9701 CHEMISTRY · TOPIC 7 · AS LEVEL

Equilibria — AS

01 · DYNAMIC EQUILIBRIUM

Reached in a **closed system** when the forward and reverse rates are equal, so the concentrations of reactants and products stay constant. Both reactions continue — it is dynamic, not stopped.

Equilibrium can be approached from either direction and gives the same position under the same conditions.

02 · LE CHATELIER'S PRINCIPLE

If a change is made to a system at equilibrium, the position shifts so as to oppose that change.

Change	Shift
[reactant] ↑	to the right
pressure ↑	to the side with fewer gas moles
temperature ↑	in the endothermic direction
catalyst	no shift — equilibrium reached sooner

Only temperature changes K_c or K_p.

Concentration and pressure move the position but leave K unchanged.

03 · K_C AND K_P

$aA + bB \rightleftharpoons cC + dD$

$K_c = [C]^c[D]^d \div [A]^a[B]^b$

$K_p = p(C)^c p(D)^d \div p(A)^a p(B)^b$

Products on top. Solids and pure liquids are left out. Work the units out each time from the powers — they may cancel entirely.

Partial pressure = mole fraction × total pressure. Mole fractions sum to 1.

04 · WORKED EXAMPLE — K_C BY ICE

1.00 mol CH_3COOH + 1.00 mol C_2H_5OH in 1.00 dm^3; at equilibrium 0.667 mol ester formed.

I 1.00 / 1.00 / 0 / 0
C −0.667 / −0.667 / +0.667 / +0.667
E 0.333 / 0.333 / 0.667 / 0.667

$K_c = (0.667 \times 0.667) \div (0.333 \times 0.333)$
K_c = **4.01, no units**

05 · INDUSTRIAL COMPROMISE

Haber $N_2 + 3H_2 \rightleftharpoons 2NH_3$, ΔH negative. High pressure favours NH_3, low temperature favours yield but is too slow — so ~450 °C, ~200 atm, Fe catalyst.

Contact $2SO_2 + O_2 \rightleftharpoons 2SO_3$, ΔH negative. ~450 °C, ~2 atm (yield is already high, so high pressure is not worth the cost), V_2O_5 catalyst.

06 · BRØNSTED–LOWRY

Acid — proton donor. **Base** — proton acceptor. Every acid has a **conjugate base** formed by losing H^+; the pairs differ by one proton.

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$ — the pairs are HCl/Cl^- and H_2O/H_3O^+.

Strong acid — fully dissociated (HCl, HNO_3, H_2SO_4). **Weak** — partially dissociated (CH_3COOH), an equilibrium. Strength is not the same as concentration.

07 · HOMOGENEOUS AND HETEROGENEOUS

Homogeneous — all species in the same phase, so every one appears in the K expression.

Heterogeneous — more than one phase; solids and pure liquids have constant concentration and are omitted. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_p = p(CO_2)$ alone.

08 · WORKED EXAMPLE — K_P

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 200 atm total. At equilibrium the mixture is 0.20 N_2, 0.60 H_2, 0.20 NH_3 by mole fraction.

$p(N_2) = 0.20 \times 200 = 40$ atm
$p(H_2) = 0.60 \times 200 = 120$ atm
$p(NH_3) = 0.20 \times 200 = 40$ atm

$K_p = 40^2 \div (40 \times 120^3)$
$K_p = 1600 \div 6.91 \times 10^7$ = **2.3×10^{-5} atm^{-2}**

09 · WHAT THE SIZE OF K TELLS YOU

Value	Position
$K \gg 1$	products dominate
$K \approx 1$	comparable amounts
$K \ll 1$	reactants dominate

K says nothing about rate. For an exothermic forward reaction K falls as temperature rises.

10 · INDICATORS

An indicator is a weak acid whose acid and conjugate-base forms have different colours: $HIn \rightleftharpoons H^+ + In^-$.

The colour changes over roughly $pK_{In} \pm 1$. Methyl orange turns red → yellow over 3.1–4.4; phenolphthalein colourless → pink over 8.3–10.0.

11 · K_C OR K_P?

Use **K_c** when the data are concentrations or moles in a stated volume. Use **K_p** when the data are partial pressures, mole fractions or a total pressure — always a gas-phase system.

For a reaction with equal numbers of gas moles on both sides the units cancel and the value is dimensionless; pressure then has no effect on the position of equilibrium either.

Both are constant at a fixed temperature no matter what starting amounts are used — that is what makes them useful.

12 · INDUSTRIAL CONDITIONS AT A GLANCE

Process	T	p	Catalyst
Haber	450 °C	200 atm	Fe
Contact	450 °C	2 atm	V_2O_5
Methanol	250 °C	50–100 atm	Cu/ZnO

Every one of these is a **compromise**: the temperature chosen is higher than the yield alone would justify, because an acceptable rate matters more than a theoretical maximum. Unreacted gases are recycled to raise the overall conversion.

13 · WORKED EXAMPLE — SHIFTING THE POSITION

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, ΔH negative.

Raise the pressure → shifts right, 3 moles of gas become 2, yield rises
Raise the temperature → shifts left, the endothermic direction, yield falls and K_p falls
Remove SO_3 → shifts right
Add V_2O_5 → no shift, equilibrium reached sooner

MARKS LOST HERE

— Saying the reaction "stops" at equilibrium.

— Claiming a catalyst increases yield or changes K.

— Putting solids or pure liquids into a K expression.

— Using moles instead of concentrations when the volume is not 1 dm^3.

9701 CHEMISTRY · TOPIC 25 · A LEVEL

Acid–Base Equilibria — A2

14 · pH and K_W

$$pH = -\log[H^+] \cdot [H^+] = 10^{-pH}$$
$$K_W = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ at } 298\text{ K}$$

For a strong base find $[OH^-]$, then $[H^+] = K_W \div [OH^-]$. K_W rises with temperature (ionisation is endothermic), so neutral water has pH below 7 above 298 K — still neutral, since $[H^+] = [OH^-]$.

15 · K_A and weak acids

$$K_a = [H^+][A^-] \div [HA] \cdot pK_a = -\log K_a$$
$$[H^+] = \sqrt{(K_a \times [HA])}$$

Assumptions: $[H^+] = [A^-]$, and $[HA]$ at equilibrium ≈ the initial value. **Larger K_a (smaller pK_a) = stronger acid.**

16 · Worked example — weak acid pH

0.100 mol dm^{-3} CH_3COOH, $K_a = 1.74 \times 10^{-5}$.

$[H^+] = \sqrt{(1.74 \times 10^{-5} \times 0.100)}$
$[H^+] = \sqrt{(1.74 \times 10^{-6})} = 1.32 \times 10^{-3}$
pH = $-\log(1.32 \times 10^{-3})$ = **2.88**

Compare 0.100 mol dm^{-3} HCl: **pH** = 1.00 — same concentration, far lower pH, because HCl is fully dissociated.

17 · Buffers

A solution that resists pH change on adding small amounts of acid or alkali. Made from a **weak acid + its salt** (CH_3COOH / CH_3COONa) or a weak base + its salt (NH_3 / NH_4Cl), or by part-neutralising a weak acid.

$$pH = pK_a + \log([\text{salt}] \div [\text{acid}])$$

Add H^+: $A^- + H^+ \rightarrow HA$. **Add OH^-:** $HA + OH^- \rightarrow A^- + H_2O$. The large reservoirs of both species absorb the change. Buffering is best when [salt] = [acid], where the **pH** equals pK_a.

18 · Titration curves

Acid + base	pH at equiv.	Indicator
strong + strong	7	either
weak + strong base	> 7	phenolphthalein
strong + weak base	< 7	methyl orange
weak + weak	~7	none suitable

The indicator's pK_{In} must lie inside the vertical section. Half-way to the equivalence point, **the pH equals pK_a** — that is the buffer region.

19 · Solubility product

$$K_{sp} = [A^{m+}]^x[B^{n-}]^y$$

Applies to a saturated solution of a sparingly soluble salt. For MX, $K_{sp} = s^2$; for MX_2, $K_{sp} = 4s^3$. A precipitate forms when the ionic product exceeds K_{sp}.

Common-ion effect: adding an ion already present shifts the equilibrium left, so solubility falls — but K_{sp} is unchanged.

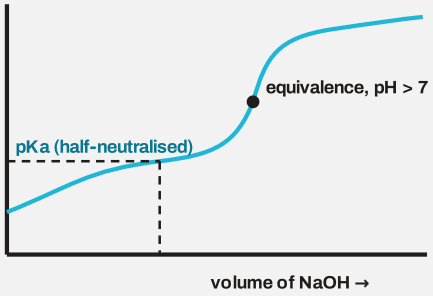
20 · Worked example — buffer

0.200 mol dm^{-3} CH_3COOH with 0.100 mol dm^{-3} CH_3COONa, $K_a = 1.74 \times 10^{-5}$.

$[H^+] = K_a \times [\text{acid}] \div [\text{salt}]$
$[H^+] = 1.74 \times 10^{-5} \times (0.200 \div 0.100)$
$[H^+] = 3.48 \times 10^{-5}$
pH = 4.46

Diluting the buffer leaves the ratio unchanged, so the pH barely moves.

21 · Titration curve — weak acid + strong base



The flat buffer region sits before the equivalence point; the vertical section is shorter than for a strong acid, so only phenolphthalein fits inside it.

22 · Worked example — K_{SP}

Solubility of $Mg(OH)_2$ is 1.44×10^{-4} mol dm^{-3}. Find K_{sp}.

$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$
$[Mg^{2+}] = s$, $[OH^-] = 2s$
$K_{sp} = s \times (2s)^2 = 4s^3$
$K_{sp} = 4 \times (1.44 \times 10^{-4})^3$
K_{sp} = **1.19×10^{-11} mol^3 dm^{-9}**

23 · Worked example — strong base

0.0500 mol dm^{-3} NaOH at 298 K.

NaOH is fully dissociated → $[OH^-] = 0.0500$
$[H^+] = K_W \div [OH^-]$
$[H^+] = 1.00 \times 10^{-14} \div 0.0500 = 2.00 \times 10^{-13}$
pH = $-\log(2.00 \times 10^{-13})$ = **12.70**

For $Ba(OH)_2$ remember $[OH^-]$ is twice the salt concentration.

24 · Worked example — common ion

Solubility of AgCl in 0.100 mol dm^{-3} NaCl, $K_{sp} = 1.8 \times 10^{-10}$.

$[Cl^-] \approx 0.100$ from the NaCl
$[Ag^+] = K_{sp} \div [Cl^-]$
$[Ag^+] = 1.8 \times 10^{-10} \div 0.100$ = **1.8×10^{-9} mol dm^{-3}**

In pure water $s = \sqrt{K_{sp}} = 1.3 \times 10^{-5}$ — about ten thousand times more soluble.

Marks lost here

— Confusing strength with concentration when comparing pH.

— Using $[H^+] = c$ directly for a weak acid.

— Forgetting K_W when going from $[OH^-]$ to pH.

— Explaining a buffer without writing the two equations for added H^+ and added OH^-.