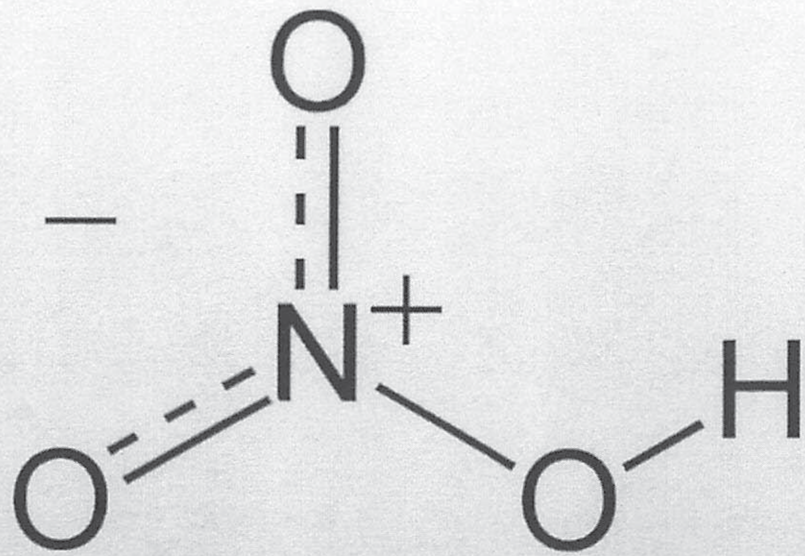
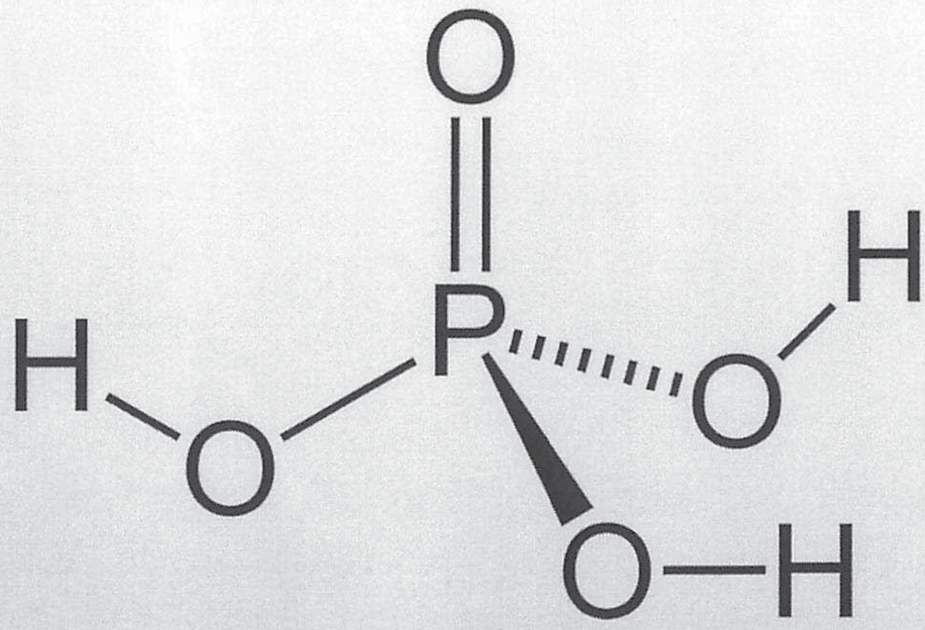
Polyprotic Acids

More than one acid/base group

Monoprotic Acid
Nitric Acid



Polyprotic Acid
Phosphoric Acid



Polyprotic Acids

Acids that have more than one proton to lose

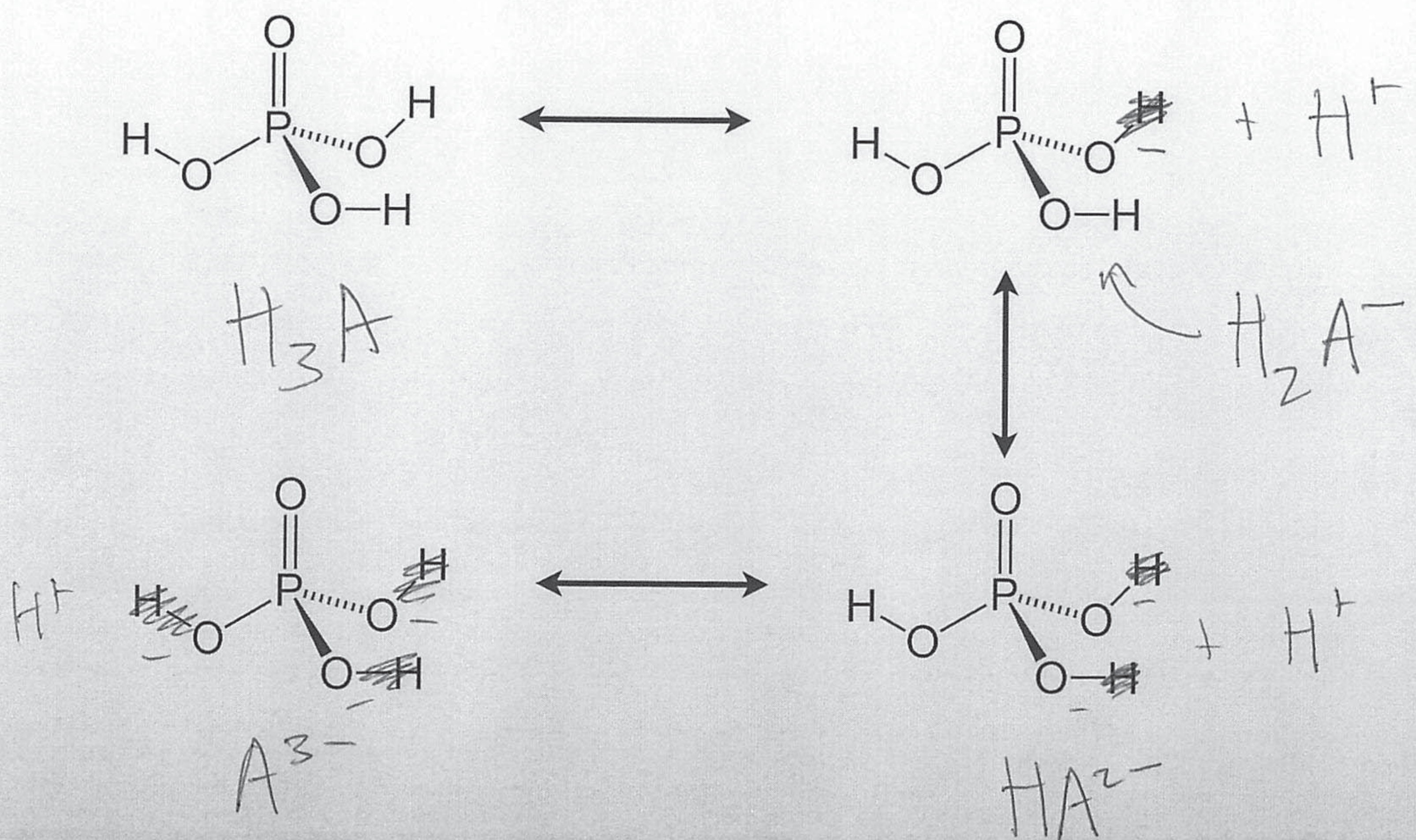
Now we need to keep track of all the "forms" of the acid

Monoprotic HA , A^-

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

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

Polyprotic Acid
Phosphoric Acid



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.

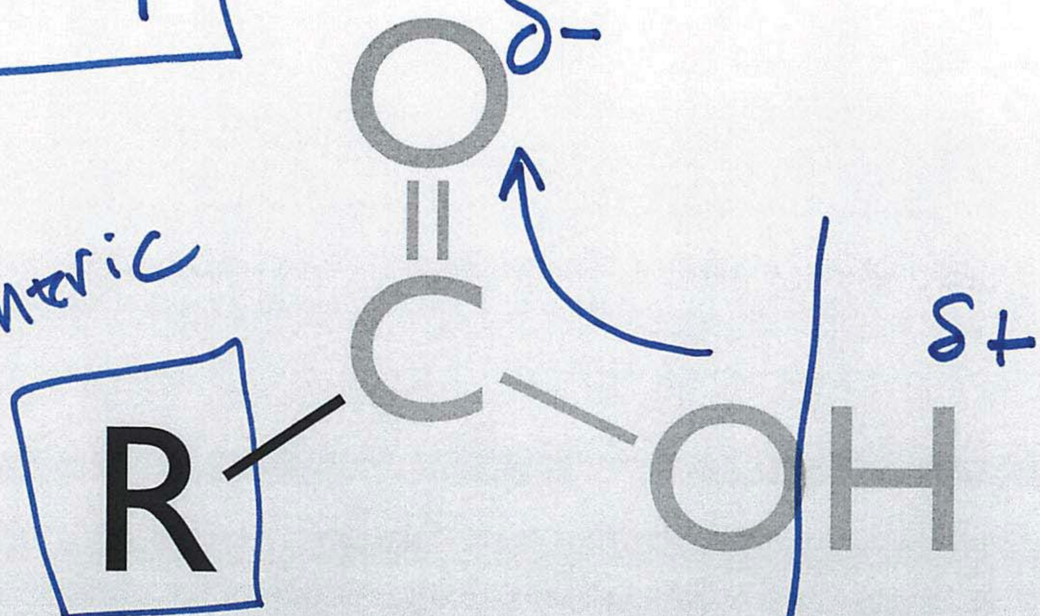
First figure out which ones will be in solution

Carboxylic Acid

$-COOH$

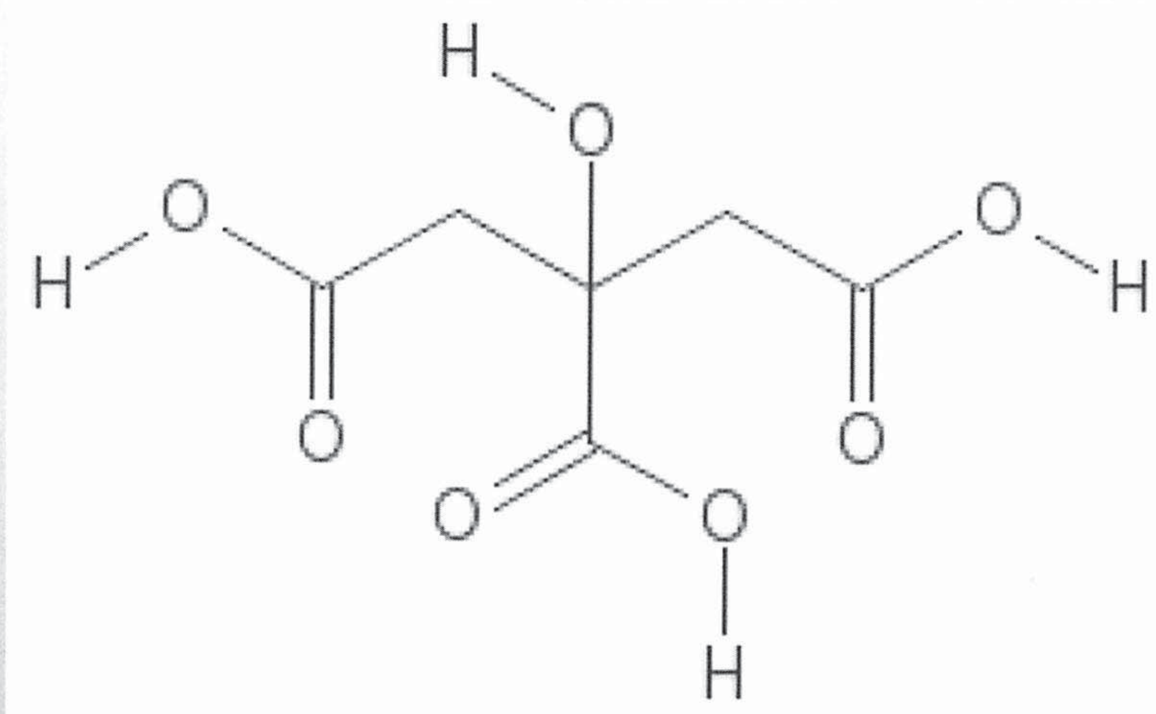
Common
Acetic Acid
(vinegar)

Generic

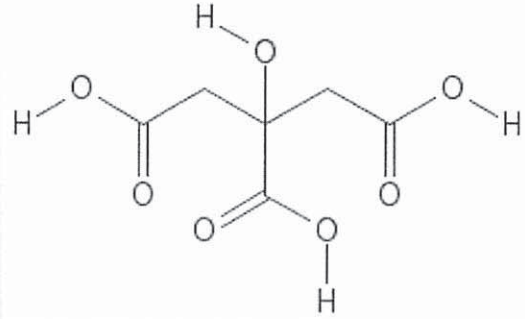


carbon double bonded to an oxygen
bonded to carbon on one side
OH on the other side

Citric Acid



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

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

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

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

Assuming that $[H^+] = .027$ what is the ratio of deprotonated to protonated for the second proton?

$$H_3A \rightarrow H^+ + H_2A^- \quad K_{a1}$$

$$H_2A^- \rightarrow H^+ + HA^{2-} \quad K_{a2}$$

$$\frac{[HA^{2-}]}{[H_2A^-]}$$

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

Assuming that $[H^+]$ =.027 what is the ratio of deprotonated to protonated for the second proton?

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

$H_2A^- \rightarrow H^+ + HA^{2-}$

Mostly H_3A tiny amount H_2A^- almost none HA^{2-}

A^{3-} inf. small.

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

Assuming that $[H^+] = .027$ what is the ratio of deprotonated to protonated for the second proton?

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

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}

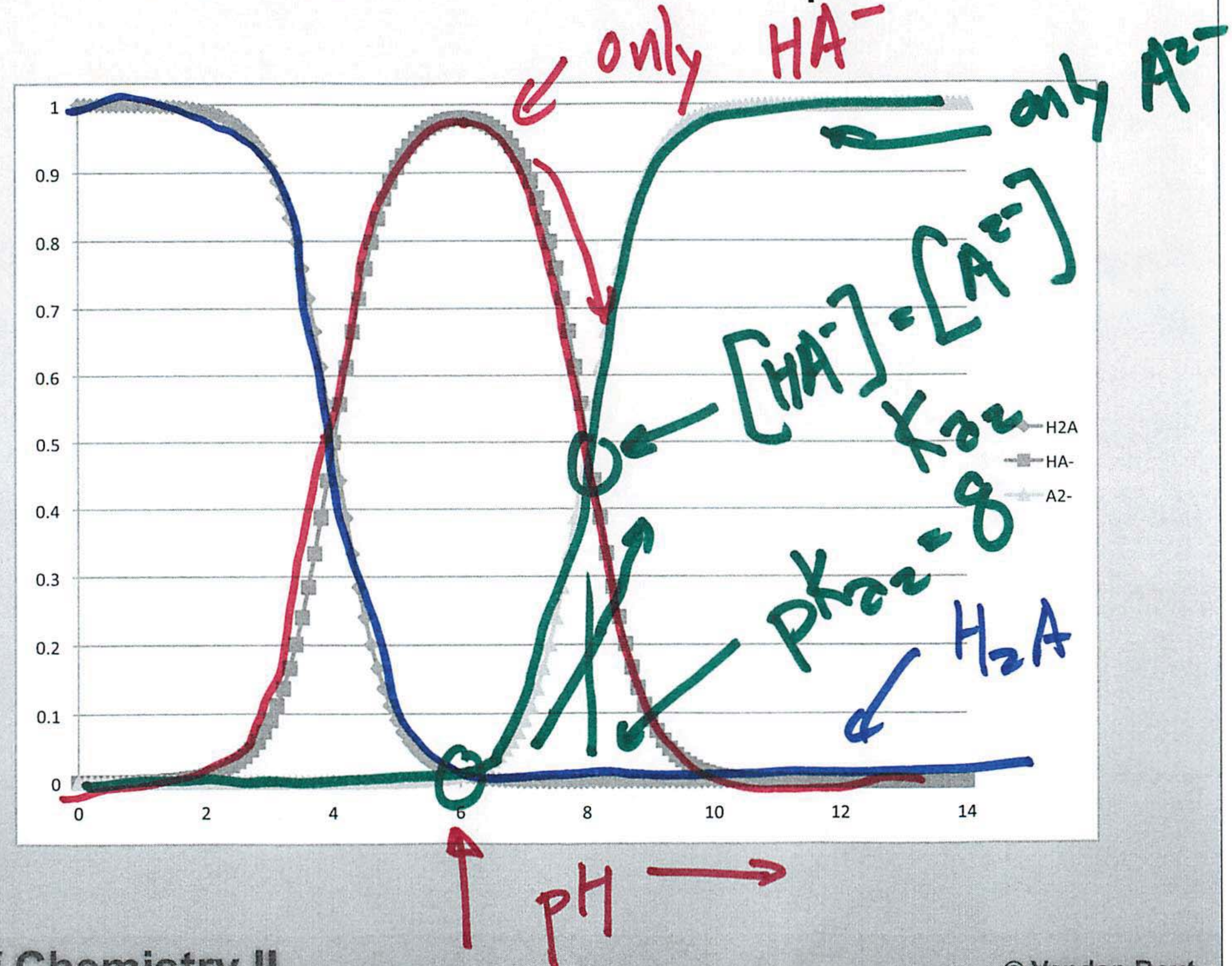
When will the other protons matter?

If we just want the pH of the solution, then it will be dominated by the first K_a

We need to consider the others if we are controlling the pH

What do I have in solution at different pH values?

% in each form



When do I care about the other protons?

When I neutralize the acid.

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

....

H_3A

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--}

$H_3A + OH^- \rightarrow H_2A^-$

H_3A	OH^-	H_2A^-
.05	.1	0
−.05	−.05	+.05
0	.05	.05

$H_2A^- + OH^- \rightarrow HA^{2-}$

H_2A^-	OH^-	HA^{2-}
.05	.05	0
−.05	−.05	+.05
0	0	+.05

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--}

What is the pH of a solution with 0.5 M Na_2HPO_4?

+2 2-

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

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

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

HA^{2-}

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

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

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

2 $H_2A^- \rightarrow H^+ + HA^{2-}$

3 $HA^{2-} \rightarrow H^+ + A^{3-}$

Species that are both acids and bases are "Amphiprotic"

Amphoteric

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

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

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

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

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

solve

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

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

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

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

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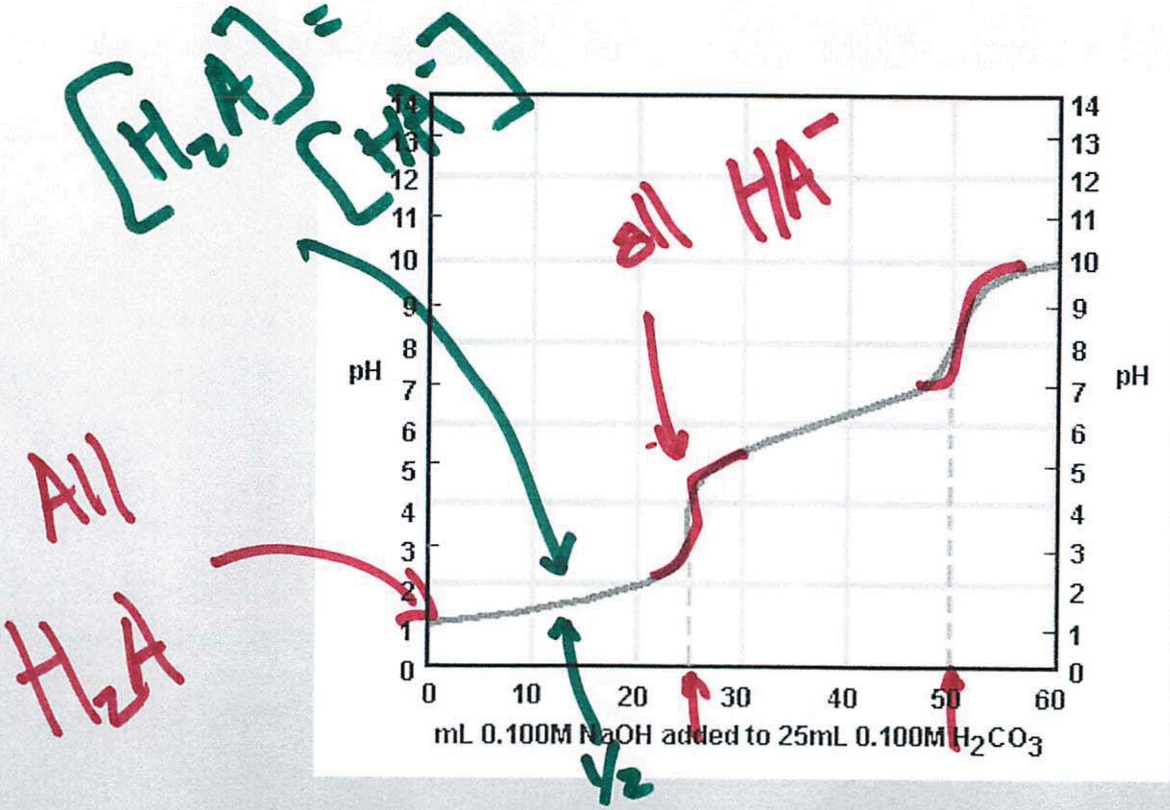
$$K_{a2} = \frac{[H^+][HA^{2-}]}{[H_2A^-]} \qquad K_{a3} = \frac{[H^+][A^{3-}]}{[HA^{2-}]}$$

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

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

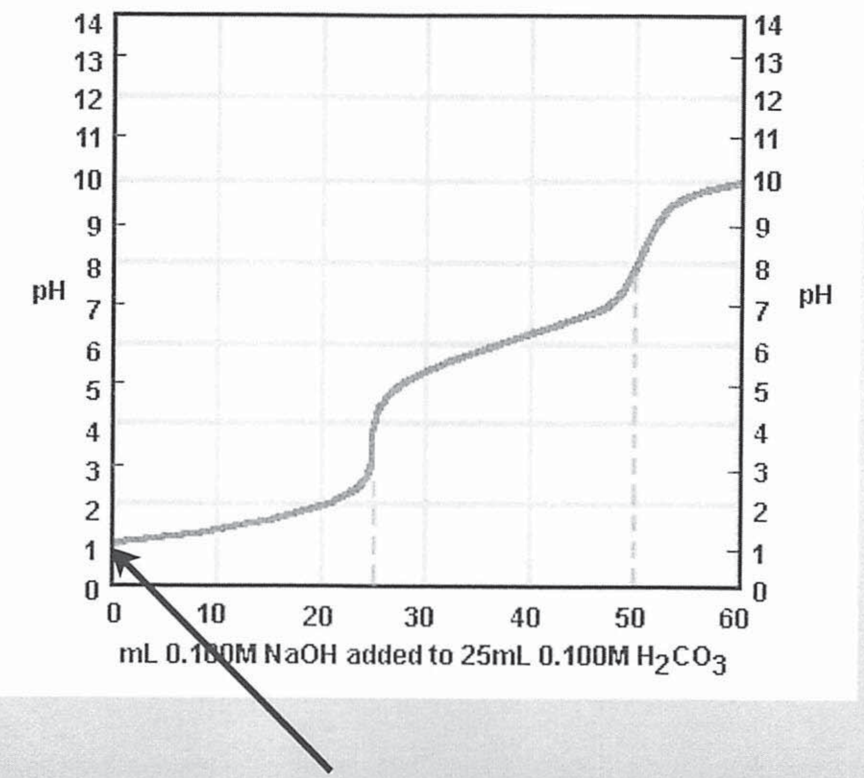
Titration of a polyprotic



Two equivalence points ← Two proton

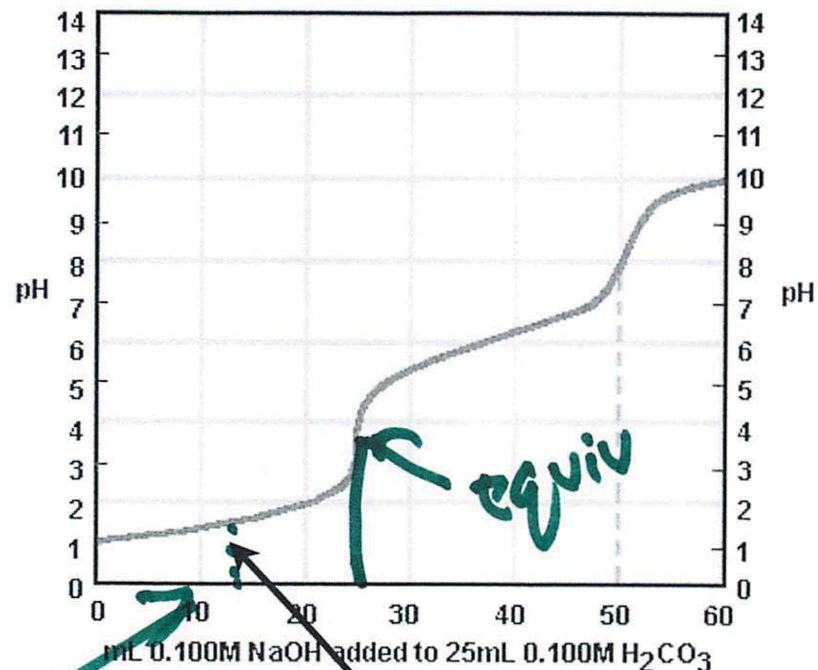
Diprotic H_2A

Titration of a polyprotic



all H_2A weak acid

Titration of a polyprotic



½ equiv.

OH$^-$ neutralizes some

H_2A to HA^-

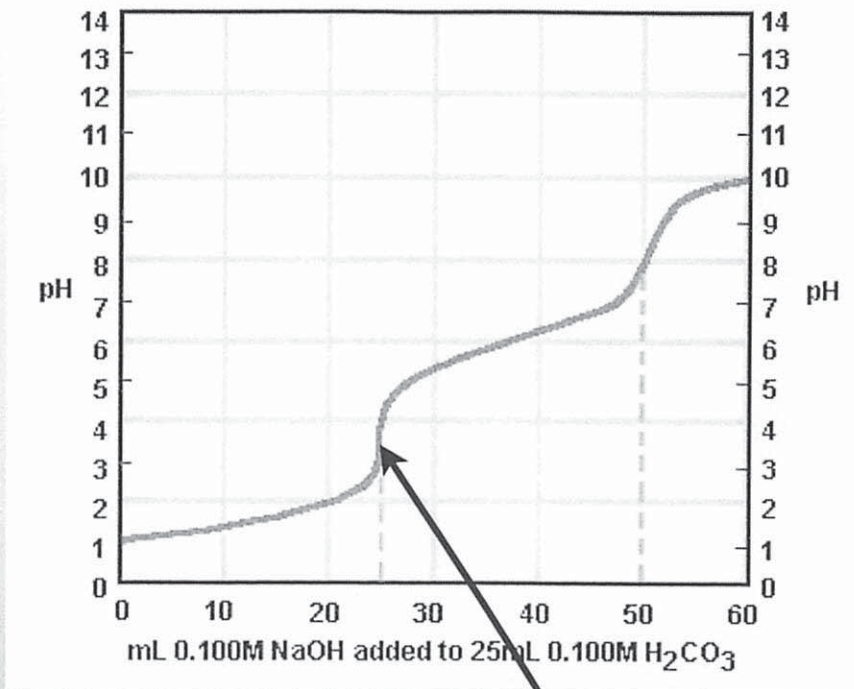
buffer around K_{a1}

halfway

to equivalence point 1

$pH = pK_{a1}$

Titration of a polyprotic

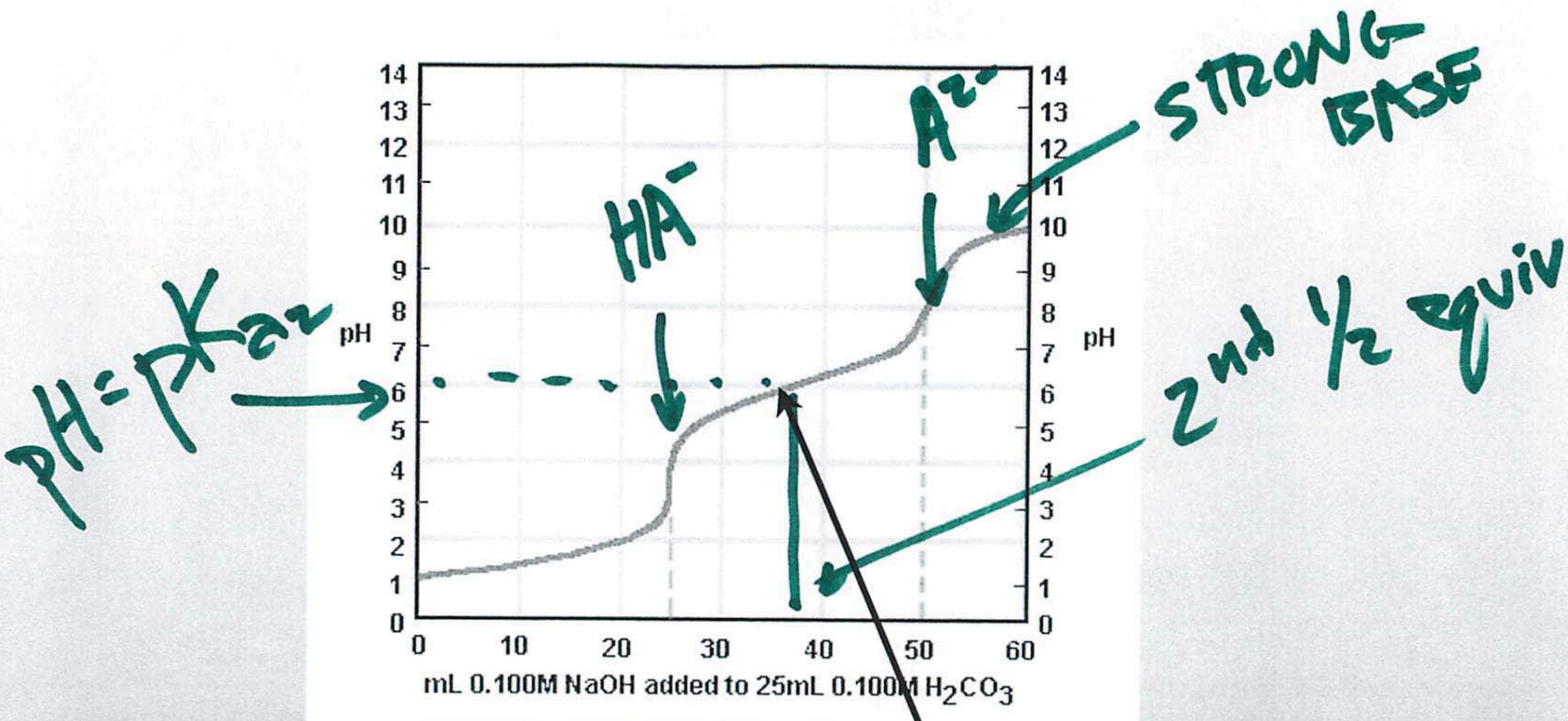


equivalence point 1

moles OH^- = moles H_2A

All H_2A converted to HA^-

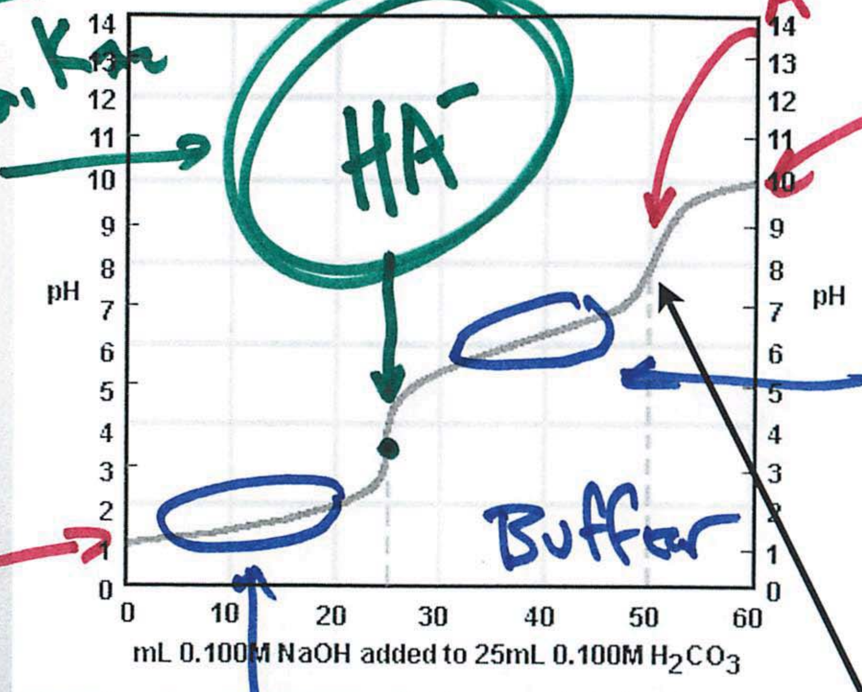
Titration of a polyprotic



halfway
to equivalence point # 2
$pH = pK_{a2}$

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

Titration of a polyprotic



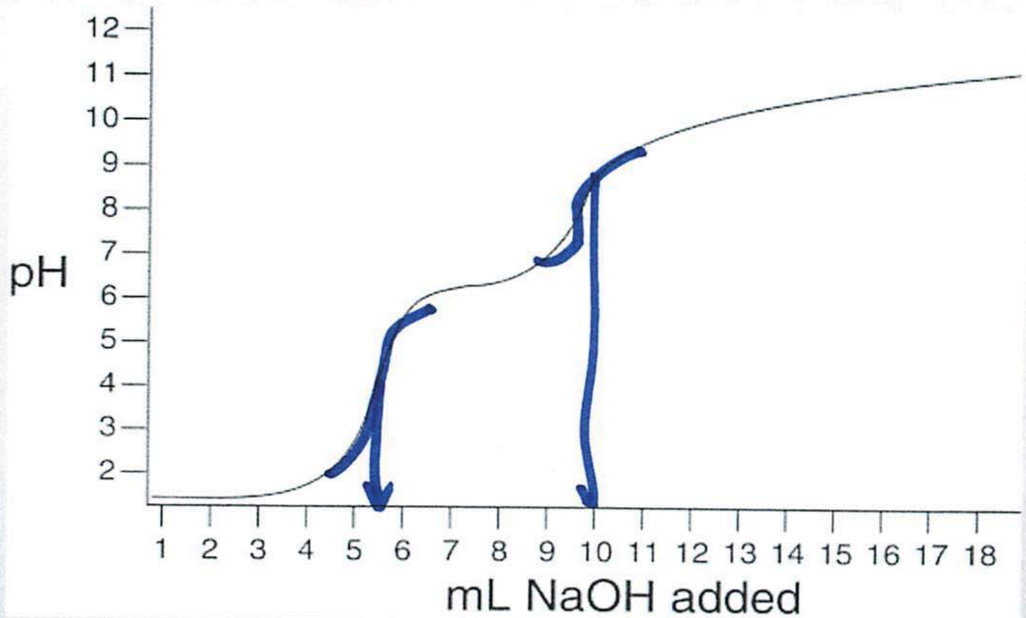
equivalence point 2

moles OH^- = 2 x moles H_2A

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

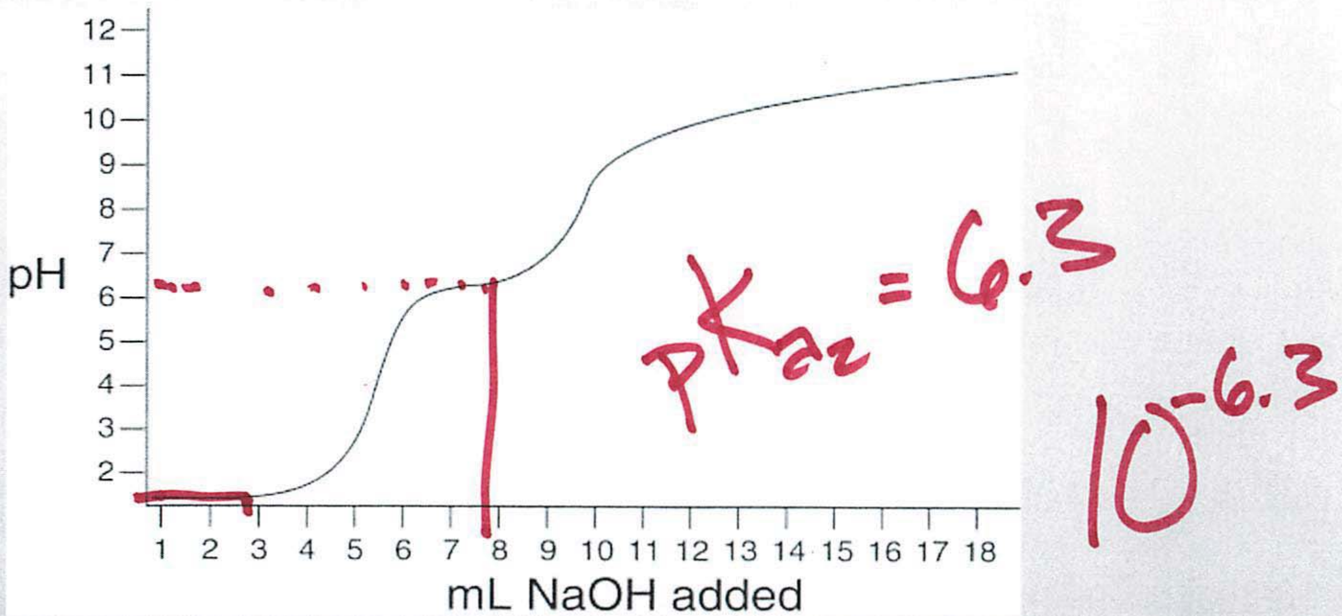
now weak base A^{2-}

How many equivalence points are in this titration?



A. 1 B. 2 C. 3 D. 4

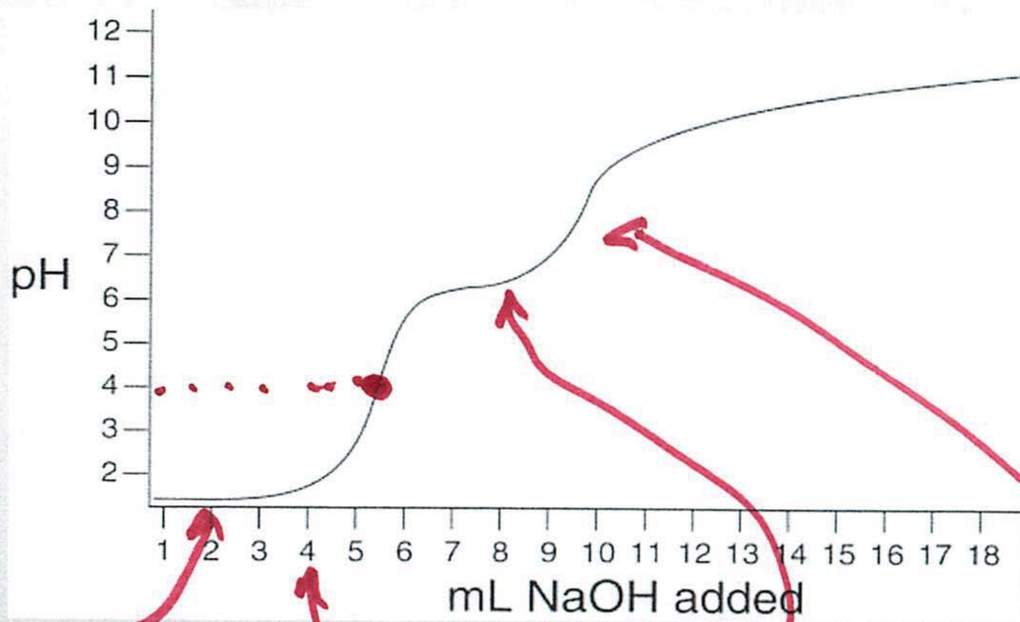
Given the following curve estimate K_{a2} for this unknown acid



A. 10^{-10} B. 10^{-4} C. 9×10^{-6} D. 5×10^{-7}

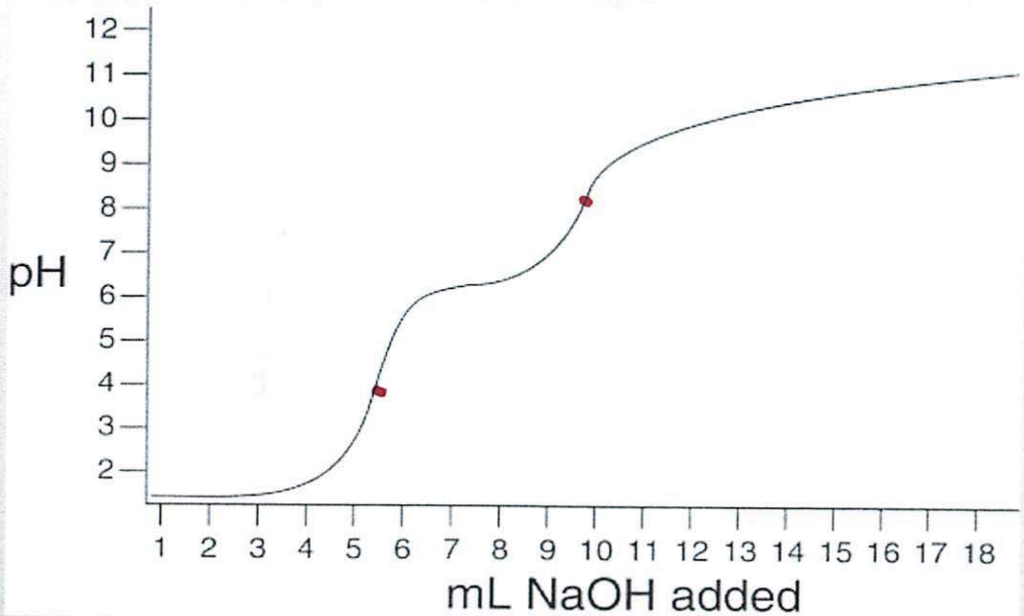
10^{-5}

What is(are) the dominate species in the solution at pH 4?



A. H_2A, HA^- B. HA^- C. HA^-, A^{2-} D. A^{2-}

How many many protons does this acid have?



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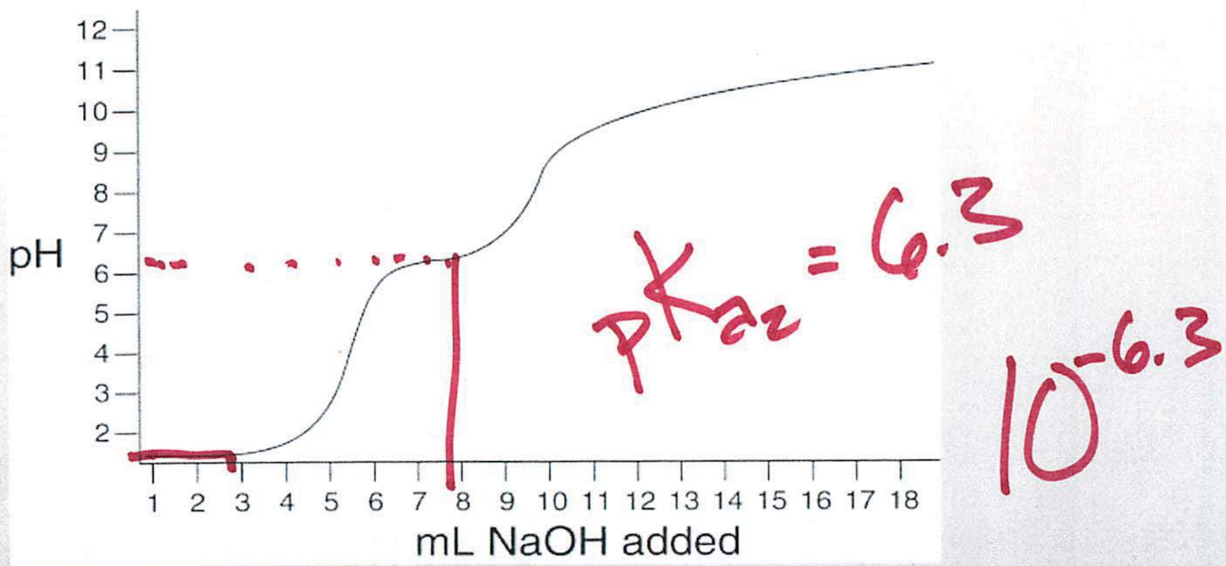

A. 10^{-10} B. 10^{-4} C. 9×10^{-6} D. 5×10^{-7}

10^{-5}