

Equilibria

A2

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What you need to know

By the end of this topic you should be able to:

Acids and bases

1. **Use the words conjugate acid and conjugate base.** When an acid gives away a proton, what is left is its conjugate base; when a base takes a proton, it becomes its conjugate acid.
2. **Define a conjugate acid–base pair** (two species that differ by one proton) and pick out both pairs in an acid–base equation.
3. **Write pH, K_a , pK_a and K_w as mathematical definitions** and use them in calculations. (K_b and $K_w = K_a \times K_b$ are not tested.)
4. **Calculate $[H^+]$ and pH** for a strong acid, a strong alkali and a weak acid.
5. **Buffers:** define a buffer solution, say how one is made, explain with equations how it keeps the pH nearly steady, and describe where buffers are used, including the hydrogencarbonate ion, HCO_3^- , in blood.
6. **Calculate the pH of a buffer** from the data given.
7. **Understand the solubility product, K_{sp} ,** of a sparingly soluble salt.
8. **Write the K_{sp} expression** for a salt, with its units.
9. **Calculate K_{sp} from concentrations,** and concentrations (the solubility) from K_{sp} .
10. **Explain the common ion effect:** a salt is less soluble in a solution that already contains one of its ions. Do calculations with K_{sp} and the concentration of that common ion.

Partition coefficients

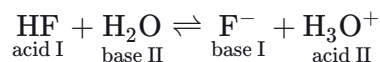
11. **State what a partition coefficient, K_{pc} , is.**
12. **Calculate and use K_{pc}** for a solute that is in the same physical state (dissolved) in both solvents.
13. **Explain what makes K_{pc} large or small,** in terms of how polar the solute and the two solvents are.

Exam questions on this topic also use a few ideas from other topics, and this note covers them where they come up: pH titration curves (AS Equilibria), how chlorine atoms and alkyl groups change the strength of a carboxylic acid (Carboxylic acids), and the stability constant K_{stab} (Transition elements).

Understand it

Conjugate acids and bases

A **Brønsted–Lowry acid** donates a proton (H^+) and a **base** accepts one. Every acid–base reaction is a proton passing from one species to another, so it can also run backwards:



When HF loses its proton it becomes F^- , which could take a proton back: F^- is the **conjugate base** of HF. In the same way H_3O^+ is the conjugate acid of H_2O . A **conjugate acid–base pair** is two species that differ by exactly one proton, so this equation has two pairs: HF/F^- and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.

To find the conjugate base, take one H^+ off (the charge drops by one); to find the conjugate acid, put one H^+ on (the charge rises by one). Some ions can do both. The hydrogensulfite ion HSO_3^- has conjugate acid H_2SO_3 and conjugate base SO_3^{2-} . Water is the same: its conjugate acid is H_3O^+ and its conjugate base is OH^- .

An amine such as ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, is a base because the lone pair on its nitrogen atom can accept a proton (forming a dative bond), giving $\text{C}_2\text{H}_5\text{NH}_3^+$.

pH and the ionic product of water

pH measures the concentration of hydrogen ions on a log scale:

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

Each pH unit is a factor of 10 in $[\text{H}^+]$, so pH 2 has ten times the $[\text{H}^+]$ of pH 3.

Water itself ionises very slightly: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$. In any aqueous solution at 298 K

$$K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}.$$

So if you know one of $[\text{H}^+]$ and $[\text{OH}^-]$ you know the other. In pure water they are equal: $[\text{H}^+] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}$, pH 7.00. A solution is **neutral** when $[\text{H}^+] = [\text{OH}^-]$, **acidic** when $[\text{H}^+]$ is larger and **alkaline** when $[\text{OH}^-]$ is larger.

The ionisation of water is **endothermic**, so heating moves the equilibrium to the right and K_w gets bigger. At 50 °C, K_w is about 5.48×10^{-14} , so pure water has $[\text{H}^+] = 2.34 \times 10^{-7}$ and pH 6.63. It is still neutral, because $[\text{H}^+] = [\text{OH}^-]$; "neutral" only means pH 7 at 298 K.

Strong acids and strong alkalis

A strong acid is fully dissociated, so $[\text{H}^+]$ equals the acid's concentration (for HCl and HNO_3). For 0.0200 mol dm^{-3} HNO_3 : $\text{pH} = -\log 0.0200 = 1.70$.

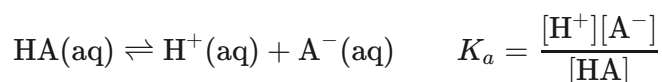
A strong alkali is fully dissociated too. Find $[\text{OH}^-]$, then use K_w :

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$$

For $0.0200 \text{ mol dm}^{-3} \text{ KOH}$, $[\text{H}^+] = 1.00 \times 10^{-14} \div 0.0200 = 5.00 \times 10^{-13}$, so $\text{pH} = 12.30$. Watch the formula: each $\text{Sr}(\text{OH})_2$ or $\text{Ba}(\text{OH})_2$ gives **two** OH^- , so $0.0200 \text{ mol dm}^{-3} \text{ Ba}(\text{OH})_2$ has $[\text{OH}^-] = 0.0400$. You can also use $\text{pOH} = -\log[\text{OH}^-]$ and $\text{pH} + \text{pOH} = 14.00$.

Weak acids, K_a and $\text{p}K_a$

A weak acid HA is only partly dissociated, and the equilibrium has its own constant, the **acid dissociation constant**:



Its units are mol dm^{-3} . A larger K_a means a stronger acid. Because K_a values are small, they are often given as $\text{p}K_a = -\log_{10} K_a$ (so $K_a = 10^{-\text{p}K_a}$); a **smaller** $\text{p}K_a$ means a **stronger** acid.

For a solution of a weak acid alone, two approximations make the calculation easy:

- every H^+ comes from the acid, so $[\text{A}^-] = [\text{H}^+]$ (the water's own H^+ is negligible);
- so little of the acid dissociates that $[\text{HA}]$ at equilibrium is still its starting concentration c .

Then $K_a = \frac{[\text{H}^+]^2}{c}$, which gives

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

The same equation works backwards: from a measured pH, $[\text{H}^+] = 10^{-\text{pH}}$ and $K_a = [\text{H}^+]^2 \div c$, or $c = [\text{H}^+]^2 \div K_a$. If the acid is fairly strong (a large fraction ionises, so $[\text{H}^+]$ is a sizeable part of c), use $[\text{HA}] = c - [\text{H}^+]$ instead of c .

Why some acids are stronger than others

Strong acids such as H_2SO_4 and HCl are fully dissociated, so they are stronger than any weak acid. Among carboxylic acids, what matters is how easily the O–H bond gives up its proton, which depends on how stable the anion left behind is:

- Chlorine atoms are electron-withdrawing.** They pull electron density away from the COO^- group, spreading its charge, so the anion is more stable and the O–H bond is weaker. Chloroethanoic acid is stronger (larger K_a) than ethanoic acid, and each extra chlorine makes it stronger again.
- Alkyl groups are electron-donating.** They push electron density onto COO^- , making the anion less stable and the O–H bond stronger, so the acid is weaker. Propanoic acid is weaker than ethanoic acid.

Buffer solutions

A **buffer solution** resists changes in pH when small amounts of acid or alkali are added. It does not keep the pH exactly constant; the pH changes only a little.

A buffer contains a weak acid **and** its conjugate base, both in reasonable amounts. There are two ways to make one:

- mix the weak acid with a salt of it, for example ethanoic acid with sodium ethanoate;
- add a strong base such as NaOH to an **excess** of the weak acid, so that part of the acid is turned into its conjugate base: $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$.

How it works, using lactic acid (HL) and lactate ions (L^-) as the example:

- **Acid added:** the extra H^+ is removed by the conjugate base: $\text{L}^- + \text{H}^+ \rightarrow \text{HL}$.
- **Alkali added:** the extra OH^- is removed by the weak acid: $\text{HL} + \text{OH}^- \rightarrow \text{L}^- + \text{H}_2\text{O}$.

Either way the added ions are used up and the ratio $[\text{HL}] \div [\text{L}^-]$ changes only slightly, so $[\text{H}^+]$ and the pH change only slightly. A buffer only works while both parts are present in large amounts compared with what is added. If too much strong acid or alkali is added, one part is used up and the pH changes sharply, towards 1 with excess strong acid or above 13 with excess strong alkali.

An ion that can both gain and lose a proton buffers on its own, with its conjugate acid and base forming as needed. The hydrogencarbonate ion does this:



Blood is kept at about pH 7.4 mainly by the $\text{H}_2\text{CO}_3/\text{HCO}_3^-$ system. Extra acid is taken up by HCO_3^- to make H_2CO_3 (which leaves the body as carbon dioxide); extra alkali reacts with H_2CO_3 to make HCO_3^- . Other uses of buffers include shampoos, food, fermentation and calibrating pH meters. Amino acids buffer in the same way: the NH_2 group takes up H^+ and the COOH group reacts with OH^- .

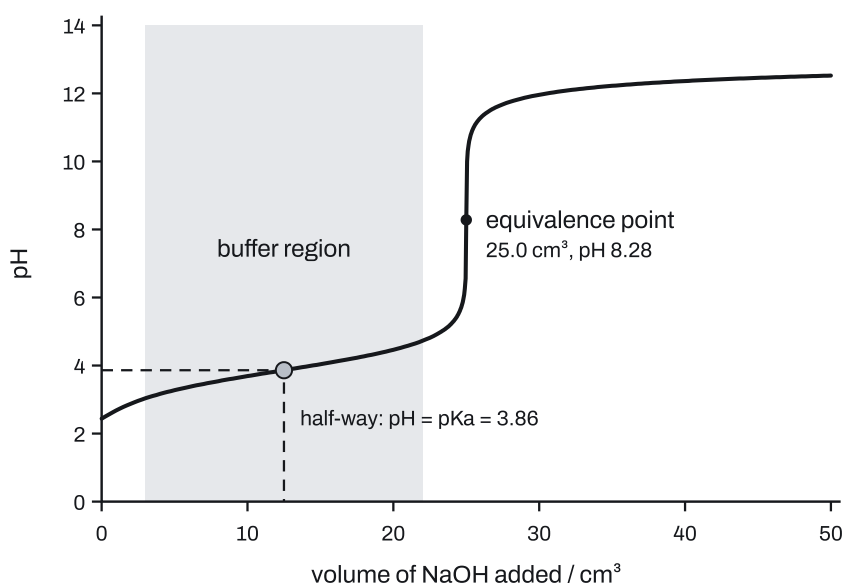
The pH of a buffer

In a buffer, $[\text{H}^+]$ and $[\text{A}^-]$ are **not** equal, so don't use $\sqrt{K_a c}$. Rearrange the K_a expression instead:

$$[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]} \quad \text{or} \quad \text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

Both forms earn the same marks. Because the acid and its salt are in the same volume, you can put **moles** into the ratio instead of concentrations. When $[\text{HA}] = [\text{A}^-]$ (an acid exactly half neutralised), the ratio is 1 and $\text{pH} = \text{p}K_a$.

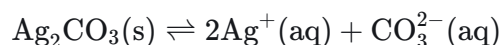
Titration curve of a weak acid with a strong base



The graph shows what happens as NaOH is added to lactic acid. At the start only the weak acid is present (pH 2.43, from $\sqrt{K_a c}$). Once some NaOH has been added, the flask holds both lactic acid and lactate ions, which is a buffer, so the pH rises only slowly: this is the **buffer region**. Half-way to the end point the two are equal and $\text{pH} = \text{p}K_a = 3.86$. At the **equivalence point** all the acid has become sodium lactate. The pH there is above 7 (8.28 here), because lactate ions are a weak base: they take a few protons from water, leaving extra OH^- .

Solubility product

A "sparingly soluble" salt such as silver carbonate dissolves only a little, and in a saturated solution the solid is in equilibrium with its ions:



The solid is left out of the expression (its concentration doesn't change), which leaves the **solubility product**:

$$K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$$

Each ion concentration is raised to the power of its number in the formula. The units follow: here $(\text{mol dm}^{-3})^3 = \text{mol}^3 \text{ dm}^{-9}$. K_{sp} is only used for sparingly soluble salts, and like every equilibrium constant it changes only with temperature.

From solubility to K_{sp} and back. If $s \text{ mol dm}^{-3}$ of Ag_2CO_3 dissolves, the solution holds $[\text{Ag}^+] = 2s$ and $[\text{CO}_3^{2-}] = s$, so $K_{sp} = (2s)^2 \times s = 4s^3$. The general pattern:

Formula type	Example	Ion concentrations	K_{sp}
AB	AgBr	s, s	s^2
AB_2 or A_2B	$\text{CaF}_2, \text{Ag}_2\text{CO}_3$	$s, 2s$	$4s^3$
AB_3	$\text{Al}(\text{OH})_3$	$s, 3s$	$27s^4$

Formula type	Example	Ion concentrations	K_{sp}
A_3B_2	$Ca_3(PO_4)_2$	$3s, 2s$	$108s^5$

Work these out from the formula each time rather than memorising the table.

The common ion effect

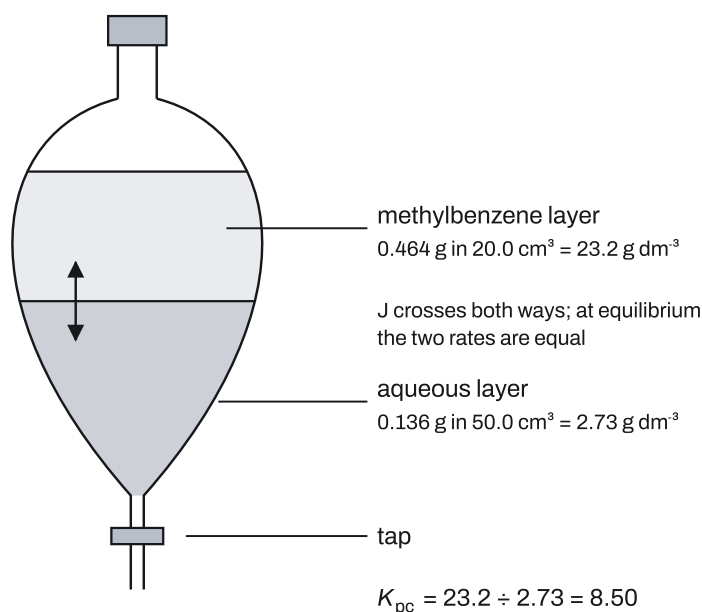
Add a soluble salt that shares an ion with the saturated solution, such as Na_2CO_3 added to saturated Ag_2CO_3 . The extra CO_3^{2-} makes $[Ag^+]^2[CO_3^{2-}]$ bigger than K_{sp} , so by Le Chatelier's principle the equilibrium moves left and solid Ag_2CO_3 **precipitates** until the product falls back to K_{sp} . So a salt is **less soluble** in a solution that already contains one of its ions. This is the **common ion effect**.

To calculate the new solubility, take the common ion's concentration from the added salt (the tiny amount from the dissolving salt is negligible) and solve for the other ion. The same idea explains why a hydroxide such as $Zn(OH)_2$ is less soluble in $NaOH(aq)$ than in water, and why adding a soluble calcium salt to saturated calcium hydroxide gives a white precipitate and lowers the pH (hydroxide ions are removed from solution).

Partition coefficients

Some solvents don't mix: water and methylbenzene form two layers, one on top of the other. Shake a solute with both and it spreads between the layers. Molecules keep crossing the boundary in both directions, and eventually they cross at equal rates in each direction. At this dynamic equilibrium the ratio of the two concentrations is fixed at a given temperature:

$$K_{pc} = \frac{\text{concentration of solute in solvent 1}}{\text{concentration of solute in solvent 2}}$$

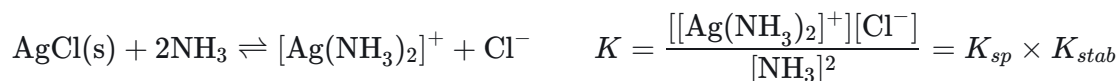


The question always says which solvent goes on top of the fraction; follow it. K_{pc} has no units, and the concentrations can be in g dm^{-3} or mol dm^{-3} (the same unit top and bottom), because the solute is the same in both.

What decides the value? Polarity: like dissolves like. A non-polar solute (a molecule with a long hydrocarbon chain, or iodine) dissolves better in a non-polar solvent such as hexane, so K_{pc} (hexane/water) is large. A polar solute that can hydrogen bond with water (a short alcohol, a small carboxylic acid) or an ionic compound stays mostly in water, so the same K_{pc} is small. If the organic solvent is itself somewhat polar (octan-1-ol, a ketone), a polar solute dissolves in it better than in hexane.

Combining equilibrium constants

The K for an overall reaction made of two steps added together is the product of the two K s. For example, silver chloride dissolving in ammonia is "dissolve" plus "form the complex":



where $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$ and $K_{stab} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$; multiplying them cancels $[\text{Ag}^+]$. A large K_{stab} means the complex is stable and its equilibrium lies far to the right.

Key facts and formulas

"Given" means it is printed in the list of important values and constants on the Paper 4 question paper (with the Periodic Table for A_r values). "Learn it" means you must remember it.

Formula	Status
$K_w = [\text{H}^+][\text{OH}^-] = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K (the value)	Given
$K_w = [\text{H}^+][\text{OH}^-]$ (the expression)	Learn it
$\text{pH} = -\log_{10}[\text{H}^+]; [\text{H}^+] = 10^{-\text{pH}}$	Learn it
$\text{pOH} = -\log_{10}[\text{OH}^-]; \text{pH} + \text{pOH} = 14.00$ at 298 K	Learn it
$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$, units mol dm^{-3}	Learn it
$\text{p}K_a = -\log_{10} K_a; K_a = 10^{-\text{p}K_a}$	Learn it
Weak acid alone: $[\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$	Learn it
Buffer: $[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$, or $\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$	Learn it
K_{sp} of $\text{A}_x\text{B}_y = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$, units $(\text{mol dm}^{-3})^{x+y}$	Learn it
$K_{pc} = \frac{[\text{solute in solvent 1}]}{[\text{solute in solvent 2}]}$ at equilibrium, no units	Learn it
Concentration = $\frac{\text{moles}}{\text{volume in dm}^3}$; moles = $\frac{\text{mass}}{M_r}$	Learn it
A_r values (Periodic Table)	Given

How to do it

In the Paper 4 questions we have tagged for this topic (55 questions, 2021–2025, of which 15 are repeats of a question in another paper of the same session), the types came up this often. 29 of the 55 questions mix several types, so the counts add up to more than 55.

Question type	Questions
Define a buffer and write equations for how it works	18
Write a K _{sp} expression and calculate K _{sp} from solubility	15
pH of a strong acid or strong alkali	14
Conjugate acid–base pairs	13
Solubility or an ion concentration from K _{sp}	12
pH of a buffer, or what is needed for a given pH	12
Partition coefficients	12
Explain the common ion effect	10
pH of a weak acid from K _a or pK _a	8
K _a , pK _a or concentration of a weak acid from its pH	7
Relative strength of acids	4
K _w and how it changes with temperature	3
Stability constants and combined K expressions	2
Weak acid–strong base titration curve	2

1. Define a buffer and write equations for how it works (18 questions)

- Definition (2 marks):** a solution that resists changes in pH **when small amounts of acid or alkali are added**. Both halves are needed.
- Name the two parts:** the weak acid and its conjugate base (usually from its sodium salt).
- Two equations**, one for each direction:
 - added acid: conjugate base + H^+ → weak acid;
 - added alkali: weak acid + OH^- → conjugate base + H_2O .

You may write them with the sodium salt, for example $\text{CH}_3\text{COONa} + \text{HCl} \rightarrow \text{CH}_3\text{COOH} + \text{NaCl}$, if you balance them.

Variations you will meet:

- **Ions that buffer on their own** (H_2PO_4^- , HPO_4^{2-} , HCO_3^- , hydrogenethanedioate HC_2O_4^-): the ion is the acid in one equation and the base in the other, for example $\text{H}_2\text{PO}_4^- + \text{H}^+ \rightarrow \text{H}_3\text{PO}_4$ and $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O}$. For a mixture of two ions of the same acid, the more protonated one reacts with OH^- and the other with H^+ .
- **Amino acids** ($\text{H}_2\text{NCH(R)COOH}$): $\text{H}_2\text{NCH(R)COOH} + \text{H}^+ \rightarrow \text{H}_3\text{NCH(R)COOH}$ and $\text{H}_2\text{NCH(R)COOH} + \text{OH}^- \rightarrow \text{H}_2\text{NCH(R)COO}^- + \text{H}_2\text{O}$. Start from the neutral molecule in both equations.
- **"Suggest a substance to add to a weak acid to make a buffer"**: its sodium salt (supplies the conjugate base), or NaOH in a smaller amount than the acid (makes the conjugate base). An organic answer is the salt, such as sodium butanoate for butanoic acid.
- **Weak acid + a neutral salt such as NaCl**: there is no conjugate base, so it can't resist added acid. It does "buffer" against added alkali, because OH^- turns some weak acid into its conjugate base: $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$.
- **The blood buffer** is HCO_3^- (with H_2CO_3).
- **Too much strong acid or alkali** (for example a buffer mixed with an equal volume of $1.00 \text{ mol dm}^{-3} \text{ KOH}$): the weak acid is all used up and excess OH^- remains, so the pH jumps above 13; the temperature rises a little because neutralisation is exothermic.

2. Write a K_{sp} expression and calculate K_{sp} from solubility (15 questions)

1. **Write the expression** from the formula: each ion to the power of its number, for example Zn(OH)_2 :

$$K_{sp} = [\text{Zn}^{2+}][\text{OH}^-]^2$$
. Never write $[\text{2OH}^-]$: the 2 is a power, not a multiplier inside the bracket.
2. **Units**: count the powers. Three concentrations multiplied gives $\text{mol}^3 \text{ dm}^{-9}$; five gives $\text{mol}^5 \text{ dm}^{-15}$.
3. **Convert the solubility to mol dm⁻³** if it is in g dm⁻³: divide by M_r .
4. **Find each ion's concentration** using the formula (for Zn(OH)_2 : $[\text{Zn}^{2+}] = s$, $[\text{OH}^-] = 2s$).
5. **Substitute and calculate**, at least 2 s.f., with the units.

Variations you will meet:

- **From a pH** of a saturated hydroxide solution: $[\text{H}^+] = 10^{-\text{pH}}$, $[\text{OH}^-] = K_w \div [\text{H}^+]$, $[\text{M}^{2+}] = \frac{1}{2}[\text{OH}^-]$, then K_{sp} .
- **From measured ion concentrations** after a precipitate forms: put the given values straight in; they don't need to be in the formula's ratio.
- **Unusual ions**: mercury(I) is Hg_2^{2+} , so Hg_2Cl_2 gives $[\text{Hg}_2^{2+}] = s$ and $[\text{Cl}^-] = 2s$, and $K_{sp} = 4s^3$.

3. pH of a strong acid or strong alkali (14 questions)

1. **Strong acid**: $[\text{H}^+] = \text{concentration of HCl or HNO}_3$; $\text{pH} = -\log[\text{H}^+]$.
2. **Strong alkali**: $[\text{OH}^-]$ from the concentration, times 2 for a Group 2 hydroxide; $[\text{H}^+] = K_w \div [\text{OH}^-]$; $\text{pH} = -\log[\text{H}^+]$. Or pOH, then $\text{pH} = 14 - \text{pOH}$.
3. Give pH to 2 decimal places if asked, otherwise at least 2 s.f.

Variations you will meet:

- **Start from a mass:** mass of solid $\div M_r$ = moles; if an oxide dissolves ($\text{SrO} + \text{H}_2\text{O} \rightarrow \text{Sr}(\text{OH})_2$), moles of hydroxide = moles of oxide; divide by the flask volume in dm^3 ; double for $[\text{OH}^-]$.
- **Work backwards from a pH:** $[\text{H}^+] = 10^{-\text{pH}}$, $[\text{OH}^-] = K_w \div [\text{H}^+]$, halve for $[\text{M}(\text{OH})_2]$, times the volume for moles, times M_r for mass.
- **Identify a Group 2 hydroxide:** from pH find $[\text{OH}^-]$, halve it, get moles, then $M_r = \text{mass} \div \text{moles}$. Subtract 34.0 for the two OH groups and match the A_r to a Group 2 metal.
- **Equal concentrations of HCl and NaOH** with pH values that differ by a given amount d : $\text{pH}(\text{acid}) = -\log c$ and $\text{pH}(\text{alkali}) = 14 + \log c$, so $d = 14 + 2 \log c$. Solve for c . Mixing equal volumes gives NaCl, pH 7; adding a little strong acid or alkali to this unbuffered solution swings the pH a long way (to about 2 or 12).
- **$[\text{OH}^-]$ in an acid solution:** $K_w \div [\text{H}^+]$, however small.
- **A strong acid with the same pH as a weak acid:** its concentration equals $[\text{H}^+]$, far less than the weak acid's concentration.

4. Conjugate acid–base pairs (13 questions)

1. **Definition:** two species that differ by one proton (H^+).
2. **In an equation**, match each reactant with the product that has one proton more or one fewer. The acid on the left pairs with a base on the right, and the base on the left pairs with an acid on the right.
3. **Conjugate base** of a species: remove one H^+ . **Conjugate acid:** add one H^+ .

Variations you will meet:

- **Amphiprotic ions:** HPO_4^{2-} has conjugate acid H_2PO_4^- and conjugate base PO_4^{3-} ; HS^- is the conjugate base of H_2S (not S^{2-} , which is two protons away).
- **Water as acid or base:** with NH_3 , water is the acid (pair $\text{H}_2\text{O}/\text{OH}^-$); with an acid, water is the base (pair $\text{H}_3\text{O}^+/\text{H}_2\text{O}$).
- **"Write the equation for the stronger acid with water":** pick the acid with the larger K_a (smaller $\text{p}K_a$), then $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$.
- **A diprotic strong acid in water** gives three pairs: $\text{H}_2\text{SO}_4/\text{HSO}_4^-$, $\text{HSO}_4^-/\text{SO}_4^{2-}$ and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.
- **A metal with excess acid** (for example calcium with ethanoic acid gives calcium ethanoate and hydrogen): the pairs in the mixture are $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.
- **Why an amine is a base:** the lone pair on N accepts a proton.

5. Solubility or an ion concentration from K_{sp} (12 questions)

1. **Write K_{sp} in terms of s** using the formula: for CaF_2 , $K_{sp} = s \times (2s)^2 = 4s^3$.
2. **Solve:** $s = \sqrt[3]{K_{sp} \div 4}$ (a square root for s^2 , a fourth root for $27s^4$).
3. **Answer what was asked:** the solubility s , an ion concentration (such as $[\text{F}^-] = 2s$), a mass per dm^3 ($s \times M_r$), or per 100 cm^3 (divide by 10).

Variation: with a common ion. Take that ion's concentration from the added solution, remembering the formula: in $0.010 \text{ mol dm}^{-3} \text{ Ba(OH)}_2$, $[\text{OH}^-] = 0.020$. Then, for Zn(OH)_2 , $[\text{Zn}^{2+}] = K_{sp} \div 0.020^2$, and that is the solubility.

6. pH of a buffer, or what is needed for a given pH (12 questions)

- Find the moles** of weak acid and of conjugate base in the final mixture.
 - Acid + its salt: moles of each from concentration $\times$ volume (or mass $\div M_r$). A salt with two anions per formula, such as calcium ethanoate $(\text{CH}_3\text{COO})_2\text{Ca}$, gives **twice** its concentration of A^- .
 - Weak acid + NaOH (acid in excess): moles of A^- formed = moles of OH^- added; moles of HA left = moles of acid at the start – moles of OH^- .
- $[\text{H}^+] = K_a \times \frac{\text{moles of HA}}{\text{moles of A}^-}$ (the volume cancels).
- $\text{pH} = -\log[\text{H}^+]$.

If exactly half the acid has been neutralised, $\text{pH} = \text{p}K_a$ with no further working.

Reverse questions (find what makes a given pH):

- $[\text{H}^+] = 10^{-\text{pH}}$.
- Rearrange: $\frac{[\text{A}^-]}{[\text{HA}]} = \frac{K_a}{[\text{H}^+]}$.
- Multiply by the known amount of HA to find the amount of A^- , then convert to what is asked (mass of salt, concentration, or the concentration of the acid before mixing, using the volumes).

Other forms: a given ratio such as $[\text{HCO}_3^-] \div [\text{H}_2\text{CO}_3]$ goes straight into the K_a expression; a salt of a weak acid with some HCl added makes HA from A^- (moles of HA formed = moles of HCl).

7. Partition coefficients (12 questions)

- Definition:** the ratio of the concentrations of a solute in two immiscible solvents, at equilibrium.
- Let x** be the mass (or moles) that ends up in one solvent; the other solvent then holds total $-x$.
- Write $K_{pc} = \frac{x \div V_1}{(\text{total} - x) \div V_2}$** , with the solvents in the order the question gives.
- Solve** for x .

Variations you will meet:

- Only part of a solution is used** (for example 40.0 cm^3 taken from a 100.0 cm^3 flask): the total mass is scaled first ($\times 40 \div 100$).
- Find K_{pc} :** the mass left in water = the starting mass – the mass extracted; divide each mass by its volume and take the ratio the right way round.
- Find a volume:** the masses are known; solve the same equation for V .
- Equal masses in each solvent:** the volume ratio must equal K_{pc} (for $K_{pc}(\text{hexane/water}) = 5$, use 5 times as much water as hexane).

- **A value measured too soon** is too low (or too high): equilibrium had not been reached, so the solute had not finished moving between the layers.
- **Polarity**: pick the least polar solute for a large K_{pc} (organic/water); predict a smaller or larger K_{pc} in a more polar organic solvent.

8. Explain the common ion effect (10 questions)

1. **State the direction**: the solubility **decreases** (or is lower than in water).
2. **Name it**: the common ion effect.
3. **Explain if asked**: the added ion raises the ionic product above K_{sp} , so the equilibrium moves left and solid precipitates.

Variations you will meet:

- **Observations**: a precipitate of the sparingly soluble salt forms, in its colour (white for $\text{Ca}(\text{OH})_2$ or CaCO_3 , yellow for PbI_2 or AgI).
- **pH after adding a calcium salt to saturated calcium hydroxide**: some OH^- precipitates as $\text{Ca}(\text{OH})_2$, so the pH falls, but stays above 7.
- **A cell potential** that depends on the concentration of an ion: the common ion lowers that ion's concentration, so predict the change in E from the lower concentration.

9. pH of a weak acid from K_a or pK_a (8 questions)

1. $K_a = 10^{-pK_a}$ if you're given pK_a .
2. **Find the acid's concentration** if needed: moles (mass $\div M_r$) $\div$ volume in dm^3 .
3. $[\text{H}^+] = \sqrt{K_a \times [\text{HA}]}$.
4. $\text{pH} = -\log[\text{H}^+]$.

Variation: the percentage of the acid that is ionised = $\frac{[\text{H}^+]}{[\text{HA}]} \times 100$.

10. K_a , pK_a or concentration of a weak acid from its pH (7 questions)

1. $[\text{H}^+] = 10^{-\text{pH}}$.
2. **For K_a** : $K_a = [\text{H}^+]^2 \div [\text{HA}]$, then $pK_a = -\log K_a$.
3. **For the concentration**: $[\text{HA}] = [\text{H}^+]^2 \div K_a$.

Variations you will meet:

- **A fairly strong acid** (low pH at a high concentration, so a lot is ionised): $[\text{HA}]_{\text{eqm}} = c - [\text{H}^+]$ and $[\text{A}^-] = [\text{H}^+]$, then $K_a = [\text{H}^+]^2 \div (c - [\text{H}^+])$.
- **Compare a strong and a weak acid of the same pH**: they have the same $[\text{H}^+]$; the ratio of their concentrations is $[\text{H}^+] \div ([\text{H}^+]^2 \div K_a) = K_a \div [\text{H}^+]$.
- **Write K_a or the K_a - pK_a link** as expressions.

11. Relative strength of acids (4 questions)

1. **Put strong acids first** (H_2SO_4 , HCl): fully dissociated.
2. **Then weak acids**, ordered by their groups: more chlorine atoms (closer to COOH) → stronger; alkyl groups → weaker.
3. **Explain the chain:** Cl is electron-withdrawing → stabilises the anion (spreads its charge) → weakens the O–H bond → H^+ is released more easily. For alkyl groups: electron-donating → destabilises the anion → strengthens O–H → weaker acid.
4. **Match K_a values:** stronger acid = larger K_a = smaller pK_a .

12. K_w and how it changes with temperature (3 questions)

1. $K_w = [\text{H}^+][\text{OH}^-]$.
2. K_w **increases with temperature**, so the ionisation of water is endothermic (the equilibrium moves right on heating).
3. **Neutral pH at another temperature:** $[\text{H}^+] = \sqrt{K_w}$, $\text{pH} = -\log \sqrt{K_w}$. Above 298 K this is below 7.
4. **"Is pH 7.00 acidic or alkaline at this temperature?"** Compare with the neutral pH, or find $[\text{OH}^-] = K_w \div 10^{-7}$ and compare with $[\text{H}^+] = 10^{-7}$. Above 298 K, pH 7.00 has $[\text{OH}^-] > [\text{H}^+]$, so it is alkaline.

13. Stability constants and combined K expressions (2 questions)

1. K_{stab} for $\text{M}^{n+} + x\text{L} \rightleftharpoons [\text{ML}_x]^{n+}$ is $\frac{[\text{ML}_x]^{n+}}{[\text{M}^{n+}][\text{L}]^x}$. Leave water out, even when the metal ion starts as an aqua complex. Units from the powers (for example $\text{mol}^{-3} \text{dm}^9$ for $x = 3$).
2. **A large K_{stab}** means the equilibrium lies far to the right and the complex is stable.
3. **Overall K** for "dissolve a salt and form a complex": write it, then show it equals $K_{sp} \times K_{stab}$ (multiply, don't divide).

14. Weak acid–strong base titration curve (2 questions)

1. **In the gently rising part** the solution contains the weak acid and its conjugate base (for example CH_3COOH and CH_3COO^-). It is a buffer, so added OH^- is removed by the acid and the pH changes slowly.
2. **At the equivalence point** the pH is above 7, because the salt's anion is a weak base that reacts with water to form some OH^- .
3. **Half-way to the equivalence point**, $\text{pH} = pK_a$.

Worked examples

The bold codes show where marks are earned, as in Cambridge mark schemes. The number is how many marks.

- **M1** method mark: for a correct method, even if the numbers slip.
 - **A1** accuracy mark: for a correct answer; it needs the M mark before it.
 - **B1** mark for a correct result on its own, with no method needed.
-

Example 1

Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, is a weak monobasic acid with $K_a = 1.38 \times 10^{-4} \text{ mol dm}^{-3}$ at 298 K.

- (a) Write the expression for the K_a of lactic acid. **[1]**
- (b) Calculate the pH of $0.0800 \text{ mol dm}^{-3}$ lactic acid at 298 K. **[2]**
- (c) Calculate the concentration of hydrochloric acid that has the same pH. **[1]**
- (d) Calculate the pH of $0.0450 \text{ mol dm}^{-3}$ potassium hydroxide at 298 K. **[2]**

$$\text{(a)} K_a = \frac{[\text{H}^+][\text{CH}_3\text{CH}(\text{OH})\text{COO}^-]}{[\text{CH}_3\text{CH}(\text{OH})\text{COOH}]} \quad \text{B1}$$

$$\text{(b)} [\text{H}^+] = \sqrt{1.38 \times 10^{-4} \times 0.0800} = 3.32 \times 10^{-3} \text{ mol dm}^{-3} \quad \text{M1}$$

$$\text{pH} = -\log(3.32 \times 10^{-3}) = 2.48 \quad \text{A1}$$

(c) HCl is fully dissociated, so its concentration equals $[\text{H}^+]$: $3.32 \times 10^{-3} \text{ mol dm}^{-3}$. **B1**

$$\text{(d)} [\text{OH}^-] = 0.0450, \text{ so } [\text{H}^+] = \frac{1.00 \times 10^{-14}}{0.0450} = 2.22 \times 10^{-13} \text{ mol dm}^{-3}. \quad \text{M1}$$

$$\text{pH} = -\log(2.22 \times 10^{-13}) = 12.65 \quad \text{A1}$$

Example 2

A student makes a buffer by adding 25.0 cm^3 of $0.200 \text{ mol dm}^{-3}$ NaOH to 60.0 cm^3 of $0.250 \text{ mol dm}^{-3}$ lactic acid, HL. K_a of lactic acid = $1.38 \times 10^{-4} \text{ mol dm}^{-3}$.

- (a) Define a buffer solution. **[2]**
- (b) Write two equations to show how this mixture acts as a buffer. **[2]**
- (c) Calculate the pH of the buffer. **[3]**
- (d) A second buffer, of pH 4.00, is made by dissolving sodium lactate, NaL (M_r 112.0), in 100 cm^3 of $0.250 \text{ mol dm}^{-3}$ lactic acid. Calculate the mass of sodium lactate needed. **[3]**

(a) A solution that resists changes in pH **B1** when small amounts of acid or alkali are added. **B1**

(b) $L^- + H^+ \rightarrow HL$ **B1** and $HL + OH^- \rightarrow L^- + H_2O$ **B1**

(c) Moles of HL at the start = $0.0600 \times 0.250 = 0.0150$. Moles of OH^- = $0.0250 \times 0.200 = 0.00500$. So moles of L^- formed = 0.00500 and moles of HL left = $0.0150 - 0.00500 = 0.0100$. **M1**

$$[H^+] = K_a \times \frac{[HL]}{[L^-]} = 1.38 \times 10^{-4} \times \frac{0.0100}{0.00500} = 2.76 \times 10^{-4} \text{ mol dm}^{-3}$$

M1. Both are in the same 85.0 cm^3 , so moles can go in the ratio.

$$\text{pH} = -\log(2.76 \times 10^{-4}) = 3.56 \text{ A1}$$

(d) $[H^+] = 10^{-4.00} = 1.00 \times 10^{-4}$, so $\frac{[L^-]}{[HL]} = \frac{K_a}{[H^+]} = \frac{1.38 \times 10^{-4}}{1.00 \times 10^{-4}} = 1.38$. **M1**

Moles of HL = $0.100 \times 0.250 = 0.0250$, so moles of L^- = $1.38 \times 0.0250 = 0.0345$. **M1**

Mass of NaL = $0.0345 \times 112.0 = 3.86 \text{ g A1}$

Example 3

Silver carbonate, Ag_2CO_3 (M_r 275.8), is sparingly soluble in water. Its K_{sp} is 8.46×10^{-12} at 298 K.

(a) Write the expression for K_{sp} of Ag_2CO_3 and give its units. **[2]**

(b) Calculate the solubility of Ag_2CO_3 in water at 298 K, in g dm^{-3} . **[3]**

(c) Calculate the solubility of Ag_2CO_3 , in mol dm^{-3} , in $0.0500 \text{ mol dm}^{-3} \text{ AgNO}_3$ at 298 K. Name the effect shown. **[3]**

(a) $K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}]$ **B1**; units $\text{mol}^3 \text{ dm}^{-9}$ **B1**

(b) Let the solubility be $s \text{ mol dm}^{-3}$: $[\text{Ag}^+] = 2s$, $[\text{CO}_3^{2-}] = s$, so $K_{sp} = (2s)^2 s = 4s^3$. **M1**

$$s = \sqrt[3]{8.46 \times 10^{-12} \div 4} = 1.28 \times 10^{-4} \text{ mol dm}^{-3} \text{ A1}$$

$$\text{Solubility} = 1.28 \times 10^{-4} \times 275.8 = 0.0354 \text{ g dm}^{-3} \text{ A1}$$

(c) $[\text{Ag}^+] = 0.0500$ from the AgNO_3 (the silver from the dissolving salt is negligible). **M1**

$$[\text{CO}_3^{2-}] = \frac{8.46 \times 10^{-12}}{0.0500^2} = 3.38 \times 10^{-9} \text{ mol dm}^{-3}, \text{ and this is the solubility of } \text{Ag}_2\text{CO}_3. \text{ A1}$$

It is far less soluble than in water: the common ion effect. **B1**

Example 4

The partition coefficient of compound J between methylbenzene and water, $K_{pc} = \frac{[\text{J in methylbenzene}]}{[\text{J in water}]}$, is 8.50 at 298 K. Methylbenzene and water are immiscible.

(a) State what is meant by partition coefficient. **[1]**

(b) 0.600 g of J is dissolved in 50.0 cm³ of water. The solution is shaken with 20.0 cm³ of methylbenzene until equilibrium is reached. Calculate the mass of J extracted into the methylbenzene. **[2]**

(c) The experiment is repeated, but this time the solution is shaken with 10.0 cm³ of methylbenzene, the layers are separated, and the water layer is shaken with a fresh 10.0 cm³ of methylbenzene. Calculate the total mass of J extracted. **[3]**

(d) Compound K is more polar than J and can form hydrogen bonds with water. Suggest, with a reason, how K_{pc} of K between methylbenzene and water compares with 8.50. **[1]**

(a) The ratio of the concentrations of a solute in two immiscible solvents at equilibrium. **B1**

(b) Let x g go into the methylbenzene; $0.600 - x$ g stays in the water. **M1**

$$8.50 = \frac{x \div 20.0}{(0.600 - x) \div 50.0} \Rightarrow 50.0x = 170(0.600 - x) \Rightarrow x = \frac{102}{220} = 0.464 \text{ g}$$

A1. The second diagram in "Understand it" shows this equilibrium.

(c) First 10.0 cm³: $8.50 = \frac{y \div 10.0}{(0.600 - y) \div 50.0}$, so $135y = 51.0$ and $y = 0.378$ g; 0.222 g is left in the water.

M1

Second 10.0 cm³: $135z = 85.0 \times 0.2222$, so $z = 0.140$ g. **M1**

Total = $0.378 + 0.140 = 0.518$ g **A1**, more than the 0.464 g from one 20.0 cm³ portion: several small extractions remove more than one large one.

(d) Smaller: K is more soluble in the polar water (hydrogen bonding) and less soluble in the non-polar methylbenzene, so the ratio is lower. **B1**

Common mistakes

- **Leaving out a proton or the charge** in a conjugate pair. The conjugate base of H₂S is HS[−], not S^{2−}. Examiners also see vague definitions such as "an acid and its base"; say "differ by one proton".
- **Defining a buffer by half.** "Keeps the pH constant" is wrong and loses the mark; it **resists** (minimises) change, and only when **small** amounts of acid **or** alkali are added.
- **Writing K_{sp} with the number inside the bracket**, such as $[\text{Fe}^{2+}][2\text{OH}^-]$, a common wrong answer. The stoichiometry is a power: $[\text{Fe}^{2+}][\text{OH}^-]^2$.
- **Forgetting the factor in K_{sp} calculations.** Using s^3 instead of $4s^3$ (or s^4 instead of $27s^4$) gives an answer that examiners see every year.
- **Using $\sqrt{K_a c}$ for a buffer.** In a buffer $[\text{A}^-]$ comes from the salt, not from the acid's own dissociation. Use $K_a \times [\text{HA}] \div [\text{A}^-]$.
- **Getting the buffer moles wrong** after adding NaOH: the acid left is the starting amount **minus** the OH[−] added. Also, not spotting that half neutralisation means $\text{pH} = \text{p}K_a$.

- **Turning the ratio upside down**, $[A^-] \div [HA]$ in $[H^+] = K_a \times \dots$ or a sign error in $pH = pK_a + \log \dots$. Check: more salt than acid must give a pH **above** pK_a .
- **Missing the 2** for $Ba(OH)_2$, $Sr(OH)_2$ and calcium ethanoate: two OH^- or two CH_3COO^- per formula.
- **Partition: forgetting to subtract**. The mass in the second solvent is the total **minus** the mass extracted; writing $\frac{x \div 50}{0.5 \div 75}$ uses the starting mass instead. Also keep the solvents the way round the question defines K_{pc} .
- **Partition definition without "concentrations" or "immiscible"**, or talking about "two solutions". It is one solute in two immiscible solvents.
- **Calling pH below 7 acidic at any temperature**. Neutral means $[H^+] = [OH^-]$; at higher temperatures neutral water has pH below 7.
- **Dividing instead of multiplying** when combining constants: $K = K_{sp} \times K_{stab}$, not $K_{stab} \div K_{sp}$.
- **Rounding too early**. Keep $[H^+]$ unrounded in your calculator until the pH.

How to get the marks

- **"Define"** needs the precise wording every time: buffer (resists pH change, small amounts of acid or alkali), conjugate pair (differ by one proton), partition coefficient (ratio of concentrations, two immiscible solvents, equilibrium), K_w , K_a and pH as expressions.
- **"Write an expression"** means square brackets for concentrations, powers from the formula, and no solids or water.
- **Units:** K_{sp} always needs them when asked ("include the units"), worked from the powers; K_a is mol dm^{-3} ; K_{pc} has none.
- **Calculations:** show $[H^+]$ (or $[OH^-]$) as a number before the pH. Each step usually carries its own mark, and later marks follow through from an earlier wrong value if the method is right.
- **Accuracy:** at least 2 significant figures unless told otherwise; give pH to 2 decimal places when the question asks, and 3 s.f. when it demands it.
- **"Show that"** a given value: work it out to more figures than printed, then state it matches.
- **"Explain"** (common ion effect, acid strength, buffer action) needs the named idea plus the reason: "less soluble due to the common ion effect"; "Cl is electron-withdrawing, so the anion is more stable and H^+ is lost more easily".
- **"Write two equations to show how it acts as a buffer"**: one with H^+ and one with OH^- , balanced, using the actual species given.
- **"Suggest"** means use the idea on something unfamiliar (a new amino acid, a new solvent). Apply the same pattern.
- **"Estimate the pH"** needs a sensible range, not a calculation: about 1–3 with excess strong acid, 11–13 with excess strong alkali.

Quick check

1. Identify the two conjugate acid–base pairs in $\text{NH}_4^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NH}_3 + \text{HCO}_3^-$.
2. Calculate the pH of $0.0180 \text{ mol dm}^{-3}$ strontium hydroxide, $\text{Sr}(\text{OH})_2$, at 298 K.
3. A $0.150 \text{ mol dm}^{-3}$ solution of pentanoic acid has pH 2.85 at 298 K. Calculate the K_a and pK_a of pentanoic acid.
4. The solubility of calcium fluoride, CaF_2 (M_r 78.1), is 0.0168 g dm^{-3} at 298 K. Calculate K_{sp} of CaF_2 , with units.
5. At 40°C , $K_w = 2.92 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. Calculate the pH of pure water at this temperature. A solution at 40°C has pH 6.90: is it acidic, neutral or alkaline?

Answers

1. NH_4^+ (acid) and NH_3 (its conjugate base); HCO_3^- (acid) and CO_3^{2-} (its conjugate base).
2. $[\text{OH}^-] = 2 \times 0.0180 = 0.0360$; $[\text{H}^+] = 1.00 \times 10^{-14} \div 0.0360 = 2.78 \times 10^{-13}$; $\text{pH} = 12.56$.
3. $[\text{H}^+] = 10^{-2.85} = 1.41 \times 10^{-3}$; $K_a = (1.41 \times 10^{-3})^2 \div 0.150 = 1.33 \times 10^{-5} \text{ mol dm}^{-3}$; $\text{p}K_a = 4.88$.
4. $s = 0.0168 \div 78.1 = 2.15 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{Ca}^{2+}] = s$, $[\text{F}^-] = 2s$; $K_{sp} = 4s^3 = 3.98 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$.
5. $[\text{H}^+] = \sqrt{2.92 \times 10^{-14}} = 1.71 \times 10^{-7}$; $\text{pH} = 6.77$, and pure water is neutral. At $\text{pH } 6.90$, $[\text{H}^+] = 1.26 \times 10^{-7}$ and $[\text{OH}^-] = 2.92 \times 10^{-14} \div 1.26 \times 10^{-7} = 2.32 \times 10^{-7}$. $[\text{OH}^-] > [\text{H}^+]$, so the solution is alkaline (its pH is above the neutral 6.77).

Past questions to try

- **9701/42/O/N/22 Q4**: solubility from K_{sp} with and without a common ion, then a weak acid's pH and a half-neutralised buffer.
- **9701/43/O/N/22 Q4**: an unknown volume from a partition coefficient, making a buffer, and K_{sp} from solubility.
- **9701/42/M/J/24 Q6**: the stronger acid's equation with water, $[\text{HA}]$ from pH , and a reverse buffer calculation.
- **9701/42/M/J/22 Q4**: the $\text{HCO}_3^-/\text{H}_2\text{CO}_3$ buffer in seawater, with its equations and pH .