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

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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.

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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.