Equilibria

Dynamic equilibrium and Le Chatelier's principle, Kc and Kp calculations, the Haber and Contact processes, and Brønsted–Lowry acids and bases, strong and weak, neutralisation and titration curves.

7.1 Chemical equilibria: reversible reactions, dynamic equilibrium

A **reversible reaction** can go in both directions, shown by ⇌. **Dynamic equilibrium** is reached when the **rate of the forward reaction equals the rate of the reverse reaction**, so the concentrations of reactants and products stay constant. It needs a **closed system**, where nothing can enter or leave.

Le Chatelier's principle

If a change is made to a system at dynamic equilibrium, the position of equilibrium moves to minimise the change.

Change	Effect on the position
Increase concentration of a reactant	Moves right, using up the reactant
Increase pressure	Moves to the side with fewer gas molecules
Increase temperature	Moves in the **endothermic** direction
Add a catalyst	No change in position; equilibrium is reached faster

The equilibrium constant, K_c

For $aA + bB \rightleftharpoons cC + dD$:

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

with equilibrium concentrations in mol dm^{-3}. Find the **units** by substituting units into the expression. Solids are left out of the expression.

Partial pressures and K_p

The **mole fraction** of a gas is $x_A = n_A/n_{total}$ and its **partial pressure** is $p_A = x_A \times p_{total}$. For gases:

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

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Units follow from the pressure units, for example $\text{Pa}^{\Delta n}$ where Δn is the change in the number of moles of gas.

> **TRY IT**
>
> In a 1.00 dm³ vessel, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium contains 0.50 mol N_2, 1.50 mol H_2 and 1.00 mol NH_3. Find K_c.

$$K_c = \frac{(1.00)^2}{(0.50)(1.50)^3} = 0.59 \text{ mol}^{-2} \text{ dm}^6.$$

Use an **ICE table** (initial, change, equilibrium) for calculations; none need a quadratic equation.

What changes K?

Only **temperature** changes the value of K_c or K_p. Concentration, pressure and a catalyst do not. For an exothermic reaction, K decreases when temperature rises.

Industrial examples

	Haber process	Contact process
Reaction	$N_2 + 3H_2 \rightleftharpoons 2NH_3$ ($\Delta H = -92$ kJ mol^{-1})	$2SO_2 + O_2 \rightleftharpoons 2SO_3$ ($\Delta H = -196$ kJ mol^{-1})
Conditions	About 450 °C, 200 atm, iron catalyst	About 450 °C, 1–2 atm, V_2O_5 catalyst

A **compromise** is used. A low temperature would favour the exothermic forward reaction, but the rate would be too slow, so about 450 °C is used with a catalyst. High pressure favours fewer gas molecules (Haber), but is expensive, so a moderate pressure is chosen. In the Contact process the yield is already high at about 1–2 atm, so higher pressure is not worth the cost. Unreacted gas is recycled in the Haber process.

What happens while equilibrium is being established?

Starting with reactants alone, the forward reaction is initially fastest and the reverse reaction cannot occur until products form. As reactants are consumed, forward rate falls; as products accumulate, reverse rate rises. At equilibrium the two rates become equal and non-zero. A concentration–time graph levels out for each species, while a rate–time graph shows the two rates meeting. Equal rates do **not** require equal concentrations: a product-favoured equilibrium can contain much more product than reactant.

The closed-system condition prevents material from being lost or added during the equilibrium experiment. A sealed vessel can still exchange heat with its surroundings. Removing a gaseous product

Note Academy

from an open vessel may favour continued forward reaction rather than allow the original equilibrium composition to persist.

Predicting disturbances carefully

After adding a reactant, its concentration first rises because of the addition; subsequent reaction uses some of it. On a concentration–time graph, distinguish this immediate jump from the gradual shift to a new equilibrium. Compressing a gas mixture immediately increases all gas concentrations or partial pressures, then the equilibrium may shift towards fewer gas molecules. If both sides have equal numbers of gaseous moles, pressure does not favour either side.

Temperature changes alter both rates, but by different factors, and also change the equilibrium constant. A catalyst accelerates both directions without changing the equilibrium composition. Therefore “higher temperature” and “a catalyst” cannot be treated as interchangeable ways of increasing yield.

> **TRY IT**
>
> For $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, predict the effect of compression at constant temperature on equilibrium yield.

Answer: No shift is predicted because each side has two gaseous moles. All partial pressures increase, but their ratio in K_p remains consistent with the same composition. The reaction may reach equilibrium faster after compression.

A complete initial–change–equilibrium calculation

Worked example: 1.00 mol ethanoic acid and 1.00 mol ethanol are mixed with no initial ester or water. At equilibrium, 0.600 mol ester has formed in a 1.00 dm^3 mixture. Treat this as an illustrative homogeneous equilibrium:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Amount / mol	Acid	Alcohol	Ester	Water
Initial	1.00	1.00	0	0
Change	−0.600	−0.600	+0.600	+0.600
Equilibrium	0.400	0.400	0.600	0.600

Here $K_c = (0.600 \times 0.600)/(0.400 \times 0.400) = 2.25$, without units because equal numbers of concentration factors occur above and below the fraction. Water is included as a reacting component of this liquid mixture; do not omit it automatically just because it is a liquid. Pure solids and pure-liquid phases are treated differently from variable concentrations in a homogeneous mixture.

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If the vessel volume were not 1.00 dm³, convert each equilibrium mole amount to concentration before substitution. Volume factors cancel only when the expression contains the same total powers in numerator and denominator. This cancellation is a result to demonstrate, not a rule to assume for every reaction.

> **TRY IT**
>
> At equilibrium, a 2.00 dm³ vessel contains 0.400 mol A, 0.400 mol B and 0.800 mol C for $A + B \rightleftharpoons C$. Find K_c and its units.

Answer: Concentrations are 0.200, 0.200 and 0.400 mol dm^{-3}. $K_c = 0.400/(0.200 \times 0.200) = 10.0$ dm³ mol^{-1}. Substituting the mole amounts directly gives an incorrect result because the volume factors do not cancel.

Partial-pressure calculations

Worked example: for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, a mixture contains 0.300 mol N_2O_4 and 0.400 mol NO_2 at a total pressure of 140 kPa. Total moles are 0.700. Therefore $p(N_2O_4) = (0.300/0.700)(140) = 60.0$ kPa and $p(NO_2) = 80.0$ kPa. Then $K_p = 80.0^2/60.0 = 107$ kPa. The partial pressures add to the stated total pressure, providing a check.

The numerical value of a dimensional equilibrium constant depends on the units used. If pressures are in Pa, the result here is 1.07×10^5 Pa. Do not calculate in kPa and label the answer Pa. The constant is fixed for a chosen temperature and unit convention; it is not the same as the product yield.

> **TRY IT**
>
> A mixture contains equal moles of two gases at a total pressure of 200 kPa. What is each partial pressure?

Answer: Each mole fraction is 0.500 and each partial pressure is 100 kPa. Equal partial pressures arise from equal mole fractions, not necessarily equal gas masses.

7.2 Brønsted–Lowry theory of acids and bases

- Common acids: hydrochloric acid HCl, sulfuric acid H_2SO_4, nitric acid HNO_3, ethanoic acid CH_3COOH.
- Common alkalis: sodium hydroxide NaOH, potassium hydroxide KOH, ammonia NH_3.

A **Brønsted–Lowry acid** is a proton (H^+) donor and a **base** is a proton acceptor.

A **strong** acid or base is fully dissociated in aqueous solution (HCl, NaOH). A **weak** acid or base is only partially dissociated (ethanoic acid, ammonia).

Note Academy

At 298 K, neutral water has pH 7; acidic solutions have lower pH and alkaline solutions higher pH. Neutral pH depends on temperature, as developed in the A Level equilibria chapter.

Strong and weak acids compared

At the same concentration a strong acid has a **lower pH** (check with a pH meter or universal indicator), a **higher conductivity**, and **reacts faster** with a reactive metal such as magnesium. The final amount of gas from the same moles of acid is the same, because the weak acid keeps dissociating as it is used up.

Neutralisation and titration curves

Neutralisation is $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$, and a **salt** is formed. Sketch pH against volume added for the four combinations:

- **Strong acid + strong base:** starts at low pH, a very steep rise through pH 7 (about 3 to 11), ends high.
- **Weak acid + strong base:** starts at about 3 (not 1), a buffer region, equivalence point above 7, steep rise about 7 to 11.
- **Strong acid + weak base:** starts at about 1, equivalence point below 7, steep rise about 3 to 7.
- **Weak acid + weak base:** no sharp rise, so no good indicator.

Choosing an indicator

The indicator must **change colour within the steep part** of the curve. **Methyl orange** (about 3 to 4.5) suits strong acid with weak base. **Phenolphthalein** (about 8 to 10) suits weak acid with strong base. Either suits strong acid with strong base.

Strong, weak, concentrated and dilute

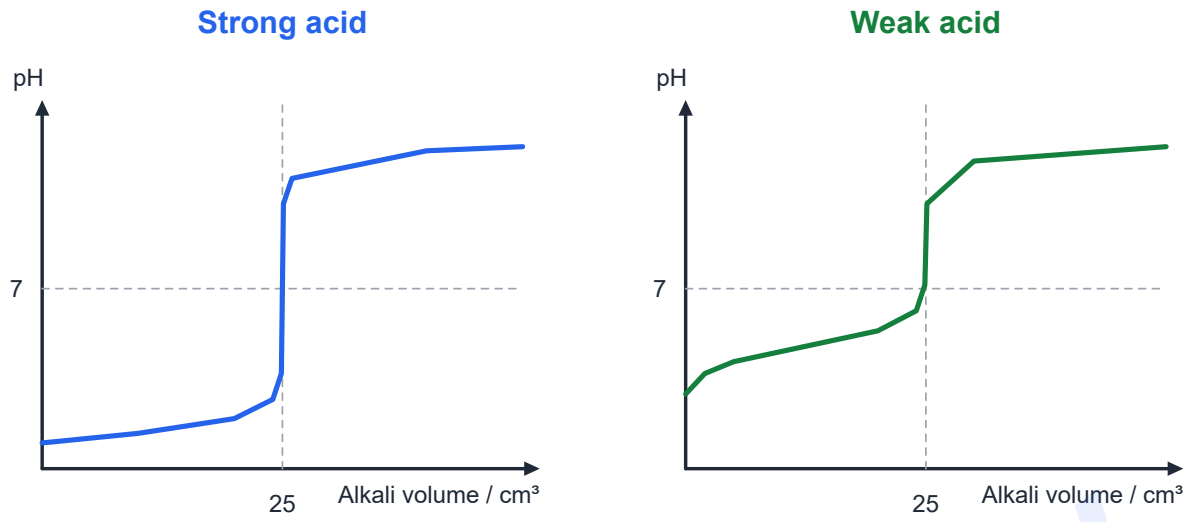
Strength describes the extent of ionisation; concentration describes amount per volume. Diluting hydrochloric acid does not turn it into a weak acid. Compare a strong and weak monoprotic acid at equal concentrations: the strong acid supplies more hydrogen ions initially, giving a lower pH and usually faster initial reaction with a metal. With enough metal, both can ultimately release the same amount of hydrogen from equal amounts of ionisable acid because weak acid continues ionising as H^+ is consumed.

In an acid–base equation, identify the proton donor and acceptor by comparing reactants with products. For $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$, ammonia accepts a proton even though it contains no hydroxide ion initially. This is why the Brønsted–Lowry definition is broader than describing bases as substances that contain OH^-.

Note Academy

Interpreting a titration curve

Acid titrated with strong alkali: compare the equivalence pH



Illustrative curves at 298 K; equivalence volumes match but equivalence pH differs.

The **equivalence point** is the stoichiometric completion of neutralisation. An indicator's **end-point** is the observed colour change. Choose an indicator whose transition lies within the steep region, so a small volume addition causes a clear change close to equivalence. An equivalence point is not automatically pH 7: the salt from a weak acid and strong base produces an alkaline solution, while a strong acid–weak base combination produces an acidic one.

For a weak acid titrated with strong base, the region before equivalence contains both acid and conjugate base and acts as a buffer. At equivalence, the acid has been consumed; beyond it, excess strong alkali dominates pH. In the weak acid–weak base case the gradual change makes a visual indicator unreliable; a pH meter provides a better way to follow the curve. The exact starting pH and steep-region limits depend on concentrations, rather than being fixed numbers for all titrations.

> **TRY IT**
>
> Why is phenolphthalein suitable for ethanoic acid titrated with NaOH, while methyl orange is unsuitable?

Answer: Phenolphthalein changes colour within the sharp alkaline pH rise near equivalence. Methyl orange changes in the acidic region, before equivalence, where a larger volume change can produce only gradual pH change.

Chapter check: distinguish rate from yield, equilibrium composition from equilibrium constant, and indicator end-point from equivalence. Detailed pH, buffers and solubility calculations follow in **A Level equilibria**.

Note Academy

References and further reading

Scope follows section 7 of the **Cambridge 9701 syllabus for 2025–2027**. **Chemguide's Cambridge topic index** links to alternative explanations. The worked exercises and added diagrams are original teaching examples; numerical examples are illustrative unless a specific source is identified.

Note Academy