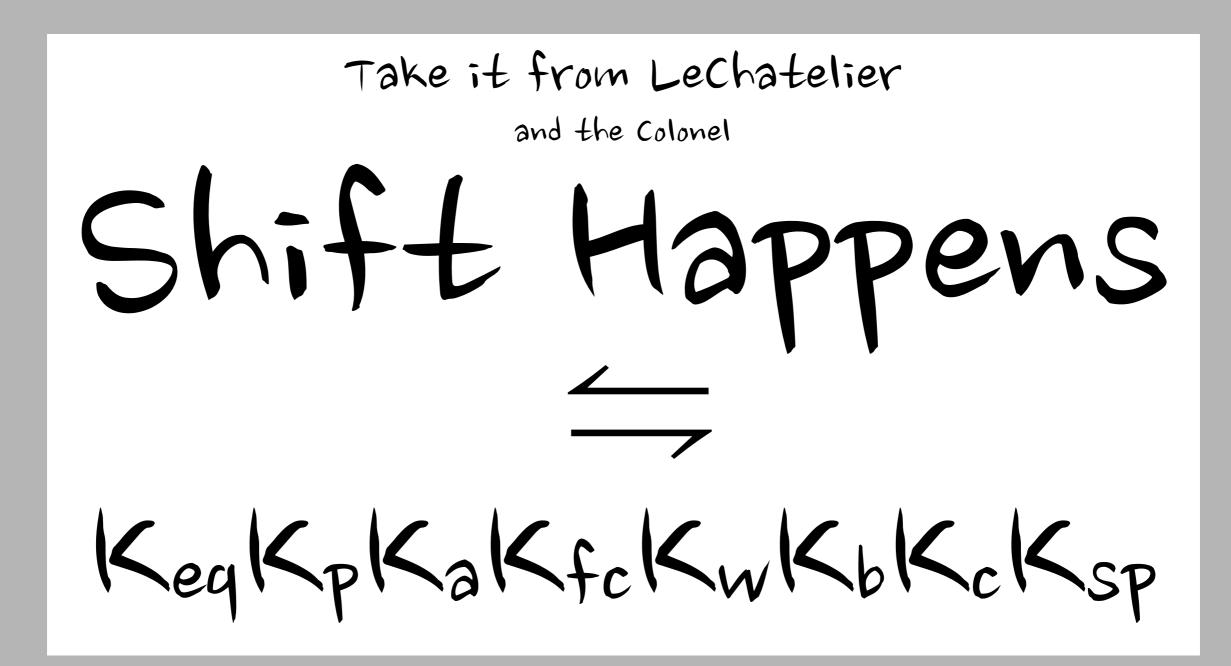
### Acid & Base Equilibrium Chapter 16



Do you know your SA & SB... **Strong Acids Strong Bases** 

- HCl
- HI
- HBr
- **HNO**<sub>3</sub>
- H<sub>2</sub>SO<sub>4</sub>
- **HCIO**<sub>4</sub>
- **HCIO**<sub>3</sub>

- LiOH
- NaOH
- KOH
- RbOH
- CsOH
- **Ba(OH)**<sub>2</sub>
- **Sr(OH)**<sub>2</sub>
- Ca(OH)<sub>2</sub>

Group hydroxides

Group II hydroxides the upper Group II hydroxides are not very soluble and thus not very useful as solutions.

#### base 10 Log Facts

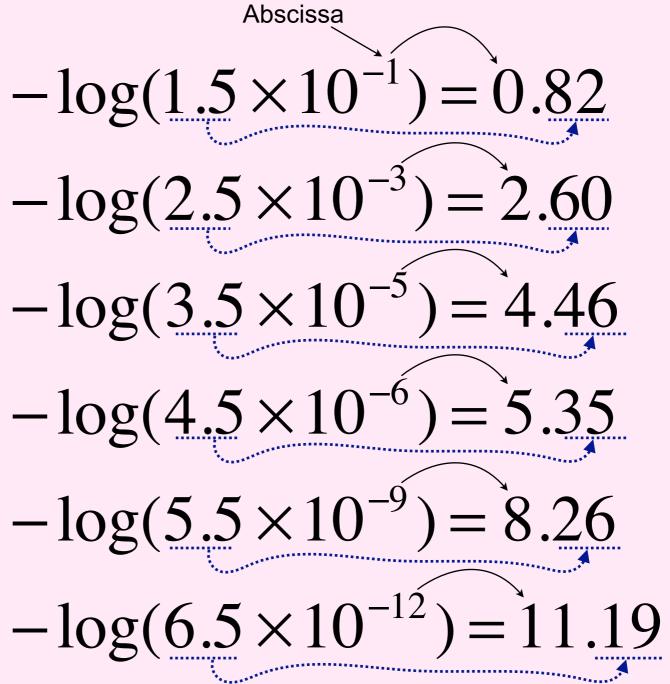
log(1×10 <sup>10</sup> )	10.0
log(1×10 <sup>3</sup> )	3.0
log(1×10 <sup>1</sup> )	1.0
log(1×10 <sup>0</sup> )	0.0
log(1×10 <sup>-1</sup> )	-1.0
log(1×10 <sup>-3</sup> )	-3.0
log(1×10 <sup>-10</sup> )	-10.0

OK, but what if the # in front is not 1??

Most of the time you would not be asked to think about logging numbers like this without a calculator, unless the MC answers were far enough apart to make your choice easy enough.

take note of the pattern of the scientific notation exponent (the abscissa) in relation to the # before decimal in the pH.

The pH will be one less than the exponent This may be helpful in MC



...and remember sig figs. In a logged number only the numbers after the decimal are Mantissa (aka significand)

- You see, the 4.6 (mantissa) is what causes the .34
- The number in front of the .34 (abscissa) is a result of the magnitude of the number that is being logged, not a part of its significant figures,
- Thus only the numbers after the decimal are the significant figure part of a logged number such as pH

- $-\log(4.6 \times 10^{-1}) = 0.34$
- $-\log(4.6 \times 10^{-3}) = 2.34$
- $-\log(4.6 \times 10^{-7}) = 6.34$
- $-\log(4.6 \times 10^{-10}) = 9.34$
- $-\log(4.6 \times 10^{-12}) = 11.34$

#### Abscissa

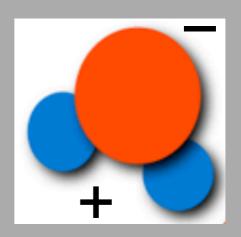
Don't spend much time on this. Sig figs with logs has shown on AP maybe once or twice in last 15 years.

**→** <sup>5</sup>

# And you thought water was just water.

#### The Water Equilibrium and

рH

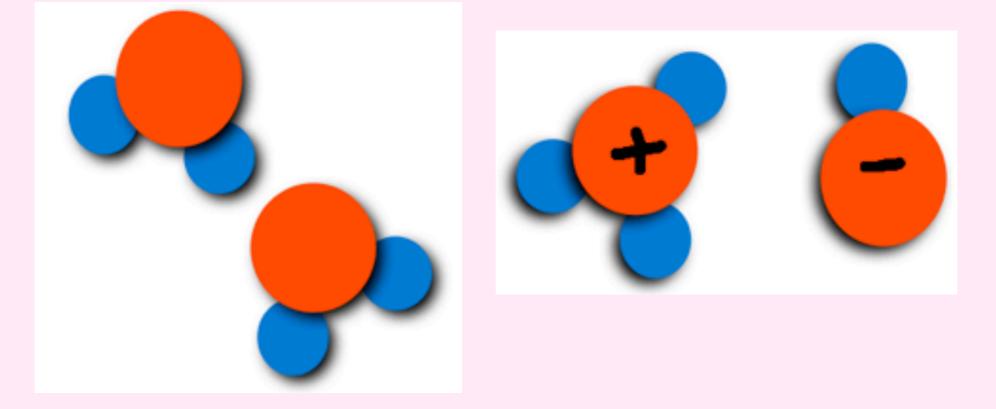


Water is a polar molecule Which end is partially+ and which is partially-?

6

Although it happens to only a very slight degree, Water molecules "crash" into each other and ionize in *every* aqueous solution.

•  $H_2O + H_2O \implies H_3O^+ + OH^-$ 



## The formation of H<sup>+</sup> and OH<sup>-</sup> ions in water is always in equibrium.

- $H_2O \leftrightarrows H^+ + OH^- OR H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$
- Write a *K<sub>eq</sub>* for these reactions above:
- *K<sub>eq</sub>* = [H<sup>+</sup>] [OH<sup>-</sup>] or [H<sub>3</sub>O<sup>+</sup>] [OH<sup>-</sup>]
   We call this equilibrium, *K<sub>w</sub>* = [H<sup>+</sup>] [OH<sup>-</sup>]
- The amount of *autoionization* is small.
   How small....?

#### *K<sub>w</sub>* The lon Product

- In pure water, [H<sup>+</sup>] = [OH<sup>-</sup>] = 1 x 10<sup>-7</sup> M (at 25°C)
- Calculate,  $K_w =$
- $K_w = [H^+] [OH^-] = 1 \times 10^{-14}$  (at 25°C)
- Does this mean that when you drink water you are drinking acid and base?
- Well, yes and no.
  - In pure water, [H<sup>+</sup>] = [OH<sup>−</sup>] = 1 x 10<sup>−7</sup> M
  - Since the amounts are equal, the water is considered "neutral."
- Here's the punch line
  - The ion product,  $K_w$  is true not just for water, but for any and all aqueous solutions.

#### The pH scale

- In most aqueous solutions, [H<sup>+</sup>] and [OH<sup>-</sup>] are often small quantities, and we would be writing out such small numbers, it is convenient to convert these small numbers to base 10 logs.
- We call this  $pH = -log [H^+]$  (or  $-log [H_3O^+]$ )
- In pure water (at  $25^{\circ}C$ ) [H<sup>+</sup>] = 1 x  $10^{-7}$ 
  - Calculate the pH of pure water.
  - The pH of water = 7
- In an acidic solution, [H<sup>+</sup>] could =  $1 \times 10^{-4} M$ ,
  - Calculate the pH of this acid solution.
  - ▶ pH = -log [1 x 10<sup>-4</sup> M] = 4

#### Other "p" scales

- While it's useful to report [H<sup>+</sup>] as a log, it can also be useful to report [OH<sup>-</sup>] as a log. We call this pOH
  - ▶ pOH = -log [OH<sup>-</sup>]
- So for the pH = 4 solution, in which  $[H^+] = 1 \times 10^{-4} M$
- Knowing K<sub>w</sub> = [H<sup>+</sup>] [OH<sup>-</sup>] = 1 x 10<sup>-14</sup>
- Calculate [OH<sup>-</sup>] and pOH
   [OH<sup>-</sup>] = 1 x 10<sup>-10</sup>, so pOH = 10
- Let's compare [H<sup>+</sup>] and [OH<sup>-</sup>] concentrations, pH and pOH of various common solutions on the next slide.

Do you notice a relationship between pH and pOH of a solution?

More acidic

More basic

Tell your mate what you notice.

		-	-	
	$1(1\times 10^{-0})$	0.0	14.0	$1 \times 10^{-14}$
	$-1(1 \times 10^{-0})$	0.0	14.0	
Gastric juice – – – – – –	$-1 \times 10^{-1}$	1.0	13.0	$1 \times 10^{-13}$
Lemon juice – – – – – –	$-1 \times 10^{-2}$	2.0	12.0	$1 \times 10^{-12}$
Cola, vinegar	$-1 \times 10^{-3}$	3.0	11.0	$1 \times 10^{-11}$
Wine Tomatoes	$- 1 \times 10^{-4}$	4.0	10.0	$1 \times 10^{-10}$
Banana Black coffee	$-1 \times 10^{-5}$	5.0	9.0	$1 \times 10^{-9}$
Rain – – – – – – – – – – – – – – – – – – –	$-1 \times 10^{-6}$	6.0	8.0	$1 \times 10^{-8}$
Milk – – – – – – – – – – – – – – – – – – –	$-1 \times 10^{-7}$	7.0	7.0	$1 \times 10^{-7}$
Egg white, seawater Baking soda	$- 1 \times 10^{-8}$	8.0	6.0	$1 \times 10^{-6}$
Borax	$- 1 \times 10^{-9}$	9.0	5.0	$1 \times 10^{-5}$
Milk of magnesia – – –	$-1 \times 10^{-10}$	10.0	4.0	$1 \times 10^{-4}$
Lime water	$-1 \times 10^{-11}$	11.0	3.0	$1 \times 10^{-3}$
Household ammonia – -	$-1 \times 10^{-12}$	12.0	2.0	$1 \times 10^{-2}$
Household bleach NaOH, 0.1 <i>M</i>	$-1 \times 10^{-13}$	13.0	1.0	$1 \times 10^{-1}$
	$- 1 \times 10^{-14}$	14.0	0.0	1 (1×10 <sup>-0</sup> )

 $[{
m H}^+](M)$ 

рΗ

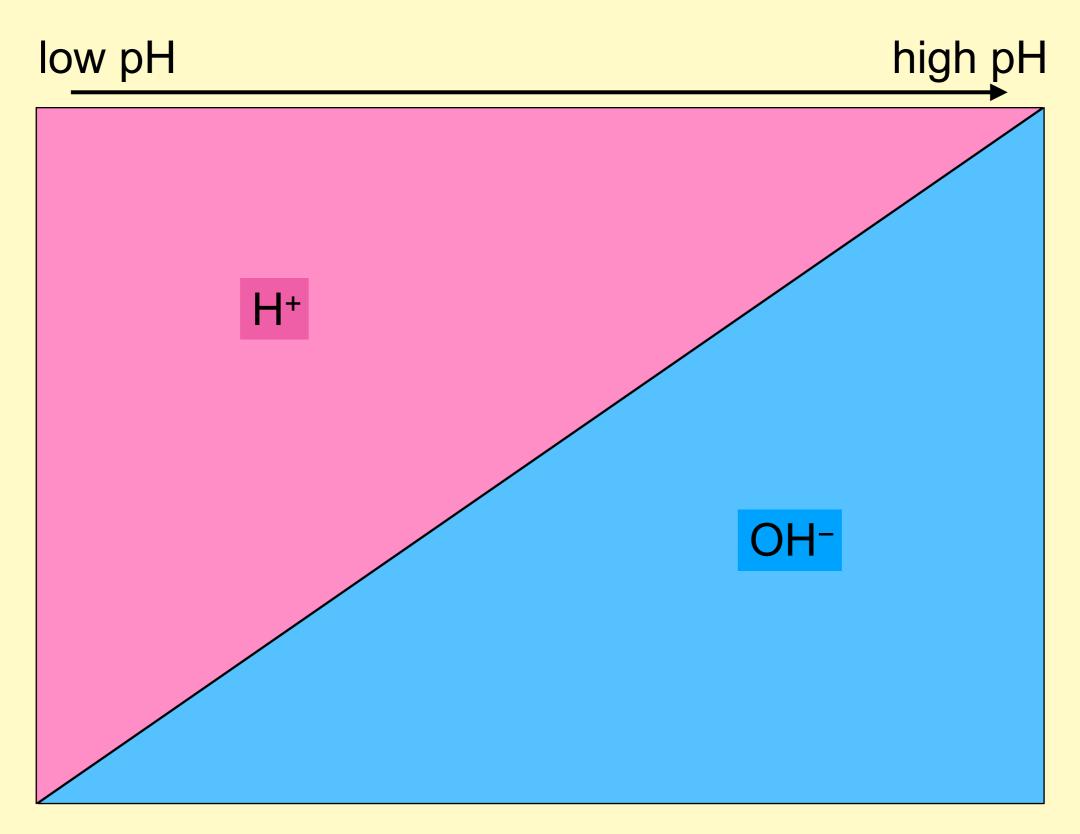
pOH

 $[OH^{-}](M)$ 

#### **The pH Loop** For ALL Aqueous Solutions

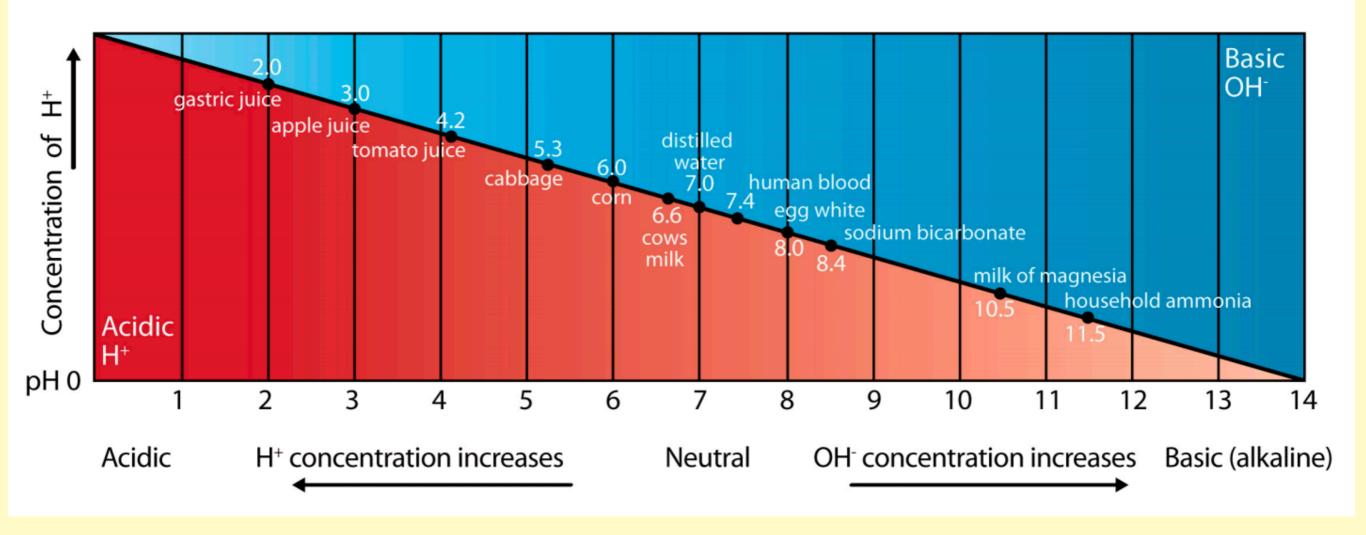
- If you know pH, you know [H+]
- Remember [H<sup>+</sup>] [OH<sup>-</sup>] =  $K_{w at 25^{\circ}} = 1 \times 10^{-14}$
- We know:  $pH = -log [H^+]$  and  $[H^+] = 10^{-pH}$
- We know pH + pOH = 14
- We know:  $pOH = -log [OH^{-}]$  and  $[OH^{-}] = 10^{-pOH}$
- So we can ride the pH Loop for ALL aqueous sol'n
- $pH \rightleftharpoons [H^+] \rightleftharpoons [OH^-] \rightleftharpoons pOH$
- very handy indeed!! `

#### H<sup>+</sup> and OH<sup>-</sup> Relative Amounts



→ 14

#### H<sup>+</sup> and OH<sup>-</sup> Relative Amounts



#### Putting pH Values into Perspective

- Because the pH scale is a logarithmic scale, changes by one pH unit are actually changes by a factor of 10, and are thus relatively large changes. Consider this comparative scale.
- Start by assuming that a solution of pH=1, in which the [H<sup>+</sup>] = 1 x 10<sup>-1</sup> is similar in size as the length of a sports field.
- As pH increases, the [H<sup>+</sup>] decreases by the same factor as the comparative scale.
- Let's take a look at the PhET pH simulation

рΗ	[H+]	Comparison
1	1 x 10 <sup>-1</sup>	100 yards
2	1 x 10-2	10 yards
3	1 x 10-3	1 yard
4	1 x 10-4	3.6 inches
5	1 x 10-5	0.36 inch
6	1 x 10-6	0.036 inch
7	1 x 10-7	0.0036 inch

## Neutralization $H^+ + OH^- \rightarrow H_2O$ reacting stoichiometric amounts of acid and base

Calculate the volume of 0.034 M potassium hydroxide required to neutralize 25.0 ml of 0.050 M nitric acid.

- Write the overall neutralization reaction.
- Write the net ionic reaction

Calculate the volume of 0.034 M potassium hydroxide required to neutralize 25.0 ml of 0.050 M nitric acid.

- KOH + HNO<sub>3</sub>  $\rightarrow$  H<sub>2</sub>O + KNO<sub>3</sub>
- $OH^-$  +  $H^+ \rightarrow H_2O$

Calculate the volume of 0.034 M potassium hydroxide required to neutralize 25.0 ml of 0.050 M nitric acid.

- KOH + HNO<sub>3</sub>  $\rightarrow$  H<sub>2</sub>O + KNO<sub>3</sub>
- OH<sup>-</sup> + H<sup>+</sup>  $\rightarrow$  H<sub>2</sub>O  $M_a V_a = M_b V_b$   $(0.05M)(25ml) = (0.034M)V_b$  $V_b = 37ml \ KOH$

$$(0.05M)(25ml) = 1.25mmolAcid \times \frac{1H^{+}}{1Acid} \times \frac{10H^{-}}{1H^{+}} = 1.25mmolOH^{-}$$
$$\frac{molBase}{V_{b}} = M \quad \frac{1.25mmolOH^{-}}{V_{b}} = 0.034M \quad V_{b} = 37ml$$

Calculate the volume of 0.034 M potassium hydroxide required to neutralize 25.0 ml of 0.050 M nitrous acid.  $K_a = 4.9 \times 10^{-4}$ 

- Write the overall neutralization reaction.
- Write the net ionic reaction

Calculate the volume of 0.034 M potassium hydroxide required to neutralize 25.0 ml of 0.050 M nitrous acid.  $K_a = 4.9 \times 10^{-4}$ 

- KOH + HNO<sub>2</sub>  $\rightarrow$  H<sub>2</sub>O + KNO<sub>2</sub>
- $OH^-$  +  $HNO_2 \rightarrow H_2O$  +  $NO_2^-$
- Though the net ionic equation (of WA + SB) is different (than SA + SB), you must represent the WA as the molecule not simply as H+, since most of the WA exists in the water at the start of the neutralization as HNO<sub>2</sub>.
- Solving for the quantity of base required for the neutralization of a weak acid would be exactly the same procedure as for SA + SB, because all the H's will be ripped off by the incoming SB.

Calculate the volume of 0.034 M potassium hydroxide required to neutralize 25.0 ml of 0.050 M nitrous acid.  $K_a = 4.9 \times 10^{-4}$ 

• 
$$OH^-$$
 +  $HNO_2 \rightarrow H_2O$  +  $NO_2^-$ 

 $M_a V_a = M_b V_b$  $(0.05M)(25ml) = (0.034M)V_b$  $V_b = 37ml \ KOH$ 

Do NOT be distracted by the WA or the  $K_a$ . There is no reason to use it. In the end, the WA will give up ALL of it H<sup>+</sup>'s

$$(0.05M)(25ml) = 1.25mmolAcid \times \frac{1H^{+}}{1Acid} \times \frac{10H^{-}}{1H^{+}} = 1.25mmolOH^{-}$$
$$\frac{molBase}{V_{b}} = M \quad \frac{1.25mmolOH^{-}}{V_{b}} = 0.034M \quad BV_{b} = 37ml$$

Calculate the volume of 0.0045 M acetic acid required to neutralize 65.0 ml of 0.0072 M barium hydroxide solution.

- Write the overall neutralization reaction.
- Write the net ionic reaction

Calculate the volume of 0.0045 M acetic acid required to neutralize 65.0 ml of 0.0072 M barium hydroxide solution.

- $Ba(OH)_2 + 2 HC_2H_3O_2 \rightarrow 2 H_2O + Ba(C_2H_3O_2)_2$
- OH<sup>-</sup> + HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>  $\rightarrow$  H<sub>2</sub>O + C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>
- Beware of the "buy-one-get-two" base
- Each mol (or molarity) of base provides double moles (or molarity) of OH-

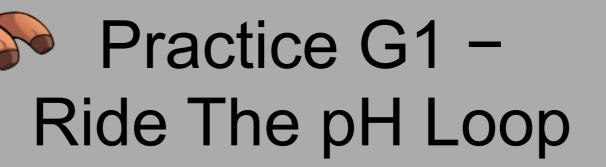
$$M_a V_a = M_b V_b \times 2$$

Calculate the volume of 0.0045 M perchloric acid required to neutralize 65.0 ml of 0.0072 M barium hydroxide.

•  $Ba(OH)_2 + 2 HC_2H_3O_2 \rightarrow 2 H_2O + Ba(CIO_4)_2$   $M_a V_a = M_b V_b \times 2$   $(0.0045M)(V_a) = (0.0072M)(65ml) \times 2$  $V_a = 210ml HCIO_4$ 

$$(0.0072M)(65ml) = 0.468mmolBase \times \frac{20H^{-}}{1Base} \times \frac{1H^{+}}{10H^{-}} = 0.936mmolH^{+}$$
$$\frac{molAcid}{V_{a}} = M \quad \frac{0.936mmolOH^{-}}{V_{a}} = 0.0045M \quad V_{a} = 210ml(208)$$

# So just what are acids and bases?



#### Let's Define Acids & Bases

- In 1880's Arrhenius defined:
  - Acid: a substance that dissolves in water to form H<sup>+</sup>
    - $\checkmark \quad \text{HCI} \ \rightarrow \ \text{H}^+ \ + \ \text{CI}^-$
  - Base: a substance that dissolves in water to form OH-
    - ✓ NaOH  $\rightarrow$  Na<sup>+</sup> + OH<sup>-</sup>
- 1923 Brønsted & Lowry expanded the definition to include molecules that did not appear to have an OH<sup>-</sup>
  - Acids as a proton (H<sup>+</sup>) donor
  - Bases as a proton (H<sup>+</sup>) acceptor
    - ✓ Isn't that acid definition pretty much the same definition as above? ...Yup
    - ✓ Why do I need this base definition?
    - ✓ I don't see how OH- from NaOH is a proton acceptor
    - ✓ Just wait...you'll see why when we look more carefully at weak bases

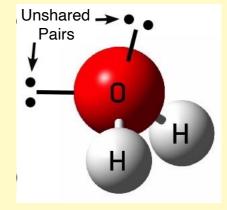
#### H+ the proton - what is it?

- H<sup>+</sup> results from the dissociation (ionization, hydrolysis) of acids in solution.
  - $\bullet \ HCI_{(aq)} \ \rightarrow \ H^{+}_{(aq)} \ + \ CI^{-}_{(aq)}$
  - The H—CI bond is loose enough to break apart in water.
  - Essentially H<sup>+</sup> is a "naked" proton.
    - ✓ But is H<sup>+</sup> really naked ????
    - ✓ No, not really....let's take a look.

#### Hydrogen ion = Hydronium Ion

 $\bullet \text{HCl}_{(aq)} \rightarrow \text{H}^+_{(aq)} + \text{Cl}^-_{(aq)}$ 

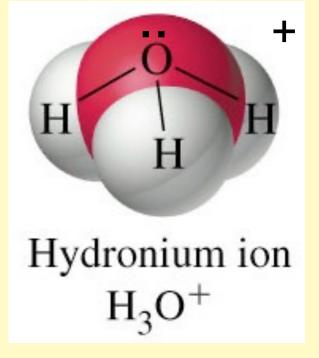
 The H<sup>+</sup> (the naked proton) is so small H<sup>+</sup> will immediately attach to one of the unshared pair of electrons on a water molecule forming H<sub>3</sub>O<sup>+</sup> Oxygen has 6 valence electrons: Two are used to make the O-H bonds, and 4 are left over as lone pairs.



 $\bullet \text{HCl}_{(aq)} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+_{(aq)} + \text{Cl}^-_{(aq)}$ 

- As far as we're concerned, we'll symbolize the hydronium ion
  - ► H<sup>+</sup> OR H<sub>3</sub>O<sup>+</sup>
  - We and AP will use these interchangeably.

Now only one lone pair is left over unbonded.

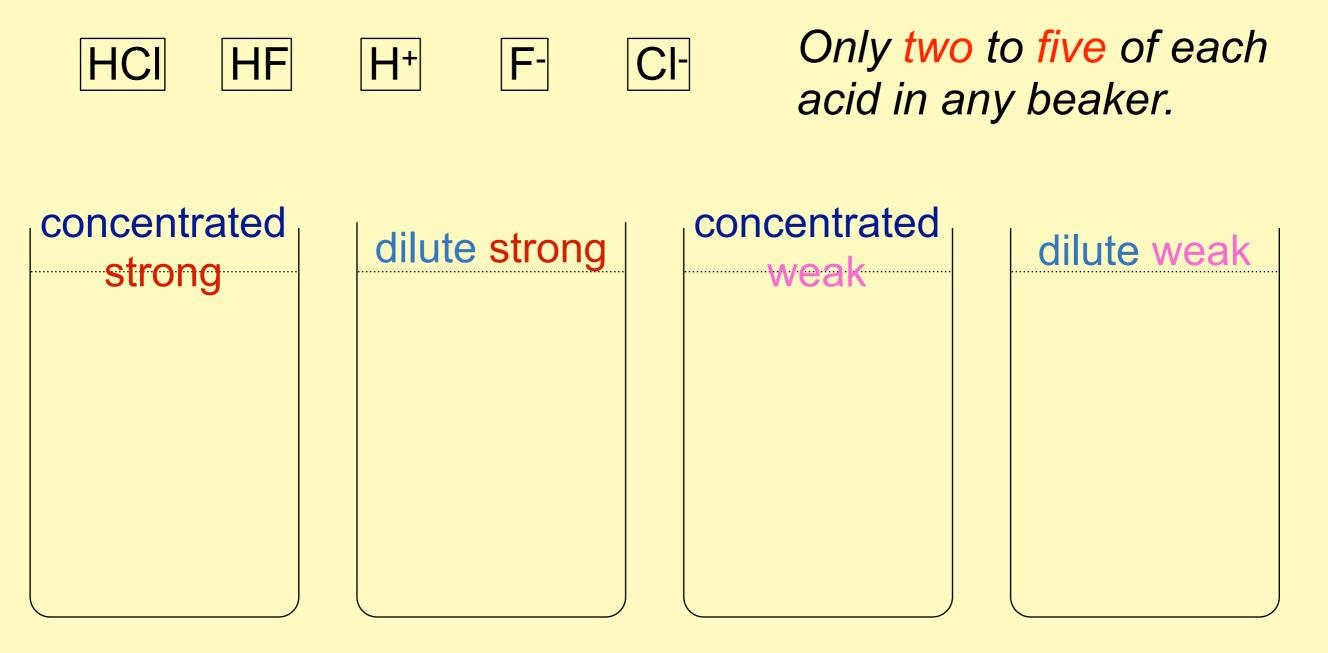


### Concentrated / Dilute Strong / Weak

Just what do these words mean?

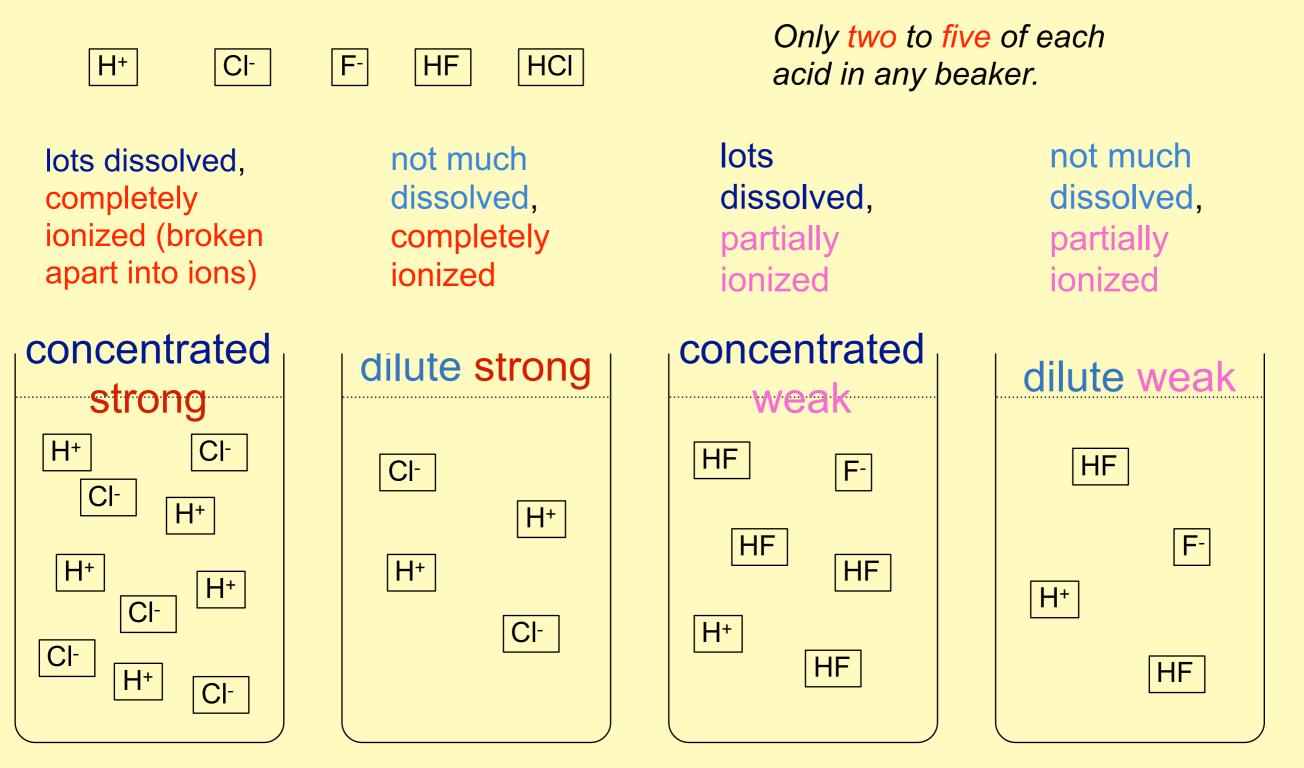
#### Weak Acids & Weak Bases

- Sketch a particulate drawing for HCI and HF in the beakers listed as appropriate.
- Your sketch should highlight the important distinctions.
  - Any particles that are touching will be considered as bonded.



Weak Acids & Weak Bases

- Sketch a particulate drawing for each of the following acids
  - Particles that are touching will be considered as bonded.



Equations to describe what acids and bases do in water

AP will as for equations that describe **lonization** aka **Hydrolysis** 

#### Reaction of a Weak Acid

$HF_{(aq)}$ +	$H_2O_{(L)} \iff$	F- <sub>(aq)</sub> +	$H_3O^+_{(aq)}$
proton	proton	proton	proton
donor	acceptor	acceptor	donor
acid	base	base	acid

- HF is the proton donor, the acid.
- H<sub>2</sub>O is the proton acceptor, the base
- This reaction happens to be one that doesn't go to completion. The reaction is reversible and reaches equilibrium.
- This reversibility of this reaction allows us to label acids and bases for the reverse reaction.

#### Reaction of a Weak Base

NH <sub>3(g)</sub> +	$H_2O_{(L)}$	$\longleftrightarrow$	NH <sub>4</sub> + <sub>(aq)</sub> +	· OH- <sub>(aq)</sub>
proton	proton		proton	proton
acceptor	donor		donor	acceptor
base	acid		acid	base

- NH<sub>3</sub> is the proton acceptor, the base.
  - As you can see, having a hydrogen does not always mean acid. CH<sub>4</sub>, AlH<sub>3</sub>,
- $H_2O$  is the proton donor, the acid.
- This reaction happens to be one that doesn't go to completion. It's reversible and therefore reaches equilibrium.
- This reversibility of this reaction allows us to label acids and bases for the reverse reaction.

### Amphoterism

• You may have noticed that in the last two reactions water has behaved both as an acid and as a base.

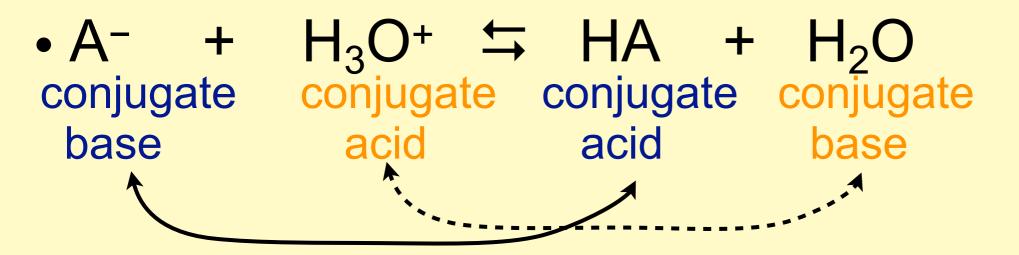
• 
$$NH_{3(g)} + H_2O_{(L)} \implies NH_4^+_{(aq)} + OH^-_{(aq)}$$
  
acid

• 
$$HF_{(aq)}$$
 +  $H_2O_{(L)}$   $\Leftrightarrow$   $H_3O_{(aq)}$  +  $F_{(aq)}$   
base

- A substance that is capable of acting as either an acid or a base is called *amphoteric* (or *amphiprotic*).
- water is not the only molecule that can do this... more on this later.

Conjugate Acid & Base Pairs

- We can write a generic reaction to represent any weak acid
- HA + H<sub>2</sub>O  $\leftrightarrows$  A<sup>-</sup> + H<sub>3</sub>O<sup>+</sup> acid base base acid
- You can also think of this in reverse....



- We call these corresponding acid/base pairs, conjugate acid/base pairs
- Notice the pairs are across the  $\rightarrow$  NOT on the same side

### K<sub>eq</sub> for Acids & Bases

 Written below are two versions of the same generic reaction to represent any weak acid, HA.

• 
$$HA_{(aq)}$$
 +  $H_2O$   $\Leftrightarrow$   $A^-$  +  $H_3O^+$   $K_a = \frac{\left\lfloor H_3O^+ \right\rfloor \left\lfloor A^- \right\rfloor}{\left\lceil HA \right\rceil}$ 

• 
$$HA_{(aq)} \xrightarrow{\leftarrow} A^- + H^+ \qquad K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$$

- Write the equilibrium expressions for these reactions
  - We will use both reactions and expressions interchangably.
  - Note what is NOT in the expression.

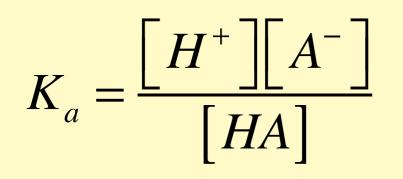
### Generic Rx's for Bases

- Write a generic reaction to represent any weak base, B. You MUST include the water.
- B +  $H_2O$   $\leftrightarrows$  HB+ + OH-

Now, write an equilibrium expression for this reaction.

$$\bullet \quad K_{b} = \frac{\left[HB^{+}\right]\left[OH^{-}\right]}{\left[B\right]}$$

(note: what is not in the expression)



Let's look for these expressions on the Formula Sheet.

# Other Acids and Bases

#### Acids can be neutral molecules or cations

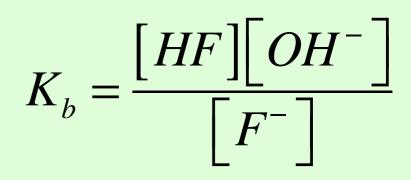
the negative ions of multiprotic acids can also be acids

Bases can be neutral molecules or anions

#### Getting Acids and Bases into water from dissolving salts

### Generic Rx's for Bases

- Since every weak acid produces a conjugate weak base, we can also represent a weak base as A<sup>-</sup>
- How can we get A<sup>-</sup> without getting it from an acid?
  - by dissolving NaF into water:  $NaF_{(s)} \rightarrow Na^+ + F^-$
  - F<sup>-</sup> is a conjugate weak base (For now, let's ignore Na<sup>+</sup>)
- Write an equation to represent the reaction of Fin water. (Remember bases are proton acceptors.)
  - $F^- + H_2O \Leftrightarrow HF_{(aq)} + OH^-$
- Write the equilibrium expression for this equation



## K<sub>eq</sub> for Acids & Bases

- Remember that conjugate acids, NH<sub>4</sub>+ form from weak bases, (NH<sub>3</sub>)
- We can get NH<sub>4</sub>+ without forming it from its base by dissolving an ammonium ionic compound?

✓ Dissolve NH<sub>4</sub>NO<sub>3</sub> into water:  $NH_4NO_{3(s)} \rightarrow NH_4^+ + NO_3^-$ 

✓  $NH_4^+$  is a conjugate weak acid (For now, let's ignore  $NO_3^-$ )

 Write an equation for the acidic reaction of NH<sub>4</sub>+ in water (Remember acids are proton donors).

 $\mathsf{NH}_4^+ + \mathsf{H}_2 \mathsf{O} \Leftrightarrow \mathsf{NH}_{3(aq)} + \mathsf{H}_3 \mathsf{O}^+ \mathsf{K}_a = \frac{[NH_3][H_3 O^+]}{[NH_4^+]}$ 

• or  $NH_4^+ \Leftrightarrow NH_{3(aq)} + H^+$ 

✓ write an equilibrium expression for the  $K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$ hydrolysis reaction of NH4<sup>+</sup> in water Just who are those acids and bases?

Just Who Are the WA & WB?

- Molecular WA generally have the formula HA
- Molecular WB generally have the formula:

► NH <sub>3</sub>		Be sure and		TABLE 16.2Some Weak Acids in Water at 25°C*		
stuff-NF	_	observe t conjugate		Acid	Structural Formula	Conjugate Base
stuff-NI	1	oonjeigeite		Hydrofluoric (HF)	H—F	F <sup>-</sup>
▶ stuff-N				Nitrous	H-O-N=O	$NO_2^-$
TABLE 16.4 Some W	Veak Base	es and Their Aq	queous Solutic	(HNO <sub>2</sub> )		
Base	Lewis Structu	ıre	Conjugate Acid	Benzoic (HC <sub>7</sub> H <sub>5</sub> O <sub>2</sub> )	$H - o - C - \langle O \rangle$	$C_7 H_5 O_2^-$
Ammonia (NH <sub>3</sub> )	H−Ň-	—н	$\mathrm{NH_4}^+$		О Н ∥	
	H	The accept locates on a	· · ·	Acetic (HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> )	н—о—ё́—с́—н ∣ н	$C_2H_3O_2^-$
Pyridine (C <sub>5</sub> H <sub>5</sub> N)	$\langle \bigcirc \rangle$	N:	$C_5H_5NH^+$	Hypochlorous (HClO)	H—O—Cl	C10 <sup>-</sup>
				Hydrocyanic (HCN)	$H - C \equiv N$	CN <sup>-</sup>
Hydroxylamine (H <sub>2</sub> NOH)	 H	—ён	H <sub>3</sub> NOH <sup>+</sup>	Phenol (HC <sub>6</sub> H <sub>5</sub> O)	H-O-	$C_6H_5O^-$
Methylamine (NH <sub>2</sub> CH <sub>3</sub> )	H—Ň·	$-CH_3$	NH <sub>3</sub> CH <sub>3</sub> <sup>+</sup>	*The proton that ionizes is sho	own in blue.	
	F1					<b>→</b> 45

# Consider the weak base, ethylamine $C_2H_5NH_2$

• Write an equation that represents the hydrolysis of ethylamine.

 $\checkmark$  aka: Write an equation that represents the ionization of ethylamine

✓ aka: Write an equation that represents ethylamine reacting with water

- $C_2H_5NH_{2(aq)}$  +  $H_2O \iff C_2H_5NH_3^+_{(aq)}$  +  $OH^-$
- Now write the equilibrium expression.

$$K_{b} = \frac{\left[C_{2}H_{5}NH_{3}^{+}\right]\left[OH^{-}\right]}{\left[C_{2}H_{5}NH_{2}\right]}$$

# Consider the weak base, (sodium nitrite) nitrite ion $NO_2^{-}$

• Write an equation that represents the hydrolysis of nitrite.

 $\checkmark$  aka: Write an equation that represents nitrite reacting with water

- $NO_2^-$  +  $H_2O \rightleftharpoons HNO_2$  +  $OH^-$
- Now write the equilibrium expression.

$$K_b = \frac{[HNO_2^-][OH^-]}{[NO_2^-]}$$

# Look up the $K_b$ expression $O_{P_0}^{c} (P_0)^{c} (P_$

- Write an equation that represents this to mula.
- B +  $H_2O \rightleftharpoons HB^+ + OH^-$
- $NH_3$  +  $H_2O \implies NH_4^+$  +  $OH^$ wb wa
- $NO_2^-$  +  $H_2O \rightleftharpoons HNO_2$  +  $OH^-$
- So Let's remember that this formula ONLY krept esents a weak base hydrolysis, NEVER a neutralization [A] reaction. [HA]
  - $pK_a = \log K , pK = \log K$  $K_a \qquad \begin{bmatrix} A \end{bmatrix}$  $K_a \qquad \begin{bmatrix} HA \end{bmatrix}$

][OH

 $K_b = \frac{[OH^-][WA]}{$ 

K

K

 $pK = \log K \cdot pK \longrightarrow 4$ 

# Consider the weak acid, lactic acid HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>

- Write an equation that represents the hydrolysis of lactic acid.
  - Aka: Write an equation that represents the ionization of lactic acid
  - Aka: Write an equation that represents lactic acid reacting with water
- $HC_3H_5O_{3(aq)}$  +  $H_2O \rightleftharpoons C_3H_5O_3^-$  +  $H_3O^+$
- $HC_3H_5O_{3(aq)} \iff C_3H_5O_3^- + H^+$
- Now write the equilibrium expression.

$$K_{a} = \frac{\left[H^{+}\right]\left[C_{3}H_{5}O_{3}^{-}\right]}{\left[HC_{3}H_{5}O_{3}\right]} \qquad K_{a} = \frac{\left[H_{3}O^{+}\right]\left[C_{3}H_{5}O_{3}^{-}\right]}{\left[HC_{3}H_{5}O_{3}\right]}$$

# Consider the weak acid, (ammonium chloride) ammonium ion NH<sub>4</sub>+

- Write an equation that represents the hydrolysis of ammonium
  - Aka: Write an equation that represents the ionization of ammonium
  - Aka: Write an equation that represents ammoniumreacting with water
- $NH_4^+$  +  $H_2O \implies NH_3$  +  $H_3O^+$
- $NH_4^+ \iff NH_3 + H^+$
- Now write the equilibrium expression.

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

## Look up the $K_a$ expression $\begin{bmatrix} C \end{bmatrix}^c \begin{bmatrix} D \end{bmatrix}^d$ the fomula sheet $(P_C)^c (P_D)^d$

• Write an equation that represents this formula. a

 $(P_{\rm A}O_{\rm H}^{a}P_{\rm B})^{b}$  ]

[H<sup>+</sup>][ wb]

 $K_a$ 

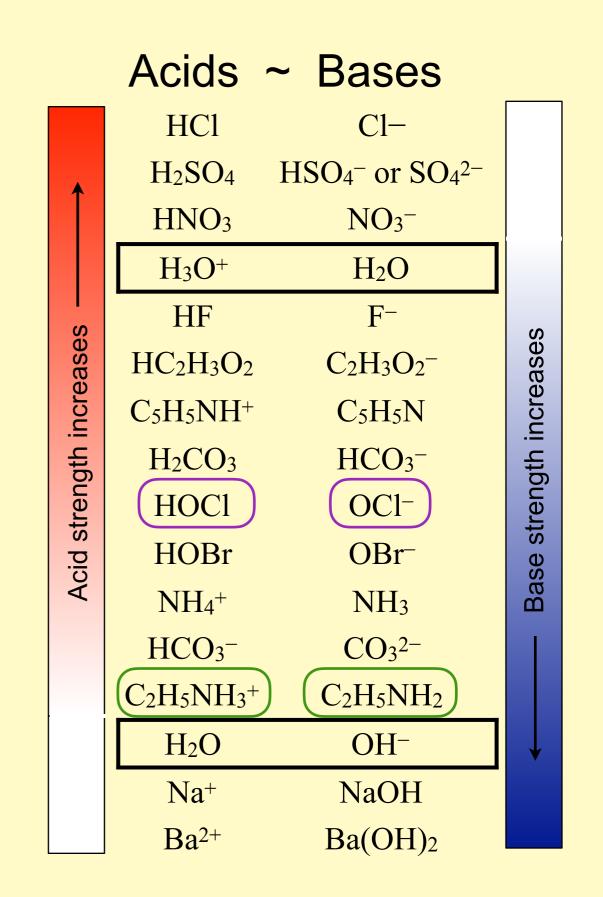
 $K_a$ 

- HA + H<sub>2</sub>O  $\leftrightarrows$  A<sup>-</sup> + H<sub>3</sub>O<sup>+</sup>
- OR HA  $\rightleftharpoons$  A<sup>-</sup> + H<sup>+</sup>
- HCIO  $\iff$  CIO<sup>-</sup> + H<sup>+</sup>
- $NH_4^+ \rightleftharpoons NH_3 + H^+$
- So Let's remember that this formula ONLY represents a weak acid hydrolysis, NEVER a neutralization reaction. K ][OH =

Understanding the relationship between strengths of conjugate A & B

weak...weaker weak....not so weak strong....incredibly weak (aka pathetic)

- Compare the inverse proportionality of the strengths of conjugate acid/base pairs.
- Turn to your mate and comment on the acid strength of HOCI compared to the base strength of OCI<sup>-</sup>
- Comment on the acid strength of C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>+ compared to the base strength of C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>



- First lets notice that hypochlorous acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> is a weak acid.
- Note that the conjugate, acetate ion, C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> is a weak base.
- It is important to remember, that the conjugate of a weak acid is NOT a strong base.

	Acids	~ Bases		
Acid strength increases	HC1	Cl-		
	$H_2SO_4$	HSO <sub>4</sub> <sup>-</sup> or SO <sub>4</sub> <sup>2-</sup>		
	HNO <sub>3</sub>	NO <sub>3</sub> -		
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O		
	HF	F-	S	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	Base strength increases	
	$C_5H_5NH^+$	$C_5H_5N$	ncre	
	$H_2CO_3$	HCO <sub>3</sub> -	gth i	
	HOCl	OC1-	tren	
	HOBr	OBr-	se s	
	$NH_{4}^{+}$	NH <sub>3</sub>	Ba	
	HCO <sub>3</sub> -	CO <sub>3</sub> 2-		
	C <sub>2</sub> H <sub>5</sub> NH <sub>3</sub> +	$C_2H_5NH_2$		
	H <sub>2</sub> O	OH-	$\downarrow$	
	Na <sup>+</sup>	NaOH		
	Ba <sup>2+</sup>	Ba(OH) <sub>2</sub>		

- Notice that ammonium,
   NH<sub>4</sub><sup>+</sup> is a weaker acid.
- Note that ammonium's conjugate, ammonia, NH<sub>3</sub> is a not a weak base.
- It is important to remember, that the conjugates of weak acids and weak bases are NOT a strong acid.

	Acids	~ Bases	
Î	HC1	Cl–	
	$H_2SO_4$	HSO <sub>4</sub> <sup>-</sup> or SO <sub>4</sub> <sup>2-</sup>	
	HNO <sub>3</sub>	NO <sub>3</sub> -	
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	
Acid strength increases -	HF	F-	S
	$HC_2H_3O_2$	$C_2H_3O_2^-$	strength increases
	$C_5H_5NH^+$	$C_5H_5N$	ncre
	$H_2CO_3$	HCO <sub>3</sub> -	gth i
	HOC1	OC1-	tren
	HOBr	OBr-	se s
	$NH_{4}^{+}$	NH <sub>3</sub>	Base
	HCO <sub>3</sub> -	CO3 <sup>2-</sup>	
	$C_2H_5NH_3^+$	$C_2H_5NH_2$	
	H <sub>2</sub> O	OH-	↓ I
	Na <sup>+</sup>	NaOH	
	Ba <sup>2+</sup>	Ba(OH) <sub>2</sub>	

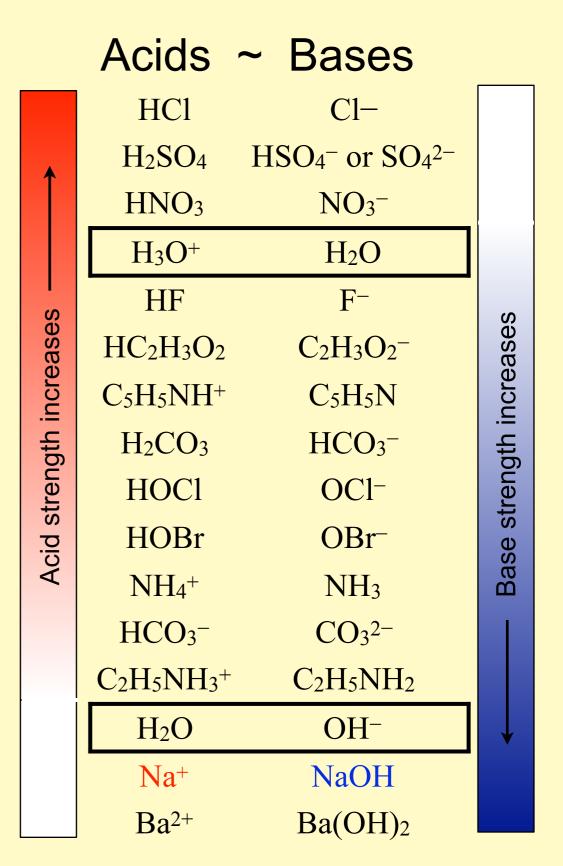
▶ 55

- Notice that hydochloric acid, HCl is a strong acid.
- Let's look at strength or weakness of HCl's "conjugate," chloride ion, Cl-?
- CI- + H<sub>2</sub>O  $\rightarrow$  HCI + OHstrong acid, totally dissociates
- It is important to remember, that the conjugate of a strong acid is an incredibly weak base....actually a nonexistent base, well call it a PATHETIC.
- All anions (other than ions of multiporotic acids) are bases.

	Acids	~ Bases	
Acid strength increases	HC1	Cl–	
	$H_2SO_4$	HSO <sub>4</sub> <sup>-</sup> or SO <sub>4</sub> <sup>2-</sup>	
	HNO <sub>3</sub>	NO <sub>3</sub> -	
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	
	HF	F-	S
	$HC_2H_3O_2$	$C_2H_3O_2^-$	ase
	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup>	C <sub>5</sub> H <sub>5</sub> N	strength increases
	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> -	gth i
	HOC1	OC1-	trenç
	HOBr	OBr-	se st
	$NH_{4}^{+}$	NH <sub>3</sub>	Base
	HCO <sub>3</sub> -	CO3 <sup>2-</sup>	
	$C_2H_5NH_3^+$	$C_2H_5NH_2$	
	H <sub>2</sub> O	OH-	$\downarrow$
	Na <sup>+</sup>	NaOH	
	Ba <sup>2+</sup>	Ba(OH) <sub>2</sub>	

- Notice that sodium hydroxide, NaOH is a strong base.
- Let's look at strength or weakness of hydroxide's "conjugate," sodium ion, Na<sup>+</sup>?

- It is important to remember, that the conjugate of a strong base is such an incredibly weak acid....actually a nonexistent acid, well call it a PATHETIC.
- All cations (other than Group I & II) are acids.



## If you know your SA & SB...

#### Strong Acids

Strong Bases

- HCI
- HI
- HBr
- HNO<sub>3</sub>
- H<sub>2</sub>SO<sub>4</sub>
- **HCIO**<sub>4</sub>
- 3 **)**4
- **IO**4
- HCIO<sub>3</sub>

- LiOH
   NaOH
- KOH
- RbOH
- CsOH
- **Ba**(OH)<sub>2</sub>
- **Sr(OH)**<sub>2</sub>
- Ca(OH)<sub>2</sub>

...then you know the pathetics. all other +ions are acids, and *nearly* all other -ions are bases.

# The Relationship between K<sub>a</sub> and K<sub>b</sub> of conjugates

The "extra" equilibrium that happens in ALL aqueous solutions.

### $K_a \ge K_b = K_w$

- HA + H<sub>2</sub>O  $\leftrightarrows$  A<sup>-</sup> + H<sub>3</sub>O<sup>+</sup>  $K_a = \frac{[A^-][H_3O^+]}{[HA]}$
- $A^- + H_2O \leftrightarrows HA + OH^- \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$
- Take a moment to notice that the pink and blue equations are *not* "opposites" of each other.
- Hess' Law, add the two equations:  $2 H_2 O \implies H_3 O^+ + OH^-$
- When adding reactions...multiply K's

$$\frac{[A^{-}][H_{3}O^{+}]}{[HA]} \times \frac{[HA][OH^{-}]}{[A^{-}]}$$

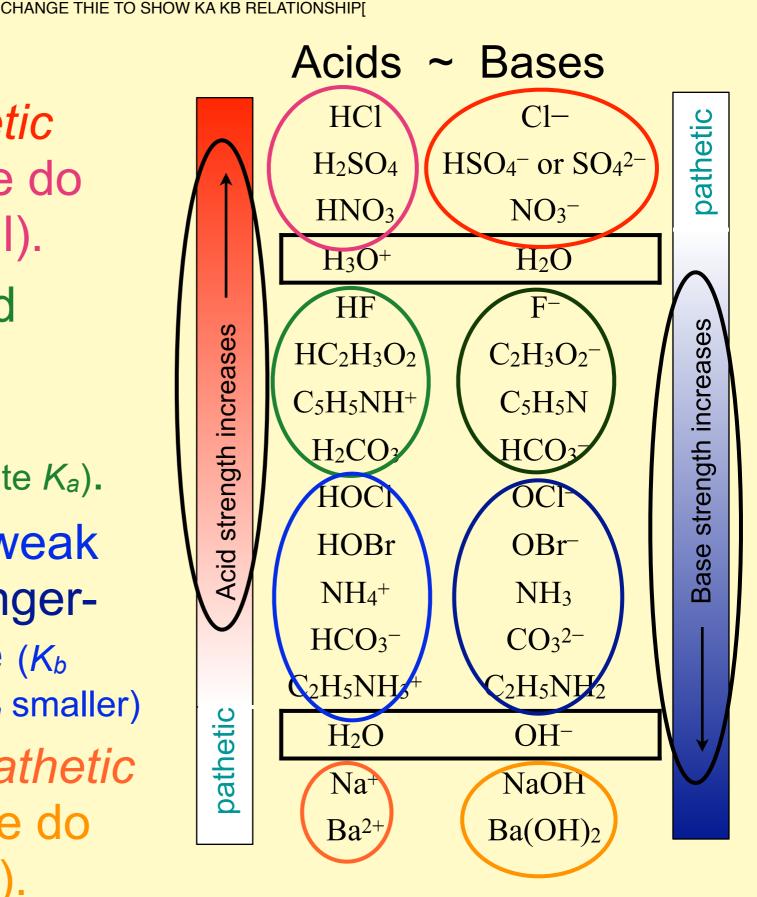
• Thus  $K_a \ge K_b = [H_3O^+][OH^-] = K_w$ 

### Why do we care about pH?

- pH is incredibly important to aqueous solutions and the reactions that take place in those solutions.
  - Body fluids must maintain a tight pH range because many metabolic reactions work only at certain [H<sup>+</sup>] and [OH<sup>-</sup>] concentrations.
  - Pool chemicals work best within a certain pH range.
  - Fish are scales and gills are sensitive to changes in concentration of [H<sup>+</sup>] and [OH<sup>-</sup>].
  - Soil pH is important for solubility and retention of particular plant nutrients.
- So as chemists, understanding, measuring, and calculating [H<sup>+</sup>] and [OH<sup>-</sup>] is very important.
- Thus the pH scale.

Strong, weak, pathetic... What does it all mean?

- A strong acid has a *pathetic* conjugate base (which we do not refer to as bases at all).
- A "stronger-ish" weak acid (K<sub>a</sub> small) has a very weak conjugate weak base (K<sub>b</sub> much smaller than the conjugate K<sub>a</sub>).
- Whereas a "weaker-ish" weak acid (K<sub>a</sub> smaller) has a "strongerish" conjugate weak base (K<sub>b</sub> small, but larger than conjugate K<sub>a</sub> smaller)
- The strong bases have *pathetic* conjugate acids (which we do not refer to as acids at all).



### Size of K<sub>a</sub> and K<sub>b</sub>

- Just as in unit F, the equilibrium position depends on the degree to which the forward reaction dominates.
- We call this the "strength" of the acid or base.
  The weaker the acid, the smaller the K<sub>a</sub>

✓ Of course a "weaker" weak acid (K<sub>a</sub> of 10-9 ish) will result in a "stronger-ish" weak conjugate base (K<sub>b</sub> of 10-5 ish).
 (but NOT a strong conjugate base)

• The weaker the base, the smaller the  $K_b$ 

 A "weaker" weak base (K<sub>b</sub> of 10<sup>-10</sup> ish) will result in a "stronger-ish" weak conjugate acid (K<sub>a</sub> of 10<sup>-4</sup> ish).
 (but NOT a strong conjugate acid)

# Polyprotic Acids "multi-hydroxide" bases

## H<sub>2</sub>A and H<sub>3</sub>A Ba(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>,

## "Multi" Acids and Bases

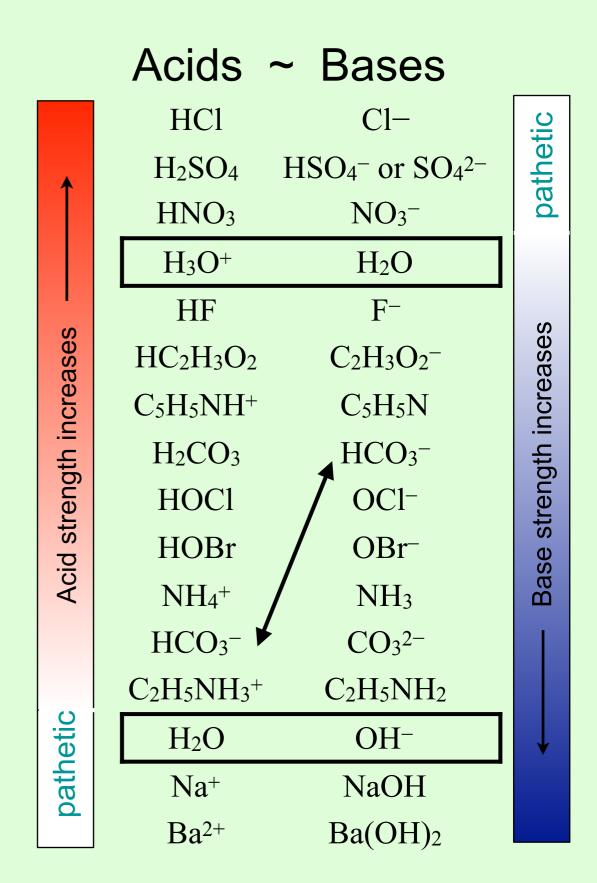
- Acids with more than one ionizable proton
  - ✓ srong sulfuric acid...we can assume both H+'s ionize
  - ✓  $H_2SO_4$
  - ✓ Most multiprotic acids are weak
  - $\checkmark H_3PO_4 \qquad H_2CO_3$
- Bases with more than one hydroxide (soluble group II hydroxides)
   ✓ Ba(OH)<sub>2</sub> Sr(OH)<sub>2</sub> Ca(OH)<sub>2</sub>
- We need to be careful when working neutralization reactions as the acids and bases are buy 1 get 2 or 3

# Another look at Amphoteric

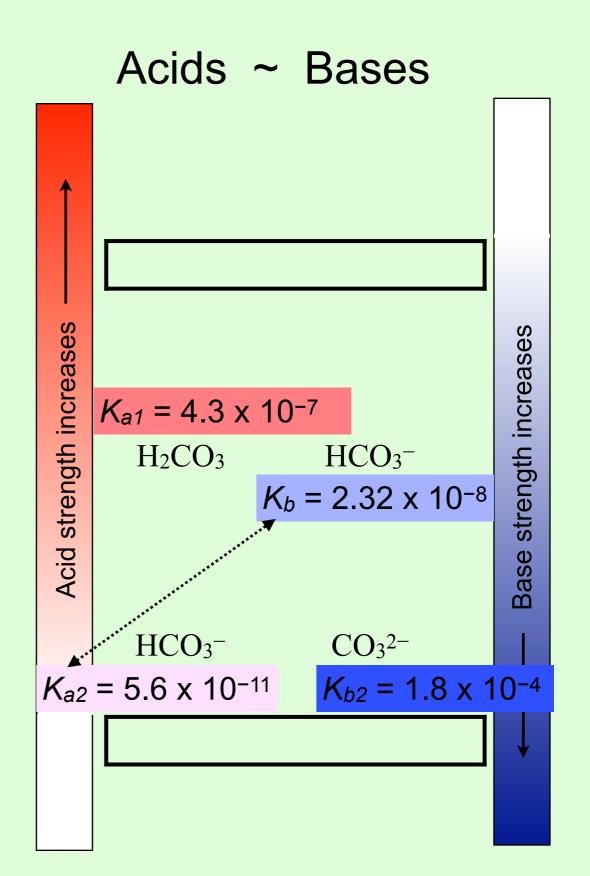
# Particles able to act as both acid or base.

#### Did you happen to notice that HCO<sub>3</sub><sup>-</sup> is in both the acid and base column?

#### Wait...whaaat??



- Why is HCO<sub>3</sub><sup>-</sup> in both the acid and base column?
- HCO<sub>3</sub><sup>-</sup> is amphoteric.
- Depending on what other substances are in the beaker, HCO<sub>3</sub><sup>-</sup> can act as either and acid or a base.
- But in water, HCO<sub>3</sub><sup>-</sup> is a better base than an acid.
- We can tell from the larger
   *K<sub>b</sub>* compared to the smaller
   *K<sub>a</sub>* of HCO<sub>3</sub><sup>-</sup>



More on this K<sub>a1</sub> and K<sub>a2</sub> stuff later

# Acid & Base Clicker Questions

Do Now or Review later ...as time allows In a 0.01 M aqueous solution of HCI, select the particles below that are in the beaker. *Select all that apply.* 

- 1. H<sub>3</sub>O<sup>+</sup>
- 2. CI<sup>-</sup>
- 3. HCI
- 4. H<sub>2</sub>O
- 5. OH-

- In a 0.01 M aqueous solution of HCI, select the particles below that are in the beaker. Select all that apply.
- 1. H<sub>3</sub>O<sup>+</sup>
- 2. CI<sup>-</sup>
- But AP really wants you to say there is NO HCI.
- because HCI is a strong acid, all of the HCI molecules have dissociated.
   4. H<sub>2</sub>O
- 5. OH-
- Every aqueous solution has both OH<sup>-</sup> and H<sup>+</sup> whether it is acidic, basic, or neutral.
  - $H_2O \rightleftharpoons H^+ + OH^-$

In a 0.01 M solution of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, select the particles below that are in solution. *Select all that apply.* 

- 1. H<sub>3</sub>O<sup>+</sup>
- 2.  $C_2H_3O_2^-$
- 3.  $HC_2H_3O_2$
- 4. H<sub>2</sub>O
- 5. OH-

In a 0.01 M solution of  $HC_2H_3O_2$ , select the particles below that are in solution. Select all that apply.

- 1. H<sub>3</sub>O<sup>+</sup>
- 2. CI-
- $3.HC_2H_3O_2$
- because HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> is a weak acid, none of the molecules have dissociated.
- **4. H**<sub>2</sub>**O**
- 5. OH-
- Every aqueous solution has both OH<sup>-</sup> and H<sup>+</sup> whether it is acidic, basic, or neutral.

If you had an aqueous solution in which  $[OH^-] = 1 \times 10^{-4} \text{ M}$ , is this solution

- 1. acidic
- 2. basic
- 3. neutral

- No calculator but be prepared to justify your answer
- 4. cannot be determined without more info

If you had an aqueous solution in which  $[OH^-] = 1 \times 10^{-4} \text{ M}$ , Is this solution

- 1. acidic
- 2. basic
- The pOH of this solution would be 4, and the pH would be 10
- 3. neutral
- 4. cannot be determined without more info
- If [OH<sup>-</sup>] > [H<sup>+</sup>] the solution is basic.
- If [OH<sup>-</sup>] < [H<sup>+</sup>] the solution is acidic.
- If  $[H^+] = [OH^-]$  the solution is neutral.

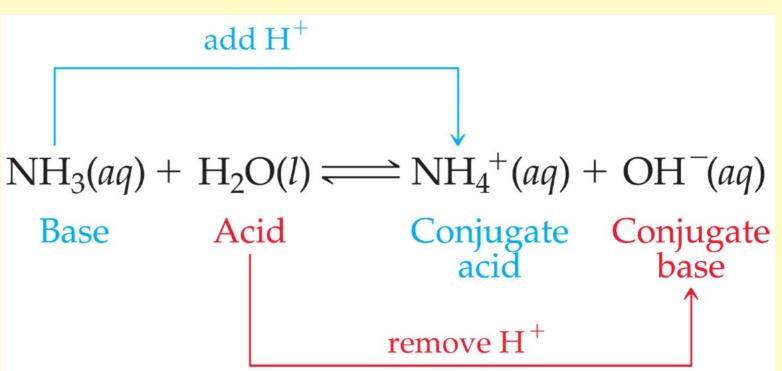
In the reaction below, which of the species are acids?  $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$ 

- 1. NH<sub>3</sub>
- 2. H<sub>2</sub>O
- 3. NH<sub>4</sub>+
- 4. There are no acids here, this is a reaction for a weak base.

# In the reaction below, which species is an acid? $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

1.NH<sub>3</sub> 2.H<sub>2</sub>O 3.NH<sub>4</sub>+

4.There are no acids here, this is a reaction for a weak base.



Let's notice the two conjugate acid/base pairs.

What would be the conjugate base for  $H_2PO_4^{-}_{(aq)}$ ?

- 1. H<sub>3</sub>O<sup>+</sup>
- 2.  $H_3PO_4$
- 3. HPO<sub>4</sub><sup>2-</sup>
- 4. PO<sub>4</sub><sup>3-</sup>
- 5. OH-
- 6. There is no conjugate base,  $H_2PO_4^-$  is not an acid, negative ions are always bases.

What would be the conjugate base for  $H_2PO_4^{-}_{(aq)}$ ?

Acid

 $H_2PO_4^- + H_2O \implies H_3O^+$ 

base

- 1. H<sub>3</sub>O<sup>+</sup>
- 2.  $H_3PO_4$
- 3. HPO<sub>4</sub><sup>2-</sup>
- 4. PO<sub>4</sub><sup>3-</sup>
- 5. OH-
- There is no conjugate base, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> is not an acid, negative ions are always bases.

HPO<sub>4</sub><sup>2-</sup>

conjugate

base

+

conjugate

acid

What would be the conjugate acid for  $H_2PO_4^{-}_{(aq)}$ ?

- 1. H<sub>3</sub>O<sup>+</sup>
- 2. H<sub>3</sub>PO<sub>4</sub>
- 3. HPO<sub>4</sub><sup>2-</sup>
- 4. PO<sub>4</sub><sup>3-</sup>
- 5. OH-

What would be the conjugate acid for  $H_2PO_4^{-}_{(aq)}$ ?

- 1. H<sub>3</sub>O<sup>+</sup>
- **2.** H<sub>3</sub>PO<sub>4</sub>
- 3. HPO<sub>4</sub><sup>2-</sup>
- 4. PO<sub>4</sub><sup>3-</sup>
- 5. OH-

#### $H_2PO_4^- + H^+ \leftrightarrows H_3PO_4$

### Which of the following particles are amphiprotic can behave as either acid or base)

- 1. H<sub>3</sub>O<sup>+</sup>
- 2.  $H_3PO_4$
- 3.  $H_2PO_4^-$
- 4. HPO<sub>4</sub><sup>2-</sup>
- 5. PO<sub>4</sub><sup>3-</sup>
- 6. OH-
- 7. H<sub>2</sub>O

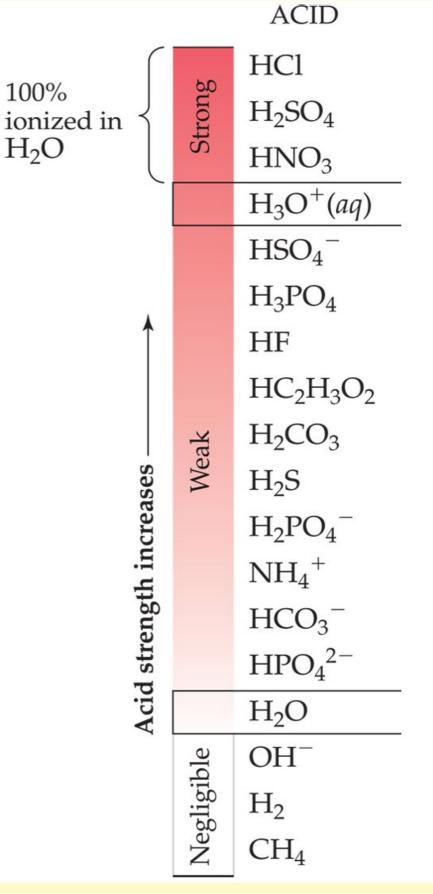
### Which of the following particles are amphoteric?

- 1. H<sub>3</sub>O<sup>+</sup>
- 2. H<sub>3</sub>PO<sub>4</sub>
- 3.  $H_2PO_4^-$
- 4. HPO<sub>4</sub><sup>2-</sup>
- 5. PO<sub>4</sub><sup>3-</sup>
- 6. OH-
- 7. H<sub>2</sub>O

$H_2PO_4^-$	+ H <sub>2</sub> O	<u></u>	H <sub>3</sub> O+	+ HPO4 <sup>2-</sup>	
Acid	Base		Acid	Base	
H <sub>2</sub> PO <sub>4</sub> -	+ H <sub>2</sub> O	<u> </u>	OH-	+ H <sub>3</sub> PO <sub>4</sub>	
Base	Acid		Base	Acid	
HPO <sub>4</sub> <sup>2-</sup>	+ H <sub>2</sub> O	$\stackrel{\checkmark}{\rightarrow}$	H <sub>3</sub> O+	+ PO <sub>4</sub> <sup>3-</sup>	
Acid	Base		acid	Base	
	+ H <sub>2</sub> O	<u> </u>		+ H <sub>2</sub> PO <sub>4</sub> -	
Base	Acid		Base	Acid	
$H_2O + H_2O \iff OH^- + H_3O^+$					
Acid	Base		Raso	Acid	

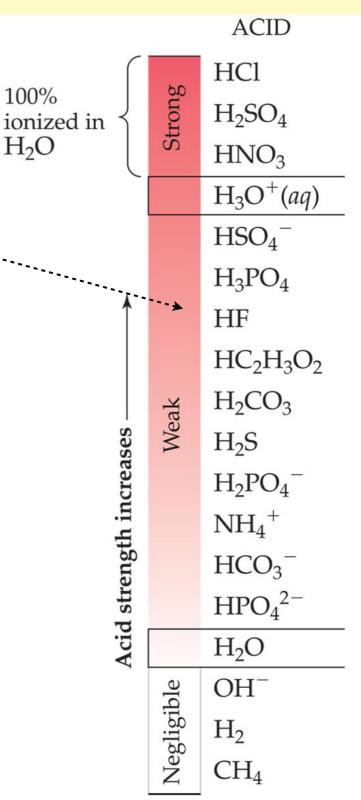
#### Which base is the weakest?

- 1.  $C_2H_3O_2^-$
- 2. CO<sub>3</sub><sup>2-</sup>
- 3. S<sup>2-</sup>
- 4. NH<sub>3</sub>
- 5.



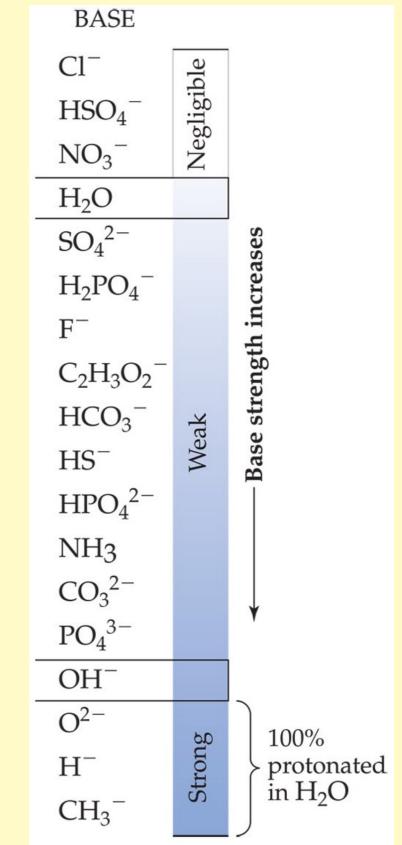
#### Which base is the weakest?

- F<sup>-</sup>
   C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>
- Z. U2H3U2
- 3. CO<sub>3</sub><sup>2-</sup>
- 4. S<sup>2-</sup>
- 5. NH<sub>3</sub>
- the conjugate base will be the weaker if its conjugate acid is stronger-ish. You must think about the conjugate acids of the bases listed, HF is the strongest of those acids, so F- is the wekest of the bases listed.



### Which acid is the strongest?

- 1. H<sub>3</sub>O<sup>+</sup>
- 2. HF
- 3.  $HC_2H_3O_2$
- 4. NH<sub>4</sub>+

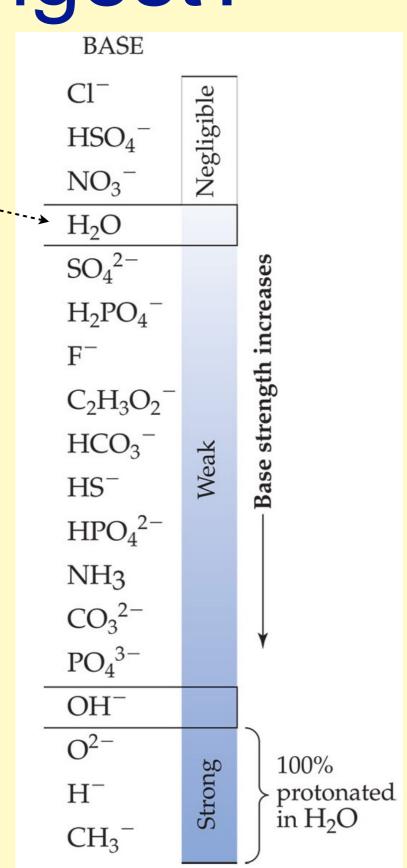


### Which acid is the strongest?

- the acid will be the stronger if its conjugate base is weaker.
- 2. HF

 $H_3$ 

- 3.  $HC_2H_3O_2$
- 4. NH<sub>4</sub>+



# Which base is the strongest of these weak bases?

1.  $NO_3^{-1}$ 2.  $C_2H_3O_2^{-1}$ 3.  $HCO_{3}^{-}$ 4.  $CO_3^{2-}$ 5. NH<sub>3</sub>

Acid	Ka	р <i>К</i> а
HNO <sub>3</sub>	Strong acid	-
HF	6.8 x 10 <sup>-4</sup>	3.17
$HC_2H_3O_2$	1.8 x 10 <sup>-5</sup>	4.7
H <sub>2</sub> CO <sub>3</sub>	4.3 x 10 <sup>-7</sup>	6.37
NH <sub>4</sub> +	5.6 x 10 <sup>-10</sup>	9.25
HCO <sub>3</sub> -	5.6 x 10 <sup>-11</sup>	10.18

#### Which base is the strongest?

- 1. NO<sub>3</sub>-
- 2.  $C_2H_3O_2^-$
- 3. HCO<sub>3</sub>-
- 4. CO<sub>3</sub><sup>2–</sup>
- The conjugate base of the weakest acid will be the strongest base
   5. NH<sub>3</sub>

pK<sub>a</sub>, is -logK<sub>a</sub>

If p*K*a is bigger,

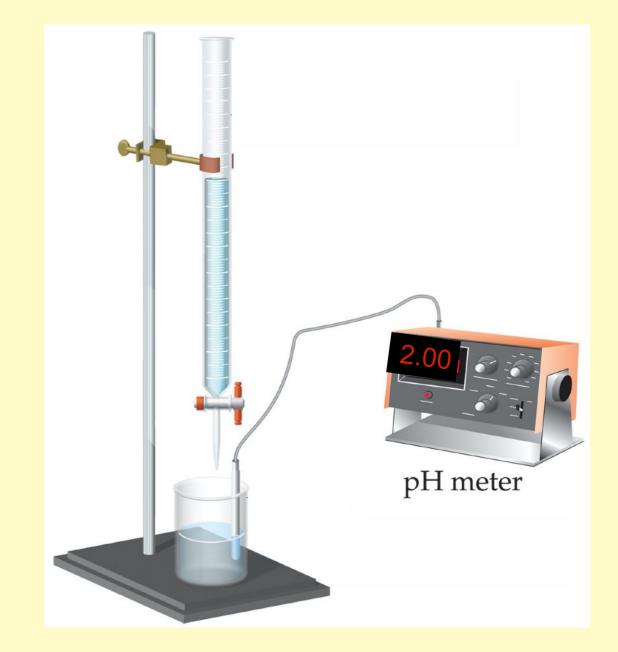
 $K_a$  is smaller which means weaker acid.

Acid	K <sub>a</sub>	р <i>К<sub>а</sub></i>
HNO <sub>3</sub>	Strong acid	-
HF	6.8 x 10⁻₄	3.17
$HC_2H_3O_2$	1.8 x 10⁻⁵	4.7
H <sub>2</sub> CO <sub>3</sub>	4.3 x 10 <sup>-7</sup>	6.37
NH <sub>4</sub> +	5.6 x 10 <sup>-10</sup>	9.25
HCO <sub>3</sub> -	5.6 x 10 <sup>-11</sup>	10.18

If the pH = 2.00 for an HNO<sub>3</sub> solution, what is the concentration of HNO<sub>3</sub>?

No calculator

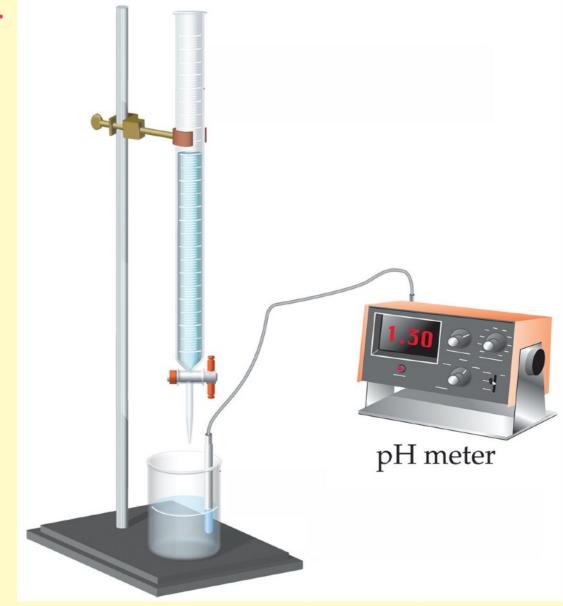
0.10
 0.20
 0.010
 0.020
 0.020
 0.0010



If the pH = 2 for an  $HNO_3$  solution, what is the concentration of  $HNO_3$ ?

No calculator

- 1. 0.102. 0.203. 0.010•  $10^{-2} = 0.01$
- 4. 0.002
   5. 0.0010



If the pH = 10 for a Ca(OH)<sub>2</sub> solution, what is the concentration of Ca(OH)<sub>2</sub>?

- **1. 1.0** x **10**<sup>-10</sup>
- 2. 5.0 x 10<sup>-11</sup>
- 3. 5.0 x 10<sup>-5</sup>
- 4. 1.0 x 10<sup>-2</sup>
- 5. 5.0 x 10<sup>-3</sup>

- 6. 1.0 x 10<sup>-4</sup>
- 7. 5.0 x 10<sup>-4</sup>
- 8. 2.0 x 10<sup>-4</sup>
- 9. 2.0 x 10<sup>-5</sup>
  10.2.0 x 10<sup>-10</sup>

Try without a calculator? If it's too hard for you, go ahead and use the calculator.

#### If the pH = 10 for a Ca(OH)<sub>2</sub> solution, what is the concentration of Ca(OH)<sub>2</sub>?

#### No calculator

1.	<b>1.0 x 10</b> <sup>-10</sup>	6.	1.0 x 10 <sup>-4</sup>
2.	5.0 x 10 <sup>-11</sup>	7.	5.0 x 10 <sup>-4</sup>
3.	5.0 x 10 <sup>-5</sup>	8.	2.0 x 10 <sup>-4</sup>
4.	1.0 x 10 <sup>-2</sup>	9.	2.0 x 10 <sup>-5</sup>
5.	5.0 x 10 <sup>-3</sup>	10.	2.0 x 10 <sup>-10</sup>

pOH = 4,  $-\log(1x10^{-4})$ , thus  $[OH^{-}] = 1x10^{-4}$ , since Ca(OH)<sub>2</sub>  $\rightarrow$  Ca<sup>+2</sup> + 2OH<sup>-</sup>, thus the concentration of dissolved Ca(OH)<sub>2</sub> = 0.5 x 10<sup>-4</sup> = 5 x 10<sup>-5</sup>

### What is the approximate pH of an aqueous solution of 0.001 M HCl?

No calculator

- 1 1. 2. 2 3. 3 7 4. 5. 11 12 6. 7. 14
- 8. None of the above

#### What is the approximate pH of an aqueous solution of 0.001 M HCI? 1. 1 No calculator 2. 2 3 3. $10^{-3} = -\log(1 \times 10^{-3}) = 3$ 4 7 5. 11 6. 12 7. 14 None of the above 8

#### Strong Acids and Bases

- Who are the strong acids?
  - HCI, HBr, HI (not HF, it's a weak acid)
  - ► HNO<sub>3</sub>, HCIO<sub>3</sub>, HCIO<sub>4</sub>
  - $H_2SO_4$
- Who are the strong bases?
  - Alkali hydroxides: KOH and NaOH
    - ✓LiOH, RbOH, and CsOH are not as common.
  - Heavy alkaline hydroxides: Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub> are quite soluble and are completely ionized.
    - ✓ Ca(OH)<sub>2</sub> is semi-soluble, Mg(OH)<sub>2</sub> is not so soluble.
       The tiny bit that does dissolve is ionized, so SB.
       ✓ The other hydroxides are very insoluble.

# Problem Types

### pH of WA, WB determining *K<sub>a</sub>*, *K<sub>b</sub>* percent ionization

- Write a reaction for the ionization of hypochlorous acid.
- Write the K<sub>a</sub> expression.

- Write a reaction for the ionization of hypochlorous acid.
  - $\checkmark$  HCIO  $\rightleftharpoons$  H<sup>+</sup> + CIO<sup>-</sup>
- Write the K<sub>a</sub> expression.

- Write a reaction for the ionization of hypochlorous acid.
  - $\checkmark$  HCIO  $\leftrightarrows$  H<sup>+</sup> + CIO<sup>-</sup>
- Write the K<sub>a</sub> expression.

$$K_a = \frac{[H^+][ClO^-]}{[HClO]}$$

 Construct an ricebox put in the concentrations we already know.....next slide please

- We can assume that the initial [H<sup>+</sup>] = 0, because the amount of H<sup>+</sup> in pure water is too small compared to any H<sup>+</sup> caused by the presence of the hypochlorous acid.
- Since we don't know what the changes are....

 $\checkmark$  call them x

And thus the equilibrium concentrations?

$$K_a = \frac{[H^+][ClO^-]}{[HClO]}$$

	HCIO =	⇒ H+ +	CIO-
	0.20	~ 0	~ 0
С			
E			

	HCIO =	⇒ H+ +	CIO-
	0.20	~ 0	0
С	-X	+χ	+χ
Ε	0.20 - x	X	X

• How will we solve? 3.

$$3.0 \times 10^{-8} = \frac{[x][x]}{[0.20 - x]}$$

✓ UGH...this is a quadratic

✓ Solving for  $x = [H^+] = 7.747 \times 10^{-5} M$ 

But wait....can we avoid the use of the quadratic??

### Calculate the pH of a 0.20 M solution of hypochlorous acid.

	HCIO =	⇒ H+ +	CIO-
Ι	0.20	~ 0	0
С	-X	+x	+χ
E	0.20 <b>-</b> X	X	Х

~0.20 In AP we will ALWAYS be able to ignore the -x when the alternative means using the quadratic

- Let's consider how significant figures allow us to avoid the quadratic formula.
  - ✓ We can consider the -x to be insignificant compared to the 0.20M for HCIO, thus the equilibrium [CIO<sup>-</sup>] = ~0.20 M

✓ x = [H<sup>+</sup>] = 7.7 x 10<sup>-5</sup> M

Use the [H<sup>+</sup>] to calculate pH
 ✓ pH = 4.11

$$3.0 \times 10^{-8} = \frac{[x][x]}{[0.20 - x]} \operatorname{x \ too \ small \ to}_{\text{worry about}}$$

Calculate the pH of a 0.20 M solution of ammonia,  $(NH_3) pK_b = 4.74$ 

- Write a chemical equation for the ionization reaction of ammonia in water.
- Write the *K*<sup>*b*</sup> expression.
- Construct a ricebox put in the concentrations we know, calculate the others, ignore insignificant x's

Calculate the pH of a 0.20 M solution of ammonia,  $pK_b = 4.74$ .

- Write a reaction for the ionization of ammonia.
  - $\checkmark NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$
- Write the *K*<sup>*b*</sup> expression.
  - $\checkmark$  What is the value for  $K_b$ ?

Calculate the pH of a 0.20 M solution of ammonia,  $(NH_3) pK_b = 4.74$ 

Write a reaction for the ionization of ammonia.

 $\checkmark NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$ 

• Write the  $K_b$  expression,  $pK_b = 4.74$  $\checkmark K_b = 10^{-4.74} = 1.8 \times 10^{-5}$ 

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Calculate the pH of a 0.20 M solution of ammonia,  $(NH_3) pK_b = 4.74$ 

Write a reaction for the ionization of ammonia.

 $\checkmark NH_3 + H_2O \iff NH_4^+ + OH^-$ 

• Write the  $K_b$  expression,  $pK_b = 4.74$  $\checkmark K_b = 10^{-4.74} = 1.8 \times 10^{-5}$ 

$$K_{b} = \frac{[NH_{4}^{+}][OH^{-}]}{[NH_{3}]} \qquad 1.8 \times 10^{-5} = \frac{[x][x]}{[0.20]} \text{ really [0.20 - x] but the x is SO tiny, we can ignore it.}$$

 $x = [OH^{-}] = 1.9 \times 10^{-3}$  if you did use the quadratic,  $x = 1.8884 \times 10^{-3}$ , pOH = 2.72, pH = 11.28

pOH = 2.72 pH = 11.28

After preparing a 0.10 M solution of nitrous acid, the pH was 2.17, calculate the  $K_a$  for this acid.

- Write the reaction for the equilibrium dissociation of nitrous acid in water.
- Write the *K*<sub>a</sub> expression.

After preparing a 0.10 M solution of nitrous acid, the pH was 2.17, calculate the  $K_a$  for this acid.

Write the reaction for the equilibrium dissociation of nitrous acid in water.

• 
$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

- $HNO_2 + H_2O \leftrightarrows H_3O^+ + NO_2^-$
- Write the K<sub>a</sub> expression.

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

• "Do we know [H<sup>+</sup>] or [NO<sub>2</sub><sup>-</sup>]"

- After preparing a 0.10 M solution of nitrous acid, the pH was 2.17, calculate the  $K_a$  for this acid.
- Write the reaction for the equilibrium dissociation of nitrous acid in water.

• 
$$HNO_2 \rightleftharpoons H^+ + NO_2^-$$

• Write the K<sub>a</sub> expression.

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

• "Un-log" the pH to determine the equilibrium [H+]

$$[H^+] = 10^{-2.17} = 6.8 \times 10^{-3} M$$

- What is the [NO<sub>2</sub>-]?
  - the same as [H<sup>+</sup>]

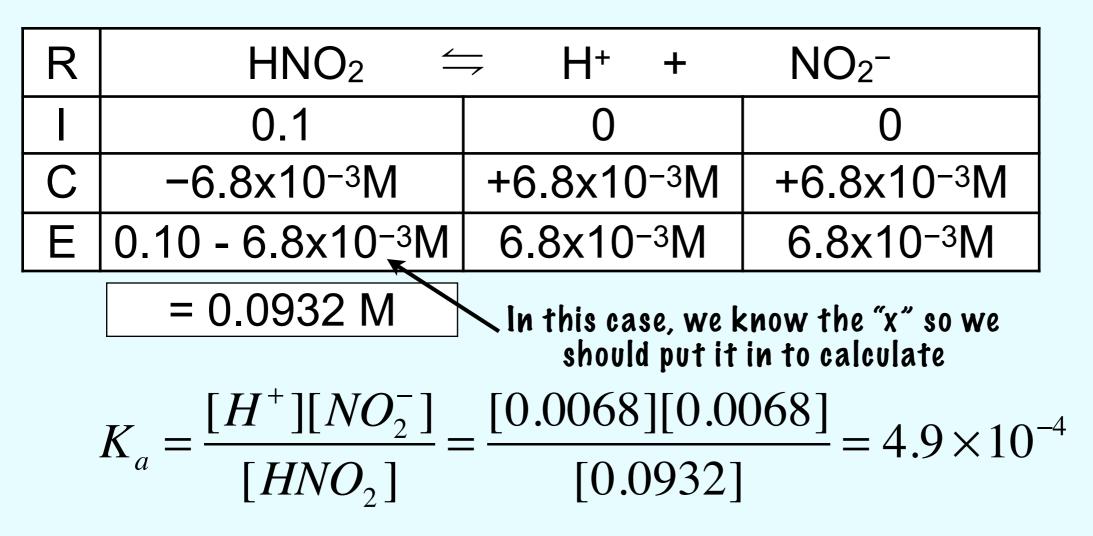
After preparing a 0.10 M solution of nitrous acid, the pH was 2.17, calculate the  $K_a$  for this acid.

- What's the equilibrium concentration of NO<sub>2</sub>-?
  - ✓ same as H<sup>+</sup>
- What do you know about the initial  $[H^+]$  and  $[NO_2^-]$ ?
  - ✓ Assume there is none in the container to start.
  - ✓ Why do we assume the initial [H<sup>+</sup>] = 0? Isn't there 1x10<sup>-7</sup>M in water?
    - 1x10<sup>-7</sup>M is so much smaller than any amounts of that will form due to the presence of the acid so sig figs allow the 1x10<sup>-7</sup> M to be considered ~0

	HNO <sub>2</sub> =	⇒ H+ +	$NO_2^-$	$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]}$
1	0.1	~ 0	0	
С				
E		6.8x10 <sup>-3</sup> M		

After preparing a 0.10 M solution of nitrous acid, the pH was 2.17, calculate the  $K_a$  for this acid.

- Now you can calculate the change row.
- Then the equilibrium concentration of  $HNO_2 = 0.0932 M$
- Fill in the equilibrium expression and calculate Ka



Calculating  $K_a$  without the subtraction = 4.6 x 10<sup>-4</sup>

## Percent Ionization

#### Another way to represent the amount of ionization as related to molarity

- $HA + H_2O \rightleftharpoons H_3O^+ + A^-$
- The amount of HA that ionizes per original amount of original amount HA present.

• %ionization = 
$$\frac{[H_3O^+]}{[HA]} \times 100$$

- For example:
  - ✓ Calculate % ionization for 0.10 M HA,  $K_a = 4.0 \times 10^{-5}$
  - ✓ First solve an x<sup>2</sup> problem, then calculate %

$$4 \times 10^{-5} = \frac{x^2}{[0.1]}$$
 %ionization =  $\frac{[2 \times 10^{-3}]}{[0.1]} \times 100 = 2\%$   
 $x = [H_3O^+] = 2 \times 10^{-3}$ 

After preparing a 0.10 M solution of nitrous acid, the pH was 2.17, calculate the  $K_a$  for this acid.

What percentage of the acid is ionized in this 0.10M solution?

- Remember that % is part out of total.
  - What part represents the part that is ionized?
  - What part represents total acid?

$$\% ionization = \frac{[H_3O^+]}{[HA]} \times 100$$

	HNO <sub>2</sub> =	⇒ H+ +	NO <sub>2</sub> -
Ι	0.1	0	0
С	−6.8x10 <sup>-3</sup> M	+6.8x10 <sup>-3</sup> M	+6.8x10 <sup>-3</sup> M
E	0.0932 M	6.8x10 <sup>-3</sup> M	6.8x10 <sup>-3</sup> M

After preparing a 0.10 M solution of nitrous acid, the pH was 2.17, calculate the  $K_a$  for this acid.

What percentage of the acid is ionized in this 0.10M solution?

- Remember that % is part out of total.
  - What part represents the part that is ionized?
  - What part represents total acid?
- Calculate  $\frac{6.8 \times 10^{-3}}{0.10} \times 100 = 6.8\%$

	HNO <sub>2</sub> =	⇒ H+ +	NO <sub>2</sub> -
Ι	0.1	0	0
С	−6.8x10 <sup>-3</sup> M	+6.8x10 <sup>-3</sup> M	+6.8x10 <sup>-3</sup> M
Ε	0.0932 M	6.8x10 <sup>-3</sup> M	6.8x10 <sup>-3</sup> M

The pH of a 0.060 M solution of pyridine,  $C_5H_5N$  is 9.00. Calculate the  $K_b$  for this base.

What is the percent ionization of this solution?

- The pH of a 0.060 M solution of pyridine, C<sub>5</sub>H<sub>5</sub>N is 9.00. Calculate the *K*<sub>b</sub> for this base.
- What is the percent dissociation of this solution?
- Write the ionization reaction for pyridine in water.
- Write the *K*<sub>b</sub> expression,
- Make a rice box.

The pH of a 0.060 M solution of pyridine,  $C_5H_5N$  is 9.00. Calculate the  $K_b$  for this base.

What is the percent dissociation of this solution?

- $C_5H_5N + H_2O \leftrightarrows C_5H_5NH^+ + OH^-$
- Set up an RICE box

$$K_{b} = \frac{[C_{5}H_{5}NH^{+}][OH^{-}]}{[C_{5}H_{5}N]}$$

• pH = 9, pOH = 5, thus [OH<sup>-</sup>] = 1 x 10<sup>-5</sup>

The pH of a 0.060 M solution of pyridine,  $C_5H_5N$  is 9.00. Calculate the  $K_b$  for this base.

What is the percent dissociation of this solution?

- $C_5H_5N + H_2O \leftrightarrows C_5H_5NH^+ + OH^-$
- Set up an RICE box

$$K_{b} = \frac{[C_{5}H_{5}NH^{+}][OH^{-}]}{[C_{5}H_{5}N]}$$

• pH = 9, pOH = 5, thus [OH<sup>-</sup>] = 1 x 10<sup>-5</sup>

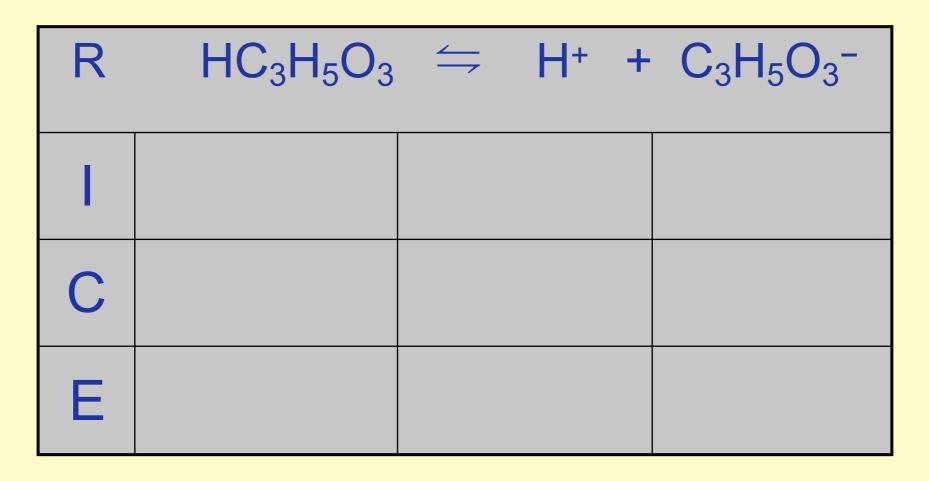
$R  C_5H_5N  \rightarrow \ C_5H_5NH^+  + \ OH^-$			$[1 \times 10^{-5}][1 \times 10^{-5}]$	
Ι	0.06	0	~ 0	$K_{b} = \frac{[1 \times 10^{-5}][1 \times 10^{-5}]}{[0.06]} = 1.7 \times 10^{-9}$
С	- 1 x 10 <sup>-5</sup>	+ 1 x 10 <sup>-5</sup>	+ 1 x 10 <sup>-5</sup>	
Е	0.06 - 1 x 10 <sup>-5</sup>	1 x 10⁻⁵	1 x 10 <sup>-5</sup>	$\frac{1 \times 10^{-5}}{100} \times 100 = 0.017\%$
	~ 0.06			$\frac{-0.06}{0.06} \times 100 = 0.017\%$

Why is  $[OH^-] \sim 0$ ? You could argue that since it is an aqueous solution, that there  $[OH^-] = 1 \times 10^{-7} \text{ OH}^-$ , but since the base will contribute more than that, we can ignore the OH<sup>-</sup> contribution from the water.

Calculate the  $K_a$  of lactic acid, HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>. The acid is 3.7% dissociated in a 0.100 M solution

### Calculate the $K_a$ of lactic acid, HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>. The acid is 3.7% dissociated in a 0.100 M solution

- Write the equilibrium reaction and K<sub>a</sub> expression.
- Set up a RICE box
- Since we are told in the problem that there is 3.7% dissociation, we can calculate [H<sup>+</sup>]



### Calculate the $K_a$ of lactic acid, HC<sub>3</sub>H<sub>5</sub>O<sub>3</sub>. The acid is 3.7% dissociated in a 0.100 M solution

- Write the equilibrium reaction and  $K_a$  expression.
- $HC_3H_5O_3 \leftrightarrows H^+ + C_3H_5O_3^-$
- Set up a RICE box

$$K_{a} = \frac{[H^{+}][C_{3}H_{5}O_{3}^{-}]}{[HC_{3}H_{5}O_{3}]}$$

- Since we are told in the problem that there is 3.7% dissociation, we know that the x is 3.7% of 0.100 M
  x = [H<sup>+</sup>] = 0.0037
- This allows you to fill in the remainder of the RICE box.
- Using the E line of the RICE box allows you to calculate K<sub>a</sub>

$R  HC_3H_5O_3  \leftrightarrows  H^+ + C_3H_5O_3^-$				
I	0.1	~ 0	0	
С	- 0.0037	+0.0037	+0.0037	
Е	0.0963	0.0037	0.0037	

$$K_a = \frac{[0.0037][0.0037]}{[0.0963]} = 1.4 \times 10^{-4}$$

## Percent Ionization



#### Practice G2 Percent Ionization Let's give it a twirl

- For varying concentrations of acetic acid
   ✓ HA + H<sub>2</sub>O ⇒ H<sub>3</sub>O<sup>+</sup> + A<sup>-</sup>
  - ✓ Consider the varying concentration, and resulting % ionization and pH values.

			1	
Conc in M	% ionization	pН		Percent Ionization
0.001	13	3.9		12
0.01	4	3.4		
0.025	2.7	3.2		
0.05	1.9	3		
0.1	1.3	2.9		0
1	0.4	2.4		0 0.02 0.04 0.06 0.08 Concentration
0.01 0.025 0.05	1.9 1.3	3.2 3 2.9		8 6 4 2 0 0 0 0.02 0.04 0.06

0.12

0.1

- Percent ionization varies with concentration changes.
- What is the correlation?

✓ As concentration decreases, percent ionization increases.

- Why? When diluting the solution, there will be less concentration of all three HA, H<sup>+</sup>, and A<sup>-</sup> in the solution. In effect the products are diluted more, thus the equilibrium will shift toward products to minimize the dilution disturbance, and because one acid molecule can produce two ions, increasing the overall concentration.
- At lower concentration, the % ionization is greater, but the [H<sup>+</sup>] is still smaller (higher pH)
  - Although greater percentage of the molecular acid is ionized, there is still much less of of the molecular acid available to providing less [H<sup>+</sup>] overall

- HA ≒ H+ + A<sup>-</sup>
- Imagine the ridiculous scenario of molar a weak acid concentration in which all were 1 M

$$K_a = \frac{[1][1]}{[1]} = 1$$

 Then diluting the solution to double the volume and all the concentrations would halved.

• 
$$K_a > Q$$
  $Q = \frac{[0.5][0.5]}{[0.5]} = 0.5$ 

- the system would shift to the right,
- thus higher percentage ionized

The pH of a 0.050 *M* weak acid is 3.00. what is the percentage ionization?

1.0.02%2.0.10% 3. 0.20% 4. 1.0% 5. 2.0% 6. 3.0%

No calculator

The pH of a 0.050 *M* weak acid is 3.00. what is the percentage ionization?

1. 0.02% No calculator 2. 0.10% Since pH = 3.00, [H<sup>+</sup>] = 1.0 x 10<sup>-3</sup> M, so 3. 0.20% % ionization =  $\frac{[H^+]_{eq}}{[HA]_{o}}$ 4. 1.0% 5. 2.0%  $\frac{10 \times 10^{-2}}{5} \qquad 2 \times 10^{-2}$  $\% ionization = \frac{0.001}{0.05}$ 6. 3.0%

# Neutralization or not? $H^+ + OH^- \rightarrow H_2O$ reacting stoichiometric

amounts of acid and base

### Calculate the pH after mixing 35 ml of 0.025 M hydrochloric acid with 40 ml of 0.030 M NaOH

- Write the neutralization reaction.
- Determine the mmol of the SA and the mmol of SB
- What do you notice? What's left over after mixing?
- What is the pH of the resulting solution?

### Calculate the pH after mixing 35 ml of 0.025 M hydrochloric acid with 40 ml of 0.030 M NaOH

- Write the neutralization reaction.
- $H^+$  +  $OH^- \rightarrow H_2O$
- What do you notice? What's left over after mixing?
- What is the pH of the resulting solution?

 $0.025M \times 35ml = 0.875mmolH^+$ 

 $0.03M \times 40ml = 1.2mmolOH^{-1}$ 

 $1.2 - 0.875 = 0.325 mmolOH^{-}LeftOver$ 

 $\frac{0.325 mmolOH^{-}}{75 ml TotalVol} = 4.3 \times 10^{-3} M OH^{-}$ pOH = 2.36 pH = 11.64

### Calculate the pH after mixing 55 ml of 0.025 M hydrochloric acid with 40 ml of 0.030 M NaOH

- Remember the SA + SB neutralization reaction.
  - $\checkmark H^+ + OH^- \rightarrow H_2O$
- Determine the mmol of the SA and the mmol of SB
- What do you notice? What's left over after mixing?
- What is the pH of the resulting solution?

### Calculate the pH after mixing 55 ml of 0.025 M hydrochloric acid with 40 ml of 0.030 M NaOH

- Remember the SA + SB neutralization reaction.
  - $\checkmark H^+ + OH^- \rightarrow H_2O$
- Determine the mmol of the SA and the mmol of SB
- What do you notice? What's left over after mixing?
- What is the pH of the resulting solution?

 $0.025M \times 55ml = 1.375mmolH^+$  $0.03M \times 40ml = 1.2mmolOH^-$ 

 $1.375 - 1.2 = 0.175 mmolH^+ Left Over$ 

 $\frac{0.175 mmolOH^{-}}{95 ml \ TotalVol} = 1.8 \times 10^{-3} M \ H^{+}$ pH = 2.73

### Calculate the pH after mixing 48 ml of 0.025 M hydrochloric acid with 40 ml of 0.030 M NaOH

- Determine the mmol of the SA and the mmol of SB
- What do you notice? What's left over after mixing?
- What is the pH of the resulting solution?

### Calculate the pH after mixing 48 ml of 0.025 M hydrochloric acid with 40 ml of 0.030 M NaOH

- Let's think about the overall SA + SB neutralization reaction.
  - $\checkmark HCI + NaOH \rightarrow H_2O + NaCI$
  - $\checkmark HCI + NaOH \rightarrow H_2O + Na^+ + CI^-$
- What species are in the beaker after this pour together?
- What is the pH of the resulting solution?

```
0.025M \times 48ml = 1.2mmolH^+
```

```
0.03M \times 40ml = 1.2mmolOH^{-1}
```

### Calculate the pH after mixing 48 ml of 0.025 M hydrochloric acid with 40 ml of 0.030 M NaOH

- Let's think about the overall SA + SB neutralization reaction.
  - $\checkmark HCI + NaOH \rightarrow H_2O + NaCI$
  - $\checkmark HCI + NaOH \rightarrow H_2O + Na^+ + CI^-$
- What species are in the beaker after this pour together?
  - ✓ just water and two pathetics
  - ✓ and so the pH??

 $0.025M \times 48ml = 1.2mmolH^+$ 

 $0.03M \times 40ml = 1.2mmolOH^{-1}$ 

★ pH = 7, no calculation necessary

#### Let's summarize what you can do so far

- Write equations to represent the reaction of SA, SB, WA or WB in water.
- Knowing [H<sup>+</sup>] allows calculation of pH, pOH, [OH-]
- Calc pH of a SA or SB
- Calc pH of a WA or WB... x<sup>2</sup> problem
- Calc *K<sub>a</sub>* or *K<sub>b</sub>* given pH or % ionization of a WA or WB
- Write an net ionic equation to represent the neutralization of SA + SB, WA + SB, WB + SA
- Calculate volume of SA or SB needed to neutralize WB/SB or WA/SA
- Calculate pH after any amount of SA mixed with SB

### **Clicker Questions**

#### Weak Acids

For a certain weak acid,  $K_a = 2.0 \times 10^{-5}$ . What is  $K_b$  for its conjugate base?

- **1.** 4.5 x 10<sup>-3</sup>
- 2. 5.0 x 10<sup>-8</sup>
- 3. 1.0 x 10<sup>-9</sup>
- **4. 4.0 x 10**<sup>-10</sup>
- 5. 5.0 x 10<sup>-10</sup>
- 6. 5.0 x 10<sup>-19</sup>

No calculator

For a certain weak acid,  $K_a = 2.0 \times 10^{-5}$ . What is  $K_b$  for its conjugate base?

- **1.** 4.5 x 10<sup>-3</sup>
- 2. 5.0 x 10<sup>-3</sup>
- 3. 1.0 x 10<sup>-9</sup>
- **4. 4.0 x 10**<sup>-10</sup>
- **5. 5.0 x 10**<sup>-10</sup>
- 6. 5.0 x 10<sup>-19</sup>

 $K_{b} = \frac{K_{w}}{K}$ 

#### Which acid is the weakest?

- 1. chlorous
- 2. nitrous
- 3. acetic
- 4. hypobromous
- 5. they are all equally weak
- 6. there is not enough information to distinguish

acid	pKa
chlorous	1.96
nitrous	3.35
acetic	4.74
hypobromous	8.6

#### Which acid is the weakest?

- 1. chlorous
- 2. nitrous
- 3. acetic
- 4. hypobromous
- 5. they are all equally weak

acid	р <i>К</i> а
chlorous	1.96
nitrous	3.35
acetic	4.74
hypobromous	8.6

- there is not enough information to distinguish
- The largest pK<sub>a</sub> is the weakest acid

# Salt Hydrolysis

#### pH above 7? pH 7? pH below 7?

#### Anions of a Strong Acid – Pathetics

- HCI, HBr, HI, HNO<sub>3</sub>,  $H_2SO_4$ , HCIO<sub>4</sub>, HCIO<sub>3</sub>
- Remember what happens if any of the anions (the pathetic conjugate base) of a SA were put into water?
- Putting XCI in water will dissolve to produce CI<sup>-</sup> ions.
   ✓ XCI → X<sup>+</sup> + CI<sup>-</sup>
- If the CI<sup>-</sup> could interact with water as a acid, this is what would occur
  - ✓  $CI^- + H_2O \rightarrow HCI + OH^-$  however, these HCI particles would immediately dissociate (They are after all a SA) to give this
  - ✓ HCI + OH<sup>-</sup> → H<sup>+</sup> + CI<sup>-</sup> + OH<sup>-</sup> these H<sup>+</sup> and OH<sup>-</sup> ions would immediately find each other
  - ✓  $H^+$  +  $CI^-$  +  $OH^-$  →  $CI^-$  +  $H_2O$  which is right back where we started, thus no change to pH.

#### Cations of a Strong Base – Pathetics

- NaOH, KOH, LiOH, Ca(OH)<sub>2</sub>, Sr(OH)<sub>2</sub>, and Ba(OH)<sub>2</sub>
- What would happen if any of the cations (the pathetic conjugate acid) of a SB were put into water?
- Putting KX into water would dissolve to produce K<sup>+</sup> ions.  $\checkmark KX \rightarrow K^+ + X^-$
- If the K<sup>+</sup> could interact with water, this is what might occur.
  - ✓  $K^+ + H_2O \rightarrow KOH + H^+$  however these KOH particles would immediately dissociate (They are after all a SB.)
  - ✓ KOH + H<sup>+</sup> → K<sup>+</sup> + OH<sup>-</sup> + H<sup>+</sup> these H<sup>+</sup> and OH<sup>-</sup> ions would immediately find each other
  - ✓ K<sup>+</sup> + OH<sup>-</sup> + H<sup>+</sup> → K<sup>+</sup> + H<sub>2</sub>O which is right back where we started, thus no change to pH

Up until now, when a soluble salt dissolved, we thought that's all there was to it, and for NaCl, that is all there is to it. But for many salts, there's more to the story.....

- When salts such as sodium fluoride or ammonium chloride dissolve, we must consider how the dissolved ions will interact with the water
   NaF → Na<sup>+</sup> + F<sup>-</sup>
  - $H_4CI \rightarrow NH_4^+ + CI^-$
- Now, knowing what you know about conjugate acids and bases, those particles hydrolyze with water. Lets look.

### Anions of a Weak Acid

- HF, HNO<sub>2</sub>, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, HC<sub>7</sub>H<sub>5</sub>O<sub>2</sub>, HCIO, HCN
- What would happen if any of the anions (attached to a metal, X instead of H) of a WA were put into water?
- Putting XNO<sub>2</sub> in water will dissolve to produce NO<sub>2</sub><sup>-</sup> ions.
   ✓ XNO<sub>2</sub> → X<sup>+</sup> + NO<sub>2</sub><sup>-</sup>
- The NO<sub>2</sub><sup>-</sup> can interact with water as a weak base
  - $\checkmark$  NO<sub>2</sub><sup>-</sup> + H<sub>2</sub>O  $\leftrightarrows$  HNO<sub>2</sub> + OH<sup>-</sup>
  - ✓ This interaction of the NO₂<sup>-</sup> ion with water causes the formation of OH<sup>-</sup> thus the pH rises above 7.

#### Cations of a Weak Base

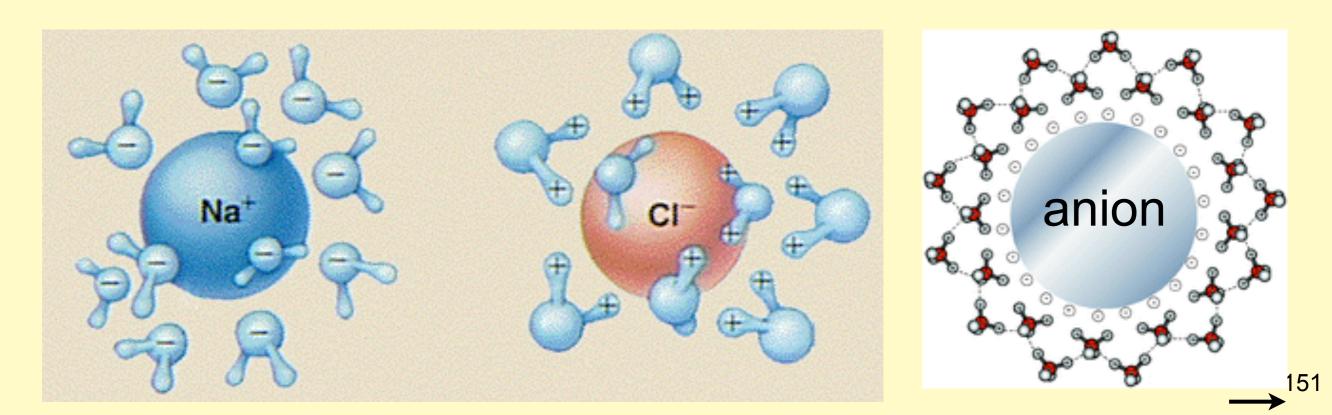
- $NH_3 \rightarrow NH_4^+$ ,  $C_5H_5N \rightarrow C_5H_5NH^+$ ,
- $H_2NOH \rightarrow H_3NOH^+$ ,  $NH_2CH_3 \rightarrow NH_3CH_3^+$
- What happens when a conjugate acid of a WB is put into water?
- Putting  $NH_4X$  in water will dissolve to produce  $NH_4^+$  ions.  $\checkmark NH_4X \rightarrow NH_4^+ + X^-$
- The NH<sub>4</sub><sup>+</sup> can interact with water as a weak acid
  - $\checkmark \mathsf{NH}_4^+ + \mathsf{H}_2\mathsf{O} \iff \mathsf{NH}_3 + \mathsf{H}_3\mathsf{O}^+$
  - ✓ This interaction NH<sub>4</sub><sup>+</sup> ion with water causes the formation of H<sup>+</sup> thus the pH drops below 7.

#### In Summary, Salts: Acidic, Basic, or Neutral?

- Anions (the pathetic conjugate base) of a strong acid
- Cation (the pathetic conjugate acid) of a strong base
  - ✓ The X<sup>-</sup> ions that are the pathetic conjugate base of a strong acid, and the M<sup>+</sup> ions that are the pathetic conjugate acid of a strong base, will *not* be able to hydrolyze in water and thus will hang around as spectator ions having no effect on pH.
- Anions (the conjugate base) of a weak acid
  - ✓ A<sup>-</sup> ions that are the conjugate bases of weak acids will hydrolyze in water causing the pH to rise.
- Cations of a weak base
  - ✓ positive ions (usually containing N) that are conjugate acids of weak bases will hydrolyze in water causing the pH to drop.
- Metallic ions (more on the next three slides Image)
  - ✓ Fe<sup>3+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup> attract the unshared pairs of e- on solvating water molecules, weakening the bonds, causing an H<sup>+</sup> to ionize causing the pH to drop.

### **Hydration Shells**

- All ions are *hydrated* in water surrounded by H<sub>2</sub>O molecules.
- hydrated cations can be represented as
  - ✓ Fe(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>
  - ✓  $Zn(H_2O)_5^{2+}$
  - ✓ The amount of waters represented around the ion vary from ion to ion. You would not be expected to predict the amount.
- Sometimes a salt solution may have higher entropy than the solid salt and water since the water molecules become more ordered.



### Hydrated Metallic Ions

- For metals other than column I and II
- Ions such as; Fe<sup>3+</sup>, Zn<sup>2+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup>
- The cation attracts the electron pairs on the water towards the cation causing the O-H bond in the water molecule to become even more polarized, weakening it enough that one H<sup>+</sup> will be released into solution.

✓  $[Fe(H_2O)_6]^{3+}$  ≒  $[Fe(H_2O)_5(OH)]^{2+} + H^+$ 

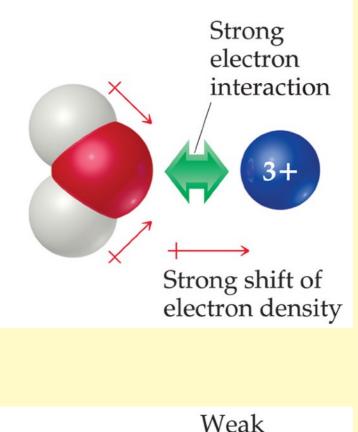
The strength of the metal ion as an acid is affected by

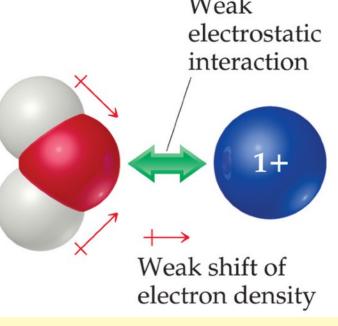
✓ charge

higher charge = stronger acid

✓ size

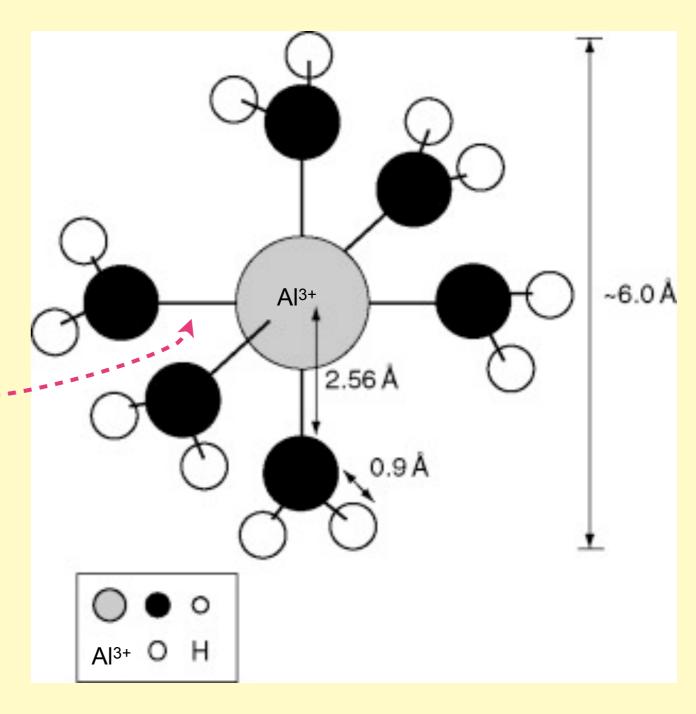
smaller size = stronger acid





### Hydrated Metallic Ions

- $Å = Angstrom = 10^{-10}$  meter
- Note the size of the hydration shell, ~6 Å
- compared to the length of the ion-dipole bond, 2.56 Å
- compared to the length of the O–H bond in water, 0.9 Å



### If you know your SA & SB...

#### **Strong Acids**

**Strong Bases** 

- HCI
- HI
- HBr
- HNO<sub>3</sub>
- H<sub>2</sub>SO<sub>4</sub>
- **HCIO**<sub>4</sub>
- **HCIO**<sub>3</sub>

- LiOH NaOH
- KOH
- RbOH
- CsOH
- **Ba(OH)**<sub>2</sub>
- **Sr(OH)**<sub>2</sub>
- Ca(OH)<sub>2</sub>

...then you know the pathetics.

all other +ions are acids, and *nearly* all other -ions are bases.

## Salt Hydrolysis

#### Negative ions are bases (or pathetic)

(unless we have the anion of a multiprotic acid)

Positive ions are acids (unless pathetic)

Which chemicals below will change pH to something other than 7 when dissolved in water? Select all that apply. *Be ready to comment.* 

1. CsI 5.  $NH_4NO_3$ 6. NaOH 2. HBr 3. KCN 7. NH<sub>3</sub> 4. HCN 8. FeCl<sub>3</sub>

Which chemicals below will change pH to something other than 7 when dissolved in water? Select all that apply. *Be ready to comment.* 1. CsI 5. NH<sub>4</sub>NO<sub>3</sub>

- pathetic / pathetic
- 2. HC1
  - SA
- 3. KCN
  - pathetic / conjWB
- 4. HCN
  - WA

- conjWA / pathetic
- 6. NaOH
  - SB
- 7. NH<sub>3</sub>
  - WB
- 8. FeCl<sub>3</sub>
  - hydrated ion / pathetic

Which chemicals below will change pH to something other than 7 when dissolved in water? Select all that apply. *Be ready to comment.* 

- $1. HC_2H_3O_2$
- 2.  $Al(NO_3)_3$
- 3.  $BaCl_2$
- 4.  $H_2SO_4$

- 5.  $NH_4ClO_4$
- $6. NaClO_2$
- 7. Sr(OH)<sub>2</sub>
- 8.  $(C_2H_3)_2NH$

Which chemicals below will change pH to something other than 7 when dissolved in water? Select all that apply. *Be ready to comment.* 

- 1.  $HC_2H_3O_2$ 
  - WA
- 2. Al(NO<sub>3</sub>)<sub>3</sub>
  - hydrated ion / pathetic
- 3. BaCl<sub>2</sub>
  - pathetic / pathetic
- 4.  $H_2SO_4$ 
  - SA
- $5. NH_4ClO_4$ 
  - conjWA / pathetic

- $6. NaClO_2$ 
  - pathetic / conjWB
- 7. Sr(OH)<sub>2</sub>
  - SB
- 8.  $(C_2H_3)_2NH$ 
  - No way AP would expect you to recognize this as a WB without a hint in the Q.

Which chemicals below will produce a solution with pH = 7 when dissolved in water? Select all that apply.

- 1.  $Ca(CN)_2$  5. RbI
- $2. AlCl_3 \qquad \qquad 6. NaNO_2$
- 3. NaCl 7. HF
- 4.  $Ba(ClO_3)_2$

8. NaBrO<sub>3</sub>

Which chemicals below will produce a solution with pH = 7 when dissolved in water? Select all that apply.

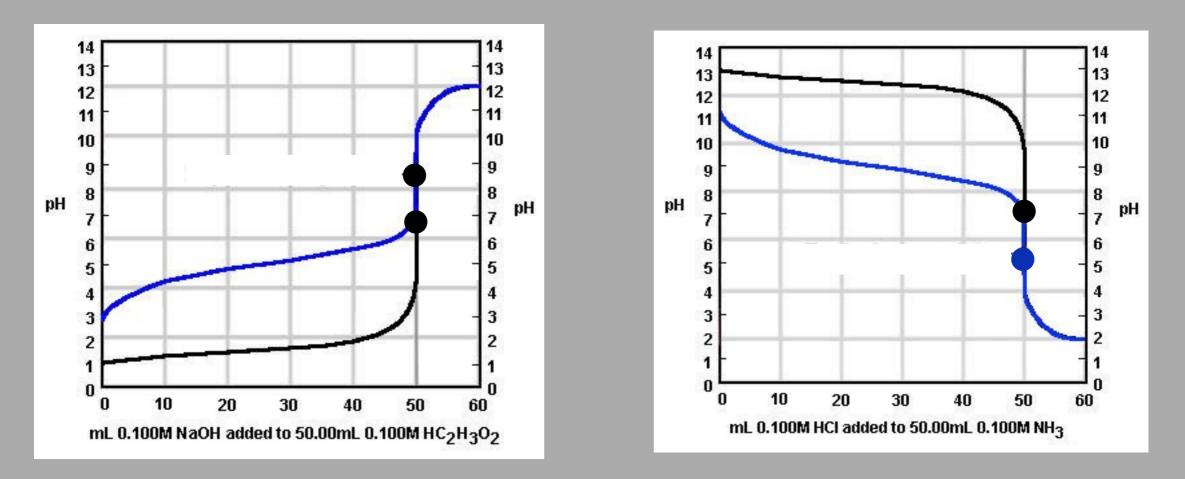
You are looking for pathetic/pathetic

- 1.  $Ca(CN)_2$  5. RbI
- $2. AlCl_3 \qquad \qquad 6. NaNO_2$
- 3. NaCl

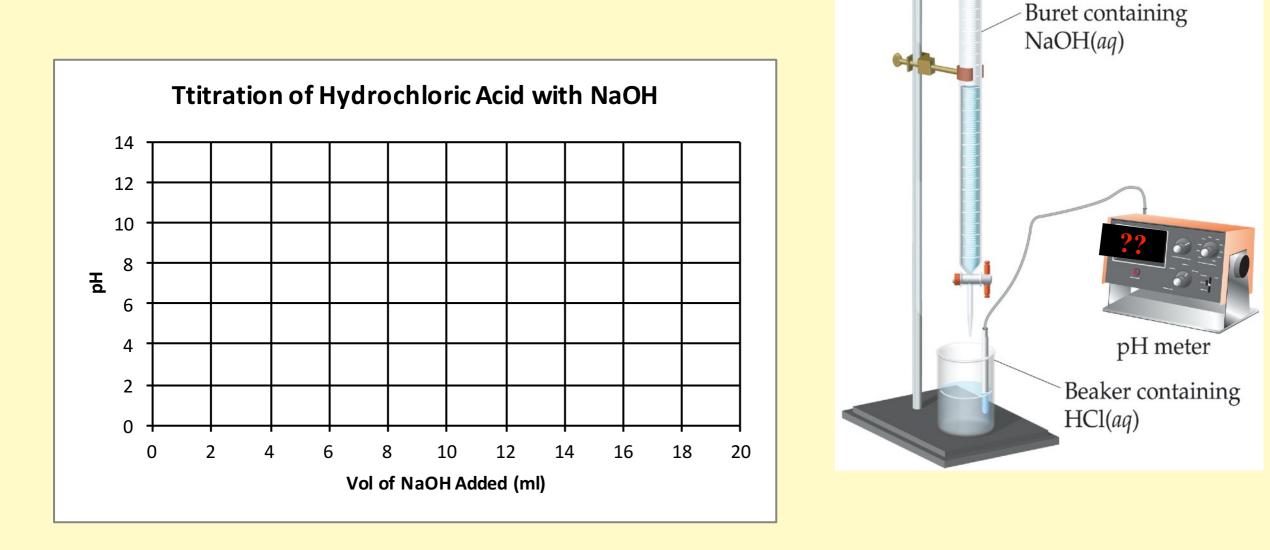
7. HF

4.  $Ba(ClO_3)_2$ 

### **Titration Curves** Watching pH vs titrant added for the following combinations: SA w/ SB, SB w/ SA WA w/ SB, WB w/ SA

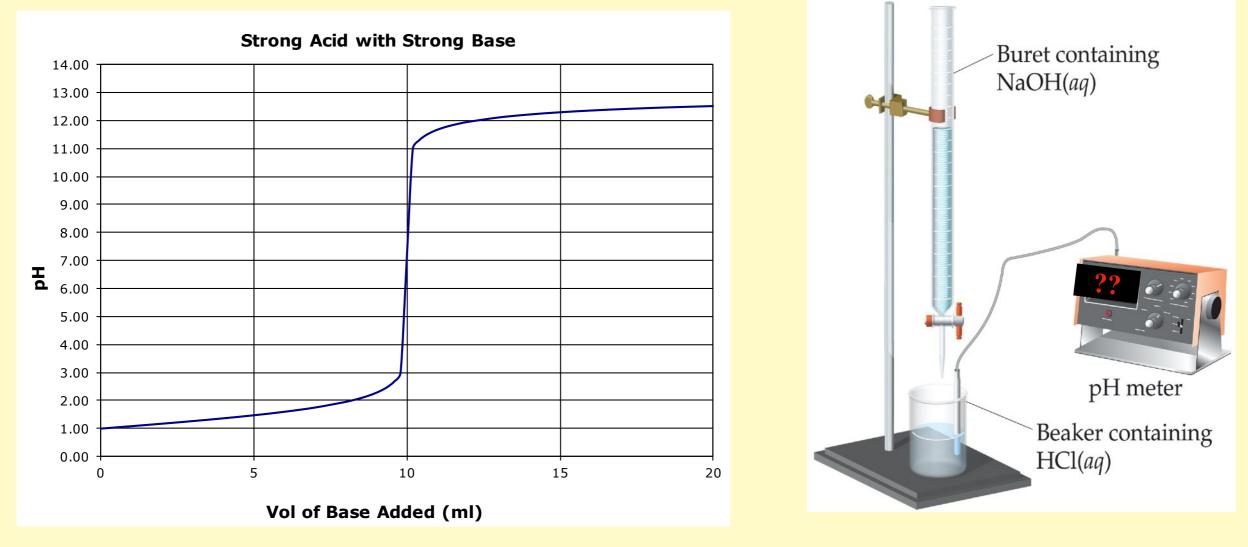


# Let's titrate 10.0 ml of 0.10 M HCl with 0.10 M NaOH



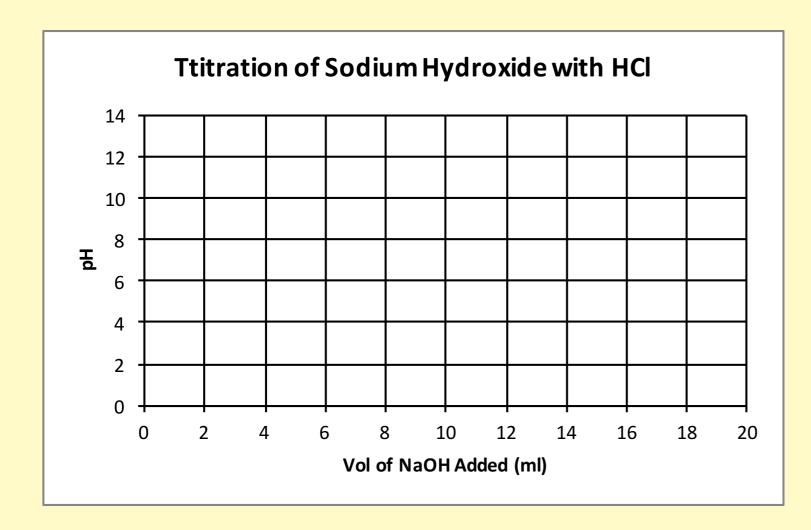
- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
- 3. What is the pH beyond the equivalence point?

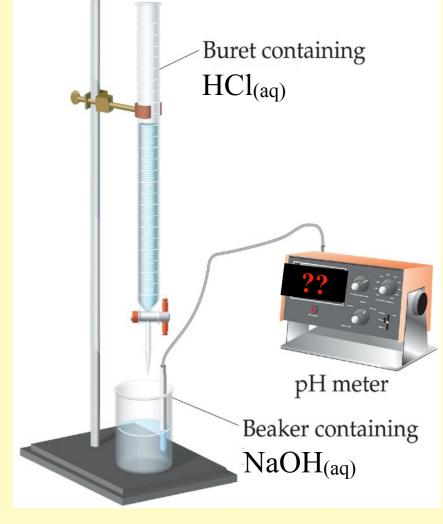
# Let's titrate 10.0 ml of 0.10 M HCl with 0.10 M NaOH



- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
- 3. What is the pH beyond the equivalence point?

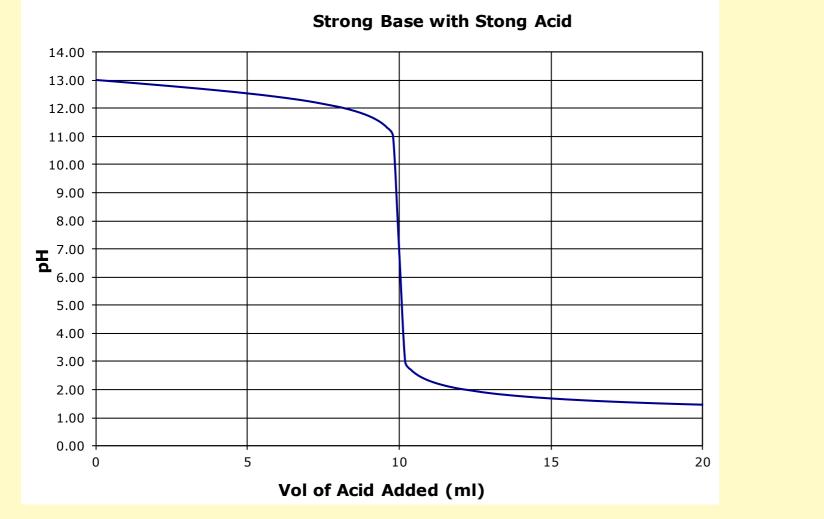
# Let's titrate 10.0 ml of 0.10 M NaOH with 0.10 M HCI

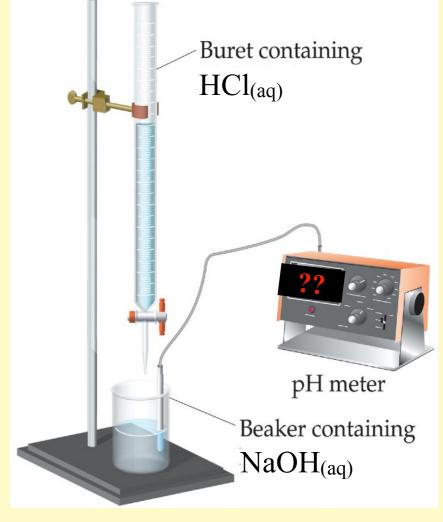




- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
- 3. What is the pH beyond the equivalence point?

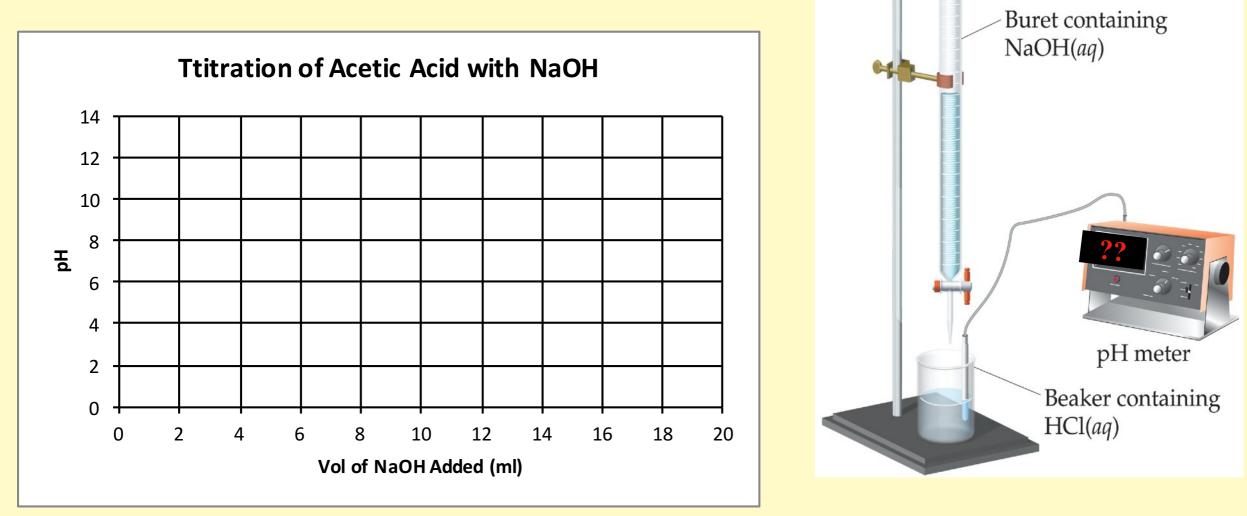
# Let's titrate 10.0 ml of 0.10 M NaOH with 0.10 M HCI





- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
- 3. What is the pH beyond the equivalence point?

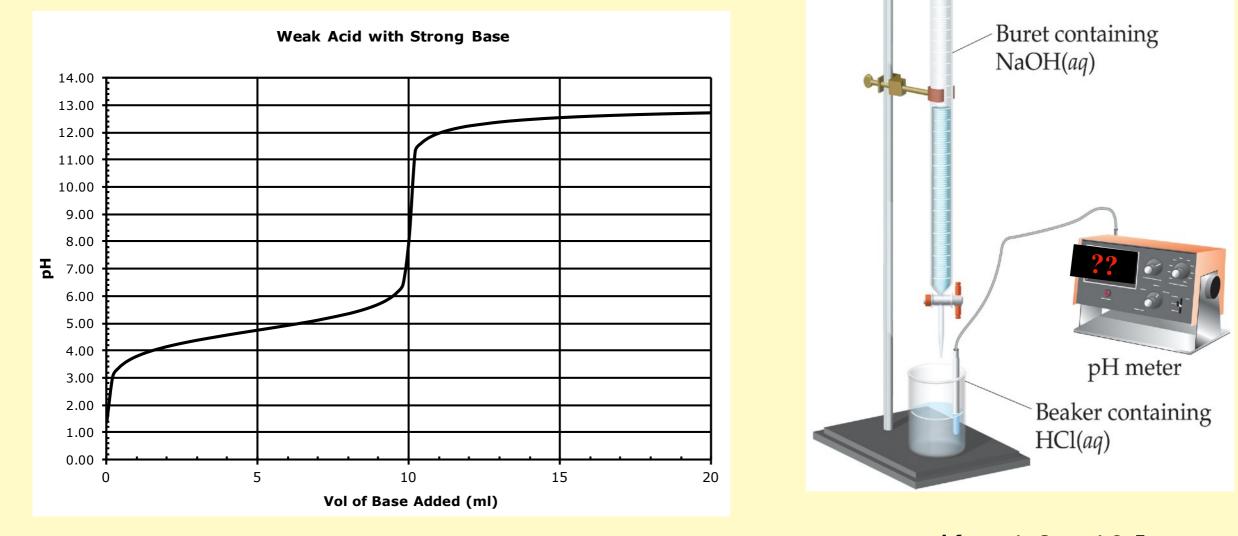
## Let's titrate 10.0 ml of 0.10 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with 0.10 M NaOH



 $K_a = 1.8 \times 10^{-5}$ 

- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
- 3. What is the pH beyond the equivalence point?

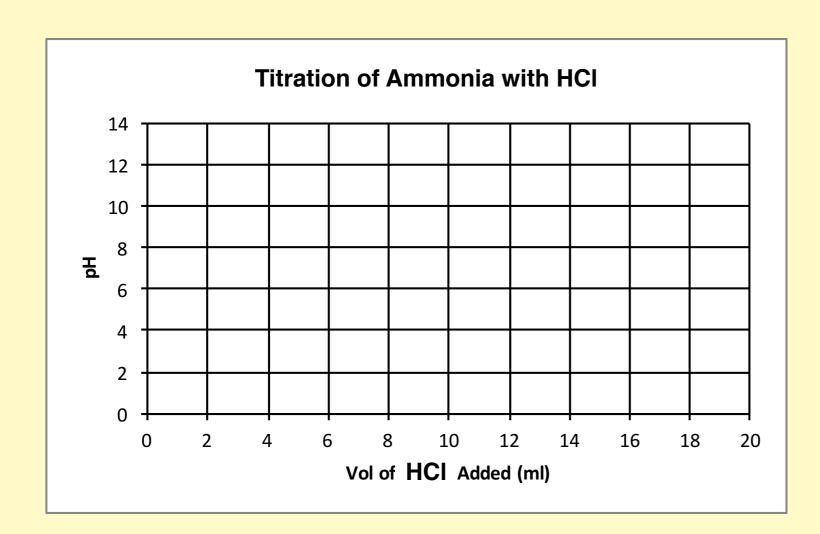
## Let's titrate 10.0 ml of 0.10 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with 0.10 M NaOH

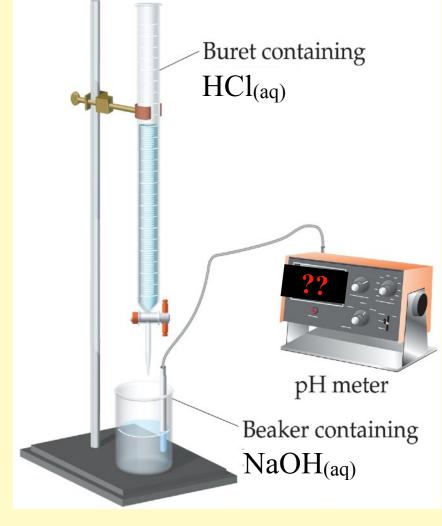


 $K_a = 1.8 \times 10^{-5}$ 

- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
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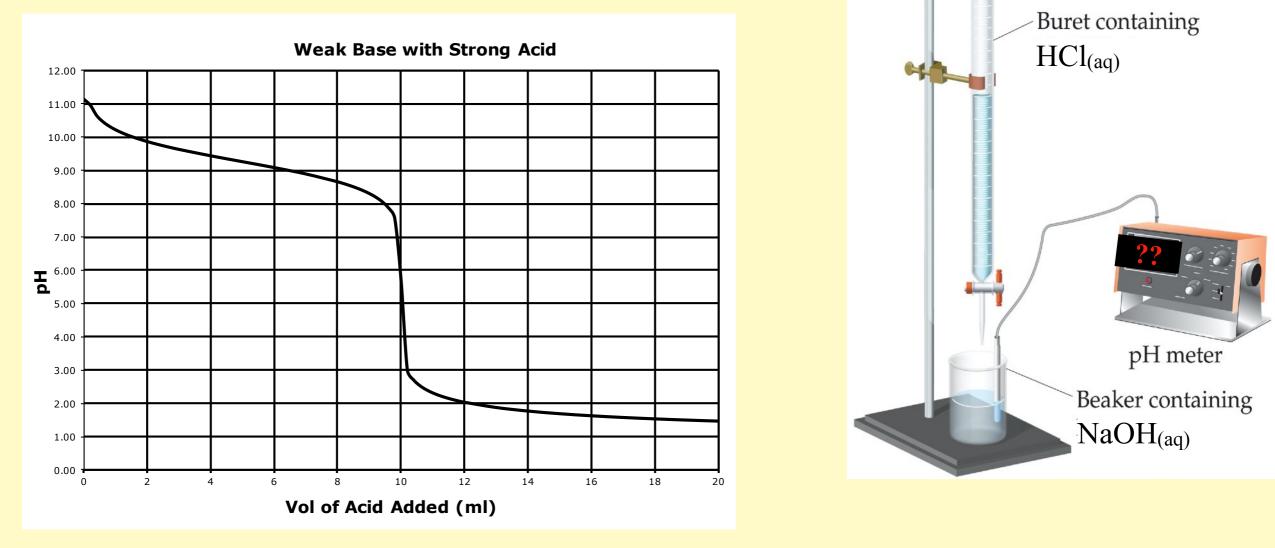
# Let's titrate 10.0 ml of 0.10 M NH<sub>3</sub> with 0.10 M HCl



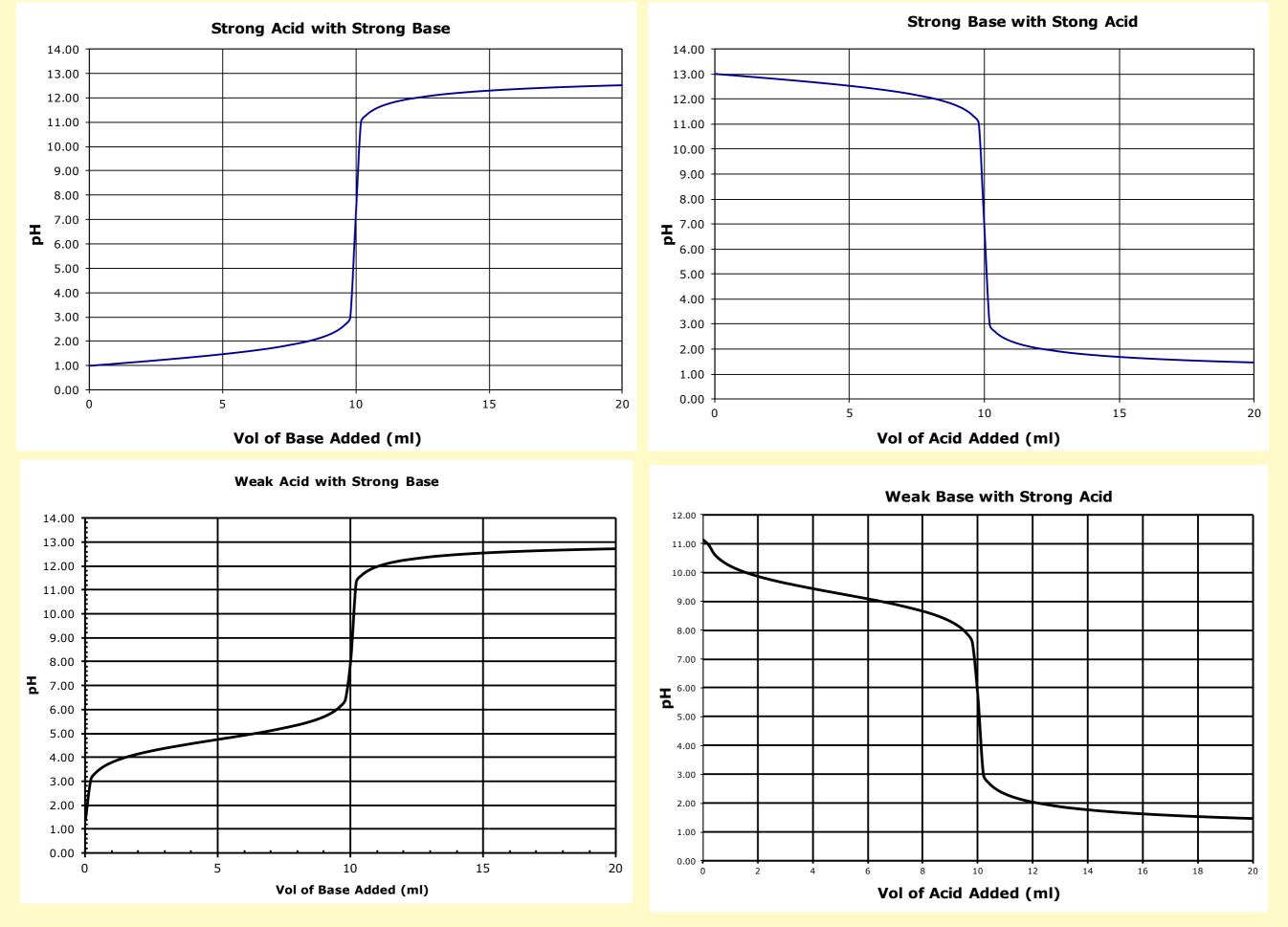


- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
- 3. What is the pH beyond the equivalence point?

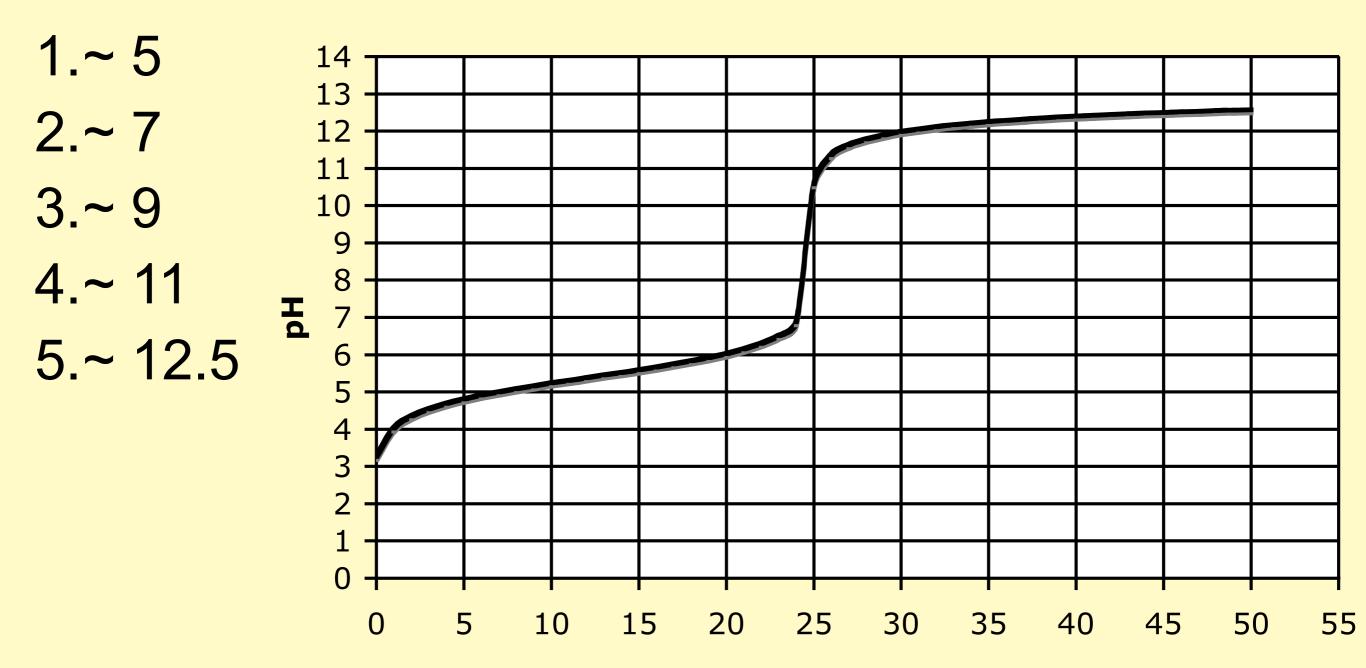
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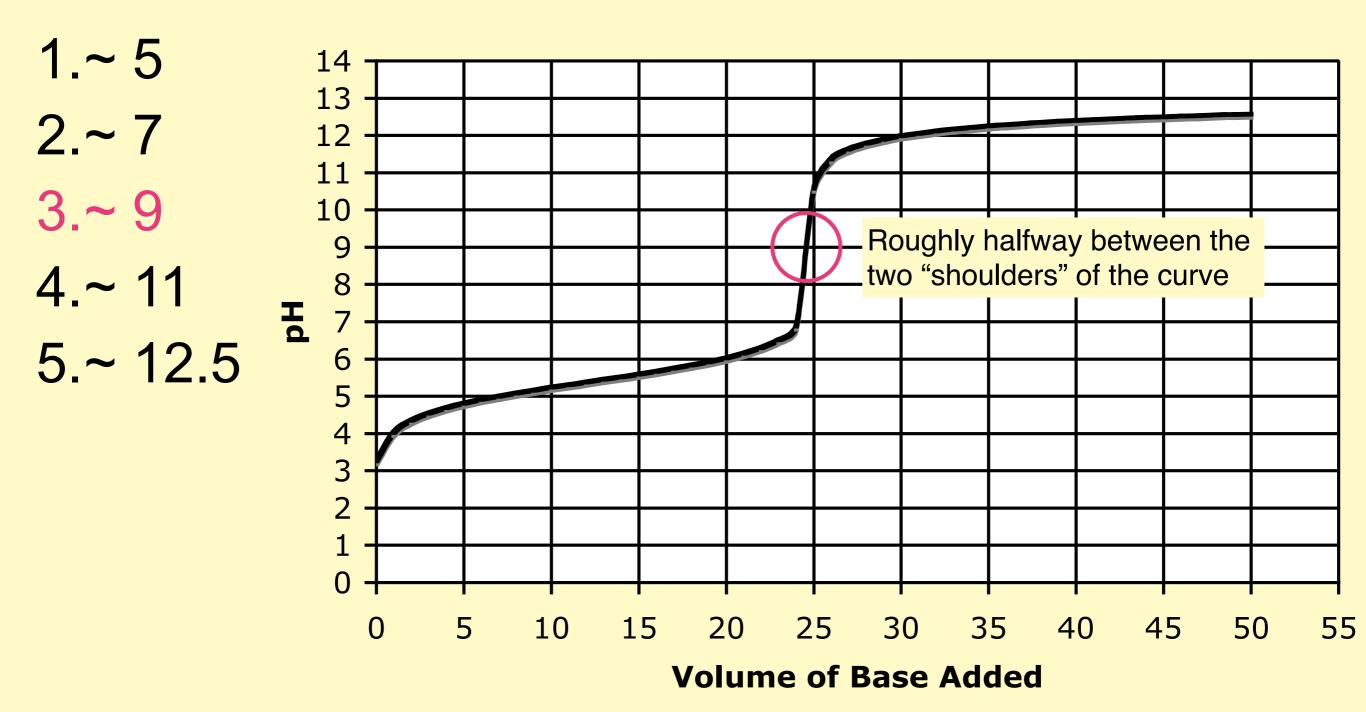
- 1. What is the pH at the start?
- 2. What is the pH at the equivalence point?
- 3. What is the pH beyond the equivalence point?



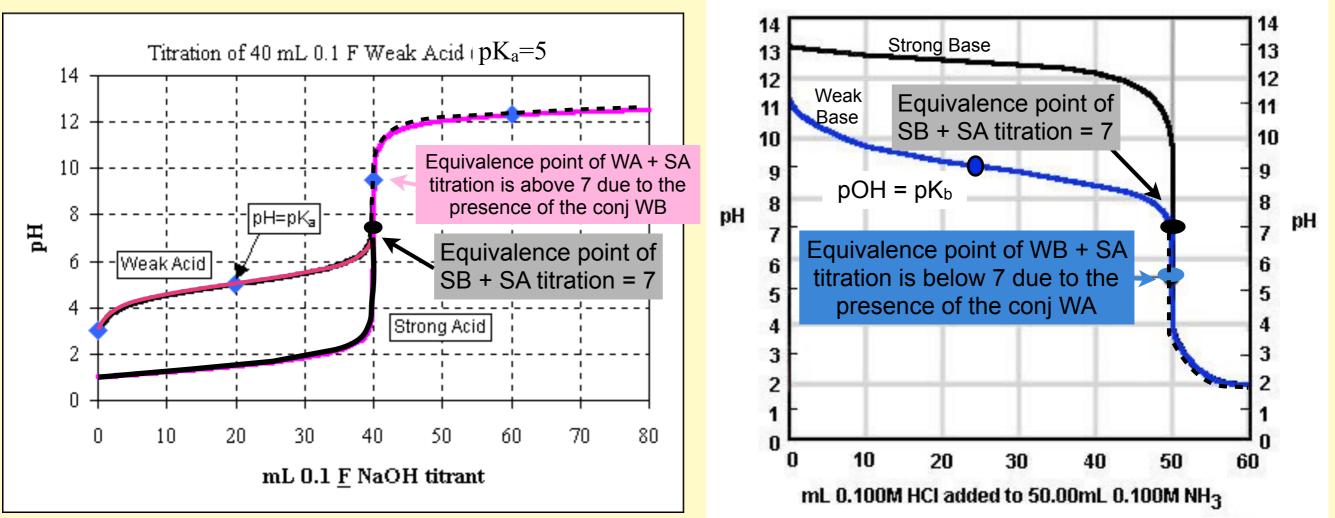
## The equivalence point of this titration curve occurs at what pH?



## The equivalence point of this titration curve occurs at what pH?

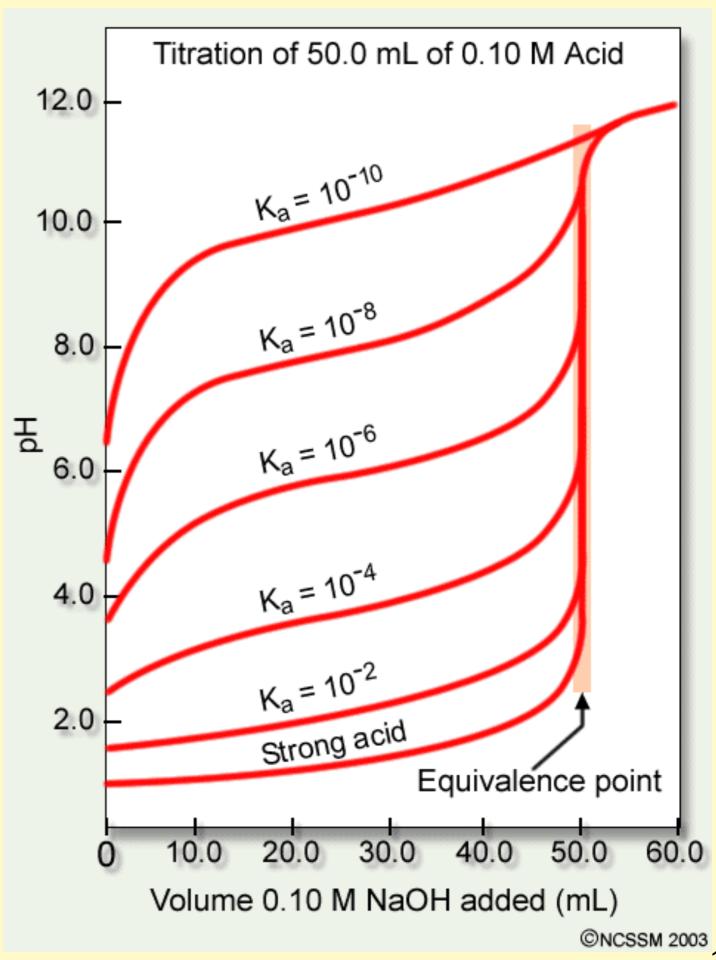


## **Comparing Titration Curves**



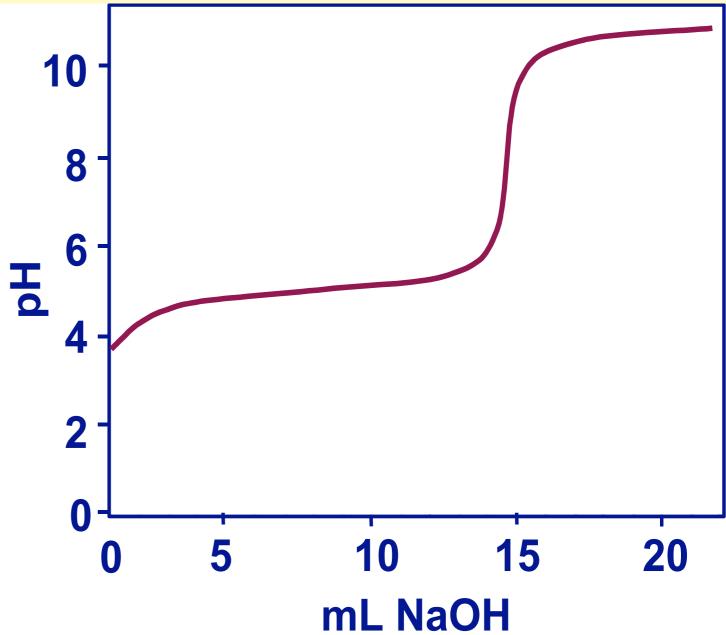
- pH at equivalence point
  - $\checkmark$  SA + SB = 7
  - ✓ WA + SB > 7
  - ✓ WB + SA < 7</p>
- Halfway to equivalence point is the easiest way to determine the K<sub>a</sub> or K<sub>b</sub>.

Titration Curves Acids with different K<sub>a</sub> values



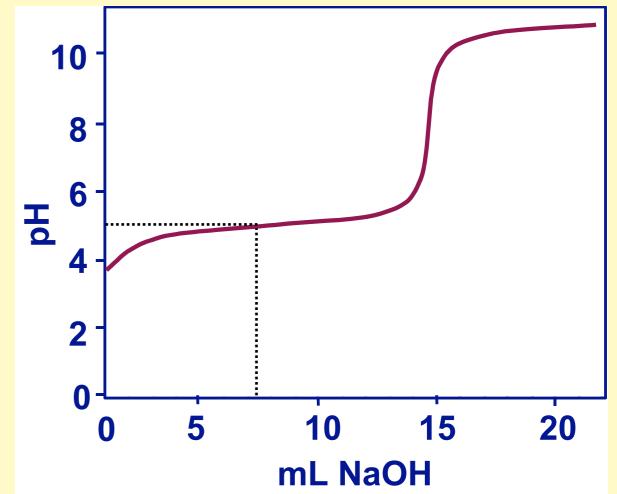
This titration curve was obtained in the titration of an unknown 0.10 M acid with 0.10 M NaOH. What is the  $K_a$  of the acid?

- 1. 1 x 10<sup>-2</sup>
- 2. 1 x 10-4
- 3. 1 x 10<sup>-5</sup>
- 4. 1 x 10<sup>-7</sup>
- 5. 1 x 10<sup>-8</sup>
- 6. 1 x 10<sup>-11</sup>
- 7. Not enough info
- 8. two Ka values
- I have NO idea how to figure this out



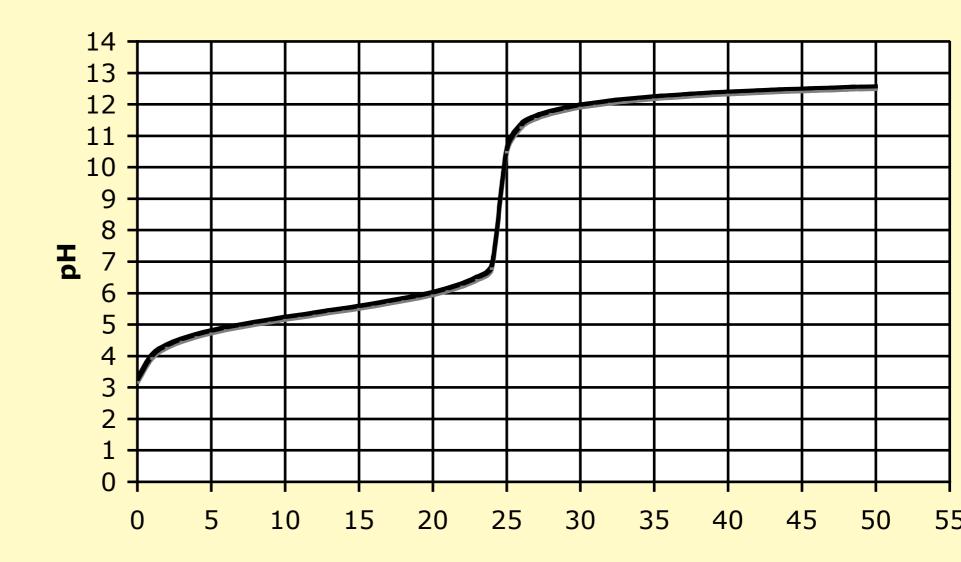
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- 1. 1 x 10<sup>-2</sup>
- 2. 1 x 10-4
- **3.** 1 x 10<sup>-5</sup>
- 4. 1 x 10<sup>-7</sup>
- 5. 1 x 10<sup>-8</sup>
- 6. 1 x 10<sup>-11</sup>
- 7. Not enough info
- Halfway to the equivalence point [H<sup>+</sup>] = K<sub>a</sub>
- Thus  $pH = pK_a$



## This is the titration curve of a titrated with a \_\_\_\_\_

- 1. WA with a SB
- 2. SB with a WA
- 3. WB with a SA
- 4. WA with a SA
- 5. SA with a SB
- 6. Can not be determined without more information.





#### This is the titration curve of a by a

Λ

#### 1. WA by a SB

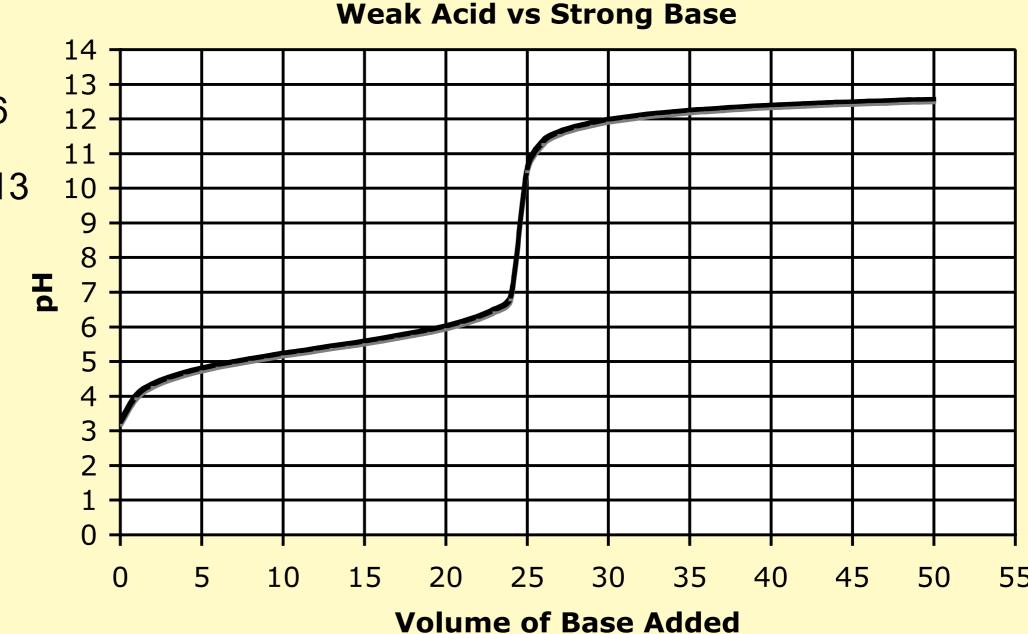
- 2. SB by a WA
- 3. WA by a SA
- 4. SA by a SB
- μd 5. Can not be determined without<sup>5</sup><sub>4</sub> more information.
- The equivalence point has a pH above 7

Weak Acid vs Strong Base



#### What is the Ka of this acid?

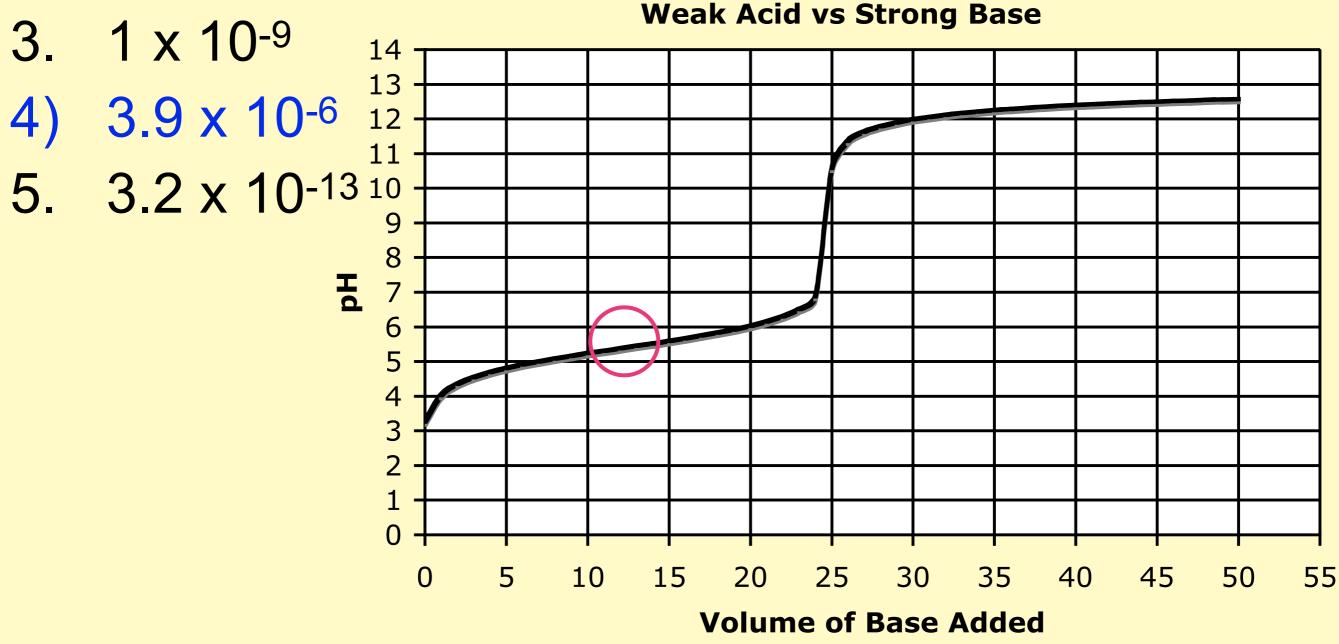
- 1. cannot be determined without more info
- 2. 6.3 x 10<sup>-4</sup>
- 3. 1 x 10<sup>-9</sup>
- 4. 3.9 x 10<sup>-6</sup>
- 5. 3.2 x 10<sup>-13</sup>



#### What is the K<sub>a</sub> of this acid?

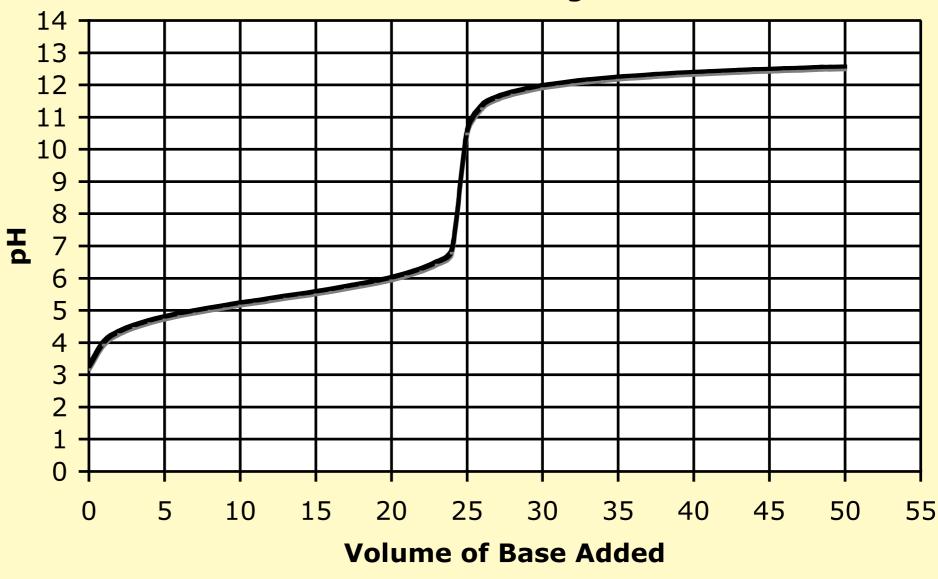
- 1. cannot be determined without more info
- 2. 6.3 x 10<sup>-4</sup>

pH halfway =  $5.4 = pK_a$ un-log for the K<sub>a</sub>



#### Determine the molar mass for this acid. 0.76 g of it was titrated with 0.15 M KOH ? Weak Acid vs Strong Base

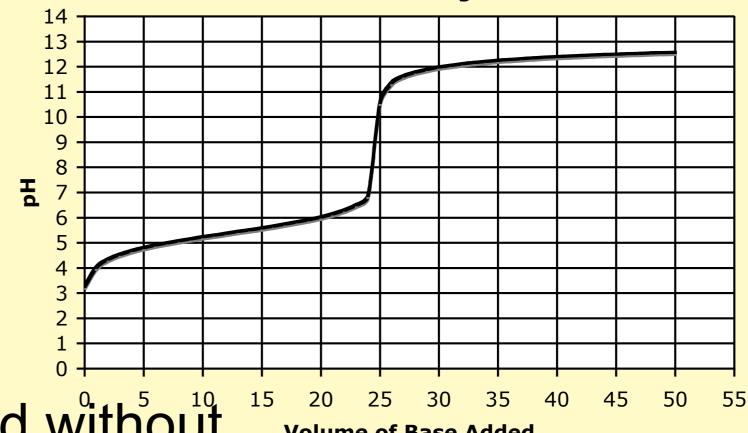
1.~100 g/mol 2.~200 g/mol 3.~300 g/mol 4.~400 g/mol 5.~500 g/mol 6.cannot be determined without more info



Assume the acid is monoprotic

#### Determine the molar mass for this acid. 0.76 g of it was titrated with 0.15 M strong base ?

- 1.~100 g/mol 2.~200 g/mol
- 3.~300 g/mol
- 4.~400 g/mol
- 5.~500 g/mol



- 6.cannot be determined without volume of Base Added more info
- 0.15 M \* 0.024 L = 0.0036 moles of base, which = moles of acid at equivalence point.
- 0.76 g/0.0036 moles = 211 g/mole

## Why is the choice of indicator more crucial for a WA-SB titration than for a SA-SB titration?

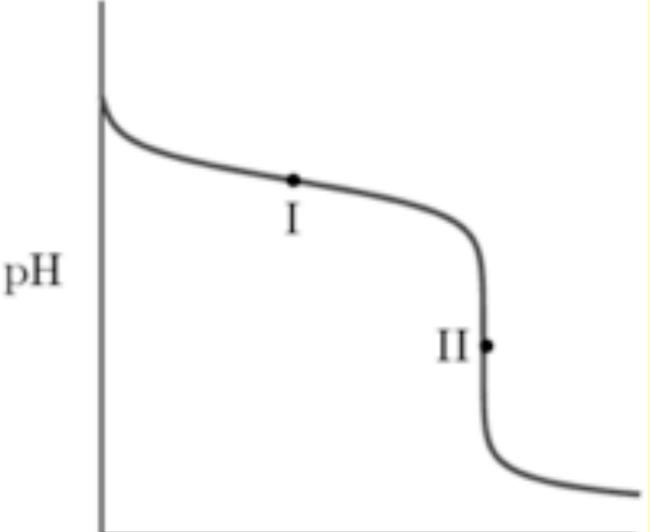
- 1. The nearly vertical equivalence point portion of the titration curve is large for a weak acid-strong base titration, and fewer indicators undergo their color change so quickly it's difficult to monitor.
- 2. The nearly vertical equivalence point portion of the titration curve is smaller for a weak acid-strong base titration, and fewer indicators undergo their color change within this narrow range.
- 3. Many indicators do not change colors at the equivalence points of weak acid-strong base titrations.
- 4. Equivalence points at pH's other than 7.00 are difficult to determine.

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- 4. Equivalence points at pH's other than 7.00 are difficult to determine.

## For the WB titration, the pH at position II is

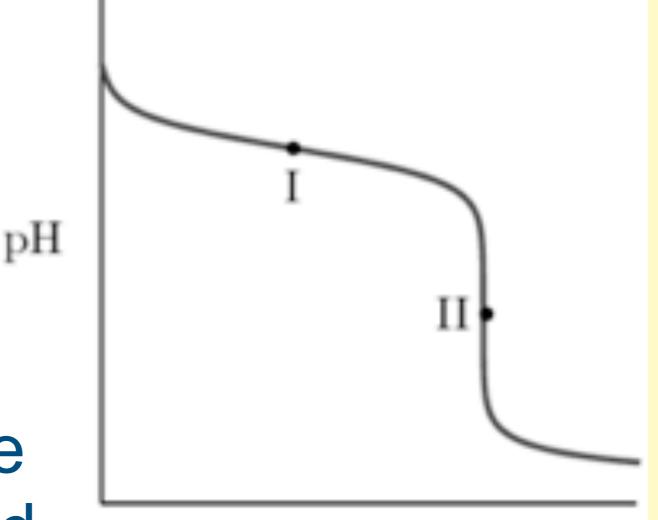
- 1. at 7
- 2. above 7
- 3. below 7
- no way of knowing



Volume of acid added

For the WB titration, the pH at position II is 1. at 7 2. above 7

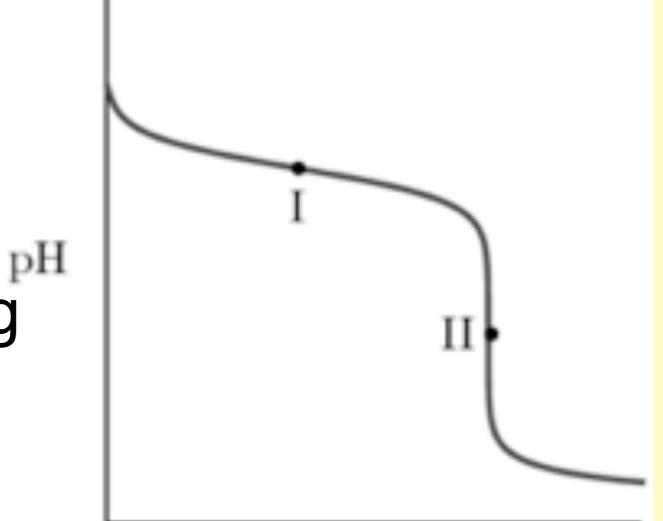
- 3. below 7
- 4. no way of knowing
- •The presence of the weak conjugate acid will make the solution acidic



Volume of acid added

# For the WB titration, the pH at position I is

- 1. at 7
- 2. above 7
- 3. below 7
- 4. no way of knowing

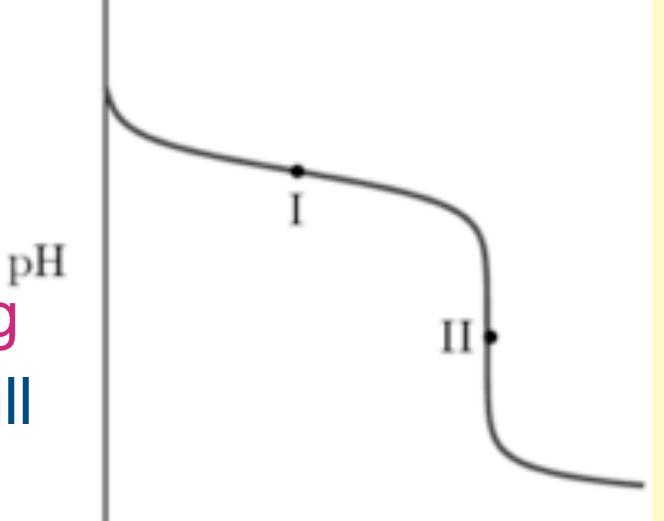


#### Volume of acid added

## For the WB titration, the pH at position I is

- 1. at 7
- 2. above 7
- 3. below 7

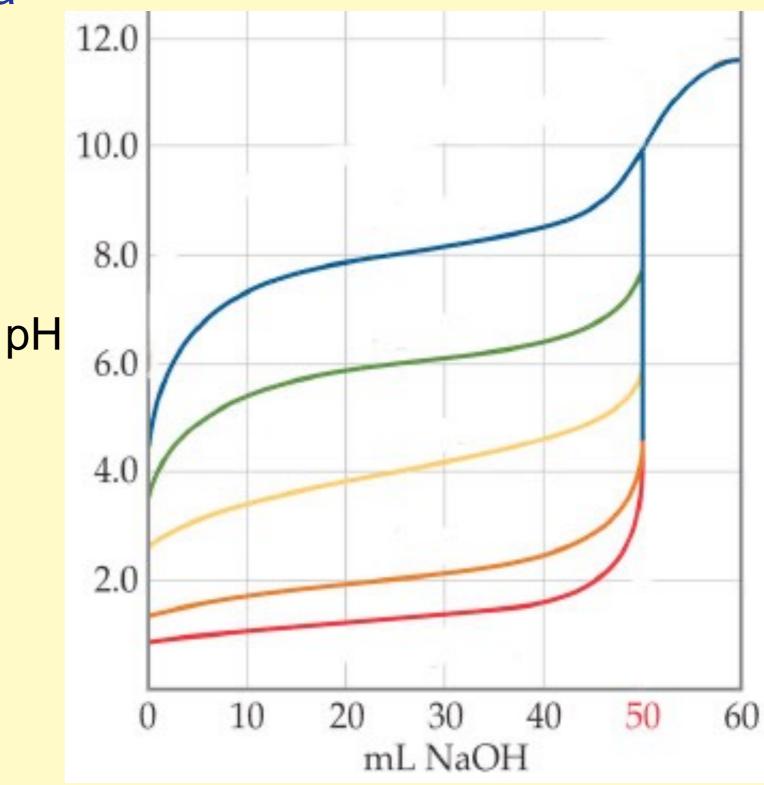
4. no way of knowing
• The size of the *K<sub>b</sub>* will determine if the pH will be above or below 7 at the half-titration point



Volume of acid added

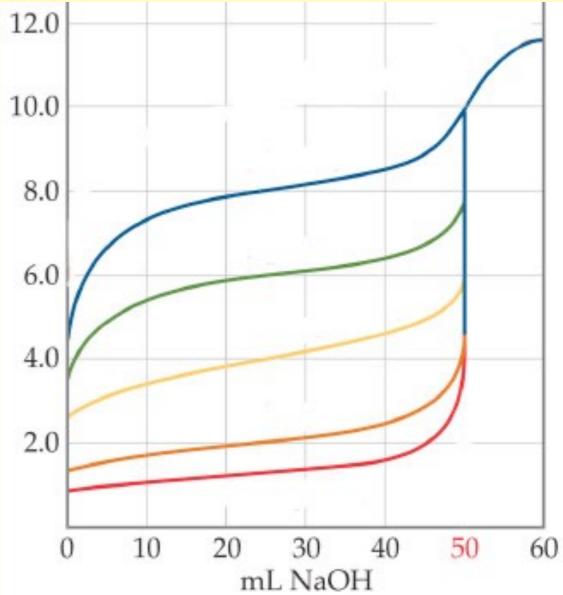
## Which titration curve represents the acid with the largest $K_a$ ?

- 1. Blue
- 2. Green
- 3. Yellow
- 4. Orange
- 5. Red



## Which titration curve represents the acid with the largest $K_a$ ? 12.0

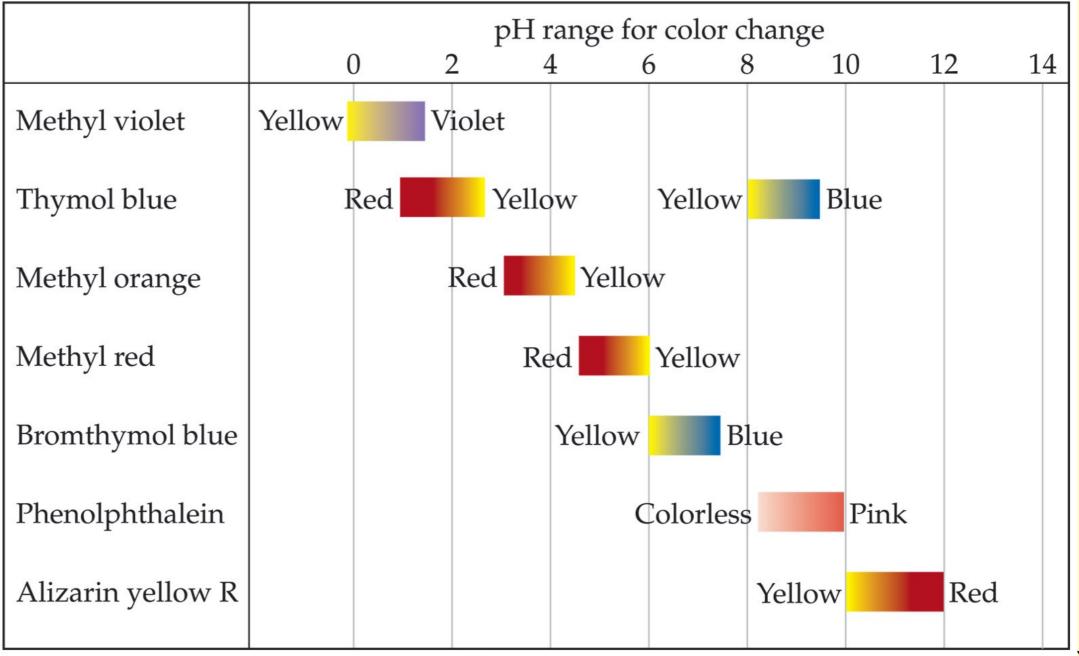
- 1. Blue
- 2. Green
- 3. Yellow
- 4. Orange
- 5. Red
- You could argue that the red curve is a SA that does not have a *K*<sub>a</sub>. All acids have *K*<sub>a</sub> values, but its *K*<sub>a</sub> is just too large to worry about any equilibrium considerations.

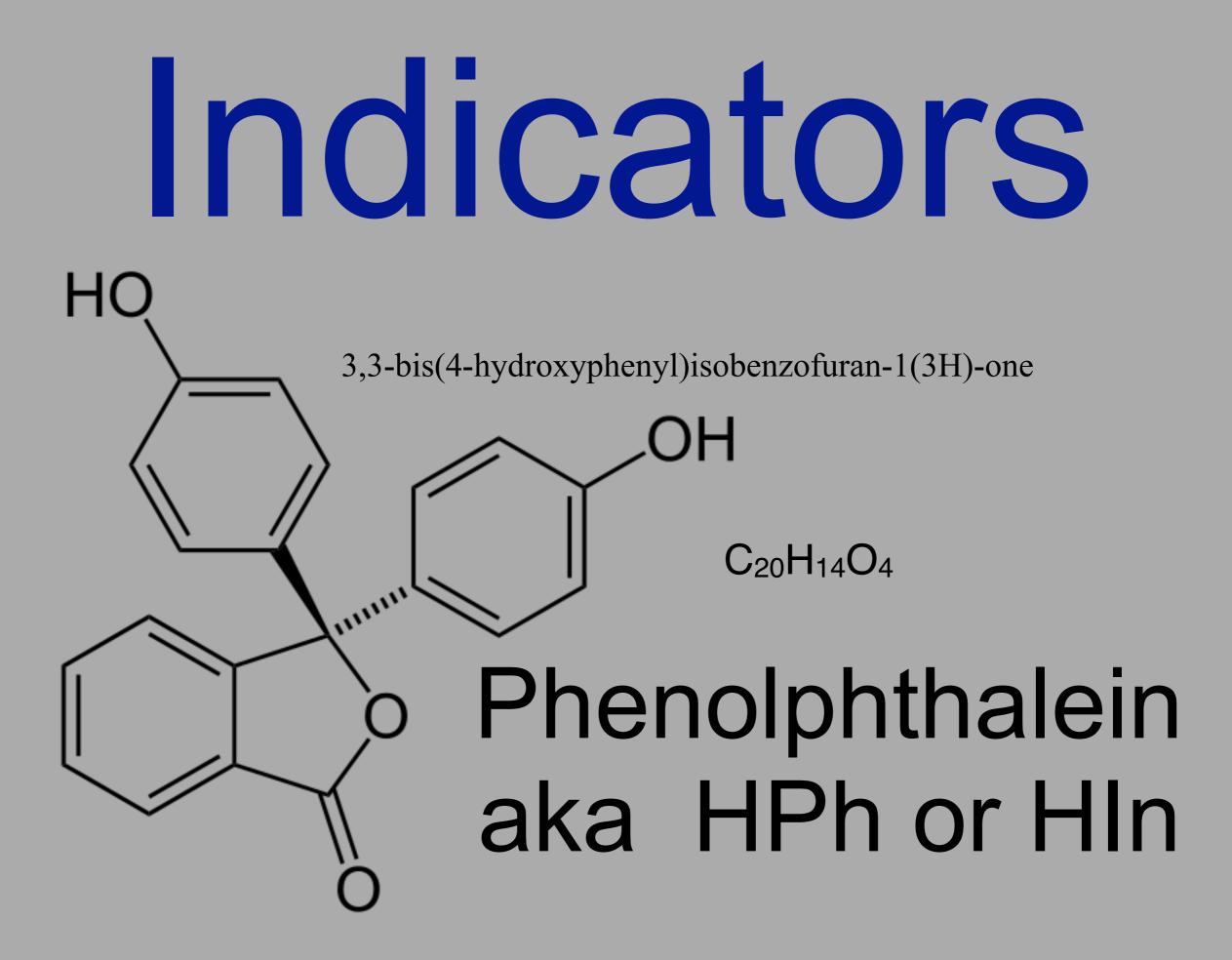


#### Measuring pH during titration curves

- pH can be accurately measured using a pH meter.
- pH can also be indicated using dyes that are different colors at different pH values and change color over a very particular pH range. These are called acid base indicators. They *indicate* when we reach a particular pH and if chosen correctly for the titration, they will accurately indicate the endpoint of a titration.







Indicators are molecules that are one color (or lack of) in molecular form, and a different color in ionized form. We can represent phenolphthalein's reaction as

#### $HPh \rightleftharpoons H^+ + Ph^-$

You should remember that phenolphthalein is colorless in acid, and pink in base.

Which form of phenolphthalein is pink, the molecular form, or the ionized form?

Hint: Think LeChatelier, and a base's effect on the reaction above

- 1. HPh
- 2. Ph-

## phenolphthalein

- It is a very complex weak acid molecule that changes structure dramatically in neutral vs ionized form.
- HIn ≒ H+ + In<sup>\_</sup>
- Adding base forces the weak acid to ionize into its pink form.



### At what pH does the color change?

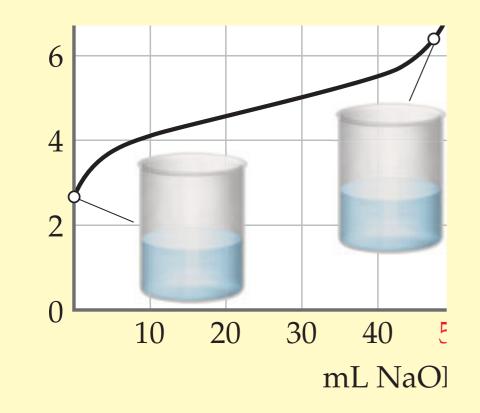
 Most indicators are weak acid molecules that are two different colors in neutral form and ionized form.

• HIn 
$$\rightleftharpoons$$
 H<sup>+</sup> + In<sup>-</sup>  $K_a = \frac{\left\lfloor H^+ \right\rfloor \left\lfloor In^- \right\rfloor}{\left[HIn\right]}$ 

- The  $K_a$  of phenolphthalein = 1 × 10<sup>-9</sup>
- 10x more or 10x less of either the neutral or ionized form is considered the range of the color change.

$$K_{a} = \frac{\left[H^{+}\right]\left[1\right]}{\left[10\right]} = 1 \times 10^{-9} \qquad K_{a} = \frac{\left[H^{+}\right]\left[10\right]}{\left[1\right]} = 1 \times 10^{-9}$$
$$pH = 8 \qquad pH = 10$$

 Pick an indicator who's pK<sub>a</sub> is near the pH of the equivalence point of the acid base titration.

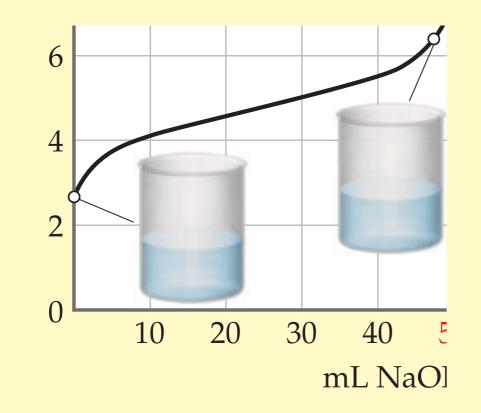


#### The substance in the beaker is

1. an acid.

T

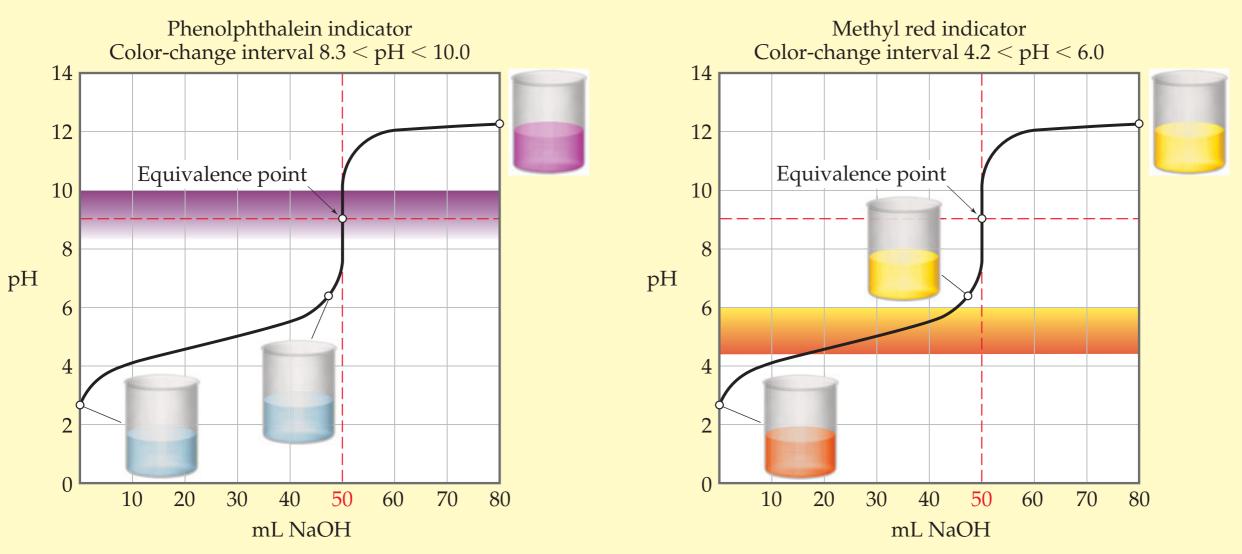
2. a base



#### The substance in the beaker is

- 1. an acid. pH is below 7
- 2. a base

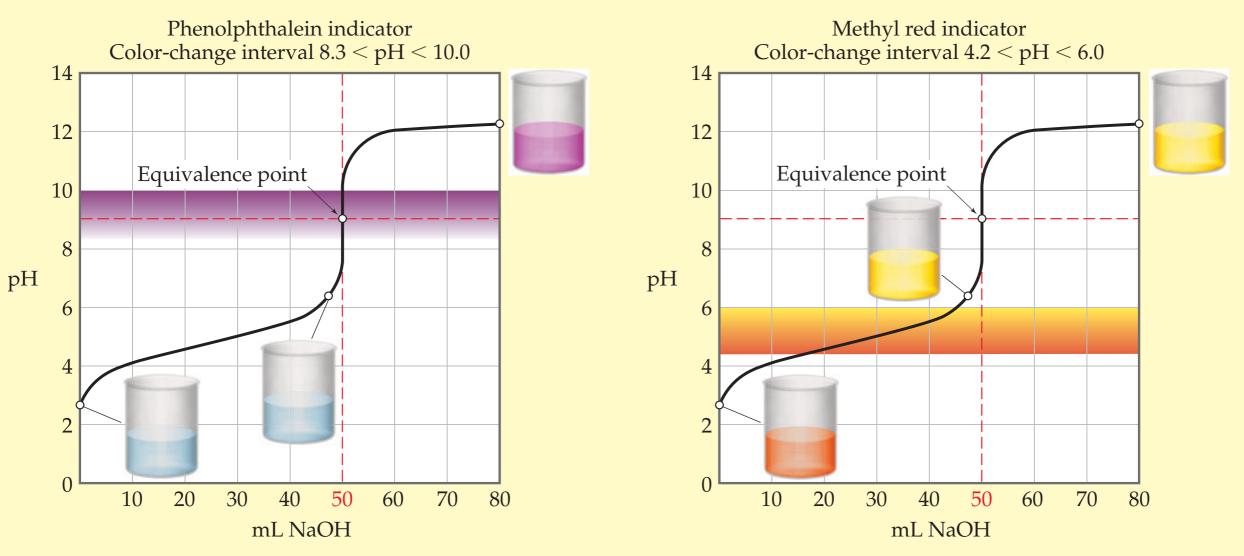
T



#### The substance in the beaker is

- 1. a strong acid.
- 2. a weak acid.

Be ready to explain the best method of knowing weak or strong

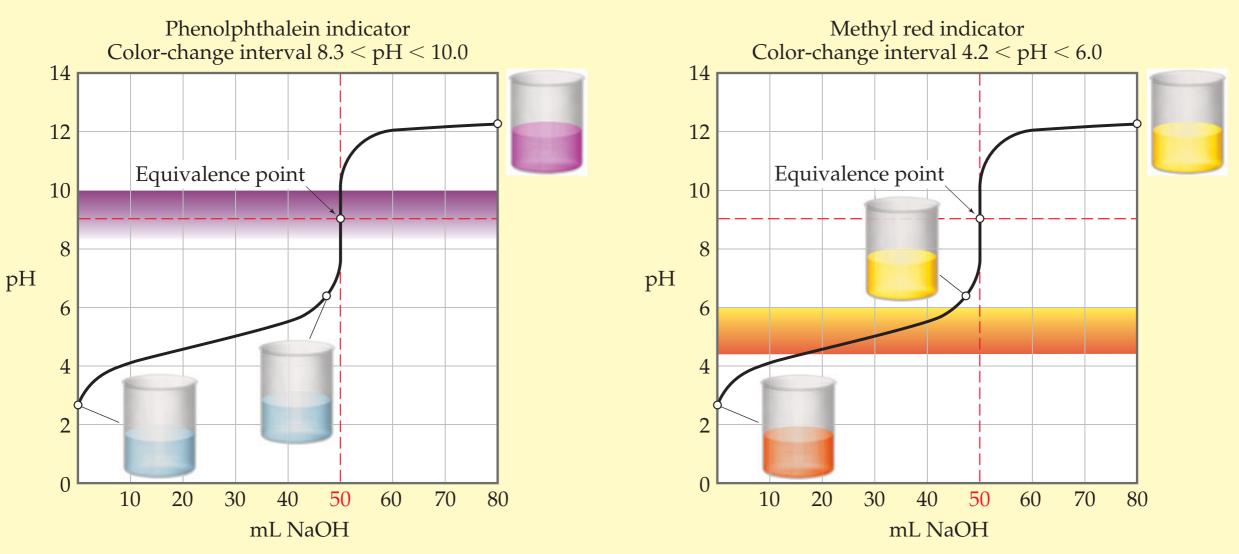


The substance in the beaker is

- 1. a strong acid.
- 2. a weak acid.

The pH at the equivalence point is above 7 due to the presence of a conjugate weak base at the equivalence point.

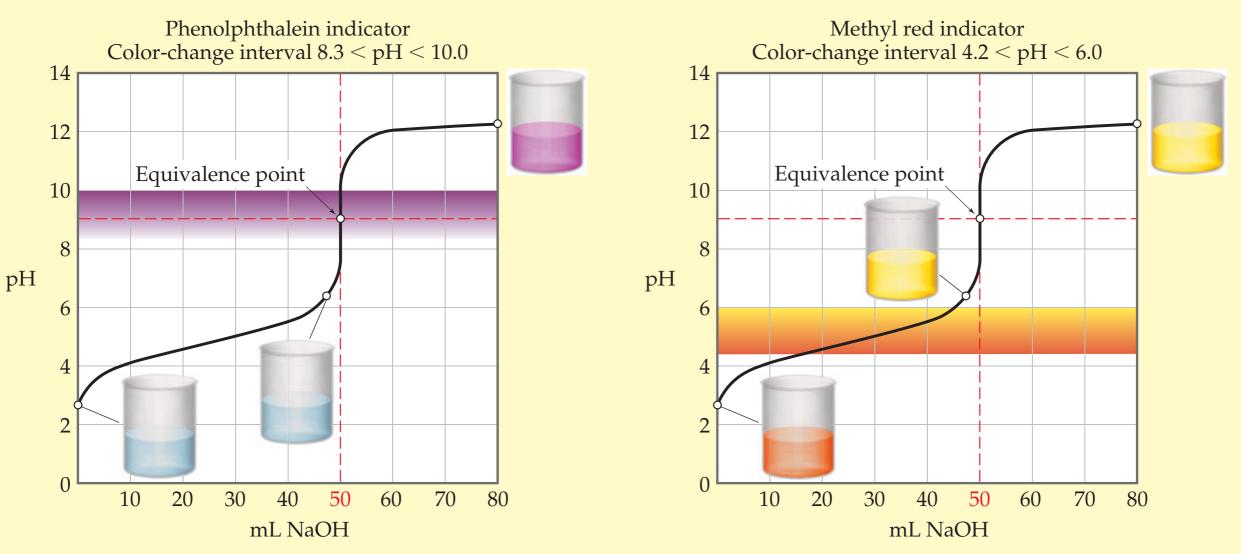
Turn to your mate and explain which indicator is best for this titration, and why.



#### Which indicator is best for this titration?

- 1. phenolphthalein
- 2. methyl red

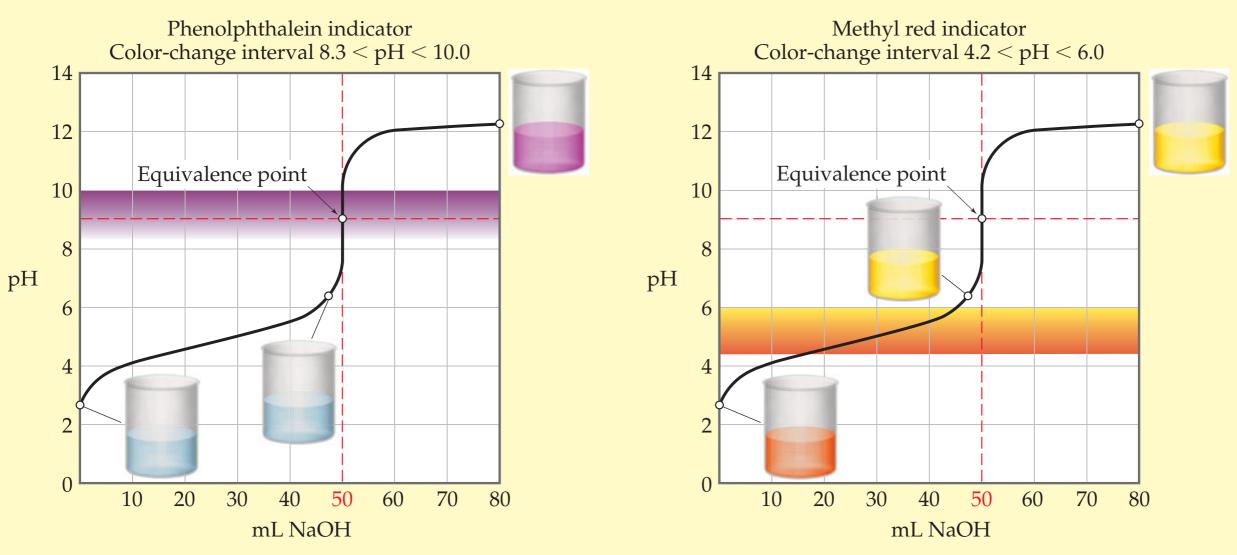
Turn to your mate and explain why you made the choice that you did.



#### Which indicator is best for this titration?

- 1. phenolphthalein
- 2. methyl red

Using methyl red the endpoint, the moment that you say "stop," does not match the equivalence point.



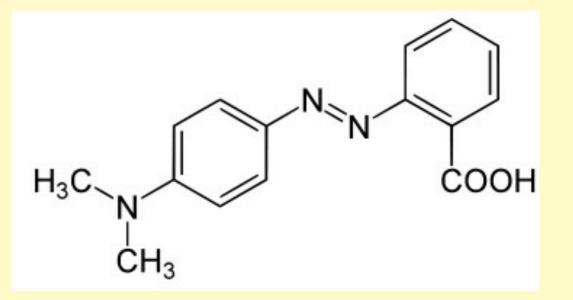
#### Phenolphthalein is the

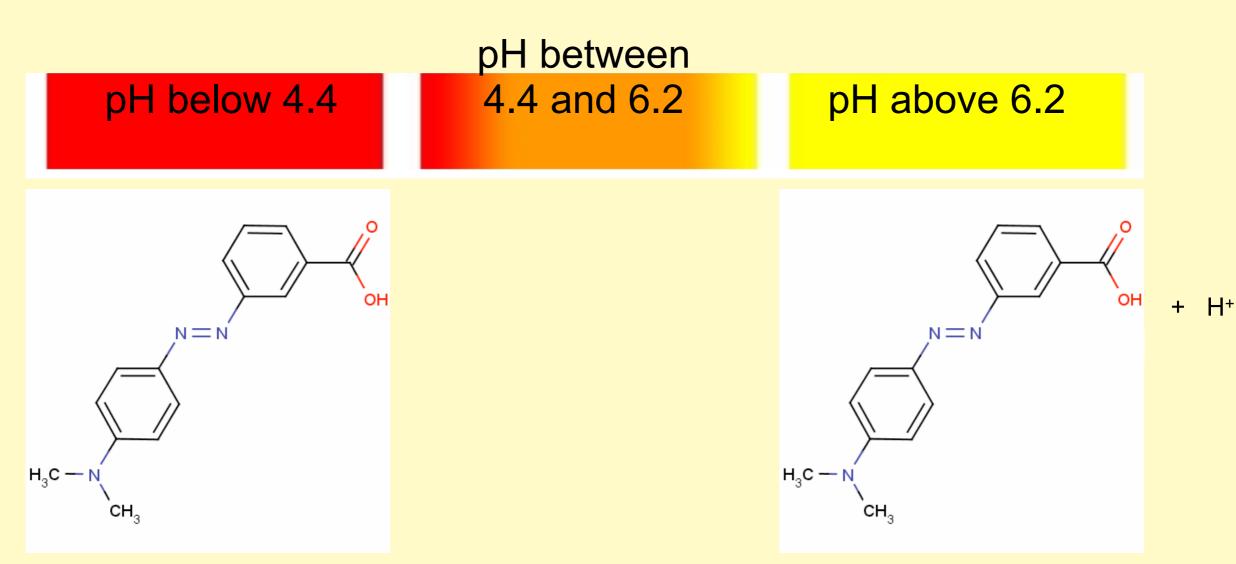
- 1. a strong acid.
- 2. a weak acid.

Using methyl red the endpoint, the moment that you say "stop," does not match the equivalence point.

## Methyl Red

- HIn ⇒ H+ + In<sup>-</sup>
- $K_a = 1 \times 10^{-5}$

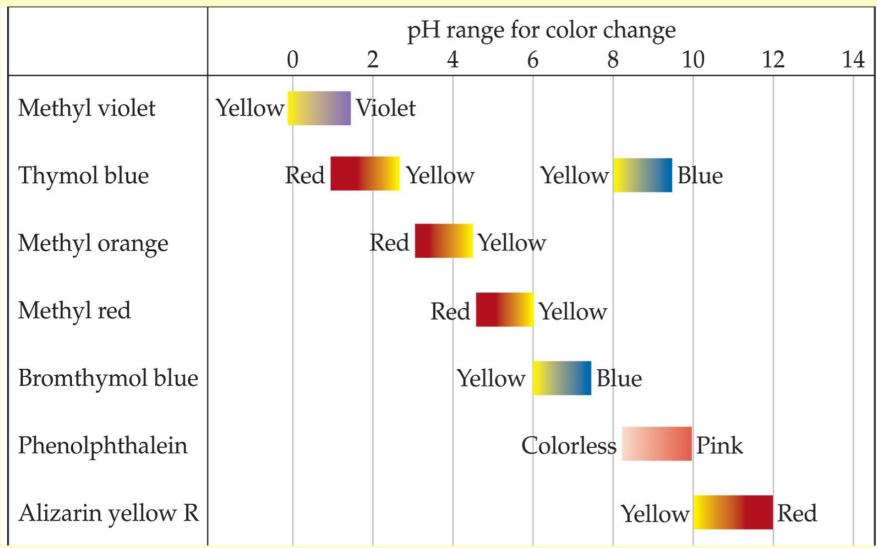




Which indicator would best determine the equivalence point of the titration of a solution of NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with HNO<sub>3</sub>?

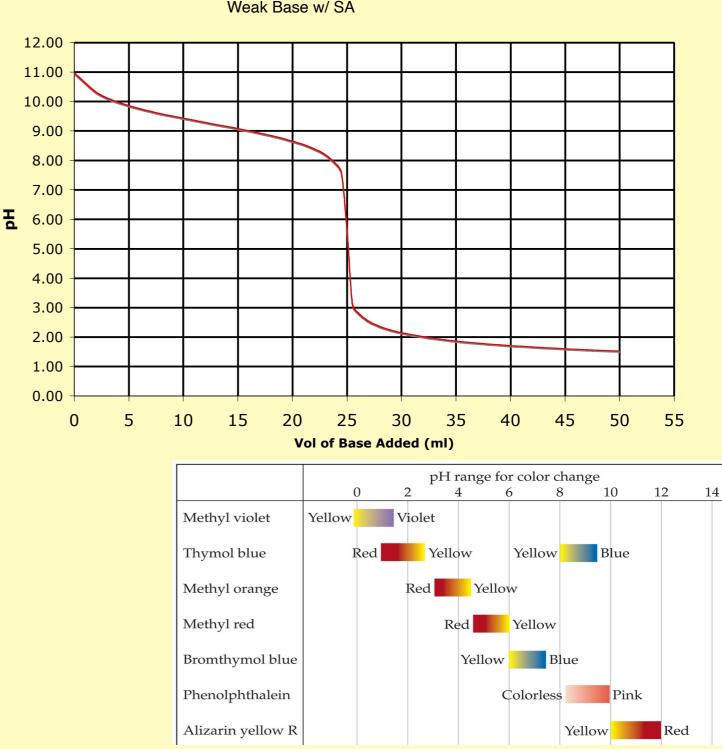
- 1. Methyl violet
- 2. Methyl red
- 3. Bromthymol blue

Phenolphthalein
 Alizarin yellow R



Which indicator would best determine the equivalence point of the titration of  $NaC_2H_3O_2$  with HNO<sub>3</sub>?

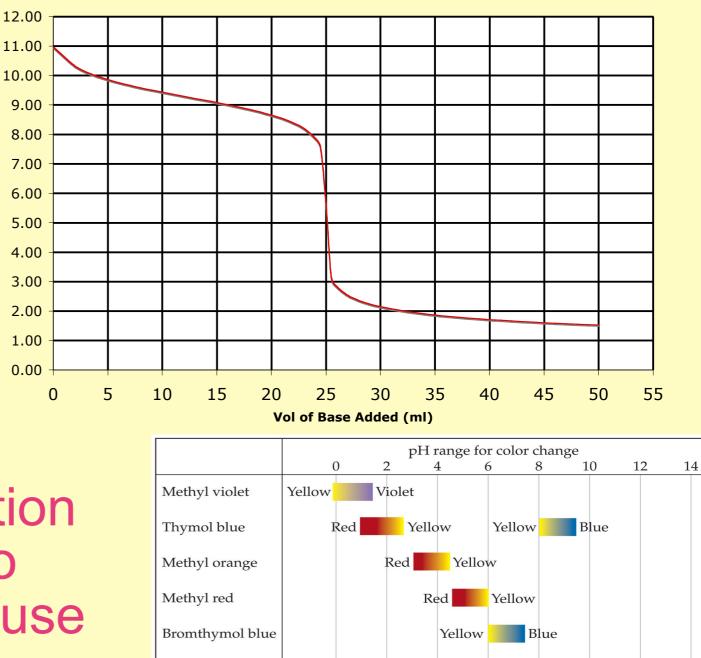
- 1. Methyl violet
- 2. Methyl red
- 3. Bromthymol blue
- 4. Phenolphthalein
- 5. Alizarin yellow R



Which indicator would best determine the equivalence point of the titration of NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> with Weak Acid vs Strong Base

Н

- 1. Methyl violet
- 2. Methyl red
- 3. Bromthymol blue
- 4. Phenolphthalein
- 5. Alizarin yellow R
- The endpoint of the titration of WB by a SA is likely to have a pH below 7 because of the presence of a conjugate acid.



Phenolphthalein

Alizarin yellow R

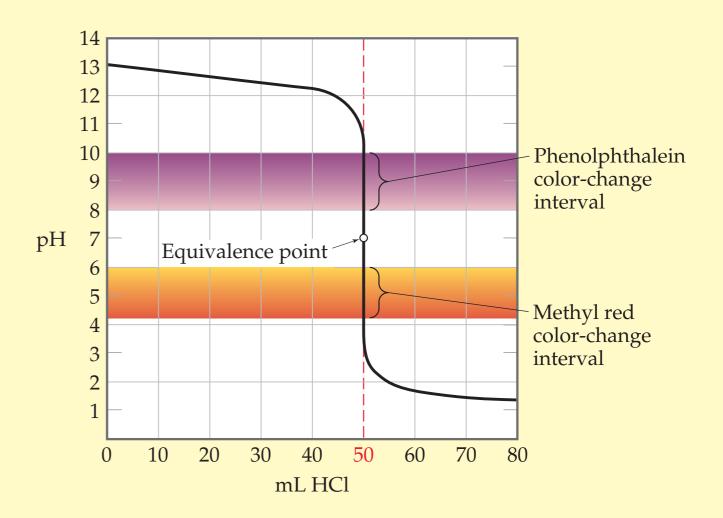
Red

Colorless

Pink

Yellow

- The moment that the indicator changes color is called the endpoint.
- It is important to pick the correct indicator so that the endpoint actually occurs the equivalence point.



# Buffers

## Made Easy

## What is a Buffer?

- When small amounts of acid or base are added to water, the pH will change several units (7 to 2ish) very quickly.
- A buffer is an aqueous solution that has a highly stable pH even upon addition of some H<sup>+</sup> or OH<sup>-</sup>.
- Clearly the solution must have some way of absorbing and neutralize the incoming acid (H<sup>+</sup>) or incoming base (OH<sup>-</sup>).
- How?

### How does a buffer work?

- The solution is able to absorb and neutralize incoming acid (H<sup>+</sup>) or incoming base (OH<sup>-</sup>).
- How??
  - ✓ Because of the presence of significant quantities of both a conjugate weak acid/base pair in the beaker.
- HA + H<sub>2</sub>O  $\leftrightarrows$  H<sup>+</sup> + A<sup>-</sup>
- $B + H_2O \leftrightarrows HB^+ + OH^-$

# Why is WA or WB alone not a buffer? Isn't there some conjugate present?

- Yest there is some....but not enough.
- A weak acid would have lots of HA, but not much A<sup>-</sup>

$$\checkmark$$
 HA  $\leftrightarrows$  H+ A-

 A weak base would have lots of B, but not much HB<sup>+</sup>

$$\checkmark B + H_2O \Leftrightarrow HB^+ + OH^-$$

### What about WA or WB

 A weak acid would have lots of HA, but not much A<sup>-</sup>

$$\checkmark HA \leftrightarrows_{H^+} + A^-$$

 A weak base would have lots of B, but not much HB<sup>+</sup>

$$\checkmark B + H_2O \leftrightarrows_{HB^+} + OH^-$$

# There are two methods to construct a buffer

- Dissolve a conjugate WB-salt or WA-salt into a solution of WA or WB.
- Titrate a WA (or WB) partway along.
- HA +  $H_2O$   $\leftrightarrows$  H<sup>+</sup> + A<sup>-</sup>
- $NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$

What is the pH of a solution made with equal moles of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>?  $K_a = 1.8 \times 10^{-5}$ 

- 1. pH = 9.26
- 2. pH = 7.00
- 3. pH = 4.74
- 4. pH = 1.80

What is the pH of a solution made with equal moles of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and C<sub>2</sub>H<sub>3</sub>O<sub>2<sup>-</sup>?  $K_a = 1.8 \times 10^{-5}$ </sub>

- 1. pH = 9.26
- 2. pH = 7.00

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$$

- 3. pH = 4.74
- When WA = WB in a buffer  $pH = pK_a$
- 4. pH = 1.80

A mixture of 0.10 mol of NH<sub>4</sub>Cl and 0.10 mole of NH<sub>3</sub> is added to enough water to make 1.0 L of solution. Which of the ions is(are) a spectator ion(s) and not involved in the equilibrium? Equilibrium? Write an equation to represent the equilibrium that is happening

- 1. There are no spectator ions.
- 2.Cl-
- 3.Both NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>
- $4.NH_{4}^{+}$

A mixture of 0.10 mol of NH<sub>4</sub>Cl and 0.10 mole of NH<sub>3</sub> is added to enough water to make 1.0 L of solution. Which of the ions is a spectator ion?

- There are no spectator ions.
   CI-
- 3.Both NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup>

 $4.NH_{4}^{+}$ 

A mixture of 0.10 mol of NH<sub>4</sub>Cl and 0.10 mole of NH<sub>3</sub> is added to enough water to make 1.0 L of solution. Which equilibrium equation(s) could we use to calculate the pH of this solution?

1. 
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^ K_b = 1.8 \times 10^{-5}$$
  
2.  $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$   $K_a = 5.6 \times 10^{-10}$   
 $(NH_4^+ \rightleftharpoons H^+ + NH_3)$ 

- 3. Neither
- 4. Either

A mixture of 0.10 mol of NH<sub>4</sub>Cl and 0.10 mole of NH<sub>3</sub> is added to enough water to make 1.0 L of solution. Which equilibrium equation(s) could we use to calculate the pH of this solution?

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$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^ K_b = 1.8 \times 10^{-5}$$
  
2.  $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$   $K_a = 5.6 \times 10^{-10}$   
 $(NH_4^+ \rightleftharpoons H^+ + NH_3)$ 

3. Neither Pick one, and calculate the pH of the solution.
4. Either Report your answer with your clicker.

A mixture of 0.10 mol of NH<sub>4</sub>Cl and 0.10 mole of NH<sub>3</sub> is added to enough water to make 1.0 L of solution. Which equilibrium equation(s) could we use to calculate the pH of this solution?

1. 
$$NH_{3(aq)} + H_2O_{(L)} \rightleftharpoons NH_4^+_{(aq)} + OH_{(aq)}^-_{(aq)}$$
  
 $K_b = \frac{\left[OH^{-}\right][cjWA]}{[WB]}$  [OH-] = 1.8 x 10<sup>-5</sup> pOH = 4.74  
pH = 9.26

2. 
$$NH_4^+(aq) + H_2O_{(L)} \rightleftharpoons H_3O_{(aq)} + NH_{3(aq)}$$
  
 $K_a = \frac{[H^+][cjWB]}{[WA]}$  [H<sup>+</sup>] = 5.6 x 10<sup>-5</sup> pH = 9.24

A mixture of 0.10 mol of NH<sub>4</sub>Cl and 0.10 mole of NH<sub>3</sub> is added to enough water to make 1.0 L of solution. *If some HCl were added, which substance responds to neutralize the incoming strong acid?* 

1. NH<sub>3</sub>

2. NH<sub>4</sub>+

- After sending in your answer, write an equation to demonstrate the neutralization reaction.
- 3. Neither
- 4. Either

A mixture of 0.10 mol of NH<sub>4</sub>Cl and 0.10 mole of NH<sub>3</sub> is added to enough water to make 1.0 L of solution. *If some HCl were added, which substance responds to neutralize the incoming strong acid?* 

- 1. NH<sub>3</sub> the base responds
- 2. NH<sub>4</sub>+

Write an equation to demonstrate the neutralization reaction that occurs.

- 3. Neither
- 4. Either

Which of the following combinations will result in a buffer? Will the pH of the solution be 7, above 7, or below 7?

- 1. 20 ml of 1 M KNO $_3$  and 20 ml of 1 M HNO $_3$
- 2. A solution of calcium acetate and acetic acid  $K_{a} = 1.8 \times 10^{-5}$
- 3. 100 ml of 0.5  $M_{K_b = 1.8 \times 10^{-5}}$  with some dissolved NH<sub>4</sub>Cl
- 4. 20 ml of 1 M NaOH and 20 ml of 1 M NaCl

# Which of the following combinations will result in a buffer?

Will the pH of the solution be 7, above 7, or below 7?

1. 20 ml of 1 M KNO $_3$  and 20 ml of HNO $_3$ 

✓ SA (HNO<sub>3</sub>) and it's pathetic (NO<sub>3<sup>-</sup></sub>) does NOT make a buffer

- 2. A solution of calcium acetate and acetic acid?
- WA (acetic acid)and it's conj WB (acetate ion) = buffer, pH < 7</li>
- 3. 100 ml of 0.5 M NH<sub>3</sub> with some dissolved NH<sub>4</sub>Cl  $K_b = 1.8 \times 10^{-5}$
- WB (NH<sub>3</sub>) and it's conj WA (NH<sub>4</sub>+) = buffer, pH > 7
- 4. 20 ml of 1 M NaOH and 20 ml of NaCl
   ✓ SB (NaOH) and it's pathetic (NO<sub>3</sub><sup>-</sup>) does NOT make a buffer

Which of the following combinations will result in a buffer? Will the pH of the solution be 7, above 7, or below 7?

- 1. 50 ml of 0.5 M NaOH with 25 ml of 0.5 M HF  $K_{a} = 6.6 \times 10^{-4}$
- 2. 20 ml of 1 M HNO<sub>3</sub> and 10 ml of 1 M NaOH
- 3. 100 ml of 0.5  $\underset{K_b = 1.8 \times 10^{-5}}{\text{ NH}}$  with 100 ml of 0.5 M HNO<sub>3</sub>
- 4. 100 ml of 0.5 M NH<sub>3</sub> with 60 ml of 0.5 M HNO<sub>3</sub>

## Which of the following combinations will result in a buffer?

Will the pH of the solution be 7, above 7, or below 7? 1. 50 ml of 0.5 M NaOH with 25 ml of 0.5 M HF  $_{K_{4}=6.6 \times 10^{4}}$ 

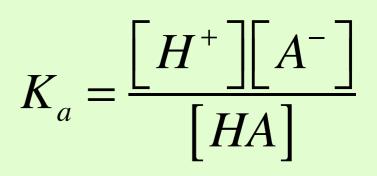
✓ WA (HF) titrated beyond equiv point = not buffer, pH > 7

- 2. 20 ml of 1 M HNO<sub>3</sub> and 10 ml of 1 M NaOH
  - ✓ SA (HNO<sub>3</sub>) and SB (NaOH) in any quantities does NOT make a buffer
- 3. 100 ml of 0.5 M NH<sub>3</sub> with 100 ml of 0.5 M HNO<sub>3</sub> √ WB (NH<sub>3</sub>) titrated to equiv point does not make a buffer
- 4. 100 ml of 0.5 M NH<sub>3</sub> with 60 ml of 0.5 M HNO<sub>3</sub>  $\checkmark$  WB (NH<sub>3</sub>) titrated partway = buffer, pH would be basic

Calculate the pH of a 0.025 M HNO<sub>2</sub> solution.  $K_a = 4.5 \times 10^{-4}$ 

Calculate the pH of a 0.025 M HNO<sub>2</sub> solution.  $K_a = 4.5 \times 10^{-4}$ 

• For the reaction:  $HA \rightleftharpoons H^+ + A^-$ 



• this is an x<sup>2</sup> problem

 $K_{a} = \frac{[H^{+}][A^{-}]}{[HA]} = 4.5 \times 10^{-4} = \frac{[x][x]}{[0.025]}$  $x = [H^{+}] = 3.3 \times 10^{-3} \quad pH = 2.47$ 

Calculate the pH of a solution made by adding 2.1 g of sodium nitrite to 2 L of 0.025 M HNO<sub>2</sub> solution.  $K_a = 4.5 \times 10^{-4}$ (Assume no volume change when the salt is added.)

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Calculate the pH of a solution made by combining 0.20 mole of sodium nitrite with 0.20 mole of HNO<sub>2</sub> in a 2.0 L solution.  $K_a = 4.5 \times 10^{-4}$ 

$$K_{a} = \frac{\left[H^{+}\right]\left[A^{-}\right]}{\left[HA\right]} = 4.5 \times 10^{-4} = \frac{\left[H^{+}\right](0.030)}{(0.050)}$$
$$x = \left[H^{+}\right] = 7.5 \times 10^{-4} \quad pH = 3.12$$

- This is a buffer solution
- Buffers can be acidic, basic, or neutral

Which of the following combinations could produce a buffer solution? Select all that apply.

- 1. HCI / NaCI
- 2. HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> / NH<sub>3</sub>
- 3. H<sub>3</sub>PO<sub>4</sub> / NaH<sub>2</sub>PO<sub>4</sub>
- 4. HNO<sub>3</sub> / Ca(OH)<sub>2</sub>
- 5. HCN / NaOH
- 6. NH<sub>4</sub>NO<sub>3</sub> / NH<sub>3</sub>

### Which of the following combinations can produce a buffer solution? Select all that apply.

- 1. HCI / NaCI
- HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> / NH<sub>3</sub> This solution can neutralize acid or base, with a WA and WB, but since they are not conjugates...you will never see them together in an AP question and we will not consider a buffer.
- 3.  $H_3PO_4$  /  $NaH_2PO_4$   $H_3PO_4^- \rightleftharpoons H^+ + H_2PO_4^{2-}$
- 4. HNO<sub>3</sub> / Ca(OH)<sub>2</sub>
- 5. HCN / NaOH Acid with ~half base
- 6. NH<sub>4</sub>NO<sub>3</sub> / NH<sub>3</sub>
- Remember, there are two ways to make a buffer
  - put in a conjugate WA /WB pair
  - put a WA with ~half of SB or WB with ~half of SA

Which of the following combinations can produce a buffer solution? Select all that apply.

- 1. KNO<sub>3</sub> / NaOH
- 2. HCN / NaOH
- 3. NH<sub>3</sub> / HCl
- 4. HCI / KOH
- 5. NH<sub>4</sub>NO<sub>3</sub> / NH<sub>3</sub>

Which of the following will produce a buffer solution?

- 1. KNO<sub>3</sub> / NaOH
- 2. HCN / NaOH
- 3. NH<sub>3</sub> / HCI
- 4. HCI/KOH
- 5. NH<sub>4</sub>NO<sub>3</sub> / NH<sub>3</sub>
- Remember: two ways to make a buffer
  - put in a conjugate WA /WB pair
  - put a WA with ~half of SB or WB with ~half of SA

What is [H<sup>+</sup>] of a 0.050 M HF solution dissolved with enough solid NaF to produce a solution 0.20 M NaF  $K_a$  (HF) = 6.8 x 10<sup>-4</sup>

- 1. 6.8 x 10-4 M
- 2. 2.7 x 10<sup>-3</sup> M
- 3. 1.4 x 10<sup>-3</sup> M
- 4. 3.4 x 10-4 M
- 5. 1.7 x 10-4 M
- Cannot be determined without knowing volumes of each, or total volume

What is [H<sup>+</sup>] of a 0.050 M HF solution dissolved with enough solid NaF to produce a solution 0.20 M NaF  $K_a$  (HF) = 6.8 x 10<sup>-4</sup>

- 1. 6.8 x 10-4 M
- 2. 2.7 x 10<sup>-3</sup> M
- 3. 1.4 x 10<sup>-3</sup> M  $x = \begin{bmatrix} x \\ y \end{bmatrix}$

$$K_{a} = \frac{\left[H^{+}\right]\left[F^{-}\right]}{\left[HF\right]} = 6.8 \times 10^{-4} = \frac{\left[H^{+}\right]\left[0.20\right]}{\left[0.05\right]}$$
$$x = \left[H^{+}\right] = 1.7 \times 10^{-4}$$

- 4. 3.4 x 10-4 M
- 5. 1.7 x 10-4 M
- 6. Cannot be determined without knowing volumes of each, or total volume

Calculate the pH of a 0.50 M solution of sodium acetate (NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> or NaAc) in 0.50 M acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> or HAc).  $pK_a$  (HAc) = 4.74

- 1. 3.74
- 2. 4.24
- 3. 4.74
- 4. 5.24
- 5. 5.74

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- 1. 3.74 2. 4.24  $K_a = \frac{\begin{bmatrix} H^+ \end{bmatrix} \begin{bmatrix} A^- \end{bmatrix}}{\begin{bmatrix} HA \end{bmatrix}}$ 3. 4.74
- 4. 5.24
- 5. 5.74
- For any buffer, when [WA] = [WB], the  $pH = pK_a$  ( $pOH = pK_b$ )

Using equal volumes and concentrations of which of the following combinations would be best to make a buffer with a pH above 7 ?

- 1. NaCl and HCl
- 2. NH<sub>3</sub> and NH<sub>4</sub>Cl
- 3. NaOH and HCI
- 4. HNO<sub>2</sub> and NaNO<sub>2</sub>
- 5. NH<sub>3</sub> and C<sub>5</sub>H<sub>5</sub>NHCI

acid	pKa
HNO <sub>2</sub>	3.35
$C_5H_5NH_2^+$	5.23
NH <sub>4</sub> +	9.25

Using equal volumes and concentrations of which of the following combinations would make a buffer with a pH above 7 ?

- 1. NaCl and HCl
- 2. NH<sub>3</sub> and NH<sub>4</sub>Cl
- 3. NaOH and HCI
- 4. HNO<sub>2</sub> and NaNO<sub>2</sub>
- 5. NH<sub>3</sub> and C<sub>5</sub>H<sub>5</sub>NHCI

acid	pKa	
HNO <sub>2</sub>	3.35	
$C_5H_5NH_2^+$	5.23	
NH4 <sup>+1</sup>	9.25	

- When the conjugate pair [base] = [acid] in the above expression
- K<sub>a</sub> = [H<sup>+</sup>], so pK<sub>a</sub> = pH

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$$

Calculate the pH of a 0.50 M solution of sodium acetate (NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> or NaAc) in 0.050 M acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> or HAc).  $pK_a$  (HAc) = 4.74

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- 3. 4.74
- 4. 5.24
- 5. 5.74
- Note that the pH was different from pKa by one unit

$$K_{a} = \frac{\left[H^{+}\right]\left[A^{-}\right]}{\left[HA\right]}$$
  
1.8×10<sup>-5</sup> =  $\frac{\left[H^{+}\right](0.5)}{(0.05)}$   
 $-H^{+} = 1.8 \times 10^{-6}$ 

#### In an NH<sub>4</sub>+/NH<sub>3</sub> buffer, what changes will occur if a small amount of OH<sup>-</sup> is added?

	[NH <sub>4</sub> +]	[NH <sub>3</sub> ]	рН	
1	Increase	Increase	Increase	
2	Decrease	Increase	Increase	
3	Increase	Decrease	Increase	
4	Increase	Decrease	Decrease	
5	Decrease	Increase	Decrease	
6	No change because this is a buffer.			
7	No change because OH <sup>-</sup> is not part of the equilibrium reaction.			

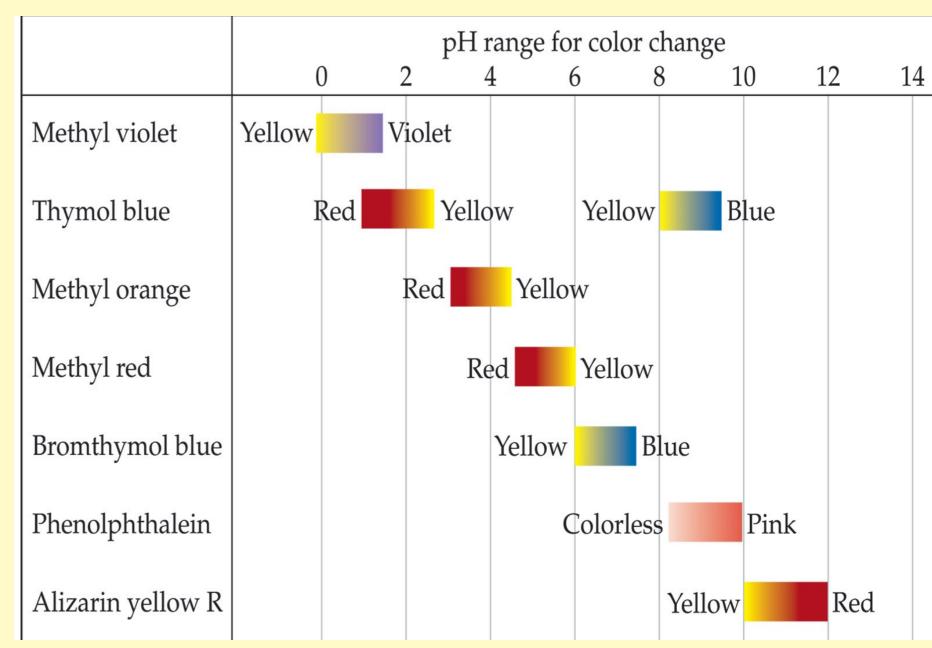
In an NH<sub>4</sub>+/NH<sub>3</sub> buffer, what concentration changes will occur if a small amount of OH- is added?

	[NH <sub>4</sub> +]	[NH <sub>3</sub> ]	рН
1	Increase	Increase	Increase
2	Decrease	Increase	Increase
3	Increase	Decrease	Increase
4	Increase	Decrease	Decrease
5	Decrease	Increase	Decrease
6	No Changes because OH <sup>-1</sup> is not part of the equilibrium reaction.		

- 1. A shift will always occur, however it may not always make any appreciable effect on the pH value.
- 2. To think about this write the equilibrium reaction (from either perspective)
  - $NH_3 + H_2O \rightleftharpoons OH^- + NH_4^+$  $\checkmark$  adding OH<sup>-</sup> shifts left
  - OR NH<sub>4</sub><sup>+</sup> *⇒* NH<sub>3</sub> + H<sup>+</sup>
     √adding OH<sup>-</sup> shifts right

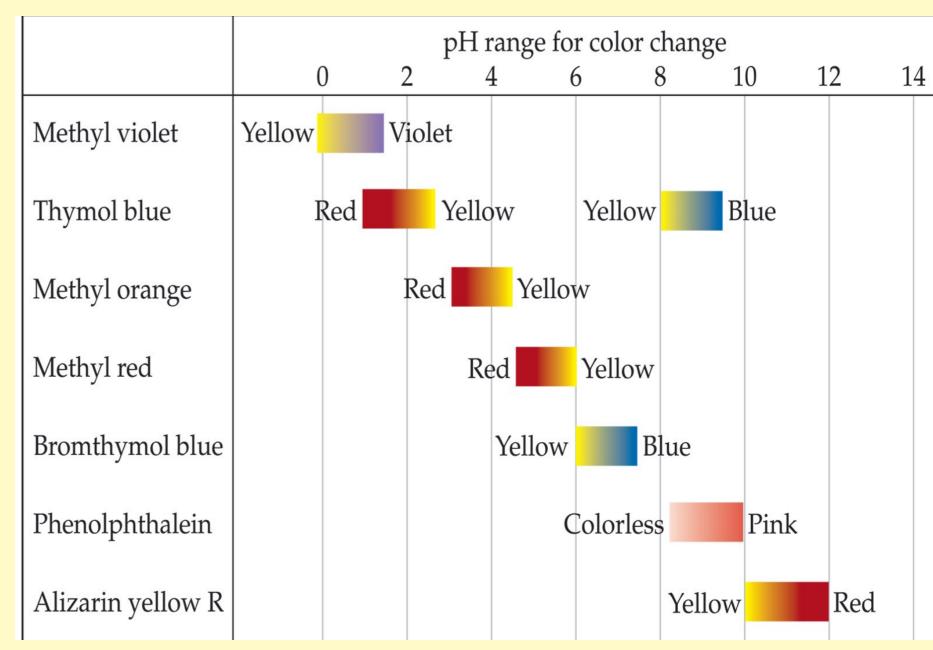
#### The pK<sub>a</sub> of phenolphthalein is likely to be HIn $\rightleftharpoons$ H<sup>+</sup> + In<sup>-</sup>

1. below 8 2.~8 3.~9 4.~10 5. above 10 6. there is not enough information to know



#### The pK<sub>a</sub> of phenolphthalein is likely to be HIn $\rightleftharpoons$ H<sup>+</sup> + In<sup>-</sup>

1. below 8 2.~8 3.~9 4.~10 5. above 10 6. there is not enough information to know



Calculate the pH of a buffer solution containing 0.20 moles sodium acetate and 0.30 moles acetic acid (HAc)  $pK_a$  (HAc) = 4.74.

- 1. 2.63Yes, you may<br/>use a calculator
- 2. 4.57
- 3. 4.74
- 4. 4.92
- 5. 5.27
- 6. not enough information, volume information must be known to calculate a pH.

Calculate the pH of a buffer solution containing 0.20 moles sodium acetate and 0.30 moles acetic acid (HAc)  $pK_a$  (HAc) = 4.74.

1. 2.63  
2. 4.57  
3. 4.74  

$$K_{a} = \frac{\left[H^{+}\right]\left[A^{-}\right]}{\left[HA\right]}$$

$$1.8 \times 10^{-5} = \frac{\left[H^{+}\right](0.2)}{(0.3)}$$

$$\left[H^{+}\right] = 2.7 \times 10^{-5}$$

- 4. 4.92
- 5. 5.27
- 6. not enough information, volume information must be known to calculate a pH.

Which of the following conjugate acid-base pairs will not function as a buffer? HCHO<sub>2</sub>/CHO<sub>2</sub><sup>-</sup> HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>-2</sup> HNO<sub>3</sub>/NO<sub>3</sub><sup>-</sup>

- 1. All acid-base pairs will function as buffers.
- 2. HCHO<sub>2</sub> and CHO<sub>2</sub><sup>-</sup> will not work as a buffer because CHO<sub>2</sub><sup>-</sup> is a spectator ion.
- 3.  $HCO_3^-$  and  $CO_3^{2-}$  will not work as a buffer because  $HCO_3^-$  is a base.
- 4.  $HNO_3$  and  $NO_3^-$  will not work as a buffer because  $HNO_3$  is a strong acid.

Which of the following conjugate acid-base pairs will not function as a buffer? HCHO<sub>2</sub>/CHO<sub>2</sub><sup>-</sup> HCO<sub>3</sub><sup>-/</sup>CO<sub>3</sub><sup>-2</sup> HNO<sub>3</sub>/NO<sub>3</sub><sup>-</sup>

- 1. All acid-base pairs will function as buffers.
- 2. HCHO<sub>2</sub> and CHO<sub>2</sub><sup>-</sup> will not work as a buffer because  $CHO_2^-$  is a spectator ion.
- 3.  $HCO_3^-$  and  $CO_3^{2-}$  will not work as a buffer because  $HCO_3^-$  is a base.
- 4.  $HNO_3$  and  $NO_3^-$  will not work as a buffer because  $HNO_3$  is a SA and  $NO_3^-$  is a pathetic.

Consider a buffer solution containing 0.30 moles sodium acetate and 0.30 moles acetic acid (HAc) to which 0.10 moles HCl are added.  $pK_a$  (HAc) = 4.74. The pH of the solution will

- 1. increase
- 2. decrease
- 3. stay exactly the same

Consider a buffer solution containing 0.30 moles sodium acetate and 0.30 moles acetic acid (HAc) to which 0.10 moles HCl are added.  $pK_a$  (HAc) = 4.74. The pH of the solution will

- 1. increase
- 2. decrease
  - When acid is added, pH always goes down, even if only a small amount.
- 3. stay exactly the same

Is the resulting solution still a buffer? 1. Yes 2. No Consider a buffer solution containing 0.30 moles sodium acetate and 0.30 moles acetic acid (HAc) to which 0.10 moles HCl are added.  $pK_a$  (HAc) = 4.74. Is the resulting solution still a buffer?

- 1. Yes
  - Since there is still ~3 mol acetic acid, and ~0.2 mole acetate, this would still be a buffer
- 2. No

When the amount of one conjugate is ~10x greater than the other conjugate, we would no longer consider a buffer.

Adding ~0.3 mole of SA or SB to this buffer, would exceed the buffer capacity

# pH of water

### at various temperatures

## pH of water at different temps

- 7.0 at 25°C
- 6.6 at 50°C
- 7.5 at 0°C
- Whaaat?
  - ✓ is hot water acidic?
  - ✓ is cold water basic?

Acidic or Basic an imbalance of H<sup>+</sup> and OH<sup>-</sup>

**Neutral** equal quantities of H<sup>+</sup> and OH<sup>-</sup>

Neutralized happens at the equivalence point

when the stoichiometric quantity of acid combined with base is equal

## pH of water

- 7.0 at 25°C
- 6.6 at 50°C
- 7.5 at 0°C
- Whaaat?
  - ✓ is hot water acidic?
  - ✓ is cold water basic?

## Predicting Strength of Acids Tighter H- bonds make WA Looser H- bonds make SA

Using the Chemical Formula to Predict Acid Strength

## Three Groups of Acids

- Oxyacids In which we will look for trends
  - ✓ HNO<sub>3</sub>, HNO<sub>2</sub>
  - ✓ H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>3</sub>
  - ✓ HCIO . . . HCIO<sub>4</sub>
- Binary acids, H-X
  - ✓ HF, HCI, HBr, HI
  - ✓ H<sub>2</sub>O, H<sub>2</sub>S
- Carboxylic Acid (organic acid, containing double bonds near the ionizable H<sup>+</sup>)
  - ✓ C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> –COOH

# 3 Factors causing acids

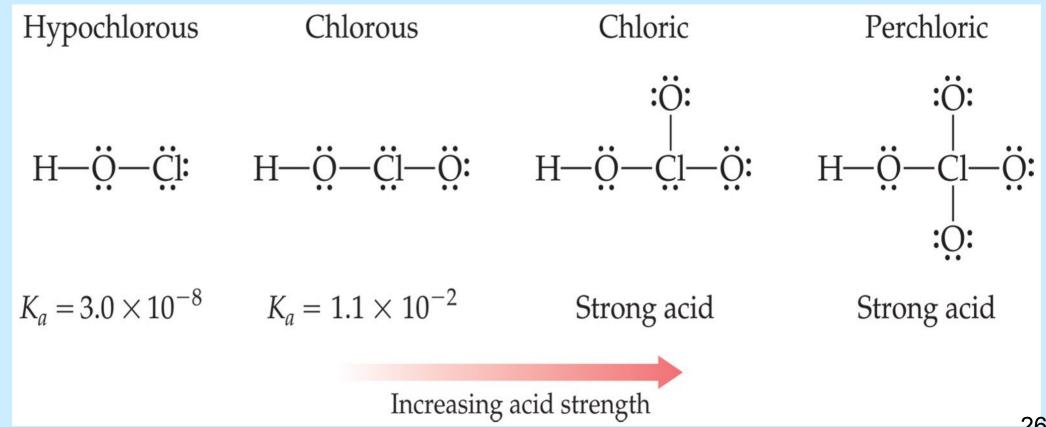
- 1. Polarizability of the –H bond
- 2. Looseness of the X–H bond
- Stability of the conjugate base (the resulting anion).

- 1. HBrO
- 2.  $HBrO_2$
- 3.  $HBrO_3$
- 4.  $HBrO_4$

- 1. HBrO
- 2. HBrO<sub>2</sub>
- 3. HBrO<sub>3</sub>
- 4. HBrO<sub>4</sub>
- Oxy acids with varying # of O atoms
  more oxygens = stronger acid
- More oxygens have more electron drawing capability (high electronegativity of oxygen), thus the -H bond is more polarized, less stable bond (looser bond), thus a weaker acid.
- Also, the additional oxygens help to stabilize the conjugate base by providing more room to "spread out" its negative charge.

## Oxyacids: HXO<sub>n</sub> (really XO<sub>n</sub>H)

- As additional oxygens attached to X, increases acidity.
- $HClO < HClO_2 < HClO_3 < HClO_4$ 
  - ✓ The additional oxygens "draw" the electrons in the H–O bond causing the bond to become even more polarized.
  - Also, the additional oxygens help to stabilize the conjugate base by providing more room to "spread out" the negative charge.



- **1. HCIO**<sub>2</sub> H-O-CI-O
- **2. HBrO**<sub>2</sub> H-O-Br-O
- **3.** HIO<sub>2</sub> H-O-I-O

- 1.  $HCIO_2$  H-O-CI-O
- 2.  $HBrO_2$  H-O-Br-O
- **3.** HIO<sub>2</sub> H–O–I–O
- Oxy acids different central atom but same # oxygens
- I is less electronegative than CI thus the -H bond is less polarized, thus the H is more likely to "hang on" and a therefore a weaker acid.
- The resulting conjugate base ion will be less stable since the presence of the less electronegative I atom is not able to distribute and stabilize the negative charge as well as a more electronegative atom.

## Oxyacids: HOX

- As the electronegativity of X increases, the acidity increases
- HOI < HOBr < HOCl
  - ✓ Because the H–O bond becomes more polarized due to greater "electron-drawing" of the nearby electronegative atom.
  - The resulting conjugate base ion will be more stable since the presence of the more electronegative CI atom can help distribute and stabilize the negative charge.

Which molecule is the weakest acid?

- H<sub>3</sub>P
   H<sub>2</sub>S
- 3. HCI

- **1.** H<sub>3</sub>P
- 2. H<sub>2</sub>S
- 3. HCI
- Binary acids across a row
- P is less electronegative than CI thus the –H bond is less polarized, thus the H is more likely to "hang on" and a weaker acid results.

- 1. H<sub>2</sub>S
- 2.  $H_2Se$
- 3.  $H_2Te$

- **1.** H<sub>2</sub>S
- 2.  $H_2Se$
- 3. H<sub>2</sub>Te
- Binary acids in a column
- S is smaller in size and thus the bond is tighter resulting in a weaker acid. (If you use the electronegativity argument, you will get to the wrong answer.)

## Making Sense of Binary Acid Strength

	GROUP				두 수
	4A	5A	6A	7A	eng
Period 2	CH <sub>4</sub> No acid or base properties	NH <sub>3</sub> Weak base	H <sub>2</sub> O 	HF Weak acid	ng acid strength base strength
Period 3	SiH <sub>4</sub> No acid or base properties	PH <sub>3</sub> Weak base	H <sub>2</sub> S Weak acid	HCl Strong acid	Increasing b

Increasing acid strength

Increasing base strength

What is the explanation....?

## Binary Acids: HX

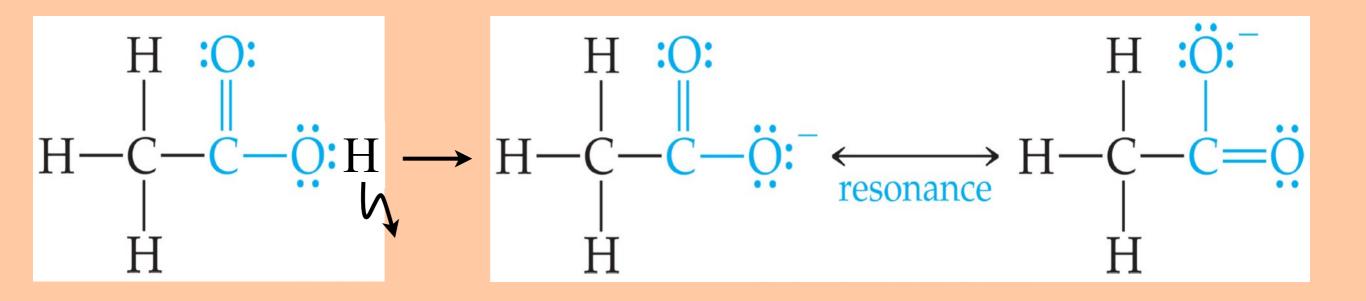
- Down a column, bond strength is the issue (or weakness) is more important:  $H_2O < H_2S < H_2Se$ 
  - ✓ As X's atomic size gets larger, bond length is longer, making the bond not as tight, causing acid strength to increase (stronger acid).
    - size changes dramatically down the column
  - ✓ the H-X bond strength decreases, because the X atoms electrons are more diffuse (spread over a larger electron cloud) and attracts the H<sup>+</sup> ion less effectively.

## Binary Acids: HX

- Across a row, bond polarity is more important: NH<sub>3</sub> < H<sub>2</sub>O < HF</li>
  - ✓ As the *electronegativity* of X *increases*,
    - size does change across the row, but the changes are far less dramatic across the row and thus have less of an effect of acidity.
  - ✓ the polarity of bond increases,
  - ✓ causing the acid strength to increase.

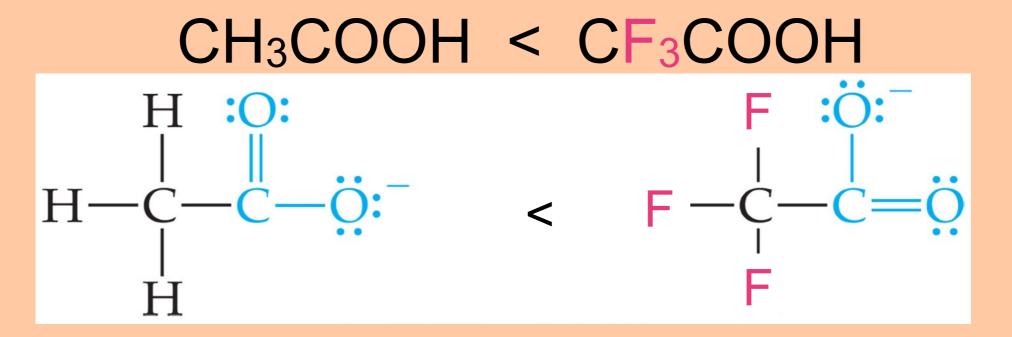
#### Carboxylic Acids: stuff-COOH Stronger acid caused by more stable conjugate

- After the H<sup>+</sup> falls off, the C=O and C-O bonds can exhibit resonance
  - ✓ Resonance is the relocation electrons in an available nearby location resulting in an "averaging" of the structures.
- Resonance allows the electrons to "spread out," distributing the charge and stabilizing the conjugate base.



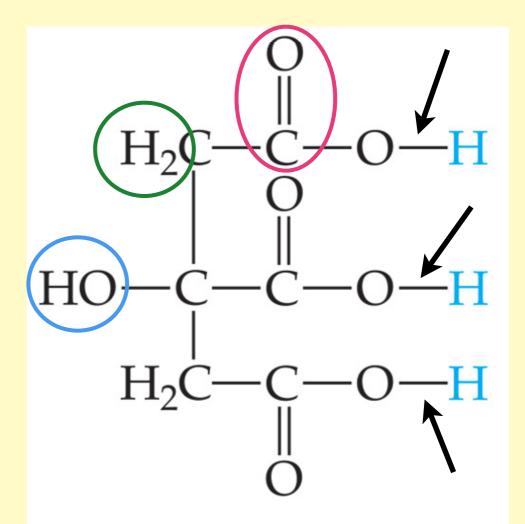
## Carboxylic Acids: Stronger acid caused by more polar –H bond *and* more stable conjugate

- Acidity increases as more electronegative atoms are attached to the root of the acid
  - ✓ because of increased electron-drawing capability and greater polarization of the O−H bond.
  - ✓ because the more electronegative F atoms the presence of the more electronegative F atom can help distribute and stabilize the negative charge.



### What Causes H+'s to Fall Off?

- Acid is only pH changing when H<sup>+</sup>s fall off
- Not every H falls off
- Not every H attached to an O falls off
- When the H falls off, the conjugate base is quite stable.
- What makes this ion stable?
  - ✓ the resonance that can occur with the nearby C=O bond.
  - ✓ Spreads out (smears) the negative charge over more atoms



Citric acid

### Notable NON-acids

- Why is *stuff*-COOH an acid,
- yet *stuff*-COH and *metal*-OH is NOT?
  - ✓ *stuff*–COH is an alcohol
    - without any nearby electron drawing C=O or C=C groups, the O-H bond is not polarized enough.
  - ✓ *metal*-OH is a hydroxide
    - with an ionic bond that is "super" polarized = ionic, thus metal-OH is a base because of the hydroxide pushed into the water.

## Acid Strength Summary

- When more oxygens attached to X
  - ✓ Oxygens draw electrons away from –O–H bond = higher acidity
  - ✓ because –O–H bond becomes more polarized
  - ✓ the resulting ion is larger and the charge can spread out
- When there are same # oxygens
  - ✓ more electronegative X = higher acidity
    - because –O–H bond becomes more polarized
    - the resulting ion has a more electronegative ion which is better at spreading out (and stabilizing) the negative charge
- Binary acids acids in a row
  - ✓ more electronegative X = higher acidity
    - because –X–H bond becomes more polarized, and H's falls of easier
- Binary acids in a column
  - ✓ it's not about electronegativity
  - ✓ Larger radius X, weaker bond = higher acidity

# Which of the following binary acids is the weakest acid in water

- $H_2S$
- H<sub>2</sub>Se
- H<sub>2</sub>Te
- HBr
- HI

## Which of the following binary acids is the weakest acid in water

- 1. H<sub>2</sub>S
  - $H_2Se$
  - H<sub>2</sub>Te
  - HBr
  - HI

We know the answer is not HBr and HI, which are both nearly completely ionized in water.

Consider the 2- ions that can be formed from the other acids.

- S<sup>2-</sup>, Se<sup>2-</sup>, and Te<sup>2-</sup>.
- Based on higher density of negative charge, the sulfide ion is the strongest of these bases.
- Therefore its conjugate acid must be the weakest, leading to the conclusion that H<sub>2</sub>S is the weakest of these acids.

For those who wish to memorize mindless rules, the strengths of binary acids increases to the right and down on the periodic table, with HI being the strongest, and H2S the weakest.

#### Which weak acid is the weakest? Do not use your *K*<sub>a</sub> chart.

- 1. hypochlorous acid
- 2. hypobromous acid
- 3. hypoiodous acid
- 4. these weak acids are all equally weak
- 5. there is not enough information to distinguish
- 6. these are not weak acids, they are all strong acids

#### Which weak acid is the weakest? Do not use your *K*<sub>a</sub> chart.

- 1. hypochlorous acid
- 2. hypobromous acid
- 3. hypoiodous acid
- Since these acids all have the same number of oxygens, the distinguishing feature is the electronegativity of the atom adjacent to the ionizing -OH bond.
- Since I is the least electronegative, it polarizes the -OH bond least making for the weakest acid.

Which of the following acids can be oxidized to form a stronger acid? (Select all that apply.)

- 1. H<sub>2</sub>SO<sub>4</sub>
- 2.  $HNO_2$
- 3.  $HBrO_2$
- 4.  $HIO_3$
- 5.  $HCIO_4$
- 6. H<sub>3</sub>PO<sub>4</sub>

# Which of the following acids can be oxidized to form a stronger acid?

- 1. H<sub>2</sub>SO<sub>4</sub>
- **2.** HNO<sub>2</sub>
- 3. HBrO<sub>2</sub>
- **4.** HIO<sub>3</sub>
- Any acid to which more oxygens can be added must attain a higher oxidation number to add those oxygens and thus would become oxidized
- 5.  $HCIO_4$
- 6. H<sub>3</sub>PO<sub>4</sub>

## Which acid is the weakest? 1. $HCIO_4$ 2. $HCIO_3$ 3. $HBrO_3$ 4. $HBrO_4$ 5. $HIO_3$ 6. $HIO_4$

- 1. HCIO<sub>4</sub>
- 2. HCIO<sub>3</sub>
- 3. HBrO<sub>3</sub>
- 4. HBrO<sub>4</sub>
- **5.** HIO<sub>3</sub>
- 6. HIO<sub>4</sub>
- Oxy acids: varying oxygens and varying central atom
- looking for less oxygens and less electronegative central atom
- AP would not force you to decide which factor trumps the other: such as HBrO<sub>2</sub> vs HIO<sub>3</sub>.

#### Which base is the strongest?

- 1. CIO<sub>4</sub>-
- 2. CIO<sub>3</sub>-
- 3. BrO<sub>3</sub>-
- 4. BrO<sub>4</sub>-
- 5. IO<sub>3</sub>-
- 6. IO<sub>4</sub>-

#### Which base is the strongest?

- 1. CIO<sub>4</sub>-
- 2. CIO<sub>3</sub>-
- 3. BrO<sub>3</sub>-
- 4. BrO<sub>4</sub>-
- 5. IO<sub>3</sub>-
- 6. IO<sub>4</sub>-
- The weaker the WA, then the stronger the cjWB

### Which acid is the weakest?

- 1. chlorous
- 2. nitrous
- 3. acetic
- 4. hypobromous
- 5. they are all equally weak
- there is not enough information to distinguish

acid	pKa	
chlorous	1.96	
nitrous	3.35	
acetic	4.74	
hypobromous	8.6	

## Which acid is the weakest?

- 1. chlorous
- 2. nitrous
- 3. acetic
- 4. hypobromous
- 5. they are all equally weak

acid	р <i>К</i> а
chlorous	1.96
nitrous	3.35
acetic	4.74
hypobromous	8.6

- there is not enough information to distinguish
- The largest pK<sub>a</sub> is the weakest acid

## What Causes H<sup>+</sup>'s to Fall Off?

- Acid is only pH changing when H<sup>+</sup>'s fall off
- Not every H falls off
- Not every H attached to an O falls off
- When the H falls off, the conjugate base is quite stable.
- What makes this ion stable?
  - ✓ the resonance that can occur with the nearby C=O bond.
  - ✓ Spreads out (smears) the negative charge over more atoms

Ascorbic acid (vitamin C)

Η

# **Polyprotic Acids**

## H<sub>2</sub>A and H<sub>3</sub>A

# **Polyprotic Acids**

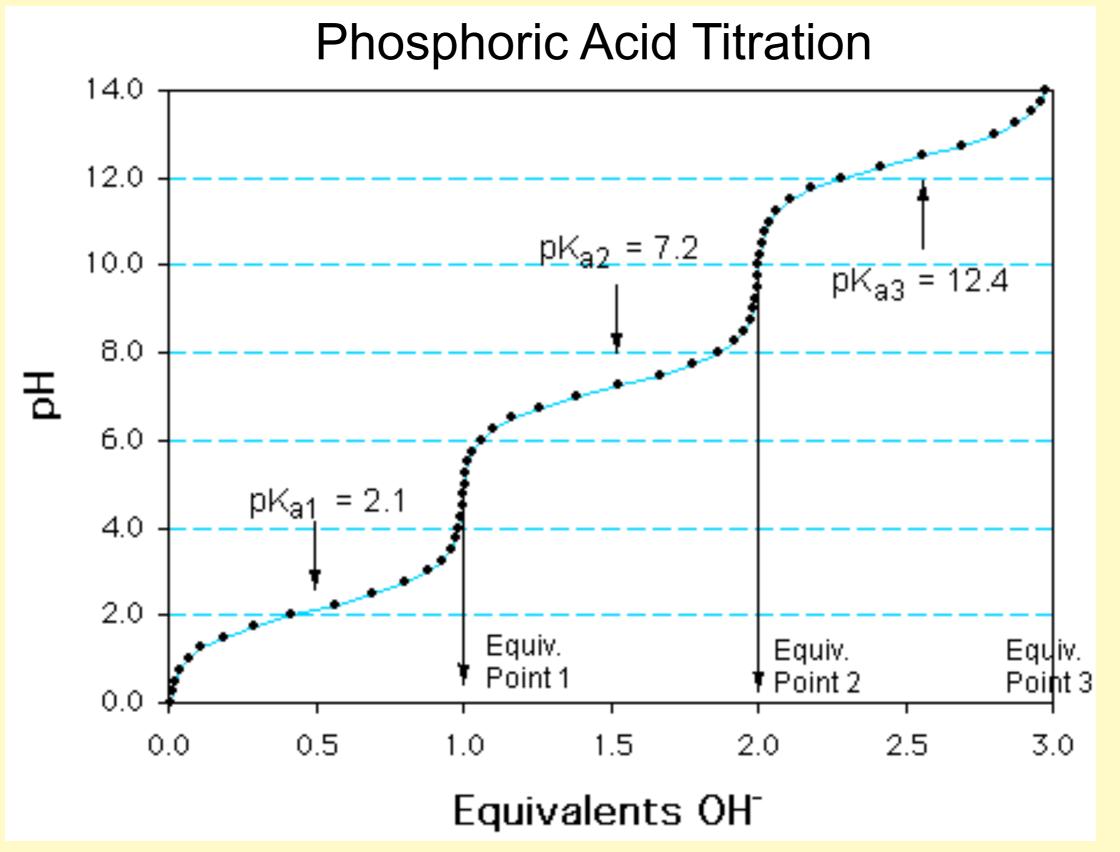
- Acids with more than one ionizable proton
- The second H<sup>+</sup> ions never ionize as easily as the first.
  - ✓ After the first ionization, the H<sup>+</sup> ion does not leave the resulting negatively charged ion as easily.
  - ✓ Successive  $K_a$  values become increasingly smaller.
- If the K<sub>a</sub> values differ by a factor of 10<sup>3</sup> or more, the pH can be calculated by considering only the first ionization.
  - ✓ Subsequent ionizations contribute a negligible amount of H<sup>+</sup> ions.

## **Examples of Polyprotic Acids**

Constants of Se

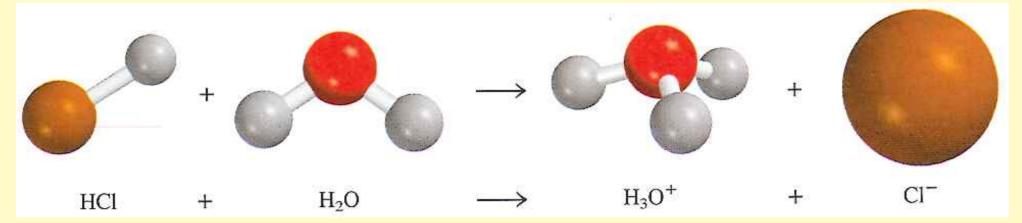
TABLE 16.3	SLE 16.3 Acid-Dissociation Constants of Some Common Polyprotic Acids					
Name	Formula	K <sub>a1</sub>	K <sub>a2</sub>	K <sub>a3</sub>		
Ascorbic Carbonic Citric Oxalic Phosphoric Sulfurous Sulfurous	$\begin{array}{c} H_{2}C_{6}H_{6}O_{6} \\ H_{2}CO_{3} \\ H_{3}C_{6}H_{5}O_{7} \\ H_{2}C_{2}O_{4} \\ H_{3}PO_{4} \\ H_{2}SO_{3} \\ H_{2}SO_{4} \end{array}$	$8.0 \times 10^{-5}$ $4.3 \times 10^{-7}$ $7.4 \times 10^{-4}$ $5.9 \times 10^{-2}$ $7.5 \times 10^{-3}$ $1.7 \times 10^{-2}$ Large	$1.6  imes 10^{-12}$ $5.6  imes 10^{-11}$ $1.7  imes 10^{-5}$ $6.4  imes 10^{-5}$ $6.2  imes 10^{-8}$ $6.4  imes 10^{-8}$ $1.2  imes 10^{-2}$	$4.0 \times 10^{-7}$ $4.2 \times 10^{-13}$		
Tartaric	$H_2C_4H_4O_6$	$1.0 \times 10^{-3}$	$4.6 \times 10^{-5}$			

## **Titration of Polyprotic Acids**



#### Brønsted & Lowry Definition as applied to a strong acid

•  $HCI_{(g)}$  +  $H_2O_{(L)}$   $\rightarrow$   $H_3O^+$  +  $CI^-$ 



- HCI is acting as the proton donor.
- H<sub>2</sub>O is acting as the proton acceptor.
- But for a strong acid, this B & L definition is not necessary, it's just as convenient and accurate to use the Arrhenius definition that defines an acid as a substance that dissolves to produce H<sup>+</sup>
  - $\bullet$  HCI<sub>(aq)</sub>  $\rightarrow$  H<sup>+</sup> + CI<sup>-</sup>

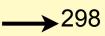
## **Brønsted & Lowry Definition**

as applied to a strong base

- $NaOH_{(s)}$  +  $H_2O_{(L)} \rightarrow Na^+$  +  $OH^-$  +  $H_2O_{(L)}$ 
  - This of course fits the Arrhenius definition by dissolving to produce OH<sup>-</sup>
- So what about the proton donor and acceptor?
- We could say that water donates a proton, and the OHaccepts a proton.
  - $\bullet$  OH<sup>-</sup> + H<sub>2</sub>O<sub>(L)</sub>  $\rightarrow$  H<sub>2</sub>O<sub>(L)</sub> + OH<sup>-</sup>
  - $H_2O_{(L)}$  is acting as the proton donor.
  - OH<sup>-</sup> is acting as the proton acceptor.
  - But of course it seems silly to even write this out because the exchange of proton turns into exactly the same thing.
- So for a strong base, this B & L definition is also not necessary, its just as convenient and accurate to use the Arrhenius definition that defines a base as a substance that dissolves to produce OH<sup>-</sup>.

#### Let's Define Acids & Bases

- In 1880's Arrhenius (same guy who studied reaction rates) defined:
   Acid: a substance that dissolves in water to form H<sup>+</sup>
   ✓ HCI → H<sup>+</sup> + CI<sup>-</sup>
  - Base: a substance that dissolves in water to form OH<sup>-</sup>
    - $\checkmark \text{ NaOH } \rightarrow \text{Na}^{+} + \text{ OH}^{-}$
- 1923 Brønsted & Lowry defined:
  - Acids as a proton (H<sup>+</sup>) donor
  - Bases as a proton (H<sup>+</sup>) acceptor
- Also in 1920's Gilbert Lewis (same guy who invented {Electron Dot} Lewis Structures) expanded the definition:
  - Acids as electron pair acceptors
  - Bases as electron pair donors
  - We have discussed this in reference to ions solvated in aqueous solution
    - ✓ maybe more on this later...

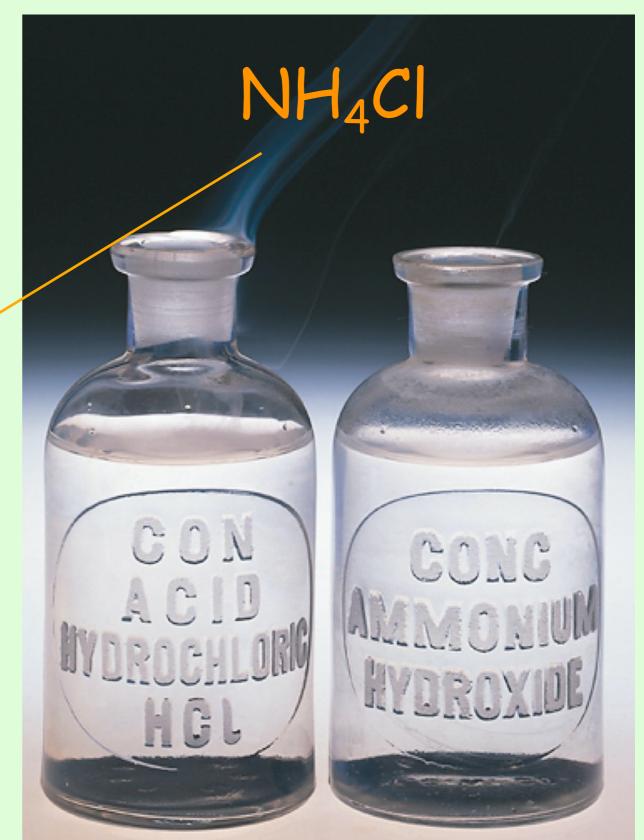


### Acids and Bases as gases?

- Most reactions we will study will be in solution, but gases can also act as acids and bases. You may recall...
  - We tested the speed of gases with the following reaction:

► 
$$HCI_{(g)} + NH_{3(g)} \rightarrow NH_4CI_{(s)}$$
  
 $HCI_{(s)} \rightarrow NH_4CI_{(s)}$ 

- Why was the white ring NOT in the middle?
- Why was it closer to the HCl end?



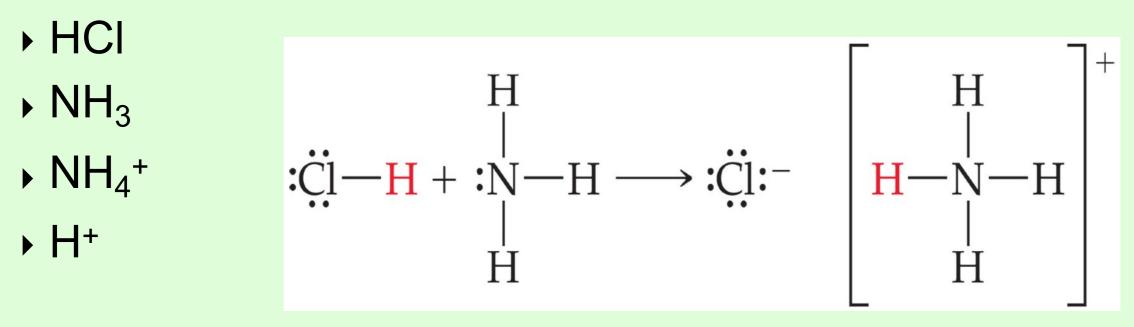
Most Acids and Bases will be in an aqueous solution, however they can occur in the gas phase as well.

- What makes the reaction on the previous slide and acid base reaction?
  - $\bullet \operatorname{HCl}_{(g)} + \operatorname{NH}_{3(g)} \to \operatorname{NH}_4\operatorname{Cl}_{(s)}$
- Draw a Lewis Structure the following particles
  - HCI
  - ► NH<sub>3</sub>
  - ▶ NH<sub>4</sub>+

► CI-

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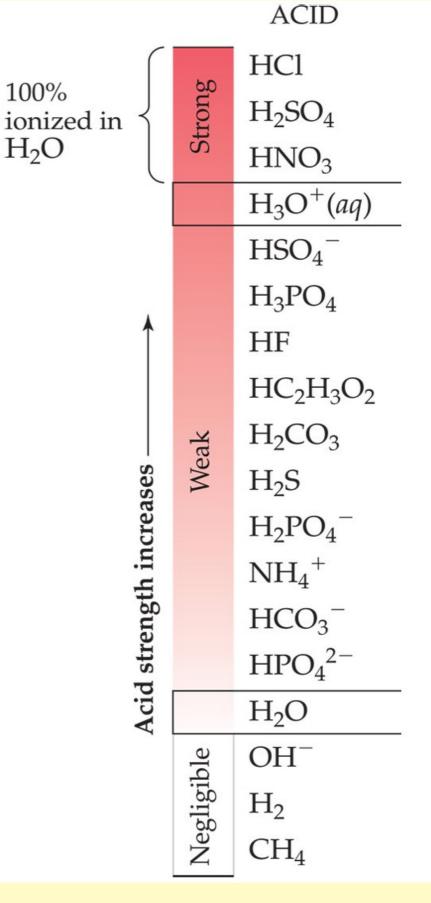


# Tricky Questions Worth Thinking

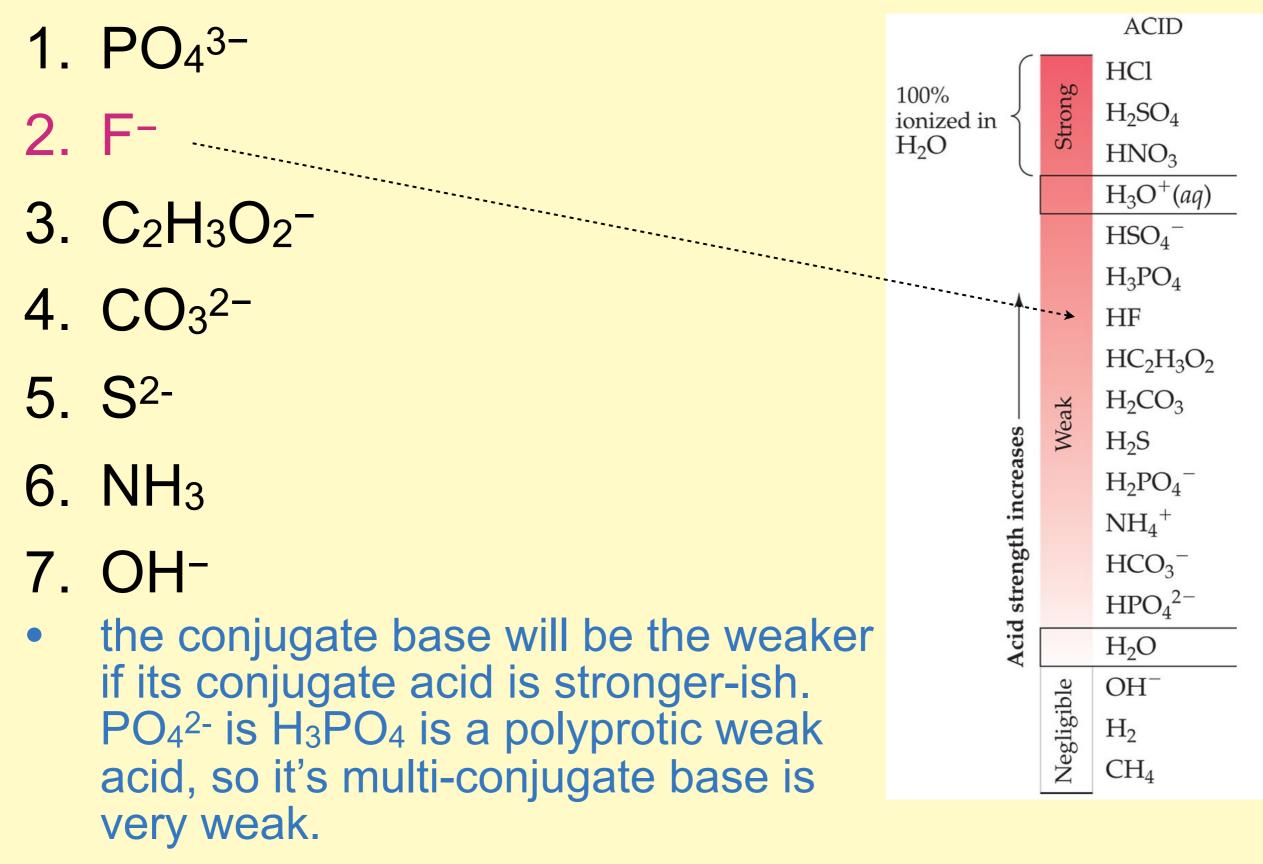
## H<sub>2</sub>A and H<sub>3</sub>A

#### Which base is the weakest?

- F<sup>-</sup>
   C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>
- 3. CO<sub>3</sub><sup>2-</sup>
- 4. S<sup>2-</sup>
- 5. NH<sub>3</sub>
- 6. OH-



#### Which base is the weakest?



#### What is the approximate pH of a 0.010 M **HF** solution? No calculator 1. 1.0 2. 2 3. 2.7 4. 7 5. 12.0 6. 11.3 7. Surely you're joking... I can't do this without a calculator.

What is the approximate pH of a 0.010 *M* HF solution?

- 1. 1.0
- 2. 2
- 3. 2.7
- We know a 0.01 M of SA would be pH = 2, thus WA would be higher pH, but not neutral
- 4. 7
- 5. 11.3