

Redox Reactions and Electrochemistry



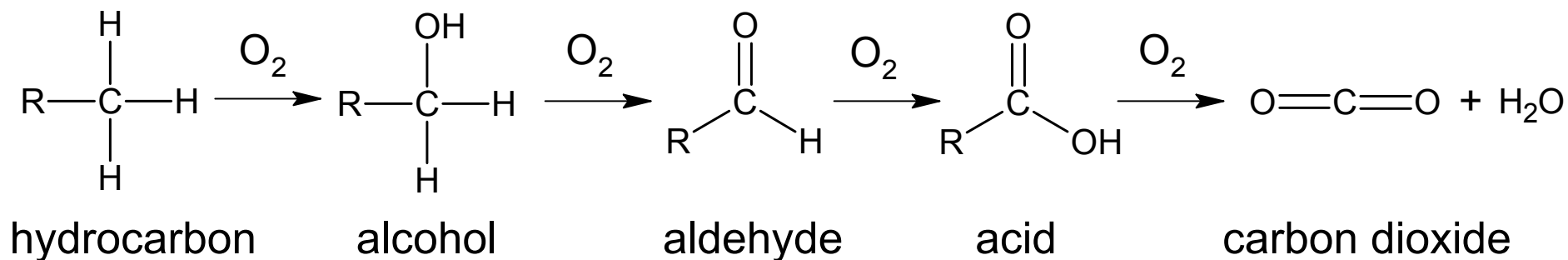
Problem Set

Chapter 5: 21-26, Chapter 21: 15-17, 32, 34, 43, 53, 72, 74

Oxidation/Reduction as Gain and Loss of Oxygen atoms

Oxidation – a reaction in which a substance gains O atoms

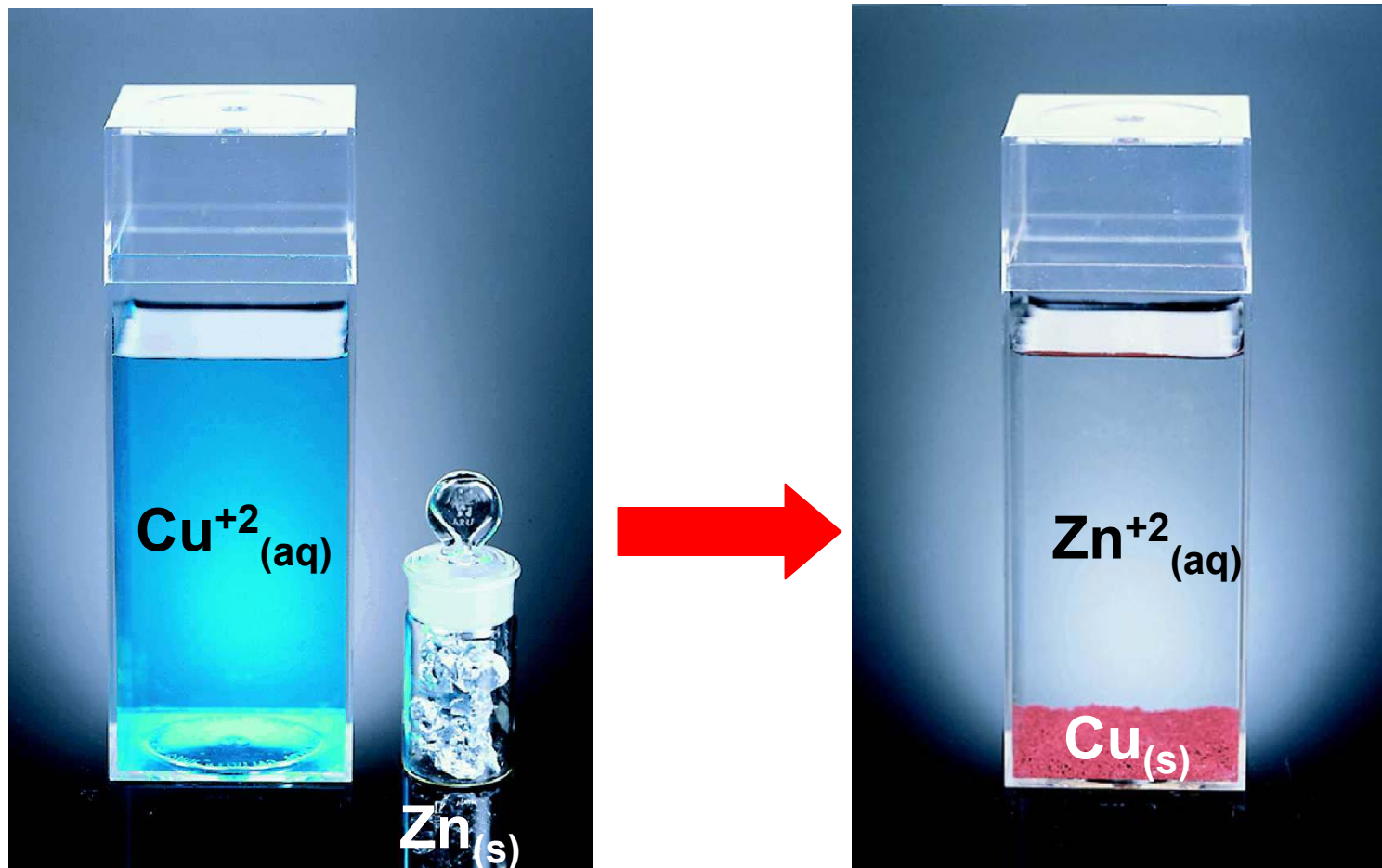
(e.g. the oxidation of a hydrocarbon)



(i.e. this is equivalent to the combustion of a hydrocarbon)

Reduction - a reaction in which a substance loses O atoms

Oxidation/Reduction as Loss or Gain of Electrons



Presentation of Redox Reaction as 2 Half-Reactions



The reaction can be represented by two $\frac{1}{2}$ reactions in which electrons are either gained or lost and the “oxidation state” of elements changes :



Reduction – a process in which electrons are gained (formally), the O.S. of an element decreases and electrons appear on the left side of the $\frac{1}{2}$ reaction

Oxidation – a process in which electrons are lost (formally), the O.S. of an element increases and electrons appear on the right side of the $\frac{1}{2}$ reaction

More electronegative atoms are less willing to change their O.S.

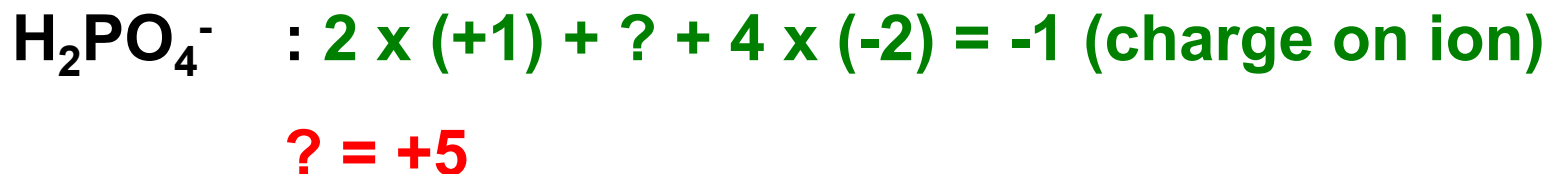
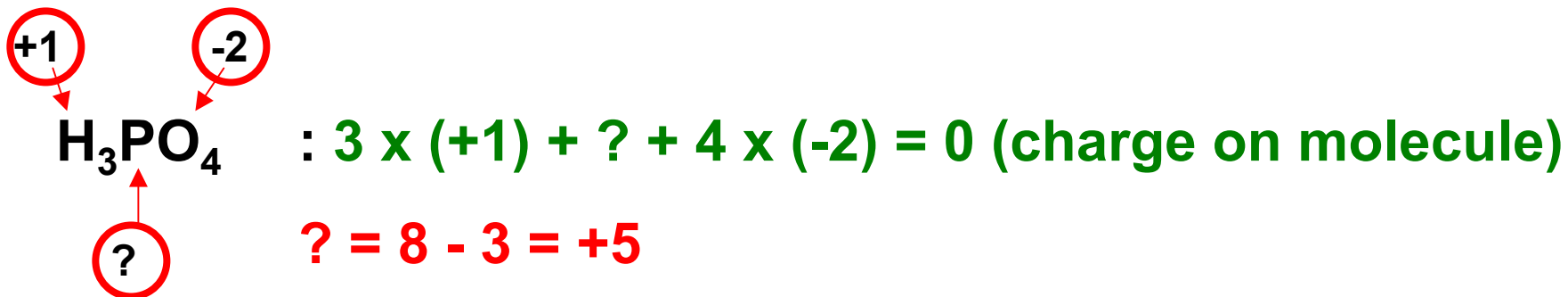
* Lanthanides: 1.1–1.3
† Actinides: 1.3–1.5

Major Rules for Oxidation States

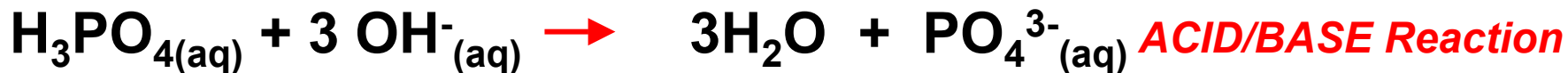
- 1) O.S. of an atom in a free element is 0
- 2) Total of the O.S.'s of atoms in a molecule or ion is equal to the total charge on the molecule or ion.
- 3) Group 1A and Group 2A metals have O.S. of +1 and +2 respectively.
- 4) F always has an O.S. of -1 . Cl also has O.S. of -1 unless it is bonded to oxygen or fluorine.
- 5) H almost always has an O.S. of +1.
- 6) O has O.S. of -2 (unless bonded to itself or F)
- 7) When bound to metals, group 7A, 6A and 5A elements have O.S.'s of -1 , -2 , -3 respectively.

Example of finding O.S.

What is the formal O.S. of P in:



If the oxidation state of elements do not change in a reaction, it is NOT a redox reaction



How to balance redox reactions?

$\frac{1}{2}$ reaction method (not the same as method in textbook)

- 1) Identify species in which the oxidation state of an element is changing. Write the skelton $\frac{1}{2}$ reactions *including balancing of the redox atoms if necessary***
- 2) Identify formal O.S. on both sides of equation for elements that have a change in O.S.**
- 3) Add appropriate # of electrones to either left or right to balance oxidation states *of redox atom(s)*.**
- 4) Balance changes on left and right side of equation by adding H^+ (if in acidic solution) or OH^- if in basic solution.**
- 5) Add appropriate number of H_2O 's to left or right to balance atoms in the $\frac{1}{2}$ reaction.**

Balancing redox reactions, cont'd

At this point, both $\frac{1}{2}$ reactions should be balanced. The next step is to combine the two $\frac{1}{2}$ reactions to form an overall equation.

- 6) Multiply through each $\frac{1}{2}$ reactions by appropriate coefficients to match e's in each $\frac{1}{2}$ reaction.
- 7) Add $\frac{1}{2}$ reactions and cancel e's and other common species on left and right.
- 8) Check Reaction. It should be balanced in terms of oxidation states, charge and atoms.

IF NOT, YOU HAVE MADE A MISTAKE!

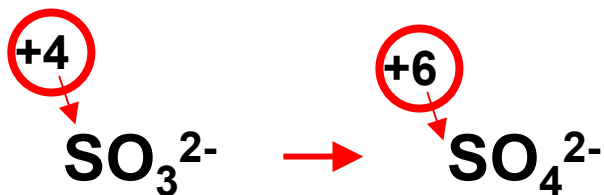
Example of balancing a redox reaction

Determining sulphite in wastewater.

Sulphite is reacted with permanganate to produce sulphate and Mn(II) ion *in acidic solution*. Balance the redox reaction.



skeleton reaction



identify oxidation states



balance O.S. with e⁻s



balance charges with H⁺



balance atoms with H₂O

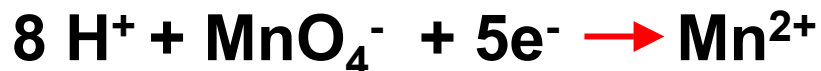
Cont'd, Mn $\frac{1}{2}$ reaction



identify oxidation states



balance O.S. with e⁻'s

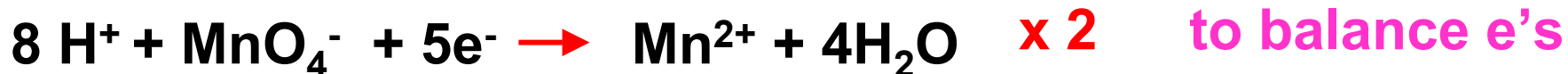
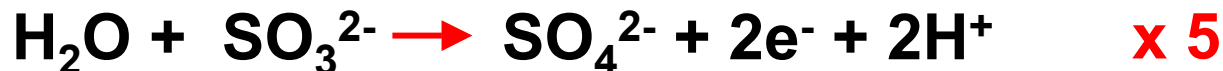


balance charges with H⁺



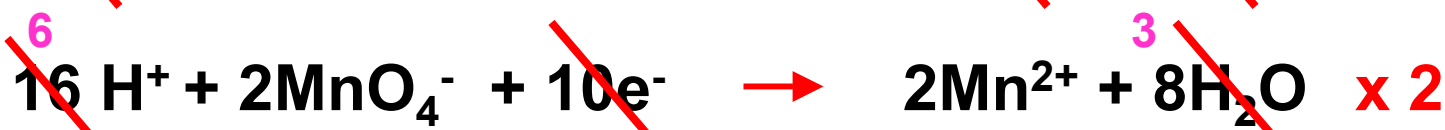
balance atoms with H₂O

Balanced $\frac{1}{2}$ Reactions



Cont'd, balancing full equation

Balanced full reaction



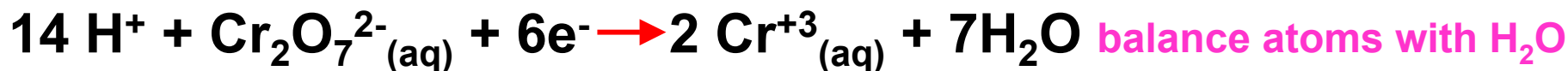
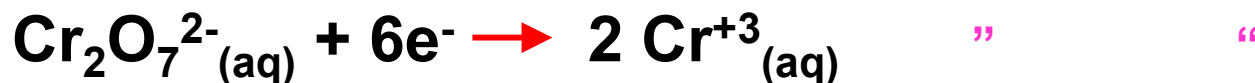
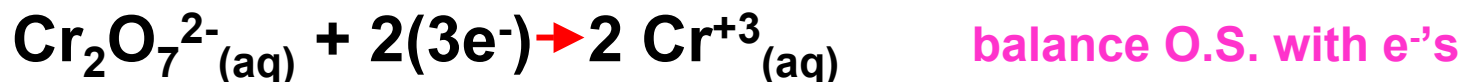
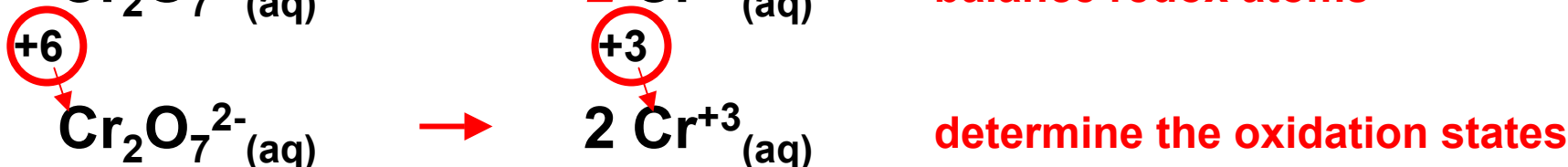
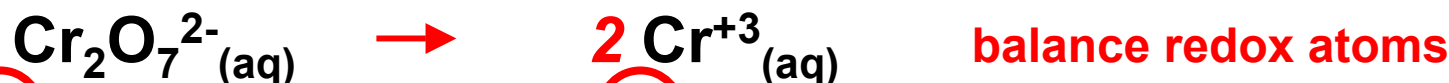
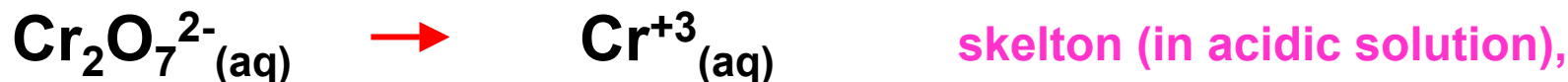
Check atom balance. OK

Try example 5.7 using this approach, use OH⁻ to balance charge in basic solution. Much easier.

This method forces you to know O.S.

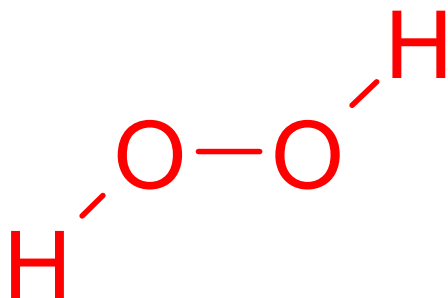
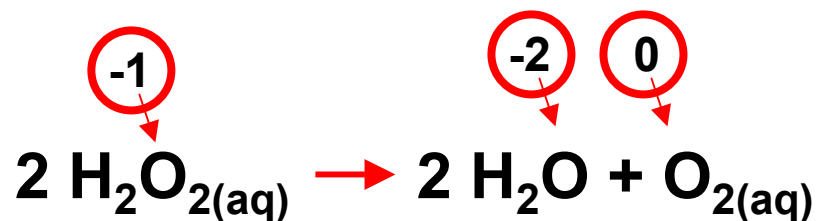
Example of balancing $\frac{1}{2}$ reaction, that requires balancing redox atoms

Write the half reaction for $\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{+3}$



Disproportionation reactions

An element in a substance is both oxidized and reduced



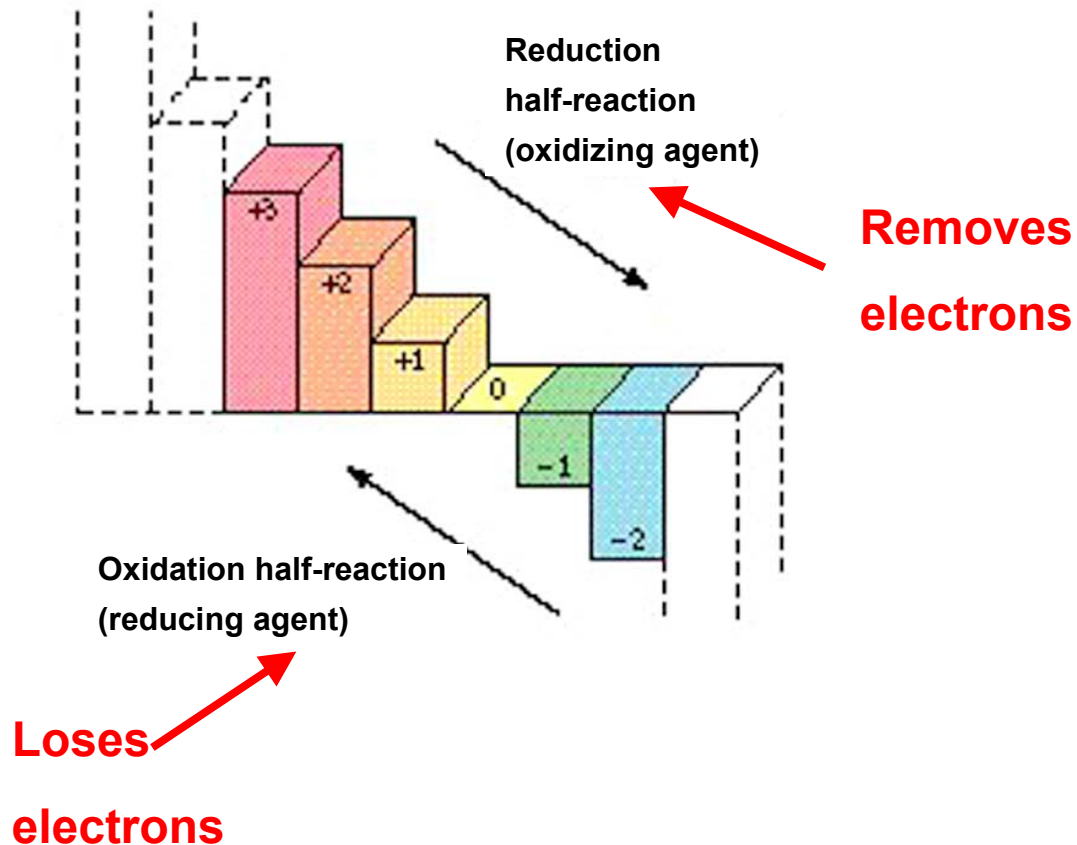
Hydrogen peroxide: antiseptic agent, O_2 acts as germicide

Ox/Red Agents

Oxidizing Agent – a chemical substance that oxidizes (removes electrons from) other substances in a chemical reaction. In the process of oxidizing something, the oxidant becomes reduced; its oxidation state decreases.

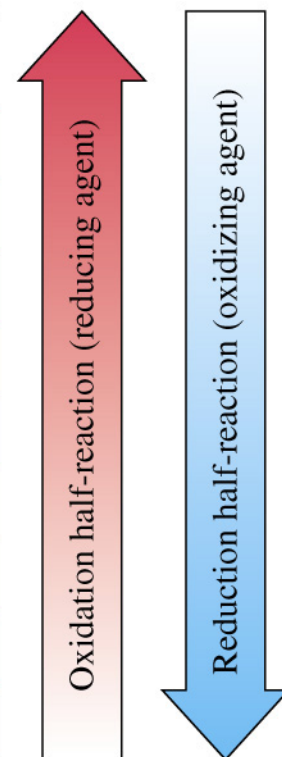
Reducing Agent – a chemical substance that reduces (loses electrons to) other substances. In the process of reducing, the oxidant becomes oxidized; its oxidation state increases.

Oxidizing and Reducing Agents



Oxidation States of Nitrogen

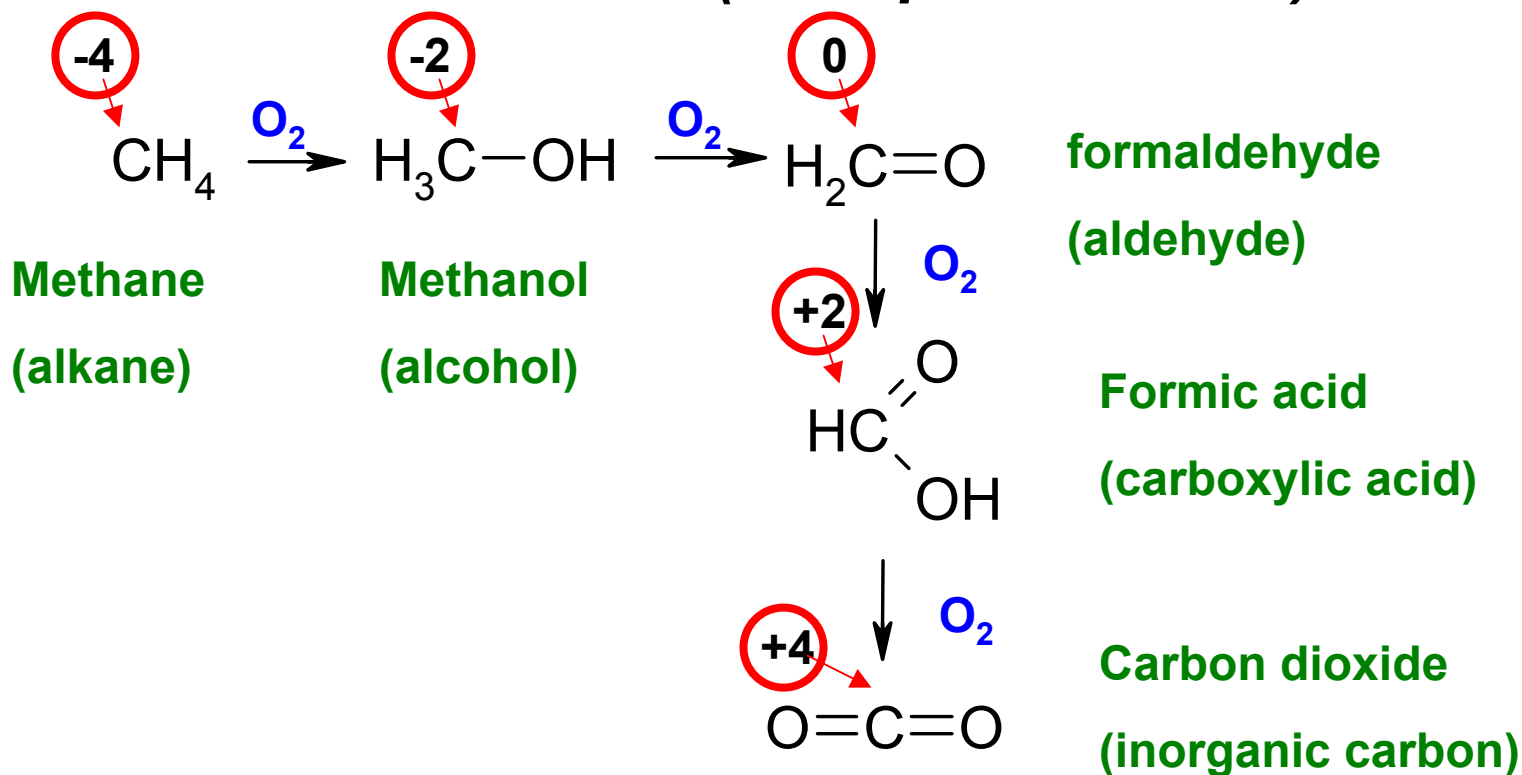
Compound or ion	Oxidation state
NO_3^-	+5
N_2O_4	+4
NO_2^-	+3
NO	+2
N_2O	+1
N_2	0
NH_2OH	-1
N_2H_4	-2
NH_3	-3



Oxidizing Agents

O_2 – *probably the most common and most important oxidant known to us. Ubiquitous.*

Organic Oxidation schemes (example- methane)



Other oxidizing agents

Oxides in their highest oxidation state are frequently strong oxidizing agents.



HNO_3 , HClO_4 – oxidizing acids

Non-oxidizing acids – HCl , HBr , HI , acids for which the only possible reduction $\frac{1}{2}$ reaction is:



HNO_3 is a much stronger oxidizing agent than H^+ .

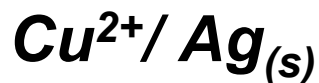
HNO_3 has been used as an oxidant of a rocket fuel in military missiles

Metals that dissolve in dilute H^+ to produce H_2	Metals that will not dissolve
Li, Na, K (1A metals) Mg, Ca (2A metals) Al, Zn Fe, Sn, Pb	Cu, Ag, Au, Hg

HNO_3 dissolves Cu

Practice problem – Cu will dissolve in HNO_3 producing Cu^{+2} in solution and a brown gas. Write a balanced equation for this process. (Hint: the brown gas is NO_2)

Electrochemistry



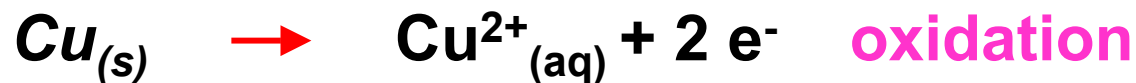
Spontaneous!

($\Delta G < 0$)



(a)

(b)



There is a flow of electrons from Cu to Ag^+ , but we cannot get use of this unless we have an electrical circuit



?

No reaction.

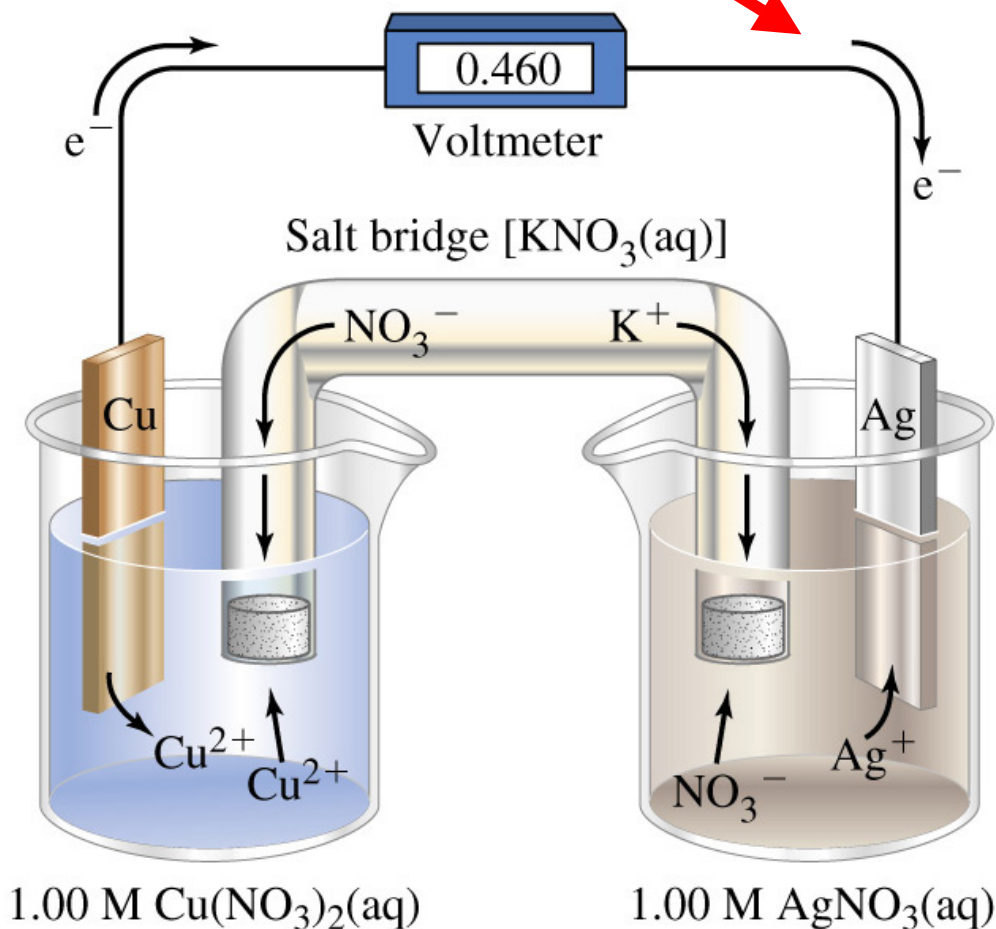
Not spontaneous!

($\Delta G > 0$)

The reverse reaction is spont.

Electrochemical Cells

Flow of electrons
(current) can do work.

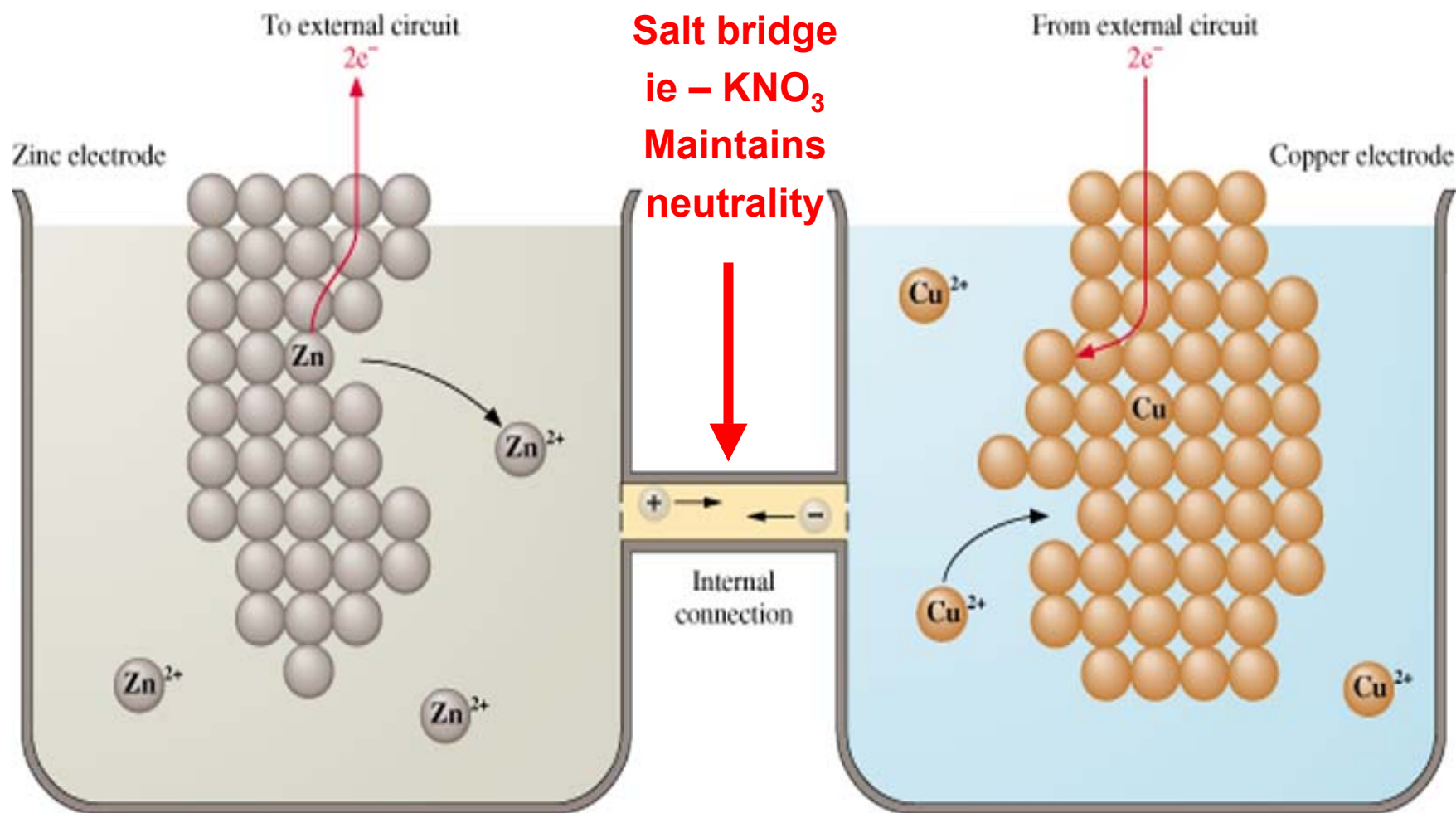


We can connect half reactions in separate containers through an electrical circuit. This will produce a current (electron flow) and voltage according to the spontaneity of the reactions.

Current depends on [], surface area of the electrodes, the resistance of the wires, etc.

$V = 0.46 = \text{const}$ for this cell

Atomic view of a Voltaic (galvanic) Cell

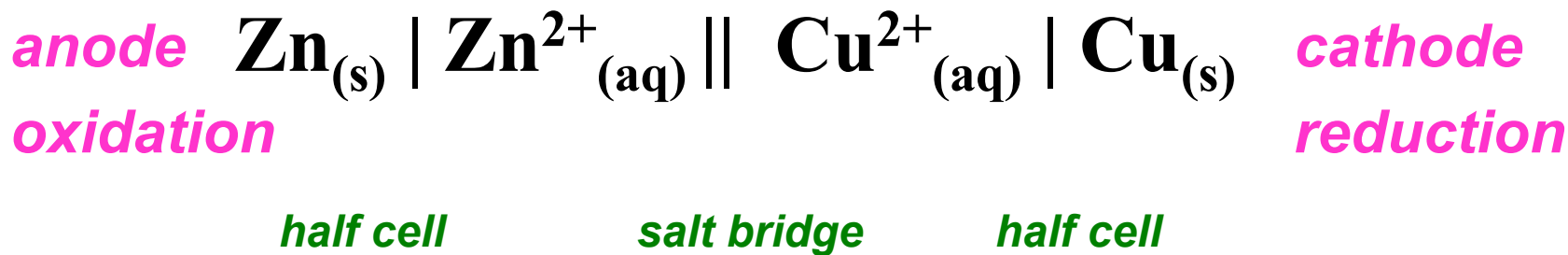


Anode – oxidation

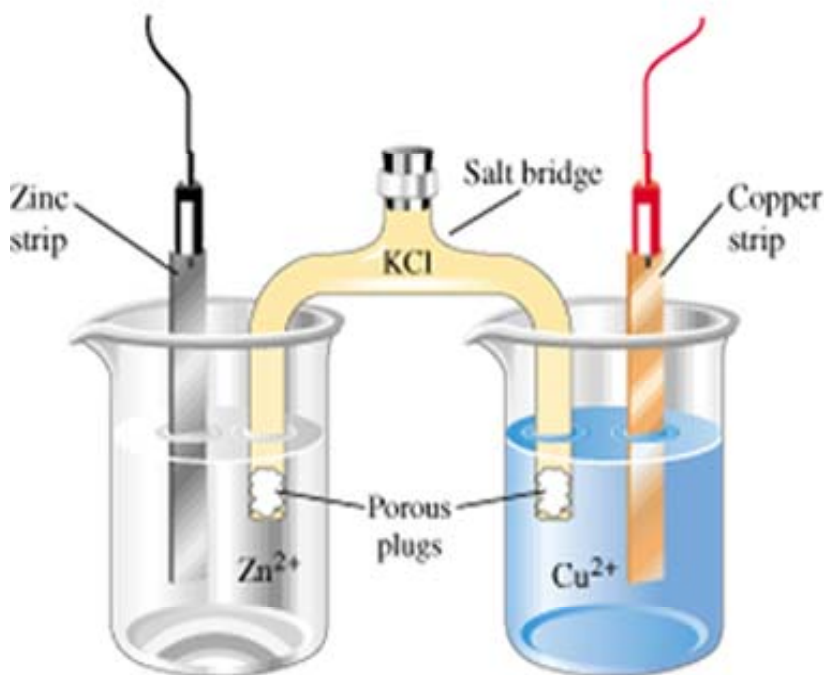
Cathode - reduction

Cell Diagrams

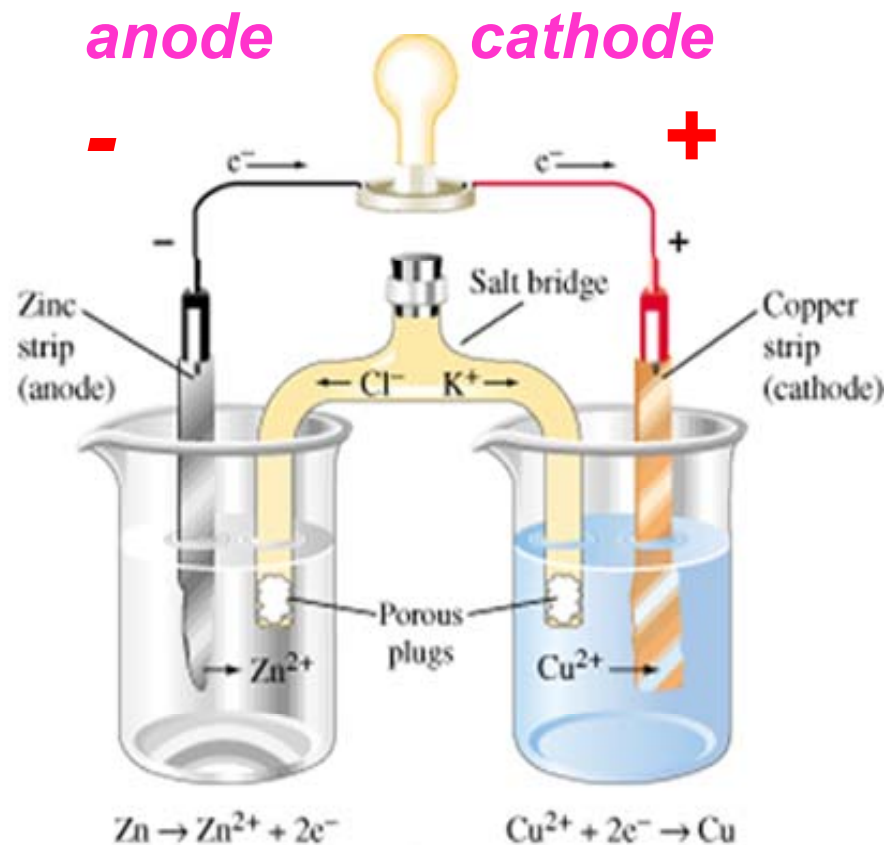
- anode (oxidation) is placed at left side of diagram
- cathode (reduction) is placed at right side of diagram
- boundary line, |, indicates a boundary between different phases (l.e. solution|solid)
- a double boundary line || indicates a boundary (l.e.- salt bridge) between different half cell compartments



Voltages and Current



A



B

Electromotive Force (EMF) - The voltage difference between two solutions provides a measure of the driving force of the electron transfer reaction.

Voltage is the difference of potentials at anode and cathode. How to determine potentials?

Standard Electrode Potentials

Absolute measurements of potential (voltage) at a single point are meaningless, **UNLESS**, they are measured against some known reference.

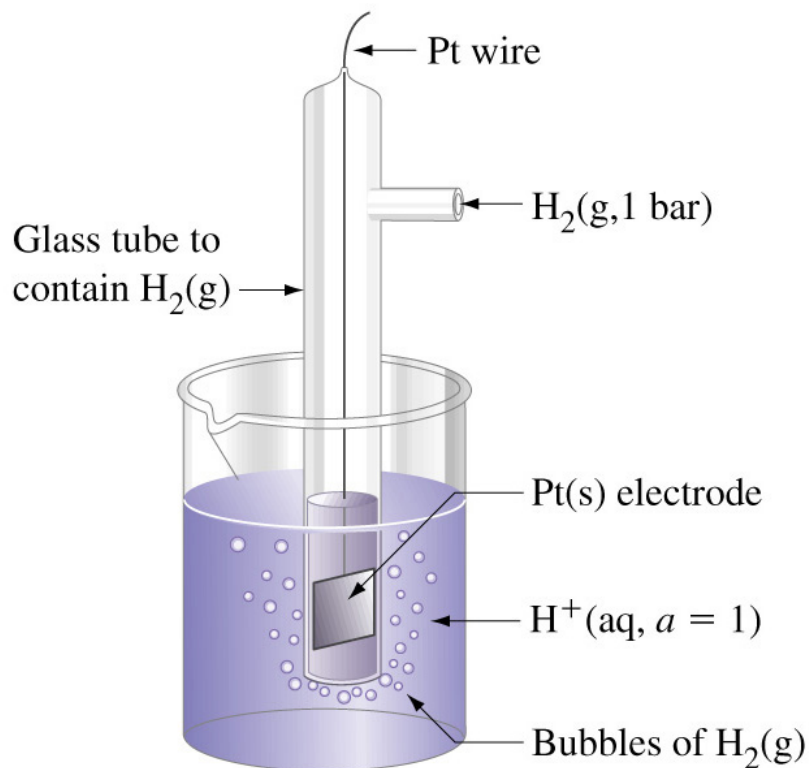
In electricity, that reference is known as “**ground**”.

In electrochemistry, that reference is the **standard hydrogen electrode** (SHE).

A standard Electrode potential, E° , measures the tendency for the **reduction** process to occur at an electrode (with respect to the SHE), when all species in solution have unit activity (~ 1.0 M) and gases are at 1 bar pressure.

The higher E° the higher the tendency of reduction on the electrode (at the expense of oxidation at the electrode with lower E°).

Standard Hydrogen Electrode (SHE)



$$P_{\text{H}_2} = 1.0 \text{ atm}$$

$$a_{\text{H}_3\text{O}^+} = a_{\text{H}^+} = 1.0$$



Convention: The potential of the SHE is zero

$$E^\circ_{\text{H}^+(\text{aq})/\text{H}_{2(\text{g})}} = 0 \text{ V}$$

TABLE 21.1 Some Selected Standard Electrode (Reduction) Potentials at 25 °C

Reduction Half-Reaction	E°, V
Acidic solution	
$\text{F}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{F}^-(\text{aq})$	+2.866
$\text{O}_3(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.075
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{SO}_4^{2-}(\text{aq})$	+2.01
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.763
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$	+1.51
$\text{PbO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.455
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \longrightarrow 2 \text{Cl}^-(\text{aq})$	+1.358
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) + 6 \text{e}^- \longrightarrow 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\text{l})$	+1.33
$\text{MnO}_2(\text{s}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l})$	+1.23
$\text{O}_2(\text{g}) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l})$	+1.229
$2 \text{IO}_3^-(\text{aq}) + 12 \text{H}^+(\text{aq}) + 10 \text{e}^- \longrightarrow \text{I}_2(\text{s}) + 6 \text{H}_2\text{O}(\text{l})$	+1.20
$\text{Br}_2(\text{l}) + 2 \text{e}^- \longrightarrow 2 \text{Br}^-(\text{aq})$	+1.065
$\text{NO}_3^-(\text{aq}) + 4 \text{H}^+(\text{aq}) + 3 \text{e}^- \longrightarrow \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.956
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+0.800
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{O}_2(\text{g}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.695
$\text{I}_2(\text{s}) + 2 \text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$	+0.535
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.340
$\text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{g})$	+0.17
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+0.154
$\text{S}(\text{s}) + 2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2\text{S}(\text{g})$	+0.14
$2 \text{H}^+(\text{aq}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.125
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.137
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.440
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.763
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.676
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.356
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.713
$\text{Ca}^{2+}(\text{aq}) + 2 \text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.84
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.924
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.040
Basic solution	
$\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{O}_2^{2-}(\text{aq}) + 2 \text{OH}^-(\text{aq})$	+1.246
$\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{Cl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq})$	+0.890
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$	+0.401
$2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.828

Easy to reduce,
hard to oxidize
(good oxidizing
agents)

Oxidation is
reverse of
reduction:

$$E^\circ_{\text{oxidation}} = - E^\circ_{\text{reduction}}$$

Hard to reduce,
easy to oxidize
(good reducing
agents)

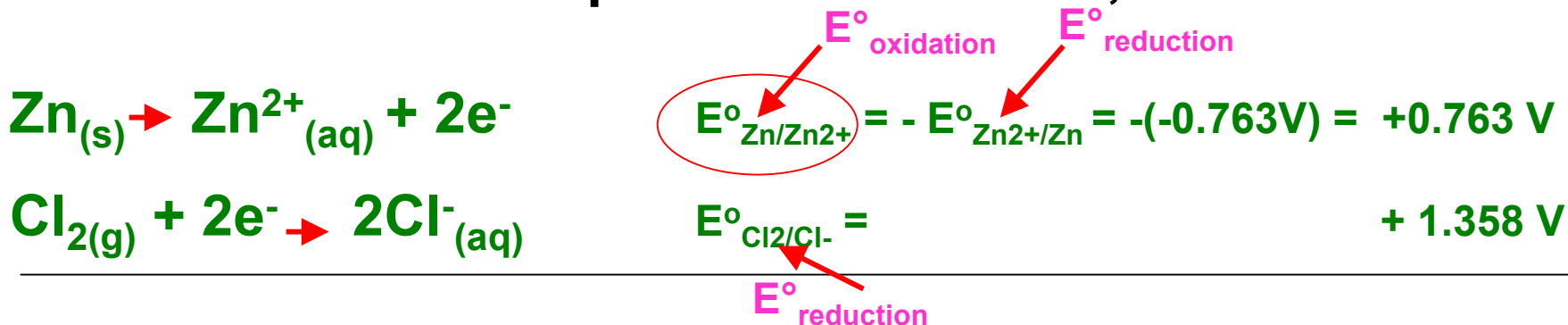
Standard Potential of Electrochemical Cell

The potential of an electrochemical cell under standard conditions may be calculated as the sum of the reduction potential and oxidation potentials for **two half cells**:

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{reduction}} + E^{\circ}_{\text{oxidation}}$$

Example 21-2: Reaction: $\text{Zn}_{(\text{s})} + \text{Cl}_{2(\text{g})} \rightarrow \text{ZnCl}_{2(\text{aq})}$

What is the standard potential of the cell, E° .



A simpler way of calculating E°_{cell}

The potential of an electrochemical cell under standard conditions may be also calculated as

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

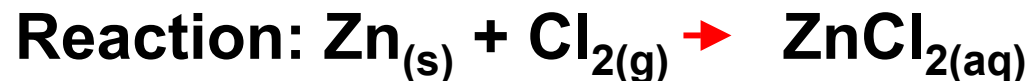
where the E° 's are standard *reduction* potentials taken from a table.

The definition of the cathode and anode depend on the direction of the reaction. Reduction occurs at the cathode (e^- 's on L.S. of equation, O.S. decreasing) while oxidation occurs at the anode (e^- 's on R.S. of equation, O.S. increasing)

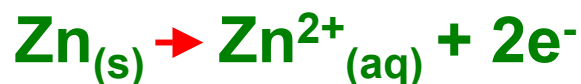
Also for a spontaneous reaction, $E^\circ_{\text{cell}} > 0$, as we will see shortly.

Example 21-2 one more time

A new battery system currently under study for possible use in electric vehicles is the ZnCl_2 battery.



What is the standard potential of the cell, E° .



Reduction potentials

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763 \text{ V}$$

Anode

$$E^\circ_{\text{Cl}_2/\text{Cl}^-} = +1.358 \text{ V}$$

Cathode



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.358 - (-0.763)\text{V} = 2.121 \text{ V}$$

Spontaneous change in a Cell

Previously, it was said $E_{\text{cell}} > 0$ for a spontaneous reaction. Where did this come from?

Electrical work:

$W_{\text{electrical}} = Fl = Eq l = \{El = V\} = qV$ **F = electrical force,**
 l = distance between two electrodes, q = charge moved,
 V = voltage

If q in coulombs and V in volts then W in joules

Related parameters:

Power $P = iV$

i = current (charge/time), V = voltage

If i - coulombs/sec (Amp), V -volts, P - joules/sec = watts

In an electrochemical cell,

$$q = n \times F$$

n = moles of electrons

F = charge of 1 mole of electrons = Faraday

$F = 96485 \text{ C/ mole electrons}$

$$V = E_{\text{cell}}$$

Spontaneous change, cont'd

$$W_{\text{electrical}} = q V = nFE_{\text{cell}}$$

This applies to a reversible process (implying that the reaction is carried out slowly enough that the system maintains equilibrium). Previously it was argued that the amount of work we can extract from a chemical process is equal $-\Delta G$ (pg 796, Petrucci “Are You Wondering” box).

$$\Delta G = -W_{\text{electrical}}$$

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

$\Delta G^\circ = -nFE^\circ_{\text{cell}}$ (standard molar \rightarrow n is number of moles of electrons per mole of reaction)

If $E^\circ_{\text{cell}} > 0$, $\Delta G^\circ < 0$ and the reaction is spontaneous

If $E^\circ_{\text{cell}} < 0$, $\Delta G^\circ > 0$ and reaction is nonspontaneous

Behavior of Metals

Previously we said that experimental evidence shows the following:

Metals of groups 1A and 2A are oxidized by H^+ .

Cu, Ag, Au, Hg are not oxidized by H^+

Metals that dissolve in dilute H^+ to produce H_2	Metals that will not dissolve
Li, Na, K (1A metals) Mg, Ca (2A metals) Al, Zn Fe, Sn, Pb	Cu, Ag, Au, Hg

Now we can better understand this:



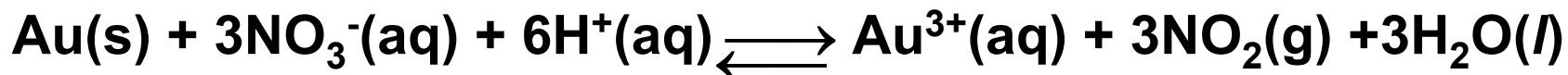
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{H^+_{(aq)}/H_{2(g)}} - E^\circ_{M^+/M} = 0 - E^\circ_{M^+/M}$$

If $E^\circ_{M^+/M} < 0$, $E^\circ_{\text{cell}} > 0$, the process is spontaneous

If $E^\circ_{M^+/M} > 0$, a stronger oxidizing agent than H^+ is required (i.e. HNO_3 , $HClO_4$).

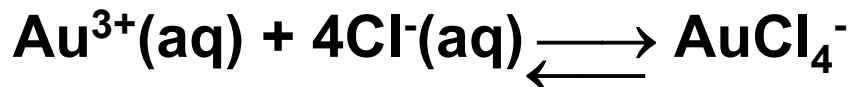
Oxidation of Gold in Aqua Regia

Nitric acid, HNO_3 , is a powerful oxidizing agent but the chemical equilibrium for its reaction with gold, Au , only permits the formation of a very small amount of Au^{3+} ion:



so the amount of gold dissolved in pure nitric acid is very low.

We know that the equilibrium can be shifted to the right if the activity of Au^{3+} at the right is decreased by the formation of a complex ion, such as the chloraurate ion, AuCl_4^- :



To form such an ion the solution has to contain Cl^- ions. It is achieved though mixing HNO_3 with HCl , this mixture is called **aqua regia**. Aqua regia can also dissolve platinum by a similar mechanisms.

Non-Standard Conditions: Nernst Equation

Previously, we have talked about standard electrode potentials, everything in standard state.

Very rarely are things in standard state.

In nonstandard state we use ΔG instead of ΔG°



$$\Delta G = \Delta G^\circ + RT \ln Q$$

R = gas constant

T = temperature (K)

Q = reaction quotient

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - RT/nF \ln Q = E^\circ_{\text{cell}} - RT/(2.303 nF) \log Q$$

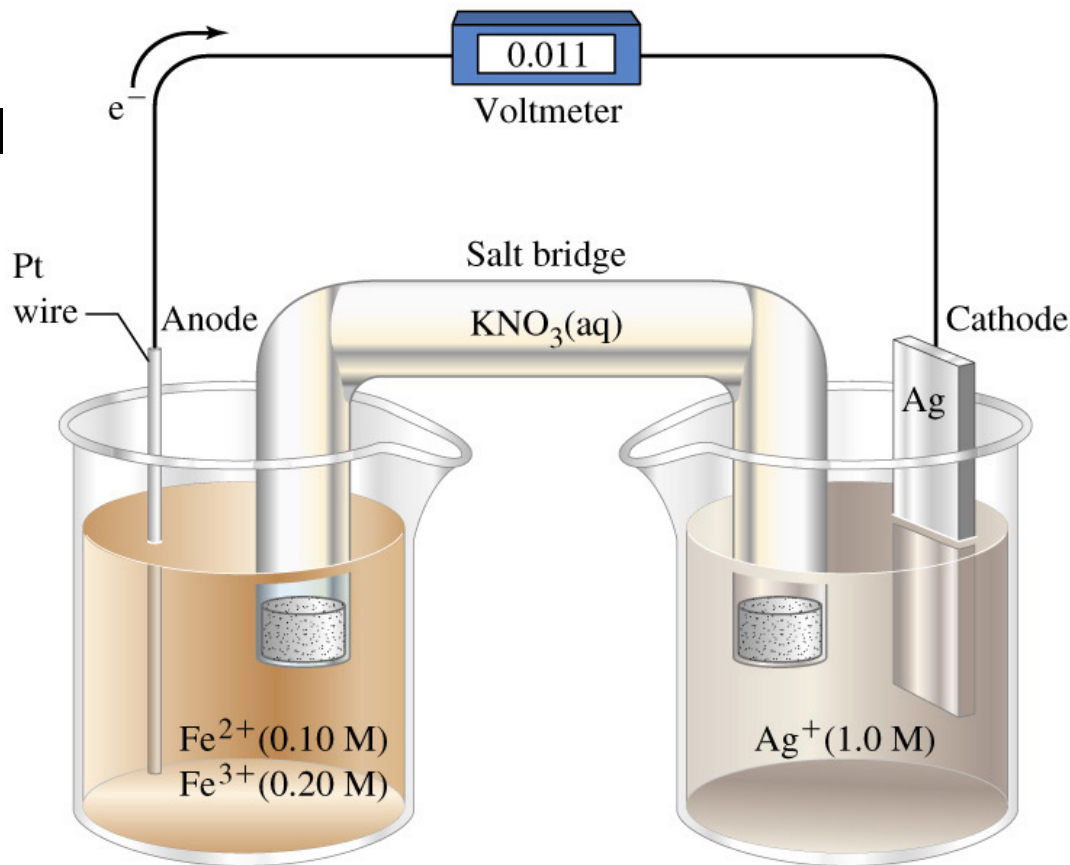
For T = 25 °C $RT/(2.303F) = \text{const} = 0.0592 \text{ V}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q, \quad \text{for } T = 25^\circ \text{C} \quad \text{Nernst Equation}$$

Applications of the Nernst Equation

Draw the condensed cell diagram for the voltaic cell pictured at right.

Calculate the value of E_{cell} for $T = 25^\circ\text{C}$



The cell is in nonstandard conditions. We need to use the Nernst equation. Thus, we need to find E°_{cell} , n , and Q .

1. To calculate E°_{cell} it is enough to recognize half-reactions:

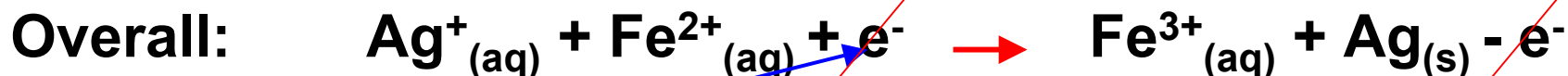
From Table of Standard Reduction Potentials:



$$E^\circ_{\text{cell}}: E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} =$$

$$E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.800\text{V} - 0.771\text{V} = 0.029\text{V}$$

2. To find both n and Q we need to write a balance overall reaction:



$$n = 1$$

$$Q = \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}][\text{Ag}^+]} = \frac{0.20\text{M}}{0.10\text{M} \times 1.0\text{M}} = 2 \text{ unitless}$$

Cont'd

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{2.303Fn} \log Q =$$
$$= 0.029 - \frac{0.0592}{1} \log 2 = 0.011 \text{ V}$$

The process is spontaneous under the stated non-standard conditions

Example A:

Calculate E_{cell} at $T = 25^\circ\text{C}$ for the following cell



$$E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 = 0.154 \text{ V}$$

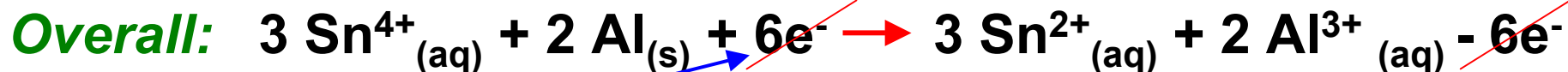


$$E_{\text{Al}^{3+}/\text{Al}}^0 = -1.676 \text{ V}$$

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^0 - E_{\text{Al}^{3+}/\text{Al}}^0$$

$$= 0.154 - (-1.676) = 1.830 \text{ V}$$

cont'd



n = 6

$$Q = \frac{[\text{Sn}^{2+}]^3 [\text{Al}^{3+}]^2}{[\text{Sn}^{4+}]^3}$$

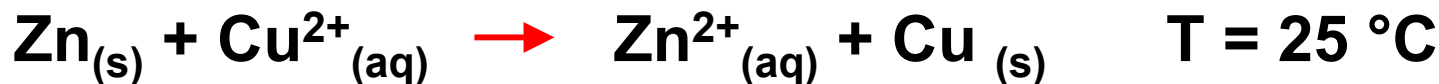
$$Q = \frac{[\text{Sn}^{2+}]^3 [\text{Al}^{3+}]^2}{[\text{Sn}^{4+}]^3} = \frac{(0.54\text{M})^3 (0.36\text{M})^2}{(0.086\text{M})^3} = 32.08 \text{ unitless}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{2.303F n} \log Q =$$

$$= 1.830 - \frac{0.0592}{6} \log 32.08 = 1.814 \text{ V}$$

The process is spontaneous under the stated non-standard conditions

Change in E_{cell} with Conditions



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q = 1.100\text{V} - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

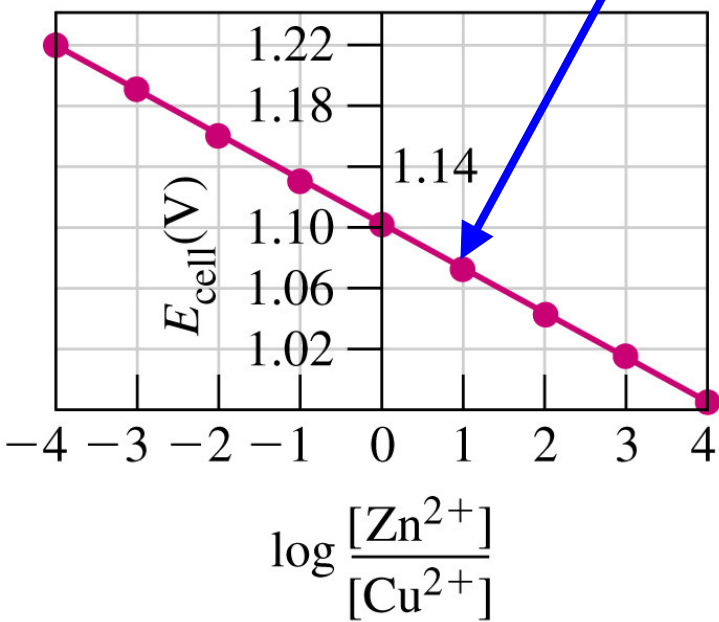
Slope = $-59/2$ mV per decade change

If we let cell reaction proceed, reaction shifts to right, $[\text{Zn}^{2+}]$ increases, $[\text{Cu}^{2+}]$ decreases and E_{cell} decreases. When does it stop?

It stops at equilibrium, $E_{\text{cell}} = 0.00\text{V}$

$$0.0 = E_{\text{cell}}^{\circ} - \frac{0.0592}{n} \log Q_{\text{eq}} \quad K_{\text{eq}} !!$$

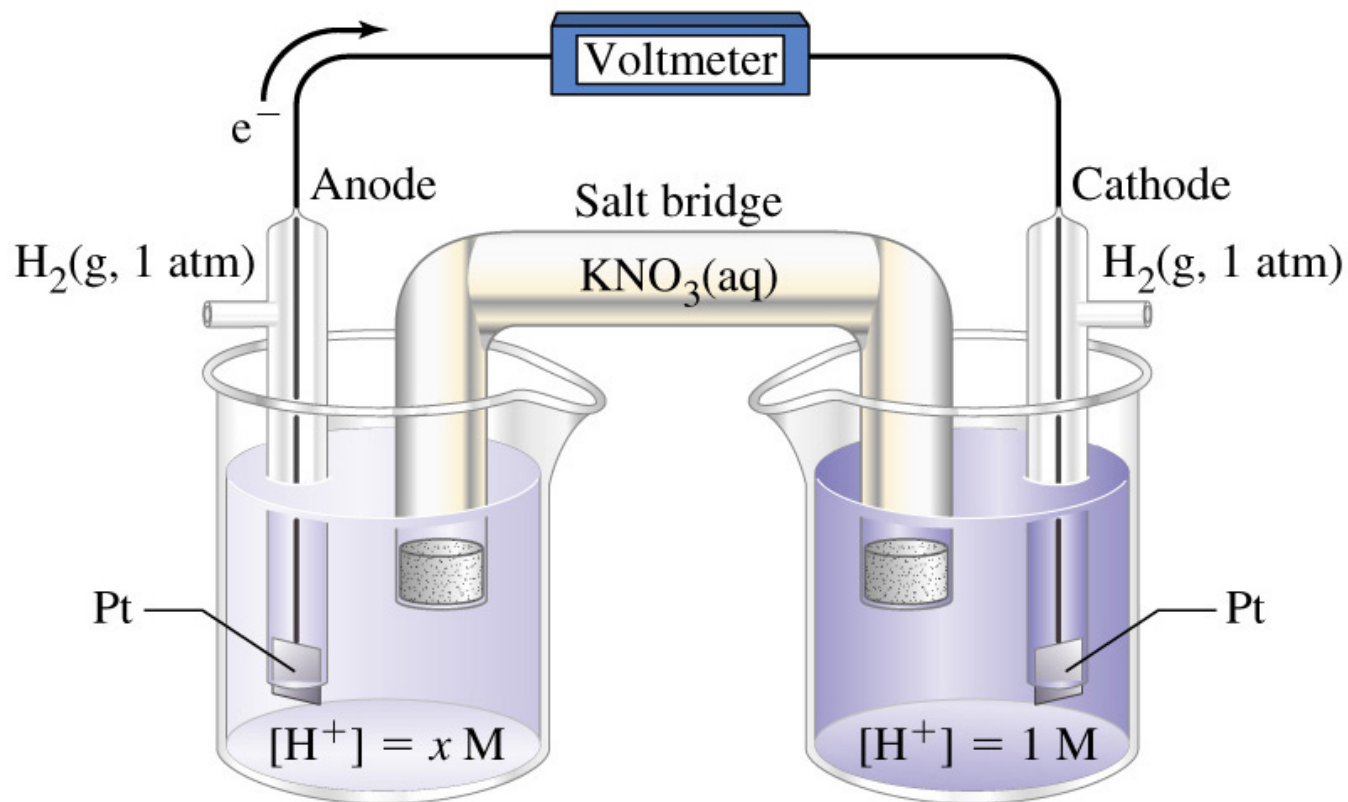
We can calculate K_{eq} from E° values! For above reaction, $K_{\text{eq}} = 1.5 \times 10^{37}$



$$K_{\text{eq}} = 10^{\left(\frac{nE_{\text{cell}}^{\circ}}{0.0592} \right)}$$

Concentration Cells

Both $\frac{1}{2}$ cells are the same chemical system, just different concentrations. The driving force (i.e. the EMF) is provided by the difference in concentrations.



Concentration Cell



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.00 - 0.00 = 0.00\text{V}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q = 0.00\text{V} - \frac{0.0592}{2} \log \frac{[\text{H}^+]^2_{\text{anode}}}{[\text{H}^+]^2_{\text{cathode}}}$$

$$= -\frac{0.0592}{2} \log \frac{x^2}{1^2} = -\left(\frac{0.0592}{2}\right)(2\log x) = -0.0592 \log x$$

Since $\text{pH} = -\log x$, $E_{\text{cell}} = 0.0592 \text{ pH}$

This concentration cell behaves as a pH meter! Other concentration cells can be used to measure unknown concentrations of other species (i.e. potentiometry).

Determination of K_{sp} (see example 21-10)

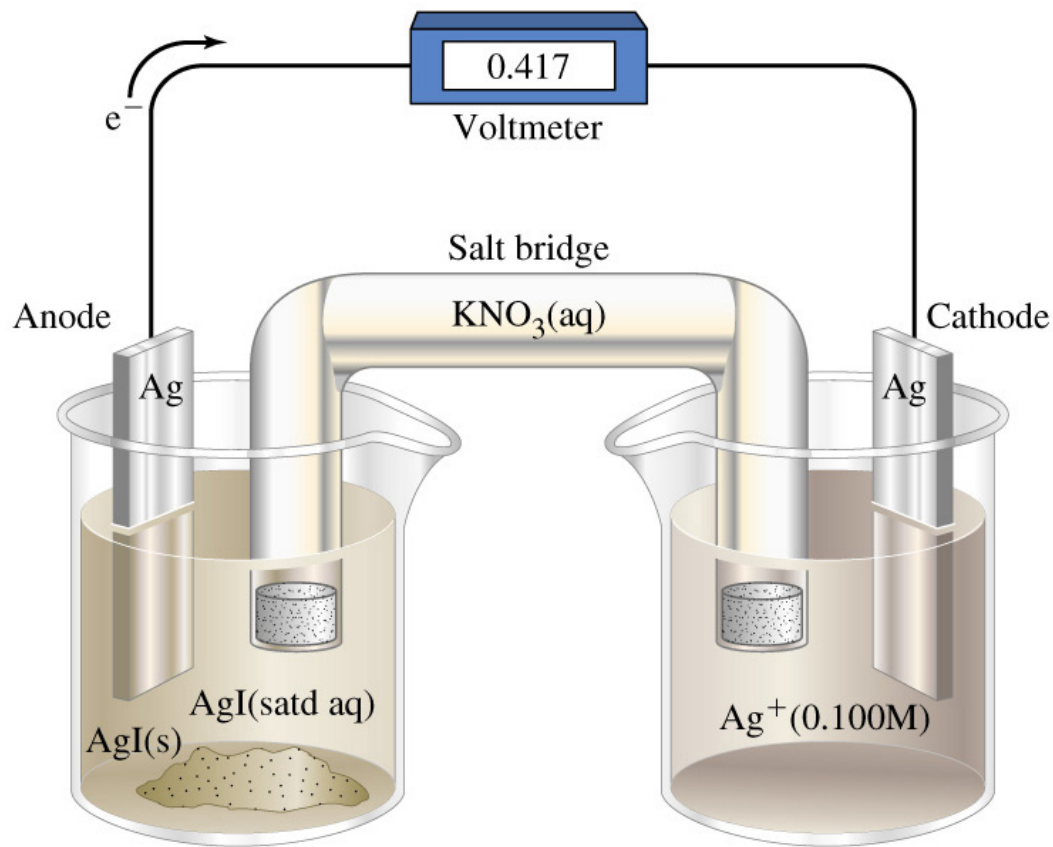
From measured E_{cell} ,
determine K_{sp} of AgI.

Solution:

Set up the voltaic cell with saturated AgI, which produces Ag^+ (aq, x M), at anode and Ag^+ (aq, 0.1 M) at cathode, by dissolving AgNO_3 for example.

Solve Nernst equation similar to how it was done in the previous example to get x.

$$x = [\text{Ag}^+] = S, [\text{I}^-] = S$$



$$K_{sp} = S^2$$

Essentials of the last Lecture

Nernst equation allows us to calculate the cell potential for non-standard conditions:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - 2.303RT/nF \log Q$$

E°_{cell} is the standard potential of the cell

n is the number of moles of electrons per mole of balanced reaction

Q is the quation

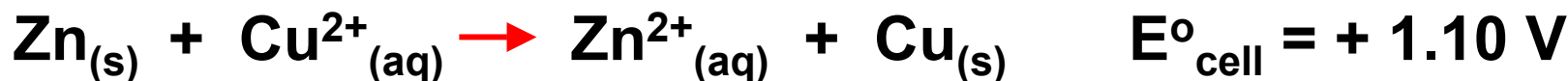
E°_{cell} is calculated from two half reactions

n and Q are found from the balanced overall redox reaction

Electrolysis

The use of an externally applied voltage to force an electrochemical reaction, even if it is naturally non-spontaneous.

Spontaneous!



What about the reverse process?

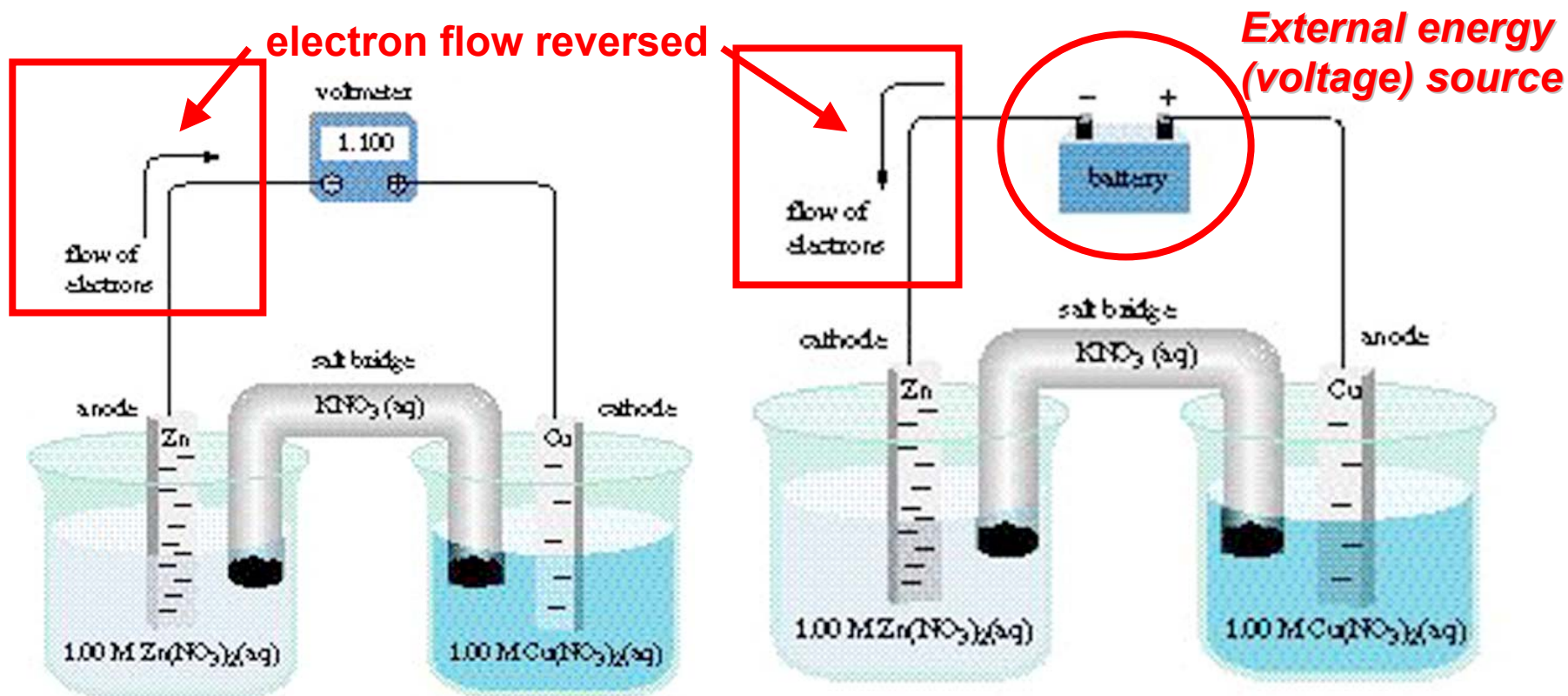
Non-spontaneous!



*But if we **apply** a potential $> 1.10 \text{ V}$ across the cell, we overcome the natural negative voltage, thus providing the driving force to make the reaction proceed.*

Current is in opposite direction of voltaic, or galvanic, cell.

Galvanic and Electrolytic Cells



Galvanic Cell

Electrolytic Cell

Regardless of the cell type, anode and cathode always defined by the process: oxidation at the anode, reduction at the cathode.

Zn/Cu²⁺ electrolysis example continued...

The amount of current that flows in the electrolytic cell tells us how much Zn has been produced or how much Cu²⁺ has dissolved.

Faraday's Law of Electrolysis:

The number of moles of product formed in an electrolysis cell by an electric current is chemically equivalent to the number of moles of electrons supplied.

or

$$Q = nF = it$$

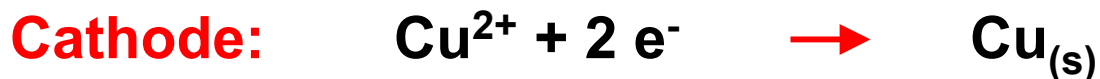
charge (coulombs) **Total #** moles of electrons current (amperes) time (seconds)

$n = it/F$

Note: 1 A = 1C/s Faradays constant = 96485 C /mole of e⁻

Example 21-12

Electrodeposition of Cu can be used to determine Cu^{2+} content of sample.



What mass of Cu is deposited in 1 hr if current = 1.62A?

Solution: find moles of electrons, find moles of Cu, find mass of Cu

$$\text{Mole of e}^- = \frac{it}{F} = 1.62 \text{ A (C/s)} \times 3600 \text{ sec} \times 1/(96485 \text{ C/mole e}^-)$$

$$\text{Mole of Cu} = \text{mole e}^- \times 1 \text{ mole Cu} / 2 \text{ mole e}^-$$

$$\text{Mass Cu} = \text{moles Cu} \times 63.456 \text{ g Cu/mole Cu}$$

Answer = 1.92 g of Cu deposited in 1 hour.

Cont'd

Example B: How long will it take to produce 2.62 L of O₂(g) at 26.2°C and 738 mmHg at a Pt anode with a constant current of 2.13A?

~~2H₂O → 4H⁺ + O₂(g) + 4e⁻~~ oxidation of O on + electrode

~~4H⁺ + 4e⁻ → 2H₂(g)~~ reduction of H on - electrode

Solution: find moles of O₂, find moles of e⁻, find charge, find time.

Mole of O₂:

$$n = \frac{PV}{RT} = \frac{\frac{738}{760} \text{ atm} \times 2.62 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 299.35 \text{ K}}$$

Mole of e⁻ = moles of O₂ x 4 mole e⁻/ mole O₂

Charge = moles of e⁻ × F (C/mole e⁻)

Time = Charge (C)/Current (C/s)

Answer = 18829 sec = 5.23 hr = 5 hr & 14min

Batteries

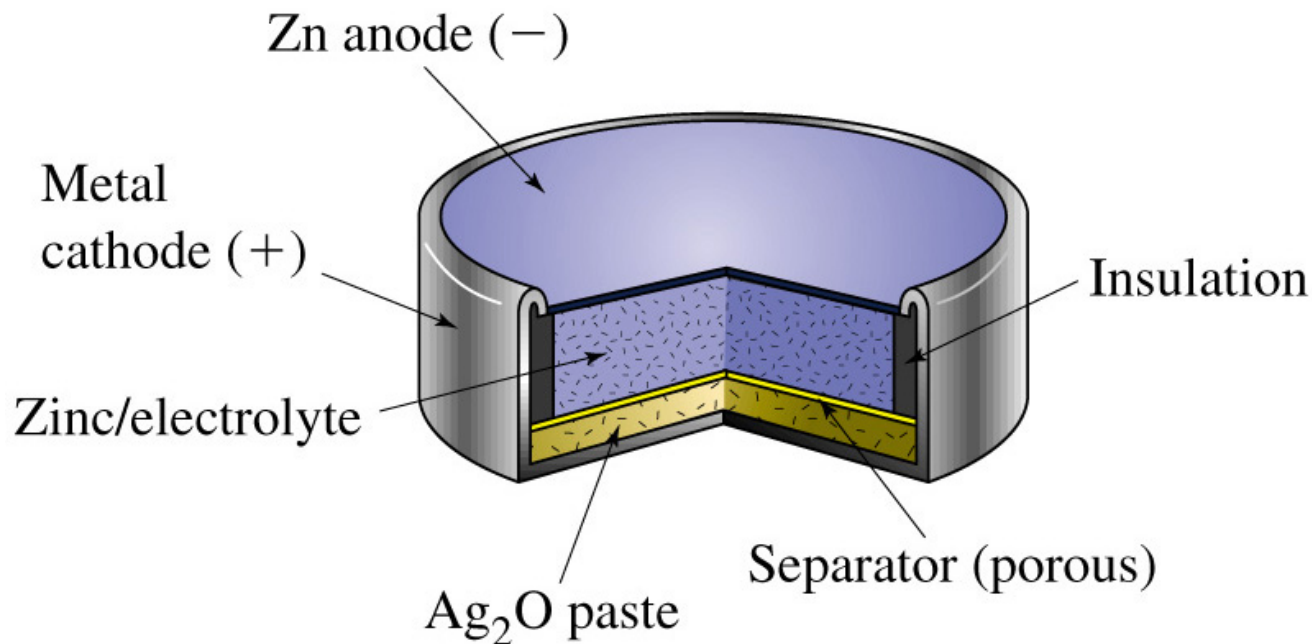
Primary batteries (one use batteries) generate current through an irreversible reaction

Secondary batteries (rechargeable batteries) generate current through a irreversible reaction.

Flow batteries serve as convertors of chemical energy to electrical while reactants (and products) flow through the batterie

Silver-Zinc Battery

1.8 V



Half reactions of discharge:

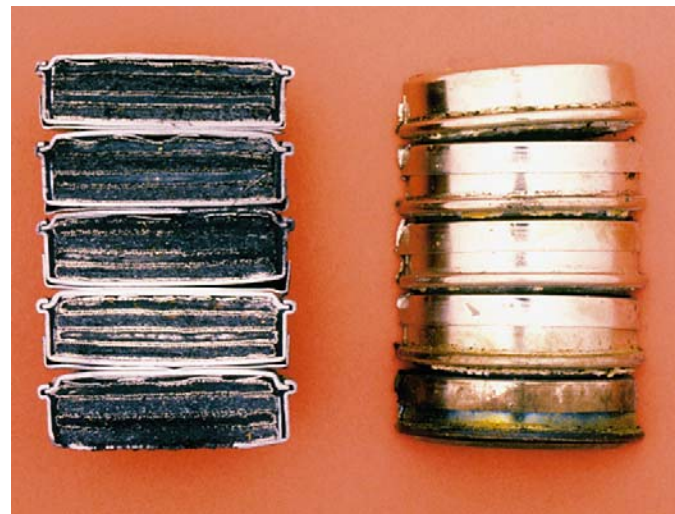
Reduction: $\text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + 2\text{OH}^-(\text{aq})$

Oxidation: $\text{Zn}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{ZnO}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^-$

Overall: $\text{Zn}(\text{s}) + \text{Ag}_2\text{O}(\text{s}) \rightarrow \text{ZnO}(\text{s}) + 2\text{Ag}(\text{s})$

The Nickel-Cadmium Rechargeable Battery

1.4 V



Half reactions of discharge:

Reduction: $2\text{NiO}(\text{OH})(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq})$

Oxidation: $\text{Cd}(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cd}(\text{OH})_2(\text{s}) + 2\text{e}^-$

Overall: $\text{Cd}(\text{s}) + 2\text{NiO}(\text{OH})(\text{s}) + 2\text{H}_2\text{O} \rightarrow 2\text{Ni}(\text{OH})_2(\text{s}) + \text{Cd}(\text{OH})_2(\text{s})$

Hydrogen-Oxygen Flow Cell

Half reactions of discharge:

Reduction: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

Oxidation: $2\{\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^-\}$

Overall: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{s})$

