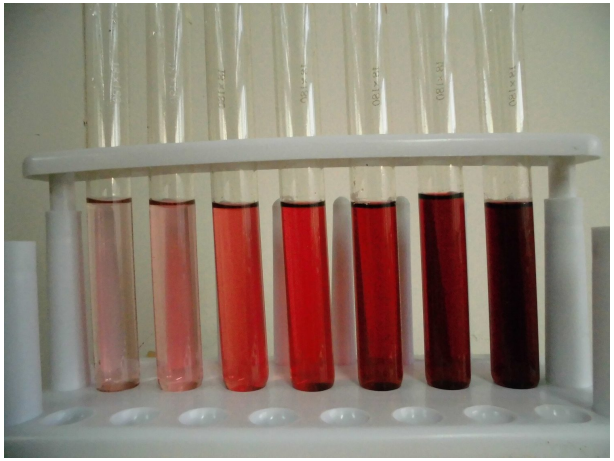
Equilibrium

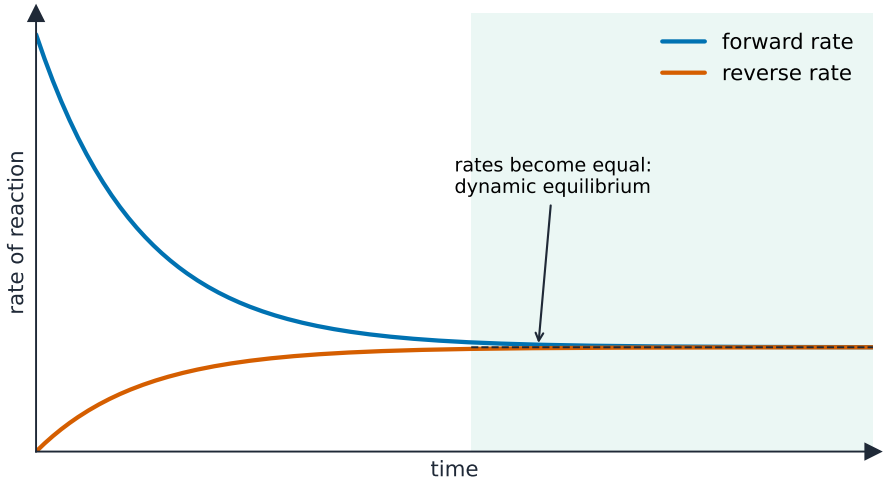
AP Chemistry

Introduction to Equilibrium



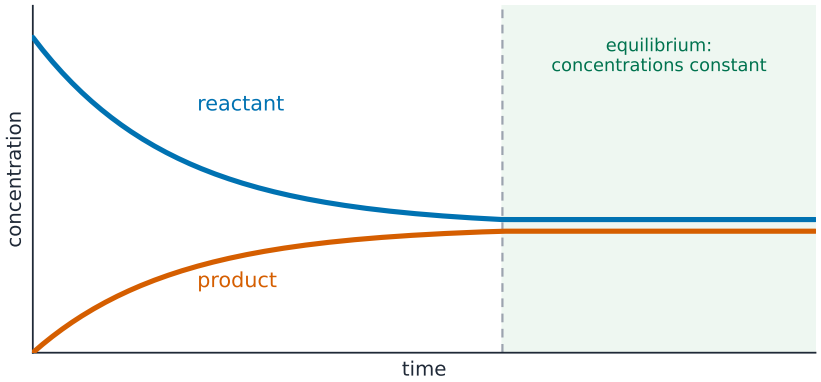
Cobalt chloride solutions: equilibrium systems shift when conditions change (Le Chatelier)

A **reversible reaction** 可逆反应 runs both ways. **Chemical equilibrium** 化学平衡 is reached when the forward and reverse rates become **equal**, so concentrations stop changing. Equilibrium is **dynamic** – both reactions continue, but at matching rates, so nothing appears to change.



Dynamic equilibrium: the forward and reverse rates become equal

The rates graph above explains *why* concentrations settle; this next graph shows *what* the concentrations do – reactants fall and products rise until, once the rates match, both hold constant (they need not be equal).



at equilibrium: $r_f = r_r \cdot K_c = \frac{[\text{products}]}{[\text{reactants}]}$

Reactant and product concentrations change, then hold constant once equilibrium is reached

Direction of Reversible Reactions

At equilibrium the amounts of reactants and products are fixed but usually **not** equal. Whether the mixture favors products or reactants depends on the reaction; you compare the current state to the equilibrium condition to predict which way it shifts.

The Reaction Quotient and Equilibrium Constant

The **reaction quotient** 反应商 Q has the same form as the equilibrium expression but uses **current** concentrations:

$$Q = \frac{[\text{products}]}{[\text{reactants}]} \text{ (each raised to its coefficient).}$$

At equilibrium Q equals the **equilibrium constant** 平衡常数 K. Comparing them predicts direction: $Q < K$ shifts **forward** (toward products); $Q > K$ shifts **reverse**; $Q = K$ means already at equilibrium.

Calculating the Equilibrium Constant

Write K from the balanced equation (pure solids and liquids are left out). From equilibrium concentrations (or partial pressures for K_p), plug in and compute. K_c uses molarities; K_p uses pressures.

Worked example. For $N_2O_4 \rightleftharpoons 2NO_2$, the equilibrium concentrations are $[N_2O_4] = 0.20$ M and $[NO_2] = 0.10$ M. Then

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.10)^2}{0.20} = 0.050.$$

The NO_2 coefficient of 2 becomes the power; N_2O_4 (coefficient 1) is just to the first power.

Magnitude of the Equilibrium Constant

- $K \gg 1$: products strongly favored (reaction nearly complete).
- $K \ll 1$: reactants favored (little reaction).
- $K \approx 1$: significant amounts of both.

The size of K tells you where the equilibrium "sits."

Properties of the Equilibrium Constant

K changes in predictable ways: reversing a reaction **inverts** K $(1/K)$; multiplying coefficients by n raises K to the nth power; adding reactions **multiplies** their K values. Only **temperature** changes the value of K itself.

Calculating Equilibrium Concentrations

Use an **ICE table** (Initial, Change, Equilibrium): fill in starting amounts, express the change with x using the mole ratios, then substitute into the K expression and solve for x. When K is small, the approximation "x is negligible" often simplifies the algebra.

Worked example. For $H_2 + I_2 \rightleftharpoons 2HI$ with $K_c = 50$, start with 0.100 M each of H_2 and I_2. The ICE table gives equilibrium $[H_2] = [I_2] = 0.100 - x$ and $[HI] = 2x$. Substitute:

$$K_c = \frac{(2x)^2}{(0.100-x)^2} = 50 \;\Rightarrow\; \frac{2x}{0.100-x} = \sqrt{50} = 7.07 \;\Rightarrow\; x = 0.078,$$

so $[HI] = 2x = 0.156$ M. Taking the square root of both sides works here because the expression is a perfect square.

Representations of Equilibrium

A particulate picture at equilibrium shows a fixed mix of reactant and product particles. Graphs of concentration vs time level off (never reaching zero) once equilibrium is reached – both curves flatten at the same moment.

Introduction to Le Chatelier's Principle

Le Chatelier's principle 勒沙特列原理: if you disturb a system at equilibrium, it shifts to **partly counteract** the change. Adding a reactant shifts forward; removing product shifts forward; increasing pressure (by reducing volume) shifts toward the side with fewer gas moles; raising temperature shifts in the endothermic direction.

the equilibrium shifts to *oppose* the change you make

increase [reactant] →	towards the **products**
increase pressure →	to the **fewer-gas-molecules** side
increase temperature →	in the **endothermic** direction

a **catalyst** speeds both directions equally, so it gives *no shift*

Le Chatelier's principle: the equilibrium shifts to oppose the change made

An ammonia plant: industrial equilibria like Haber's process are driven by pressure, temperature and catalysts

The Reaction Quotient and Le Chatelier's Principle

You can justify every Le Chatelier shift with Q versus K: a disturbance changes Q, and the system reacts to bring Q back to K. This quantitative view backs up the qualitative rule and is the fuller answer on the exam.

Introduction to Solubility Equilibria

For a slightly soluble salt, the **solubility product** 溶度积 K_{sp} is the equilibrium constant for its dissolving:

$$\mathrm{M}_a\mathrm{X}_b(s) \rightleftharpoons a\,\mathrm{M}^{b+} + b\,\mathrm{X}^{a-}, \qquad K_{sp} = [\mathrm{M}^{b+}]^a[\mathrm{X}^{a-}]^b.$$

A smaller K_{sp} means less soluble. The **common-ion effect** – adding an ion already in the salt – pushes the equilibrium back and **lowers** solubility.

Worked example. Silver chloride has $K_{sp} = 1.8 \times 10^{-10}$. If its molar solubility is s, then $[\mathrm{Ag}^+] = [\mathrm{Cl}^-] = s$, so $K_{sp} = s^2$ and

$$s = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}\ \mathrm{M}.$$

Adding NaCl (a common ion) would raise $[\mathrm{Cl}^-]$, forcing s down – far less AgCl would dissolve.

Exam tips

- At equilibrium the forward and reverse **rates** are equal, but the **amounts** are usually not.
- Leave pure solids and liquids out of the K expression; a large K favours products, a small K favours reactants.
- Apply **Le Chatelier**: add reactant → shift forward; raise pressure → shift toward fewer gas moles; raise temperature → shift in the **endothermic** direction.
- A **catalyst does not shift** the position of equilibrium — it only speeds the approach.
- Use an **ICE table** for equilibrium concentrations, and the small-x approximation when K is small.