

Equilibria

A-Level Chemistry 9701 · Topic 7 revision notes

Everything from the 5 lessons of this topic on a few pages: the key idea of each lesson, the diagram to remember, the points to learn and the traps examiners set. Read it, cover it, test yourself.

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|--|---|
| 1. <u>Dynamic equilibrium and Le Chatelier's principle</u> | 3. <u>The equilibrium constant K_p</u> |
| 2. <u>The equilibrium constant K_c</u> | 4. <u>Brønsted-Lowry acids and bases</u> |
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1 Dynamic equilibrium and Le Chatelier's principle

Syllabus 7.1

In a **closed system** a reversible reaction reaches **dynamic equilibrium**: the forward and reverse reactions continue at **equal rates**, so the concentrations stay constant. **Le Chatelier's principle**: if a condition of a system at equilibrium is changed, the position of equilibrium shifts to **minimise** the change. Adding a reactant shifts it right; raising the pressure shifts it towards fewer gas molecules; raising the temperature shifts it in the **endothermic** direction. A catalyst speeds up both reactions equally, so it does not move the position; it only gets there faster.

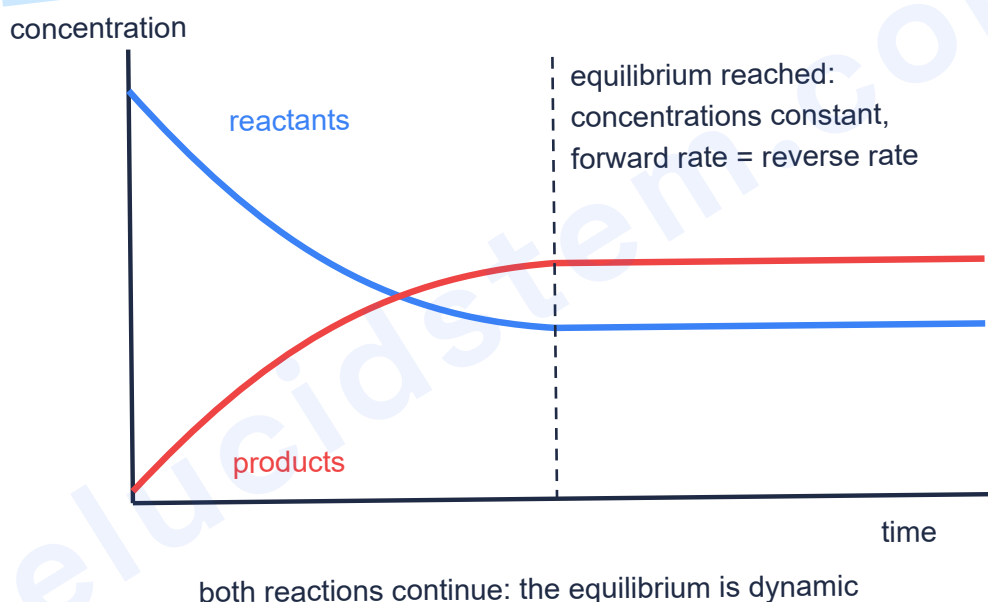


Fig. 1: concentrations level off once the forward and reverse rates are equal

The system opposes the change.

- ✓ **Dynamic:** equal rates, constant concentrations, closed system.
- ✓ **Pressure:** count moles of gas on each side.
- ✓ **Temperature:** heating favours the endothermic direction.
- ✓ **Catalyst:** no shift, faster to equilibrium.

Watch out!

A catalyst does **not** change the position of equilibrium or the yield; it increases the rate of the forward and reverse reactions equally. And when explaining a pressure change, always count the **moles of gas** on each side of the equation; if they are equal, pressure has no effect on the position.

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2 The equilibrium constant K_c

Syllabus 7.1

For $aA + bB \rightleftharpoons cC + dD$, $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$, using **equilibrium** concentrations in mol dm^{-3} . Products go on top, and each concentration is raised to the power of its coefficient. The units come from cancelling the concentration units, and may be none at all. A large K_c means the position lies to the right. K_c changes **only with temperature**; concentration, pressure and catalysts leave it unchanged.



amount / mol	PCl_5	PCl_3	Cl_2
initial	0.500	0	0
change	-0.200	+0.200	+0.200
equilibrium	0.300	0.200	0.200
$\div 2.00 \text{ dm}^3$	0.150	0.100	0.100

$$K_c = (0.100 \times 0.100) \div 0.150 = 0.0667 \text{ mol dm}^{-3}$$

Fig. 1: finding K_c from initial amounts with an initial, change, equilibrium table

Products over reactants, powers from the equation.

- ✓ **Equilibrium** concentrations only.
- ✓ **Table:** initial, change, equilibrium, then $\div$ volume.
- ✓ **Units:** cancel mol dm^{-3} each time.
- ✓ **Only temperature** changes K_c .

Watch out!

Use **equilibrium** concentrations, not initial amounts, and convert moles to concentrations by dividing by the volume unless the volumes cancel. Products always go on top. Work out the units separately each time by cancelling, rather than guessing.

3 The equilibrium constant K_p

Syllabus 7.1

The **partial pressure** of a gas is the pressure it would exert alone in the container: $p = \text{mole fraction} \times \text{total pressure}$, where $\text{mole fraction} = \text{moles of that gas} \div \text{total moles of gas}$. The partial pressures add up to the total pressure. K_p is written like K_c but with partial pressures: for $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$, $K_p = p(\text{NO}_2)^2 \div p(\text{N}_2\text{O}_4)$. Units come from the pressure units (Pa, kPa or atm). Like K_c , K_p changes only with temperature.

$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ total pressure 100 kPa

N_2O_4 0.80 mol

NO_2 0.40 mol

mole fraction: $0.80 \div 1.20 = 0.667$

$0.40 \div 1.20 = 0.333$

partial pressure: 66.7 kPa

33.3 kPa

$$K_p = p(\text{NO}_2)^2 \div p(\text{N}_2\text{O}_4) = 33.3^2 \div 66.7 = 16.7 \text{ kPa}$$

partial pressure = mole fraction $\times$ total pressure

Fig. 1: from equilibrium amounts to mole fractions, partial pressures and

K_p

Moles, fractions, pressures, then K_p .

- ✓ **Mole fraction** = $n \div \text{total equilibrium moles}$.
- ✓ **Partial pressure** = mole fraction $\times$ total pressure.
- ✓ **Units** from the pressure unit, cancelled like K_c .
- ✓ **Only temperature** changes K_p .

Watch out!

Partial pressure uses the mole fraction of the **equilibrium** mixture, so first find the equilibrium moles and the new total. A common slip is dividing by the initial number of moles. Also remember that increasing the total pressure changes the position of equilibrium but **not** the value of K_p .

4 Brønsted-Lowry acids and bases

Syllabus 7.2

A **Brønsted-Lowry acid** is a **proton (H^+) donor**; a **base** is a **proton acceptor**. When an acid donates a proton it becomes its **conjugate base**; when a base accepts one it becomes its **conjugate acid**. Each pair differs by one H^+ . A **strong acid** dissociates **fully** in water (HCl , HNO_3 , H_2SO_4); a **weak acid** dissociates only **partially**, setting up an equilibrium (CH_3COOH). Strength is about the extent of dissociation, not concentration.

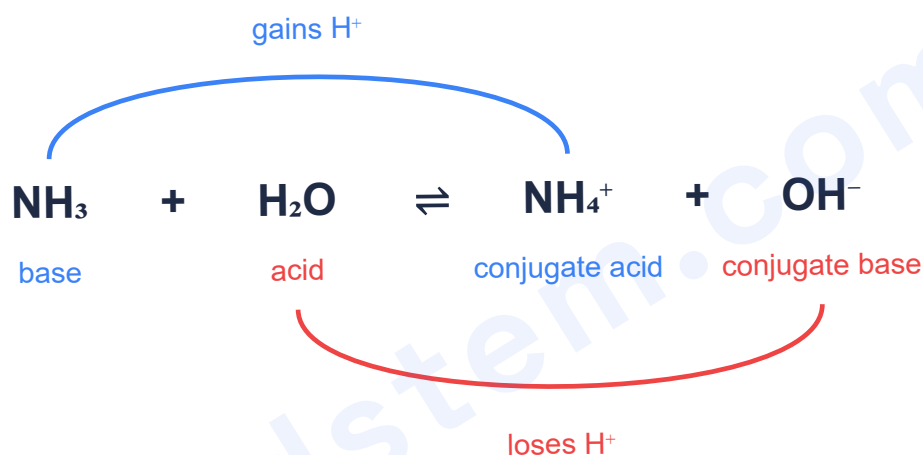


Fig. 1: the two conjugate acid-base pairs when ammonia reacts with water

Acid gives H^+ ; base takes it.

- ✓ **Conjugate pairs** differ by one H^+ .
- ✓ **Water** can act as acid or base.
- ✓ **Strong** = fully dissociated; **weak** = partially.
- ✓ **Strong $\neq$ concentrated.**

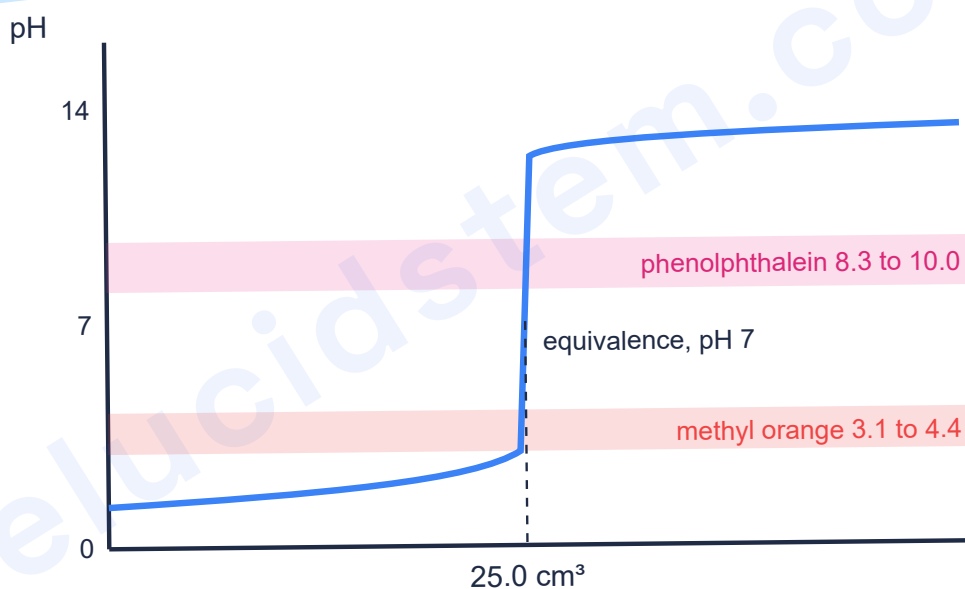
Watch out!

Strong and **concentrated** mean different things. Strong means fully dissociated; concentrated means a lot of acid per dm^3 . A dilute solution of HCl is still a strong acid. Also, in a conjugate pair the formulae differ by exactly one H^+ : the conjugate base of H_2SO_4 is HSO_4^- , not SO_4^{2-} .

5 pH, strong and weak acids, titration curves

Syllabus 7.2

$\text{pH} = -\log_{10}[\text{H}^+]$. For a strong monobasic acid, $[\text{H}^+]$ equals the acid concentration, so $0.0100 \text{ mol dm}^{-3}$ HCl has pH 2.00; each tenfold dilution raises the pH by one. A **titration curve** plots pH against volume added. Near the equivalence point the pH changes sharply, and the vertical section sits around pH 7 for strong acid/strong base, below 7 for strong acid/weak base, and above 7 for weak acid/strong base. A suitable **indicator** must change colour entirely within that vertical section: methyl orange (3.1 to 4.4) for strong acid/weak base, phenolphthalein (8.3 to 10.0) for weak acid/strong base, either for strong/strong, and none for weak/weak.



strong acid titrated with strong base: both indicators work

Fig. 1: titration curve for 25.0 cm^3 of a strong acid with a strong base of equal concentration

The indicator must change within the jump.

- ✓ **pH = $-\log[H^+]$** ; strong acid $[H^+] =$ concentration.
- ✓ **Strong/weak base:** equivalence below 7, methyl orange.
- ✓ **Weak acid/strong base:** above 7, phenolphthalein.
- ✓ **Weak/weak:** no sharp end point.

Watch out!

The equivalence point is where the acid and base have reacted in exactly the ratio of the equation; it is **not** always pH 7. And the end point of an indicator is where it changes colour, which is only a good estimate of equivalence if the indicator's range lies inside the steep part of the curve.

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