B9 · Electrolysis of aqueous solutions

Completed notes | Notes 1/3

Decide what reacts at each electrode when water is present, explain the chloride exception and why E° must be used with caution, and predict products and observations.

1. Water joins the competition

Choose by table value

In B8 the cells held a molten salt, so only its ions could react. In a water solution, water is in the beaker too, and it can react at either electrode.

Water can be reduced: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, **−0.83 V**. Water can be oxidized: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, which is the O_2 row run backward, from the **+1.23 V** row.

At the cathode, the strongest oxidizing agent is reduced, and it has the **highest** value. At the anode, the strongest reducing agent is oxidized, and it has the **lowest** value.

Na^+ (−2.71 V) is lower than water, so **water** is reduced at the cathode. It makes H_2 gas and **OH^-**, so the solution turns basic and the pH **rises**. Red litmus turns blue there. Sodium metal never forms from a water solution.

On the diploma: list every ion, and water. At the cathode pick the highest value. At the anode pick the lowest. Picking the highest at the anode is a common wrong choice.

Watch: Electrolysis of water (Tyler DeWitt, “Electrolysis”, 19:02)

Cathode examples

Cu^{2+} (+0.34 V) is higher than water, so **Cu^{2+}** is reduced to copper metal. The cathode **gains** mass and the blue colour fades as Cu^{2+} is used up.

The dividing line is −0.83 V. A cation above it, like Ag^+ or Cu^{2+}, is reduced before **water**. A cation below it, like Na^+, Mg^{2+} or Al^{3+}, loses to water.

Zn^{2+} (−0.76 V) is just above the line, so it is predicted to win by a small margin. This is a prediction from the table, so compare numbers every time.

On the diploma: the wrong options usually reduce a metal that sits below water.

> Cathode choices: Cu^{2+} +0.34 V or water −0.83 V. Reduced: Cu^{2+}
>
> Anode choices: sulfate (not oxidized) or water +1.23 V. Oxidized: water
>
> Products: cathode Cu(s); anode O_2(g)
>
> Near the anode the pH falls because H^+ is made.

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2. Anodes and the chloride exception

Choose the anode reaction

Take NaI(aq) with inert electrodes, which means electrodes that do not react, like carbon or platinum. I^- (+0.54 V) is lower than water (+1.23 V), so $\mathbf{I^-}$ is oxidized: $2I^- \rightarrow \mathbf{I_2} + 2e^-$.

We observe a brown colour near the anode and infer that **iodine** forms. The Na^+ ions are spectator ions, which means they do not react at either electrode.

In $CuSO_4(aq)$, sulfate appears in the booklet only as a product, in the $S_2O_8^{2-}$ row at +2.01 V. That is higher than water, so sulfate is not oxidized and **water** is: $2H_2O \rightarrow O_2 + \mathbf{4H^+} + 4e^-$.

Oxygen bubbles form, and H^+ is made, so the pH **falls** near the anode. Blue litmus turns red there.

A reactive electrode can react itself. A copper anode (+0.34 V) is lower than water, so copper is the stronger reducing agent: $Cu \rightarrow Cu^{2+} + 2e^-$. The anode **dissolves** and loses mass.

On the diploma: sulfate and nitrate are not oxidized, so water reacts. Always check what the electrode is made of. A wrong option ignores a reactive anode.

The chloride anomaly

In NaCl(aq), Cl^- is +1.36 V and water is +1.23 V. Water has the lower value, so the table predicts oxygen. But chlorine gas is **observed**: $2Cl^- \rightarrow Cl_2 + 2e^-$.

This is the chloride **anomaly**. The reason is overvoltage, the extra voltage some reactions need to run at a useful rate. Oxidizing water needs a **greater** overvoltage than oxidizing chloride, so chloride reacts.

So think of a table value as a minimum, not a promise. E° values must be used with **caution**. The table minimum is **not** enough on its own, because an extra overvoltage must be applied.

On the diploma: write the table prediction first, then check for exceptions. In a chloride solution the observed product is chlorine gas. An option saying the table minimum is enough is a wrong choice.

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3. Predict products and observations

Sodium bromide

Take NaBr(aq) with inert electrodes. At the cathode, water (−0.83 V) beats Na^+ (−2.71 V), so **water** is reduced: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$.

At the anode, Br^- (+1.07 V) is lower than water (+1.23 V), so **Br^-** is oxidized: $2Br^- \rightarrow Br_2 + 2e^-$. This is not a chloride case, so there is no exception.

Both halves move two electrons, so no multiplier is needed. The cell reaction is $2Br^- + 2H_2O \rightarrow Br_2 + H_2 + \mathbf{2OH^-}$. Atoms and charge check: Br 2, H 4, O 2, charge −2 on each side.

$E°cell = -0.83 - 1.07 = \mathbf{-1.90\ V}$. The pH rises near the **cathode**, because OH^- is made there.

On the diploma: E°cell is in volts, and the sign matters.

Observations and inferences

What we can see is an **observation**: bubbles at the cathode and a brown-orange colour near the anode.

Hydrogen gas, bromine and a rising pH are **inferences** from the half-reactions. A pH **indicator**, a dye that changes colour with pH, can test the pH.

On the diploma: keep observation and inference apart. You see colour and bubbles. From them you work out each product.

Watch: Twice as much hydrogen as oxygen (Tyler DeWitt, “Electrolysis”, 22:58)

Copper sulfate and sodium sulfate

$CuSO_4(aq)$ with inert electrodes: copper forms at the **cathode**, $Cu^{2+} + 2e^- \rightarrow Cu$. O_2 forms at the anode and the pH **falls**.

The water half moves four electrons and each copper half only two, so multiply the copper half by 2. Then add: $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 + \mathbf{4H^+}$.

E°cell = 0.34 − 1.23 = −0.89 V, so the source must supply more than 0.89 V. The blue colour fades and the solution turns more acidic.

$Na_2SO_4(aq)$: neither ion reacts, so water reacts at both electrodes. The ions only carry charge through the solution.

Double the cathode half to match four electrons: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$. Adding gives $6H_2O \rightarrow 2H_2 + O_2 + 4OH^- + 4H^+$.

The $4OH^-$ and $4H^+$ make $4H_2O$, so the overall reaction is $2H_2O \rightarrow \mathbf{2H_2} + O_2$, a 2 : 1 ratio of H_2 to O_2.

On the diploma: expect the 2 to 1 ratio of H_2 to O_2 in a numerical-response item. H^+ on the product side means the pH goes down.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 1-2 of 12

State symbols: (s) solid, (aq) dissolved in water, (l) liquid, (g) gas. Use the supplied reaction and conditions. B4 values name the Alberta Chemistry 30 Data Booklet table where used.

B9-P01 · Easy · Explain why there are more possible reactions in an aqueous solution than in a molten salt.

1. A molten salt has only its own ions.

2. An aqueous solution also contains water, and water can be reduced or oxidized, so it competes at each electrode.

B9-P02 · Easy · Given $NaNO_3(aq)$ with inert electrodes (Na^+ −2.71 V; water −0.83 V). Decide what is reduced at the cathode, write the half-reaction and state the change in pH near the cathode.

1. Water is reduced, because −0.83 V is higher than −2.71 V.

2. Reduction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$. Hydroxide ions are made, so the pH rises near the cathode.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 3-4 of 12

B9-P03 · Easy · Given $CuSO_4(aq)$ with inert electrodes (Cu^{2+} +0.34 V; water −0.83 V). Decide what is reduced at the cathode and predict the change in mass of the cathode and the colour of the solution near it.

1. Cu^{2+} is reduced because +0.34 V is higher than −0.83 V. $Cu^{2+} + 2e^- \rightarrow Cu$.

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

B9-P04 · Easy · Given NaI(aq) with inert electrodes (I_2/I^- +0.54 V; O_2/H_2O +1.23 V). Decide what is oxidized at the anode, write the half-reaction and describe the observation and the inference.

1. Iodide is oxidized because +0.54 V is lower than +1.23 V.

2. Oxidation: $2I^- \rightarrow I_2 + 2e^-$. We observe a brown colour near the anode and infer that iodine forms.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 5-6 of 12

B9-P05 · Medium · In $CuSO_4(aq)$ with inert electrodes, water is oxidized at the anode. Write the half-reaction and predict the observation at the anode and the change in pH near it.

1. Oxidation: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

2. Oxygen gas bubbles form at the anode, and hydrogen ions are made, so the pH falls near the anode.

B9-P06 · Medium · Given $CuSO_4(aq)$ with a copper anode and an inert cathode (Cu^{2+}/Cu +0.34 V; O_2/H_2O +1.23 V). Decide what is oxidized at the anode and predict the change in its mass.

1. Copper has a lower value than water, so copper is the stronger reducing agent.

2. $Cu \rightarrow Cu^{2+} + 2e^-$. The copper anode dissolves, so it loses mass.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 7-8 of 12

B9-P07 · Medium · 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.

1. The table predicts oxygen from water, because +1.23 V is lower than +1.36 V.

2. Chlorine gas is observed. The overvoltage for oxidizing water is greater than for oxidizing chloride, so chloride reacts.

B9-P08 · Medium · Given NaBr(aq) with inert electrodes (water −0.83 V; Br_2/Br^- +1.07 V; O_2/H_2O +1.23 V). Write the cell reaction and calculate E°cell.

1. Water is reduced at the cathode and bromide is oxidized at the anode. Each half moves two electrons.

2. The cell reaction is $2Br^- + 2H_2O \rightarrow Br_2 + H_2 + 2OH^-$.

3. $E°_{cell} = -0.83 - 1.07 = -1.90$ V.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 9-10 of 12

B9-P09 · Challenging · Given $CuSO_4(aq)$ with inert electrodes. Match the electrons in the half-reactions, write the cell reaction and calculate E°cell (Cu^{2+}/Cu +0.34 V; O_2/H_2O +1.23 V).

1. The water oxidation moves four electrons and each copper reduction takes two, so multiply the copper half by 2.

2. The cell reaction is $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 + 4H^+$. E°cell = 0.34 − 1.23 = −0.89 V.

B9-P10 · Challenging · Given $Na_2SO_4(aq)$ with inert electrodes. Write the half-reactions with matched electrons and the overall reaction, and say which gas forms in the larger amount.

1. Reduction: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$. Oxidation: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

2. Add, and combine $4H^+$ with $4OH^-$ to make water. The overall reaction is $2H_2O \rightarrow 2H_2 + O_2$.

3. Hydrogen forms in the larger amount, in a ratio of 2 mol of H_2 to 1 mol of O_2.

B9 · Worked practice

Electrolysis of aqueous solutions | Questions 11-12 of 12

B9-P11 · Challenging · A student says that applying the minimum voltage from the table guarantees the predicted reaction. Use aqueous NaCl to explain why this is not correct.

1. The table minimum is not enough for a reaction to happen at a useful rate. An extra overvoltage is needed.

2. In NaCl(aq) the table predicts water, but chlorine forms because water needs a larger overvoltage than chloride does.

B9-P12 · Challenging · Given $AgNO_3(aq)$ with inert electrodes (Ag^+ +0.80 V; water −0.83 V; O_2/H_2O +1.23 V). State what is reduced and what is oxidized and write the cell reaction.

1. Ag^+ is reduced at the cathode, because +0.80 V is higher than −0.83 V. Nitrate is not oxidized, so water is oxidized at the anode.

2. Match the electrons by multiplying the silver half by 4: $4Ag^+ + 2H_2O \rightarrow 4Ag + O_2 + 4H^+$.