Additional Aspects of Aqueous Equilibria

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The Common-Ion Effect

- Consider a solution of acetic acid:

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \leftrightarrows H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)}$$

- If acetate ion is added to the solution, Le Châtelier's Principle says the equilibrium will shift to the left.
- Acetate ion can be added in the form of a strong electrolyte such as sodium acetate, $NaC_2H_3O_2$

$$NaC_2H_3O_{2\,(aq)} \rightarrow Na^+_{(aq)} + C_2H_3O_{2\,(aq)}^-$$

Sodium acetate is 100% ionic in solution

The Common-Ion Effect

The extent of ionization of a weak electrolyte can be decreased by adding a strong electrolyte to the solution that has an ion in common with the weak electrolyte.

The Common-Ion Effect

Example:

Calculate the fluoride ion concentration and pH of a solution that is 0.20 *M* in HF and 0.10 *M* in HCl.

K_a for HF is 6.8×10^{-4}.

Solution:

$$HF_{(aq)} + H_2O_{(l)} \rightleftarrows H_3O^+_{(aq)} + F^-_{(aq)}$$

The equilibrium constant expression is

$$K_a = \frac{[H_3O^+]\,[F^-]}{[HF]} = 6.8 \times 10^{-4}$$

The Common-Ion Effect

Because HCl, a strong acid, is also present,

$$\mathrm{HCl}_{(aq)} + \mathrm{H_2O}_{(l)} \rightarrow \mathrm{H_3O^+}_{(aq)} + \mathrm{Cl^-}_{(aq)}$$

the initial $[H_3O^+]$ is not 0, but rather 0.10 *M*.

	$[HF]$, *M*	$[H_3O^+]$, *M*	$[F^-]$, *M*
Initial concentration	0.20	0.10 (from the HCl)	0
Change	$-x$	$+x$	$+x$
Equilibrium concentration	$0.20 - x$ ≈ 0.20	$0.10 + x$ ≈ 0.10	x

Remember, x is small and can be ignored

The Common-Ion Effect

$$6.8 \times 10^{-4} = \frac{(0.10)\,(x)}{(0.20)}$$

Solve for x. Rearrange to:

$$\frac{(0.20)\,(6.8 \times 10^{-4})}{(0.10)} = x$$

$$1.4 \times 10^{-3}\ \mathrm{M} = x$$

The Common-Ion Effect

Therefore, $[F^-] = x = 1.4 \times 10^{-3}$ M

If we add x to 0.10 M

$$[H_3O^+] = 0.10 + x$$

$$= 0.10 + (1.4 \times 10^{-3})$$

$$= 0.10\ M$$

and $\quad$ $pH = -\log (0.10)$

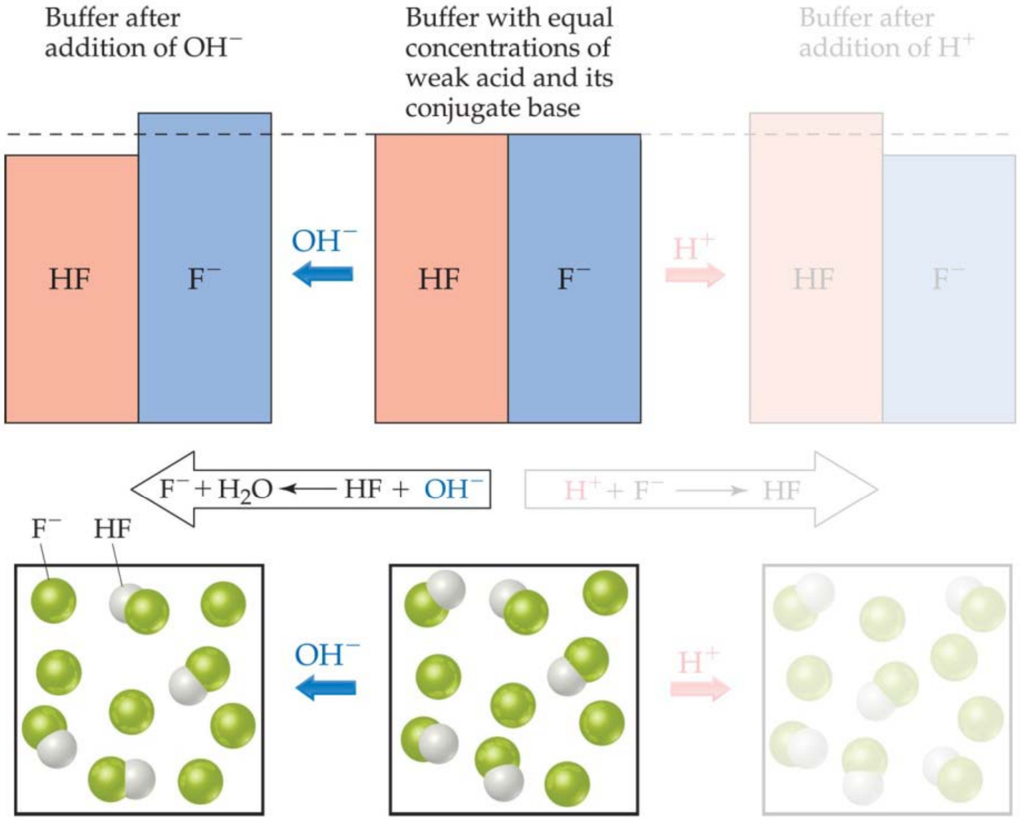
$pH = 1.00$

Buffer Solutions

- A buffer is an application of the common ion effect
- Because the common ion shifts the equilibrium in one direction, a buffer is resistant to pH changes, even when small amounts of a strong acid or base is added.

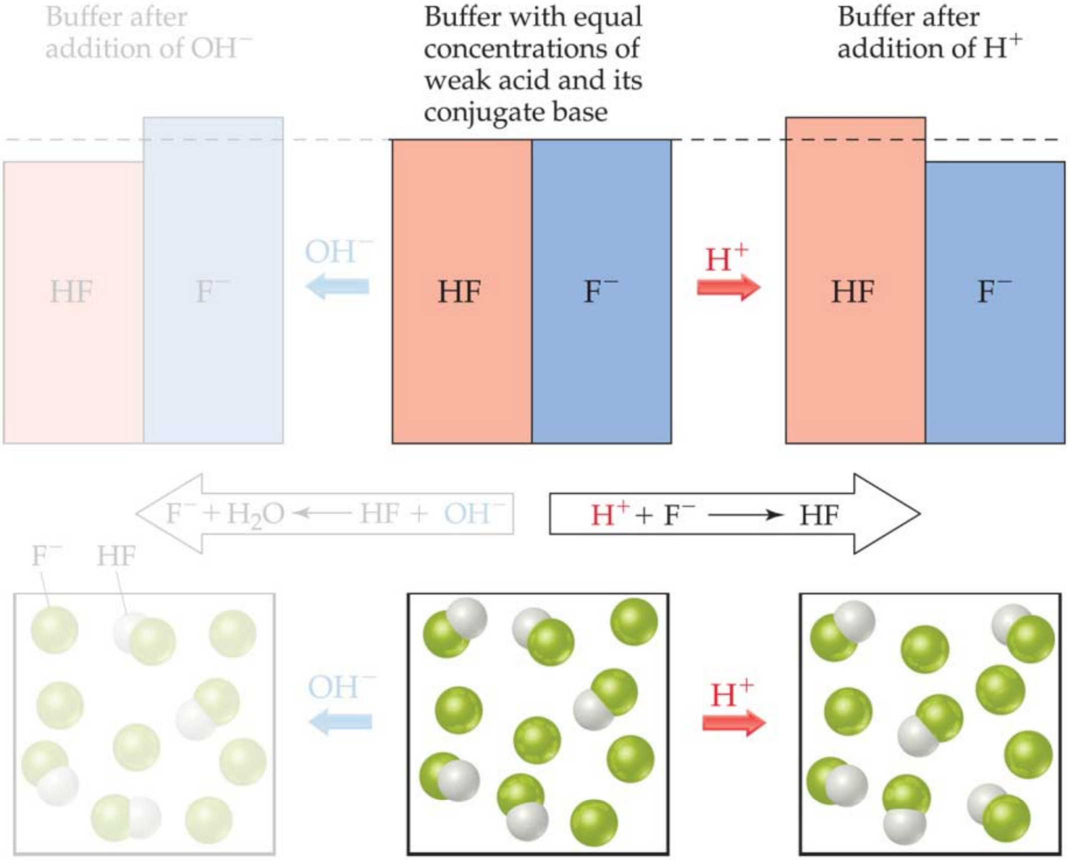
Buffer Solutions

If a small amount of hydroxide is added to an equimolar solution of HF in NaF, for example, the HF reacts with the OH^- to make F^- and water.



Buffer Solutions

If acid is added, the F⁻ reacts to form HF and water.



Buffer Calculations

Consider the equilibrium constant expression for the dissociation of a generic acid, HA:

$$HA + H_2O \rightleftarrows H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

Rearrange this to separate out the $[H_3O^+]$

$$K_a = [H_3O^+]\,\frac{[A^-]}{[HA]}$$

Buffer Calculations

$$K_a = [H_3O^+]\,\frac{[A^-]}{[HA]}$$

Take the negative log of both sides

$$\underbrace{-\log K_a}_{\mathrm{p}K_a} = \underbrace{(-\log [H_3O^+])}_{\mathrm{pH}} + \left(-\log \frac{\overset{\text{base}}{[A^-]}}{\underset{\text{acid}}{[HA]}}\right)$$

and

$$\mathrm{p}K_a = \mathrm{pH} - \log \frac{[\text{base}]}{[\text{acid}]}$$

Buffer Calculations

Rearrange the equation to solve for pH

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

The equation, in this form is known as the **Henderson–Hasselbalch equation**.

Henderson–Hasselbalch Equation

Example:

What is the pH of a buffer that is 0.12 *M* in lactic acid, $HC_3H_5O_3$, and 0.10 *M* in sodium lactate?

K_a for lactic acid is 1.4×10^{-4}.

Solution:

$$HC_3H_5O_3 + H_2O \leftrightarrows C_3H_5O_3^- + H_3O^+$$

Conc.	0.12 M			0.10 M	x

(What happened to x for the $HC_3H_5O_3$ concentration?)

Henderson–Hasselbalch Equation

Substitute the concentrations into the Henderson-Hasselbalach equation

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

$$= -\log\left(1.4 \times 10^{-4}\right) + \log \frac{(0.10)}{(0.12)}$$

$$= 3.85 + (-0.08)$$

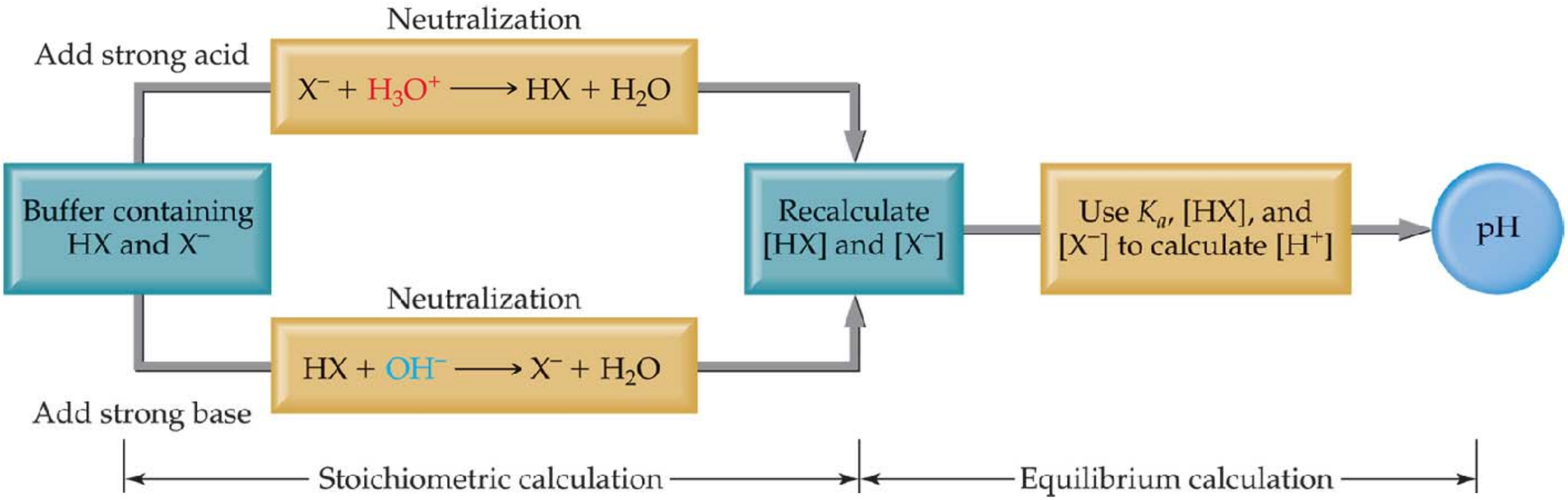
$$\mathrm{pH} = 3.77$$

Buffer Capacity

- The buffer capacity is the amount of acid or base that the buffer can neutralize before the pH changes to an appreciable degree.
- The pH range is the range of pH values over which a buffer system works effectively.
- It is best to choose an acid with a pK_a close to the desired pH.

When Strong Acids or Bases Are Added to a Buffer

Assume that all of the strong acid or base is consumed in the reaction.



Add strong acid

Neutralization

$X^- + H_3O^+ \longrightarrow HX + H_2O$

Buffer containing HX and X^-

Neutralization

$HX + OH^- \longrightarrow X^- + H_2O$

Add strong base

Recalculate [HX] and $[X^-]$

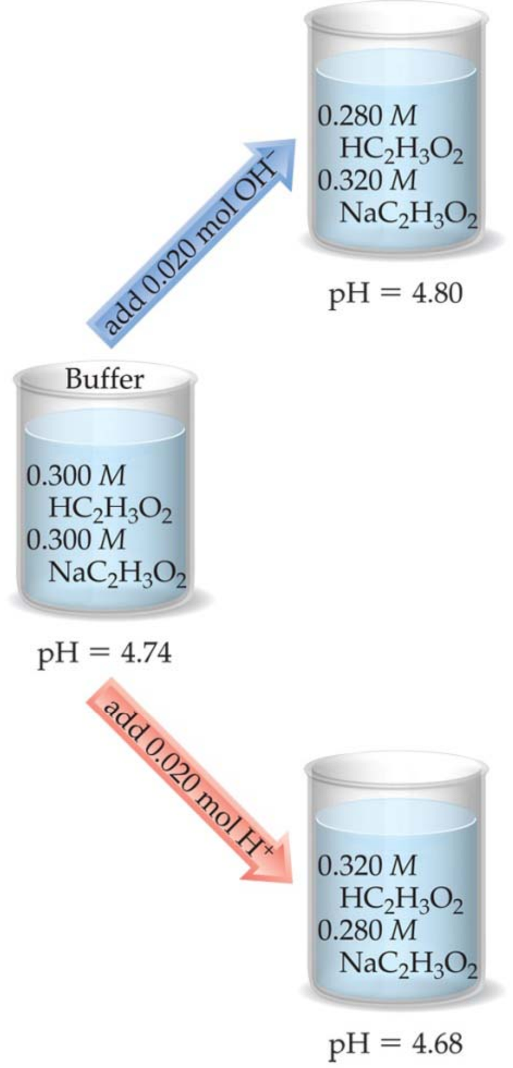
Use K_a, [HX], and $[X^-]$ to calculate $[H^+]$

pH

Stoichiometric calculation

Equilibrium calculation

Addition of Strong Acid or Base to a Buffer



1. Determine how the neutralization reaction affects the amounts of the weak acid and its conjugate base in solution.
2. Use the Henderson–Hasselbalch equation to determine the new pH of the solution.

Calculating pH changes when adding strong acid or base to a Buffer

Sample problem:

A buffer is made by adding 0.300 mol $HC_2H_3O_2$ and 0.300 mol $NaC_2H_3O_2$ to enough water to make 1.00 L of solution. The pH of the buffer is 4.74. Calculate the pH of this solution after 0.020 mol of NaOH is added.

$K_{a\ HC_2H_3O_2} = 1.8 \times 10^{-5}$

Calculating pH changes when adding strong acid or base to a Buffer

Initial data, before the reaction:

mol $HC_2H_3O_2$ = mol $C_2H_3O_2^-$ = 0.30 M

From the acetic acid from the sodium acetate

and

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

Since [base] = [acid]

$$pH = pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Calculating pH changes when adding strong acid or base to a Buffer

The 0.020 mol NaOH will react with 0.020 mol of the acetic acid:

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \rightarrow C_2H_3O_2^-{}_{(aq)} + H_2O_{(l)}$$

This reduces the amount of acetic acid by 0.020 mole and increases the acetate ion concentration by 0.020 mole

	$HC_2H_3O_2$	$C_2H_3O_2^-$	OH^-
Before reaction	0.300 mol	0.300 mol	0.020 mol
After reaction	0.280 mol	0.320 mol	0.000 mol

Calculating pH changes when adding strong acid or base to a Buffer

Use the Henderson–Hasselbalch equation to calculate the new pH:

$$\text{pH} = 4.74 + \log \frac{(0.320)}{(0.\ 280)}$$

$$= 4.74 + 0.06$$

$$\text{pH} = 4.80$$

Calculating pH changes when adding strong acid or base to a Buffer

Sample Problem: What is the pH when 1.00 mL of 1.00 M HCl is added to

a) 1.00 L of pure water (before HCl, pH = 7.00)

b) 1.00 L of buffer that has [HOAc] = 0.700 M and $[OAc^-]$ = 0.600 M. The pH = 4.68

Calculating pH changes when adding strong acid or base to a Buffer

Solution to Part (a)

HCl is 100% ionic.

Calc. [HCl] after adding 1.00 mL of 1.00 M HCl to 1.00 L of water

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

$$1.00\ M \bullet 1.00\ mL = M_2 \bullet 1001\ mL$$

$$M_2 = 1.00 \times 10^{-3}\ M = [H_3O^+]$$

$$pH = -\log(1.00 \times 10^{-3})$$

$$pH = 3.00$$

Calculating pH changes when adding strong acid or base to a Buffer

Solution to Part (b)

Step 1 — The H_3O^+ (from HCl) reacts with OAc^- (from buffer) to yield HOAc

The reaction occurs completely because K is very large.

	$[H_3O^+]$ +	$[OAc^-]$	$[HOAc]$
Before rxn	0.0010 M	0.600 M	0.700 M
Change	-0.0010 M	-0.0010M	+0.0010M
After rxn	0	0.599 M	0.701 M

Calculating pH changes when adding strong acid or base to a Buffer

Solution to Part (b):

Step 2 - Set up a concentration table (similar to equilibrium-type calculation or ICE) using calculated concentrations [HOAc] and [OAc^-] – Solve for [H_3O^+]

$$HOAc + H_2O \leftrightarrows H_3O^+ + OAc^-$$

	[HOAc]	[H_3O^+]	[OAc^-]
I: Before rxn	0.701 M	0	0.599 M
Change	-x	+x	+x
E: After rxn	0.701 – x M ≈ 0.701 M	x	0.599 + x M ≈ 0.599 M

Calculating pH changes when adding strong acid or base to a Buffer

Solution to Part (b):

Step 2 - Solve for pH using the Henderson-Hasselbalch Equation

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

$$\mathrm{pH} = -\log(1.8 \times 10^{-5}) + \log \frac{[0.599]}{[0.701]}$$

$$\mathrm{pH} = -(-4.74) + (-0.0685)$$

$$\mathrm{pH} = 4.67$$

The original pH was 4.68, so the pH is essentially unchanged.

Preparing a Buffer

How would you prepare a buffer solution with a pH of 4.30 ?

Solution:

First, calculate the $[H_3O^+]$

$$pH = -\log [H_3O^+]$$

$$4.30 = -\log [H_3O^+]$$

$$-4.30 = \log [H_3O^+]$$

$$[H_3O^+] = 10^{-4.30}$$

$$[H_3O^+] = 5.0 \times 10^{-5}\ M$$

Choose an acid such that $[H_3O^+] \approx K_a$

Preparing a Buffer

Next, consult a list of weak acids:

Weak Acid	Formula	K_a
Formic acid	HCO_2H	1.8×10^{-4}
Benzoic acid	HC_6H_5COO	6.3×10^{-5}
Acetic acid	$HC_2H_3O_2$	1.8×10^{-5}
Propanoic acid	$HC_2H_5O_2$	1.3×10^{-5}

Since $[H_3O^+] = 5.0 \times 10^{-5}$ M

Choose an acid such that $[H_3O^+] \approx K_a$

For this problem, I am selecting acetic acid

Preparing a Buffer

Solution (continued):

Use the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Solve for the [base]/[acid] ratio

$$4.30 = -\log(1.8 \times 10^{-5}) + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$4.30 = 4.74 + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$-0.44 = \log \frac{[\text{base}]}{[\text{acid}]}$$

Preparing a Buffer

Solution (continued):

$$3.63 = \frac{[\text{base}]}{[\text{acid}]}$$

A typical laboratory solution of acetic acid is **0.10 M** – substitute 0.10 M for the [acid] and solve for [base]

$$[\text{base}] = 0.363\ \text{M}$$

You would need 0.363 mole of acetate ion added to 1.0 L of 0.10 M acetic acid

If you used sodium acetate (MW = 82 g/mol):

0.363 mol x 82 g/mol = 29.8 g sodium acetate/L

Preparing a Buffer

In the preparation of a buffer, the important thing to remember is the RATIO OF THE CONJUGATE BASE TO THE ACID determines the pH of the buffer

CONCENTRATION of the acid and conjugate base are not important.

Diluting a buffer solution does not change its pH

Commercial Buffers

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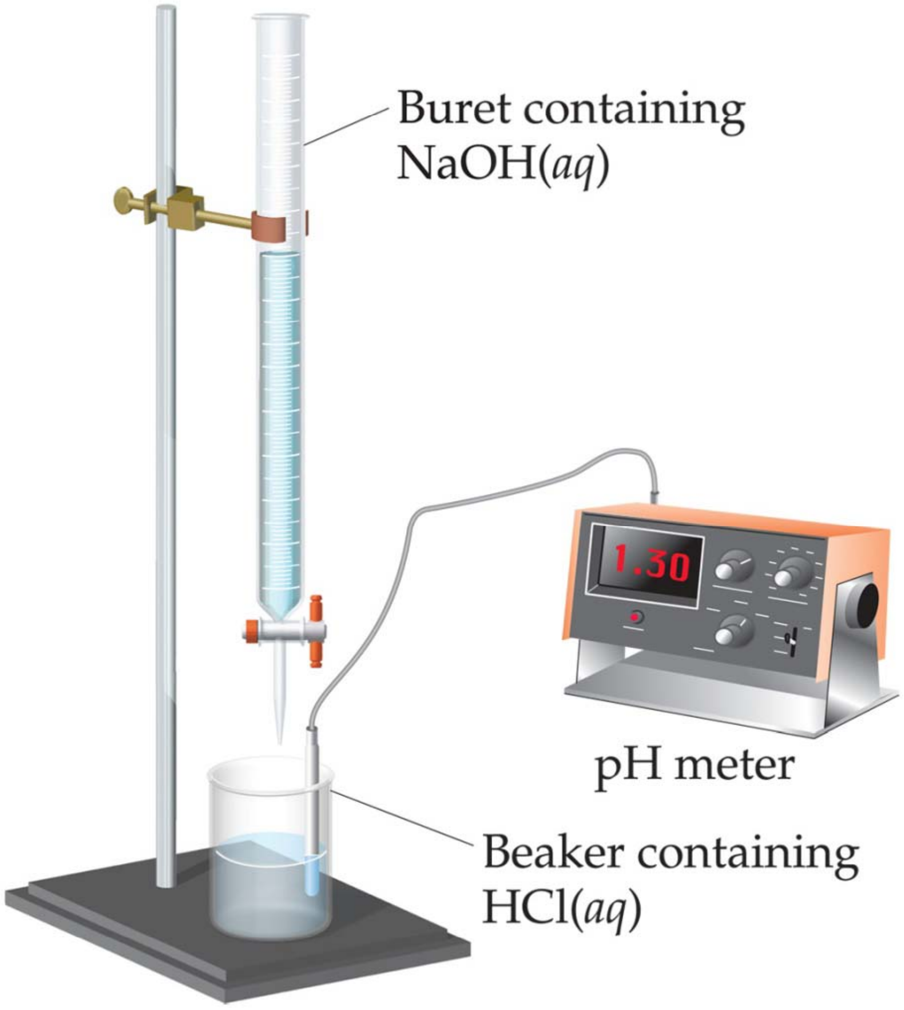
- **The solid acid and a salt of the acid (containing the conjugate base) are in a premeasured packet.**
- **The solid acid and conjugate base in the packet are mixed with a specified amount of water to give a buffer of a specified pH.**
- **Although the quantity of water does not affect the pH of the buffer, only the recommended volume of buffer should be prepared.**

Titration

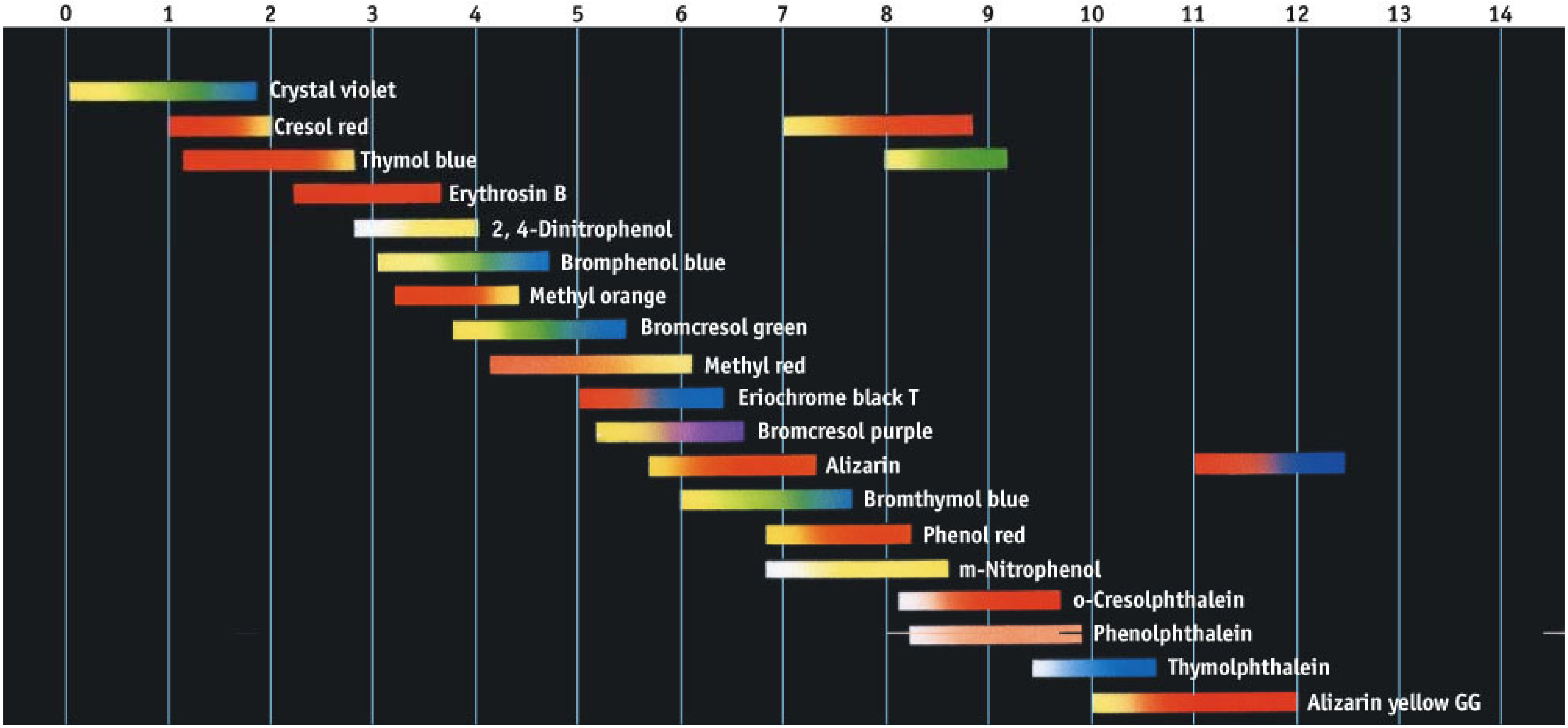


- A known concentration of base (or acid) is slowly added to a solution of acid (or base).
- The progress of the reaction is observed using a pH meter and/or an indicator

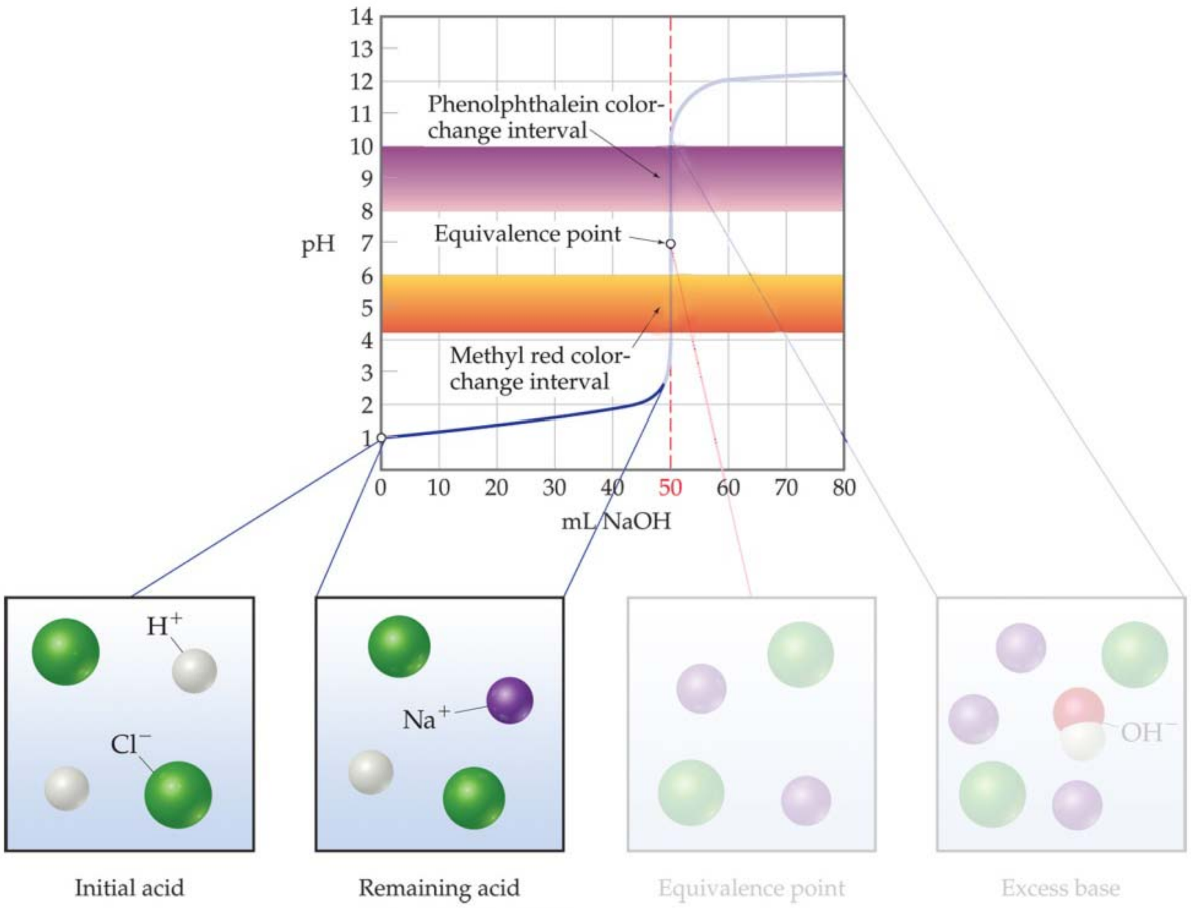
Titration

- A pH meter or indicators are used to determine when the solution has reached the equivalence point, at which the stoichiometric amount of acid equals that of base.
- If an indicator is used, it is chosen so that its color change occurs close to the pH of the equivalence point of the titration.

Indicators for Acid-Base Titrations

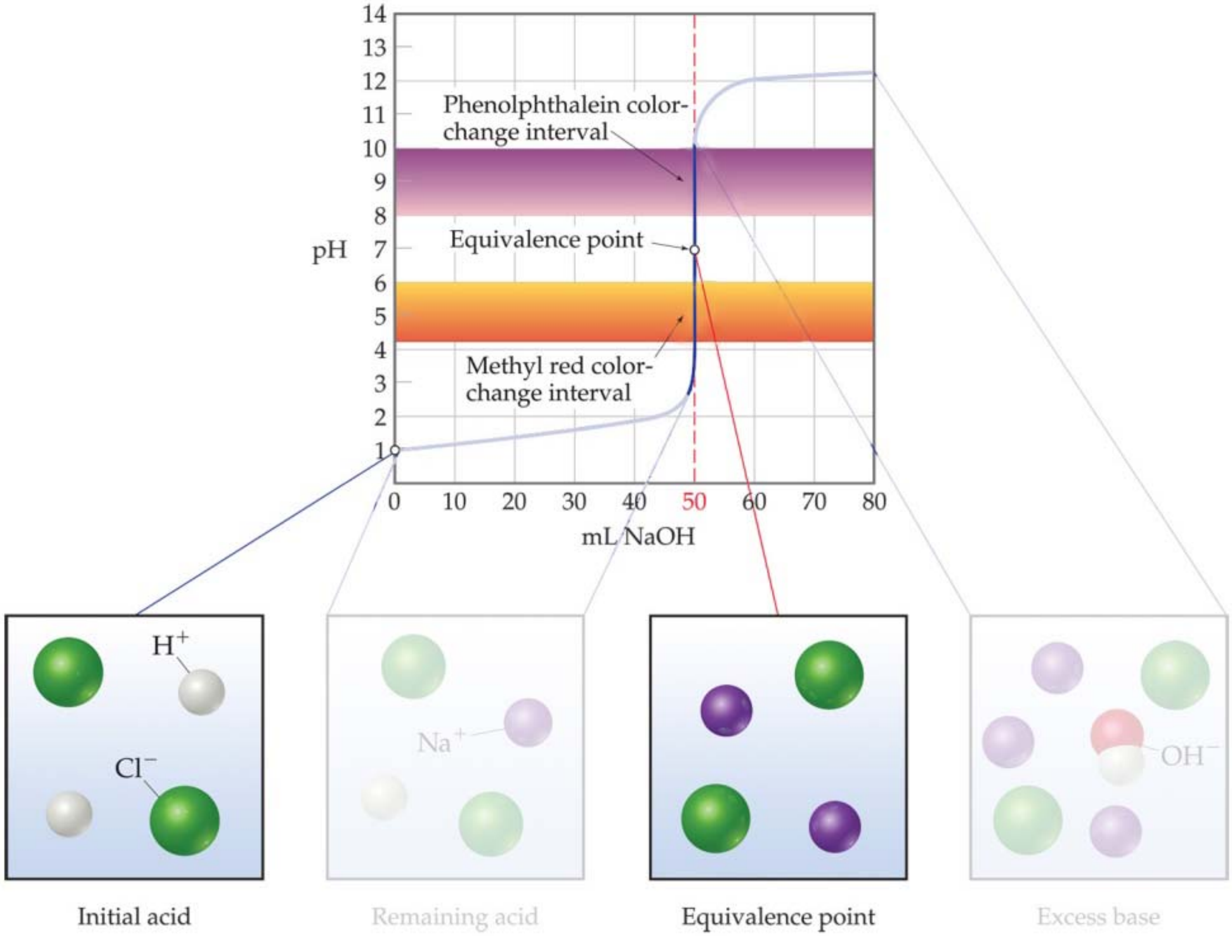


Titration of a Strong Acid with a Strong Base



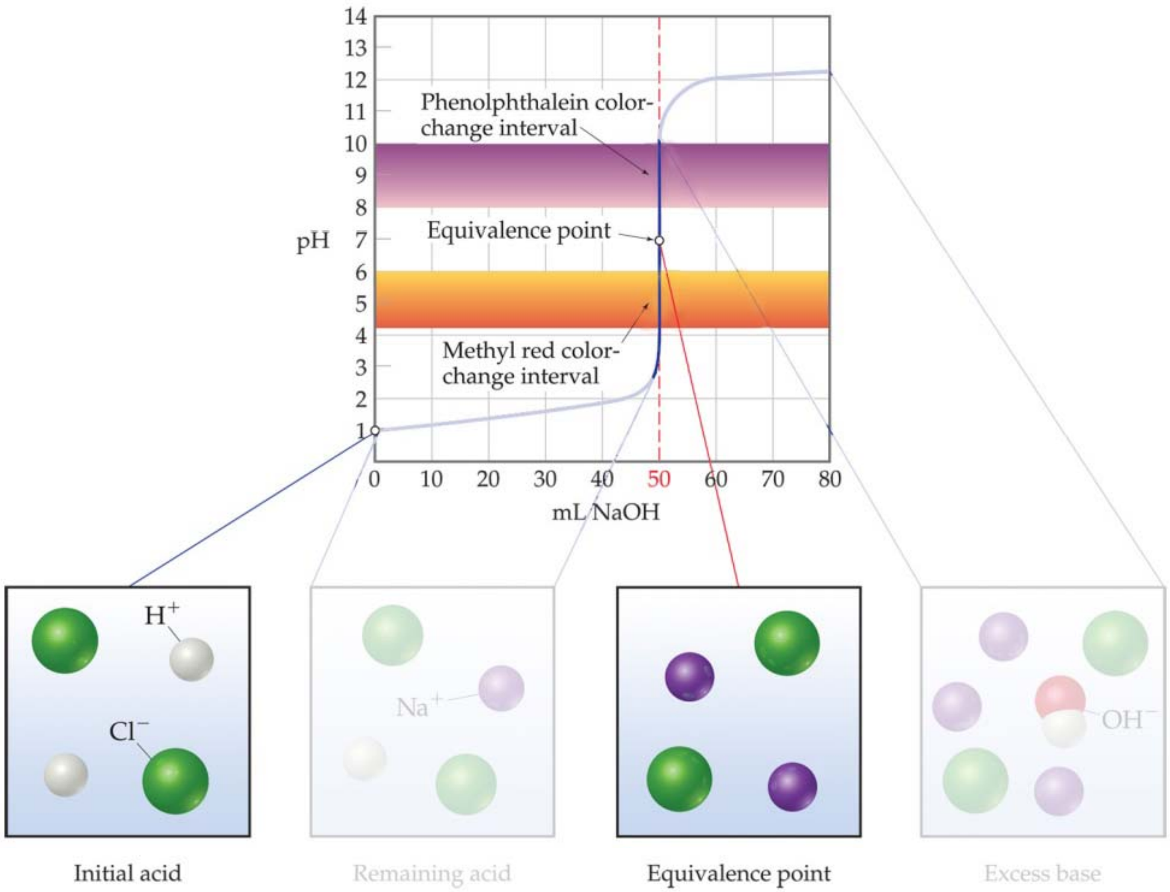
From the start of the titration to near the equivalence point, the pH goes up slowly.

Titration of a Strong Acid with a Strong Base



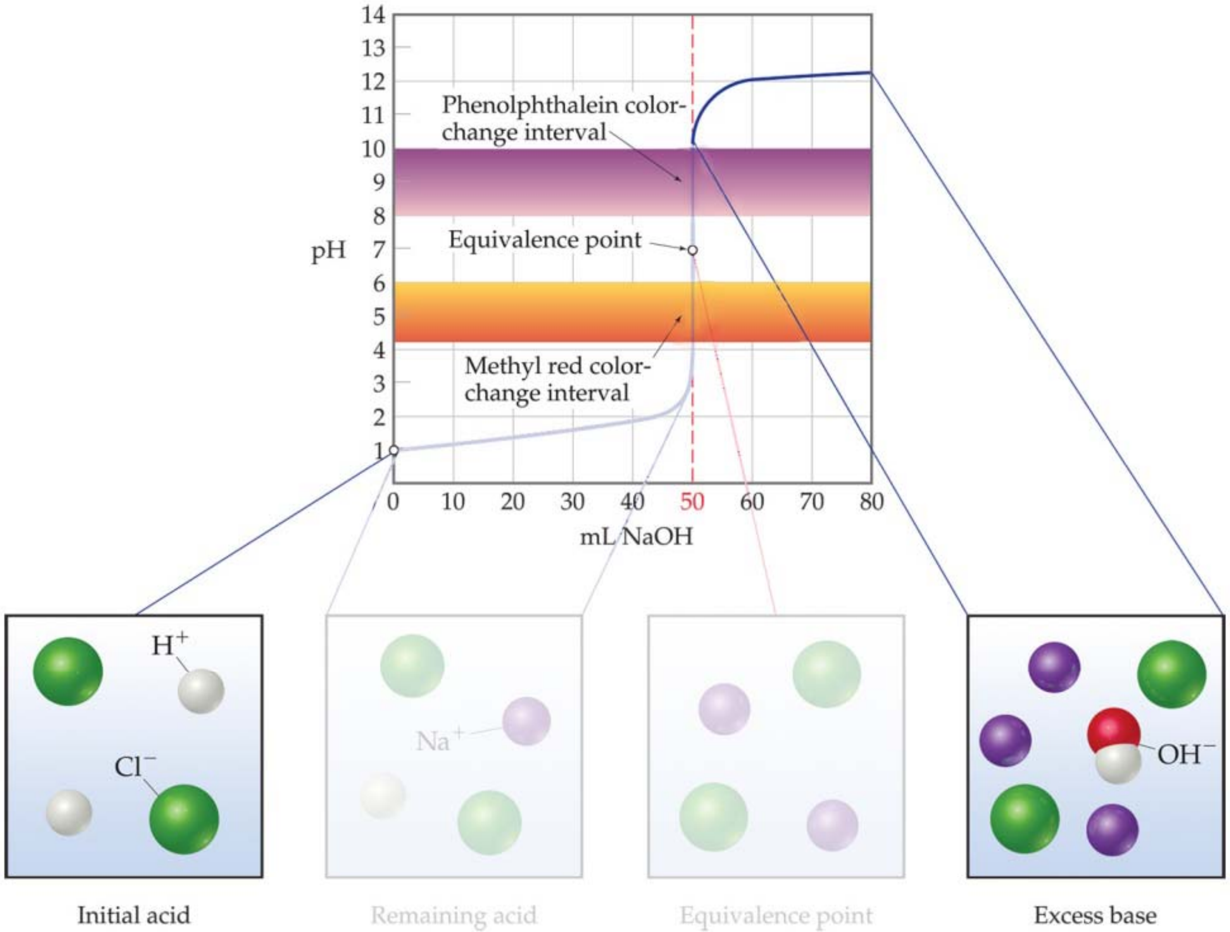
Just before and after the equivalence point, the pH increases rapidly.

Titration of a Strong Acid with a Strong Base



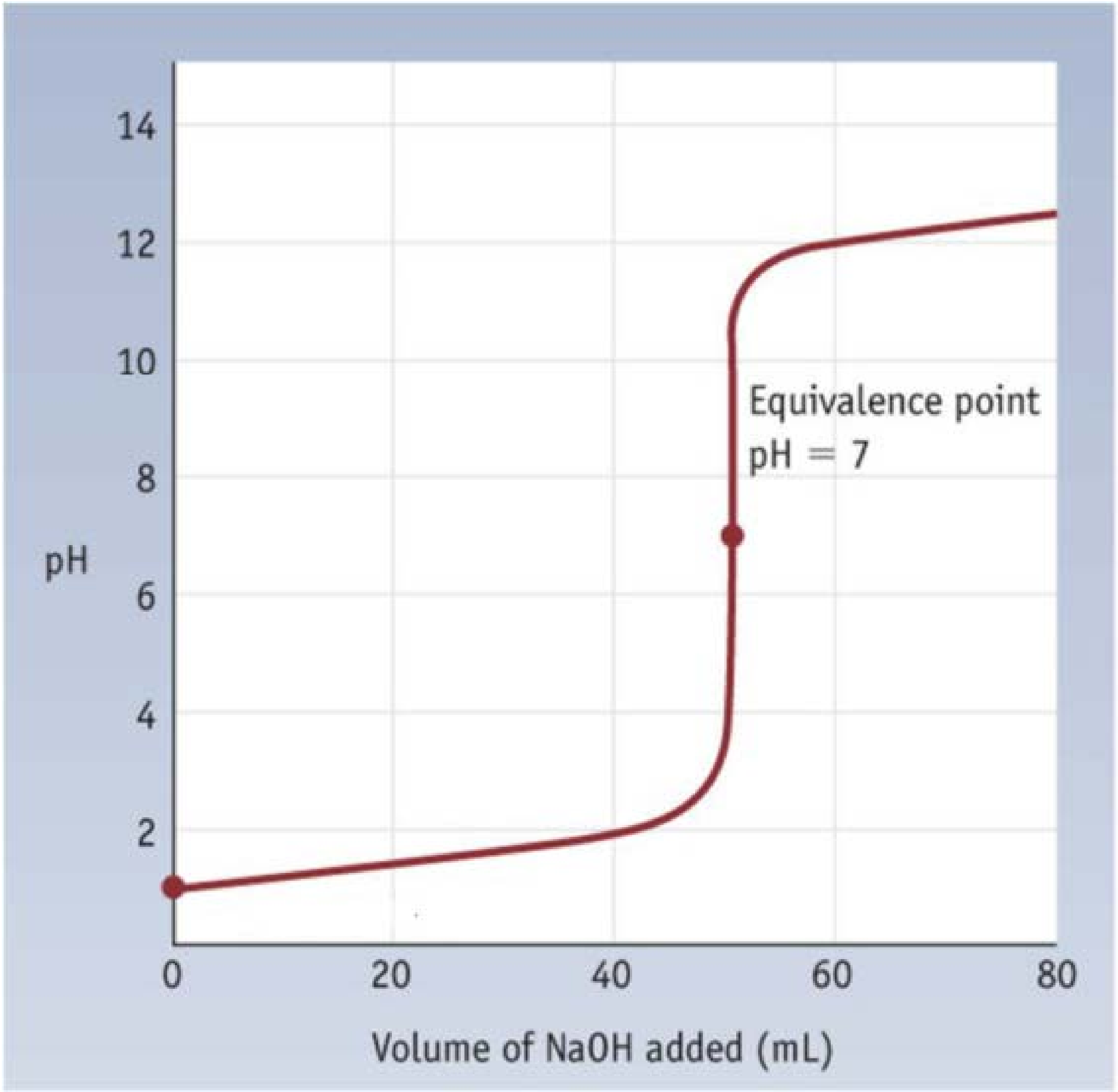
At the equivalence point, moles acid = moles base, and the solution contains only water and the salt from the cation of the base and the anion of the acid.

Titration of a Strong Acid with a Strong Base



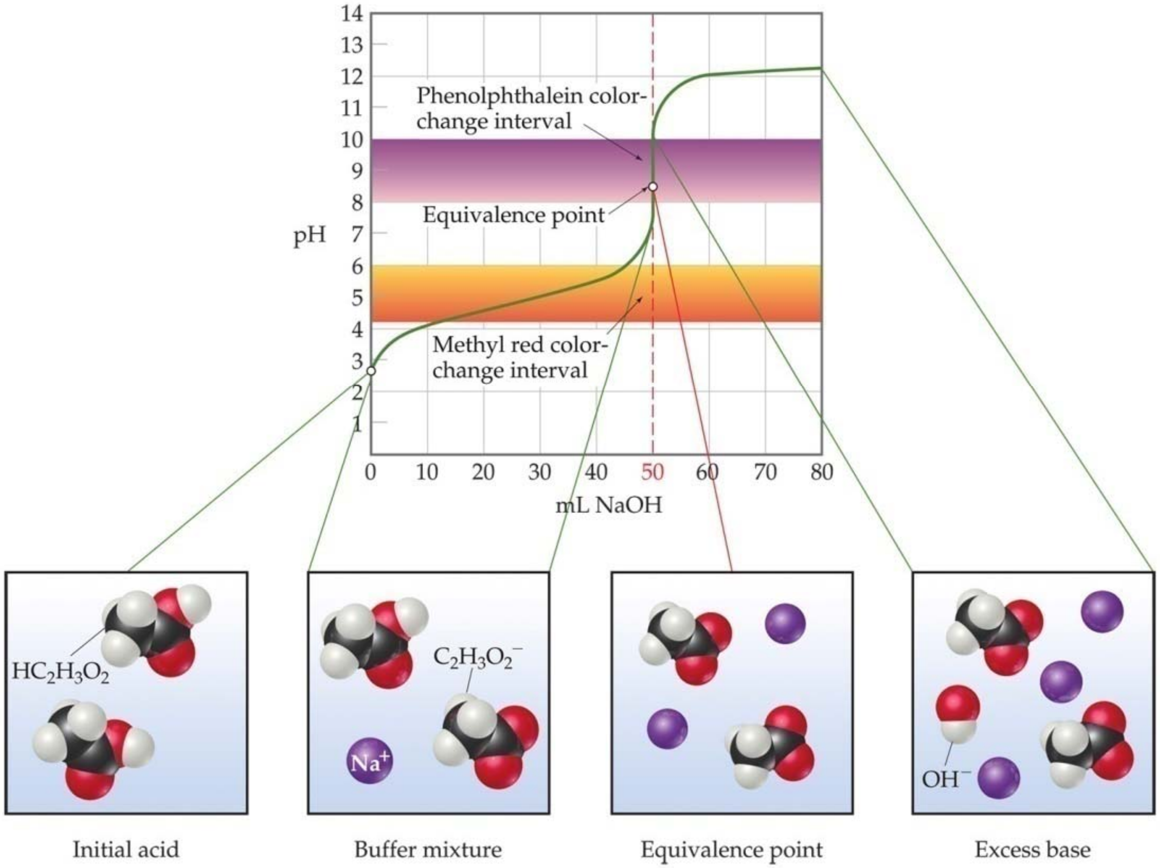
As more base is added, the increase in pH again levels off.

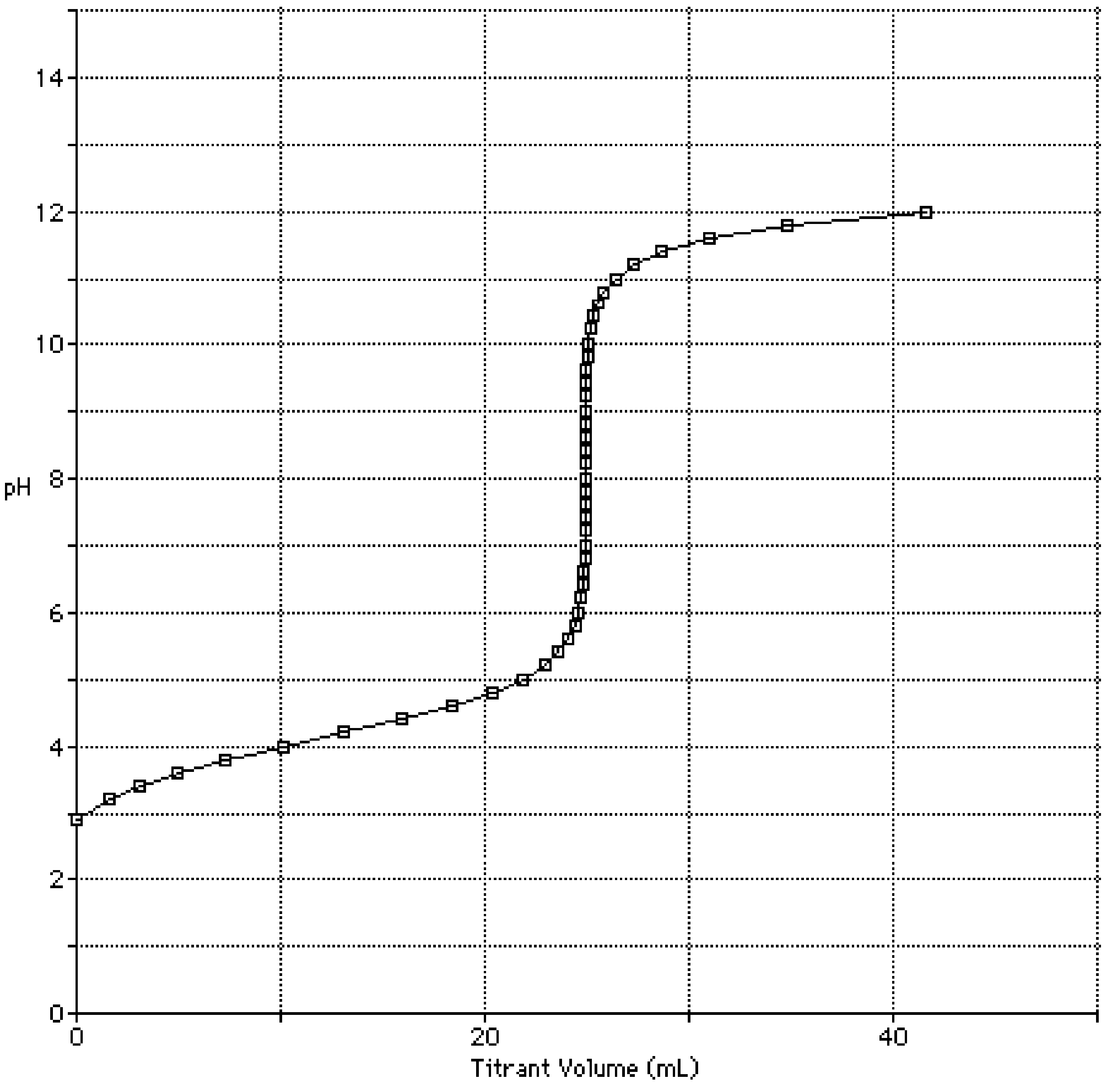
Strong acid titrated with a strong base



Titration of a Weak Acid with a Strong Base

- Unlike in the previous case, the conjugate base of the acid affects the pH when it is formed.
- The pH at the equivalence point will be >7.
- Phenolphthalein is commonly used as an indicator in these titrations.

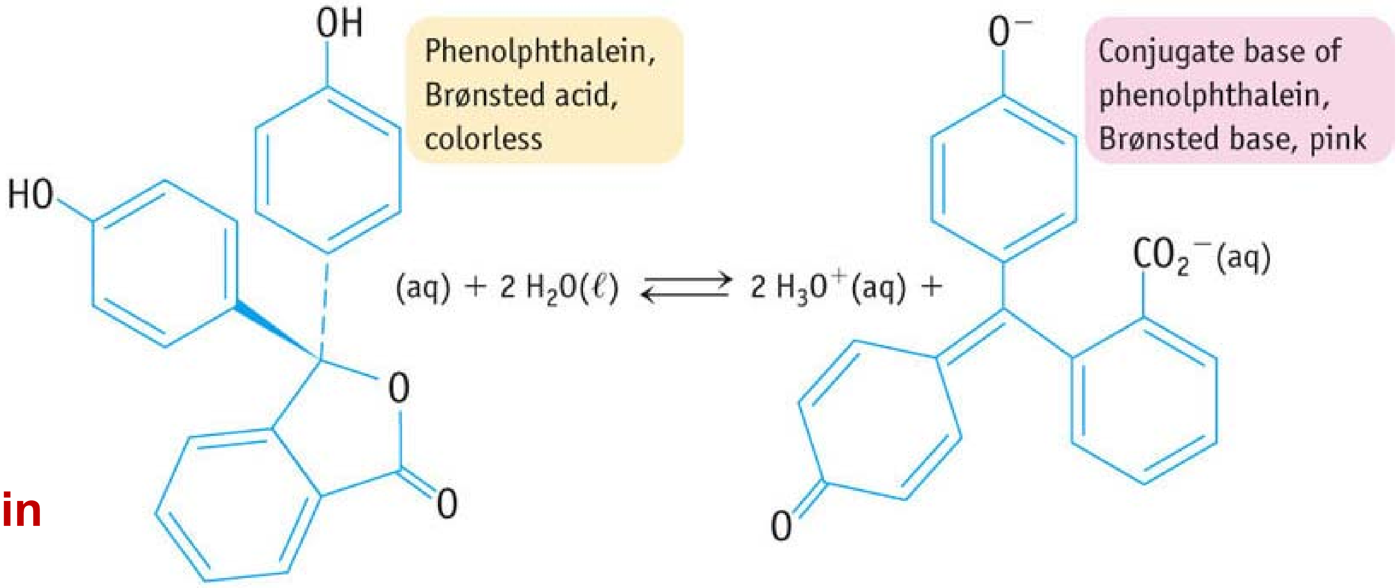




pH

Titrant volume, mL

How phenolphthalein works



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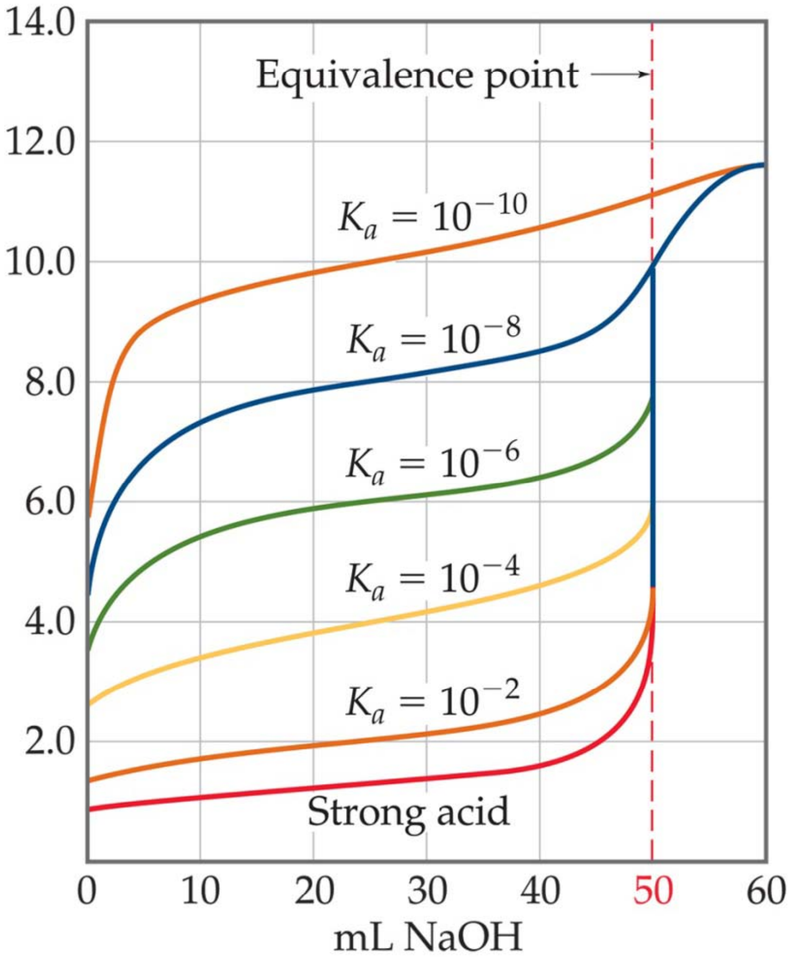
Titration of a Weak Acid with a Strong Base

- In the titration of a weak acid with a strong base, at each point below the equivalence point, the pH of the solution during titration is determined from the amounts of the acid and its conjugate base present at that particular point of the titration.
- To calculate the pH, treat the solution as a buffer

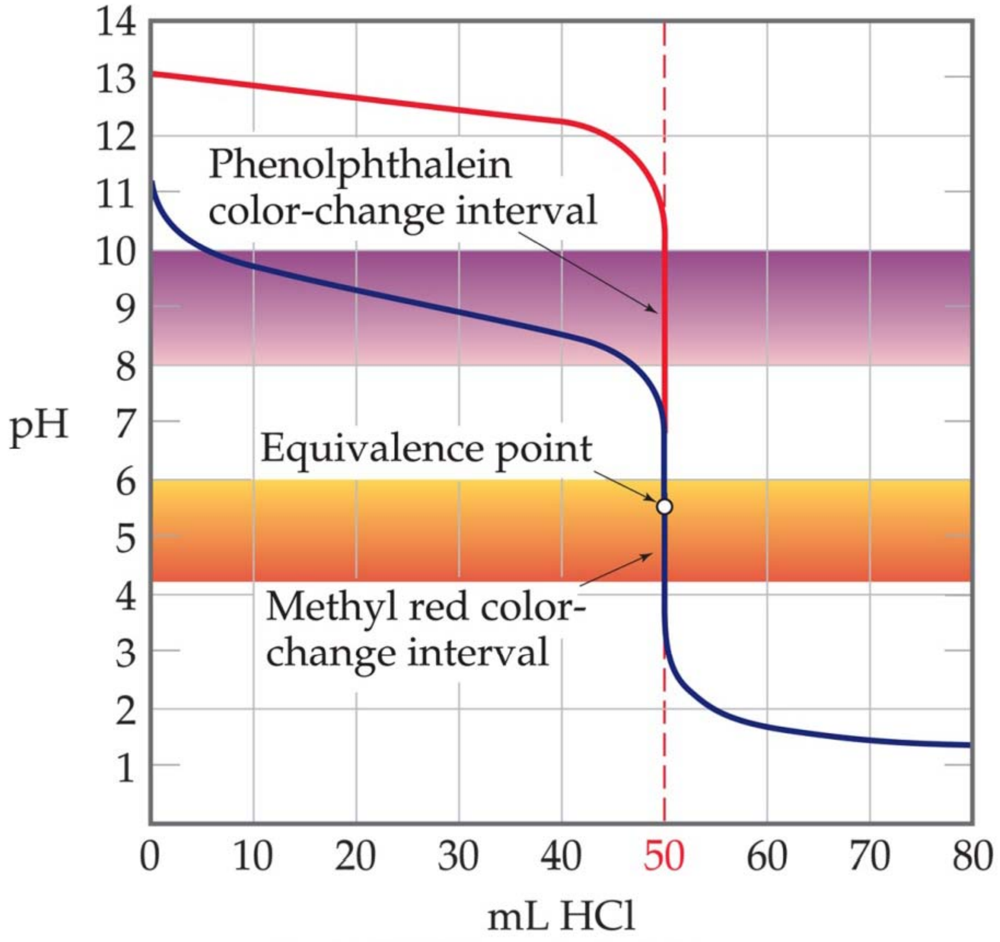
Titration of a Weak Acid with a Strong Base



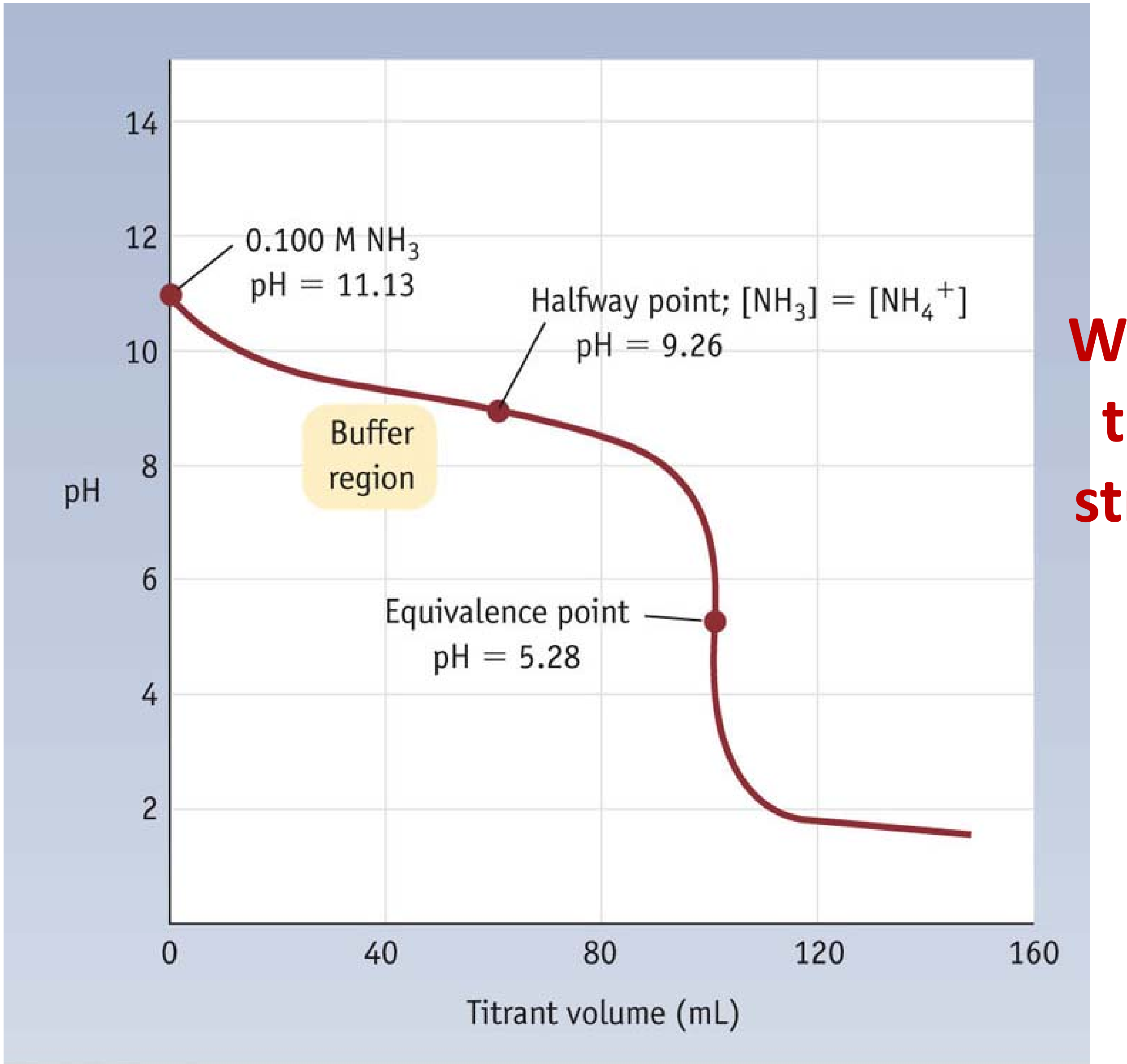
- With weaker acids (lower K_a), the initial pH is higher
- pH changes near the equivalence point are smaller

Titration of a Weak Base with a Strong Acid

- The pH at the equivalence point in these titrations is < 7.
- Methyl red is a suitable indicator for this titration.

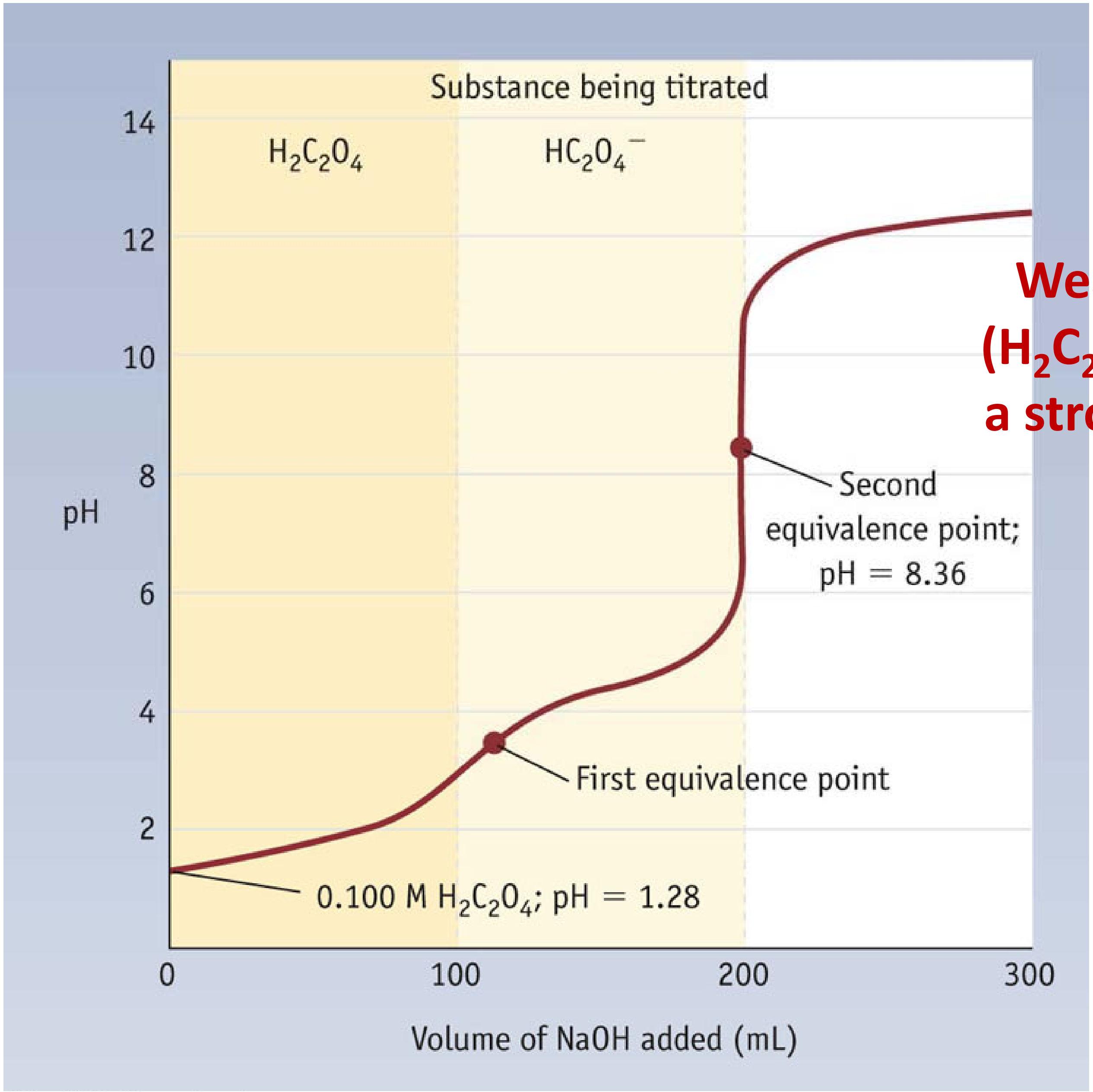


Titration of a Weak Base with a Strong Acid



Weak base (NH_3) titrated with a strong acid (HCl)

Titration of Polyprotic Acids



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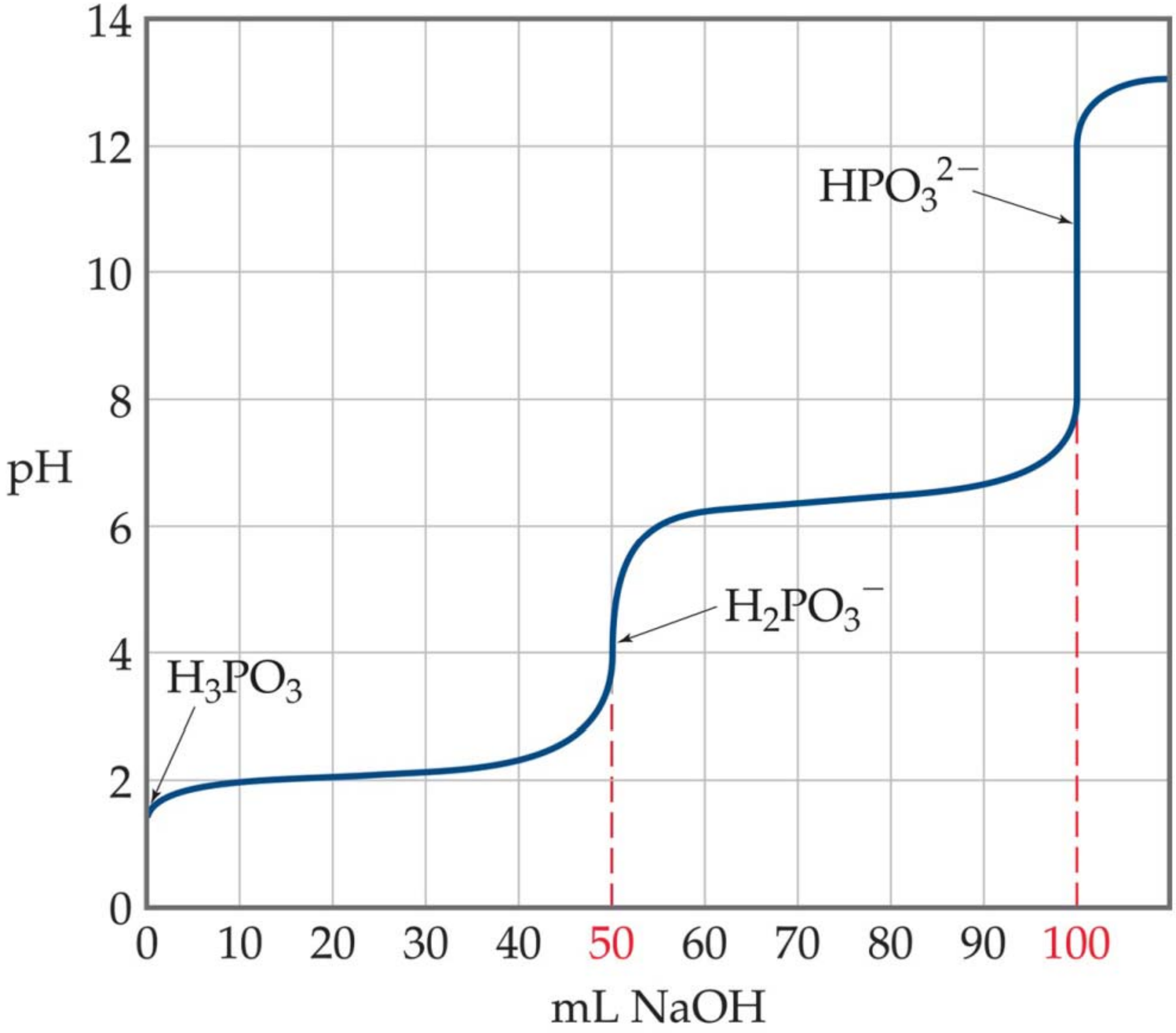
Weak diprotic acid ($H_2C_2O_4$) titrated with a strong base (NaOH)

Titration of Polyprotic Acids



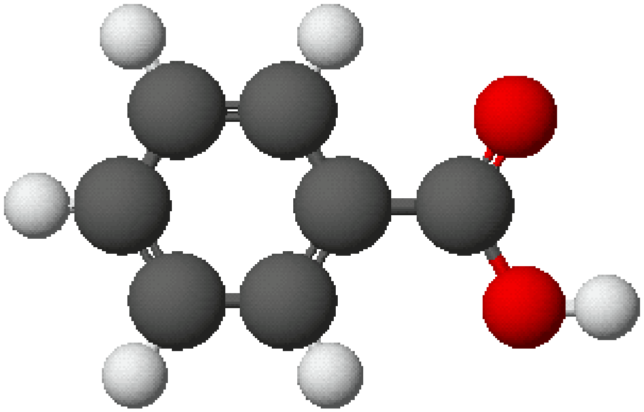
For a triprotic acid, H_3PO_3, phosphorous acid, there is an equivalence point for each dissociation

QUESTION: You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. $K_{a\ HBz} = 6.3 \times 10^{-5}$

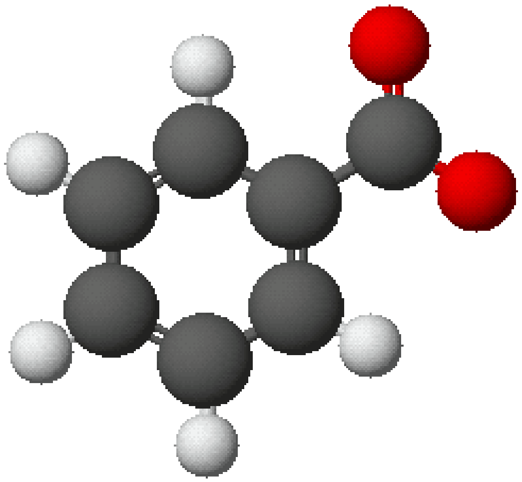
a) What is the pH of the solution when the benzoic acid is 50% neutralized?

b) What is the pH of the solution at the equivalence point?

$$\mathrm{HBz} + \mathrm{NaOH} \rightarrow \mathrm{Na}^+ + \mathrm{Bz}^- + \mathrm{H_2O}$$



$C_6H_5CO_2H$ = HBz

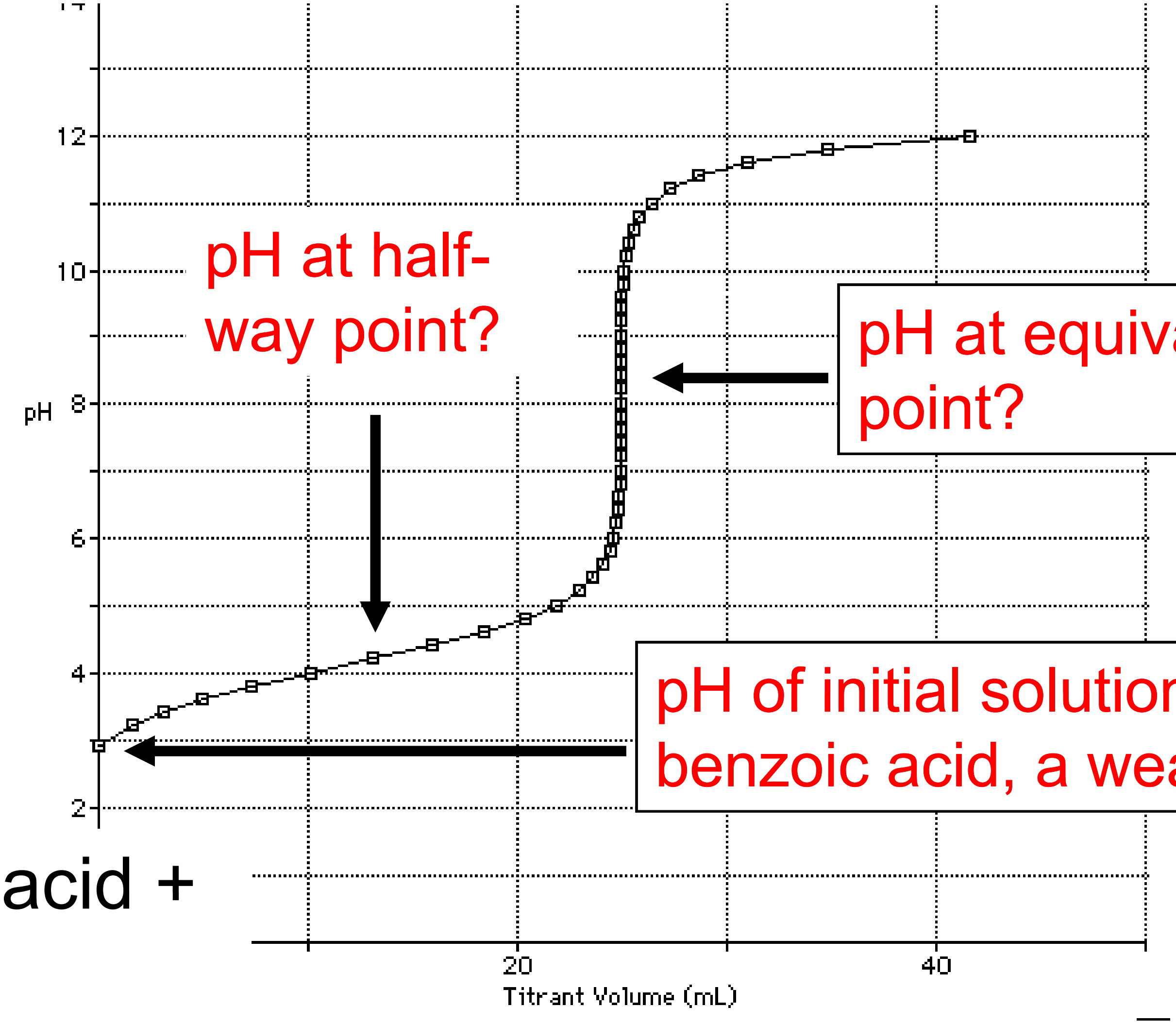


Benzoate ion = Bz^-

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH.**

a) What is the pH of the solution when the benzoic acid is 50% neutralized?

b) What is the pH of the solution at the equivalence point?



pH at half-way point?

pH at equivalence point?

pH of initial solution of benzoic acid, a weak acid

Benzoic acid + NaOH

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH.** **$K_{a\ HBz} = 6.3 \times 10^{-5}$**

a) What is the pH of the solution when the benzoic acid is 50% neutralized?

Solution:

Amount of benzoic acid reacted = 50.0 mL of a 0.025 M solution

Calculate Volume of NaOH used:

$$M_{HBz} \times V_{HBz} = M_{NaOH} \times V_{NaOH}$$

$$0.025\ M \times 50.0\ mL = 0.100\ M \times V_{NaOH}$$

$$V_{NaOH} = 12.5\ mL$$

Calculate new volume of solution:

100. mL HBz sol'n + 12.5 mL NaOH = 112.5 mL

Calculate Molarity of remaining benzoic acid

$$M_{1\ HBz} \times V_{1\ HBz} = M_{2\ HBz} \times V_{2\ HBz}$$

$$0.025\ M \times 50.0\ mL = M_{2\ HBz} \times 112.5\ mL$$

$$= 0.011\ M$$

Calculate concentration of Bz^-

$$HBz + NaOH \rightarrow Na^+ + Bz^- + H_2O$$

Conc. 0.011 M 0.011 M

Use the Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

Since [base] = [acid], log 1 = 0 and pH = pK_a

$$pH = -\log (6.3 \times 10^{-5})$$

$$pH = 4.2$$

Solution:

b) What is the pH of the solution at the equivalence point?

$$HBz + NaOH \rightarrow Na^+ + Bz^- + H_2O$$

At the equivalence point, all the benzoic acid has reacted and is in the form of sodium benzoate. There is no excess of acid or base. (25.0 mL NaOH was used)

$$Bz^- + H_2O \leftrightarrows HBz + OH^-$$

The benzoate concentrations is:

$$M_{1\ Bz} \text{ x } V_{1\ Bz} = M_{2\ Bz} \text{ x } V_{2\ Bz}$$

$$0.025 \text{ M x } 100 \text{ mL} = M_{2\ HBz} \text{ x } 125 \text{ mL}$$

$$M_{2\ Bz} = [Bz^-] = 0.020 \text{ M}$$

This is treated as a hydrolysis reaction

$$K_h = \frac{K_w}{K_a} = \frac{[HBz][OH^-]}{[Bz^-]}$$

$$K_h = \frac{1 \times 10^{-14}}{6.3 \times 10^{-5}} = \frac{[x][x]}{[0.020]}$$

$$x^2 = 3.17 \times 10^{-12}$$

$$x = 1.8 \times 10^{-6}$$

pOH = -log (1.8×10^{-6})

pOH = 5.7

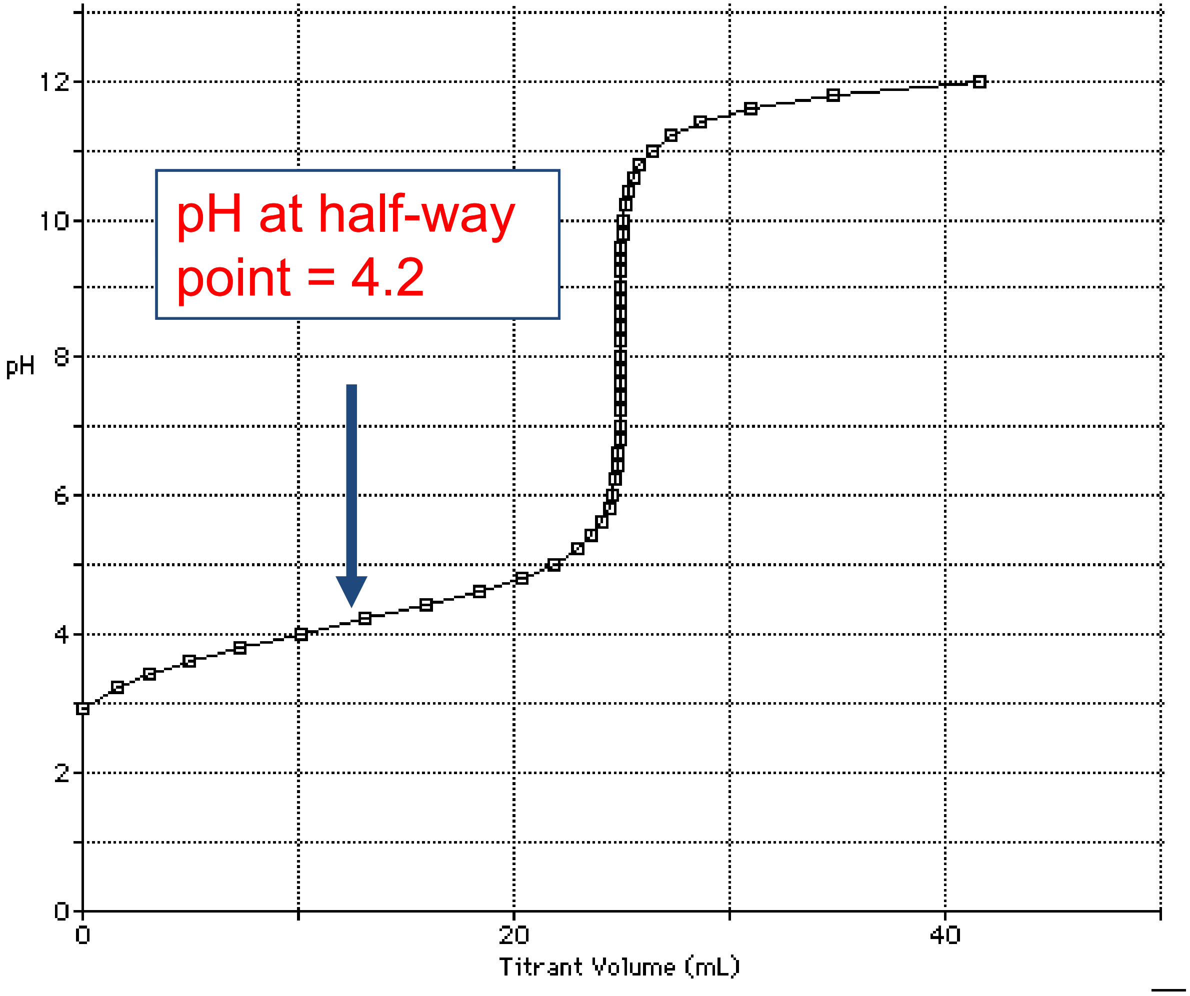
Solve for pH

pH = 14 – pOH = 14 – 5.7

pH = 8.26

QUESTION: You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH. $K_{a\ HBz} = 6.3 \times 10^{-5}$

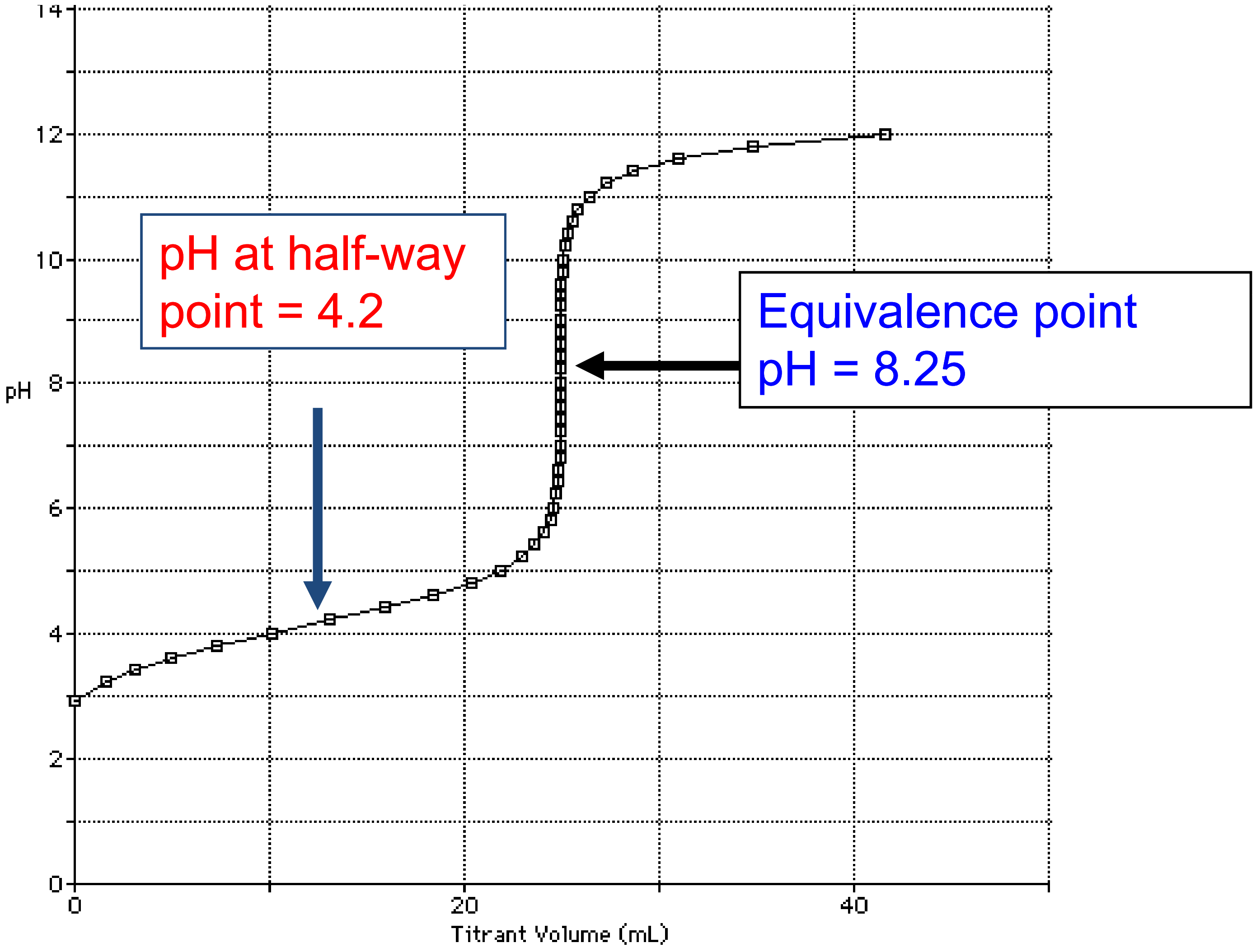
a)What is the pH of the solution when the benzoic acid is 50% neutralized?



pH at half-way point = 4.2

QUESTION: **You titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH.** **$K_{a\ HBz} = 6.3 \times 10^{-5}$**

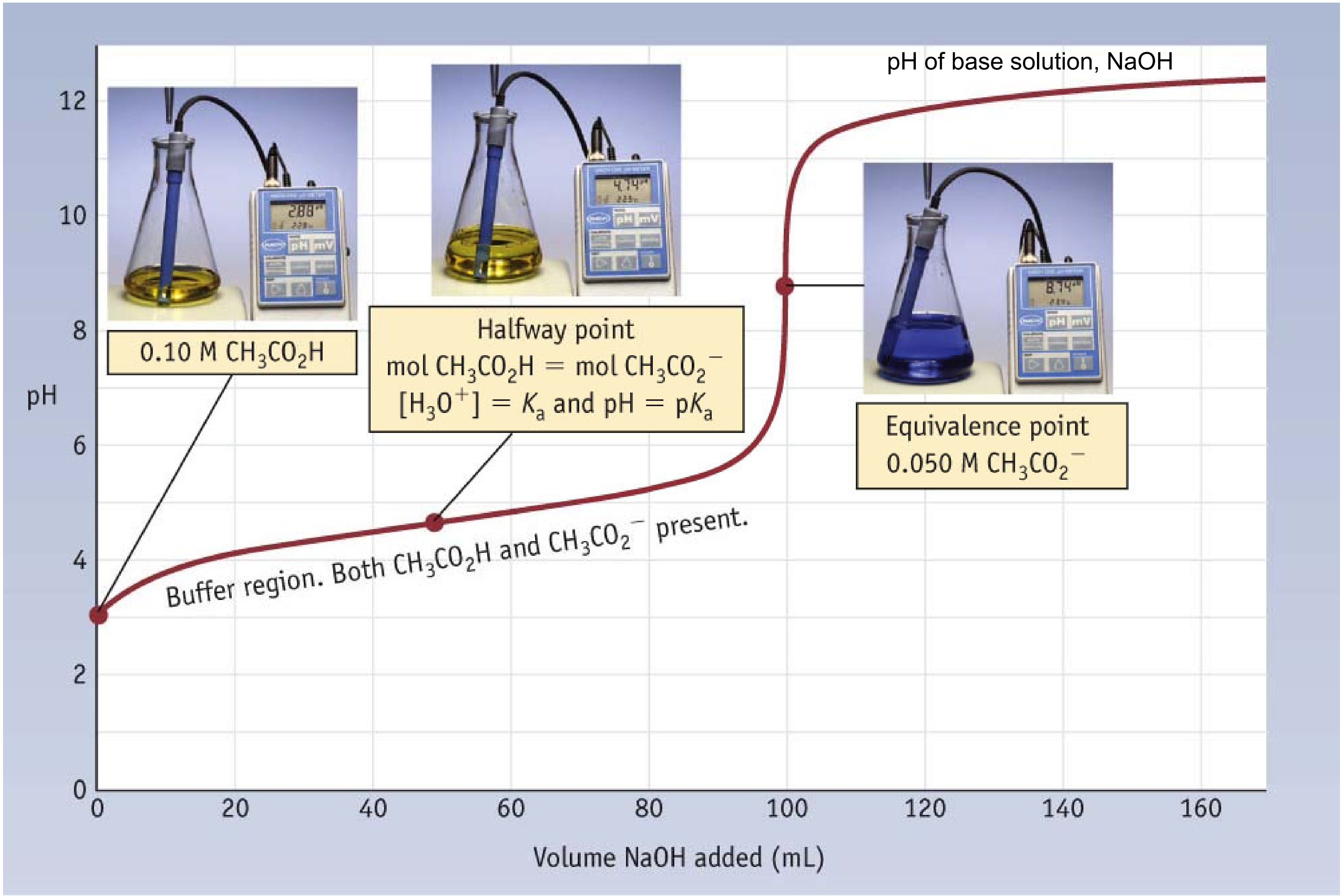
b) What is the pH of the solution at the equivalence point?



pH at half-way point = 4.2

Equivalence point pH = 8.25

Acetic acid titrated with NaOH



Solubility Products

- When an insoluble compound, such as $BaSO_4$, is added to water, a very small amount of the solid dissolves.
- The solution is saturated with the $BaSO_4$
- The solubility of the $BaSO_4$ is treated as an equilibrium :

$$BaSO_{4\,(s)} \leftrightarrows Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

- Note that this is a heterogeneous equilibrium

Solubility Products

The equilibrium constant expression for this equilibrium system is

$$K_{sp} = [\mathrm{Ba}^{2+}]\,[\mathrm{SO_4}^{2-}]$$

where the equilibrium constant is given a special symbol, K_{sp}

K_{sp} is called the **solubility product**.

Solubility Products

- K_{sp} is *not* the same as solubility.
- Solubility is most commonly expressed as the mass of solute dissolved in 100 mL (g/100 mL) of solution.
- The K_{sp} is the product of the concentration of the ions in a saturated solution of an “insoluble” substance.

Solubility Products

Sample problem:

Calculate the solubility of $BaSO_4$. $K_{sp\ BaSO4} = 1.1 \times 10^{-10}$

Solution:

$$BaSO_{4\,(s)} \rightleftarrows Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

Concentration	-	x	x

$$K_{sp} = [Ba^{2+}]\,[SO_4{}^{2-}]$$

$$1.1 \times 10^{-10} = [x]\,[x] = x^2$$

$$1.05 \times 10^{-5}\ M = x = [Ba^{2+}] = [SO_4{}^{2-}]$$

Solubility Products

Sample problem:

Calculate the solubility of $Ca(OH)_2$ $K_{sp\ Ca(OH)2} = 5.5 \times 10^{-5}$

Solution:

$$Ca(OH)_{2\,(s)} \leftrightarrows Ca^{2+}_{(aq)} + 2\,OH^{-}_{(aq)}$$

Concentration - x 2x

$$K_{sp} = [Ca^{2+}]\,[OH^{-}]^2$$

$$5.5 \times 10^{-5} = [x]\,[2x]^2 = 4x^3$$

$$1.38 \times 10^{-5}\ M = x^3$$

$$2.4 \times 10^{-2}\ M = x = [Ca^{2+}]$$

Factors Affecting Solubility

- The Common-Ion Effect
  - If one of the ions in a solution equilibrium is already dissolved in the solution, the equilibrium will shift to the left and the solubility of the salt will decrease.

$$BaSO_{4(s)} \leftrightarrows Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Factors Affecting Solubility

Sample problem:

Calculate the solubility of $BaSO_4$ in a 0.050 M solution of H_2SO_4 $K_{sp\ BaSO4} = 1.1 \times 10^{-10}$

Solution:

$$BaSO_{4(s)} \leftrightarrows Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

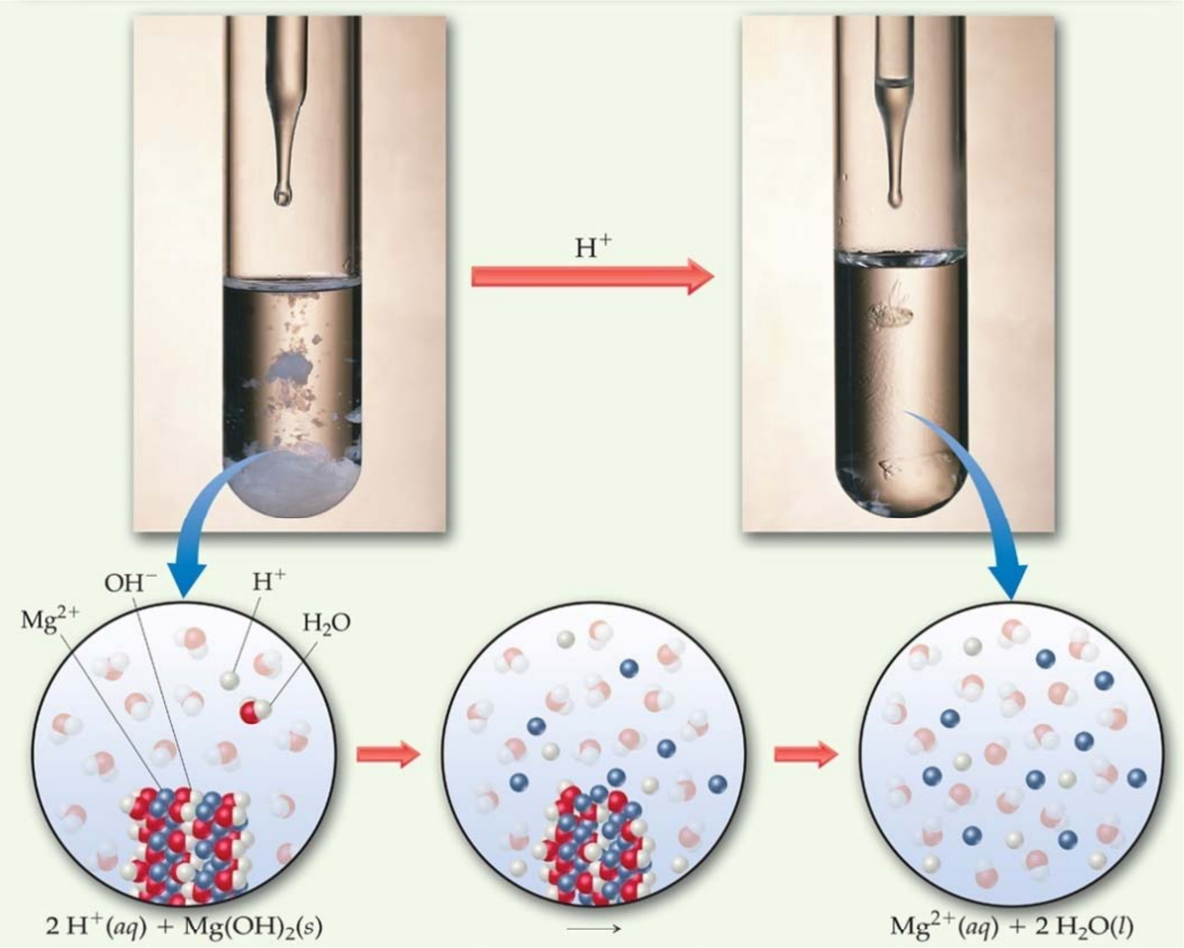
Concentration - x 0.050M

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

$$1.1 \times 10^{-10} = [x]\,[0.050]$$

$$2.2 \times 10^{-9}\ M = x = [Ba^{2+}]$$

Factors Affecting Solubility



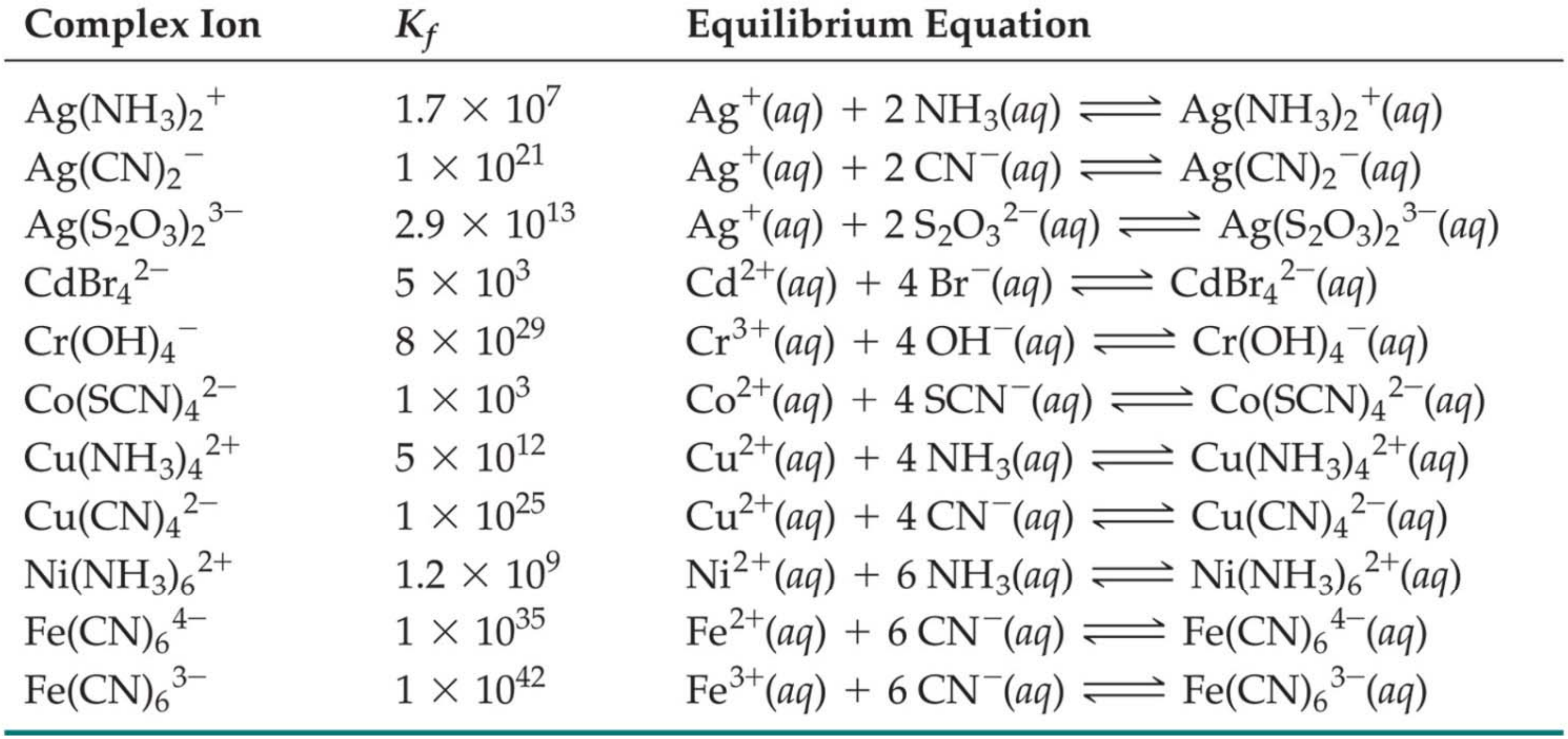
pH

- If a substance has a basic anion, it will be more soluble in an acidic solution.
- Substances with acidic cations are more soluble in basic solutions.

$K_{sp\ Mg(OH)2} = 5.6 \times 10^{-12}$

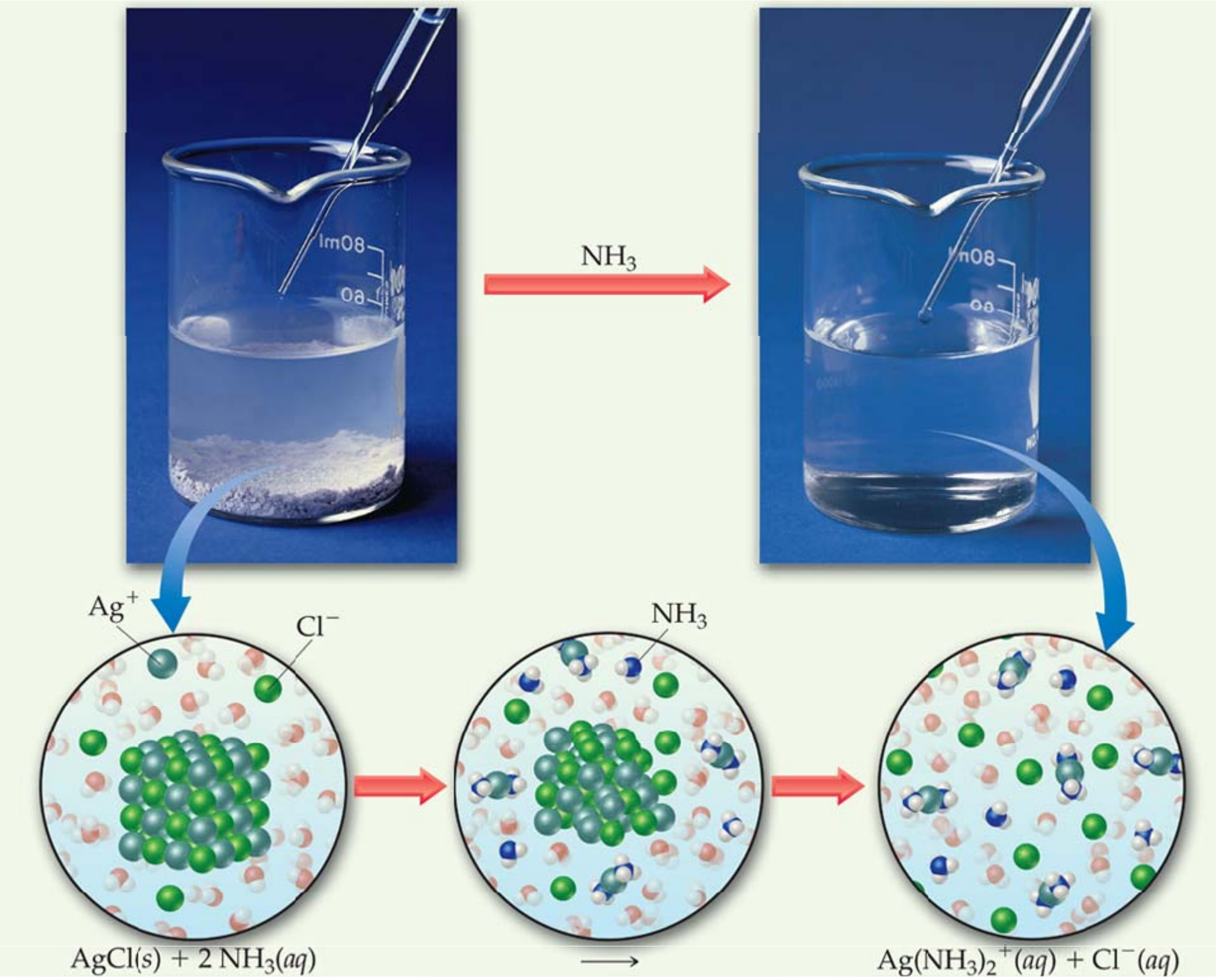
Factors Affecting Solubility

- Complex Ions
  - Metal ions can act as Lewis acids and form complex ions with Lewis bases in the solvent.



Complex Ion	K_f	**Equilibrium Equation**
$Ag(NH_3)_2{}^{+}$	1.7×10^{7}	$Ag^{+}(aq) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2{}^{+}(aq)$
$Ag(CN)_2{}^{-}$	1×10^{21}	$Ag^{+}(aq) + 2\,CN^{-}(aq) \rightleftharpoons Ag(CN)_2{}^{-}(aq)$
$Ag(S_2O_3)_2{}^{3-}$	2.9×10^{13}	$Ag^{+}(aq) + 2\,S_2O_3{}^{2-}(aq) \rightleftharpoons Ag(S_2O_3)_2{}^{3-}(aq)$
$CdBr_4{}^{2-}$	5×10^{3}	$Cd^{2+}(aq) + 4\,Br^{-}(aq) \rightleftharpoons CdBr_4{}^{2-}(aq)$
$Cr(OH)_4{}^{-}$	8×10^{29}	$Cr^{3+}(aq) + 4\,OH^{-}(aq) \rightleftharpoons Cr(OH)_4{}^{-}(aq)$
$Co(SCN)_4{}^{2-}$	1×10^{3}	$Co^{2+}(aq) + 4\,SCN^{-}(aq) \rightleftharpoons Co(SCN)_4{}^{2-}(aq)$
$Cu(NH_3)_4{}^{2+}$	5×10^{12}	$Cu^{2+}(aq) + 4\,NH_3(aq) \rightleftharpoons Cu(NH_3)_4{}^{2+}(aq)$
$Cu(CN)_4{}^{2-}$	1×10^{25}	$Cu^{2+}(aq) + 4\,CN^{-}(aq) \rightleftharpoons Cu(CN)_4{}^{2-}(aq)$
$Ni(NH_3)_6{}^{2+}$	1.2×10^{9}	$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons Ni(NH_3)_6{}^{2+}(aq)$
$Fe(CN)_6{}^{4-}$	1×10^{35}	$Fe^{2+}(aq) + 6\,CN^{-}(aq) \rightleftharpoons Fe(CN)_6{}^{4-}(aq)$
$Fe(CN)_6{}^{3-}$	1×10^{42}	$Fe^{3+}(aq) + 6\,CN^{-}(aq) \rightleftharpoons Fe(CN)_6{}^{3-}(aq)$

Factors Affecting Solubility



$K_{sp\ AgCl} = 1.8 \times 10^{-10}$

soluble

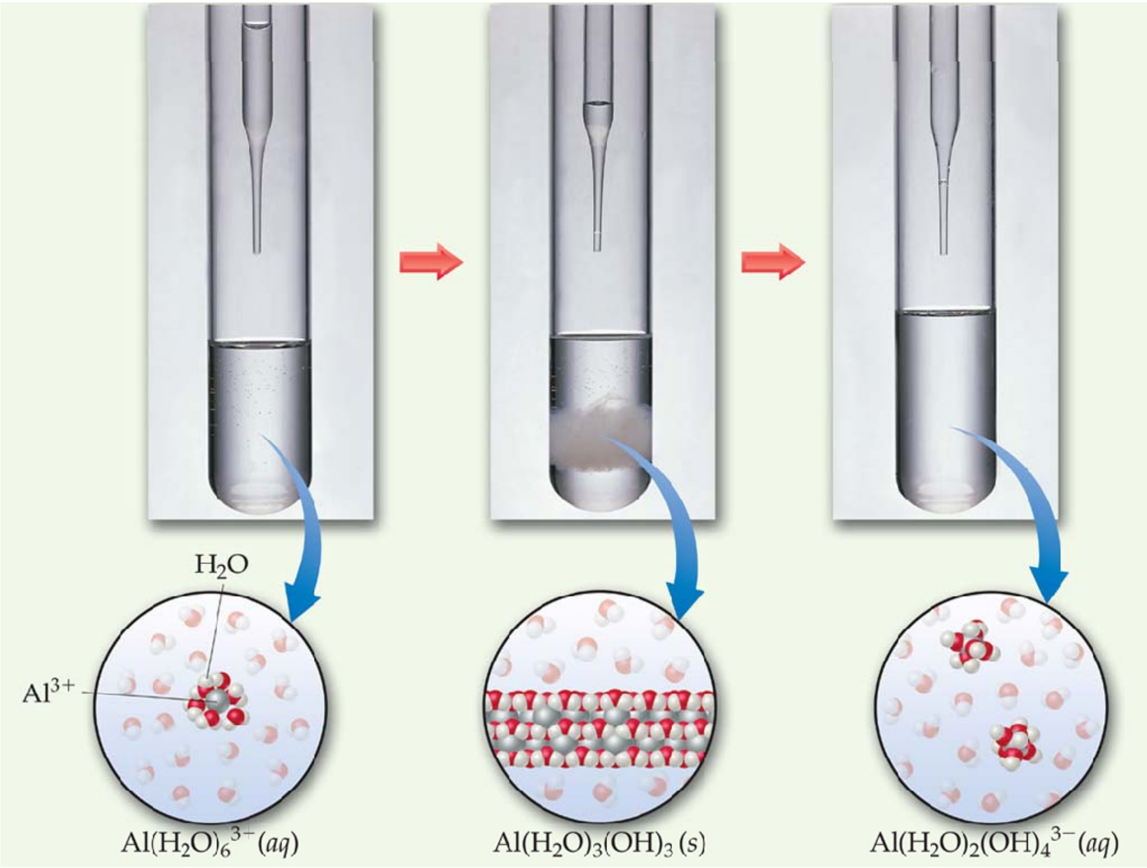
Complex Ions

- The formation of these complex ions increases the solubility of these salts.

Factors Affecting Solubility

Amphoterism

- Amphoteric metal oxides and hydroxides are soluble in strong acid or base, because they can act either as acids or bases.
- Examples of such cations are Al^{3+}, Zn^{2+}, and Sn^{2+}.

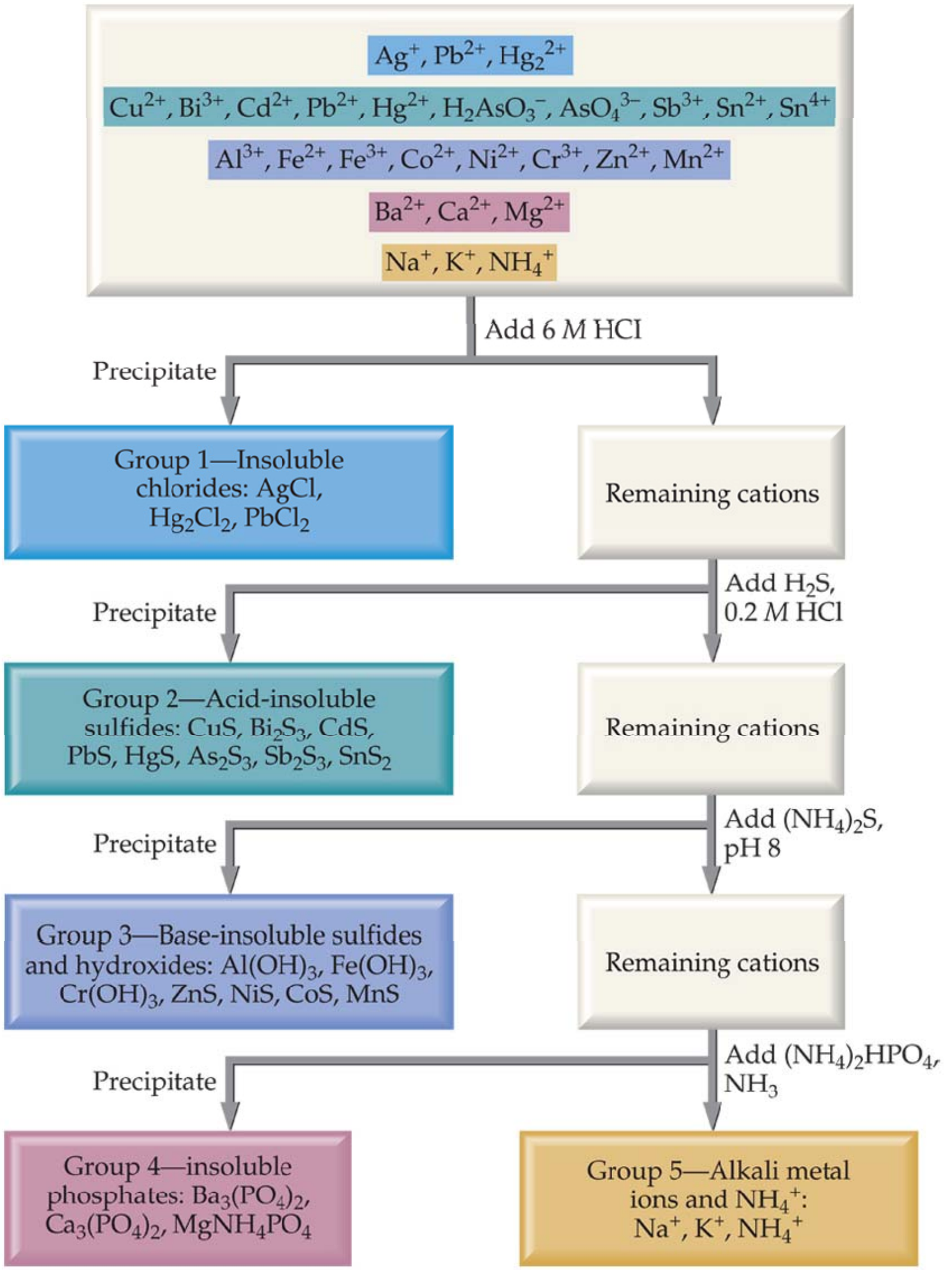


→ Addition of base → → → →

Will a Precipitate Form?

- Using the reaction quotient, Q, in a solution,
  - If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated. (both solid and ions are present)
  - If $Q < K_{sp}$, more solid will dissolve until $Q = K_{sp}$. (only ions are present)
  - If $Q > K_{sp}$, the salt will precipitate until $Q = K_{sp}$. (there are excess ions present in solution, so a precipitate will form)

Selective Precipitation of Ions



Ag^+, Pb^{2+}, Hg_2^{2+}

Cu^{2+}, Bi^{3+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, $H_2AsO_3^-$, AsO_4^{3-}, Sb^{3+}, Sn^{2+}, Sn^{4+}

Al^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Mn^{2+}

Ba^{2+}, Ca^{2+}, Mg^{2+}

Na^+, K^+, NH_4^+

Add 6 *M* HCl

Precipitate

Group 1—Insoluble chlorides: AgCl, Hg_2Cl_2, $PbCl_2$

Remaining cations

Add H_2S, 0.2 *M* HCl

Precipitate

Group 2—Acid-insoluble sulfides: CuS, Bi_2S_3, CdS, PbS, HgS, As_2S_3, Sb_2S_3, SnS_2

Remaining cations

Add $(NH_4)_2S$, pH 8

Precipitate

Group 3—Base-insoluble sulfides and hydroxides: $Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$, ZnS, NiS, CoS, MnS

Remaining cations

Add $(NH_4)_2HPO_4$, NH_3

Precipitate

Group 4—insoluble phosphates: $Ba_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$

Group 5—Alkali metal ions and NH_4^+: Na^+, K^+, NH_4^+

In the process of qualitative analysis, we use the differences in solubilities of salts to separate ions in a mixture.

Analysis of the Silver Group

- The silver group consists of three ions: Ag^+, Hg_2^{2+} and Pb^{2+}
- All three ions form precipitates with Cl^-

$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ $K_{sp} = 1.8 \times 10^{-10}$

$Hg_2^{2+}{}_{(aq)} + 2\,Cl^-_{(aq)} \rightarrow Hg_2Cl_{2\,(s)}$ $K_{sp} = 1.4 \times 10^{-18}$

$Pb^{2+}_{(aq)} + 2\,Cl^-_{(aq)} \rightarrow PbCl_{2\,(s)}$ $K_{sp} = 1.7 \times 10^{-5}$

Analysis of the Silver Group

6 M HCl is added dropwise to a solution containing 0.025 M concentrations of Ag^+, Hg_2^{2+} and Pb^{2+}

a) What is the concentration of Cl^- when the first ion precipitates?

b) When the second ion precipitates, what is the concentration of the ion that precipitated first?

c) What is the concentration of Cl^- needed to precipitate 99% of the Pb^{2+}?

$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$ $K_{sp} = 1.8 \times 10^{-10}$

$Hg_2^{2+}{}_{(aq)} + 2\,Cl^-_{(aq)} \rightarrow Hg_2Cl_{2\,(s)}$ $K_{sp} = 1.4 \times 10^{-18}$

$Pb^{2+}_{(aq)} + 2\,Cl^-_{(aq)} \rightarrow PbCl_{2\,(s)}$ $K_{sp} = 1.7 \times 10^{-5}$

Analysis of the Silver Group

6 M HCl is added dropwise to a solution containing 0.025 M concentrations of Ag^+, Hg_2^{2+} and Pb^{2+}

a) What is the concentration of Cl^- when the first ion precipitates?

Solution:

Generally, the compound with the smallest K_{sp} precipitates first, so calculate concentration of Cl^- necessary to precipitate the Hg_2^{2+}

$$Hg_2Cl_{2\,(s)} \rightarrow Hg_2^{2+}{}_{(aq)} + 2\,Cl^-{}_{(aq)}$$

Concentrations 0.025 M 2x

$$K_{sp\ Hg2Cl2} = 1.4 \times 10^{-18} = [Hg_2^{2+}]\,[Cl^-]^2$$

$$1.4 \times 10^{-18} = [0.025]\,[2x]^2$$

$$4x^2 = 5.6 \times 10^{-17}$$

$$x^2 = 1.4 \times 10^{-17}$$

$$x = 3.7 \times 10^{-9}\ M$$

$$[Cl^-] = 2x = 7.4 \times 10^{-9}\ M$$

Analysis of the Silver Group

6 M HCl is added dropwise to a solution containing 0.025 M concentrations of Ag^+, Hg_2^{2+} and Pb^{2+}

a) What is the concentration of Cl^- when the first ion precipitates?

Solution Part a) (continued):

Next, calculate the Cl^- concentration needed to precipitate Ag^+ (Although the K_{sp} for AgCl is larger than the K_{sp} for Hg_2Cl_2, the difference in reaction stoichiometry does have an effect.)

$$AgCl_{(s)} \rightarrow Ag^+_{(aq)} + Cl^-_{(aq)} \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$K_{sp\ AgCl} = 1.8 \times 10^{-10} = [Ag^+]\,[Cl^-]$$

$$1.8 \times 10^{-10} = [0.025]\,[x]$$

$$x = 7.2 \times 10^{-9}\ M$$

The concentration of Cl^- needed to precipitate the Ag^+ is less than that for Hg_2^{2+} , so, Ag^+ precipitates first.

Analysis of the Silver Group

6 M HCl is added dropwise to a solution containing 0.025 M concentrations of Ag^+, Hg_2^{2+} and Pb^{2+}

b) When the second ion precipitates, what is the concentration of the ion that precipitated first?

Solution, Part b):

Hg_2^{2+} precipitates second when $[Cl^-] = 7.4 \times 10^{-9}$ M

Calculate the concentration of Ag^+

$$K_{sp\ AgCl} = 1.8 \times 10^{-10} = [Ag^+]\,[Cl^-]$$

$$1.8 \times 10^{-10} = [Ag^+]\,[7.4 \times 10^{-9}]$$

$$[Ag^+] = 2.4 \times 10^{-2}\ M$$

Analysis of the Silver Group

6 M HCl is added dropwise to a solution containing 0.025 M concentrations of Ag^+, Hg_2^{2+} and Pb^{2+}

c) What is the concentration of Cl^- needed to precipitate 99% of the Pb^{2+}?

Solution Part c):

If 1% of the Pb^{2+} will remain in solution, calculate that amount (Note 1% = 0.01)

$$0.01 \times 0.025\ M = 2.5 \times 10^{-4}\ M$$

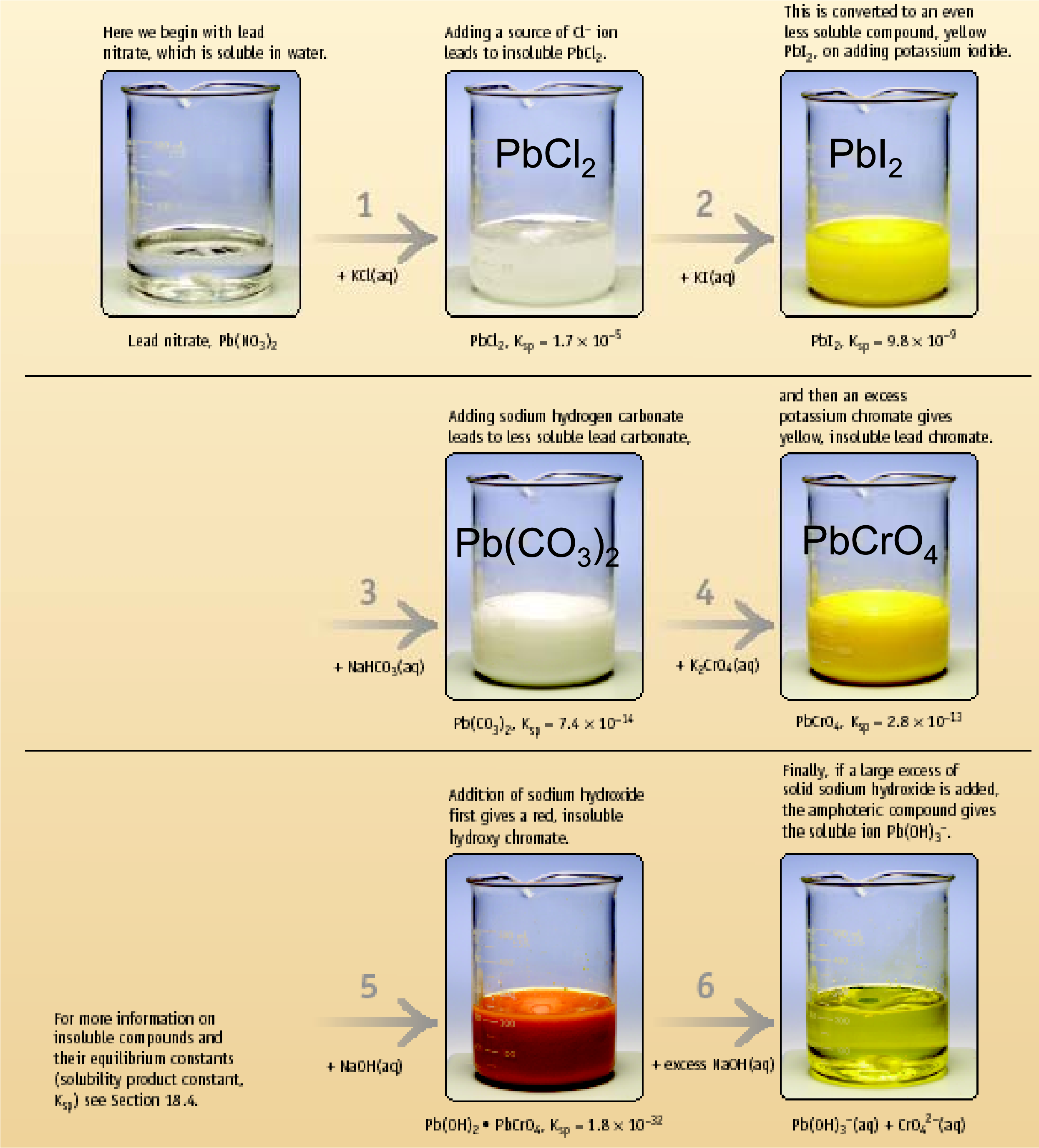
Calculate the concentration of Cl^-

$$K_{sp\ PbCl2} = 1.7 \times 10^{-5} = [Pb^{2+}]\,[Cl^-]^2$$

$$1.7 \times 10^{-5} = [2.5 \times 10^{-4}]\,[Cl^-]^2$$

$$[Cl^-]^2 = 6.8 \times 10^{-2}$$

$$[Cl^-] = 0.26\ M$$



Here we begin with lead nitrate, which is soluble in water.

Lead nitrate, $Pb(NO_3)_2$

Adding a source of Cl^- ion leads to insoluble $PbCl_2$.

$PbCl_2$, $K_{sp} = 1.7 \times 10^{-5}$

This is converted to an even less soluble compound, yellow PbI_2, on adding potassium iodide.

PbI_2, $K_{sp} = 9.8 \times 10^{-9}$

Adding sodium hydrogen carbonate leads to less soluble lead carbonate,

$Pb(CO_3)_2$, $K_{sp} = 7.4 \times 10^{-14}$

and then an excess potassium chromate gives yellow, insoluble lead chromate.

$PbCrO_4$, $K_{sp} = 2.8 \times 10^{-13}$

Addition of sodium hydroxide first gives a red, insoluble hydroxy chromate.

$Pb(OH)_2 \bullet PbCrO_4$, $K_{sp} = 1.8 \times 10^{-32}$

Finally, if a large excess of solid sodium hydroxide is added, the amphoteric compound gives the soluble ion $Pb(OH)_3^-$.

$Pb(OH)_3^-(aq) + CrO_4^{2-}(aq)$

For more information on insoluble compounds and their equilibrium constants (solubility product constant, K_{sp}) see Section 18.4.

Lead Chemistry

Illustrates the transformation of one insoluble compound into an even less soluble compound.

$K_{sp\ PbCl2} = 1.7 \times 10^{-5}$

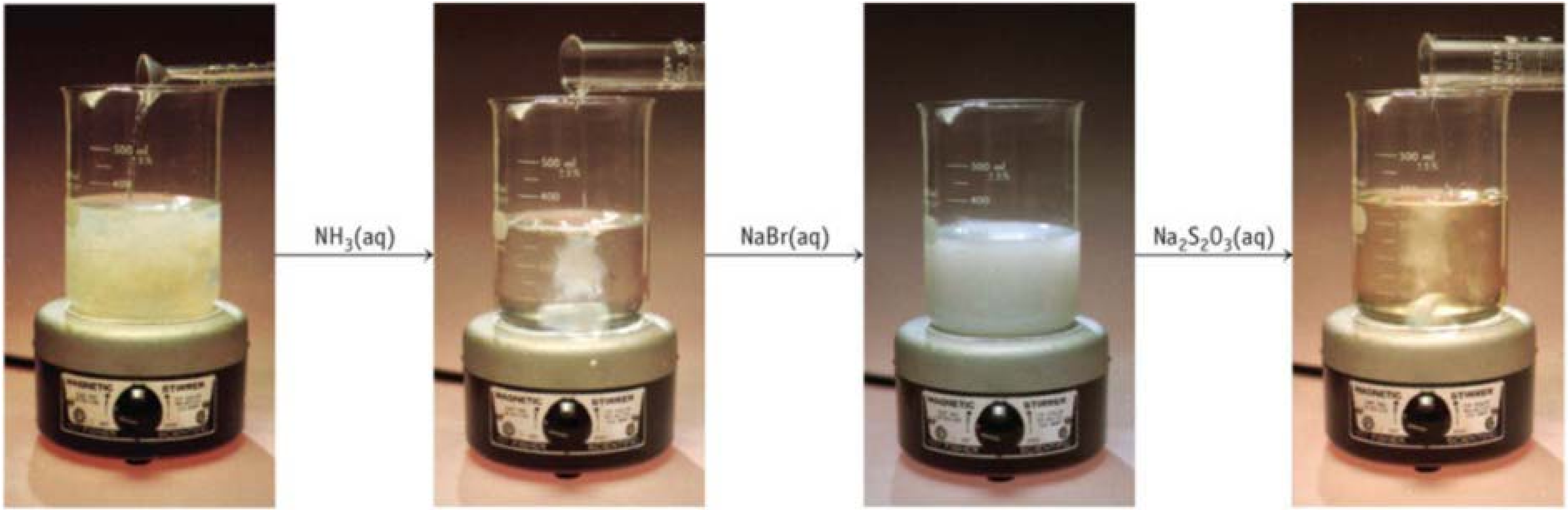
$K_{sp\ PbI2} = 9.8 \times 10^{-9}$

$K_{sp\ Pb(CO3)2} = 7.4 \times 10^{-14}$

$K_{sp\ PbCrO4} = 2.8 \times 10^{-13}$

$K_{sp\ PbCrO4 \bullet Pb(OH)2} =$
1.8×10^{-32}

Separations by Difference in K_{sp}



$AgCl(s)$, $K_{sp} = 1.8 \times 10^{-10}$

(a) AgCl precipitates on adding $NaCl(aq)$ to $AgNO_3(aq)$

$[Ag(NH_3)_2]^+(aq)$

(b) The precipitate of AgCl dissolves on adding aqueous NH_3 to give water-soluble $[Ag(NH_3)_2]^+$.

$AgBr(s)$, $K_{sp} = 5.4 \times 10^{-13}$

(c) The silver-ammonia complex ion is changed to insoluble AgBr on adding $NaBr(aq)$.

$[Ag(S_2O_3)_2]^{3-}(aq)$

(d) Solid AgBr is dissolved on adding $Na_2S_2O_3(aq)$. The product is the water-soluble complex ion $[Ag(S_2O_3)_2]^{3-}$.