

Unit 9: Applications of Thermodynamics

Unit 9 answers the question every chemistry student eventually asks: will this reaction actually happen? It covers entropy, Gibbs free energy, the link between free energy and the equilibrium constant, coupled reactions, and electrochemical cells, including galvanic cells, electrolytic cells, cell potentials, and Faraday's laws.

AP Chemistry

Applications of Thermodynamics

About 13 minutes to read

How to use this guide

Read it in order the first time because the ideas stack. Entropy and enthalpy feed into Gibbs free energy, free energy tells you whether a reaction is favored and how far it goes, and then the second half of the unit applies all of that to electrochemical cells. The worked examples are the core of this unit, so work each calculation yourself before reading the result.

After the first read, use the trap boxes and the comparison tables to review the distinctions exam questions test most often. Finish with the practice questions, then complete the recall check on the last page out loud and note any items you cannot explain yet.

What this unit is worth. Applications of Thermodynamics is about 7 to 9 percent of the AP Chemistry exam. It also rewards you for earlier units, because the equilibrium constant from Unit 7 and redox from Unit 4 both return here in new form. If K and oxidation numbers feel solid, this unit is mostly new vocabulary on top of ideas you already own.

9.1 Entropy (S)

Entropy is a measure of the dispersal of matter and energy. Matter disperses when a solid becomes a liquid or a liquid becomes a gas, when a gas expands into a larger volume, and when a reaction produces more moles of gas than it consumes. Energy disperses as temperature rises, because the same thermal energy spreads across more available microstates.

The fastest way to predict the sign of an entropy change is to count moles of gas. For $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$, three moles of gas become a liquid, so matter is far less dispersed and ΔS is negative. For $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, a gas appears where there was none, so ΔS is positive. When the moles of gas do not change, the sign is harder to call and you need actual data.

Trap. Entropy is not disorder in the messy-room sense. Ice melting into water increases entropy because the molecules can occupy more positions and the energy spreads out, not because anything looks messier. On the exam, justify entropy claims with particle dispersal or moles of gas, not with how orderly something appears.

9.2 Standard Entropy

The **standard molar entropy (S°)** of a substance is the absolute entropy of one mole of it in its **standard state**: pure substances, solutions at 1.0 M, and gases at 1.0 atm. Unlike enthalpy, absolute entropies exist because entropy has a true zero at 0 K, where a perfect crystal has exactly one microstate.

The **standard entropy change** of a reaction comes from the same products-minus-reactants pattern you know from enthalpy: $\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants})$, using the absolute entropies from a table and multiplying by the stoichiometric coefficients. Watch the units. Tables list S° in J/mol·K while ΔH° is usually in kJ/mol, so convert one of them before combining them in the Gibbs equation.

Trap. The most common arithmetic error in this unit is mixing J and kJ in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. If ΔS° is $-198.7\text{ J/mol}\cdot\text{K}$, convert it to $-0.1987\text{ kJ/mol}\cdot\text{K}$ before multiplying by T in kelvin. A factor-of-1000 slip here ruins an otherwise perfect setup.

9.3 Gibbs Free Energy and Thermodynamic Favorability

Gibbs free energy is the quantity that determines whether a process is favored at constant temperature and pressure: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, with T in kelvin. A process with $\Delta G^\circ < 0$ is **thermodynamically favored**. The CED prefers that phrase over "spontaneous," because a favored process can still be extremely slow. Diamond converting to graphite is favored at room temperature, and you will wait longer than the age of the universe to watch it happen.

You can also get ΔG° from tables of **standard Gibbs free energies of formation (ΔG_f°)**, the free energy change when one mole of a compound forms from its elements in their standard states: $\Delta G^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants})$. Elements in their standard states have $\Delta G_f^\circ = 0$, exactly as with enthalpy of formation.

The signs of ΔH° and ΔS° tell you how temperature affects favorability, because the $-T\Delta S^\circ$ term grows with T:

SIGNS	RESULT
$\Delta H^\circ < 0, \Delta S^\circ > 0$	Favored at all temperatures. Both terms push the same way.
$\Delta H^\circ > 0, \Delta S^\circ < 0$	Favored at no temperature. Both terms push against it.
$\Delta H^\circ > 0, \Delta S^\circ > 0$	Favored at high temperature, where $-T\Delta S^\circ$ wins.
$\Delta H^\circ < 0, \Delta S^\circ < 0$	Favored at low temperature, where ΔH° wins.

Worked example. For $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$, $\Delta H^\circ = -92.2 \text{ kJ}$ and $\Delta S^\circ = -198.7 \text{ J/K} = -0.1987 \text{ kJ/K}$. At 298 K: $\Delta G^\circ = -92.2 - (298)(-0.1987) = -92.2 + 59.2 = -33.0 \text{ kJ}$. Negative, so the reaction is favored at room temperature. But $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$ means it is favored only at low temperature, which is why the Haber process runs hot for speed yet needs high pressure to push the equilibrium toward ammonia anyway.

Trap. Thermodynamically favored does not mean fast, and it does not mean the reaction goes to completion. Favorability is about ΔG° and the equilibrium position. Speed is about activation energy. Those are separate questions, and the exam loves asking them in the same problem.

9.4 Kinetic Control

A reaction can be thermodynamically favored and still not happen on any timescale you care about. A mixture of hydrogen and oxygen at room temperature has a very negative ΔG° for forming water, but nothing happens until a spark supplies the activation energy. When a favored process is held back by a high activation energy, it is under **kinetic control**. It is not at equilibrium. It is stuck waiting.

This is the idea behind catalysts in Unit 5 returning here. A catalyst cannot change ΔG° or K , but it can move a reaction from kinetic control into something that actually proceeds by lowering the activation energy barrier.

9.5 Free Energy and the Equilibrium Constant

Free energy and equilibrium are two views of the same thing: $\Delta G^\circ = -RT \ln K$, or equivalently $K = e^{-\Delta G^\circ/RT}$. A negative ΔG° means products are favored at equilibrium ($K > 1$). A positive ΔG° means reactants are favored ($K < 1$). When ΔG° is near zero, K sits near 1, and when ΔG° is much larger or smaller than RT , K deviates strongly from 1.

Keep the direction of the logic straight. ΔG° describes the reaction under standard conditions and tells you where equilibrium lies. It does not tell you the composition of a mixture that is not at equilibrium, and $K > 1$ does not mean every reactant molecule converts. A K of 10^6 still leaves a tiny fraction of reactants at equilibrium.

Trap. Students read $\Delta G^\circ < 0$ as "the reaction goes." It means the equilibrium constant favors products. If you start with pure products, the reaction runs backward toward that same equilibrium. ΔG° sets the destination, not the starting point.

9.6 Free Energy of Dissolution

Dissolving a solid involves three energy contributions: breaking the solid's intermolecular interactions, reorganizing the solvent to make room, and forming new solute-solvent interactions. Predicting the total ΔG of dissolution is difficult because these terms partially cancel each other. This is why solubility trends have so many exceptions and why the exam tests the pattern qualitatively rather than asking you to calculate it.

9.7 Coupled Reactions

An unfavorable reaction can be driven by **coupling** it to a favorable one. The two reactions share intermediates, and what matters is the sum: if the overall ΔG° is negative, the pair proceeds. Biology runs on this. The hydrolysis of ATP to ADP has a ΔG° of about -30.5 kJ/mol , and cells couple it to biosynthesis steps that would never run on their own.

The same idea works with external energy input. An **electrolytic cell** uses electrical energy to force an unfavorable redox reaction to occur, which is how rechargeable batteries recharge. Photosynthesis uses light energy to drive CO_2 and water uphill into glucose. In every case, something pays the free energy bill.

9.8 Electrochemical Cells

A **galvanic (voltaic) cell** runs a thermodynamically favored redox reaction and turns it into electric current. The voltage is positive and the cell does work on its surroundings. An **electrolytic cell** does the reverse: an externally applied voltage forces an unfavorable redox reaction to occur. Galvanic cells discharge batteries. Electrolytic cells recharge them and drive electroplating.

The vocabulary is the same for both cell types, and that is deliberate. The **anode** is where oxidation occurs and the **cathode** is where reduction occurs, in every electrochemical cell. Each **half-cell** is one electrode plus its surrounding solution, hosting one of the two half-reactions. A **salt bridge** lets ions flow between the half-cells, completing the circuit while keeping the solutions from mixing. **Electrons flow through the external wire from the anode to the cathode.**

Trap. The anode is oxidation and the cathode is reduction in both cell types. What changes between galvanic and electrolytic cells is the sign of each electrode, not which process happens there. If you memorize "anode is negative," you will get every electrolytic cell question wrong. Memorize the process, not the sign.

9.9 Standard Cell Potential

The **standard cell potential (E°)** is the voltage under standard conditions. Find it from the **standard reduction potentials**, each measured against the standard hydrogen electrode: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both. The half-reaction with the higher reduction potential gets reduced (cathode), and the other gets oxidized (anode).

Worked example. For the zinc-copper cell, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$ and $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$. Copper has the higher reduction potential, so copper is reduced at the cathode and zinc is oxidized at the anode: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$. $E^\circ_{\text{cell}} = 0.34 - (-0.76) = 1.10 \text{ V}$.

Cell potential and free energy are the same story in different units: $\Delta G^\circ = -nFE^\circ$, where n is the moles of electrons transferred and F is Faraday's constant (96,485 C/mol). A positive E° gives a negative ΔG° , a favored reaction. For the zinc-copper cell with $n = 2$: $\Delta G^\circ = -(2)(96,485)(1.10) = -212,000 \text{ J}$, or -212 kJ . A negative E° gives a positive ΔG° , an unfavored reaction that needs an external voltage, which is exactly what an electrolytic cell supplies.

Trap. $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ uses reduction potentials for both electrodes. Do not flip the sign of the anode's reduction potential before subtracting. That double-flips it and gives you $E^\circ_{\text{cathode}} + E^\circ_{\text{anode}}$, which is wrong. Pick the cathode, write both reduction potentials, subtract.

9.10 The Nernst Equation and Concentration Cells

Standard conditions rarely hold once a cell starts running. The **Nernst equation**, $E = E^\circ - (RT/nF) \ln Q$, adjusts the potential for the actual reaction quotient. As the cell runs, reactants are consumed and products build up, so Q moves toward K and the cell potential shrinks. A dead battery is a cell at equilibrium: $Q = K$ and $E = 0$.

A **concentration cell** is the limiting case. Both half-cells contain the same species at different concentrations, so $E^\circ_{\text{cell}} = 0$, yet the cell still produces a voltage because $Q \neq 1$. Electrons flow in the direction that evens out the concentrations, moving the system toward equilibrium. This is also why **Le Châtelier's principle does not apply to electrochemical cells**: they are not at equilibrium, so deviations from standard conditions change the potential through the Nernst equation instead.

9.11 Faraday's Laws

Faraday's laws connect charge to chemistry. Current is charge per time, $I = q/t$, so the charge that flows is $q = It$. Dividing by Faraday's constant gives moles of electrons, q/F , and the half-reaction stoichiometry converts that to moles of substance deposited or consumed. This is the math behind electroplating.

Worked example. A current of 2.00 A runs through a Cu^{2+} solution for 30.0 minutes. Charge: $q = (2.00)(1800) = 3600$ C. Moles of electrons: $3600 / 96,485 = 0.0373$ mol. The half-reaction $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ needs two electrons per copper atom, so moles of Cu = $0.0373 / 2 = 0.0187$ mol. Mass: $(0.0187)(63.55) = 1.19$ g of copper plated out.

Trap. The half-reaction's electron count is not optional. Forgetting the 2 in $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ doubles your answer. Write the balanced half-reaction first, then convert moles of electrons to moles of substance through it.

Confusions That Cost Points

PAIR	HOW TO KEEP THEM STRAIGHT
Favored vs fast	$\Delta G^\circ < 0$ means favored. Speed is activation energy. Diamond to graphite is favored and takes effectively forever.
Anode and cathode across cell types	Oxidation at the anode, reduction at the cathode, always. The electrode signs flip between galvanic and electrolytic cells; the processes do not.
E°_{cell} calculation	$E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ with reduction potentials for both. Do not flip the anode sign first.
$\Delta G^\circ < 0$ vs complete reaction	Negative ΔG° means $K > 1$, products favored at equilibrium. It never means 100 percent conversion.
Nernst vs Le Châtelier	Cells are not at equilibrium, so Le Châtelier does not apply. Concentration changes shift E through the Nernst equation.
Units in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	T in kelvin, and ΔS° in kJ/K if ΔH° is in kJ. Convert J to kJ first.
Sign of ΔS°	Count moles of gas. More gas in products means positive ΔS° ; less gas means negative.

Practice Questions

Original questions written for this guide in the style of the AP exam. Answers and explanations are on the next page, so complete the questions before checking them.

- For the reaction $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, the sign of ΔS° is
 - Positive, because a gas is produced from a solid
 - Negative, because one solid becomes another solid
 - Zero, because the number of product species equals the number of reactant species
 - Cannot be determined without table values
- For $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$, $\Delta H^\circ = -92.2 \text{ kJ}$ and $\Delta S^\circ = -198.7 \text{ J/K}$. What is ΔG° at 298 K?
 - 151 kJ
 - 33.0 kJ
 - +33.0 kJ
 - 92.2 kJ
- A reaction has $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$. It is thermodynamically favored
 - At all temperatures
 - At no temperature
 - At high temperature only
 - At low temperature only
- A galvanic cell is built from the half-reactions $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ ($E^\circ = +0.34 \text{ V}$) and $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ ($E^\circ = -0.76 \text{ V}$). The standard cell potential is
 - 1.10 V
 - 1.10 V
 - 0.42 V
 - 0.42 V
- For the cell in question 4, with $n = 2 \text{ mol}$ of electrons transferred, ΔG° is closest to
 - 212 kJ
 - 106 kJ
 - +212 kJ
 - 424 kJ
- A current of 2.00 A is passed through a solution of Cu^{2+} for 30.0 minutes. The mass of copper deposited is closest to
 - 2.37 g
 - 1.19 g
 - 0.59 g
 - 4.74 g

Answer Key

- 1. A.** A gas appears where there was none, so matter is more dispersed in the products and ΔS° is positive. B looks only at the solids and ignores the CO_2 . C counts species instead of counting moles of gas, which is the actual predictor. D is overcautious; the sign is clear from the phases alone.
- 2. B.** Convert ΔS° to kJ: $-198.7 \text{ J/K} = -0.1987 \text{ kJ/K}$. Then $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92.2 - (298)(-0.1987) = -92.2 + 59.2 = -33.0 \text{ kJ}$. A slips the sign on ΔS° , treating it as $+0.1987 \text{ kJ/K}$, which gives $-92.2 - 59.2 = -151 \text{ kJ}$. C flips the sign of the $T\Delta S^\circ$ term. D ignores entropy entirely.
- 3. C.** With $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$, the $-T\Delta S^\circ$ term is the only thing that can make ΔG° negative, and it grows with temperature, so the reaction is favored at high temperature only. A and B describe the cases where both terms agree. D is the pattern for $\Delta H^\circ < 0$ and $\Delta S^\circ < 0$.
- 4. B.** Copper has the higher reduction potential, so Cu^{2+} is reduced at the cathode and Zn is oxidized at the anode. $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = 1.10 \text{ V}$. A flips the sign of the whole result, which would describe an electrolytic cell. C and D come from adding or subtracting the wrong pair.
- 5. A.** $\Delta G^\circ = -nFE^\circ = -(2)(96,485)(1.10) = -212,000 \text{ J} \approx -212 \text{ kJ}$. B uses $n = 1$, forgetting the balanced half-reactions each transfer 2 electrons. C flips the sign; a positive E° always gives a negative ΔG° . D doubles n to 4.
- 6. B.** Charge $q = It = (2.00)(1800) = 3600 \text{ C}$. Moles of electrons $= 3600 / 96,485 = 0.0373 \text{ mol}$. The half-reaction needs 2 e^- per Cu, so moles of Cu $= 0.0187 \text{ mol}$, and $(0.0187)(63.55) = 1.19 \text{ g}$. A skips the 2-electron stoichiometry. C and D come from misplacing the time conversion or the molar mass.

One-Page Recall Check

- Define entropy in terms of dispersal of matter and energy, and give two ways it increases.
- Predict the sign of ΔS° for a reaction by counting moles of gas, with an example.
- Write the formula for ΔS° from standard molar entropies.
- State the standard state for pure substances, solutions, and gases.
- Write $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and state the units each term needs.
- Explain why the CED says "thermodynamically favored" instead of "spontaneous."
- State the four $\Delta H^\circ/\Delta S^\circ$ sign combinations and the temperature dependence of each.
- Explain kinetic control and give an example of a favored reaction that does not proceed.
- Write $\Delta G^\circ = -RT \ln K$ and explain what the sign of ΔG° says about K.
- Explain how coupled reactions drive an unfavorable process, with the ATP example.
- Distinguish a galvanic cell from an electrolytic cell.
- State which process happens at the anode and which at the cathode, in both cell types.
- Calculate E°_{cell} from two reduction potentials and convert it to ΔG° with $\Delta G^\circ = -nFE^\circ$.
- Explain qualitatively what the Nernst equation says happens to E as a cell runs.
- Describe a concentration cell and explain where its voltage comes from.
- Use Faraday's laws to find the mass deposited by a given current and time.

Study this unit in Rycal. Open the Unit 9 deck under AP Chemistry at rycal.web.app/apchem. The deck covers the terms in this guide, and its practice questions target the same traps named here. If you have a test date, add it in the Test Planner. You can also start your next review with a Brain Dump, then check what you missed against this guide.

Key terms for this unit

Entropy (S), Standard molar entropy (S°), Standard entropy change, Standard state, Gibbs free energy (ΔG°), Thermodynamically favored, Standard Gibbs free energy of formation (ΔG_f°), Predicting favorability from ΔH° and ΔS° , Kinetic control, Free energy and the equilibrium constant, Estimating K from ΔG° , Free energy of dissolution, Coupled reactions, Driving unfavorable processes with energy input, Galvanic (voltaic) cell, Electrolytic cell, Anode, Cathode, Salt bridge, Half-cell, Electron flow in electrochemical cells, Standard cell potential (E°), Standard reduction potential, Cell potential and free energy, Nernst equation (qualitative), Concentration cell, Electrochemical cells are not at equilibrium, Faraday's laws, Current equation.

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