Equilibria (A Level)

Understand acid–base equilibria, calculate pH and buffer composition, use solubility products and the common ion effect, and solve solvent-extraction problems with partition coefficients.

Equilibrium calculations connect a chemical explanation to a numerical prediction. Why does a weak acid have a higher pH than a strong acid of the same concentration? How can a buffer absorb added acid? Why does a salt dissolve less readily when one of its ions is already present? Begin with the equilibrium equation, identify what changes, and then choose the appropriate expression.

Before starting, revise dynamic equilibrium and acids and bases, the mole equation $n = cV$, and converting cm³ into dm³. Concentrations in square brackets are in mol dm^{-3}. Unless another value is given, these pH examples use $K_w = 1.00 \times 10^{-14}$ mol² dm^{-6} at 298 K. The worked examples use illustrative data and are original practice problems.

25.1 Acids and bases

Conjugate acid–base pairs

A Brønsted–Lowry acid donates a proton; a base accepts one. After donating H^+, an acid becomes its **conjugate base**. After accepting H^+, a base becomes its **conjugate acid**. The two members of a conjugate pair differ by exactly one proton: their charges differ by one, but their other atoms are unchanged.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Ethanoic acid donates a proton to water. In the reverse reaction, ethanoate accepts a proton from the hydroxonium ion.

Acid	Its conjugate base	Relationship
CH_3COOH	CH_3COO^-	Acid loses H^+
H_3O^+	H_2O	Acid loses H^+
NH_4^+	NH_3	Acid loses H^+
HCO_3^-	CO_3^{2-}	Acid loses H^+

The acid and base reacting together are usually **not** a conjugate pair. In the equation above, the pairs are CH_3COOH/CH_3COO^- and H_3O^+/H_2O, rather than CH_3COOH/H_2O.

Note Academy

TRY IT

Identify both conjugate pairs in $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$.

Answer: NH_4^+/NH_3 and H_2O/OH^-. Ammonia accepts a proton, so it is the base in the forward reaction. Water donates a proton, so it acts as the acid. Water can take either role depending on its reaction partner.

pH and hydrogen ion concentration

The mathematical definition used for these aqueous calculations is:

$$pH = -\log_{10}[H^+] \qquad [H^+] = 10^{-pH}$$

$H^+(aq)$ is shorthand for a hydrated proton, often represented as H_3O^+. pH has no units. Keep the negative sign: $[H^+] = 10^{-3}$ mol dm^{-3} gives pH 3, not −3. A decrease of one pH unit means a tenfold increase in hydrogen ion concentration.

Worked example — converting in both directions. If $[H^+] = 3.20 \times 10^{-4}$ mol dm^{-3}:

$$pH = -\log_{10}(3.20 \times 10^{-4}) = 3.49$$

If a different solution has pH 4.25:

$$[H^+] = 10^{-4.25} = 5.62 \times 10^{-5} \text{ mol dm}^{-3}$$

Keep unrounded calculator values during intermediate steps. State concentration units and normally report a final pH to two decimal places unless instructed otherwise.

TRY IT

Solution A has pH 2.80 and solution B has pH 4.80. Which has more hydrogen ions per unit volume, and by what factor?

Answer: A has $10^{4.80-2.80} = 100$ times the hydrogen ion concentration of B. A difference in pH is a logarithmic comparison; do not divide the pH numbers.

Water, Kw and the meaning of neutral

Water undergoes a small amount of ionisation:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Its ionic product is:

$$K_w = [H^+][OH^-]$$

Note Academy

At 298 K, $K_w = 1.00 \times 10^{-14}$ mol² dm⁻⁶. In a **neutral** solution, $[H^+] = [OH^-]$, so each concentration is $\sqrt{K_w} = 1.00 \times 10^{-7}$ mol dm⁻³ and pH is 7.00.

Neutral does not always mean pH 7. Water's ionisation is endothermic, so raising the temperature increases K_w. Both ion concentrations increase in pure water, but remain equal. The water stays neutral even though its pH falls.

Worked example — neutral water at another temperature. Given $K_w = 4.00 \times 10^{-14}$ mol² dm⁻⁶:

$$[H^+] = \sqrt{4.00 \times 10^{-14}} = 2.00 \times 10^{-7} \text{ mol dm}^{-3}$$

$$pH = -\log_{10}(2.00 \times 10^{-7}) = 6.70$$

A solution is neutral when its hydrogen and hydroxide ion concentrations are equal. Use the value of K_w for the stated temperature.

TRY IT

At 298 K, a solution has $[OH^-] = 2.50 \times 10^{-3}$ mol dm⁻³. Find $[H^+]$ and pH.

Answer: $[H^+] = K_w/[OH^-] = 4.00 \times 10^{-12}$ mol dm⁻³. Its pH is **11.40**. Calculate hydrogen ion concentration before applying the pH definition.

Strong acids and strong alkalis: a calculation method

Strong describes essentially complete ionisation or dissociation in water; **concentrated** describes the amount of solute per unit volume. A dilute solution of HCl is still a strong acid. Do not use these terms interchangeably.

For a strong monoprotic acid such as HCl, one mole of acid produces one mole of H^+. Provided the acid is not so dilute that water's contribution matters, $[H^+]$ equals the acid concentration. For a strong alkali, count hydroxide ions per formula unit: dissolved NaOH provides one; dissolved $Ba(OH)_2$ provides two.

Worked example — acid after dilution. Dilute 20.0 cm³ of 0.150 mol dm⁻³ HCl to a total volume of 250.0 cm³.

1. Moles before dilution: $n = 0.150 \times 0.0200 = 3.00 \times 10^{-3}$ mol.
2. Dilution changes volume but not moles: $[H^+] = (3.00 \times 10^{-3})/0.2500 = 0.0120$ mol dm⁻³.
3. Apply the definition: $pH = -\log_{10}(0.0120) = \mathbf{1.92}$.

Worked example — two hydroxide ions. A solution contains 0.00400 mol dm⁻³ dissolved $Ba(OH)_2$.

$$[OH^-] = 2(0.00400) = 0.00800 \text{ mol dm}^{-3}$$

Note Academy

$[H^+] = \frac{1.00\times10^{-14}}{0.00800} = 1.25 \times 10^{-12}\ \text{mol dm}^{-3}$

Its pH is **11.90**. Taking $-\log[OH^-]$ gives pOH, not pH.

When an acid and alkali are mixed, first use $H^+ + OH^- \rightarrow H_2O$ to find **excess moles**, then divide by the **combined volume**. For example, mixing 30.0 cm³ of 0.100 mol dm⁻³ HCl with 20.0 cm³ of 0.100 mol dm⁻³ NaOH leaves $0.00300 - 0.00200 = 0.00100$ mol H^+ in 0.0500 dm³. Thus $[H^+] = 0.0200$ mol dm⁻³ and pH = **1.70**.

> **NOTE**
>
> For polyprotic acids, establish how many protons are released under the question's assumptions. Sulfuric acid's first ionisation is effectively complete, but the second is an equilibrium. Use $[H^+] = 2c$ when complete release of both protons is specified or is the intended approximation; it is not a universal rule for all concentrations or all dibasic acids.

> **TRY IT**
>
> Dilute 10.0 cm³ of 0.200 mol dm⁻³ NaOH to 100.0 cm³. Calculate the final pH at 298 K.

Answer: Moles of OH^- are $0.200 \times 0.0100 = 0.00200$. The final $[OH^-] = 0.00200/0.1000 = 0.0200$ mol dm⁻³, giving $[H^+] = 5.00 \times 10^{-13}$ mol dm⁻³ and pH = **12.30**.

Weak acids, Ka and pKa

A weak acid is only partially ionised. For a monoprotic acid:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad pK_a = -\log_{10} K_a \qquad K_a = 10^{-pK_a}$$

Use **equilibrium** concentrations in K_a. Its units here are mol dm⁻³; pK_a has no units. Water is the solvent and is omitted. At the same temperature, a larger K_a means a greater tendency to donate a proton and therefore a stronger acid; a smaller pK_a means the same thing. Dilution changes concentrations and the degree of ionisation, but not K_a at fixed temperature.

To calculate the pH of a solution containing just weak acid and water, let its initial concentration be c and equilibrium $[H^+]$ be x:

Note Academy

Concentration / mol dm^{-3}	HA	H^+	A^-
Initially, ignoring water's ions	c	0	0
Change	$-x$	$+x$	$+x$
At equilibrium	$c-x$	x	x

Thus $K_a = x^2/(c-x)$. For small ionisation, $x \ll c$, so $c - x \approx c$:

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

This assumes water supplies negligible H^+ and only a small fraction of HA ionises. Check $100x/c$: if it is only a few percent or less, the small-ionisation approximation is reasonable. Do not apply this expression to a buffer, where added salt supplies a separate source of A^-.

Worked example — weak-acid pH. A 0.0800 mol dm^{-3} acid has $K_a = 1.60 \times 10^{-5}$ mol dm^{-3}.

$$[H^+] \approx \sqrt{(1.60 \times 10^{-5})(0.0800)} = 1.13 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pH = 2.95 \qquad \%\text{ ionised} \approx \frac{1.13\times10^{-3}}{0.0800} \times 100 = 1.41\%$$

The small percentage supports the approximation. The same concentration of a strong monoprotic acid would have pH 1.10. The difference comes from the equilibrium position, not from fewer acid molecules having been added initially.

Worked example — finding acid strength from measured pH. A 0.0500 mol dm^{-3} weak monoprotic acid has pH 3.20. First, $x = 10^{-3.20} = 6.31 \times 10^{-4}$ mol dm^{-3}. Taking $[HA] \approx 0.0500$:

$$K_a \approx \frac{(6.31\times10^{-4})^2}{0.0500} = 7.96 \times 10^{-6} \text{ mol dm}^{-3}$$

Then $pK_a = 5.10$. If greater precision is needed, retain $c - x$ in the denominator; state which approximation you used.

> **TRY IT**
>
> A 0.125 mol dm^{-3} weak acid has $K_a = 2.00 \times 10^{-5}$ mol dm^{-3}. Estimate its pH and percentage ionisation.

Answer: $[H^+] = \sqrt{2.50 \times 10^{-6}} = 1.58 \times 10^{-3}$ mol dm^{-3}. pH = **2.80**, and percentage ionisation is **1.26%**, supporting $[HA] \approx c$.

Making a buffer and explaining its action

A **buffer solution** resists a large change in pH when a small amount of acid or alkali is added. An acidic buffer contains substantial amounts of a weak acid and its conjugate base, usually supplied by a soluble

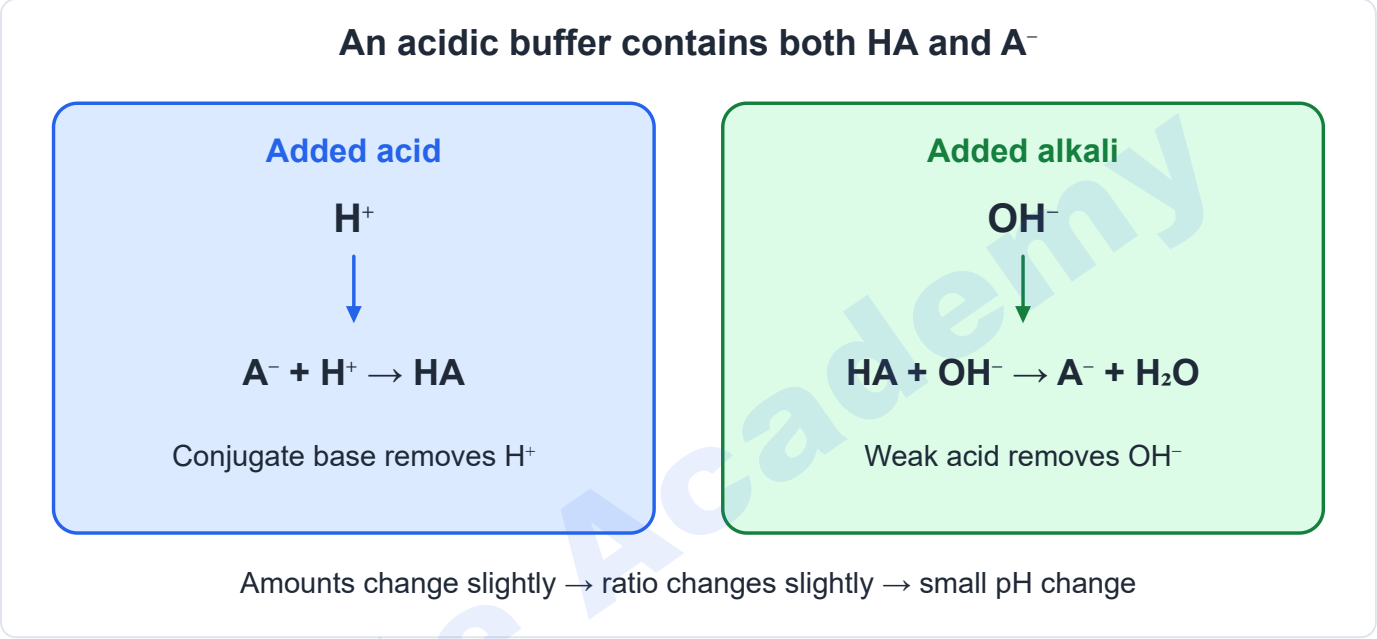
Note Academy

salt. Ethanoic acid with sodium ethanoate is an example. The salt dissociates to supply CH_3COO^-; Na^+ is a spectator ion.

Two preparation routes are useful:

1. Mix a weak acid solution with a solution of its salt.
2. **Partly neutralise** a weak acid with a strong alkali. Some acid must remain, while some becomes its conjugate base: $HA + OH^- \rightarrow A^- + H_2O$.

A weak acid alone has too little conjugate base to remove much added acid. A strong acid and its salt do not supply the weak-acid/conjugate-base reservoir required for an acidic buffer. Complete neutralisation of HA leaves mainly its salt, rather than a useful mixture of both components.



When acid is added, conjugate base removes most of the added hydrogen ions:

$$CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$$

When alkali is added, weak acid removes most of the added hydroxide:

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

Both reactions change the amounts of acid and conjugate base slightly. The pH changes a little; it is not held exactly constant. Buffer **capacity** is limited: enough acid exhausts A^-, while enough alkali exhausts HA. A more concentrated buffer with the same ratio can neutralise more added acid or alkali per unit volume before a large change occurs.

Buffer pH: mixtures and partial neutralisation

Rearrange the acid equilibrium expression:

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

Note Academy

Taking logarithms gives the equivalent form:

$$pH = pK_a + \log_{10} \frac{[A^-]}{[HA]}$$

Both components share the same final volume, so their concentration ratio equals their mole ratio. You may use $n(A^-)/n(HA)$ **after any neutralisation reaction**. If $[A^-] = [HA]$, pH = pK_a; more conjugate base gives a higher pH.

Worked example — mixing acid and salt. Mix 40.0 cm³ of 0.200 mol dm⁻³ HA with 60.0 cm³ of 0.100 mol dm⁻³ sodium A. Given $K_a = 1.80 \times 10^{-5}$ mol dm⁻³:

1. $n(HA) = 0.200 \times 0.0400 = 0.00800$ mol; $n(A^-) = 0.100 \times 0.0600 = 0.00600$ mol.
2. The final volume is 0.1000 dm³: $[HA] = 0.0800$ and $[A^-] = 0.0600$ mol dm⁻³.
3. $[H^+] = (1.80 \times 10^{-5})(0.00800/0.00600) = 2.40 \times 10^{-5}$ mol dm⁻³.
4. pH = **4.62**. Using the original concentrations directly gives the wrong ratio because the mixed volumes were different.

Worked example — partial neutralisation. Add 20.0 cm³ of 0.100 mol dm⁻³ NaOH to 50.0 cm³ of 0.100 mol dm⁻³ HA, which has $pK_a = 4.76$.

Amount / mol	HA	OH^-	A^-
Before reaction	0.00500	0.00200	0
Reaction change	−0.00200	−0.00200	+0.00200
After reaction	0.00300	0	0.00200

The strong alkali is used up. Remaining acid and newly formed conjugate base make a buffer:

$$pH = 4.76 + \log_{10} \frac{0.00200}{0.00300} = 4.58$$

Adding acid or alkali to a buffer

Worked example — added acid. A buffer contains 0.0100 mol HA and 0.0100 mol A^-, with $pK_a = 4.76$. Add 0.00100 mol HCl with negligible volume change. Initially pH = 4.76. Added H^+ reacts with A^-, giving:

$$n(A^-) = 0.00900 \text{ mol}, \qquad n(HA) = 0.0110 \text{ mol}$$

$$pH = 4.76 + \log_{10} \frac{0.00900}{0.0110} = 4.67$$

The fall is only 0.09 pH unit. If alkali is added instead, subtract its moles from HA and add them to A^- before calculating pH. Check that neither component has been exhausted.

Dilution reduces both concentrations by the same factor, leaving the ratio and approximate pH unchanged. It reduces buffering capacity **per unit volume**. At extreme dilution, water's own ions matter and these approximations fail.

Note Academy

TRY IT

A buffer has 0.0200 mol HA and 0.0100 mol A^-, with $pK_a = 4.80$. Add 0.00200 mol NaOH. Find the new pH.

Answer: OH^- converts HA into A^-. The amounts become 0.0180 mol acid and 0.0120 mol conjugate base. pH $= 4.80 + \log(0.0120/0.0180) =$ **4.62**, compared with 4.50 initially. Using the original ratio would ignore neutralisation.

Buffer uses and hydrogencarbonate in blood

Blood must maintain a narrow pH range for normal protein and enzyme function. One contributing buffer involves dissolved carbon dioxide and hydrogencarbonate:

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Increased $[H^+]$ shifts this equilibrium left: HCO_3^- removes added hydrogen ions, producing dissolved CO_2 and water. Added alkali removes H^+, allowing the equilibrium to move right and replenish it. This is a simplified account: blood has other buffers, and the body also regulates carbon dioxide and hydrogencarbonate.

Laboratory buffers provide stable reference solutions for **calibrating pH meters**. They are also used in enzyme experiments so that changes in activity can be attributed to the variable being studied rather than unintended pH drift. In exam explanations, identify the species and show how added acid or alkali is consumed. Saying only “the equilibrium shifts” leaves the mechanism unclear.

Solubility products: expressions and units

A sparingly soluble ionic solid establishes an equilibrium with its aqueous ions in a saturated solution:

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

The **solubility product**, K_{sp}, is the product of the equilibrium ion concentrations, each raised to its stoichiometric coefficient. The pure solid is omitted:

$$K_{sp} = [Ag^+][Cl^-]$$

Ions continue leaving and returning to the solid at equal rates. Adding more solid to a saturated solution does not increase equilibrium ion concentrations at the same temperature.

Note Academy

Dissolution equation	Expression	Units
$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$	$[Ag^+][Cl^-]$	mol² dm⁻⁶
$CaF_2(s) \rightleftharpoons Ca^{2+} + 2F^-$	$[Ca^{2+}][F^-]^2$	mol³ dm⁻⁹
$Ag_2CO_3(s) \rightleftharpoons 2Ag^+ + CO_3^{2-}$	$[Ag^+]^2[CO_3^{2-}]$	mol³ dm⁻⁹

For CaF_2, the exponent 2 comes from the **two fluoride ions** released, not an ionic charge. The units come from three concentration factors: $(\text{mol dm}^{-3})^3$.

> **TRY IT**
>
> Write the expression and units for the solubility product of $Mg(OH)_2$.

Answer: $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$, so $K_{sp} = [Mg^{2+}][OH^-]^2$, with units **mol³ dm⁻⁹**. Leave out the solid.

Calculating solubility from Ksp and back again

Molar solubility, s, is the amount of solid that dissolves per dm³ of solution. In pure water, assuming no other reaction consumes the ions, use the dissolution equation to express each ion concentration in terms of s.

Worked example — solubility to constant. An illustrative CaF_2 sample has molar solubility 2.00×10^{-4} mol dm⁻³. Each mole produces one mole of calcium ions and two of fluoride:

$$[Ca^{2+}] = s, \qquad [F^-] = 2s$$

$$K_{sp} = s(2s)^2 = 4s^3 = 4(2.00 \times 10^{-4})^3 = 3.20 \times 10^{-11}\ \text{mol}^3\ \text{dm}^{-9}$$

Worked example — constant to solubility. For an illustrative $Mg(OH)_2$ system, $K_{sp} = 3.20 \times 10^{-11}$ mol³ dm⁻⁹. Ignoring water's contribution to $[OH^-]$:

$$K_{sp} = s(2s)^2 = 4s^3 \qquad s = \sqrt[3]{\frac{3.20 \times 10^{-11}}{4}} = 2.00 \times 10^{-4}\ \text{mol dm}^{-3}$$

If the molar mass is 58.3 g mol⁻¹, the mass solubility is $sM_r = 0.0117$ g dm⁻³. Convert mass solubility into molar solubility before substituting into a concentration-based expression.

> **K_{sp} is an equilibrium constant; solubility is an amount per volume. They have different units. Do not rank solubilities of salts with different ion ratios simply by comparing their K_{sp} values.**

Note Academy

TRY IT

A salt MX dissolves as $MX(s) \rightleftharpoons M^{+}(aq) + X^{-}(aq)$ and has $K_{sp} = 9.00 \times 10^{-10}$ mol² dm⁻⁶. Find its molar solubility in pure water.

Answer: Both concentrations equal s, so $s^2 = K_{sp}$ and $s = \mathbf{3.00 \times 10^{-5}}$ mol dm⁻³. Unlike an MX_2 salt, this needs a square root.

The common ion effect and precipitation

Consider solid AgCl in aqueous NaCl. Both supply Cl^{-}, the **common ion**. Increasing its concentration drives

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

to the left, reducing the silver ion concentration and the amount of AgCl that dissolves. K_{sp} **stays constant at fixed temperature**; solubility changes instead.

Worked example — common-ion solubility. Take $K_{sp}(AgCl) = 1.80 \times 10^{-10}$ mol² dm⁻⁶. In pure water:

$$s = \sqrt{K_{sp}} = 1.34 \times 10^{-5} \text{ mol dm}^{-3}$$

In 0.0200 mol dm⁻³ NaCl, let extra dissolved AgCl have concentration s. Then $[Ag^{+}] = s$ and $[Cl^{-}] = 0.0200 + s$. Approximate the chloride concentration as 0.0200:

$$s \approx \frac{1.80 \times 10^{-10}}{0.0200} = 9.00 \times 10^{-9} \text{ mol dm}^{-3}$$

This is much less than in pure water. The result is tiny compared with 0.0200, confirming the approximation. Here we assume no significant complex formation or other reactions involving the ions.

To predict precipitation, calculate the **ionic product**, Q, from concentrations immediately after mixing, before precipitation. Use the same powers as in K_{sp}:

- $Q < K_{sp}$: unsaturated; precipitation is not predicted.
- $Q = K_{sp}$: at the saturation boundary.
- $Q > K_{sp}$: precipitation is favoured until remaining ion concentrations satisfy the equilibrium condition.

Worked example — dilution on mixing. Mix equal volumes of 2.00×10^{-4} mol dm⁻³ $AgNO_3$ and 2.00×10^{-4} mol dm⁻³ NaCl. Each original concentration halves, giving $[Ag^{+}] = [Cl^{-}] = 1.00 \times 10^{-4}$ mol dm⁻³.

$$Q = (1.00 \times 10^{-4})^2 = 1.00 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

This exceeds 1.80×10^{-10}, so AgCl precipitates. Q tests the mixture's initial composition; it is not a new value of K_{sp}.

Note Academy

TRY IT

An MX_2 salt has $K_{sp} = 4.00 \times 10^{-12}$ mol³ dm⁻⁹. Estimate its molar solubility in a solution already containing 0.0100 mol dm⁻³ X^-.

Answer: $K_{sp} \approx s(0.0100)^2$, giving $s = \mathbf{4.00 \times 10^{-8}}$ mol dm⁻³. The extra $2s$ of X^- is negligible. Dividing by 0.0100 rather than its square misses the stoichiometric exponent.

25.2 Partition coefficients

Distribution between immiscible solvents

When a solute dissolves in two **immiscible solvents**, shaking increases contact and helps it reach equilibrium. Particles continue crossing both ways, but at equilibrium their transfer rates are equal and each concentration stays constant. The concentrations need not be equal.

The **partition coefficient**, K_{pc}, is the equilibrium ratio of a solute's concentrations in two solvents at fixed temperature. Always specify the order. Here:

$$K_{pc} = \frac{\text{concentration of X in organic solvent}}{\text{concentration of X in water}}$$

Concentration units must match, so the ratio has no units. You may use g cm⁻³ in both numerator and denominator, or mol dm⁻³ in both. A coefficient of 5 means five times the **concentration** in the organic layer, not necessarily five times the mass: the volumes may differ.

The simple treatment assumes dilute solutions and the solute in the same molecular form and physical state in both solvents, without significant reaction, ionisation or association. Do not apply a single simple ratio to a solute that ionises in one layer or forms dimers in the other.

Polarity and choice of extraction solvent

Predict the preferred solvent by comparing intermolecular attractions. A non-polar molecular solute is often more soluble in a non-polar solvent, where dispersion forces replace similar attractions. A polar solute capable of hydrogen bonding may interact strongly with water. Ionic species generally favour water through ion–dipole attractions.

“Like dissolves like” is a starting point; explain **which interactions** stabilise the solute. For K_{pc} defined as organic/water, stronger relative attraction to water lowers it; stronger relative attraction to the organic phase raises it. Reversing the solvent order gives the reciprocal coefficient. Temperature may also change the ratio.

An extraction solvent should dissolve the desired solute effectively and form a separate layer from the original solvent. The organic layer is not always the top layer: position depends on density.

Note Academy

Finding a coefficient and solving a single extraction

Worked example — coefficient from measured masses. Initially, 0.600 g of solute is in 60.0 cm³ water. After shaking with 20.0 cm³ organic solvent, 0.400 g is in that layer. Assuming unchanged volumes, water retains $0.600 - 0.400 = 0.200$ g:

$$K_{pc} = \frac{0.400/20.0}{0.200/60.0} = 6.00$$

Using $0.400/0.200$ alone gives a mass ratio of 2, not a concentration ratio of 6.

Worked example — mass extracted. A solute has $K_{pc} = 5.00$ for organic/water. Initially 1.20 g is in 100 cm³ water. Shake with 40.0 cm³ organic solvent, assuming unchanged layer volumes. Let x g transfer:

Layer	Equilibrium mass / g	Concentration / g cm^{-3}
Organic	x	$x/40.0$
Water	$1.20 - x$	$(1.20 - x)/100$

$$5.00 = \frac{x/40.0}{(1.20-x)/100}$$

$$5.00(40.0)(1.20 - x) = 100x \quad \Rightarrow \quad 240 - 200x = 100x$$

Thus **0.800 g** is extracted, leaving **0.400 g** in water. Check: $(0.800/40.0)/(0.400/100) = 5.00$. The extracted fraction is $0.800/1.20 = 66.7\%$.

> **TRY IT**
>
> A solute has $K_{pc} = 3.00$ for organic/water. Shake 0.900 g in 90.0 cm³ water with 30.0 cm³ organic solvent. How much is extracted?

Answer: $3.00 = (x/30.0)/((0.900 - x)/90.0)$, giving $x = \mathbf{0.450}$ g. Concentrations differ threefold, but masses are equal because the aqueous volume is three times larger.

Repeated extraction with fresh solvent

Several smaller fresh portions can extract more solute than one larger portion of the same total volume. Each fresh portion begins with no solute and establishes a new equilibrium with what **remains in the water**.

Use the previous worked example: 1.20 g in 100 cm³ water, $K_{pc} = 5.00$. Replace one 40.0 cm³ extraction with two separate 20.0 cm³ extractions, removing the first organic layer before adding the second.

First extraction:

$$5.00 = \frac{x/20.0}{(1.20-x)/100} \quad \Rightarrow \quad x = 0.600 \text{ g}$$

Note Academy

There are 0.600 g left in water. For the second extraction, let y g transfer to **fresh** solvent:

$$5.00 = \frac{y/20.0}{(0.600-y)/100} \quad \Rightarrow \quad y = 0.300 \text{ g}$$

Together the organic layers contain $0.600 + 0.300 = \mathbf{0.900}$ g, or **75.0%** of the original solute, compared with 0.800 g and 66.7% for one extraction. The coefficient has not changed; the sequence of equilibrium distributions has.

Fresh portions extract more solute

Start: 1.20 g in 100 cm³ water; Kpc (organic/water) = 5.00

One 40.0 cm³ portion

0.800 g extracted

0.400 g left in water

Total extracted: 0.800 g (66.7%)

Two fresh 20.0 cm³ portions

First: 0.600 g extracted

0.600 g remains in water

↓

Second: 0.300 g extracted

0.300 g remains in water

Total extracted: 0.900 g (75.0%)

Remove each organic layer before adding the next fresh portion.

Note Academy

TRY IT

Repeat the preceding practice problem using two fresh 15.0 cm³ portions instead of one 30.0 cm³ portion. Compare the total mass extracted.

Answer: The first extraction removes 0.300 g, leaving 0.600 g. The second removes 0.200 g, leaving 0.400 g. Total extracted = **0.500 g**, compared with **0.450 g** in one extraction. Start the second calculation with the remaining 0.600 g, not the original 0.900 g.

Choosing the right equilibrium method

Situation	Start with	Essential check
Strong acid or alkali	Ion stoichiometry, then pH or K_w	Ions per formula unit; final volume
Weak acid alone	$K_a = [H^+][A^-]/[HA]$	Small ionisation; negligible water contribution
Buffer	Neutralisation moles, then $[H^+] = K_a[HA]/[A^-]$	Both components remain; use amounts after reaction
Salt in pure water	Dissolution equation, then concentrations in terms of s	Ion ratio and powers
Common ion present	K_{sp} and total concentration of that ion	Is its contribution from dissolution negligible?
Extraction	Mass balance and concentrations in both layers	Ratio direction; mass remaining after each extraction

Check that equations balance, units match the expression, calculated masses do not exceed the starting mass, and your explanation agrees with the result. A buffer given acid should decrease in pH; a common ion should reduce solubility under the assumptions used here.

References and further reading

Coverage follows section 25 of the **Cambridge 9701 syllabus for 2025–2027**. Alternative explanations are available in Chemguide's **acid–base theory**, **acid strength**, **ionic product of water**, **buffers**, **solubility-product guide** and **partition-coefficient guide**. Explanations, numerical exercises and diagrams were written for Note Academy.

Note Academy