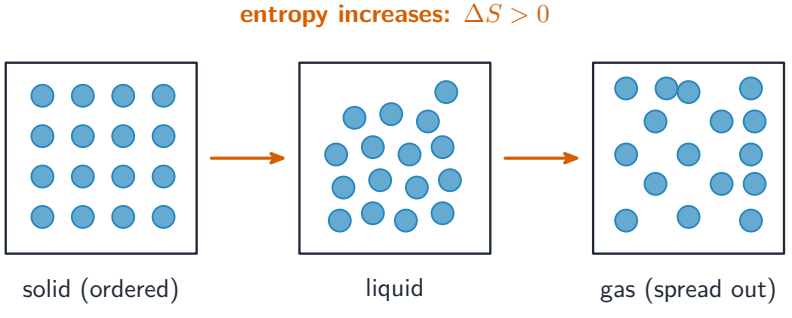
Thermodynamics and Electrochemistry

AP Chemistry

Introduction to Entropy

Household batteries: electrochemical cells convert chemical free energy into electrical work

Entropy 熵 S measures the dispersal of energy and matter – loosely, the number of ways to arrange a system. Entropy **increases** when a substance goes solid → liquid → gas, when a solid dissolves, when gas moles increase, or when temperature rises. More disorder means higher entropy.



Entropy rises from solid to liquid to gas

Absolute Entropy and Entropy Change

Every substance has a positive absolute entropy S°. For a reaction,

$$\Delta S^\circ = \sum S^\circ(\text{products}) - \sum S^\circ(\text{reactants}).$$

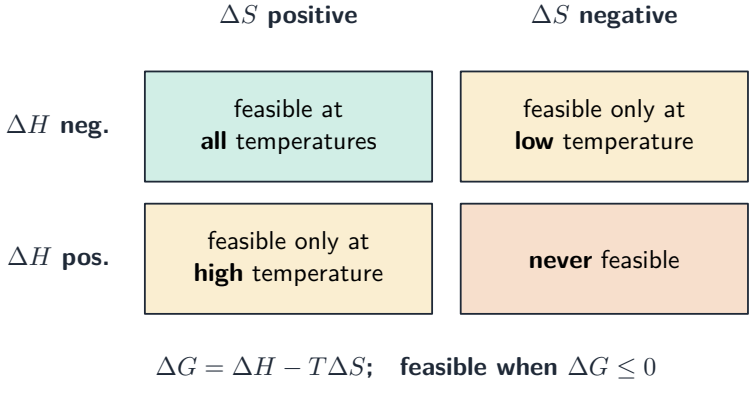
Predict its **sign** from the change in gas moles: making more gas raises entropy ($\Delta S > 0$).

Gibbs Free Energy and Thermodynamic Favorability

Gibbs free energy 吉布斯自由能 combines enthalpy and entropy:

$$\Delta G = \Delta H - T\Delta S.$$

A process is **thermodynamically favorable** 热力学有利 when $\Delta G < 0$. So exothermic ($\Delta H < 0$) and entropy-increasing ($\Delta S > 0$) reactions are always favorable; when the two oppose, **temperature** decides.



Whether a reaction is favorable, from the signs of the enthalpy and entropy change

Worked example. A reaction has $\Delta H = +40$ kJ/mol and $\Delta S = +120$ J/(mol K). It is endothermic (unfavorable enthalpy) but entropy-increasing, so it becomes favorable only when hot enough. Setting $\Delta G = \Delta H - T\Delta S < 0$ and matching units ($\Delta S = 0.120$ kJ):

$$T > \frac{\Delta H}{\Delta S} = \frac{40}{0.120} = 333 \text{ K } (60\,^\circ\text{C}).$$

Thermodynamic and Kinetic Control

$\Delta G < 0$ says a reaction *can* happen, not that it *will* happen fast. A reaction can be thermodynamically favorable yet **kinetically** slow because of a high activation energy (diamond $\rightarrow$ graphite). Thermodynamics gives the direction; kinetics gives the speed.

Free Energy and Equilibrium

Free energy links to the equilibrium constant:

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

So $\Delta G^\circ < 0$ gives $K > 1$ (products favored), and $\Delta G^\circ > 0$ gives $K < 1$. At equilibrium $\Delta G = 0$.

A battery converts free energy of a spontaneous redox reaction into electrical work

Free Energy of Dissolution

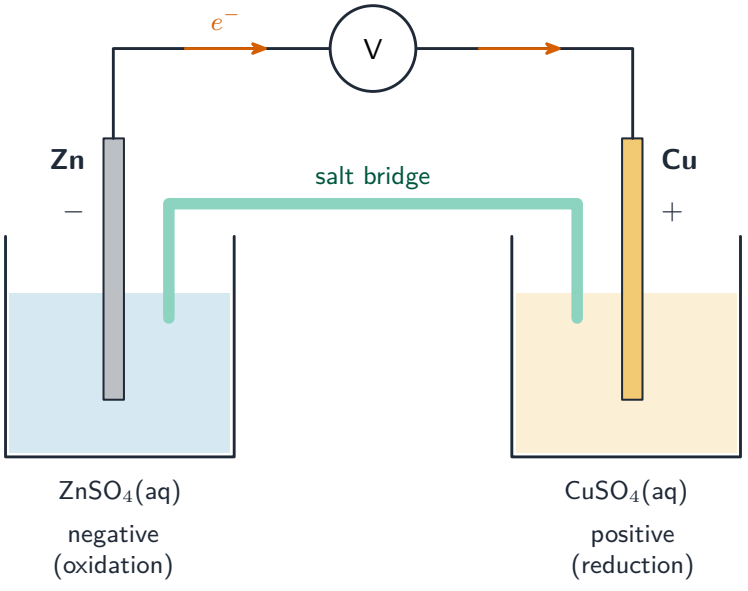
Whether a salt dissolves depends on the free-energy change of dissolving. Dissolving often increases entropy (ordered solid $\rightarrow$ dispersed ions) but may cost enthalpy; the sign of ΔG (and thus K_{sp}) follows from $\Delta H - T\Delta S$.

Coupled Reactions

An unfavorable reaction ($\Delta G > 0$) can be driven by **coupling** it to a favorable one ($\Delta G < 0$) that shares a common intermediate, as long as the **sum** has $\Delta G < 0$. This is how cells use ATP to power otherwise unfavorable processes.

Galvanic and Electrolytic Cells

Redox reactions can move electrons through a wire:



A galvanic cell with a salt bridge and voltmeter

- A **galvanic (voltaic) cell** 原电池 uses a **favorable** reaction ($\Delta G < 0$) to produce electricity – a battery.
- An **electrolytic cell** 电解池 uses electricity to **force** an unfavorable reaction ($\Delta G > 0$).

In both, **oxidation** happens at the **anode** 阳极 and **reduction** at the **cathode** 阴极.

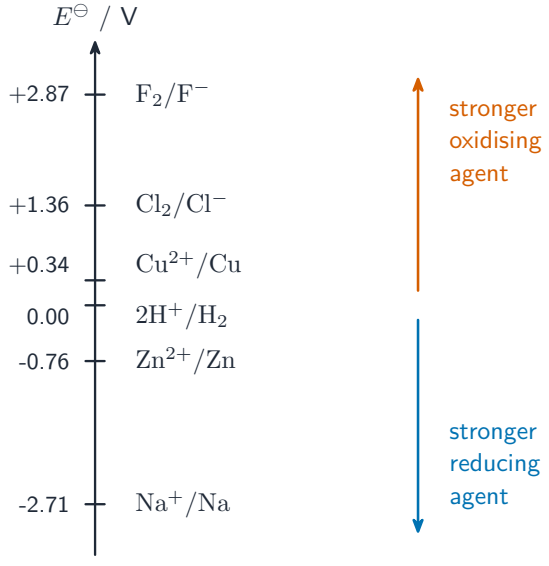
Commercial batteries: galvanic cells convert chemical free energy into electrical work

Cell Potential and Free Energy

The **cell potential** 电池电势 E°_{cell} measures the driving force in volts, found from standard reduction potentials ($E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$). It links to free energy by

$$\Delta G^\circ = -nFE^\circ_{\text{cell}},$$

where n is moles of electrons and F the Faraday constant. A **positive** E°_{cell} means a favorable (galvanic) reaction.



The electrochemical series of standard electrode potentials

Worked example. A cell pairs a copper cathode ($Cu^{2+} + 2e^- \to Cu$, $E^\circ = +0.34$ V) with a zinc anode ($Zn^{2+} + 2e^- \to Zn$, $E^\circ = -0.76$ V). The cell potential is

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 - (-0.76) = 1.10 \text{ V}.$$

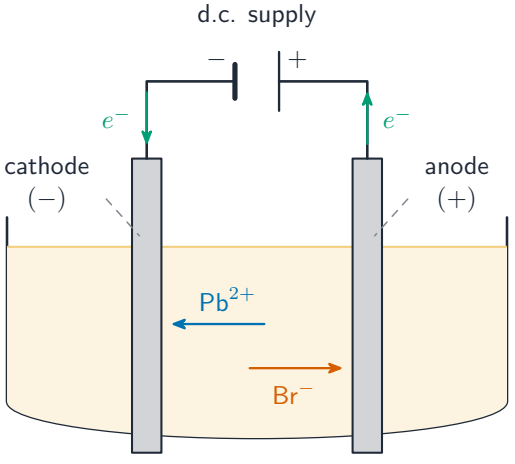
It is positive, so the reaction is spontaneous and the cell (a Daniell cell) acts as a battery.

Cell Potential Under Nonstandard Conditions

Away from standard conditions, the potential shifts with concentration – the **Nernst equation** 能斯特方程 (qualitatively): as reactants are consumed, Q rises and E_{cell} falls, reaching zero at equilibrium (a dead battery). Changing a concentration shifts E_{cell} the way Le Chatelier predicts.

Electrolysis and Faraday's Law

In **electrolysis** 电解, the charge passed determines how much substance is deposited or produced – **Faraday's law** 法拉第定律. Convert current × time to charge, charge to moles of electrons ($F = 96{,}485$ C/mol), then use the half-reaction's electron ratio to get moles (and mass) of product.



molten lead(II) bromide, $PbBr_2$

cathode: $Pb^{2+} + 2e^- \to Pb$ (silvery lead)

anode: $2Br^- \to Br_2 + 2e^-$ (red-brown bromine)

Electrolysis: ions move to the electrodes and are discharged

Worked example. A current of 2.0 A flows for 30 minutes through copper(II) sulfate ($Cu^{2+} + 2e^- \rightarrow Cu$). How much copper is deposited? The charge is $Q = It = 2.0 \times 1800 = 3600$ C, giving $3600/96485 = 0.0373$ mol of electrons. Since each Cu needs 2 electrons, 0.0187 mol of Cu forms, a mass of $0.0187 \times 63.5 = 1.2$ g.

Exam tips

- A process is **thermodynamically favourable** when $\Delta G < 0$; combine enthalpy and entropy with $\Delta G = \Delta H - T\Delta S$ (match units — kJ vs J).
- Entropy **increases** solid→liquid→gas and when more gas moles are produced.
- Favourable does **not** mean fast — a high activation energy can make a $\Delta G < 0$ reaction extremely slow (kinetic control).
- In electrochemistry a **positive** $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ means a spontaneous (galvanic) cell; oxidation is at the **anode**, reduction at the **cathode**.
- In electrolysis the charge passed ($Q = It$) fixes the amount deposited (Faraday's law).