B8 · Electrolytic cells

Completed notes | Notes 1/3

Explain how an electrolytic cell uses electrical energy to drive a reaction that is not spontaneous, label its parts, write its reactions and compare it with a voltaic cell.

1. A power source drives the reaction

A reaction that does not go by itself

Look at $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$. Zn^{2+} is reduced at the cathode (−0.76 V) and copper is oxidized at the anode (+0.34 V).

$E°cell = -0.76 - (+0.34) =$ **−1.10 V**. A negative value means the reaction is **not spontaneous** as written, so it will not go by itself.

But a power source can push it, like pushing a ball uphill. A cell that uses **electrical** energy to drive a reaction that is not spontaneous is an electrolytic cell.

The source must supply more than **1.10 V**. We ignore the sign, because the size of the negative value is the minimum push needed.

On the diploma: give a minimum voltage as a positive number. A negative one is a common wrong choice.

Watch: A reaction that is not spontaneous (Tyler DeWitt, “Electrolysis”, 3:58)

Watch: Splitting water needs electrical energy (Alberta Chemistry Teacher, “Chemistry 30 - Predicting redox reaction from species in the reduction table”, 20:04)

Watch: Why the battery must push the electrons (Tyler DeWitt, “Introduction to Electrochemistry”, 13:46)

Anode and cathode

In every cell, **reduction** happens at the cathode and **oxidation** happens at the anode. Those names come from the chemical change, not from a plus or minus sign.

In an electrolytic cell, the power source sets the signs. A terminal is where a wire joins the source. The negative terminal pushes electrons out, and they arrive at the electrode joined to it.

Electrons arriving means that electrode gains electrons, which is reduction. So the cathode is joined to the **negative** terminal and the anode to the **positive** terminal.

Cations (positive ions) move toward the **cathode**. Anions (negative ions) move toward the **anode**.

Electrons move only in the **wires**. In the liquid, the moving ions carry the charge. Both electrodes sit in one container, so no salt bridge is needed. In a drawing, a power source in the wire means electrolytic, and a voltmeter means voltaic.

On the diploma: a diagram may show only the power source. Label the terminals first, then the electrodes. The wrong option usually swaps the two electrodes.

Watch: Anode and cathode in an electrolytic cell (Tyler DeWitt, “Electrolysis”, 8:02)

Watch: A way to remember anode and cathode (Tyler DeWitt, “Introduction to Electrochemistry”, 10:44)

Cathode joins the negative terminal; anode joins the positive terminal.

Cathode (reduction): $Na^+ + e^- \rightarrow Na$

Anode (oxidation): $2Cl^- \rightarrow Cl_2 + 2e^-$

$E°cell = -2.71 - 1.36 = -4.07$ V; source must exceed 4.07 V

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Completed notes | Notes 2/3

2. Molten salts

Molten sodium chloride

Molten NaCl is the ionic solid heated until it melts, so its ions can move. It has only Na^+ and Cl^- ions and no water.

Na^+ is attracted to the negative **cathode** and gains one electron: $Na^+ + e^- \rightarrow$ **Na**.

Cl^- goes to the positive anode. Cl_2 has two atoms, so two chloride ions each give up one electron: $2Cl^- \rightarrow$ **Cl_2** $+ 2e^-$.

The anode gives 2 electrons and the cathode takes only 1, so double the cathode half. The cell reaction is $2Na^+ + 2Cl^- \rightarrow$ **$2Na + Cl_2$**.

$E°cell = -2.71 - (+1.36) =$ **-4.07 V**, so the source must supply more than **4.07 V**. We do not double E° when we double a half-reaction.

On the diploma: list the ions first, then send the cation to the cathode. Doubling E° with the half-reaction is a common wrong choice.

Watch: Splitting sodium chloride (Tyler DeWitt, “Electrolysis”, 0:46)

Watch: A battery forces the reaction (Tyler DeWitt, “Electrolysis”, 4:46)

Watch: Why the salt must be molten (Tyler DeWitt, “Electrolysis”, 7:10)

Watch: The two half-reactions (Tyler DeWitt, “Electrolysis”, 11:56)

Watch: The final equation (Tyler DeWitt, “Electrolysis”, 14:19)

Molten zinc bromide

$ZnBr_2(l)$ has only Zn^{2+} and Br^-. Zn^{2+} goes to the **cathode**: $Zn^{2+} + 2e^- \rightarrow Zn$. Br^- goes to the **anode**: $2Br^- \rightarrow Br_2 + 2e^-$.

Both halves move two electrons, so they cancel when we add them. The cell reaction is $Zn^{2+} + 2Br^- \rightarrow$ **$Zn + Br_2$**.

$E°cell = -0.76 - (+1.07) =$ **-1.83 V**. A negative value shows that a power **source** is needed, one that supplies more than 1.83 V.

On the diploma: reporting +1.83 V would suggest the cell runs by itself. Check the electrode order before you subtract, and give the sign.

B8 · Electrolytic cells

Completed notes | Notes 3/3

3. Compare cells, plating and refining

Side by side

The same two half-cells can run either way. In the Zn / Cu voltaic cell, zinc is oxidized and E°cell is +1.10 V. In the electrolytic cell, copper is oxidized and E°cell is −1.10 V for the forced reaction.

Voltaic cell: **chemical** energy to electrical energy, E°cell **positive**, anode **negative**. It needs a **salt bridge** or porous barrier.

Electrolytic cell: electrical energy to **chemical** energy, E°cell for the forced reaction **negative**, anode **positive**. It **does not** need a salt bridge.

The voltaic anode is negative because that cell makes electrons there. The electrolytic anode is positive because it is joined to the positive terminal.

On the diploma: many wrong choices copy the voltaic sign onto an electrolytic cell. Check which cell type the question describes.

Watch: Electrolytic cell versus voltaic cell (Tyler DeWitt, “Introduction to Electrochemistry”, 11:30)

Plating and refining

To plate a spoon with silver, make the spoon the **cathode**. Reduction deposits metal there: $Ag^+ + e^- \rightarrow$ **Ag**, so the spoon gains mass.

A silver anode **loses** mass as $Ag \rightarrow Ag^+ + e^-$. It replaces the Ag^+ the cathode used up, so the ion concentration stays nearly constant. A carbon anode would not dissolve.

To refine copper, impure copper is the anode and a thin pure sheet is the cathode. Pure metal builds up on the **cathode**. Impurities above copper on the table, like silver and gold, fall as solid. Those below it dissolve.

Two electrodes of the same metal in its own ion give E°cell = **0.00 V**, because the same half-reaction is reversed at the anode. Only a small voltage is needed, plus a little extra to beat resistance.

On the diploma: the electrode that gains mass is where ions are reduced, the cathode. Same metal at both electrodes means E°cell = 0.00 V.

Watch: Plating a copper ring with silver (Tyler DeWitt, “Electroplating”, 1:30)

Watch: Which terminal the object connects to (Tyler DeWitt, “Electroplating”, 3:00)

Watch: Half-reaction at the ring (Tyler DeWitt, “Electroplating Part 2”, 1:27)

Watch: Half-reaction at the silver (Tyler DeWitt, “Electroplating Part 2”, 2:36)

Watch: Anode and cathode in electroplating (Tyler DeWitt, “Electroplating Part 2”, 6:23)

B8 · Worked practice

Electrolytic cells | 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.

B8-P01 · Easy · Given $Ni^{2+} + 2e^- \rightarrow Ni$ (−0.26 V) and $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34 V). A power source is used to drive $Cu + Ni^{2+} \rightarrow Cu^{2+} + Ni$. Calculate E°cell and state the smallest voltage that the source must exceed.

1. Ni^{2+} is reduced at the cathode (−0.26 V) and copper is oxidized at the anode (+0.34 V).

2. E°cell = −0.26 − 0.34 = −0.60 V, so the source must supply more than 0.60 V.

B8-P02 · Easy · In an electrolytic cell, which electrode is joined to the negative terminal of the power source? Name the process there and give the direction in which cations move.

1. The cathode is joined to the negative terminal.

2. Reduction happens there, and cations move toward the cathode.

B8 · Worked practice

Electrolytic cells | Questions 3-4 of 12

B8-P03 · Easy · Explain why electrons do not travel through the electrolyte, and why an electrolytic cell does not need a salt bridge.

1. Electrons travel only in the wires. In the liquid the charge is carried by ions.

2. Both electrodes are in the same liquid, so ions can move between them. No salt bridge is needed to complete the circuit.

B8-P04 · Easy · Write the half-reactions, the cell reaction and the product at each electrode for the electrolysis of molten NaCl.

1. Cathode: $Na^+ + e^- \rightarrow Na$, so sodium metal forms. Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$, so chlorine gas forms.

2. Double the cathode half to match two electrons. The cell reaction is $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$.

B8 · Worked practice

Electrolytic cells | Questions 5-6 of 12

B8-P05 · Medium · Given molten $ZnBr_2(l)$ with inert electrodes (Zn^{2+}/Zn −0.76 V; Br_2/Br^- +1.07 V). Write the cell reaction and calculate E°cell.

1. Zn^{2+} is reduced at the cathode. Bromide is oxidized at the anode.

2. The cell reaction is $Zn^{2+} + 2Br^- \rightarrow Zn + Br_2$. E°cell = −0.76 − 1.07 = −1.83 V.

B8-P06 · Medium · Given molten $MgCl_2$ with inert electrodes (Mg^{2+}/Mg −2.37 V; Cl_2/Cl^- +1.36 V). Write the cell reaction and calculate the smallest voltage that the source must exceed.

1. Mg^{2+} is reduced at the cathode and Cl^- is oxidized at the anode. Each half moves two electrons.

2. The cell reaction is $Mg^{2+} + 2Cl^- \rightarrow Mg + Cl_2$. E°cell = −2.37 − 1.36 = −3.73 V, so the source must exceed 3.73 V.

B8 · Worked practice

Electrolytic cells | Questions 7-8 of 12

B8-P07 · Medium · Compare a voltaic cell and an electrolytic cell for the Zn / Cu pair. Use the energy change, the sign of the cell value for the reaction that runs, and the sign of the anode.

1. Voltaic: chemical to electrical energy, E°cell +1.10 V, anode negative.

2. Electrolytic: electrical to chemical energy, E°cell −1.10 V for the forced reaction, anode positive.

B8-P08 · Medium · A student says the anode in an electrolytic cell is negative because it is negative in a voltaic cell. Explain the error.

1. The anode is defined by oxidation, not by its sign.

2. In an electrolytic cell the anode is joined to the positive terminal of the source, so it is positive.

B8 · Worked practice

Electrolytic cells | Questions 9-10 of 12

B8-P09 · Challenging · A silver spoon is plated in $AgNO_3(aq)$ with a silver bar. Say which is the cathode, write the half-reaction at each electrode and predict the mass change of each.

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

2. The silver bar is the anode: $Ag \rightarrow Ag^+ + e^-$. It loses mass and replaces the Ag^+ that was used.

B8-P10 · Challenging · Describe a cell for refining impure copper and name the electrode that gains mass.

1. The impure copper is the anode and a thin pure copper sheet is the cathode, in a copper(II) solution.

2. $Cu \rightarrow Cu^{2+} + 2e^-$ at the anode and $Cu^{2+} + 2e^- \rightarrow Cu$ at the cathode. The pure copper cathode gains mass.

B8 · Worked practice

Electrolytic cells | Questions 11-12 of 12

B8-P11 · Challenging · Silver electrodes are placed in silver nitrate solution and connected to a power source. Calculate E°cell for the reaction in this cell and say how much voltage is needed in principle.

1. The same half-cell, Ag^+/Ag (+0.80 V), is reduced at the cathode and reversed at the anode.

2. E°cell = 0.80 − 0.80 = 0.00 V. Only a small applied voltage is needed, plus a little more to overcome resistance.

B8-P12 · Challenging · A student says that a negative E°cell means a reaction cannot happen at all. Use the idea of an electrolytic cell to correct this.

1. A negative value means the reaction is not spontaneous by itself.

2. A power source with a voltage greater than the magnitude of the negative value can drive it, as in an electrolytic cell.