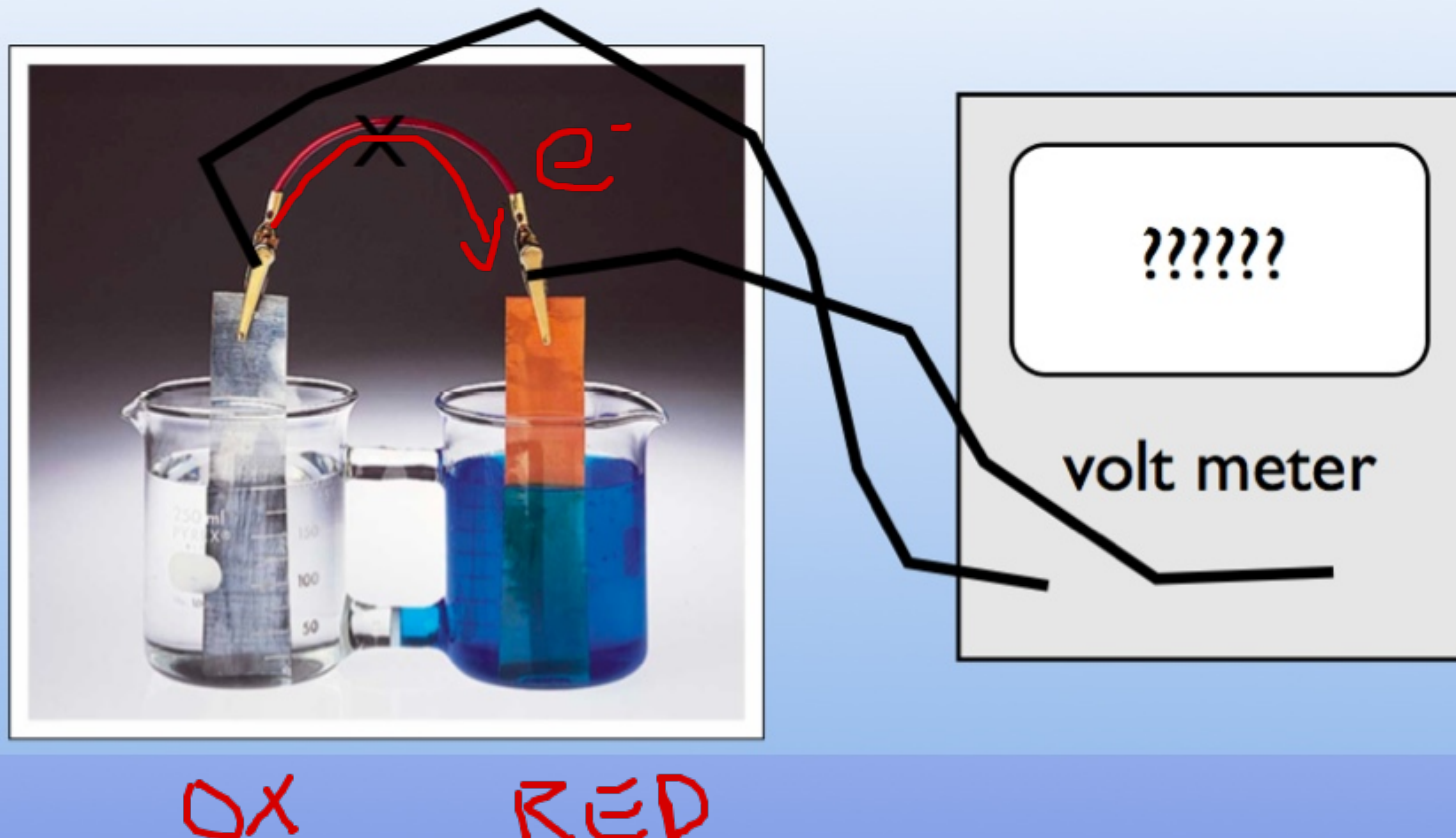
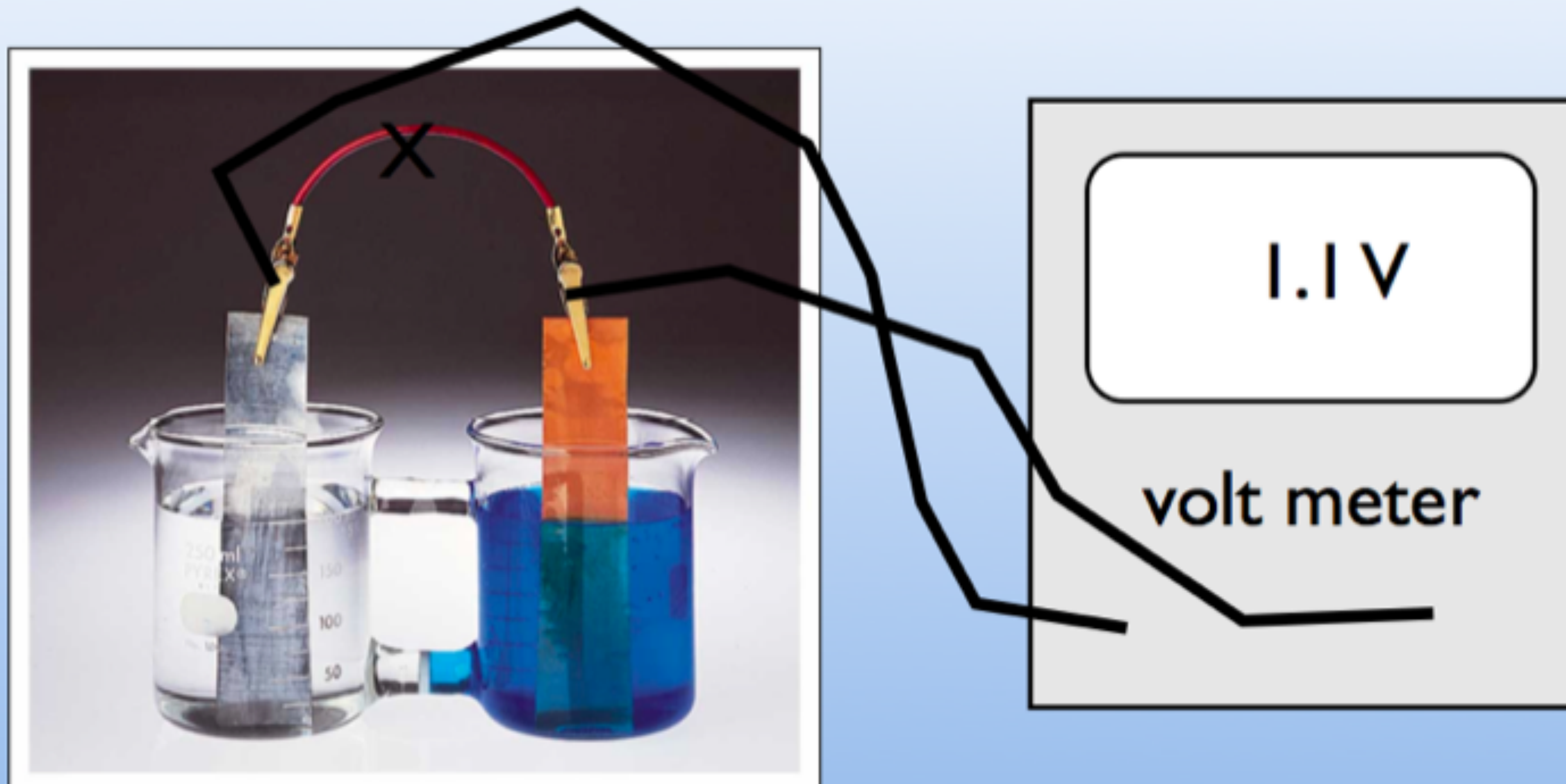
Today

Voltage and Equilibria

How do we know what the voltage is?



The voltage depends on the concentrations
(we've all had dead batteries)



Mix up "standard" concentrations

1 M Zn^{2+} and 1 M Cu^{2+}

(note this is very concentrated)

Let’s look at an actual cell

On which side of the cell are the electrons at a higher potential energy at these concentrations?

A. the anode

B. the cathode

C. they are the same

$\bar{e}$ flow

spontaneous

to cathode

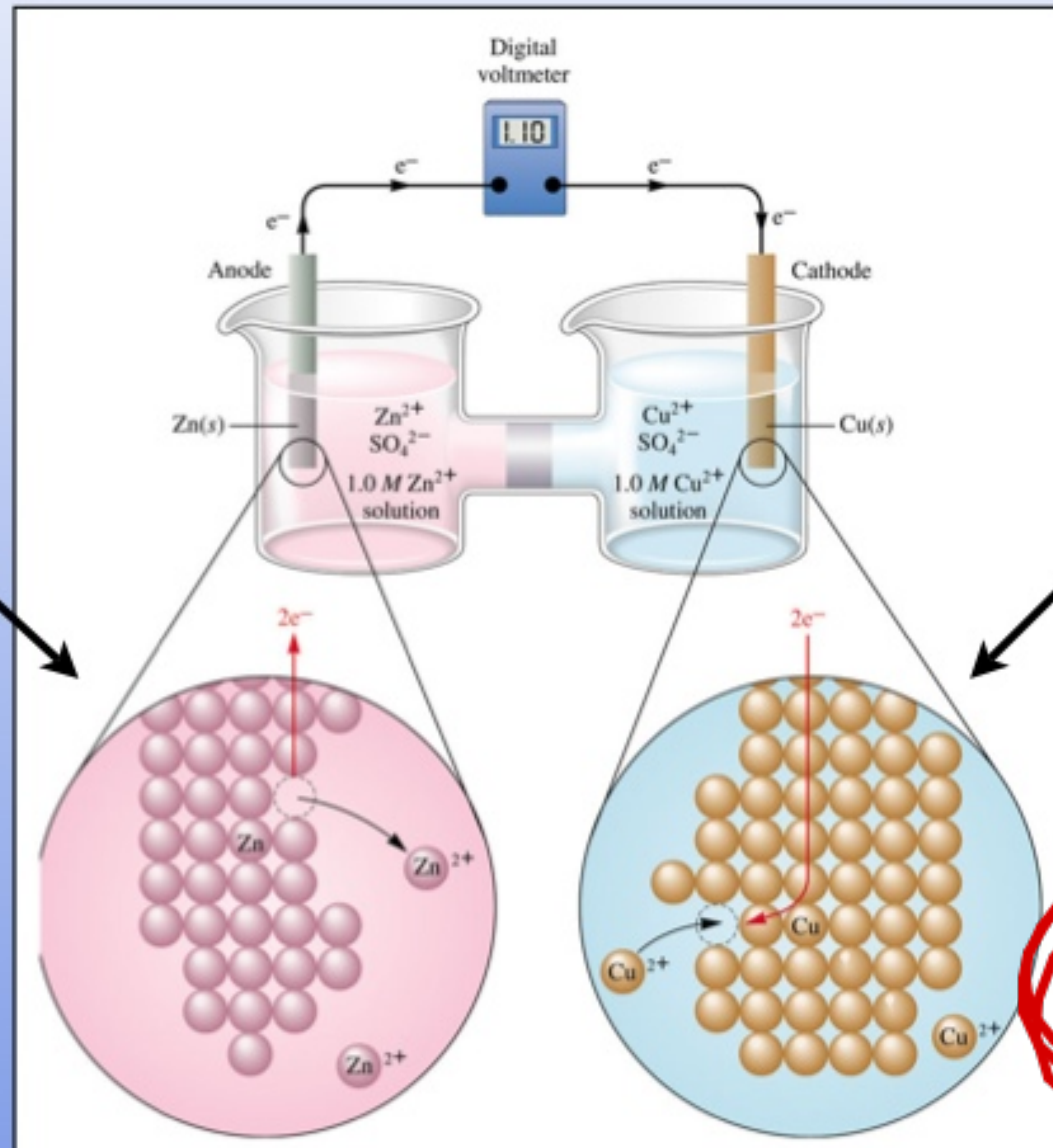
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

$$Zn(s) \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$$

E > D

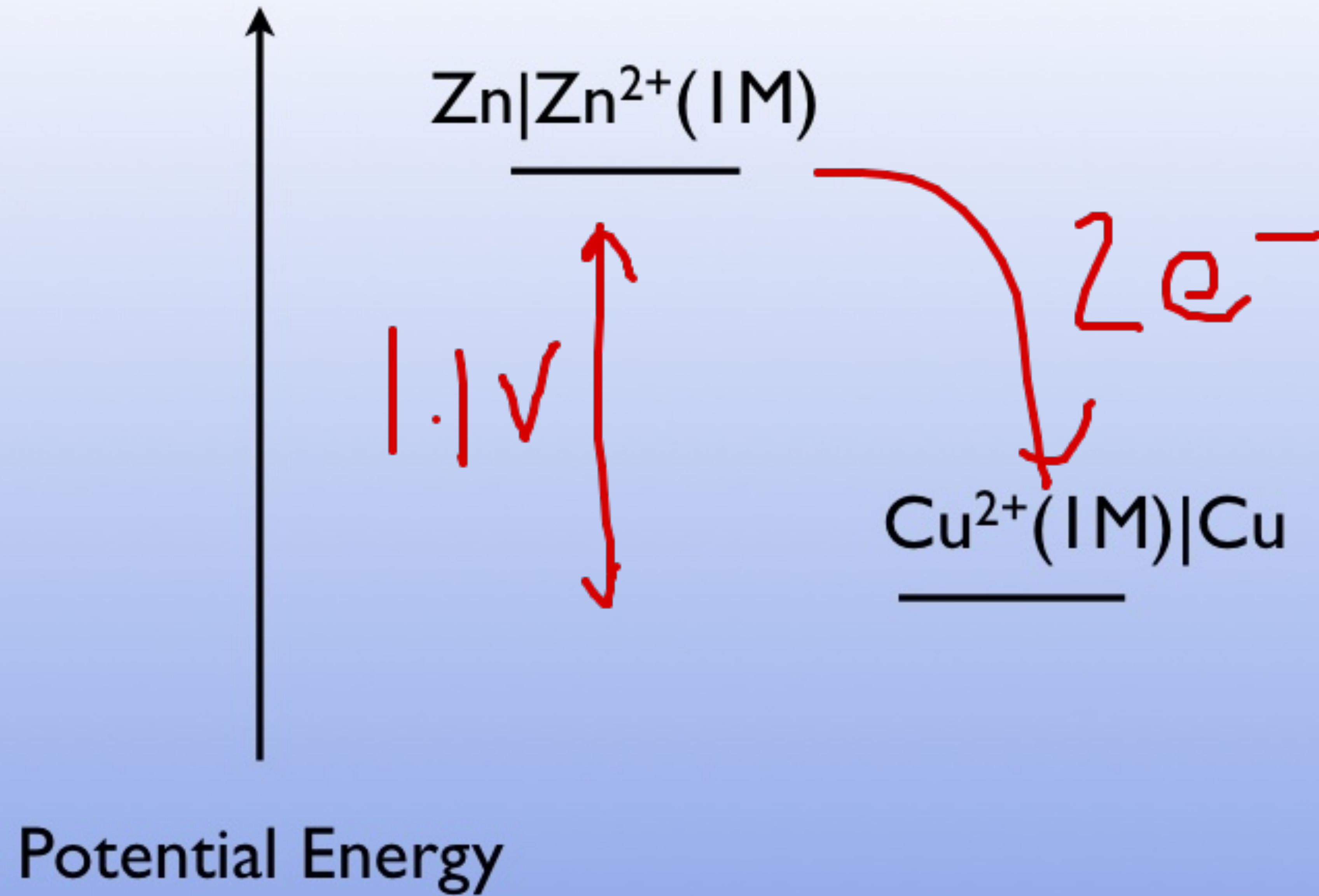
Oxidation
Anode

Reduction
Cathode



voltaic
galvanic

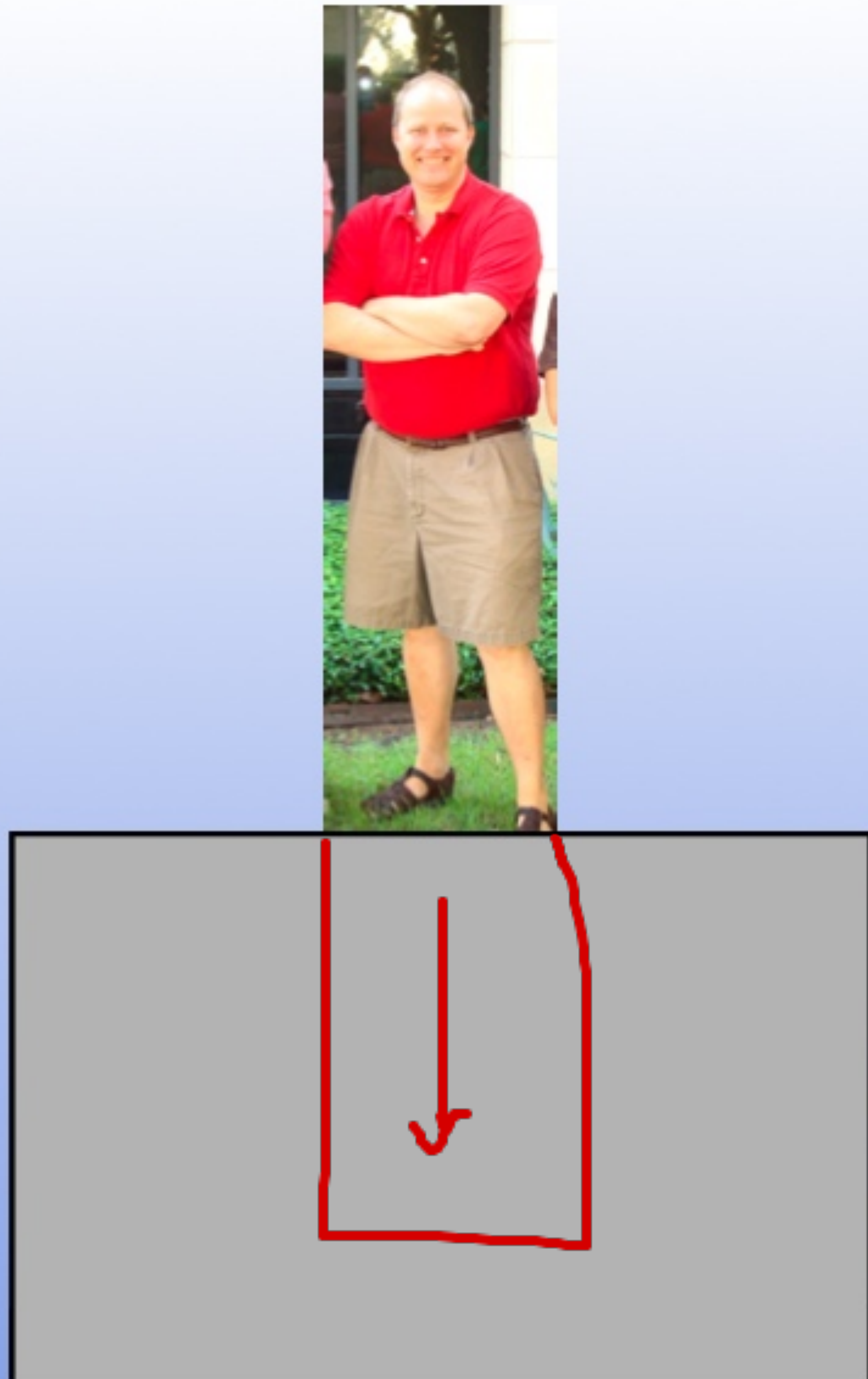
We've made a 1.1 V battery!


Zn|Zn2+(1M)
Cu2+(1M)|Cu
Potential Energy
1.1V
2e−

Now we can measure every possible combination of electrochemical cells!

What if I would like to predict
the voltage from a cell
for any reaction at standard conditions?

First we need to think about potential energy



What is my gravitational potential energy?
zero if I am on the ground

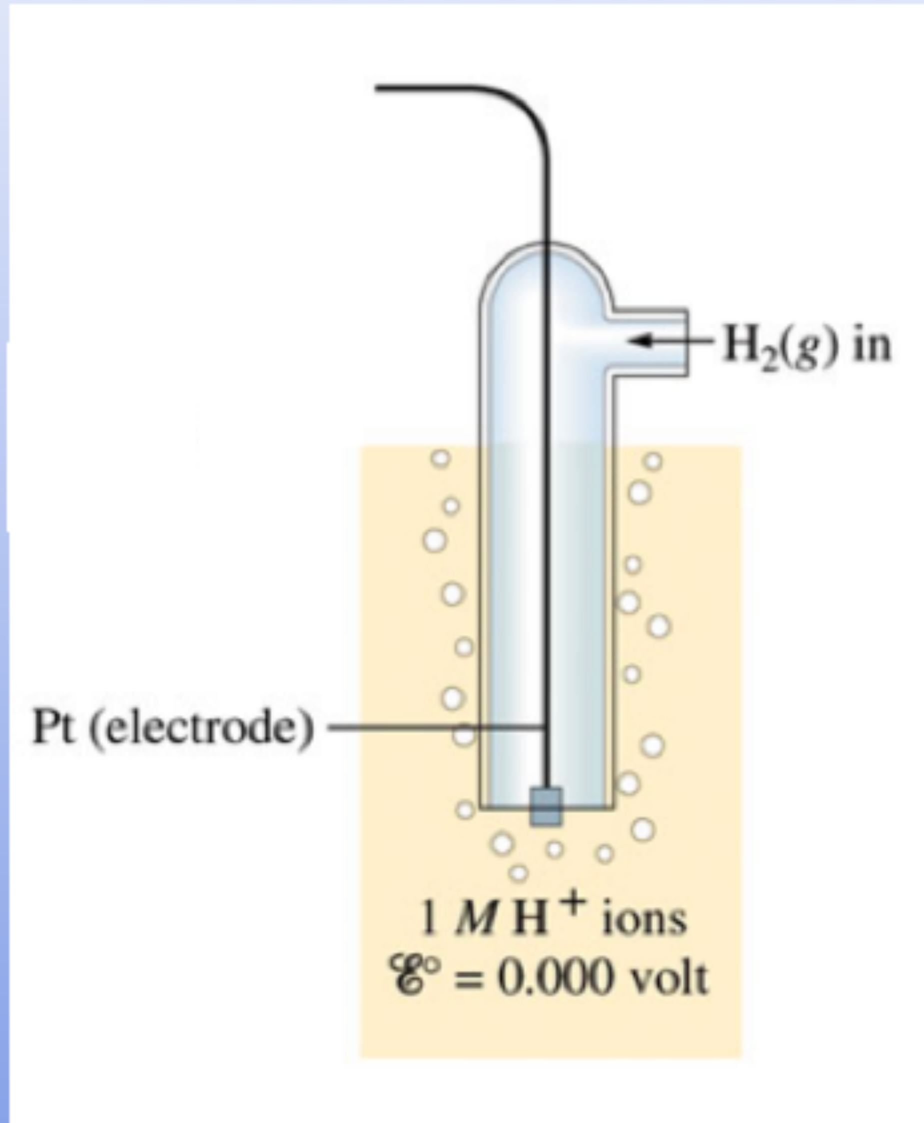
But if a hole appears beneath me?
then it is no longer zero

Energy is relative!

We pick where zero is

We need to pick a zero potential for electrochemistry

We chose this reaction



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

note standard conditions

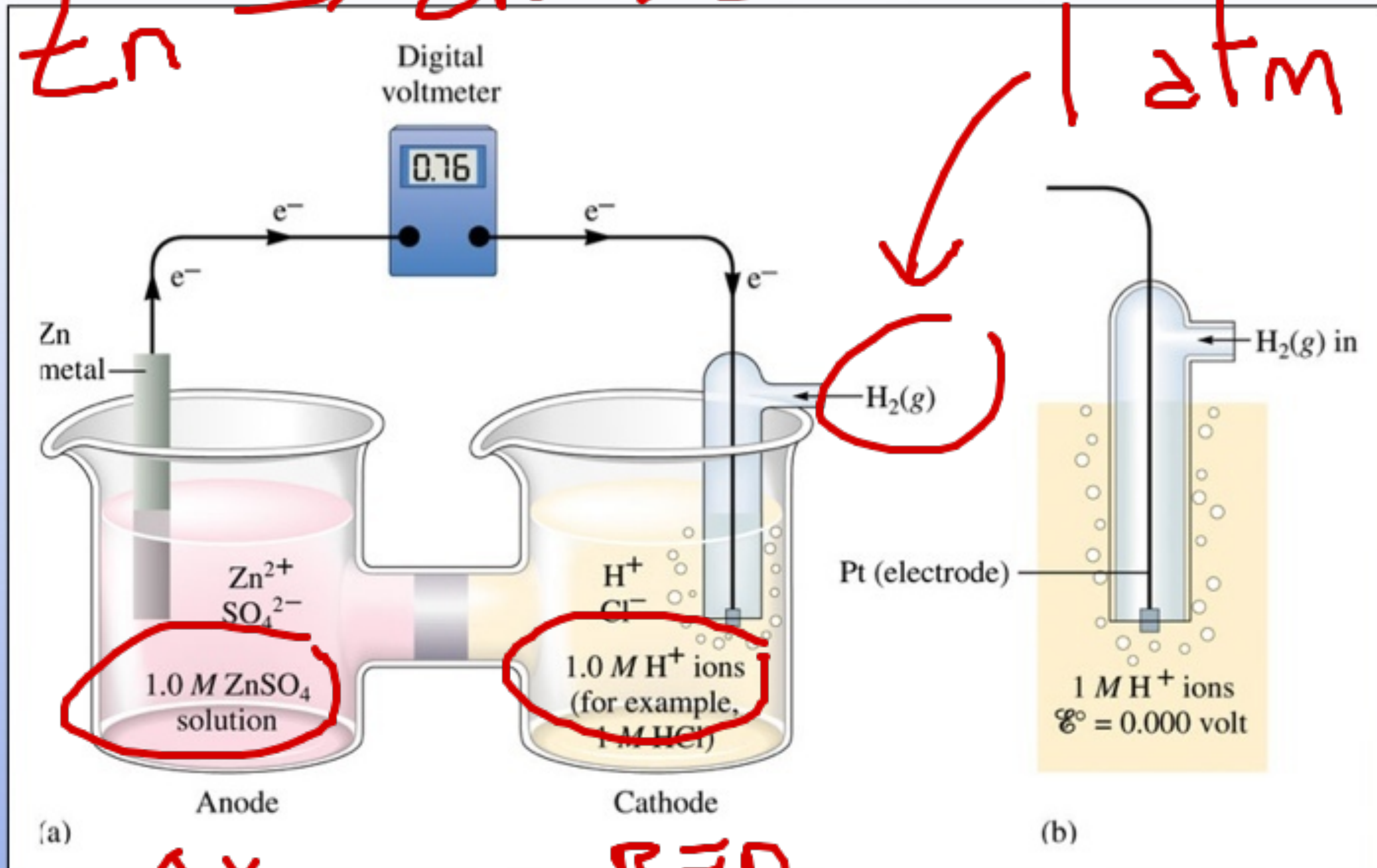
we pick this as E°= 0V

potential energy

Now compare everything to this

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

1 atm



OX RED

So potential for $Zn \longrightarrow Zn^{2+} + 2e^-$
is 0.76 V

If the potential for

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{is } 0.76V$$

what is the potential for

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

A. -0.76 V

B. 0.76 V

C. 0 V

D. it can't be measured

Backward

= - Forward

Write everything as a reduction reaction

TABLE 11.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

EASY RED

Easy to OX

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

Standard Potential (V)	Reduction Half-Reaction
+2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$
+1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
+1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$
+1.33	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
+1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$
+1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$
+0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$
+0.80	$Ag^+(aq) + e^- \longrightarrow Ag(s)$
+0.77	$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$
+0.68	$O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
+0.59	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$
+0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$
+0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$
+0.34	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$
−0.28	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$
−0.44	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$
−0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
−1.66	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$
−2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$
−3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$

Easy to reduce (Strongest oxidizing agents)

Most positive

Most negative

Easy to oxidize (strongest reducing agents)

Given that $E^0_{1/2\ RED}$

$Fe^{2+} + 2e^- \longrightarrow Fe$ -0.44 V

$Zn^{2+} + 2e^- \longrightarrow Zn$ -0.76V

which is easier to oxidize?

A. Zn

B. Fe

C. Zn^{2+}

D. Fe^{2+}

$E^0_{1/2}$ for Zn is more negative

Zn^{2+} harder to reduce

Zn easier to oxid.

STD

½ RED TABLE

How to find E°cell?

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

Use the reduction potential for both half reactions

The number of electrons does not matter

only the half-reactions

(2 ⟶

How to find E°cell?

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

ANODE CATHODE

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

$Zn^{2+} + 2e^- \longrightarrow Zn$ $E^\circ = -0.76$

$Cu^{2+} + 2e^- \longrightarrow Cu$ $E^\circ = +0.34$

$E^\circ = 0.34 - (-0.76) = +1.1V$

E > 0 Battery, Voltaic.

How to find E°cell?

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

ANODE CATHODE

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

$Zn^{2+} + 2e^- \rightarrow Zn$ E°= $-.76$

$Cu^{2+} + 2e^- \rightarrow Cu$ E°= $+.34$

$$E^\circ = -.76 - (.34) = -1.1\ V$$

Electrolytic E<0

How to find E°cell?

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

ANODE CATHODE

$Pt \mid H_2(g) \mid 2H^+ \parallel O_2(g) \mid H_2O \mid Pt$

$2H^+ + 2e^- \longrightarrow H_2$ E°= 0 V

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ E°= +1.23 V

$E^\circ = 1.23 - 0 = 1.23\ V$

What is cell notation for the following reaction?

$$Ni(s) + 2Fe^{3+}(aq) \longrightarrow Ni^{2+}(aq) + 2Fe^{2+}(aq)$$

A. $Ni^{2+} | Ni || Fe^{2+} | Fe^{3+} | Pt$

B. $Ni | Ni^{2+} || Fe^{3+} | Fe^{2+} | Pt$

C. $Ni | Ni^{2+} || Fe^{2+} | Fe^{3+} | Pt$

D. $Ni | Ni^{2+} || 2Fe^{2+} | 2Fe^{3+} | Pt$

E. $Ni | Ni^{2+} || 2Fe^{3+} | 2Fe^{2+} | Pt$

What is E° for the following reaction?

$$Ni(s) + 2Fe^{3+}(aq) \longrightarrow Ni^{2+}(aq) + 2Fe^{2+}(aq)$$

A. +0.54 V

B. +0.77 V

C. +1.0 V

D. -1.0 V

E. -0.54 V

AN: $Ni | Ni^{2+}$ || CATH: $Fe^{3+} | Fe^{2+} | Pt$

$$E^{\circ} = 0.77 - (-0.23)$$
$$= +1.0\,V$$

Could the following reaction make a battery?

$$Ni(s) + 2Fe^{3+}(aq) \longrightarrow Ni^{2+}(aq) + 2Fe^{2+}(aq)$$

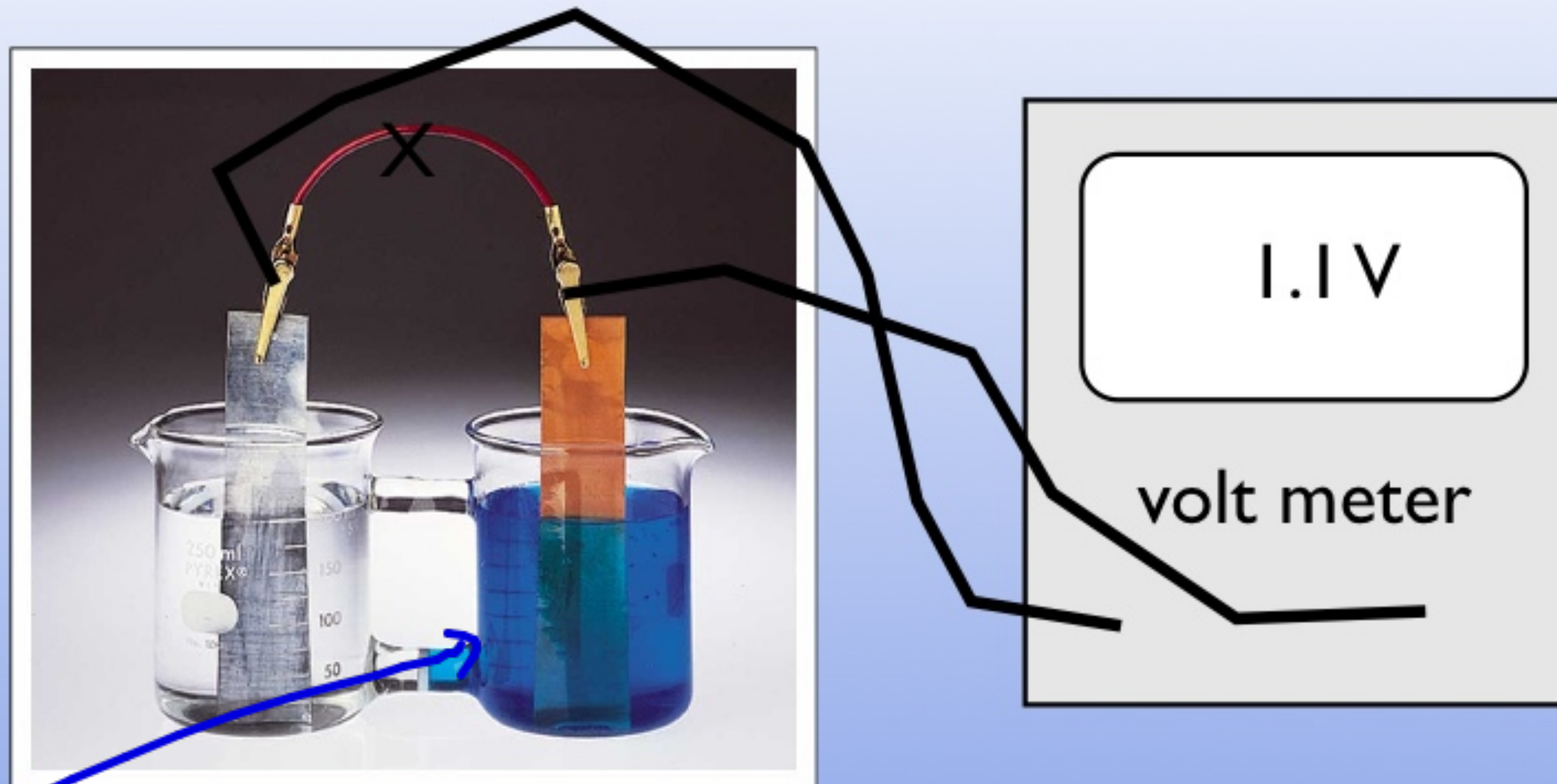
A. yes

B. no

E > 0

We'll look at standard concentrations

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



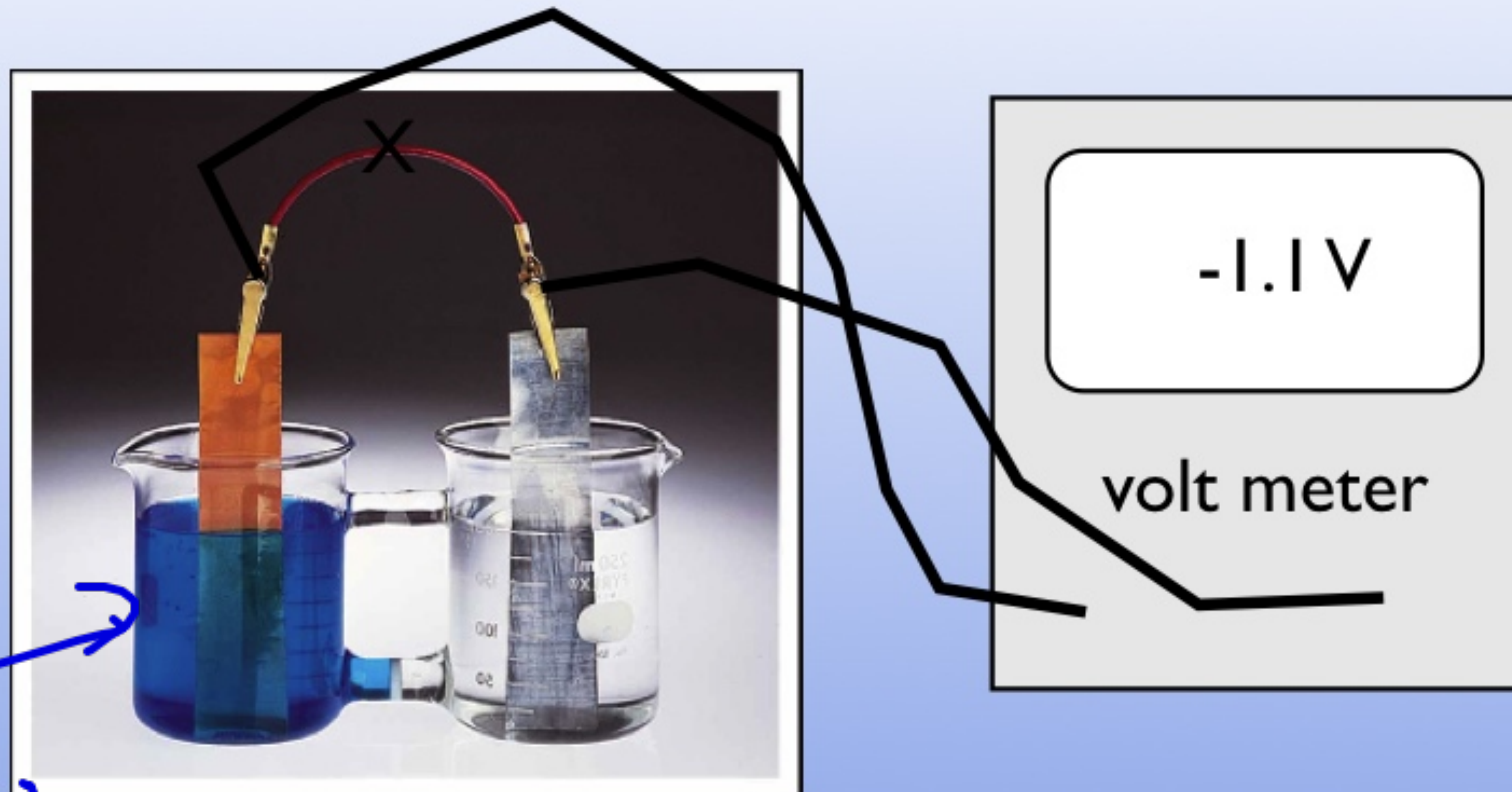
Cu
Cathode

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

BACKWARD

We'll look at standard concentrations

Cu | Cu^{2+} || Zn^{2+} | Zn



Cu now ANODE

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

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

At equilrium
NO current
Why? no potential
$E = 0$

Relationship between E and ΔG

ΔG is energy
E is electrical potential

Electric work (energy) is -charge x potential

work = -charge x E

$\Delta G = work_{max}$
$\Delta G = -\ charge \times E_{max}$

From now on we'll now the Potential we calculate
is the theoretical maximum
Real world never actually that good

Free Energy & Potential are directly related

Relationship between E and ΔG

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

What is the charge?

charge = n X F

n is number of moles of electrons (per mole rxn)
F is the charge of one mole of electrons
F = 96,485 C (Faraday's Constant)

$$\Delta G = - nFE$$

Other concentrations and equilibrium
Let's remember equlibrium!

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

at equilibrium $\Delta G = 0$

so $\Delta G^\circ = -RT\ln K$

$$-nFE = -nFE^\circ + RT\ln Q$$

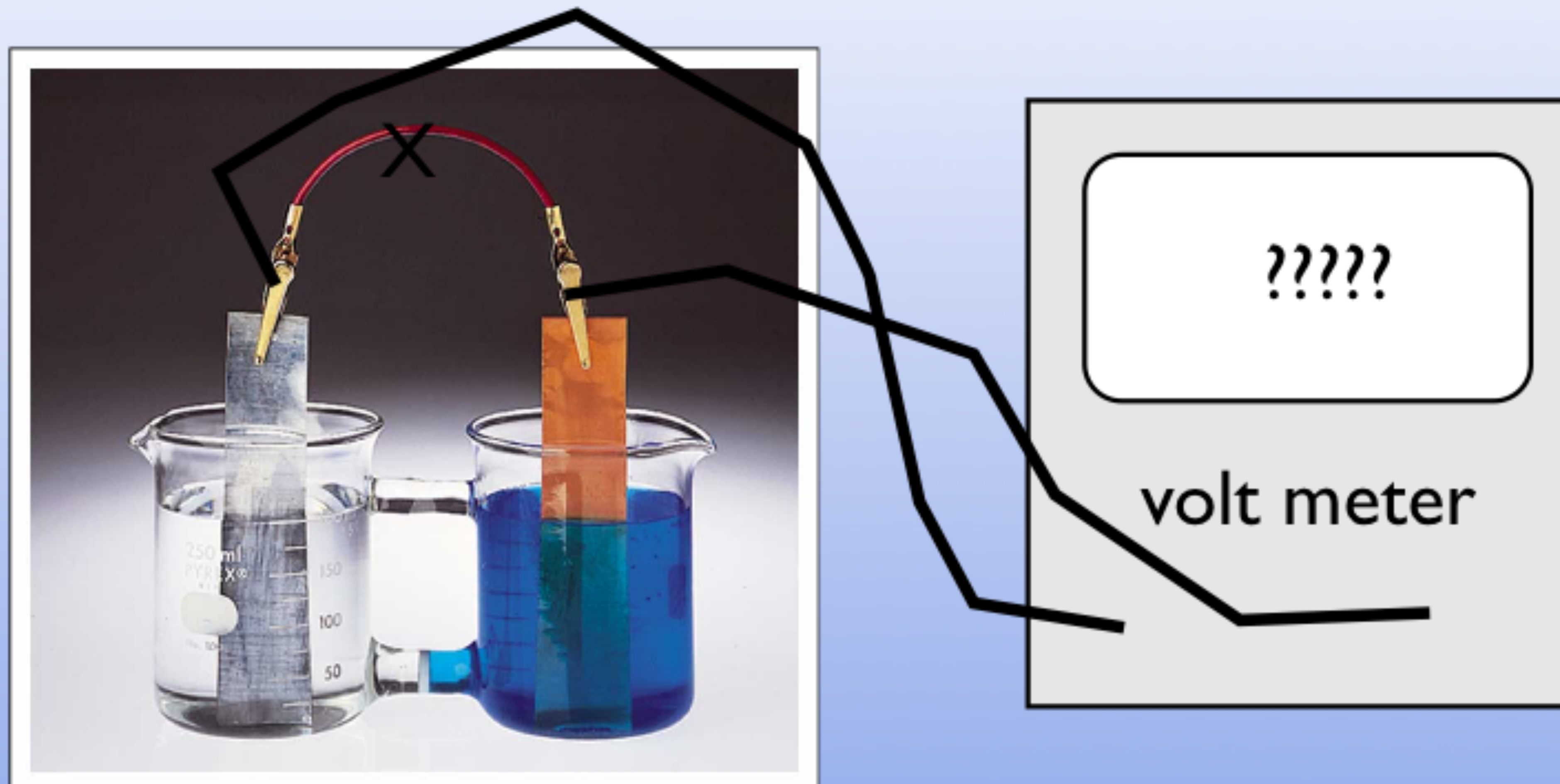
$$E = E^\circ - \frac{RT}{nF}\ln Q$$

assume 25°C

log!

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

What about other concentrations?



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

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

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

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

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

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

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

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

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

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

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

Current will flow until E = 0

Equilibrium

$$E^\circ = \quad + \frac{0.0591}{n} \log K$$

$$\log K = \frac{nE^\circ}{0.0591}$$

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