

Today

**Titration**

determining something about an unknown  
by reacting it with a known solution

**Polyprotic Acids**

## Titration

Why do a titration.

You have a solution with an unknown property

Unknown Concentration?

Unknown  $K_a$  ( $K_b$ )?

Both.

Slowly neutralize the solution by adding  
a strong base (acid)  
monitor the pH with each addition

## Neutralize first

Then look at the neutralization from last class equilibrium

imagine a 100 mL solution with 0.1 M Acetic Acid (initial .01 moles)  
we add 10 mL of 0.1M NaOH in each titration step (add 0.001 moles)

Initial (moles)			After Neutralization			Volume (L)	Equilibrium
HA	OH <sup>-</sup>	A <sup>-</sup>	HA	OH <sup>-</sup>	A <sup>-</sup>		pH
0.010	0.000	0.00	0.010	0.000	0.000	0.10	2.87
only HA			$[H^+] = \sqrt{K_a C_a}$				
0.010	0.001	0.00	0.009	0.000	0.001	0.11	3.79

Both HA & A<sup>-</sup> Buffer  $[H^+] = K_a \frac{C_a}{C_b}$

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0.010	0.001	0.00	0.009	0.000	0.001	0.11	3.79
0.009	0.001	0.00	0.008	0.000	0.002	0.12	4.15

↑  
keep adding  
OH<sup>-</sup>

HA neutralizes  
to A<sup>-</sup>

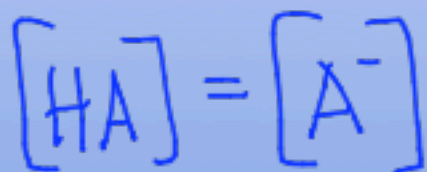
Buffer

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.....							
0.006	0.001	0.005	0.005	0.000	0.005	0.15	4.75



Equal

Buffer

$$pH = pK_a$$

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.....							
0.006	0.001	0.005	0.005	0.000	0.005	0.15	4.75
.....							
0.001	0.001	0.009	0.000	0.000	0.010	0.15	8.78

HA all neutralized NOW all A<sup>-</sup> weak base

## Neutralize first

Then look at the neutralization from last class equilibrium

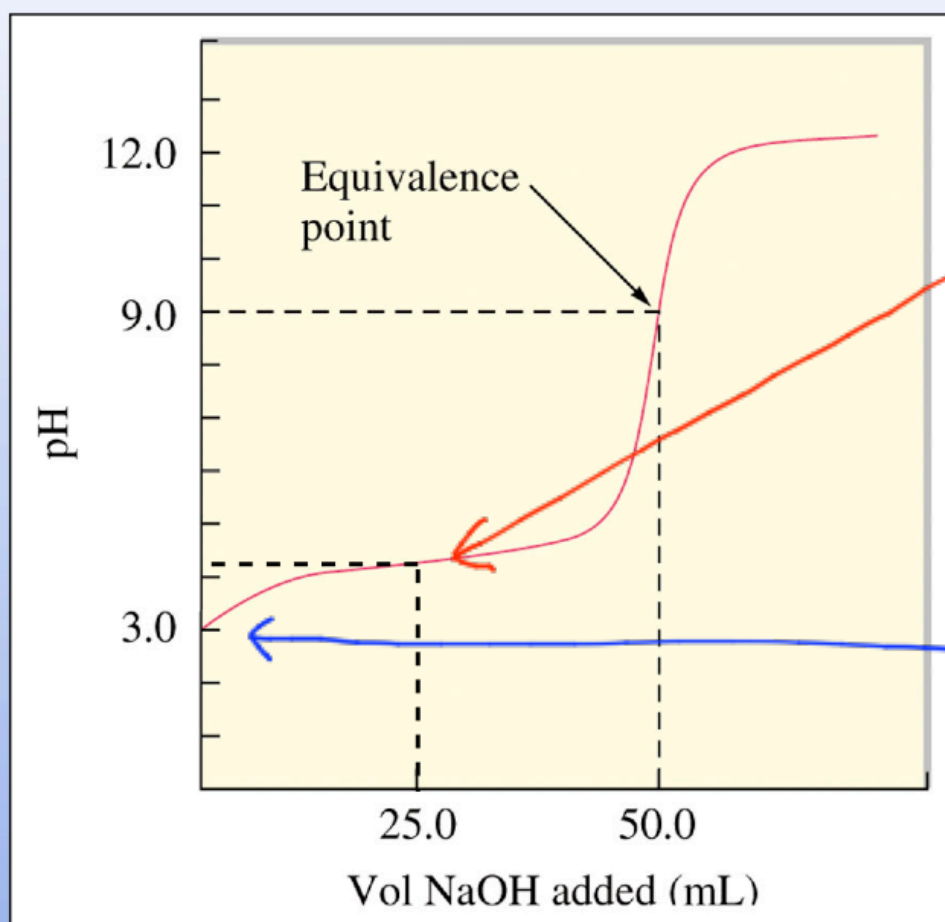
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.....							
0.006	0.001	0.005	0.005	0.000	0.005	0.15	4.75
.....							
0.001	0.001	0.009	0.000	0.000	0.010	0.15	8.78
0.000	0.001	0.010	0.000	0.001	0.010	0.16	12.8

Both A<sup>-</sup> & OH<sup>-</sup>

STRONG BASE

## Titrating a weak acid

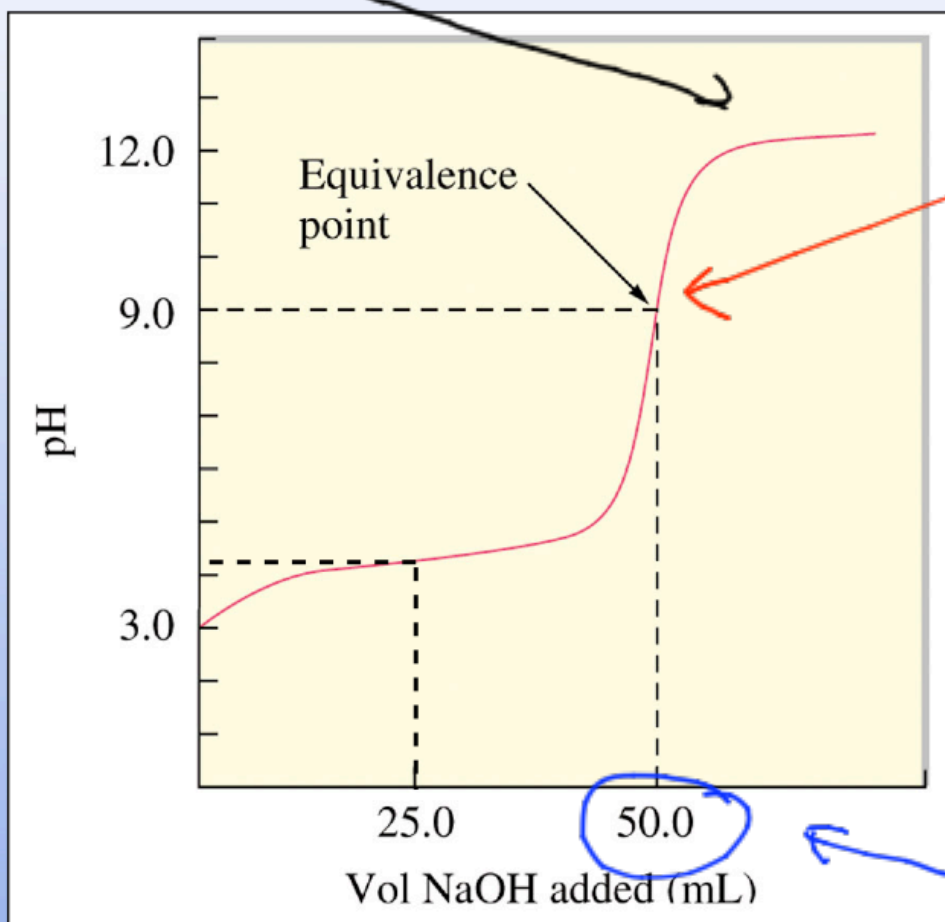


Buffer  
Both HA & A<sup>-</sup>

all HA.  
weak acid



# strong base Titrating a weak acid

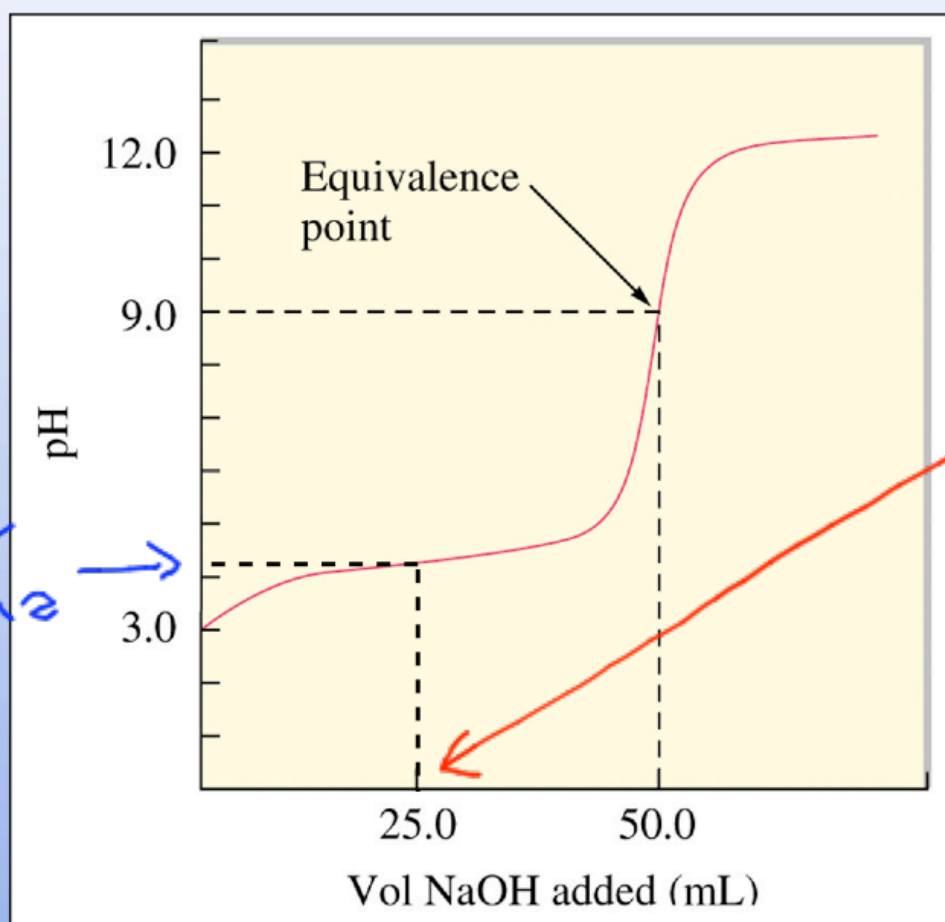


Equivalence Pt.  
all HA neutralized  
to  $A^-$

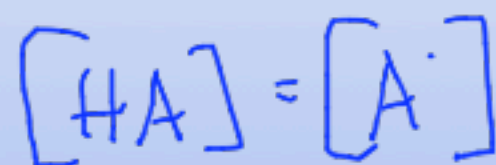
Equal moles  
initial HA  
added  $OH^-$

information on  
concentration  
of initial sol'n

## Titrating a weak acid

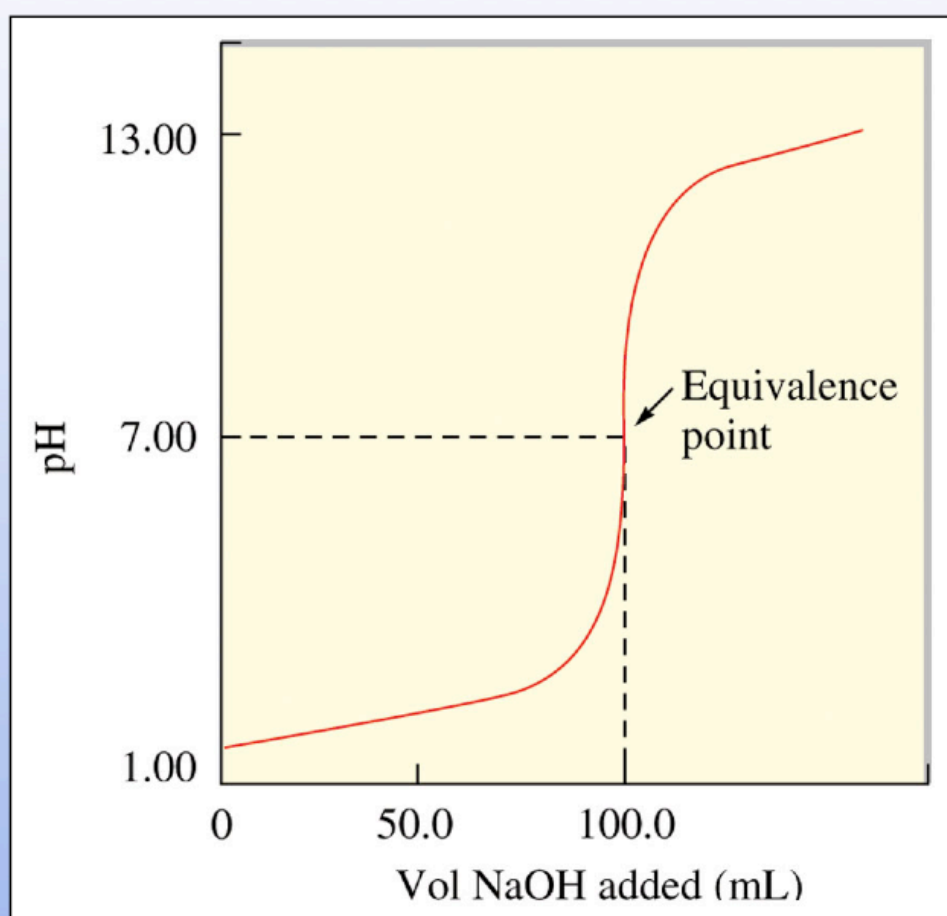


1/2 equivalence



$$pH = pK_a$$

## Easier Version Strong Acid/Strong Base



HCl titrated with NaOH

No Buffer  
(conjugate base is infinitely weak)

no  $\frac{1}{2}$  equiv.  
only determine  
conc.

at the equivalence point we have  
equal number of moles of acid and base

## Neutralize first Then look at the equilibrium

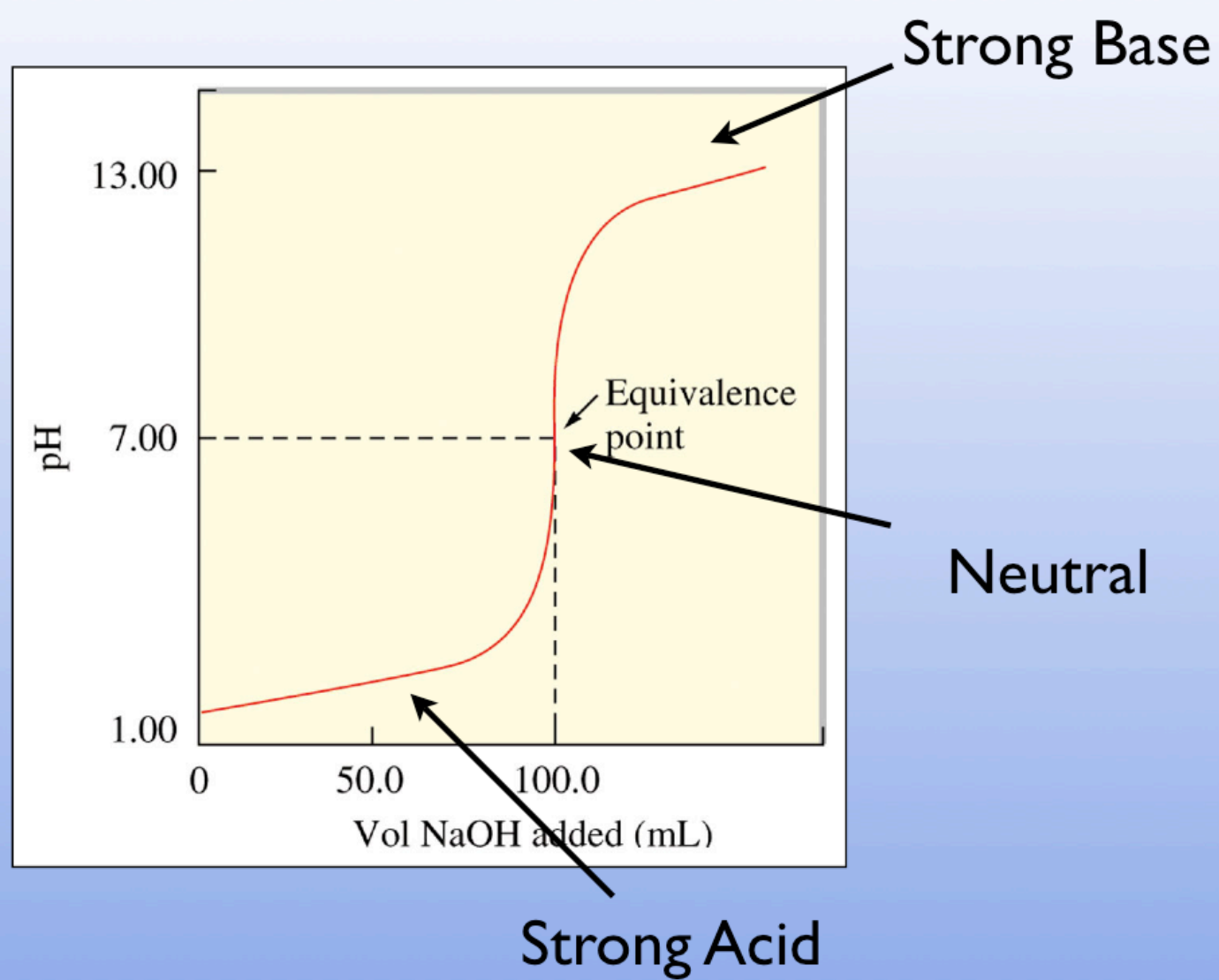
imagine a 100 mL solution with 0.1 moles of HCl  
we add .01 moles of NaOH in each titration step (10 mL of 1M)

Initial		After Neutralization		Volume (L)	Equilibrium	
mol H <sup>+</sup>	mol OH <sup>-</sup>	mol H <sup>+</sup>	mol OH <sup>-</sup>		pH	pOH
0.1	0.01	0.09	0.00	0.11	0.09	13.91
0.09	0.01	0.08	0.00	0.12	0.18	13.82
0.08	0.01	0.07	0.00	0.13	0.27	13.76
.....						
0.02	0.01	0.01	0.00	0.19	1.28	12.72
0.01	0.01	0.00	0.00	0.20	7.00	7.00
0.0	0.01	0.0	0.01	0.21	12.67	1.33
0.0	0.02	0.0	0.02	0.22	12.86	1.04

*until all H<sup>+</sup> is neutralized*

*small changes*

## Strong Acid/Strong Base Titration



At the endpoint of your titration you have added 40 mL of a 1 M NaOH solution to 200 mL of an unknown HCl solution. What was the concentration of the HCl?

A. 0.1 M

B. 0.2 M

C. 0.4 M

D. 1 M

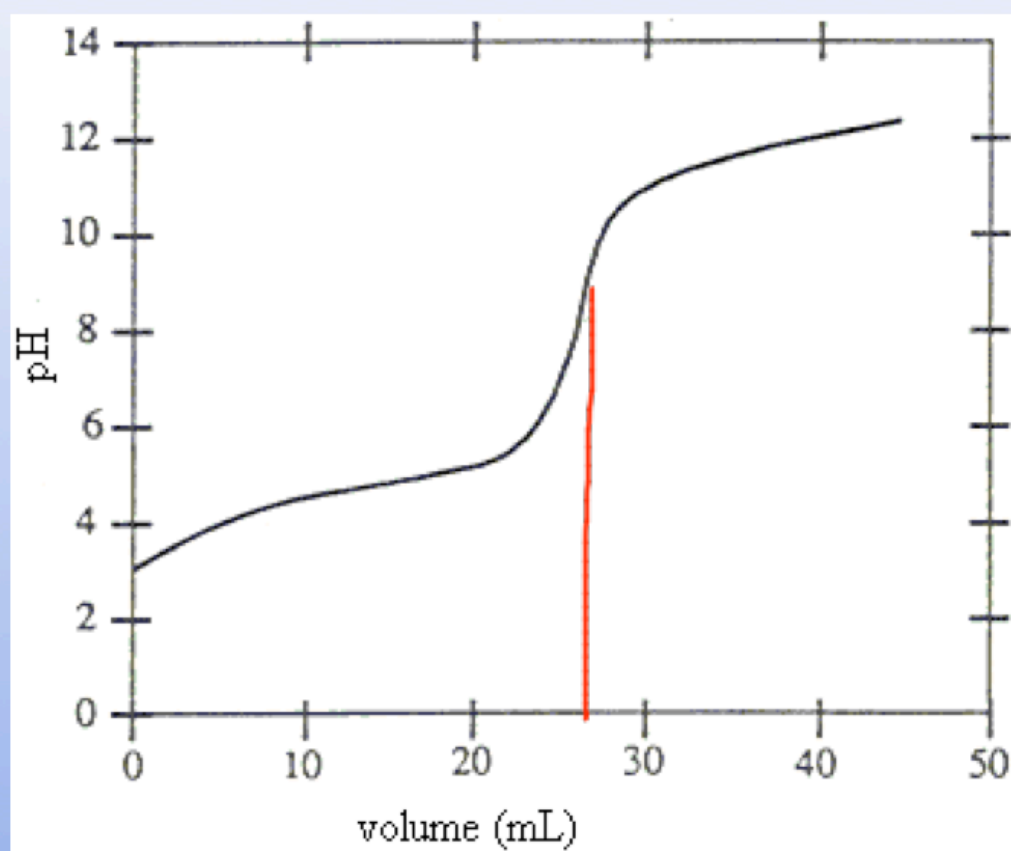
E. 2 M

At equiv. pt. Added  $\text{OH}^-$   
= init.  $\text{H}^+$

$$\text{moles OH}^- = (.04)(1\text{ M}) = .04$$

$$\frac{.04 \text{ moles}}{.2 \text{ L}} = .2 \text{ M}$$

The equivalence point in this titration is at



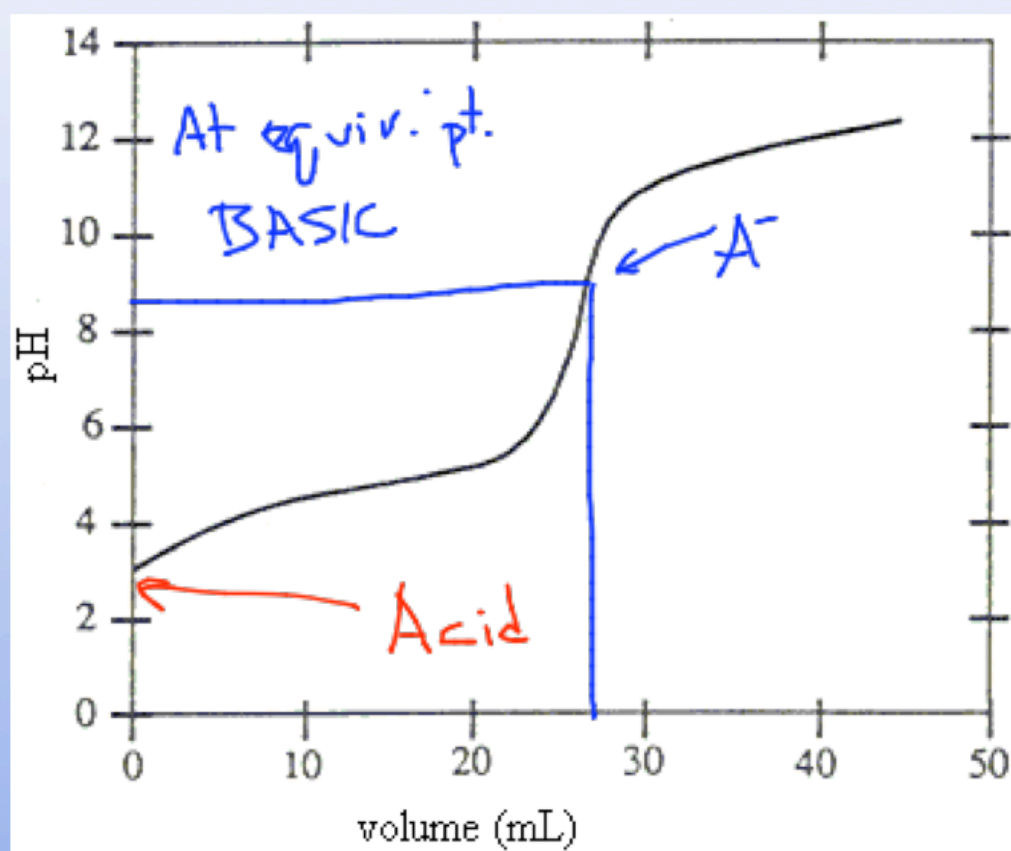
A. 5 mL

B. 14 mL

C. 28 mL

D. 44 mL

Below is a titration curve of a \_\_\_\_\_



A. weak acid  
with a strong base

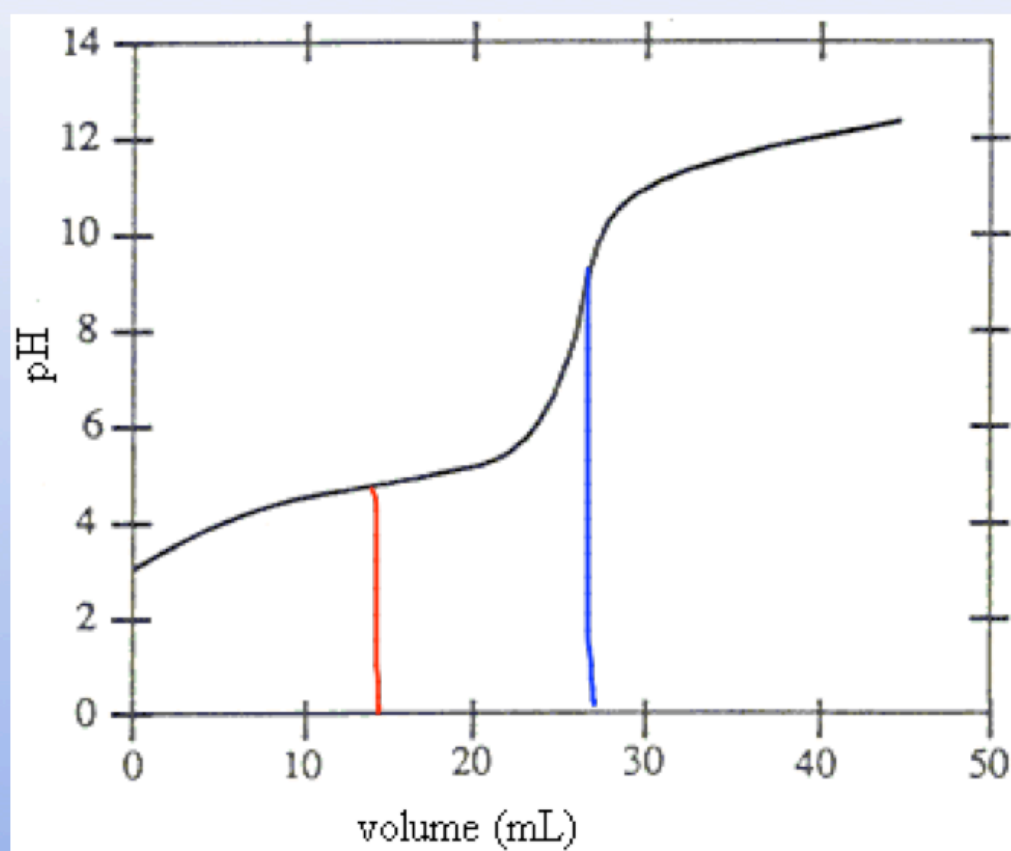
B. weak base  
with a strong acid

C. strong acid  
with a strong base

D. strong base  
with a strong acid



The half-equivalence point in this titration is at



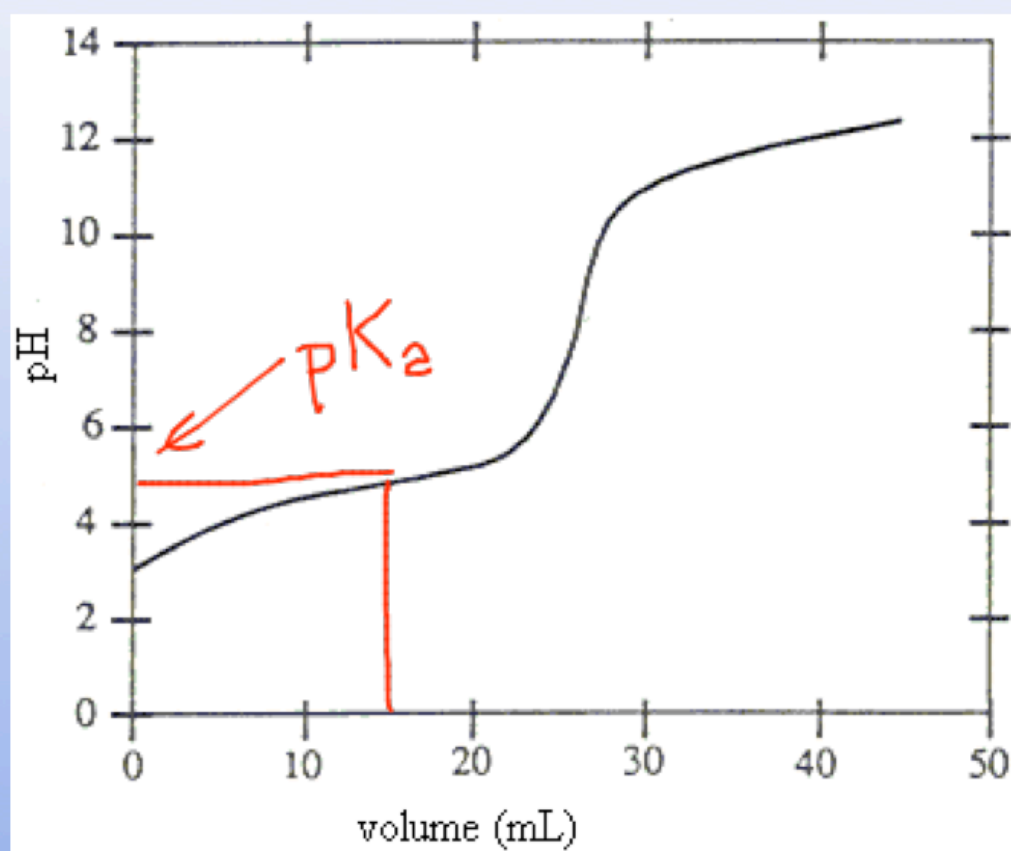
A. 5 mL

B. 14 mL =  $28/2$

C. 28 mL

D. 44 mL

The  $pK_a$  of this weak acid is \_\_\_\_\_



A. 3.1

B. 4.7

C. 8

D. 12.1

## Finding the endpoint (equivalence point)

### Indicator dye

#### Phenolphthalein

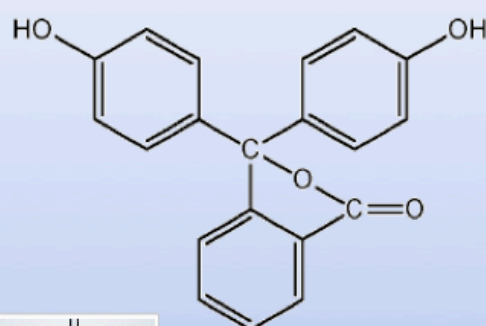
amount of indicator is so small it doesn't affect the pH, but the equilibrium of the dye is strongly affected by the pH

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

$$= [H^+] \times \frac{\text{Pink}}{\text{Clear}}$$

$$pK_a = 8.2$$

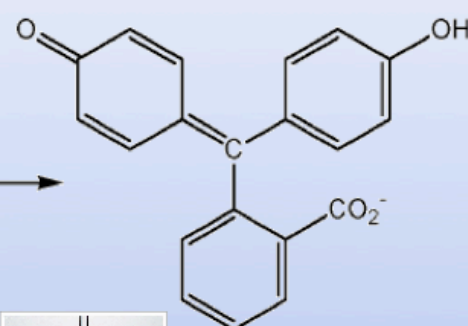
$$K_a = 6.3 \times 10^{-9}$$



Colourless  
HA

$$[H^+] > 6.3 \times 10^{-9}$$
$$pH < 8.2$$

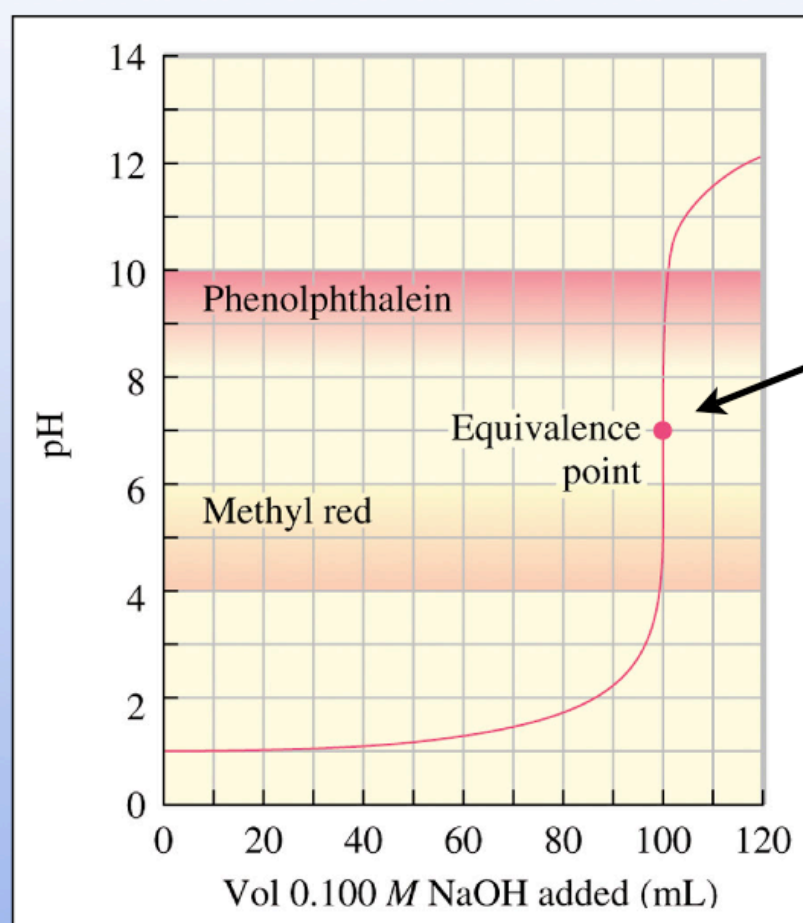
$$\frac{\text{Pink}}{\text{Clear}} < 1$$



Pink  
A<sup>-</sup>

$$[H^+] < 6.3 \times 10^{-9}$$
$$pH > 8.2$$

$$\frac{\text{Pink}}{\text{Clear}} > 1$$



color just barely  
changing for  
Phenolphthalein

Better yet just  
use a pH meter

Bromophenol Blue has a  $pK_a$  of around 4. When it is protonated (HA form) it is green, when it is deprotonated ( $A^-$  form) it is blue.

What color would it be in a solution in which the pH was 8?

A. blue

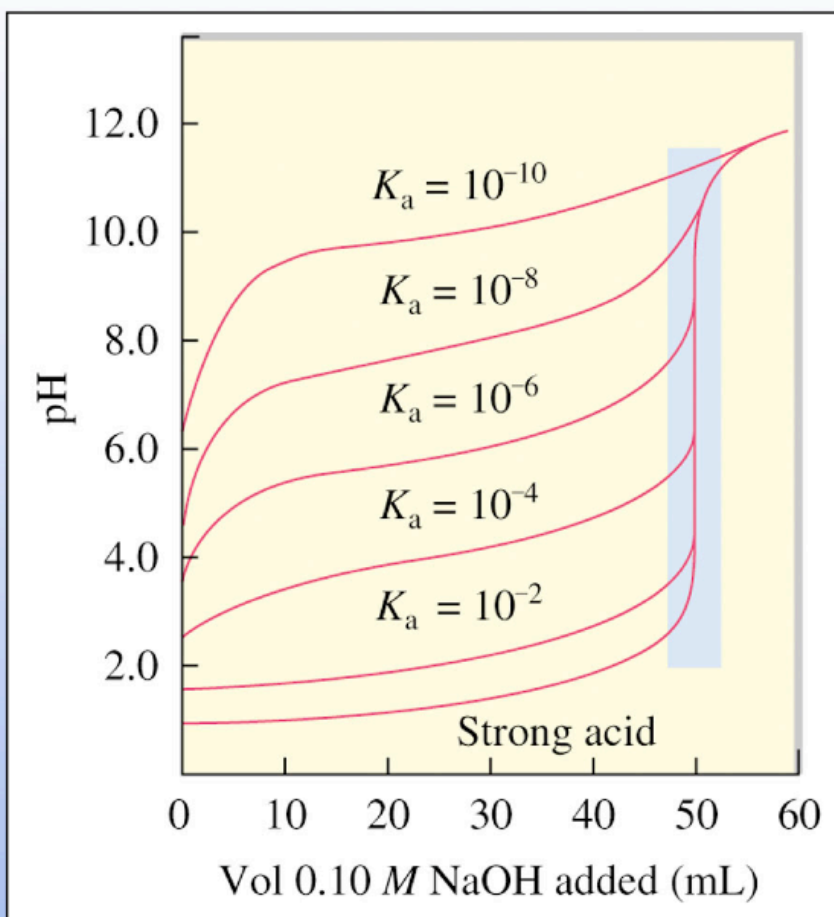
B. green

C. a mix of blue and green

More Basic than

$pK_a \rightarrow A^-$

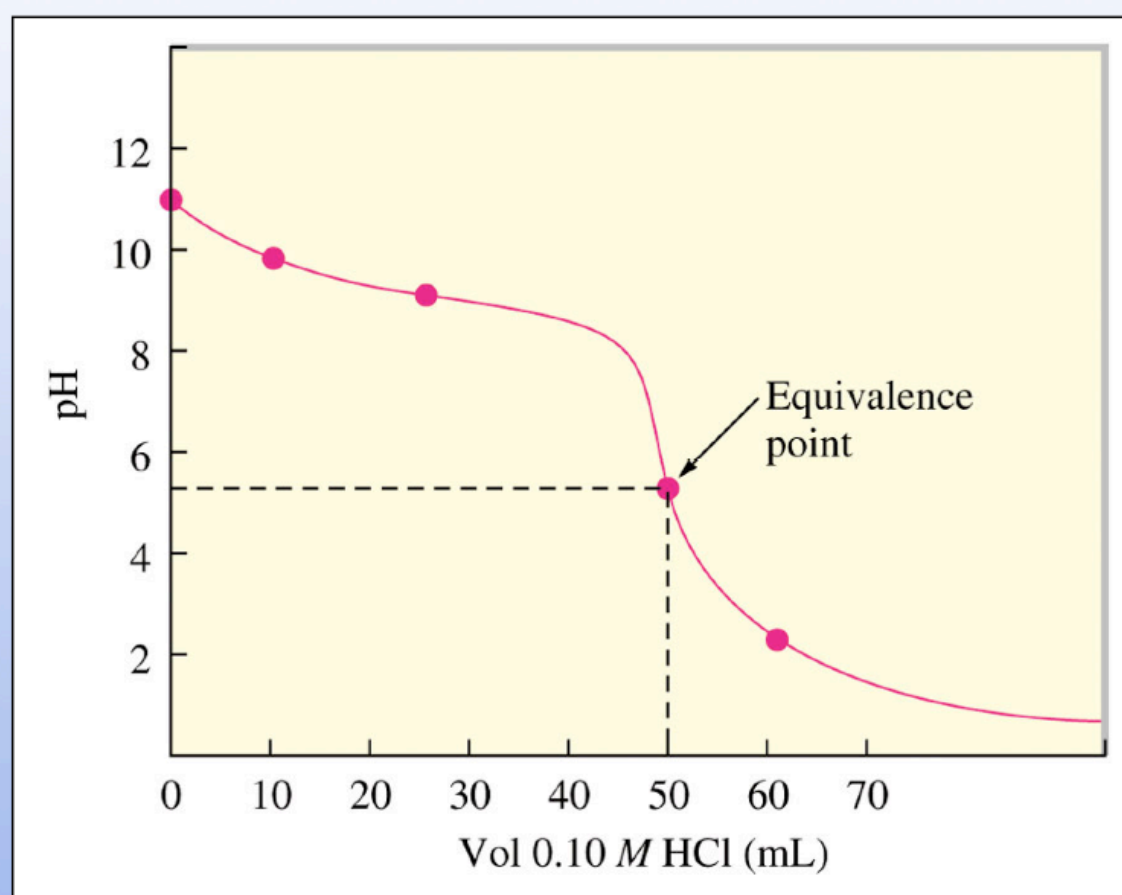
predominates



$\frac{1}{2}$  equiv. pt.  
 $\hookrightarrow$   $pK_a$

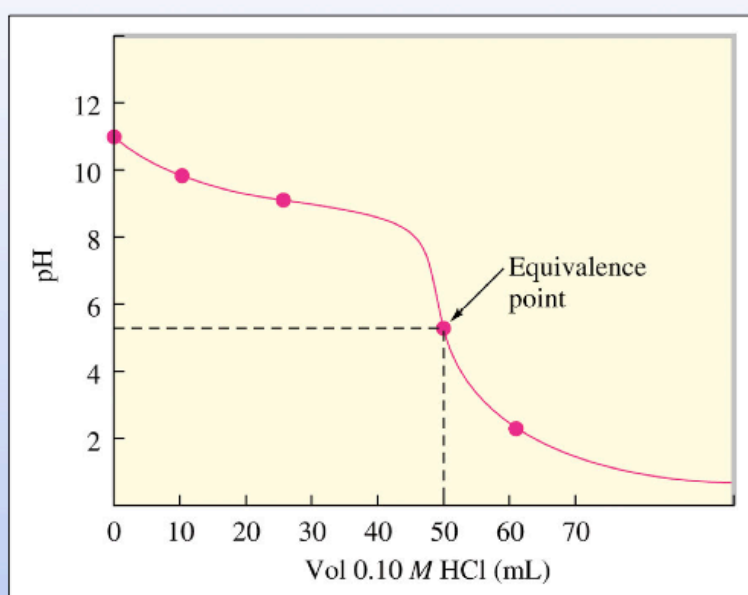
Example of 6 acids with different  $K_a$ 's but  
 the same concentration  
 Same concentration will produce the  
 same equivalence point

## Weak base titrated with strong acid



Basic solution starts at high pH (basic) goes to low (acid)

## Weak base titrated with strong acid



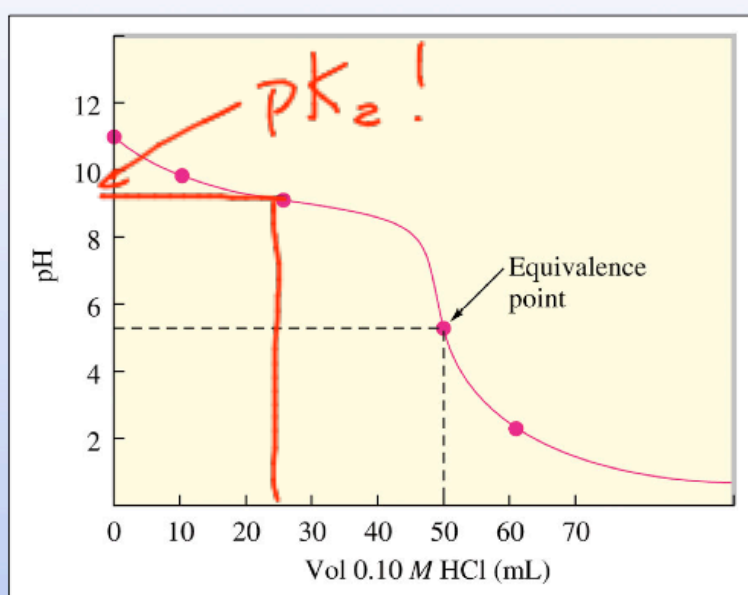
Original Base solution had a volume of  
100 mL.  
What is the concentration?

- A. 0.05 M
- B. 0.1 M
- C. 0.15 M
- D. 0.20 M

moles added  $H^+$  = init. base  
 $(.1 M)(.05 L) = .005$  moles  
 $\frac{.005}{.1} = 0.05 M$



## Weak base titrated with strong acid



What is the  $K_b$  of the base?

$$K_b = \frac{K_w}{K_2}$$

$$pK_2 + pK_b = 14$$

- A.  $1 \times 10^{-3}$
- B.  $1 \times 10^{-5}$
- C.  $1 \times 10^{-8}$
- D.  $1 \times 10^{-9}$

$$pK_2 = 9 \quad K_2 = 1 \cdot 10^{-9}$$

$$K_b = 1 \cdot 10^{-5}$$

## Polyprotic Acids

Acids that have more than one proton to lose

Now we need to keep track of all the "forms" of the acid

Monoprotic     $\text{HA}$  ,  $\text{A}^-$

Diprotic     $\text{H}_2\text{A}$ ,  $\text{HA}^-$ ,  $\text{A}^{2-}$

Triprotic     $\text{H}_3\text{A}$ ,  $\text{H}_2\text{A}^-$ ,  $\text{HA}^{2-}$ ,  $\text{A}^{3-}$