B9 · Electrolysis of aqueous solutions

Completed notes

Goals: Decide what is reduced and what is oxidized when a solution is electrolyzed, using the table. Explain the chloride exception and why E° values are used with caution. Predict products, colour, mass and pH changes and write the cell reaction.

Slide 1 of 8 · Water joins the competition

In a molten salt only the salt ions can react. In a water solution, **water** molecules are present too, so water can react at either electrode.

At the cathode, water can be reduced: $2H_2O + 2e^- \rightarrow$ **$H_2 + 2OH^-$**. Its table value is **−0.83 V**.

At the anode, water can be oxidized: $2H_2O \rightarrow$ **$O_2 + 4H^+ + 4e^-$**. This is the +1.23 V row written **in reverse**.

At the cathode, whatever has the **highest** table value is reduced. At the anode, whatever has the **lowest** value is oxidized.

Example. An ionic compound is dissolved in water. The cell has two inert electrodes and a power source. What competes to be reduced at the cathode, and what competes to be oxidized at the anode?

1. Cathode: the cations compete with water (−0.83 V). The highest value is reduced.

2. Anode: the anions compete with water (+1.23 V row, reversed). The lowest value is oxidized.

3. Inert electrodes do not react, so they are not in the competition.

Try it. In molten NaCl only Na^+ and Cl^- can react. List everything that can react at each electrode when NaCl is dissolved in water instead.

1. Cathode: Na^+ and water can be reduced.

2. Anode: Cl^- and water can be oxidized.

3. Water is the extra competitor at both electrodes.

Slide 2 of 8 · Choose the cathode reaction

Inert means the electrode does **not react**. Compare each cation with water at −0.83 V, and the one with the **higher** value is reduced.

In NaCl(aq), Na^+ is −2.71 V and water is −0.83 V, so **water** is reduced. The pH near the cathode **rises**, because OH^- is made.

In $CuSO_4$(aq), Cu^{2+} is **+0.34 V**, higher than water, so $Cu^{2+} + 2e^- \rightarrow$ **Cu**. The cathode gains mass and the blue colour fades.

A cation with a value above **−0.83 V** is predicted to be reduced before water. A close call such as Zn^{2+} (−0.76 V) is only a **weak** prediction. Sodium, magnesium and aluminium lose to water.

Example. Aqueous NaCl is electrolyzed with inert electrodes. The table values are Na^+ −2.71 V and water −0.83 V. What is reduced at the cathode, what is the half-reaction, and what happens to the pH near the cathode?

1. Water (−0.83 V) is higher than Na^+ (−2.71 V), so water is reduced.

2. Reduction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

3. OH^- is made, so the pH near the cathode rises. No sodium metal forms.

Try it. Aqueous $CuSO_4$ is electrolyzed with inert electrodes. The table values are Cu^{2+} +0.34 V and water −0.83 V. What is reduced, and what happens to the cathode mass and the blue colour?

1. Cu^{2+} (+0.34 V) is higher than water (−0.83 V), so Cu^{2+} is reduced.

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

3. Copper deposits, so the cathode gains mass. The blue colour fades as Cu^{2+} is used up.

Slide 3 of 8 · Choose the anode reaction

At the anode, compare the anions, water and a reactive **electrode**. The one with the **lowest** value is oxidized.

In NaI(aq), I^- (+0.54 V) is lower than water (+1.23 V), so $2I^- \rightarrow I_2 + \mathbf{2e^-}$. Iodine makes the solution near the anode **brown**.

Sulfate has **no row** in the table as an oxidation, so only water reacts: $2H_2O \rightarrow O_2 + \mathbf{4H^+} + 4e^-$. The pH near the anode falls.

An ion that does not react at either electrode, such as Na^+, is a **spectator** ion. A reactive metal anode can be oxidized **itself**.

Example. Aqueous NaI is electrolyzed with inert electrodes. The values are I_2/I^- +0.54 V and water +1.23 V (O_2/H_2O row). What is oxidized at the anode, and what is seen near it?

1. I^- (+0.54 V) is lower than water (+1.23 V), so iodide is oxidized.

2. Oxidation: $2I^- \rightarrow I_2 + 2e^-$

3. Iodine forms, so the solution near the anode turns brown.

Try it. $CuSO_4$(aq) has a copper anode. The values are Cu^{2+}/Cu +0.34 V and water +1.23 V (O_2/H_2O row). What is oxidized at the anode, and what happens to the anode mass?

1. Cu (+0.34 V) is lower than water (+1.23 V), so the copper anode is oxidized.

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

3. The anode dissolves, so it loses mass.

Slide 4 of 8 · The chloride exception and caution with E°

In NaCl(aq) the anode choices are Cl^- at **+1.36 V** and water at +1.23 V. Water is lower, so the table predicts **oxygen**.

In a real cell, **chlorine** gas forms: $2Cl^- \rightarrow Cl_2 + \mathbf{2e^-}$. This difference is called the chloride **anomaly**.

Overvoltage is the **extra voltage** a reaction needs to run at a useful rate. Water oxidation needs a **greater** overvoltage than chloride oxidation.

A table value is a first prediction, not a promise. The table minimum voltage **may not** be enough to make water react. Predict from the table, then check for known exceptions, like chloride.

Example. Aqueous NaCl is electrolyzed with inert electrodes. The values are Cl_2/Cl^- +1.36 V and O_2/H_2O +1.23 V. What gas does the table predict at the anode, what gas is observed, and why?

1. Water (+1.23 V) is lower than Cl^- (+1.36 V), so the table predicts water is oxidized and O_2 forms.

2. Observed: Cl_2 forms, $2Cl^- \rightarrow Cl_2 + 2e^-$. This is the chloride anomaly.

3. Reason: oxidizing water needs a greater overvoltage than oxidizing chloride.

Try it. In aqueous NaCl, by how many volts do $E°(Cl_2/Cl^-)$ = +1.36 V and $E°(O_2/H_2O)$ = +1.23 V differ? Which gas actually forms at the anode?

1. Difference: 1.36 − 1.23 = 0.13 V.

2. The values are close, but overvoltage makes chloride react, so Cl_2 forms, not O_2.

Slide 5 of 8 · Method: how to predict the products of electrolysis of a solution

Step 1. List every ion, and **water**.

Step 2. Cathode: choose the reduction with the **higher** E°. Water is at **−0.83 V**.

Step 3. Anode: choose the oxidation with the **lower** E°. Water is at **+1.23 V**.

Step 4. Check for exceptions: **chloride** and a reactive electrode.

Step 5. Write the halves, the overall equation and the observations. Close E° values are a **weak** prediction.

Example. Use the method on $CuSO_4(aq)$ with inert carbon electrodes. Predict the product at each electrode and what is seen.

1. Step 1: Cu^{2+}, SO_4^{2-} and H_2O.

2. Step 2: Cu^{2+} (+0.34 V) is higher than water (−0.83 V), so $Cu^{2+} + 2e^- \rightarrow Cu$.

3. Step 3: sulfate is not oxidized, so $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

4. Steps 4 and 5: no exception applies. $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 + 4H^+$. Copper deposits, oxygen bubbles form, the blue fades and the pH falls.

Try it. Use the method on KI(aq) with inert electrodes. $E°(I_2/I^-) = +0.54$ V. What forms at each electrode?

1. Cathode: K^+ is far lower than water, so water is reduced: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$.

2. Anode: iodide (+0.54 V) is lower than water (+1.23 V), so $2I^- \rightarrow I_2 + 2e^-$.

3. Hydrogen forms at the cathode and iodine at the anode.

Slide 6 of 8 · Your turn: aqueous sodium bromide

At the cathode, Na^+ is −2.71 V and water is −0.83 V. Water is **higher**, so $2H_2O + 2e^- \rightarrow H_2 + \mathbf{2OH^-}$, and the pH rises.

At the anode, Br^- is +1.07 V and water is +1.23 V. Bromide is **lower**, so $2Br^- \rightarrow Br_2 + \mathbf{2e^-}$. Brown-orange colour is observed near the anode.

Both half-reactions move **2** electrons, so no multiplier is needed. Add the halves and cancel the electrons.

E°reaction = E°cathode − E°anode = −0.83 − (+1.07) = **−1.90** V. The power source must supply more than **1.90 V**.

Example. Aqueous NaBr is electrolyzed with inert electrodes. The values are Na^+ −2.71 V, water −0.83 V, Br_2/Br^- +1.07 V and O_2/H_2O +1.23 V. Predict the product at each electrode, write the cell reaction and find E°reaction and the minimum voltage.

1. Cathode: water (−0.83 V) is higher than Na^+, so $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

2. Anode: Br^- (+1.07 V) is lower than water, so $2Br^- \rightarrow Br_2 + 2e^-$

3. Cell reaction: $2Br^- + 2H_2O \rightarrow Br_2 + H_2 + 2OH^-$ (atoms and a charge of −2 match on both sides).

4. E°reaction = E°cathode − E°anode = −0.83 − (+1.07) = −1.90 V

5. The source must supply more than 1.90 V. The pH rises near the cathode.

Try it. Aqueous $CuBr_2$ is electrolyzed with inert electrodes. The values are Cu^{2+} +0.34 V, water −0.83 V, Br_2/Br^- +1.07 V and O_2/H_2O +1.23 V. Write the cell reaction and find E°reaction.

1. Cathode: Cu^{2+} (+0.34 V) is higher than water, so $Cu^{2+} + 2e^- \rightarrow Cu$

2. Anode: Br^- (+1.07 V) is lower than water, so $2Br^- \rightarrow Br_2 + 2e^-$

3. Cell reaction: $Cu^{2+} + 2Br^- \rightarrow Cu + Br_2$ (a charge of 0 on both sides).

4. E°reaction = 0.34 − 1.07 = −0.73 V, so the source must supply more than 0.73 V.

Slide 7 of 8 · Predict observations: copper sulfate

At the cathode, Cu^{2+} (+0.34 V) beats water (−0.83 V): $Cu^{2+} + 2e^- \rightarrow$ **Cu**. The cathode **gains** mass and the blue colour fades.

At the anode, sulfate is not oxidized, so water is: $2H_2O \rightarrow O_2 +$ **4H**$^+ + 4e^-$. Oxygen bubbles form and the pH **falls**.

The copper half moves 2 electrons and the water half moves 4. Multiply the copper half by **2** so the electrons match. E° values are never **multiplied**.

Overall: $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 +$ **4H**$^+$. E°reaction = 0.34 − 1.23 = **−0.89** V.

Example. $CuSO_4(aq)$ is electrolyzed with inert carbon electrodes. The values are Cu^{2+} +0.34 V, water −0.83 V and O_2/H_2O +1.23 V. Predict what is seen at each electrode, write the cell reaction and find E°reaction.

1. Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$. The cathode gains mass and the blue colour fades.

2. Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. Oxygen bubbles form and the pH falls near the anode.

3. Multiply the cathode half by 2 so that both halves move 4 electrons.

4. Cell reaction: $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 + 4H^+$ (a charge of +4 on both sides).

5. E°reaction = 0.34 − 1.23 = −0.89 V, so the source must supply more than 0.89 V.

Try it. $AgNO_3(aq)$ is electrolyzed with inert electrodes. The values are Ag^+ +0.80 V, water −0.83 V and O_2/H_2O +1.23 V. Nitrate is not oxidized. Write the cell reaction and find E°reaction.

1. Cathode: Ag^+ (+0.80 V) is higher than water, so $Ag^+ + e^- \rightarrow Ag$

2. Anode: water is oxidized, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

3. Multiply the silver half by 4: $4Ag^+ + 4e^- \rightarrow 4Ag$

4. Cell reaction: $4Ag^+ + 2H_2O \rightarrow 4Ag + O_2 + 4H^+$ (a charge of +4 on both sides).

5. E°reaction = 0.80 − 1.23 = −0.43 V. The pH falls near the anode.

Slide 8 of 8 · Sodium sulfate: when neither ion reacts

In $Na_2SO_4(aq)$, Na^+ is lower than water and sulfate is **not oxidized**. So **water** reacts at both electrodes.

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, so the pH **rises** and red litmus turns blue. Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, so the pH **falls** and blue litmus turns red.

Double the cathode half so both halves move **4** electrons: $4H_2O + 4e^- \rightarrow \mathbf{2H_2} + 4OH^-$.

Adding the halves, $4OH^-$ and $4H^+$ make $4H_2O$. The overall reaction is $2H_2O \rightarrow 2H_2 + O_2$, so the mole ratio of H_2 to O_2 is **2 to 1**.

Example. $Na_2SO_4(aq)$ is electrolyzed with inert electrodes. Neither ion reacts. What happens at each electrode, and what is the overall reaction?

1. Cathode: water is reduced, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. The pH rises.

2. Anode: water is oxidized, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. The pH falls.

3. Double the cathode half: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

4. Add: $6H_2O \rightarrow 2H_2 + O_2 + 4OH^- + 4H^+$. Then $4OH^- + 4H^+ \rightarrow 4H_2O$.

5. Overall: $2H_2O \rightarrow 2H_2 + O_2$

Try it. A cell with $Na_2SO_4(aq)$ and inert electrodes makes 0.0300 mol of O_2. How many moles of H_2 form at the same time?

1. The overall reaction $2H_2O \rightarrow 2H_2 + O_2$ gives 2 mol H_2 for each 1 mol O_2.

2. $n(H_2) = 2 \times 0.0300 = 0.0600$ mol

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 1-2 of 7

1. Given $NaNO_3(aq)$ with inert electrodes, decide what is reduced at the cathode and write the half-reaction (Data Booklet table values: Na^+ −2.71 V; water −0.83 V).

Water is reduced because −0.83 V is higher than −2.71 V. Reduction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$.

2. Given aqueous NaI with inert electrodes (Data Booklet table values: I_2/I^- +0.54 V; O_2/H_2O +1.23 V; water −0.83 V; Na^+ −2.71 V). Write the half-reaction at each electrode, the cell reaction and E°reaction.

Use Method: how to predict the products of electrolysis of a solution. Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. Anode: $2I^- \rightarrow I_2 + 2e^-$. Cell reaction: $2I^- + 2H_2O \rightarrow I_2 + H_2 + 2OH^-$. E°reaction = −0.83 − 0.54 = −1.37 V.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 3-4 of 7

3. Aqueous NaCl is electrolyzed with inert electrodes. State the product at the anode that the table predicts, the product that is observed, and the reason for the difference.

The table predicts oxygen from water (+1.23 V is lower than +1.36 V). Chlorine is observed. The overvoltage for oxidizing water is greater than for chloride, so chloride is oxidized.

4. Given NaBr(aq) with inert electrodes. Predict the colour change near the anode and the pH change near the cathode, and explain both with half-reactions.

We would observe a brown-orange colour near the anode and bubbles at the cathode. We infer that $2Br^- \rightarrow Br_2 + 2e^-$ makes bromine, and that $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ makes hydroxide, so the pH near the cathode rises.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 5-6 of 7

5. Given $CuSO_4(aq)$ with a copper cathode and a copper anode. Predict the change in mass of each electrode and the change in the blue colour (Data Booklet table values: Cu^{2+}/Cu +0.34 V; O_2/H_2O +1.23 V; water −0.83 V).

The cathode gains mass ($Cu^{2+} + 2e^- \rightarrow Cu$). The copper anode loses mass ($Cu \rightarrow Cu^{2+} + 2e^-$), because copper is lower than water. The blue colour stays about the same because Cu^{2+} is replaced as it is used.

6. Given $Na_2SO_4(aq)$ with inert electrodes. Write the overall cell reaction and say which gas forms in the larger amount.

Reduction: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$. Oxidation: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. Overall: $2H_2O \rightarrow 2H_2 + O_2$. Hydrogen forms in the larger amount, 2 mol for each 1 mol of O_2.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 7-7 of 7

7. Challenge: Given a solution that contains $Cu(NO_3)_2(aq)$ and $Zn(NO_3)_2(aq)$, electrolyzed with inert electrodes. Nitrate ions do not react. Data Booklet table values: Cu^{2+}/Cu +0.34 V; Zn^{2+}/Zn −0.76 V; water reduced −0.83 V; O_2/H_2O +1.23 V. Which metal plates on the cathode first? Write both half-reactions and predict the pH change near the anode.

Cathode: list what can be reduced: Cu^{2+} (+0.34 V), Zn^{2+} (−0.76 V) and water (−0.83 V). The highest value is reduced first, so copper plates first: $Cu^{2+} + 2e^- \rightarrow Cu$. Zinc plates only after the Cu^{2+} is used up. Anode: nitrate does not react and the electrodes are inert, so water is oxidized: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$. H^+ forms, so the pH near the anode falls.