

Unit

9

AP Chemistry

Thermodynamics and Electrochemistry

Unit 1

7–9%
Atomic
structure

Unit 2

7–9%
Compound
structure

Unit 3

18–22%
Substances
and
mixtures

Unit 4

7–9%
Chemical
reactions

Unit 5

7–9%
Kinetics

Unit 6

7–9%
Thermo-
chemistry

Unit 7

7–9%
Equilibrium

Unit 8

11–15%
Acids and
bases

Unit 9

7–9%
Thermo-
dynamics,
electro-
chemistry

Unit 9 is 7–9% of the multiple-choice section. Its ideas also turn up in the free-response section almost every year, usually as parts of a longer question: explaining the sign of ΔS° , finding the temperatures at which a reaction is favored, or working with a galvanic or electrolytic cell.

9.1

Entropy

9.2

Absolute entropy

9.3

Gibbs free energy

9.4

Thermodynamic
and kinetic control

9.5

Free energy and
equilibrium

9.6

Free energy of
dissolution

9.7

Coupled reactions

9.8

Galvanic and
electrolytic cells

9.9

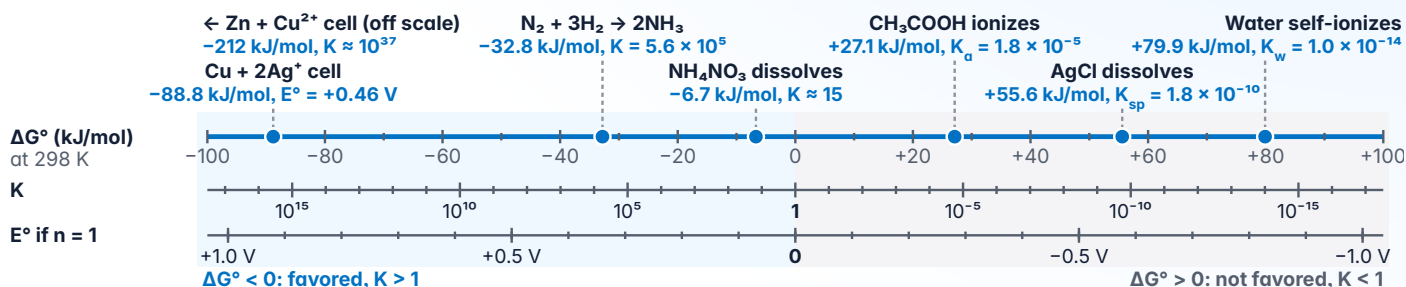
Cell potential and
free energy

9.10

Nonstandard cell
potential

9.11

Electrolysis and Faraday's law



Each dot is a real reaction at 298 K. ΔG° , K and E° are three ways of describing how far a reaction goes, and they always agree: a negative ΔG° goes with $K > 1$ and a positive E° . Each 5.7 kJ/mol drop in ΔG° multiplies K by 10 (one tick on the K line). The E° line is for a cell whose reaction transfers $n = 1$ mol of electrons; with $n = 2$, each E° is half as large.

What the exam asks most

- 1 Explain the sign of ΔS° with particles.** Name each substance and its phase. For $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$: " ΔS° is negative because 2 mol of gas become a solid, whose particles have far fewer possible arrangements." "More disorder" earns nothing. (9.1)
- 2 Say at what temperatures a reaction is favored.** Give the signs of ΔH° and ΔS° , and say which term in $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ helps make ΔG° negative and which works against it. In calculations, convert ΔS° from J to kJ (divide by 1000) and use T in kelvins. (9.2) (9.3)
- 3 Explain why a favored reaction seems not to happen.** A negative ΔG° says which way a reaction goes, not how fast. Its activation energy is high, so few collisions have enough energy and it is too slow to see. (9.4)
- 4 Find E° and ΔG° for a cell.** $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using the two reduction potentials as given, never multiplied by coefficients. Then $\Delta G^\circ = -nFE^\circ$, with n from the balanced equation; give ΔG° in kJ/mol. (9.9)
- 5 Explain how a concentration change affects the voltage.** Adding a reactant ion lowers Q and raises E ; adding a product ion does the opposite. Argue with Q , not Le Châtelier's principle: a working cell isn't at equilibrium. (9.10)
- 6 Read a cell diagram and count electrons.** Oxidation is at the anode, reduction at the cathode; electrons go through the wire, ions through the salt bridge. For plating, take $q = It$, divide by 96,485 C per mole of electrons and by the electrons per ion, then multiply by the molar mass. (9.8) (9.11)

The equations for this unit
Given on the equation sheet

- $\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$, and ΔG° from ΔG°_f the same way
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- $\Delta G^\circ = -RT \ln K = -nFE^\circ$
- $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$ and $I = \frac{q}{t}$
- $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $F = 96,485 \text{ C per mole of electrons}$, $1 \text{ V} = 1 \text{ J/C}$, $1 \text{ A} = 1 \text{ C/s}$

Not given, so know them by heart

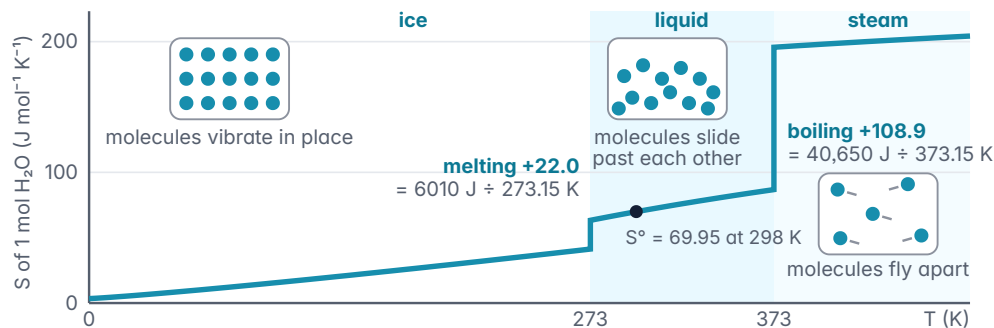
- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
- Where a reaction switches between favored and not: $T = \Delta H^\circ / \Delta S^\circ$ (when the two signs match).
- Oxidation at the anode, reduction at the cathode.
- At equilibrium, $\Delta G = 0$ and $E = 0$, but ΔG° and E° don't become zero.

Not on the exam

Labeling electrodes positive or negative. You never have to memorize S° , ΔG°_f or E° values: the question gives them.

9.1 Introduction to entropy

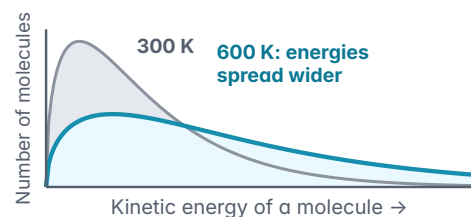
Entropy, S , measures how spread out matter and energy are. The more ways a substance's particles and their energy can be arranged, the higher its entropy.



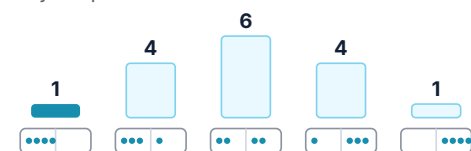
The jump when water boils is about five times the jump when ice melts, because a gas is far more spread out than a liquid. At a melting or boiling point the two phases are at equilibrium, so $\Delta G = 0$ and $\Delta S = \Delta H/T$.

Entropy goes up when ...

- **A solid melts or a liquid boils.** For one substance, the gas has far more entropy than the liquid, and the liquid more than the solid. This holds for water too, though liquid water is denser than ice.
- **A gas spreads into a bigger volume at the same temperature:** each molecule has more places to be.
- **A reaction makes more moles of gas than it uses.** Count only the (g) coefficients.
- **The temperature rises.** The molecules' energies spread over a wider range, so there are more ways to share the energy:



Ways to place 4 molecules in two halves



Only 1 of the 16 ways to place four molecules (the dark bar) has all four on the left. With 100 molecules the chance is about 1 in 10^{30} , so a gas never gathers in one half.

Quick check

Predict the sign of ΔS° for $2 \text{H}_2\text{O}_2(\text{l}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ and for $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$.

Answer: the first is **positive**, as 1 mol of gas forms from none; the second is **negative**, as 2 mol of gas become a solid.

Process and the reason	ΔS
$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ 1 mol of gas forms from none	+
$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$ 3 mol of gas become 2	-
$\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$ 5 mol of gas end up in a solid	-
$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$ 2 mol of gas on each side, so calculate it from S° values (Topic 9.2)	can't tell

Explaining a negative ΔS° in words

For $\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$, ΔS° is negative because 5 mol of O_2 gas are used up to form a solid. Gas particles are far more dispersed than the particles of a solid, so the products have fewer possible arrangements.

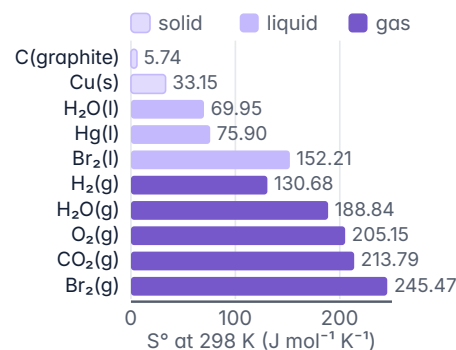
"Fewer microstates" (possible arrangements) or "fewer positions available" also earns the point.

Exam trap

- **Writing "more disorder" and stopping.** It says nothing about the particles, so it earns nothing. Write: " ΔS° is positive because 1 mol of CO_2 gas forms from solid CaCO_3 , and gas particles have far more possible positions."
- **Counting all moles instead of moles of gas.** Solids and liquids add little entropy, so count only the (g) coefficients. $\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$ goes from 6 mol to 7 mol in total, but the gas drops from 6 mol to 3, so $\Delta S^\circ < 0$.
- **Saying the gas freezes.** In the P_4O_{10} reaction the O_2 doesn't freeze; it reacts. Describe a reaction, not a phase change.

9.2 Absolute entropy and entropy change

Entropy has a true zero: a perfect crystal at 0 K. S° is the entropy of 1 mol of a substance at standard conditions, counted up from that zero, in $\text{J mol}^{-1} \text{K}^{-1}$. Every pure substance has $S^\circ > 0$.



A substance has the most entropy as a gas (Br_2 : 152 as a liquid, 245 as a gas). Liquid Br_2 still has more entropy than gaseous H_2 , because its molecules are bigger and heavier.

On the equation sheet

$$\Delta S^\circ_{\text{rxn}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

Worked example

S° values: $\text{SO}_2(\text{g})$ 248.22, $\text{O}_2(\text{g})$ 205.15, $\text{SO}_3(\text{g})$ 256.77 $\text{J mol}^{-1} \text{K}^{-1}$. Find ΔS° for $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$.

- 1 Predict the sign first: 3 mol of gas become 2, so $\Delta S^\circ < 0$.
- 2 Products: $2(256.77) = 513.54$
- 3 Reactants: $2(248.22) + 205.15 = 701.59$

$$\Delta S^\circ = 513.54 - 701.59 = -188.05 \text{ J mol}^{-1} \text{K}^{-1}, \text{ negative as predicted}$$

Exam trap

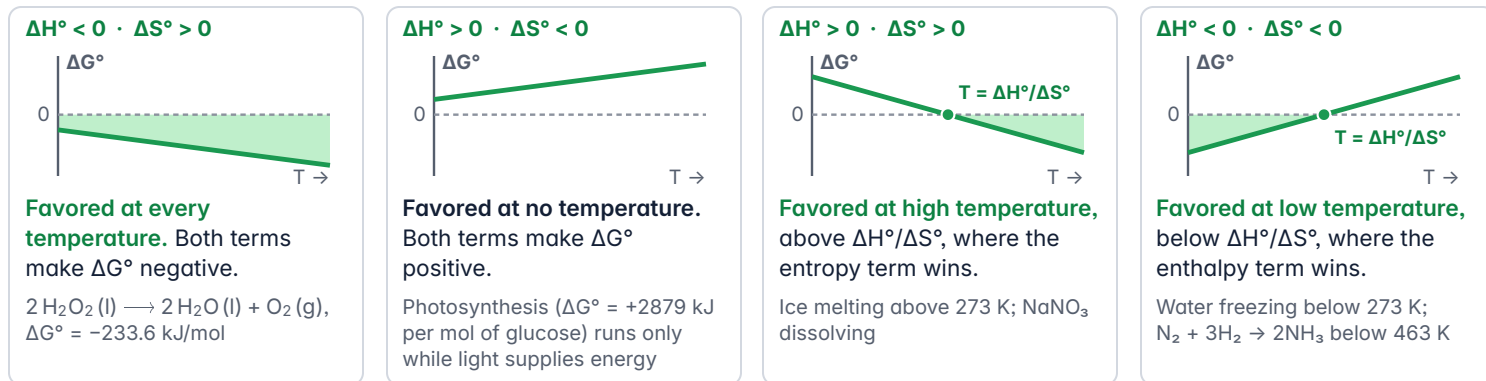
- **Leaving out O_2 "because it's an element."** An element's ΔH°_f and ΔG°_f are zero, but its S° is not. Leaving out O_2 's 205.15 in the worked example gives +17.10, the wrong sign.
- **Forgetting the coefficients.** Using one SO_2 and one SO_3 gives -196.60: right sign, wrong number. Write out both sums before you subtract.

Quick check

S° in $\text{J mol}^{-1} \text{K}^{-1}$: N_2 191.61, H_2 130.68, NH_3 192.77. Find ΔS° for $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$.

Answer: $2(192.77) - [191.61 + 3(130.68)] = 385.54 - 583.65 = -198.11 \text{ J mol}^{-1} \text{K}^{-1}$. It is negative, as expected when 4 mol of gas become 2.

9.3 Gibbs free energy and thermodynamic favorability

shaded: $\Delta G^\circ < 0$, so favored

A reaction with $\Delta G^\circ < 0$ is **thermodynamically favored**: at standard conditions it runs forward, and products are favored at equilibrium ($K > 1$). The $^\circ$ means standard conditions: gases at 1 atm, solutions at 1.0 M, and pure solids and liquids. The temperature is given separately, usually 298 K, and T is always in kelvins. The exam says "favored", not "spontaneous", and neither word says anything about speed.

On the equation sheet

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ_{\text{rxn}} = \sum \Delta G^\circ_{f, \text{products}} - \sum \Delta G^\circ_{f, \text{reactants}}$$

Worked example

For $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$, $\Delta H^\circ = +178.3 \text{ kJ/mol}$ and $\Delta S^\circ = +160.6 \text{ J mol}^{-1} \text{ K}^{-1}$. Is it favored at 298 K? Above what temperature is it favored?

- Put ΔS° in kJ: $0.1606 \text{ kJ mol}^{-1} \text{ K}^{-1}$
- $\Delta G^\circ = 178.3 - (298)(0.1606) = 178.3 - 47.9 = +130.4 \text{ kJ/mol}$: not favored at 298 K
- $\Delta G^\circ = 0$ where $T = \Delta H^\circ/\Delta S^\circ = 178.3 \div 0.1606 = 1110 \text{ K}$

Not favored at 298 K; favored above about 1110 K. That's why limestone (CaCO_3) is roasted in a kiln.

The 1110 K estimate assumes ΔH° and ΔS° barely change with temperature.

Why water freezes only below 273 K

For freezing, $\Delta H^\circ = -6.01 \text{ kJ/mol}$ and $\Delta S^\circ = -22.0 \text{ J mol}^{-1} \text{ K}^{-1}$, so each ΔG° below is -6.01 plus $-T\Delta S^\circ$ (all in kJ/mol).

T	$-T\Delta S^\circ$	ΔG°	What happens
263 K	+5.79	-0.22	water freezes
273 K	+6.01	0.00	water and ice coexist
283 K	+6.23	+0.22	water stays liquid

Saying what drives a reaction

For $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ at 298 K:

$\Delta H^\circ < 0$, so the enthalpy term favors the reaction. $\Delta S^\circ < 0$, so $-T\Delta S^\circ$ is positive and the entropy term opposes it. $\Delta G^\circ < 0$ at 298 K, so the reaction is driven by enthalpy.

If a question asks whether a student is right that a reaction is driven by enthalpy, say yes or no, then give both signs and what each does to ΔG° .

Exam trap

- **Saying "both drive it."** When ΔH° and ΔS° have the same sign, one term helps and the other hurts. For $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$, $\Delta H^\circ < 0$ helps, but $\Delta S^\circ < 0$ makes $-T\Delta S^\circ$ positive, which hurts. Say "driven by enthalpy, opposed by entropy."

- **Mixing kJ and J.** With $\Delta H^\circ = -91.8 \text{ kJ/mol}$ and $\Delta S^\circ = -198.1 \text{ J mol}^{-1} \text{ K}^{-1}$, writing $-91.8 - (298)(-198.1)$ gives +58,942, which is nonsense. Write ΔS° as $-0.1981 \text{ kJ mol}^{-1} \text{ K}^{-1}$ first: $-91.8 - (298)(-0.1981) = -32.8 \text{ kJ/mol}$. Use T in kelvins: 25 $^\circ\text{C}$ is 298 K.

Finding the sign of ΔH° from the temperatures

$\text{P}_4(\text{g}) \rightleftharpoons 2\text{P}_2(\text{g})$ is favored only at high temperature. It makes 2 mol of gas from 1, so $\Delta S^\circ > 0$. A reaction with $\Delta S^\circ > 0$ that is favored only when hot must have $\Delta H^\circ > 0$, so it is **endothermic**.

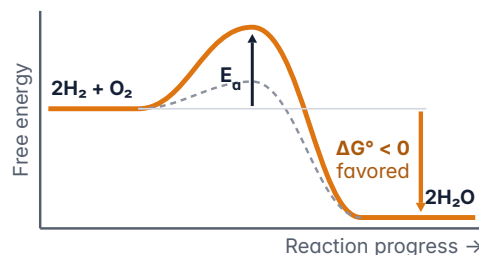
Quick check

For $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$, $\Delta H^\circ = -57.2 \text{ kJ/mol}$ and $\Delta S^\circ = -175.8 \text{ J mol}^{-1} \text{ K}^{-1}$. Find ΔG° at 298 K and the highest temperature at which it is favored.

Answer: $-57.2 - (298)(-0.1758) = -4.8 \text{ kJ/mol}$. It switches at $57.2 \div 0.1758 = 325 \text{ K}$ and is favored below it.

9.4 Thermodynamic and kinetic control

ΔG° tells you **which way** a reaction goes; activation energy sets **how fast**. A favored reaction too slow to see is under **kinetic control**.



A spark supplies the activation energy; the heat released keeps it going. A catalyst (dashed) lowers the barrier but not ΔG° or K .

Favored, but too slow to see

H_2 and O_2 can sit mixed for years even though $\Delta G^\circ = -474.2 \text{ kJ}$ for 2 mol of $\text{H}_2\text{O}(\text{l})$. Write:

The reaction is thermodynamically favored because $\Delta G^\circ < 0$, but its **activation energy is large**. At 298 K too few collisions have enough energy, so the rate is too slow to observe.

Exam trap

- **Thinking an unchanging mixture is at equilibrium.** At equilibrium $Q = K$, so compare them. In an H_2 and O_2 mixture Q is near 1 but K is about 10^{83} : the mixture is far from equilibrium, just too slow to react.

Quick check

Diamond $\rightarrow$ graphite: $\Delta G^\circ = -2.900 \text{ kJ/mol}$ at 298 K. Why do diamonds last?

Answer: it is favored, but the activation energy is enormous, so it is immeasurably slow: **kinetic control**, not equilibrium.

9.5 Free energy and equilibrium

ΔG° and K both tell you how far a reaction goes before it reaches equilibrium. A negative ΔG° means $K > 1$, so products are favored at equilibrium.



For $A \rightleftharpoons B$ at 298 K, each curve is the free energy of the mixture. From either end, the mixture runs downhill to the lowest point (the dot), which is equilibrium: $\Delta G = 0$ and $Q = K$. Making ΔG° 5.7 kJ/mol more negative moves that point toward B and multiplies K by 10.

On the equation sheet

$$\Delta G^\circ = -RT \ln K$$

Rearranged, not on the sheet: $K = e^{-\Delta G^\circ/RT}$

ΔG° (kJ/mol)	-11.4	-5.7	0	+5.7	+11.4
K	100	10	1	0.1	0.01

Worked example

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ has $\Delta G^\circ = -32.8$ kJ/mol at 298 K. Find K .

1 Put ΔG° in joules to match R : -32,800 J/mol

$$2 \quad -\frac{\Delta G^\circ}{RT} = \frac{32,800}{(8.314)(298)} = 13.24$$

$K = e^{13.24} = 5.6 \times 10^5$, so NH_3 is strongly favored

Exam trap

- Leaving ΔG° in kJ when R is in J. ΔG° must be in joules too. Using -32.8 gives $K = e^{0.0132} \approx 1.01$ instead of 5.6×10^5 .
- Using 10^x instead of e^x . The equation uses $\ln$, so undo it with e^x (keys on page 7): $10^{13.24}$ would give 1.7×10^{13} .
- Mixing up ΔG and ΔG° . At equilibrium $\Delta G = 0$, but ΔG° doesn't change: a reaction with $K = 100$ sits at equilibrium with $\Delta G^\circ = -11.4$ kJ/mol.

Using ΔG° to support a claim about K

Claim: $K < 1$ at 350 K for $2NO_2 \rightleftharpoons N_2O_4$ ($\Delta H^\circ = -57.2$ kJ/mol, $\Delta S^\circ = -175.8$ J mol $^{-1}$ K $^{-1}$).

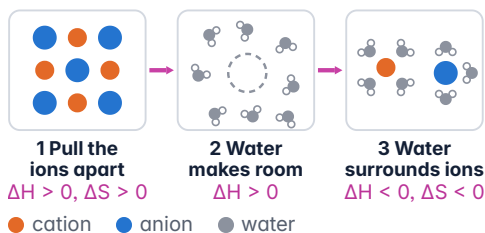
$$\Delta G^\circ = -57.2 - (350)(-0.1758) = +4.3 \text{ kJ/mol}$$

is positive, so by $\Delta G^\circ = -RT \ln K$, $K < 1$: the data support the claim.

"Nothing happened when we mixed them, so K is small" is not evidence: the reaction may just be slow.

9.6 Free energy of dissolution

Pulling the ions apart takes energy, and water surrounding them gives energy back. These two energies are often close, so you need data to know whether dissolving is favored.



	kJ/mol	ΔH°	$-T\Delta S^\circ$	ΔG°	Driven by
NH_4NO_3	+25.7	-32.4	-6.7		entropy
$CaCl_2$	-81.3	+13.3	-68.0		enthalpy
$AgCl$	+65.4	-9.8	+55.6		not favored

Exam trap

- Assuming dissolving always raises entropy. The ions spread out, but water molecules line up around them, and that ordering can outweigh the spreading. For $CaCl_2$, $\Delta S^\circ = -44.7$ J mol $^{-1}$ K $^{-1}$, so its $-T\Delta S^\circ$ above is positive. Take the sign of ΔS° from data.

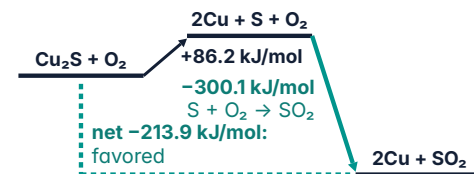
Why does a cold pack work?

Dissolving NH_4NO_3 absorbs heat from the water, so the pack gets cold. Being endothermic opposes dissolving, but $\Delta S^\circ > 0$ as the ions spread out, and $T\Delta S^\circ$ (32.4 kJ/mol) outweighs ΔH° (25.7 kJ/mol). So $\Delta G^\circ < 0$: dissolving is driven by entropy.

9.7 Coupled reactions

A reaction with $\Delta G^\circ > 0$ can still be made to run, but only while something supplies the energy it needs:

- Outside energy can keep it going: electricity (electrolysis, charging a battery) or light (photosynthesis).
- A coupled reaction can pay for it: a favored reaction that shares a substance with the unfavored one, so the two add up to $\Delta G^\circ < 0$.



Roasting copper ore. Splitting Cu_2S into copper and sulfur is uphill ($\Delta G^\circ = +86.2$ kJ/mol), but burning that sulfur (-300.1 kJ/mol) more than pays for it.

Adding reactions and their ΔG° values

- Add the equations, cancel what appears on both sides, and add the ΔG° values.
- Reversing a reaction changes the sign of ΔG° ; doubling it doubles ΔG° .

Showing that coupling works

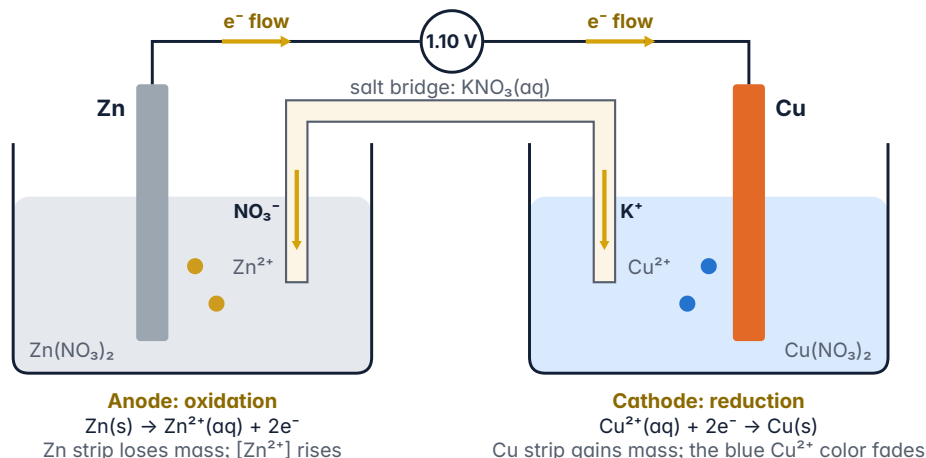
$ATP + H_2O \rightarrow ADP + P_i$ has $\Delta G^\circ = -30.5$ kJ/mol, and glucose + $P_i \rightarrow$ glucose 6-phosphate + H_2O has +13.8 kJ/mol. (P_i is phosphate; the ' marks biochemists' standard state, at pH 7.)

The reactions share P_i , so adding them gives glucose + $ATP \rightarrow$ glucose 6-phosphate + ADP , with $\Delta G^\circ = +13.8 + (-30.5) = -16.7$ kJ/mol < 0 . The coupled process is thermodynamically favored.

Exam trap

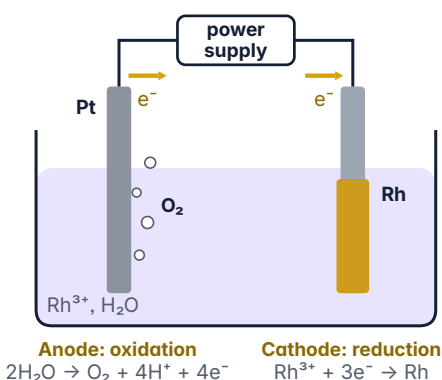
- Coupling reactions that share nothing. A favored reaction in the same flask does nothing for an unfavored one unless it makes or uses one of its substances. ATP breaking down beside glucose makes no glucose 6-phosphate unless an enzyme links the two through their shared phosphate.
- Thinking a one-time push is enough. Electrolysis needs current the whole time it runs; a push past the activation energy only starts a reaction that is already favored.

9.8 Galvanic (voltaic) and electrolytic cells



True in every cell, galvanic or electrolytic

- Oxidation at the anode, reduction at the cathode ("an ox, red cat").
- Electrons travel only through the wire, from the anode to the cathode.
- Ions carry charge between the half-cells, through a salt bridge or a shared solution: anions move toward the anode, cations toward the cathode.
- A metal anode that dissolves loses mass, and a cathode being plated gains mass. An inert Pt or graphite electrode keeps its mass; a gas may form there instead.



An electrolytic cell plating rhodium. The supply pushes electrons onto the object being plated (grey, with its new rhodium layer in gold). Water is oxidized at the inert Pt anode, so O_2 bubbles off and the Pt keeps its mass.

Exam trap

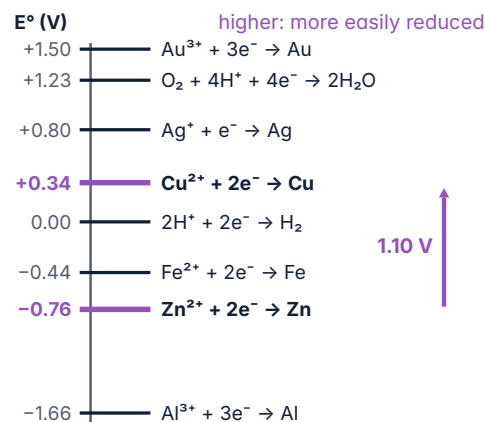
- Sending electrons through the salt bridge. Electrons move only through the wire; ions move in the bridge and keep each half-cell's charge balanced.

9.9 Cell potential and free energy

Not on the equation sheet

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

Use both reduction potentials as the question's table gives them, never multiplied by coefficients. A positive E°_{cell} means the reaction is favored at standard conditions, so it can run as a galvanic cell.



higher: more easily reduced
 lower: the metal is more easily oxidized
 The zinc-copper cell above uses the two purple half-reactions: $E^\circ = 0.34 - (-0.76) = 1.10 \text{ V}$.

Why plating needs a power source

Plating silver from Ag^+ , with water oxidized at an inert anode:

$E^\circ_{\text{cell}} = 0.80 - 1.23 = -0.43 \text{ V}$, so $\Delta G^\circ = -nFE^\circ$ is positive: the reaction is not thermodynamically favored. The power source must supply energy continuously to drive it.

Exam trap

- Multiplying E° by coefficients. E° is energy per coulomb, so multiplying a half-reaction doesn't change it. In silver plating, multiplying 0.80 V by 4 to match water's 4 electrons gives $(4)(0.80) - 1.23 = +1.97 \text{ V}$, the wrong sign; the right value is -0.43 V .
- Using the wrong n . n is the moles of electrons in the balanced overall equation, 2 for $\text{Cu} + 2\text{Ag}^+$. Using $n = 1$ (from $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$) gives -44.4 kJ/mol , half the right value.

Worked example

Find E° and ΔG° for $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$. Reduction potentials: $\text{Ag}^+/\text{Ag} +0.80 \text{ V}$, $\text{Cu}^{2+}/\text{Cu} +0.34 \text{ V}$.

- 1 Ag^+ is reduced (the cathode) and Cu is oxidized (the anode).
- 2 $E^\circ = 0.80 - 0.34 = +0.46 \text{ V}$. The 2 in 2Ag^+ doesn't change E° .
- 3 $n = 2$, so $\Delta G^\circ = -nFE^\circ = -(2)(96,485)(0.46) = -88,766 \text{ J/mol}$.

$E^\circ = +0.46 \text{ V}$ and $\Delta G^\circ = -88,766 \text{ J/mol} \div 1000 = -88.8 \text{ kJ/mol}$: favored

Quick check

Zinc is the anode in the zinc-copper cell. Paired with Al^{3+}/Al (-1.66 V), is zinc the anode or the cathode? Find E°_{cell} .

Answer: the cathode. Zn^{2+}/Zn (-0.76 V) is higher, so Zn^{2+} is reduced: $E^\circ_{\text{cell}} = -0.76 - (-1.66) = +0.90 \text{ V}$.

	Galvanic (voltaic)	Electrolytic
Reaction	favored: $\Delta G < 0$, $E > 0$	unfavored: $\Delta G > 0$, $E < 0$
Energy	gives electrical energy	needs a power supply the whole time
Examples	batteries, the zinc-copper cell	plating, recharging, making Al

Comparing electrode mass changes



Per mole of reaction, the Al anode loses $2 \text{ mol} \times 26.98 \text{ g/mol} = 53.96 \text{ g}$, while the Zn cathode gains $3 \text{ mol} \times 65.38 \text{ g/mol} = 196.1 \text{ g}$, so the Zn electrode changes more.

"3 Zn for every 2 Al" on its own doesn't earn the point: use the molar masses too.

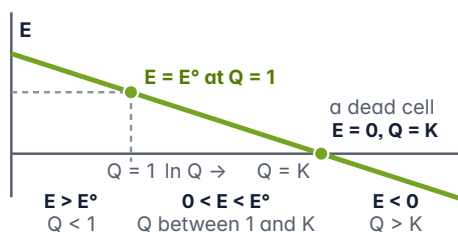
9.10 Cell potential under nonstandard conditions

A cell makes a voltage only because its reaction hasn't reached equilibrium. The smaller Q is compared with K, the larger E. At Q = K, E = 0 and the cell is dead.

On the equation sheet

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

This is the Nernst equation. Q is built like K: products over reactants, with solids and pure liquids left out. For the zinc-copper cell, $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$.



[Zn ²⁺]	[Cu ²⁺]	Q	E (V)	What it shows
0.010	1.0	0.010	1.16	above E°
1.0	1.0	1	1.10	standard
0.10	0.10	1	1.10	diluted: same Q
1.0	0.010	100	1.04	below E°
1.99	0.010	199	1.03	99% used up
at equilibrium		$K \approx 10^{37}$	0	dead, not empty

These values are for the zinc-copper cell at 298 K. A hundredfold change in Q moves E by only 0.06 V, so a battery holds its voltage most of its life.

Change to the running cell	Q	E
Add Cu ²⁺ to the cathode side	↓	↑
Add Zn ²⁺ to the anode side	↑	↓
Precipitate Cu ²⁺ (add S ²⁻)	↑	↓
Bigger Zn or Cu strip (solids aren't in Q)	same	same

Explaining a voltage change with Q

Adding Cu²⁺ lowers $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$, so the cell is farther from equilibrium and E increases (ln Q gets smaller in the Nernst equation).

To compare E with E°, compare Q with 1: Q < 1 gives E > E°, and Q > 1 gives E < E°.

Exam trap

- **Using Le Châtelier's principle.** "The equilibrium shifts right" describes a system at equilibrium, and a working cell isn't one. Say whether Q rises or falls, and connect that to E. Concentrations change E, never E°.
- **Expecting dilution to change the voltage.** In a cell like zinc-copper, where both ions have the same charge, diluting both half-cells equally leaves $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$, and so E, unchanged.
- **Thinking a dead cell is empty.** E = 0 means Q = K: the cell is at equilibrium and can still hold plenty of ions.

Worked example

A concentration cell joins Cu in 0.0010 M Cu²⁺ to Cu in 1.0 M Cu²⁺ at 298 K. Find E and the direction of electron flow.

- 1 The same half-reaction runs on both sides, so $E^{\circ} = 0$ V.
- 2 Cu dissolves on the dilute side (the anode), so that side's Cu²⁺ is the product: $Q = [\text{dilute}]/[\text{concentrated}] = 0.0010/1.0 = 1.0 \times 10^{-3}$.
- 3 $E = 0 - \frac{(8.314)(298)}{(2)(96,485)} \ln(1.0 \times 10^{-3}) = +0.089$ V

E = +0.089 V. Electrons flow from the dilute side to the concentrated side until the two concentrations match (Q = K = 1).

Where K ≈ 10³⁷ comes from

Set the equation sheet's two forms of ΔG° equal: $-nFE^{\circ} = -RT \ln K$, so $\ln K = \frac{nFE^{\circ}}{RT} = \frac{(2)(96,485)(1.10)}{(8.314)(298)} = 85.7$, and $K = e^{85.7} = 1.6 \times 10^{37}$ (keys for ln and e^x on page 7). A positive E° always means K > 1.

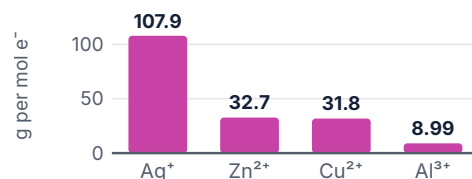
9.11 Electrolysis and Faraday's law

In electrolysis you count electrons with a current and a time: $q = It$ gives the charge, dividing by F gives moles of electrons, and the half-reaction gives the electrons per ion.

On the equation sheet

$$I = \frac{q}{t}$$

Here q is charge in coulombs, not heat. 1 A = 1 C/s, and F = 96,485 C per mole of electrons.



Mass deposited by one mole of electrons (96,485 C). Each Ag⁺ takes one electron, Cu²⁺ two and Al³⁺ three, so aluminum takes the most charge per gram.

Exam trap

- **Forgetting the electrons per ion.** The ion's charge, or the metal's oxidation state, gives the number: 3 for Rh³⁺, 6 for Cr in CrO₃. Leaving out the 3 in the rhodium example below gives about 1300 s instead of 3.9×10^3 s.
- **Using minutes or hours.** $I = q/t$ needs seconds: 30.0 min is 1800 s.

Quick check

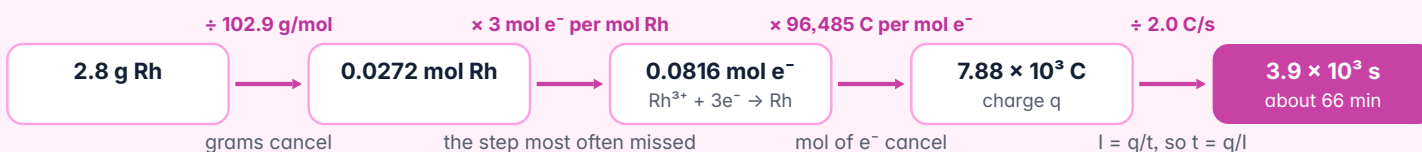
2.00 A runs for 30.0 min through a Cu²⁺ plating bath. What mass of Cu (63.55 g/mol) plates out?

Answer: $2.00 \times 1800 = 3600$ C, which is 0.0373 mol of electrons. Each Cu²⁺ takes 2, so $0.01866 \text{ mol} \times 63.55 = 1.19$ g.

How fast industry makes aluminum

One modern aluminum cell runs at 4.20×10^5 A. Every 72 s it passes 3.04×10^7 C (315 mol of electrons) and makes about 2.83 kg of aluminum. At 100 A, the same 2.83 kg would take 84 hours.

Worked example: how long does a 2.0 A current take to plate 2.8 g of rhodium from Rh³⁺?



What earns points on the free-response questions

When a question asks you to ...	What earns the point
Explain, using particles, why ΔS° is negative (9.1)	Name the substances and their phases: "In $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$, 3 mol of gas become 2, so the particles have fewer possible arrangements." "More disorder" on its own earns nothing.
Say whether a reaction is favored at all temperatures (9.3)	Give both signs and use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. $\Delta H^\circ < 0$ with $\Delta S^\circ > 0$ is favored at every temperature and $\Delta H^\circ > 0$ with $\Delta S^\circ < 0$ at none. With the same signs, it is favored only when hot (both +) or only when cold (both -).
Say whether it is driven by enthalpy, entropy or both (9.3)	Say which term makes ΔG° negative and which works against it. Answer "both" only when $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$.
Calculate ΔS° or ΔG° (9.2) (9.3)	Take products minus reactants, multiplying each value by its coefficient. Convert ΔS° to kJ before you combine it with ΔH° , use T in kelvins, and give the sign and units.
Explain why a favored reaction isn't observed (9.4)	$\Delta G^\circ < 0$, but the activation energy is high, so too few collisions have enough energy and the rate is too slow to see. Don't say it is at equilibrium or not favored.
Say whether data support a claim about K (9.5)	Find the sign of ΔG° , then use $\Delta G^\circ = -RT \ln K$: a negative ΔG° means $K > 1$. "Nothing happened when they were mixed" is not evidence about K.
Write the half-reaction at the anode (9.8)	Write the oxidation, with the electrons as products: $\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{e}^-$.
Write the balanced equation for the cell (9.8)	Multiply the half-reactions until the electrons match (2 Al give up 6e^- and 3 Zn^{2+} take 6e^-), add them and cancel. The final equation shows no electrons and no spectator ions.
Say which electrode's mass changes more (9.8)	For each electrode, multiply its moles in the balanced equation by its molar mass, then compare grams, not moles.
Calculate E°_{cell} , then ΔG° (9.9)	Subtract E°_{anode} from E°_{cathode} , without multiplying either by a coefficient. Then $\Delta G^\circ = -nFE^\circ$, with n from your balanced equation; it comes out in joules, so divide by 1000 for kJ.
Explain why a cell needs a power source (9.9)	$E < 0$, so $\Delta G > 0$ and the reaction is not favored. The source must supply energy the whole time it runs, not just enough to get past the activation energy.
Say how E changes when a concentration changes (9.10)	Write Q. If Q falls, the cell is farther from equilibrium and E rises; if Q rises, E falls. Don't use Le Châtelier's principle: a working cell isn't at equilibrium.
Find a time, current or mass in electrolysis (9.11)	$q = It$ with t in seconds. Divide by 96,485 C per mole of electrons, then by the electrons each ion needs, then multiply by the molar mass. For a time, work backward and finish with $t = q/I$. Show units at every step.

Use ln and e^x

TI-84 Plus CE. For ln, press **[ln]**, type the number and press **[enter]**. For e^x, press **[2nd] [ln]**, which types e⁽. Put the whole exponent inside the parentheses: e^{(32800/(8.314×298))} shows 561724.97, which is 5.6×10^5 .

TI-Nspire CX. Press **[e^x]** for e to a power, or **[ctrl] [e^x]** for ln. Type the exponent inside the parentheses and press **[enter]**.

Desmos. Type ln(...) or e^(...), with the whole exponent in parentheses: e^{(32800/(8.314*298))}.

Enter powers of ten

TI-84 Plus CE. Type 1.8, then **[2nd] [10^x]** (EE), then **[(-)]** 10. The screen shows 1.8E-10. Use **[(-)]** for a negative sign, never the subtraction key.

TI-Nspire CX. Type 1.8 **[x]** 10 **[^]** **[(-)]** 10. Use **[(-)]** for a negative sign, never the subtraction key.

Desmos. Type 1.8*10⁻¹⁰.

Units to check before you answer

$S^\circ, \Delta S^\circ$	J mol ⁻¹ K ⁻¹ ; divide by 1000 before combining with kJ
$\Delta H^\circ, \Delta G^\circ$	kJ per mole of reaction as written
E°, E	volts (1 V = 1 J/C), never multiplied by coefficients
n	moles of electrons in the balanced equation
q	coulombs = amperes × seconds (charge, not heat)
K	no units

Galvanic cells in the real world

The Statue of Liberty. Its iron frame touched its copper skin in salty air, making a galvanic cell: the iron (-0.44 V) was the anode and corroded. The 1980s restoration swapped in stainless steel, with Teflon between the metals.

Sacrificial anodes. Zinc blocks bolted to a ship's steel hull are oxidized instead of the iron, because zinc (-0.76 V) is lower than iron on the page 5 ladder.

What Unit 9 uses from earlier units

- **Unit 3:** ion–water attractions set the energy of dissolving (9.6).
- **Unit 4:** oxidation numbers and half-reactions start every cell question.
- **Unit 5:** activation energy is why a favored reaction can still be slow.
- **Unit 6:** ΔH° came from ΔH°_f values, the same way ΔG° comes from ΔG°_f here.
- **Unit 7:** K and Q return, tied to ΔG° and E.
- **Unit 8:** K_a and K_w give ΔG° values too; K_w gives +79.9 kJ/mol.

Useful numbers at 298 K

RT	2.48 kJ/mol
K ten times larger	ΔG° falls by 5.7 kJ/mol
Q ten times larger	E falls by 0.0592/n V
$E^\circ = 1\text{ V}, n = 1$	$\Delta G^\circ = -96.5\text{ kJ/mol}$
1 mol of electrons	96,485 C, or 26.8 amp-hours
1 A for 1 hour	3600 C = 0.0373 mol of electrons