

Today

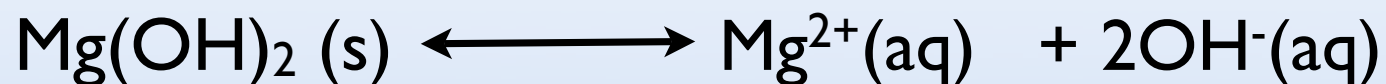
Solubility

The easiest of all the equilibria

Polyprotic Acids

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

Solubility Equilibria



$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^{-}]^2$$

solubility product



example

In which solution with $\text{Mg}(\text{OH})_2$ have the highest solubility?


A. pure water

B. 1 M NaOH

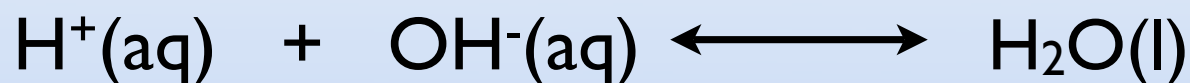
C. 1 M MgCl_2

D. 1 M HCl

The acid will neutralize the OH^- allowing more to dissolve



If I add 1 mole of $\text{Al}(\text{OH})_3$ to
1 L of a 1 M HCl solution
what is the pH?



$$K_{\text{sp}} = 4.6 \times 10^{-33}$$

First neutralize. Even though the $[\text{OH}^{-}]$ concentration will be small, whatever dissolves will neutralize

Then you can solve the equilibrium

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 B & C

Precipitation

Like neutralization problems

First react, then solve the equilibrium

K_{sp} is generally small.

First assume as much solid as possible forms
Then look at what "re-dissolves" into solution

Problem

Polyprotic Acids

Acids that have more than one proton to lose

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

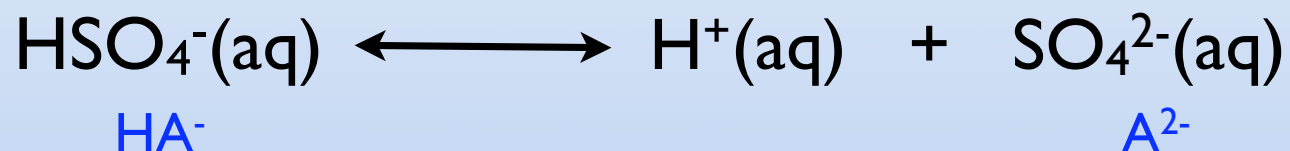
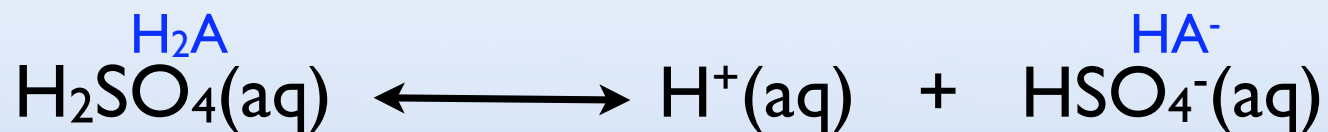
Monoprotic HA , A^-

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

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

For example

Sulfuric Acid



$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} = 10^3$$

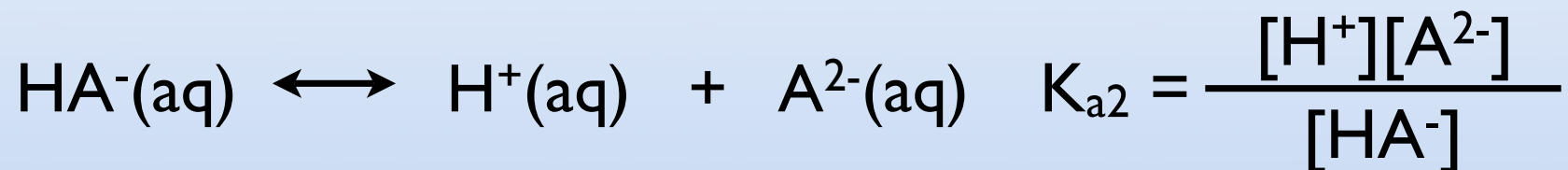
Equilibrium for the first
proton coming "off"

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1.2 \times 10^{-2}$$

Equilibrium for the next
proton coming "off"

Key Question

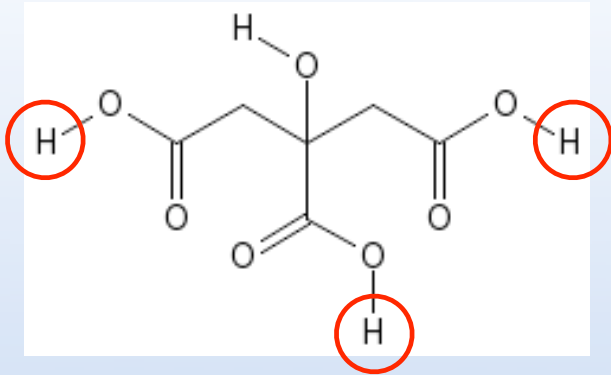
What is in solution!



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

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

Citric Acid

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

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}

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

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

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-}

.05 moles OH would
neutralize all the
 H_3PO_4

making 0.5 moles of H_2PO_4^-

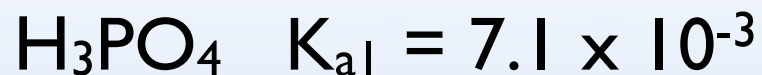
.05 moles would neutralize all the
 H_2PO_4^-

making 0.5 moles of HPO_4^{2-}
OH⁻ no all neutralized

what is left? 0.5 moles of HPO_4^{2-}



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



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

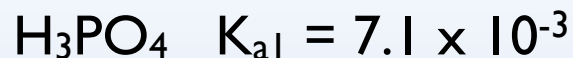
$$K_{a3} = 4.5 \times 10^{-13}$$

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

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

$$K_{a2} = \frac{[\text{H}^+][\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]} \quad K_{a3} = \frac{[\text{H}^+][\text{A}^{3-}]}{[\text{HA}^{2-}]}$$

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



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

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

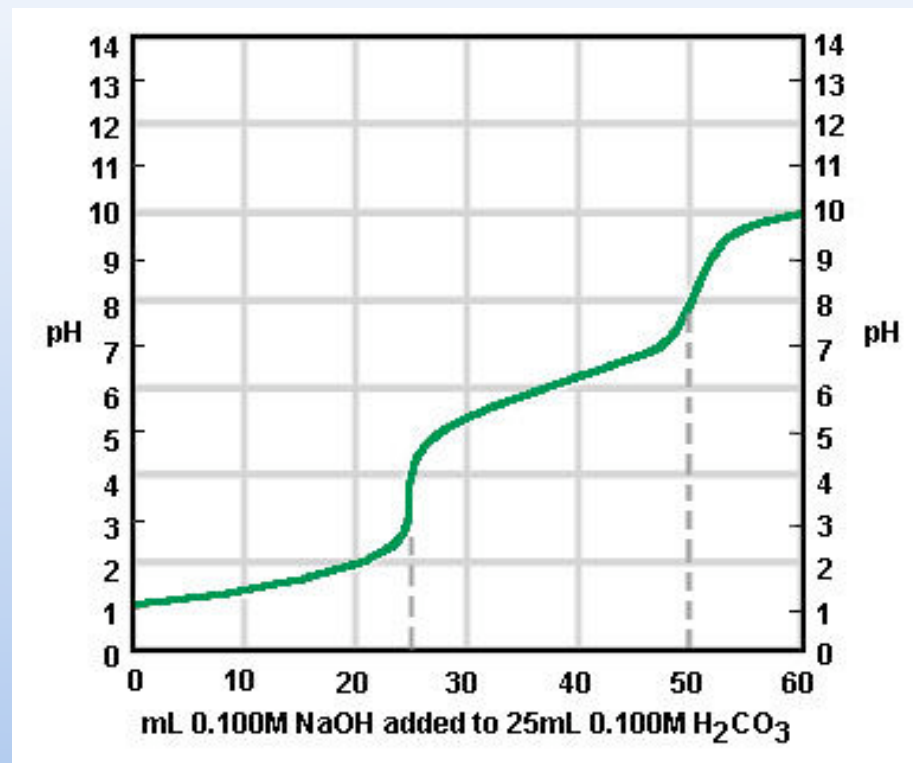
$$K_{a2} = \frac{[\text{H}^+][\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]} \quad K_{a3} = \frac{[\text{H}^+][\text{A}^{3-}]}{[\text{HA}^{2-}]}$$

$$[\text{HA}^{2-}] = \frac{[\text{H}^+][\text{A}^{3-}]}{K_{a3}} \quad K_{a2} = \frac{[\text{H}^+][\text{H}^+][\text{A}^{3-}]}{[\text{H}_2\text{A}^-] K_{a3}}$$

assume the
small change in
forming both acid
and base

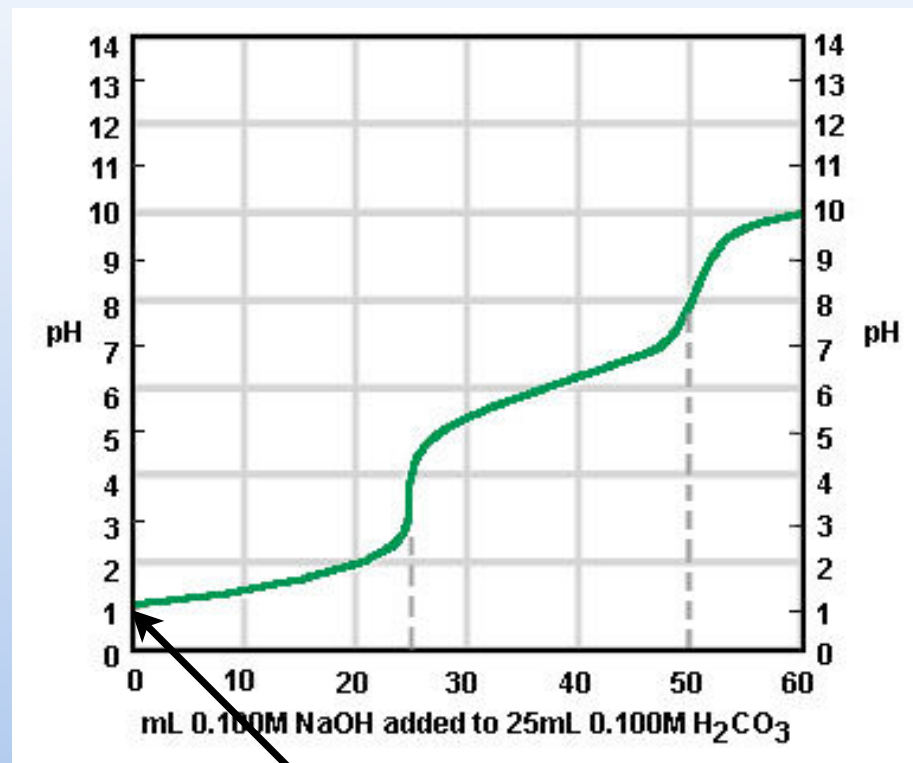
$$[\text{H}^+] = \sqrt{K_{a2} \times K_{a3}}$$

Titration of a polyprotic



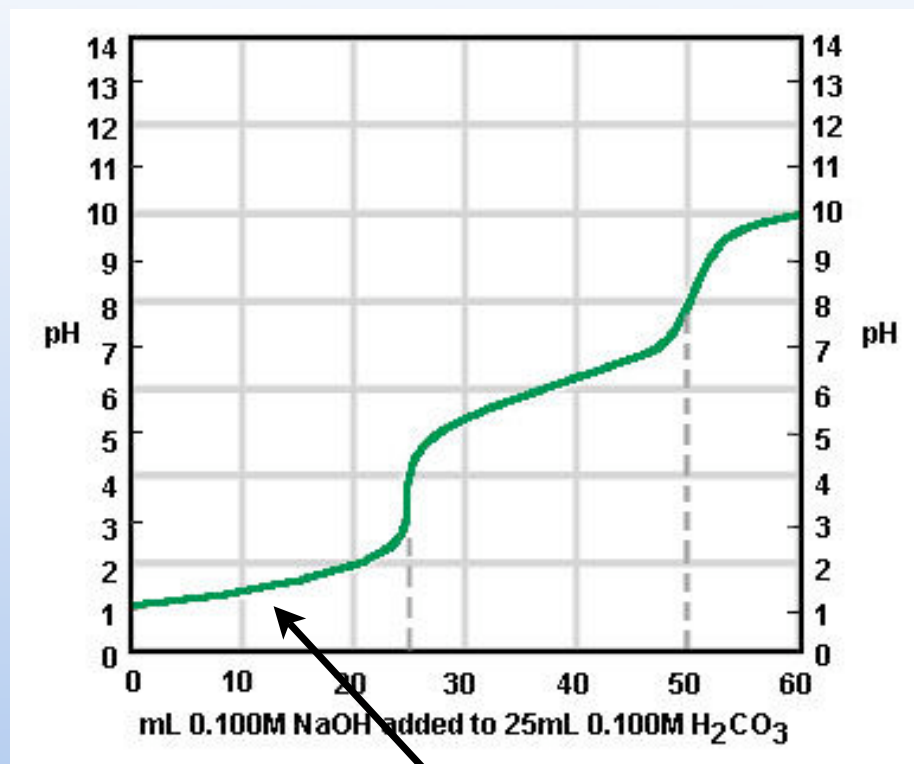
Two equivalence
points
Diprotic H₂A

Titration of a polyprotic



all H₂A weak acid

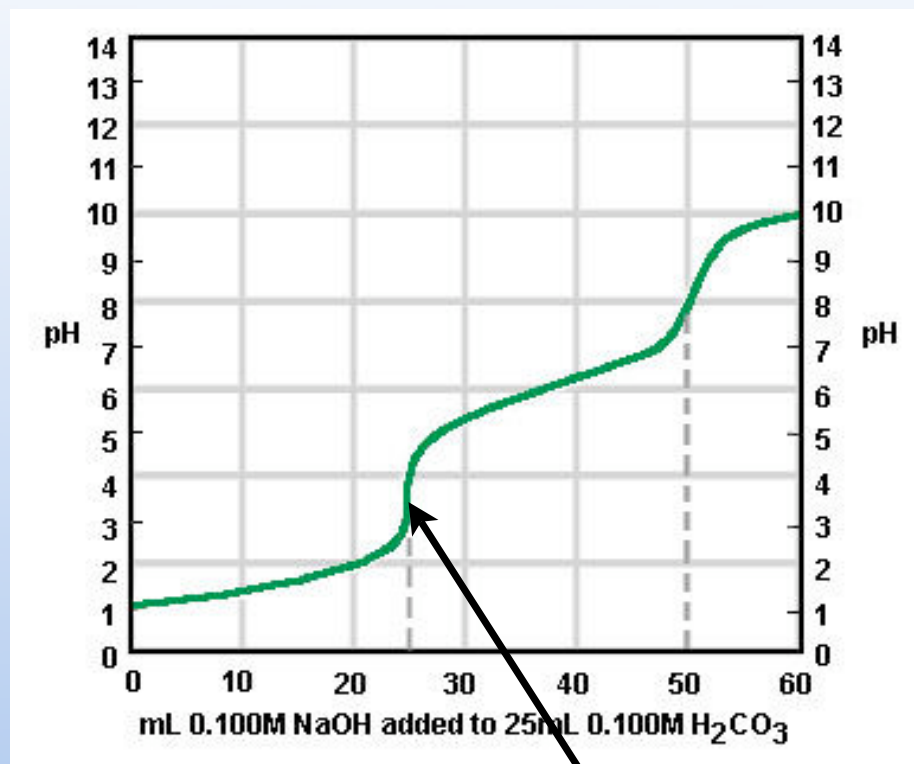
Titration of a polyprotic



OH⁻ neutralizes some
H₂A to HA⁻
buffer around K_{a1}

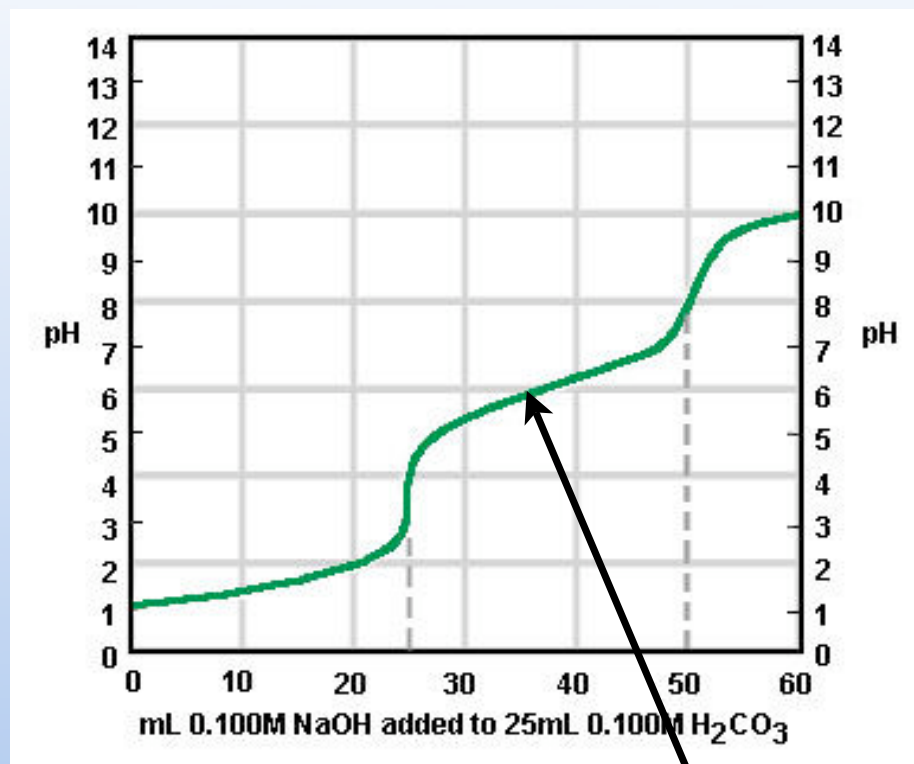
halfway
to equivalence point I
pH = pK_{a1}

Titration of a polyprotic



equivalence point I
moles OH⁻ = moles H₂A
All H₂A converted to HA⁻

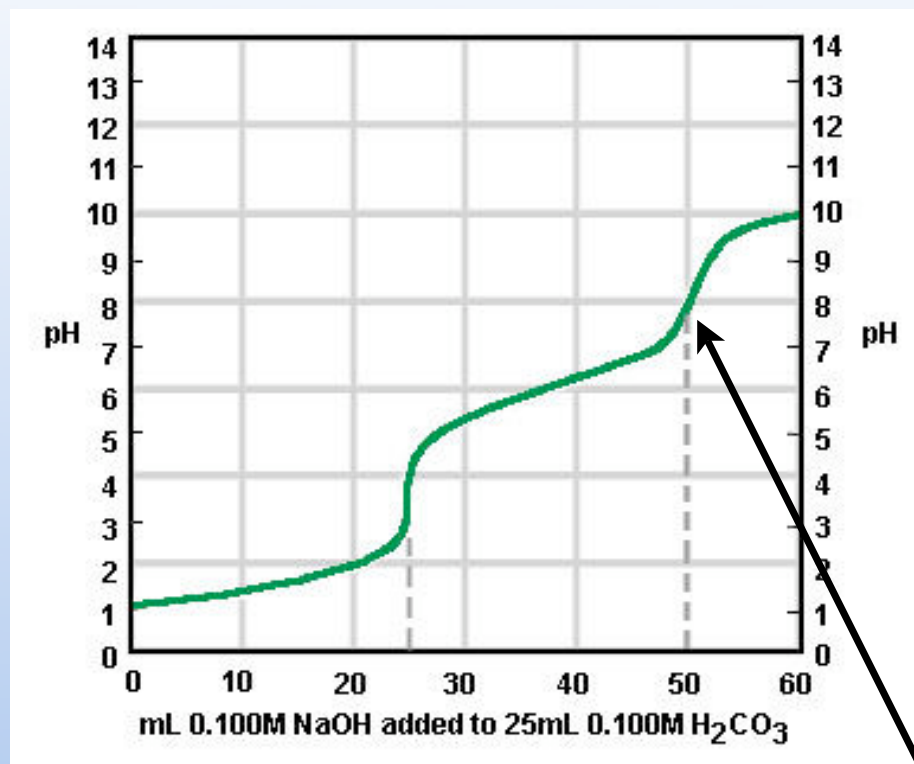
Titration of a polyprotic



halfway
to equivalence point I
 $\text{pH} = \text{pK}_{a2}$

OH^- neutralizes HA^- to A^{2-}
 HA^- and A^{2-}
buffer around K_{a2}

Titration of a polyprotic



equivalence point 2
moles $\text{OH}^- = 2 \times$ 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-}

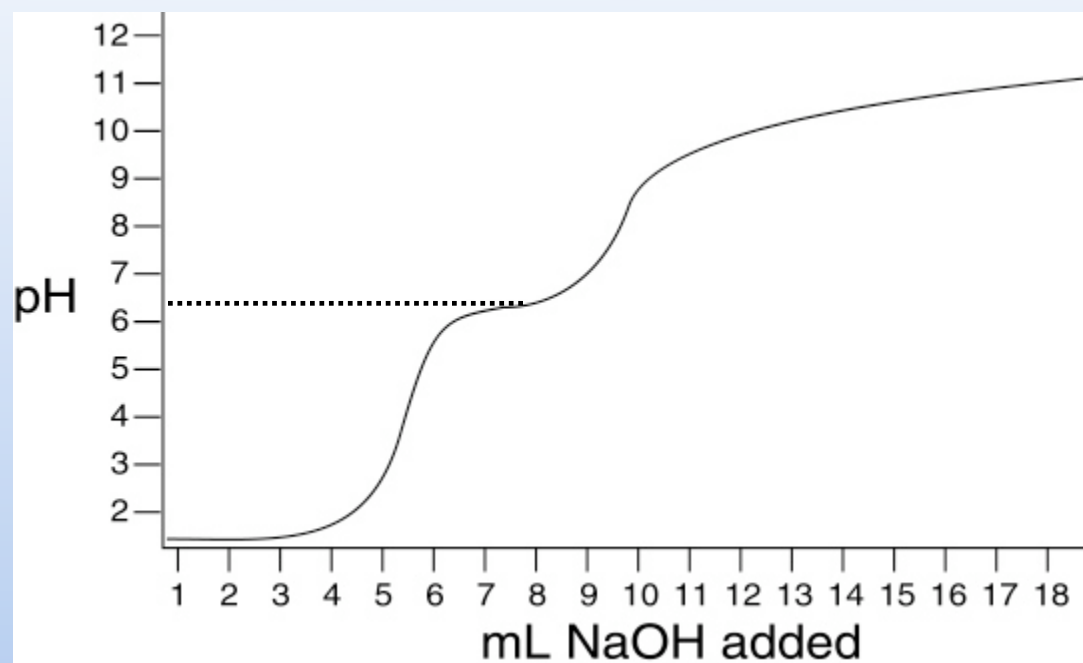
D. HPO_4^{2-}

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

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



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



at 1/2 equiv
 $\text{pH} = \text{pK}_a$
 $\text{pH} = 6.3$
 $\text{pK}_a = 6.3$
 $K_a = 5 \times 10^{-7}$



A. 1

B. 6.3

C. 5×10^{-6}

D. 5×10^{-7}