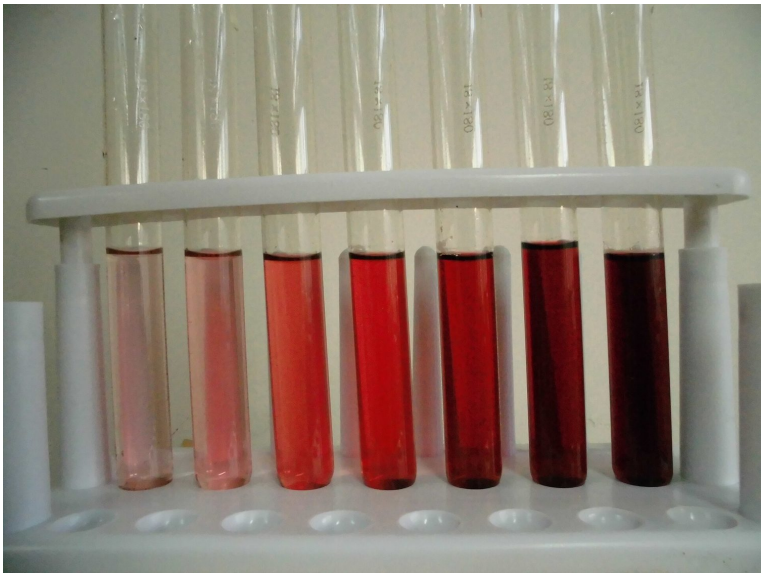
Equilibrium

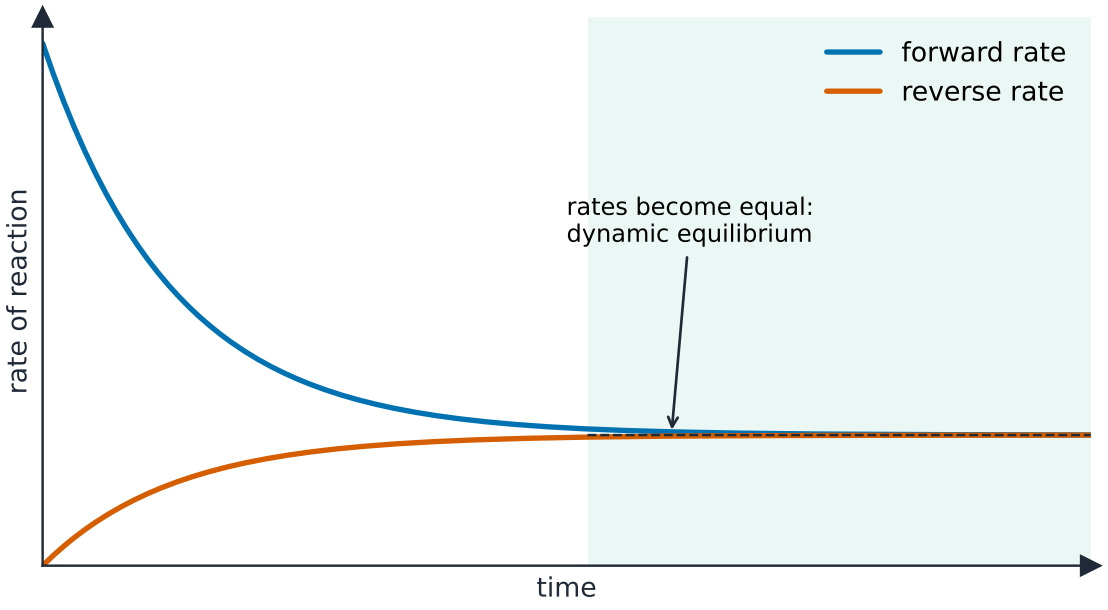
AP Chemistry

Introduction to Equilibrium



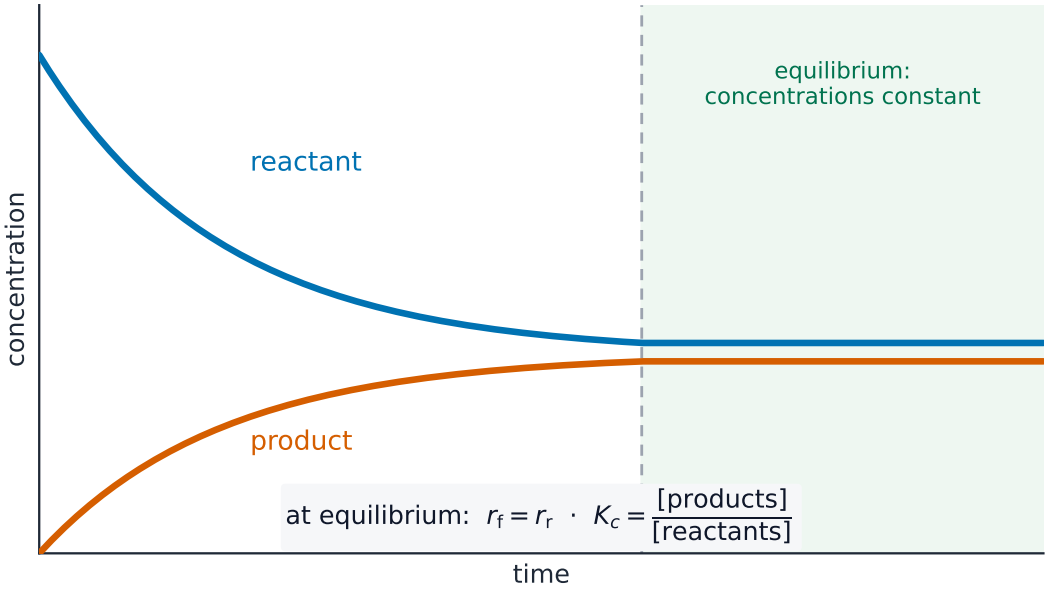
Cobalt chloride solutions: equilibrium systems shift when conditions change (Le Chatelier)

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).



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:

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

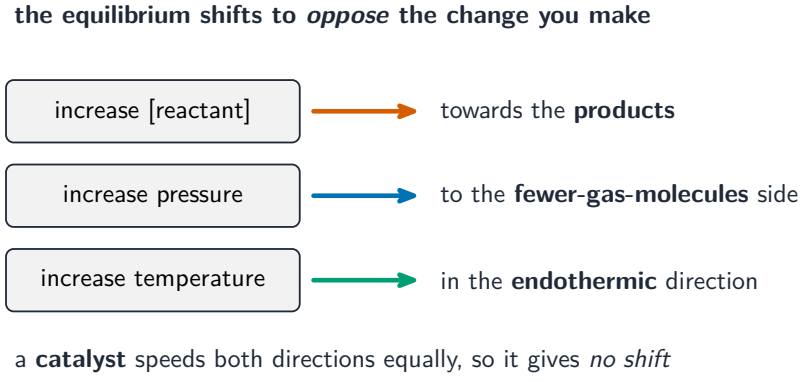
so $[HI] = 2x = 0.156$ M. Taking the square root of both sides works here because the expression is a perfect square.

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.



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.