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Topic 9.8: Galvanic (Voltaic) and Electrolytic Cells

Revision Notes · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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A Galvanic Cell Turns a Favorable Reaction Into Current

A spontaneous redox reaction can do electrical work. In a galvanic cell, the two half reactions sit in separate half cells, joined by a wire and a salt bridge. Electrons released by oxidation travel through the wire to the cathode, where reduction consumes them.

Favorable means the cell runs on its own. A galvanic cell is built around a thermodynamically favorable reaction: negative free energy change and positive cell potential.

An Ox, Red Cat: The Assignment That Never Changes

Oxidation always happens at the anode; reduction always happens at the cathode. This rule holds in every cell, galvanic or electrolytic. The mnemonics are worth memorizing exactly: An Ox, Red Cat.

What flips between cell types is the sign, never the role. In a galvanic cell the anode is negative and the cathode positive; in an electrolytic cell the reverse.

Why the galvanic anode is negative. Oxidation releases electrons into the anode faster than the wire carries them away, so the anode sits electron rich and negative.

Electrons in the Wire, Ions in the Bridge

Electrons use the wire only. They leave the anode through the external circuit and arrive at the cathode.

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Ions balance the charge. As a galvanic cell runs, the anode compartment gains metal ions and the cathode compartment loses them. Without a salt bridge, charge would build up and the current would stop. The bridge lets spectator ions migrate, anions toward the anode compartment and cations toward the cathode compartment, keeping each side neutral.

Cell Notation: One Line That Names the Whole Cell

The anode goes on the left, the cathode on the right. A single vertical bar marks a phase boundary, and a double bar marks the salt bridge. The classic example:

$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$

Concentrations ride with the ions.

$Zn(s)|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu(s)$

This marks standard conditions, which is what tabulated potentials assume.

Inert electrodes appear when both species are in solution. Platinum conducts electrons without reacting.

$Pt|Fe^{2+}(aq),\ Fe^{3+}(aq)||MnO_4^-(aq),\ H^+(aq),\ Mn^{2+}(aq)|Pt$

The two platinums serve the iron and permanganate half reactions.

Electrode Mass and Solution Concentration as the Cell Runs

The galvanic anode is consumed. Solid metal atoms lose electrons and enter solution as ions, so the anode loses mass and its compartment grows more concentrated.

The galvanic cathode gains mass. Metal ions gain electrons and plate out, so the cathode grows heavier and its compartment grows less concentrated.

A running cell heads toward equilibrium. As the anode compartment concentrates and the cathode compartment dilutes, the cell potential falls to zero at equilibrium and the cell is dead.

Electrolytic Cells: Forcing the Reverse with a Power Supply

An external supply pays the free energy bill. An electrolytic cell drives a reaction whose free energy change is positive, so it cannot run on its own. The supply pushes electrons onto the cathode and pulls them from the anode.

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The sign rule flips, the role rule does not. The electrolytic anode is positive and the cathode negative. Oxidation still happens at the anode and reduction still at the cathode.

A negative cell potential is the signature. A reaction written with E°cell < 0 is nonspontaneous as written and must be driven electrolytically.

Two Electrolysis Cases the File Tests

Molten sodium chloride. With no water present, the ions themselves react. At the cathode, liquid sodium metal forms.

$Na^+ + e^- \rightarrow Na(l)$

At the anode, chlorine gas forms.

$2Cl^- \rightarrow Cl_2(g) + 2e^-$

Copper refining. Impure copper is the anode and pure copper the cathode, in copper sulfate solution. At the anode, impure copper dissolves.

$Cu \rightarrow Cu^{2+} + 2e^-$

At the cathode, pure copper plates out.

$Cu^{2+} + 2e^- \rightarrow Cu$

Impurities fall away as sludge or stay in solution; they do not plate out with the copper.

Potentials and Free Energy: The Numbers the File Tests

The higher reduction potential wins the cathode. The species with the more positive standard reduction potential is reduced, and the other is oxidized. For magnesium and silver, $E°(Ag^+/Ag) = +0.80$ V beats $E°(Mg^{2+}/Mg) = -2.37$ V, so silver ions are reduced at the cathode and magnesium metal is oxidized at the anode.

Cell potential is cathode minus anode, never scaled.

$E°cell = E°cathode - E°anode$

Use the reduction potentials exactly as tabulated; the subtraction handles the anode's reversal. For zinc and copper, $E°cell = (+0.34) - (-0.76) = +1.10$ V. Potentials are intensive: doubling a half reaction to balance electrons leaves its E° unchanged.

Free energy follows from the potential.

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$\Delta G° = -nFE°$

Here n is the moles of electrons transferred and F = 96,485 C mol^{-1}. For the aluminum copper reaction below, six electrons move and E°cell = +2.00 V, so $\Delta G° = -(6)(96{,}485)(2.00) = -1{,}158{,}000$ J mol^{-1}, about −1160 kJ mol^{-1}.

$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$

A concentration cell runs on concentration alone. Identical copper electrodes in 0.10 M and 1.0 M Cu^{2+} still produce a voltage. Oxidation happens in the dilute compartment and reduction in the concentrated compartment, until the two concentrations match.

Worked Examples

Example 1: The zinc copper cell, end to end. Anode:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Cathode:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Both move two electrons, so they add directly:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

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Cell potential: E°cell = (+0.34) − (−0.76) = +1.10 V, positive, so the cell is galvanic. As it runs, the zinc electrode loses mass and the copper electrode gains mass.
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Example 2: The mislabeled lead nickel cell. A student labels nickel the cathode in a Pb/Pb^{2+} and Ni/Ni^{2+} cell. Lead has the higher reduction potential, −0.13 V against nickel's −0.25 V, so lead is reduced at the cathode and nickel oxidized at the anode: the labels are backwards. Correct potential: E°cell = (−0.13) − (−0.25) = +0.12 V, and the cell is galvanic.

Example 3: Magnesium and silver. Silver has the higher reduction potential, +0.80 V against magnesium's −2.37 V, so Ag^+ is reduced at the cathode and Mg is oxidized at the anode. Then E°cell = (+0.80) − (−2.37) = +3.17 V: positive, so the cell is galvanic.

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Example 4: Free energy from a cell potential. For the aluminum copper reaction below, six electrons move and E°cell = +2.00 V.

$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$

Then $\Delta G° = -nFE° = -(6)(96{,}485)(2.00) = -1{,}157{,}820\ J\ mol^{-1} = -1158\ kJ\ mol^{-1}$: negative, so the reaction is spontaneous.

Traps That Cost Marks in Topic 9.8

Flipping the redox roles instead of the signs. Oxidation is at the anode in both cell types; only the electrode charge changes.

Sending electrons through the salt bridge. Electrons travel through the wire only; ions through the bridge only.

Scaling a potential with its half reaction. Doubling a half reaction doubles the electrons, never the potential.

Reading a negative E°cell as a faulty galvanic cell. A negative standard potential means the reaction as written is nonspontaneous and the setup is electrolytic.

Confusing the oxidizing agent with the species oxidized. The oxidizing agent is the species reduced: in the permanganate iron cell, MnO_4^- is the oxidizing agent and Fe^{2+} the reducing agent.

Assuming the concentrated side of a concentration cell is the anode. Oxidation happens in the dilute compartment; concentrated is the cathode.

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Key Relationships to Remember

- Oxidation at the anode, reduction at the cathode, in galvanic and electrolytic cells alike
- Galvanic: anode negative, cathode positive; electrolytic: anode positive, cathode negative
- Electrons flow through the wire from anode to cathode; bridge ions flow anions toward the anode compartment, cations toward the cathode compartment
- Cell notation: anode left, cathode right, single bars for phase boundaries, double bar for the salt bridge; Pt electrodes where both redox species are in solution
- Galvanic anode loses mass and concentrates its compartment; cathode gains mass and dilutes its compartment; potential falls to zero at equilibrium
- Electrolytic cells use an external supply to drive a positive ΔG° reaction; negative E°_{cell} marks a nonspontaneous reaction as written
- $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$, potentials never scaled by coefficients; the species with the higher reduction potential is reduced
- $\Delta G^\circ = -nFE^\circ$: positive E°_{cell} means negative ΔG° and a spontaneous, galvanic reaction
- Concentration cells: identical electrodes, different concentrations; oxidation in the dilute compartment, reduction in the concentrated compartment, until concentrations equalize

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Topic 9.8 Worksheet

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