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Topic 9.8: Galvanic (Voltaic) and Electrolytic Cells

Worksheet · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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How to Use This Worksheet

Work in order. Section A checks the ideas: which electrode does what in each cell type, where electrons and ions travel, how to read cell notation, and what a concentration cell does. Section B practices the working: half reactions and overall reactions, cell potentials from tabulated values, free energy from a cell potential, the mislabeled cell, the platinum electrode cell, and the two electrolysis cases. Section C is exam style: judging a batch of student claims, a cell running down toward equilibrium, and a negative cell potential handled three ways.

Reference facts. oxidation always happens at the anode and reduction always at the cathode, in both cell types. Electrode signs flip with cell type: galvanic anode negative and cathode positive, electrolytic anode positive and cathode negative. Potentials are in volts, free energies in kJ mol^{-1}, F = 96,485 C mol^{-1}. Potentials are intensive: never multiply an E° by a stoichiometric coefficient. Values given for a reaction are for the reaction exactly as written: reverse it and the sign of E°cell flips with it.

One working habit ties the sheet together: roles first, signs second, numbers last. Name the anode and cathode from the chemistry before touching any sign, then assign charges from the cell type, then compute. Finally, check: every overall reaction balances for atoms and charge, and every electron count matches between the two half reactions.

The answer key gives the full working for every part. Do not look at the answer key until you have attempted every question.

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Section A: Recall and Concepts

A1. (a) State the rule that assigns oxidation and reduction to electrodes, and say whether it changes between galvanic and electrolytic cells. (b) State the electrode signs in a galvanic cell and in an electrolytic cell. (c) In a galvanic cell, explain in one sentence why the anode is negative. (d) Judge the claim: "The anode is always the negative electrode."

A2. In a galvanic cell: (a) state the direction of electron flow through the external wire; (b) state the direction of anion flow and of cation flow through the salt bridge; (c) state what happens to the current if the salt bridge is removed, and why.

A3. Read the notation $Zn(s)|Zn^{2+}(1\ M)||Cu^{2+}(1\ M)|Cu(s)$. (a) Name the anode and the cathode. (b) Write both half reactions. (c) Write the overall cell reaction. (d) State how many electrons are transferred per formula unit of reaction.

A4. In an electrolytic cell: (a) state which electrode is positive; (b) state where reduction happens; (c) judge the claim: "Electrons flow from the cathode to the anode through the external wire in an electrolytic cell."

A5. A concentration cell has copper electrodes in 0.10 M and 1.0 M Cu^{2+} solutions. (a) State which compartment is the anode. (b) State the direction of electron flow through the wire. (c) State what happens to the Cu^{2+} concentration in each compartment as the cell runs. (d) State when the cell stops producing current.

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Section B: Core Practice

B1. A galvanic cell is built from Zn(s)|Zn^{2+}(aq) and Cu(s)|Cu^{2+}(aq) half cells. $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Cu^{2+}/Cu) = +0.34$ V. (a) Write both half reactions and the overall reaction. (b) Calculate E°cell, showing the subtraction. (c) State whether the cell is galvanic or electrolytic, with the sign reason.

B2. A galvanic cell is made from Mg/Mg^{2+} and Ag/Ag^{+}. $E°(Mg^{2+}/Mg) = -2.37$ V and $E°(Ag^{+}/Ag) = +0.80$ V. (a) State which half reaction occurs at the cathode, and write it. (b) Write the anode half reaction and the overall reaction, scaled so the electrons match. (c) Calculate E°cell.

B3. The standard cell potential for $2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$ is +2.00 V. (a) State how many electrons are transferred. (b) Calculate ΔG° in kJ mol^{-1}, showing the substitution. (c) State what the sign of ΔG° tells you about the reaction. (d) State E°cell and ΔG° for the reverse reaction, and state whether the reverse reaction is spontaneous.

B4. A student builds a cell from Pb/Pb^{2+} ($E° = -0.13$ V) and Ni/Ni^{2+} ($E° = -0.25$ V) and labels nickel the cathode. (a) State the error and name the true cathode. (b) Write both half reactions. (c) Calculate the correct E°cell. (d) State which electrode loses mass as this cell runs.

B5. A galvanic cell is written Pt|Fe^{2+}(aq), Fe^{3+}(aq)||MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)|Pt. (a) Name the oxidizing agent and the reducing agent. (b) Explain why platinum electrodes are used here. (c) Write both half reactions. (d) Write the overall reaction, scaled so the electrons match, and verify that it balances for charge.

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B6. (a) During electrolysis of molten NaCl, state the product at each electrode and write both half reactions and the overall reaction. (b) In copper refining, impure copper is the anode and pure copper the cathode in copper sulfate solution. State what happens at each electrode, state the net effect, and state where the impurities end up. (c) State the electrode signs in the copper refining cell, and justify them from the cell type.

Section C: Exam Style

C1. A student builds the zinc copper galvanic cell and makes five claims. Judge each claim, giving the correct statement where a claim is wrong. (i) The copper electrode is the anode because it is the positive electrode. (ii) Electrons flow through the salt bridge from the anode side to the cathode side. (iii) The zinc electrode gains mass as the cell runs. (iv) Removing the salt bridge increases the cell voltage. (v) The cell potential stays constant until the cell suddenly dies.

C2. A galvanic cell runs for several hours. (a) State how the mass of each electrode changes and how the concentration of each compartment changes. (b) State what happens to the cell potential as the cell runs, and why. (c) State the condition under which the current stops, and what that condition means for ΔG. (d) A second, identical cell is built but left disconnected, with no wire joining its electrodes. State whether its electrodes change mass, with a reason.

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C3. A reaction as written has E°cell = −0.46 V. (a) State whether the reaction is spontaneous as written. (b) State what kind of setup drives it, and state the electrode signs in that setup. (c) State E°cell for the reverse of the reaction as written. (d) In the driven setup, state the direction of electron flow through the external wire.

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Answer Key

A1. (a) Oxidation always occurs at the anode and reduction always at the cathode: An Ox, Red Cat. The rule does not change between galvanic and electrolytic cells. (b) Galvanic: anode negative, cathode positive. Electrolytic: anode positive, cathode negative. (c) Oxidation releases electrons into the anode faster than the wire carries them away, leaving the anode electron rich and negative. (d) The claim is false. The anode is negative only in a galvanic cell; in an electrolytic cell the anode is positive, because the external supply strips electrons from it. What never changes is the role: oxidation happens at the anode in both cell types.

A2. (a) Electrons flow through the external wire from the anode to the cathode. (b) Anions in the salt bridge migrate toward the anode compartment; cations migrate toward the cathode compartment. (c) The current stops. The anode compartment gains positive ions and the cathode compartment loses them, so without the bridge charge builds up and the circuit cannot be completed.

A3. (a) Anode: zinc, on the left of the notation. Cathode: copper, on the right. (b) Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$. Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. (c) Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. (d) Two electrons per formula unit: both half reactions move $2e^-$, so no scaling is needed.

A4. (a) The anode is positive in an electrolytic cell. (b) Reduction happens at the cathode, as in every cell. (c) The claim is false. Electrons flow from the anode to the cathode through the external wire in both cell types; in an electrolytic cell the external supply drives that flow, pushing electrons onto the cathode and pulling them from the anode. Cathode to anode flow through the wire never happens.

A5. (a) The dilute compartment, 0.10 M Cu^{2+}, is the anode. (b) Electrons flow through the wire from the dilute compartment toward the concentrated compartment. (c) The dilute compartment's Cu^{2+} concentration rises, because oxidation produces Cu^{2+} there; the concentrated compartment's concentration falls, because Cu^{2+} is reduced there. (d) The cell stops when the two concentrations become equal: there is then no free energy left to gain from evening them out, so the potential is zero.

B1. (a) Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$. Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$. (b) $E°cell = E°cathode - E°anode = (+0.34) - (-0.76) = +1.10$ V. The subtraction handles the anode's reversal; no sign is flipped by hand. (c) Galvanic. $E°cell$ is positive, so the reaction is spontaneous as written and the cell runs on its own.

B2. (a) Silver has the higher reduction potential, so Ag^+ is reduced at the cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$. (b) Anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$. The silver half reaction must be doubled to match the two electrons: $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$. Overall: $Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$. Charge check: left

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+2, right +2. (c) E°cell = E°cathode − E°anode = (+0.80) − (−2.37) = +3.17 V. Note that doubling the silver half reaction does not change its E°: potentials are intensive.

B3. (a) Six electrons are transferred: each aluminum atom loses 3 electrons and two aluminum atoms react, while each copper ion gains 2 electrons and three copper ions react, so $6e^-$ move in total. (b) $\Delta G° = -nFE° = -(6)(96{,}485)(2.00) = -1{,}157{,}820$ J mol^{-1} = −1158 kJ mol^{-1}, about −1160 kJ mol^{-1}. (c) The negative sign means the reaction is spontaneous as written, consistent with its positive cell potential: the cell is galvanic. (d) The reverse reaction has E°cell = −2.00 V and $\Delta G°$ = +1160 kJ mol^{-1}: reversing a reaction flips the sign of both quantities. The reverse reaction is not spontaneous; it would need an electrolytic setup to be driven.

B4. (a) The error is the cathode label. Lead has the higher reduction potential, −0.13 V against nickel's −0.25 V, so lead is reduced at the cathode and nickel is oxidized at the anode. Nickel is the anode, not the cathode. (b) Anode: Ni(s) → Ni^{2+}(aq) + $2e^-$. Cathode: Pb^{2+}(aq) + $2e^-$ → Pb(s). (c) E°cell = E°cathode − E°anode = (−0.13) − (−0.25) = +0.12 V. (d) The nickel electrode loses mass: nickel metal is oxidized to Ni^{2+} ions that enter solution.

B5. (a) The oxidizing agent is MnO_4^-: it is reduced at the cathode, so it takes electrons from the other reactant. The reducing agent is Fe^{2+}: it is oxidized at the anode, so it gives electrons. (b) Platinum electrodes are used because both redox species in each half cell are in solution: there is no metal electrode to supply or receive electrons, so an inert conductor is needed. The platinum itself is neither oxidized nor reduced. (c) Anode: Fe^{2+}(aq) → Fe^{3+}(aq) + e^-. Cathode: MnO_4^-(aq) + $8H^+$(aq) + $5e^-$ → Mn^{2+}(aq) + $4H_2O$(l). (d) Scale the iron half reaction by 5 to match the five electrons: $5Fe^{2+}$(aq) + MnO_4^-(aq) + $8H^+$(aq) → $5Fe^{3+}$(aq) + Mn^{2+}(aq) + $4H_2O$(l). Charge check: left (5 × +2) + (−1) + (+8) = +17; right (5 × +3) + (+2) = +17. Atoms: Fe 5 = 5, Mn 1 = 1, O 4 = 4, H 8 = 8. Balanced.

B6. (a) Cathode product: liquid sodium metal. Cathode: Na^+(l) + e^- → Na(l). Anode product: chlorine gas. Anode: $2Cl^-$(l) → Cl_2(g) + $2e^-$. Overall, with the sodium half reaction doubled to match the two electrons: 2NaCl(l) → 2Na(l) + Cl_2(g). Reduction gives the metal, oxidation gives the gas. (b) At the anode, impure copper dissolves: Cu(s) → Cu^{2+}(aq) + $2e^-$. At the cathode, copper ions plate out pure: Cu^{2+}(aq) + $2e^-$ → Cu(s). Net effect: copper moves from the impure anode to the pure cathode, so the cathode gains pure copper. Impurities fall away as sludge beneath the anode or stay dissolved in solution; they do not plate out with the copper. (c) Copper refining is an electrolytic process, driven by an external supply, so the anode is positive and the cathode negative. Oxidation still happens at the anode and reduction at the cathode: the cell type sets the signs, never the roles.

C1. (i) Wrong. Copper is the positive electrode, but it is the cathode, not the anode: reduction happens at the cathode, and Cu^{2+} is reduced to Cu. The anode is zinc, which is negative in a galvanic cell. The claim confuses sign with role. (ii) Wrong. Electrons never travel through the salt bridge; they travel through the external wire from anode to cathode. Ions travel through the bridge. (iii) Wrong. The zinc electrode loses mass: zinc metal is oxidized to Zn^{2+} ions that leave the electrode and enter solution. It is the copper cathode that gains mass. (iv) Wrong. Removing the

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salt bridge stops the current: charge builds up in the compartments and the circuit cannot be completed. The bridge supplies no voltage at all, so removing it cannot raise the voltage. (v) Wrong. The cell potential falls gradually as the cell runs, because the anode compartment concentrates and the cathode compartment dilutes, moving the reaction toward equilibrium. It reaches zero only when equilibrium is reached; there is no sudden death at full voltage.

C2. (a) The anode loses mass as its metal is oxidized to ions; the cathode gains mass as metal ions plate out. The anode compartment grows more concentrated in metal cations; the cathode compartment grows less concentrated as its cations are consumed. (b) The cell potential falls. The reaction is moving toward equilibrium, so the free energy driving the current shrinks as the concentrations move toward their equilibrium values. (c) The current stops when the reaction reaches equilibrium: at that point $E = 0$ and $\Delta G = 0$, so there is no drive left in either direction and the cell is dead. (d) No. With no wire joining the electrodes, electrons have no path from anode to cathode, so neither half reaction can proceed and the electrodes keep their mass. A spontaneous reaction still needs a completed circuit to deliver current.

C3. (a) Not spontaneous as written. A negative $E°_{cell}$ means a positive $\Delta G°$, so the reaction as written does not run on its own. (b) An electrolytic setup drives it: an external power supply forces the reaction. In that setup the anode is positive and the cathode negative, while oxidation still happens at the anode and reduction at the cathode. (c) The reverse reaction has $E°_{cell} = +0.46$ V: reversing a reaction flips the sign of its cell potential. (d) Electrons flow through the external wire from the anode to the cathode, driven by the supply, exactly as in a galvanic cell; only the signs of the electrodes and the spontaneity of the reaction differ.

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Topic 9.8 Revision Notes

Topic 9.8 Quiz: Galvanic (Voltaic) and Electrolytic Cells

Previous Worksheet: Topic 9.7 Coupled Reactions

Next Worksheet: Topic 9.9 Cell Potential and Free Energy

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