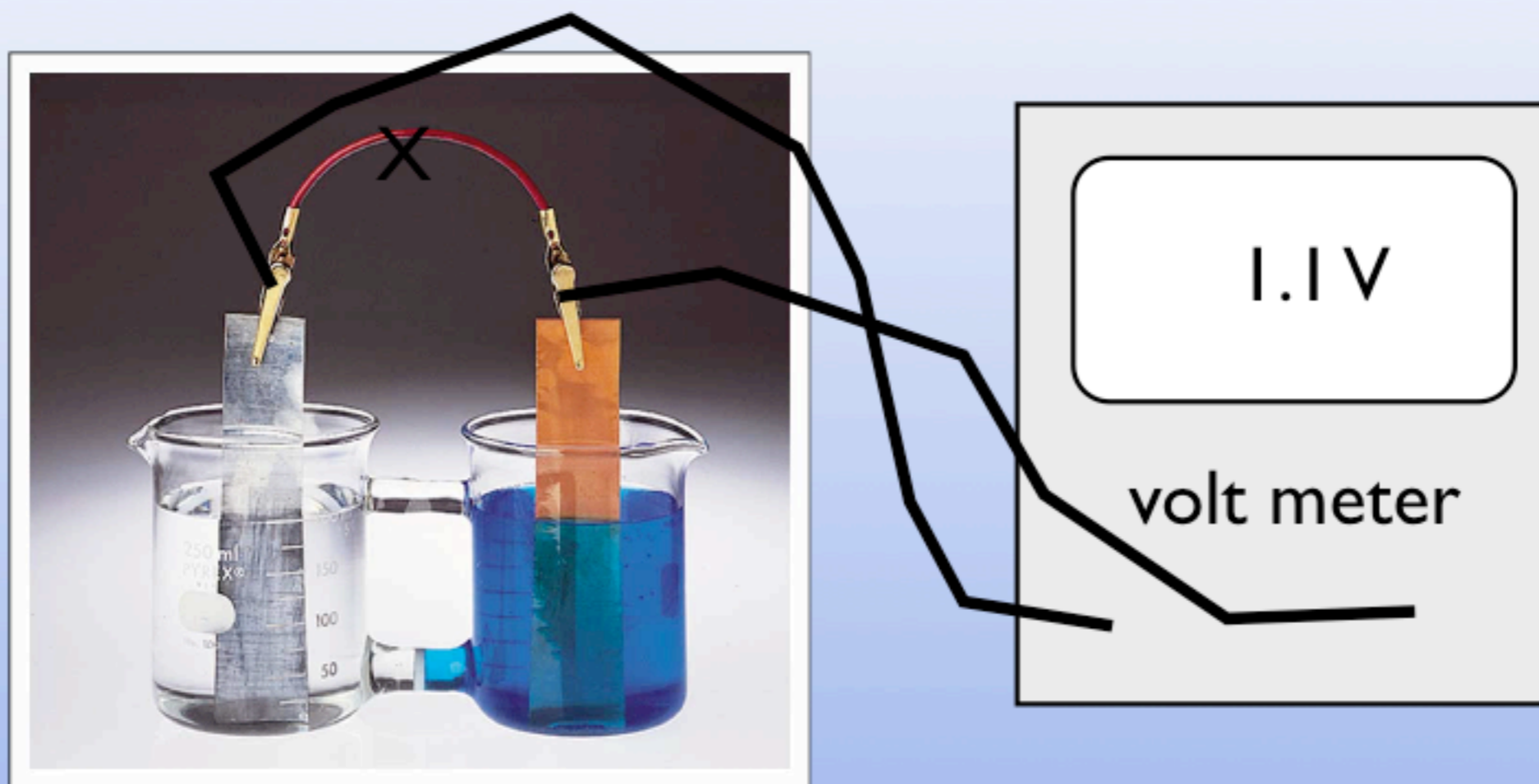# Today
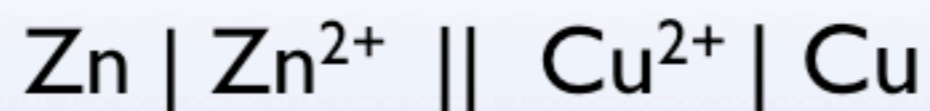
Voltage and Equilibria (again)
Batteries and Fuel Cells

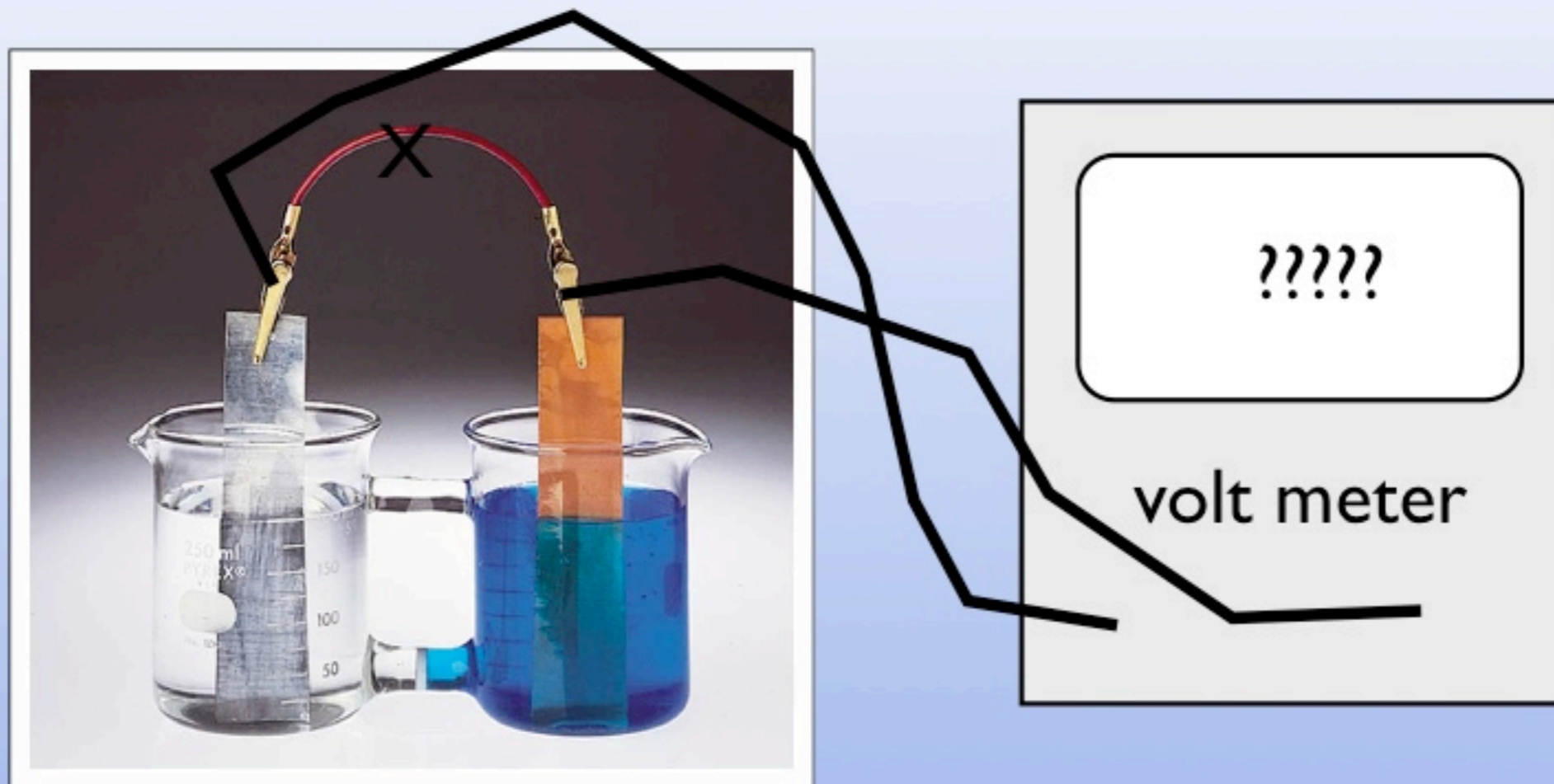## Electrolytic Cells

We'll look at standard concentrations

$$Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

1 M Zn^{2+} (aq) and 1 M Cu^{2+} (aq)
(note this is ridiculously concentrated)

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What about other concentrations?

$E \neq E^{\circ}$

X

?????

volt meter

$$[Zn^{2+}] \neq 1M \text{ and } [Cu^{2+}] \neq 1M \text{ ???}$$

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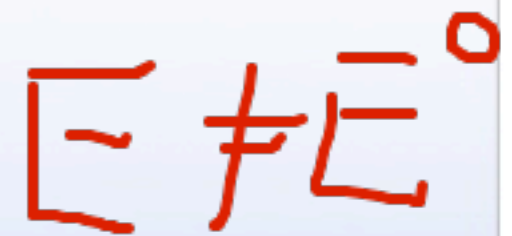
What is voltage for the following reaction at equilibrium?

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

A. 1.1 V

B. zero

C. -1.1 V

D. something between 0 and 1.1 V

What is voltage for the following reaction
if $[Cu^{2+}] = 10^{-4}$ M   and $[Zn^{2+}] = 1.9$ M

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

A. 1.1 V

B. zero

C. -1.1 V

D. something between 0 and 1.1 V

start @ std (1.1 v)

moving → equil

we really need to know K

Relationship between E and ΔG

$$\Delta G = - \text{charge} \times E$$

$$\Delta G = - nFE$$

mole é
per mole rxn

Potential
Voltage
EMF

Free
Energy

charge
of 1 mol
e⁻

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Other concentrations and equilibrium
Let's remember equilbrium!

$$\Delta G = \Delta G° + RT\ln Q$$

at equilibrium $\Delta G = 0$

so $\Delta G° = -RT\ln K$

$$-nFE = -nFE° + RT\ln Q$$

$$E = E° - \frac{RT}{nF}\ln Q$$

assume 25°C

$$E = E° - \frac{0.0591}{n}\log Q$$

R;F T=298K

log!

NERST EQUATION

What about other concentrations?
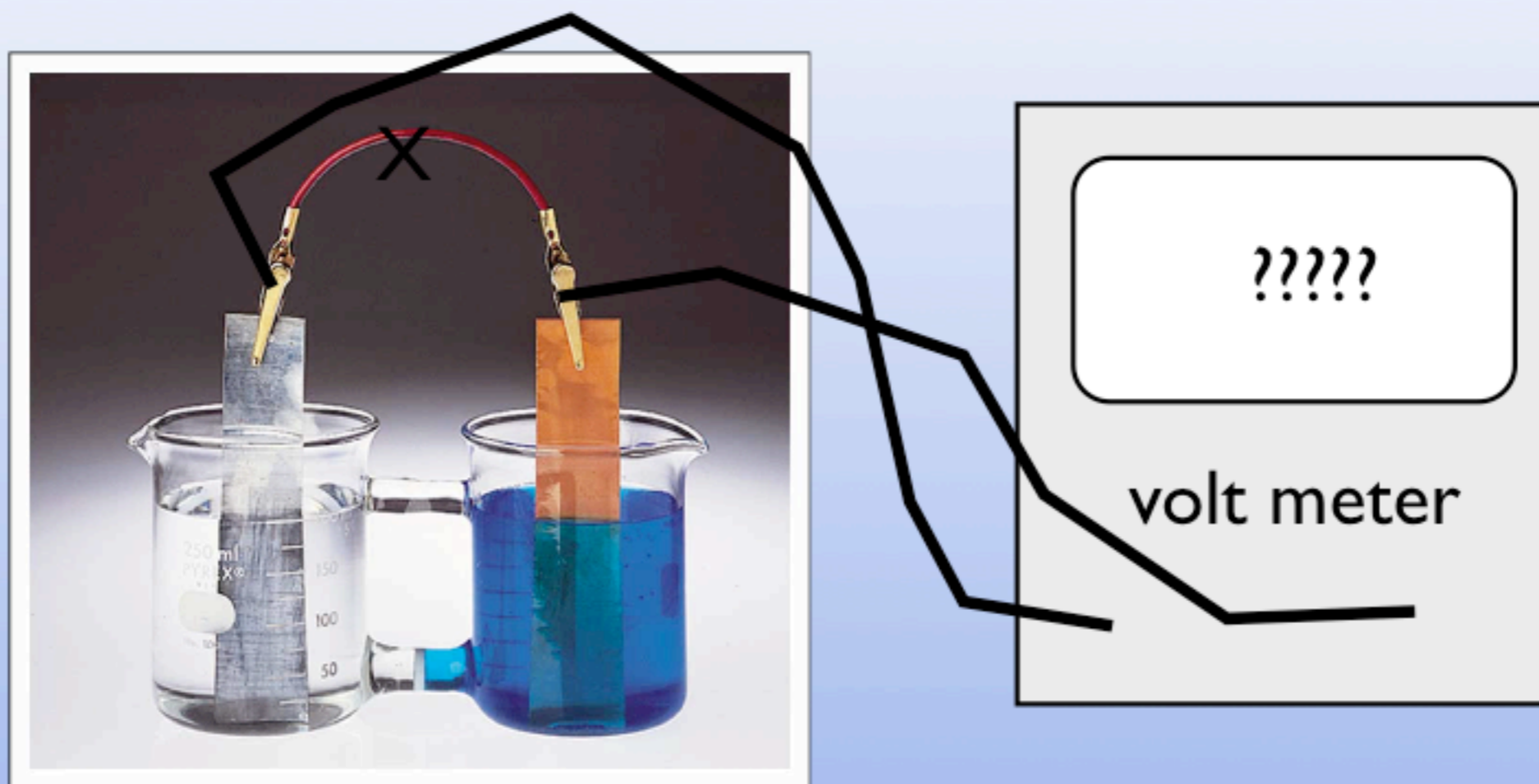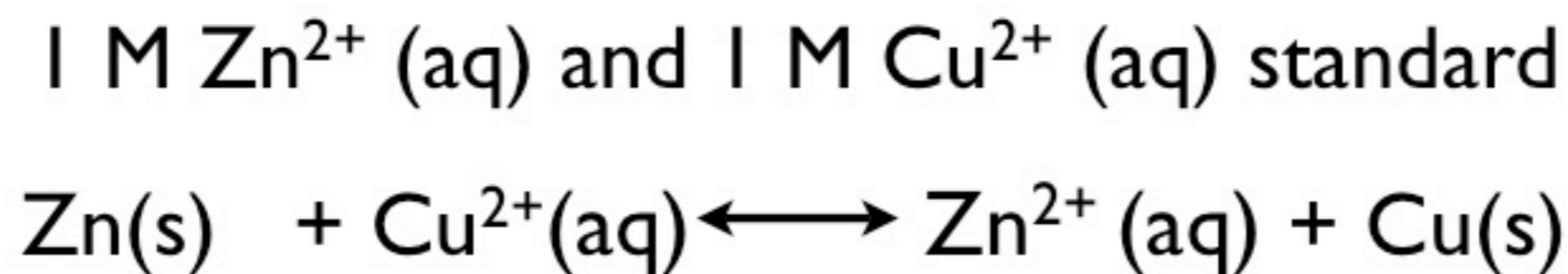
X

?????

volt meter

10^{-3} M Zn^{2+} (aq) and 10^{-1} M Cu^{2+} (aq) ???

1 M Zn^{2+} (aq) and 1 M Cu^{2+} (aq) standard

$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{1} = 1$$

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

this is std

$$\therefore E = E^\circ$$

$$E = 1.10V - \frac{0.0591}{2} \log(1) = 1.10V$$

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$$10^{-3} \text{ M } Zn^{2+} \text{ (aq) and } 10^{-1} \text{ M } Cu^{2+} \text{ (aq) } ???$$

$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$
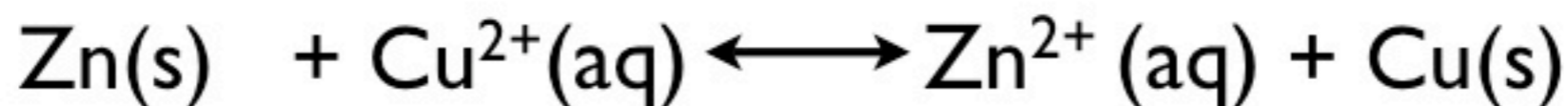
$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{(10^{-3})}{(10^{-1})} = 10^{-2}$$

more

R than ?

E > E°

$$E = E° - \frac{0.0591}{n} \log Q$$

$$E = 1.10\,V - \frac{0.0591}{2} \log(10^{-2}) = 1.16\,V$$

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$$E = E° - \frac{0.0591}{n} \log Q$$

Current will flow until E = 0
Equilibrium

$$E° = + \frac{0.0591}{n} \log K$$

$$\log K = \frac{nE°}{0.0591}$$

What will happen to the voltage if I lower the Zn^{2+} concentration?

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

A.   the voltage will increase

B.   the voltage will decrease

C.   the voltage will stay the same

$R\uparrow$ or $P\downarrow$ $E\uparrow$
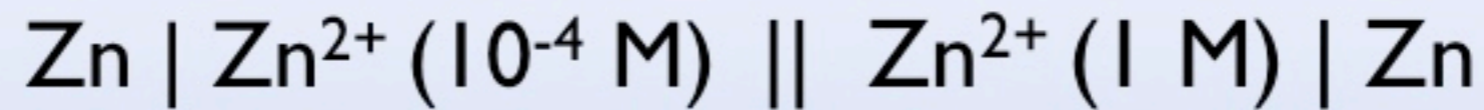
$R\downarrow$ or $P\uparrow$ $E\downarrow$

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What about this cell?

$$Zn \mid Zn^{2+} \parallel Zn^{2+} \mid Zn$$
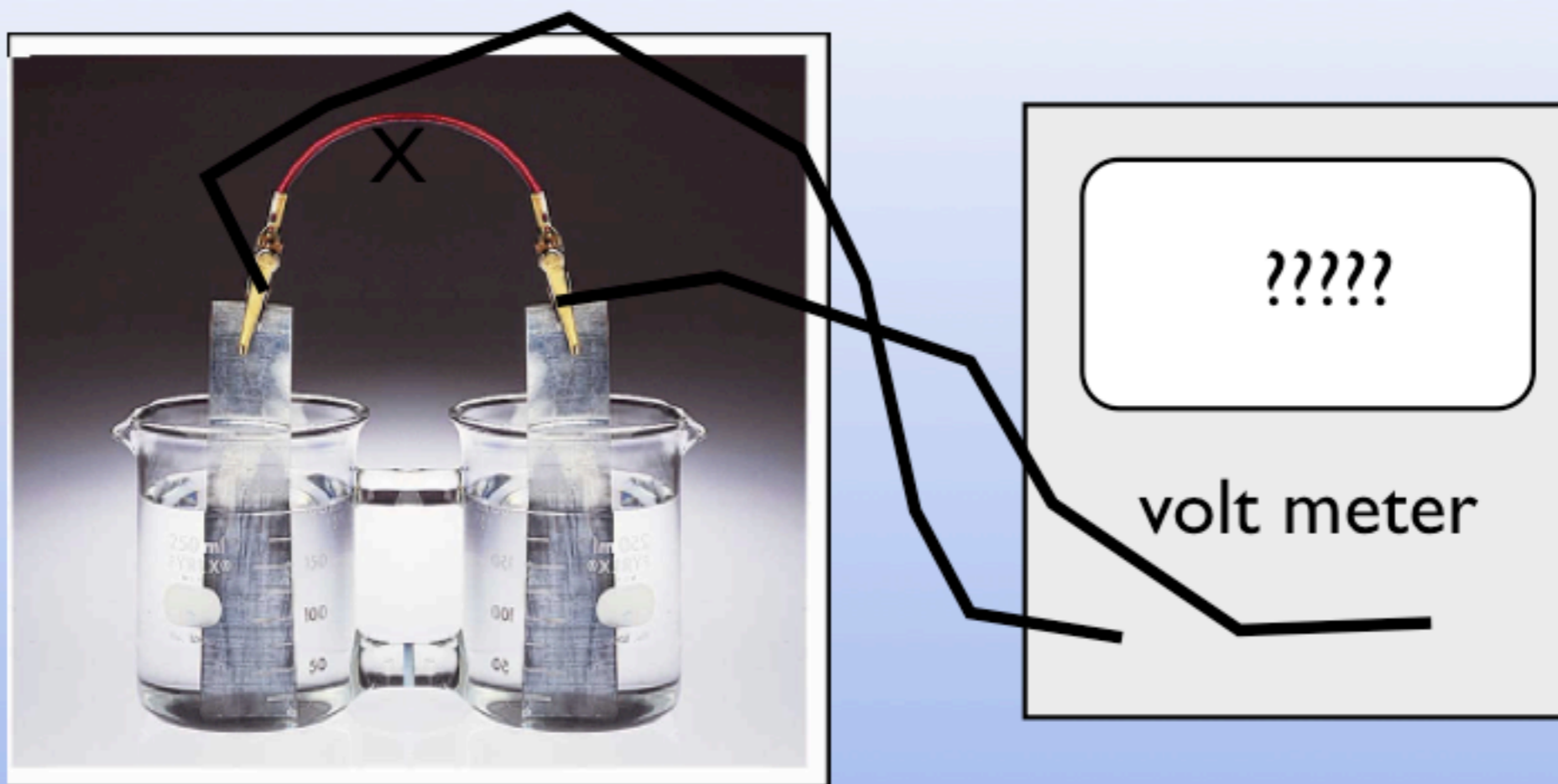
$$10^{-4} \text{ M } Zn^{2+} \text{ (aq) and } 1 \text{ M } Zn^{2+} \text{ (aq) ???}$$

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Does this cell have a non-zero voltage?

$$Zn \mid Zn^{2+} (10^{-4} \text{ M}) \parallel Zn^{2+} (1 \text{ M}) \mid Zn$$

A. yes

B. no

Which side has the lower free energy?

$$Zn \mid Zn^{2+} (10^{-4} \text{ M}) \parallel Zn^{2+} (1 \text{ M}) \mid Zn$$
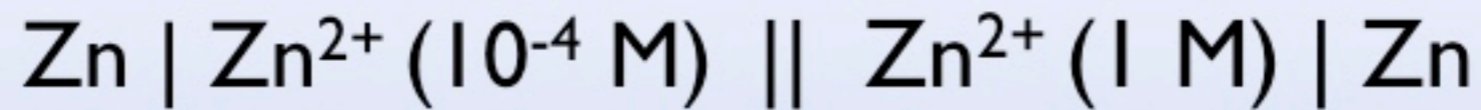
A. 1 M solution

B. 10^{-4} M solution

C. they are the same (its at equilibrium)

More conc

higher S

LOWER G

Will electrons flow spontaneously to the cathode?

$$Zn \mid Zn^{2+} (10^{-4} M) \; \| \; Zn^{2+} (1 M) \mid Zn$$
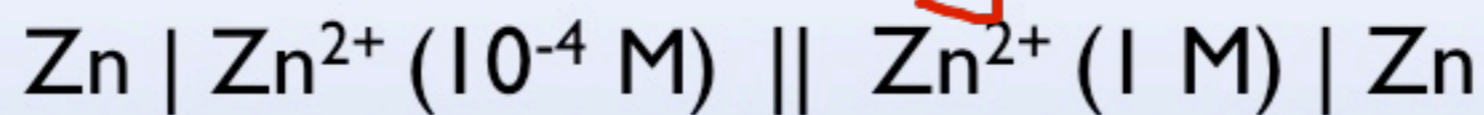
HIGH G   LOW G

A.   yes

B.   no

Will the potential for this cell be positive?

$$Zn \mid Zn^{2+} (10^{-4}\ M) \parallel Zn^{2+} (1\ M) \mid Zn$$
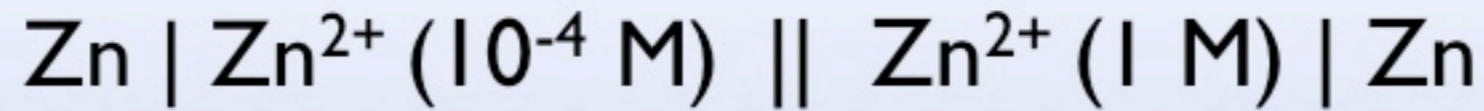
A.   yes, $E > 0$

B.   no, $E < 0$

C.   it is the same reaction so $E = 0$

$$Zn \mid Zn^{2+} (10^{-4} \text{ M}) \mid\mid Zn^{2+} (1 \text{ M}) \mid Zn$$
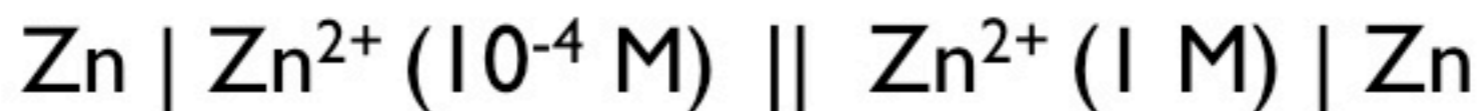
Same reaction! $E° = 0 \text{ V}$

$$Q = \frac{[Zn^{2+}]_{\text{anode}}}{[Zn^{2+}]_{\text{cathode}}} = \frac{10^{-4}}{1} = 10^{-4}$$

$$E = E° - \frac{0.0591}{n} \log Q$$

$$E = 0 \text{ V} - \frac{0.0591}{2} \log(10^{-4}) = 0.118 \text{V}$$

fairly small

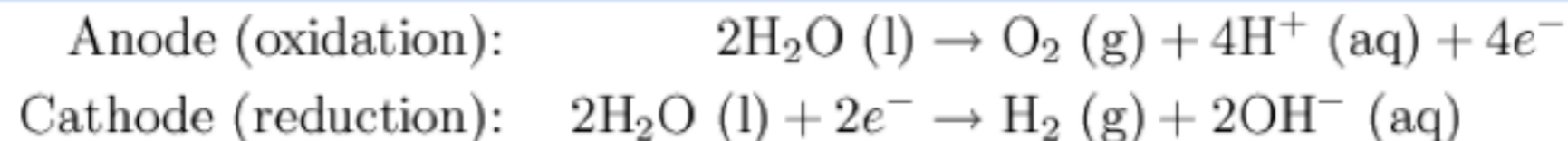each factor of ten will be another 0.0591 V

Take home message!

Voltage is a direct measure of the free energy

Therefore it is a direct measure of Q!

If you set up a system where one half of the cell is known, the the other half can be used as a sensor!

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Let's look at this reaction

$$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$$

Anode (oxidation):	$2H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$
Cathode (reduction):	$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$

$$E°_{cell} = -2.06\ V$$

Not spontaneous, but if we apply a
voltage > 2.06 we can force the reaction to go!

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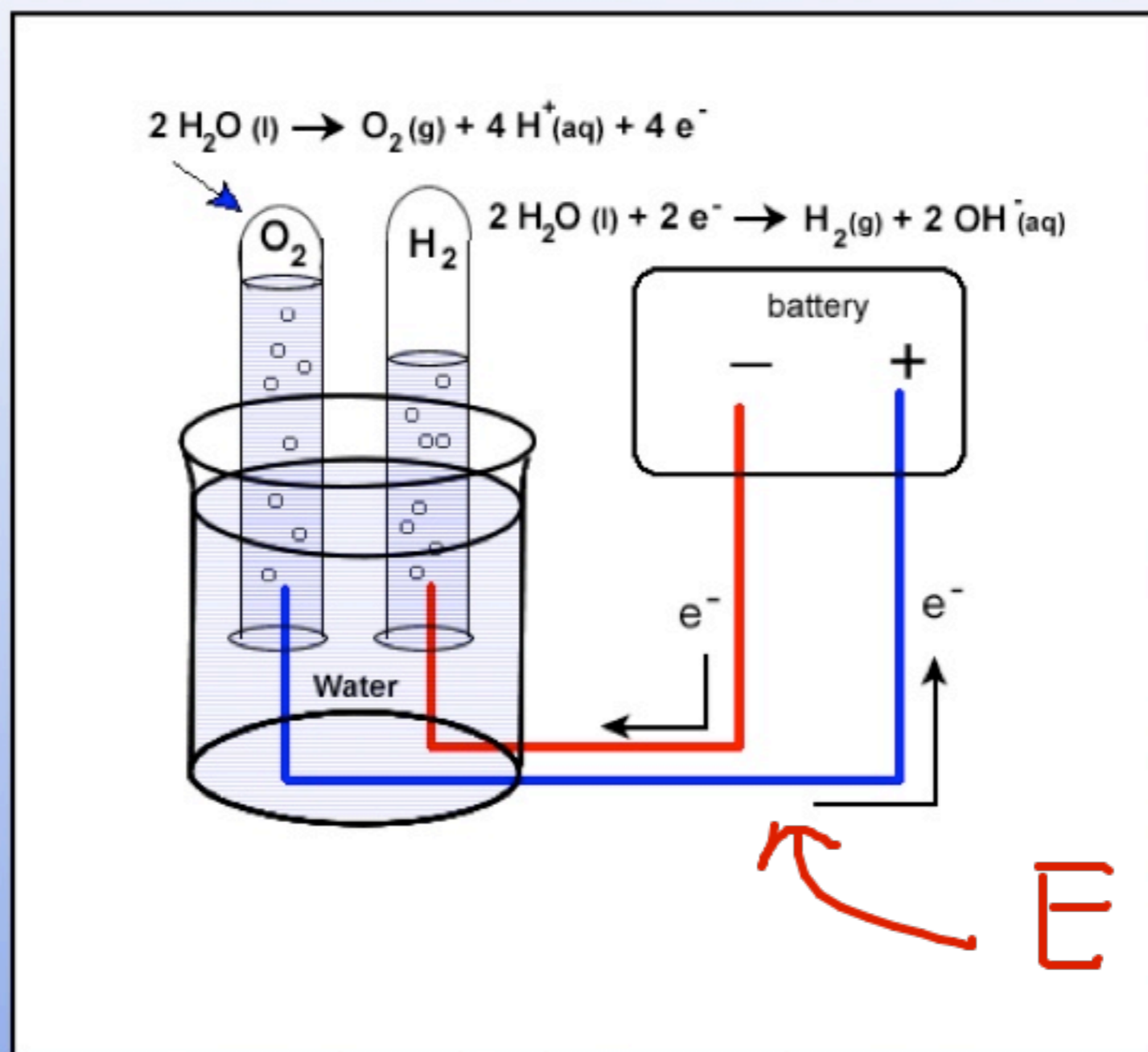
You reduce H^+ to H_2 in an electrochemical cell.
Your cell has a current of 1 Amp for 10 minutes
What is the total charge that is passed through the cell?

A.   1 C

B.   10 C

C.   600 C

D.   6000 C

$$(1 \ C \ s^{-1})(600 \ s)$$

$$= 600 \ C$$

You reduce H^+ to H_2 in an electrochemical cell.
Your cell has a current of 1 Amp for 10 minutes
How many moles of electrons pass through the cell?

A.   600 C / F

B.   600 C x F

C.   1 A x F

$$F = 96,485 \ C \ mol^{-1}_{e^-}$$

$$= 6.2 \cdot 10^{-3}$$

You reduce H^+ to H_2 in an electrochemical cell. The number of moles of electrons that pass through the cell is 6.2×10^{-3}. How many moles of H_2 are formed?

$$2H^+ + 2e^- \text{-----}> \quad H_2(g)$$

A. 6.2×10^{-3}

B. 3.1×10^{-3}

C. 1.2×10^{-2}

Need 2 mole e⁻ for each mole H₂

You reduce H^+ to H_2 in an electrochemical cell. Your cell has a current of 1 Amp for 10 minutes. How many moles of H_2 are formed?
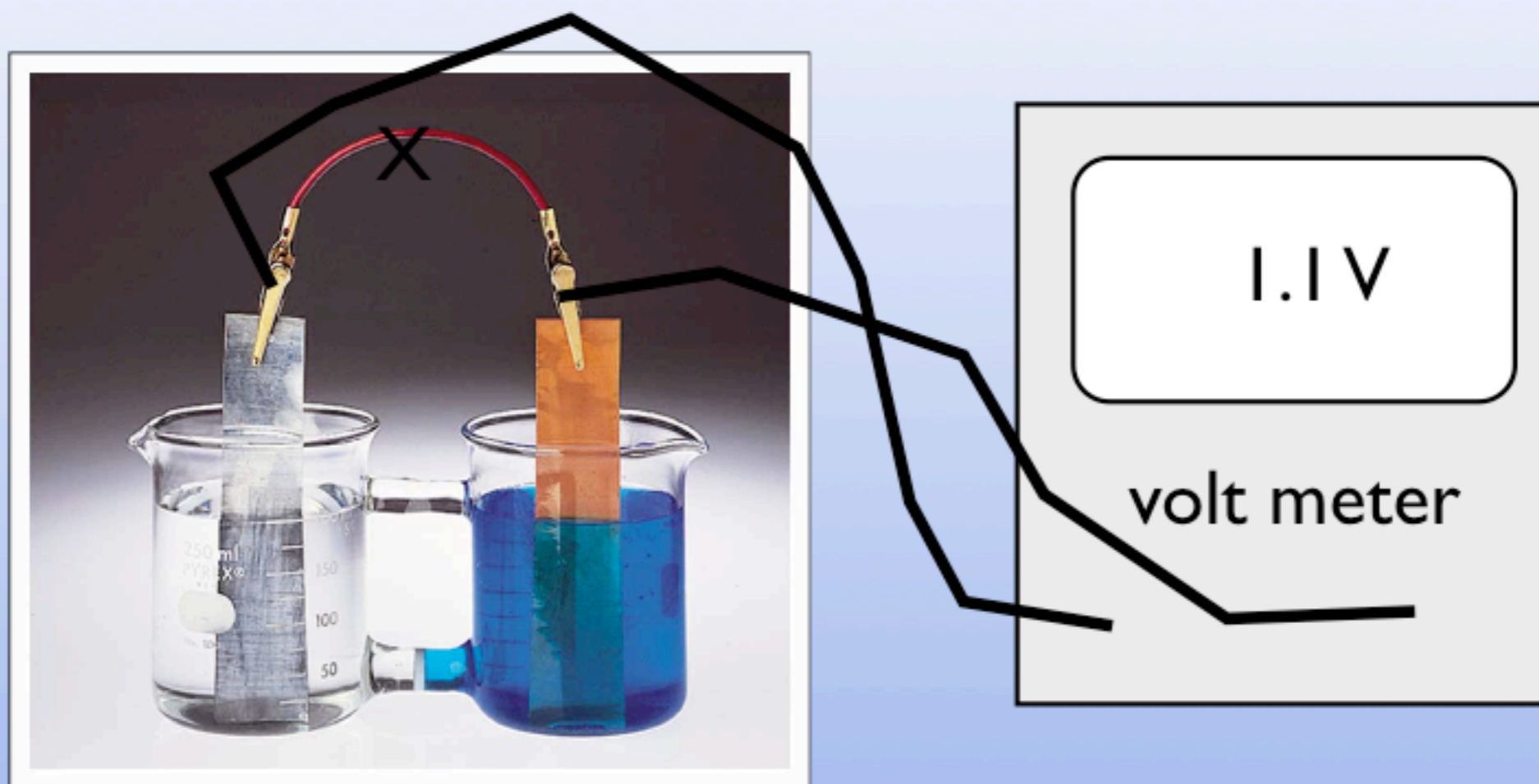
$$2H^+ + 2e^- \text{-----}> \quad H_2(g)$$

A. 6.2×10^{-3}

B. 3.1×10^{-3}

C. 1.2×10^{-2}
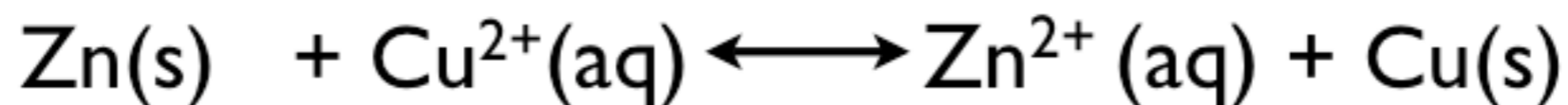
SAME QUESTION

This is the most impractical 1.1 V battery

X

1.1 V

volt meter

How can we get rid of the beaker and salt bridge?

What is the voltage when 90% of the Cu^{2+} has reacted?

$$Zn(s) + Cu^{2+}(aq) \longleftrightarrow Zn^{2+}(aq) + Cu(s)$$

1.9 M Zn^{2+} (aq) and 0.1 M Cu^{2+} (aq) ???
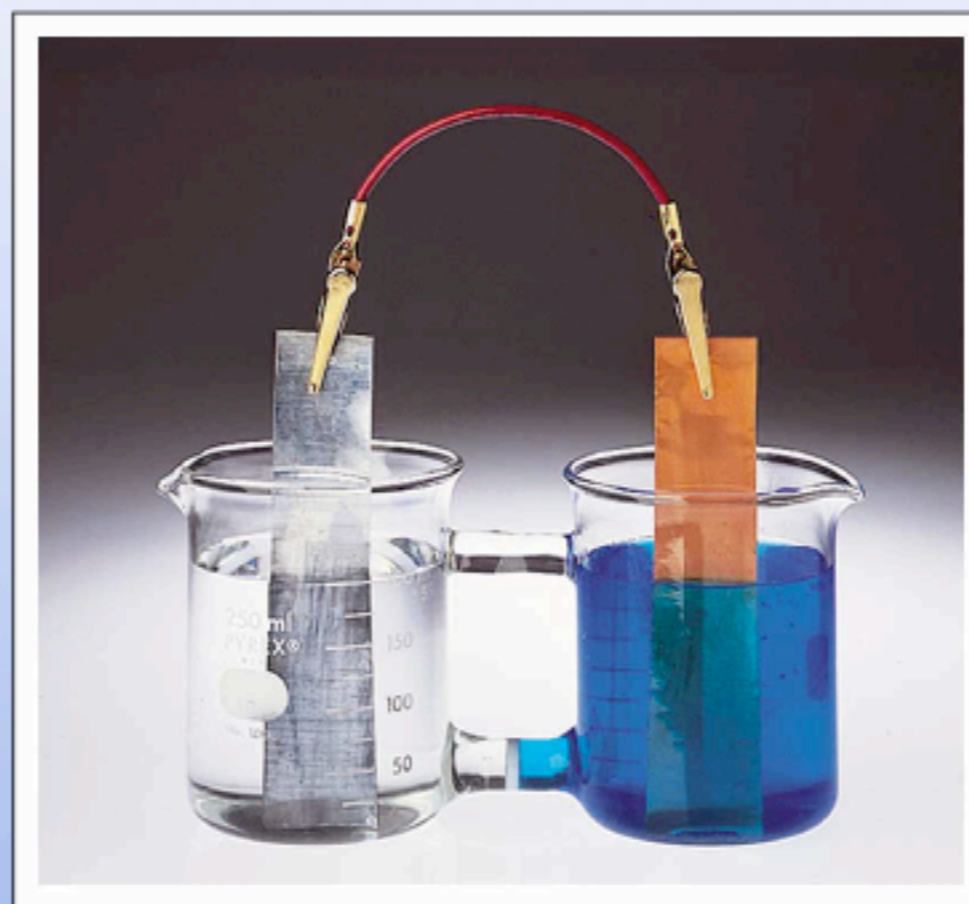
$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{(1.9)}{(.1)} = 19$$

$$E = E° - \frac{0.0591}{n} \log Q$$

$$E = 1.10 V - \frac{0.0591}{2} \log(19) = 1.06 V$$

Issue to deal with

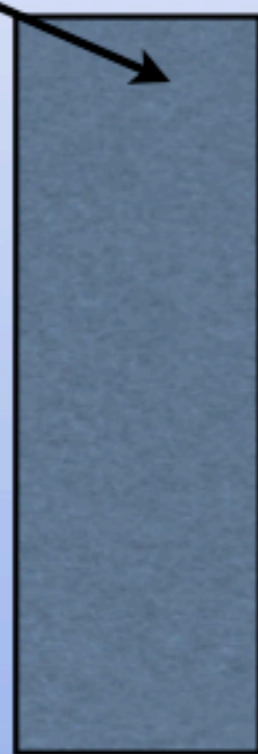Beakers keep the oxidation and reduction reactions physically separated from one another

Salt bridge connect the circuits by allowing ions to flow between the two regions

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No Beakers is easy. Put chemical into a porous medium

Water and ions can flow in and out
Solids can't

Many many tiny holes

Pb

PbO$_2$
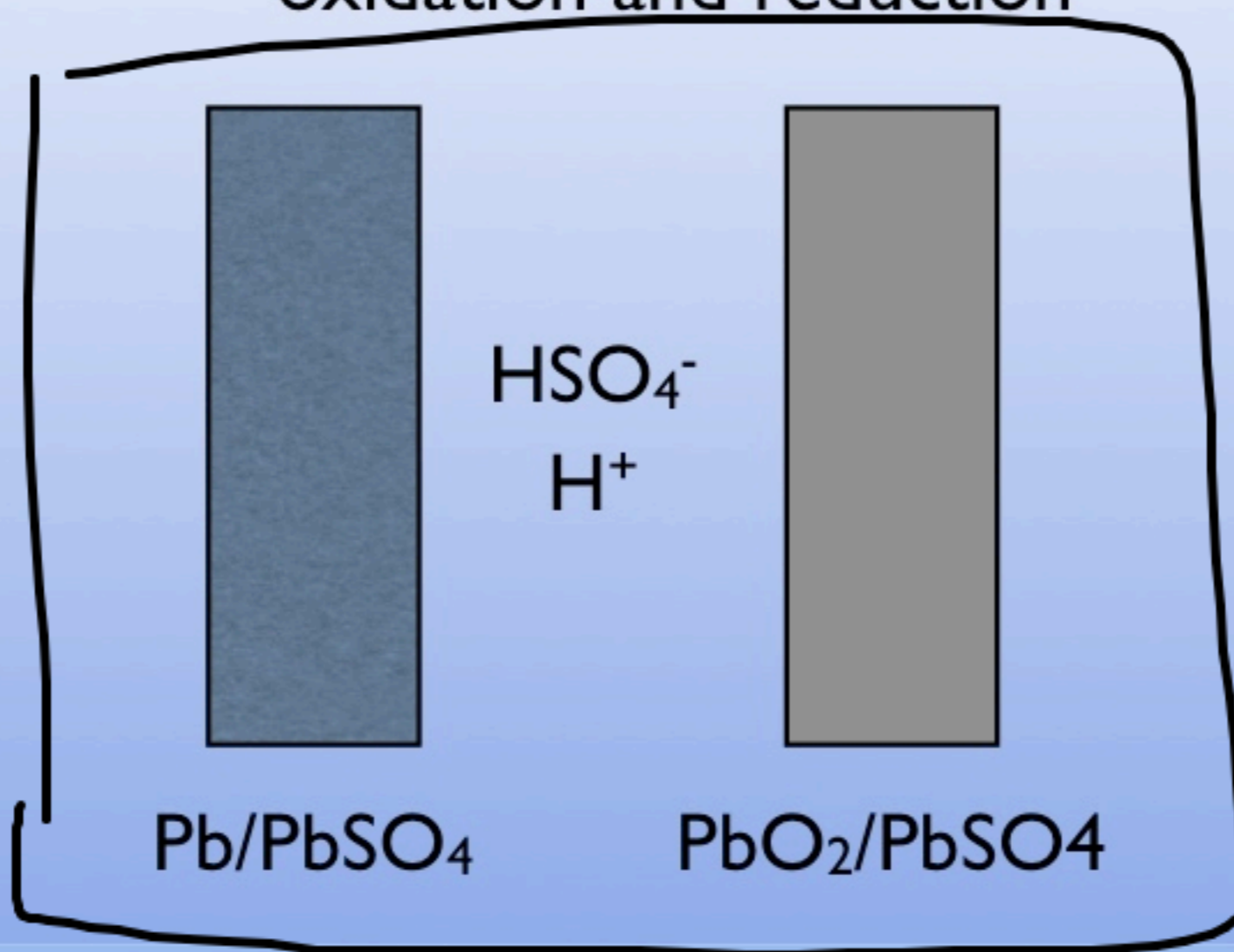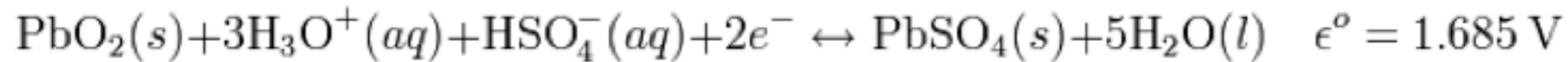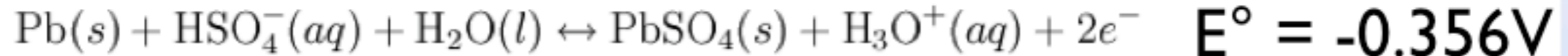
How to connect them?

Use a common electrolyte
Same chemical is common to both the
oxidation and reduction

HSO_4^-

H^+

Pb/PbSO₄

PbO₂/PbSO4

all in
one
container

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Lead Acid Battery

Anode

reduction potential

$$Pb(s) + HSO_4^-(aq) + H_2O(l) \leftrightarrow PbSO_4(s) + H_3O^+(aq) + 2e^-$$ $E° = -0.356V$

$$PbO_2(s) + 3H_3O^+(aq) + HSO_4^-(aq) + 2e^- \leftrightarrow PbSO_4(s) + 5H_2O(l)$$ $\epsilon^o = 1.685\ V$

Cathode

H_2SO_4 electrolyte solution

Anode (lead grid filled with spongy lead)
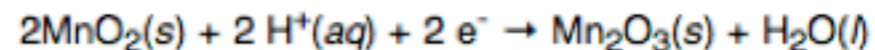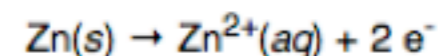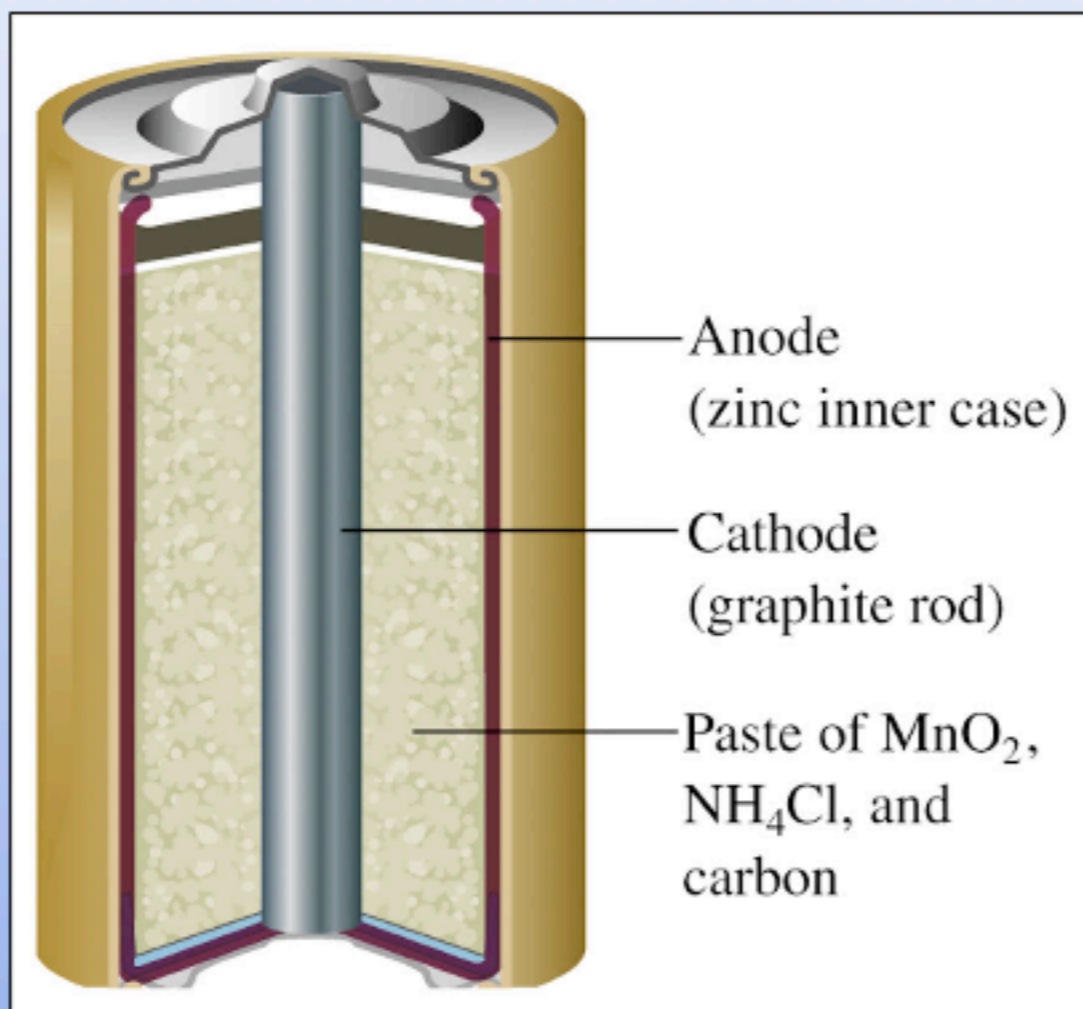
Cathode (lead grid filled with spongy PbO₂)
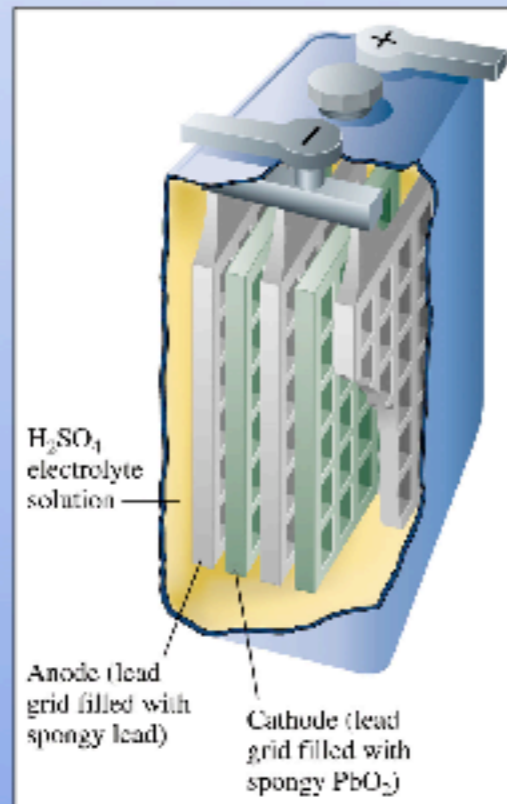
$E°_{cell} = 1.685 - (-.356) = 2.041\ V$

Everything in liquid
Therefore the reaction can be fast!

Fast = High current

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Batteries without liquids

Dry Cell

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

$$2MnO_2(s) + 2\ H^+(aq) + 2\ e^- \rightarrow Mn_2O_3(s) + H_2O(l)$$

Anode
(zinc inner case)

Cathode
(graphite rod)

Paste of MnO_2,
NH_4Cl, and
carbon

The Key
Solid Electrolyte
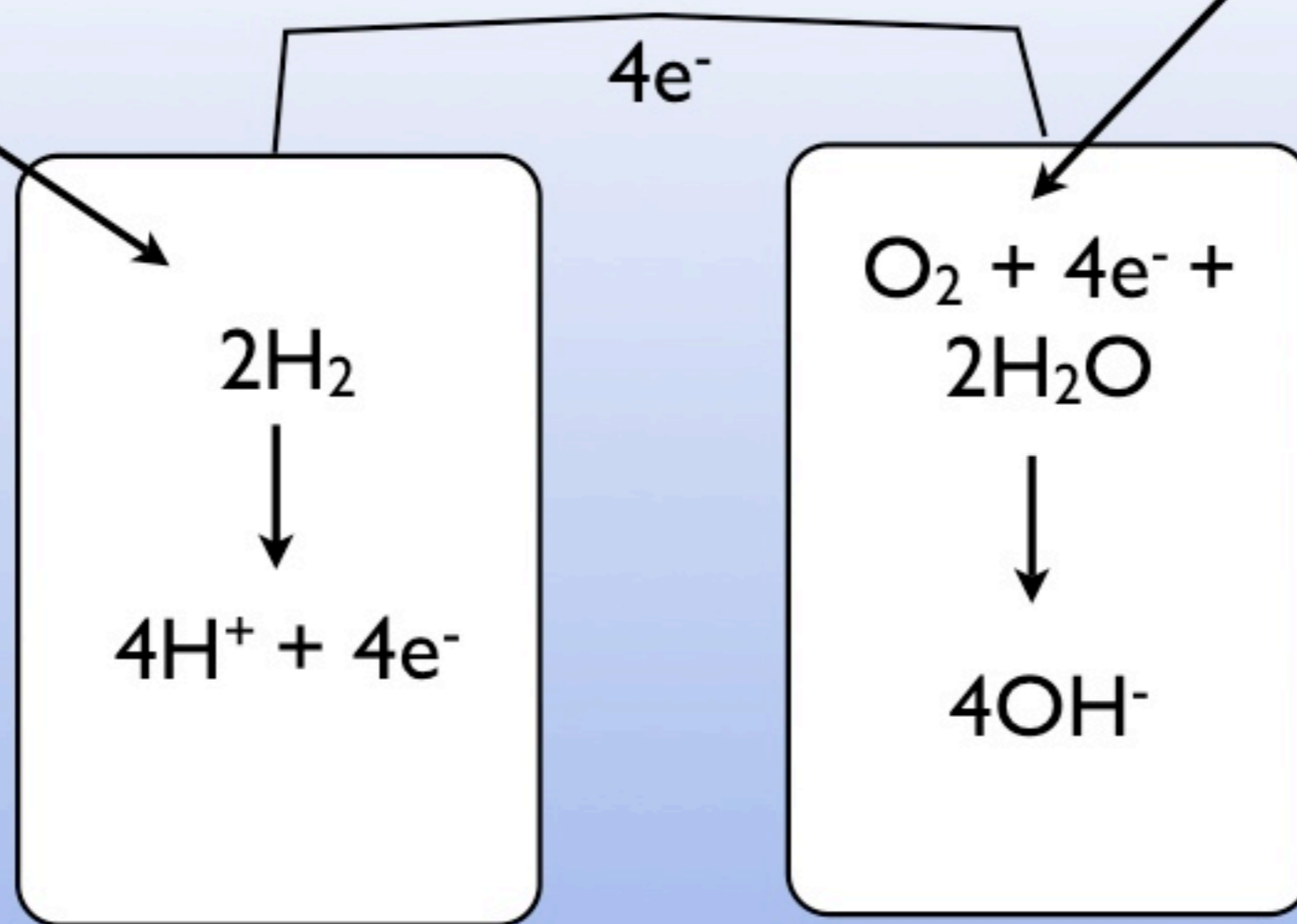Paste
NH_4^+, NH_3, H_2O

Carbon makes
electrical connection

Very slow reaction. Constant V.   Very low current

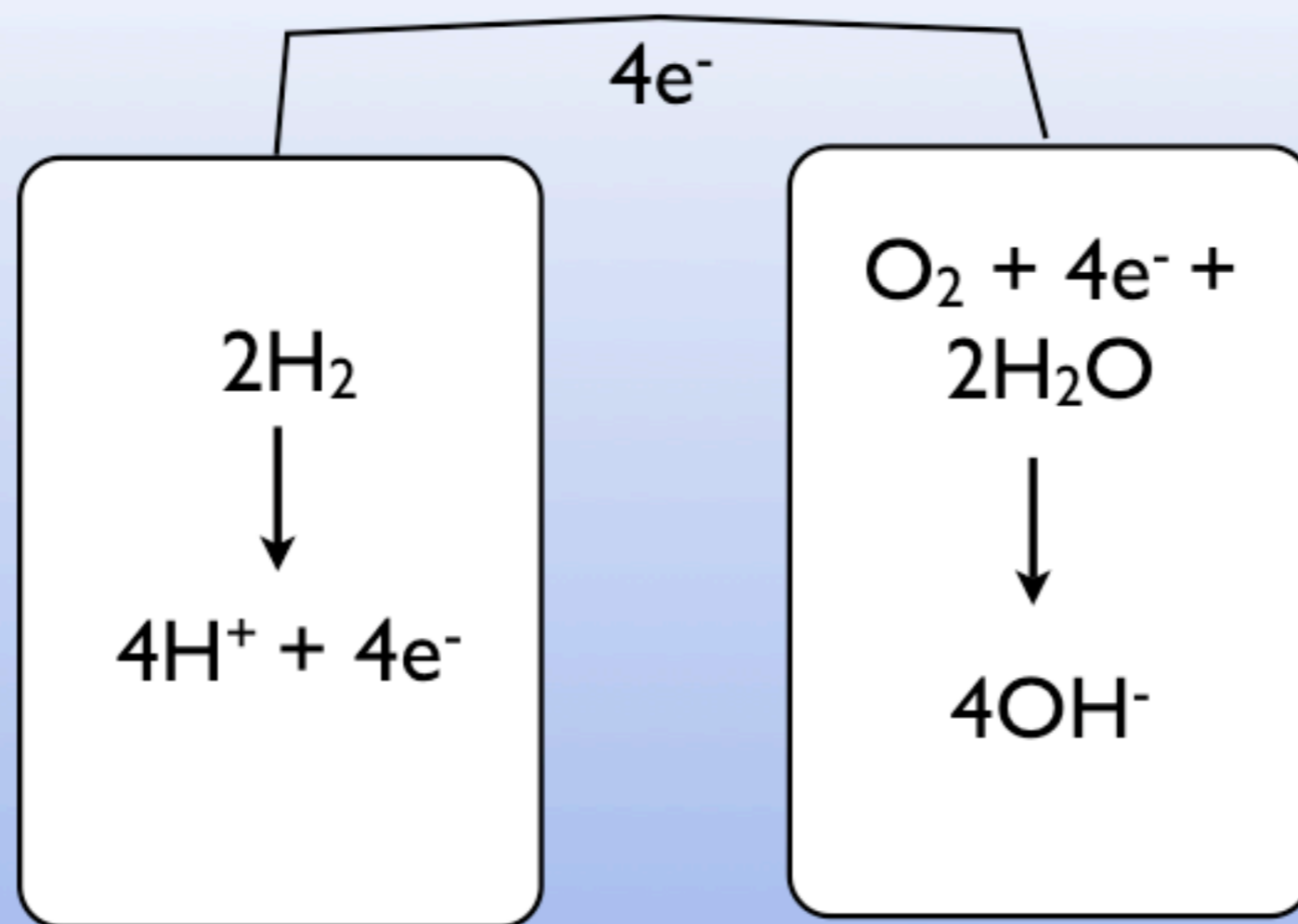like a battery you can refill

"fill up" with
H_2

Fuel Cells

O_2 from air

$4e^-$

$2H_2$

$\downarrow$

$4H^+ + 4e^-$

$O_2 + 4e^- + 2H_2O$

$\downarrow$

$4OH^-$

Anode
oxidation

Cathode
reduction

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Fuel Cells

4e⁻

$2H_2$

$\downarrow$

$4H^+ + 4e^-$

$O_2 + 4e^- + 2H_2O$

$\downarrow$

$4OH^-$

We need a salt Bridge!

$4e^-$ ⟶

$2H_2$

↓

$4H^+ + 4e^-$

$O_2 + 4e^- + 2H_2O$

↓

$4OH^-$

H^+ ⟶

Proton Transport Membrane

Water out

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