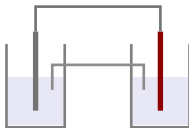


Thermodynamics and Electrochemistry

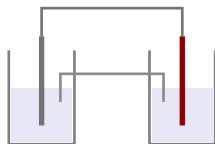
AP Chemistry ■ Unit 9

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



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

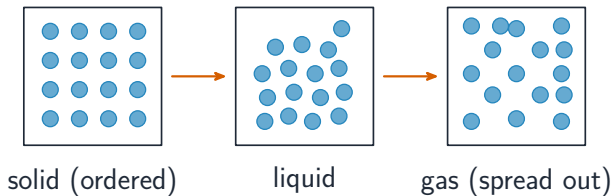
Products minus reactants

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

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

Entropy

entropy increases: $\Delta S > 0$



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*

Gibbs free energy

	ΔS positive	ΔS negative
ΔH neg.	feasible at all temperatures	feasible only at low tem- perature
ΔH pos.	feasible only at high tem- perature	never feasible

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

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.

Galvanic and electrolytic cells

Galvanic 原电池: a **spontaneous** redox reaction makes electricity (a battery).

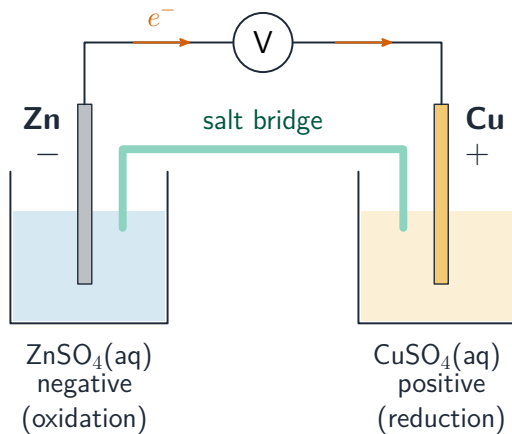
Electrolytic 电解池: an external voltage **drives** a nonspontaneous one.

Oxidation at the **anode** 阳极, reduction at the **cathode** 阴极. Electrons flow anode $\rightarrow$ cathode.



Cells convert chemical energy to electricity

Galvanic and electrolytic cells



Cell potential and electrolysis

Cell potential and free energy

$$E_{\text{cell}}^{\circ} = E_{\text{cath}}^{\circ} - E_{\text{an}}^{\circ}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

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

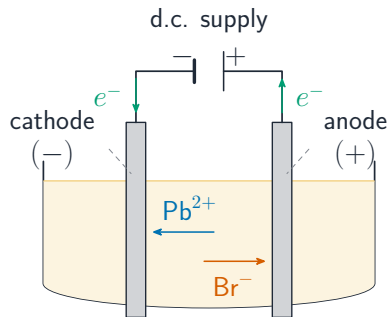
Nernst & Faraday

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

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

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

Cell potential and electrolysis



molten lead(II) bromide, PbBr_2

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

anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2e^-$ (red-brown bromine)

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

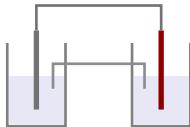
$\Delta G^\circ = -RT \ln K$; couple to drive
uphill steps

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