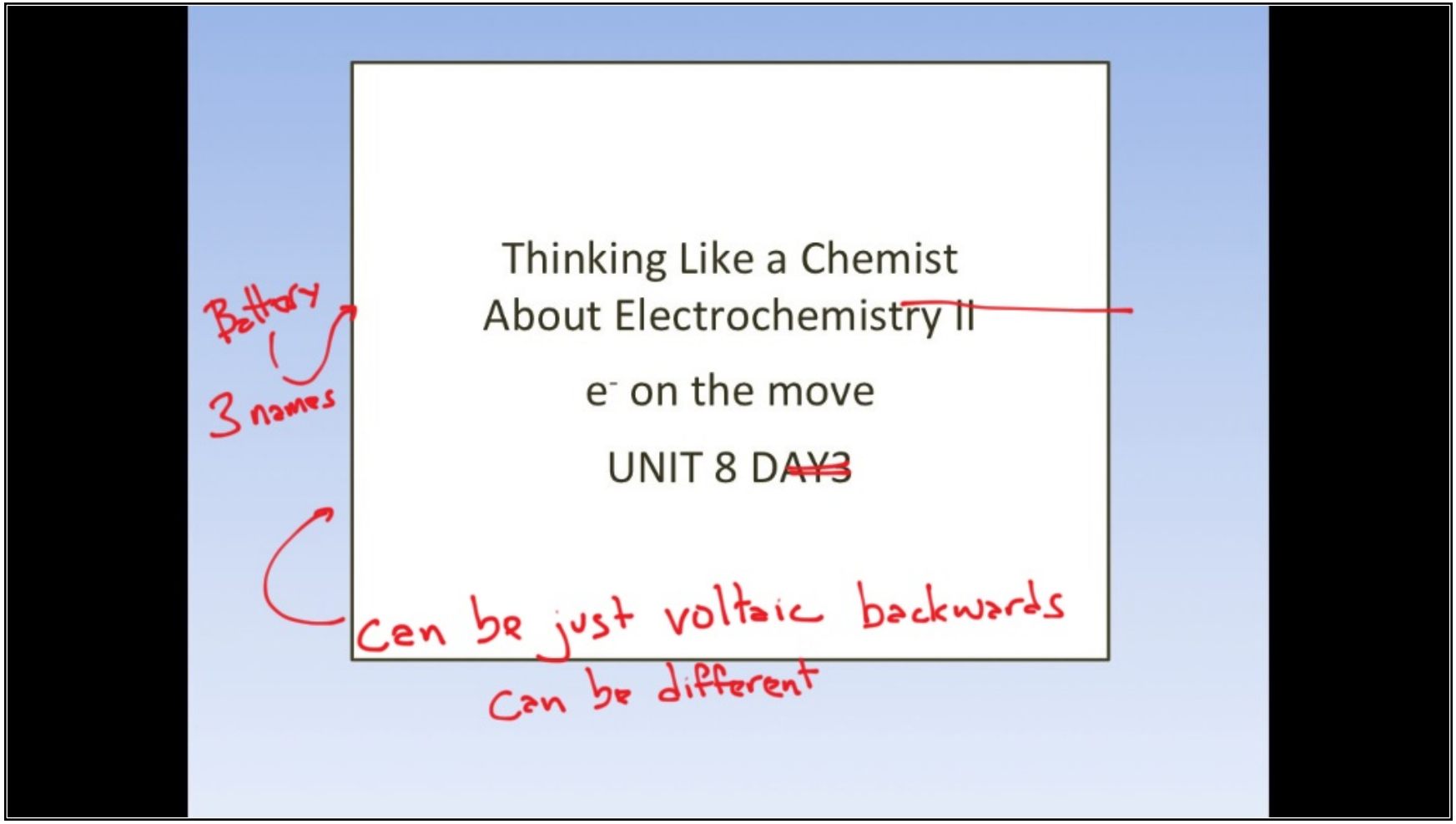
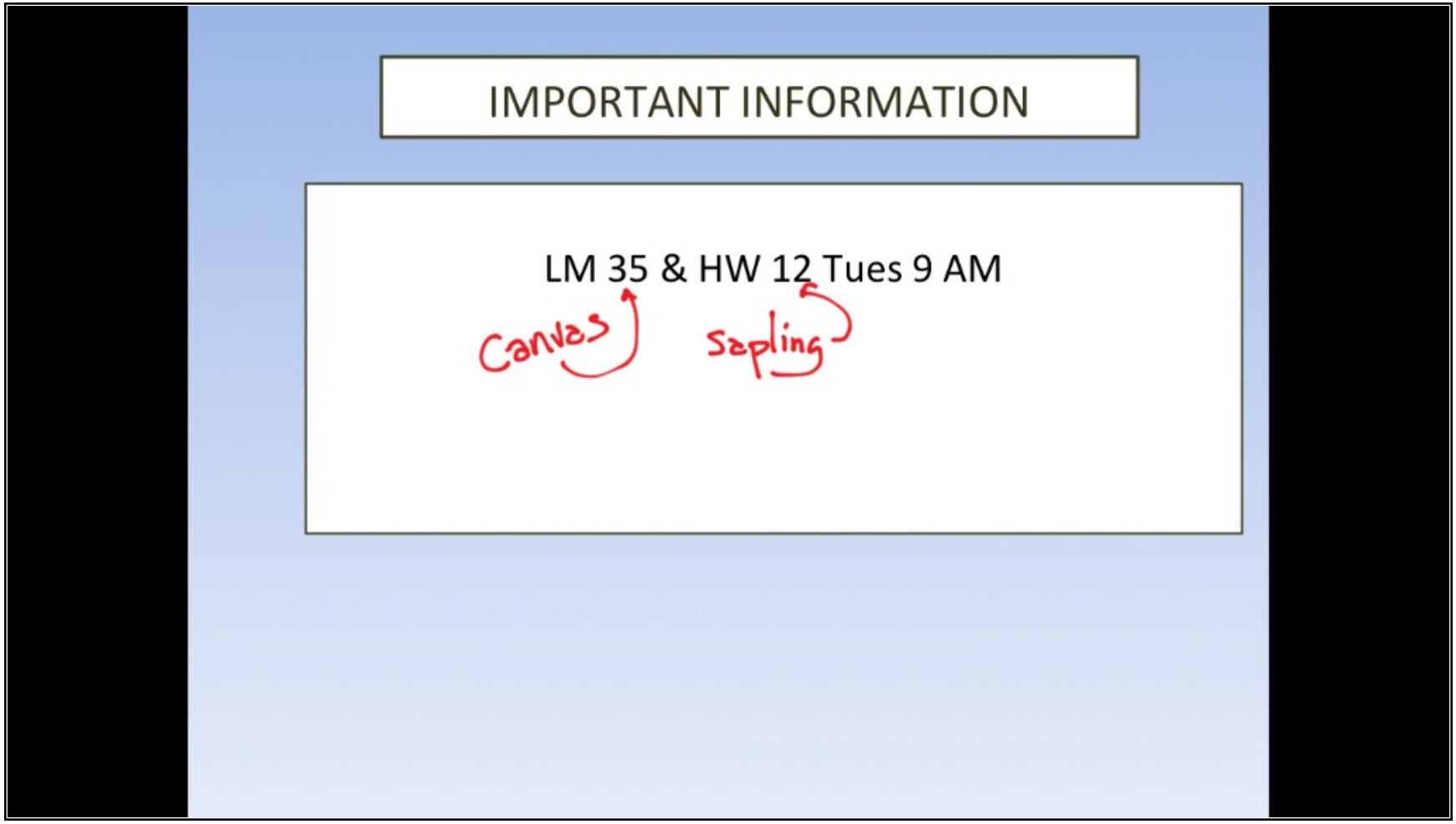
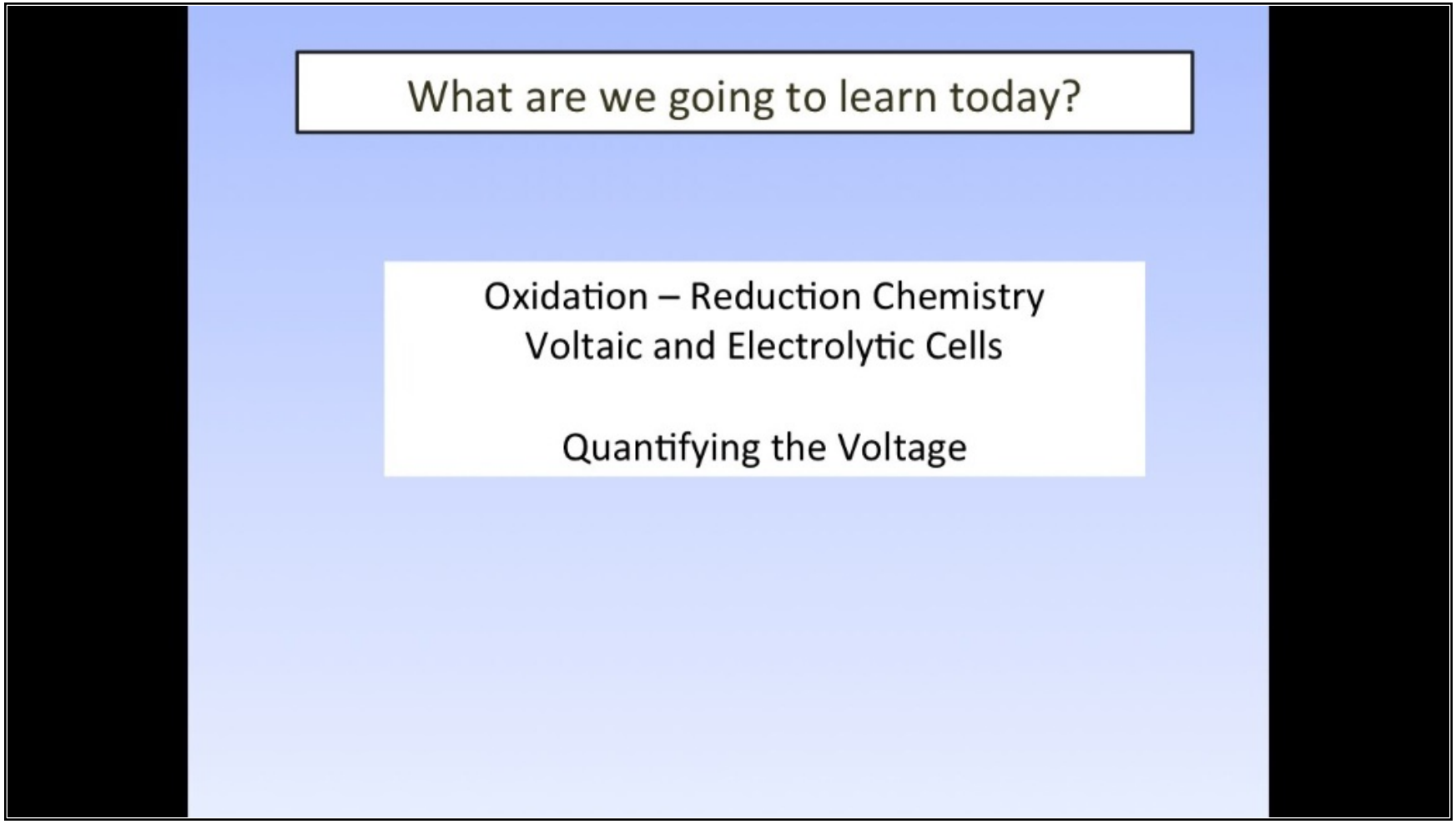

Thinking Like a Chemist
About Electrochemistry II
e⁻ on the move
UNIT 8 DAY3
Battery
3 names
can be just voltaic backwards
can be different


IMPORTANT INFORMATION
LM 35 & HW 12 Tues 9 AM
Canvas
Sapling


What are we going to learn today?
Oxidation – Reduction Chemistry
Voltaic and Electrolytic Cells
Quantifying the Voltage

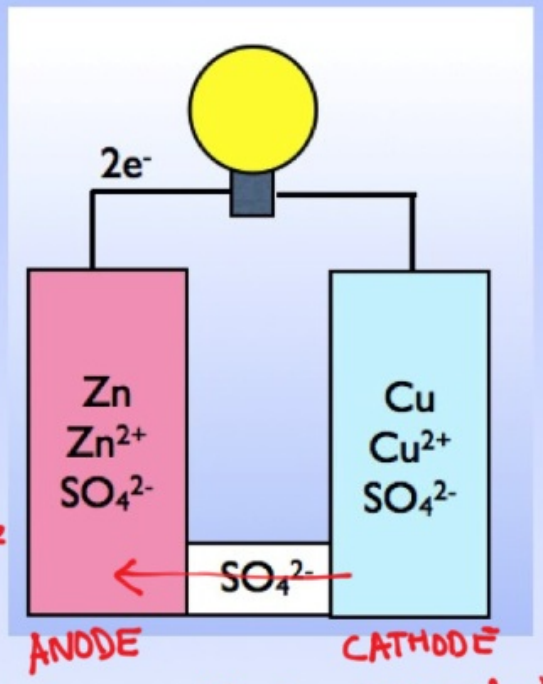
Quiz: Clicker Question

1. The following is a sketch of a voltaic cell. In which direction will the sulfate anions flow?

A. Toward the anode
B. Toward the cathode
C. Depends, could go either way to balance charge

2. Is it possible for the "counter ions" to flow through the external wire to balance the charge?

A. Yes
B. No



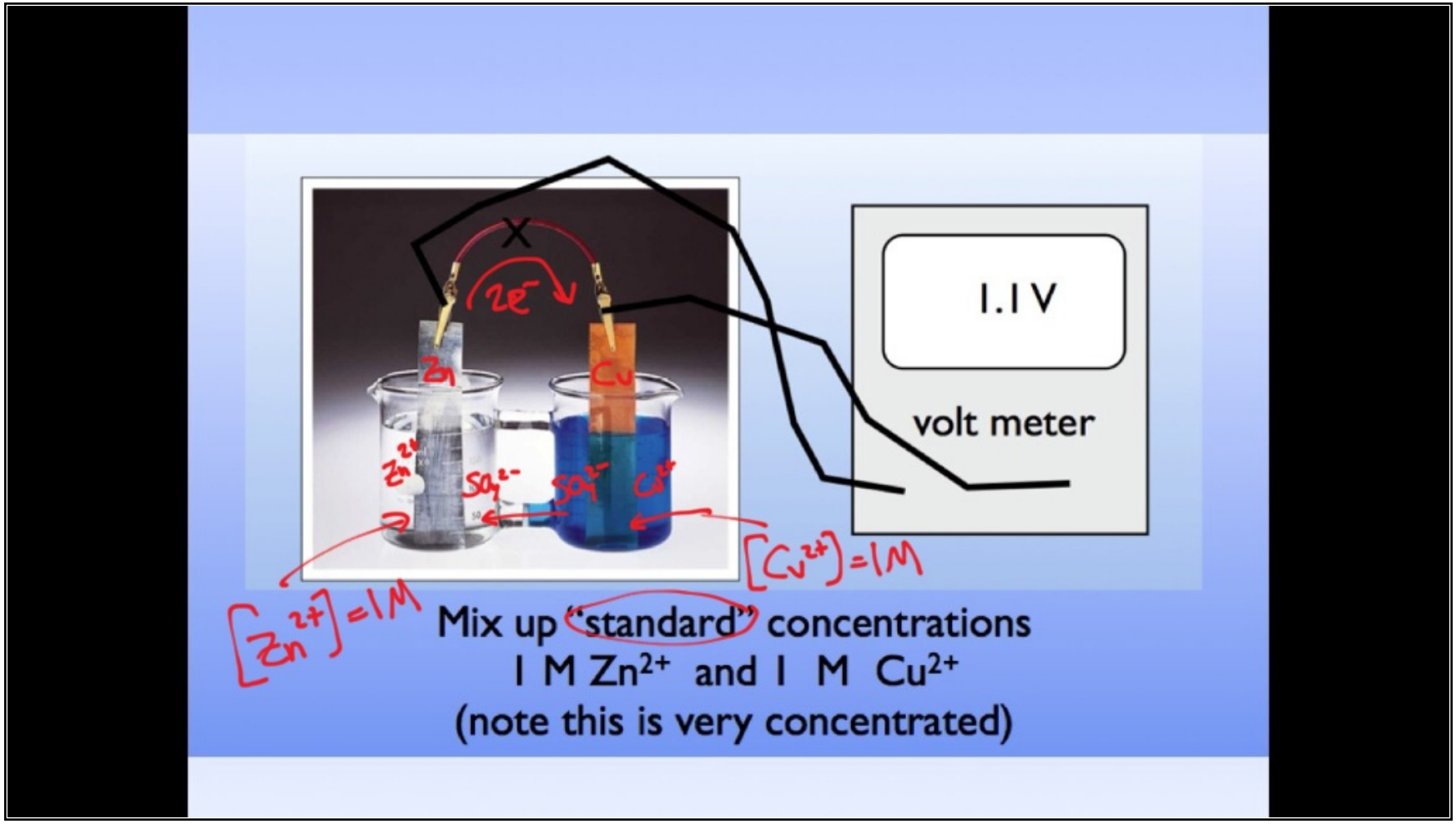
By definition e⁻ flow Anode → Cathode

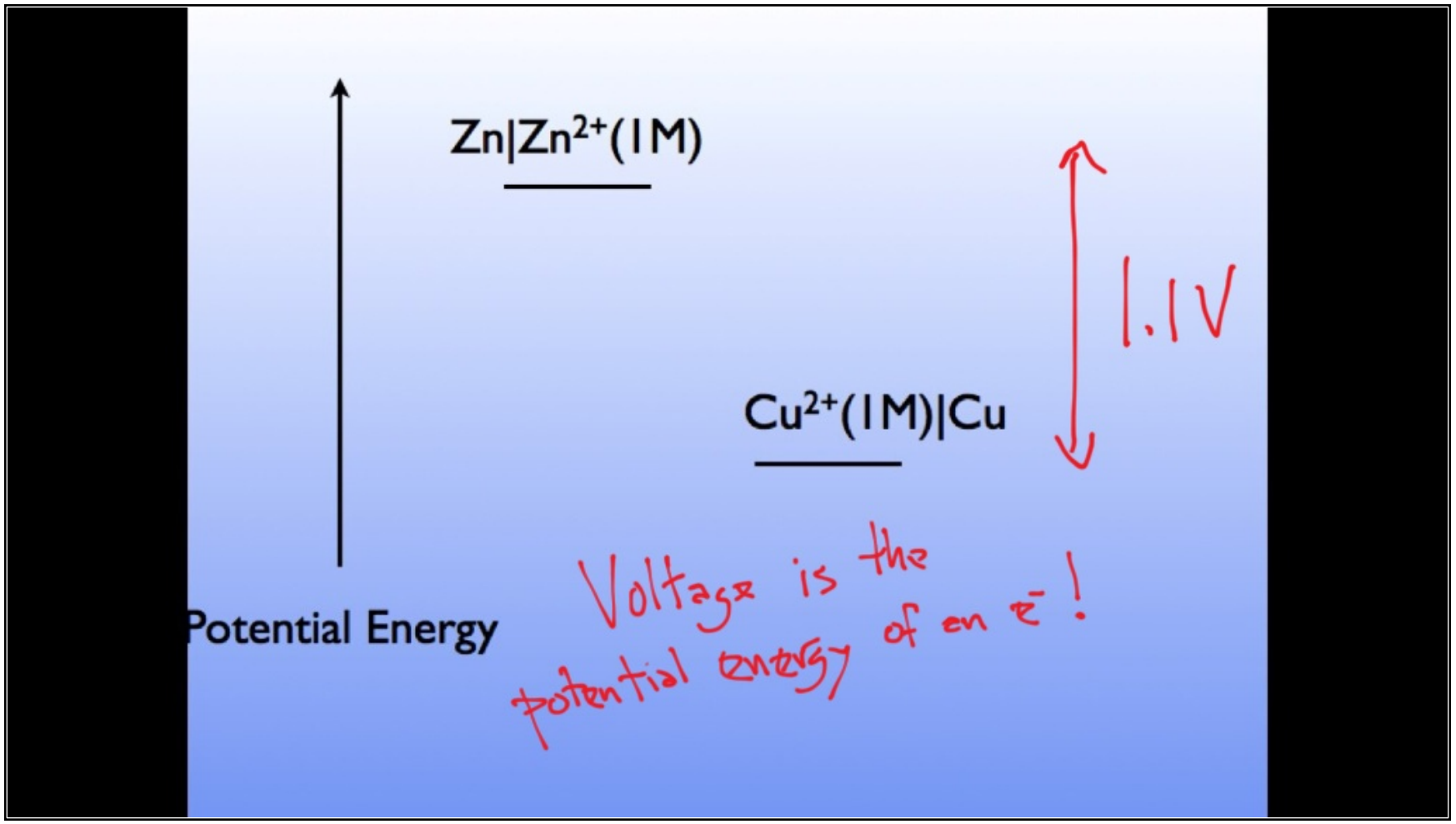
therefore Anion flow CAT → AN

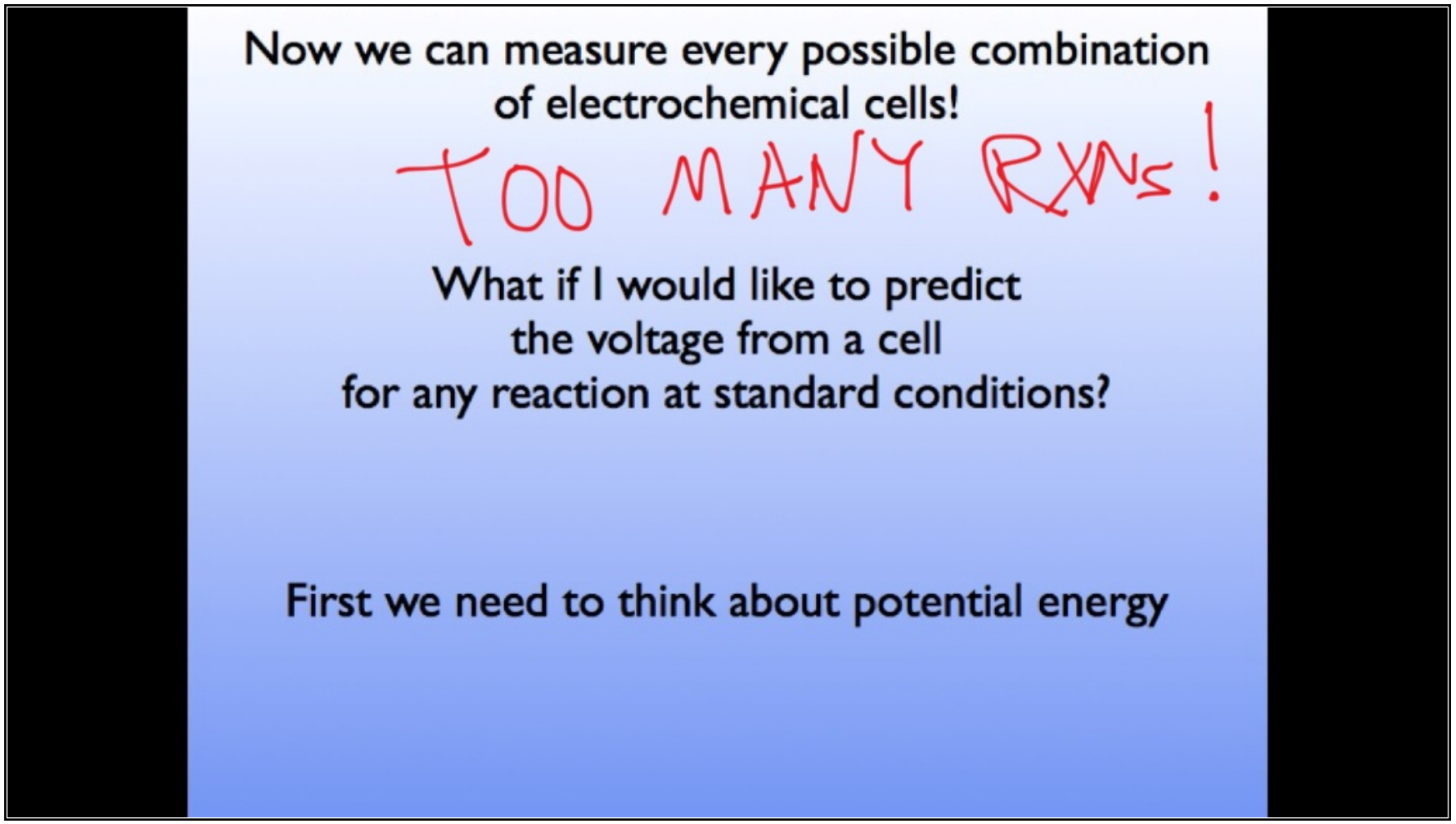
metal wire → e⁻ conductor
electrolyte → ion conductor

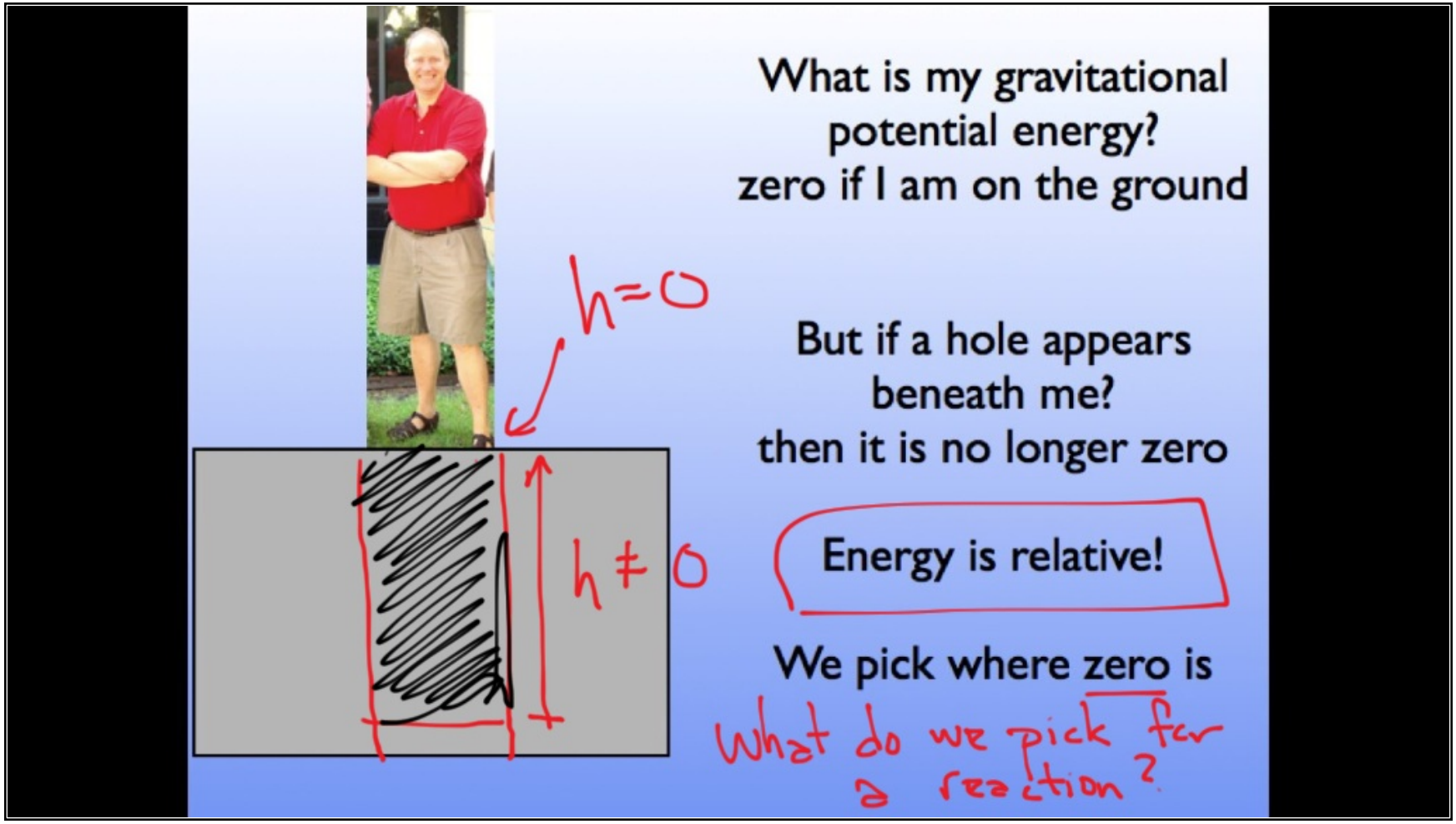
Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	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		

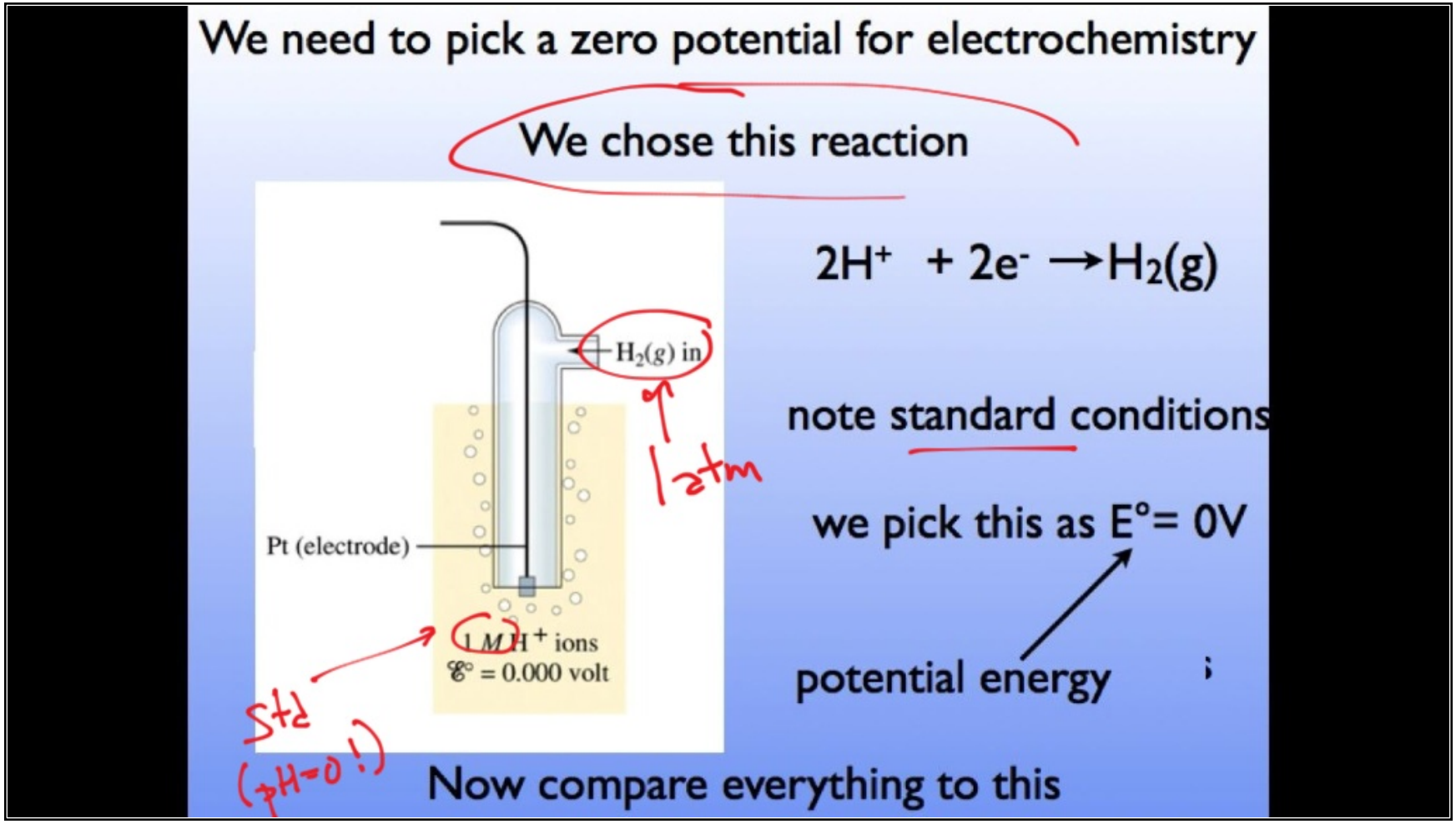
Comparing lots of reactions

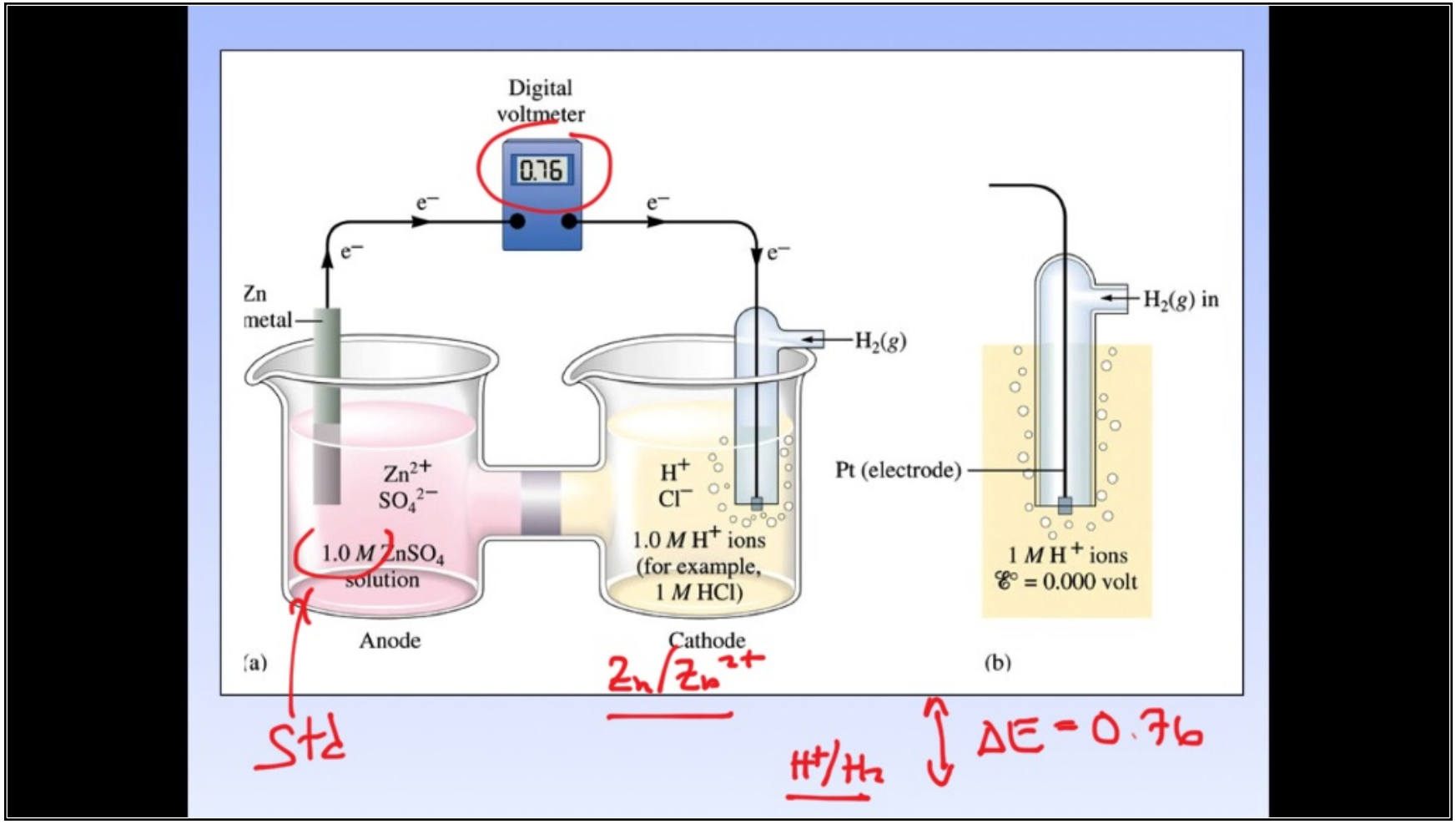

X
2e⁻
Zn
Cu
1.1 V
volt meter
$[Zn^{2+}]=1M$
$[Cu^{2+}]=1M$
Mix up "standard" concentrations
1 M Zn^{2+} and 1 M Cu^{2+}
(note this is very concentrated)

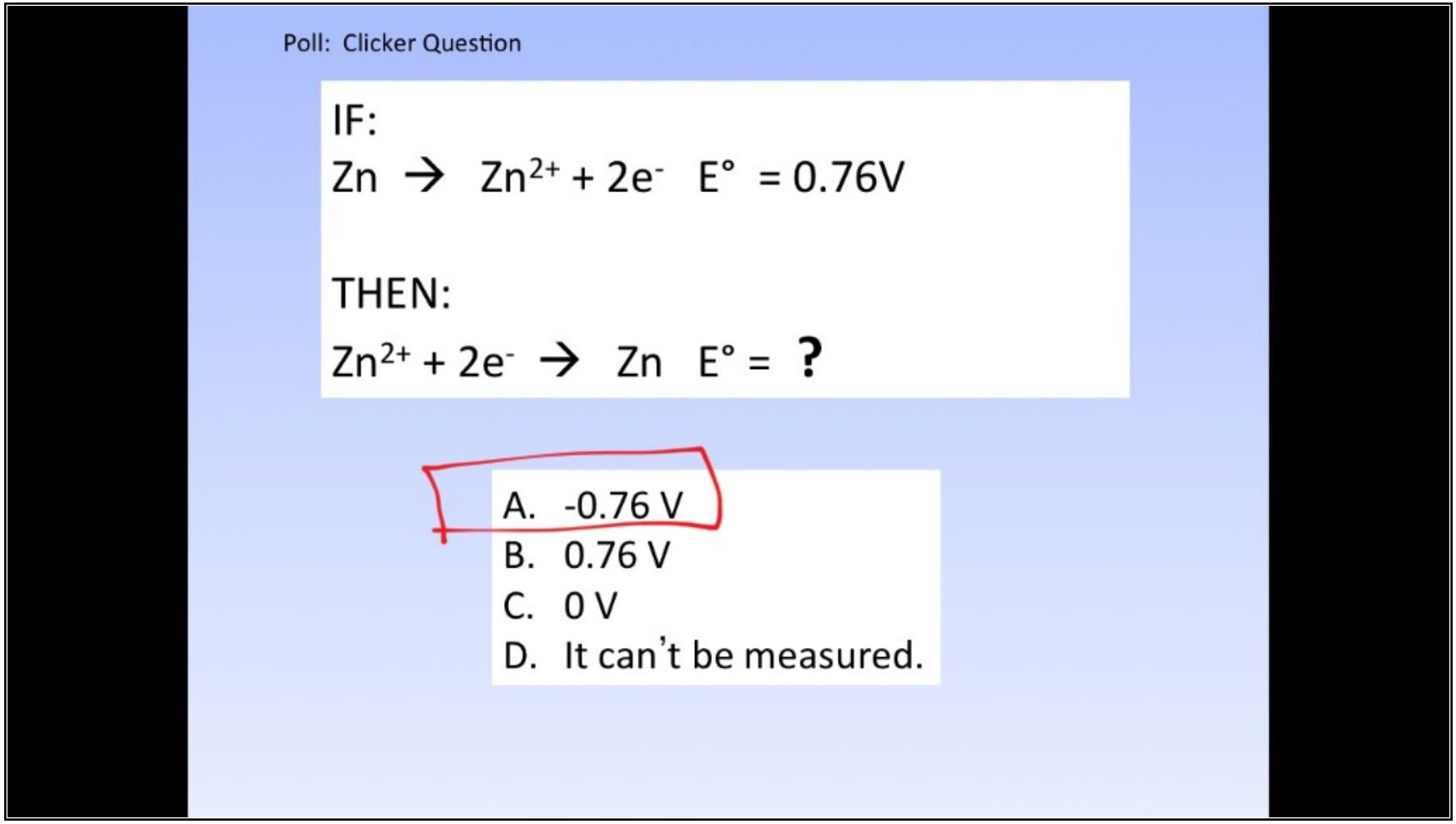

Zn|Zn2+(1M)
Cu2+(1M)|Cu
1.1V
Potential Energy
Voltage is the potential energy of an e-!

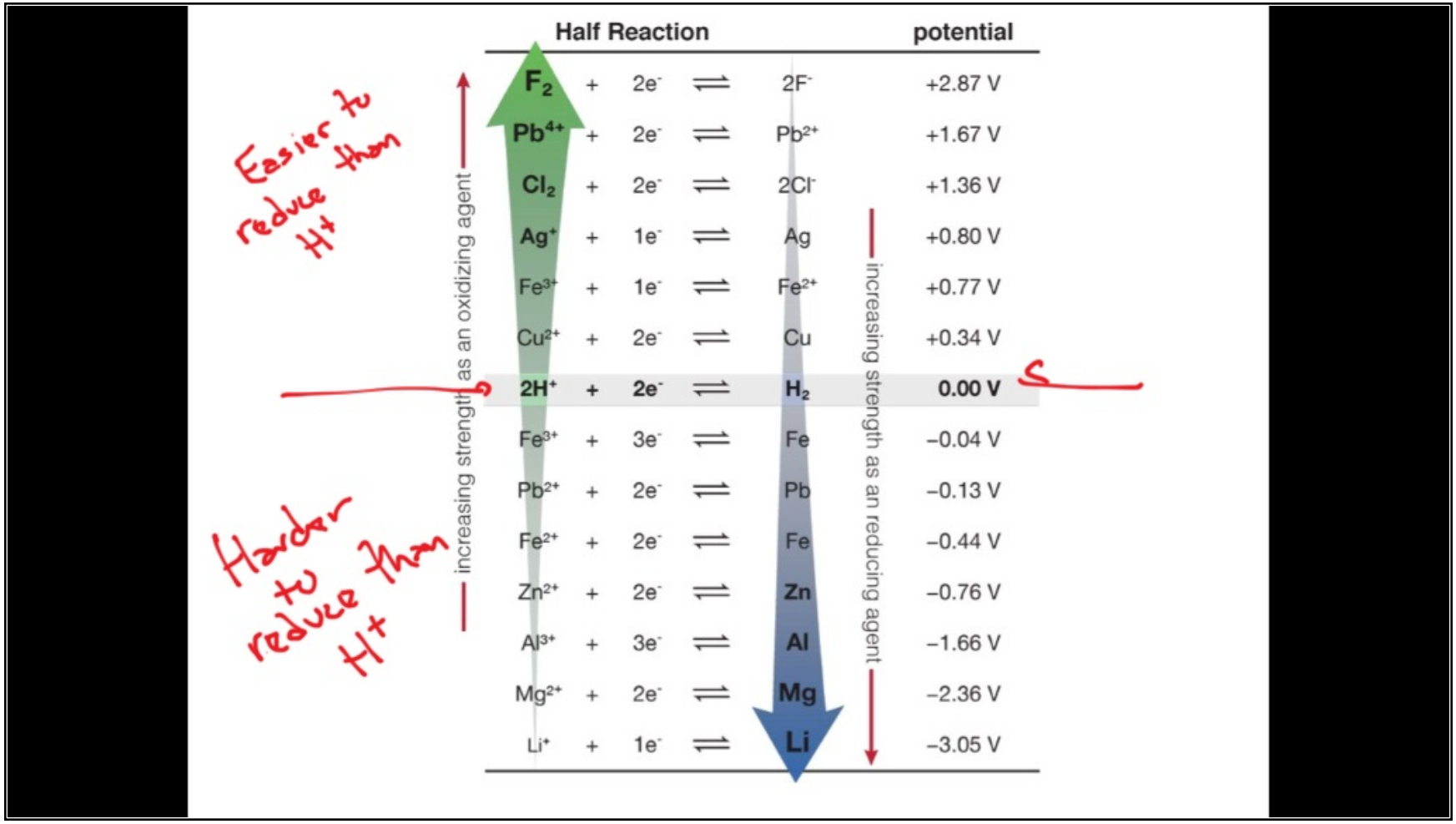

Now we can measure every possible combination of electrochemical cells!
TOO MANY RXNs!
What if I would like to predict the voltage from a cell for any reaction at standard conditions?
First we need to think about potential energy

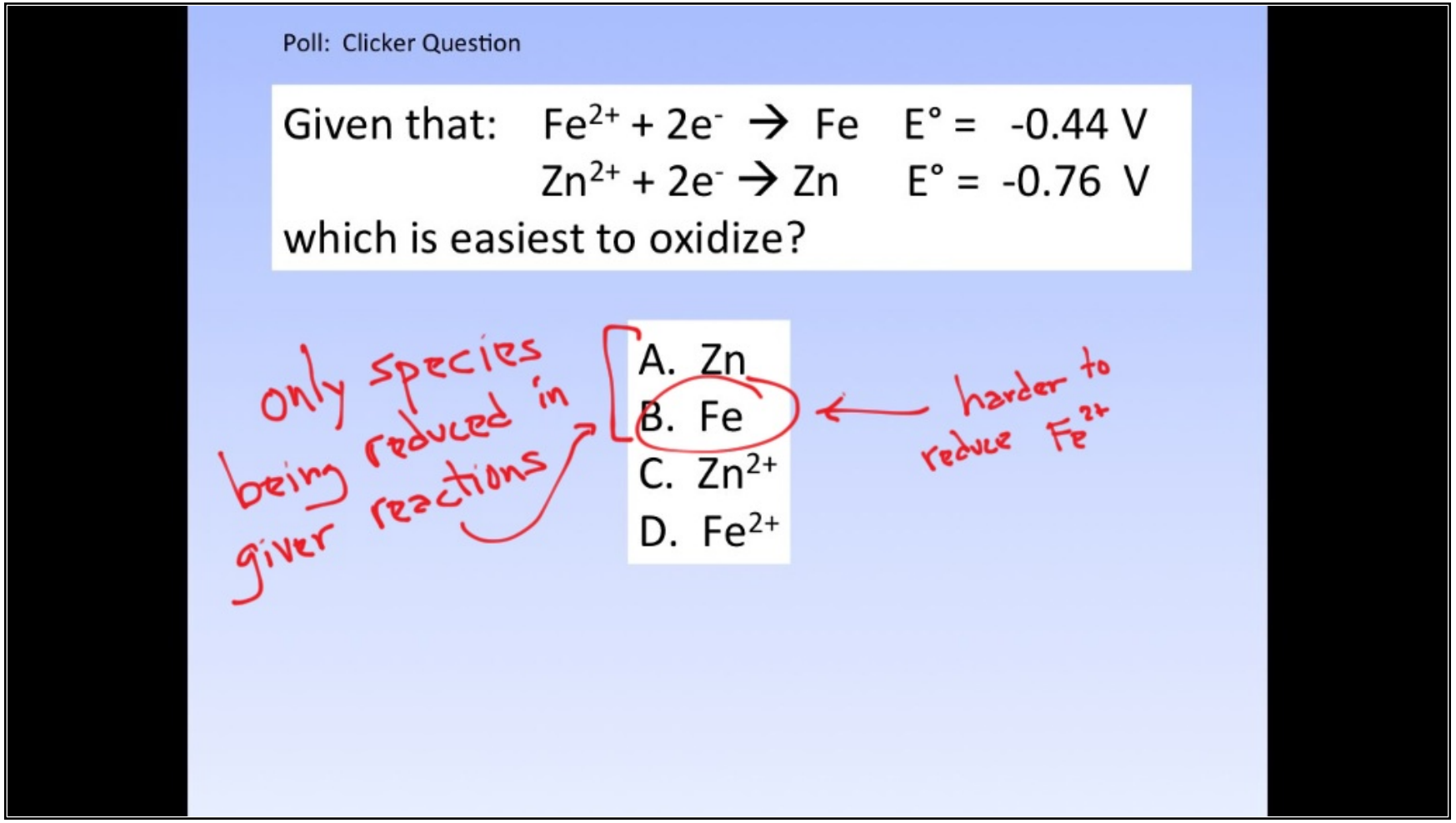

What is my gravitational potential energy?
zero if I am on the ground
h=0
But if a hole appears beneath me?
then it is no longer zero
h ≠ 0
Energy is relative!
We pick where zero is
What do we pick for a reaction?

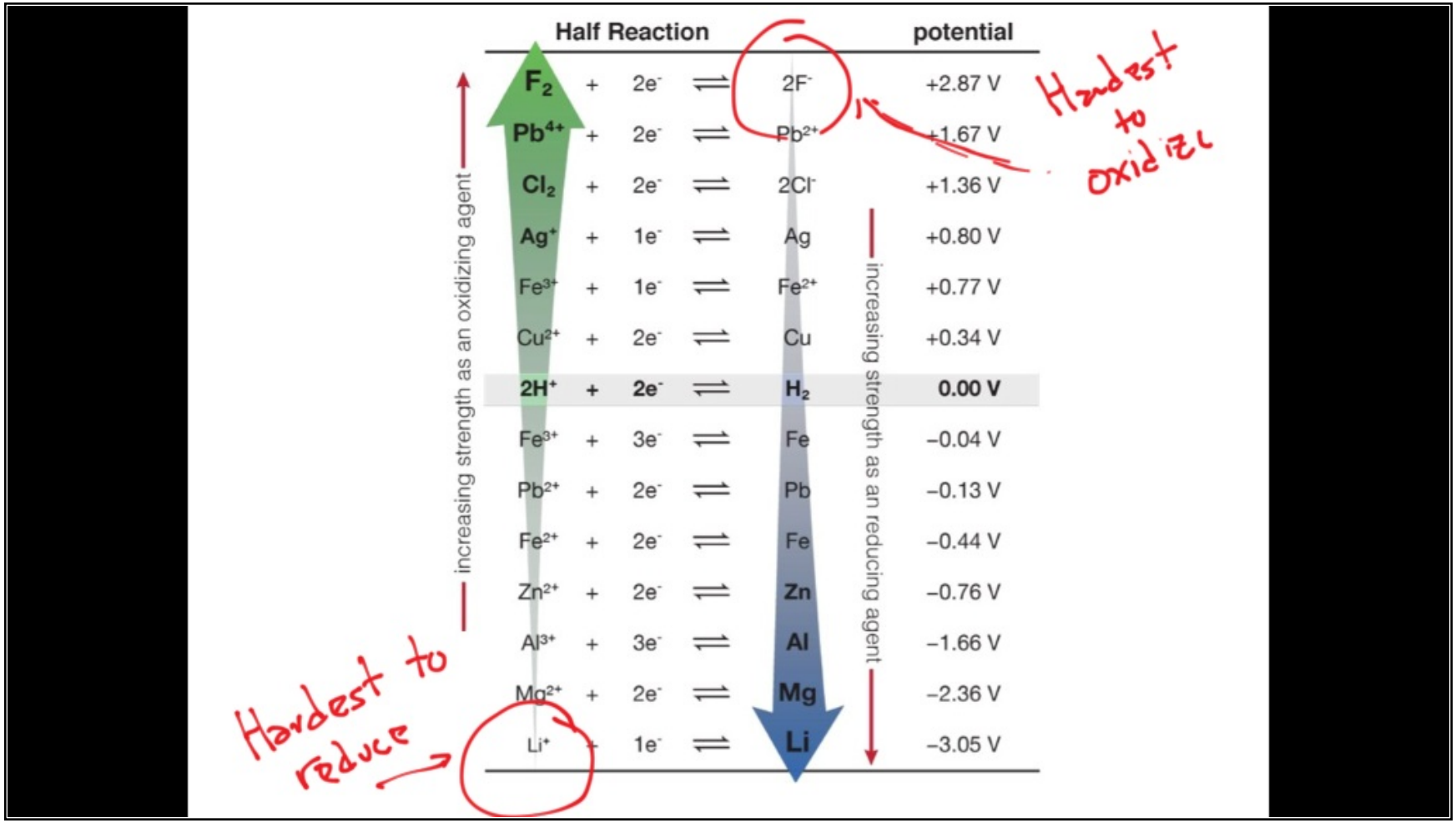

We need to pick a zero potential for electrochemistry
We chose this reaction
$2H^+ + 2e^- \rightarrow H_2(g)$
$H_2(g)$ in
1 atm
note standard conditions
we pick this as E°= 0V
Pt (electrode)
1 M H^+ ions
$\mathscr{E}^\circ$ = 0.000 volt
potential energy
Std
(pH=0!)
Now compare everything to this

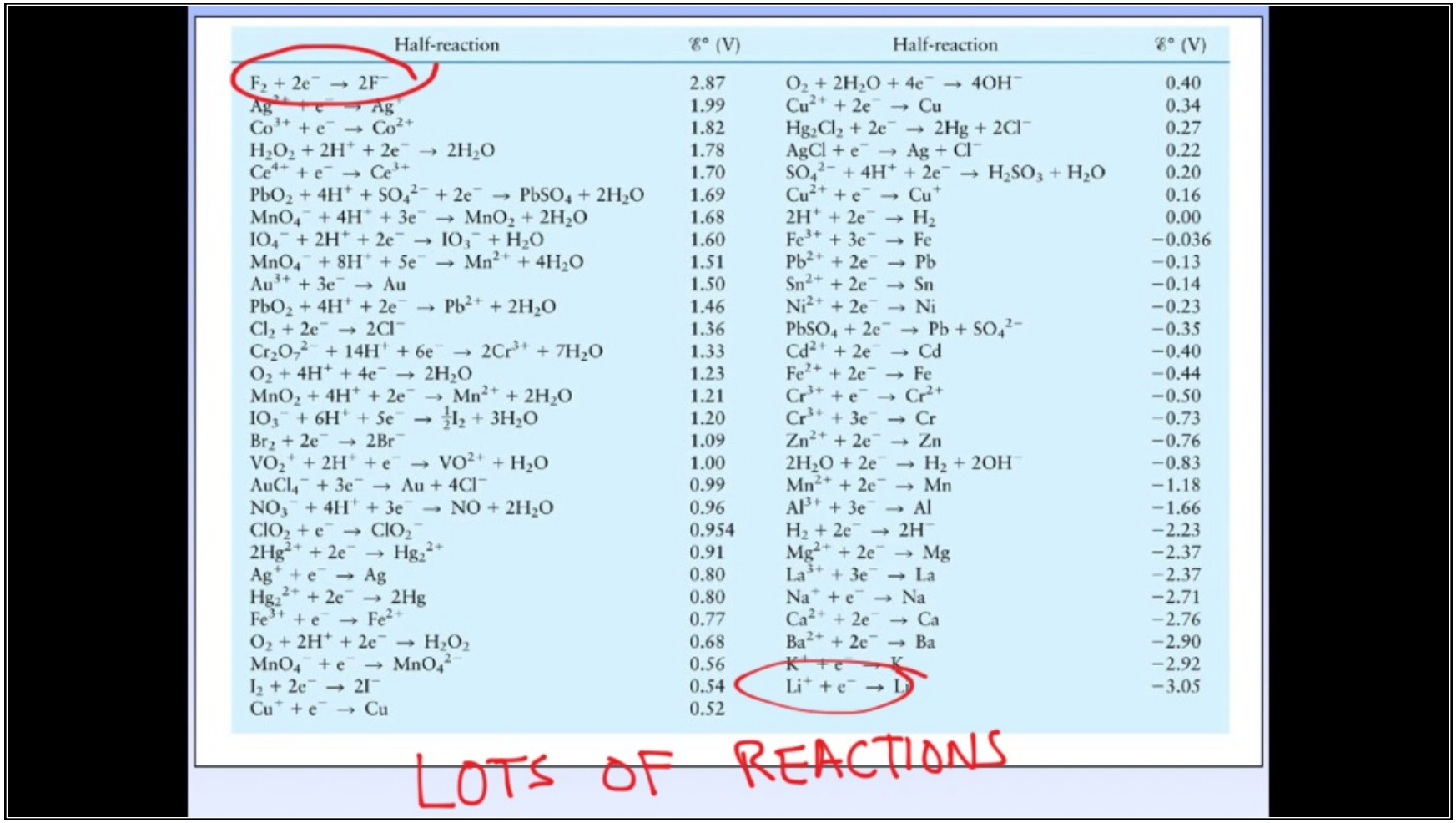

Digital voltmeter
0.76
e⁻
e⁻
e⁻
e⁻
Zn metal
$H_2(g)$
Zn^{2+}
SO_4^{2-}
1.0 M $ZnSO_4$ solution
H^+
Cl^-
1.0 M H^+ ions (for example, 1 M HCl)
Anode
Cathode
(a)
Pt (electrode)
$H_2(g)$ in
1 M H^+ ions
$\mathscr{E}^\circ$ = 0.000 volt
(b)
Std
Zn/Zn²⁺
H⁺/H₂
ΔE = 0.76


Poll: Clicker Question
IF:
Zn → Zn2+ + 2e- E° = 0.76V
THEN:
Zn2+ + 2e- → Zn E° = ?
A. -0.76 V
B. 0.76 V
C. 0 V
D. It can't be measured.


Half Reaction
potential
F2 + 2e- ⇌ 2F- +2.87 V
Pb4+ + 2e- ⇌ Pb2+ +1.67 V
Cl2 + 2e- ⇌ 2Cl- +1.36 V
Ag+ + 1e- ⇌ Ag +0.80 V
Fe3+ + 1e- ⇌ Fe2+ +0.77 V
Cu2+ + 2e- ⇌ Cu +0.34 V
2H+ + 2e- ⇌ H2 0.00 V
Fe3+ + 3e- ⇌ Fe −0.04 V
Pb2+ + 2e- ⇌ Pb −0.13 V
Fe2+ + 2e- ⇌ Fe −0.44 V
Zn2+ + 2e- ⇌ Zn −0.76 V
Al3+ + 3e- ⇌ Al −1.66 V
Mg2+ + 2e- ⇌ Mg −2.36 V
Li+ + 1e- ⇌ Li −3.05 V
increasing strength as an oxidizing agent
increasing strength as an reducing agent
Easier to reduce H+
Harder to reduce H+
S


Poll: Clicker Question
Given that: $Fe^{2+} + 2e^- \rightarrow Fe$ E° = -0.44 V
$Zn^{2+} + 2e^- \rightarrow Zn$ E° = -0.76 V
which is easiest to oxidize?
A. Zn
B. Fe
C. Zn^{2+}
D. Fe^{2+}
only species being reduced in giver reactions
harder to reduce Fe^{2+}


Half Reaction
potential
increasing strength as an oxidizing agent
increasing strength as an reducing agent
F2 + 2e- ⇌ 2F- +2.87 V
Pb4+ + 2e- ⇌ Pb2+ +1.67 V
Cl2 + 2e- ⇌ 2Cl- +1.36 V
Ag+ + 1e- ⇌ Ag +0.80 V
Fe3+ + 1e- ⇌ Fe2+ +0.77 V
Cu2+ + 2e- ⇌ Cu +0.34 V
2H+ + 2e- ⇌ H2 0.00 V
Fe3+ + 3e- ⇌ Fe −0.04 V
Pb2+ + 2e- ⇌ Pb −0.13 V
Fe2+ + 2e- ⇌ Fe −0.44 V
Zn2+ + 2e- ⇌ Zn −0.76 V
Al3+ + 3e- ⇌ Al −1.66 V
Mg2+ + 2e- ⇌ Mg −2.36 V
Li+ + 1e- ⇌ Li −3.05 V
Hardest to oxidize
Hardest to reduce



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		

LOTS OF REACTIONS

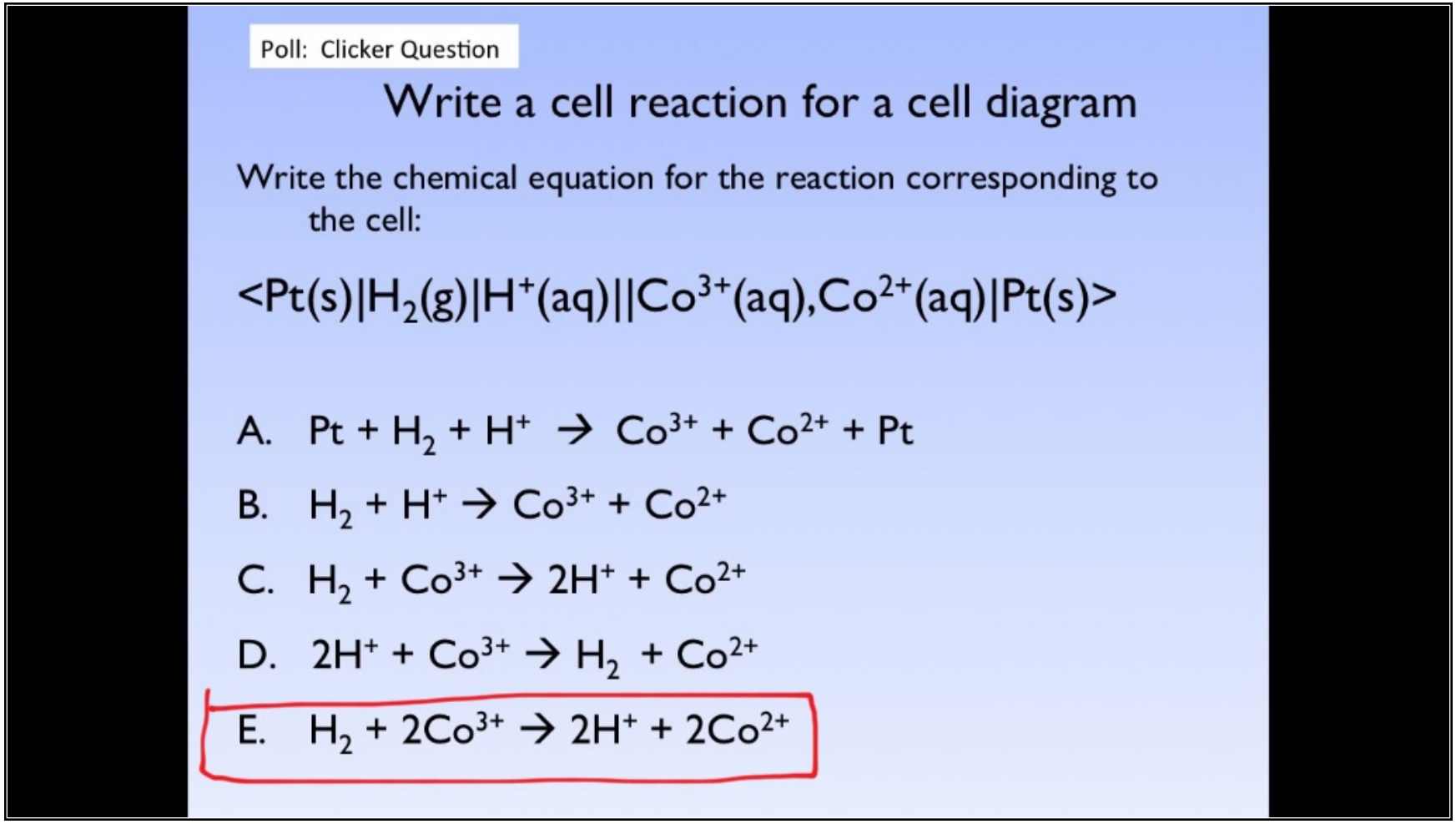
Standard ½ reactions are listed as REDUCTION ½ reactions

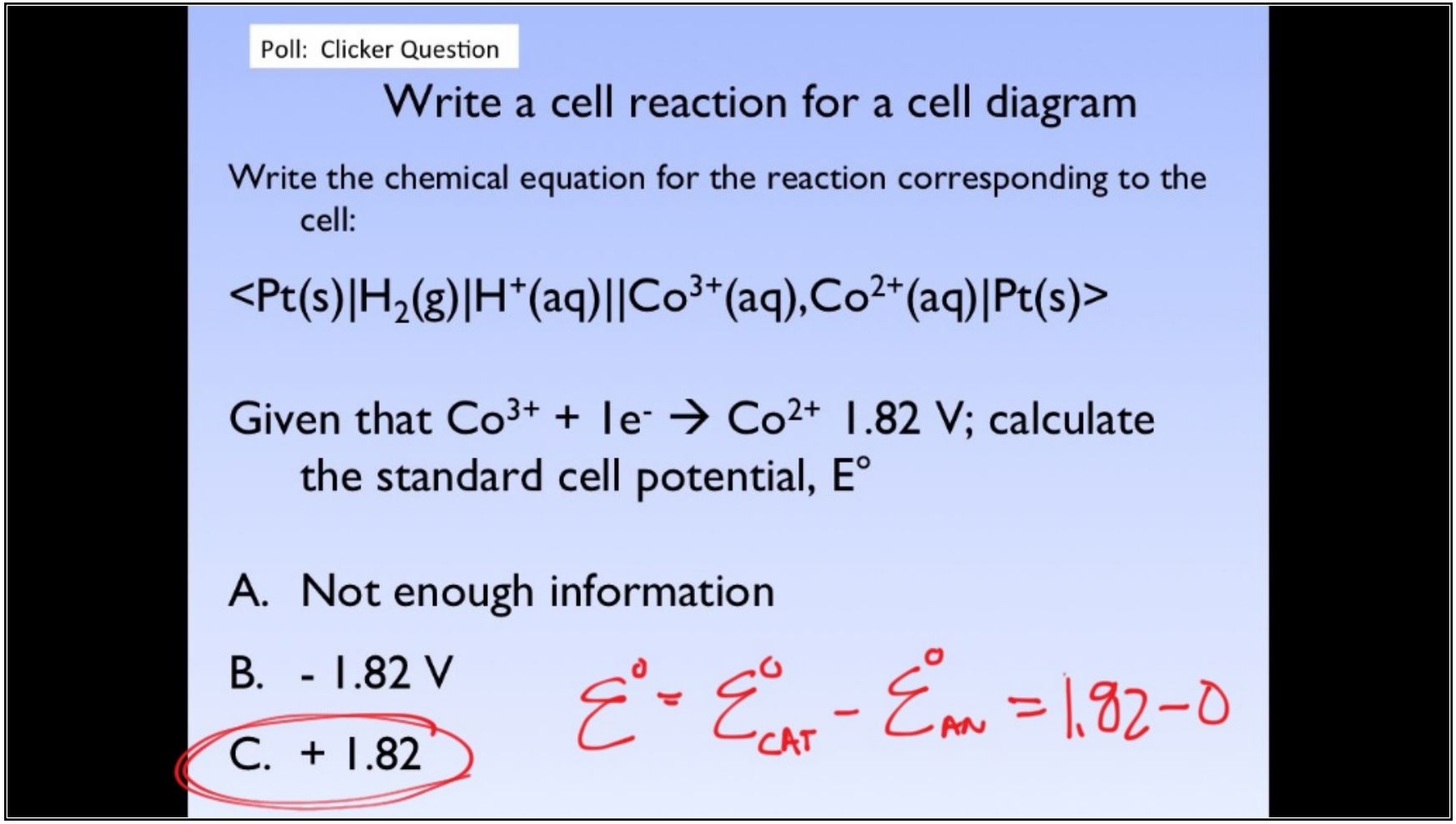
HOW CAN YOU CALCULATE THE STANDARD POTENTIAL OF AN ELECTROCHEMICAL CELL?

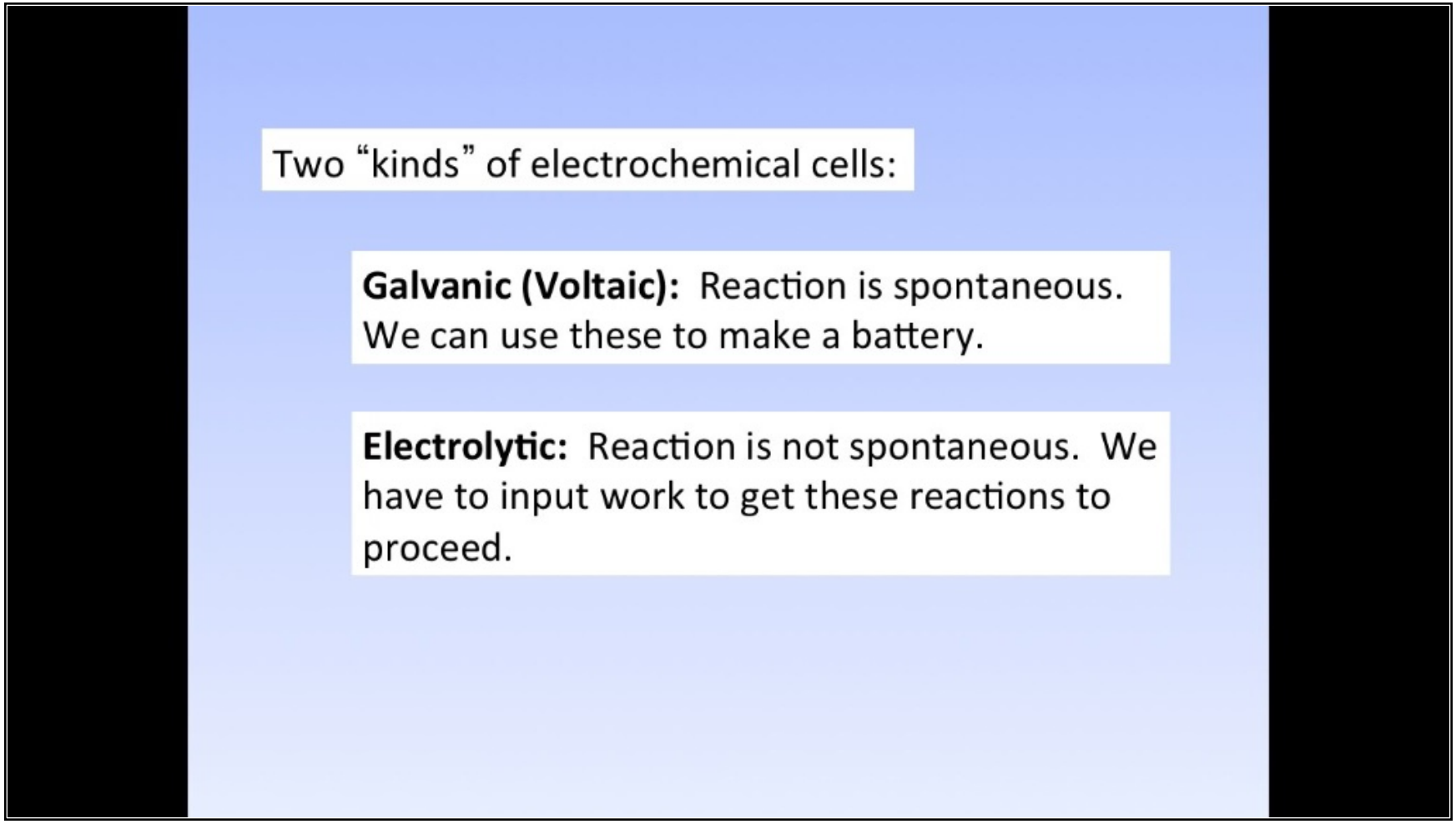
Use the tabulated reduction potentials for each ½ reaction…

THE # OF ELECTRONS DOES NOT MATTER

$E°(cell) = E^{o}(cathode) - E^{o}(anode)$

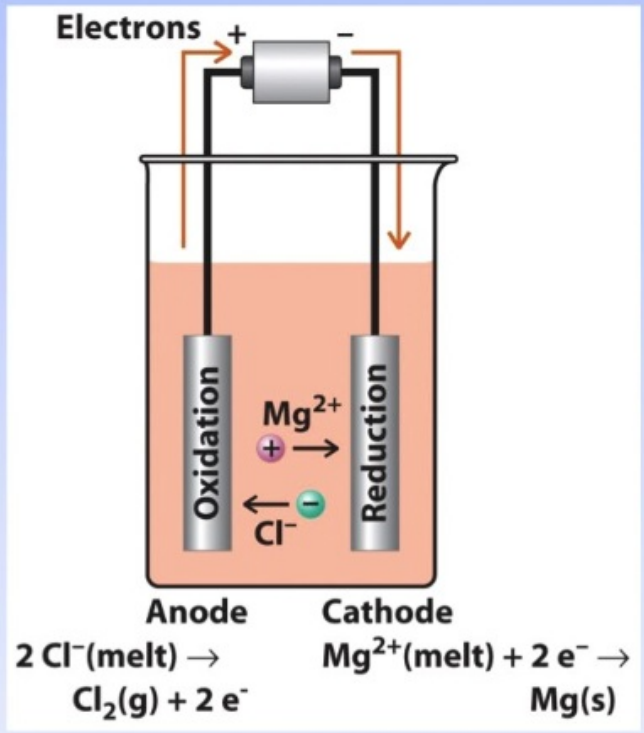

Poll: Clicker Question
Write a cell reaction for a cell diagram
Write the chemical equation for the reaction corresponding to the cell:
<Pt(s)|H2(g)|H+(aq)||Co3+(aq),Co2+(aq)|Pt(s)>
A. Pt + H2 + H+ → Co3+ + Co2+ + Pt
B. H2 + H+ → Co3+ + Co2+
C. H2 + Co3+ → 2H+ + Co2+
D. 2H+ + Co3+ → H2 + Co2+
E. H2 + 2Co3+ → 2H+ + 2Co2+

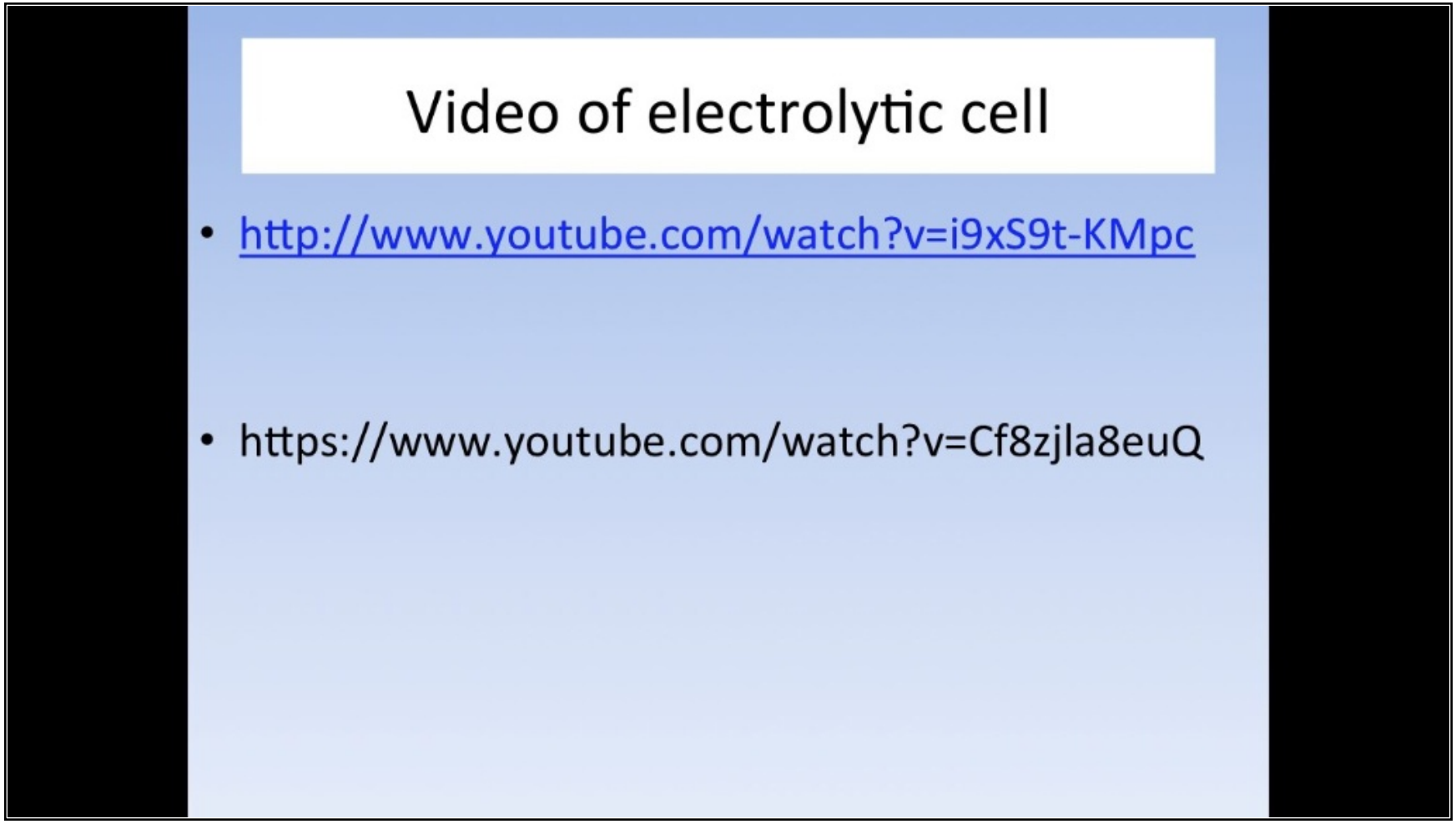

Poll: Clicker Question
Write a cell reaction for a cell diagram
Write the chemical equation for the reaction corresponding to the cell:
<Pt(s)|H2(g)|H+(aq)||Co3+(aq),Co2+(aq)|Pt(s)>
Given that Co3+ + 1e- → Co2+ 1.82 V; calculate the standard cell potential, E°
A. Not enough information
B. - 1.82 V
C. + 1.82
E° = E°CAT - E°AN = 1.82 - 0

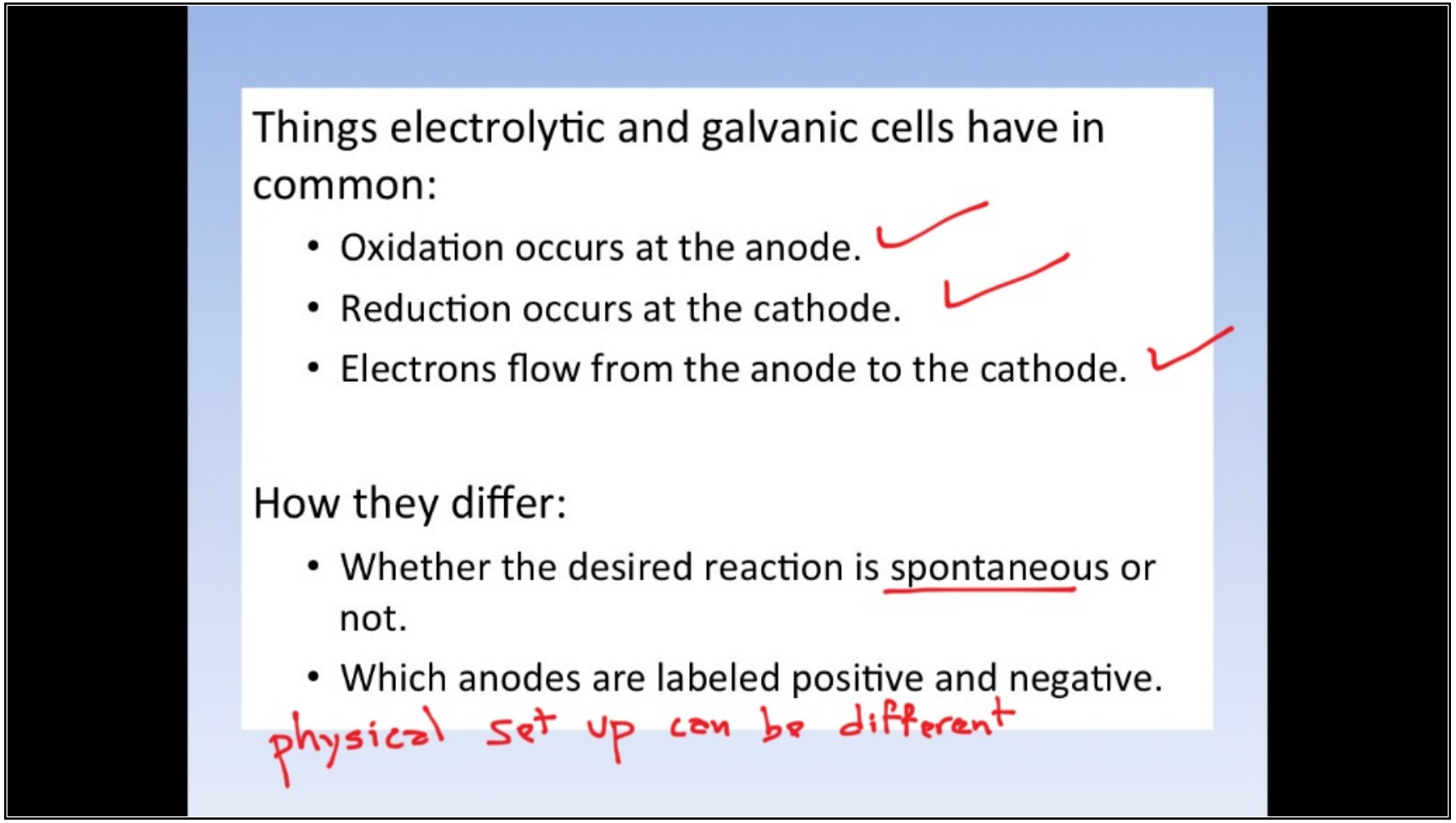

Two "kinds" of electrochemical cells:
Galvanic (Voltaic): Reaction is spontaneous. We can use these to make a battery.
Electrolytic: Reaction is not spontaneous. We have to input work to get these reactions to proceed.

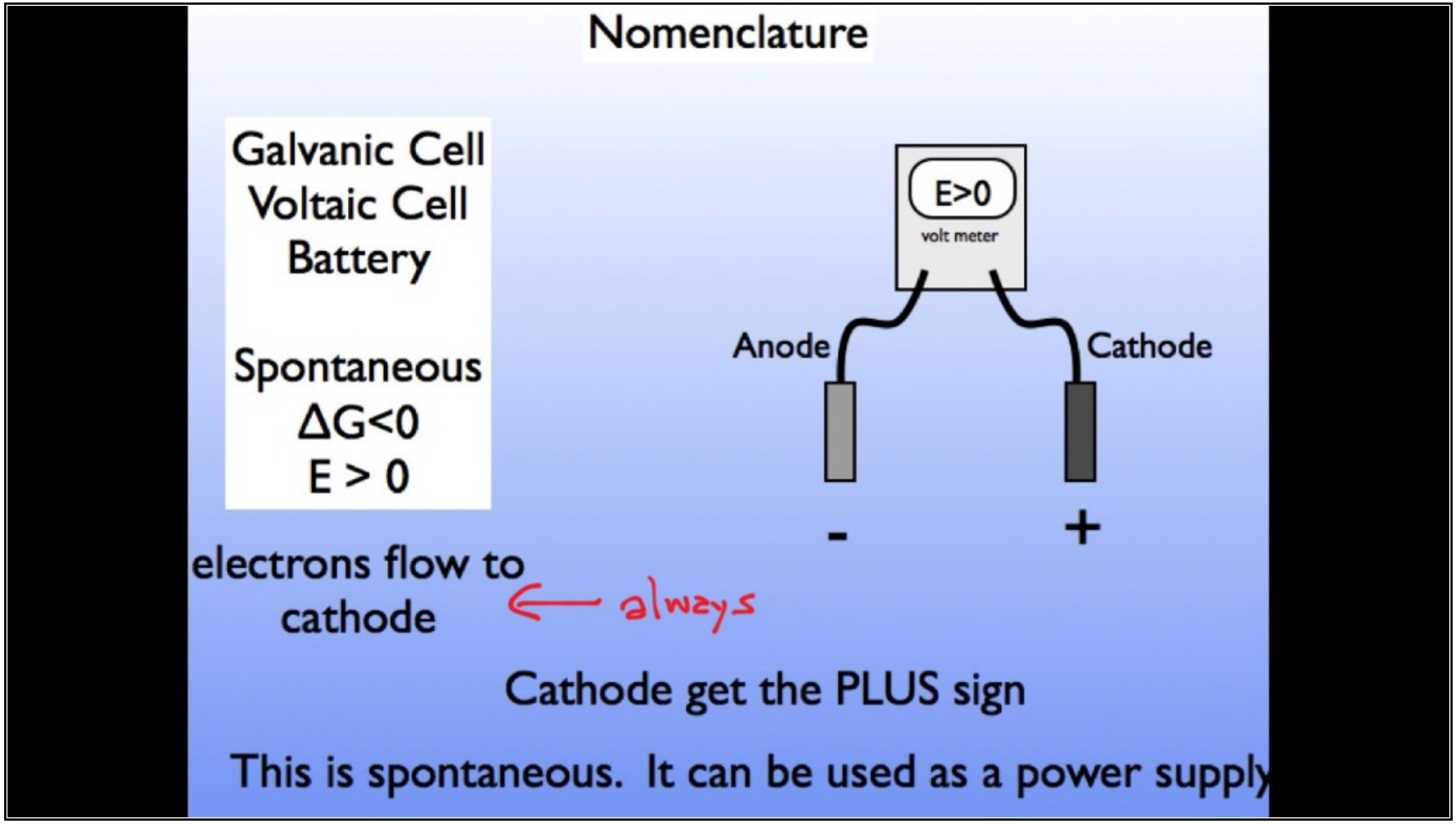
Electrolytic Cells

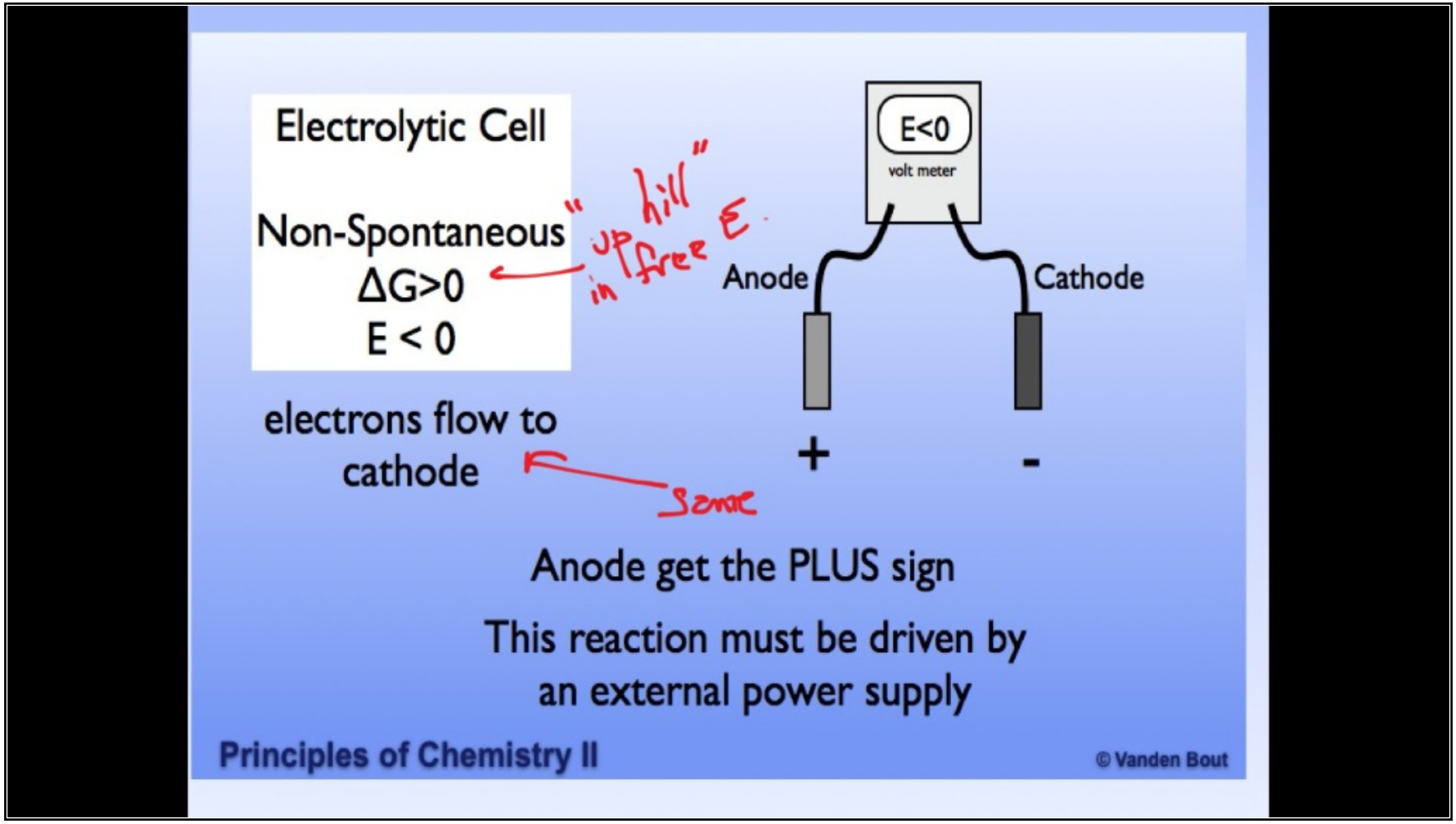
- Reaction is driven in a nonspontaneous direction by using an electric current.
- Anode is site of oxidation but labeled with "+", and cathode is site of reduction but labeled with a "-".
- Over potential is the extra emf over the emf of the cell that is needed to push the reaction in a nonspontaneous direction.




Video of electrolytic cell
• http://www.youtube.com/watch?v=i9xS9t-KMpc
• https://www.youtube.com/watch?v=Cf8zjla8euQ


Things electrolytic and galvanic cells have in common:
• Oxidation occurs at the anode.
• Reduction occurs at the cathode.
• Electrons flow from the anode to the cathode.
How they differ:
• Whether the desired reaction is spontaneous or not.
• Which anodes are labeled positive and negative.
physical set up can be different


Nomenclature
Galvanic Cell
Voltaic Cell
Battery
Spontaneous
ΔG<0
E > 0
E>0
volt meter
Anode
Cathode
-
+
electrons flow to
cathode
always
Cathode get the PLUS sign
This is spontaneous. It can be used as a power supply


Electrolytic Cell
Non-Spontaneous
ΔG>0
E < 0
"up hill" in free E
E<0
volt meter
Anode
Cathode
+
-
electrons flow to cathode
same
Anode get the PLUS sign
This reaction must be driven by an external power supply
Principles of Chemistry II
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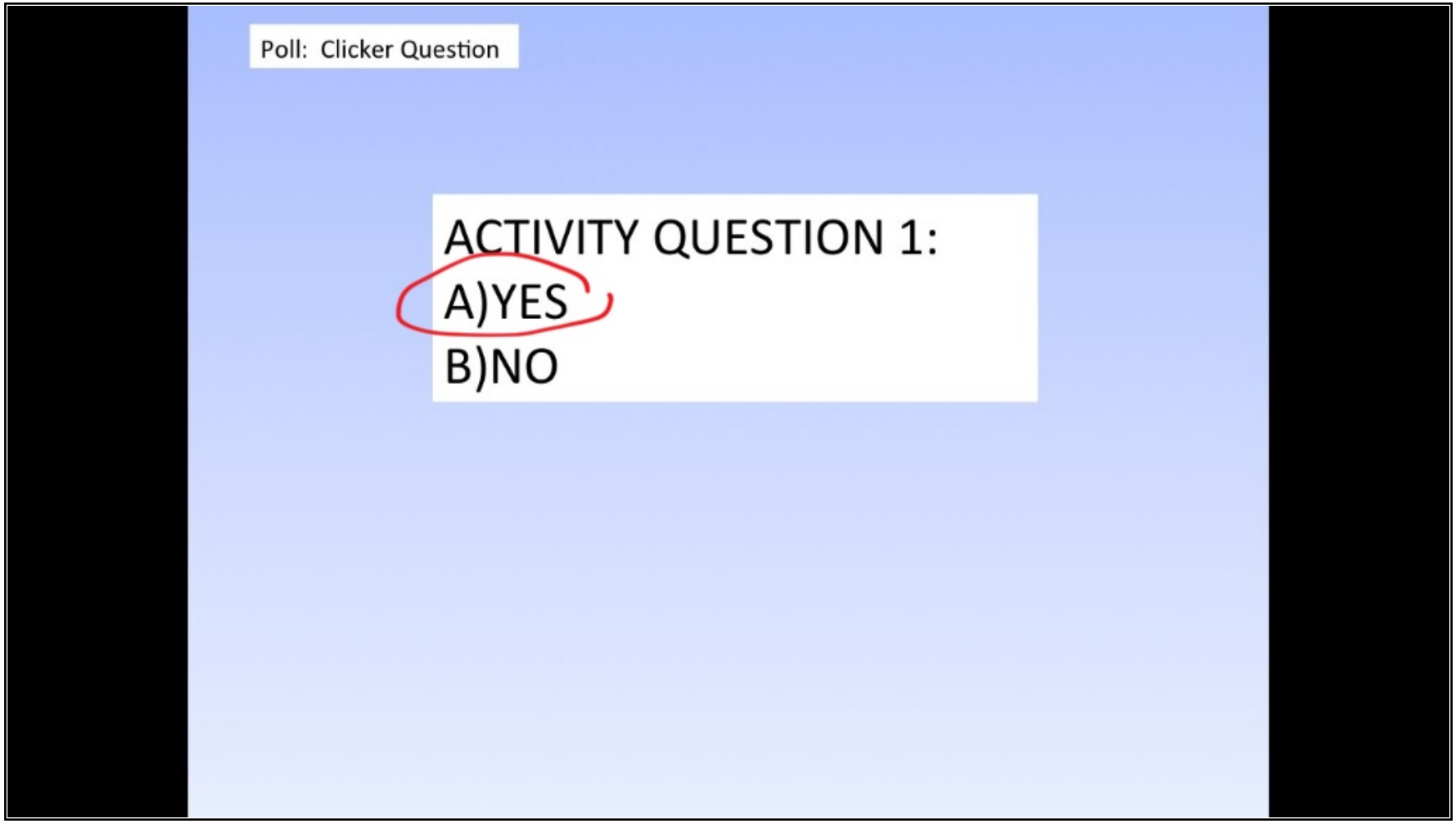
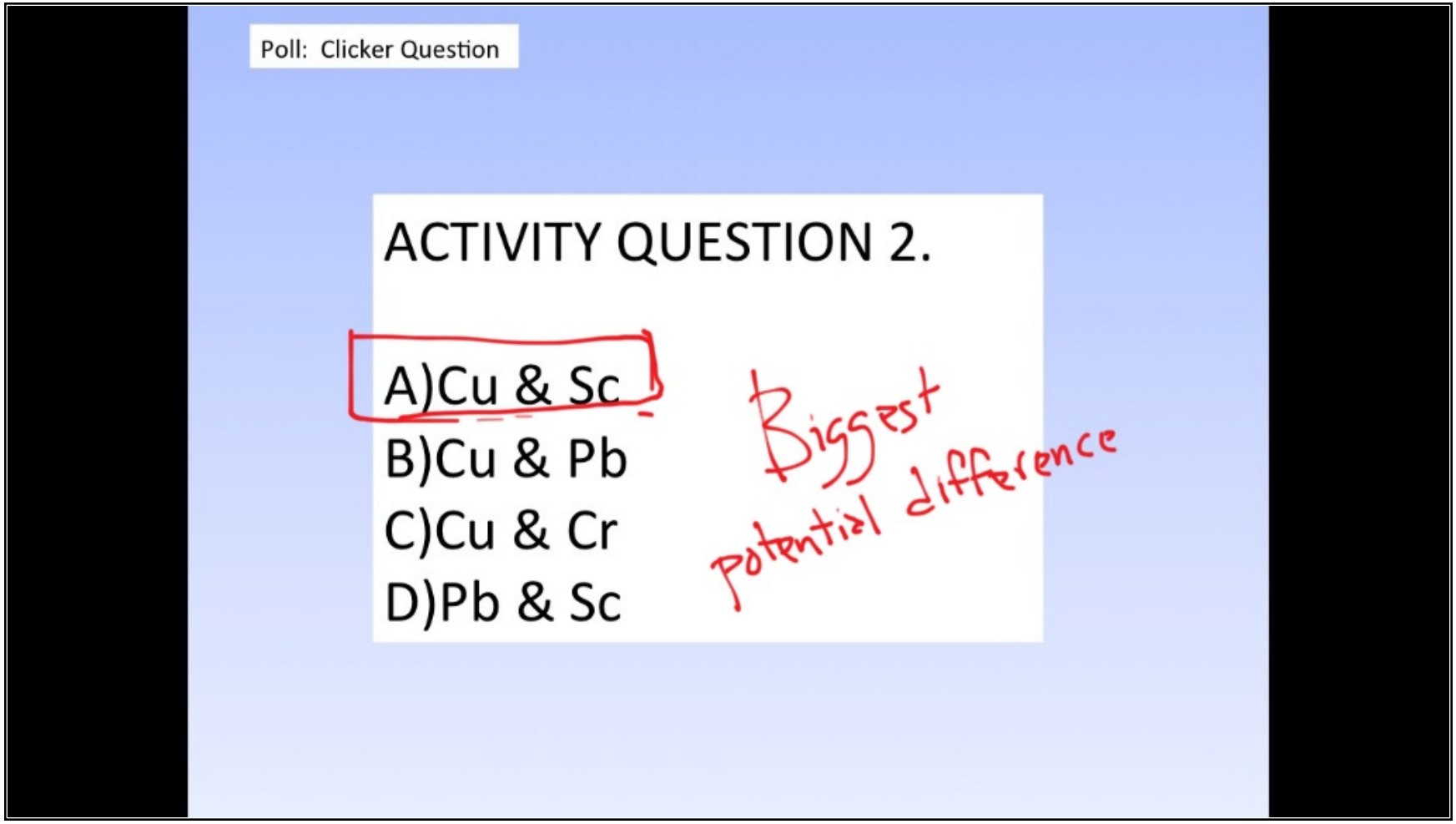
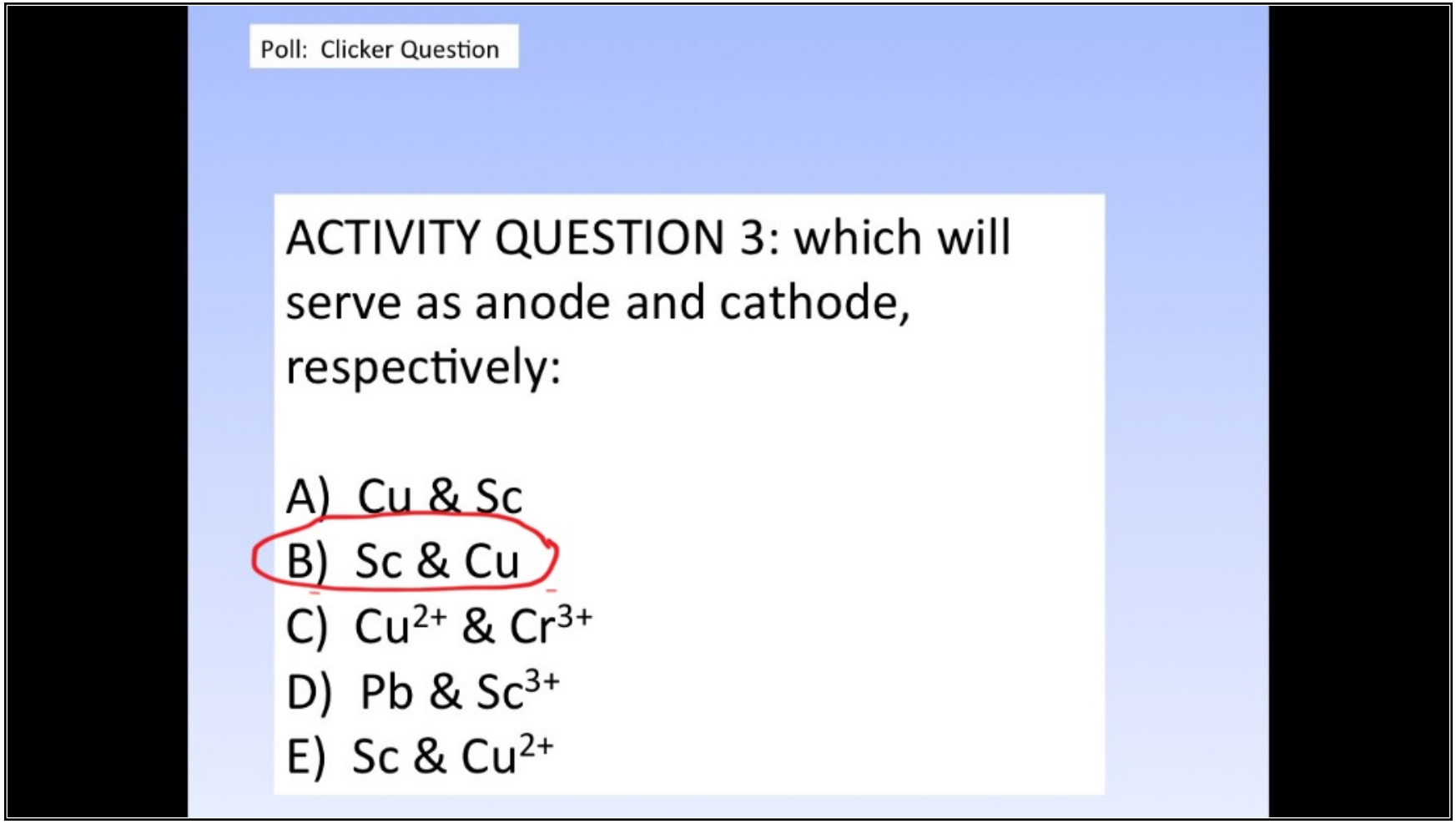
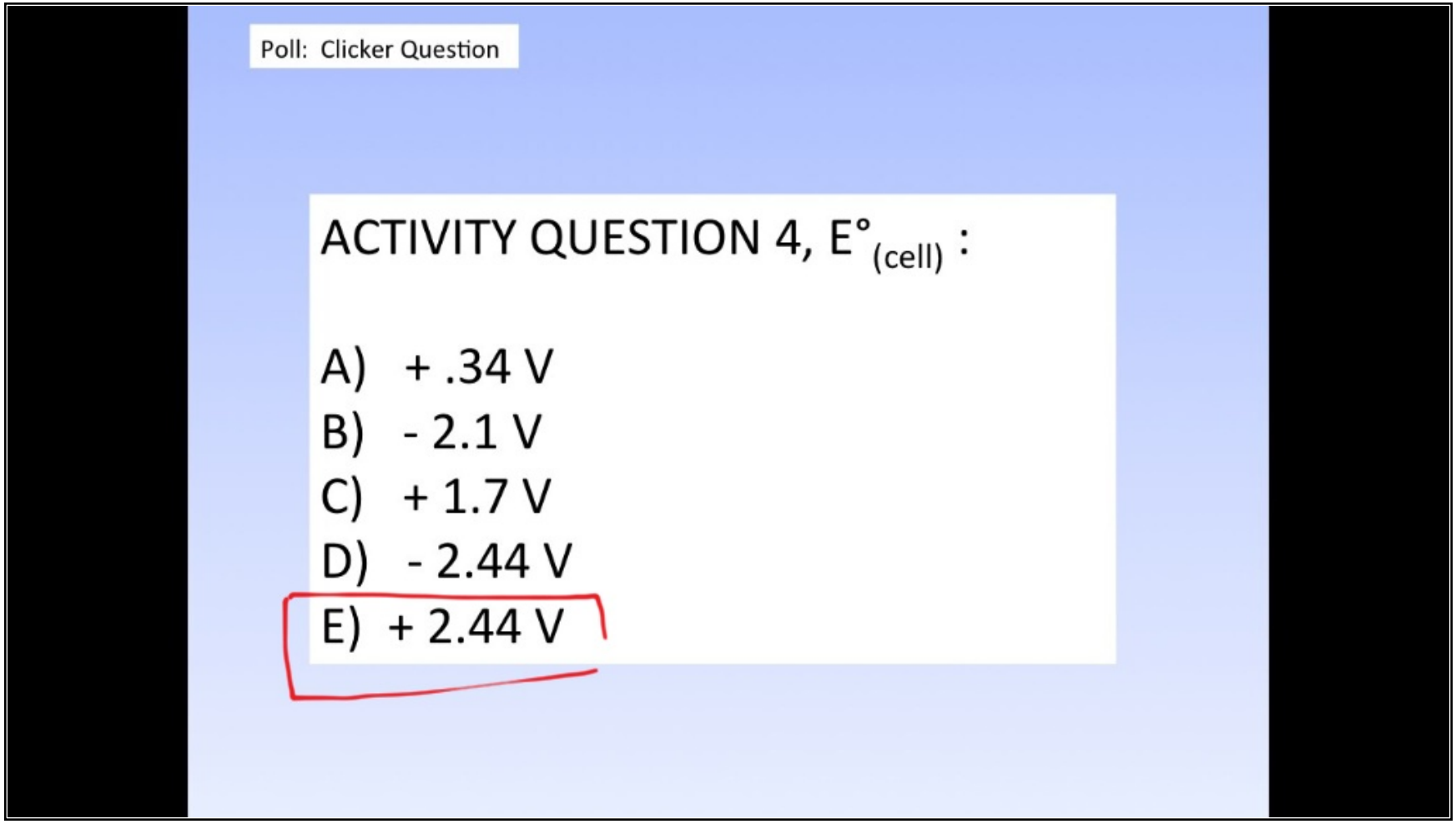
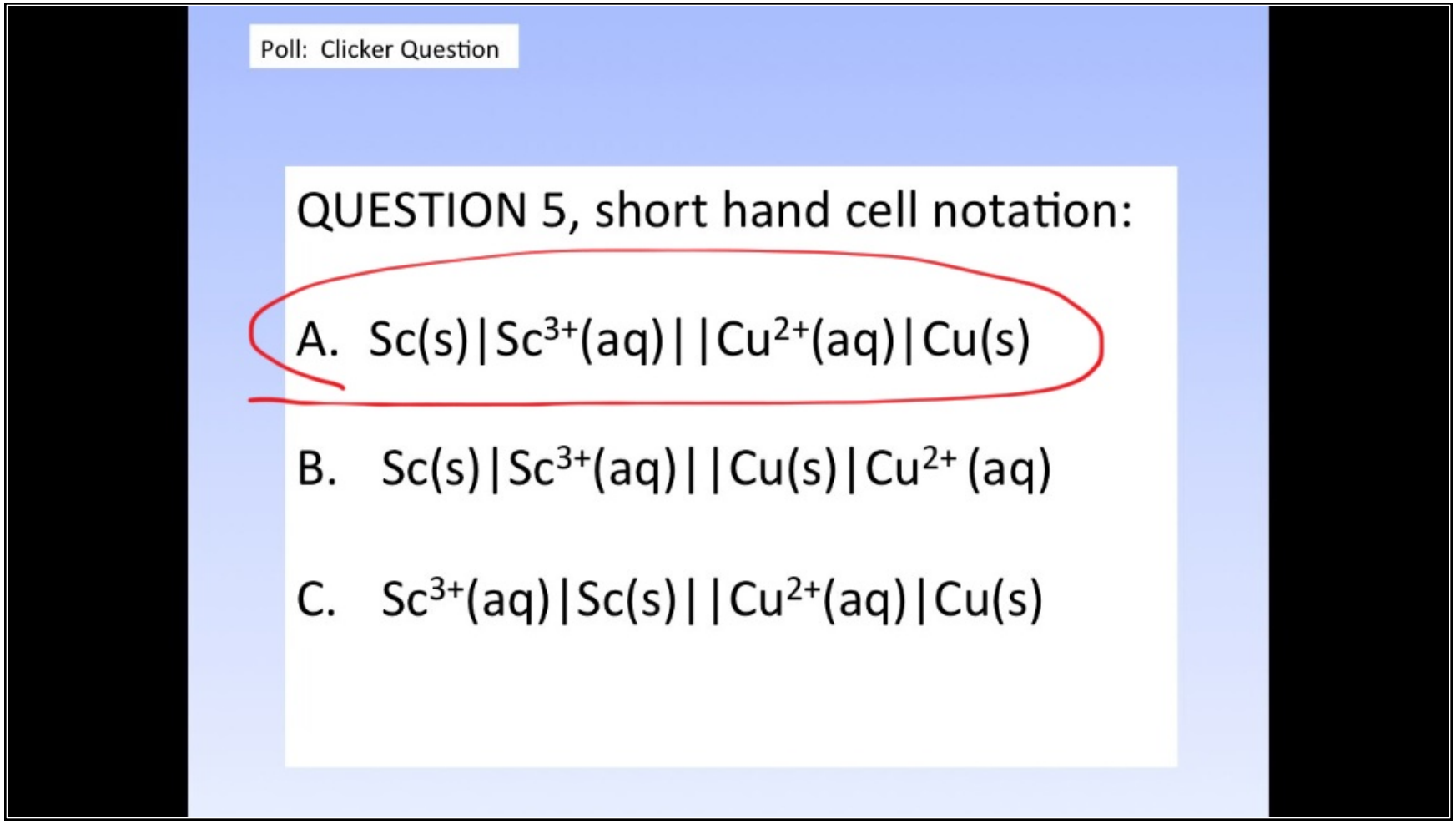
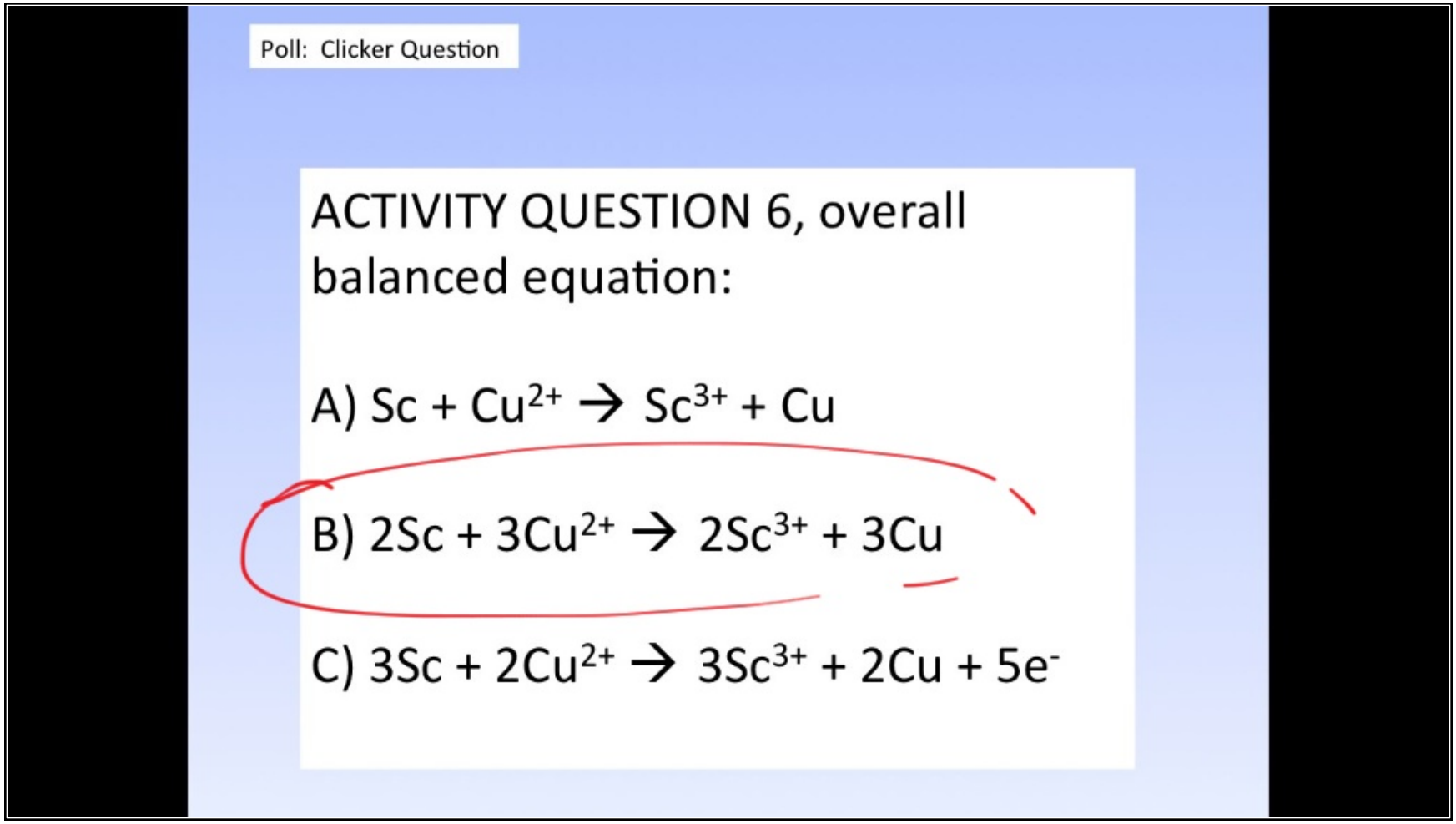

Poll: Clicker Question
ACTIVITY QUESTION 1:
A)YES
B)NO

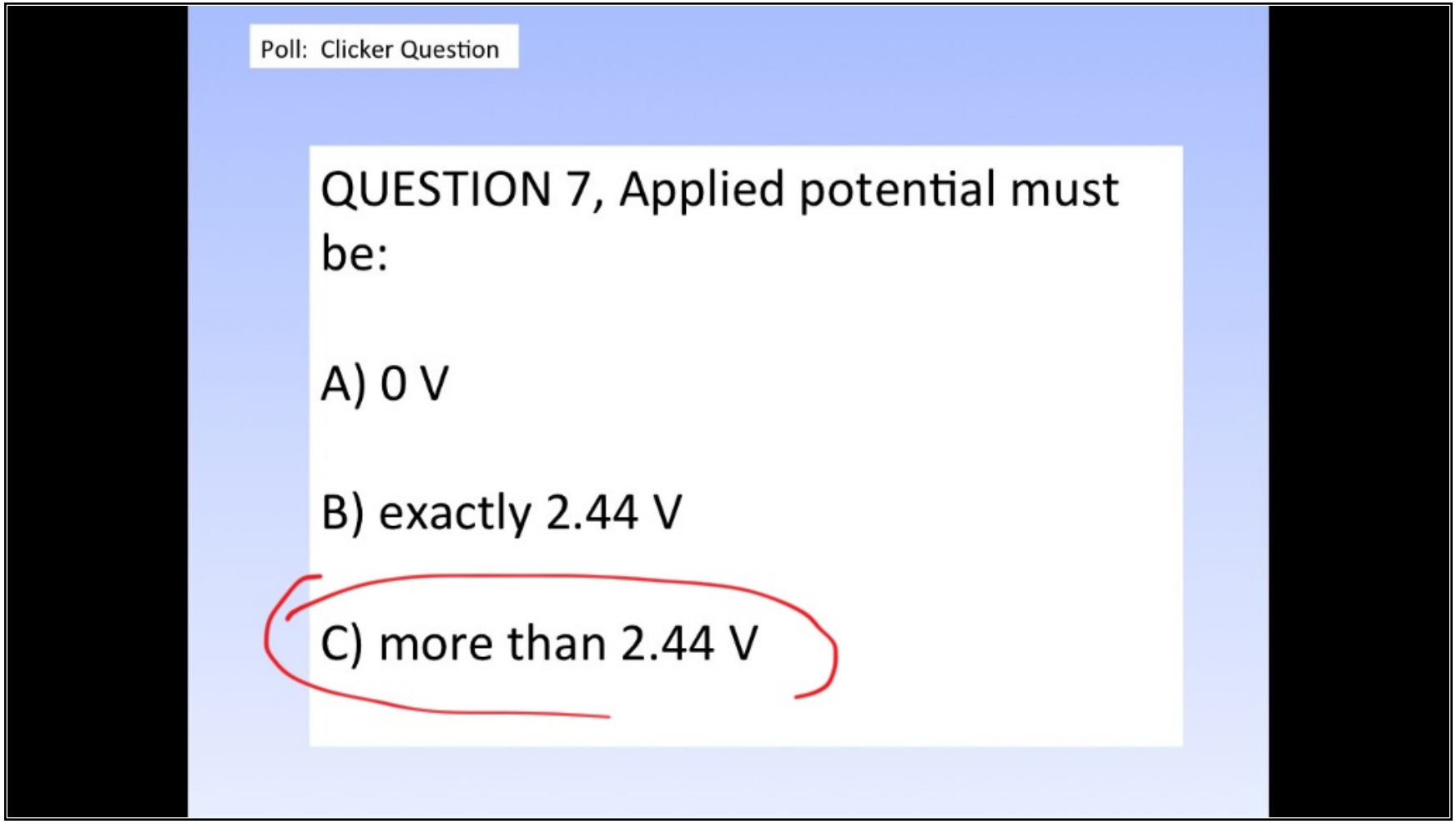

Poll: Clicker Question
ACTIVITY QUESTION 2.
A)Cu & Sc
B)Cu & Pb
C)Cu & Cr
D)Pb & Sc
Biggest potential difference

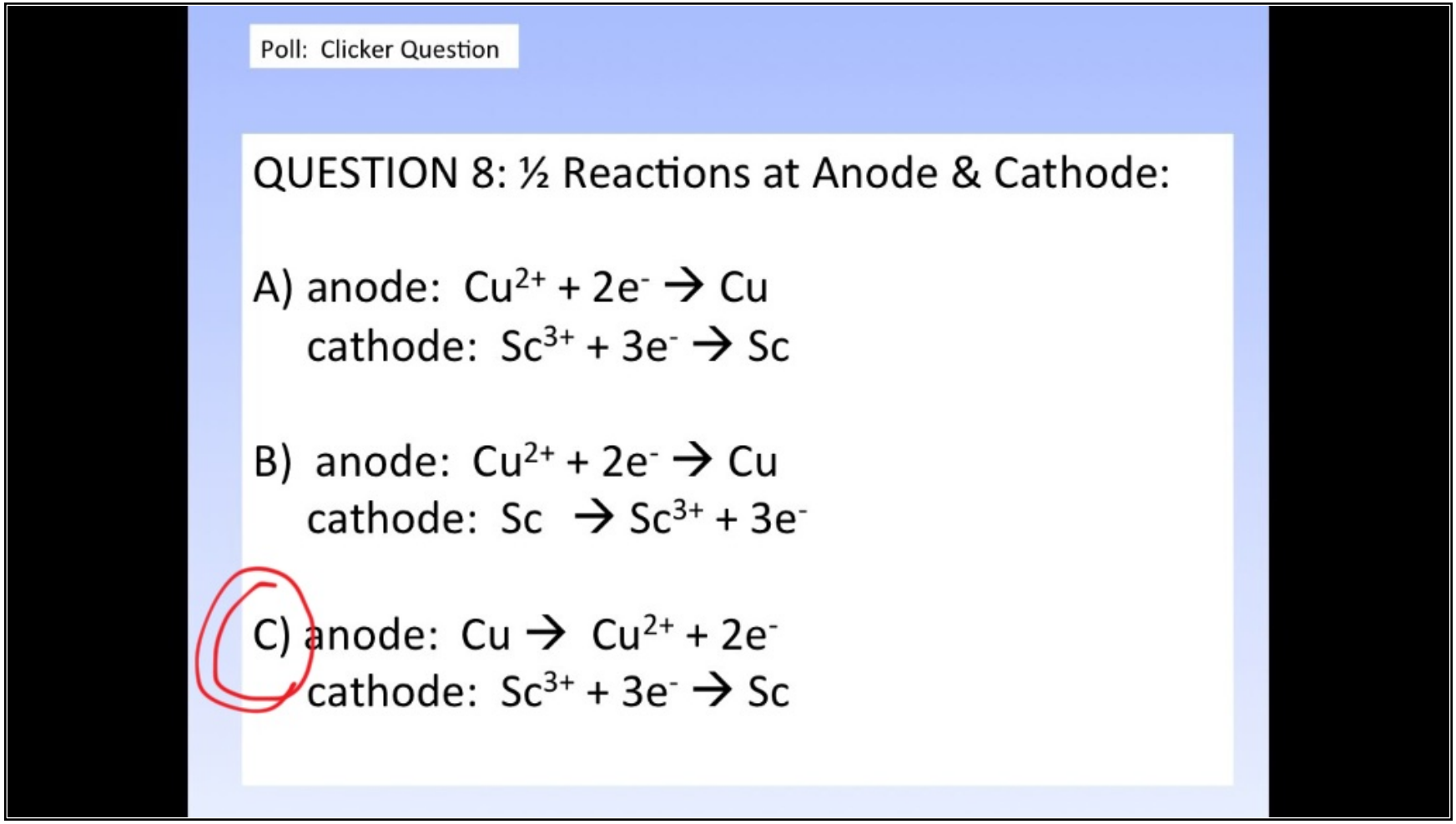

Poll: Clicker Question
ACTIVITY QUESTION 3: which will serve as anode and cathode, respectively:
A) Cu & Sc
B) Sc & Cu
C) Cu^{2+} & Cr^{3+}
D) Pb & Sc^{3+}
E) Sc & Cu^{2+}


Poll: Clicker Question
ACTIVITY QUESTION 4, E°(cell) :
A) + .34 V
B) - 2.1 V
C) + 1.7 V
D) - 2.44 V
E) + 2.44 V


Poll: Clicker Question
QUESTION 5, short hand cell notation:
A. Sc(s)|Sc3+(aq)||Cu2+(aq)|Cu(s)
B. Sc(s)|Sc3+(aq)||Cu(s)|Cu2+(aq)
C. Sc3+(aq)|Sc(s)||Cu2+(aq)|Cu(s)


Poll: Clicker Question
ACTIVITY QUESTION 6, overall balanced equation:
A) $Sc + Cu^{2+} \rightarrow Sc^{3+} + Cu$
B) $2Sc + 3Cu^{2+} \rightarrow 2Sc^{3+} + 3Cu$
C) $3Sc + 2Cu^{2+} \rightarrow 3Sc^{3+} + 2Cu + 5e^-$


Poll: Clicker Question
QUESTION 7, Applied potential must be:
A) 0 V
B) exactly 2.44 V
C) more than 2.44 V


Poll: Clicker Question
QUESTION 8: ½ Reactions at Anode & Cathode:
A) anode: $Cu^{2+} + 2e^- \rightarrow Cu$
cathode: $Sc^{3+} + 3e^- \rightarrow Sc$
B) anode: $Cu^{2+} + 2e^- \rightarrow Cu$
cathode: $Sc \rightarrow Sc^{3+} + 3e^-$
C) anode: $Cu \rightarrow Cu^{2+} + 2e^-$
cathode: $Sc^{3+} + 3e^- \rightarrow Sc$

Example of Electrolytic Cell

Consider the electrolysis of aqueous copper(II)bromide. The observations are: one electrode becomes coated with copper metal, and the color of the solution around the electrode fades; around the other electrode the solution turns brown, as the bromine is formed and some O_2 bubbles are formed.

Design the cell, label electrodes, flow of e^-, and ½ reactions.