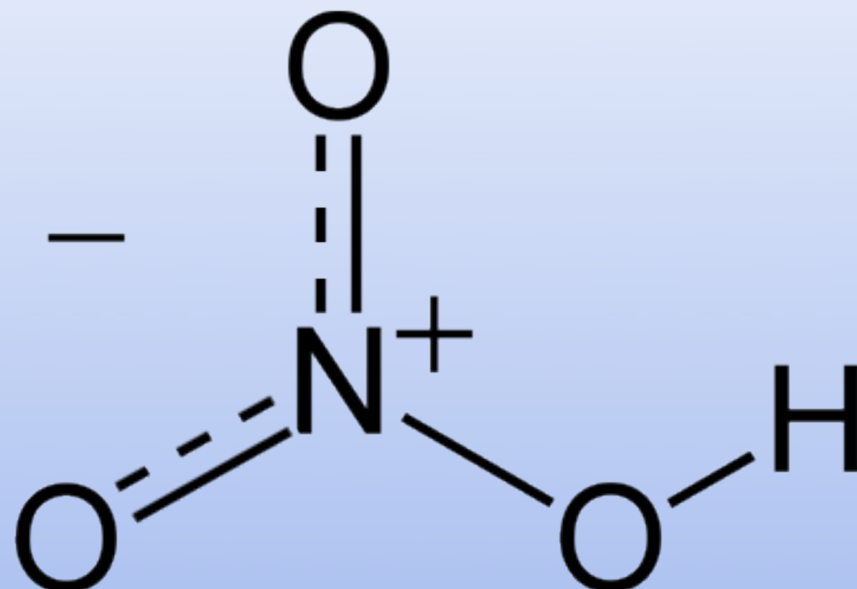
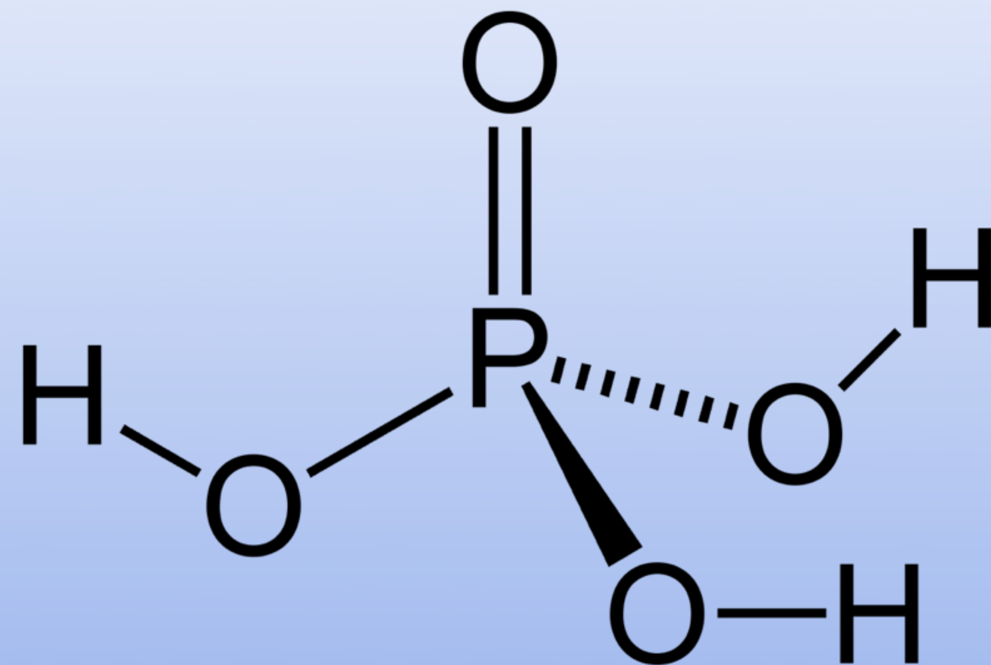
Polyprotic Acids

More than one acid/base group

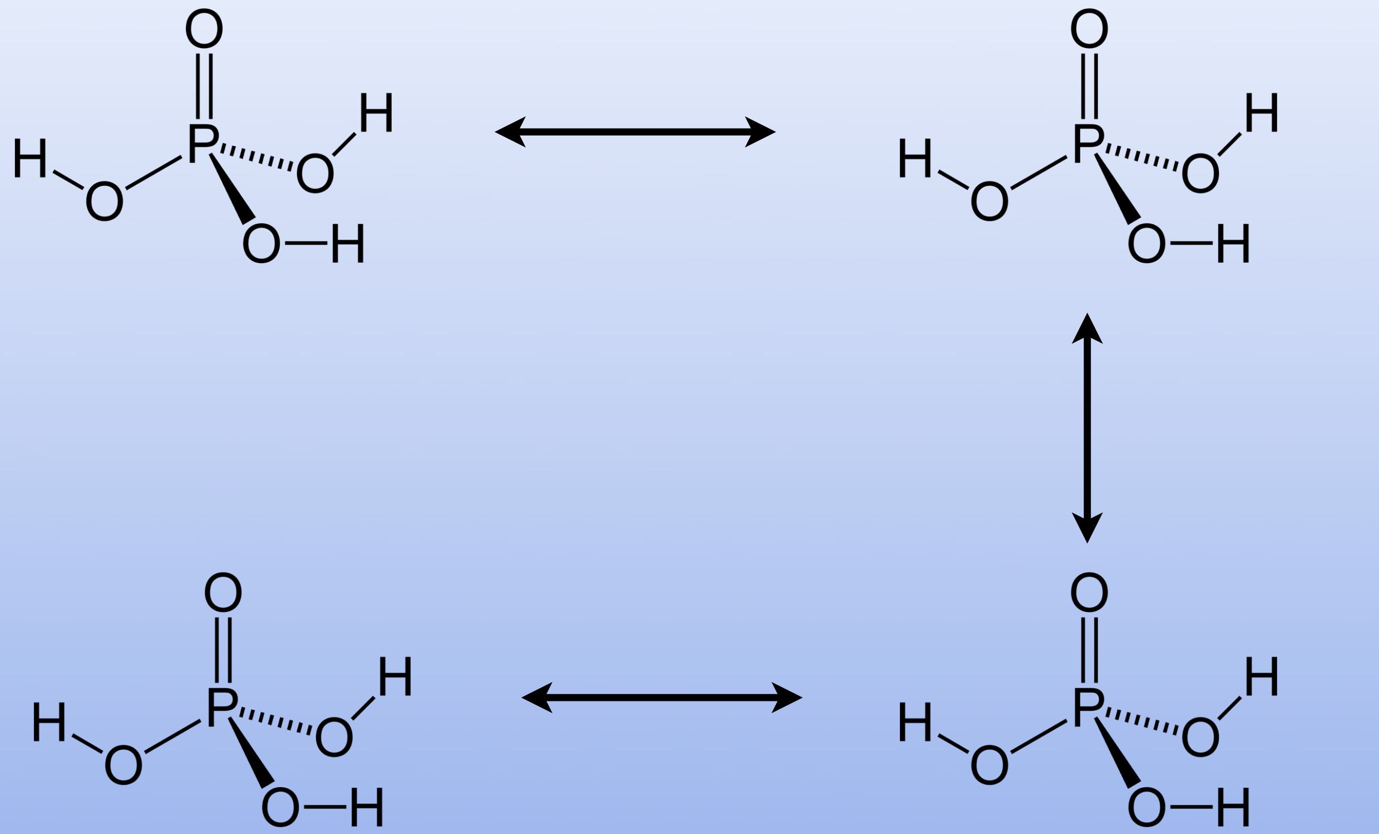
Monoprotic Acid
Nitric Acid



Polyprotic Acid
Phosphoric Acid



Polyprotic Acid
Phosphoric Acid



Polyprotic Acids

Acids that have more than one proton to lose

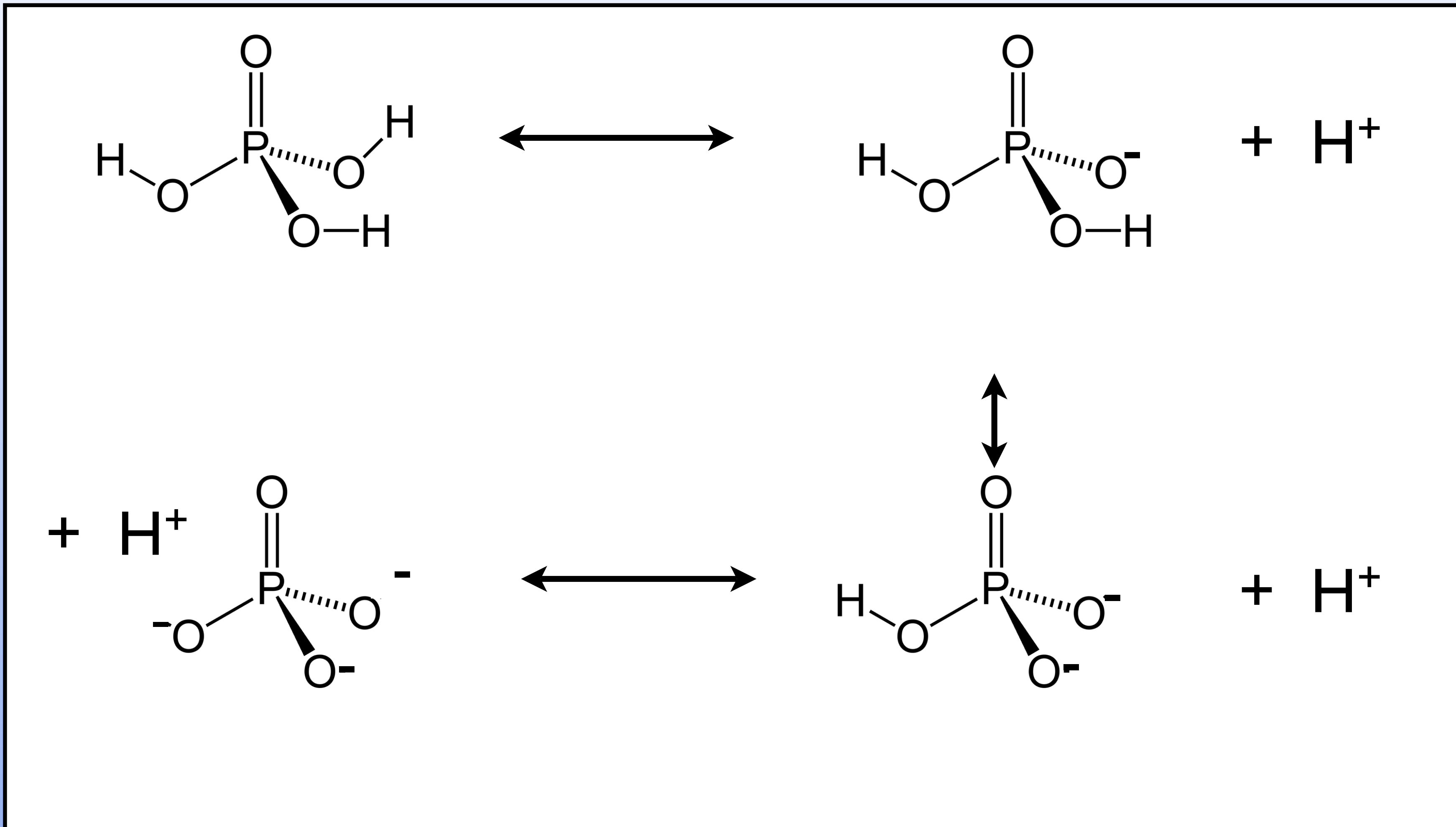
Now we need to keep track of all the "forms" of the acid

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!

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

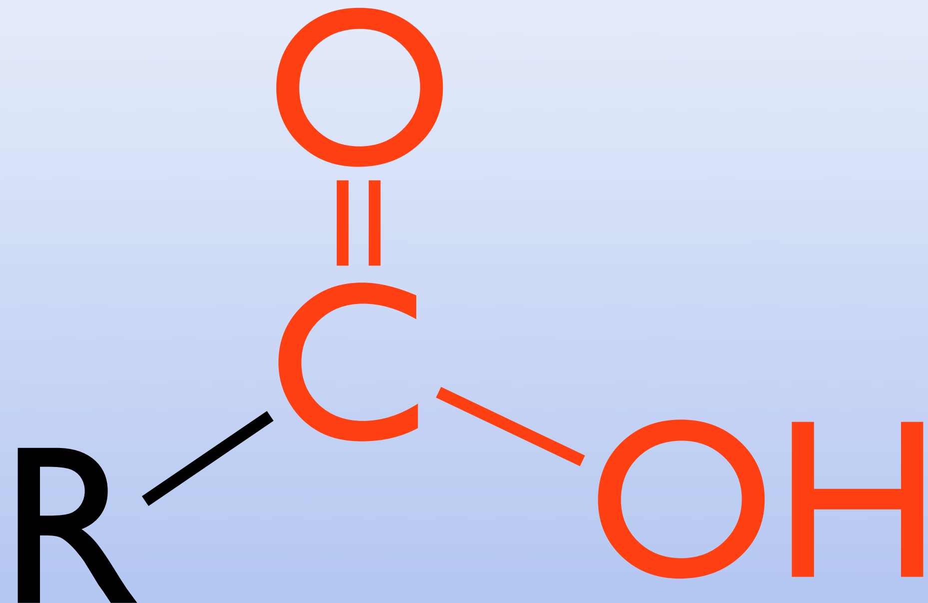
$$HA^-(aq) \longleftrightarrow H^+(aq) + A^{2-}(aq) \qquad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

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

First figure out which ones will be in solution

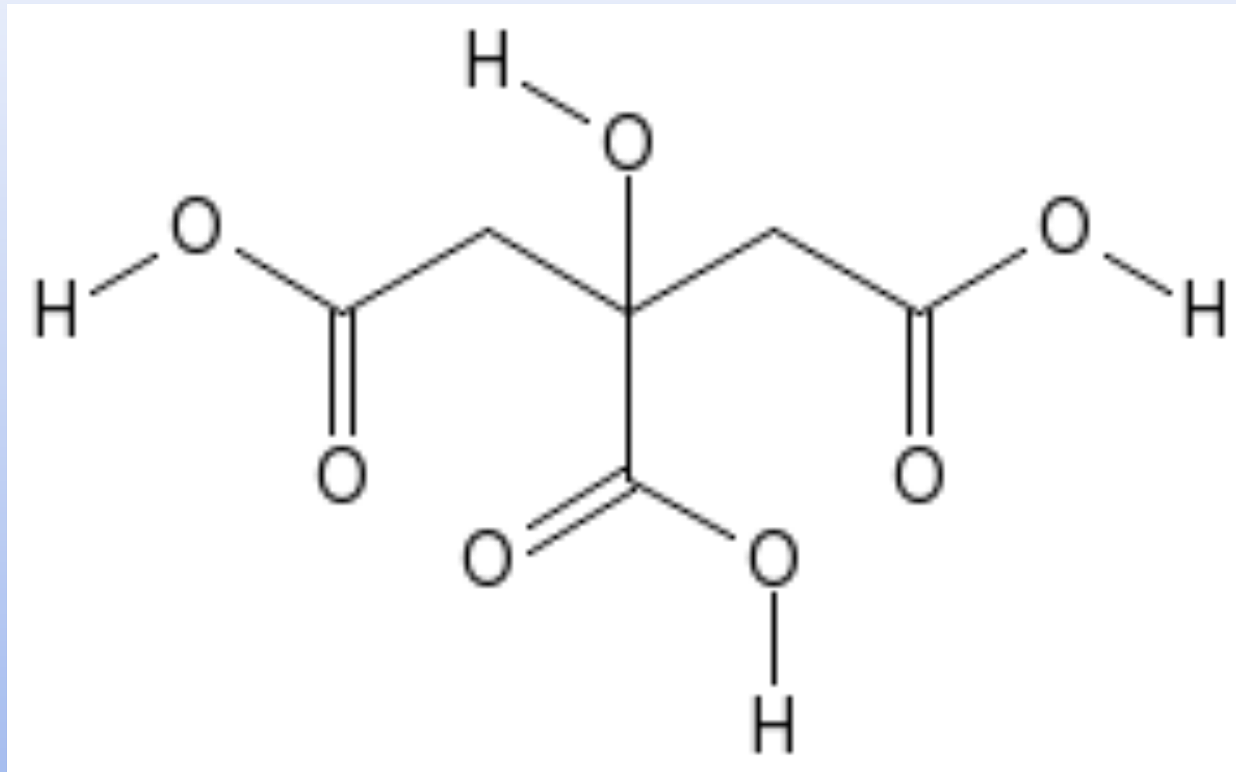
Carboxylic Acid

Common
Acetic Acid
(vinegar)

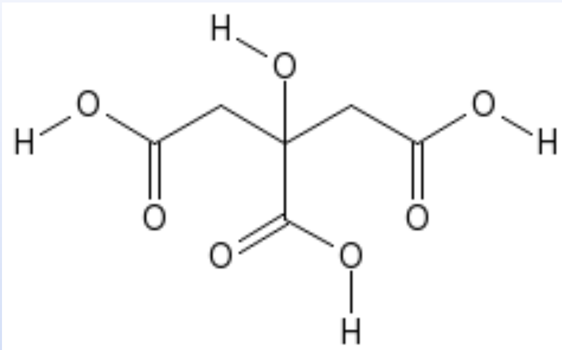


carbon double bonded to an oxygen
bonded to carbon on one side
OH on the other side

Citric Acid



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?

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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

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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}

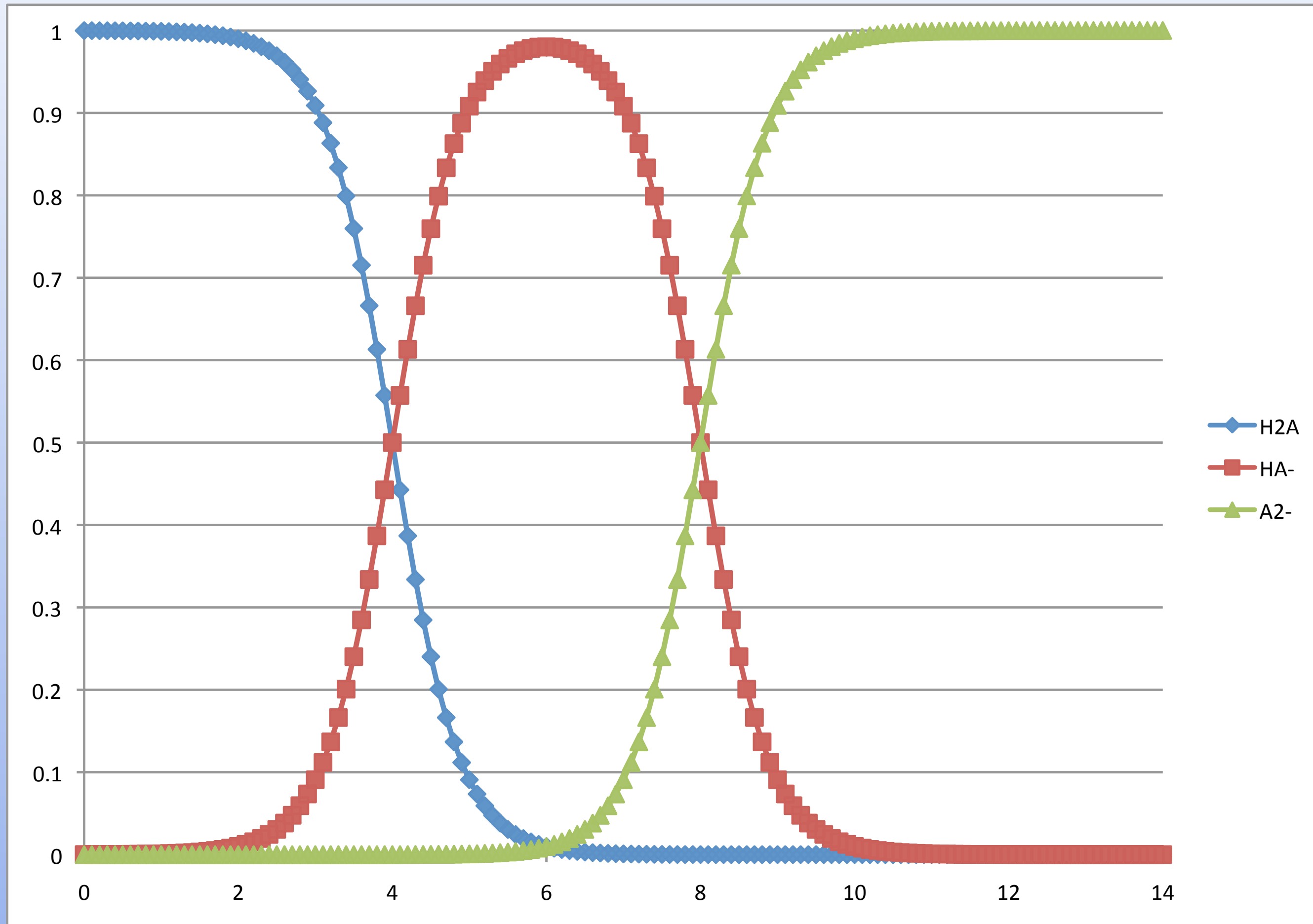
When will the other protons matter?

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



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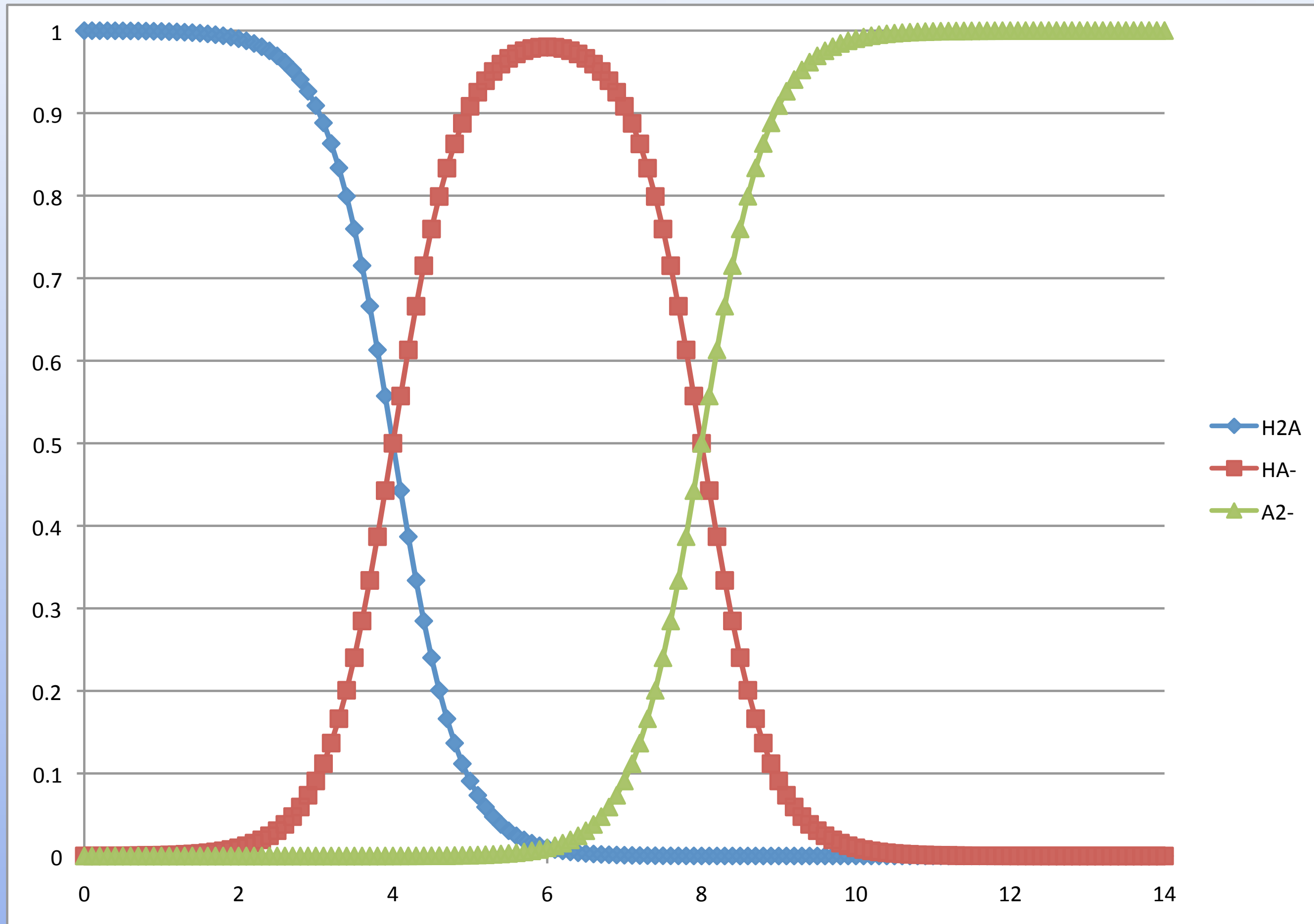

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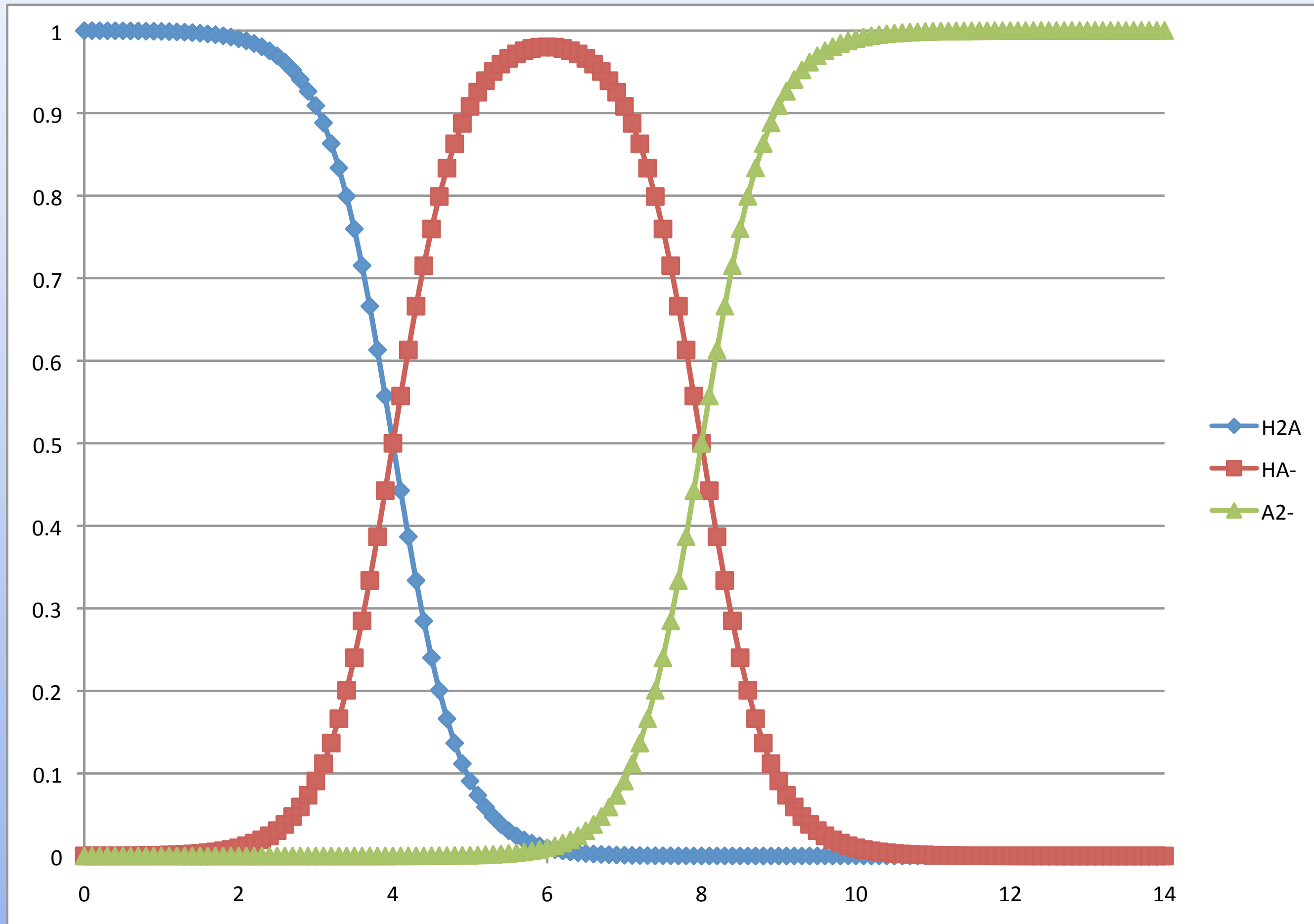

When do I care about the other protons?

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?

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?

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

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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 $H_2PO_4^-$

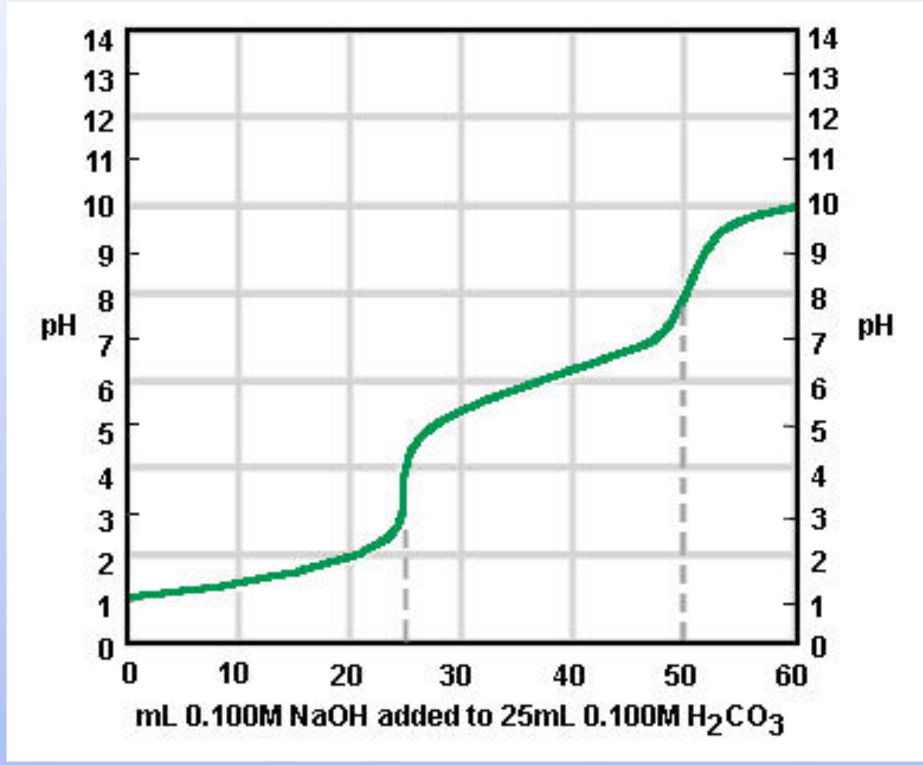
B. $H_2PO_4^-$

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

D. HPO_4^{2-}

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

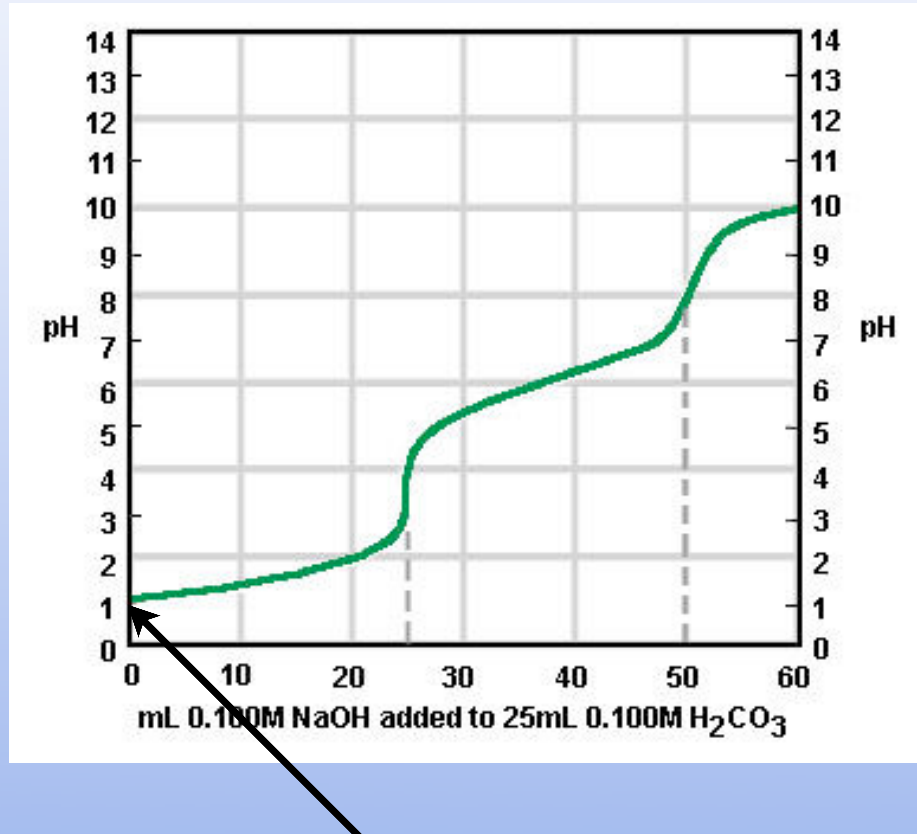
Titration of a polyprotic



Two equivalence points

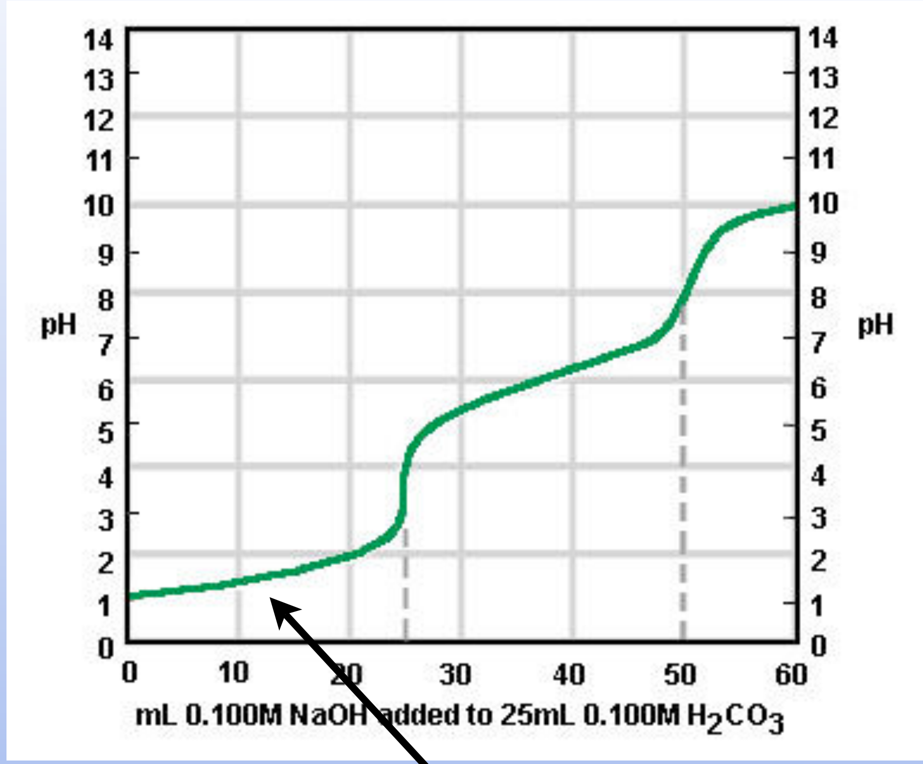
Diprotic H_2A

Titration of a polyprotic



all H_2A weak acid

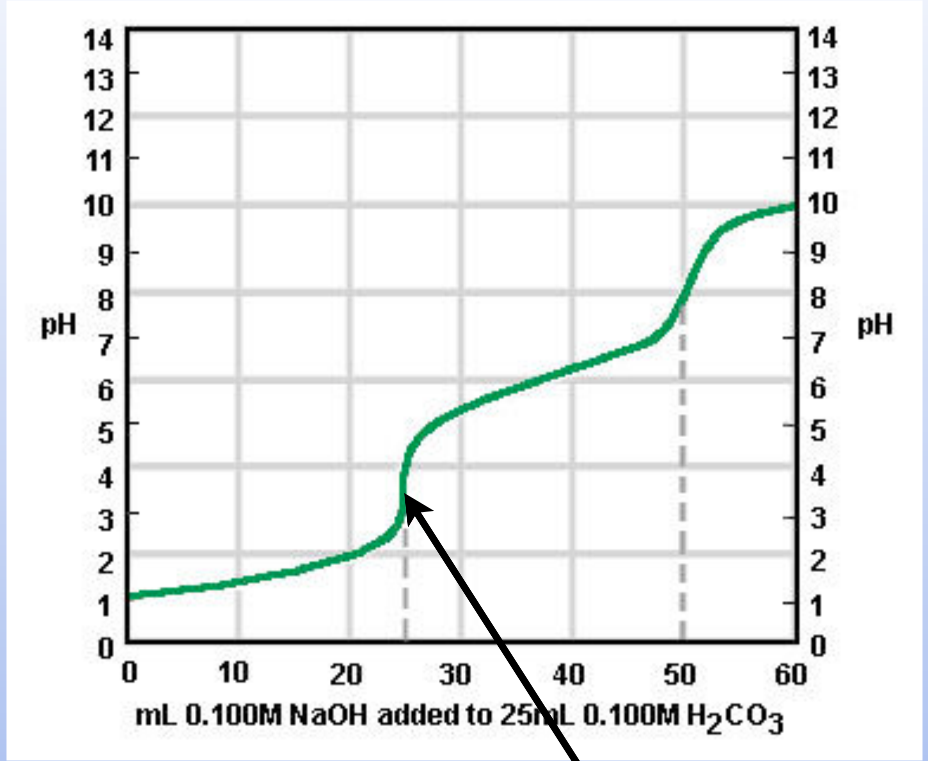
Titration of a polyprotic



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

halfway
to equivalence point 1
pH = pK_{a1}

Titration of a polyprotic

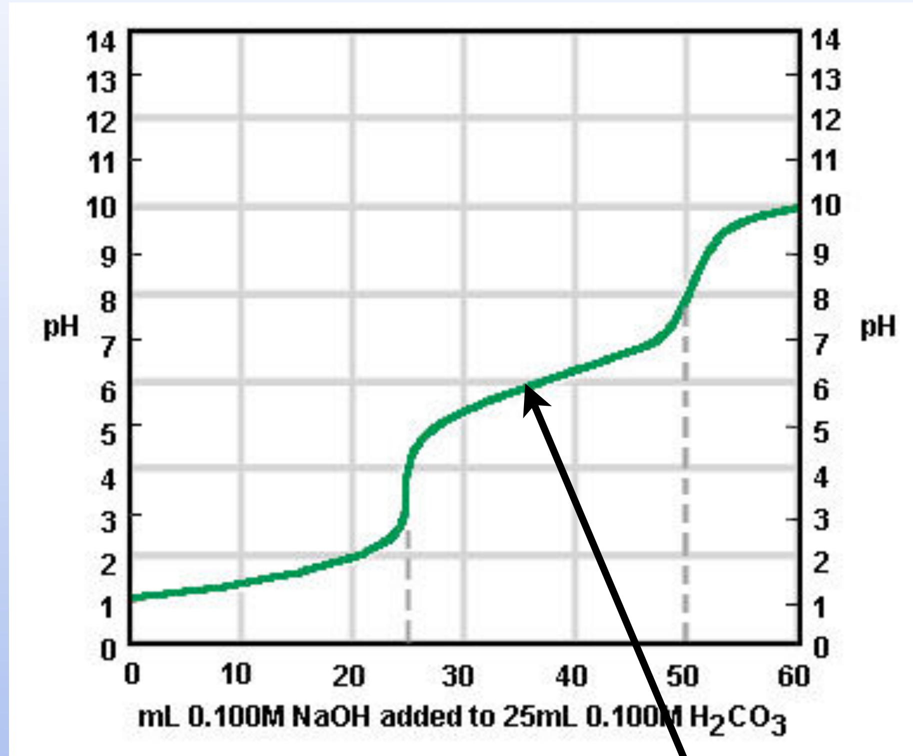


equivalence point 1

moles OH^- = moles H_2A

All H_2A converted to HA^-

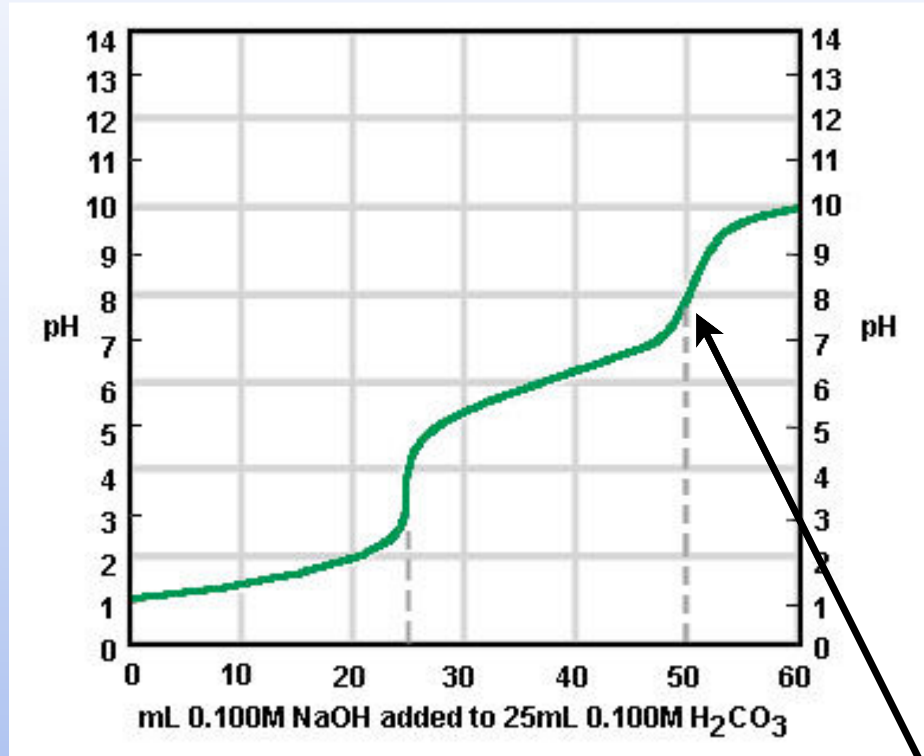
Titration of a polyprotic



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

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

Titration of a polyprotic



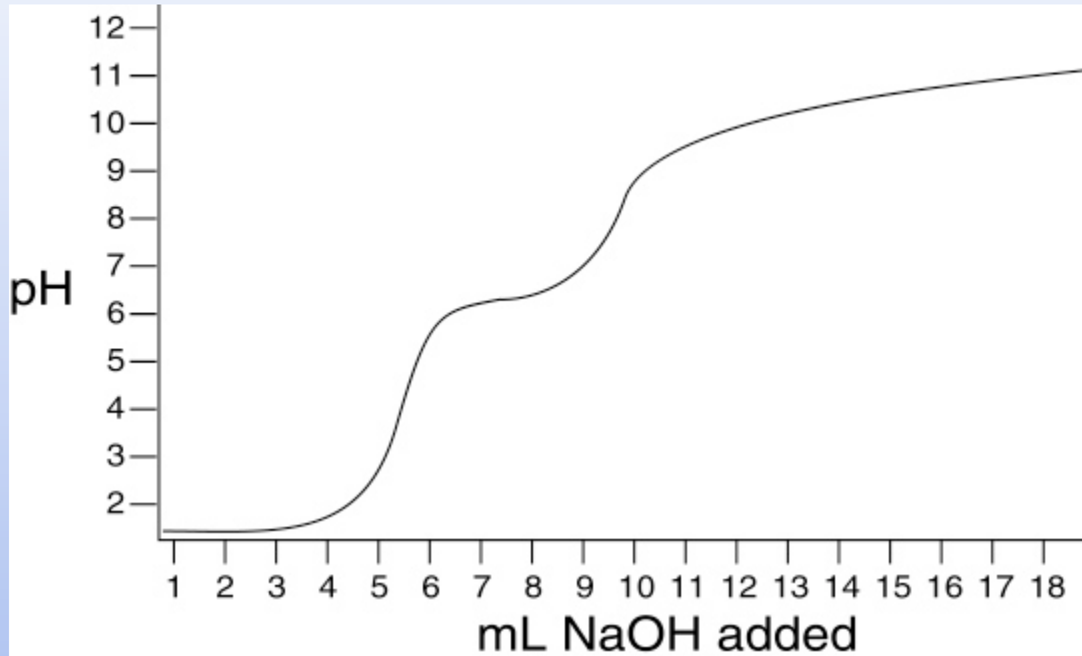
equivalence point 2

moles OH^- = 2 x moles H_2A

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

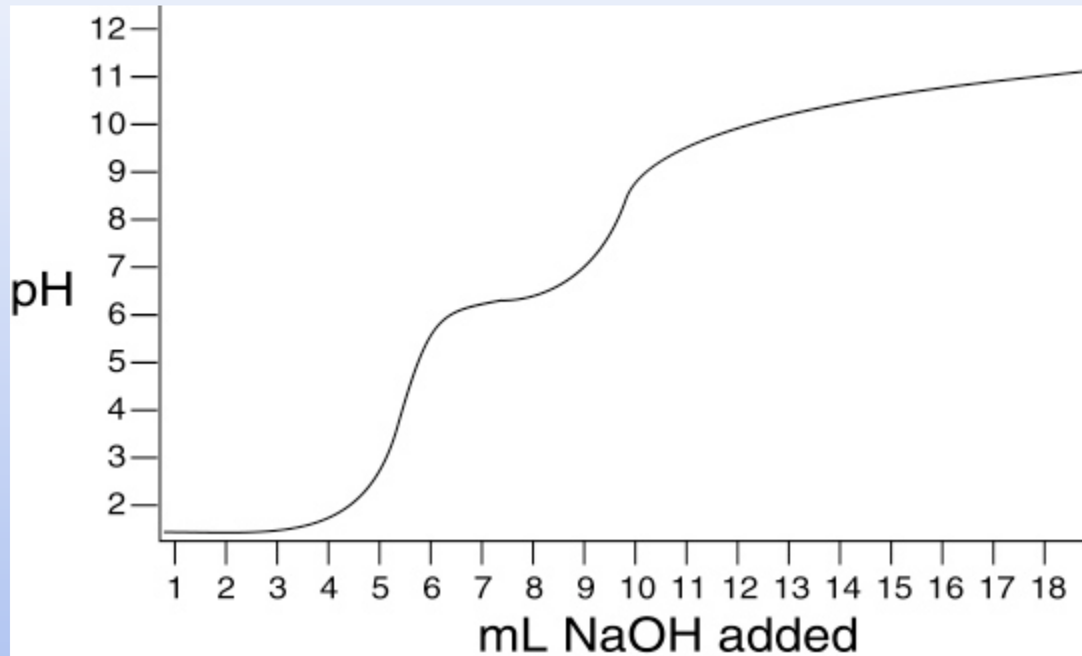
now weak base A^{2-}

How many equivalence points are in this titration?



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

How many many protons does this acid have?



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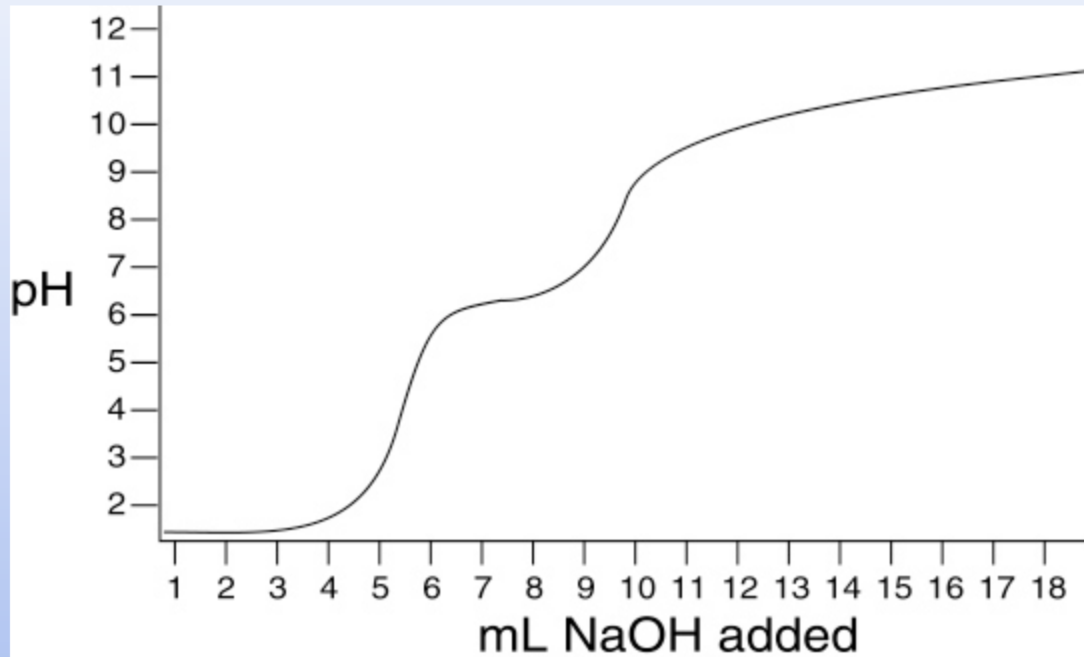
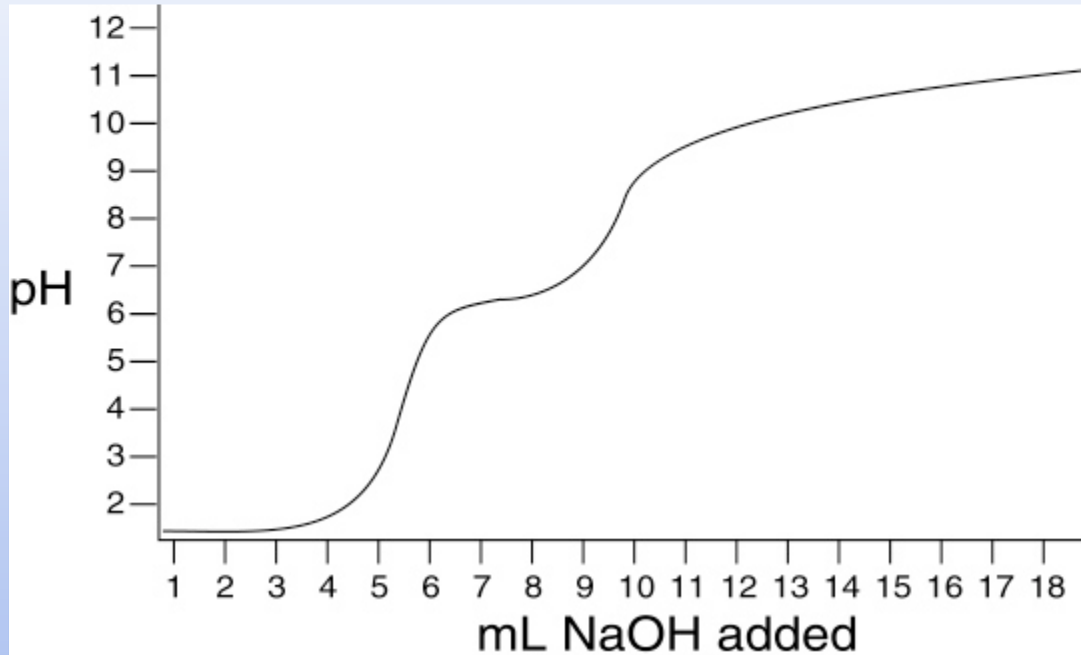


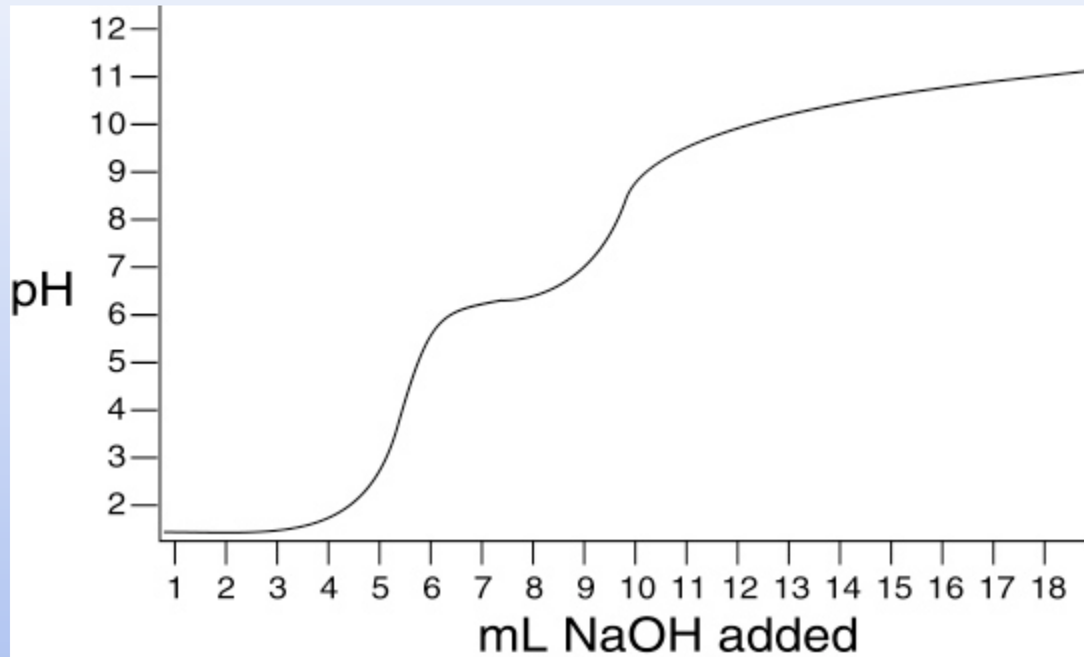
A. 1 B. 2 C. 3 D. 4

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-}

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

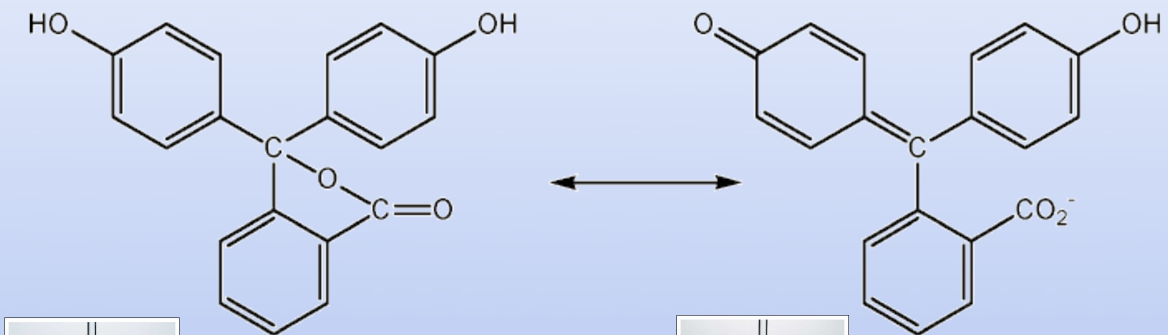


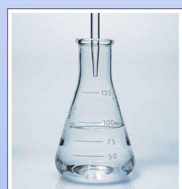
A. 10^{-10} B. 10^{-4} C. 9×10^{-6} D. 5×10^{-7}

Thinking about acid/base chemistry

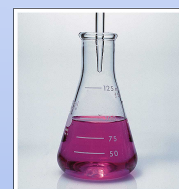
Phenolphthalein

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





Colourless
HA



Pink
A^-

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

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

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

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

What happens in our bubbling experiment to make the solution clear?

A. the indicator dye evaporates

B. the solution becomes more acidic

C. the solution becomes more alkaline (basic)

D. the solution becomes too dilute to see the color

What makes the solution acidic?

A. dissolved oxygen gas

B. dissolved nitrogen gas

C. dissolved carbon dioxide gas

D. saliva

What is one consequence of increased CO_2 in the Earth's atmosphere?

A. oceans becoming more acidic

B. oceans becoming more alkaline

What makes the solution acidic?

$$CO_2(g) \longleftrightarrow CO_2(aq)$$

$$CO_2(aq) + H_2O(l) \longleftrightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \longleftrightarrow HCO_3^-(aq) + H^+(aq)$$

$$HCO_3^-(aq) \longleftrightarrow CO_3^{2-}(aq) + H^+(aq)$$

$$CO_3^{2-}(aq) + Ca^{2+}(aq) \longleftrightarrow CaCO_3(s)$$