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Topic 9.10: Cell Potential Under Nonstandard Conditions

Worksheet · AP Chemistry

UNIT 9 · THERMODYNAMICS AND ELECTROCHEMISTRY

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How to Use This Worksheet

Work the questions in order, and do not look at the answer key until you have attempted every question. Section A checks the equation, the sign rules, and the concentration cell picture that the whole topic rests on. Section B practices the calculations: E from Q, concentration cell potentials, the E = 0 threshold, and a negative E. Section C combines them the way exam questions do, with concentration changes, a concentration cell, and a measured potential worked back to Q and compared with K.

Reference facts. R = 8.314 J mol^{-1} K^{-1}; F = 96,485 C mol^{-1}; at 25 °C, RT/F = 0.0257 V and the log form factor is 0.0592 V. For the zinc copper cell, E°cell = 1.10 V with n = 2, so one decade of Q shifts E by 0.0296 V.

Use the same working order every time. First, write the balanced overall cell reaction and read n, the moles of electrons transferred. Second, build Q: products over reactants for the reaction as written, each raised to its stoichiometric coefficient, solids and pure liquids omitted, aqueous ions as molarities, gases as partial pressures in atm. Third, pick the form: the log form below at 25 °C, the ln form below it anywhere else.

$$E = E^\circ - (0.0592/n) \log Q$$

$$E = E^\circ - (RT/nF) \ln Q$$

Fourth, compute log Q or ln Q and keep its sign visible; the sign decides whether E lands above or below E°. Fifth, check the answer: Q > 1 must give E below E°, Q < 1 must give E

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above E°, and a concentration cell must give a positive E with the cathode on the concentrated side. If any check fails, the error is usually a flipped Q, a missing n, or a dropped minus sign.

Two slip points deserve a deliberate pause. Q is built for the reaction exactly as written: if you reverse the reaction, Q inverts and E changes sign, so a reversed cell is not a different answer to the same question, it is a different cell. And n comes from the balanced overall equation, not from one half reaction alone: in the zinc copper cell, zinc loses 2 electrons and copper gains 2, so n = 2. Doubling a half reaction to balance electrons never changes its potential, because potentials are intensive, but it does change the electron count you carry into the equation, so balance first and read n last.

Section A: Recall and Concepts

A1. State the Nernst equation in both its ln form and its log base 10 form. Define every symbol in the equation, and state the value of RT/F at 25 °C and what the 0.0592 V factor is.

A2. A cell has E° = 1.10 V. State whether the measured E is above, below, or equal to E° in each case, and explain each answer with the sign of log Q: (a) Q = 10, (b) Q = 0.010, (c) Q = 1.

A3. Write the expression for Q for each reaction, and state why any solid species do not appear: (a) $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$; (b) $2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$, with P_H_2 = 2.0 atm and $[H^{+}]$ = 1.0 M. Evaluate Q for part (b).

A4. Explain, in terms of Q and K, what happens to the cell potential E as a galvanic cell operates, and state what E is at equilibrium. Does E° change as the cell runs? Explain.

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A5. A concentration cell is built as Cu(s)|Cu^{2+}(0.0010 M)||Cu^{2+}(1.0 M)|Cu(s). Which compartment is the cathode, and why? What is E° for this cell, and what happens to E as the cell runs?

Section B: Core Practice

B1. A cell has E° = 1.10 V and n = 2. At 25 °C with Q = 10, calculate Ecell. Show the log form working, and confirm it with the ln form.

B2. A cell has E° = 0.76 V, n = 2, and Q = 0.010 at 25 °C. Calculate Ecell, showing the intermediate step where the sign of log Q matters.

B3. For the concentration cell Cu(s)|Cu^{2+}(0.0010 M)||Cu^{2+}(1.0 M)|Cu(s) at 25 °C, calculate Ecell. State Q, n, and E° as part of your working.

B4. For the concentration cell Ag(s)|Ag^{+}(0.10 M)||Ag^{+}(1.0 M)|Ag(s) at 25 °C, calculate Ecell. Explain why the answer is positive even though E° = 0.

B5. A cell has E° = 0.20 V and n = 1 at 25 °C. (a) Find the value of Q at which Ecell = 0. (b) For Q = 1.0×10^{2} and Q = 1.0×10^{4}, calculate Ecell in each case and state which value makes Ecell negative.

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B6. A cell has E° = 0.34 V, n = 1, and Q = 1.0×10^{6} at 25 °C. Calculate Ecell, and interpret the sign of your answer: what does it mean for the direction of the reaction under these conditions?

Section C: Exam Style

C1. For the cell Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s) with E°cell = 1.10 V at 25 °C: (a) With [Zn^{2+}] = 0.010 M and [Cu^{2+}] = 0.10 M, calculate Q and Ecell. (b) The Zn^{2+} solution is then diluted to 0.0010 M while Cu^{2+} stays at 0.10 M. Calculate the new Q and Ecell, and explain in one sentence why E moved in that direction.

C2. A concentration cell is built with [Ag^{+}] = 1.0 M in one half cell and [Ag^{+}] = 1.0×10^{-5} M in the other at 25 °C. (a) Calculate Ecell. (b) Identify the anode and the cathode, with a reason. (c) Describe what happens to the two concentrations and to Ecell as the cell runs, and state the value of Ecell once the concentrations have equalized.

C3. A galvanic cell with E° = 1.10 V and n = 2 shows a measured Ecell of 0.95 V at 25 °C. (a) Calculate the reaction quotient Q. (b) Calculate the equilibrium constant K for the cell reaction from E°. (c) Compare Q with K and state, with a reason, whether the cell is close to equilibrium and which way the reaction is still running.

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Answer Key

A1. The ln form is $E = E° - (RT/nF) \ln Q$. The log form is $E = E° - (0.0592/n) \log Q$. E is the cell potential under the actual conditions; E° is the standard cell potential; R = 8.314 J mol^{-1} K^{-1} is the gas constant; T is the temperature in kelvin; n is the moles of electrons transferred in the balanced cell reaction; F = 96,485 C mol^{-1} is Faraday's constant; Q is the reaction quotient under the actual conditions. At 25 °C (298 K), RT/F = (8.314)(298)/96,485 = 0.0257 V. The 0.0592 V factor is (RT/F) × ln(10) = 0.0257 × 2.303 at 25 °C, and it converts the natural log form into the log base 10 form. The two forms are the same equation, not two different rules: ln Q = 2.303 × log Q, so (RT/nF) ln Q and (0.0592/n) log Q are the same correction written two ways. The 0.0592 V factor is specific to 25 °C: at any other temperature, use the ln form with the given T.

A2. (a) Q = 10 gives log Q = +1, so the correction term (0.0592/n) log Q is positive and subtracted, so E is below E°. (b) Q = 0.010 gives log Q = −2, so the correction term is negative and subtracting it adds to E°, so E is above E°. (c) Q = 1 gives log Q = 0, so the correction term vanishes and E = E°. The rule in one line: Q > 1 lowers E, Q < 1 raises E, Q = 1 leaves E unchanged.

A3. (a) For $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, $Q = [Zn^{2+}]/[Cu^{2+}]$. The product ion is on top, the reactant ion below, each to the power 1. (b) For $2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$, $Q = P_H_2/[H^{+}]^2$. The gas product enters as its partial pressure, and the hydrogen ion concentration is squared because its coefficient is 2. With P_H_2 = 2.0 atm and $[H^{+}]$ = 1.0 M, $Q = 2.0/(1.0)^2 = 2.0$. Solids do not appear in Q because a pure solid has a fixed activity of 1 under standard conditions; changing how much solid is present does not change its concentration in any meaningful sense, so it drops out of the quotient. The same applies to pure liquids.

A4. As the cell operates, reactants are consumed and products accumulate, so Q grows toward K. The Nernst correction term (0.0592/n) log Q grows with Q, so E falls steadily. At equilibrium, Q = K and E = 0: there is no net driving force left. E° does not change as the cell runs. E° is the potential under the fixed standard conditions, 1 M, 1 atm, 25 °C, and it is a property of the reaction, not of the cell's current state. Only the actual potential E changes, falling to zero when the cell dies.

A5. The right hand compartment, with $[Cu^{2+}]$ = 1.0 M, is the cathode. The spontaneous change in a concentration cell is dilution: the concentrated ion is reduced, plating out as metal, while the metal is oxidized in the dilute compartment. The cathode therefore gains mass as copper plates out, and the anode loses mass as copper dissolves. E° = 0 for this cell, because both half reactions are the same reaction and their potentials cancel exactly. As the cell runs, Cu^{2+} is consumed on the concentrated side and produced on the dilute side, so the two concentrations move toward each other and E falls. When they equalize, Q = 1 and E = 0.

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B1. Log form: E = 1.10 − (0.0592/2) log 10 = 1.10 − 0.0296 × 1 = 1.0704 V, about 1.07 V. Ln form check: E = 1.10 − (0.0257/2) ln 10 = 1.10 − 0.0129 × 2.303 = 1.10 − 0.0296 = 1.0704 V. The two forms agree. Q > 1, so E below E°, as expected.

B2. log Q = log(0.010) = −2. E = 0.76 − (0.0592/2) × (−2) = 0.76 − (0.0296)(−2) = 0.76 + 0.0592 = 0.8192 V, about 0.82 V. The intermediate step is the point: subtracting a negative number adds, so a Q below 1 lifts E above E°. The ln form confirms: E = 0.76 − (0.0257/2) ln(0.010) = 0.76 − 0.0129 × (−4.605) = 0.76 + 0.0592 = 0.8192 V.

B3. E° = 0 for a concentration cell, because both half reactions are identical. The overall change is Cu^{2+}(1.0 M) → Cu^{2+}(0.0010 M), so Q = 0.0010/1.0 = 0.0010 and n = 2. E = 0 − (0.0592/2) log(0.0010) = −0.0296 × (−3) = +0.0888 V, about +0.089 V. The ln form confirms: E = −(0.0257/2) ln(0.0010) = −0.0129 × (−6.908) = +0.0887 V, which rounds to the same +0.089 V.

B4. E° = 0, Q = 0.10/1.0 = 0.10, n = 1. E = 0 − 0.0592 × log(0.10) = −0.0592 × (−1) = +0.0592 V, about +0.059 V. The ln form confirms: E = −0.0257 × ln(0.10) = −0.0257 × (−2.303) = +0.0592 V. The answer is positive even though E° = 0 because Q is below 1: the correction term is negative, and subtracting it gives a positive potential. The driving force is purely the concentration difference, with the system running toward equal concentrations.

B5. (a) Set E = 0: 0 = 0.20 − 0.0592 log Q, so log Q = 0.20/0.0592 = 3.38, and Q = $10^{3.38}$ = 2.4 × 10^3. At this Q the cell is at equilibrium. (b) For Q = 1.0 × 10^2: E = 0.20 − 0.0592 × 2 = 0.20 − 0.1184 = +0.082 V, still positive. For Q = 1.0 × 10^4: E = 0.20 − 0.0592 × 4 = 0.20 − 0.2368 = −0.037 V, negative. Only Q = 1.0 × 10^4 makes E negative, because only it exceeds the equilibrium value of about 2.4 × 10^3.

B6. E = 0.34 − 0.0592 × log(1.0 × 10^6) = 0.34 − 0.0592 × 6 = 0.34 − 0.3552 = −0.0152 V, about −0.015 V. The ln form confirms: E = 0.34 − 0.0257 × ln(1.0 × 10^6) = 0.34 − 0.0257 × 13.816 = 0.34 − 0.3551 = −0.0149 V, which rounds to the same −0.015 V. A negative E means the forward reaction is no longer spontaneous under these conditions: the product buildup is so extreme that the reaction would run backward if it ran at all. In Q and K language, a negative E means Q has passed K, so the reverse direction is now the favored one. E crosses zero exactly when Q reaches K.

C1. (a) The overall reaction is Zn(s) + Cu^{2+}(aq) → Zn^{2+}(aq) + Cu(s), so Q = [Zn^{2+}]/[Cu^{2+}] = 0.010/0.10 = 0.10, and n = 2. E = 1.10 − (0.0592/2) log 0.10 = 1.10 − 0.0296 × (−1) = 1.10 + 0.0296 = 1.1296 V, about 1.13 V. (b) After dilution, Q = 0.0010/0.10 = 0.010, so log Q = −2 and E = 1.10 − 0.0296 × (−2) = 1.10 + 0.0592 = 1.1592 V, about 1.16 V. E rose because diluting the product ion lowered Q further below 1, turning the correction term into a larger bonus instead of a penalty.

C2. (a) E° = 0 for a concentration cell. The overall change is Ag^+(1.0 M) → Ag^+(1.0 × 10^{-5} M), so Q = 1.0 × 10^{-5}/1.0 = 1.0 × 10^{-5} and n = 1. E = 0 − 0.0592 × log(1.0 × 10^{-5}) = −0.0592 × (−5) = +0.2960 V, about +0.30 V. The ln form confirms: E = −0.0257 × ln(1.0 × 10^{-5}) = −0.0257 × (−11.513) = +0.2958 V, the same +0.30 V. (b) The 1.0 M compartment is the cathode, because the concentrated ion is reduced there; the 1.0 × 10^{-5} M compartment is the anode, where silver metal is oxidized. The system dilutes the concentrated side and concentrates the dilute side. (c) As the cell runs, [Ag^+]

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falls on the concentrated side and rises on the dilute side, so Q rises toward 1 and E falls. Once the concentrations equalize, Q = 1 and Ecell = 0: the cell is dead.

C3. (a) Rearranging the Nernst equation: log Q = (E° − E)/(0.0592/n) = (1.10 − 0.95)/0.0296 = 0.15/0.0296 = 5.07, so $Q = 10^{5.07} = 1.2 \times 10^{5}$. (b) At equilibrium E = 0, so log K = nE°/0.0592 = (2)(1.10)/0.0592 = 37.16, and $K = 10^{37.16} = 1.5 \times 10^{37}$. (c) $Q = 1.2 \times 10^{5}$ is enormously smaller than $K = 1.5 \times 10^{37}$, so the cell is nowhere near equilibrium. The reaction is still running forward, because Q < K means the forward direction is still favored, and E will keep falling from 0.95 V toward zero as Q climbs the long way toward K. Put the two logarithms side by side to see how far there is to go: log Q = 5.07 against log K = 37.16, so the cell has covered only a small part of the logarithmic distance to equilibrium, even though its voltage has already dropped 0.15 V from standard.

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