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PHYSICAL

CH 06

# Ionic Equilibrium — pH, Buffers & Solubility Product

06

Acid–base theories, Kw and pH, weak acids and Ostwald dilution, salt hydrolysis, buffers and the Henderson equation, common-ion effect, solubility product and indicators — with every numerical type solved, an exam trap gallery, graded MCQs and a one-page revision sheet.

## WHAT YOU WILL BE ABLE TO DO

- Use Arrhenius, Brønsted–Lowry and Lewis definitions and identify conjugate pairs
- Calculate pH for strong and weak acids and bases, including very dilute solutions
- Find the pH of salt solutions and buffers with the hydrolysis and Henderson equations
- Relate Ksp to solubility, apply the common-ion effect and predict precipitation
- Choose the right indicator for a titration

## INSIDE

A The big picture
B Acid–base definitions
C Relative strength of acids and bases
D Kw and the pH scale
E Weak acids and bases
F Salt hydrolysis

HOW TO USE THESE NOTES

| | | |
|---|---|---|
| **IN ONE LINE**<br>The core idea of a section | **KEY IDEA**<br>The concept to remember | **EXAM TRAP**<br>Where marks are usually lost |
| **SOLVED EXAMPLE**<br>Worked step by step | **CHECK YOURSELF**<br>Quick self-test | **MEMORY HOOK**<br>A line that sticks |

SECTION A

# The big picture

A

*Pick the situation, then the formula.*

**IN ONE LINE**

Strong electrolytes ionise fully; weak ones set up an equilibrium described by Ka, Kb or Ksp. pH, hydrolysis, buffers and precipitation are all that equilibrium seen from different angles.

| Situation | Formula |
|---|---|
| Strong acid, concentration C | $[H^+] = C$ (add water's $10^{-7}$ only if $C < 10^{-6}$ M) |
| Weak acid | $[H^+] = \sqrt{(Ka\ C)}$; $\alpha = \sqrt{(Ka / C)}$ |
| Salt of weak acid + strong base | $pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log C$ |
| Salt of strong acid + weak base | $pH = 7 - \frac{1}{2}pKb - \frac{1}{2}\log C$ |
| Salt of weak acid + weak base | $pH = 7 + \frac{1}{2}pKa - \frac{1}{2}pKb$ |
| Acidic buffer | $pH = pKa + \log([salt]/[acid])$ |
| Sparingly soluble salt | Ksp from s; precipitate if ionic product > Ksp |

**THINK OF IT LIKE THIS**

A weak acid in water is like a crowd at a gate where only a few people pass through at a time. Add more people at the gate (a common ion) and even fewer get through. Add more water (dilution) and a larger fraction passes, even though the total number per litre falls.

SECTION B

# Acid–base definitions

B

*Three definitions, each wider than the last.*

| Theory | Acid | Base | Example |
|---|---|---|---|
| Arrhenius | Gives $H^+$ in water | Gives $OH^-$ in water | HCl, NaOH |
| Brønsted–Lowry | Proton donor | Proton acceptor | $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ |

| Theory | Acid | Base | Example |
|---|---|---|---|
| Lewis | Electron-pair acceptor | Electron-pair donor | $BF_3$ (acid), $NH_3$ (base) |

- **Conjugate pairs** differ by one $H^+$: $HCl/Cl^-$, $NH_4^+/NH_3$, $H_2O/OH^-$, $H_3O^+/H_2O$.
- **Strong acid → very weak conjugate base**, and vice versa.
- **Ka × Kb = Kw** for a conjugate pair; so pKa + pKb = 14 at 298 K.
- **Amphiprotic species** can both give and accept $H^+$: $H_2O$, $HCO_3^-$, $HSO_4^-$, $H_2PO_4^-$.
- Lewis acids include electron-deficient molecules ($BF_3$, $AlCl_3$), cations ($Ag^+$, $Fe^{3+}$) and molecules with polar multiple bonds ($CO_2$, $SO_2$).

SECTION C

# Relative strength of acids and bases

*What makes one acid stronger than another.*

- **Down a group, bond strength decides:** HF < HCl < HBr < HI in acid strength. The H–I bond is longest and weakest, so it releases $H^+$ most easily, even though F is the most electronegative.
- **Across a period, electronegativity decides:** $CH_4$ < $NH_3$ < $H_2O$ < HF. The more electronegative atom stabilises the negative charge left behind.
- **Oxyacids of one element:** more oxygen atoms → stronger acid, because the negative charge on the anion spreads over more O atoms. HClO < $HClO_2$ < $HClO_3$ < $HClO_4$.
- **Oxyacids with the same structure:** more electronegative central atom → stronger. HOCl > HOBr > HOI; $H_2SO_4$ > $H_2SeO_4$.
- **Levelling effect:** in water, HCl, HBr, HI, $HNO_3$, $H_2SO_4$ and $HClO_4$ all appear equally strong — each converts completely to $H_3O^+$, the strongest acid that can exist in water. In a less basic solvent such as acetic acid their differences show: $HClO_4$ is the strongest.

| Acid | Ka (298 K) | pKa |
|---|---|---|
| HF | $3.5 \times 10^{-4}$ | 3.45 |
| $HNO_2$ | $4.5 \times 10^{-4}$ | 3.35 |
| HCOOH | $1.8 \times 10^{-4}$ | 3.74 |
| $CH_3COOH$ | $1.8 \times 10^{-5}$ | 4.74 |
| HCN | $4.9 \times 10^{-10}$ | 9.31 |
| Phenol | $1.3 \times 10^{-10}$ | 9.89 |

| Base | Kb (298 K) | pKb |
|---|---|---|
| $NH_3$ | $1.8 \times 10^{-5}$ | 4.74 |
| $CH_3NH_2$ | $4.4 \times 10^{-4}$ | 3.36 |

| Base | Kb (298 K) | pKb |
|---|---|---|
| $(CH_3)_2NH$ | $5.4 \times 10^{-4}$ | 3.27 |
| $C_6H_5NH_2$ | $4.3 \times 10^{-10}$ | 9.37 |
| Pyridine | $1.8 \times 10^{-9}$ | 8.75 |

**CHECK YOURSELF**

C1 Arrange $HClO$, $HClO_3$ and $HClO_4$ in increasing acid strength.

C2 Why is HF a weaker acid than HCl in water?

*Answers at the end of the chapter.*

SECTION D

D

# Kw and the pH scale

*Water ionises a little, and that sets the scale.*

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 298 \text{ K}$$

$$pH = -\log[H^+] \quad pOH = -\log[OH^-] \quad pH + pOH = 14$$

pKw changes with temperature

**KEY IDEA**

**Kw increases with temperature** (ionisation of water is endothermic). At higher temperature, neutral water has pH below 7 — but it is still neutral because $[H^+] = [OH^-]$.

**SOLVED EXAMPLE 01** — A VERY DILUTE STRONG ACID

Find the pH of $1.0 \times 10^{-8}$ M HCl.

SOLUTION

1. Writing pH = 8 would make an acid basic — wrong. Water's own $H^+$ cannot be ignored.
2. Let $[H^+] = 10^{-8} + x$ and $[OH^-] = x$, with $(10^{-8} + x)x = 10^{-14}$.
3. Solving: $x \approx 0.95 \times 10^{-7}$, so $[H^+] \approx 1.05 \times 10^{-7}$ M.

ANSWER pH ≈ 6.98 — slightly acidic, as it must be.

**SOLVED EXAMPLE 02** — MIXING STRONG ACID AND BASE

50 mL of 0.10 M HCl is mixed with 50 mL of 0.08 M NaOH. Find the pH.

SOLUTION

1. Moles $H^+$ = 5.0 mmol; moles $OH^-$ = 4.0 mmol; excess $H^+$ = 1.0 mmol.
2. Total volume = 100 mL → $[H^+]$ = 0.010 M.

ANSWER pH = 2.

## pH of mixtures

- **Two strong acids:** add the moles of $H^+$ and divide by the total volume.
- **Strong acid + weak acid:** the strong acid fixes $[H^+]$; the weak acid's ionisation is suppressed (common ion) and can usually be ignored.
- **Strong acid + strong base:** find the excess moles of $H^+$ or $OH^-$ and divide by the total volume.
- **Weak acid + strong base (not in excess):** a buffer forms — use the Henderson equation (see Buffers).

**SOLVED EXAMPLE 03** — STRONG AND WEAK ACID TOGETHER

Find the pH of a solution 0.10 M in HCl and 0.10 M in $CH_3COOH$, and the degree of ionisation of acetic acid in it. Ka = $1.8 \times 10^{-5}$.

SOLUTION

1. HCl is fully ionised: $[H^+] \approx 0.10$ M → pH = 1.
2. For acetic acid: $Ka = [H^+][CH_3COO^-] / [CH_3COOH]$ → $[CH_3COO^-] = 1.8 \times 10^{-5} \times 0.10 / 0.10 = 1.8 \times 10^{-5}$ M.
3. $\alpha = 1.8 \times 10^{-5} / 0.10 = 1.8 \times 10^{-4}$.

ANSWER pH = 1; α of acetic acid falls from 1.3% (alone) to 0.018%.

SECTION E

# Weak acids and bases

E

*Partial ionisation, governed by Ka or Kb.*

$$HA \rightleftharpoons H^+ + A^- \quad Ka = C\alpha^2 / (1 - \alpha) \approx C\alpha^2$$

$$\alpha = \sqrt{(Ka / C)} \quad [H^+] = C\alpha = \sqrt{(Ka\ C)}$$

Ostwald's dilution law; the approximation holds when α < about 5%

- **Dilution increases** α but decreases $[H^+]$: diluting 100 times raises α 10 times while $[H^+]$ falls 10 times.
- For a weak base: $[OH^-] = \sqrt{(Kb\ C)}$, then pH = 14 − pOH.

- **Polyprotic acids** ($H_2S$, $H_3PO_4$, $H_2CO_3$): $Ka_1 \gg Ka_2 \gg Ka_3$; the pH comes almost entirely from the first step.
- **Common-ion effect:** adding a salt with a shared ion ($CH_3COONa$ to $CH_3COOH$) suppresses ionisation of the weak electrolyte.

**SOLVED EXAMPLE 04** — PH OF A WEAK ACID

Find the pH and degree of ionisation of 0.10 M acetic acid. Ka = $1.8 \times 10^{-5}$.

SOLUTION

1. $\alpha = \sqrt{(1.8 \times 10^{-5} / 0.10)} = \sqrt{(1.8 \times 10^{-4})} = 1.34 \times 10^{-2}$ (1.34%).
2. $[H^+] = C\alpha = 1.34 \times 10^{-3}$ M.
3. $pH = -\log(1.34 \times 10^{-3}) = 3 - 0.127$.

ANSWER pH ≈ 2.87; α ≈ 1.3%.

## Polyprotic acids in detail

$$H_2S \rightleftharpoons H^+ + HS^- \quad Ka_1 = 9.1 \times 10^{-8}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \quad Ka_2 = 1.2 \times 10^{-13}$$

$$Ka_1 \times Ka_2 = [H^+]^2 [S^{2-}] / [H_2S]$$

The combined expression is what group analysis uses

- Each step is weaker than the one before: removing $H^+$ from a negative ion is harder.
- In a solution of $H_2S$ alone, $[S^{2-}] \approx Ka_2$ — independent of concentration.
- Adding a strong acid raises $[H^+]$ and drives $[S^{2-}]$ down by the square of $[H^+]$.

**SOLVED EXAMPLE 05** — SULPHIDE ION IN ACID

Saturated $H_2S$ is 0.10 M. Find $[S^{2-}]$ when the solution also contains 0.10 M HCl.

SOLUTION

1. $[H^+]$ = 0.10 M (from HCl).
2. $[S^{2-}] = Ka_1Ka_2[H_2S] / [H^+]^2 = (9.1 \times 10^{-8})(1.2 \times 10^{-13})(0.10) / (0.10)^2$.
3. $= 1.09 \times 10^{-21} / 0.010$.

ANSWER $[S^{2-}] \approx 1.1 \times 10^{-19}$ M — tiny, so only sulphides with very small Ksp (group II) precipitate.

CHECK YOURSELF

C3 What is the conjugate base of $HSO_4^-$?

C4 A weak acid is diluted 4 times. By what factor does α change?

*Answers at the end of the chapter.*

SECTION F

# Salt hydrolysis

F

*Ions of weak partners react with water.*

| Salt from | Example | Ion that hydrolyses | Solution | pH |
|---|---|---|---|---|
| Strong acid + strong base | NaCl, $KNO_3$ | None | Neutral | 7 |
| Weak acid + strong base | $CH_3COONa$, $Na_2CO_3$ | Anion (gives $OH^-$) | Basic | 7 + ½pKa + ½log C |
| Strong acid + weak base | $NH_4Cl$, $CuSO_4$ | Cation (gives $H^+$) | Acidic | 7 − ½pKb − ½log C |
| Weak acid + weak base | $CH_3COONH_4$ | Both | Depends on Ka vs Kb | 7 + ½pKa − ½pKb |

KEY IDEA

**For a weak acid–weak base salt the pH does not depend on concentration.** $CH_3COONH_4$ has pKa ≈ pKb ≈ 4.75, so its solution is almost exactly neutral — yet it is hydrolysed.

SOLVED EXAMPLE 06 — PH OF SODIUM ACETATE

Find the pH of 0.10 M $CH_3COONa$. pKa ($CH_3COOH$) = 4.74.

SOLUTION

1. Weak acid + strong base → pH = 7 + ½pKa + ½log C.
2. = 7 + 2.37 + ½(−1) = 7 + 2.37 − 0.50.

ANSWER pH ≈ 8.87 (basic).

## Degree of hydrolysis

| Salt type | Hydrolysis constant Kh | Degree of hydrolysis h |
|---|---|---|
| Weak acid + strong base | Kw / Ka | √(Kh / C) |
| Strong acid + weak base | Kw / Kb | √(Kh / C) |
| Weak acid + weak base | Kw / (Ka × Kb) | √Kh (independent of C) |

**SOLVED EXAMPLE 07** — HYDROLYSIS OF AMMONIUM CHLORIDE

Find the hydrolysis constant, degree of hydrolysis and pH of 0.10 M $NH_4Cl$. Kb ($NH_3$) = 1.8 × $10^{-5}$.

SOLUTION

1. Kh = Kw / Kb = $10^{-14}$ / 1.8 × $10^{-5}$ = 5.6 × $10^{-10}$.
2. h = √(5.6 × $10^{-10}$ / 0.10) = 7.5 × $10^{-5}$.
3. $[H^+]$ = Ch = 7.5 × $10^{-6}$ M → pH = 5.13.

ANSWER Kh = 5.6 × $10^{-10}$; h = 7.5 × $10^{-5}$; pH ≈ 5.13 (the formula 7 − ½pKb − ½log C gives the same).

SECTION G

# Buffers

G

*Solutions that resist a change in pH.*

Acidic buffer: pH = pKa + log ([salt] / [acid])

Basic buffer: pOH = pKb + log ([salt] / [base])

Henderson–Hasselbalch equation

- **Acidic buffer:** weak acid + its salt with a strong base ($CH_3COOH$ + $CH_3COONa$). **Basic buffer:** weak base + its salt with a strong acid ($NH_4OH$ + $NH_4Cl$).
- Added $H^+$ is taken up by the conjugate base; added $OH^-$ by the weak acid.
- **Maximum buffer capacity** when [salt] = [acid], i.e. pH = pKa. The useful range is pKa ± 1.
- A buffer is also made by **partly neutralising** a weak acid with a strong base: half-neutralisation gives pH = pKa.
- Blood is buffered near pH 7.4 mainly by $H_2CO_3/HCO_3^-$.

**SOLVED EXAMPLE 08** — BUFFER PH

Find the pH of a solution 0.10 M in $CH_3COOH$ and 0.20 M in $CH_3COONa$. pKa = 4.74.

SOLUTION

1. pH = 4.74 + log(0.20 / 0.10) = 4.74 + log 2.
2. = 4.74 + 0.30.

ANSWER pH ≈ 5.04.

**SOLVED EXAMPLE 09** — ADDING ACID TO A BUFFER

To 1.0 L of buffer containing 0.10 mol $CH_3COOH$ and 0.10 mol $CH_3COONa$, 0.010 mol HCl is added. Find the new pH (pKa = 4.74).

SOLUTION

1. $H^+$ reacts with acetate: $CH_3COO^- + H^+ \rightarrow CH_3COOH$.
2. Acid: 0.10 + 0.010 = 0.11 mol; salt: 0.10 − 0.010 = 0.09 mol.
3. pH = 4.74 + log(0.09 / 0.11) = 4.74 − 0.087.

ANSWER pH ≈ 4.65. The same HCl in 1 L of pure water would give pH 2 — a drop of 5 units instead of 0.09.

**SOLVED EXAMPLE 10** — DESIGNING A BUFFER

In what ratio must sodium acetate and acetic acid be mixed to get a buffer of pH 5.74? (pKa = 4.74)

SOLUTION

1. 5.74 = 4.74 + log([salt]/[acid]).
2. log([salt]/[acid]) = 1.

ANSWER [salt] : [acid] = 10 : 1.

CHECK YOURSELF

C5 What pH does a buffer have when [salt] = [acid]?

C6 Is a mixture of HCl and NaCl a buffer?

*Answers at the end of the chapter.*

SECTION H

# Titration curves

H

*How pH changes as base is added to acid.*

| Point in the titration | Weak acid (HA) + NaOH | What to calculate |
|---|---|---|
| Start | Weak acid alone | $[H^+] = \sqrt{(Ka\ C)}$ |
| Before equivalence | Buffer of HA + $A^-$ | Henderson equation |
| Half-way to equivalence | $[HA] = [A^-]$ | pH = pKa |
| Equivalence point | Salt NaA only | Hydrolysis: pH = 7 + ½pKa + ½log C |
| After equivalence | Excess $OH^-$ | $[OH^-]$ from excess base |

**SOLVED EXAMPLE 11** — POINTS ON A TITRATION CURVE

25 mL of 0.10 M $CH_3COOH$ is titrated with 0.10 M NaOH (pKa = 4.74). Find the pH (a) at the start, (b) after 12.5 mL, (c) at 25 mL.

SOLUTION

1. (a) $[H^+] = \sqrt{(1.8 \times 10^{-5} \times 0.10)} = 1.34 \times 10^{-3}$ → pH 2.87.
2. (b) Half-neutralised: [salt] = [acid] → pH = pKa = 4.74.
3. (c) All acid is now 2.5 mmol of acetate in 50 mL → C = 0.050 M; pH = 7 + 2.37 + ½log 0.050 = 9.37 − 0.65.

ANSWER (a) 2.87 (b) 4.74 (c) 8.72 — so phenolphthalein is the right indicator.

KEY IDEA

**Half-equivalence point gives pKa directly.** This is how Ka of a weak acid is measured in the lab: titrate, find the volume at equivalence, read the pH at half that volume.

SECTION I

# Solubility product

*Equilibrium between a solid and its ions in a saturated solution.*

$$A_xB_y(s) \rightleftharpoons xA^{y+} + yB^{x-} \quad Ksp = (xs)^x\,(ys)^y = x^x\,y^y\,s^{x+y}$$

s = molar solubility (mol $L^{-1}$)

| Type | Example | Ksp in terms of s | s in terms of Ksp |
|---|---|---|---|
| AB | AgCl, $BaSO_4$ | $s^2$ | √Ksp |
| $AB_2$ or $A_2B$ | $PbCl_2$, $Ag_2CrO_4$ | $4s^3$ | $\sqrt[3]{(Ksp/4)}$ |
| $AB_3$ | $Fe(OH)_3$, $Al(OH)_3$ | $27s^4$ | (Ksp/27) to the ¼ |
| $A_3B_2$ | $Ca_3(PO_4)_2$ | $108s^5$ | (Ksp/108) to the ⅕ |

KEY IDEA

**Compare solubilities only through s, not Ksp,** unless the salts are of the same type. $Ag_2CrO_4$ ($Ksp \approx 1.1 \times 10^{-12}$) is more soluble than AgCl ($Ksp \approx 1.8 \times 10^{-10}$) because its formula type is different.

- **Precipitation rule:** if the ionic product Q > Ksp, a precipitate forms; if Q < Ksp, more solid can dissolve.
- **Common-ion effect** lowers solubility: AgCl is far less soluble in NaCl solution than in water.

- **Group analysis:** group II sulphides (CuS, PbS) have very small Ksp, so they precipitate with $H_2S$ in acid, where HCl (common $H^+$) keeps $[S^{2-}]$ low; group IV sulphides (ZnS, MnS) need ammoniacal solution, where $[S^{2-}]$ is higher.
- Purification of common salt: passing HCl gas into a saturated NaCl solution precipitates pure NaCl (common $Cl^-$).

### SOLVED EXAMPLE 12 — SOLUBILITY AND COMMON ION

Ksp of AgCl = $1.8 \times 10^{-10}$. Find its solubility (a) in water, (b) in 0.10 M NaCl.

SOLUTION

1. (a) $K_{sp} = s^2 \rightarrow s = \sqrt{(1.8 \times 10^{-10})} = 1.34 \times 10^{-5}$ M.
2. (b) $[Cl^-] \approx 0.10$ M from NaCl; $s \times 0.10 = 1.8 \times 10^{-10}$.

ANSWER (a) $1.34 \times 10^{-5}$ M. (b) $1.8 \times 10^{-9}$ M — about 7400 times less.

### SOLVED EXAMPLE 13 — WILL IT PRECIPITATE?

Equal volumes of $2 \times 10^{-4}$ M $AgNO_3$ and $2 \times 10^{-4}$ M NaCl are mixed. Does AgCl precipitate? ($K_{sp} = 1.8 \times 10^{-10}$)

SOLUTION

1. Mixing halves each concentration: $[Ag^+] = [Cl^-] = 1 \times 10^{-4}$ M.
2. $Q = (1 \times 10^{-4})^2 = 1 \times 10^{-8}$.
3. $Q\ (10^{-8}) > K_{sp}\ (1.8 \times 10^{-10})$.

ANSWER Yes, AgCl precipitates.

### SOLVED EXAMPLE 14 — KSP FROM GRAMS PER LITRE

The solubility of $BaSO_4$ is $2.45 \times 10^{-3}$ g $L^{-1}$ at 298 K. Find Ksp. (Molar mass 233 g $mol^{-1}$)

SOLUTION

1. $s = 2.45 \times 10^{-3} / 233 = 1.05 \times 10^{-5}$ mol $L^{-1}$.
2. $K_{sp} = s^2 = (1.05 \times 10^{-5})^2$.

ANSWER $K_{sp} \approx 1.1 \times 10^{-10}$.

**SOLVED EXAMPLE 15** — AT WHAT PH DOES A HYDROXIDE PRECIPITATE?

A solution is 0.010 M in $Mg^{2+}$. Above what pH does $Mg(OH)_2$ begin to precipitate? ($K_{sp} = 1.8 \times 10^{-11}$)

SOLUTION

1. $K_{sp} = [Mg^{2+}][OH^-]^2 \rightarrow [OH^-]^2 = 1.8 \times 10^{-11} / 0.010 = 1.8 \times 10^{-9}$.
2. $[OH^-] = 4.2 \times 10^{-5}$ M → pOH = 4.37.

ANSWER Above pH ≈ 9.63.

- **Why $NH_4Cl$ is added with $NH_4OH$ in group III:** the common $NH_4^+$ ion lowers $[OH^-]$, so only the very insoluble hydroxides ($Fe^{3+}$, $Al^{3+}$, $Cr^{3+}$) precipitate; $Mg(OH)_2$ and the group IV–VI hydroxides stay in solution.

CHECK YOURSELF

C7 How does the solubility of AgCl change in 0.1 M $AgNO_3$ compared with water?

C8 A salt $AB_2$ has solubility s. Write its $K_{sp}$.

*Answers at the end of the chapter.*

SECTION J

# Indicators and titrations

J

*Choose an indicator that changes colour at the equivalence-point pH.*

| Indicator | pH range | Colour change (acid → base) |
|---|---|---|
| Methyl orange | 3.1 – 4.4 | Red → yellow |
| Methyl red | 4.2 – 6.3 | Red → yellow |
| Phenolphthalein | 8.2 – 10.0 | Colourless → pink |

$$HIn \rightleftharpoons H^+ + In^- \quad pH = pK_{In} + \log([In^-] / [HIn])$$

The colour changes over about $pK_{In} \pm 1$, where one form is ten times the other

An indicator is itself a weak acid (or base) whose two forms have different colours. Phenolphthalein's HIn form is colourless and its $In^-$ form pink; in acid it stays as HIn, in base it changes to $In^-$.

| Titration | pH at equivalence | Suitable indicator |
|---|---|---|
| Strong acid – strong base | 7 | Either (sharp jump from about 4 to 10) |
| Weak acid – strong base | > 7 | Phenolphthalein |

| Titration | pH at equivalence | Suitable indicator |
|---|---|---|
| Strong acid – weak base | < 7 | Methyl orange |
| Weak acid – weak base | ≈ 7, no sharp jump | No simple indicator works well |

SECTION K

# Exam trap gallery

K

*Where marks are lost in ionic equilibrium.*

**✗ TRAP 01 · WHAT STUDENTS WRITE**
pH of $10^{-8}$ M HCl is 8.

**✓ WHAT IS ACTUALLY CORRECT**
About 6.98.

**WHY** Water's own $H^+$ ($10^{-7}$ M) is larger than the acid's.

**✗ TRAP 02 · WHAT STUDENTS WRITE**
Dilution increases $[H^+]$ of a weak acid because α increases.

**✓ WHAT IS ACTUALLY CORRECT**
α increases but $[H^+] = \sqrt{(K_a C)}$ decreases.

**WHY** The concentration falls faster than α rises.

**✗ TRAP 03 · WHAT STUDENTS WRITE**
Comparing Ksp directly tells which salt is more soluble.

**✓ WHAT IS ACTUALLY CORRECT**
Only for salts of the same formula type; otherwise compare s.

**WHY** $Ag_2CrO_4$ is more soluble than AgCl despite a smaller Ksp.

**✗ TRAP 04 · WHAT STUDENTS WRITE**
$CH_3COONH_4$ is not hydrolysed because its solution is neutral.

**✓ WHAT IS ACTUALLY CORRECT**
It is hydrolysed; the acid and base effects cancel.

**WHY** pKa ≈ pKb.

**✗ TRAP 05 · WHAT STUDENTS WRITE**
HCl + NaCl is a buffer.

**✓ WHAT IS ACTUALLY CORRECT**
No: a buffer needs a weak acid (or base) and its conjugate.

**WHY** A strong acid has no reserve to absorb added $OH^-$.

**✗ TRAP 06 · WHAT STUDENTS WRITE**
Pure water at 350 K with pH 6.6 is acidic.

**✓ WHAT IS ACTUALLY CORRECT**
It is neutral: $[H^+] = [OH^-]$.

**WHY** Kw rises with temperature.

| ✗ TRAP 07 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| Phenolphthalein is suitable for a strong acid – weak base titration. | Use methyl orange (equivalence pH < 7). |
| **WHY** Phenolphthalein changes colour above pH 8. | |

| ✗ TRAP 08 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| Adding NaCl increases the solubility of AgCl. | It decreases it (common ion). |
| **WHY** Q rises above Ksp until AgCl precipitates. | |

| ✗ TRAP 09 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| HI is a weaker acid than HF because I is less electronegative. | HI is the strongest hydrohalic acid. |
| **WHY** Bond strength, not electronegativity, decides down a group. | |

| ✗ TRAP 10 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| At the equivalence point of any acid–base titration, pH = 7. | Only for strong acid – strong base. |
| **WHY** Salt hydrolysis shifts the pH. | |

| ✗ TRAP 11 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| At half-equivalence, pH = 7. | At half-equivalence, pH = pKa. |
| **WHY** [salt] = [acid] in the Henderson equation. | |

| ✗ TRAP 12 · WHAT STUDENTS WRITE | ✓ WHAT IS ACTUALLY CORRECT |
|---|---|
| Adding $NH_4Cl$ to $NH_4OH$ increases $[OH^-]$. | It decreases $[OH^-]$. |
| **WHY** Common-ion effect of $NH_4^+$. | |

MEMORY HOOK

"Weak acid: root of Ka C."

"Seven plus half pKa plus half log C" — salt of weak acid, strong base.

"Equal salt and acid → pH = pKa."

"Same type, compare Ksp; different type, compare s."

SECTION L

# Practice MCQs

L

*Levels: Easy, Moderate, Tough.*

**Q01** The conjugate base of $H_2O$ is: [EASY]

(a) $H_3O^+$ (b) $OH^-$
(c) $O^{2-}$ (d) $H_2$

**Q02** $BF_3$ is a: [EASY]

(a) Brønsted acid (b) Lewis acid
(c) Lewis base (d) Arrhenius base

**Q03** pH of 0.001 M NaOH is: [EASY]

(a) 3 (b) 11
(c) 10 (d) 14

**Q04** An aqueous solution of $NH_4Cl$ is: [EASY]

(a) neutral (b) acidic
(c) basic (d) amphoteric

**Q05** Ksp of a salt $AB_2$ with solubility s is: [EASY]

(a) $s^2$ (b) $2s^3$
(c) $4s^3$ (d) $s^3$

**Q06** pH of $10^{-8}$ M HCl is closest to: [MODERATE]

(a) 8.0 (b) 7.0
(c) 6.98 (d) 6.0

**Q07** A buffer of $CH_3COOH$ and $CH_3COONa$ has pH = pKa when: [MODERATE]

(a) [salt] = 2[acid] (b) [salt] = [acid]
(c) [acid] = 0 (d) [salt] = 0

**Q08** pH of 0.1 M $CH_3COONa$ (pKa = 4.74) is about: [MODERATE]

(a) 8.87 (b) 5.13
(c) 9.87 (d) 7.00

**Q09** Indicator for titrating $NH_4OH$ with HCl: [MODERATE]

(a) phenolphthalein (b) methyl orange
(c) either (d) none

**Q10** Solubility of AgCl (Ksp = $1.8 \times 10^{-10}$) in 0.01 M NaCl is: [MODERATE]

(a) $1.8 \times 10^{-8}$ M (b) $1.34 \times 10^{-5}$ M
(c) $1.8 \times 10^{-12}$ M (d) $1.8 \times 10^{-6}$ M

**Q11** Group II sulphides are precipitated in acidic medium because: [MODERATE]

(a) acid increases $[S^{2-}]$ (b) acid lowers $[S^{2-}]$ so only low-Ksp sulphides precipitate
(c) acid dissolves group IV cations (d) $H_2S$ is a strong acid

**Q12** Which salt solution has pH independent of concentration? [MODERATE]

(a) $NH_4Cl$ (b) $CH_3COONa$
(c) $CH_3COONH_4$ (d) $Na_2CO_3$

**Q13** A weak acid HA (0.01 M) is 1% ionised. Its Ka is about: [TOUGH]

(a) $10^{-4}$ (b) $10^{-6}$
(c) $10^{-8}$ (d) $10^{-2}$

**Q14** Which is the most soluble in water (molar solubility)? AgCl (Ksp $1.8 \times 10^{-10}$), AgBr ($5 \times 10^{-13}$), $Ag_2CrO_4$ ($1.1 \times 10^{-12}$) [TOUGH]

(a) AgCl (b) AgBr
(c) $Ag_2CrO_4$ (d) all equal

**Q15** 50 mL of 0.2 M $CH_3COOH$ is mixed with 50 mL of 0.1 M NaOH (pKa = 4.74). The pH is: [TOUGH]

(a) 4.74 (b) 2.87
(c) 8.72 (d) 7.00

**Q16** Strongest acid in water among these: [EASY]

(a) HF (b) HCl
(c) HBr (d) HI

**Q17** Strongest oxyacid: [EASY]

(a) HClO (b) $HClO_2$
(c) $HClO_3$ (d) $HClO_4$

**Q18** pH of a solution with $[OH^-] = 10^{-5}$ M is: [EASY]

(a) 5 (b) 9
(c) 10 (d) 4

**Q19** At the half-equivalence point of $CH_3COOH$ vs NaOH, pH equals: [MODERATE]

(a) 7 (b) pKa
(c) pKb (d) 14 − pKa

**Q20** Kh for $CH_3COONa$ equals: [MODERATE]

(a) Ka/Kw (b) Kw/Ka
(c) Kw/Kb (d) Ka × Kb

**Q21** The degree of hydrolysis of $CH_3COONH_4$ depends on: [MODERATE]

(a) concentration only (b) Ka and Kb only
(c) concentration and Ka (d) nothing

**Q22** $NH_4Cl$ is added before $NH_4OH$ in group III analysis to: [MODERATE]

(a) increase $[OH^-]$ (b) decrease $[OH^-]$
(c) increase $[NH_3]$ (d) dissolve $Fe(OH)_3$

**Q23** Ksp of $Ca_3(PO_4)_2$ in terms of solubility s is: [MODERATE]

(a) $108s^5$ (b) $27s^4$
(c) $6s^5$ (d) $36s^5$

**Q24** Solubility of $Ag_2CrO_4$ (Ksp = $1.1 \times 10^{-12}$) in 0.10 M $AgNO_3$ is: [TOUGH]

(a) $1.1 \times 10^{-10}$ M (b) $1.1 \times 10^{-11}$ M
(c) $6.5 \times 10^{-5}$ M (d) $1.1 \times 10^{-6}$ M

**Q25** pH at the equivalence point when 0.10 M $CH_3COOH$ is titrated with 0.10 M NaOH (pKa 4.74): [TOUGH]

(a) 7.00 (b) 8.72
(c) 4.74 (d) 10.0

## Answer key with explanations

Q01 **(b) $OH^-$** — Remove one $H^+$.

Q02 **(b) Lewis acid** — Accepts an electron pair.

Q03 **(b) 11** — pOH = 3.

Q04 **(b) acidic** — Strong acid + weak base salt.

Q05 **(c) $4s^3$** — $(s)(2s)^2$.

Q06 **(c) 6.98** — Include water's $H^+$.

Q07 **(b) [salt] = [acid]** — log 1 = 0.

Q08 **(a) 8.87** — 7 + 2.37 - 0.5.

Q09 **(b) methyl orange** — Equivalence pH < 7.

Q10 **(a) $1.8 \times 10^{-8}$ M** — Ksp / 0.01.

Q11 **(b) acid lowers $[S^{2-}]$ so only low-Ksp sulphides precipitate** — Common-ion effect of $H^+$.

Q12 **(c) $CH_3COONH_4$** — Weak acid – weak base salt.

Q13 **(b) $10^{-6}$** — $Ka = C\alpha^2 = 0.01 \times 10^{-4}$.

Q14 **(c) $Ag_2CrO_4$** — $s = \sqrt[3]{(Ksp/4)} \approx 6.5 \times 10^{-5}$ M.

Q15 **(a) 4.74** — Half-neutralised → equal acid and salt.

Q16 **(d) HI** — Weakest H–X bond.

Q17 **(d) $HClO_4$** — Most O atoms to spread the charge.

Q18 **(b) 9** — pOH 5 → pH 9.

Q19 **(b) pKa** — Equal acid and salt.

Q20 **(b) Kw/Ka** — Anion of a weak acid hydrolyses.

Q21 **(b) Ka and Kb only** — $h = \sqrt{(Kw/KaKb)}$.

Q22 **(b) decrease $[OH^-]$** — Common ion suppresses $NH_4OH$.

Q23 **(a) $108s^5$** — $(3s)^3(2s)^2$.

Q24 **(a) $1.1 \times 10^{-10}$ M** — $Ksp = (0.10)^2$ s.

Q25 **(b) 8.72** — 0.050 M acetate.

SECTION M

# Advanced problems

M

*Each needs two ideas from the chapter.*

### SOLVED EXAMPLE 16 — KA FROM PH

A 0.050 M solution of a weak monobasic acid has pH 3.0. Find Ka and α.

SOLUTION

1. $[H^+] = 1.0 \times 10^{-3}$ M; $\alpha = 10^{-3} / 0.050 = 0.02$ (2%).
2. $Ka \approx C\alpha^2 = 0.050 \times (0.02)^2 = 2.0 \times 10^{-5}$.

ANSWER $Ka \approx 2.0 \times 10^{-5}$; α = 2%.

### SOLVED EXAMPLE 17 — SELECTIVE PRECIPITATION

A solution is 0.01 M in both $Cl^-$ and $CrO_4^{2-}$. $AgNO_3$ is added slowly. Which precipitates first? (Ksp: AgCl $1.8 \times 10^{-10}$; $Ag_2CrO_4$ $1.1 \times 10^{-12}$)

SOLUTION

1. $[Ag^+]$ needed for AgCl: $1.8 \times 10^{-10} / 0.01 = 1.8 \times 10^{-8}$ M.
2. $[Ag^+]$ needed for $Ag_2CrO_4$: $\sqrt{(1.1 \times 10^{-12} / 0.01)} = \sqrt{(1.1 \times 10^{-10})} \approx 1.05 \times 10^{-5}$ M.
3. The smaller $[Ag^+]$ is reached first.

ANSWER AgCl precipitates first — the basis of Mohr's titration, where red $Ag_2CrO_4$ appears only after the chloride is used up.

### SOLVED EXAMPLE 18 — COMMON ION WITH A 2:1 SALT

Find the solubility of $Ag_2CrO_4$ in 0.10 M $AgNO_3$. Ksp = $1.1 \times 10^{-12}$.

SOLUTION

1. $[Ag^+] \approx 0.10$ M from $AgNO_3$; $[CrO_4^{2-}] = s$.
2. $Ksp = (0.10)^2 \times s \rightarrow s = 1.1 \times 10^{-12} / 0.010$.

ANSWER $s = 1.1 \times 10^{-10}$ M — about 600 000 times lower than in water ($6.5 \times 10^{-5}$ M).

**SOLVED EXAMPLE 19** — BASIC BUFFER

Find the pH of a solution 0.20 M in $NH_3$ and 0.10 M in $NH_4Cl$. pKb = 4.74.

SOLUTION

1. pOH = pKb + log([salt]/[base]) = 4.74 + log(0.10/0.20) = 4.74 − 0.30 = 4.44.
2. pH = 14 − 4.44.

ANSWER pH ≈ 9.56.

## Check-yourself answers

C1 $HClO < HClO_3 < HClO_4$.

C2 The H–F bond is very strong (and $F^-$ is strongly hydrated by H bonding to HF), so HF releases $H^+$ far less readily.

C3 $SO_4^{2-}$.

C4 α = √(Ka/C): C becomes C/4, so α doubles.

C5 pH = pKa.

C6 No — HCl is a strong acid; there is no weak acid/conjugate base pair.

C7 It decreases (common $Ag^+$ ion): $s = Ksp/[Ag^+] = 1.8 \times 10^{-9}$ M in 0.1 M $AgNO_3$.

C8 $Ksp = (s)(2s)^2 = 4s^3$.

QUICK REVISION

# One-page revision

*Read this page the night before the exam.*

## Definitions

- Arrhenius, Brønsted ($H^+$), Lewis ($e^-$ pair)
- Conjugate pair differs by one $H^+$
- Ka × Kb = Kw; pKa + pKb = 14
- Amphiprotic: $H_2O$, $HCO_3^-$, $HSO_4^-$

## pH basics

- Kw = $10^{-14}$ at 298 K; rises with T
- pH + pOH = 14
- $10^{-8}$ M HCl: pH ≈ 6.98
- Mix: find excess moles ÷ total volume

## Weak electrolytes

- α = √(Ka/C); $[H^+]$ = √(Ka C)
- Dilution: α ↑, $[H^+]$ ↓
- Polyprotic: first step dominates
- Common ion suppresses ionisation

## Hydrolysis and buffers

- WA–SB: 7 + ½pKa + ½log C
- SA–WB: 7 − ½pKb − ½log C
- WA–WB: 7 + ½pKa − ½pKb
- pH = pKa + log(salt/acid)

## Solubility product

- AB: $s^2$; $AB_2$: $4s^3$; $AB_3$: $27s^4$; $A_3B_2$: $108s^5$
- Q > Ksp → precipitate
- Common ion lowers s
- Group II: $H_2S$ in acid; group IV: in $NH_3$

## Indicators

- Methyl orange 3.1–4.4
- Phenolphthalein 8.2–10
- WA–SB: phenolphthalein
- SA–WB: methyl orange

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