B7 · Reduction potentials and the hydrogen reference

Completed notes | Notes 1/3

Use the hydrogen reference and the reduction table to build a cell from any two half-cells, write its notation, predict observations and say what E° means.

1. The hydrogen reference and the table

One reference for every half-cell

A voltmeter reads the push between **two** half-cells, so one half-cell alone can't have a measured value.

So chemists picked the standard hydrogen half-cell ($2H^+ + 2e^- \rightarrow H_2$, 1.0 mol/L, H_2 gas at 101.325 kPa) as the reference. They set it to exactly **0.00 V**, like sea level for heights.

Join zinc to it and the meter reads 0.76 V, with electrons flowing from zinc to hydrogen. Electrons leave the anode, so zinc is the **anode**.

Use $E°cell = E°cathode - E°anode$. That gives $0.76 = 0.00 - E°(Zn^{2+}/Zn)$, so $E°(Zn^{2+}/Zn) =$ **-0.76 V**. Negative means zinc ions are poorer than hydrogen ions at gaining electrons.

Now join copper. The meter reads 0.34 V, but electrons flow toward copper. Electrons go toward the cathode, so copper is the **cathode**.

So $0.34 = E°(Cu^{2+}/Cu) - 0.00$ and $E°(Cu^{2+}/Cu) =$ **+0.34 V**. Positive means copper ions are better than hydrogen ions at gaining electrons.

On the diploma: electron flow tells you which half is the anode, and that decides the sign. Name the anode before you write the equation.

Read the table

Every row is written as a **reduction**, with the electrons on the left.

A higher value means the particle on the left gains electrons better, so it is a stronger **oxidizing agent**. A lower value means the particle on the right gives electrons better, so it is a stronger reducing agent.

Ag^+ (+0.80 V) is a stronger oxidizing agent than Cu^{2+} (+0.34 V). Zn is the strongest reducing agent of the three, because Zn^{2+}/Zn is lowest at −0.76 V. You built this same ranking from experiments in B4.

If something is oxidized in a cell, we still use its printed **reduction** value and we never change its **sign**.

The subtraction in E°cell = E°cathode − E°anode already handles the sign. If you flip the sign first, you count it twice.

On the diploma: the strongest oxidizing agent has the highest value on the left. The strongest reducing agent has the lowest value on the right. Flipping the anode's sign is a common wrong option.

Reference: $2H^+ + 2e^- \rightarrow H_2$ is set at 0.00 V

Zn half-cell joined to the reference reads 0.76 V and Zn is the anode: E° = -0.76 V

Fe^{3+}/Fe^{2+} +0.77 V cathode; I_2/I^- +0.54 V anode: E°cell = +0.23 V

E°cell = E°cathode − E°anode. Do you multiply E° by the electron count? No

B7 · Reduction potentials and the hydrogen reference

Completed notes | Notes 2/3

2. Cells from any two half-cells

Choose the cathode and the anode

Given $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V) and $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V). It is the same rule as the Zn / Cu cell: the half with the **higher** value is reduced at the cathode.

So **Fe^{3+}** is reduced and **I^-** is oxidized. The iodine row runs backward at the anode.

Each I_2 made gives 2 electrons, and each Fe^{3+} takes only 1. So multiply the iron half by **2** to match the electrons.

Add the halves and cancel the electrons. The cell reaction is $2Fe^{3+} + 2I^- \rightarrow$ **$2Fe^{2+} + I_2$**. Check the charge: +6 − 2 = +4 on the left and +4 on the right.

$E°_{cell}$ = **+0.77** − (+0.54) = **+0.23 V**. We did not double 0.77 V. A potential is a push per electron, not a total, so never **multiply** a table value by a coefficient.

On the diploma: write the two values side by side before anything else, and count electrons before you balance. Multiplying E° by a coefficient is a typical wrong option.

Watch: Which metal pulls electrons harder (Tyler DeWitt, “Introduction to Electrochemistry”, 6:06)

Inert electrodes and notation

In B6 both halves had a solid metal to connect the wire. The Fe^{3+}/Fe^{2+} half-cell has only dissolved ions, so it needs an **inert** electrode, which means one that does not react.

Carbon is the usual choice, written C(s). It only gives electrons a surface to enter or leave. Iron metal would not work, because it could react itself.

Take MnO_4^-/Mn^{2+} (+1.51 V) and Fe^{3+}/Fe^{2+} (+0.77 V). The higher value is the cathode, so permanganate is reduced and the iron half is the anode.

C(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^-(aq), H^+(aq), Mn^{2+}(aq) | C(s). The **anode** is on the far left, and a **comma** separates ions in one solution. H^+ is there because the permanganate half needs it.

The reduction is $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. Each Fe^{2+} gives 1 electron and each MnO_4^- takes 5, so multiply the iron half by 5.

$E°_{cell}$ = 1.51 − 0.77 = **+0.74 V**. This is the same reaction as the titration of iron(II) with permanganate.

On the diploma: put the anode on the left, the double line in the middle, and each dissolved ion in its own solution. A half-cell with no solid metal needs a carbon electrode.

B7 · Reduction potentials and the hydrogen reference

Completed notes | Notes 3/3

3. Predict and interpret

Predict observations

We predict what we would see the same way as in B6. Read each half-reaction and ask what is used up and what is made.

At the cathode, purple MnO_4^- is reduced to almost colourless **Mn^{2+}**, so the purple fades. The half-reaction has $8H^+$ on the left, so H^+ is used up and the pH **rises**.

At the anode, lime green Fe^{2+} is oxidized to Fe^{3+}, and the solution turns **orange-yellow**.

Carbon is inert, so it is in no half-reaction and its **mass** does not change. A mass change only happens if a solid is made or used up.

On the diploma: pH goes up when H^+ is used up and down when H^+ is made. Say which one the half-reaction does.

What the sign of E° means

Try $2Ag + Cu^{2+} \rightarrow 2Ag^+ + Cu$. Cu^{2+} is reduced, so Cu^{2+}/Cu (+0.34 V) is the cathode. Silver is oxidized, so Ag^+/Ag (+0.80 V) is the anode.

$E°_{cell} = 0.34 - 0.80 =$ **−0.46 V**. The reaction is not **spontaneous** as written. The reverse, $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$, has E° = +0.46 V, so it is spontaneous.

E° predicts the spontaneous **direction** under standard conditions, meaning 1.0 mol/L and 25 °C. It does not predict **speed**, because a spontaneous reaction can still be very slow.

E° also says nothing about other concentrations. The Nernst equation is **not** part of this course.

On the diploma: if $E°_{cell}$ is negative, say the reaction is not spontaneous as written and give the reverse reaction. A claim that positive E° means fast is a wrong option.

B7 · Worked practice

Reduction potentials and the hydrogen reference | 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.

B7-P01 · Easy · A silver half-cell is joined to the standard hydrogen half-cell and the voltmeter reads 0.80 V. Electrons flow toward the silver electrode. Find E° for $Ag^+ + e^- \rightarrow Ag$ and name the anode.

1. Electrons flow toward the cathode, so silver is the cathode and hydrogen is the anode.

2. $E°_{cell} = E°_{cathode} - E°_{anode}$, so $0.80 = E°(Ag^+/Ag) - 0.00$. Then $E°(Ag^+/Ag) = +0.80$ V.

B7-P02 · Easy · Explain why a table cannot list a measured voltage for a single half-cell, and what the standard hydrogen half-cell is used for.

1. A voltmeter reads the difference between two half-cells, not the value of one alone.

2. The standard hydrogen half-cell is set to 0.00 V. Every other value is the voltage measured against it.

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 3-4 of 12

B7-P03 · Easy · Given $Cl_2 + 2e^- \rightarrow 2Cl^-$ (+1.36 V), $Br_2 + 2e^- \rightarrow 2Br^-$ (+1.07 V) and $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V). Name the strongest oxidizing agent and the strongest reducing agent among Cl_2, Br_2, I_2, Cl^-, Br^- and I^-.

1. The strongest oxidizing agent is Cl_2, because it has the highest table value.

2. The strongest reducing agent is I^-, because I_2/I^- has the lowest value, so I^- gives up electrons most easily.

B7-P04 · Easy · A student reverses the zinc row to $Zn \rightarrow Zn^{2+} + 2e^-$ and uses +0.76 V for the cell calculation. Which value should be used, and why?

1. The printed table value, −0.76 V, should be used.

2. All table values are table values. We never change the sign for an oxidation, because the subtraction E°cathode − E°anode already handles it.

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 5-6 of 12

B7-P05 · Medium · Given $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V) and $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V). Write the cell reaction and calculate E°cell.

1. Fe^{3+}/Fe^{2+} has the higher value, so Fe^{3+} is reduced at the cathode and I^- is oxidized at the anode.

2. Multiply the iron half by 2 to match two electrons: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$.

3. E°cell = 0.77 − 0.54 = +0.23 V.

B7-P06 · Medium · Given $Cl_2 + 2e^- \rightarrow 2Cl^-$ (+1.36 V) and $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V). Write the cell reaction in which chlorine oxidizes iodide and calculate E°cell.

1. Each half moves two electrons, so no multiplier is needed.

2. The cell reaction is $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$.

3. E°cell = 1.36 − 0.54 = +0.82 V.

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 7-8 of 12

B7-P07 · Medium · In the cell $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$, a student multiplies 0.77 V by 2 because the iron half was doubled. Explain the error.

1. A table value does not depend on how many copies of the half-reaction are written.

2. The correct calculation is $0.77 - 0.54 = +0.23$ V, with no multiplication.

B7-P08 · Medium · Why does the Fe^{3+}/Fe^{2+} half-cell need an inert electrode, and why is carbon a suitable choice?

1. The half-cell has no solid metal. Something must carry electrons to and from the dissolved ions.

2. Carbon is inert, so it does not react itself and only provides a surface. In cell notation it is written C(s).

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 9-10 of 12

B7-P09 · Challenging · Write the cell notation for the cell in which acidified MnO_4^- oxidizes Fe^{2+}, using carbon electrodes. Name the anode and give E°cell (MnO_4^-/Mn^{2+} +1.51 V; Fe^{3+}/Fe^{2+} +0.77 V).

1. The anode is the iron half, because Fe^{2+} is oxidized.

2. C(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^-(aq), H^+(aq), Mn^{2+}(aq) | C(s).

3. E°cell = 1.51 − 0.77 = +0.74 V.

B7-P10 · Challenging · Given $Br_2 + 2e^- \rightarrow 2Br^-$ (+1.07 V) and $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V). Will Br_2 oxidize Fe^{2+} under standard conditions? Write the equation and E°cell.

1. Br_2 has the higher value, so it is reduced and Fe^{2+} is oxidized. Multiply the iron half by 2.

2. The cell reaction is $Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$. E°cell = 1.07 − 0.77 = +0.30 V, so it is spontaneous.

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 11-12 of 12

B7-P11 · Challenging · In the cell C(s) | $Fe^{2+}(aq)$, $Fe^{3+}(aq)$ || $MnO_4^-(aq)$, $H^+(aq)$, $Mn^{2+}(aq)$ | C(s), predict three things. Give the pH change near the cathode, the colour change at each electrode and the mass change of the electrodes.

1. At the cathode $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ uses H^+, so the pH rises, and the purple colour fades.

2. At the anode, $Fe^{2+} \rightarrow Fe^{3+} + e^-$ makes the solution orange-yellow. The carbon electrodes are inert, so their mass does not change.

B7-P12 · Challenging · A student calculates $E°_{cell} = -0.46$ V for $2Ag + Cu^{2+} \rightarrow 2Ag^+ + Cu$ and says the reaction is impossible and very fast in reverse. Explain what the sign does and does not tell us.

1. A negative value says the reaction is not spontaneous as written under standard conditions. The reverse, $Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$, is spontaneous (+0.46 V).

2. The sign says nothing about the speed. A spontaneous reaction can still be slow, and E° applies to 1.0 mol/L solutions only.

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

B8 · Electrolytic cells

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.

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.

B9 · Electrolysis of aqueous solutions

Completed notes | Notes 2/3

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.

B9 · Electrolysis of aqueous solutions

Completed notes | Notes 3/3

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: $4Ag^+ + 2H_2O \rightarrow 4Ag + O_2 + 4H^+$.