Chemical equilibria

Equilibrium constants Kc and Kp, calculations from data, what changes the equilibrium constant, and the link between equilibrium constant and total entropy change.

The equilibrium constant Kc

For a reaction $aA + bB \rightleftharpoons cC + dD$ at equilibrium:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

with **equilibrium concentrations** in mol dm^{-3}. Units depend on the equation, and are found by substituting units into the expression.

For a **heterogeneous** equilibrium, solids (and pure liquids) are not included in the expression, because their concentration is constant. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_c = [CO_2]$.

The equilibrium constant Kp

For gaseous equilibria use **partial pressures**. The partial pressure of a gas is its mole fraction times the total pressure:

$$p_A = x_A \times P_{total} \qquad x_A = \frac{n_A}{n_{total}}$$

$$K_p = \frac{p_C^c\, p_D^d}{p_A^a\, p_B^b}$$

(pressures in atm, as the question states; units depend on the equation).

> **TRY IT**
>
> For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, 1.00 mol of N_2O_4 is 20% dissociated at equilibrium at a total pressure of 1.00 atm. Find K_p.

At equilibrium: N_2O_4 0.80 mol, NO_2 0.40 mol, total 1.20 mol. $p(N_2O_4) = (0.80/1.20) \times 1.00 = 0.667$ atm. $p(NO_2) = 0.333$ atm. $K_p = \dfrac{0.333^2}{0.667} = 0.167$ atm.

Calculations from experimental data

1. Write the balanced equation and the expression for K.
2. Make a table of **initial moles, change and equilibrium moles**, using the reaction ratio.
3. Convert to concentrations (divide by volume) or partial pressures.
4. Substitute into the expression, and work out the units.

Note Academy

TRY IT

1.00 mol of ethanoic acid and 1.00 mol of ethanol react in a total volume of V dm^3 to give ethyl ethanoate and water. At equilibrium 0.667 mol of ester is present. Find K_c.

The equation $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ has the same number of moles on each side, so V cancels. At equilibrium, acid and alcohol are each $1.00 - 0.667 = 0.333$ mol and ester and water are each 0.667 mol. $K_c = \dfrac{0.667 \times 0.667}{0.333 \times 0.333} = 4.0$ (no units).

What changes K and what does not

Change	Effect on equilibrium position	Effect on K
Concentration	Shifts to oppose the change	**None**
Pressure	Shifts to the side with fewer moles of gas (if different)	**None**
Catalyst	None, the rate to reach equilibrium is faster	**None**
Temperature	Shifts	**Changes**

Temperature

- For an **exothermic** reaction, raising the temperature **decreases** K, so the position moves to the left.
- For an **endothermic** reaction, raising the temperature **increases** K, so the position moves to the right.

The position of equilibrium changes with temperature because the value of the equilibrium constant changes. With concentration or pressure changes, the constant stays the same and the concentrations adjust to restore it.

If a reactant concentration is increased, the system is no longer at equilibrium: the ratio is less than K, and the reaction goes forward until the ratio equals K again.

The link with entropy

For a reaction at equilibrium, the total entropy change is related to K:

$$\Delta S_{total} = R \ln K$$

- If K is **large**, $\ln K$ is positive, so ΔS_{total} is positive and the reaction goes essentially to completion.
- If K is **small**, ΔS_{total} is negative and little product forms.
- $K \approx 1$ means about equal amounts.

Note Academy

This links with temperature. $\Delta S_{total} = \Delta S_{system} - \Delta H/T$, so for an **exothermic** reaction a higher temperature reduces the magnitude of $-\Delta H/T$, so ΔS_{total} falls, $\ln K$ falls and K decreases. The reverse applies to an endothermic reaction.

Predicting the extent of reaction

Value of K	Extent
$K \gg 1$ (e.g. 10^{10})	Almost complete
$K \approx 1$	Reactants and products both significant
$K \ll 1$ (e.g. 10^{-10})	Hardly any reaction

> **NOTE**
>
> K says nothing about the **rate**. A reaction with a large K may be extremely slow without a catalyst.

Suggested practicals include the equilibrium between ethanol and ethanoic acid (with an acid catalyst, followed by titration), the Fe^{2+}/Ag^{+} system, and the distribution of iodine between two immiscible solvents.

Note Academy