B8 · Electrolytic cells

Completed notes

Goals: Explain how an electrolytic cell uses electrical energy to drive a reaction that is not spontaneous. Identify the anode, cathode, polarity and ion movement, and write half-reactions for molten salts and plating. Compare voltaic and electrolytic cells.

Slide 1 of 8 · Driving a reaction that will not go by itself

E°reaction = E°cathode − E°anode. A **positive** value means the reaction goes by itself. A **negative** value means it does not.

A power source can force a reaction that is not spontaneous. A cell that uses electrical energy to do this is an **electrolytic** cell.

A voltaic cell does the opposite. It turns a spontaneous reaction into **electrical** energy.

If E°reaction = −1.10 V, the source must supply more than **1.10** V. Give a minimum voltage as a **positive** number.

Example. Given Cu + Zn^{2+} → Cu^{2+} + Zn, with E°(Zn^{2+}/Zn) = −0.76 V and E°(Cu^{2+}/Cu) = +0.34 V. Find E°reaction. Does the reaction go by itself? What minimum voltage must a power source exceed to force it?

1. Zn^{2+} is reduced (cathode, −0.76 V). Cu is oxidized (anode, +0.34 V).

2. E°reaction = E°cathode − E°anode = −0.76 V − (+0.34 V) = −1.10 V

3. The value is negative, so the reaction does not go by itself.

4. A power source must supply more than 1.10 V.

Try it. Given Cu + Mg^{2+} → Cu^{2+} + Mg, with E°(Mg^{2+}/Mg) = −2.37 V and E°(Cu^{2+}/Cu) = +0.34 V. Find E°reaction. Does the reaction go by itself? What minimum voltage must a power source exceed to force it?

1. Mg^{2+} is reduced (cathode, −2.37 V). Cu is oxidized (anode, +0.34 V).

2. E°reaction = −2.37 V − (+0.34 V) = −2.71 V

3. The value is negative, so the reaction does not go by itself.

4. A power source must supply more than 2.71 V.

Slide 2 of 8 · Anode, cathode and the power source

Oxidation happens at the **anode** and reduction happens at the **cathode**, in every cell, voltaic or electrolytic.

In an electrolytic cell, the power source sets the signs. The negative terminal pushes electrons to the **cathode**, so the cathode is **negative**.

The electrode joined to the positive terminal hands electrons back to the source. That is oxidation, so it is the **anode** and it is **positive**.

Cations move toward the **cathode** and anions move toward the **anode**. Electrons travel only in the **wires**, and ions carry the charge in the liquid.

Example. A power source is joined by wires to two electrodes in a liquid that has ions. Which electrode is the cathode and which is the anode? Which way do cations and anions move, and where do the electrons travel?

1. The electrode joined to the negative terminal gains electrons (reduction), so it is the cathode.

2. The electrode joined to the positive terminal loses electrons (oxidation), so it is the anode.

3. Cations move toward the cathode. Anions move toward the anode.

4. Electrons travel only in the wires: from the anode to the positive terminal, and from the negative terminal to the cathode.

Try it. Two inert electrodes dip in molten KBr. Electrode X is joined to the negative terminal of a power source. Name electrode X, name the process at X, and say whether K^+ moves toward or away from X.

1. Electrode X is the cathode, because it is joined to the negative terminal.

2. Reduction happens at X.

3. K^+ is a cation, so it moves toward X.

Slide 3 of 8 · A molten salt cell

Molten NaCl has only **Na^+ and Cl^-** ions and no water, so each electrode has only one ion that can react.

Na^+ moves to the negative cathode: $Na^+ + e^- \rightarrow$ **Na**. Cl^- moves to the positive anode: $2Cl^- \rightarrow$ **Cl_2** $+ 2e^-$.

The anode loses **2** electrons and the cathode half gains 1, so double the cathode half. Cell reaction: $2Na^+ + 2Cl^- \rightarrow$ **$2Na + Cl_2$**.

$E°_{reaction} = -2.71 - (+1.36) =$ **−4.07** V. E° is never multiplied by **a coefficient**. The source must supply more than 4.07 V.

Example. Molten sodium chloride, NaCl(l), has two inert electrodes joined to a power source. Given $E°(Na^+/Na) = -2.71$ V and $E°(Cl_2/Cl^-) = +1.36$ V. Write both half-reactions and the cell reaction, name the product at each electrode, and find E°reaction.

1. Cathode (negative): $Na^+ + e^- \rightarrow Na$. Sodium metal forms.

2. Anode (positive): $2Cl^- \rightarrow Cl_2 + 2e^-$. Chlorine gas forms.

3. Double the cathode half: $2Na^+ + 2e^- \rightarrow 2Na$. Overall: $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$

4. $E°_{reaction} = E°_{cathode} - E°_{anode} = -2.71\text{ V} - (+1.36\text{ V}) = -4.07\text{ V}$

5. The source must supply more than 4.07 V.

Try it. Molten potassium bromide, KBr(l), has two inert electrodes joined to a power source. Given $E°(K^+/K) = -2.93$ V and $E°(Br_2/Br^-) = +1.07$ V. Write the cell reaction, name the product at each electrode, and find E°reaction.

1. Cathode: $K^+ + e^- \rightarrow K$. Potassium metal forms.

2. Anode: $2Br^- \rightarrow Br_2 + 2e^-$. Bromine forms.

3. Double the cathode half. Overall: $2K^+ + 2Br^- \rightarrow 2K + Br_2$

4. $E°_{reaction} = -2.93\text{ V} - (+1.07\text{ V}) = -4.00\text{ V}$

5. The source must supply more than 4.00 V.

Slide 4 of 8 · Method: how to describe an electrolytic cell

Step 1. List the **ions** present. A molten salt has no water.

Step 2. Send **cations** to the cathode. Reduction happens at the cathode.

Step 3. Send **anions** to the anode. Oxidation happens at the anode.

Step 4. Write the halves and the overall equation. Match the **electrons** first.

Step 5. Find E°reaction = E°cathode − E°anode. The source must be **larger** than its size, and the cathode joins the **negative** terminal.

Example. Use the method on molten NaCl with inert electrodes and a power source. What forms at each electrode?

1. Step 1: Na^+ and Cl^- only. No water.

2. Step 2: $Na^+ + e^- \rightarrow Na$ at the cathode.

3. Step 3: $2Cl^- \rightarrow Cl_2 + 2e^-$ at the anode.

4. Steps 4 and 5: $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$. E°reaction = −2.71 − (+1.36) = −4.07 V, so the source must be above 4.07 V.

Try it. Use the method on molten $MgCl_2$ with inert electrodes. $E°(Mg^{2+}/Mg) = -2.37$ V and $E°(Cl_2/Cl^-) = +1.36$ V. What forms, and what is the minimum voltage?

1. Mg^{2+} goes to the cathode: $Mg^{2+} + 2e^- \rightarrow Mg$. Cl^- goes to the anode: $2Cl^- \rightarrow Cl_2 + 2e^-$.

2. Overall: $Mg^{2+} + 2Cl^- \rightarrow Mg + Cl_2$.

3. E°reaction = −2.37 − (+1.36) = −3.73 V, so the source must be above 3.73 V.

Slide 5 of 8 · Voltaic and electrolytic cells side by side

The same two half-cells can run either way. In the voltaic Zn / Cu cell, the reaction is spontaneous and E°reaction = **+1.10** V.

In the electrolytic cell, a power source forces the reverse reaction, $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$. Then E°reaction = **−1.10** V.

Energy changes from chemical to **electrical** in a voltaic cell, and from electrical to **chemical** in an electrolytic cell.

In both cells, oxidation happens at the **anode**. The anode is negative in a **voltaic** cell and positive in an electrolytic cell. In a drawing, a voltmeter means voltaic and a power source means electrolytic.

Example. The Zn^{2+}/Zn (−0.76 V) and Cu^{2+}/Cu (+0.34 V) half-cells run first as a voltaic cell and then as an electrolytic cell. For each, write the overall reaction and E°reaction, and give the sign of the anode.

1. Voltaic: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$. E°reaction = +0.34 V − (−0.76 V) = +1.10 V. The anode (Zn) is negative.

2. Electrolytic: $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$. E°reaction = −0.76 V − (+0.34 V) = −1.10 V. The anode (Cu) is positive.

Try it. A cell runs a reaction with E°reaction = −0.46 V. Is it a voltaic or an electrolytic cell? Give the energy change, say whether the reaction is spontaneous, and give the sign of the anode.

1. It is an electrolytic cell, because a negative E°reaction means the reaction is not spontaneous and needs a power source.

2. The energy changes from electrical to chemical.

3. The reaction is not spontaneous. The anode is positive.

Slide 6 of 8 · Your turn: molten zinc bromide

Write the ion movement first. Molten $ZnBr_2$ has Zn^{2+} and Br^- ions. Positive ions go to the negative electrode, the **cathode**. Br^- goes to the **anode**.

Cathode: $Zn^{2+} + \mathbf{2}e^- \rightarrow Zn$. Anode: $\mathbf{2Br^-} \rightarrow Br_2 + 2e^-$.

Both halves move 2 electrons, so they cancel when added. Cell reaction: $Zn^{2+} + 2Br^- \rightarrow$ **$Zn + Br_2$**.

$E°_{reaction} = -0.76 - 1.07 =$ **-1.83** V. Swapping the electrodes would wrongly give **+1.83** V, as if the cell ran by itself.

Example. Molten zinc bromide, $ZnBr_2(l)$, has two inert electrodes joined to a power source. Given $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Br_2/Br^-) = +1.07$ V. Decide the product at each electrode, write the cell reaction and find the minimum voltage.

1. Zn^{2+} goes to the cathode and Br^- goes to the anode.

2. Cathode: $Zn^{2+} + 2e^- \rightarrow Zn$. Anode: $2Br^- \rightarrow Br_2 + 2e^-$

3. Overall: $Zn^{2+} + 2Br^- \rightarrow Zn + Br_2$. Zn is 1, Br is 2 and charge is 0 on each side.

4. $E°_{reaction} = E°_{cathode} - E°_{anode} = -0.76\text{ V} - (+1.07\text{ V}) = -1.83$ V

5. The source must supply more than 1.83 V.

Try it. Molten copper(II) bromide, $CuBr_2(l)$, has two inert electrodes joined to a power source. Given $E°(Cu^{2+}/Cu) = +0.34$ V and $E°(Br_2/Br^-) = +1.07$ V. Decide the product at each electrode, write the cell reaction and find the minimum voltage.

1. Cu^{2+} goes to the cathode and Br^- goes to the anode.

2. Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. Anode: $2Br^- \rightarrow Br_2 + 2e^-$

3. Overall: $Cu^{2+} + 2Br^- \rightarrow Cu + Br_2$. Charge is 0 on each side.

4. $E°_{reaction} = +0.34\text{ V} - (+1.07\text{ V}) = -0.73$ V

5. The source must supply more than 0.73 V.

Slide 7 of 8 · Electroplating and refining

To plate an object, make it the **cathode**. It is joined to the **negative** terminal, metal ions gain electrons there, and the object gains mass.

In silver plating, the cathode half-reaction is $Ag^+ + e^- \rightarrow$ **Ag**. A silver bar as the anode dissolves: Ag → **Ag^+** + e^-, so the Ag^+ concentration stays nearly constant.

In copper refining, impure copper is the **anode** and a sheet of pure copper is the **cathode**. Cu is oxidized at one and Cu^{2+} is reduced at the other.

Impurities with a more **positive** E° than Cu^{2+}/Cu, such as silver and gold, stay solid. Impurities with a more negative E°, such as zinc, **dissolve**.

Example. A steel spoon and a bar of silver are placed in silver nitrate solution, $AgNO_3$(aq), and joined to a power source. How can a thin layer of silver be placed on the spoon? Name the cathode and anode, write both half-reactions and state each mass change.

1. Make the spoon the cathode by joining it to the negative terminal. The silver bar is the anode.

2. Cathode: $Ag^+ + e^- \rightarrow Ag$. Silver deposits on the spoon, so the spoon gains mass.

3. Anode: $Ag \rightarrow Ag^+ + e^-$. The silver bar dissolves, so it loses mass.

4. Silver moves from the anode to the spoon, and Ag^+ stays nearly constant in the solution.

Try it. A metal key is to be plated with nickel. The cell has a nickel bar and nickel(II) sulfate solution, $NiSO_4$(aq), joined to a power source. Name the cathode, write both half-reactions and state each mass change.

1. The key is the cathode, joined to the negative terminal. The nickel bar is the anode.

2. Cathode: $Ni^{2+} + 2e^- \rightarrow Ni$. Nickel deposits on the key, so the key gains mass.

3. Anode: $Ni \rightarrow Ni^{2+} + 2e^-$. The nickel bar dissolves, so it loses mass.

Slide 8 of 8 · The same method with two silver electrodes

The same rule works for any metal. At the cathode, $Ag^+ + e^- \rightarrow$ **Ag**, so the cathode gains mass. At the anode, Ag $\rightarrow$ **Ag**$^+ + e^-$, so the anode loses mass.

Silver moves from one electrode to the other, so the Ag^+ concentration stays about the **same**.

Both electrodes use the same half-cell, so E°reaction = +0.80 − (+0.80) = **0.00** V.

Real cells need a **small** voltage above 0.00 V to beat resistance. That is why plating and refining use little energy.

Example. Two silver electrodes dip in $AgNO_3$(aq). Electrode 1 is joined to the negative terminal of a power source and electrode 2 to the positive terminal. Given E°(Ag^+/Ag) = +0.80 V. Name each electrode, give its half-reaction and mass change, and find E°reaction.

1. Electrode 1 is the cathode. $Ag^+ + e^- \rightarrow$ Ag. It gains mass.

2. Electrode 2 is the anode. Ag $\rightarrow Ag^+ + e^-$. It loses mass.

3. Both electrodes use the Ag^+/Ag half-cell: E°reaction = +0.80 V − (+0.80 V) = 0.00 V

Try it. Two copper electrodes dip in $CuSO_4$(aq) and are joined to a power source. Given E°(Cu^{2+}/Cu) = +0.34 V. Write the half-reaction at the cathode and at the anode, and find E°reaction.

1. Cathode: $Cu^{2+} + 2e^- \rightarrow$ Cu. The cathode gains mass.

2. Anode: Cu $\rightarrow Cu^{2+} + 2e^-$. The anode loses mass.

3. E°reaction = +0.34 V − (+0.34 V) = 0.00 V

B8 · Worked practice

Electrolytic cells | Questions 1-2 of 7

1. Given the Data Booklet table values Mg^{2+}/Mg at −2.37 V and Zn^{2+}/Zn at −0.76 V. A student wants to drive $Zn^{2+} + Mg \rightarrow Zn + Mg^{2+}$ backwards in an electrolytic cell, so $Mg^{2+} + Zn \rightarrow Mg + Zn^{2+}$. Find E°reaction for the reaction in the cell and the smallest voltage that must be exceeded.

Mg^{2+} is reduced at the cathode (−2.37 V) and zinc is oxidized at the anode (−0.76 V). E°reaction = −2.37 − (−0.76) = −1.61 V. The applied voltage must be greater than 1.61 V.

2. In an electrolytic cell with inert electrodes, which electrode is joined to the positive terminal of the power source? Name the process that happens there and the direction in which anions move.

The anode is joined to the positive terminal. Oxidation happens there, and the anions move toward the anode.

B8 · Worked practice

Electrolytic cells | Questions 3-4 of 7

3. Write the half-reactions and the cell reaction for molten NaCl and name the product at each electrode.

Use Method: how to describe an electrolytic cell. Cathode: $Na^+ + e^- \rightarrow Na$ (sodium metal). Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$ (chlorine gas). Cell reaction: $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$.

4. Given molten $ZnBr_2(l)$ with inert electrodes (Data Booklet table values: $E°(Zn^{2+}/Zn) = -0.76$ V; $E°(Br_2/Br^-) = +1.07$ V). Write the half-reaction at each electrode and calculate $E°_{reaction}$.

Cathode: $Zn^{2+} + 2e^- \rightarrow Zn$. Anode: $2Br^- \rightarrow Br_2 + 2e^-$. $E°_{reaction} = -0.76 - 1.07 = -1.83$ V, so the source must supply more than 1.83 V.

B8 · Worked practice

Electrolytic cells | Questions 5-6 of 7

5. A copper bar and a metal key are placed in copper(II) sulfate solution to plate the key with copper. Say which one is the cathode, write its half-reaction and predict the mass change of each.

The key is the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. The key gains mass. The copper bar is the anode: $Cu \rightarrow Cu^{2+} + 2e^-$, so it loses mass.

6. Compare a voltaic cell and an electrolytic cell for the Zn / Cu pair. Give the sign of E°reaction, the energy change and the sign of the anode in each.

Voltaic: E°reaction +1.10 V, chemical to electrical energy, anode negative. Electrolytic: E°reaction −1.10 V for the reaction that is forced, electrical to chemical energy, anode positive.

B8 · Worked practice

Electrolytic cells | Questions 7-7 of 7

7. Challenge: Given molten $CaCl_2(l)$ with inert electrodes (Data Booklet table values: $E°(Ca^{2+}/Ca) = -2.87$ V; $E°(Cl_2/Cl^-) = +1.36$ V). Write the half-reaction at each electrode, name each product, and find $E°_{reaction}$ in volts. Then state the least voltage the power source must supply.

Only Ca^{2+} and Cl^- are present. Cathode (reduction): $Ca^{2+} + 2e^- \rightarrow Ca$. Calcium metal forms. Anode (oxidation): $2Cl^- \rightarrow Cl_2 + 2e^-$. Chlorine gas forms. $E°_{reaction} = E°_{cathode} - E°_{anode} = -2.87 - (+1.36) = -4.23$ V. It is negative, so the reaction does not run by itself. The power source must supply more than 4.23 V. The table values are for standard conditions, so this is a first estimate for a molten salt.