ELECTROCHEMISTRY
2: GALVANIC CELLS

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ELECTROCHEMICAL CELLS

An **electrochemical cell** is a system consisting of electrodes that dip into an electrolyte and in which a chemical reaction either uses or generates an electric current.

- A **voltaic** or **galvanic cell** is an electrochemical cell in which a spontaneous reaction generates an electric current.
- An **electrolytic cell** is an electrochemical cell in which an electric current drives an otherwise nonspontaneous reaction.

VOLTAIC OR GALVANIC CELLS

A **galvanic cell** employs a spontaneous oxidation–reduction reaction as a source of energy.

- The redox reactions studied here are electron transfers: oxidation – loss of electrons and reduction – gain of electrons.
- It separates the reaction into two half–reactions, physically separating one half–reaction from the other.
- There are various ways of representing a galvanic cell.

But first, lets learn the terms.

GALVANIC CELLS TERMS

- **Electrodes**
  - Anode – Where oxidation occurs; electrons are produced; is negative.
  - Cathode – Where reduction occurs; electrons are accepted; is positive.
- **Half-cell -** combination of container, electrode and solution
- **Salt bridge -** conducting medium through which the cations and anions can move from one half-cell to the other.
- **Ion migration**
  - Cations – migrate toward the cathode.
  - Anions – migrate toward the anode.
- **Cell potential (E_{cell}) –** difference in electrical potential between the anode and cathode
  - Concentration dependent.
  - Temperature dependent.
  - Determined by nature of reactants.

GALVANIC CELLS CONSTRUCTION

Construct a Zn-Cu cell where zinc getting oxidized.

Zn loses two electrons forming Zn^{2+} ions.

oxidation/loss of e^-

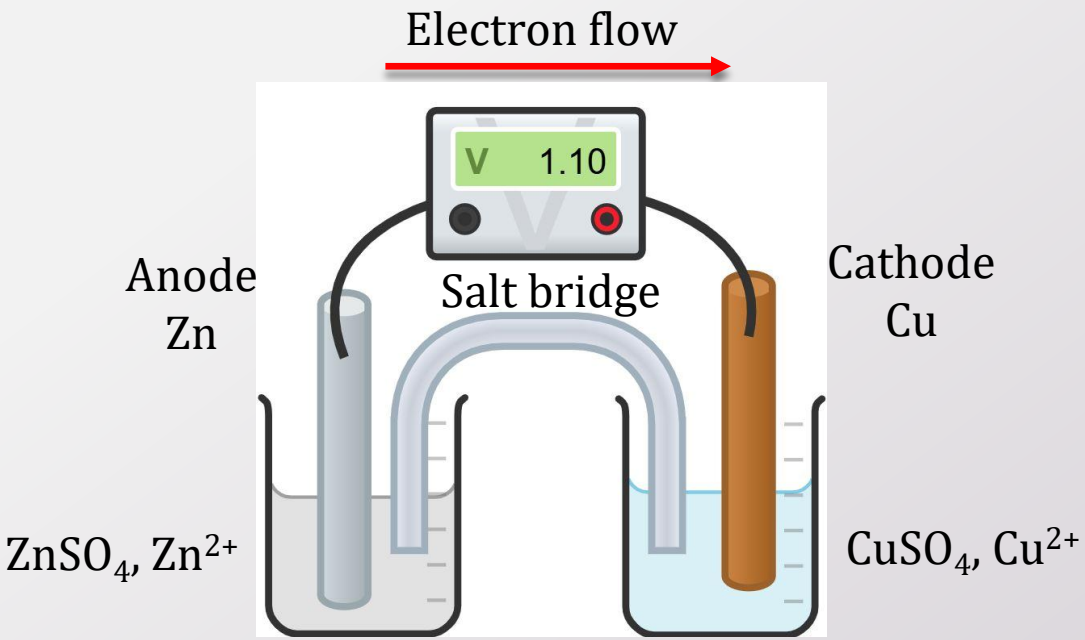
anode

Cu^{2+} ions gain two electrons, forming solid copper

reduction/gain of e^-

cathode

Electrons flow from anode to cathode



EXAMPLE: CONSTRUCT A Al/Cu GALVANIC CELL

Sketch the voltaic cell for aluminum (anode) and copper and label the anode and the cathode; show the half–reactions; and indicate the direction of electron flow.

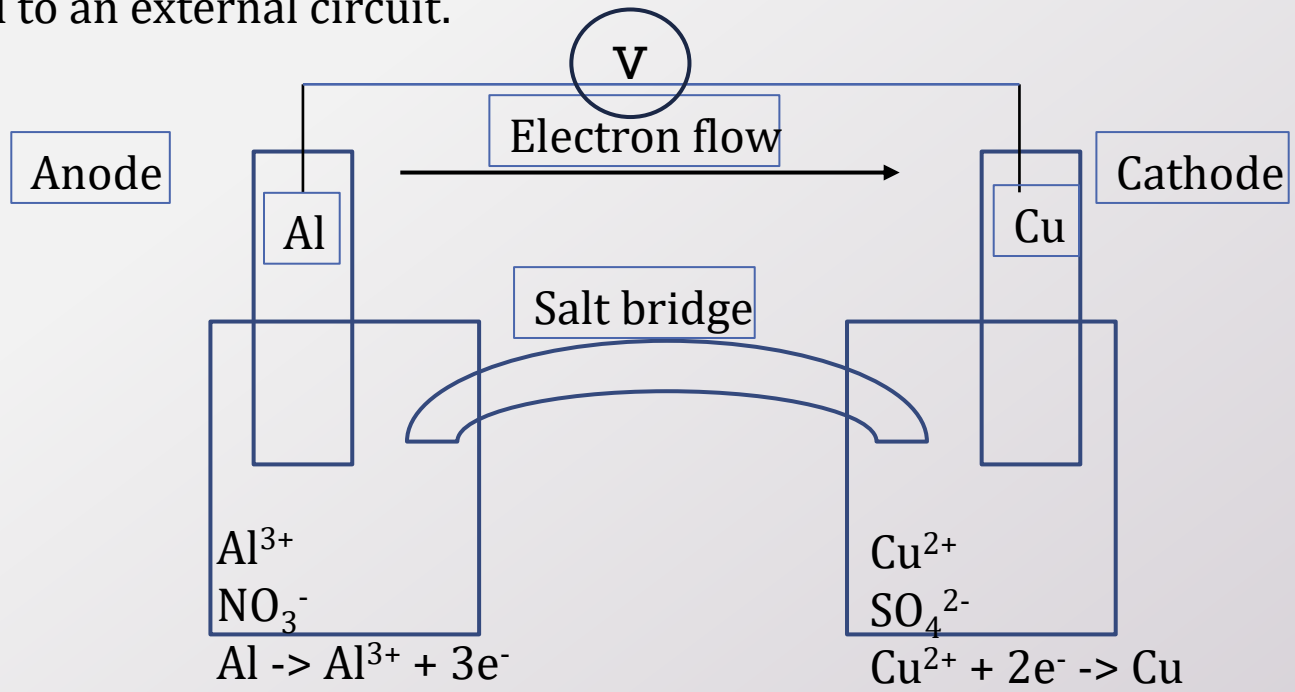
Answer:

1)Construct a half–cell by inserting an aluminum metal strip in a solution of aluminum nitrate and write the equation. (Anode)

2) Construct the other half–cell of a voltaic cell by inserting a copper metal strip into a solution of copper(II) sulfate and write the equation. (Cathode)

3) Connect the half–cells by a salt bridge.

4) Connected to an external circuit.



VOLTAIC CELL NOTATION

This is a shorthand way of writing a cell instead of drawing the cell.

- The oxidation half–cell, the anode, is written on the left.

  Anode, the oxidation of $Zn(s)$ to $Zn^{2+}(aq)$ is shown as $Zn(s) \mid Zn^{2+}(aq)$.

- The reduction half–cell, the cathode, is written on the right.

  Cathode, the reduction of $Cu^{2+}(aq)$ to $Cu(s)$ is shown as $Cu^{2+}(aq) \mid Cu(s)$.

- The cell terminal with the phase, is written on the outside left for the anode and right for the cathode.
- Phase boundaries are shown with a single vertical bar, |.
- Between the anode and cathode, the salt bridge is represented by two vertical bars, ||.
- The complete notation for the redox reaction of Zn and Cu^{2+} is:

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

losing electrons gaining electrons

VOLTAIC CELL NOTATION WITH GASES

When the half–reaction involves a gas, the electrode is an inert material such as platinum, Pt. It is included as a third substance in the half–cell.

- For the oxidation of $H_2(g)$ to $H^+(aq)$, the notation is

  $$Pt(s) \mid H_2(g) \mid H^+(aq)$$

- In this case, the electrode appears on the far left.
- In half–reaction of Cl_2 being reduced to Cl^- is written as follows:

  $$Cl_2(g) \mid Cl^-(aq) \mid Pt(s)$$

- Because this is a reduction, the electrode appears on the far right.

Cell Notation: $Pt(s) \mid H_2(g) \mid H^+(aq) \parallel Cl_2(g) \mid Cl^-(aq) \mid Pt(s)$

With Concentrations:

To completely specify a voltaic cell, concentrations of the solutions are also written. For example, the oxidation of $Cu(s)$ to $Cu^{2+}(aq)$ at the anode and the reduction of $F_2(g)$ to $F^-(aq)$ at the cathode is written as follows:

$Cu(s) \mid Cu^{2+}(1.0\ M) \parallel F_2(1.0\ atm) \mid F^-(1.0\ M) \mid Pt(s)$

EXAMPLE: VOLTAIC CELL TO EQUATION

Write the cell reaction for the following cell notation for a voltaic cell.

$$Al(s) \mid Al^{3+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

Answer:

Write and balance each half–reaction, and then to combine the half–reactions to give the overall cell reaction.

- The skeleton oxidation reaction is $Al(s) \longrightarrow Al^{3+}(aq)$.
  - Balanced eq.: $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$
- The skeleton reduction reaction is $Cu^{2+}(aq) \longrightarrow Cu(s)$.
  - Balanced eq.: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- Balance the electrons in the equations by multiplying by 2 and 3 respectively.
- Add the two equations by cancelling the electrons.

$$2Al(s) \longrightarrow 2Al^{3+}(aq) + \cancel{6e^-}$$

$$\underline{3Cu^{2+}(aq) + \cancel{6e^-} \longrightarrow 3Cu(s)}$$

$$2Al(s) + 3Cu^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Cu(s)$$

KEY CONCEPTS

- Constructing a galvanic cell.
- Writing cell notations.