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 Ka (Kb)?
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^-	A^-	HA	OH^-	A^-		pH
0.010	0.000	0.00	0.010	0.000	0.000	0.10	2.87
0.010	0.001	0.00	0.009	0.000	0.001	0.11	3.79

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

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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

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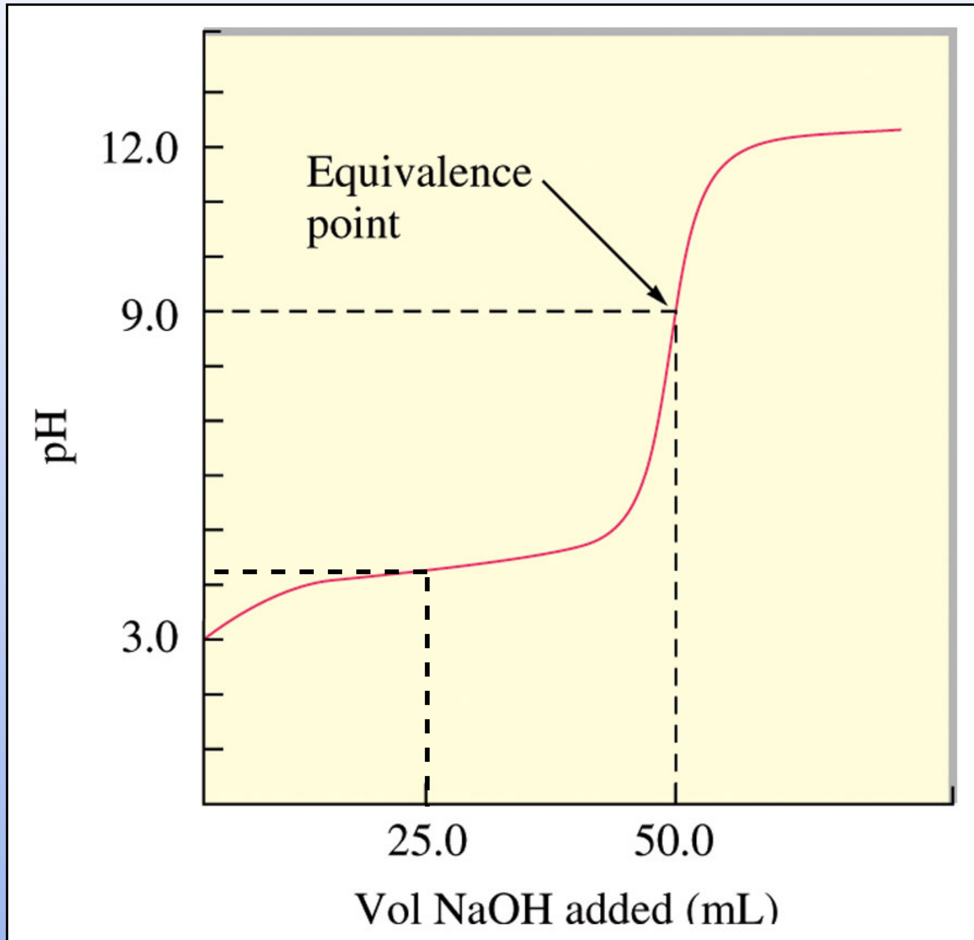
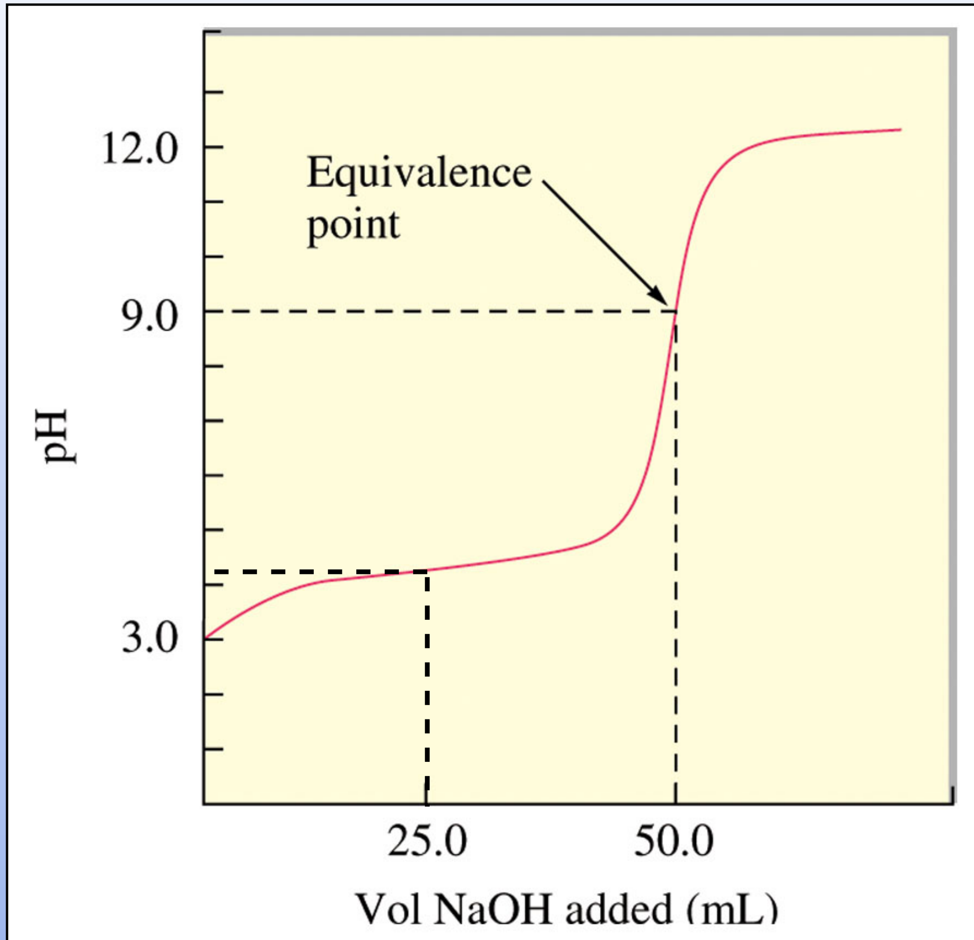
	....						
0.001	0.001	0.009	0.000	0.000	0.010	0.15	8.78
0.000	0.001	0.010	0.000	0.001	0.010	0.16	12.8

Titrating a weak acid



Titrating a weak acid



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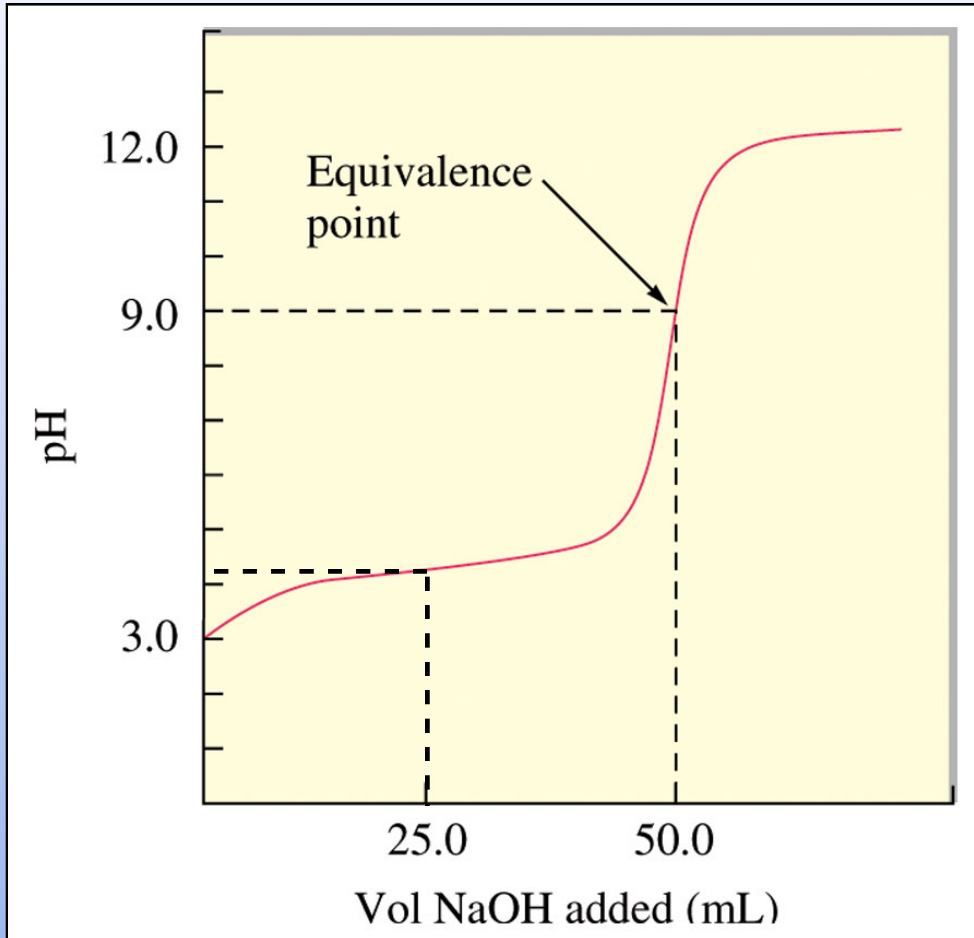
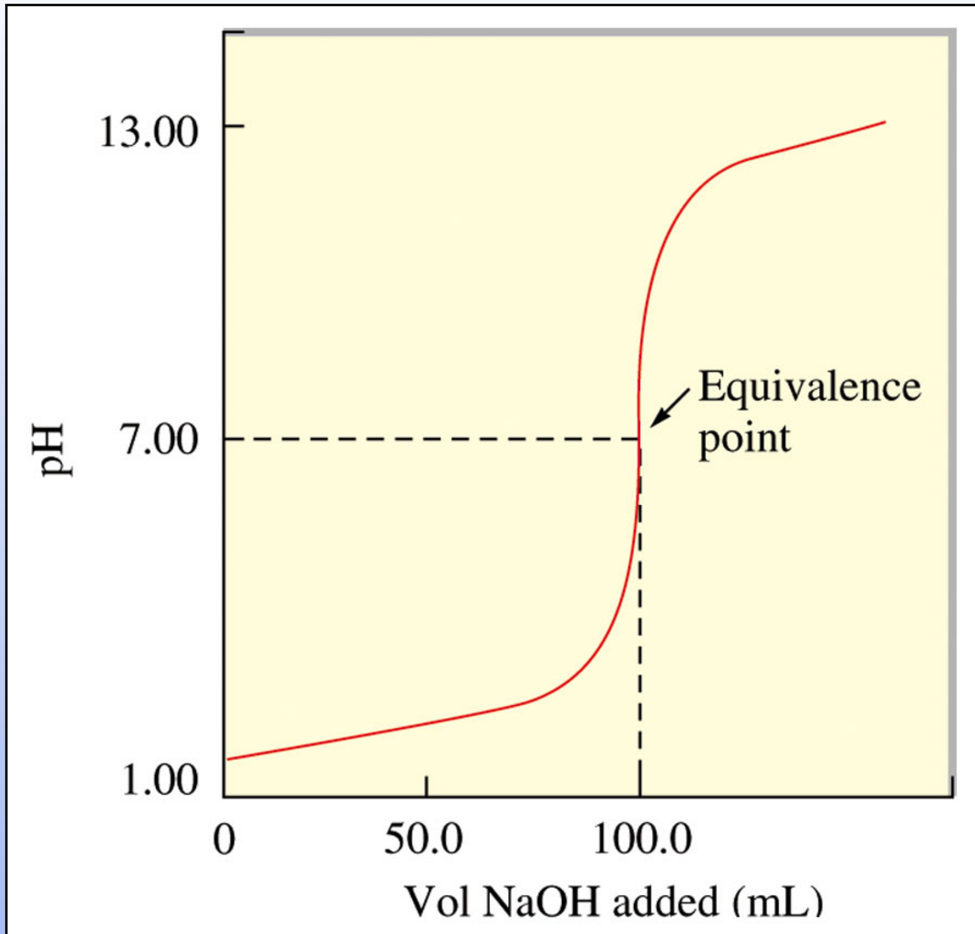


Easier Version   Strong Acid/Strong Base



HCl titrated with NaOH

No Buffer
(conjugate base is infinitely weak)

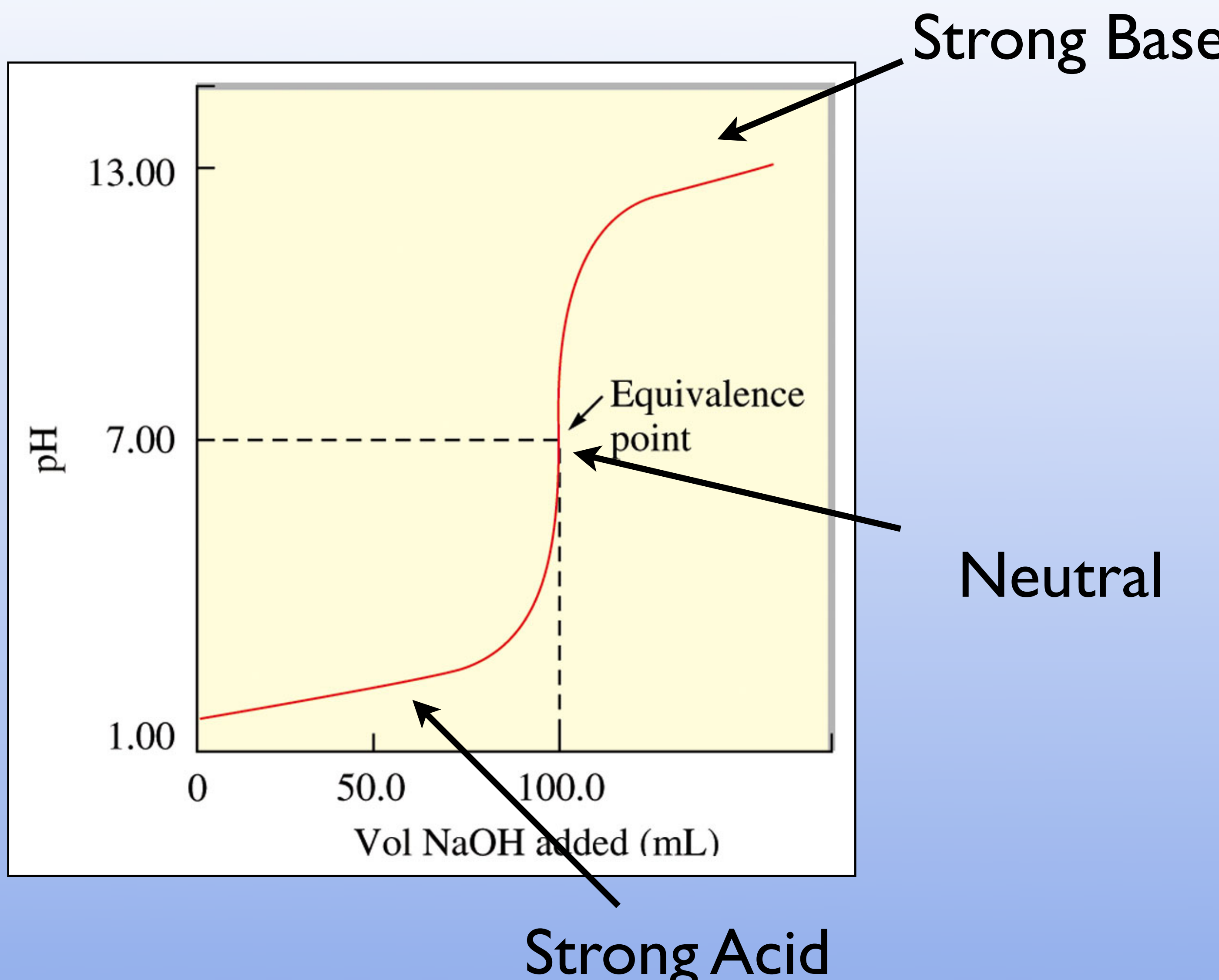
at the equivalence point we have
equal number of moles of acid and base

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^+	mol OH^-	mol H^+	mol OH^-		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

Strong Acid/Strong Base Titration



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

A. 0.1 M

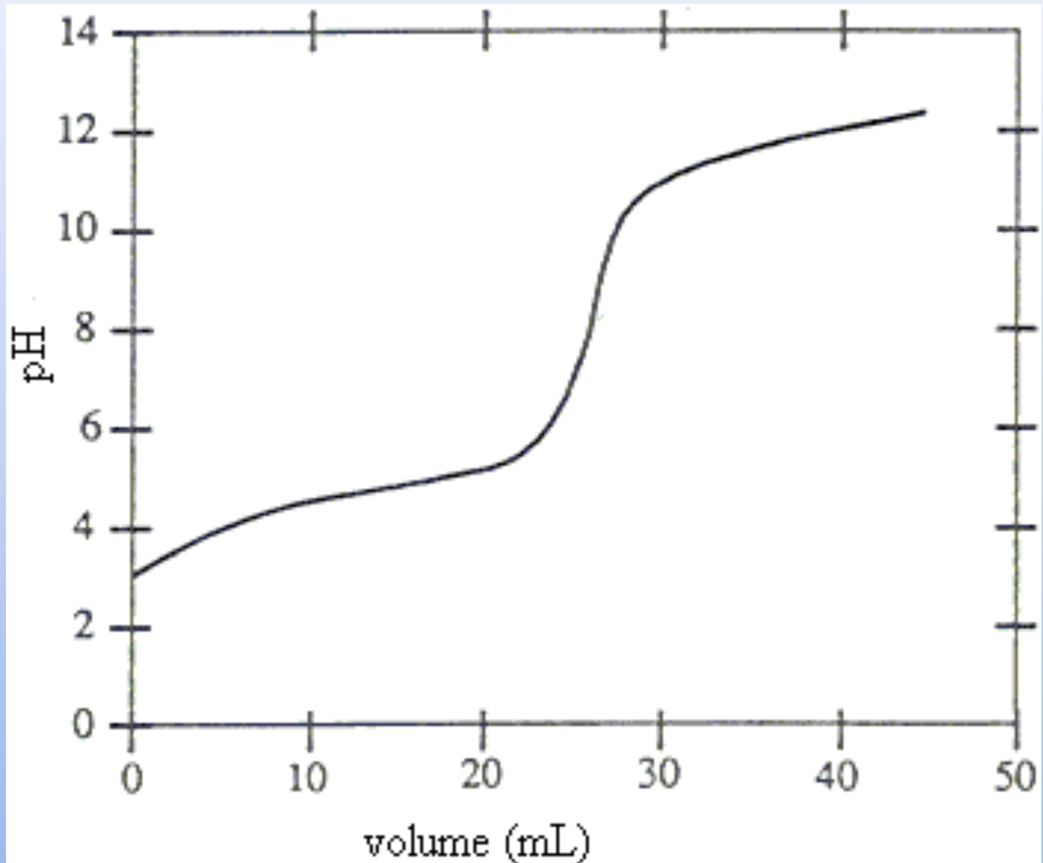
B. 0.2 M

C. 0.4 M

D. 1 M

E. 2 M

The equivalence point in this titration is at



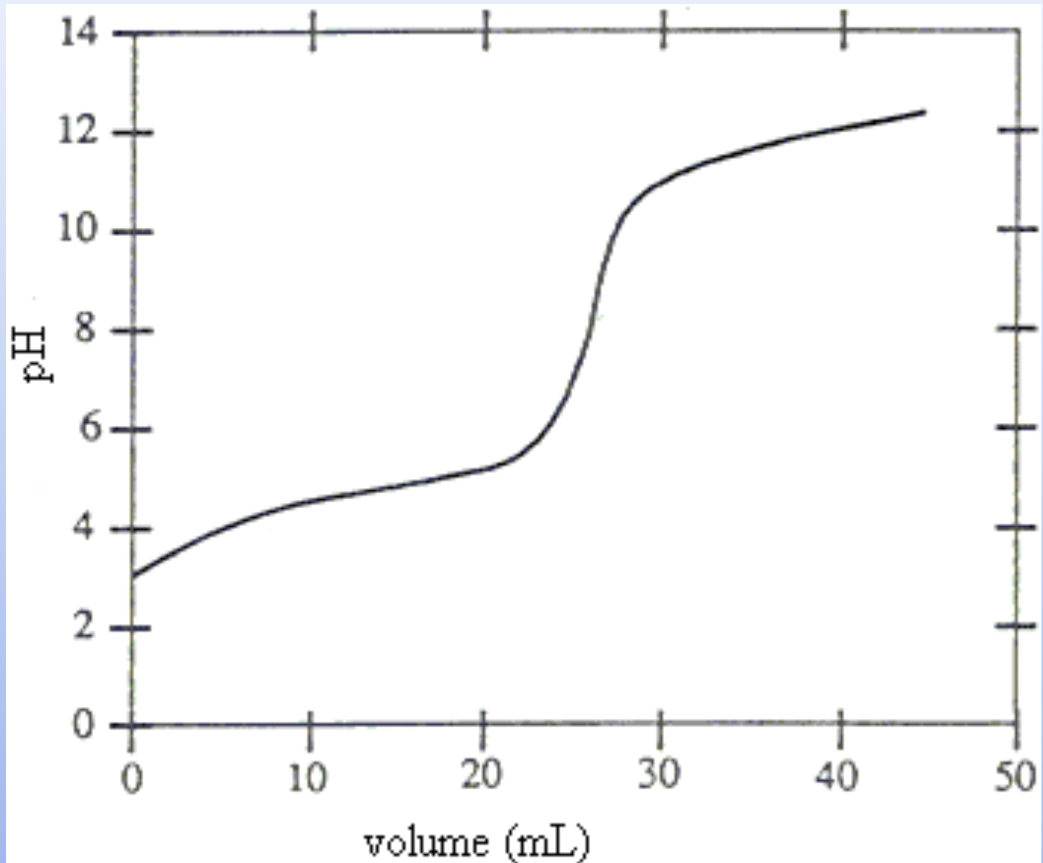
A. 5 mL

B. 14 mL

C. 28 mL

D. 44 mL

Below is a titration curve of a ______________



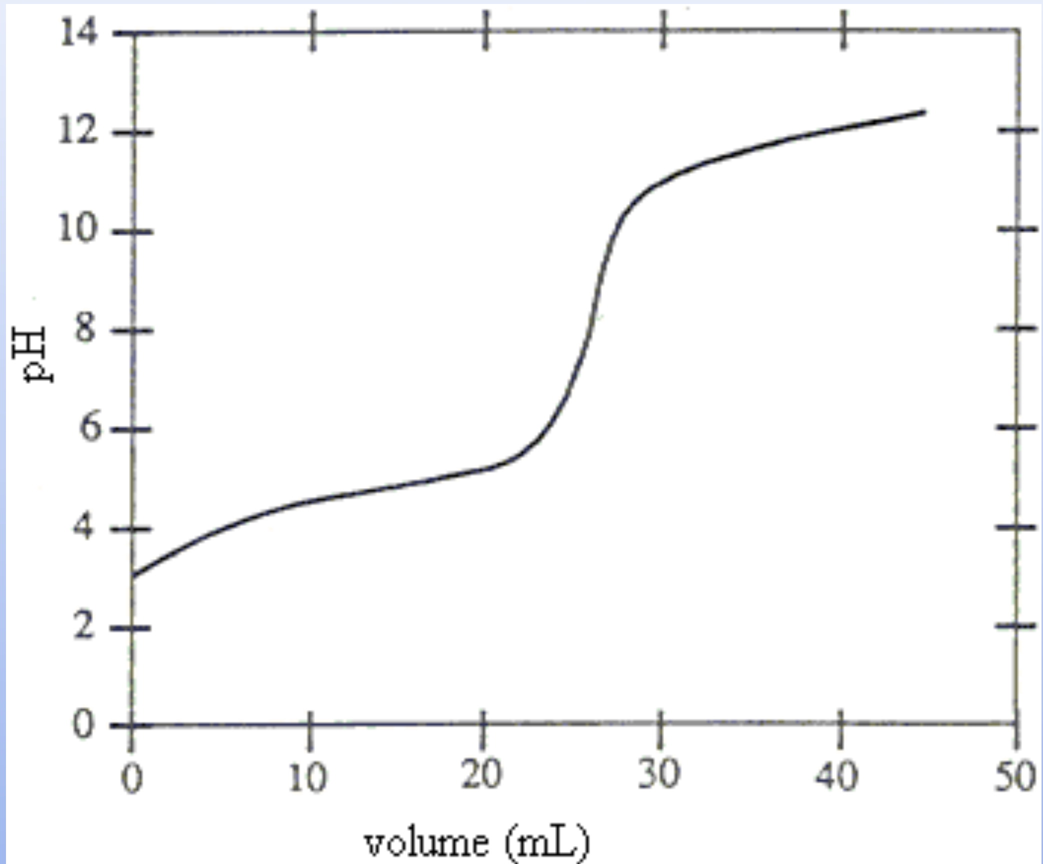
A. weak acid
with a strong base

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



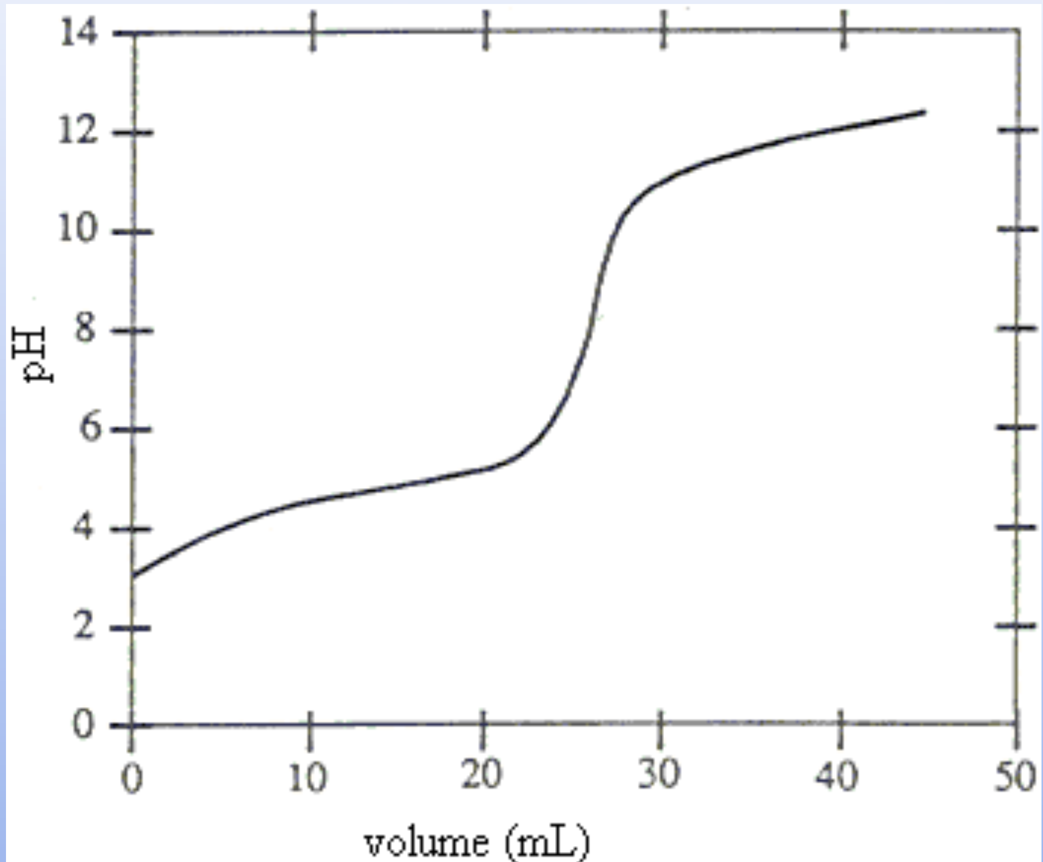
A. 5 mL

B. 14 mL

C. 28 mL

D. 44 mL

The pKa of this weak acid is________



A. 3.1

B. 4.7

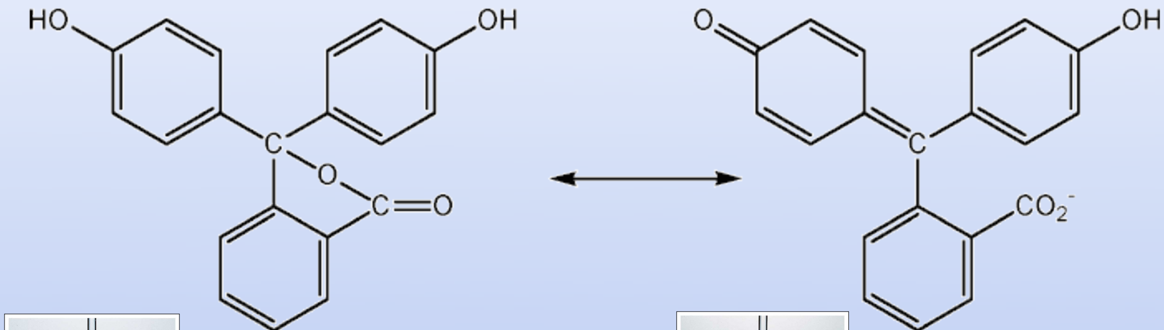
C. 8

D. 12.1

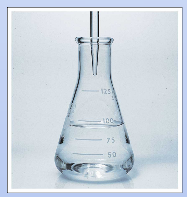
Finding the endpoint (equivalence point)
Indicator dye

Phenolphthalein

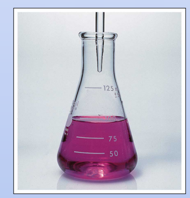
pKa = 8.2 $K_a = 6.3 \times 10^{-9}$



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



Colourless
HA



Pink
A^-

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

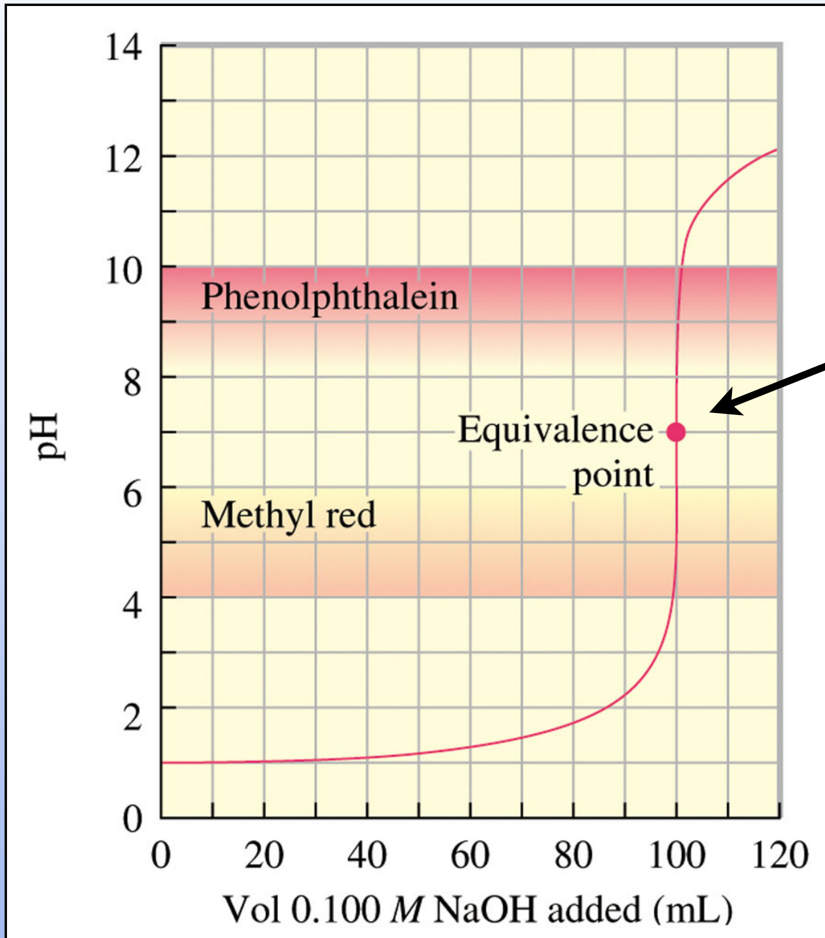
$$= [H^+] \times \frac{\text{Pink}}{\text{Clear}}$$

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

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

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

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



color just barely changing for Phenolpthalein

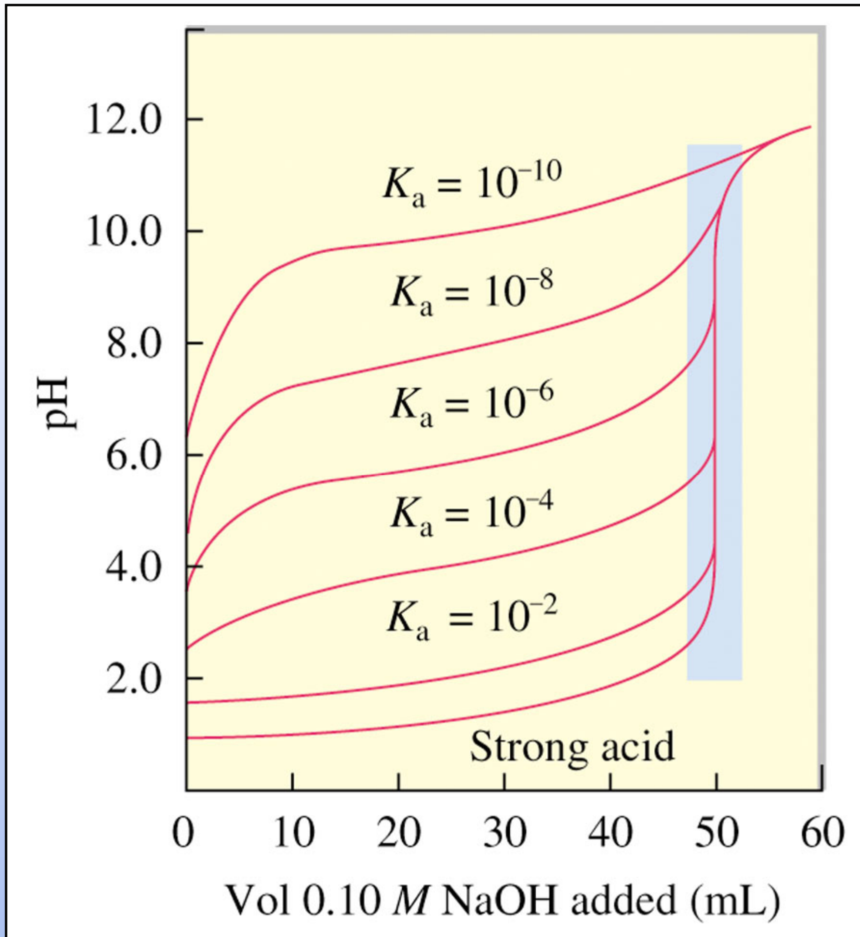
Bromophenol Blue has a pK_a of around 4. When it is protonated (HA form) it is green, when it is deprotonated (A^- form) it is blue.

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

A. blue

B. green

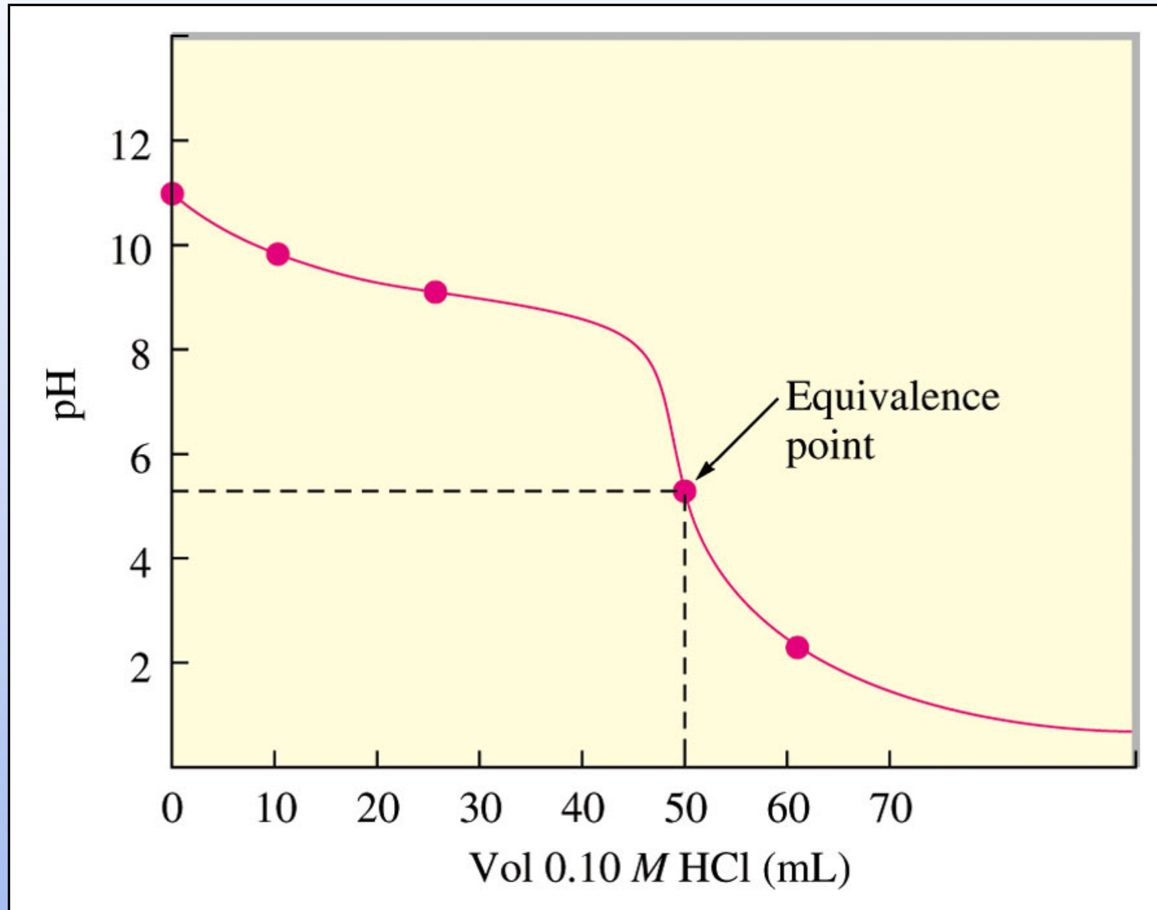
C. a mix of blue and green



Example of 6 acids with different Ka's but the same concentration

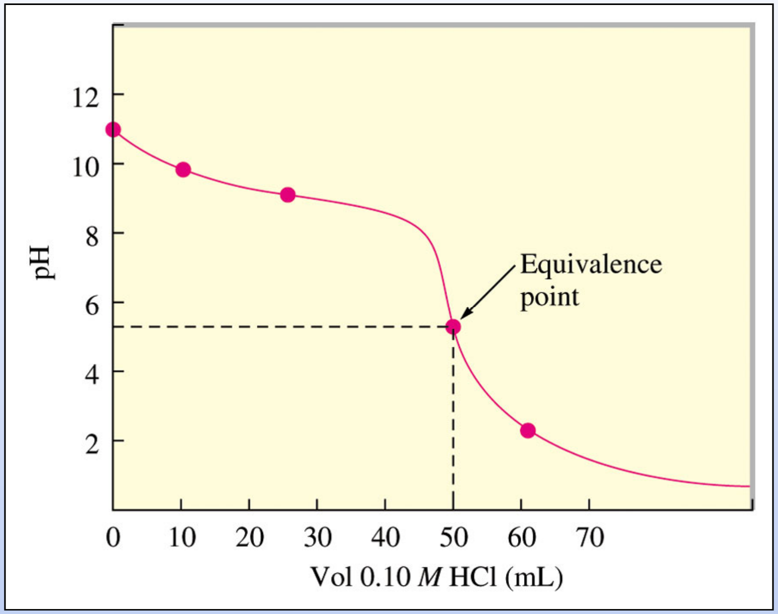
Same concentration will produce the same equivalence point

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?

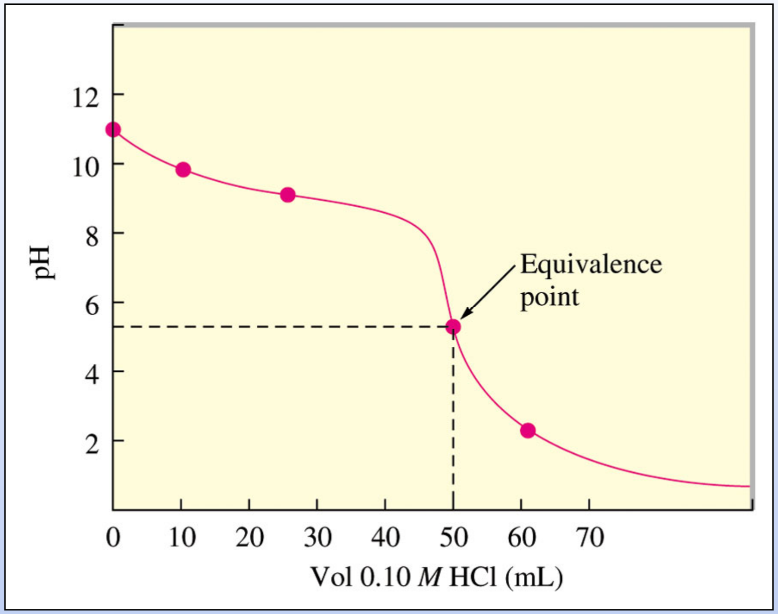
A. 0.05 M

B. 0.1 M

C. 0.15 M

D. 0.20 M

Weak base titrated with strong acid



What is the Kb of the base?

A. 1×10^{-3}

B. 1×10^{-5}

C. 1×10^{-8}

D. 1×10^{-9}

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 HA , A^-

Diprotic H_2A, HA^-, A^{2-}

Triprotic H_3A, H_2A^-, HA^{2-}, A^{3-}

For example

Sulfuric Acid

$$H_2SO_4(aq) \longleftrightarrow H^+(aq) + HSO_4^-(aq)$$

$$HSO_4^-(aq) \longleftrightarrow H^+(aq) + SO_4^{2-}(aq)$$

$$K_{a1} = \frac{[H^+][HSO_4^-]}{[H_2SO_4]} = 10^3$$

Equilibrium for the first proton coming "off"

$$K_{a2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1.2 \times 10^{-2}$$

Equilibrium for the next proton coming "off"

Key Question

What is in solution!

$$H_2A(aq) \longleftrightarrow H^+(aq) + HA^-(aq) \quad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

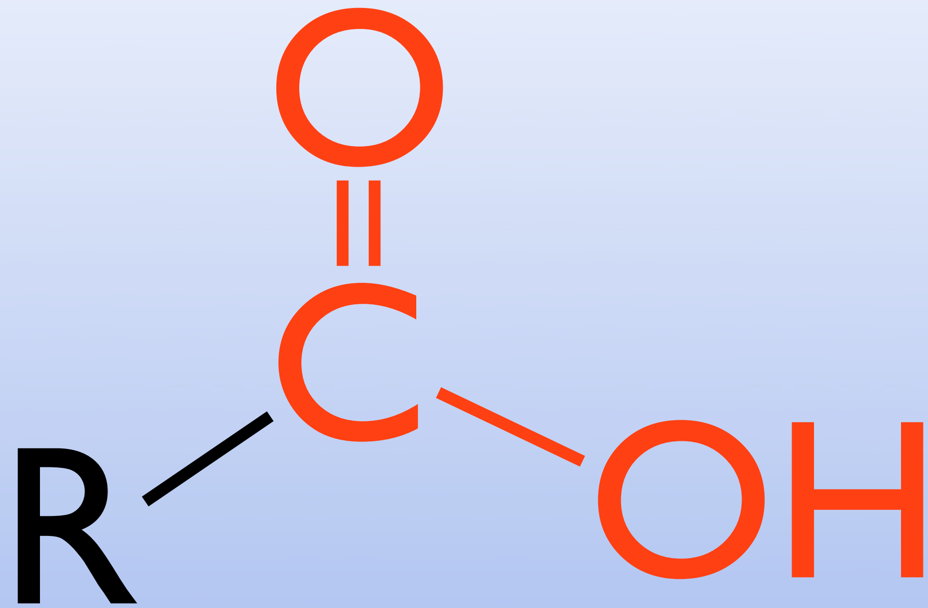
$$HA^-(aq) \longleftrightarrow H^+(aq) + A^{2-}(aq) \quad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

we'll reduce all such problems to 1 or 2 major forms of the acid.

First figure out which ones will be in solution

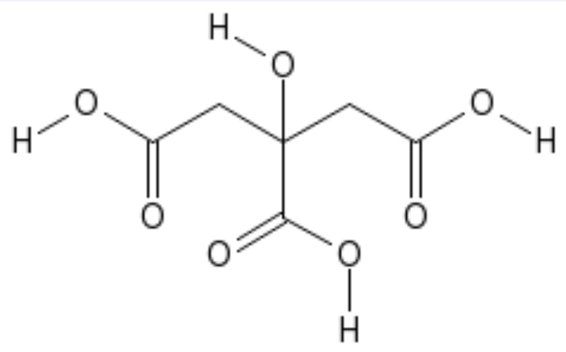
Carboxylic Acid

Common
Acetic Acid
(vinegar)



carbon double bonded to an oxygen
bonded to carbon on one side
OH on the other side

Citric Acid



$K_{a1} = 7.4 \times 10^{-4}$

$K_{a2} = 1.7 \times 10^{-5}$

$K_{a3} = 4.0 \times 10^{-7}$

What is the pH of 1M Citric Acid?

Imagine that it was monoprotic

Weak Acid

$$K_{a1} = \frac{[H^+][H_2A^-]}{[H_3A]} = \frac{(x)(x)}{Ca - x} = \frac{(x)(x)}{Ca}$$

$$[H^+] = x = \sqrt{K_a C_a} = \sqrt{(7.4 \times 10^{-4})(1)} = 0.027$$

Citric Acid

$K_{a1} = 7.4 \times 10^{-4}$ $K_{a2} = 1.7 \times 10^{-5}$ $K_{a3} = 4.0 \times 10^{-7}$

Lets look at K_{a2}

$$K_{a2} = [H^+]\frac{[HA^{2-}]}{[H_2A^-]} \qquad \frac{[HA^{2-}]}{[H_2A^-]} = \frac{K_{a2}}{[H^+]} = \frac{1.7 \times 10^{-5}}{0.027} = 6.3 \times 10^{-4}$$

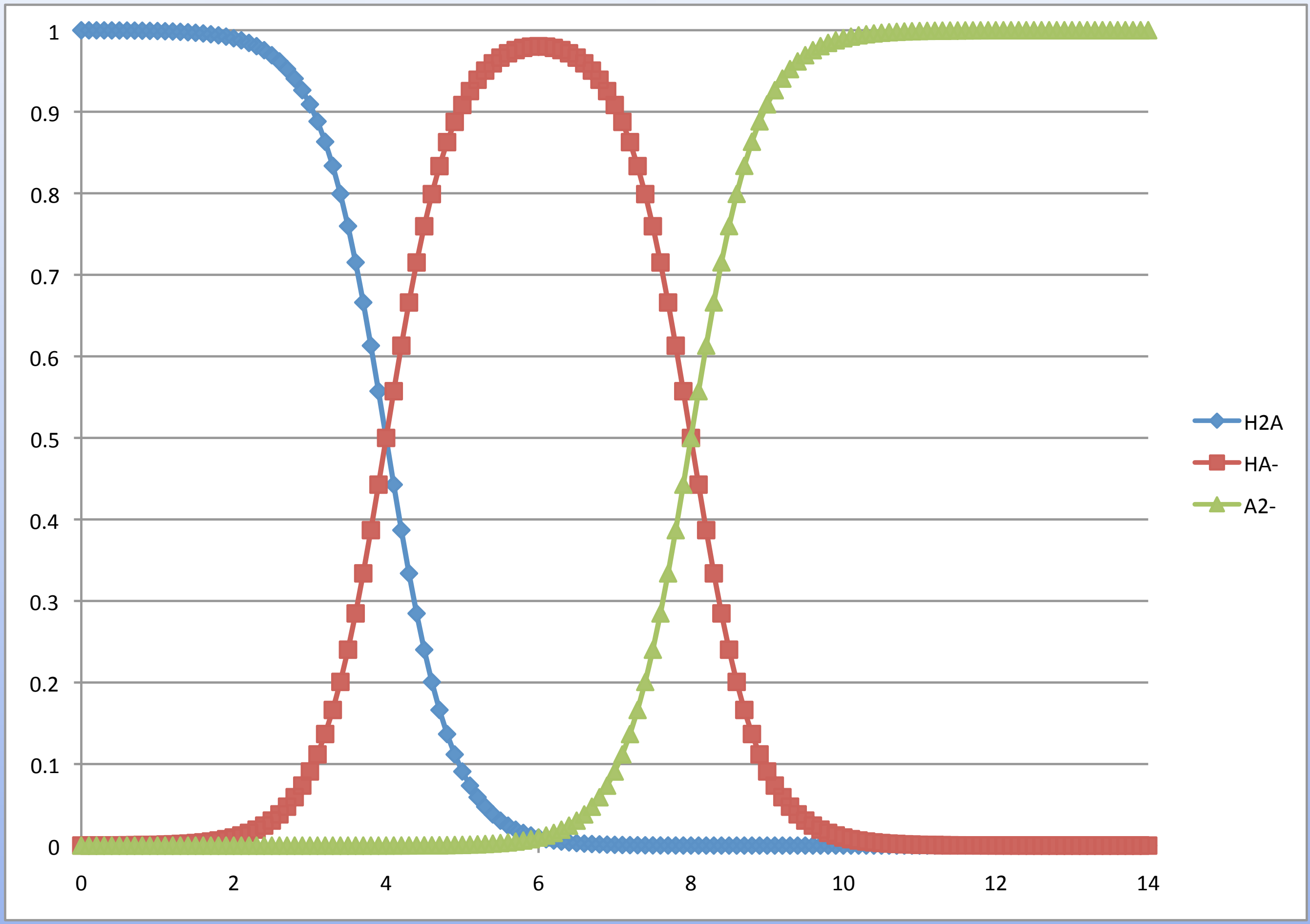
This is a very small number

very very little HA^{2-} the second proton doesn't come off
pH is dominated by the first proton equilibrium

So we really only need to consider
the $[H^+]$ concentration changing due to K_{a1}

What do I have in solution at different pH values?

% in each form



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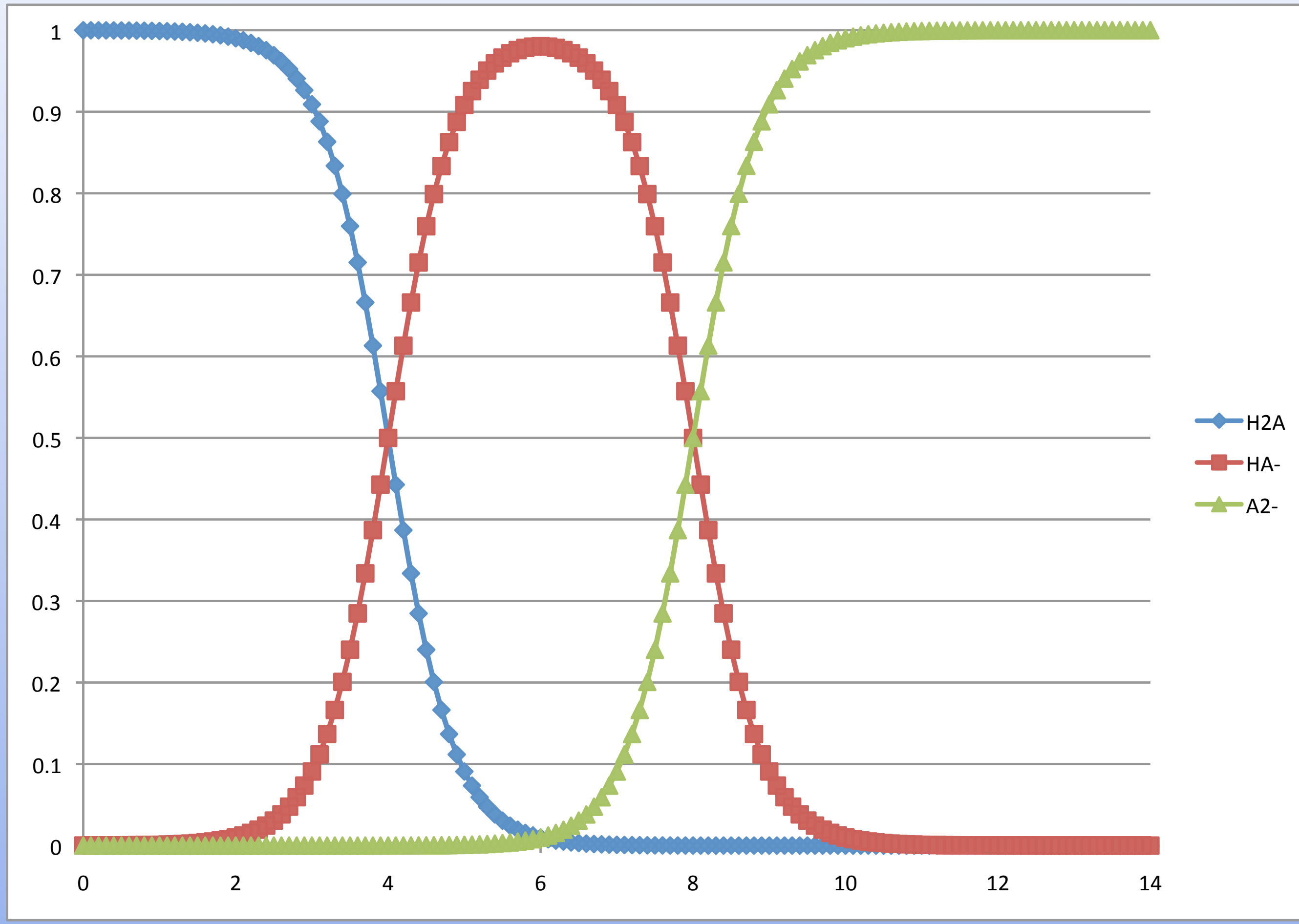

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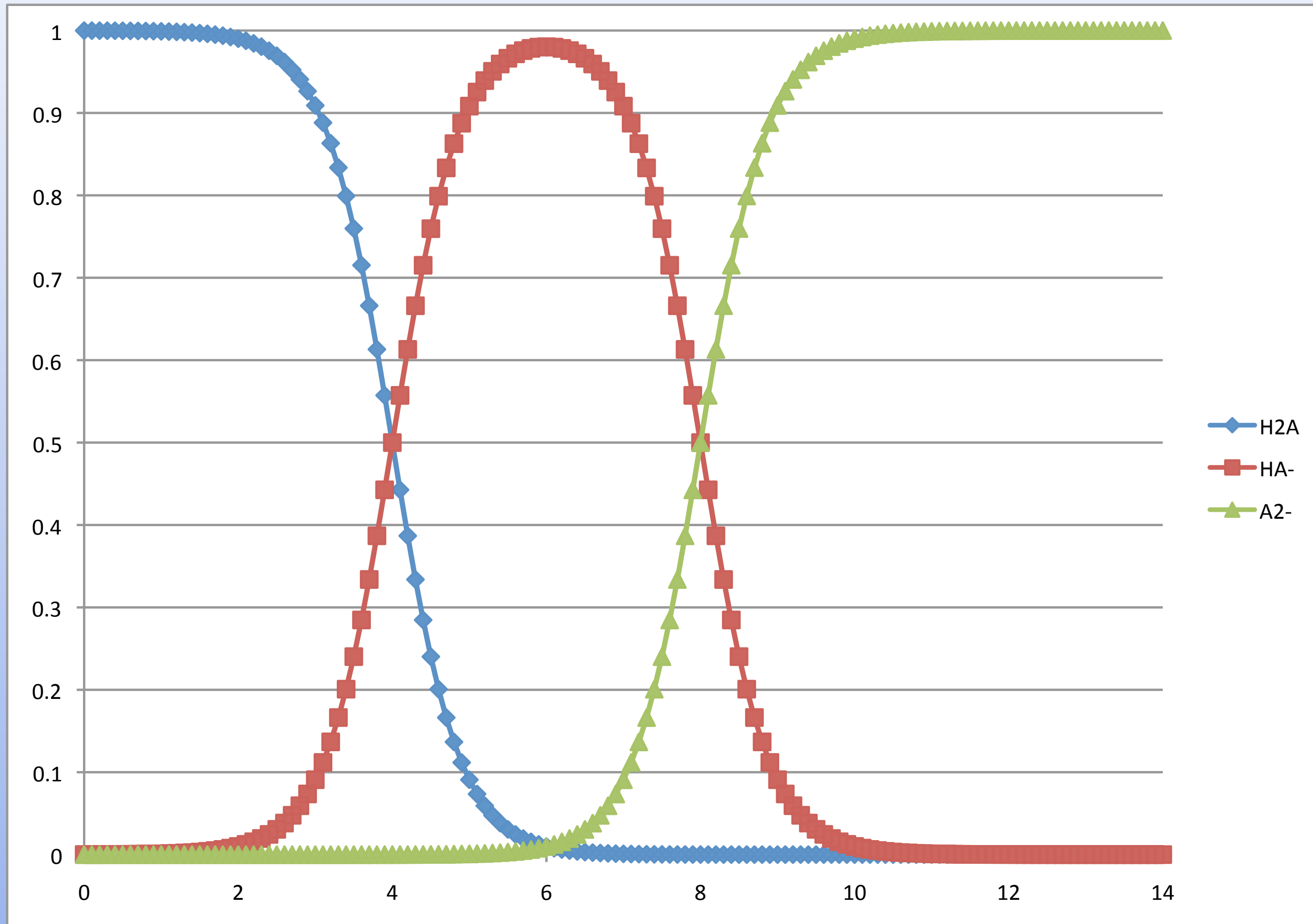

When do I care about the other protons?

When I neutralize the acid.

As you neutralize the first protons,
the second will come off,
....

If I add 0.1 moles of NaOH to 0.05 moles of H_3PO_4
what will be the dominant species in solution?

If I add 0.1 moles of NaOH to 0.05 moles of H_3PO_4 what will be the dominant species in solution?

A. H_3PO_4 and $H_2PO_4^-$

B. $H_2PO_4^-$

C. $H_2PO_4^-$ and HPO_4^{2-}

D. HPO_4^{2-}

E. HPO_4^{2-} and PO_4^{3--}

What is the pH of a solution with 0.5 M HPO_4^{2-}?

H_3PO_4 $K_{a1} = 7.1 \times 10^{-3}$

$K_{a2} = 6.3 \times 10^{-8}$

$K_{a3} = 4.5 \times 10^{-13}$

to simplify we'll use the generic notation HPO_4^{2-} is HA^{2-}

HA^{2-} is found in equilibria 2 & 3

$$K_{a2} = \frac{[H^+][HA^{2-}]}{[H_2A^-]} \qquad K_{a3} = \frac{[H^+][A^{3-}]}{[HA^{2-}]}$$

Species that are both acids and bases are "Amphiprotic"

What is the pH of a solution with 0.5 M HPO_4^{2-}?

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$$K_{a2} = \frac{[H^+][HA^{2-}]}{[H_2A^-]} \qquad K_{a3} = \frac{[H^+][A^{3-}]}{[HA^{2-}]}$$

$$[HA^{2-}] = \frac{[H^+][A^{3-}]}{K_{a3}} \qquad K_{a2} = \frac{[H^+][H^+][A^{3-}]}{[H_2A^-]\, K_{a3}}$$

$$[H^+] = \sqrt{K_{a2} \times K_{a3}}$$

If I add 0.1 moles of NaOH to 0.07 moles of H_3PO_4 what will be the dominant species in solution?

A. H_3PO_4 and $H_2PO_4^-$

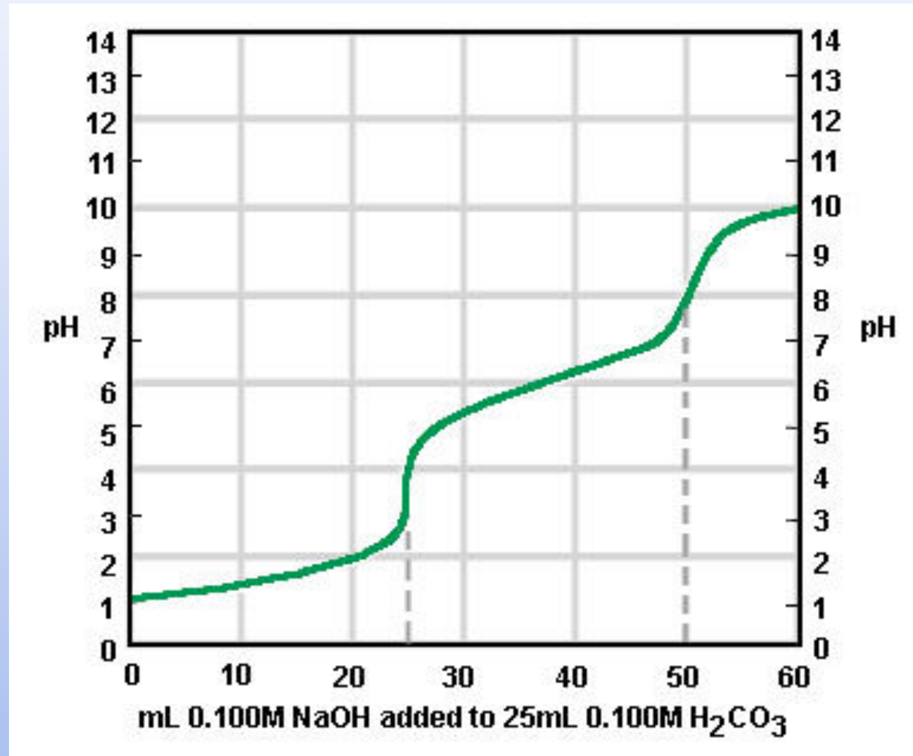
B. $H_2PO_4^-$

C. $H_2PO_4^-$ and HPO_4^{2-} ← .04 moles $H_2PO_4^-$ .03 moles HPO_4^{2-}

D. HPO_4^{2-}

E. HPO_4^{2-} and PO_4^{3--}

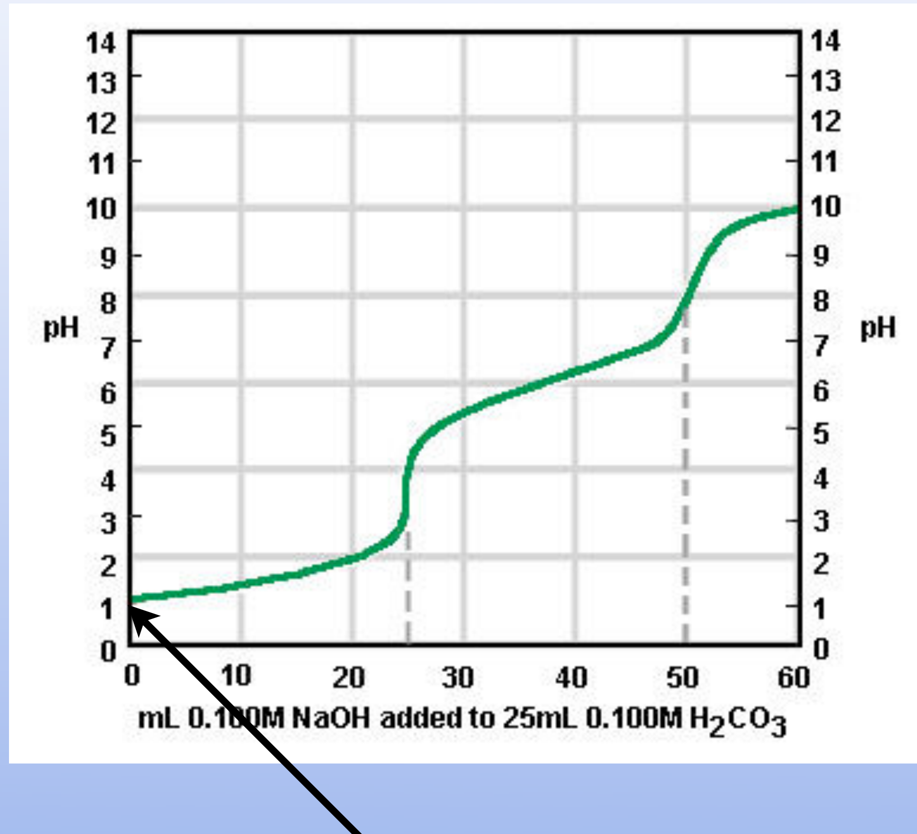
Titration of a polyprotic



Two equivalence points

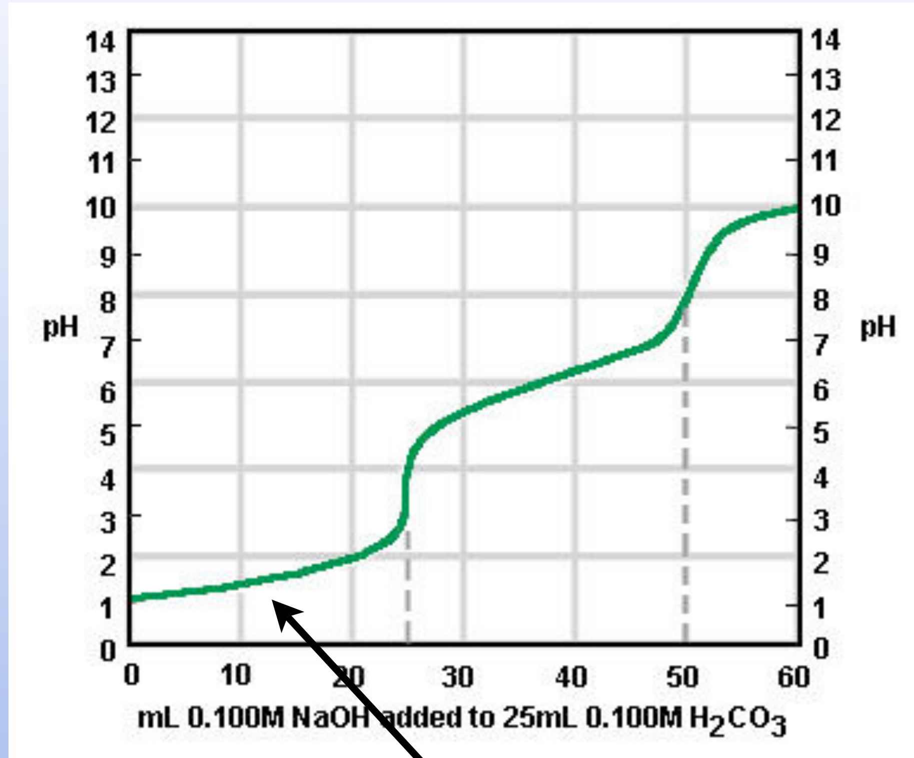
Diprotic H_2A

Titration of a polyprotic



all H_2A weak acid

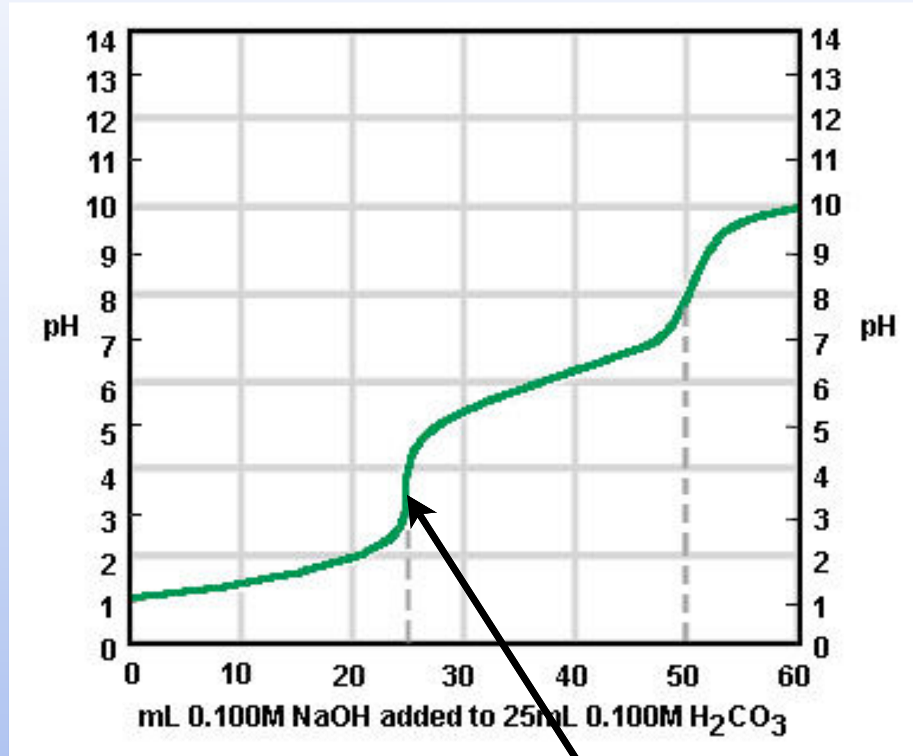
Titration of a polyprotic



OH^- neutralizes some
H_2A to HA^-
buffer around K_{a1}

halfway
to equivalence point 1
$pH = pK_{a1}$

Titration of a polyprotic

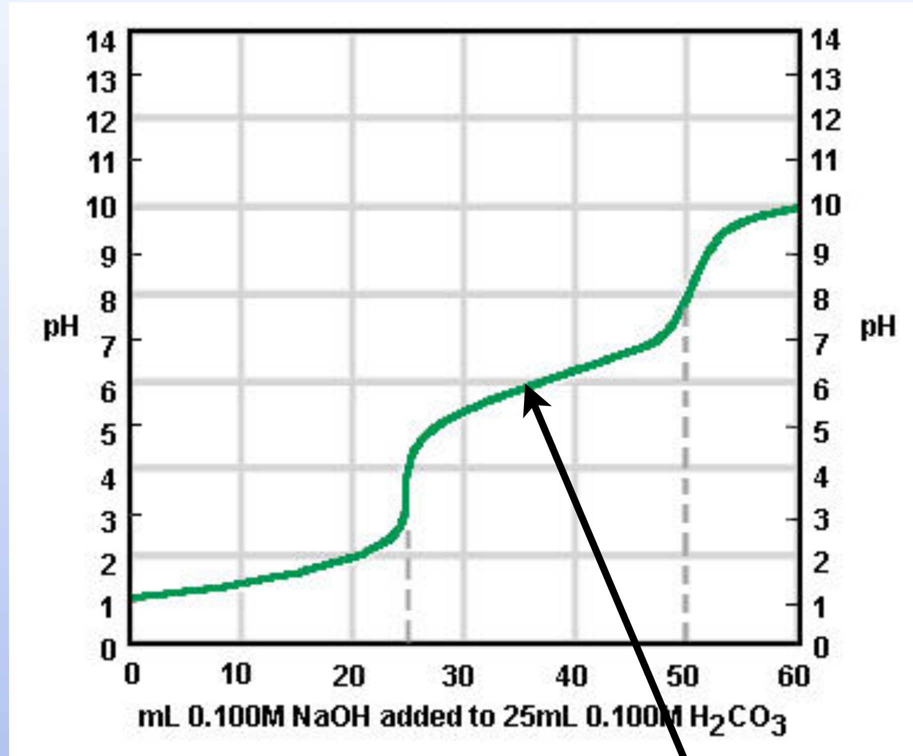


equivalence point 1

moles OH^- = moles H_2A

All H_2A converted to HA^-

Titration of a polyprotic



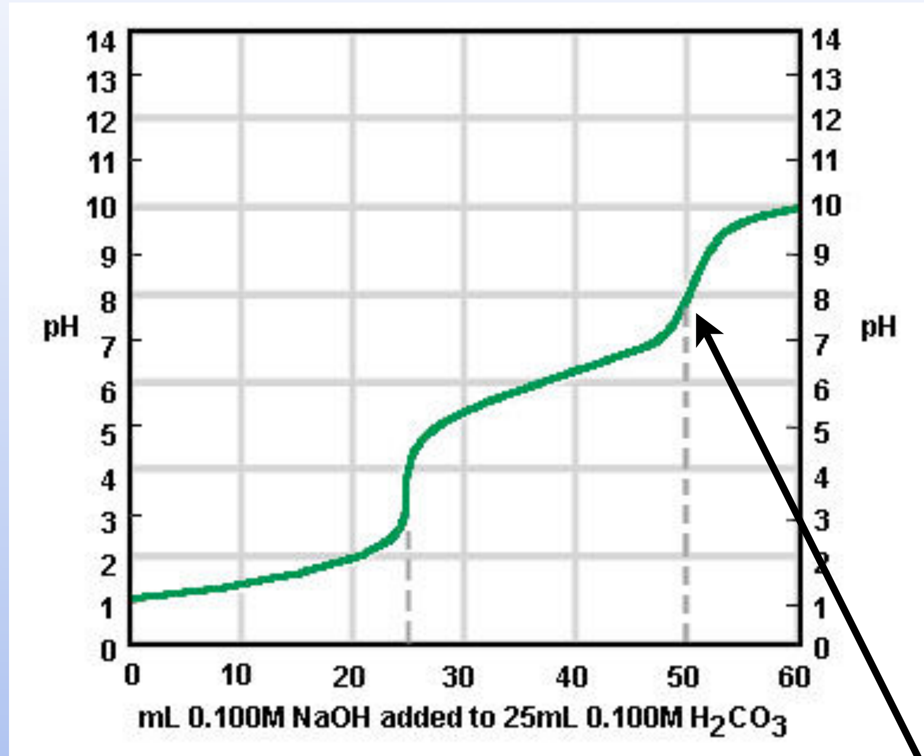
halfway
to equivalence point 1
pH = pK_{a2}

OH^- neutralizes HA^- to A^{2-}

HA^- and A^{2-}

buffer around K_{a2}

Titration of a polyprotic



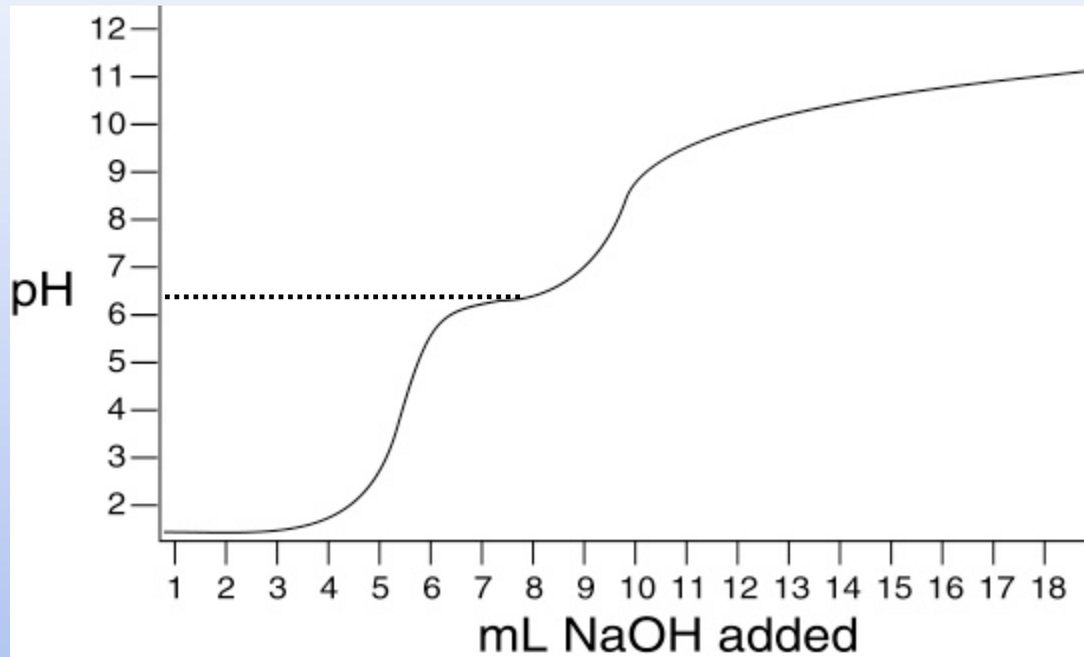
equivalence point 2

moles OH^- = 2 x moles H_2A

now all H_2A is converted to A^{2-}

now weak base A^{2-}

Given the following curve estimate K_{a2} for this unknown acid



at 1/2 equiv
pH = pKa
pH = 6.3
pKa = 6.3
Ka = 5×10^{-7}

A. 1 B. 6.3 C. 5×10^{-6} D. 5×10^{-7}