

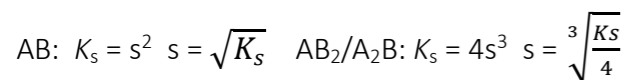
No Brain Too Small

AQUEOUS CHEMISTRY

Sparingly soluble ionic solids

AB and AB₂/A₂B type

Equation for equilibrium occurring in a saturated solution:

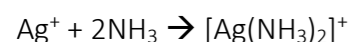
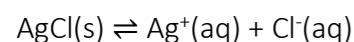


s in mol L⁻¹

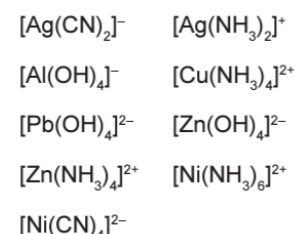
Solubility DECREASES in solutions containing one of the ions A²⁺ or B²⁻ (**common ion**); AB(s) ⇌ A²⁺(aq) + B²⁻(aq). An increase in either favours the back reaction to USE up the extra ion, making more solid, so solubility decreases.

Solubility INCREASES due to:

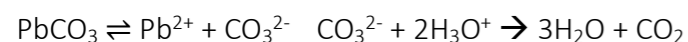
1 Complex ion



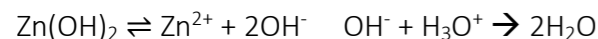
Formation of **complex ion** favours forward reaction of eqm. to REPLACE used up Ag⁺, making less solid, hence solubility increases.



2 Reaction of basic anion (OH⁻ or CO₃²⁻) with added acid.



The CO₃²⁻ ion reacts with added acid. Removal of CO₃²⁻ favours forward reaction of equilibrium to REPLACE used up CO₃²⁻ making less solid, hence solubility increases.



The OH⁻ ion reacts with added acid. Removal of OH⁻ ion favours forward reaction to REPLACE used up OH⁻, making less solid, hence solubility increases.

Watch out for @ low pH i.e. [H₃O⁺] is high, or at high pH i.e. [OH⁻] is high. Excess "..." normally suggests complex ion is formed.

Predicting precipitation

When mixing volumes take into account the dilution factor.

e.g. 20.0 mL of 2.50 × 10⁻² mol L⁻¹ Ca(NO₃)₂(aq), is mixed with 35.0 mL of 6.50 × 10⁻² mol L⁻¹ NaOH(aq).

Determine whether a precipitate of calcium hydroxide, Ca(OH)₂(s), forms. K_s(Ca(OH)₂) = 6.40 × 10⁻⁶

Q = [Ca²⁺][OH⁻]² Q = (20/55 × 2.50 × 10⁻²) × (35/55 × 6.50 × 10⁻²)²
If Q > K_s ppt forms, if Q = K_s saturated solution forms, if Q < K_s no ppt forms

$$\text{pH} = -\log[\text{H}_3\text{O}^+] \quad \text{pOH} = -\log[\text{OH}^-] \quad [\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C} \quad [\text{OH}^-] = 10^{-\text{pOH}}$$

$$\text{p}K_a = -\log K_a \quad K_a = 10^{-\text{p}K_a}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

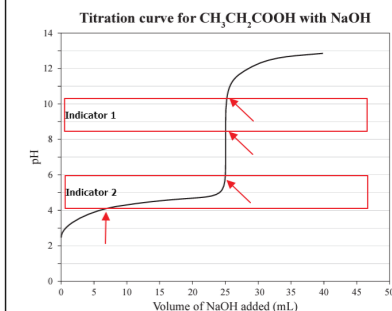
$$\text{pH} + \text{pOH} = 14$$

$$n = cV$$

$$n = \frac{m}{M}$$

Titration curves: A titration curve is the plot of the pH versus volume as the titration progresses. The equivalence point is reached when the moles of acid and base are equal.

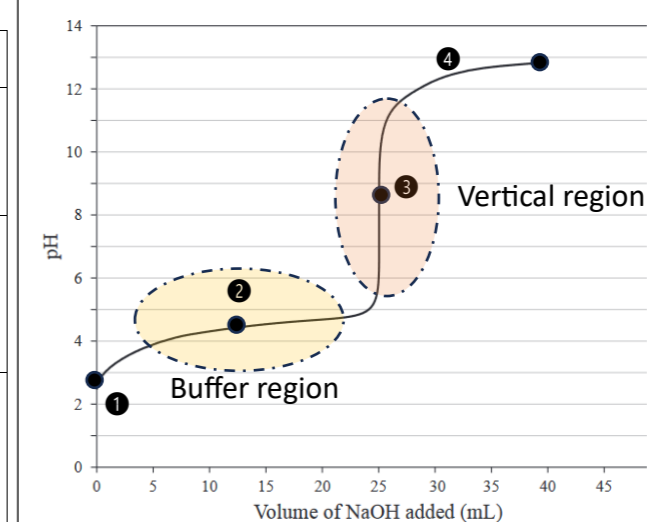
pH range of indicator is its pK_a ± 1 pH unit. Indicator needs to change colour in the VERTICAL region of titration curve, as close to pH at equivalence point as possible to get the correct volume of titrant (stuff added from burette) needed for equivalence point.



Want **indicator** with pK_a ± 1 EP pH to change colour in vertical region. Indicator 1 changes colour too soon (between 7-25 mL). Indicator 1 is a good choice.

- Initial pH – no NaOH added, calculate as a WA.
- Halfway to EP - [acid]=[base] and pH = pK_a
- EP - all WA has been converted to its conjugate WB. Do a WB calculation.
- Past EP – calculate as diluted strong base.

Weak acid / acidic salt	Buffer solution	Weak base / basic salt
$[\text{H}_3\text{O}^+] = \sqrt{K_a[\text{HA}]}$	$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$	$[\text{H}_3\text{O}^+] = \sqrt{\frac{K_a K_w}{[\text{B}]}}$
E.g. CH ₃ COOH or a solution of NH ₄ Cl containing NH ₄ ⁺ ion	Remember: if [base] = [acid], log 1. Log 1 = 0 so pH = pK _a	E.g. NH ₃ or a solution of CH ₃ COONa containing CH ₃ COO ⁻ ion
Rearrange as needed e.g. $[\text{HA}] = \frac{[\text{H}_3\text{O}^+]^2}{K_a}$	If pH < pK _a then the buffer contains more acid than base. Better at 'absorbing' base than acid. (And vice versa)	Or... $[\text{OH}^-] = \sqrt{K_b[\text{B}]}$ Remember K _a × K _b = K _w and pK _w = pK _a + pK _b

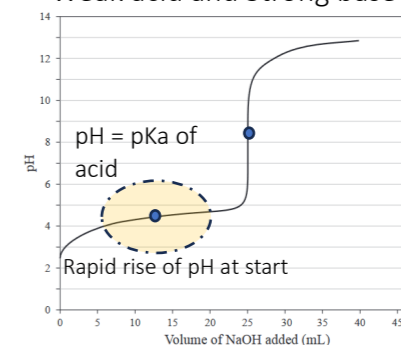


EP = equivalence point

Species in solution HCOOH + NaOH → HCOONa + H₂O

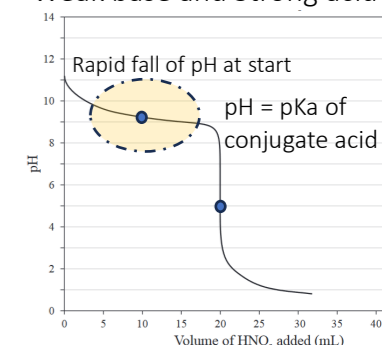
- [HCOOH] > [HCOO⁻] = [H₃O⁺] > [OH⁻]
- [Na⁺] ≈ [HCOO⁻] > [HCOOH] = [OH⁻] > [H₃O⁺]

Weak acid and Strong base



Initial pH < 7 due to WA
pH at EP > 7 as WB formed

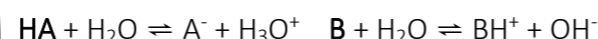
Weak base and Strong acid



Rapid fall of pH at start
pH = pK_a of conjugate acid
Initial pH > 7 due to WB
pH at EP < 7 as WA formed

Electrical conductivity depends on mobile charge carriers. In aqueous solutions it depends on the concentration of ions.

SA and SB and ALL salts are all GOOD conductors as their ionisation / dissociation is complete. WA and WB are POOR conductors as their reaction with H₂O is incomplete and so [ions] is low.



pH depends on the extent of the reaction with water.

For a weak acid, lower K_a / higher pK_a means a weaker acid. So if there are two weak acids of the same concentration, the one with lower K_a / higher pK_a will have the higher pH as it will be less dissociated. so [H₃O⁺] will be less, hence pH will be higher.

Buffers: solutions that resist change in pH when small amounts of acid and base are added.

Contain a weak acid and its conjugate base e.g. CH₃COOH & CH₃COO⁻ OR a weak base and its conjugate acid e.g. CH₃NH₂ and CH₃NH₃⁺.

- Buffer range is pK_a ± 1 pH unit. Outside a 10x or 1/10x they are not effective. The closer the pH is to the pK_a the more effective the buffer.
- Are most effective when concentrated AND [acid] ≈ [base]
- Buffers do not change pH if diluted as ratio [acid] : [base] is unaltered BUT the buffering ability (or capacity) is reduced as the mol (acid) and mol (base) are less. A concentrated buffer can neutralise more added acid or base than a dilute one.
- HA + OH⁻ → H₂O + A⁻. pH doesn't rise much as OH⁻ is turned to neutral H₂O
- A⁻ + H₃O⁺ → HA + H₂O. pH doesn't drop much as H₃O⁺ is turned to neutral H₂O
- pH = pK_a + log $\frac{[\text{base}]}{[\text{acid}]}$ or pH = pK_a + log $\frac{\text{mol}(\text{base})}{\text{mol}(\text{acid})}$
or ratio e.g. NH₃ and NH₄⁺ in a 5:1 ratio pH = pK_a + log $\frac{5}{1}$
- If dissolving x g of CH₃COONa in 400 mL of 0.100 mol L⁻¹ CH₃COOH, calculate (1) n(CH₃COONa) using n = m/M (2) c(CH₃COONa) using c = n/V (3) substitute in buffer equation.

pH at EP (for WA-SB)

(1) Calculate n(base) formed using n = cV of the starting weak acid. (2) Calculate the total volume at EP. (3) Determine [base] using c = n/V. (4) Solve for pH using equation for WB.

pH after EP (for WA-SB)

(1) Calculate how many "extra" mL of unreacted base you are adding. (2) Calculate n(base) using n = cV, where V is the "extra" mL. (3) Calculate [base] using c = n/V, where V is total volume. (4) Calculate pH for a strong base using [OH⁻].