B6 · Voltaic cells

Completed notes

Goals: Explain why a voltaic cell separates the half-reactions and needs a salt bridge. Identify the anode and cathode, and write cell notation and half-reactions. Predict observations and calculate the standard cell potential.

Slide 1 of 9 · Why separate the halves?

Zinc atoms give up electrons and Cu^{2+} ions take them, so zinc in copper(II) sulfate solution is a **redox** reaction.

When zinc touches the ions, electrons jump straight across the surface and the energy spreads out as **heat**.

To get useful work, keep the two halves **apart** and let the electrons travel only through a **wire**.

A cell that turns chemical energy into electrical energy is a **voltaic** cell (also called a galvanic cell). One electrode plus its solution is a **half-cell**.

Example. Zinc placed in copper(II) sulfate solution slowly becomes coated with copper, and the solution warms. How could we use that electron transfer to run a device? Sketch the cell.

1. Put the zinc in its own $Zn^{2+}(aq)$ solution and the copper in its own $Cu^{2+}(aq)$ solution.

2. Join the two metals with a wire, so the electrons must travel through it.

3. A device or voltmeter in the wire uses the energy. This is a voltaic cell.

Try it. Zinc metal is placed directly in $Cu^{2+}(aq)$. What happens to the energy released? Name the energy change when the same reaction runs in a voltaic cell.

1. The energy is released as heat, because the electrons jump straight from zinc to Cu^{2+}.

2. In a voltaic cell, chemical energy becomes electrical energy.

Slide 2 of 9 · Which electrode is which?

The ion with the **higher** table value is the stronger oxidizing agent, so it is reduced. The metal in the other row is oxidized.

The **anode** is where oxidation happens. The **cathode** is where reduction happens. Memory aid: AN OX (anode, oxidation) and RED CAT (reduction, cathode).

In a voltaic cell the anode is **negative** and the cathode is **positive**.

Electrons leave the anode, travel through the **wire** and are used up at the cathode. Ions carry the charge in the **solutions**.

Example. Given $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Cu^{2+}/Cu) = +0.34$ V. A voltaic cell joins the two half-cells. Which metal is oxidized? Name the anode and cathode, give their signs, and say which way the electrons travel.

1. Cu^{2+}/Cu has the higher value (+0.34 V), so Cu^{2+} is reduced. Zinc is oxidized.

2. Anode: zinc, negative. $Zn \rightarrow Zn^{2+} + 2e^-$

3. Cathode: copper, positive. $Cu^{2+} + 2e^- \rightarrow Cu$

4. Electrons travel from the zinc electrode through the wire to the copper electrode.

Try it. Given $E°(Mg^{2+}/Mg) = -2.37$ V and $E°(Zn^{2+}/Zn) = -0.76$ V. A voltaic cell joins the two half-cells. Which metal is the anode, which electrode is positive, and which way do the electrons travel?

1. Zn^{2+}/Zn has the higher value (−0.76 V), so Zn^{2+} is reduced at the cathode. Magnesium is oxidized.

2. Magnesium is the anode (negative). Zinc is the cathode (positive).

3. Electrons travel from the magnesium electrode through the wire to the zinc electrode.

Slide 3 of 9 · The salt bridge keeps charge balanced

At the anode, Zn atoms make Zn^{2+} ions, so that beaker gains **positive** charge. At the cathode, Cu^{2+} ions leave, so extra **negative** ions (anions) remain.

The charge build-up pushes back on the electrons, and the voltmeter reading falls to **zero**.

A salt bridge holds unreactive ions, such as sodium nitrate. It joins the two solutions and carries **ions** but no electrons. A porous barrier does the same job.

Anions move toward the **anode** beaker, which gains positive charge. Cations move toward the **cathode** beaker, which loses positive charge.

Example. A Zn / Cu cell is joined with wires only. After a short time the voltmeter reading falls to zero. What stops the cell, and how does a salt bridge fix it?

1. Zn^{2+} ions build up in the anode beaker. Cu^{2+} ions leave the cathode beaker, so extra negative ions remain there.

2. The build-up of charge pushes back on the electrons, and they stop.

3. A salt bridge lets ions move between the beakers: anions toward the anode and cations toward the cathode. The circuit is complete and the cell keeps running.

Try it. In the Zn / Cu cell, the salt bridge contains $NaNO_3(aq)$. Toward which beaker do the Na^+ ions move, and why?

1. The Na^+ ions move toward the copper (cathode) beaker.

2. Cu^{2+} ions are leaving that beaker, so positive ions move in to balance the charge.

Slide 4 of 9 · Cell notation

In cell notation, the **anode** goes on the far left and the **cathode** goes on the far right.

Each half is written from the **solid** metal to its ion. A single line | separates two different **phases**.

The double line || stands for the **salt bridge** or porous barrier. Always include **state symbols** such as (s) and (aq).

To write the overall reaction, take the left half as **oxidation** and the right half as reduction. Match the electrons, add the halves and cancel them.

Example. In a Zn / Cu cell, zinc is the anode and copper is the cathode. Write the cell notation and the overall reaction.

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

2. Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

3. Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$

4. Both halves move 2 electrons, so they cancel. Overall: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

Try it. Given the cell notation $Mg(s) \mid Mg^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$. Write the oxidation half-reaction, the reduction half-reaction and the overall reaction.

1. Oxidation (left half): $Mg \rightarrow Mg^{2+} + 2e^-$

2. Reduction (right half): $Ag^+ + e^- \rightarrow Ag$. Double it to take 2 electrons: $2Ag^+ + 2e^- \rightarrow 2Ag$

3. Overall: $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$. Charge is +2 on each side.

Slide 5 of 9 · Your turn: copper and silver

Compare the table values first. Ag^+/Ag is **+0.80** V and Cu^{2+}/Cu is +0.34 V, so silver ions are reduced at the **cathode**.

Each Ag^+ takes **1** electron but the copper anode gives **2**. Multiply the silver half by 2: $2Ag^+ + 2e^- \rightarrow$ **2Ag**.

E° is **never** multiplied by a coefficient. The doubled silver half still has the value +0.80 V. Overall: $Cu + 2Ag^+ \rightarrow$ **Cu^{2+} + 2Ag**.

Notation: Cu(s) | Cu^{2+}(aq) **||** Ag^+(aq) | Ag(s). Cell notation has no **coefficients**.

Example. Given $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34 V) and $Ag^+ + e^- \rightarrow Ag$ (+0.80 V). A cell has a copper electrode in Cu^{2+}(aq), a silver electrode in Ag^+(aq), a wire and a salt bridge. Name the anode, write the half-reactions and overall reaction, and write the cell notation.

1. Ag^+/Ag has the higher value, so silver is the cathode. Copper is the anode.

2. Oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$

3. Reduction: $2Ag^+ + 2e^- \rightarrow 2Ag$

4. Overall: $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

5. Notation: Cu(s) | Cu^{2+}(aq) || Ag^+(aq) | Ag(s)

Try it. Given $Al^{3+} + 3e^- \rightarrow Al$ (−1.66 V) and $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34 V). A cell has an aluminium electrode in Al^{3+}(aq), a copper electrode in Cu^{2+}(aq) and a salt bridge. Name the anode, write the overall reaction and write the cell notation.

1. Cu^{2+}/Cu has the higher value, so copper is the cathode. Aluminium is the anode.

2. Oxidation: $Al \rightarrow Al^{3+} + 3e^-$. Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$

3. Multiply the oxidation by 2 and the reduction by 3 so each moves 6 electrons.

4. Overall: $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$. Charge is +6 on each side.

5. Notation: Al(s) | Al^{3+}(aq) || Cu^{2+}(aq) | Cu(s)

Slide 6 of 9 · Predict what you would observe

Every prediction comes from a **half-reaction**. Ask what is made and what is used up at each electrode.

At the copper anode, $Cu \rightarrow Cu^{2+} + 2e^-$, so the electrode **loses** mass and the Cu^{2+} concentration goes **up**. The Data Booklet lists Cu^{2+} as blue (p. 11), so the blue gets deeper.

At the silver cathode, $2Ag^+ + 2e^- \rightarrow 2Ag$, so the electrode **gains** mass and the Ag^+ concentration goes **down**.

Ag^+ is **colourless** in water, so there is no colour change at the cathode. A metal anode loses mass and a metal cathode gains mass.

Example. The Cu / Ag cell $Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$ is running. Predict what happens to each electrode and each solution as the cell operates.

1. Anode (Cu): $Cu \rightarrow Cu^{2+} + 2e^-$. The copper electrode loses mass. Cu^{2+} increases and the blue colour deepens.

2. Cathode (Ag): $2Ag^+ + 2e^- \rightarrow 2Ag$. The silver electrode gains mass. Ag^+ falls in concentration and the solution stays colourless.

Try it. The Zn / Cu cell $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$ is running. Predict the mass change of each electrode and the change in the blue colour of the copper solution.

1. Anode (Zn): $Zn \rightarrow Zn^{2+} + 2e^-$. The zinc electrode loses mass.

2. Cathode (Cu): $Cu^{2+} + 2e^- \rightarrow Cu$. The copper electrode gains mass.

3. Cu^{2+} is used up, so the blue colour of the copper solution fades.

Slide 7 of 9 · Cell potential

Standard conditions mean **1.0** mol/L solutions, 25.00 °C (298.15 K) and **101.325** kPa for gases.

E°cell = E°**cathode** − E°**anode**. Use each table value as printed, even for the anode.

For the Zn / Cu cell, E°cell = 0.34 − (−0.76) = **+1.10** V. Subtracting a negative number **adds**.

A positive E°cell means the cell reaction runs as **written**. A negative value warns that the anode and cathode are **swapped**. Never multiply E° by a coefficient.

Example. Given E°(Zn^{2+}/Zn) = −0.76 V and E°(Cu^{2+}/Cu) = +0.34 V. Zinc is the anode and copper is the cathode. Calculate E°cell. Then swap the electrodes and say what the sign tells you.

1. E°cell = E°cathode − E°anode = +0.34 V − (−0.76 V) = +1.10 V

2. Swapped: E°cell = −0.76 V − (+0.34 V) = −1.10 V

3. The negative value means the cell does not run that way. The half with the higher value must be the cathode.

Try it. Given E°(Fe^{2+}/Fe) = −0.45 V and E°(Ag^{+}/Ag) = +0.80 V. Iron is the anode and silver is the cathode. Calculate E°cell and say whether the cell reaction runs as written.

1. E°cell = E°cathode − E°anode = +0.80 V − (−0.45 V) = +1.25 V

2. The value is positive, so the cell reaction runs as written.

Slide 8 of 9 · Method: how to describe a voltaic cell

Step 1. Write the two **halves**. Oxidation happens at the **anode**. Reduction happens at the cathode.

Step 2. Trace the **electrons**. They travel through the wire from the anode to the cathode.

Step 3. Place the salt bridge ions. **Anions** move toward the anode. Cations move toward the cathode.

Step 4. Write the cell **notation**, with the anode on the left and the cathode on the right.

Step 5. $E°_{cell} = E°_{\textbf{cathode}} - E°_{anode}$.

Step 6. Predict what you would see. Check: $E°_{cell}$ is **positive** for a working cell.

Example. Use the method on a cell with Cu in $Cu^{2+}(aq)$ and Ag in $Ag^{+}(aq)$. $E°(Cu^{2+}/Cu) = +0.34$ V and $E°(Ag^{+}/Ag) = +0.80$ V. Describe the cell.

1. Step 1: $Cu \rightarrow Cu^{2+} + 2e^{-}$ at the anode. $2Ag^{+} + 2e^{-} \rightarrow 2Ag$ at the cathode.

2. Steps 2 and 3: electrons go from Cu to Ag through the wire. Anions move toward Cu and cations toward Ag.

3. Step 4: $Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$.

4. Steps 5 and 6: $E°_{cell} = +0.80 - (+0.34) = +0.46$ V. Copper loses mass and the blue deepens. Silver gains mass.

Try it. Use the method on a cell with Zn in $Zn^{2+}(aq)$ and Cu in $Cu^{2+}(aq)$. $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Cu^{2+}/Cu) = +0.34$ V. Find the anode, the notation and $E°_{cell}$.

1. Zn has the lower E°, so Zn is the anode and Cu is the cathode.

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

3. $E°_{cell} = +0.34 - (-0.76) = +1.10$ V.

Slide 9 of 9 · A cell drawn the other way

Where an electrode is drawn does **not** show which one is the anode. Use the table values.

$E°(Ag^+/Ag) = +0.80$ V is higher than $E°(Zn^{2+}/Zn) =$ **−0.76** V, so silver is the **cathode** and zinc is the anode.

If the anode is drawn on the right, the electrons travel through the wire from **right** to left.

In cell notation the anode is always on the **far left**. $E°_{cell} = E°_{cathode} - E°_{anode} =$ **+1.56** V, and redrawing the cell does not change it.

Example. Given $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Ag^+/Ag) = +0.80$ V. A drawing shows the silver half-cell on the left and the zinc half-cell on the right. Find the anode, write the cell notation and find $E°_{cell}$.

1. Ag^+/Ag has the higher value (+0.80 V), so silver is the cathode. Zinc is the anode, even though it is drawn on the right.

2. Notation puts the anode first: $Zn(s) \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$

3. $E°_{cell} = E°_{cathode} - E°_{anode} = +0.80\text{ V} - (-0.76\text{ V}) = +1.56$ V

Try it. Given $E°(Cu^{2+}/Cu) = +0.34$ V and $E°(Mg^{2+}/Mg) = -2.37$ V. A drawing shows the copper half-cell on the left and the magnesium half-cell on the right. Find the anode, write the cell notation and find $E°_{cell}$.

1. Cu^{2+}/Cu has the higher value (+0.34 V), so copper is the cathode. Magnesium is the anode, drawn on the right.

2. Notation: $Mg(s) \mid Mg^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

3. $E°_{cell} = +0.34\text{ V} - (-2.37\text{ V}) = +2.71$ V

B6 · Worked practice

Voltaic cells | Questions 1-2 of 7

1. Given the Data Booklet table values $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Ag^{+}/Ag) = +0.80$ V. A cell has a zinc electrode in $Zn^{2+}(aq)$ and a silver electrode in $Ag^{+}(aq)$. Name the anode and the cathode, and state the direction of electron flow in the wire.

Use Method: how to describe a voltaic cell. Zinc is the anode (lower table value, oxidized). Silver is the cathode (higher value, reduced). Electrons go from the zinc electrode through the wire to the silver electrode.

2. Given a cell in which Mg(s) is oxidized and $Cu^{2+}(aq)$ is reduced, with a salt bridge. Write the cell notation.

$Mg(s) \mid Mg^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$. The anode is on the far left, the double line is the salt bridge, and the cathode is on the far right.

B6 · Worked practice

Voltaic cells | Questions 3-4 of 7

3. Given the Cu / Ag cell, Cu(s) | $Cu^{2+}(aq)$ || $Ag^{+}(aq)$ | Ag(s), with a salt bridge containing $NaNO_3(aq)$. Toward which beaker do the NO_3^- ions move, and why?

NO_3^- ions move toward the copper (anode) beaker. Cu^{2+} ions are being made there, so positive charge builds up and the anions balance it.

4. Given the Cu / Ag cell, Cu(s) | $Cu^{2+}(aq)$ || $Ag^{+}(aq)$ | Ag(s), running. Predict the change in mass of each electrode and the change in the blue colour of the copper solution.

The copper electrode loses mass ($Cu \rightarrow Cu^{2+} + 2e^-$). The silver electrode gains mass ($Ag^+ + e^- \rightarrow Ag$). The Cu^{2+} solution gets a deeper blue because Cu^{2+} is produced.

B6 · Worked practice

Voltaic cells | Questions 5-6 of 7

5. A student builds the Zn / Cu cell with wires but no salt bridge or porous barrier. The voltmeter reading drops to zero after a moment. Explain why.

Zn^{2+} ions build up positive charge in the anode beaker, and the cathode beaker is left with extra negative charge. Without a bridge the ions cannot balance the charge, so the electrons stop flowing.

6. Given the Data Booklet table values $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Ag^{+}/Ag) = +0.80$ V. Find $E°_{cell}$ for the cell with zinc as the anode and silver as the cathode.

$E°_{cell} = E°_{cathode} - E°_{anode} = 0.80 - (-0.76) = +1.56$ V.

B6 · Worked practice

Voltaic cells | Questions 7-7 of 7

7. Challenge: Given the Data Booklet table values E°(Al^{3+}/Al) = −1.66 V and E°(Ni^{2+}/Ni) = −0.26 V. Both values are negative. A voltaic cell is built from these two half-cells. Name the anode, write the cell notation and the net equation, and find E°cell in volts.

The lower table value is the reducing agent. Aluminium (−1.66 V) is lower, so Al is oxidized and is the anode. Nickel is the cathode. Notation: Al(s) | Al^{3+}(aq) || Ni^{2+}(aq) | Ni(s). Halves: Al → Al^{3+} + $3e^{-}$ and Ni^{2+} + $2e^{-}$ → Ni. Match 6 electrons: 2Al(s) + $3Ni^{2+}$(aq) → $2Al^{3+}$(aq) + 3Ni(s). E°cell = E°cathode − E°anode = −0.26 − (−1.66) = +1.40 V. Two negative table values can still give a positive cell voltage.