Today

Quick solubility question

Polyprotic Acids

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

Silver Nitrate ($AgNO_3$) and Potassium Chloride (KCl) are both soluble salts. What will happen if I mix 100 mL of 1 M $AgNO_3$ solution with 200 ml of 1 M KCl solution given that K_{sp} for $AgCl$ is 1.8×10^{-10}

A. I'll have a solution with Ag^+, Cl^-, K^+, and NO_3^- ions

B. some solid $AgCl$ will form

C. both A & B

Precipitation

Like neutralization problems

First react, the solve the equilibrium

K_{sp} is generally small.
First assume as much solid as possible forms
Then look at what "re-dissolves" into solution

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

$$\overset{H_2A}{H_2SO_4(aq)} \longleftrightarrow H^+(aq) + \overset{HA^-}{HSO_4^-(aq)}$$

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

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

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!

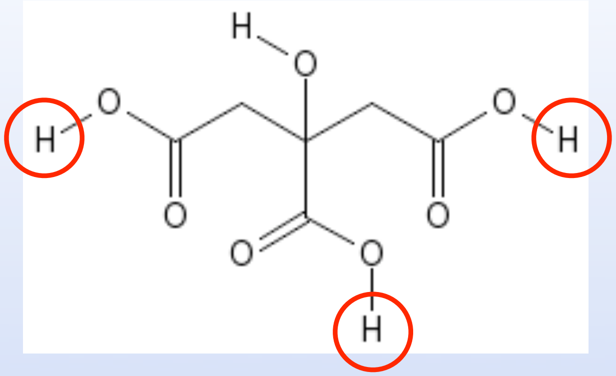
$$H_2A(aq) \longleftrightarrow H^+(aq) + HA^-(aq) \quad K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

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

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

First figure out which ones will be in solution

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

	H_3A	H^+	H_2A^-
I	Ca	0	0
C	-x	+x	+x
E	Ca-x	+x	+x

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

$$[H^+] = x = \sqrt{K_a C_a}$$

Citric Acid

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

Imagine that it was monoprotic

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

Lets look at K_{a2}

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

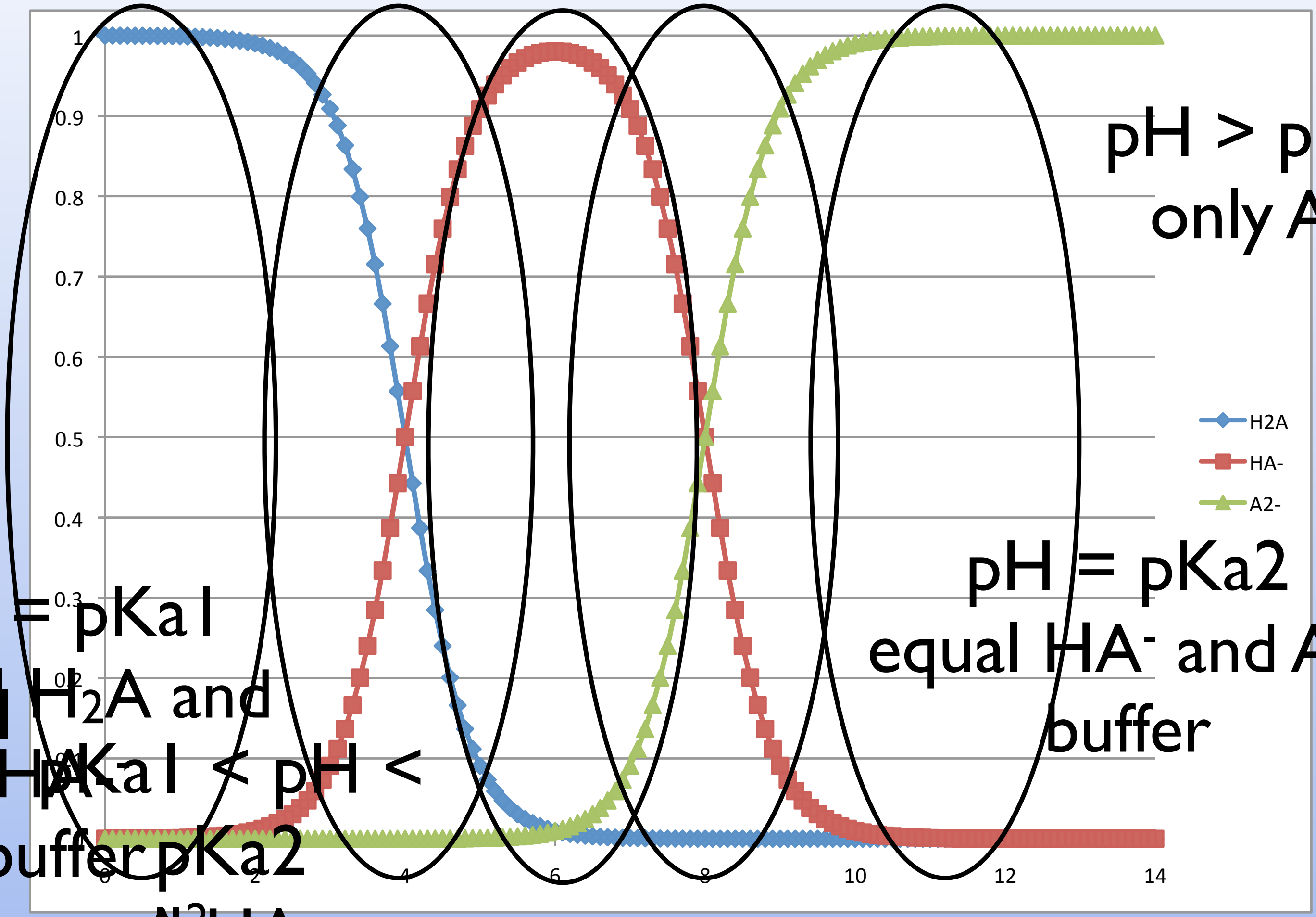
This is a very small number

very very little HA^{2-} the second proton doesn't come off

pH is dominated by the first proton equilibrium

What do I have in solution at different pH values?

% in each form



pH < pKa1
all H_2A

pH = pKa1
equal H_2A and HA^-
buffer

pKa1 < pH < pKa2
all HA^-
note no A^{2-}

pH = pKa2
equal HA^- and $A2^-$
buffer

pH > pKa2
only $A2^-$

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?

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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--}

.05 moles OH would
neutralize all the
H_3PO_4
making 0.5 moles of $H_2PO_4^-$

.05 moles would neutralize all the
$H_2PO_4^-$
making 0.5 moles of HPO_4^{2-}
OH^- no all neutralized

what is left? 0.5 moles of HPO_4^-

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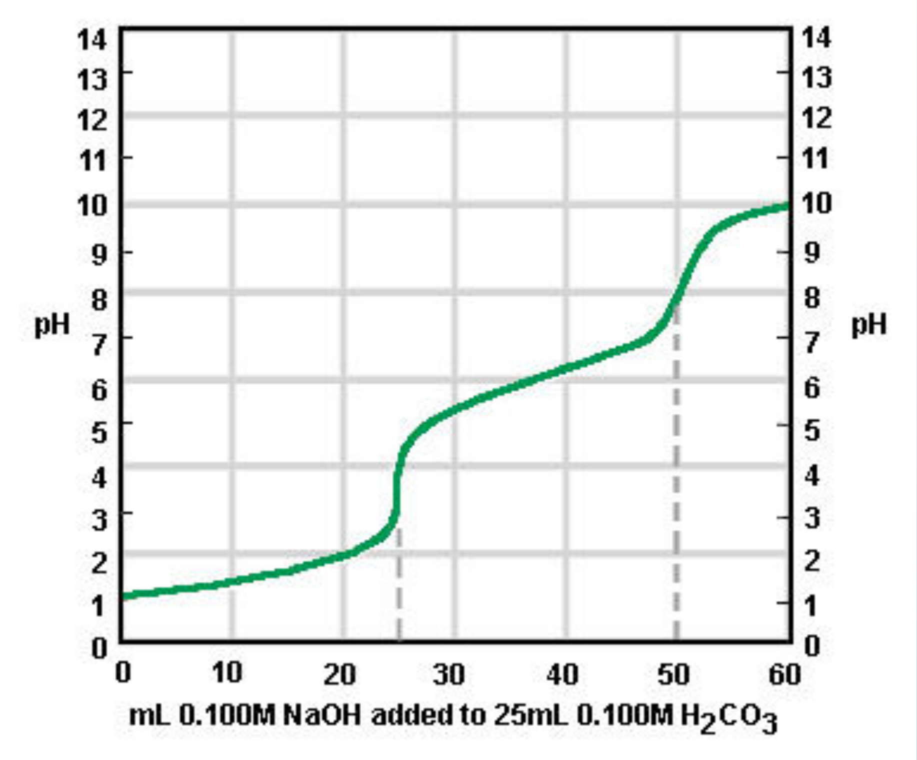
$$K_{a2} = \frac{[H^+][HA^{2-}]}{[H_2A^-]} \qquad K_{a3} = \frac{[H^+][A^{3-}]}{[HA^{2-}]}$$

$$[HA^{2-}] = \frac{[H^+][A^{3-}]}{K_{a3}} \qquad K_{a2} = \frac{[H^+][H^+][\cancel{A^{3-}}]}{[\cancel{H_2}A^-]\,K_{a3}}$$

assume the
small change in
forming both acid
and base

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

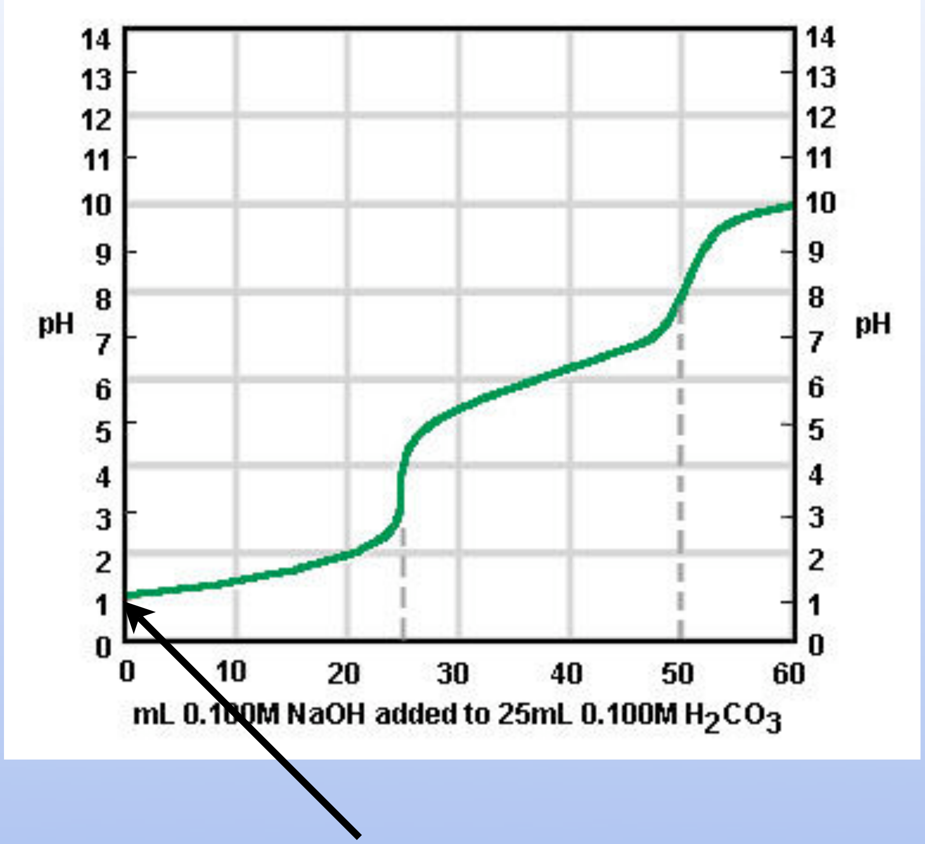
Titration of a polyprotic



Two equivalence points

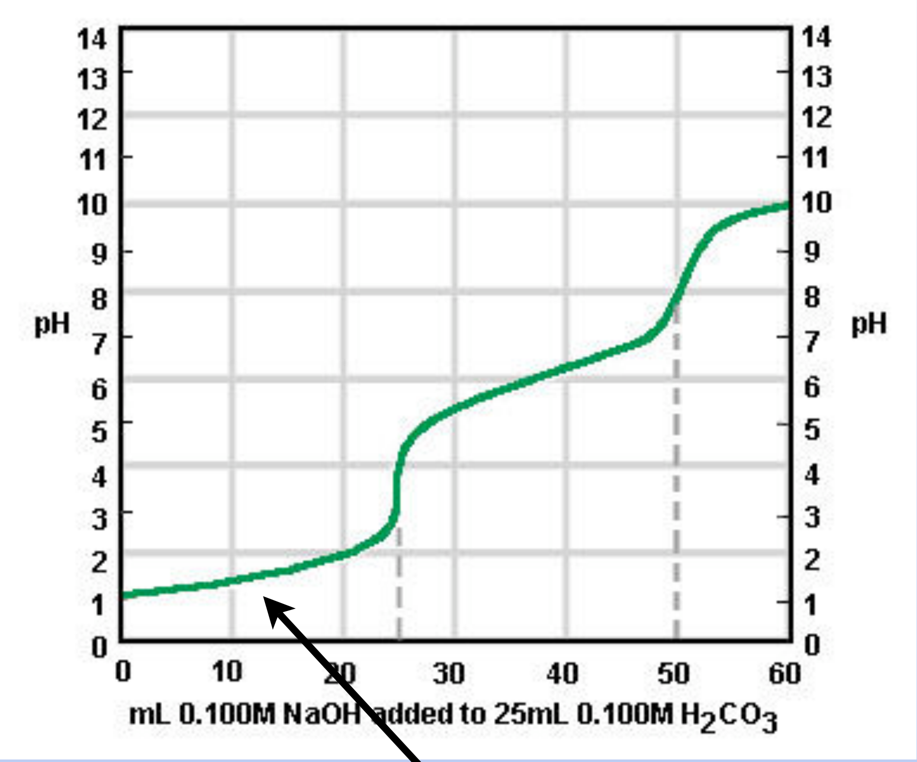
Diprotic H_2A

Titration of a polyprotic



all H_2A weak acid

Titration of a polyprotic



OH$^-$ neutralizes some

H_2A to HA^-

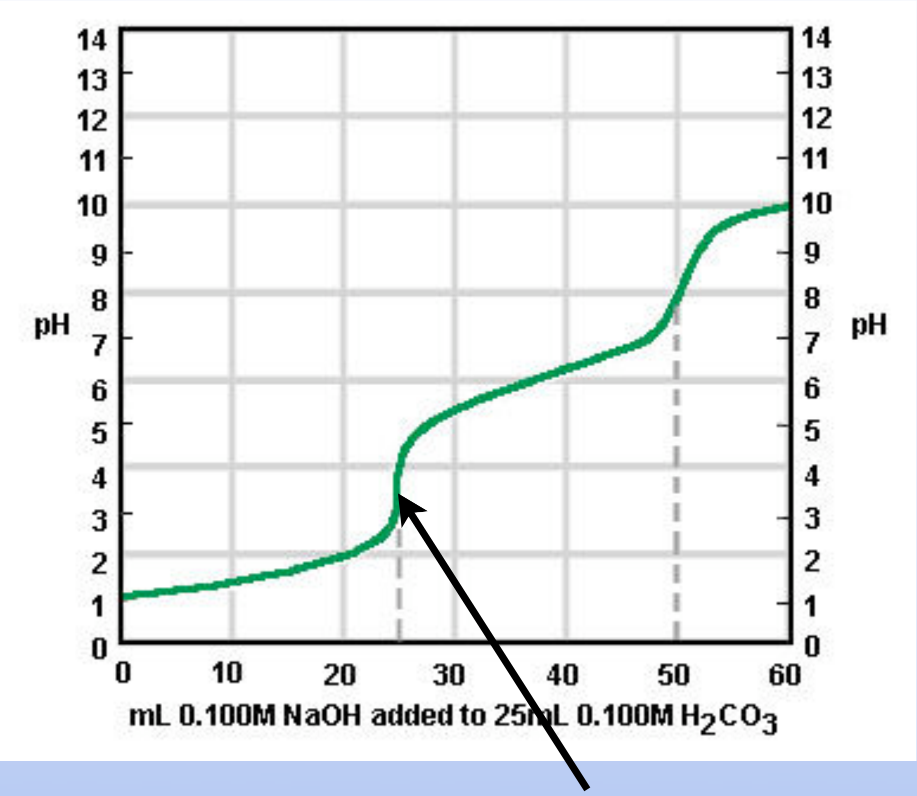
buffer around K_{a1}

halfway

to equivalence point 1

pH = pK_{a1}

Titration of a polyprotic

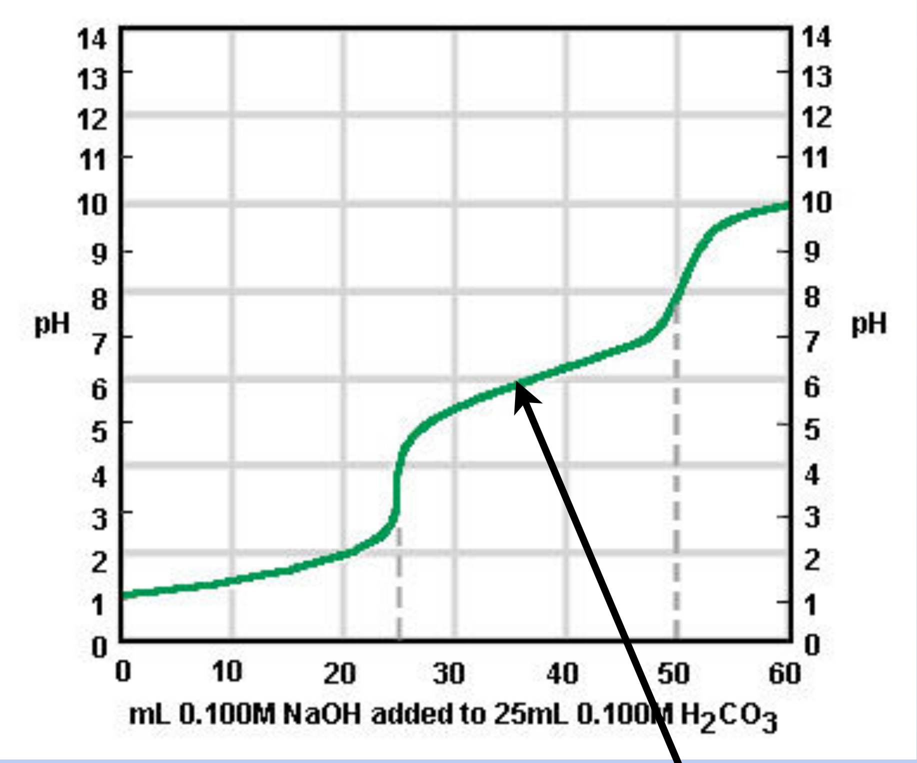


equivalence point 1

moles OH^- = moles H_2A

All H_2A converted to HA^-

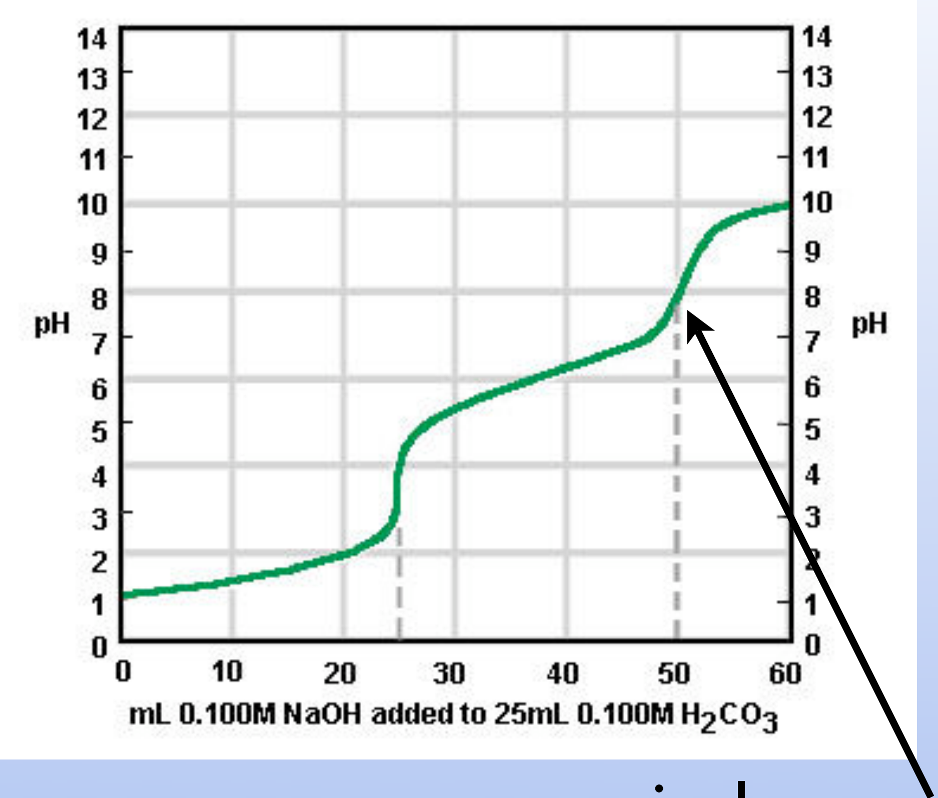
Titration of a polyprotic



halfway
to equivalence point I
$pH = pK_{a2}$

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-}

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. $H_2PO_4^-$

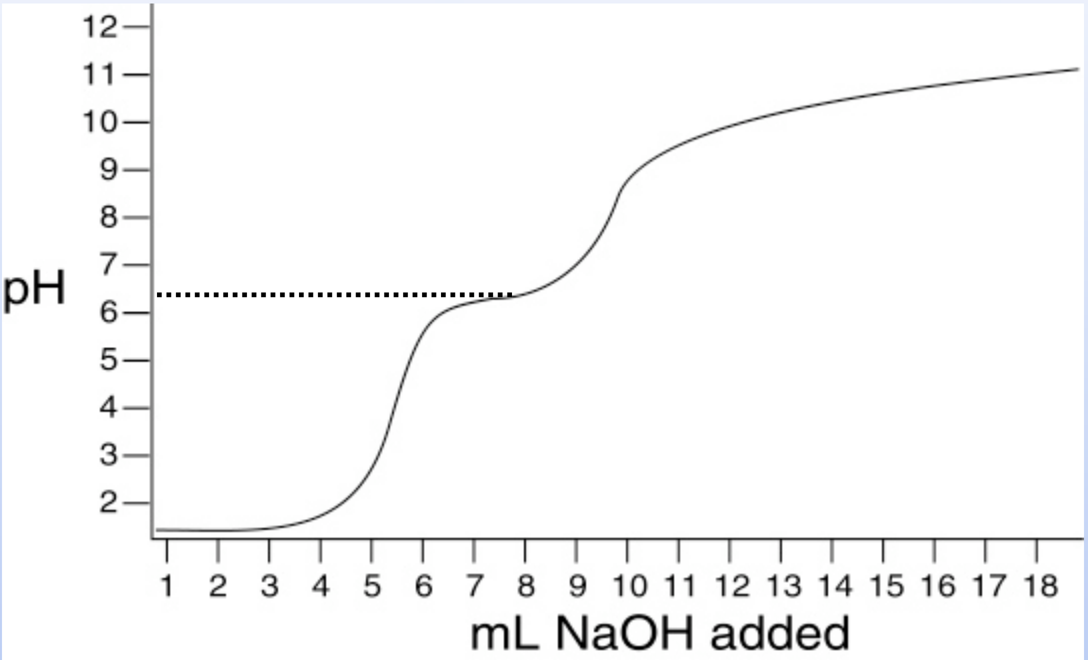
C. $H_2PO_4^-$ and HPO_4^{2-} ←

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

D. HPO_4^{2-}

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

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}