Electricity from Chemical reactions

Electrochemistry is…

Oxidation–Reduction (it's all about the electrons)

- Reactions where electrons are transferred from one atom to another are called oxidation–reduction reactions.
  - Redox reactions for short
- Atoms that lose electrons are being oxidized (OIL); atoms that gain electrons are being reduced (RIG).

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

$Cu(s)$ was oxidized

Cu^{2+} ion

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

Zn^{2+} ion reduced to atomic $Zn(s)$

Half-Reactions

- split the redox reaction into two separate **half-reactions**—a reaction just involving oxidation or reduction.
  - The oxidation half-reaction has electrons as products.
  - The reduction half-reaction has electrons as reactants.

$Cu^{2+} + 2e^- \rightarrow Cu$

$Zn \rightarrow Zn^{2+} + 2e^-$

Cu^{2+} ion is reduced

Zn is oxidized

ClO_3^- balanced for mass

ClO_4^-

redox 1/2 reactions balance for mass and charge

*redox reaction is the sum of the 1/2 rxns after balancing for mass and charge

red ½ rxn. $Cu^{2+} + 2e^- \rightarrow Cu$

ox. ½ rxn $Zn \rightarrow Zn^{2+} + 2e^-$

$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$

redox reaction

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oxidation numbers (state)

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① Hydrogen is always +1 except when in a metal hydride. NaH (-1)

② oxygen is usually -2 except in peroxides

③ group I cations +1
group II cations +2
transition metals need
to tell you the charge
of the ion
Al^{3+} cation

④ Fluorine is always −1

Example

SiO_4 (−2, 2−)

+6 ; (−8)

O is 2−

S is 6^+

$KMnO_4$ (2−)

+1 ; +7 ; (−8)

Balancing Oxidation-Reduction reactions in acidic solution

the final redox reaction you may have H^+ rxn. is @ pH 2-7 in lab

- Separate into 2 half equations
- Balance all atoms except O and H
- Add water molecules and H^+ to the equation to balance O and H atoms
- Balance for charge (add up charges on both, sides add e- as needed)
- Write the redox equation by adding two half reactions (making sure the e- cancel out when adding the two half reactions

Balancing Oxidation-Reduction Reactions in Acidic Solution

$H_2O_2 + Sn^{2+} \longrightarrow H_2O + Sn^{4+}$

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

$2e^- + 2H^+ + H_2O_2 \rightarrow H_2O + H_2O$

add the 2 1/2 rxns.

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

$+2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O$

$Sn^{2+}_{(aq)} + 2H^+_{(aq)} + H_2O_{2(aq)} \rightarrow Sn^{4+}_{(aq)} + 2H_2O_{(\ell)}$

Balancing Oxidation-Reduction reactions in bas solution

basic solution
pH 7
* can't free H+ in overall redox rxn.

- Separate into two half reactions
- Balance atoms except O and H
- Balance O and H by adding water and/or H+
- Add OH- to neutralize H+
- If OH- and H+ on same side combine to form H_2O, simplify
- Balance for charge (add up charge on both sides, add e- as needed
- Add two half reactions to get redox reaction

Balancing Oxidation-Reduction Reactions in Basic Solution

$SO_3^{2-}(aq)+Cu(OH)_2(s)\longrightarrow SO_4^{2-}(aq)+Cu(OH)(s)$

1) separate into 1/2 reactions

$H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

$Cu(OH)_2 \rightarrow Cu(OH)$

$H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

$e^- + H^+ + Cu(OH)_2 \rightarrow CuOH + H_2O$

$H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^-$

$(e^- + H^+ + Cu(OH)_2 \rightarrow CuOH + H_2O) \times 2$

$+2e^- + 2H^+ + 2Cu(OH)_2 \rightarrow 2CuOH + 2H_2O$

$H_2O + SO_3^{2-} + 2Cu(OH)_2 \rightarrow$

$2Cu(OH) + SO_4^{2-} + 2H_2O$

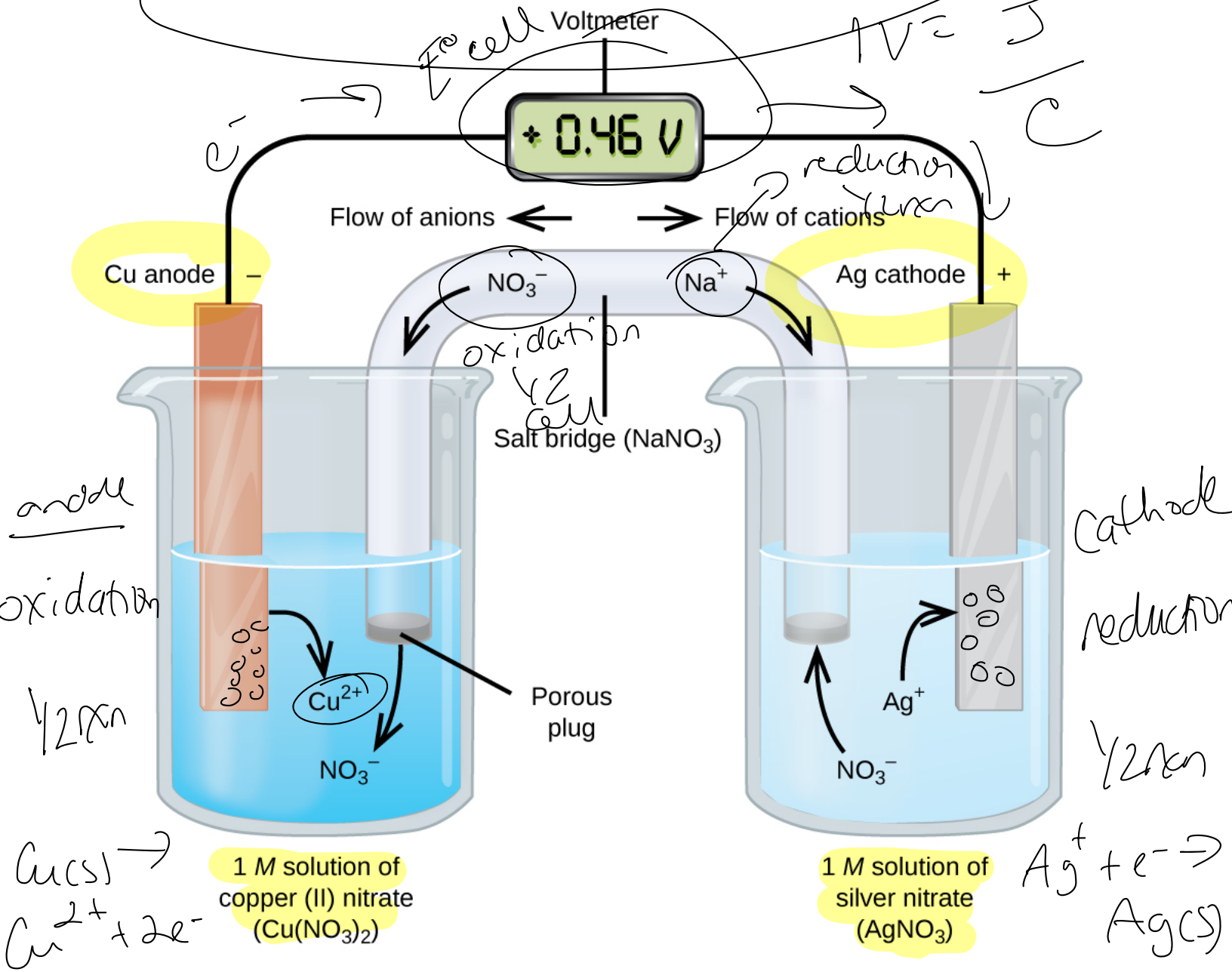
Simplify H_2O molecules

$SO_3^{2-} + 2Cu(OH)_2 \rightarrow$

$2Cu(OH) + SO_4^{2-} + H_2O$

Voltaic cell (chemical energy→electrical)

$Cu + 2Ag^+ \rightarrow Ag + Cu^{2+}$ (redox reaction)



Spontaneous process has a + voltage (Ecell) because

$\Delta G = -nFE$, where F is Faraday's constant 96 500 C/mol

How do we calculate E°_{cell}?

- 25.0°C
- 1.0 M solution

Cell Potential

- Measured in reference to a standard hydrogen electrode (SHE) that has an Ecell of 0

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

- The cell potential under standard conditions is called the **standard emf, $E°_{cell}$**.
  - 25 °C, 1 atm for gases, 1 M concentration of solution
  - Sum of the cell potentials for the half-reactions

Reduction reaction	E^θ / V
$Au^+ + e^- \rightarrow Au$	+1.69
$Au^{3+} + 3e^- \rightarrow Au$	+1.40
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0,92
$Hg^{2+} + 2e^- \rightarrow Hg$	+0,86
$Ag^+ + e^- \rightarrow Ag$	**+0,80**
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,77
$Cu^{2+} + e^- \rightarrow Cu+$	+0,16
$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
$Na^+ + e^- \rightarrow Na$	-2,71

intrinsic

voltaic cell

spon. redox reaction

$\Delta G = -nFE_{cell}$

Columbs

Calculating Cell Potentials under Standard Conditions

$\Delta G^\circ = -nFE^\circ$

n is the moles of e- in the redox rxn.

F is Faraday's constant 96,500 C/mole

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

anode → salt bridge ← cathode

Cu(s)|1MCu(NO3)2(aq)||1MAgNO3(aq)|Ag(s)

E°_{cell} @ 25°C & 1M aq. solutions

Voltaic (galvanic) cell E°cell is + (spontaneous redox rxn)

Electrolytic cell E°cell is – (non-spontaneous redox rxn)

b/c $\Delta G^\circ = -nFE^\circ_{cell}$

Full redox reaction

$$Cu(s) + 2Ag^{+}(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

½ reactions

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

cathode (+) $Ag^{+} + e^- \rightarrow Ag$

Calculate voltaic (spon)

$+E^\circ_{cell}$, $\Delta G < 0$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ ← from reduction table

cathode

E°_{cell} Ag^+ red: 0.80V

anode

E°_{cell} Cu^{2+} red: 0.34V

$E^\circ_{cell} = +0.80V - 0.34V$

$= E^\circ_{cell} = 0.46V$

overall rxn spontaneous

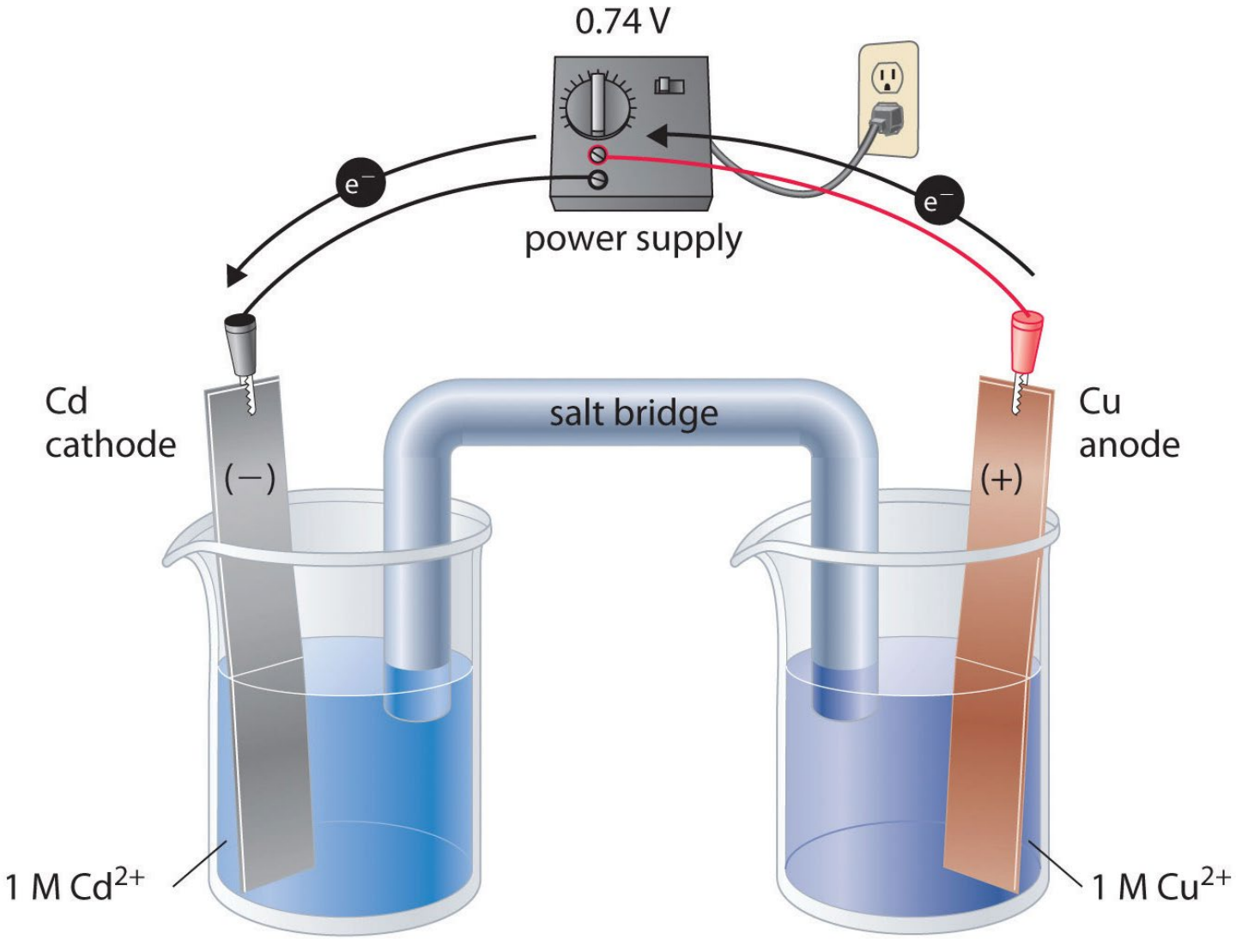
$\Delta G = -nFE^\circ_{cell}$

$\Delta G^\circ = -2\,\text{mol } e^- \left(96{,}500\,\frac{C}{\text{mol } e^-}\right)\left(0.46\,\frac{J}{C}\right)$

$\Delta G = -88{,}780\,J$

or $-88.8\,kJ$

Electrolytic Cells



cathode:
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$

anode:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Overall reaction: $Cd^{2+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2+}(aq)$

Electrolysis

- In electrolysis we use electrical energy to overcome the energy barrier of a nonspontaneous reaction, allowing it to occur.

- The reaction that takes place is the opposite of the spontaneous process.

  $2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l)$ spontaneous

  $2\ H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$ electrolysis

- Some applications are (1) metal extraction from minerals and purification, (2) production of H_2 for fuel cells, and (3) metal plating.

Deposition

- Example 1 : In the electrolysis of a solution of Ni^{2+} (aq), metallic Ni(s) deposits on a cathode. Using a current of 0.150 A for 12.2 min, what mass of nickel will form?

$F = 96,500 \frac{C}{mole^-}$

$Ampere\ (A) = \frac{C}{s}$

The Nernst Equation

- For a cell under non-standard conditions
- $E = E^{o} - (RT/nF) \ln Q$,
  - Where R is the gas law constant 8.314472 J/K mol, n is the number of moles of electrons transferred , F is the Faraday constant (9.6485338×10^{4} C/mol) , Q is the reaction quotient
  - RT/nFlnQ “corrects” the standard potential under non-standard conditions or concentrtations

E^o cell and the equilibrium constant (K)

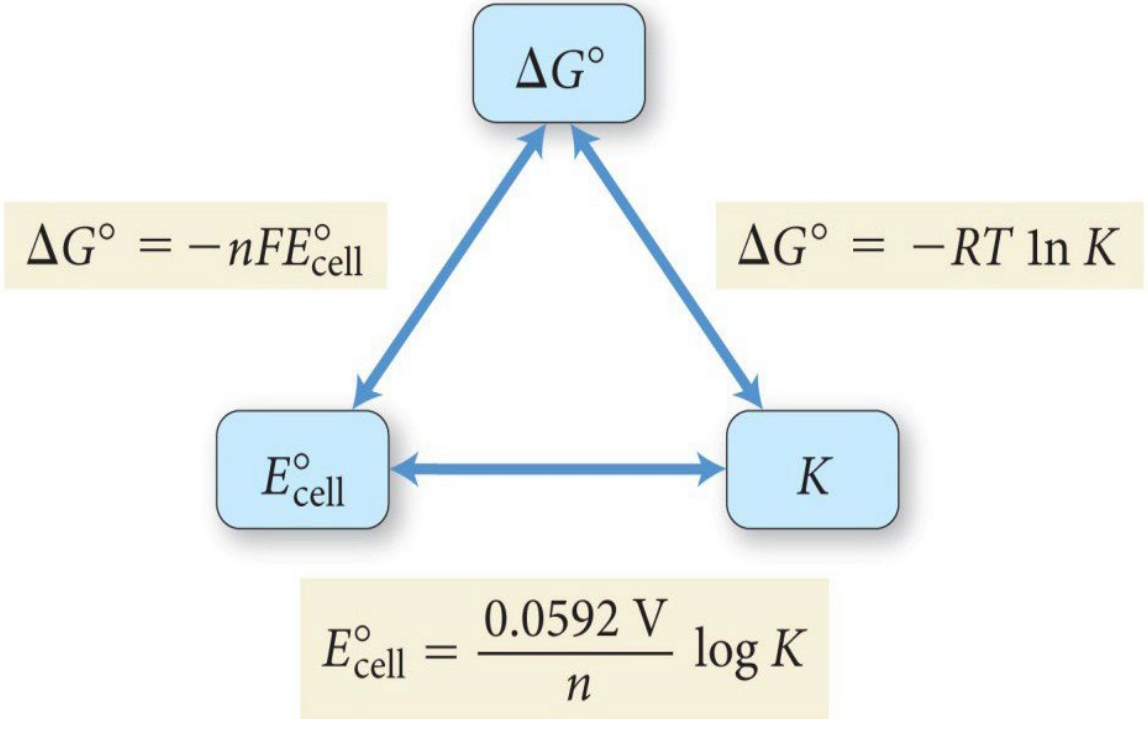
- When E cell = 0 , the reactants and products are at equilibrium , so Q = K
- Substituting the into the Nernst equation :

- $\ln K = nE^o/0.0257$ at 25ºC

ΔG and $E°_{cell}$

$\Delta G° = -nFE°_{cell}$

$E°_{cell}$, $\Delta G°$, and K



Ecell = - (0.0257/n) ln K