

Equilibria (A Level)

A-Level Chemistry 9701 · Topic 25 revision notes

Everything from the 4 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.

1. K_a, pK_a and the pH of weak acids

2. Buffer solutions

3. Solubility product and the common ion effect

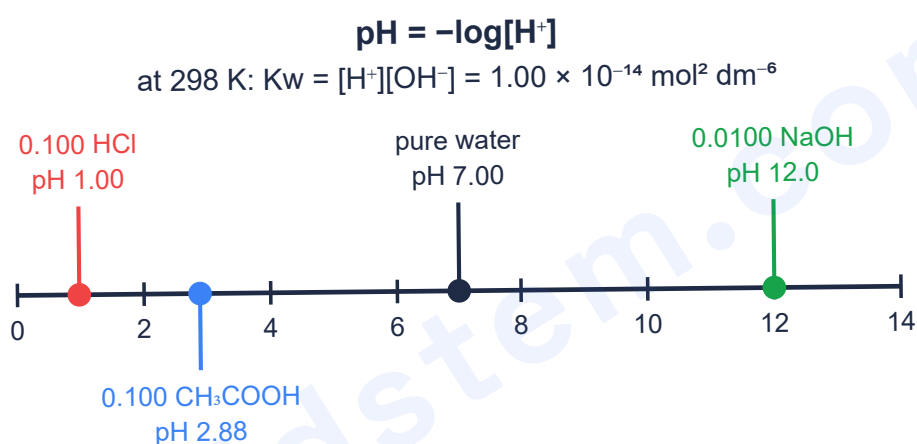
4. Partition coefficients

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1 K_a , pK_a and the pH of weak acids

Syllabus 25.1

Water ionises slightly: $H_2O \rightleftharpoons H^+ + OH^-$, and the **ionic product of water** $K_w = [H^+][OH^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K. **$pH = -\log[H^+]$** ; for a strong acid $[H^+]$ equals the acid concentration, and for a strong base $[H^+] = K_w \div [OH^-]$, so $0.0100 \text{ mol dm}^{-3}$ NaOH has pH 12.0. A weak acid HA is only partly ionised, described by the **acid dissociation constant** $K_a = \frac{[H^+][A^-]}{[HA]}$, and **$pK_a = -\log K_a$** (smaller pK_a , stronger acid). Assuming $[H^+] = [A^-]$ and that very little HA ionises, **$[H^+] = \sqrt{K_a \times c}$** : $0.100 \text{ mol dm}^{-3}$ ethanoic acid ($K_a = 1.74 \times 10^{-5} \text{ mol dm}^{-3}$) has pH 2.88.



strong acid

$[H^+] = c$ (fully ionised)

weak acid

$[H^+] = \sqrt{K_a \times c}$

Fig. 1: the pH scale at 298 K, with a strong acid, a weak acid of the same concentration and a strong base

Strong: $[H^+] = c$. **Weak:** $[H^+] = \sqrt{K_a c}$.

✓ **pH** = $-\log[H^+]$; $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$.

✓ **Strong base:** $[OH^-]$ first, then $[H^+] = K_w \div [OH^-]$.

✓ **Weak acid:** $K_a = [H^+]^2 \div [HA]$.

✓ **pK_a** = $-\log K_a$: smaller pK_a, stronger acid.

Watch out!

Do **not** set $[H^+]$ equal to the concentration of a weak acid; that is only true for strong acids. For a strong base, find $[OH^-]$ first, then use K_w ; quoting $-\log[OH^-]$ as the pH is the classic slip (that is pOH). Remember that $Ba(OH)_2$ releases two OH^- per formula unit, and that pure water is neutral at every temperature even when its pH is not 7.

2 Buffer solutions

Syllabus 25.1

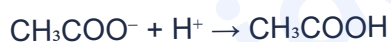
A **buffer solution** is a solution that **resists changes in pH** when small amounts of acid or alkali are added. An **acidic buffer** contains a weak acid and its conjugate base, for example CH_3COOH with CH_3COONa : added H^+ is removed by $\text{CH}_3\text{COO}^- + \text{H}^+ \rightarrow \text{CH}_3\text{COOH}$, and added OH^- is removed by $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$. An **alkaline buffer** such as NH_3 with NH_4Cl works the same way using NH_3 and NH_4^+ . Because both reservoirs are large, their ratio hardly changes, so the pH, given by $[\text{H}^+] = K_a \times [\text{HA}] \div [\text{A}^-]$, hardly changes. Blood is buffered by $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$.

an acid buffer: large reservoirs of HA and A^-



HA from the acid, A^- from the salt

add a little H^+



H^+ is removed by A^-
pH barely falls

add a little OH^-



OH^- is removed by HA
pH barely rises

Fig. 1: how the ethanoic acid and ethanoate buffer removes added H^+ and OH^-

*Weak acid + conjugate base,
both in large amounts.*

- ✓ **Added H^+ :** $A^- + H^+ \rightarrow HA$.
- ✓ **Added OH^- :** $HA + OH^- \rightarrow A^- + H_2O$.
- ✓ **pH:** $[H^+] = K_a \times [HA] \div [A^-]$.
- ✓ **Indicator:** its range must lie in the steep section of the curve.

Watch out!

A buffer is **not** a solution whose pH never changes: it resists change from **small** additions, and fails once one reservoir is used up. In buffer calculations use the **salt concentration for $[A^-]$** , not $[H^+]$; the $\sqrt{K_a c}$ shortcut is for a weak acid on its own. When acid and alkali are mixed to make a buffer, work in **moles after reaction** before taking the ratio.

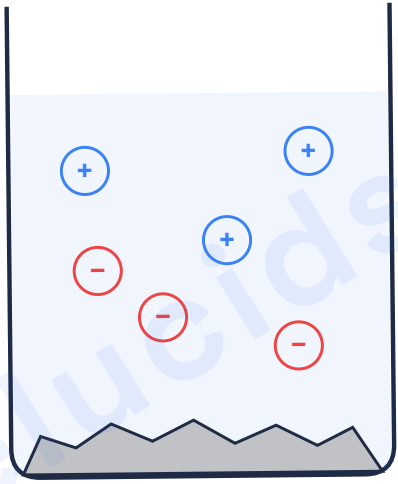
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3 Solubility product and the common ion effect

Syllabus 25.1

In a saturated solution of a sparingly soluble salt, the solid is in **dynamic equilibrium** with its ions: $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$. The **solubility product** is the product of the ion concentrations, each raised to the power of its coefficient: $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$ ($\text{mol}^2 \text{dm}^{-6}$), $K_{sp} = [\text{Pb}^{2+}][\text{I}^-]^2$ ($\text{mol}^3 \text{dm}^{-9}$). The solid does not appear. From a solubility s : AgCl has $s = 1.34 \times 10^{-5} \text{ mol dm}^{-3}$, so $K_{sp} = s^2 = 1.80 \times 10^{-10} \text{ mol}^2 \text{dm}^{-6}$; for PbI_2 , $K_{sp} = 4s^3$. Adding a **common ion** shifts the equilibrium to the left and **lowers the solubility**. If the **ionic product** of mixed solutions **exceeds K_{sp}** , a precipitate forms.

$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$



saturated solution over solid AgCl

$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$
 $= 1.80 \times 10^{-10} \text{ mol}^2 \text{dm}^{-6}$

ionic product > K_{sp}
precipitate forms

ionic product < K_{sp}
no precipitate

Fig. 1: a saturated solution of silver chloride, its solubility product and the precipitation rule

Ions only, powers from the formula.

- ✓ **AB:** $K_{sp} = s^2$, $\text{mol}^2 \text{dm}^{-6}$.
- ✓ **AB₂:** $K_{sp} = 4s^3$, $\text{mol}^3 \text{dm}^{-9}$.
- ✓ **Common ion:** lowers solubility, K_{sp} unchanged.
- ✓ **Mixing:** dilute first; ionic product $> K_{sp}$ means precipitate.

Watch out!

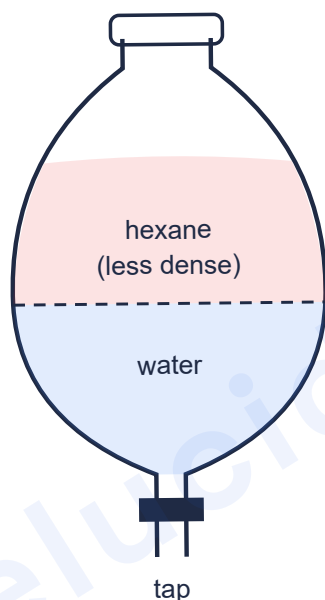
Square or cube the right terms: for PbI_2 , $[\text{I}^-] = 2s$ and $K_{sp} = 4s^3$, not s^3 or s^2 . When two solutions are **mixed**, each concentration is **diluted** (halved for equal volumes) before you work out the ionic product. The common ion lowers the **solubility**, not K_{sp} . Units of K_{sp} depend on the formula: $\text{mol}^2 \text{dm}^{-6}$ for AB, $\text{mol}^3 \text{dm}^{-9}$ for AB₂.

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4 Partition coefficients

Syllabus 25.2

When a solute X is shaken with two **immiscible solvents**, such as hexane and water, it distributes itself between them and reaches a **dynamic equilibrium**, $X(aq) \rightleftharpoons X(\text{organic})$. The **partition coefficient** is the ratio of the equilibrium concentrations, $K_{pc} = [X]_{\text{organic}} \div [X]_{\text{aqueous}}$, which is **constant at a fixed temperature** and has no units. A **non-polar** solute such as iodine is more soluble in a non-polar solvent, so K_{pc} (organic over water) is greater than 1; a **polar** solute such as ammonia, which hydrogen bonds to water, has K_{pc} less than 1. Because the amount extracted depends on the volumes as well as K_{pc} , **several small portions** of solvent extract more than one large portion.



$K_{pc} = [X]_{\text{organic}} \div [X]_{\text{aqueous}}$
at equilibrium, fixed temperature
no units (same units cancel)

non-polar solute
prefers hexane: $K_{pc} > 1$

polar solute
prefers water: $K_{pc} < 1$

Fig. 1: a solute partitioned between hexane and water in a separating funnel

Concentrations, not masses.

- ✓ $K_{pc} = [X]_{\text{organic}} \div [X]_{\text{aqueous}}$, no units.
- ✓ **Divide by volume:** each layer's amount over its own volume.
- ✓ **Polarity:** non-polar solute, $K_{pc} > 1$; polar solute, $K_{pc} < 1$.
- ✓ **Several small portions** extract more than one large one.

Watch out!

K_{pc} is a ratio of **concentrations**, not masses: divide each amount by its own layer's volume. Keep the order as stated (organic over aqueous here); inverting it gives $1 \div K_{pc}$. The amount left in water after extraction is the starting amount minus x, and each new portion starts from what is left. A large K_{pc} means the solute prefers the organic layer, which needs a **non-polar** solute.