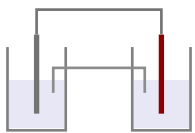
Thermodynamics and Electrochemistry

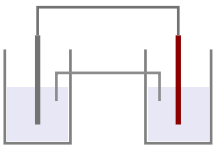
AP Chemistry ▪ Unit 9

AP Chemistry



What we will cover

1. Entropy
2. Gibbs free energy
3. Free energy and equilibrium
4. Coupled reactions
5. Galvanic and electrolytic cells
6. Cell potential and electrolysis



1 Entropy

Entropy

Entropy 熵 S measures how spread out matter and energy are among **microstates** 微观状态. $\Delta S > 0$ for more freedom:

- solid $\rightarrow$ liquid $\rightarrow$ gas
- dissolving a solid
- more gas molecules

Products minus reactants

$$\Delta S^\circ = \sum S^\circ(\text{prod}) - \sum S^\circ(\text{react})$$

Gases have the highest S°; a reaction making a gas has $\Delta S > 0$.

When entropy increases

entropy 熵 S	measures the dispersal of energy and matter – loosely, the number of ways to arrange a system
phase	increases solid $\rightarrow$ liquid $\rightarrow$ gas, and the gas step is by far the largest
particle count	more moles of gas on the product side means $\Delta S > 0$
dissolving	usually increases entropy, as an ordered lattice disperses
temperature	raising it increases entropy, because more energy levels become accessible
volume	expanding a gas increases it

Count the moles of gas on each side first. That single comparison predicts the sign of ΔS for most reactions on the paper.

2

Gibbs

Gibbs free energy

Favorability depends on both energy and entropy:

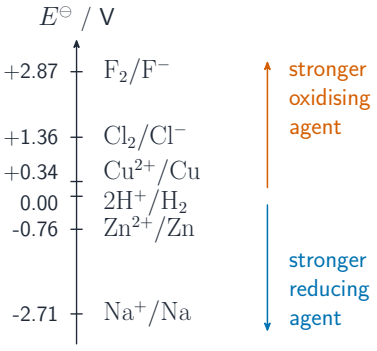
Gibbs free energy

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

$\Delta G^\circ < 0$ is **thermodynamically favorable** 热力学有利的. If ΔH and ΔS oppose, T can flip it.

Free energy drives spontaneous change

Cell Potential and Free Energy



The electrochemical series of standard electrode potentials

3 Free energy & equilibrium

Free energy and equilibrium

Free energy connects to the equilibrium constant:

Standard and nonstandard

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

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$\Delta G^\circ < 0 \Rightarrow K > 1$. At **equilibrium** 平衡, $\Delta G = 0$ and $Q = K$.

Coupled reactions

Add the ΔG° values. An unfavorable step $(+20)$ coupled to -50:

$$+20 + (-50) = -30\,\text{kJ}$$

In cells, the "downhill" partner is ATP breakdown.

4 Cells

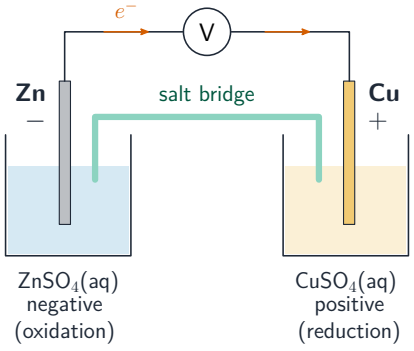
Galvanic and electrolytic cells

Galvanic 原电池: a spontaneous redox reaction makes electricity (a battery).
Electrolytic 电解池: an external voltage drives a nonspontaneous one.

> Oxidation at the **anode** 阳极, reduction at the **cathode** 阴极. Electrons flow anode → cathode.

Cells convert chemical energy to electricity

A galvanic cell with a salt bridge and voltmeter



A galvanic cell with a salt bridge and voltmeter

The two kinds of electrochemical cell

Galvanic (voltaic) cell	A **galvanic (voltaic) cell** runs a spontaneous reaction ($\Delta G < 0$, $E^\circ_{cell} > 0$) and delivers electrical work – a battery.
Electrolytic cell	An electrolytic cell drives a non-spontaneous reaction with an external supply – plating, and the extraction of aluminium.
What is shared	Oxidation at the anode, reduction at the cathode, in both. Only the signs of the electrodes swap.
The link	$\Delta G^\circ = -nFE^\circ$ ties the cell potential to the free-energy change directly.

Sign of E°_{cell} decides which cell you have. Everything else about the two is the same chemistry.

5 Potential

Cell potential and electrolysis

Cell potential and free energy

$$E^\circ_{cell} = E^\circ_{cath} - E^\circ_{an}$$

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

Positive $E^\circ \Rightarrow$ negative ΔG (spontaneous). Zn-Cu: $0.34 - (-0.76) = +1.10\,\mathrm{V}$.

Nernst & Faraday

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$q = It, \quad n_{e^-} = \frac{q}{F}$$

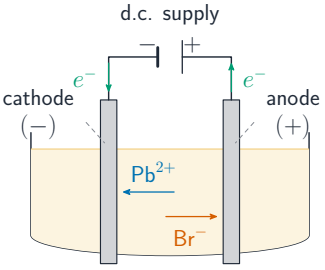
A dead battery is $Q = K$, $E = 0$. **Electrolysis** 电解: charge $\rightarrow$ mass of metal.

Coupling, the Nernst shift, and electrolysis

coupled reactions	an unfavourable reaction ($\Delta G > 0$) can be driven by a favourable one ($\Delta G < 0$) sharing a common intermediate
the condition	the total ΔG of the pair must be negative – ATP hydrolysis is the biological case
the Nernst equation 能斯特方程	away from standard conditions the cell potential shifts with concentration
qualitatively	as reactants are consumed and products build up, the potential falls toward zero – a dead battery is a cell at equilibrium
electrolysis 电解	the charge passed determines how much substance is deposited – **Faraday's law** 法拉第定律
the route	current × time → coulombs → moles of electrons → moles of substance → mass

A 2.0 A current for 30 minutes passes 3600 C, which is 0.0373 mol of electrons – and for Cu^{2+} that is half as many moles of copper.

Electrolysis



molten lead(II) bromide, $PbBr_2$

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

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

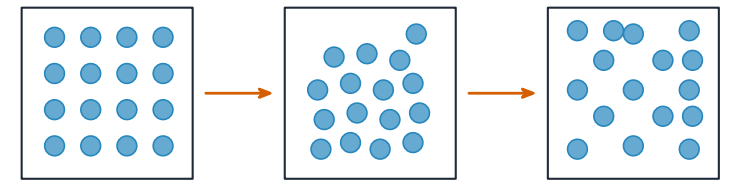
Electrolysis: ions move to the electrodes and are discharged

Galvanic and Electrolytic Cells, continued

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

Introduction to Entropy

entropy increases: $\Delta S > 0$



Entropy rises from solid to liquid to gas

Gibbs Free Energy and Thermodynamic Favorability

	ΔS **positive**	ΔS **negative**
ΔH **neg.**	feasible at **all** temperatures	feasible only at **low** temperature
ΔH **pos.**	feasible only at **high** temperature	**never** feasible

$$\Delta G = \Delta H - T\Delta S; \quad \textbf{feasible when } \Delta G \leq 0$$

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

Worked example – when does an endothermic reaction go?

$\Delta H = +40$ kJ/mol and $\Delta S = +120$ J/(mol K). Above what temperature is it favourable?

- $\Delta G = \Delta H - T\Delta S$; favourable when $\Delta G < 0$
- $T > \dfrac{\Delta H}{\Delta S} = \dfrac{40{,}000}{120}$
- $= 333$ K

Unfavourable enthalpy, favourable entropy: temperature decides. Convert ΔS from J to kJ before dividing – the factor of 1000 is the standard slip.

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).

6 Recap

Unit 9 – key takeaways

1 Entropy

S = spread of matter and energy; gas raises it

2 Gibbs

$\Delta G = \Delta H - T\Delta S$; $\Delta G < 0$ favorable

3 Equilibrium

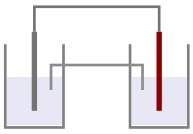
$\Delta G^\circ = -RT \ln K$; couple to drive uphill steps

4 Cells

anode oxidizes, cathode reduces; $\Delta G^\circ = -nFE^\circ$

Check yourself

1. A reaction produces a gas – what is the sign of ΔS?
2. What sign of ΔG° is thermodynamically favorable?
3. Where does oxidation happen in an electrochemical cell?
4. A positive E°_{cell} means the reaction is…?



Answers **1.** positive **2.** negative **3.** the anode **4.** spontaneous