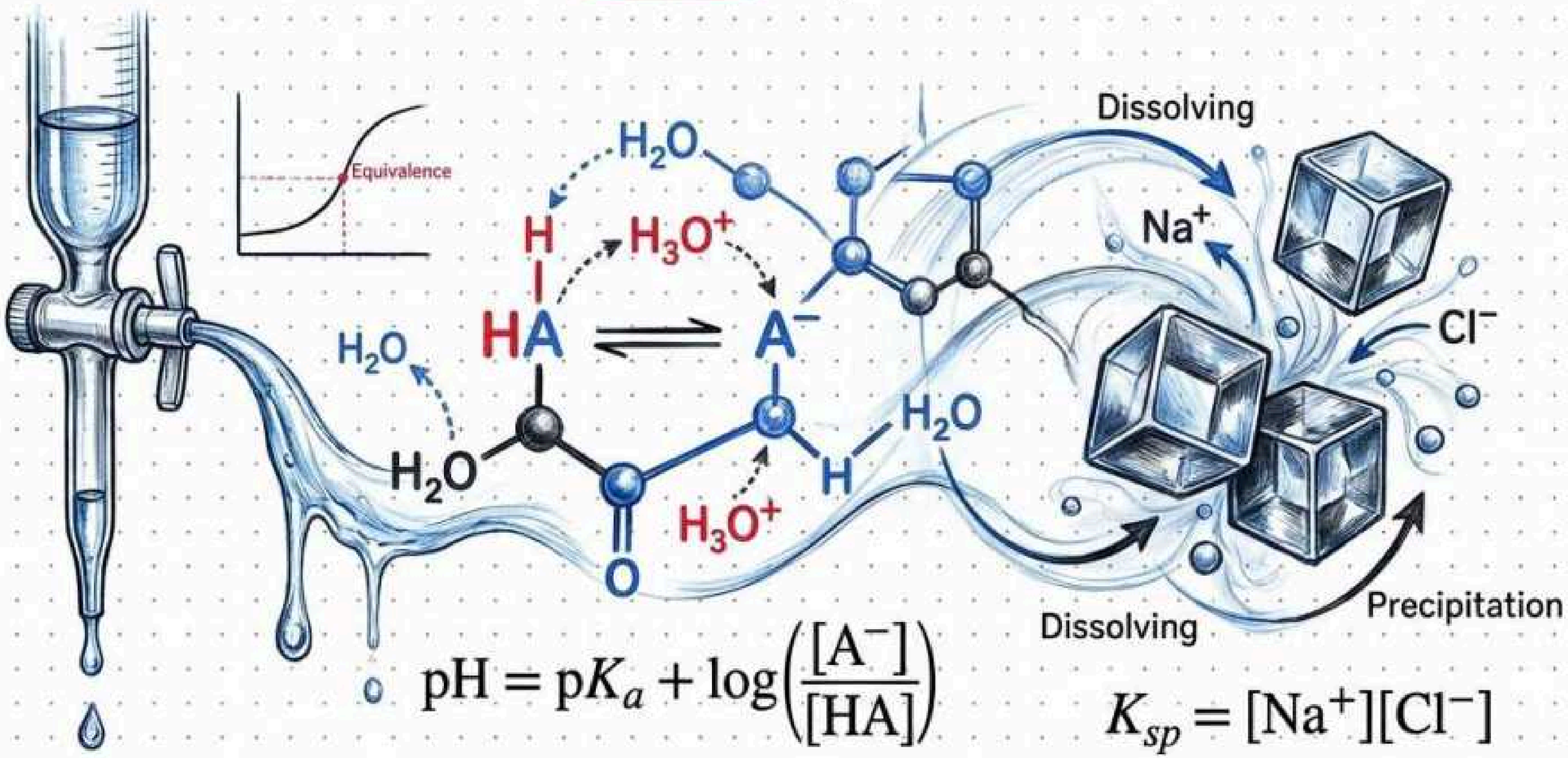
Lecture 4: Buffers, Titrations and Solubility

¶ 4.1

At a glance — Buffers (Henderson-Hasselbalch & capacity) | Titrations (Strong vs. Weak curves) | Solubility (K_{sp}, common ion & precipitation)



$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

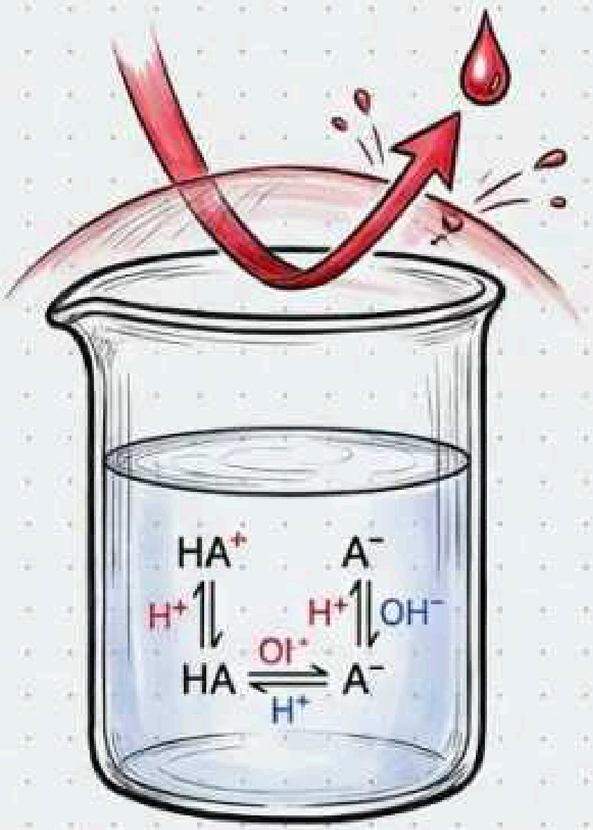
$$K_{sp} = [\mathrm{Na}^+][\mathrm{Cl}^-]$$

One Equilibrium Tool, Three Practical Questions

¶ 4.2

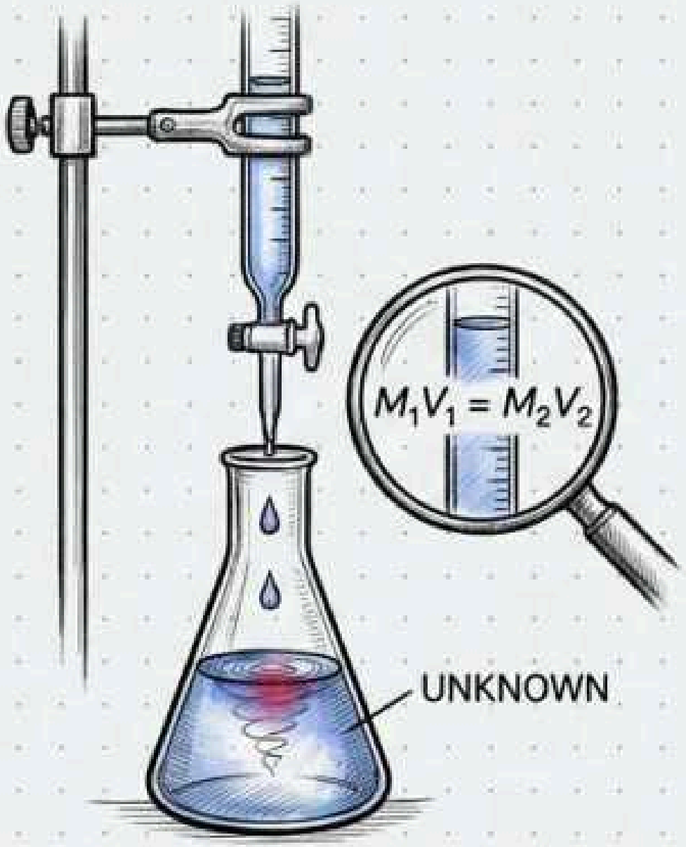
Buffers

How does a solution resist changes in pH?



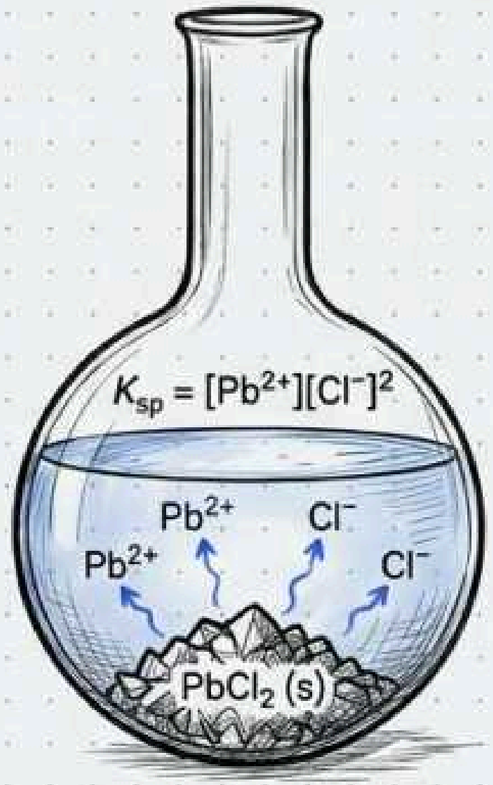
Titrations

How do we measure an unknown acid or base?



Solubility

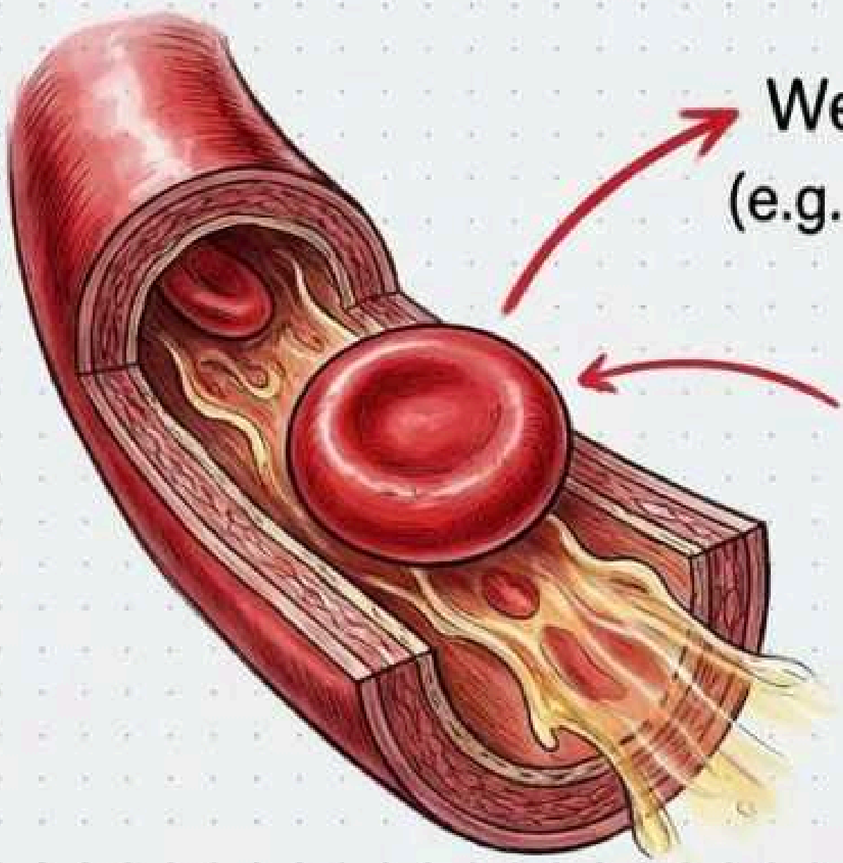
How much of an “insoluble” salt actually dissolves?



What is a Buffer?

¶ 4.3

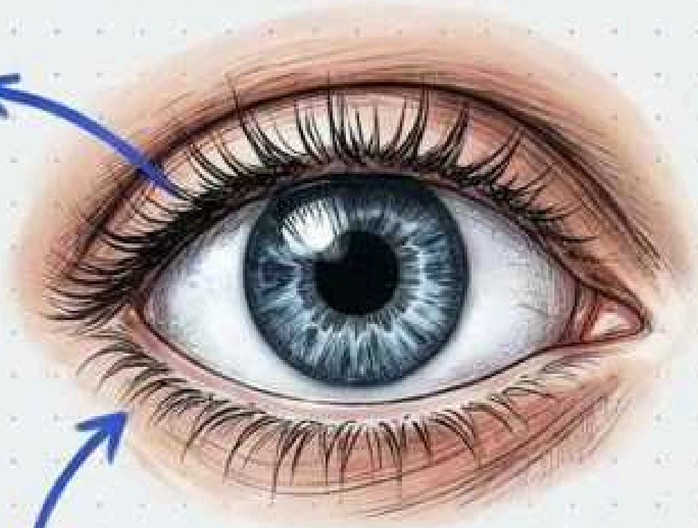
A solution that resists changes in pH when small amounts of acid or base are added. It contains a weak acid and its conjugate base in good amounts.



Weak Acid + Conjugate Base

(e.g., Acetic acid + Sodium acetate)

Blood is buffered by carbonic acid and bicarbonate; small drifts are dangerous.

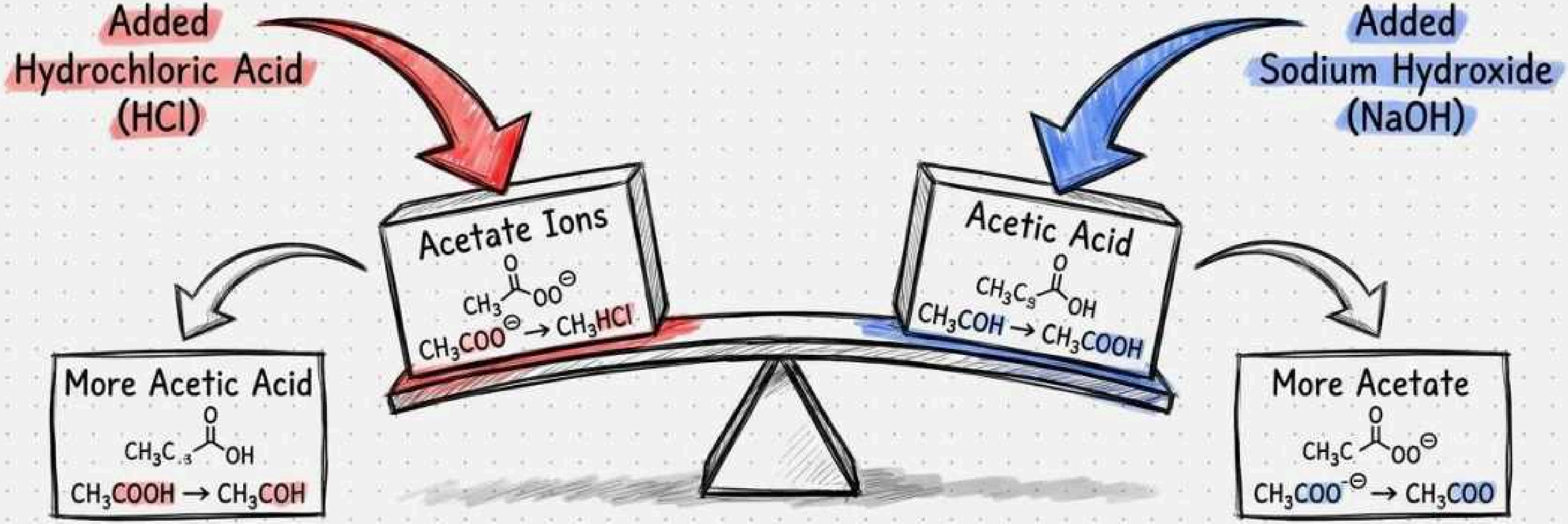


Eye drops, shampoos, and injectable drugs use buffers to protect tissues.

The Mechanism of Neutralization

¶ 4.4

The overall ratio of the conjugate pair shifts only slightly.



Conjugate base neutralizes added acid.

Weak acid neutralizes added base.

The Henderson-Hasselbalch Equation



$$pH = pKa + \log\left(\frac{[\text{Base}]}{[\text{Acid}]}\right)$$

Rearranging the Ka expression yields this ratio. The ratio controls the pH.

Derived in the early 20th century for blood chemistry.



The Mathematics of the Ratio



Equal Base and Acid

$$\frac{0.10\ \text{M acetate}}{0.10\ \text{M acetic acid}}$$

$$\text{Ratio} = 1$$

$$\text{pH} = 4.74 + \log(1)$$

$\log(1) = 0$, therefore $\text{pH} = \text{p}K_a$

$$\boxed{\text{pH} = 4.74}$$

Base is 10x the Acid

$$\text{Ratio} = 10$$

$$\text{pH} = 4.74 + \log(10)$$

+1

$$\boxed{\text{pH} = 5.74}$$

The pH rises exactly one unit.

Testing the Buffer: Adding Acid



Scenario: Add 0.010 moles of HCl to 1 Litre of the previous buffer.

Component	Before (moles)	After (moles)
Acetate (Base)	0.10	0.090 ↓
Acetic Acid	0.10	0.110 ↑

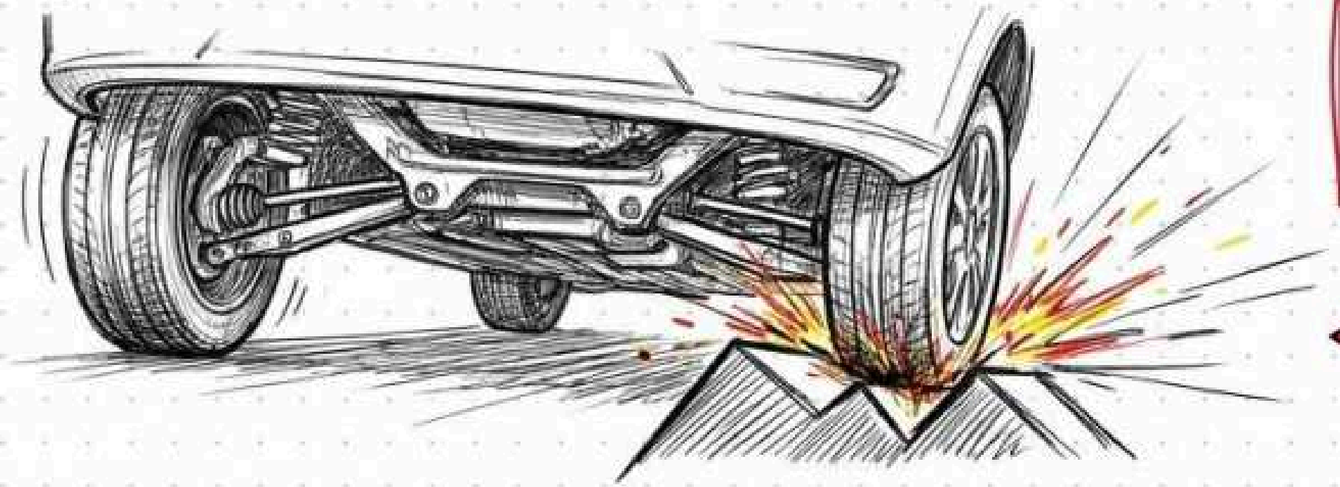
$$pH = 4.74 + \log\left(\frac{0.090}{0.110}\right)$$

pH = 4.66

The Shock Absorber Metaphor

¶ 4.8

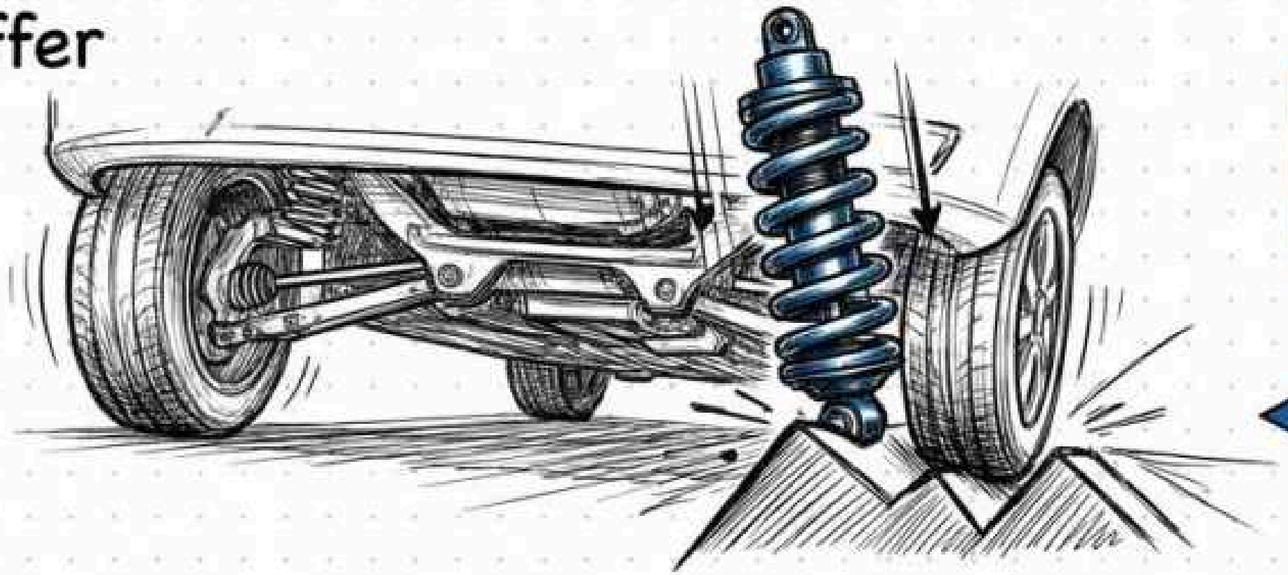
Top Panel (Pure Water)



Add the same acid to 1L pure water.
pH plummets from 7 to 2.

A violent 5-unit crash.

Buffer



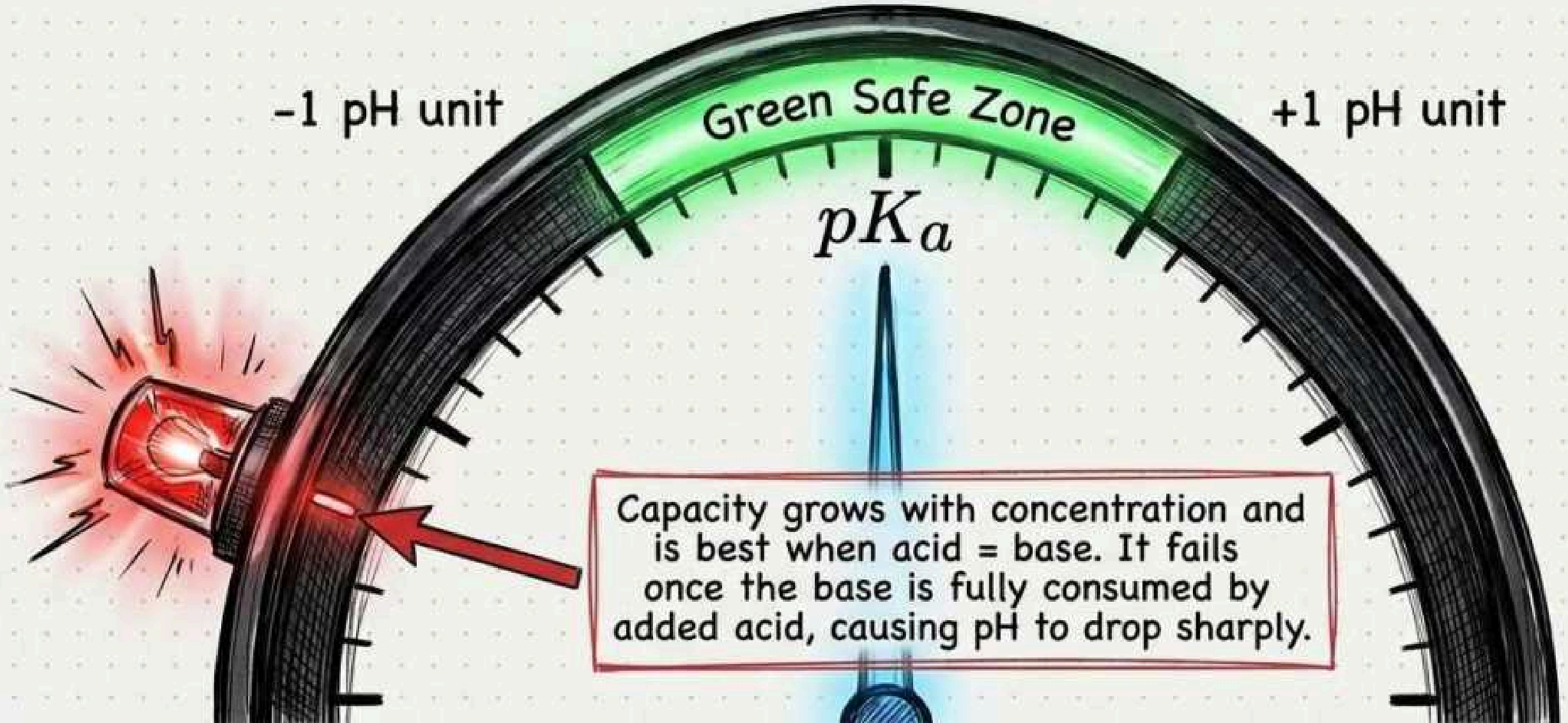
Buffer pH moved by only ~0.09 units (4.74 to 4.66).

It holds the pH far better than nothing.

Buffer Capacity and Working Limits

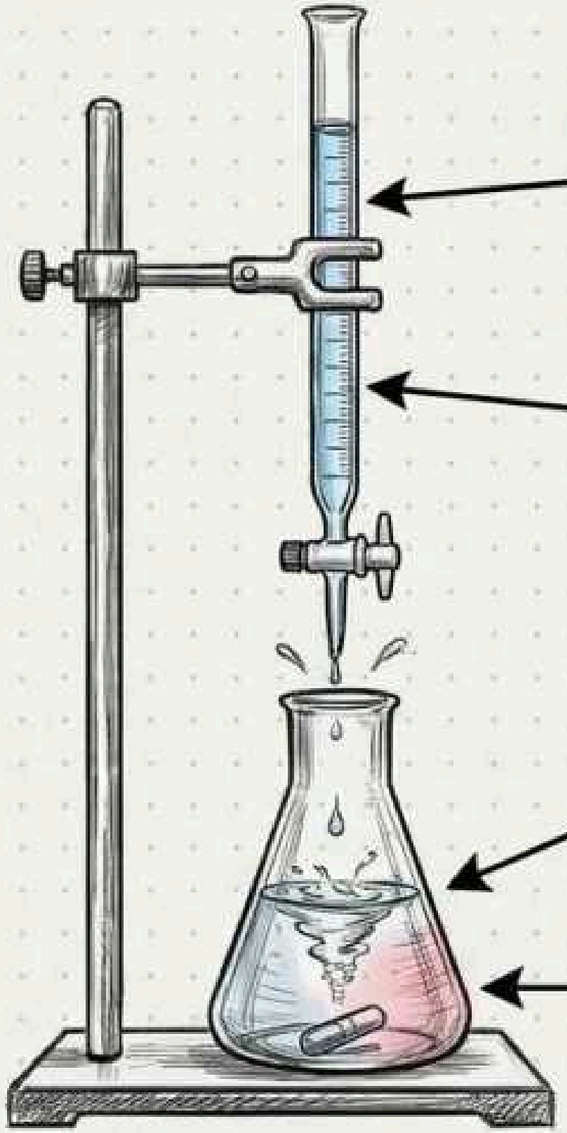
¶ 4.9

Buffer works well within 1 pH unit of pK_a;
choose your weak acid accordingly.



Anatomy of a Titration

¶ 4.10



Titrant: The solution of known concentration in the burette.

Burette: Long glass tube to read volume before & after (difference = added volume).

Equivalence Point: The point of exact chemical balance.

Endpoint: The visual color change of the indicator dye near equivalence.

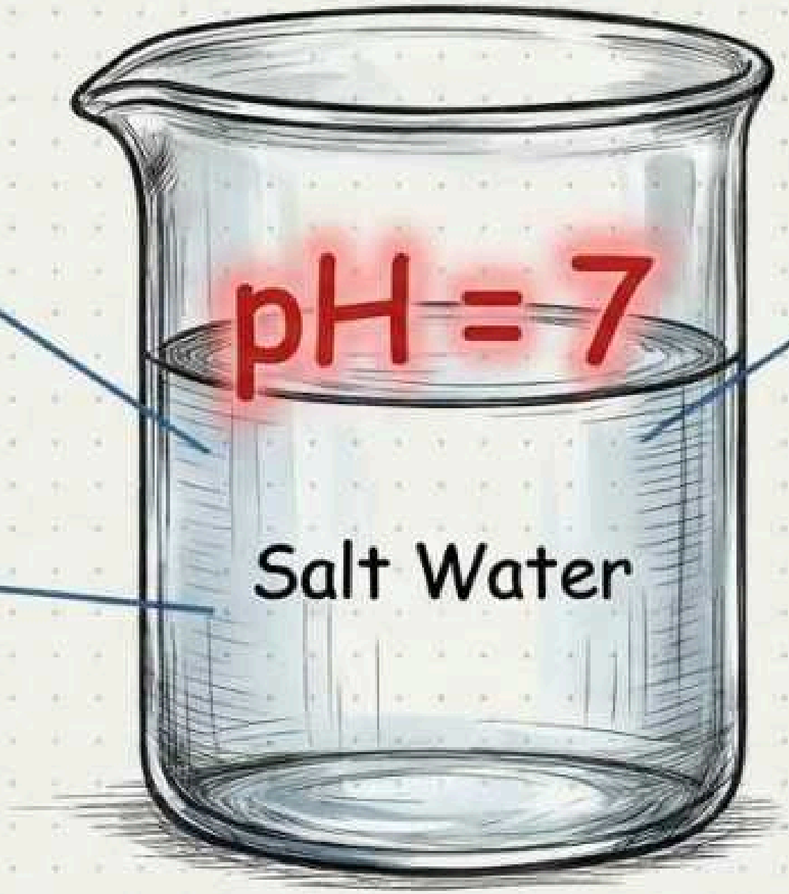
Strong Acid + Strong Base

¶ 4.11

$$HCl + NaOH \rightarrow NaCl + H_2O$$

25.0 mL of 0.100 M HCl

Titrated with 0.100 M NaOH

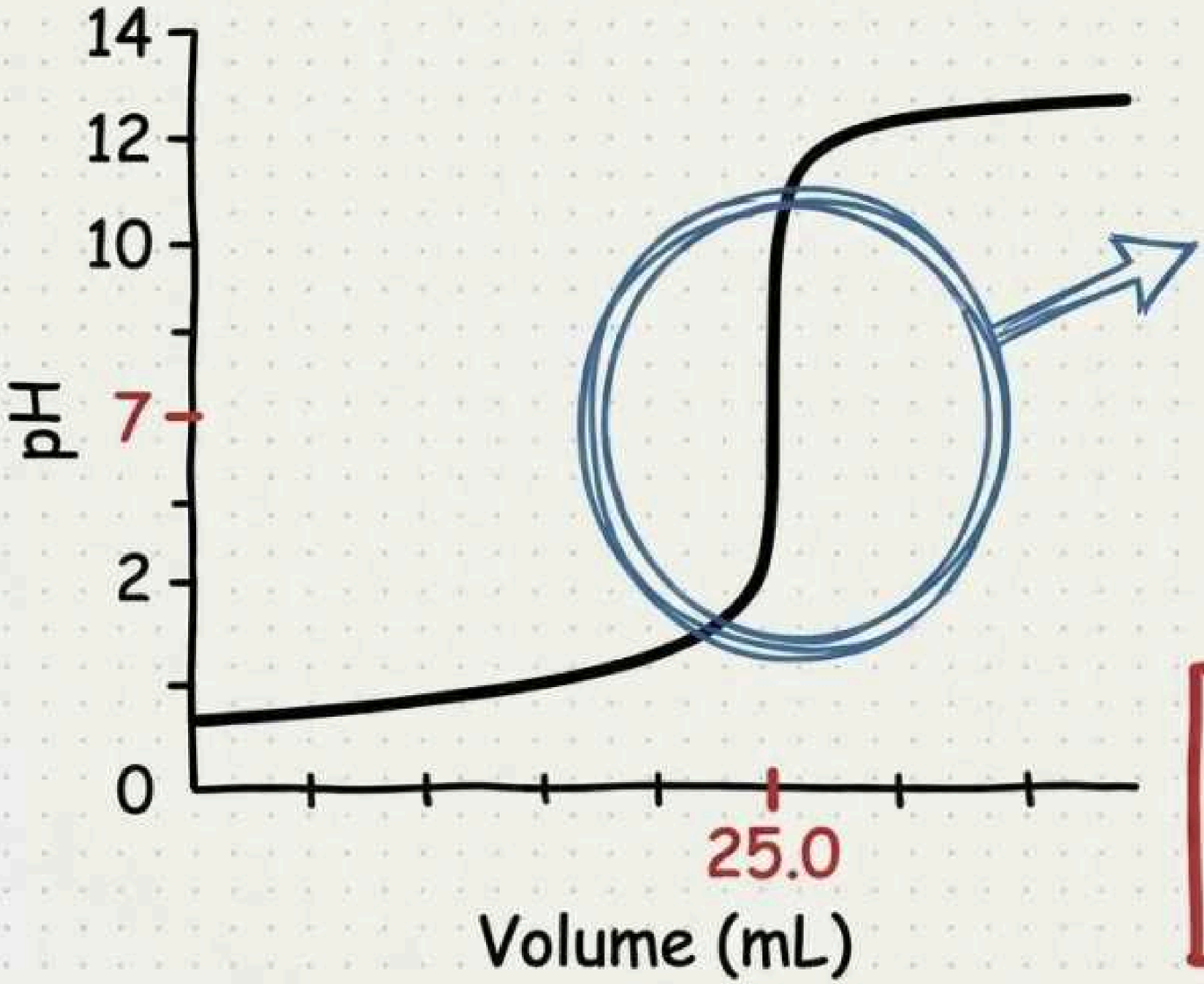


They react 1:1, so equivalence hits exactly at 25.0 mL.

This perfect neutrality is only true for strong acid with a strong base.

The Strong Titration Curve

¶ 4.12



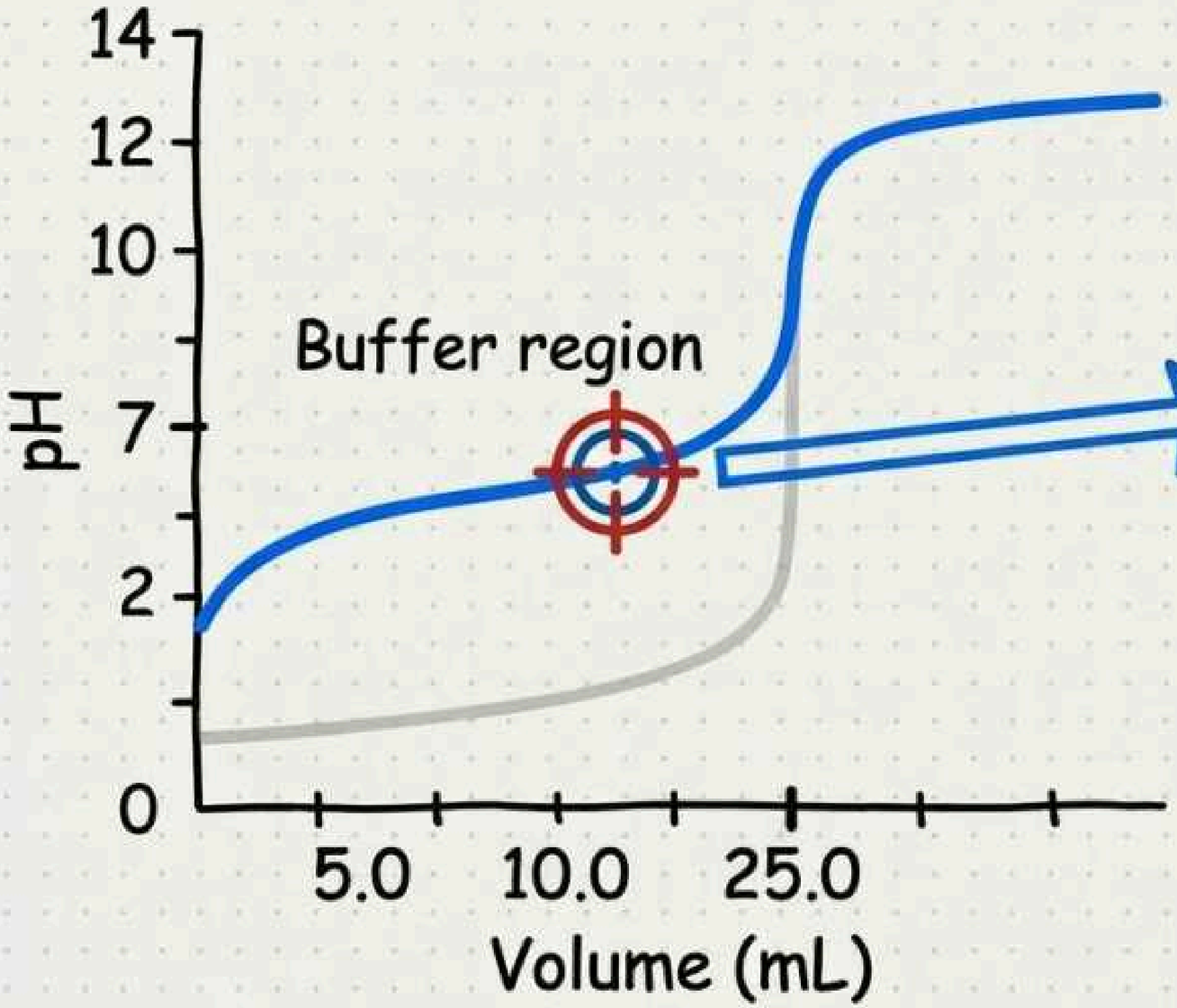
The Vertical Swing

- At 24.9 mL (0.1 mL short): excess acid → pH 3.7
- At 25.1 mL (0.1 mL over): excess base → pH 10.3

A single drop swings the pH by 6 units. That steep jump is why indicators work.

Weak Acid Titration & The Halfway Point

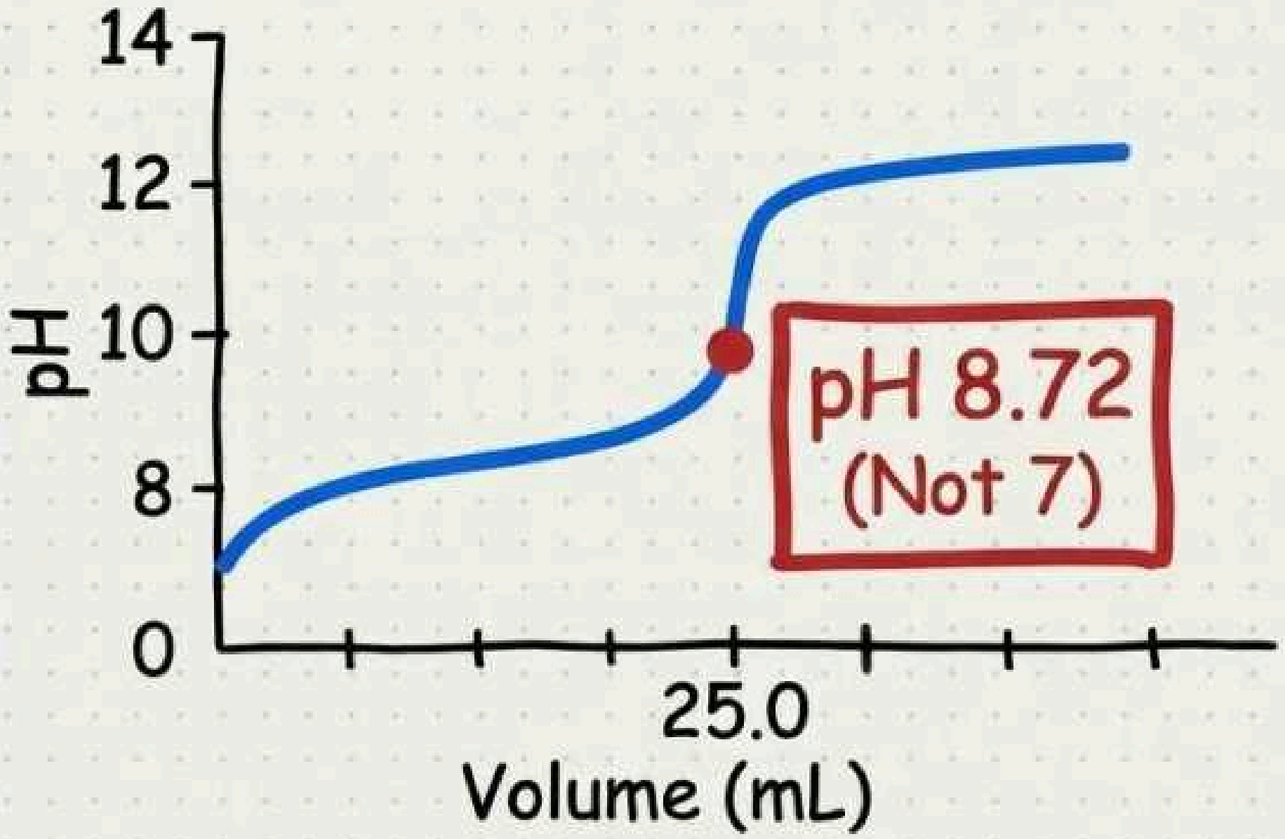
¶ 4.13



1. Half the acid has become acetate.
2. Base = Acid.
3. Therefore, $\mathrm{pH} = pK_a$.

(This is a highly effective way to measure pK_a).

Equivalence for a Weak Acid



25 mL of 0.10 M acid leaves 0.050 M acetate after mixing. Acetate is a weak base, so the equivalence point is above 7.

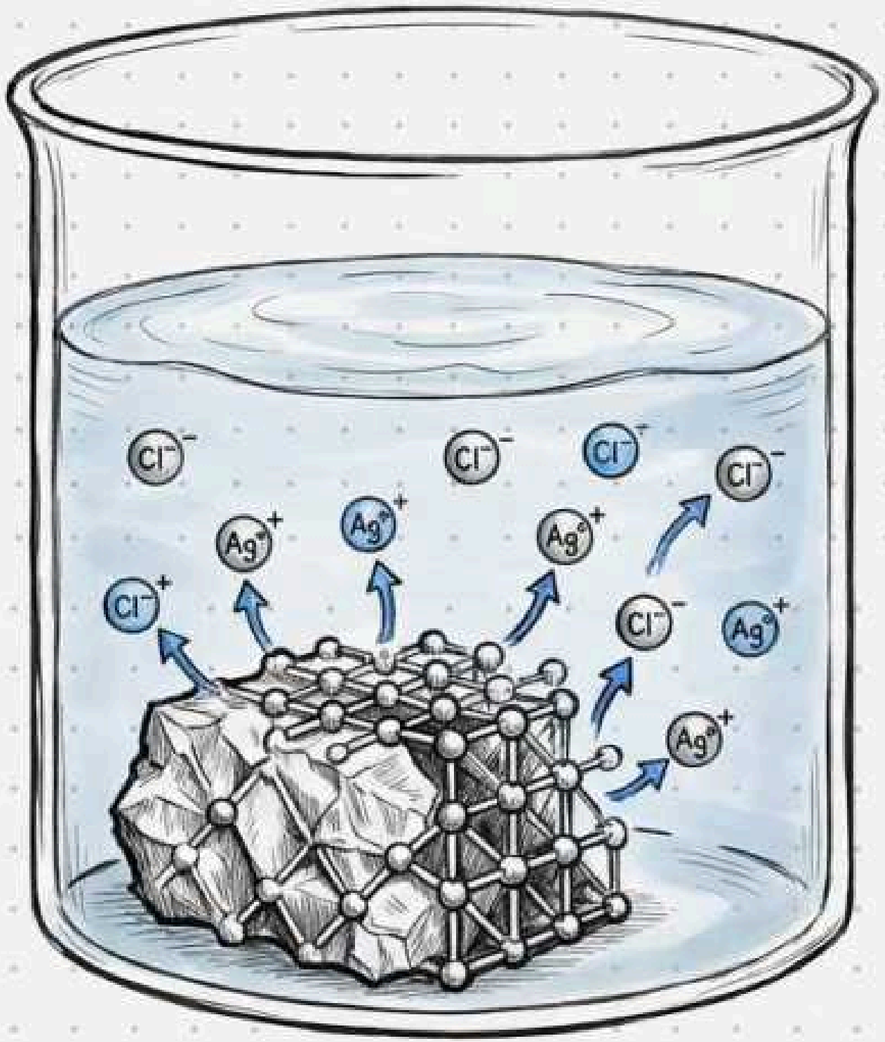
Indicator must change color in the basic range.



Phenolphthalein does.

Introduction to Solubility (K_{sp})

¶ 4.15



The equilibrium constant becomes the Solubility Product.

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

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

Because the solid is left out, K_{sp} relies only on the ion concentrations.

K_{sp} Variations by Formula

¶ 4.16

1:1 Formula: Silver Chloride

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

$$K_{sp} = (s)(s) = s^2$$

$$s^2 = 1.8 \times 10^{-10}$$

$$s = 1.3 \times 10^{-5}\ M$$

1:2 Formula: Magnesium Hydroxide

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$K_{sp} = (s)(2s)^2 = 4s^3$$

For a salt with a different formula, the powers change.

¶ 4.17

Solving for Molar Solubility ('s')

Working the math for Magnesium Hydroxide.

Step 1: $K_{sp} = 5.6 \times 10^{-12} = 4s^3$

↓

Step 2: $s^3 = \dfrac{5.6 \times 10^{-12}}{4}$

↓

Step 3: $s = 1.1 \times 10^{-4}\, M$



Compare salts only with care: K_{sp} values be compared directly only when the salts the salts have the same formula type.

¶ 4.18

The Common Ion Effect

Le Chatelier's principle in action.

Extra Chloride
(from 0.10 M NaCl)

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



$$[\mathrm{Ag^+}] = \frac{K_{sp}}{0.10}$$

$$[\mathrm{Ag^+}] = 1.8 \times 10^{-9}\ M$$

Solubility drops by
a factor of 7,000.

¶ 4.19

Predicting Precipitation (Q_{sp} vs K_{sp})

Compute Reaction Quotient (Q_{sp}) from mixture.

Compare Q_{sp} to K_{sp}

If $Q_{sp} > K_{sp}$

YES: Solid Forms (Precipitates)

If $Q_{sp} < K_{sp}$

NO: Stays Dissolved

Example: Q_{sp} $(1 \times 10^{-6}) > K_{sp}$ (1.8×10^{-10})
→ Silver chloride precipitates.

pH Effects on Solubility

¶ 4.20

A salt whose anion is a base (hydroxide or carbonate) dissolves better in acid.



Acid rain dissolves limestone (carbonate base)



Stomach acid dissolves antacids.

Next: Why do these changes happen at all?
→ Thermodynamics