

A dramatic, dark purple and blue stormy sky with multiple bright white lightning bolts striking down. The clouds are heavy and dark, creating a high-contrast, atmospheric scene.

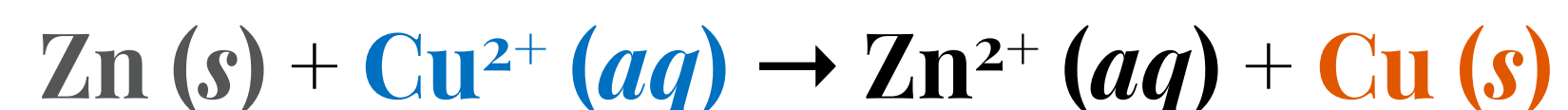
10 **ELECTROCHEMISTRY**

REDUCTION-OXIDATION (REDOX) REACTIONS

CHEMISTRY 136L // FALL 2019

SPONTANEITY

General ideas



This redox reaction is spontaneous.

How can we know this?

When you bring Zn metal and aqueous Cu^{2+} , there will be a visible, spontaneous change.

Activity Series

Zn metal can reduce Cu^{2+} to Cu metal.

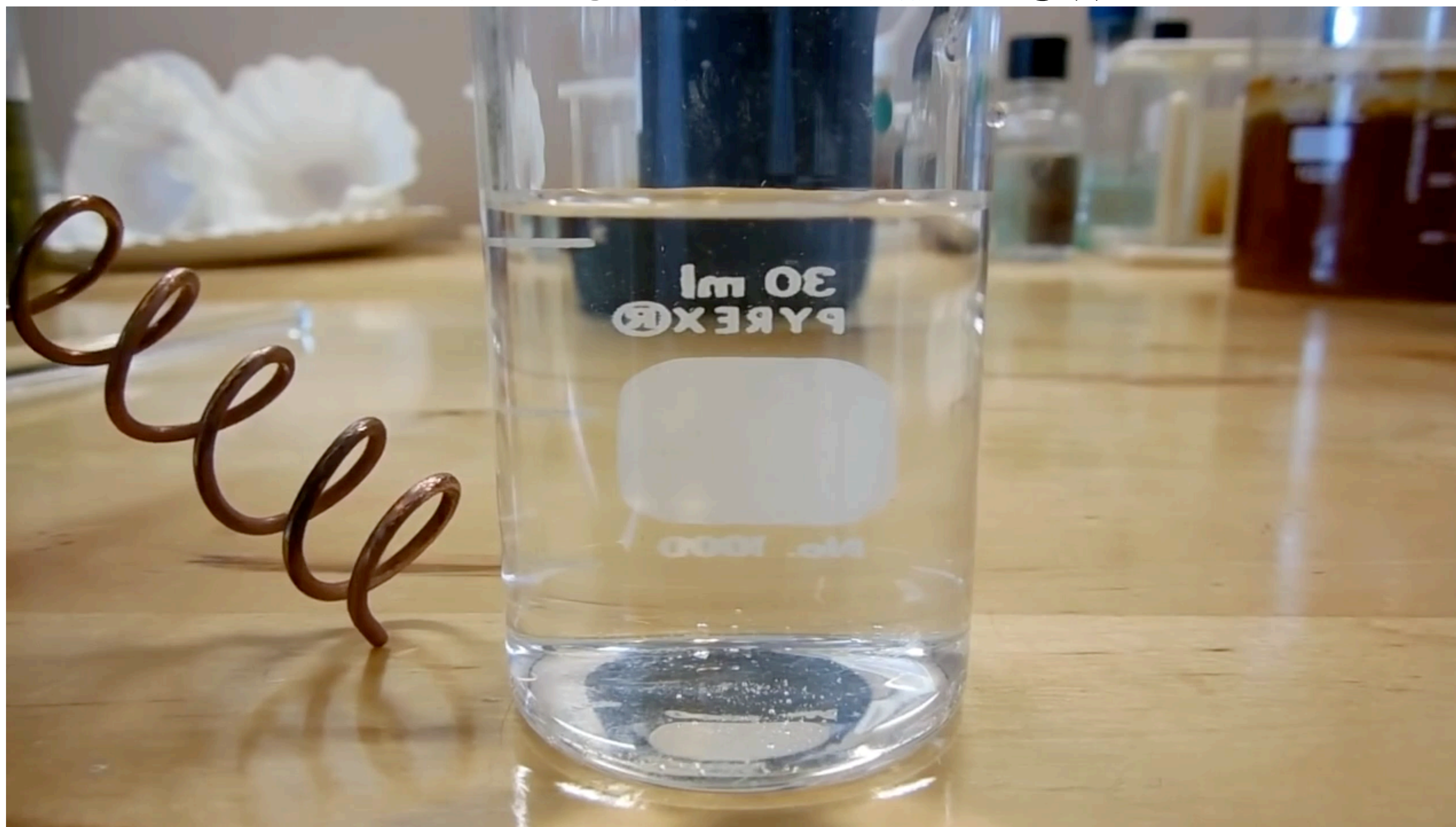
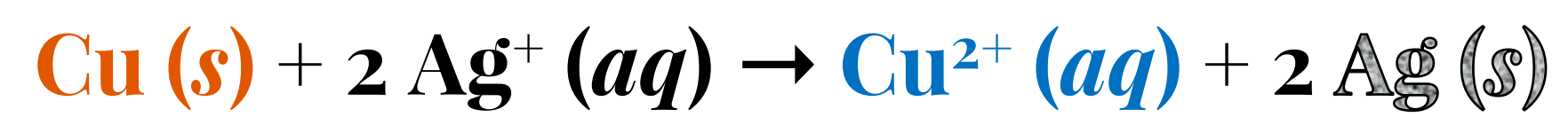
This implies Cu metal is unable to reduce Zn^{2+} to Zn metal.

In other words, the reverse (redox) reaction is *nonspontaneous*.

Zn metal is a stronger reducing agent than Cu metal.

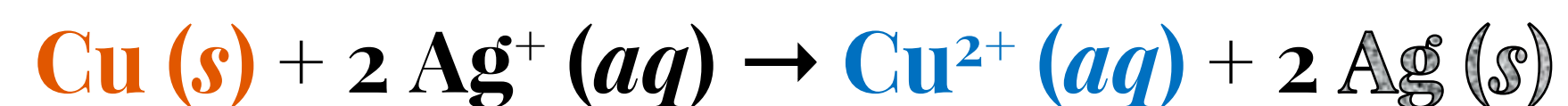
SPONTANEITY

General ideas



SPONTANEITY

General ideas



This redox reaction is spontaneous.

Activity Series

Cu metal can reduce Ag^+ to **Ag** metal.

Cu metal is a stronger reducing agent than **Ag** metal.

Zn metal is the strongest reducing agent (reductant).

Ag metal is the weakest reducing agent (reductant).

VOLTAIC/GALVANIC CELLS

Spontaneous redox reactions

Zn electrode – the negative electrode where oxidation occurs:



Cu electrode – the positive electrode where reduction occurs:



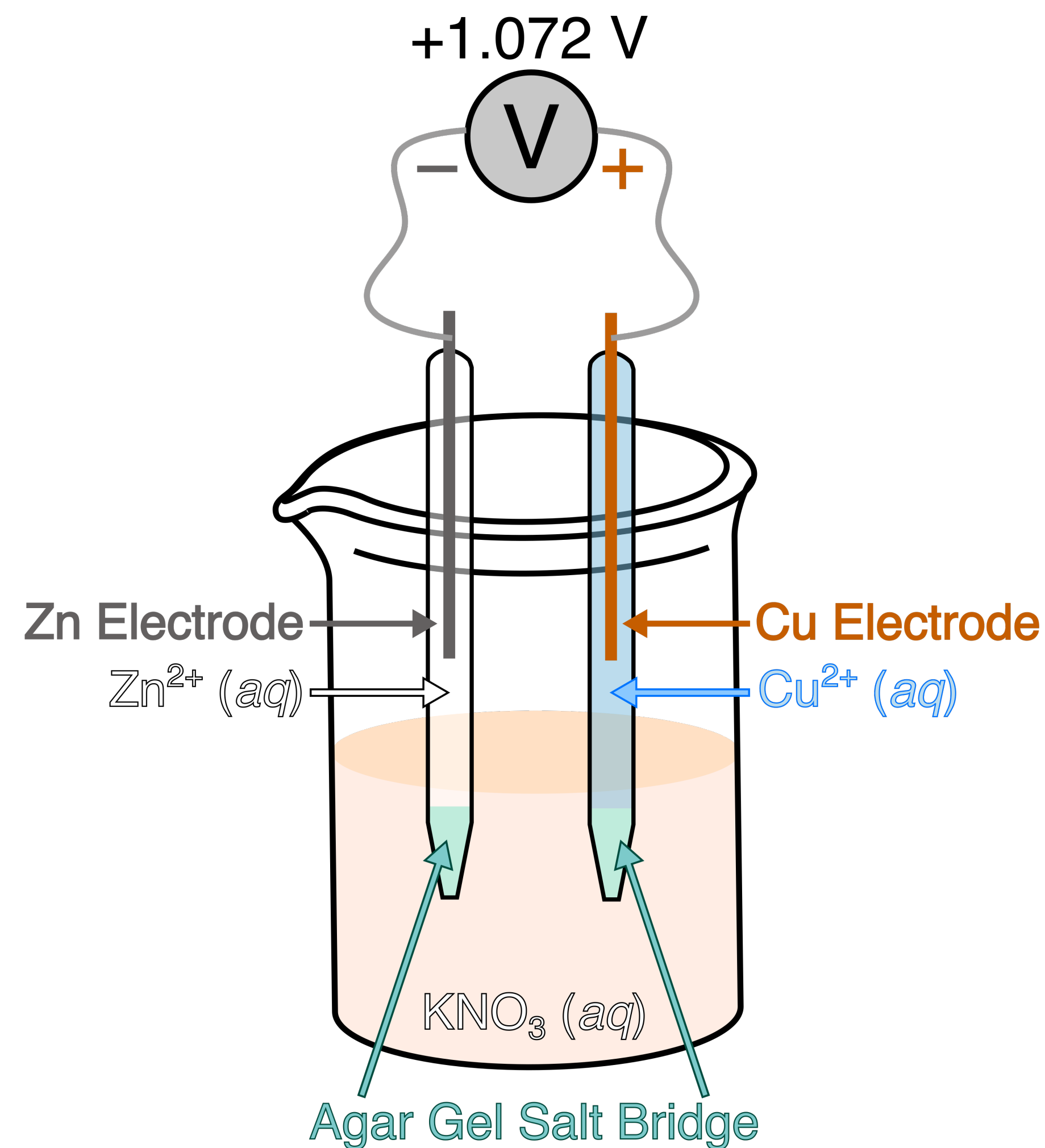
The **electrons** released from oxidation of Zn metal makes the Zn electrode the negative electrode.



These **electrons** leave the Zn electrode and flow through the external circuit (a voltmeter).



When these **electrons** arrive at the positive **Cu** electrode, **Cu²⁺** ions are reduced to **Cu** metal.



ELECTROLYTIC CELLS

Nonspontaneous redox reactions

The opposite is true in electrolytic cells, where a *nonspontaneous* redox reaction is forced (driven) to occur by electrical energy input.

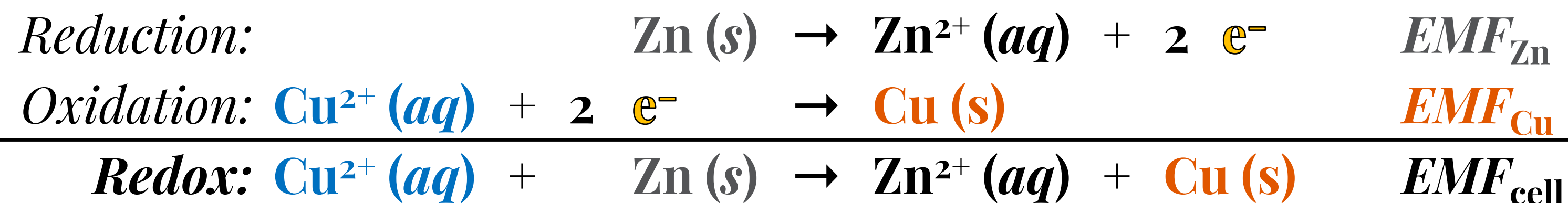


Oxidation now takes place at the positive electrode.
Reduction now takes place at the negative electrode.

CELL POTENTIAL

Galvanic/Voltaic cells

Since the overall redox reaction is the sum of the two half-reactions, we have:



$$EMF_{\text{cell}} = EMF_{\text{Zn}} + EMF_{\text{Cu}} \quad \text{—or—} \quad E_{\text{cell}} = E_{\text{Zn}} + E_{\text{Cu}}$$

where *EMF* stands for electromotive force and is measured in volts (V).

For Voltaic/Galvanic Cells:

$$\Delta G = nFE_{\text{cell}} \quad \text{where} \quad \left\{ \begin{array}{l} n = \text{moles of electrons} \\ F = \text{Faraday's constant (charge, C, of 1 mol e}^{-}\text{)} \\ E_{\text{cell}} = EMF \text{ of cell} \end{array} \right.$$

$$\text{Spontaneous} \quad \Delta G < 0 \quad E_{\text{cell}} > 0$$

$$\text{Nonspontaneous} \quad \Delta G > 0 \quad E_{\text{cell}} < 0$$

VOLTAIC/GALVANIC CELLS

Spontaneous redox reactions

Zn electrode – the negative electrode where oxidation occurs:

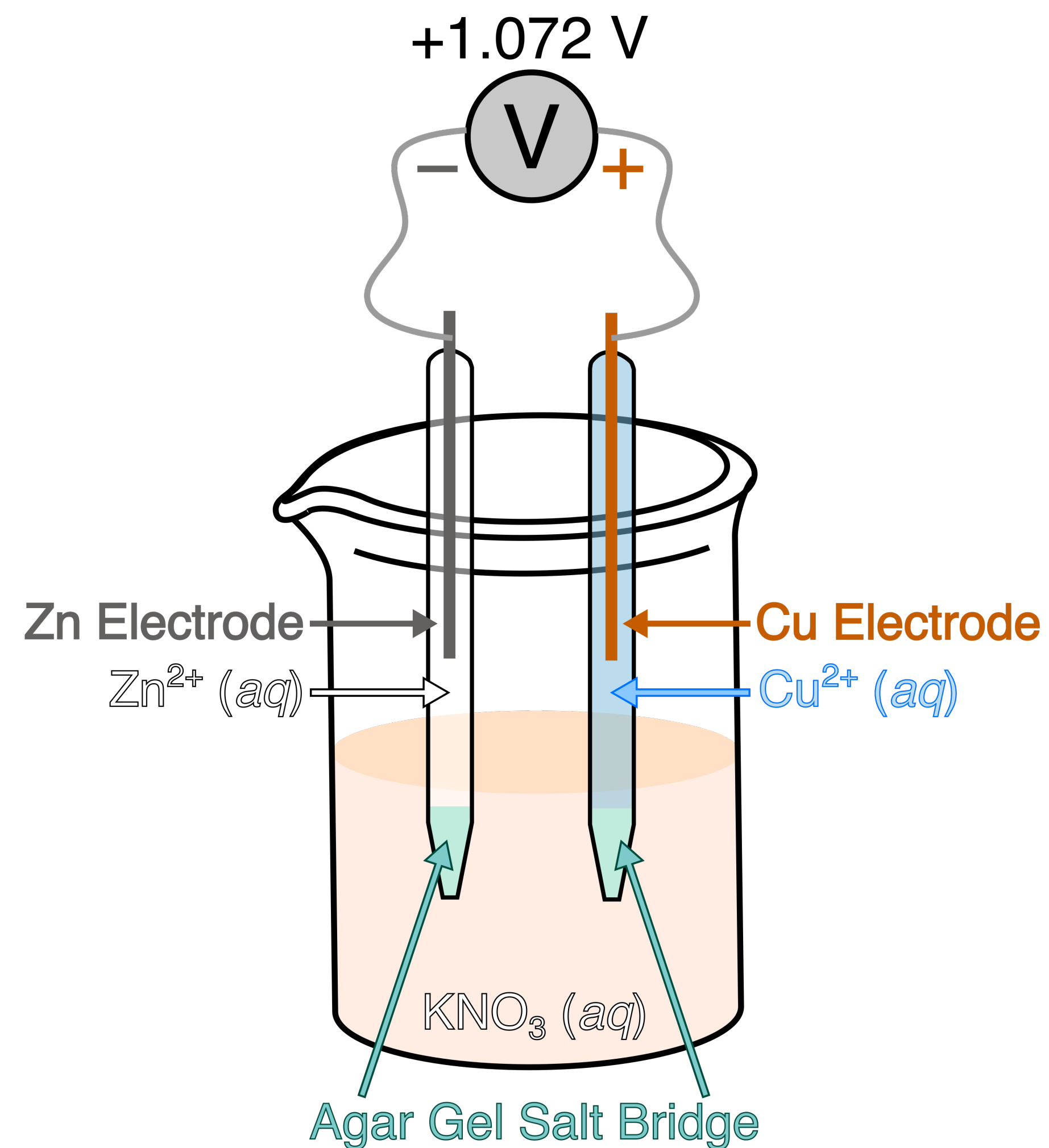


Cu electrode – the positive electrode where reduction occurs:



We can measure the E_{cell} using a voltmeter.

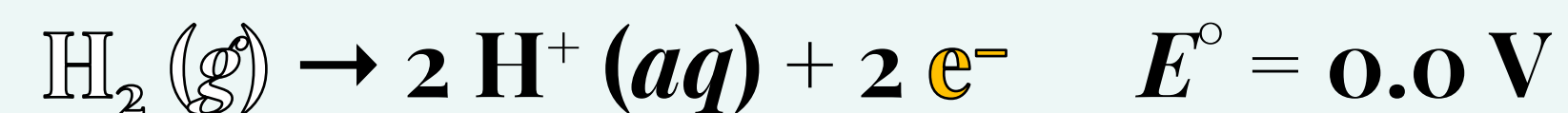
Can we assign individual half-cell potentials (EMFs)?



STANDARD HYDROGEN ELECTRODE (SHE)

A convention

The standard hydrogen electrode (SHE) convention:



Combine the **Cu** half-cell with the H_2 half-cell (SHE).



The measured E_{cell} is then
+0.342 V with SHE as the negative electrode.



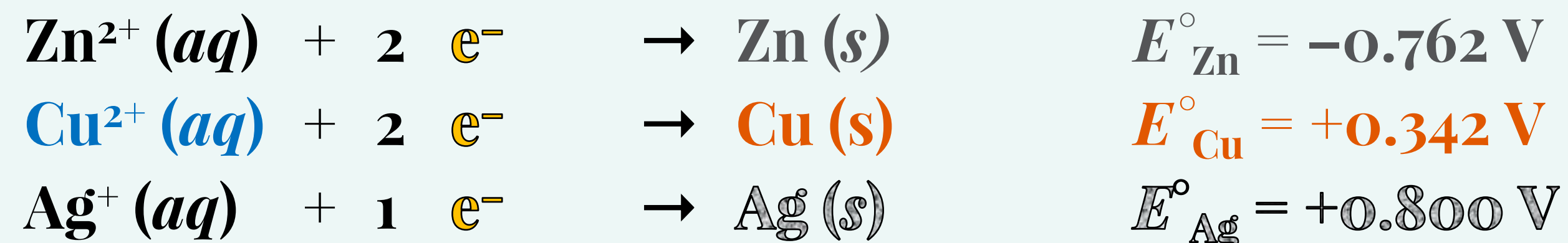
Therefore, we know that



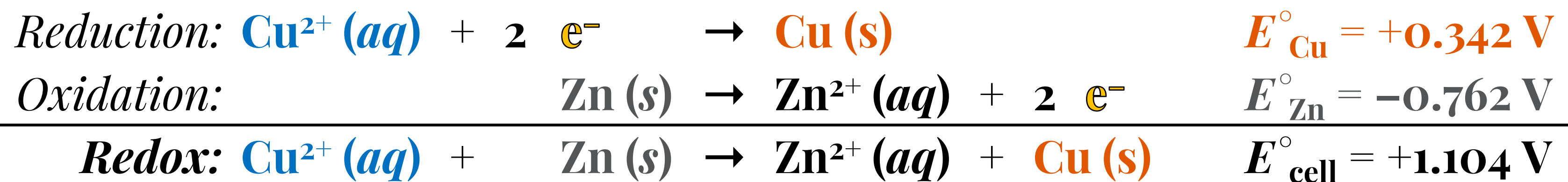
The H_2/H^+ half-cell is the primary reference half-cell.
The **Cu**/**Cu²⁺** half-cell is the secondary reference half-cell.

STANDARD REDUCTION POTENTIALS

Combining half-cells



If we combine a standard Zn half-cell with a standard Cu half-cell:



If we combine a standard Cu half-cell with a standard Ag half-cell:

