B9 · Electrolysis of aqueous solutions

Student notes - follow the slides, fill the blanks, work the questions

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.

Name: _____ Date: _____

Slide 1 of 8 · Water joins the competition

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

At the cathode, water can be reduced: $2H_2O + 2e^- \rightarrow$ _____. Its table value is _____.

At the anode, water can be oxidized: $2H_2O \rightarrow$ _____. This is the +1.23 V row written _____.

At the cathode, whatever has the _____ table value is reduced. At the anode, whatever has the _____ 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?

Work:

Answer: _____

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.

Work:

Answer: _____

Sketch (draw and label the diagram):

Slide 2 of 8 · Choose the cathode reaction

Inert means the electrode does _____. Compare each cation with water at −0.83 V, and the one with the _____ value is reduced.

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

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

A cation with a value above _____ is predicted to be reduced before water. A close call such as Zn^{2+} (−0.76 V) is only a _____ 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?

Work:

Answer: _____

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?

Work:

Answer: _____

Slide 3 of 8 · Choose the anode reaction

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

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

Sulfate has _____ in the table as an oxidation, so only water reacts: $2H_2O \rightarrow O_2 +$ _____ $+ 4e^-$. The pH near the anode falls.

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

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?

Work:

Answer: _____

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?

Work:

Answer: _____

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

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

In a real cell, _____ gas forms: $2Cl^- \rightarrow Cl_2 +$ _____. This difference is called the chloride _____.

Overvoltage is the _____ a reaction needs to run at a useful rate. Water oxidation needs a _____ overvoltage than chloride oxidation.

A table value is a first prediction, not a promise. The table minimum voltage _____ 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?

Work:

Answer: _____

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?

Work:

Answer: _____

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

Step 1. List every ion, and _____.

Step 2. Cathode: choose the reduction with the _____ E°. Water is at _____.

Step 3. Anode: choose the oxidation with the _____ E°. Water is at _____.

Step 4. Check for exceptions: _____ and a reactive electrode.

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

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

Work:

Answer: _____

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

Work:

Answer: _____

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 _____, so $2H_2O + 2e^- \rightarrow H_2 +$ _____, and the pH rises.

At the anode, Br^- is +1.07 V and water is +1.23 V. Bromide is _____, so $2Br^- \rightarrow Br_2 +$ _____. Brown-orange colour is observed near the anode.

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

$E°_{reaction} = E°_{cathode} - E°_{anode} = -0.83 - (+1.07) =$ _____ V. The power source must supply more than _____.

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.

Work:

Answer: _____

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 $E°_{reaction}$.

Work:

Answer: _____

Slide 7 of 8 · Predict observations: copper sulfate

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

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

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

Overall: $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 +$ _____. E°reaction = 0.34 − 1.23 = _____ 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.

Work:

Answer: _____

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.

Work:

Answer: _____

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

In $Na_2SO_4(aq)$, Na^+ is lower than water and sulfate is _____. So _____ reacts at both electrodes.

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

Double the cathode half so both halves move _____ electrons: $4H_2O + 4e^- \rightarrow$ _____ $+ 4OH^-$.

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 _____.

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

Work:

Answer: _____

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?

Work:

Answer: _____

B9 · 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).

Work:

Final answer (with unit): _____

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.

Work:

Final answer (with unit): _____

B9 · 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.

Work:

Final answer (with unit): _____

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.

Work:

Final answer (with unit): _____

B9 · 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).

Work:

Final answer (with unit): _____

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

Work:

Final answer (with unit): _____

B9 · 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.

Work:

Final answer (with unit): _____