

Equilibrium constants and shifts

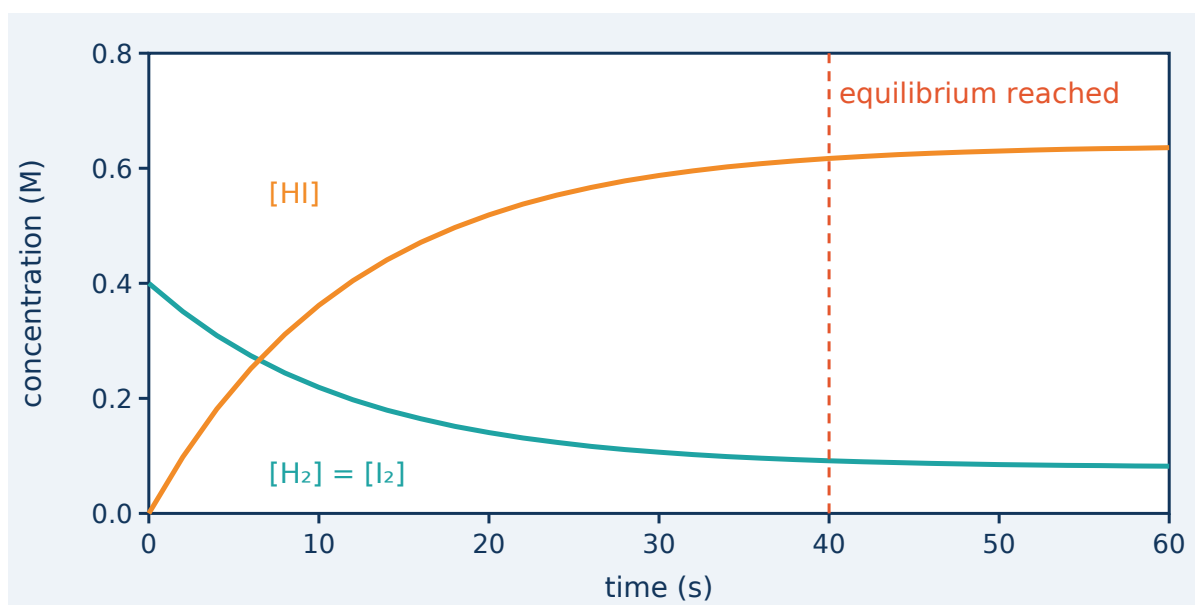
AP Chemistry · Lesson

Quick answer: At chemical equilibrium the forward and reverse reaction rates are equal, so concentrations stay constant. The equilibrium constant K = products over reactants (each raised to its coefficient) depends only on temperature. Comparing Q with K predicts the direction of change, ICE tables find equilibrium concentrations, and Le Chatelier's principle predicts the shift after a disturbance.

Level: AP Chemistry · **Curriculum:** AP Chem Unit 7

What is chemical equilibrium?

Many reactions are reversible: products re-form reactants. In a closed vessel the forward and reverse rates become equal, and the concentrations stay constant even though both reactions continue. This is dynamic equilibrium; nothing looks as if it were happening, but molecules are still reacting.



$H_2 + I_2 \rightleftharpoons 2 HI$: concentrations change, then stay constant when the forward and reverse rates are equal.

Definition

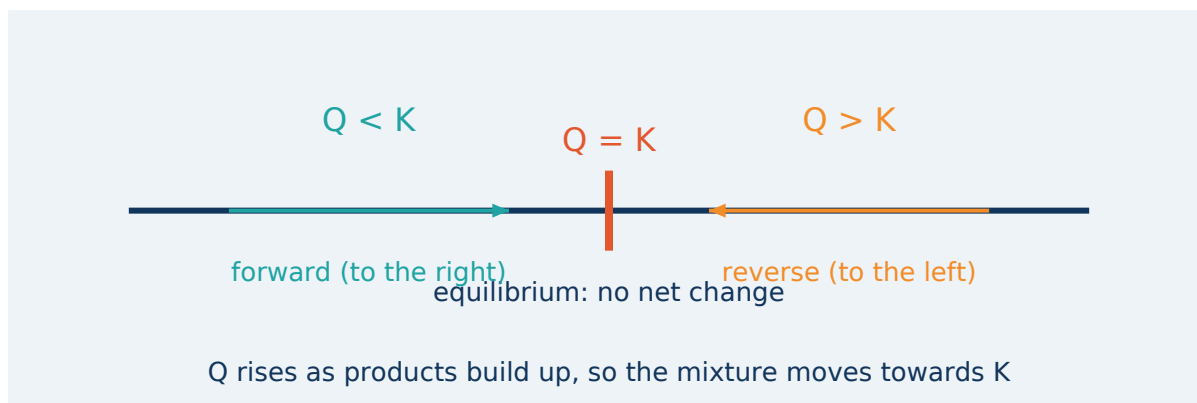
The **equilibrium constant** for $aA + bB \rightleftharpoons cC + dD$ is $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, using equilibrium concentrations in mol/L. Pure solids and pure liquids are left out because their concentration is constant. For gases, K_p uses partial pressures.

The value of K depends only on temperature. A large K (above about 10^3) means products dominate; a small K (below about 10^{-3}) means reactants dominate. If you reverse a reaction, K becomes $1/K$; if you multiply the equation by n , K becomes K^n ; if you add two reactions, you multiply their K values. The two constants are linked by $K_p = K_c(RT)^{\Delta n}$, where Δn is moles of gas

on the right minus moles on the left.

How do you use the reaction quotient Q ?

The reaction quotient Q has the same form as K but uses the concentrations at any moment. Comparing Q with K tells you which way the mixture will move.



Compare Q with K to predict the direction in which a mixture changes.

Worked example 1

Bilal in Lahore has $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$ with $K_c = 0.50$ at a certain temperature. A mixture contains $[\text{H}_2] = 0.40 \text{ M}$, $[\text{CO}_2] = 0.40 \text{ M}$, $[\text{H}_2\text{O}] = 0.30 \text{ M}$ and $[\text{CO}] = 0.30 \text{ M}$.

$$Q = (0.30 \times 0.30)/(0.40 \times 0.40) = 0.0900/0.160 = 0.56.$$

Since $Q > K$, there are too many products: the reaction shifts **in reverse** (to the left).

How do you solve an ICE table?

An ICE table lists Initial, Change and Equilibrium concentrations. Let the change be x , scaled by the coefficients, then substitute the equilibrium row into K . If the equation is a perfect square, take square roots; otherwise use the quadratic formula, or an approximation when K is very small and x is under 5 % of the initial value.

Worked example 2

For $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$, $K_c = 64$. Start with 0.40 M H_2 and 0.40 M I_2 and no HI.

Change: $\text{H}_2 -x$, $\text{I}_2 -x$, $\text{HI} +2x$. Then $(2x)^2/(0.40 - x)^2 = 64$, so $2x/(0.40 - x) = 8$, which gives $2x = 3.2 - 8x$ and $x = 0.32$.

$[\text{H}_2] = [\text{I}_2] = 0.08 \text{ M}$ and $[\text{HI}] = \mathbf{0.64 \text{ M}}$. Check: $0.64^2/0.08^2 = 64 \checkmark$.

Worked example 3

$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ has $K_c = 0.20$. Start with $0.50 \text{ M N}_2\text{O}_4$ only.

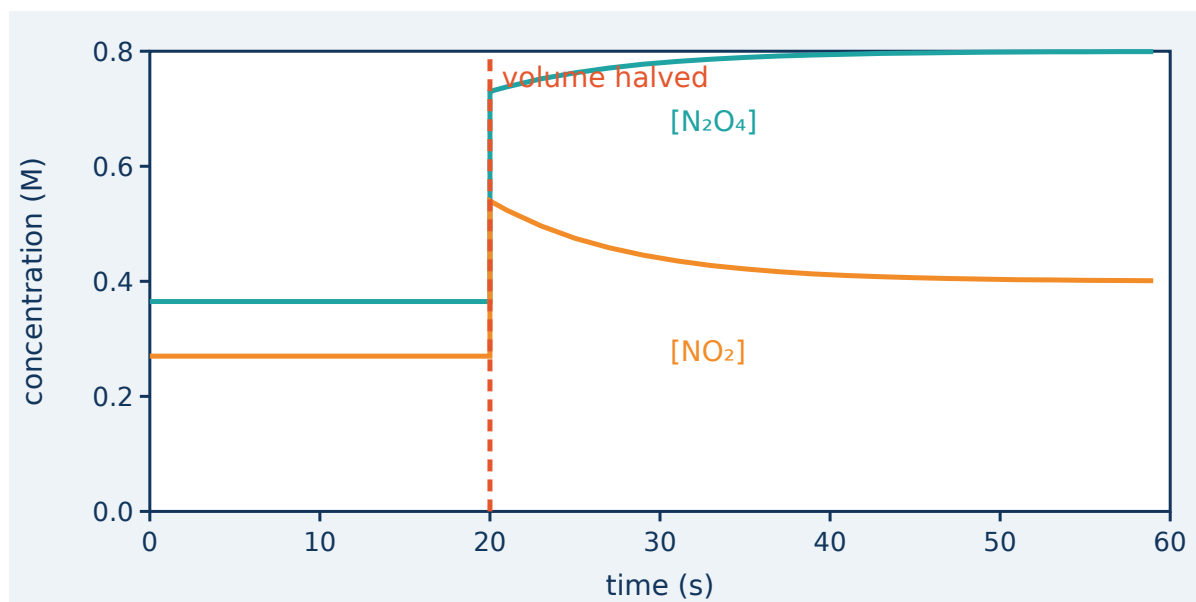
$(2x)^2/(0.50 - x) = 0.20$, so $4x^2 + 0.20x - 0.10 = 0$. The quadratic formula gives $x = [-0.20 + \sqrt{(0.04 + 1.60)}/8 = 0.135$.

$[\text{NO}_2] = 2x = \mathbf{0.27 \text{ M}}$ and $[\text{N}_2\text{O}_4] = 0.50 - 0.135 = \mathbf{0.365 \text{ M}}$. Check: $0.270^2/0.365 = 0.20 \checkmark$.

What does Le Chatelier's principle predict?

When a system at equilibrium is disturbed, it shifts to partly oppose the change. Only a change in temperature alters K ; other disturbances change Q and the system moves until $Q = K$ again.

Disturbance	Shift	Does K change?
Add reactant or remove product	To the right	No
Add product or remove reactant	To the left	No
Compress (smaller volume)	Towards fewer moles of gas	No
Raise temperature	In the endothermic direction	Yes
Add catalyst or inert gas (constant volume)	No shift	No



After compression, Q is greater than K , so the system shifts towards fewer moles of gas (N_2O_4).

Worked example 4

The equilibrium mixture of Example 3 is $[\text{N}_2\text{O}_4] = 0.365$ M and $[\text{NO}_2] = 0.270$ M. The volume is halved at constant temperature. Concentrations double at once: 0.730 M and 0.540 M.

$Q = 0.540^2/0.730 = 0.40 > K = 0.20$, so the system shifts left, towards the side with fewer moles of gas. The new equilibrium is $[\text{N}_2\text{O}_4] = 0.80$ M and $[\text{NO}_2] = 0.40$ M, which satisfies $0.40^2/0.80 = 0.20 \checkmark$.

Common mistake

A catalyst does not shift an equilibrium or change K : it speeds up both directions equally. Also, adding an inert gas at constant volume does not change the partial pressures, so nothing shifts. And remember that K only changes with temperature, even when the position of the equilibrium moves.

Lina's tip

When a problem says “predict the shift”, compute Q whenever you have numbers. Q below K means the forward reaction runs; Q above K means the reverse reaction runs. It works for every disturbance, not only for concentrations.

Key points to remember

- $K = \frac{\text{coefficients}}{\text{coefficients}}$; solids and pure liquids are omitted.
- $Q < K$: forward reaction; $Q > K$: reverse reaction; $Q = K$: equilibrium.
- $K_p = K_c(RT)^{\Delta n}$, with $\Delta n = \text{moles of gas products} - \text{moles of gas reactants}$.
- Reversing a reaction gives $1/K$; multiplying by n gives K^n ; adding reactions multiplies K .
- Only temperature changes K ; catalysts and inert gases do not shift the equilibrium.

Equilibrium constants and shifts: frequently asked questions

Does equilibrium mean the concentrations are equal?

No. At equilibrium the rates are equal and the concentrations are constant, but they are usually different. The size of K tells you which side is favoured.

Why are solids not included in K ?

The concentration of a pure solid or liquid is fixed by its density, so it does not change during the reaction. It is absorbed into the value of K .

What is the difference between Q and K ?

Q uses the concentrations at any moment, while K uses only equilibrium concentrations. Comparing them shows which direction the reaction will move.

How does temperature change K ?

Increasing the temperature favours the endothermic direction. K rises for an endothermic reaction and falls for an exothermic one.

When can you use the small- x approximation?

When K is very small compared with the initial concentration, so x is under about 5 % of it. Always check the assumption after you have solved.