

Unit 1 – Deck 3

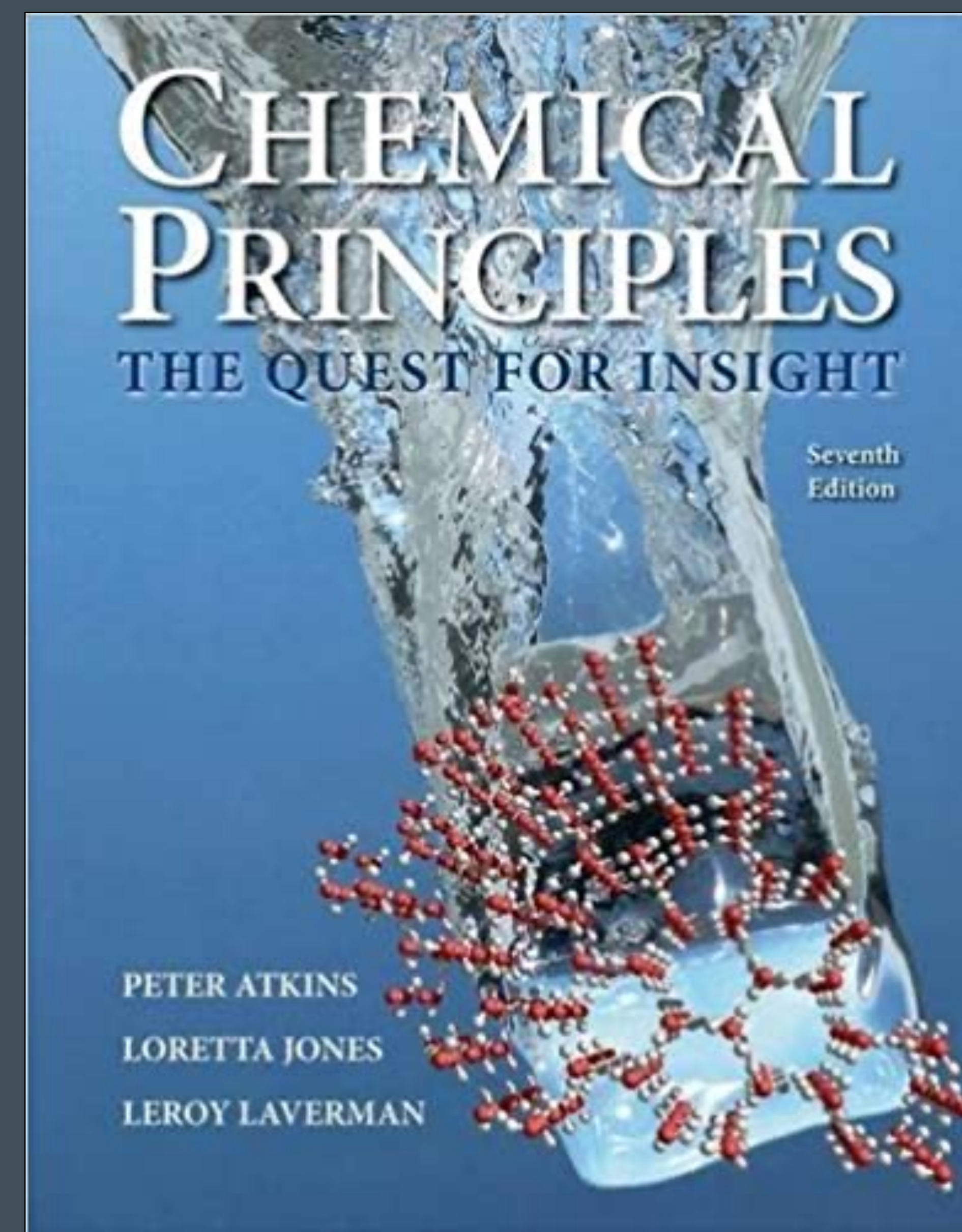
ELECTROCHEMISTRY

Electrochemical cells and their potentials



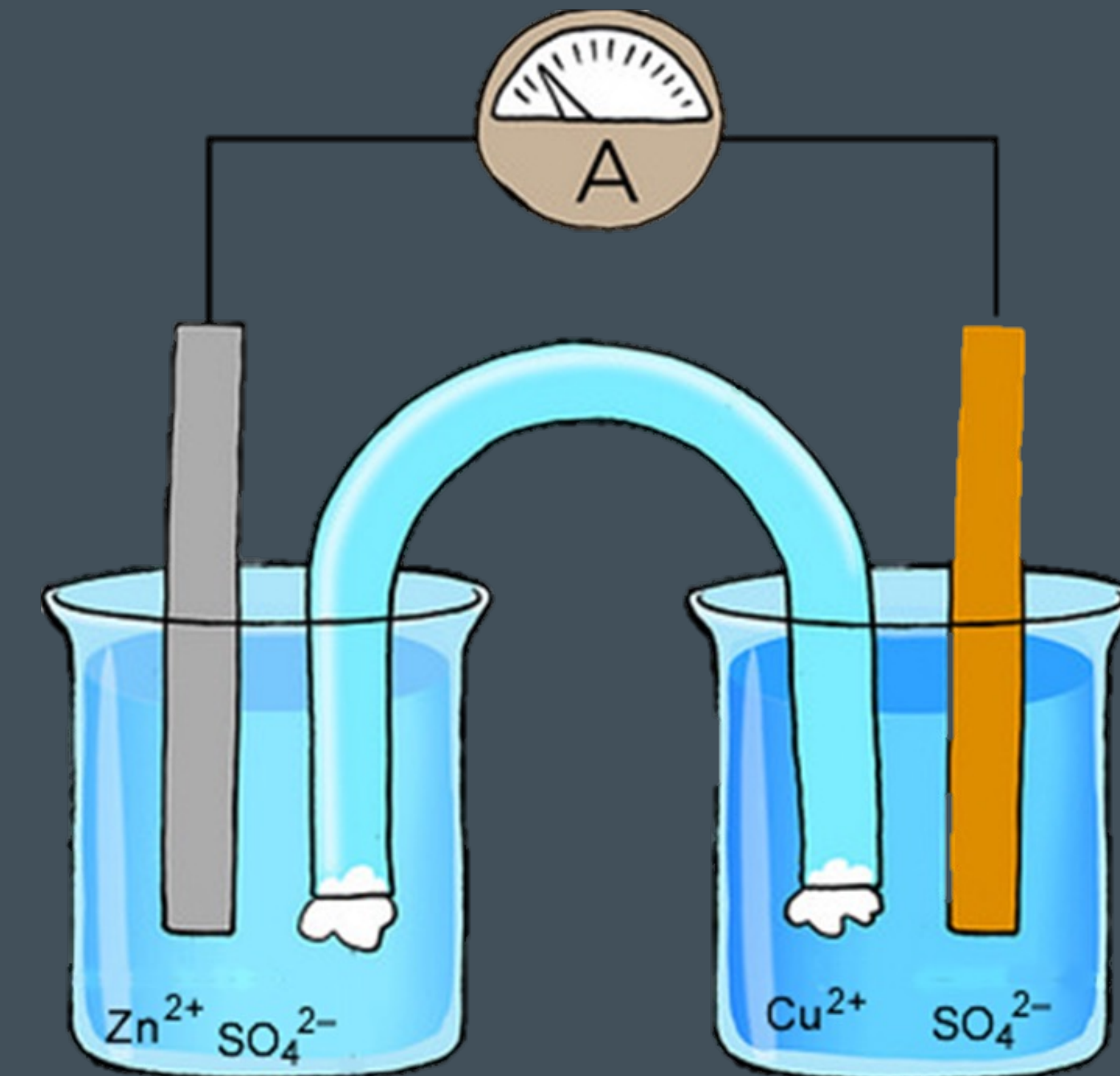
Unit 1 Reading

- ① *Chemical Principles*
by Atkins Jones & Laverman
Chapter K & 13
- ② *Inorganic Chemistry*
Housecroft & Sharpe
Chapter 8



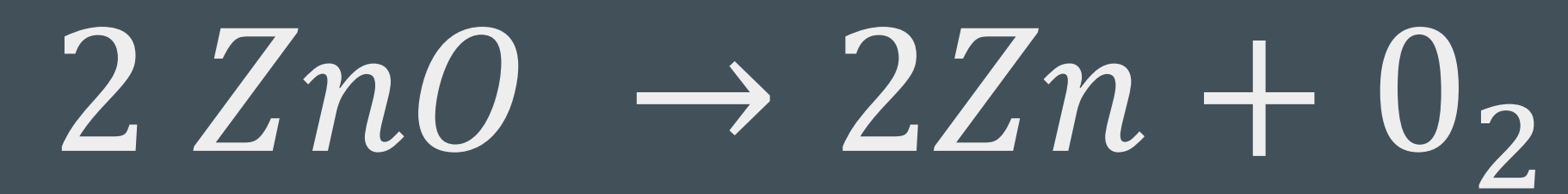
Topics

- ① Stoichiometry in electrochemical cells
- ② Galvanic and electrolytic cells
- ③ Standard electrode potentials
- ④ Calculating cell potentials
- ⑤ The microscopic view of a cell



Stoichiometry in electrochemical cells

How much (g) Zn
if you apply x amps for y hours?



1. Write the (and balance) the half reactions

2. Determine how much charge in mol e^- you have

F: 96485 C/mol

3. Use molecular mass and the stoichiometry of the half reactions to get grams of Zn

Electricity

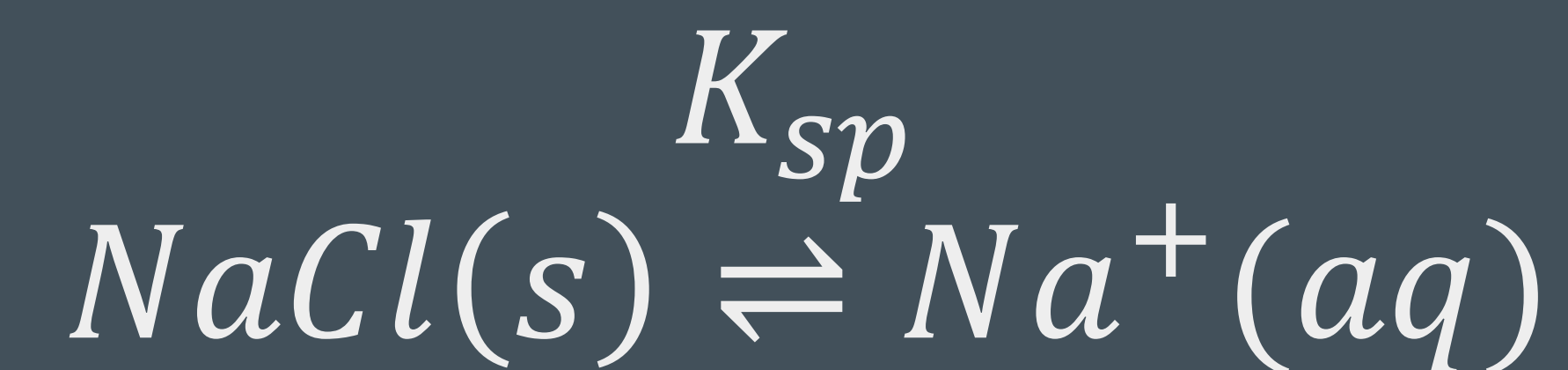
Electricity from electrons:

1. There are + and – charges
2. Charge much balance
3. Charge can flow like fluid
4. Current is measure of + flow
5. Charge flow through wires as e^-

Electricity from ions:

1. Molten Salt : NaCl @ 800 °C
2. Dissolved Salts

1885 - Svante Arrhenius



Electrochemistry

DEF: Interactions of molten salts/electrolyte solutions in an electric field

Charge: Property of subatomic particles p^+ and e^-

Unit = **Coulomb** (C)

$$1e^- = 1.6 \times 10^{-19} C$$

$$\times 6.022 \cdot 10^{23}$$


Faraday (F): 1 mol $e^- = 96485 C$

Current – the flow of electrons

Unit of Current : $C/s = A$ (Amp)

Engineering Units of Charge:

mAh (milliamp hour)

or

Ah (amp hour)

Voltage – Potential (V) ≠ Energy (J)

Unit of Potential: Volt (V) : J/C

$$\Delta G = -nFE$$

$$\text{Energy} = \text{Volts} \cdot \text{Charge}$$

Engineering Units of Energy:

Wh (watt-hour)

or

kWh (kilowatt-hour)

Watt is a unit of Power:

$$1 \text{ Watt (W)} = 1 \text{ J/s}$$

$$\text{Power} = \frac{\text{Energy}}{\text{time}}$$

$$\text{Charge} \quad 1 \text{ A h} = \frac{1 \text{ C h}}{\text{s}}$$

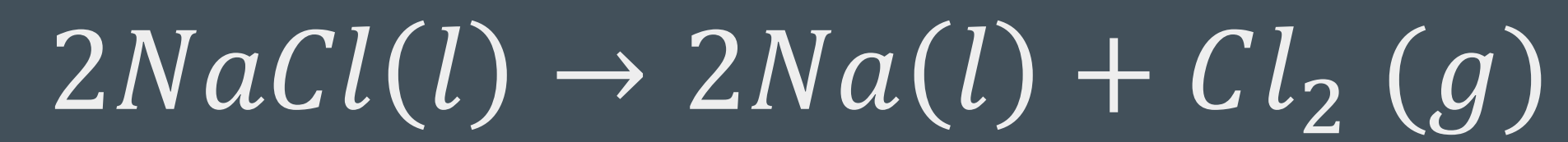
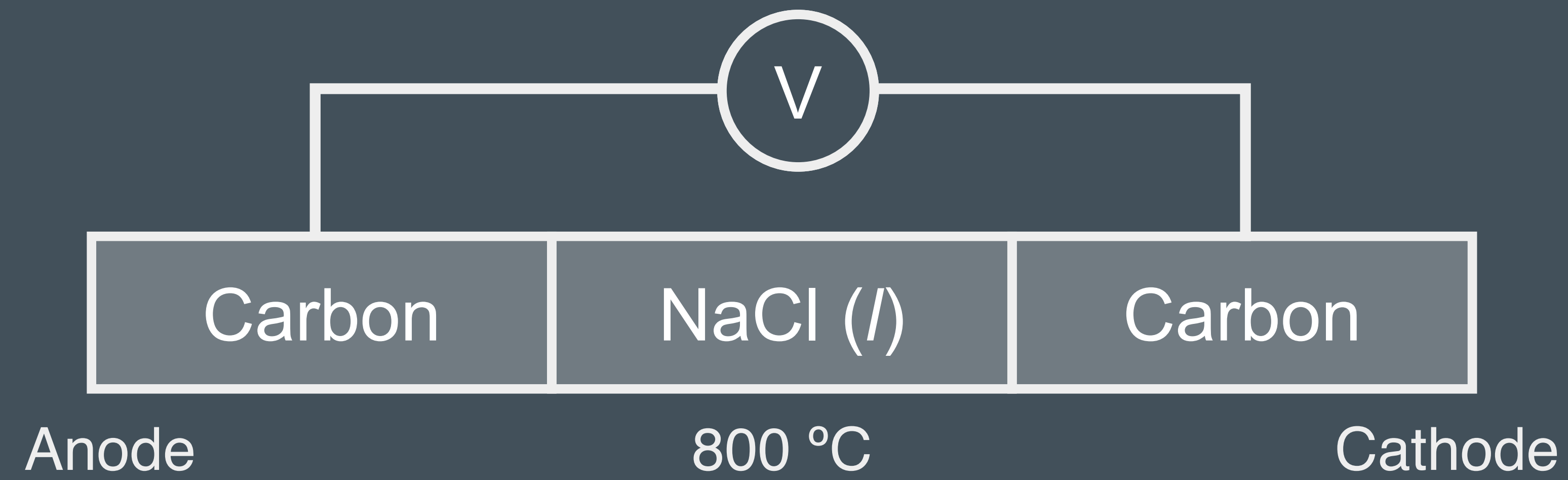
$$\text{Energy} \quad 1 \text{ V} * 1 \text{ A h} = \left(\frac{1 \text{ J}}{\text{C}}\right) \frac{1 \text{ C h}}{\text{s}} = \left(\frac{1 \text{ J}}{\text{s}}\right) (1 \text{ h}) = 1 \text{ Wh}$$

Electrochemical Potential

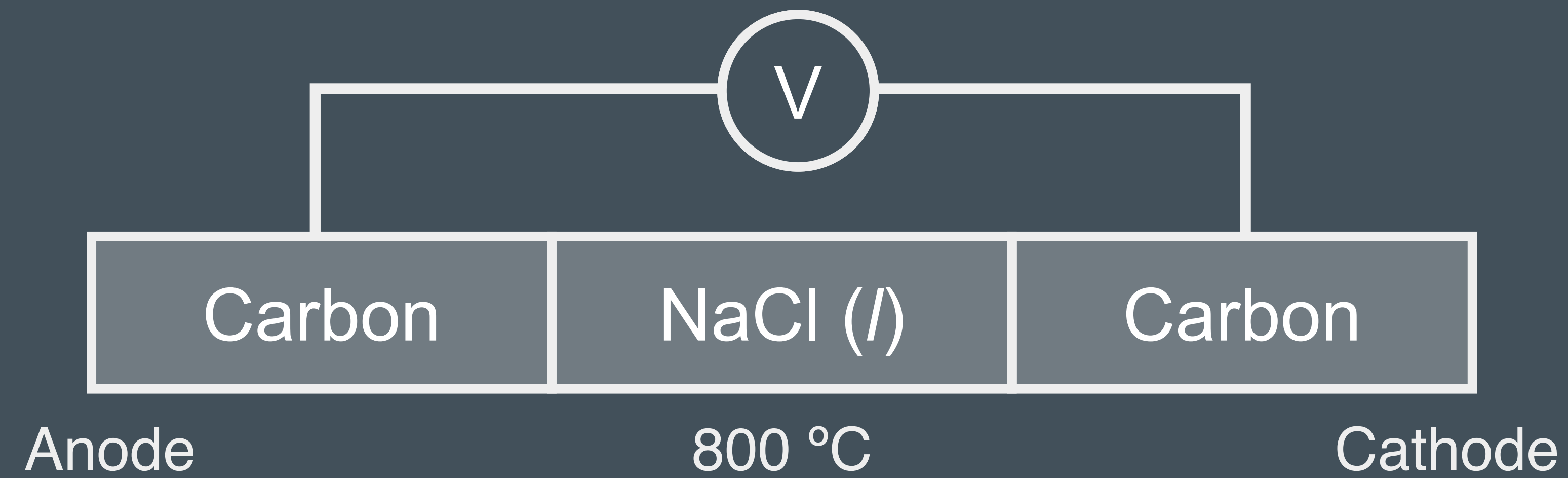
Electrochemical Potential : A voltage measured between two different electrodes in chemically distinct environments @ Zero Current (V_{oc})

Electrochemical potentials fall between _____ V and _____ V

Example: The Downs Process



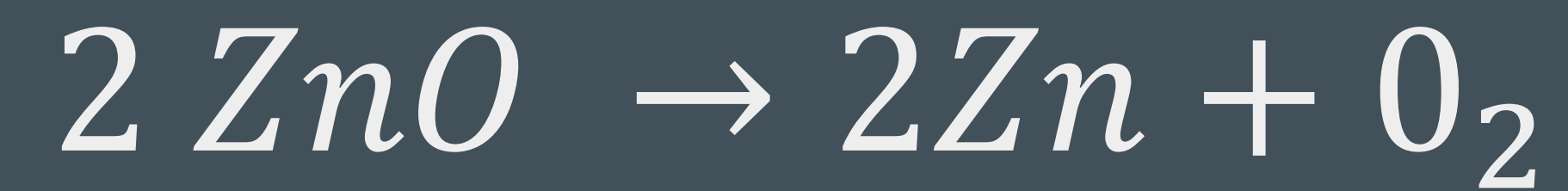
Example: The Downs Process



Question: If you push 10 A of current through the cell how long will it take you to make 23 g of Na?

Stoichiometry in electrochemical cells

How many hours to make x g Zn
if your cell is running at y amps?



1. Write the (and balance) the half reactions

2. Determine how much charge in mol e^- you need

F: 96485 C/mol

3. Convert mole e^- to Amp·hours, divide by given current to get time of reaction in hours

Poll: How much Ag can be deposited?



Your phone's battery has a charge capacity of 3.2 Ah. Converting this charge instead to make silver:



Ag: 107.9 g/mol

Cu: 63.5 g/mol

F: 96485 C/mol

how much silver, in grams, can be deposited. How much would be copper consumed?

Electrochemical cells under the hood

CONDUCTIVITY

OHM'S LAW

$$V = IR \quad V \propto I$$

$\frac{V}{A} = R \cdot \frac{I}{A}$



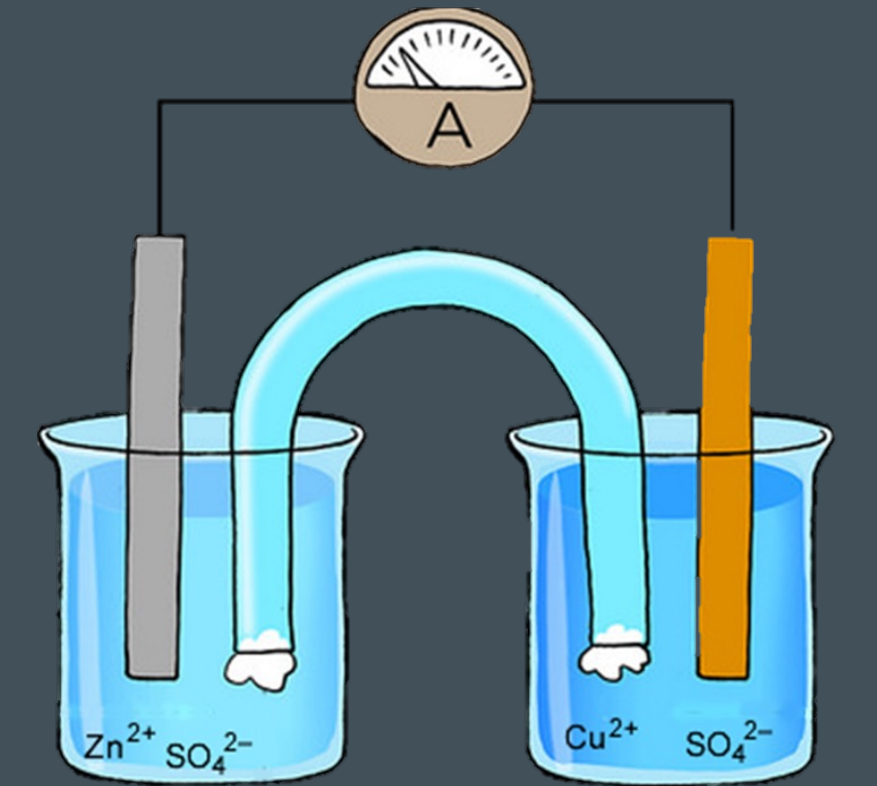
NORMALIZE TO DIMENSIONS
TO GET INTRINSIC PROPERTY
OF SOLUTION:

$$E = j \rho$$

$\frac{V}{cm} = \frac{A}{cm^2} \cdot \Omega \cdot cm$

CONDUCTIVITY $\sigma = 1/\rho \rightarrow \frac{1}{\Omega \cdot cm} = \frac{S}{cm}$ SIEMAN

HOW EASY IT IS
FOR A VOLTAGE
TO DRIVE CHARGE
THROUGH A SOLUTION
OR MATERIAL



Under the hood - Electrodes

Electrode *must* move electrons

① METALS - WIRES



e⁻ flow FREELY

ONLY SLOWED BY SCATTERING OFF ATOMS IN LATTICE.

"e⁻ gas"

100 S/cm

100,000 S/cm

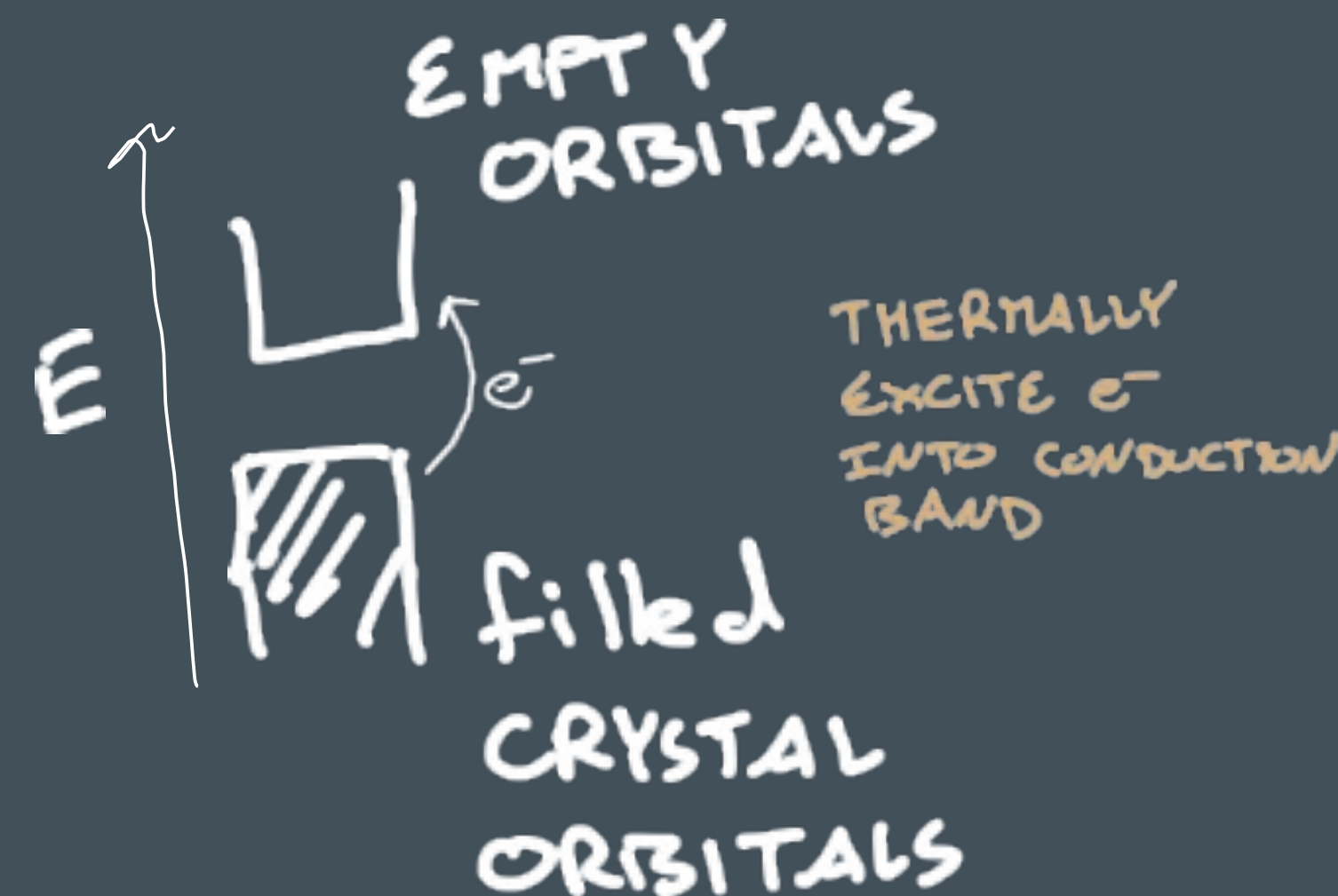
T ↑ σ ↓
σ is very HIGH

② SEMICONDUCTORS

ELECTRODES THAT ARE NOT METALS

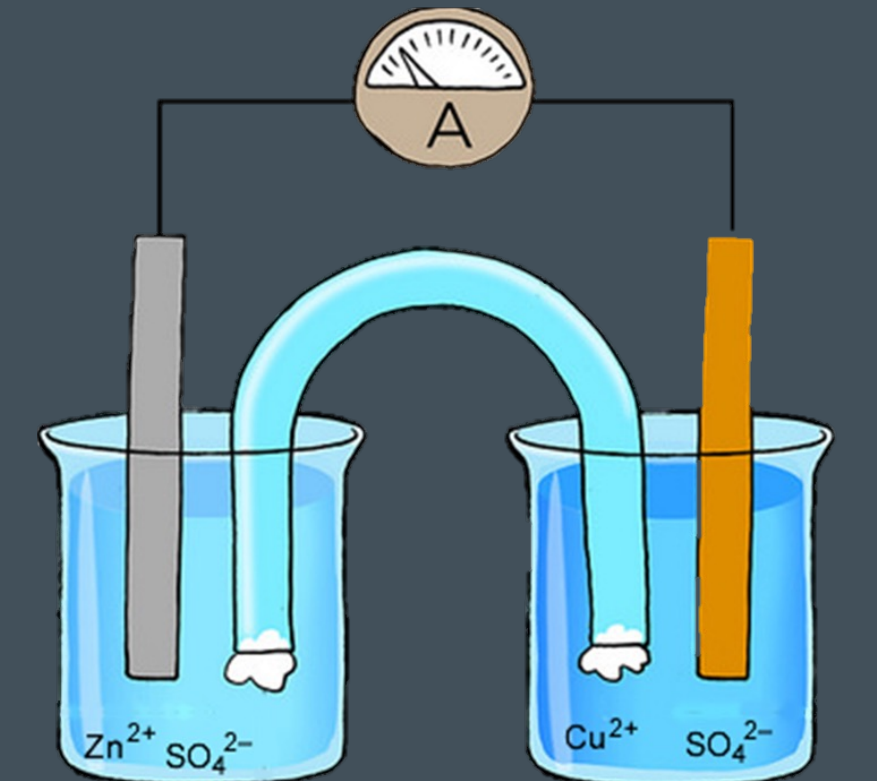
LiFePO₄ : 10⁻⁹ S/cm

Doped Si : 1 S/cm



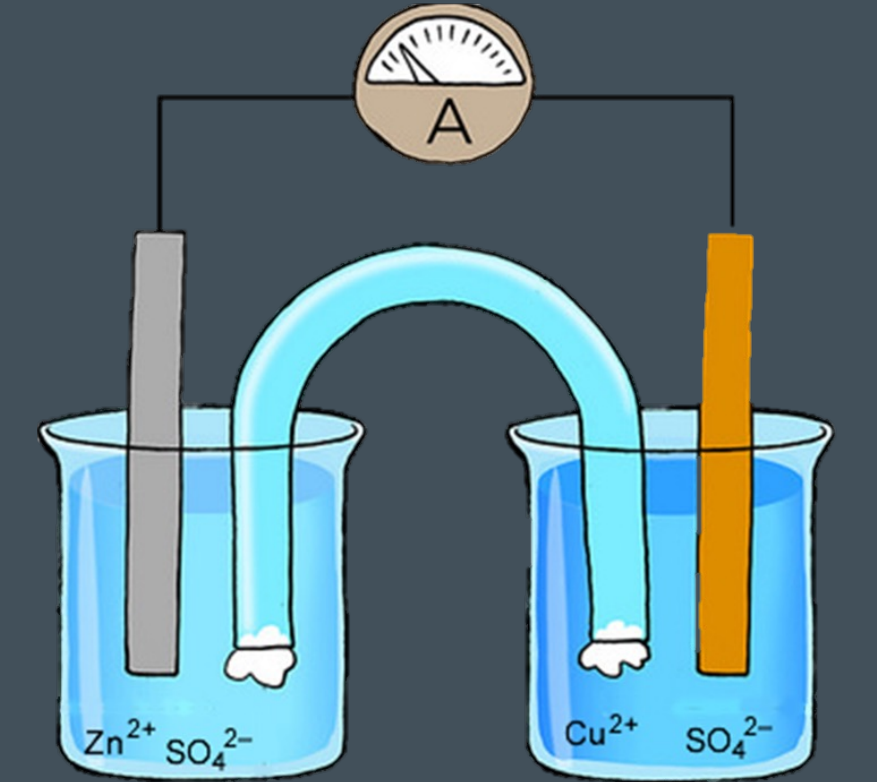
As T ↑ σ ↑

σ is LOW TO MODERATE



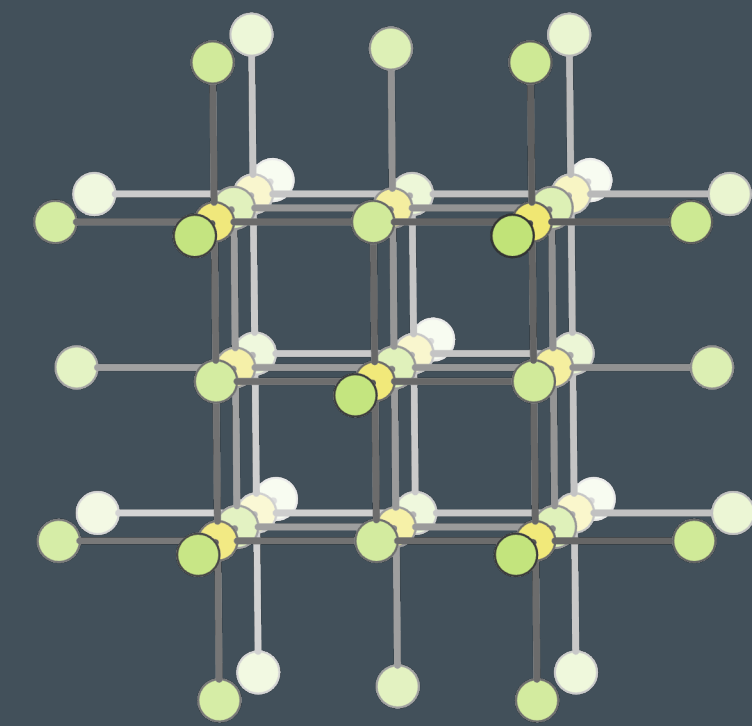
Under the hood - Electrolytes

Electrolytes *must* move ions and only ions



③ IONIC CRYSTALS

A STARTING POINT FOR DESCRIBING ION IN SOLUTION



HAPPENS CLOSE TO MELTING POINT OR IN RARE/SPECIAL MATERIALS VIA DEFECTS



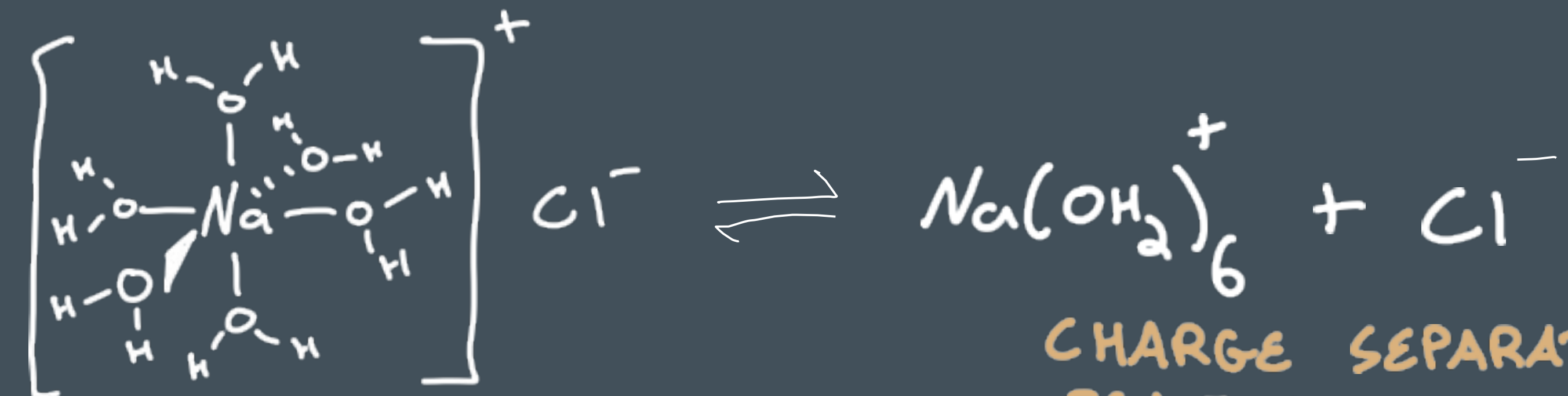
$$\sigma \uparrow \text{ as } T \uparrow$$

$$\sigma T = \sigma_0 e^{-E_A/RT}$$

10^{-5} to 10^{-1} S/cm

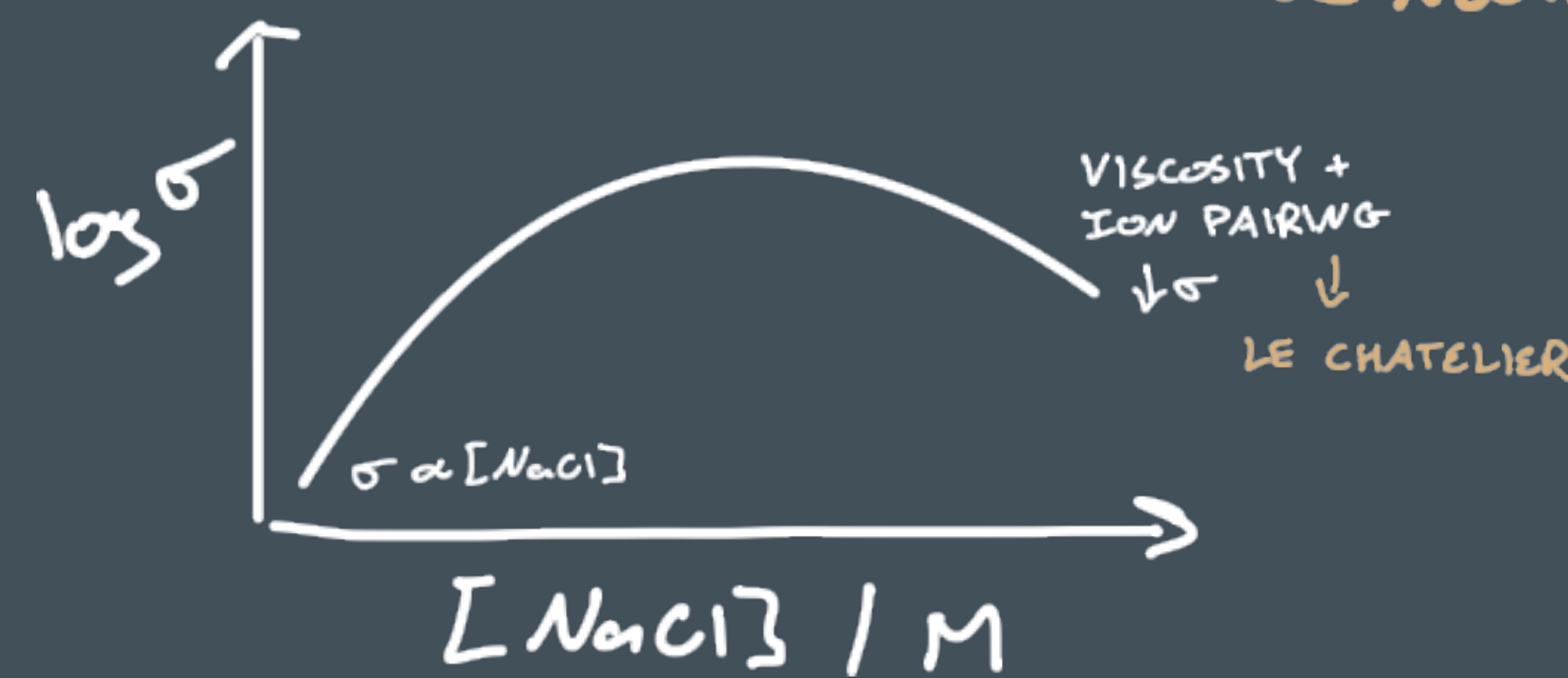
④ IONS IN SOLUTION

"ELECTROLYTES"
NaCl in H₂O



CHARGE SEPARATED
REACTS/MOVES IN E-FIELD

ELECTROSTATICALLY BOUND
"CONTACT ION PAIR"
INVISIBLE TO E-FIELD
APPEARS TO BE CHARGE NEUTRAL

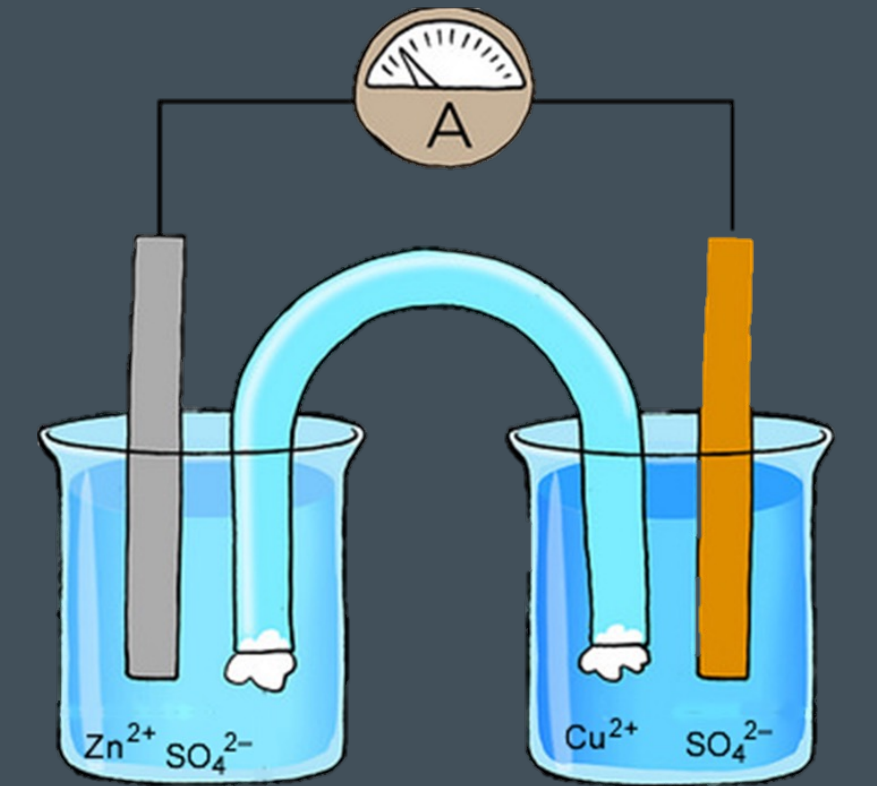


$$\sigma \uparrow \quad T \uparrow$$

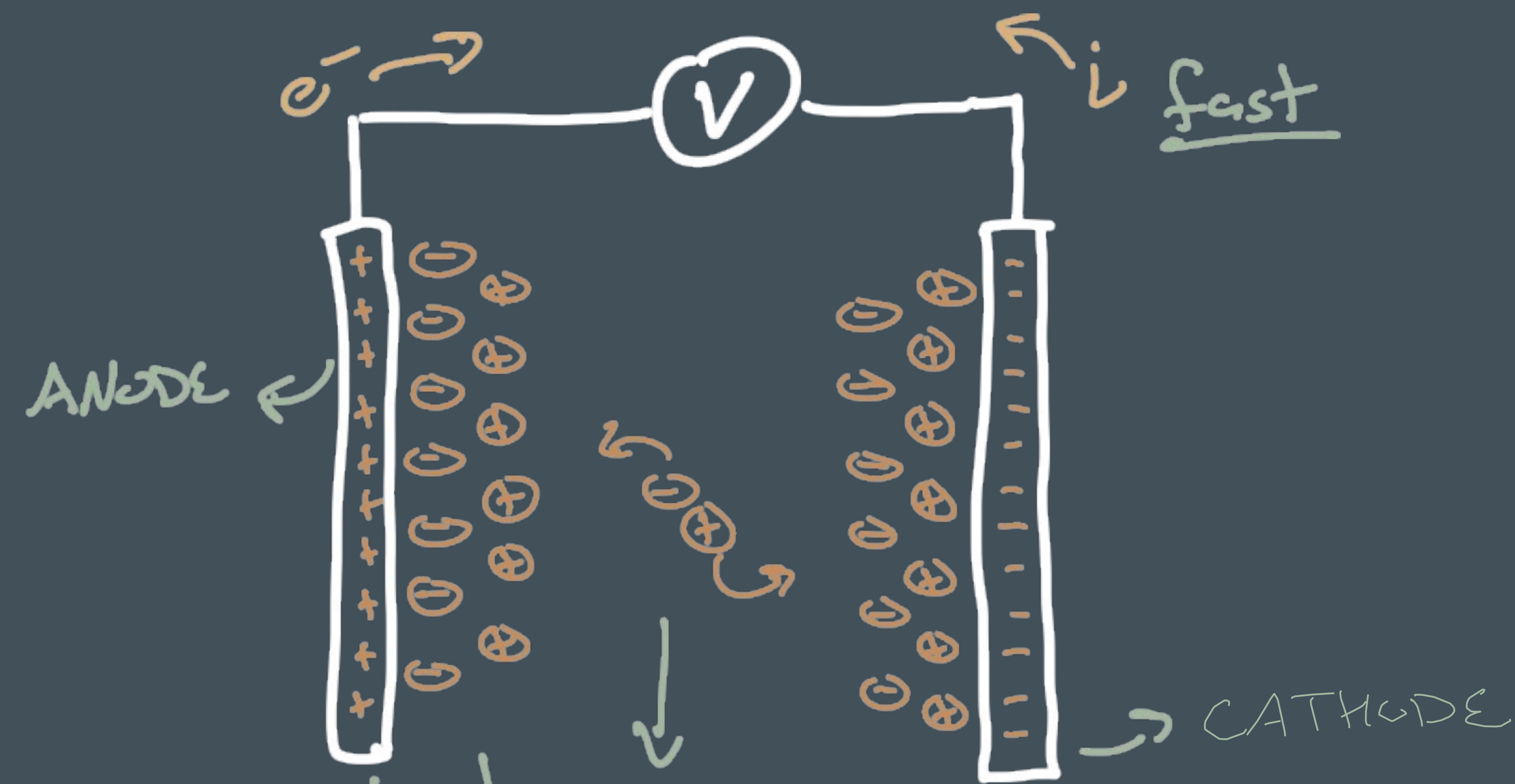
10^{-6} to 10^{-1} S/cm

Under the hood - Electrolytes

Electrolytes *must* move ions and only ions



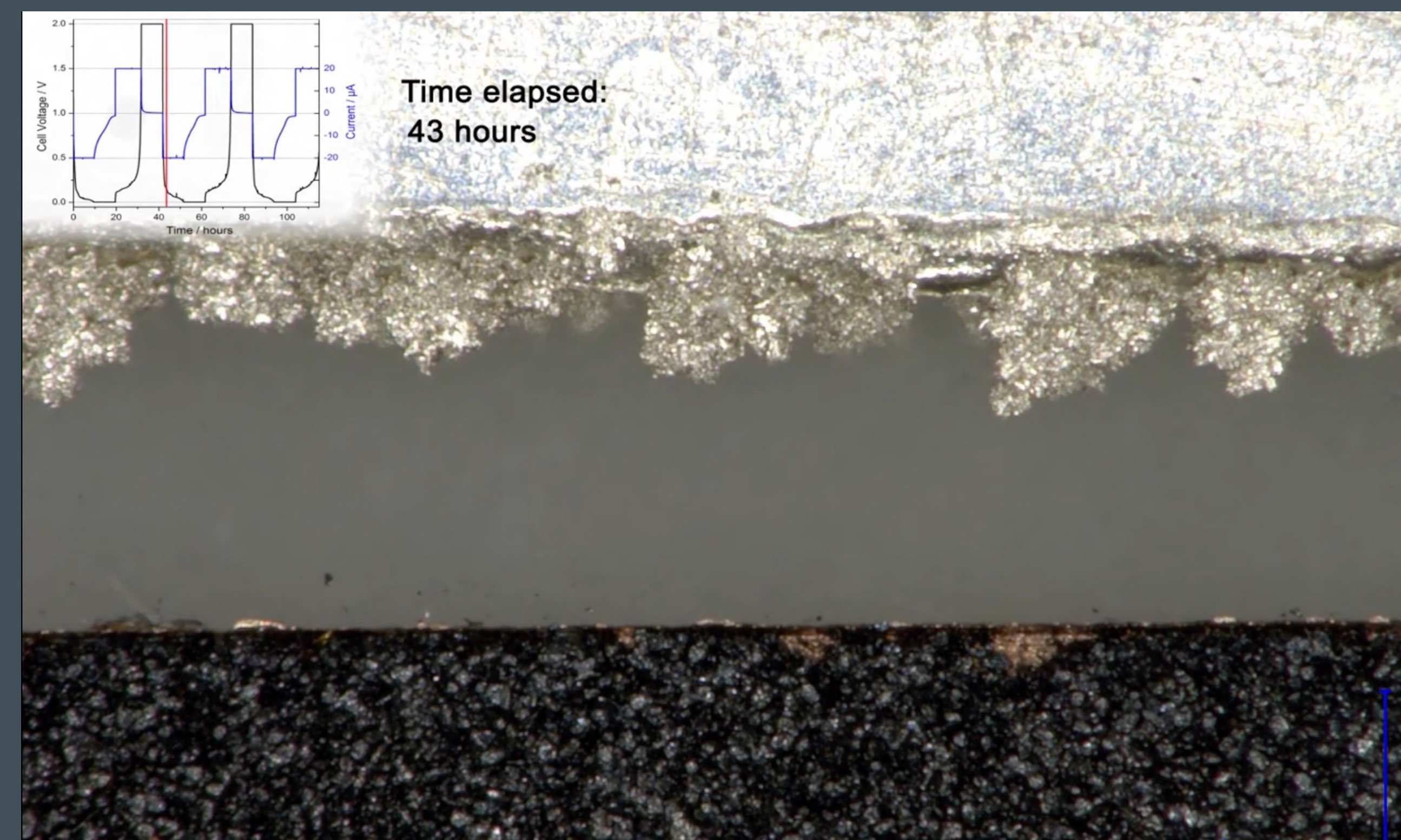
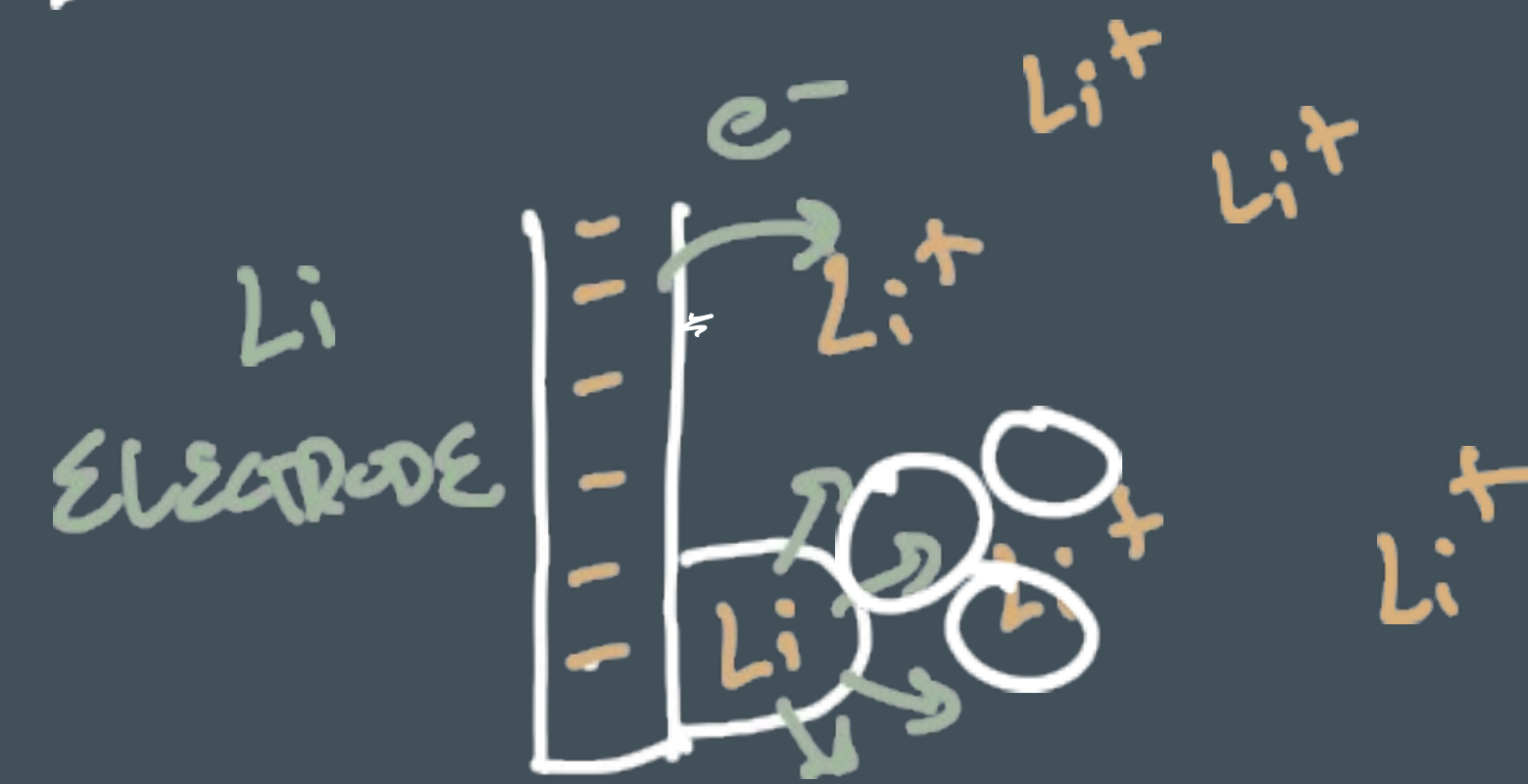
MOTION OF CHARGE IN A CELL



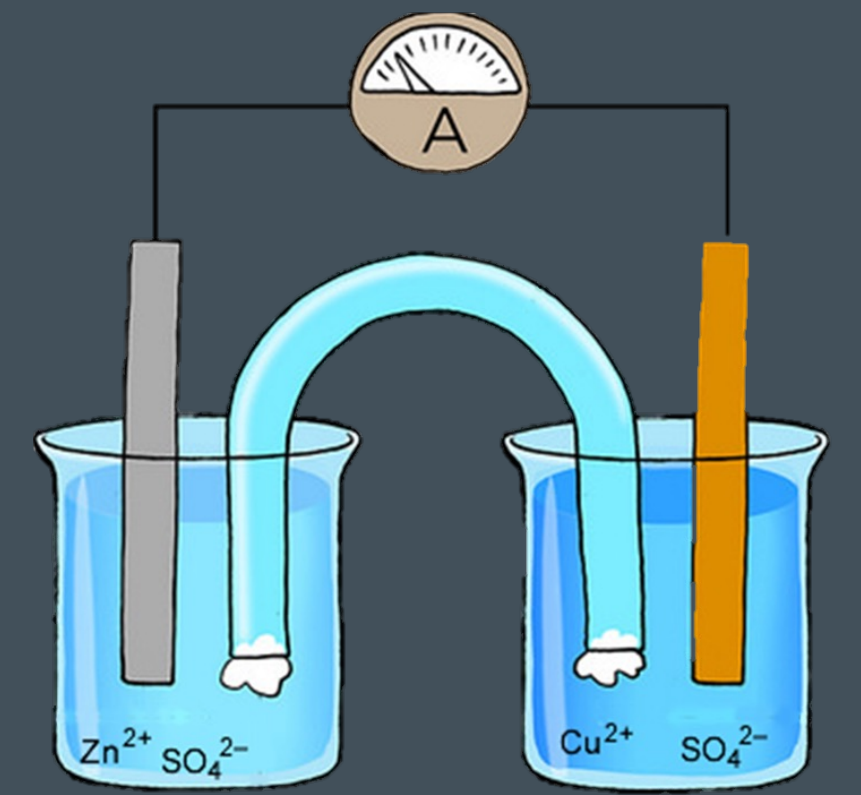
"ELECTRICAL DOUBLE LAYER"

ION'S SEPARATE, DIFFUSE AND POLARIZE THE SOLUTION

ORIGIN OF LITHIUM DENDRITES



Under the hood - Terminology



DEF **Electrochemical Cell** | A device that forces electrons through one path (circuit) and ions through another (electrolyte)

DEF **Metal** | Material in which electrons flow freely. Conductivity increases as temperature decreases

DEF **Semiconductor** | Material that conducts electrons but not freely. Need heat to conduct electrons (thermal excitation). Conductivity increases as temperature increases.

DEF **Ohm** | SI unit of resistance. Units of R in Ohm's law relating current observed to voltage applied ($V=IR$)

DEF **Siemen** | SI unit of conductivity equal to $1/\text{Ohm}$.

DEF **Conductivity** | A measure of how easy it is for charge (ionic or electronic) to flow through a material or solution $\sigma = \frac{1}{R}$

DEF **Contact Ion Pair** | A + and a - charged pair of ions that are in solution but electrostatically bond to one another and "appear" to be charge neutral in the presence of an externally applied voltage.

DEF **Electrical Double Layer** | The layer of ions right at an electrode surface under applied voltage that forms multiple layers of ions of opposite charges.

DEF **Dendrite** | Tree-like metallic structures that sometimes form when electrodepositing a metal in an electrochemical cell

Spontaneity in Electrochemical Cells

Galvanic cell

- A spontaneous redox reaction occurs and generates an electric current

Electrolytic cell

- A nonspontaneous reaction
- However, we can use an electric current to cause a chemical reaction to occur

Galvanic Cells

A Spontaneous Reaction



$$\Delta G = -nFE$$

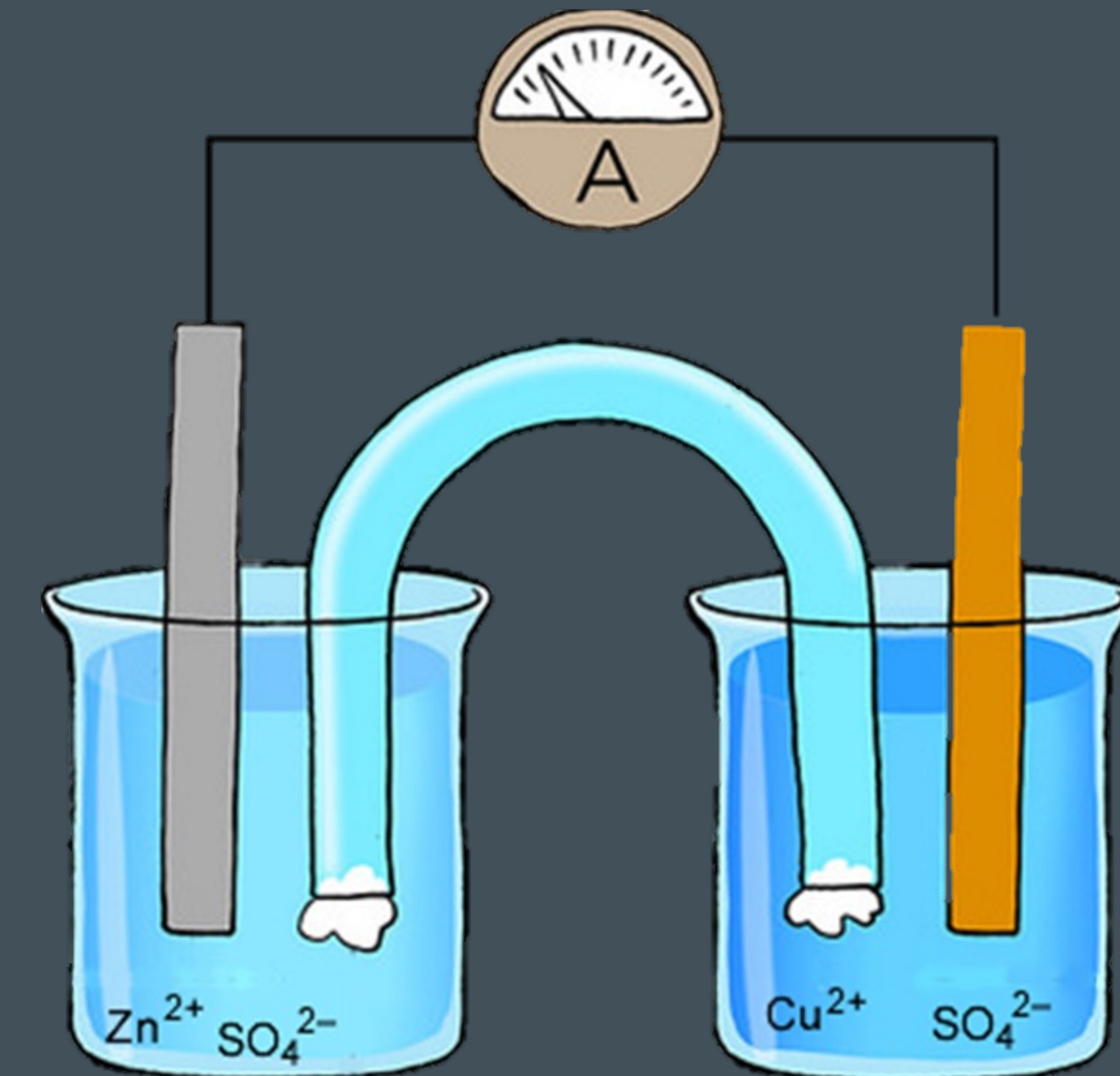
Recall: $\Delta G = \Delta H - T\Delta S$
 $\Delta G = -RT\ln(K_{eq})$

$n = \# e^-$ transferred (equiv)
 $F = 96485 \text{ C/mol}$
 $E = \text{Potential in units of } V = \text{J/C}$

Cell Potential

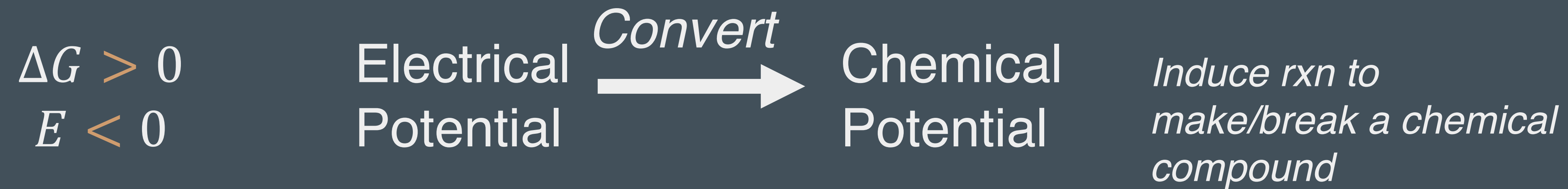
$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} \quad E^{\circ} \text{ defined for } \frac{1}{2} \text{ rxn's for interoperability}$$

If $E_{cell}^{\circ} > 0$ then *Spontaneous*



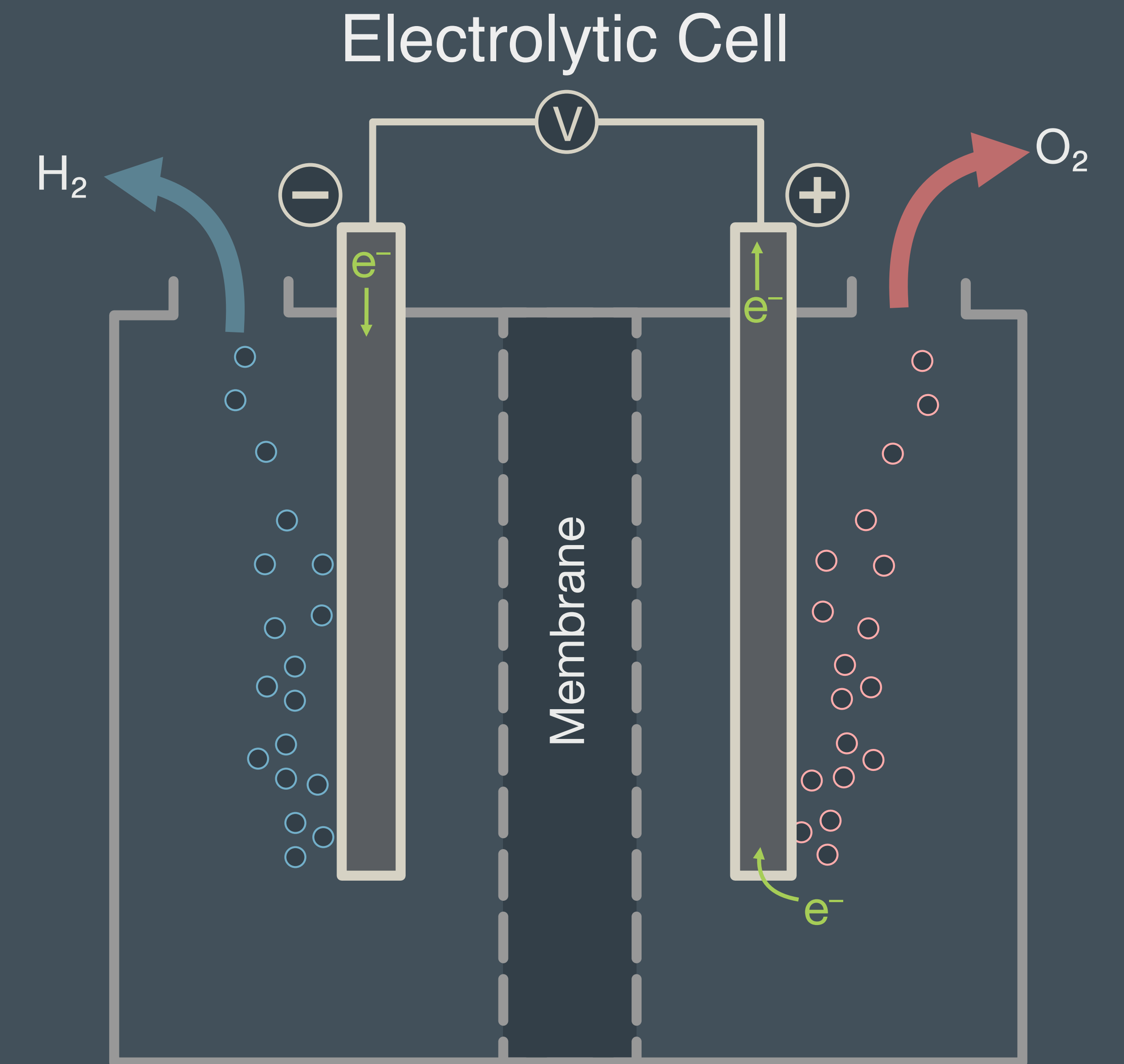
Electrolytic Cells

A Non-Spontaneous Reaction



Cell Potential

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$$



Galvanic vs. Electrolytic Cells

Galvanic cells are spontaneous reactions that generate electricity.
Electrolytic cells are galvanic cells being forced to run backward.

In both cases

- Oxidation occurs at the anode and reduction occurs at the cathode.
- Electrons flow from the anode to the cathode

Differences

- Galvanic: anode is (–), cathode is (+)
- Electrolytic: anode is (+), cathode is (–)

Summary

Galvanic cell (spontaneous)

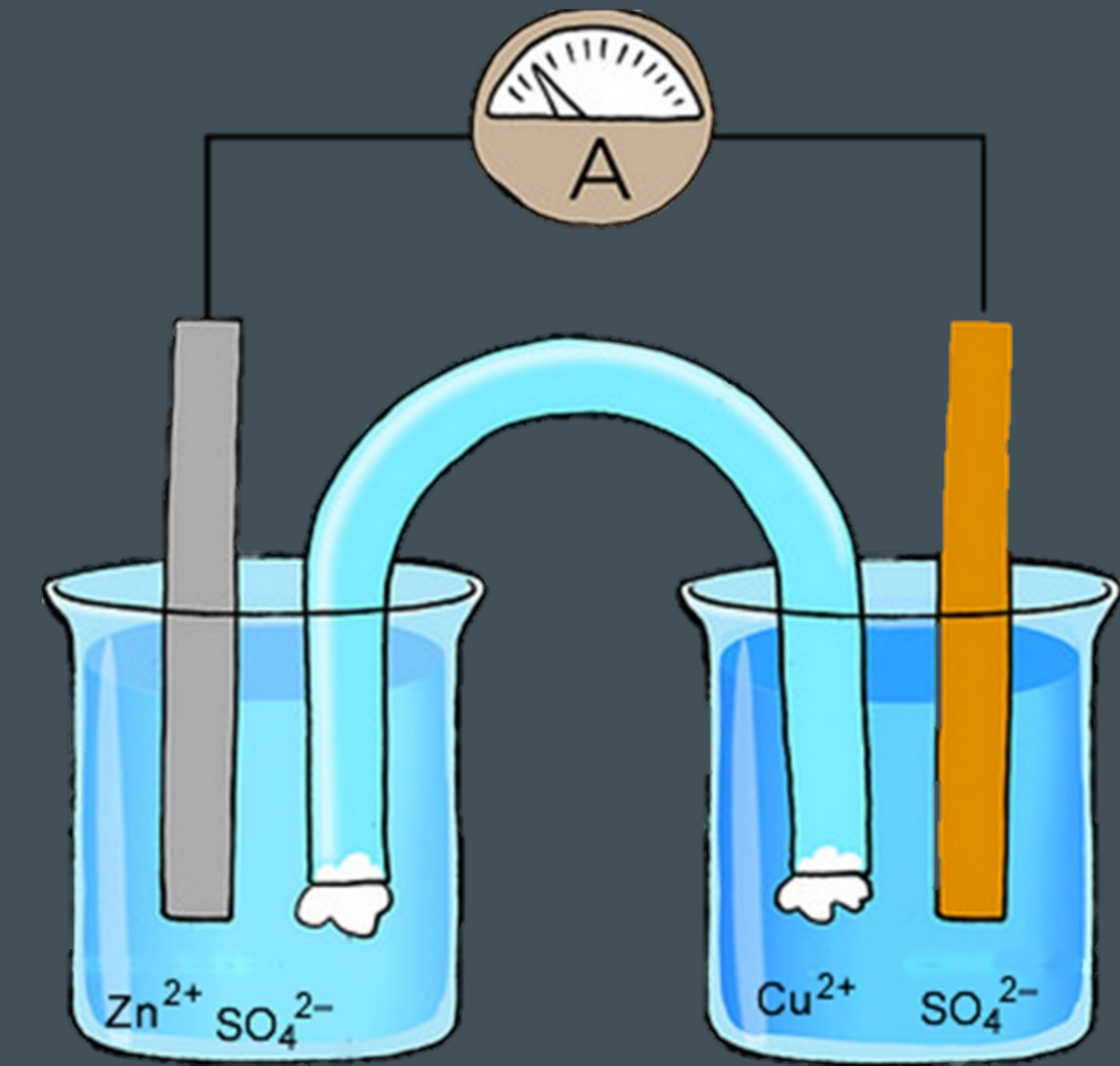
- E_{cell}° is positive
- ΔG° is negative
- $K > 1$

Electrolytic cell (nonspontaneous)

- E_{cell}° is negative
- ΔG° is positive
- $K < 1$

Free Energy of the Cell

Example: What is K_{eq} for the reaction?

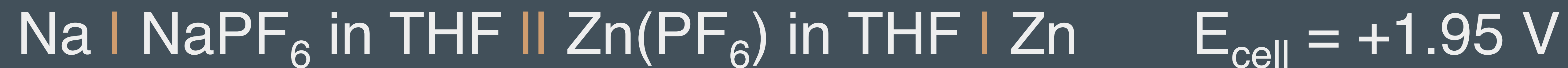


$$E_{cell}^{\circ} = 1.10 \text{ V}$$

Voltage and Equilibrium Constants



For the electrochemical cell below what is the equilibrium constant?



How Much Na is left once the reaction has reached equilibrium?



Standard Reduction Potentials

E° : A value for a half-reaction that corresponds to a single electrode

E°_{cell} : A value for a galvanic or electrolytic cell
(a combination of two E° values)

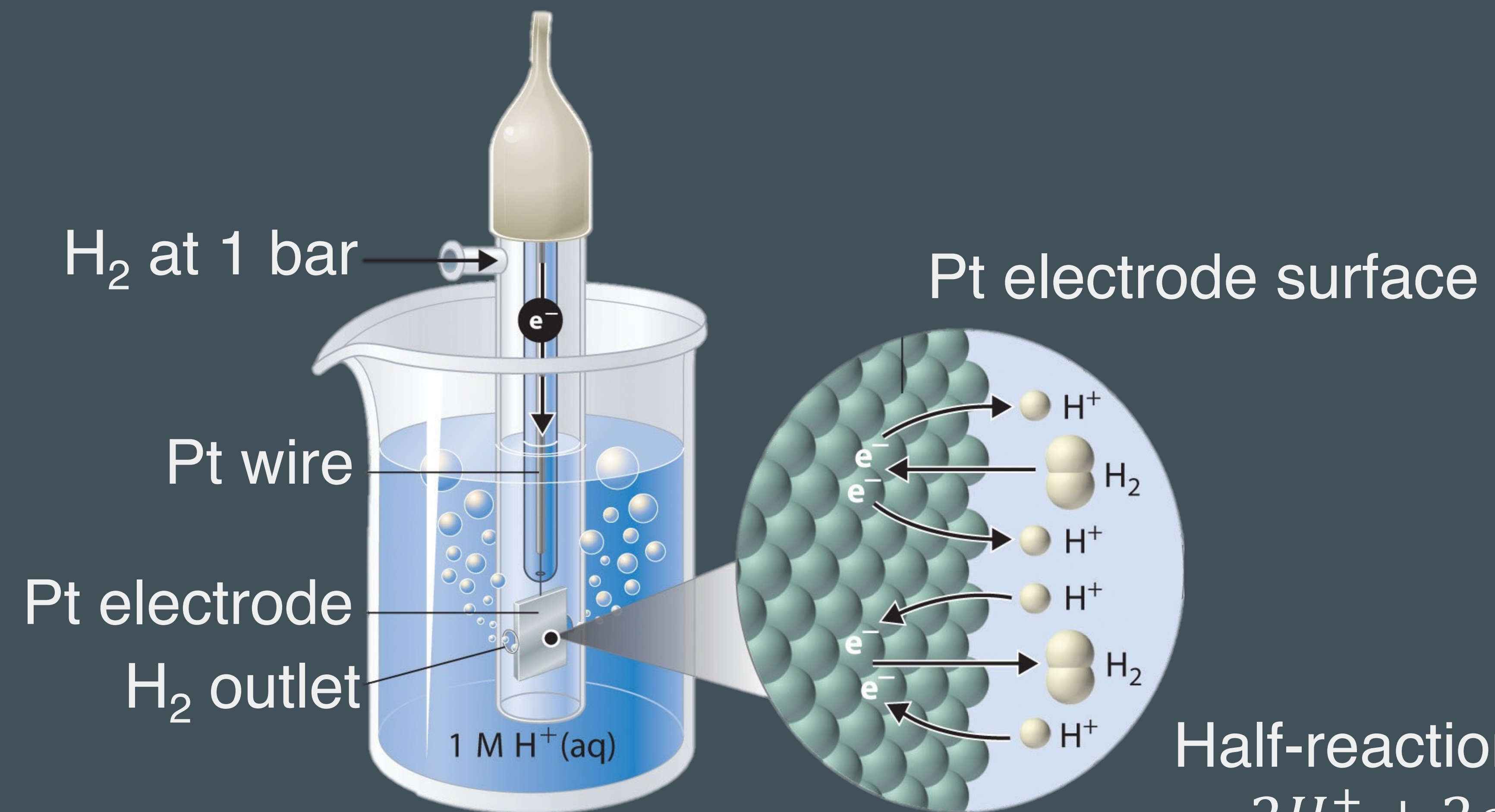
Standard Conditions

There are four standard conditions that you need to know:

- Temperature = 298 K
- Pressure = 1 bar
- Solutions = Aqueous & 1 Molarity
- Solids are in their standard state

Standard Hydrogen Electrode (SHE)

A platinum wire immersed in a 1M solution of hydronium ions



A sensible definition but impractical to measurement tool. Other simpler reference electrodes are more reliable.

Half-reaction at Pt surface
 $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$

Poll

Which is a stronger Reductant?

- Fe^{2+} or Pb^{2+} ?
- Ag or Zn ?

Which is a stronger oxidant?

- H^+ or Al^{3+}
- Cu^{2+} or Ag^+

For full table of standard potentials: Atkins Appendix 2B



	Half Reaction	Potential
Increasing strength of oxidant ↑	$\text{F}_2 + 2e^- \rightleftharpoons 2\text{F}^-$	+2.87 V
	$\text{Pb}^{4+} + 2e^- \rightleftharpoons \text{Pb}^{2+}$	+1.67 V
	$\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1.36 V
	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+0.80 V
	$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$	+0.77 V
	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+0.34 V
	$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0.00 V
	$\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe}$	-0.04 V
	$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	-0.13 V
	$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.44 V
	$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0.76 V
↓ Increasing strength of reductant	$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	-1.66 V
	$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2.36 V
	$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3.05 V

Calculating Cell Potentials

If you have 2 compounds from The Electrochemical Series you can determine:

The full balanced redox reaction & $\Delta E_{rxn} \rightarrow$ Spontaneity (galvanic vs electrolytic)

Compare the two half-reactions:

1. Identify the best oxidizing agent
2. Identify the reduction half-reaction
3. Flip the direction of the oxidation half-reaction. Make sure to flip the sign of the standard potential too!
4. Add the two potentials to determine the standard cell potential

Example



Calculate the standard cell potential for an electrochemical cell made from a standard hydrogen electrode half cell and a zinc half cell.





Question

Using a standard potentials, which of these reactions occurs spontaneously?



C. Neither

D. Both

2B STANDARD POTENTIALS AT 25°C

Potentials in Electrochemical Order

Reduction half-reaction	E° (V)	Reduction half-reaction	E° (V)
<i>Strongly oxidizing</i>			
$\text{H}_4\text{XeO}_6 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{XeO}_3 + 3 \text{H}_2\text{O}$	+3.0	$\text{NO}_3^- + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{NO}_2^- + 2 \text{OH}^-$	+0.01
$\text{F}_2 + 2 \text{e}^- \rightarrow 2 \text{F}^-$	+2.87	$\text{Ti}^{4+} + \text{e}^- \rightarrow \text{Ti}^{3+}$	0.00
$\text{O}_3 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07	$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$	0, by definition
$\text{S}_2\text{O}_8^{2-} + 2 \text{e}^- \rightarrow 2 \text{SO}_4^{2-}$	+2.05	$\text{Fe}^{3+} + 3 \text{e}^- \rightarrow \text{Fe}$	-0.04
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	+1.98	$\text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.08
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	+1.81	$\text{Pb}^{2+} + 2 \text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$	+1.78	$\text{In}^+ + \text{e}^- \rightarrow \text{In}$	-0.14
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69	$\text{Sn}^{2+} + 2 \text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{Pb}^{4+} + 2 \text{e}^- \rightarrow \text{Pb}^{2+}$	+1.67	$\text{AgI} + \text{e}^- \rightarrow \text{Ag} + \text{I}^-$	-0.15
$2 \text{HClO} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Cl}_2 + 2 \text{H}_2\text{O}$	+1.63	$\text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	+1.61	$\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$	-0.26
$2 \text{HBrO} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Br}_2 + 2 \text{H}_2\text{O}$	+1.60	$\text{Co}^{2+} + 2 \text{e}^- \rightarrow \text{Co}$	-0.28
$\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	+1.51	$\text{In}^{3+} + 3 \text{e}^- \rightarrow \text{In}$	-0.34
$\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$	+1.51	$\text{Tl}^+ + \text{e}^- \rightarrow \text{Tl}$	-0.34
$\text{Au}^{3+} + 3 \text{e}^- \rightarrow \text{Au}$	+1.40	$\text{PbSO}_4 + 2 \text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.36
$\text{Cl}_2 + 2 \text{e}^- \rightarrow 2 \text{Cl}^-$	+1.36	$\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$	-0.37
$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	+1.33	$\text{In}^{2+} + \text{e}^- \rightarrow \text{In}^+$	-0.40
$\text{O}_3 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{O}_2 + 2 \text{OH}^-$	+1.24	$\text{Cd}^{2+} + 2 \text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$	+1.23	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.41
$\text{MnO}_2 + 4 \text{H}^+ + 2 \text{e}^- \rightarrow \text{Mn}^{2+} + 2 \text{H}_2\text{O}$	+1.23	$\text{Fe}^{2+} + 2 \text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{ClO}_4^- + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	+1.23	$\text{In}^{3+} + 2 \text{e}^- \rightarrow \text{In}^+$	-0.44
$\text{Pt}^{2+} + 2 \text{e}^- \rightarrow \text{Pt}$	+1.20	$\text{S} + 2 \text{e}^- \rightarrow \text{S}^{2-}$	-0.48
$\text{Br}_2 + 2 \text{e}^- \rightarrow 2 \text{Br}^-$	+1.09	$\text{In}^{3+} + \text{e}^- \rightarrow \text{In}^{2+}$	-0.49
		$\text{Ga}^+ + \text{e}^- \rightarrow \text{Ga}$	-0.53

Next Time

Section 8.3

- Nernst Equation
- Tools and visualizations for analyzing cell potentials