

Chapter 17: Acid-Base Equilibria and Solubility Equilibria

Key topics:

Common ion effect

Buffers

Acid-base equilibria

Solubility equilibria; complex ion formation

The Common Ion Effect

If we have *two solutes each containing the same ion*, the equilibrium is affected. This is called the common ion effect.

Consider adding acetic acid (CH_3COOH) and sodium acetate (NaCH_3COO) to water. The acetate anion from sodium acetate will inhibit acetic acid from dissociating (Le Chatelier).

First consider the situation with only acetic acid, at 0.10 M

	CH_3COOH	$\rightleftharpoons \text{H}^+ +$	CH_3COO^-
Initial	0.10	0	0
Change	-x	+x	+x
Equilibrium	0.10 - x	x	x

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} \Rightarrow x = 1.34 \times 10^{-3}$$

which means the **pH = 2.87** and the **% ionization = 1.34%**

Next, consider adding 0.050 moles of sodium acetate to 1.00 L of our acetic acid solution (assume volume does not change).

	CH ₃ COOH	\rightleftharpoons H ⁺ +	CH ₃ COO ⁻
Initial	0.09866	1.34 x 10 ⁻³	5.134 x 10 ⁻²
Change	+x	-x	-x
Equilibrium	0.09866 + x	1.34 x 10 ⁻³ - x	5.134 x 10 ⁻² - x

(note: the equilibrium must shift to the left from Le Chatelier)

$$K_a = 1.8 \times 10^{-5} = \frac{(0.00134 - x)(0.05134 - x)}{0.09866 + x} \Rightarrow x = 1.305 \times 10^{-3}$$

This gives [H⁺] = 3.5 x 10⁻⁵ (using the quadratic equation)

which means the pH = 4.46 and the % ionization = 0.035%

The common ion effect is significant !

Comment: The last calculation was hard because we had to use the quadratic equation. We can redo the last calculation by adding both of our solutes at the same time. This simplifies the math but does not affect the final equilibrium.

	CH ₃ COOH	\rightleftharpoons H ⁺ +	CH ₃ COO ⁻
Initial	0.10	0	0.050
Change	-x	+x	+x
Equilibrium	0.10 - x	x	0.050 + x

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.050 + x)}{0.10 - x} \approx \frac{(x)(0.050)}{0.10} \Rightarrow x = 3.6 \times 10^{-5}$$

Buffer Solutions

A buffer is a solution that contains comparable amounts of a weak acid and its conjugate base, or a weak base and its conjugate acid.

Buffers *resist* changes in pH upon addition of acid or base.

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(0.9 + x)}{1.1 - x} \approx \frac{(x)(0.9)}{1.1} \Rightarrow x = 2.2 \times 10^{-5}$$

so the pH is 4.66 (a change of 0.08 pH units)

We can derive a simple equation for buffer calculations:

For $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ we have

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

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

$$\Rightarrow \text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

This is called the *Henderson – Hasselbalch equation*.

Important points:

1. “x” is small, so we can use the initial [] for HA and A⁻
2. since you have a ratio, you can use M or moles
3. dilution won't change [A⁻] / [HA], so pH won't change

For a weak base / conjugate acid buffer it reads:

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{conjugate acid}]}{[\text{weak base}]}$$

e.g., How much HCl must be added to a liter of buffer that is 1.5 M in acetic acid and 0.75 M in sodium acetate to give a buffer pH of 4.10? ($\text{p}K_a = 1.8 \times 10^{-5}$)

Solution:

Adding x moles of HCl gives (0.75 - x) moles sodium acetate and (1.5 + x) moles acetic acid. Thus

$$\text{pH} = \text{p}K_a + \log \frac{(0.75 - x)}{(1.5 + x)}$$

$$4.10 = 4.74 + \log \frac{(0.75 - x)}{(1.5 + x)}$$

$$10^{-0.64} = \frac{(0.75 - x)}{(1.5 + x)} \Rightarrow x = 0.33$$

Buffer Capacity: how much acid or base can be adsorbed before the buffer is spent.

Buffer Range:

Buffers are most effective (maximum buffering capacity) when $[\text{HA}] = [\text{A}^-]$. When $[\text{HA}]$ and $[\text{A}^-]$ differ by more than a factor of 10, the buffer has lost its ability to absorb acid / base.

$$10 \geq \frac{\text{conjugate base}}{\text{weak acid}} \geq 0.1 \Rightarrow \text{pH} = \text{p}K_a \pm 1$$

Weak Acid	K_a	$\text{p}K_a$
HF	7.1×10^{-4}	3.15
HNO_2	4.5×10^{-4}	3.35
HCOOH	1.7×10^{-4}	3.77
$\text{C}_6\text{H}_5\text{COOH}$	6.5×10^{-5}	4.19
CH_3COOH	1.8×10^{-5}	4.74
HCN	4.9×10^{-10}	9.31
$\text{C}_6\text{H}_5\text{OH}$	1.3×10^{-10}	9.89

Preparing a buffer solution with a specific pH:

e.g., Prepare a $\text{pH} = 9.50$ buffer using phenol.

Solution:

We have

$$9.50 = 9.89 + \log \frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} \Rightarrow \frac{[\text{C}_6\text{H}_5\text{O}^-]}{[\text{C}_6\text{H}_5\text{OH}]} = 10^{-0.39} = 0.41$$

We could therefore dissolve 0.41 moles of $\text{NaC}_6\text{H}_5\text{O}$ and 1.00 mol of $\text{C}_6\text{H}_5\text{OH}$ in 1 L of water.

Acid-Base Titrations

Titration: reaction of an acid with a base (neutralization)

Specifically, the addition of a solution of accurately known concentration (e.g. acid) to a solution of unknown concentration (e.g. base) until the reaction is complete.

From the known concentration, the concentration of the other species can be calculated from the stoichiometry.

Definitions:

- **Standard solution:** one of known concentration.
- **Equivalence point:** point when stoichiometrically equivalent amounts of acid and base are present.
- **Endpoint:** the point in the laboratory when the titration is stopped (often around the equivalence point); typically signaled by the color change of an indicator.
- **Titrant** = the solution that is placed in the buret (typically the one of known concentration)
- **Titration Curve:** pH vs. volume (or moles) of titrant added

Types of titration systems that will be considered:

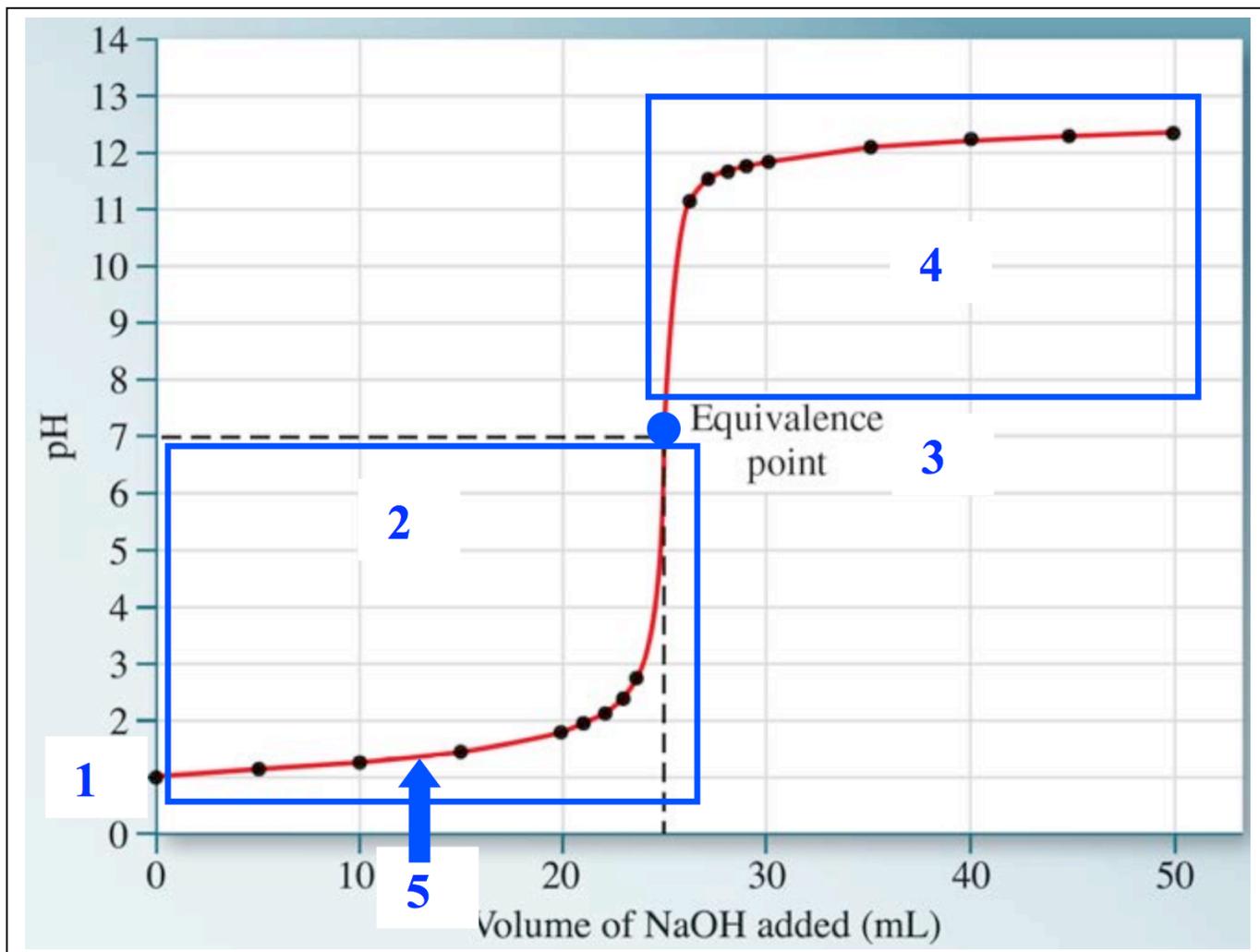
- strong acid – strong base
- weak acid – strong base
- strong acid – weak base

Items to keep track of during a titration:

- reaction taking place (what is in the beaker)
- moles of acid or base in the beaker
- moles of base or acid added from the buret
- total volume

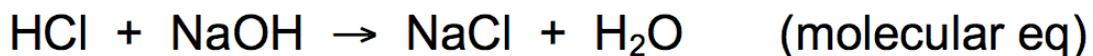
Different places to do a pH calculation in a titration:

1. beginning
2. between the beginning and the equivalence point
3. equivalence point
4. after the equivalence point
5. $\frac{1}{2}$ equivalence point



Titration of Strong Acid with Strong Base:

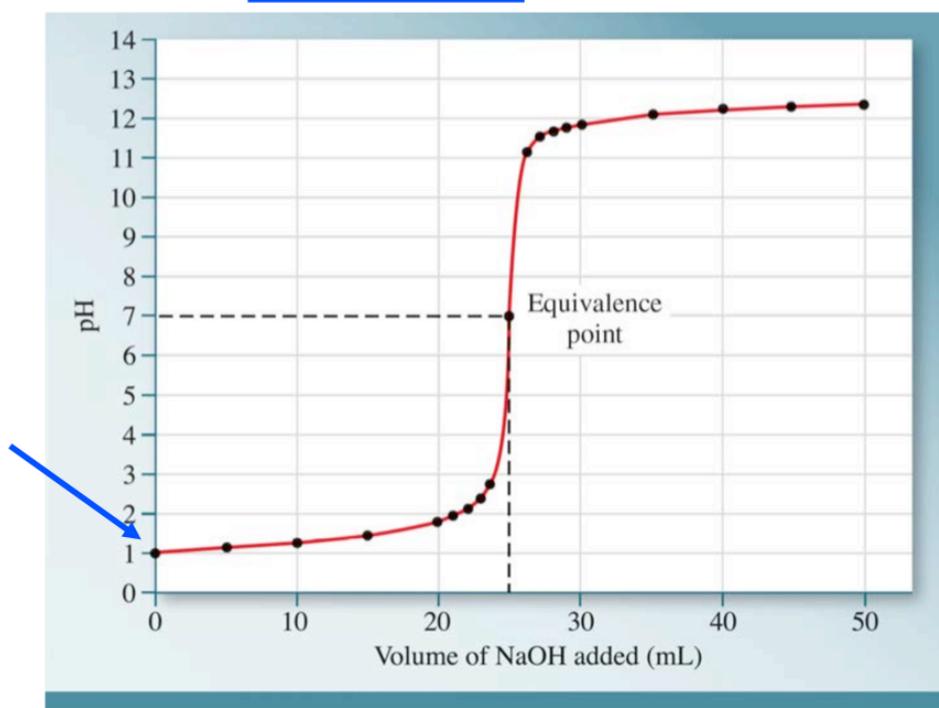
- reaction:



- titration of 25.00 mL 0.100 M HCl (beaker) with 0.100 M NaOH (in buret)

1. initial pH: $[\text{HCl}] = [\text{H}^+] = 0.100 \text{ M}$

$$\text{pH} = 1.00$$



$$(0.100 \text{ M}) (0.02500 \text{ L}) = 2.50 \times 10^{-3} \text{ mol H}^+ \text{ in beaker}$$

2. add 10.00 mL of 0.100 M NaOH (total):

2.50×10^{-3} mol H^+ in beaker

$(0.100 \text{ M})(0.01000 \text{ L}) = 1.00 \times 10^{-3}$ mol OH^- added

-- *how do you know where you are in titration??*

= compare moles H^+ in beaker to moles OH^- added

→ if mol $\text{H}^+ >$ mol OH^- → before equiv. pt.

→ if mol $\text{H}^+ <$ mol OH^- → after equiv. pt.

→ if mol $\text{H}^+ =$ mol OH^- → at equiv pt.

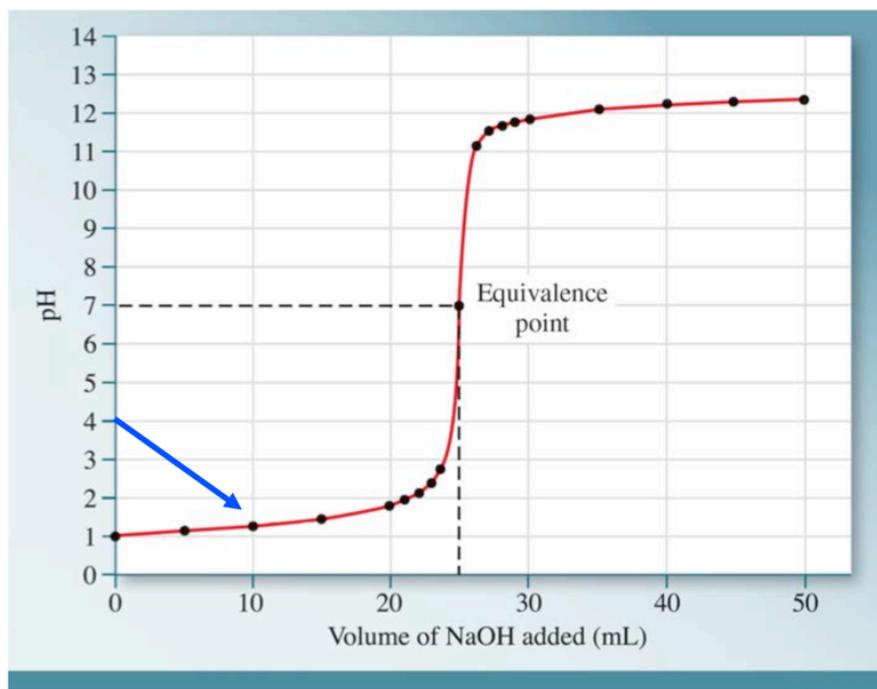
• mol H^+ excess = $(2.50 \times 10^{-3}) - (1.00 \times 10^{-3})$

= 1.50×10^{-3} mol H^+

• total volume = 25.00 + 10.00 mL = 35.00 mL

• $[\text{H}^+] = (1.50 \times 10^{-3} \text{ mol}) / (0.03500 \text{ L}) = 0.0429 \text{ M}$

pH = 1.364



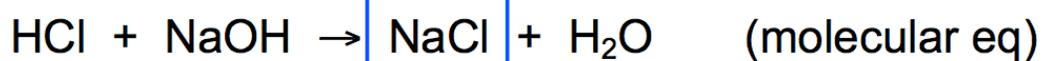
3. add 25.00 mL of 0.100 M NaOH (total):

2.50×10^{-3} mol H^+ in beaker initially

$(0.100 \text{ M})(0.02500 \text{ L}) = 2.50 \times 10^{-3}$ mol OH^- added

→ mol H^+ = mol OH^- → at equivalence point

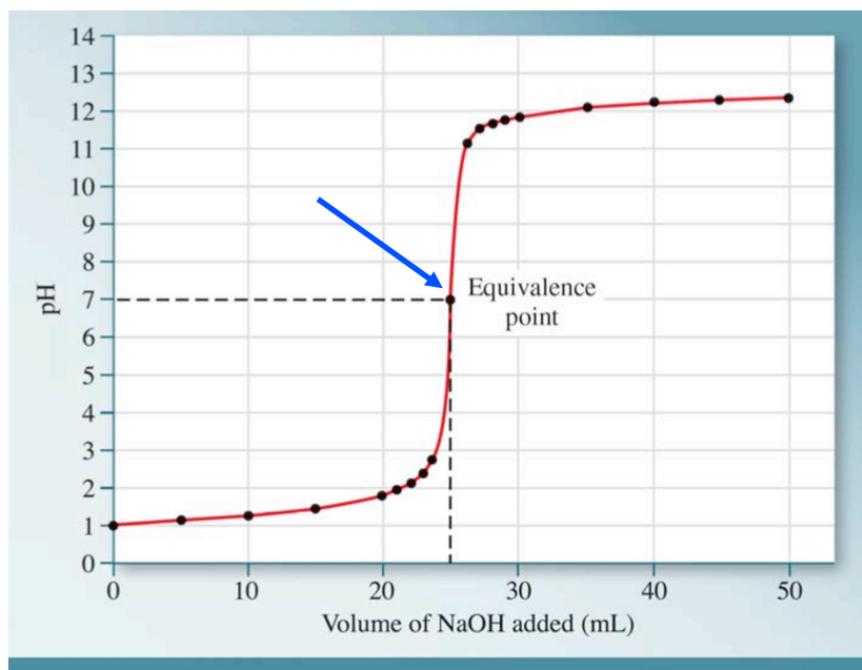
- when at the equivalence point, look at what's left in solution



→ neither affect pH → neutral

→ $\text{pH} = 7.00$

for ANY
strong acid/
strong base
titration,
pH at equiv. pt.
= 7.00



4. add 35.00 mL of 0.100 M NaOH (total):

2.50×10^{-3} mol H^+ in beaker initially

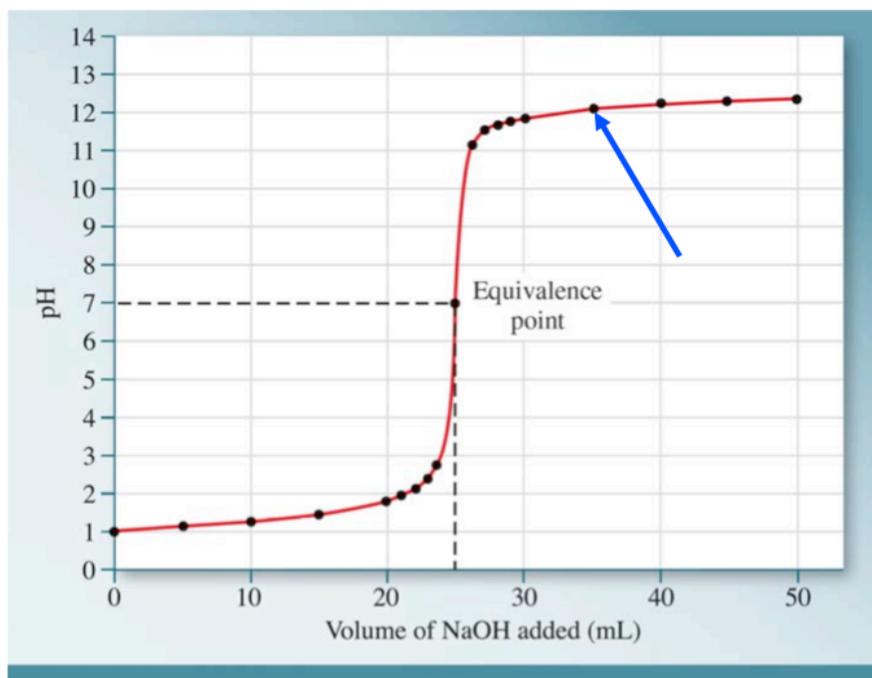
$(0.100 \text{ M})(0.03500 \text{ L}) = 3.50 \times 10^{-3}$ mol OH^- added

→ mol H^+ < mol OH^- → after equivalence point

= excess OH^- in solution → basic solution

- mol OH^- excess = $(3.50 \times 10^{-3}) - (2.50 \times 10^{-3})$
= 1.00×10^{-3} mol OH^-
- total volume = 25.00 + 35.00 mL = 60.00 mL
- $[\text{OH}^-] = (1.00 \times 10^{-3} \text{ mol}) / (0.06000 \text{ L}) = 0.0167 \text{ M}$
- pOH = 1.778

pH = 12.22

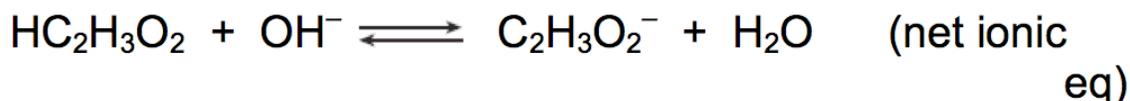
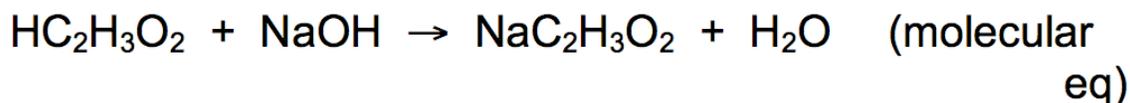


• Variations:

- strong base titrated with strong acid:
= handled same way → titration curve is just inverted
- H_2SO_4 vs HCl or $\text{Ba}(\text{OH})_2$ vs NaOH
- different concentrations of acid and base

Titration of Weak Acid with Strong Base:

- more complex due to equilibrium
- reaction:



- titration of 25.00 mL 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ (beaker) with 0.100 M NaOH (in buret)

1. initial pH: weak acid equilibrium

$$K_a = 1.8 \times 10^{-5}$$



Initial concentration (M):

0.10	0	0
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Change in concentration (M):

-x	+x	+x
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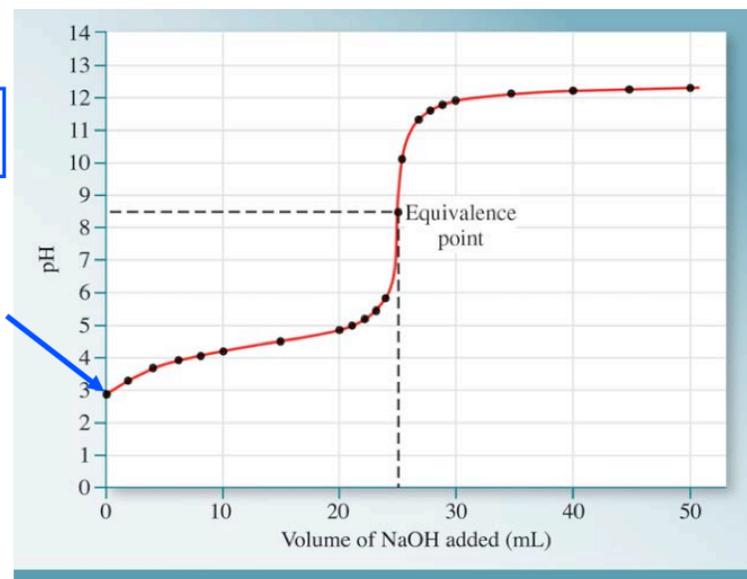
Equilibrium concentration (M):

0.10 - x	x	x
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$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

$$[\text{H}^+] = 1.34 \times 10^{-3}$$

$$\text{pH} = -\log(1.34 \times 10^{-3}) = 2.87$$

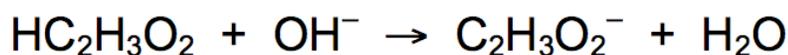


2. add 10.00 mL of 0.100 M NaOH (total):

~ 2.50×10^{-3} mol $\text{HC}_2\text{H}_3\text{O}_2$ in beaker

$(0.100 \text{ M})(0.01000 \text{ L}) = 1.00 \times 10^{-3}$ mol OH^- added

→ mol $\text{HC}_2\text{H}_3\text{O}_2 >$ mol OH^- → before equiv. pt.



2.50×10^{-3} 1.00×10^{-3} 0

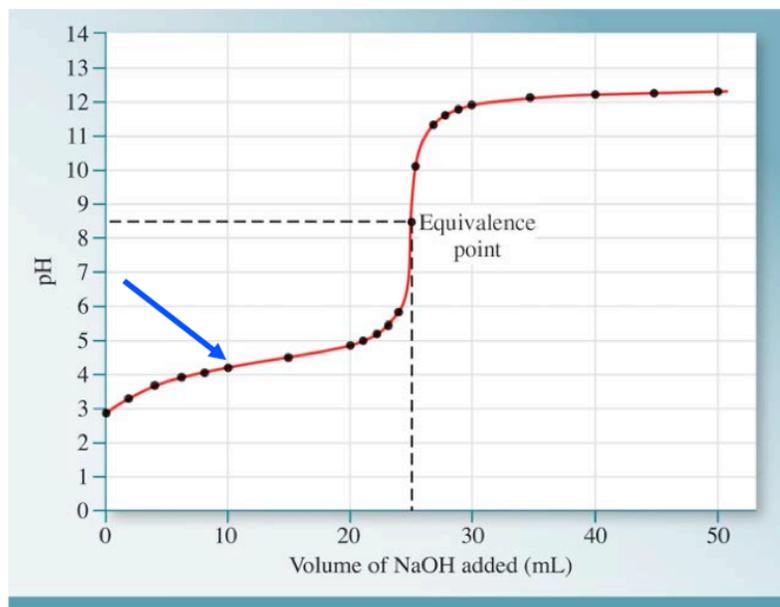
-1.00×10^{-3} -1.00×10^{-3} $+1.00 \times 10^{-3}$

1.50×10^{-3} 0 1.00×10^{-3} ***BUFFER!!***

- total volume = 25.00 + 10.00 mL = 35.00 mL

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \text{pH} = 4.74 - \log(1.00 \times 10^{-5} / 1.50 \times 10^{-5})$$

- | |
|-----------|
| pH = 4.56 |
|-----------|



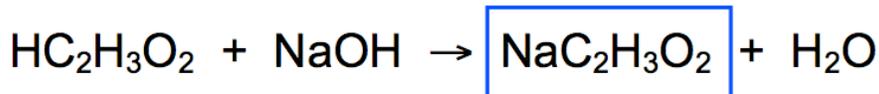
3. add 25.00 mL of 0.100 M NaOH (total):

~ 2.50×10^{-3} mol HC₂H₃O₂ in beaker

$$(0.100 \text{ M})(0.02500 \text{ L}) = 2.50 \times 10^{-3} \text{ mol OH}^- \text{ added}$$

→ mol HC₂H₃O₂ = mol OH⁻ → at equivalence point

- when at the equivalence point, look at what's left in solution



→ C₂H₃O₂⁻ is weak base → basic

→ pH > 7.00

- weak base calculation:

$$K_b = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \quad [\text{CH}_3\text{COO}^-] = \frac{2.50 \text{ mmol}}{50.0 \text{ mL}} = 0.050 \text{ M}$$

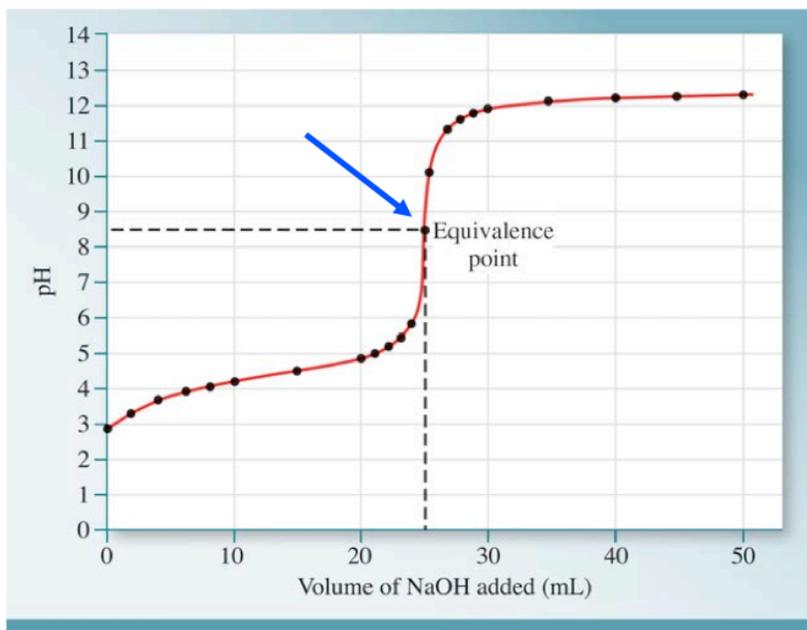
	CH ₃ COO ⁻ (aq)	+ H ₂ O(l)	⇌	OH ⁻ (aq)	+ CH ₃ COOH(aq)
Initial concentration (M):	0.050			0	0
Change in concentration (M):	-x			+x	+x
Equilibrium concentration (M):	0.050 - x			x	x

$$K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050} = 5.6 \times 10^{-10}$$

$$[\text{OH}^-] = 5.3 \times 10^{-6} \text{ M} \quad \text{pOH} = 5.28$$

$$\text{pH} = 14.00 - 5.28 = 8.72$$

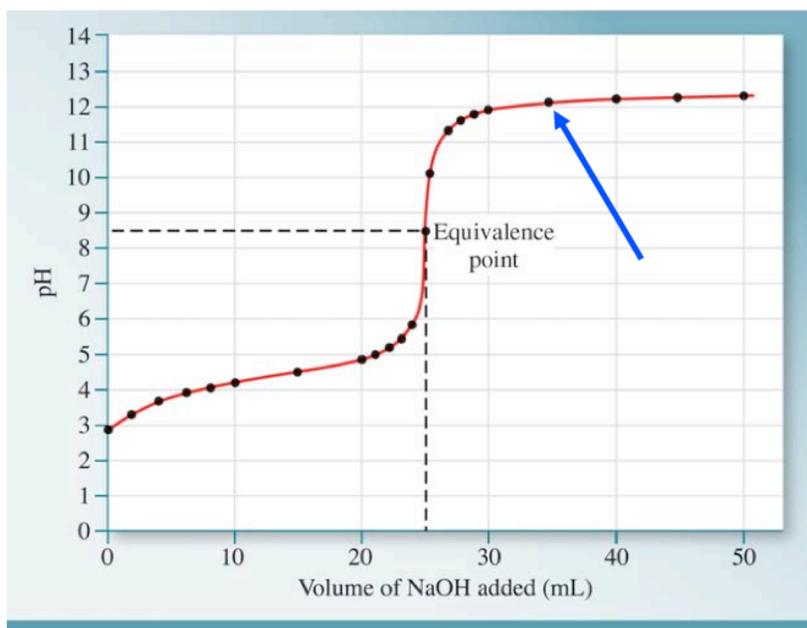
for ANY
weak acid/
strong base
titration,
pH at equiv. pt.
> 7.00



4. add 35.00 mL of 0.100 M NaOH (total):

- after equivalence point identical to strong acid/strong base titration → OH⁻ in solution
- $[\text{OH}^-] = (1.00 \times 10^{-3} \text{ mol}) / (0.06000 \text{ L}) = 0.0167 \text{ M}$
- pOH = 1.778

pH = 12.22

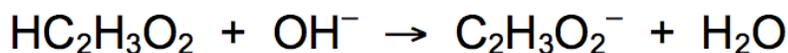


5. add 12.50 mL of 0.100 M NaOH (total):

~ 2.50×10^{-3} mol $\text{HC}_2\text{H}_3\text{O}_2$ in beaker

$(0.100 \text{ M})(0.01250 \text{ L}) = 1.25 \times 10^{-3}$ mol OH^- added

→ mol $\text{HC}_2\text{H}_3\text{O}_2 = 2$ (mol OH^-) → $\frac{1}{2}$ equivalence point



2.50×10^{-3} 1.25×10^{-3} 0

-1.25×10^{-3} -1.25×10^{-3} $+1.25 \times 10^{-3}$

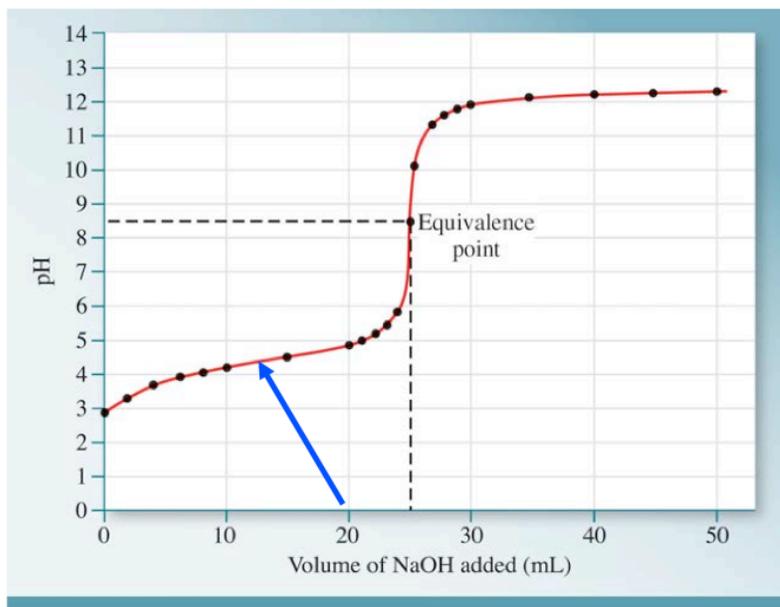
1.25×10^{-3} 0 1.25×10^{-3} **BUFFER!!**

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\begin{aligned} \text{pH} &= 4.74 - \log(1.25 \times 10^{-5} / 1.25 \times 10^{-5}) \\ &= 4.74 - \log(1) \end{aligned}$$

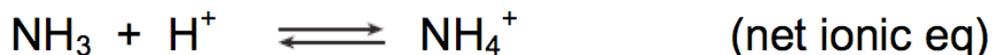
• $\text{pH} = \text{pK}_a = 4.74$

for ANY
weak acid/
strong base
titration,
pH at $\frac{1}{2}$ equiv. pt.
= pKa



Titration of Weak Base with Strong Acid:

- similar to weak acid/strong base
- reaction:



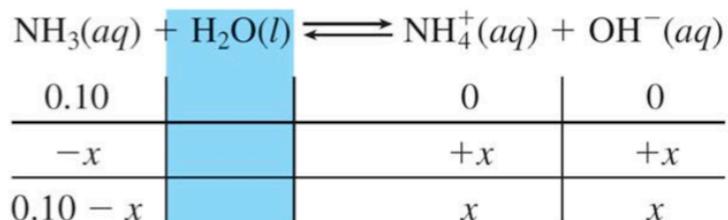
- titration of 25.00 mL 0.100 M NH_3 (beaker) with 0.100 M HCl (in buret)

1. initial pH: weak base equilibrium

Initial concentration (M):

Change in concentration (M):

Equilibrium concentration (M):

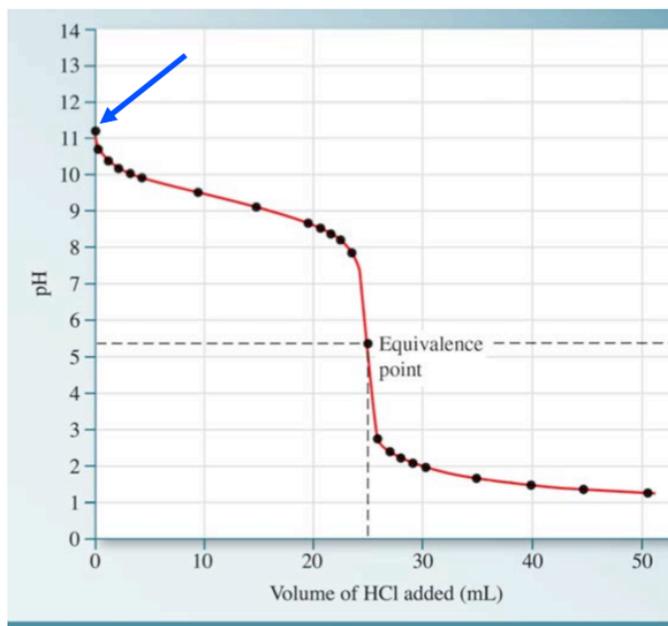


$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

$$[\text{OH}^-] = 1.34 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.87$$

$$\text{pH} = 14.00 - 2.87 = 11.13$$

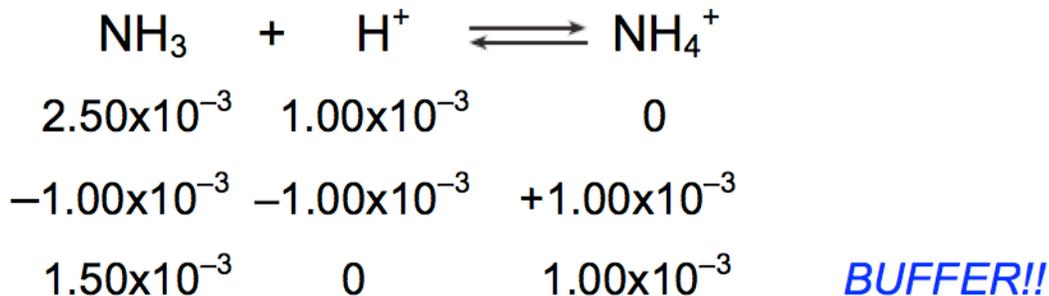


2. add 10.00 mL of 0.100 M HCl (total):

~ 2.50×10^{-3} mol NH_3 in beaker

$(0.100 \text{ M})(0.01000 \text{ L}) = 1.00 \times 10^{-3}$ mol H^+ added

→ mol $\text{NH}_3 >$ mol H^+ → before equiv. pt.



- total volume = 25.00 + 10.00 mL = 35.00 mL

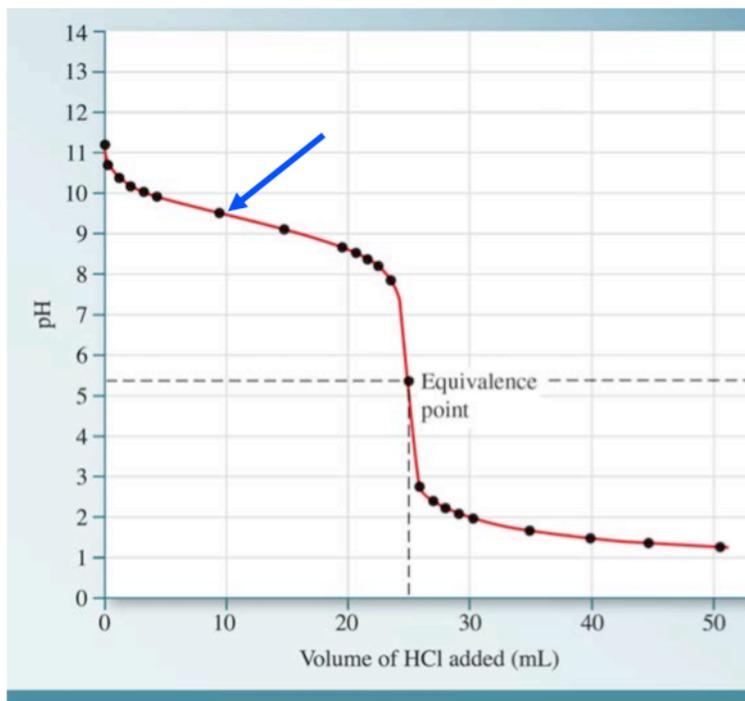


$$K_b = 1.8 \times 10^{-5} = [\text{OH}^-](1.00 \times 10^{-5} \text{ mol}) / (1.50 \times 10^{-5} \text{ mol})$$

$$[\text{OH}^-] = 2.7 \times 10^{-5} \text{ M}$$

$$\text{pOH} = 4.56$$

$$\text{pH} = 9.43$$



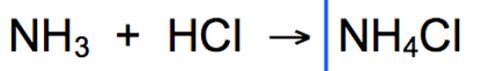
3. add 25.00 mL of 0.100 M HCl (total):

~ 2.50×10^{-3} mol NH_3 in beaker

$$(0.100 \text{ M}) (0.02500 \text{ L}) = 2.50 \times 10^{-3} \text{ mol H}^+ \text{ added}$$

→ mol NH_3 = mol H^+ → at equivalence point

- when at the equivalence point, look at what's left in solution



→ NH_4^+ is weak acid → acidic

→ pH < 7.00

- weak acid calculation:

$$K_a = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \quad [\text{NH}_4^+] = \frac{2.50 \text{ mmol}}{50.0 \text{ mL}} = 0.050 \text{ M}$$

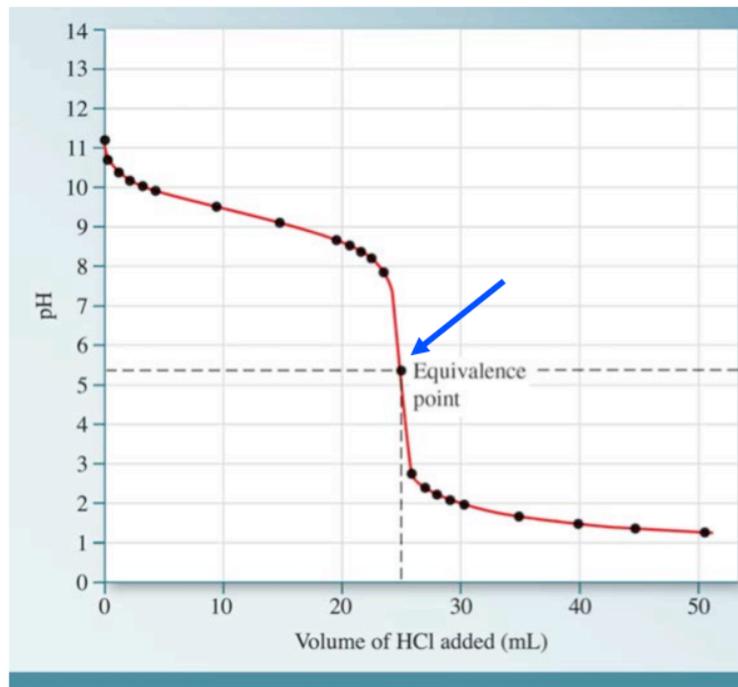
	$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)$	
Initial concentration (M):	0.0500		0	0
Change in concentration (M):	-x		+x	+x
Equilibrium concentration (M):	0.0500 - x		x	x

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050} = 5.6 \times 10^{-10}$$

$$[\text{H}^+] = 5.29 \times 10^{-6} \text{ M}$$

$$\boxed{\text{pH} = 5.28}$$

for ANY
weak base/
strong acid
titration,
pH at equiv. pt.
< 7.00

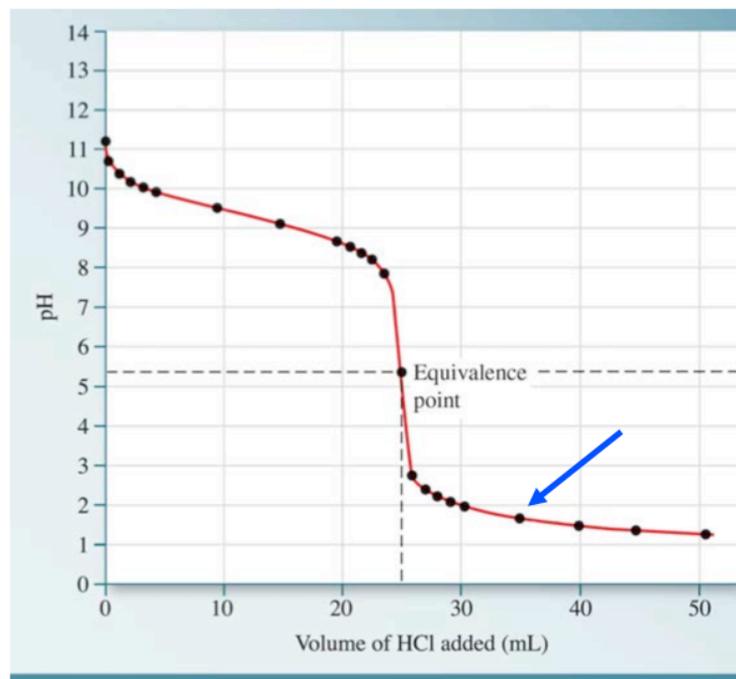


4. add 35.00 mL of 0.100 M HCl (total):

- after equivalence point identical to strong base/strong acid titration → H^+ in solution

- $[H^+] = (1.00 \times 10^{-3} \text{ mol}) / (0.06000 \text{ L}) = 0.0167 \text{ M}$

- $pH = 1.778$

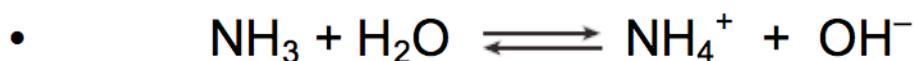
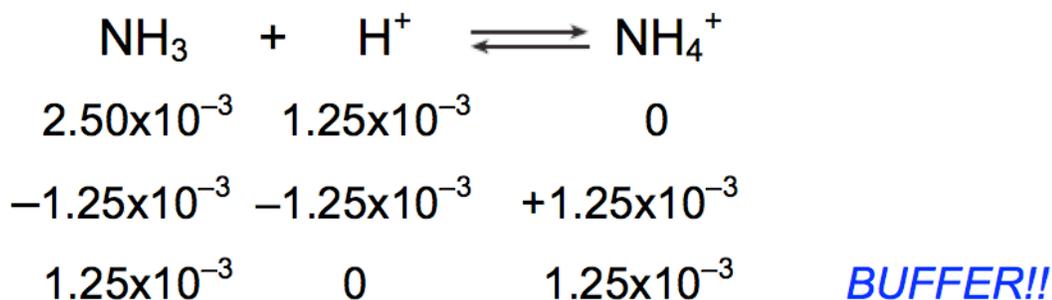


5. add 12.50 mL of 0.100 M HCl (total):

~ 2.50×10^{-3} mol NH_3 in beaker

$(0.100 \text{ M})(0.01250 \text{ L}) = 1.25 \times 10^{-3}$ mol H^+ added

→ mol $\text{NH}_3 = 2(\text{mol } \text{H}^+) \rightarrow 1/2$ equiv. pt.

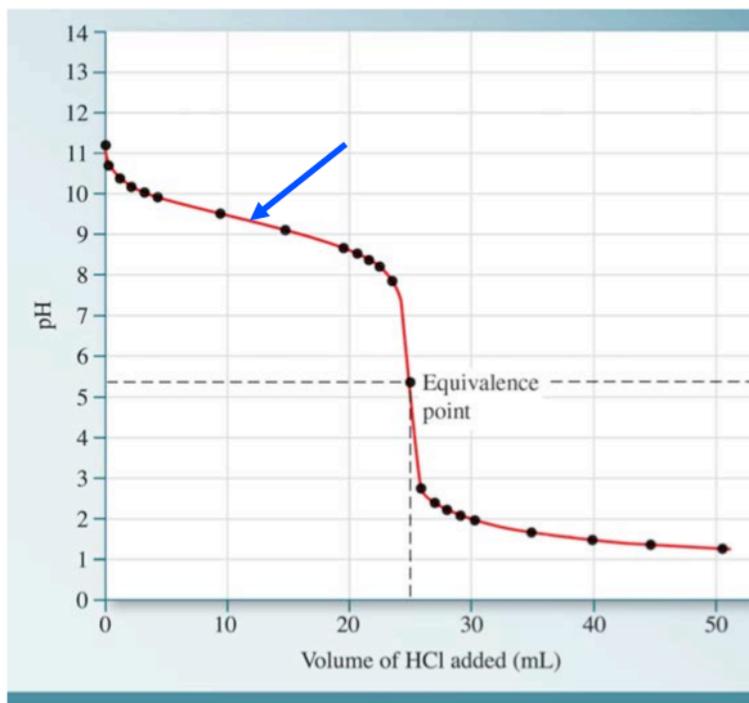


$$K_b = 1.8 \times 10^{-5} = [\text{OH}^-](1.25 \times 10^{-5} \text{ mol}) / (1.25 \times 10^{-5} \text{ mol})$$

$$[\text{OH}^-] = K_b$$

$$\text{pOH} = 4.74$$

$$\text{pH} = 9.26$$



Acid-base indicator:

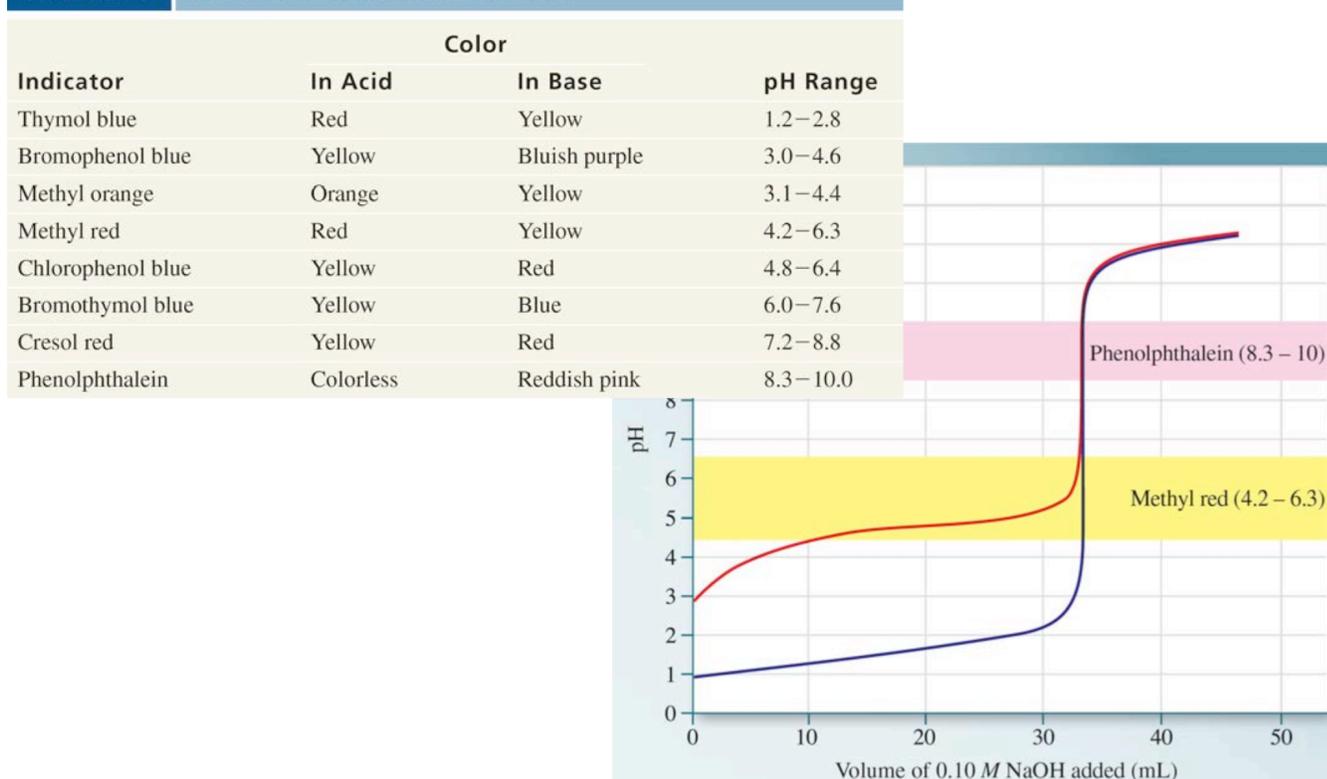
is a weak organic acid or base for which the ionized and un-ionized forms (i.e. weak acid and conjugate base, or weak base and conjugate acid) are **different colors**

The pH range over which the indicator changes color depends on the value of its K_a or K_b

The color change is used to signal endpoints during a titration. **Therefore want this to occur at the steepest part of the titration (need $pK_{\text{indicator}}$ to be within ± 1 pH units of equiv. point)**

The pH at the equivalence point of the titration must be within the pH range where the indicator changes color.

TABLE 17.3 Some Common Acid-Base Indicators



Phenolphthalein can be used for both strong acid – strong base (blue curve) and for weak acid – strong base (red curve). But methyl red is not appropriate for the weak acid – strong base case because its color change is not on the steepest part of the curve.

Solubility Equilibria

- solubility rules introduced in chapter 9:

TABLE 9.2

Solubility Guidelines: Soluble Compounds

Water-Soluble Compounds	Insoluble Exceptions
Compounds containing an alkali metal cation (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) or the ammonium ion (NH_4^+)	
Compounds containing the nitrate ion (NO_3^-), acetate ion ($\text{C}_2\text{H}_3\text{O}_2^-$), or chlorate ion (ClO_3^-)	ClO_4^-
Compounds containing the chloride ion (Cl^-), bromide ion (Br^-), or iodide ion (I^-)	Compounds containing Ag^+ , Hg_2^{2+} , or Pb^{2+}
Compounds containing the sulfate ion (SO_4^{2-})	Compounds containing Ag^+ , Hg_2^{2+} , Pb^{2+} , Ca^{2+} , Sr^{2+} , or Ba^{2+}

TABLE 9.3

Solubility Guidelines: Insoluble Compounds

Water-Insoluble Compounds	Soluble Exceptions
Compounds containing the carbonate ion (CO_3^{2-}), phosphate ion (PO_4^{3-}), chromate ion (CrO_4^{2-}), or sulfide ion (S^{2-})	Compounds containing Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , or NH_4^+
Compounds containing the hydroxide ion (OH^-)	Compounds containing Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , or Ba^{2+}
O^{2-}	Ca^{2+} , Sr^{2+}

- view presented in chapter 9 a little too simplistic
 - the *most soluble compounds* can be made **insoluble** if you put **enough** solute in
 - the *most insoluble compounds* can be made **soluble** if you put **little enough** solute in
- better view: gradient of solubilities



- use concept of equilibrium to get the gradient

Solubility product = K_{sp}

Consider the equilibrium between undissolved silver chloride and a saturated silver chloride solution:



Since this is a heterogeneous equilibrium, the equilibrium constant is

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

- always write the K_{sp} expression with the solid on the left
- *Molar solubility*: moles of solute in 1L of saturated solution
- *Solubility*: grams of solute in 1 L of saturated solution

e.g., Calculate the molar solubility and the solubility of PbF_2 , given that $K_{sp} = 4.0 \times 10^{-8}$

Solution:

	$\text{PbF}_2(s) \rightleftharpoons$	Pb^{2+}	+	2F^-
Initial	lots	0		0
Change	-x	+x		+2x
Equilibrium		x		2x

This gives $K_{sp} = (x)(2x)^2 = 4x^3 \Rightarrow x = 2.15 \times 10^{-3} M$

This is the molar solubility. For the solubility we multiply by the molar mass of $207.2 + 2(19.00) = 245.2$ to give 0.527 g/L.

e.g., Given that the solubility of Ag_2SO_3 is 4.6×10^{-3} g/L, what is the solubility product constant K_{sp} ?

Solution:

We first convert to molar solubility:

$$(4.6 \times 10^{-3} \text{ g/L}) / (295.87 \text{ g/mol}) = 1.55 \times 10^{-5} \text{ M}$$

	$\text{Ag}_2\text{SO}_3 \rightleftharpoons$	$2\text{Ag}^+ +$	SO_3^{2-}
Initial	lots	0	0
Change	-x	+2x	+x
Equilibrium		2x	x

We know that $x = 1.55 \times 10^{-5} \text{ M}$. Thus $K_{\text{sp}} = 4x^3 = 1.5 \times 10^{-14}$

e.g., What is the maximum mass (in grams) of $(\text{NH}_4)_2\text{SO}_4$ that can be added to 150 mL of 0.050 M BaCl_2 without causing a precipitate to form?

Solution:

First, we have to examine a K_{sp} table (e.g., Table 17.4 in the textbook). We can find that the K_{sp} for BaSO_4 is 1.1×10^{-10}

This means that if $[\text{Ba}^{2+}][\text{SO}_4^{2-}] > K_{\text{sp}}$, we get a precipitate. Since $[\text{Ba}^{2+}] = 0.050 \text{ M}$, we can have at most $[\text{SO}_4^{2-}] = K_{\text{sp}}/0.050 = 2.2 \times 10^{-9} \text{ M}$.

Then we multiply by the volume and the molar mass:

$$(2.2 \times 10^{-9} \text{ mol/L}) \times (0.150 \text{ L}) \times (132.154 \text{ g/mol}) = 4.4 \times 10^{-8} \text{ g}$$

Factors Affecting Solubility

The common ion effect

Consider the solubility of AgCl:



in a solution that already has dissolved AgNO₃ in it.

From Le Chatelier's Principle we know that AgCl will be significantly less soluble in 0.10 M AgNO₃ than in pure water.

Work out the numbers:

Since K_{sp} for AgCl is 1.6×10^{-10} ,
the molar solubility is just the square root of this: 1.3×10^{-5} .

Now consider the solubility of AgCl in 0.10 M AgNO₃

	AgCl \rightleftharpoons	Ag ⁺ +	Cl ⁻
Initial	lots	0.10	0
Change	-x	+x	+x
Equilibrium		0.10 + x	x

$$K_{sp} = 1.6 \times 10^{-10} = (x)(0.10 + x) \approx (x)(0.10) \Rightarrow x = 1.6 \times 10^{-9}$$

pH

The solubility of a substance can depend on pH.

For example, consider $\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$

At equilibrium, if we add OH⁻ ions (increase the pH) the equilibrium will shift to the left, decreasing the solubility of Mg(OH)₂.

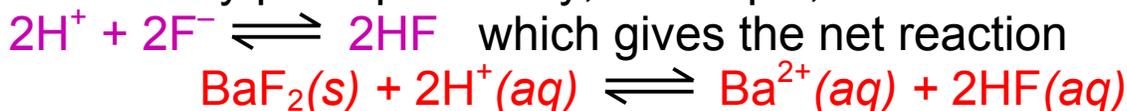
If we add H^+ ions (decrease the pH), $Mg(OH)_2$ will become more soluble. This is why insoluble bases tend to dissolve in acidic solutions.

Adding H^+ results in the reaction $2H^+ + 2OH^- \rightleftharpoons 2H_2O(l)$ which gives the net reaction



Another example: consider $BaF_2(s) \rightleftharpoons Ba^{2+} + 2F^-$

Since F^- has acid/base properties, this equilibrium is also affected by pH. Specifically, at low pH, we can write



Separation of Ions using Differences in Solubility

Fractional precipitation

If we have two or more ions in solution we can separate them by using a compound that can form a precipitate with each of them (with different K_{sp} values).

e.g., we can separate $Cl^-(aq)$ and $Br^-(aq)$ by using $AgNO_3$.

Compound	K_{sp}
AgCl	1.6×10^{-10}
AgBr	7.7×10^{-13}
AgI	8.3×10^{-17}

Silver nitrate is added to a solution containing 0.020 M Cl^- and 0.020 M Br^- . Calculate the concentration of Ag^+ ions needed to initiate precipitation of AgBr without precipitating AgCl .

Also, when the more soluble species begins to precipitate, what is $[\text{Br}^-]$?

Solution:

AgBr will precipitate first because its K_{sp} is smaller than AgCl .

From the expression $[\text{Ag}^+][\text{Br}^-] = K_{\text{sp}} = 7.7 \times 10^{-13}$

We get $[\text{Ag}^+] = 7.7 \times 10^{-13} / 0.020 = 3.9 \times 10^{-11}\text{ M}$.

Any higher value for $[\text{Ag}^+]$ will cause AgBr to precipitate.

From the expression $[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}} = 1.6 \times 10^{-10}$

We get $[\text{Ag}^+] = 1.6 \times 10^{-10} / 0.020 = 8.0 \times 10^{-9}\text{ M}$.

Any higher value for $[\text{Ag}^+]$ will cause AgCl to precipitate.

Therefore we can precipitate the maximum amount of AgBr without causing any AgCl to precipitate if we use $[\text{Ag}^+] = 8.0 \times 10^{-9}\text{ M}$

At this point, what is $[\text{Br}^-]$?

It is $7.7 \times 10^{-13} / 8.0 \times 10^{-9} = 9.6 \times 10^{-5}\text{ M}$.

This is less than 0.5 % of the original $[\text{Br}^-]$ so we are able to effectively separate Cl^- and Br^- (by filtration to remove AgBr).