B7 · Reduction potentials and the hydrogen reference

Completed notes

Goals: Explain why every potential is measured against the standard hydrogen reference. Use the table to build a cell from any two half-cells, with inert electrodes when needed. Calculate E°cell, predict observations and say what the sign does and does not tell us.

Slide 1 of 8 · One reference point for every half-cell

A voltmeter reads the push between **two** half-cells, so chemists chose one half-cell as the reference and set its value to exactly **0.00** V.

The standard hydrogen half-cell is $2H^+ + 2e^- \rightarrow H_2$, with H^+ at **1.0** mol/L and H_2 gas at **101.325** kPa.

Electrons flow away from the **anode** and toward the cathode. Use E°cell = E°cathode − E°anode and solve for the unknown half-cell value.

When the reference is the cathode, the unknown value is **negative**. When the reference is the anode, the unknown value is **positive**.

Example. A zinc half-cell is joined to the standard hydrogen half-cell. The voltmeter reads 0.76 V and electrons flow from the zinc half-cell toward the hydrogen half-cell. Find $E°(Zn^{2+}/Zn)$.

1. Electrons leave the anode, so zinc is the anode and hydrogen is the cathode.

2. E°cell = E°cathode − E°anode, so 0.76 V = 0.00 V − $E°(Zn^{2+}/Zn)$

3. $E°(Zn^{2+}/Zn) = -0.76$ V

Try it. A copper half-cell is joined to the standard hydrogen half-cell. The voltmeter reads 0.34 V and electrons flow toward the copper half-cell. Find $E°(Cu^{2+}/Cu)$.

1. Electrons go toward the cathode, so copper is the cathode and hydrogen is the anode.

2. E°cell = E°cathode − E°anode, so 0.34 V = $E°(Cu^{2+}/Cu)$ − 0.00 V

3. $E°(Cu^{2+}/Cu) = +0.34$ V

Slide 2 of 8 · Reading the table: all values are reductions

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

The strongest oxidizing agent is on the **left** side and has the **highest** value.

The strongest reducing agent is on the **right** side and has the **lowest** value.

If something is oxidized in a cell, still use its reduction row value as **printed**. Flipping the sign and then subtracting counts the sign change **twice**.

Example. Given $Ag^+ + e^- \rightarrow Ag$ (+0.80 V), $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34 V) and $Zn^{2+} + 2e^- \rightarrow Zn$ (−0.76 V). Which of these is the strongest oxidizing agent and which is the strongest reducing agent? Rank each group.

1. Strongest oxidizing agent: Ag^+, on the left with the highest value (+0.80 V).

2. Strongest reducing agent: Zn, on the right with the lowest value (−0.76 V).

3. Oxidizing agents: $Ag^+ > Cu^{2+} > Zn^{2+}$. Reducing agents: Zn > Cu > Ag.

Try it. Given $Br_2 + 2e^- \rightarrow 2Br^-$ (+1.07 V), $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V) and $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V). Name the strongest oxidizing agent and the strongest reducing agent among all six.

1. Strongest oxidizing agent: Br_2, on the left of the row with the highest value (+1.07 V).

2. Strongest reducing agent: I^-, on the right of the row with the lowest value (+0.54 V).

Slide 3 of 8 · A cell from any two half-cells

Compare the two table values. The half with the **higher** value is reduced at the cathode. The other half runs **backwards** as the oxidation at the anode.

The anode half $2I^- \rightarrow I_2 + 2e^-$ gives **2** electrons, and each Fe^{3+} takes **1**, so multiply the iron half by 2.

The cell reaction is $\mathbf{2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2}$. Check the charge: both sides total +4.

$E°cell = E°cathode - E°anode =$ **+0.23** V. E° is energy for each unit of charge, so it is **not** multiplied when a half-reaction is.

Example. Given $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V) and $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V). Build the cell reaction and find E°cell.

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

2. Reduction: $Fe^{3+} + e^- \rightarrow Fe^{2+}$. Oxidation: $2I^- \rightarrow I_2 + 2e^-$

3. Multiply the iron half by 2: $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$

4. Overall: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$. Charge is +4 on each side.

5. E°cell = +0.77 V − (+0.54 V) = +0.23 V

Try it. Given $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V) and $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34 V). Build the cell reaction in which Fe^{3+} is reduced and copper is oxidized, and find E°cell.

1. Fe^{3+}/Fe^{2+} has the higher value, so it is the cathode. Copper is the anode.

2. Reduction: $Fe^{3+} + e^- \rightarrow Fe^{2+}$. Oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$

3. Multiply the iron half by 2: $2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+}$

4. Overall: $2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$. Charge is +6 on each side.

5. E°cell = +0.77 V − (+0.34 V) = +0.43 V

Slide 4 of 8 · Method: how to find E°cell from any two half-cells

Step 1. Write the two table **values**. Each one is E° for its pair.

Step 2. The **lower** E° is the anode, so that half is oxidized.

Step 3. The **higher** E° is the cathode, so that half is reduced.

Step 4. E°cell = E°**cathode** − E°anode. Do not multiply by **coefficients**.

Step 5. A **positive** E°cell means the cell runs by itself.

Example. Use the method on $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V) and $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V). Find E°cell.

1. Step 1: +0.77 V and +0.54 V.

2. Step 2: the lower value is I_2/I^-, so iodide is oxidized.

3. Step 3: the higher value is Fe^{3+}/Fe^{2+}, so Fe^{3+} is reduced.

4. Steps 4 and 5: E°cell = +0.77 − (+0.54) = +0.23 V. It is positive, so the cell runs by itself.

Try it. Use the method on $Br_2 + 2e^- \rightarrow 2Br^-$ (+1.07 V) and $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V). Find E°cell.

1. Br_2/Br^- has the higher value, so it is the cathode. Fe^{3+}/Fe^{2+} is the anode.

2. E°cell = +1.07 − (+0.77) = +0.30 V.

3. It is positive, so the cell runs by itself.

Slide 5 of 8 · Inert electrodes and notation

An **inert** electrode does not react. It only gives electrons a surface to enter or leave. Use one when a half-cell has no solid **metal**.

Carbon is written **C(s)** in cell notation. Iron metal would not work, because it could **react**.

In cell notation, a **comma** separates ions in the same solution. The anode goes on the far left.

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.

Example. Given $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (+1.51 V) and $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V). Neither half-cell has a solid metal. Name the electrode, write the cell notation and the overall reaction, and find E°cell.

1. Use inert carbon electrodes, written C(s).

2. MnO_4^-/Mn^{2+} has the higher value, so it is the cathode. The iron half is the anode.

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

4. Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. Oxidation: $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

5. Overall: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

6. $E°cell = +1.51\ V - (+0.77\ V) = +0.74\ V$

Try it. Given $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V) and $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34 V). Write the cell notation for the cell in which Fe^{3+} is reduced. Say which electrode is carbon, and find E°cell.

1. Fe^{3+}/Fe^{2+} has the higher value, so it is the cathode. Copper is the anode.

2. The iron half-cell has no solid metal, so it uses a carbon electrode. Copper uses a copper electrode.

3. Notation: Cu(s) | Cu^{2+}(aq) || Fe^{3+}(aq), Fe^{2+}(aq) | C(s)

4. $E°cell = +0.77\ V - (+0.34\ V) = +0.43\ V$

Slide 6 of 8 · Your turn: will bromine oxidize iron(II)?

To oxidize something, an oxidizing agent must itself be **reduced**, because an oxidizing agent takes electrons.

Br_2 (+1.07 V) has a **higher** value than Fe^{3+}/Fe^{2+} (+0.77 V), so Br_2 is reduced at the cathode.

The iron half gives 1 electron and bromine takes 2, so multiply the iron half by **2**. Overall: $Br_2 + 2Fe^{2+} \rightarrow \mathbf{2Br^- + 2Fe^{3+}}$.

$E°cell = 1.07 - 0.77 = \mathbf{+0.30}$ V. A positive sign says the reaction is **spontaneous**. It predicts direction only, not **speed**.

Example. Given $Br_2 + 2e^- \rightarrow 2Br^-$ (+1.07 V) and $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V). Does Br_2 oxidize Fe^{2+} to Fe^{3+} under standard conditions? Write the cell reaction and find E°cell.

1. Br_2/Br^- has the higher value, so Br_2 is reduced at the cathode.

2. Reduction: $Br_2 + 2e^- \rightarrow 2Br^-$. Oxidation: $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$

3. Overall: $Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$. Br is 2 and Fe is 2 on each side. Charge is +4 on each side.

4. $E°cell = +1.07\ V - (+0.77\ V) = +0.30\ V$

5. The value is positive, so yes, Br_2 oxidizes Fe^{2+} under standard conditions.

Try it. Given $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V) and $Fe^{3+} + e^- \rightarrow Fe^{2+}$ (+0.77 V). Does I_2 oxidize Fe^{2+} to Fe^{3+} under standard conditions? Write the reaction and find E°cell for it as written.

1. For I_2 to oxidize Fe^{2+}, I_2 is reduced (cathode, +0.54 V) and Fe^{2+} is oxidized (anode, +0.77 V).

2. Overall: $I_2 + 2Fe^{2+} \rightarrow 2I^- + 2Fe^{3+}$. Charge is +4 on each side.

3. $E°cell = +0.54\ V - (+0.77\ V) = -0.23\ V$

4. The value is negative, so the reaction is not spontaneous as written. I_2 does not oxidize Fe^{2+}.

Slide 7 of 8 · Predict what you would see in a cell

At the cathode, purple MnO_4^- is reduced to Mn^{2+}, which is **colourless** at 0.010 mol/L (pale pink at 1.0 mol/L), so the purple fades.

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ uses up H^+, so the pH **rises**. Less H^+ means a higher pH.

At the anode, $Fe^{2+} \rightarrow Fe^{3+} + e^-$. The Data Booklet (p. 11) lists iron(III) as **orange-yellow**, so the solution turns that colour.

Carbon electrodes are **inert**, so their mass does not change. A mass change needs a **solid** that is made or used up.

Example. The cell C(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^-(aq), H^+(aq), Mn^{2+}(aq) | C(s) is running. Predict the colour change at each electrode, the pH change near the cathode and the mass change of the electrodes.

1. Cathode: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$. The purple fades to colourless, since Mn^{2+} is colourless at 0.010 mol/L.

2. H^+ is used up, so the pH rises near the cathode.

3. Anode: $Fe^{2+} \rightarrow Fe^{3+} + e^-$. Fe^{3+} is made, so the solution turns orange-yellow.

4. Both carbon electrodes are inert, so their masses do not change.

Try it. The cell Cu(s) | Cu^{2+}(aq) || Fe^{3+}(aq), Fe^{2+}(aq) | C(s) is running. Predict the mass change of each electrode and the change in the blue colour of the copper solution.

1. Anode (Cu): $Cu \rightarrow Cu^{2+} + 2e^-$. The copper electrode loses mass.

2. Cu^{2+} is made, so the blue colour of the copper solution deepens.

3. Cathode (C): $Fe^{3+} + e^- \rightarrow Fe^{2+}$. The carbon electrode is inert, so its mass does not change.

Slide 8 of 8 · What E° tells us, and what it does not

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

E°cell = 0.34 − 0.80 = **−0.46** V. A negative value means the reaction is **not spontaneous** as written under standard conditions.

The reverse reaction, $Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag$, has E°cell = **+0.46** V, so it is spontaneous.

E° gives the spontaneous direction under **standard** conditions. It does not give **speed**, and it does not give voltages at other concentrations.

Example. Given $E°(Ag^{+}/Ag)$ = +0.80 V and $E°(Cu^{2+}/Cu)$ = +0.34 V. A student studies $2Ag + Cu^{2+} \rightarrow 2Ag^{+} + Cu$. Calculate E°cell for the reaction as written. What does the sign tell you, and which reaction is spontaneous?

1. Cu^{2+} is reduced (cathode, +0.34 V). Ag is oxidized (anode, +0.80 V).

2. E°cell = E°cathode − E°anode = +0.34 V − (+0.80 V) = −0.46 V

3. The value is negative, so the reaction is not spontaneous as written.

4. The reverse, $Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag$, has E°cell = +0.46 V and is spontaneous.

Try it. Given $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ (+0.77 V) and $Zn^{2+} + 2e^{-} \rightarrow Zn$ (−0.76 V). A student studies $Zn^{2+} + 2Fe^{2+} \rightarrow Zn + 2Fe^{3+}$. Calculate E°cell as written. Is the reaction spontaneous, and does the sign tell us its speed?

1. Zn^{2+} is reduced (cathode, −0.76 V). Fe^{2+} is oxidized (anode, +0.77 V).

2. E°cell = −0.76 V − (+0.77 V) = −1.53 V

3. The value is negative, so the reaction is not spontaneous as written. The reverse reaction is spontaneous.

4. The sign gives direction only, not speed.

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 1-2 of 7

1. A cell is built from the standard hydrogen half-cell and a nickel half-cell. The voltmeter reads 0.26 V and electrons flow from the nickel electrode toward the hydrogen half-cell. Find E° for $Ni^{2+} + 2e^- \rightarrow Ni$.

Nickel is the anode and hydrogen is the cathode. E°cell = E°cathode − E°anode, so 0.26 = 0.00 − E°(Ni^{2+}/Ni). Then E°(Ni^{2+}/Ni) = −0.26 V.

2. Given these Data Booklet table rows: $Ag^+ + e^- \rightarrow Ag$ (+0.80 V), $Cu^{2+} + 2e^- \rightarrow Cu$ (+0.34 V) and $Zn^{2+} + 2e^- \rightarrow Zn$ (−0.76 V). Which of these is the strongest reducing agent, and which is the strongest oxidizing agent?

The strongest reducing agent is Zn, because Zn^{2+}/Zn has the lowest value. The strongest oxidizing agent is Ag^+, because it has the highest value.

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 3-4 of 7

3. Given these Data Booklet table rows: $I_2 + 2e^- \rightarrow 2I^-$ (+0.54 V) and $Cl_2 + 2e^- \rightarrow 2Cl^-$ (+1.36 V). Write the cell reaction for the cell in which chlorine oxidizes iodide and calculate E°cell.

Use Method: how to find E°cell from any two half-cells. Cl_2 has the higher value, so it is the cathode. Reduction: $Cl_2 + 2e^- \rightarrow 2Cl^-$. Oxidation: $2I^- \rightarrow I_2 + 2e^-$. Cell reaction: $Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$. E°cell = 1.36 − 0.54 = +0.82 V.

4. Write the cell notation for the cell in which MnO_4^- (acidic) oxidizes Fe^{2+}, using carbon electrodes. Name the anode and give E°cell (Data Booklet table values: MnO_4^-/Mn^{2+} +1.51 V; Fe^{3+}/Fe^{2+} +0.77 V).

The anode is the iron half (Fe^{2+} is oxidized). The notation is C(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^-(aq), H^+(aq), Mn^{2+}(aq) | C(s). E°cell = 1.51 − 0.77 = +0.74 V.

B7 · Worked practice

Reduction potentials and the hydrogen reference | Questions 5-6 of 7

5. Given these Data Booklet table rows: $Cl_2 + 2e^- \rightarrow 2Cl^-$ (+1.36 V) and $Br_2 + 2e^- \rightarrow 2Br^-$ (+1.07 V). Will Cl_2 oxidize Br^- to Br_2 under standard conditions? Write the equation and E°cell.

Cl_2 has the higher value, so it is reduced, and Br^- is oxidized. The reaction is $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$. E°cell = 1.36 − 1.07 = +0.29 V, so it is spontaneous.

6. In the cell C(s) | Fe^{2+}(aq), Fe^{3+}(aq) || MnO_4^-(aq), H^+(aq), Mn^{2+}(aq) | C(s), predict the change in pH and in colour near the cathode. Explain with a half-reaction.

The pH rises and the purple colour fades. At the cathode, $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ uses H^+ and changes purple MnO_4^- to colourless Mn^{2+} at 0.010 mol/L.

B7 · Worked practice

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

7. Challenge: Given the Data Booklet table values $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Cu^{2+}/Cu) = +0.34$ V. Suppose chemists had chosen the zinc half-cell as the zero reference instead of hydrogen. What would $E°(Cu^{2+}/Cu)$ be on that new scale, in volts? Would $E°_{cell}$ for the zinc and copper cell change? Explain.

Moving the zero shifts every value by the same amount. Zinc must become 0.00 V, so every value goes up by 0.76 V. New $E°(Cu^{2+}/Cu) = +0.34 + 0.76 = +1.10$ V. $E°_{cell}$ on the hydrogen scale $= +0.34 - (-0.76) = +1.10$ V. On the new scale it is $+1.10 - 0.00 = +1.10$ V. It does not change. A cell voltage is a difference, so the choice of zero does not matter.