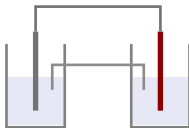


Thermodynamics and Electrochemistry

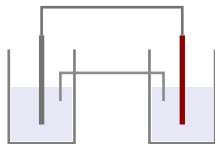
AP Chemistry ■ Unit 9

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 S measures how spread out matter and energy are among **microstates** . $\Delta S > 0$ 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 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.



Gibbs free energy

Favorability depends on **both** energy and entropy:

Gibbs free energy

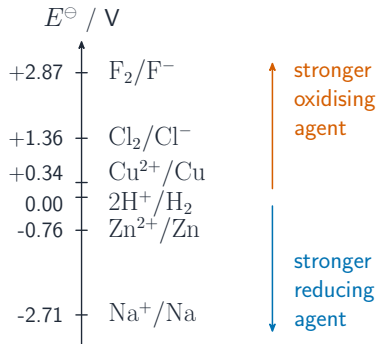
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$\Delta G^\circ < 0$ is **thermodynamically favorable**. 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



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**,
 $\Delta G = 0$ 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

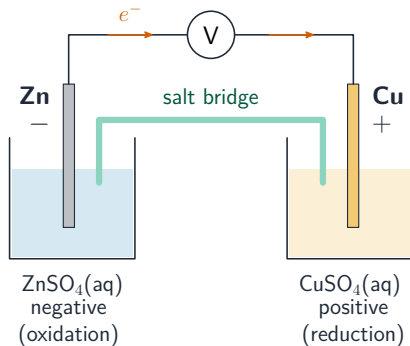
Galvanic : a **spontaneous** redox reaction makes electricity (a battery). **Electrolytic** : an external voltage **drives** a nonspontaneous one.

Oxidation at the **anode** , reduction at the **cathode** . Electrons flow anode $\rightarrow$ 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 ($\Delta G < 0$, $E_{cell}^{\circ} > 0$) 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.



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** : 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

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

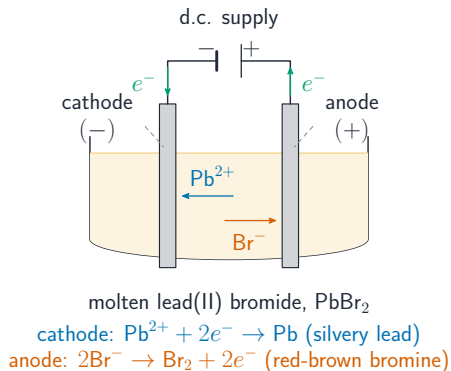
the **charge passed** determines how much substance is deposited – **Faraday's law**

the route

current $\times$ time $\rightarrow$ coulombs $\rightarrow$ moles of electrons $\rightarrow$ moles of substance $\rightarrow$ 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



Electrolysis: ions move to the electrodes and are discharged

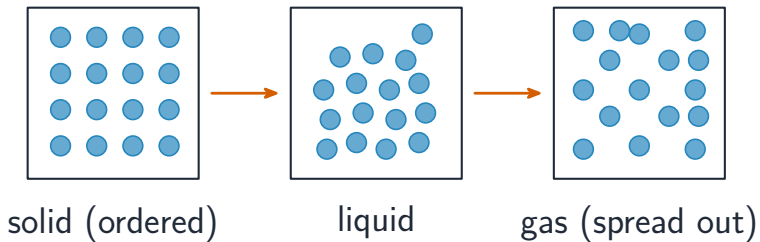
Galvanic and Electrolytic Cells, continued



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 tem- perature
ΔH pos.	feasible only at high tem- perature	never feasible

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

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

Worked example – when does an endothermic reaction go?

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

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

Unfavourable enthalpy,
favourable entropy: **tem-
perature 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).



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

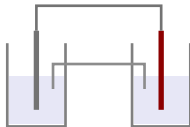
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Cells

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