

Equilibrium constants and shifting equilibria

Chemistry grades 11-12 (A Level · IB · Class 11-12) · Lesson

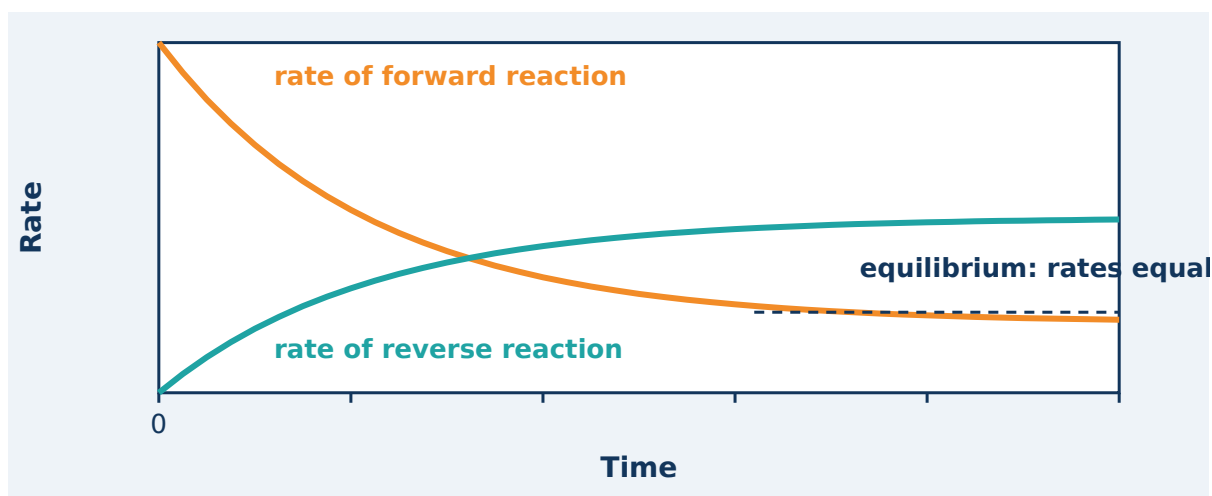
Quick answer: Chemical equilibrium is reached when forward and reverse reactions occur at the same rate, so concentrations stay constant. The equilibrium constant K_c , products over reactants raised to their coefficients, depends only on temperature. Le Chatelier's principle predicts the direction of shift when concentration, pressure or temperature changes.

Level: Chemistry grades 11-12 (A Level · IB · Class 11-12) · **Curriculum:** IB R2.3

What is a dynamic equilibrium?

Definition

A dynamic equilibrium is the state of a reversible reaction in a closed system in which the forward and reverse reactions occur at equal rates, so the concentrations of all species stay constant. Both reactions continue; nothing stops.



The two rates become equal at equilibrium; both reactions continue.

How do you write and use K_c ?

Formula

For $aA + bB \rightleftharpoons cC + dD$: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Concentrations are equilibrium values in mol/dm^3 ; K_c depends only on temperature. Pure solids and liquids are left out of the expression.

Equilibrium	K_c expression	Units of K_c
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	$[\text{NO}_2]^2 / [\text{N}_2\text{O}_4]$	mol dm^{-3}
$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$	$[\text{HI}]^2 / ([\text{H}_2][\text{I}_2])$	none

Equilibrium	Kc expression	Units of Kc
$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$	$[\text{NO}_2]^2 / ([\text{NO}]^2[\text{O}_2])$	$\text{dm}^3 \text{mol}^{-1}$
$\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	$[\text{CO}_2]$	mol dm^{-3}

Worked example

1.00 mol of H_2 and 1.00 mol of I_2 react in a 2.0 dm^3 vessel at 720 K. At equilibrium 1.56 mol of HI is present. Calculate Kc.

HI formed = 1.56 mol, which used 0.78 mol of each reactant. Remaining H_2 and I_2 = 0.22 mol each. Concentrations: $[\text{HI}] = 0.78$, $[\text{H}_2] = [\text{I}_2] = 0.11 \text{ mol/dm}^3$. $K_c = 0.78^2 / (0.11 \times 0.11) = 0.6084 / 0.0121 = \mathbf{50.3}$ (no units).

A large Kc (above 10^3) means the equilibrium mixture is mostly products. A small Kc (below 10^{-3}) means mostly reactants. Values near 1 give a mixture of both.

What is Kp for gas equilibria?

Kp has the same form as Kc but uses partial pressures. The partial pressure of a gas is its mole fraction times the total pressure: $p(\text{A}) = x(\text{A}) \times P$.

Worked example

1.00 mol of N_2O_4 is 20 % dissociated into NO_2 at a total pressure of 100 kPa. Calculate Kp for $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$.

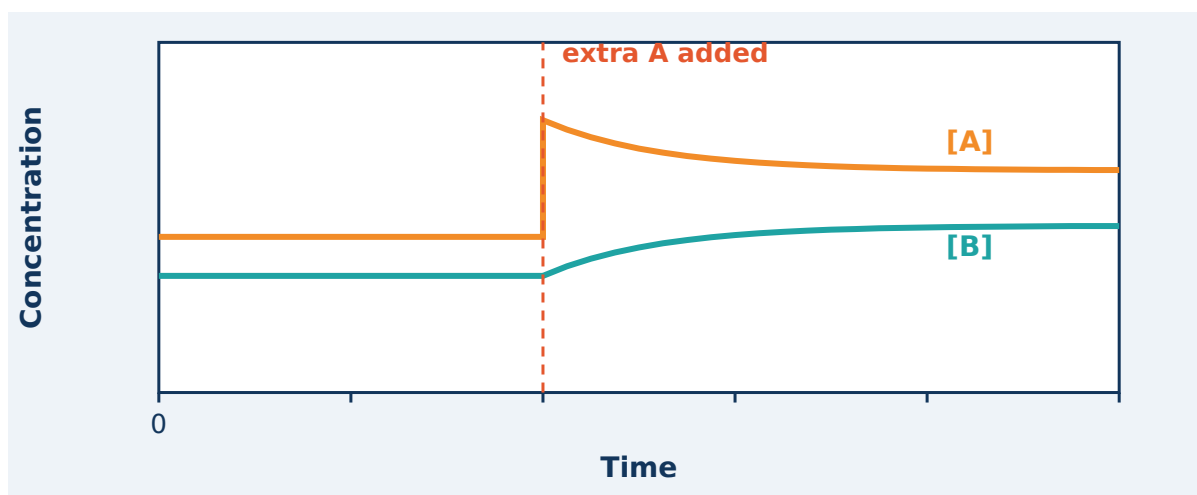
Moles: $\text{N}_2\text{O}_4 = 0.80$, $\text{NO}_2 = 0.40$, total 1.20. Mole fractions: 0.667 and 0.333. Partial pressures: 66.7 kPa and 33.3 kPa. $K_p = p(\text{NO}_2)^2 / p(\text{N}_2\text{O}_4) = 33.3^2 / 66.7 = \mathbf{16.7 \text{ kPa}}$.

How does Le Chatelier's principle predict shifts?

Key law

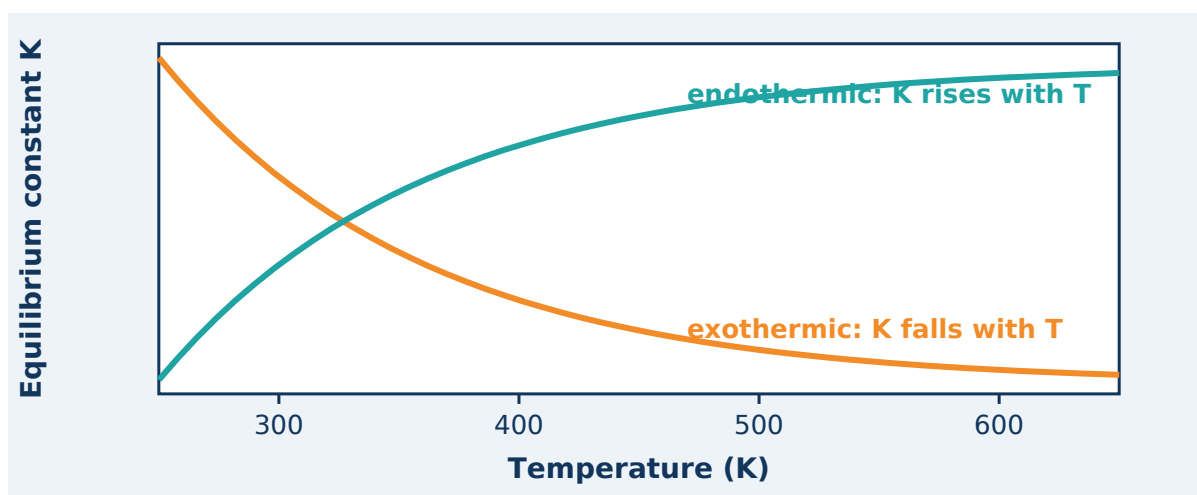
Le Chatelier's principle: when a change is made to a system at equilibrium, the position of equilibrium shifts to oppose the change. The reaction quotient Q, calculated like Kc with current concentrations, tells you the direction: if Q is less than K the reaction goes right, and if Q is greater than K it goes left.

Change	Shift of equilibrium	Effect on K
Add reactant or remove product	to the right	none
Increase pressure (gas)	to the side with fewer gas moles	none
Raise temperature, forward ΔH positive	to the right	K increases
Raise temperature, forward ΔH negative	to the left	K decreases
Add a catalyst	no shift	none



After extra A is added the system shifts to the right and settles at a new equilibrium.

Temperature is the only factor that changes the value of K . A rise in temperature favours the endothermic direction, so K increases for a positive forward ΔH and decreases for a negative one.



Temperature is the only change that alters the value of K .

Common mistake

A catalyst does not change K or the position of equilibrium. It speeds up both reactions equally so equilibrium is reached sooner. Changing concentration or pressure shifts the position, but K_c stays the same.

Lina's tip

Use an ICE table: Initial, Change, Equilibrium. Write the change using the mole ratio from the balanced equation, then substitute the equilibrium line into K_c .

Key points to remember

- At dynamic equilibrium the forward and reverse rates are equal and concentrations are constant.
- $K_c = \frac{\text{coefficients}}{\text{coefficients}}$; solids and pure liquids are omitted.
- K_p uses partial pressures: $p = \text{mole fraction} \times \text{total pressure}$.

- Only a change in temperature changes the value of K ; catalysts do not.
- If Q is less than K the reaction shifts right; if Q is greater than K it shifts left.

Equilibrium constants and shifting equilibria: frequently asked questions

What does the equilibrium constant K_c tell you?

K_c shows how far a reversible reaction goes at a given temperature. A large value means mostly products at equilibrium, and a small value means mostly reactants.

Why are solids not included in the K_c expression?

The concentration of a pure solid or liquid is constant, so it does not change with the amount present. It is absorbed into the value of K and left out of the expression.

How does temperature change the value of K ?

For an endothermic forward reaction K increases as temperature rises, and for an exothermic forward reaction K decreases. Concentration, pressure and catalysts do not change K .

How do you find the direction of shift with Q ?

Calculate the reaction quotient Q with the current concentrations. If Q is less than K the system moves to the right to form more products, and if Q is greater than K it moves to the left.

What is the difference between K_c and K_p ?

K_c uses equilibrium concentrations in mol/dm^3 , whereas K_p uses partial pressures of gases. Both are constant at a given temperature and have the same form.