

Today

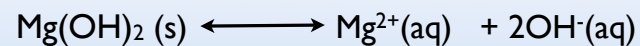
### Solubility

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

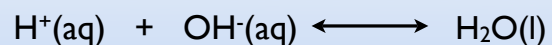
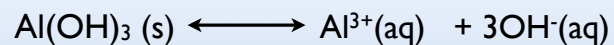
example

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

- A. pure water
- B. 1 M NaOH
- C. 1 M  $\text{MgCl}_2$
- D. 1 M HCl

The acid will neutralize the  $\text{OH}^{-}$   
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 ( $\text{AgNO}_3$ ) and Potassium Chloride ( $\text{KCl}$ ) are both soluble salts. What will happen if I mix 100 mL of 1 M  $\text{AgNO}_3$  solution with 200 mL of 1 M  $\text{KCl}$  solution given that  $K_{\text{sp}}$  for  $\text{AgCl}$  is  $1.8 \times 10^{-10}$

- A. I'll have a solution with  $\text{Ag}^{+}$ ,  $\text{Cl}^{-}$ ,  $\text{K}^{+}$ , and  $\text{NO}_3^{-}$  ions
- B. some solid  $\text{AgCl}$  will form
- C. both B & C

## Precipitation

Like neutralization problems

First react, then solve the equilibrium

$K_{\text{sp}}$  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

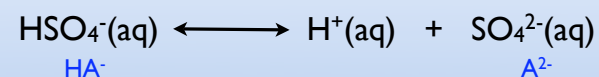
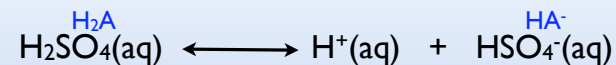
Monoprotic HA, A<sup>-</sup>

Diprotic H<sub>2</sub>A, HA<sup>-</sup>, A<sup>2-</sup>

Triprotic H<sub>3</sub>A, H<sub>2</sub>A<sup>-</sup>, HA<sup>2-</sup>, A<sup>3-</sup>

For example

Sulfuric Acid

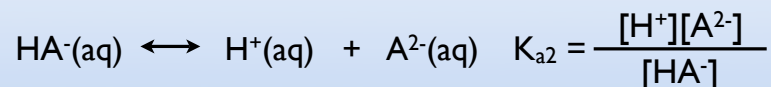


$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} = 10^3 \quad \text{Equilibrium for the first proton coming "off"}$$

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1.2 \times 10^{-2} \quad \text{Equilibrium for the next proton coming "off"}$$

## Key Question

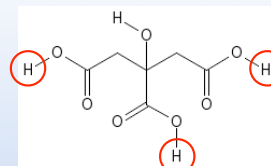
What is in solution!



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 <sub>3</sub> A	H <sup>+</sup>	H <sub>2</sub> A <sup>-</sup>	
I	Ca	0	0	$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]} = \frac{(x)(x)}{\text{Ca} - x} = \frac{(x)(x)}{\text{Ca}}$
C	-x	+x	+x	
E	Ca-x	+x	+x	

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

### 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?

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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<sup>-</sup> no all neutralized

what is left? 0.5 moles of  $HPO_4^-$

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

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

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

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

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

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

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

What is the pH of a solution with 0.5 M  $\text{HPO}_4^{2-}$ ?

$$\begin{aligned} \text{H}_3\text{PO}_4 \quad K_{a1} &= 7.1 \times 10^{-3} \\ K_{a2} &= 6.3 \times 10^{-8} \\ K_{a3} &= 4.5 \times 10^{-13} \end{aligned}$$

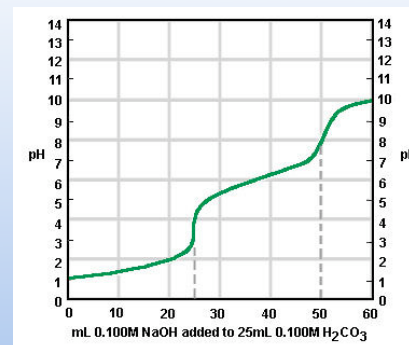
$$K_{a2} = \frac{[\text{H}^+][\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]} \quad K_{a3} = \frac{[\text{H}^+][\text{A}^{3-}]}{[\text{HA}^{2-}]}$$

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

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

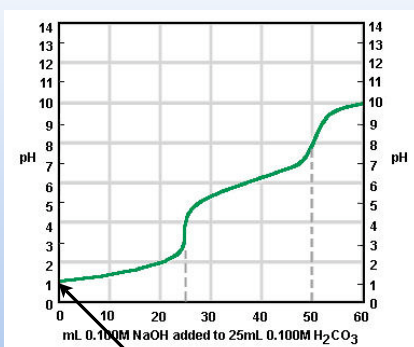
assume the small change in forming both acid and base

### Titration of a polyprotic



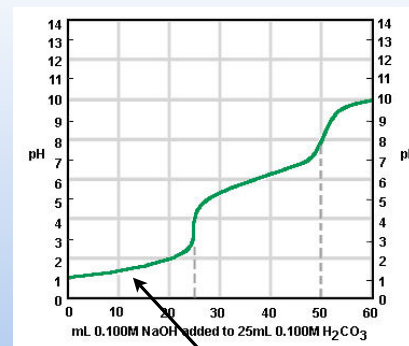
Two equivalence points  
Diprotic  $\text{H}_2\text{A}$

### Titration of a polyprotic



all  $\text{H}_2\text{A}$  weak acid

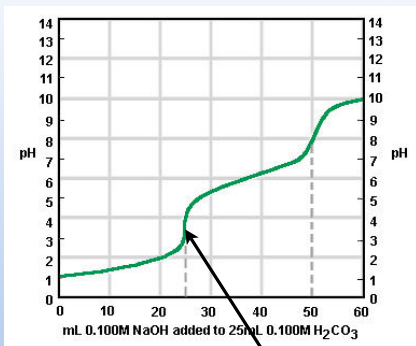
### Titration of a polyprotic



$\text{OH}^-$  neutralizes some  $\text{H}_2\text{A}$  to  $\text{HA}^-$  buffer around  $K_{a1}$

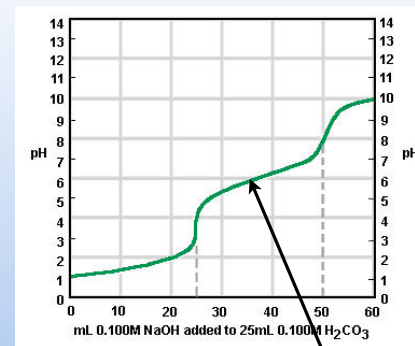
halfway to equivalence point I  
 $\text{pH} = \text{p}K_{a1}$

### Titration of a polyprotic



equivalence point I  
 moles  $\text{OH}^-$  = moles  $\text{H}_2\text{A}$   
 All  $\text{H}_2\text{A}$  converted to  $\text{HA}^-$

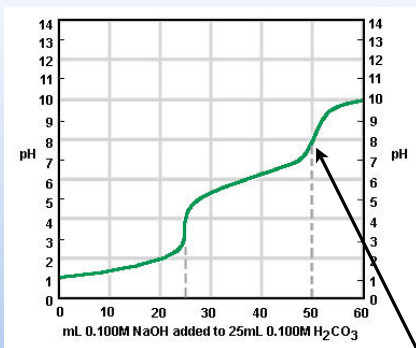
### Titration of a polyprotic



halfway  
 to equivalence point I  
 $\text{pH} = \text{p}K_{a2}$

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

### Titration of a polyprotic



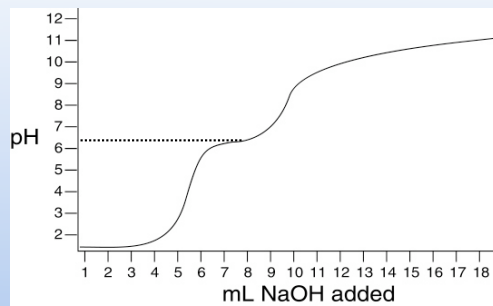
equivalence point 2  
 moles  $\text{OH}^-$  = 2 x moles  $\text{H}_2\text{A}$   
 now all  $\text{H}_2\text{A}$  is converted to  $\text{A}^{2-}$   
 now weak base  $\text{A}^{2-}$

If I add 0.1 moles of  $\text{NaOH}$  to 0.07 moles of  $\text{H}_3\text{PO}_4$   
 what will be the dominant species in solution?

- A.  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{PO}_4^-$
- B.  $\text{H}_2\text{PO}_4^-$
- C.  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$
- D.  $\text{HPO}_4^{2-}$
- E.  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$

.04 moles  $\text{H}_2\text{PO}_4^-$   
 .03 moles  $\text{HPO}_4^{2-}$

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.  $5 \times 10^{-6}$       D.  $5 \times 10^{-7}$