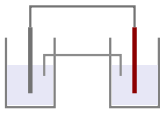
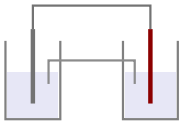
Thermodynamics and Electrochemistry

AP Chemistry ▪ Unit 9

AP Chemistry



What we will cover



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 → liquid → 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 $\Delta S > 0$.

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

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:

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

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

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° ⇒ 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 → mass of metal.

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

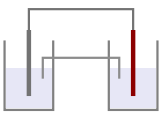
$\Delta G^\circ = -RT \ln K$; couple to drive uphill steps

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