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Topic 9.9: Cell Potential and Free Energy

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 definitions and the sign rules that the whole topic rests on. Section B practices the three calculations of the topic: cell potential from a table, free energy from a potential, and ranking agents from a table. Section C combines them the way exam questions do, with multi-step chains where one answer feeds the next.

Reference facts. F = 96,485 C mol^{-1}; R = 8.314 J mol^{-1} K^{-1}; at 298 K, RT ln 10 = 5.70 kJ mol^{-1}, so every 5.7 kJ mol^{-1} of ΔG° is one factor of 10 in K. Standard conditions are 1 M, 1 atm, 25 °C. E°(Zn^{2+}/Zn) = −0.76 V, E°(Cu^{2+}/Cu) = +0.34 V, E°(Ag^{+}/Ag) = +0.80 V, E°(Fe^{2+}/Fe) = −0.44 V.

Use the same working order every time. First, compare the two reduction potentials and pick the cathode: the more positive value is reduced. Second, subtract using the equation below, with the potentials exactly as tabulated.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

Third, balance the overall reaction and read n, the moles of electrons transferred, from the balanced half reactions. Fourth, apply the equation below with F = 96,485 C mol^{-1}, and convert joules to kilojoules at the end.

$$\Delta G° = -nFE°$$

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Fifth, check the sign chain: a positive E° must go with a negative ΔG° and K greater than 1. If any link in the chain disagrees with the others, something in the working is wrong, and the error is usually a flipped sign or a scaled potential.

Section A: Recall and Concepts

A1. State what is meant by the standard hydrogen electrode, and give the standard conditions that every tabulated reduction potential assumes. Explain briefly why a reference electrode is needed at all: why can a single half reaction's potential never be measured on its own?

A2. A cell is built from two half reactions: $Mn^{2+} + 2e^- \rightarrow Mn$ with $E° = -1.18$ V, and $Sn^{2+} + 2e^- \rightarrow Sn$ with $E° = -0.14$ V. Which electrode is the cathode, and which species is oxidized at the anode? Give a reason based on the potentials, and write the two half reactions as they actually run in the cell.

A3. A student doubles the half reaction $Cu^{2+} + 2e^- \rightarrow Cu$ and claims its E° doubles to +0.68 V. Is the student right? Explain, and state what does double when the half reaction is doubled. Give the doubled reaction's ΔG° in terms of the undoubled reaction's ΔG°.

A4. A reaction under standard conditions has $E°_{cell} < 0$. State the signs of ΔG° and the size of K relative to 1, and state whether the reaction is spontaneous as written. What kind of setup would be needed to make this reaction run?

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A5. A galvanic cell has been running for a long time and has reached equilibrium. State the values of Ecell and ΔG at that point, and explain why E°cell and ΔG° are not zero at the same time. A student argues that a dead cell must have E°cell = 0: explain the student's error.

Section B: Core Practice

B1. For the cell $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$, $E°(Zn^{2+}/Zn) = -0.76$ V and $E°(Cu^{2+}/Cu) = +0.34$ V. Write both half reactions as they run in the cell, calculate E°cell, and state whether the cell is galvanic.

B2. For the zinc copper cell in B1, n = 2. Calculate ΔG° in kJ mol^{-1}, showing the joule-to-kilojoule conversion. State what the sign of your answer means for the spontaneity of the reaction.

B3. $E°(Ag^{+}/Ag) = +0.80$ V and $E°(Fe^{2+}/Fe) = -0.44$ V. For the galvanic cell built from these half cells: (a) identify the cathode and the anode, (b) calculate E°cell, (c) write the balanced overall reaction and state n, and (d) calculate ΔG° in kJ mol^{-1}.

B4. A reaction run forward has E°cell = +0.55 V and ΔG° = −106 kJ mol^{-1}. State E°cell and ΔG° for the reverse reaction, and explain why the magnitudes are unchanged. State whether K for the reverse reaction is greater than or less than 1, with a reason.

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B5. A reaction has $\Delta G^\circ = -237$ kJ mol^{-1} and transfers n = 2 mol of electrons. Calculate E°_{cell}, showing the joule conversion explicitly. Then check your answer against the sign chain: does a negative ΔG° go with the sign of E° you found?

B6. A table gives $E^\circ(Mg^{2+}/Mg) = -2.37$ V, $E^\circ(Zn^{2+}/Zn) = -0.76$ V, $E^\circ(Cu^{2+}/Cu) = +0.34$ V, and $E^\circ(Ag^{+}/Ag) = +0.80$ V. (a) Identify the strongest oxidizing agent and the strongest reducing agent in the table, with reasons. (b) Calculate E°_{cell} for a galvanic cell built from magnesium and silver half cells. (c) Write the balanced overall reaction, state n, and calculate ΔG° in kJ mol^{-1}. (d) State whether K for this cell is greater than or less than 1.

Section C: Exam Style

C1. Cell X has $E^\circ_{cell} = 0.80$ V with n = 2. Cell Y has $E^\circ_{cell} = 0.45$ V with n = 6. (a) Calculate ΔG° for each cell in kJ mol^{-1}. (b) State which cell is more spontaneous under standard conditions. (c) Explain why the answer is not simply the cell with the larger voltage, and state the general rule for comparing spontaneity between cells.

C2. A reaction at 298 K has an equilibrium constant $K = 1.0 \times 10^{20}$. (a) Calculate ΔG° in kJ mol^{-1} from $\Delta G^\circ = -RT \ln K$, showing the value of ln K. (b) State whether E°_{cell} for this reaction is positive or negative, with a reason based on the sign chain. (c) If the reaction transfers n = 2 mol of electrons, calculate E°_{cell}. (d) Explain in words why an equilibrium constant of 10^{20} goes with a voltage of the size you found, using the 5.70 kJ mol^{-1} per factor of 10 rule at 298 K.

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C3. For the cell Pb(s)|Pb^{2+}(aq)||Cu^{2+}(aq)|Cu(s), $E°(Pb^{2+}/Pb) = -0.13$ V and $E°(Cu^{2+}/Cu) = +0.34$ V. (a) Calculate E°cell, identifying the cathode first. (b) With n = 2, calculate ΔG° in kJ mol^{-1}. (c) Use $\Delta G° = -RT \ln K$ at 298 K to find ln K and hence K, and comment on what the size of K means for how far the reaction goes. (d) State what happens to E°cell, ΔG°, and K if the balanced equation is doubled, with a reason for each.

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Answer Key

A1. The standard hydrogen electrode is the reference half cell, $2H^+(aq) + 2e^- \rightarrow H_2(g)$, assigned E° = 0.00 V by definition. Standard conditions are 1 M concentrations for aqueous species, 1 atm pressure for gases, pure solids and liquids, and 25 °C. A reference is needed because a voltmeter measures a potential difference between two electrodes, never the absolute potential of one half reaction alone: every tabulated value is really the voltage of that half cell against the hydrogen half cell. Setting hydrogen to zero gives every other half reaction a number on a single comparable scale.

A2. Tin is the cathode. Sn^{2+} has the more positive reduction potential, −0.14 V against −1.18 V for Mn^{2+}, so Sn^{2+} is reduced and manganese metal is oxidized. As run in the cell, the half reactions are: anode, $Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$; cathode, $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$. The rule is always the same: the species with the larger reduction potential is reduced, and the other half reaction is forced to run backwards as oxidation. Note that both potentials are negative, which does not matter: only the comparison between them decides the roles.

A3. No, the student is wrong. Standard reduction potentials are intensive properties, so doubling $Cu^{2+} + 2e^- \rightarrow Cu$ leaves E° at +0.34 V. Voltage behaves like temperature here, not like heat: doubling the system does not double the voltage. What does double is the extensive quantity, the free energy change: the doubled reaction has ΔG° exactly twice the undoubled reaction's ΔG°, because twice as many moles of electrons move at the same potential. This distinction is the point of the question, and it is tested again in C3 part (d).

A4. ΔG° is positive, because $\Delta G^\circ = -nFE^\circ$ flips the sign of E°: a negative cell potential always gives a positive free energy change. K is less than 1, because $\Delta G^\circ = -RT \ln K$ gives a negative ln K for a positive ΔG°, and a negative logarithm means a constant below 1. The reaction is nonspontaneous as written under standard conditions. To make it run, an external power supply is needed: the setup is electrolytic, driving the reaction in the direction the chemistry resists.

A5. At equilibrium, Ecell = 0 and ΔG = 0: there is no driving force left, no net electron flow, and the forward and reverse rates are equal. E°cell and ΔG° are not zero at the same time because they are standard values, fixed by the reaction and the table, and they do not change as the cell runs. Only the actual, nonstandard quantities fall as the concentrations move toward their equilibrium values. The student's error is confusing the two sets of quantities: E°cell describes the cell under standard conditions, which is a fixed reference state, while Ecell describes the cell as it actually is, and it is Ecell that reaches zero when the cell dies.

B1. Copper has the more positive reduction potential, so it is the cathode and zinc is the anode. As run in the cell: anode, $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; cathode, $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$. Cell potential: $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = (+0.34) - (-0.76) = +1.10$ V. The subtraction of a negative number adds its

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magnitude, which is why the cell voltage exceeds either half reaction's potential. The potential is positive, so the cell is galvanic and runs on its own, with electrons flowing through the wire from the zinc anode to the copper cathode.

B2. $\Delta G° = -nFE° = -(2)(96{,}485)(1.10) = -212{,}267$ J mol^{-1}. Dividing by 1000 gives about −212 kJ mol^{-1}. The negative sign means the reaction is spontaneous under standard conditions, which agrees with the positive cell potential from B1: the sign chain holds, $E° > 0$ with $\Delta G° < 0$. If the two signs had disagreed, that would have been the signal of an arithmetic error, most likely a flipped sign in the subtraction.

B3. (a) Silver has the more positive reduction potential, +0.80 V against −0.44 V for iron, so silver is the cathode and iron is the anode. (b) $E°_{cell} = (+0.80) - (-0.44) = +1.24$ V. (c) Half reactions: anode $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$; cathode $2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$. The silver half reaction is doubled so the electrons match, but its potential stays +0.80 V: potentials are never scaled. Overall: $Fe(s) + 2Ag^+(aq) \rightarrow Fe^{2+}(aq) + 2Ag(s)$, so n = 2. (d) $\Delta G° = -(2)(96{,}485)(1.24) = -239{,}283$ J mol^{-1}, about −239 kJ mol^{-1}. Check: positive E° with negative ΔG° fits the sign chain, and K is far above 1.

B4. Reverse reaction: $E°_{cell} = -0.55$ V and $\Delta G° = +106$ kJ mol^{-1}. Reversing swaps the cathode and anode, so the sign of the cell potential flips, and ΔG° flips with it because $\Delta G° = -nFE°$. Magnitudes are unchanged because the same electron transfer and the same potential difference are involved, only in the opposite direction: the reverse reaction is the same hill climbed backwards. K for the reverse reaction is less than 1, because its ΔG° is positive, and a positive ΔG° gives ln K negative through $\Delta G° = -RT \ln K$. The forward reaction's K is above 1 by exactly the reciprocal factor.

B5. $E° = -\Delta G°/(nF)$. First convert to joules: $\Delta G° = -237$ kJ mol^{-1} = −237,000 J mol^{-1}. Then $E° = -(-237{,}000)/((2)(96{,}485)) = 237{,}000/192{,}970 = +1.23$ V. Check against the sign chain: a negative ΔG° must go with a positive E°, and +1.23 V is positive, so the answer is consistent. The common error here is forgetting the joule conversion, which would give an answer 1000 times too small, or dropping the negative sign in the rearrangement, which would give −1.23 V and contradict the sign chain.

B6. (a) The strongest oxidizing agent is Ag^+, with the most positive reduction potential, +0.80 V: it is the species most readily reduced, so it oxidizes other species most strongly. The strongest reducing agent is Mg metal, whose half reaction has the most negative reduction potential, −2.37 V: it is the species most readily oxidized, so it reduces other species most strongly. (b) Silver is the cathode: $E°_{cell} = (+0.80) - (-2.37) = +3.17$ V, a large voltage because the two potentials sit at opposite ends of the table. (c) Overall: $Mg(s) + 2Ag^+(aq) \rightarrow Mg^{2+}(aq) + 2Ag(s)$, so n = 2. $\Delta G° = -(2)(96{,}485)(3.17) = -611{,}715$ J mol^{-1}, about −612 kJ mol^{-1}. (d) K is greater than 1, because ΔG° is negative, and a negative ΔG° gives a positive ln K. With ΔG° near −612 kJ mol^{-1}, K is astronomically large, and the reaction goes essentially to completion.

C1. (a) Cell X: $\Delta G° = -(2)(96{,}485)(0.80) = -154{,}376$ J mol^{-1}, about −154 kJ mol^{-1}. Cell Y: $\Delta G° = -(6)(96{,}485)(0.45) = -260{,}510$ J mol^{-1}, about −261 kJ mol^{-1}. (b) Cell Y is more spontaneous under

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standard conditions, because its ΔG° is more negative. (c) The answer is not the cell with the larger voltage because spontaneity is measured by ΔG°, and ΔG° = −nFE° depends on n as well as E°. Cell Y's smaller voltage is outweighed by its six transferred electrons against cell X's two. The general rule: compare ΔG° values when n differs, and compare voltages directly only when n is the same.

C2. (a) $\ln(1.0 \times 10^{20}) = 20 \times \ln 10 = 20 \times 2.303 = 46.05$. $\Delta G° = -RT \ln K = -(8.314)(298)(46.05) = -114{,}096$ J mol^{-1}, about −114 kJ mol^{-1}. (b) E°cell is positive, because the sign chain ties a negative ΔG° to a positive E° through ΔG° = −nFE°: the negative sign in that equation flips the free energy's sign into the potential's. (c) $E° = -\Delta G°/(nF) = 114{,}096/((2)(96{,}485)) = 114{,}096/192{,}970 = +0.59$ V. (d) The size makes sense through the 5.70 kJ mol^{-1} rule: at 298 K, every 5.70 kJ mol^{-1} of free energy is one factor of 10 in K, and 114 kJ mol^{-1} divided by 5.70 gives 20 factors of 10, exactly $K = 10^{20}$. A voltage near 0.6 V with n = 2 carries about 114 kJ mol^{-1}, so a constant of 10^{20} is what the arithmetic demands, not a surprise.

C3. (a) Copper has the more positive reduction potential, +0.34 V against −0.13 V for lead, so copper is the cathode and lead is the anode. E°cell = (+0.34) − (−0.13) = +0.47 V. (b) With n = 2, $\Delta G° = -(2)(96{,}485)(0.47) = -90{,}696$ J mol^{-1}, about −90.7 kJ mol^{-1}. (c) $\ln K = -\Delta G°/(RT) = 90{,}696/((8.314)(298)) = 90{,}696/2{,}477.6 = 36.6$, so $K = e^{36.6} = 7.9 \times 10^{15}$. A constant this large means the reaction goes essentially to completion: at equilibrium, products dominate reactants by fifteen orders of magnitude, and for practical purposes the lead is consumed. (d) Doubling the balanced equation leaves E°cell unchanged at +0.47 V, because potentials are intensive. ΔG° doubles to about −181 kJ mol^{-1}, because twice as many moles of electrons move at the same potential. K is squared, to about 6.2×10^{31}, because ln K doubles when ΔG° doubles, and doubling a logarithm squares its argument. All three answers follow from the same rule: voltage intensive, energy and log K extensive.

Continue Revising

Topic 9.9 Revision Notes

Topic 9.9 Quiz: Cell Potential and Free Energy

Previous Worksheet: Topic 9.8 Galvanic (Voltaic) and Electrolytic Cells

Next Worksheet: Topic 9.10 Cell Potential Under Nonstandard Conditions

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