AGENDA

- Bellwork
- 8.1
- 8.2
- 8.3
- 8.4
- Gallery walk

BELLWORK

- Name 4 of the strong acids

8.1 Introduction to Acids and Bases

ENDURING UNDERSTANDING:	
SAP-9	The chemistry of acids and bases involves reversible proton-transfer reactions, with equilibrium concentrations being related to the strength of the acids and bases involved
LEARNING OBJECTIVE:	
SAP-9.A	Calculate the values of pH and pOH, based on Kw and the concentration of all species present in a neutral solution of water.

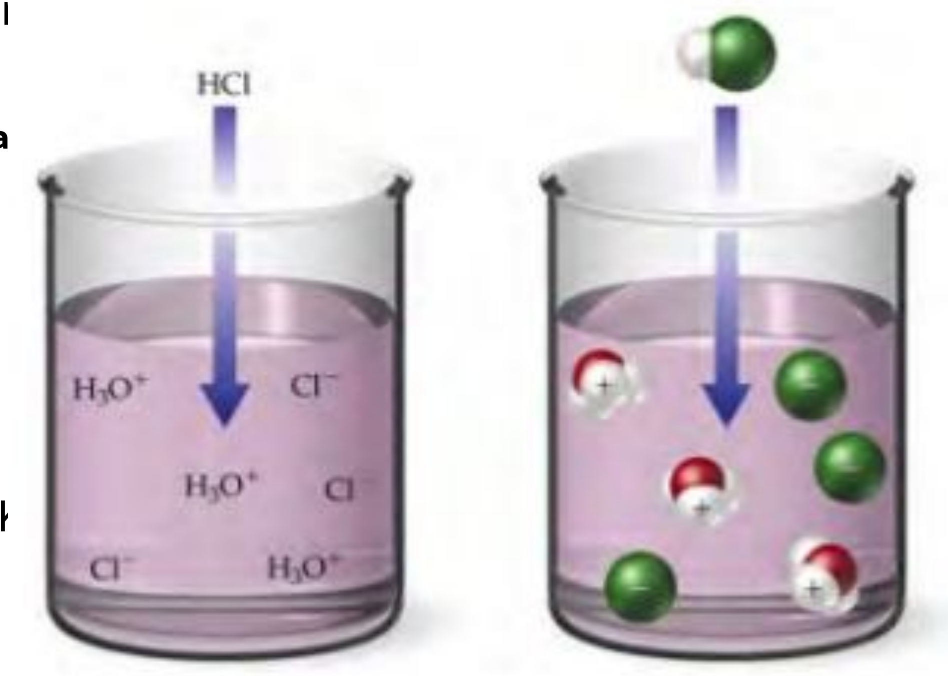
Acids

Brønsted-Lowry acid is a substance that donates hydrogen ions (H^+) to a solution. When the hydrogen ion interacts with water it forms the hydronium io

$$\mathbf{HCl_{(aq)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(a}}$$

Notice the single headed arrow!
This means HCl is a strong acid and will ionize 100%.
All acids start as COVALENT molecules.

If you see ⇄ it indicates a WEA acid that does not completely ionize.



BASES

Brønsted-Lowry bases are substances that can accept a hydrogen ion (H^+).

$$\mathbf{NaOH_{(s)} \rightarrow Na^{+}_{(aq)} + OH^{-}_{(aq)}}$$

Notice the single headed arrow - this indicates the base has dissolved 100% and we would define the base as a strong base

Apart from ammonia, most bases are ionic.

STRONG ACIDS AND STRONG BASES

As a reminder, when a substance completely dissociates/ionizes we describe it as being a **strong** acid or base.

There are six strong acids: HCl, HBr, HI, HNO_3, H_2SO_4 (for the first hydrogen ion), and $HClO_4$.

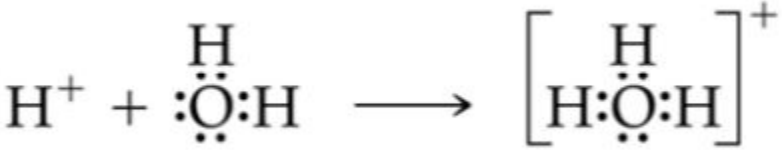
(The mnemonic is “SO, I Brought NO Clean ClOthes)

The strong bases are metal hydroxides from Group 1 and 2 on the periodic table.

WATER

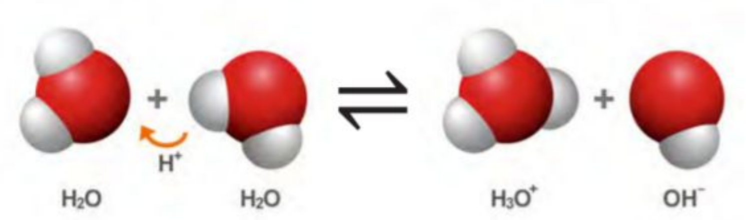
Hydrogen ions are too small (basically they are just a single proton) to exist as stable particles.

Instead they form a covalent bond with a water molecule.



WATER

Water also AUTOIONIZES!



$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

We can write an equilibrium expression for the autoionization of water:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

WATER CONSTANT, K_w

Remember pure liquids and solids can be treated as having an “effective concentration” of 1.

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

becomes $K_w = [H_3O^+][OH^-]$

or $K_w = [H^+][OH^-]$

$= \mathit{1.0 \times 10^{-14}}$ *at 25° C*

PH AND POH

$$2H_2O \leftrightharpoons H_3O^+ + OH^-$$

Pure water is neutral because $[H_3O^+]$ is equal $[OH^-]$.

At 25°C, $[H_3O^+][OH^-] = 1\text{x}10^{-14} = K_w$.

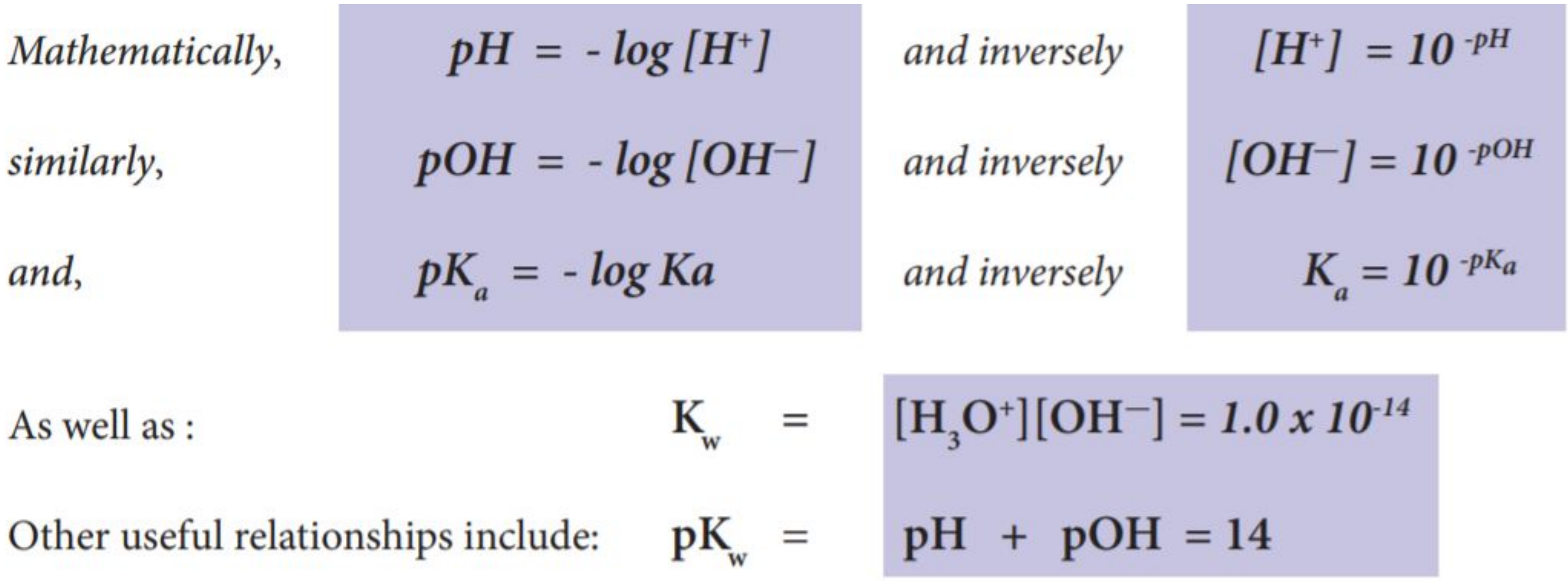
What is the concentration of hydronium ions? hydroxide ions?

p(anything) = -log of (anything)

What is the pH?

What is the pOH?

I PROMISE THIS GETS EASY IF YOU PRACTICE!



Mathematically, $pH = -\log [H^+]$ *and inversely* $[H^+] = 10^{-pH}$

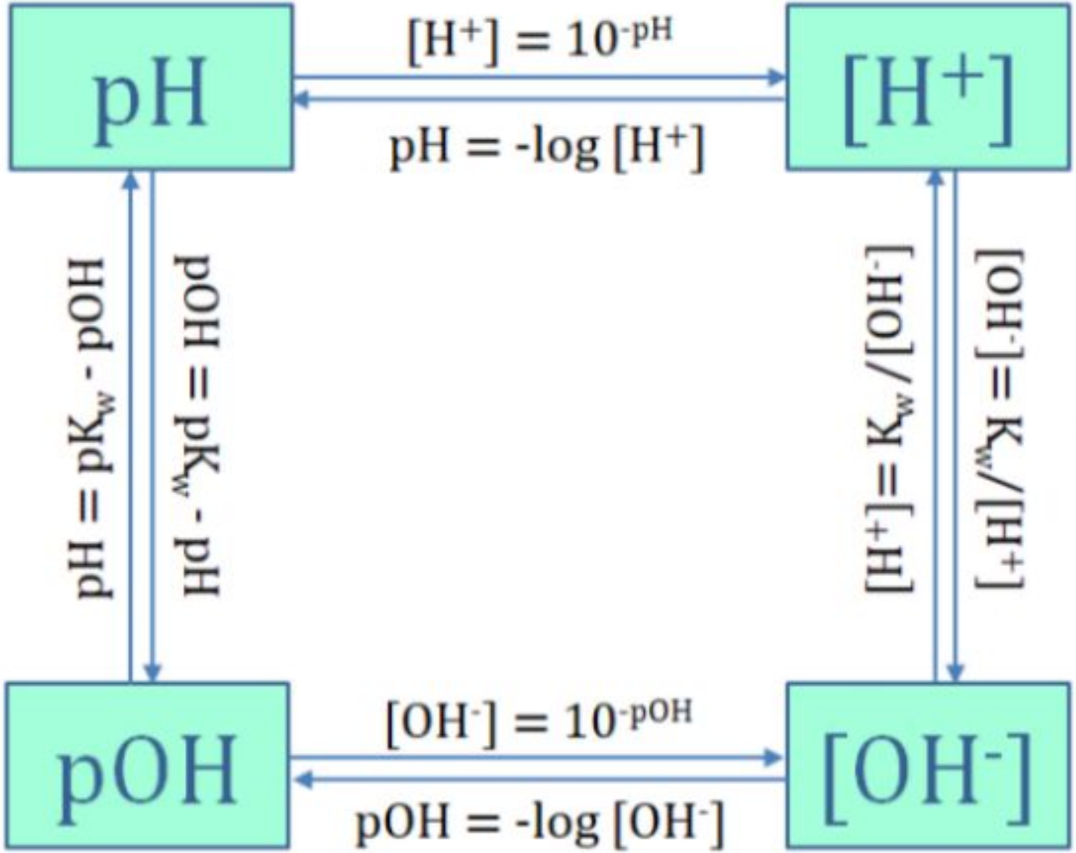
similarly, $pOH = -\log [OH^-]$ *and inversely* $[OH^-] = 10^{-pOH}$

and, $pK_a = -\log Ka$ *and inversely* $K_a = 10^{-pK_a}$

As well as : $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Other useful relationships include: $pK_w = pH + pOH = 14$

Calculations



$[H^+] = 10^{-pH}$

$pH = -\log [H^+]$

$pH = pK_w - pOH$

$pOH = pK_w - pH$

$[H^+] = K_w/[OH^-]$

$[OH^-] = K_w/[H^+]$

$[OH^-] = 10^{-pOH}$

$pOH = -\log [OH^-]$

At 25°C:

$K_w = 1.0 \times 10^{-14}$

$pK_w = 14.00$

What is the only thing that can change an equilibrium constant?

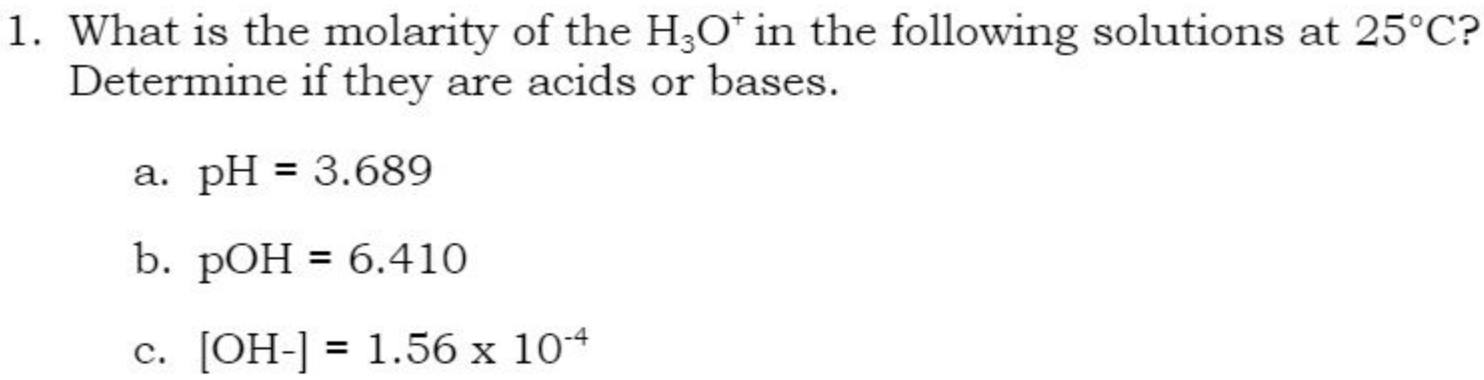
Same for K_w

$$\text{Heat} + 2\ H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

The autoionization of water is endothermic.

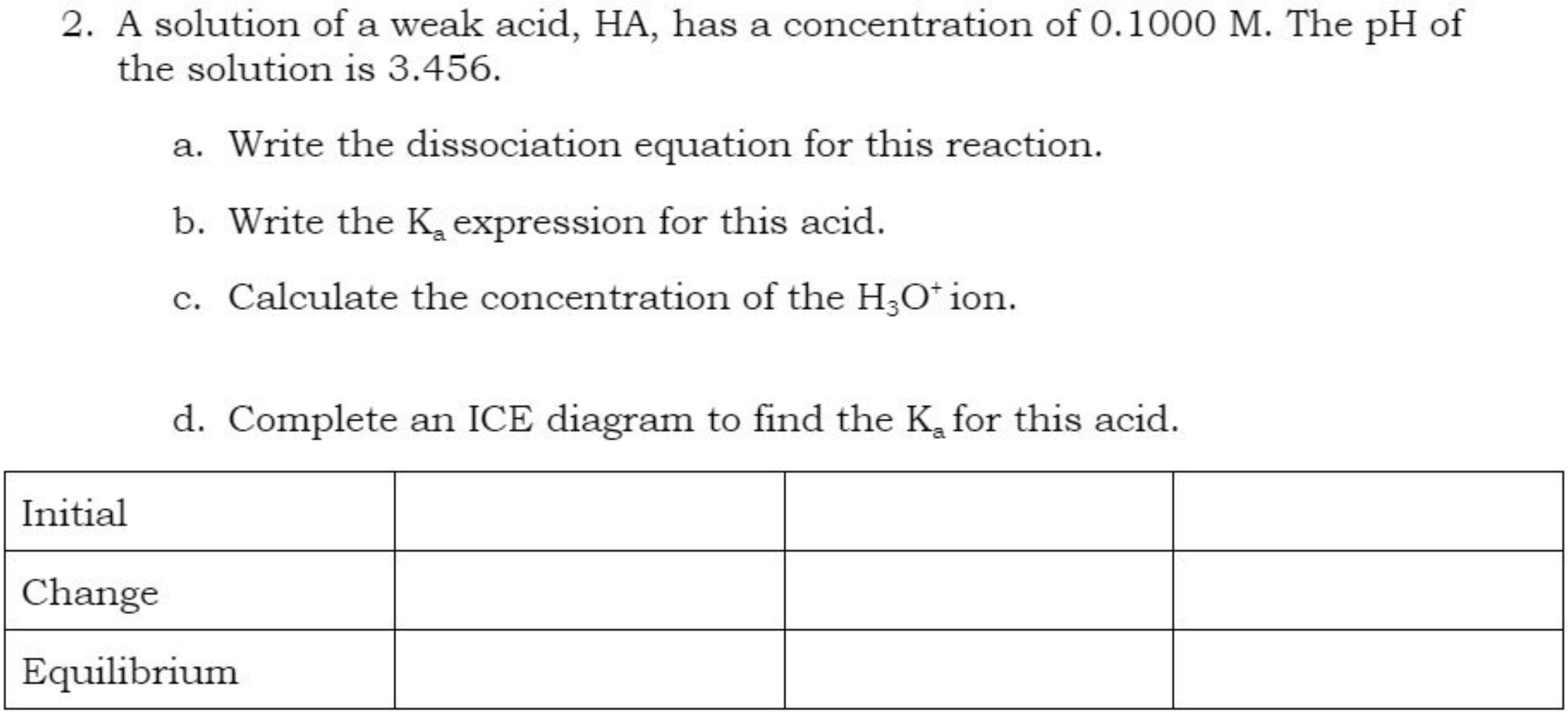
At 100 ℃ the pH of water is 6.14. Does that mean that water is acidic at high temperatures?

Together



1. What is the molarity of the H_3O^+ in the following solutions at 25°C? Determine if they are acids or bases.
   a. pH = 3.689
   b. pOH = 6.410
   c. [OH-] = 1.56×10^{-4}

YOU DO, WE REVIEW



2. A solution of a weak acid, HA, has a concentration of 0.1000 M. The pH of the solution is 3.456.
   a. Write the dissociation equation for this reaction.
   b. Write the K_a expression for this acid.
   c. Calculate the concentration of the H_3O^+ ion.

   d. Complete an ICE diagram to find the K_a for this acid.

Initial			
Change			
Equilibrium			

8.2 pH and pOH of Strong Acids and Bases

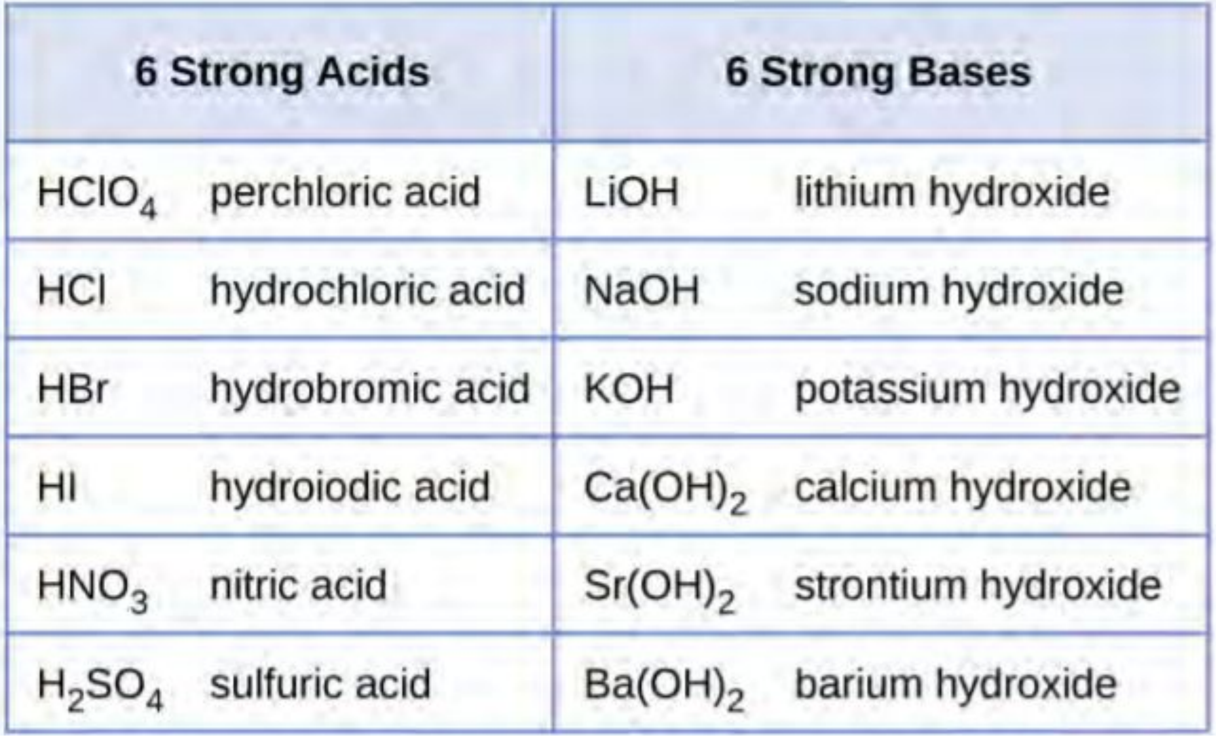
ENDURING UNDERSTANDING:

SAP-9	The chemistry of acids and bases involves reversible proton-transfer reactions, with equilibrium concentrations being related to the strength of the acids and bases involved.

LEARNING OBJECTIVE:

SAP-9.B	Calculate pH and pOH based on concentrations of all species in a solution of a strong acid or a strong base.

STRONG ACIDS AND STRONG BASES



6 Strong Acids		**6 Strong Bases**	
$HClO_4$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

$$pH = -\log[H^+]$$
$$pOH = -\log[OH^-]$$

$$K_w = [H_3O^+][OH^-] = 10^{-14}$$
$$pK_w = pH + pOH = 14$$

a *change of one pH unit* represents a *10 fold increase or decrease* in *ion concentration*

STRONG ACIDS

- Strong acids are **strong electrolytes** and when added to water dissociate into their ions to form an aqueous solution. Electrolytes can conduct electricity when they are in a solution.
- For monoprotic strong acids, the concentration of the acid is equal to the concentration (molarity) of the hydronium ions.

$$[H_3O^+] = [acid]$$

- For H_2SO_4, only the first hydrogen dissociates completely: $H_2SO_{4\,(aq)} + H_2O_{(l)}$ □ $HSO_4^-{}_{(aq)} + H_3O^+{}_{(aq)}$ However, in a reaction with a base, both hydrogen ions will react.

QUICK CHECK:

- What is the pH of 0.010M solution of hydrochloric acid, HCl?
- What is the pH of 0.00001M solution of HI?

Strong Bases

- Strong bases are the soluble hydroxides; they dissociate completely in water, and are therefore **strong electrolytes**.
- They are group 1, alkali metal hydroxides, and the group 2, alkaline earth metal hydroxides (Ca^{2+}, Sr^{2+}, and Ba^{2+}).
- For strong bases, you can calculate the concentration of the hydroxide, using the initial concentration (molarity) **and the ratio of hydroxide ions** in the formula.

Remember that bases are IONIC!

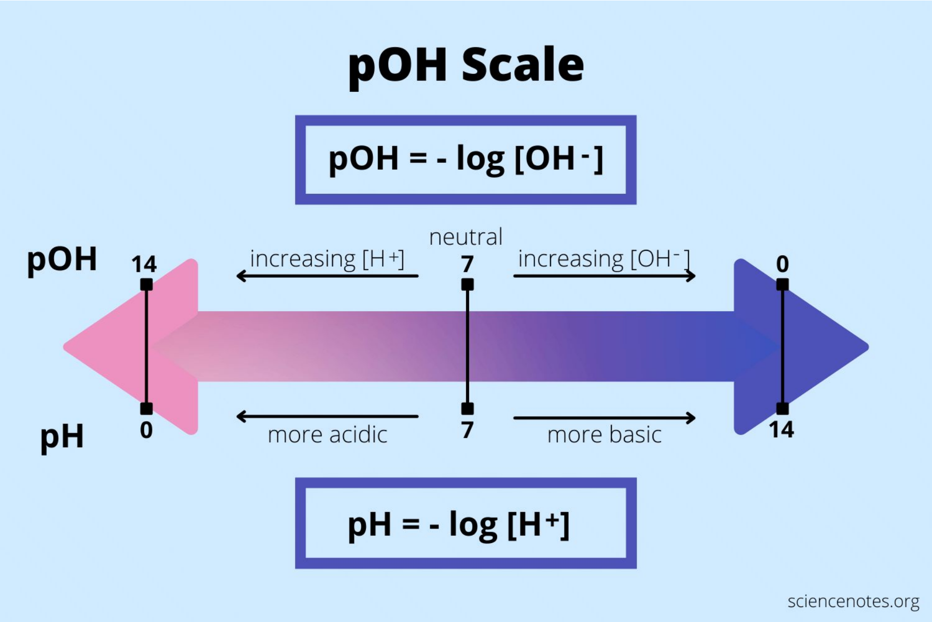
$$[OH^-] = [base]$$

QUICK CHECK:

- What is the pOH of 0.0001M solution of NaOH?
- What is the pOH of 0.01M solution of KOH?
- What is the pOH of 0.1M solution of $Ca(OH)_2$?

pH & pOH

- The more concentrated an acid is, the lower the pH will be.
- The more concentrated the base is, the lower the pOH will be and the higher the pH will be.
- Acids have pH values that are lower than 7 while bases have pH values that are greater than 7.



Temperature

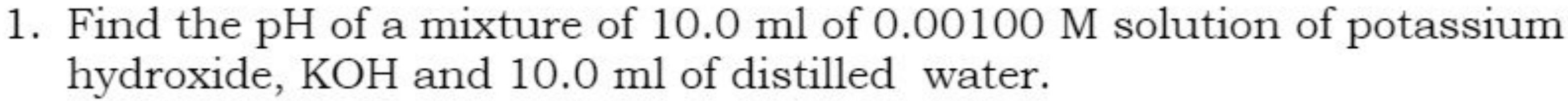
Yesterday we saw that K_w is temperature dependent.

Changing temperature **has no effect** on stoichiometry and our calculations of pH and pOH do not change.

At ~0°C, $pK_w = 14.8$

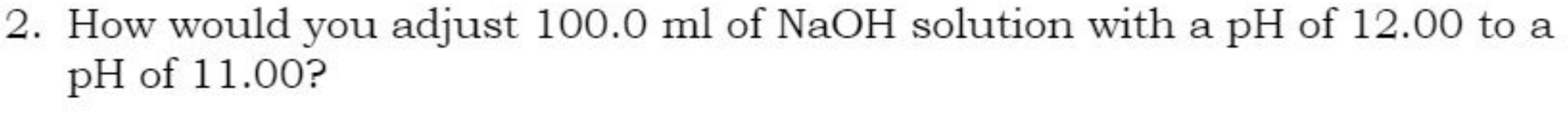
What is the **pOH** of a 0.20 M HCl solution at 0°C?

TOGETHER



1. Find the pH of a mixture of 10.0 ml of 0.00100 M solution of potassium hydroxide, KOH and 10.0 ml of distilled water.

YOU DO, WE REVIEW



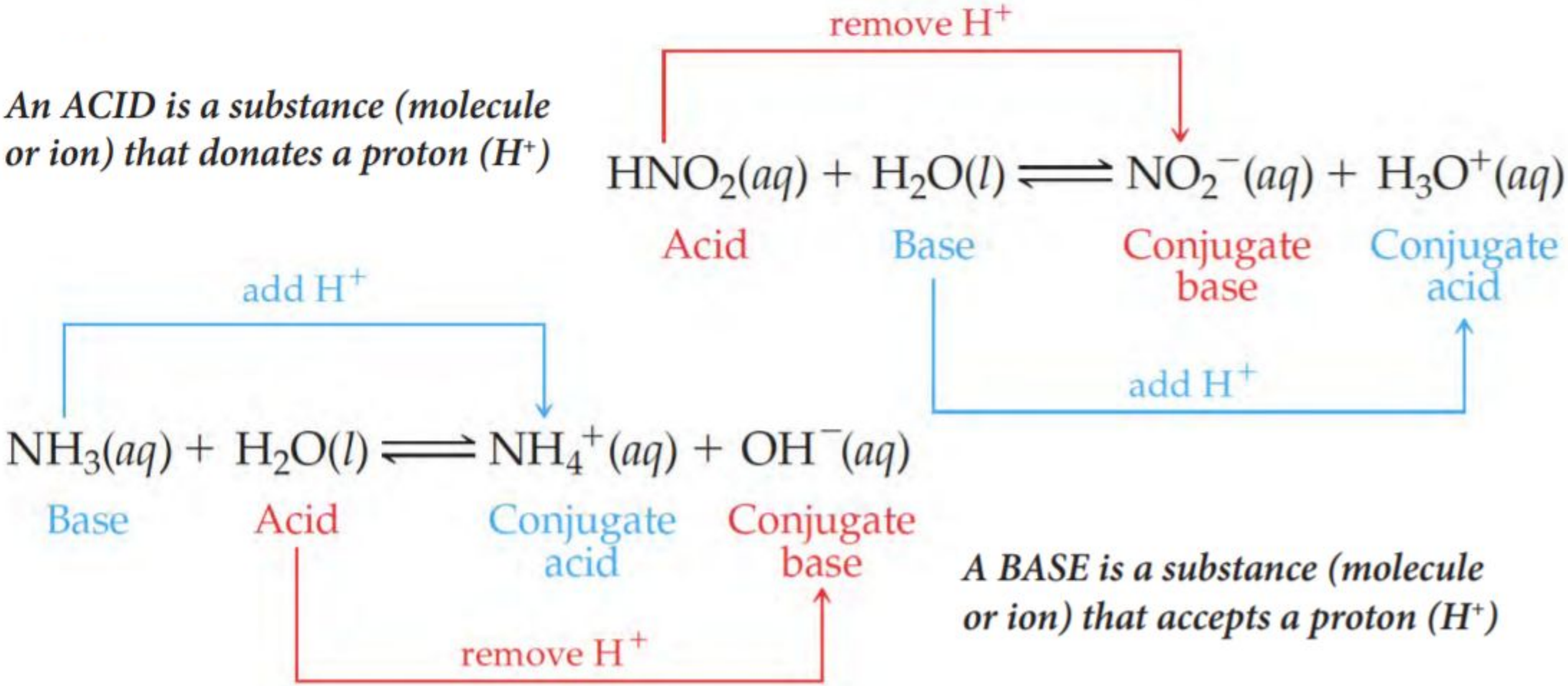
2. How would you adjust 100.0 ml of NaOH solution with a pH of 12.00 to a pH of 11.00?

8.3 Weak Acid and Base Equilibrium

ENDURING UNDERSTANDING:	
SAP-9	The chemistry of acids and bases involves reversible proton-transfer reactions, with equilibrium concentrations being related to the strength of the acids and bases involved.
LEARNING OBJECTIVE:	
SAP-9.C	Explain the relationship among pH, pOH, and concentrations of all species in a solution of a monoprotic weak acid or weak base.

Some Reminders

An ACID is a substance (molecule or ion) that donates a proton (H⁺)



remove H^+

$$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$$

Acid

Base

Conjugate base

Conjugate acid

add H^+

add H^+

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Base

Acid

Conjugate acid

Conjugate base

remove H^+

A BASE is a substance (molecule or ion) that accepts a proton (H⁺)

Weak Acids

- There are six strong acids: HCl, HBr, HI, $HClO_4$, H_2SO_4, and HNO_3.
- All other acids are considered weak acids.
- When a weak acid is dissolved in water only a small amount of ionization will occur according to the following general equation (note: HA represents any acid):

$$\mathbf{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)}$$

K_A

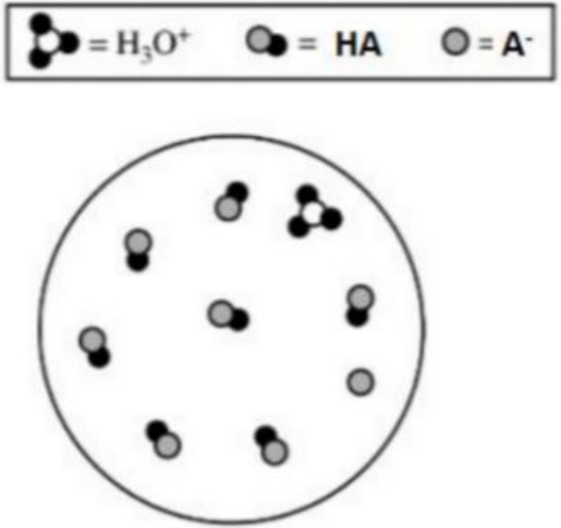
$$\mathbf{HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)}$$

The equilibrium constant associated with weak acids is designated as $\mathbf{K_a}$ and is called the **acid ionization constant**.

Since these constants are generally very small, the pK_a is often reported instead of Ka.

For acids, the smaller the K_a, the larger the pK_a, the weaker the acid.

A weak acid will exist primarily in its molecular form (unionized).



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

Weak Bases

- Strong bases include group I and group II hydroxides.
- All other bases can be considered weak bases.
- When a weak base is dissolved in water a small amount of base will react with water to produce hydroxide according to the following general equation (note: B represents any base):

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

K_B

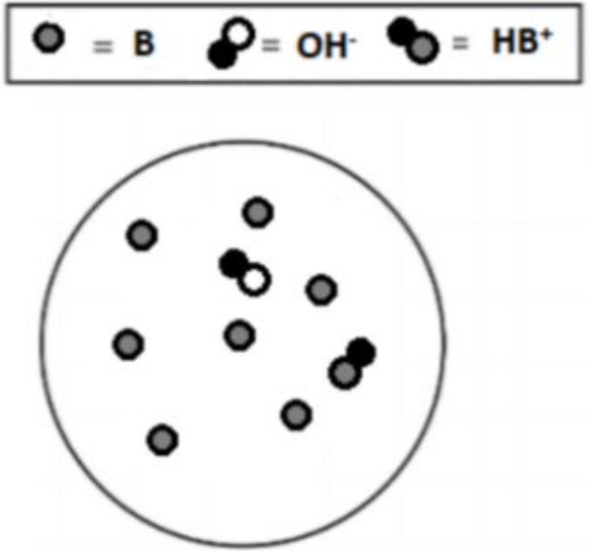
$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

The equilibrium constant associated with weak bases is designated as $\mathbf{K_b}$ and is called the **base ionization constant**.

Since these constants are generally very small, the pK_b is often reported instead of K_b.

For bases, the smaller the K_b, the larger the pK_b, the weaker the base.

A weak base will exist primarily in its un-ionized form in solution.



$$= \frac{[BH^+][OH^-]}{[B]}$$

PERCENT IONIZATION

Percent ionization is a measurement of the extent of ionization of an acid. A strong acid will have 100% ionization, while a weak acid will have a much lower percent ionization which can be calculated using the equation:

$$\text{Percent Ionization} = \frac{[H_3O^+]_{equilibrium}}{[HA]_{initial}} \text{ x } 100\%$$

PERCENT IONIZATION

$$\text{Percent Ionization} = \frac{[H_3O^+]_{equilibrium}}{[HA]_{initial}} \text{ x } 100\%$$

Percent ionization is dependent on both the strength of the acid or base and the initial concentration.

If acids are of equal concentration, the weaker acid will have a lower percent ionization.

If two samples of the same acid are of different concentrations, the solution of lower concentration will have a higher percent ionization.

QUICK CHECK

The pH of a 0.036 M nitrous acid (HNO_2) solution is measured as 2.4.

$$HNO_{2(aq)} \rightleftharpoons H^{+}_{(aq)} + NO_{2}^{-}{}_{(aq)}$$

Calculate the percent ionization for nitrous acid.

EQUATION SHEET

Acid Equations

$$K_a = \frac{[H^+][A^-]}{[HA]}$$ ①

$$pH = -\log[H^+]$$ ②

$$pK_a = -\log K_a$$ ③

Base Equations

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$ ④

$$pOH = -\log[OH^-]$$ ⑤

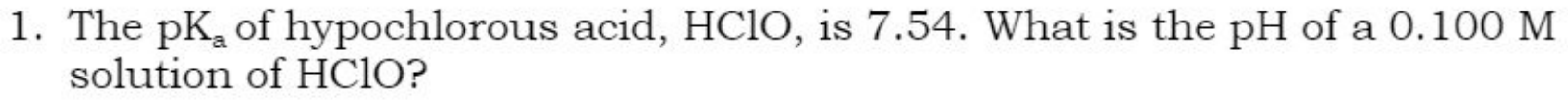
$$pK_b = -\log K_b$$ ⑥

General Equations

⑦ $$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} = K_a \times K_b$$

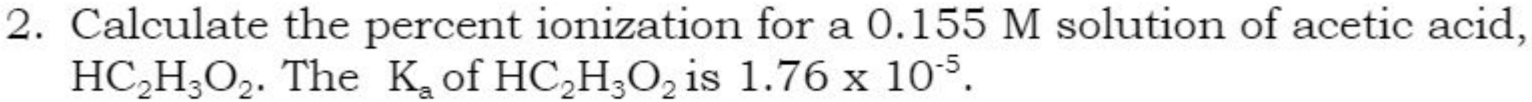
$$14 = pH + pOH$$ ⑧

Together



1. The pK_a of hypochlorous acid, HClO, is 7.54. What is the pH of a 0.100 M solution of HClO?

YOU DO, WE REVIEW



2. Calculate the percent ionization for a 0.155 M solution of acetic acid, $HC_2H_3O_2$. The K_a of $HC_2H_3O_2$ is 1.76 x 10^{-5}.

8.4 Acid-Base reactions and Buffers

ENDURING UNDERSTANDING:	
SAP-9	The chemistry of acids and bases involves reversible proton-transfer reactions, with equilibrium concentrations being related to the strength of the acids and bases involved.
LEARNING OBJECTIVE:	
SAP-9.D	Explain the relationship among the concentrations of major species in a mixture of weak and strong acids and bases.

STRONG ACID, STRONG BASE NEUTRALIZATION

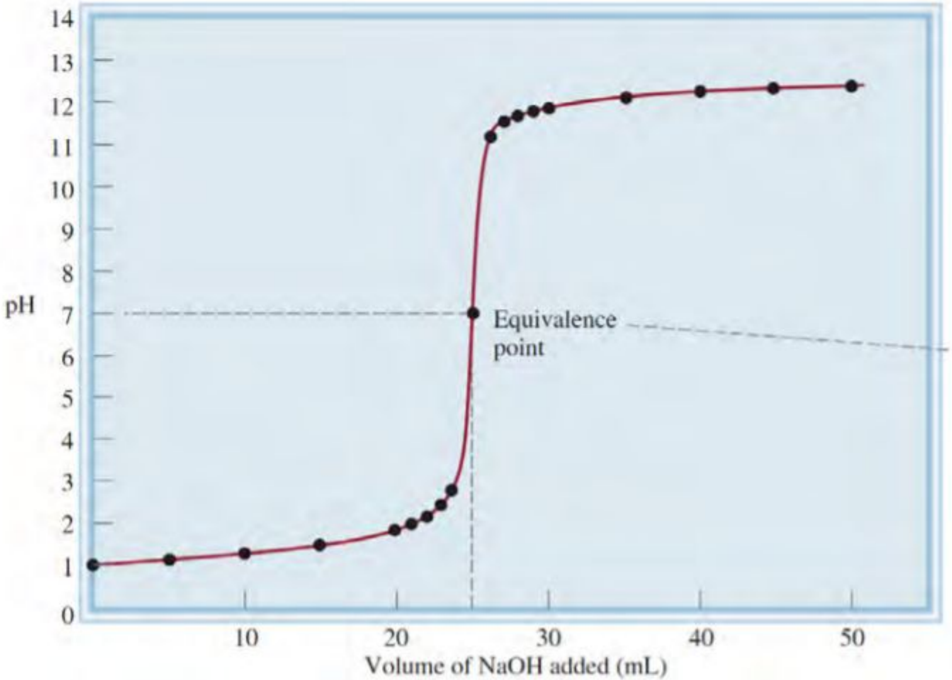
The reaction between a strong acid (like HCl) and a strong base (like NaOH) can be represented by:

$\mathbf{NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}}$

Or, the net ionic equation: $\mathbf{H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}}$

STRONG ACID, STRONG BASE NEUTRALIZATION

Changes in pH can be monitored by setting the reaction up as a titration and using a pH meter to measure the pH throughout.

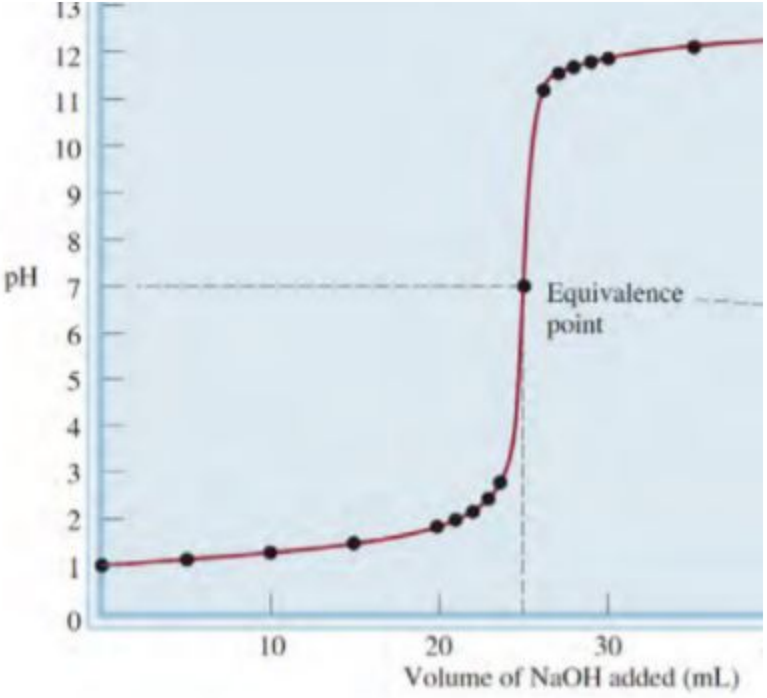


Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

A 0.100 M NaOH solution is added from a buret to 25.0 mL of a 0.100 M HCl solution in an Erlenmeyer flask. This curve is sometimes referred to as a *titration curve*.

Strong Acid, Strong Base Neutralization

- The equivalence point represents the stoichiometric balance when $[H^+] = [OH^-]$.
- Only for strong acid / strong base titrations will pH = 7 at equivalence point.
- Reactions involving weak acids or weak bases will produce acidic salts or basic salts , so pH ≠ 7



STRONG ACID/STRONG BASE EXAMPLE:

A 25.0 mL sample of HI requires 46.23 mL of 0.203M NaOH solution to reach the equivalence point. Calculate the [HI].

Step 1: Calculate number of moles of OH^- ions added.

Step 2: Use the stoichiometry of the balanced equation to convert to moles of HI.

Step 3: Calculate [HI].

Weak Acid, Strong Base Neutralization

The calculations in the previous sections are made 'easier' by the fact that everything ionizes 100%.

Next in difficulty is where we have one weak/one strong.

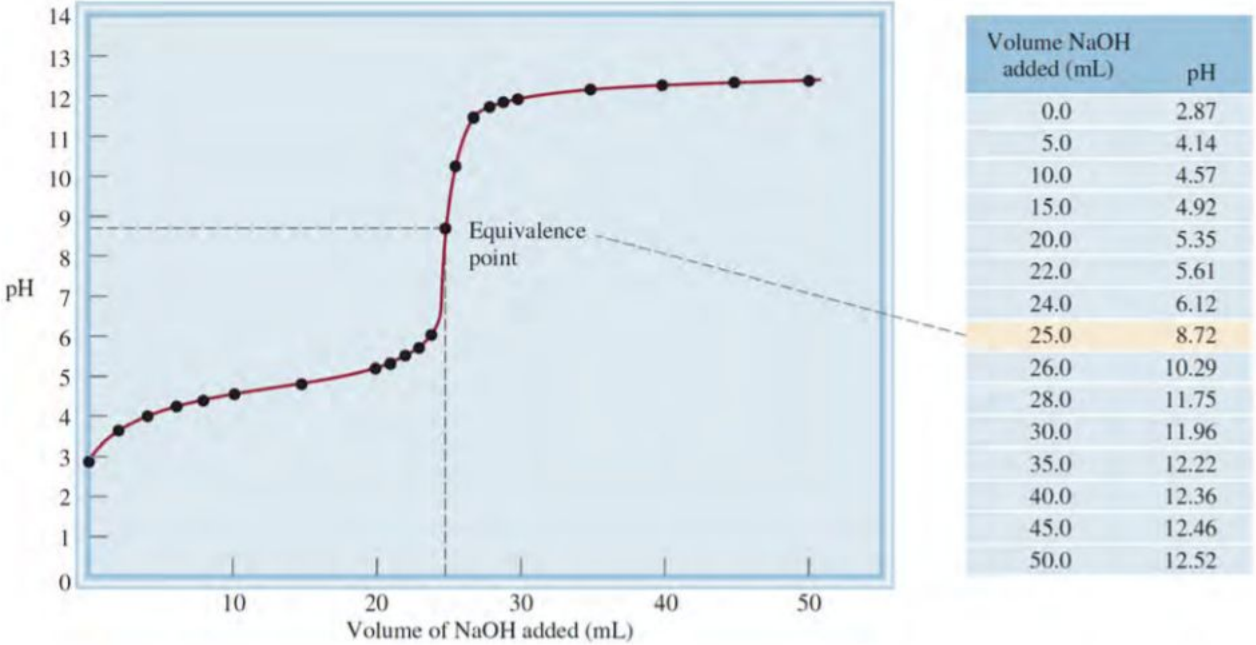
The reaction between a weak acid (say, CH_3COOH) and a strong base (say, NaOH) can be represented by:

$NaOH_{(aq)} + CH_3COOH_{(aq)} \rightleftharpoons NaCH_3COO_{(aq)} + H_2O_{(l)}$

or the net ionic equation: **$OH^{-}_{(aq)} + HA_{(aq)} \rightleftharpoons A^{-}_{(aq)} + H_2O_{(l)}$**

Weak Acid, Strong Base Neutralization

Changes in pH can be monitored by setting the reaction up as a titration and using a pH meter to measure the pH throughout:

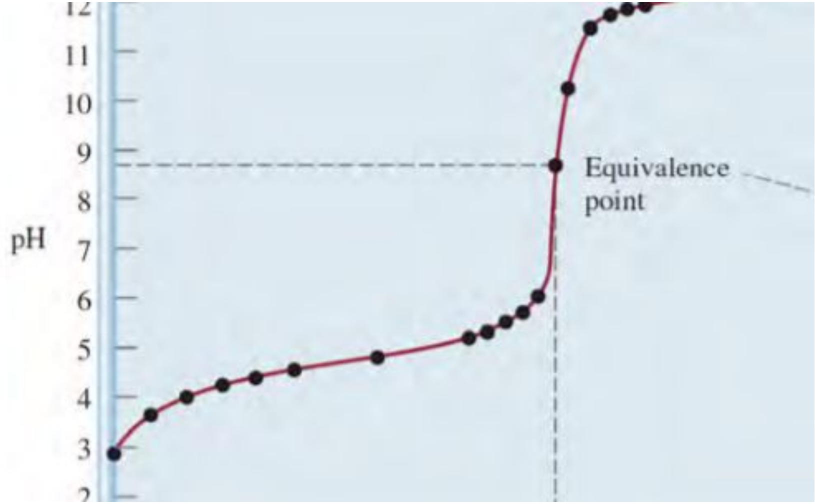


Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

A 0.100 M NaOH solution is added from a buret to 25.0 mL of a 0.100 M CH_3COOH solution in an Erlenmeyer flask.

Weak Acid, Strong Base Neutralization

- The **equivalence point** represents the stoichiometric balance when **moles of CH_3COOH present at start = moles of NaOH added**.
- Only for strong acid/strong base titrations will pH = 7 at equivalence point.
- When a **weak acid/strong base** is used the salt formed will be basic so **pH > 7**.



WEAK ACID/STRONG BASE EXAMPLE

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid by sodium hydroxide after the addition to the acid solution of 35.0 mL of 0.100 M NaOH. $K_a = 1.8 \times 10^{-5}$.

Step 1: Calculate number of moles of OH^- ions added.

Step 2: Calculate the number of moles of CH_3COOH present at start.

Step 3: Calculate the number of moles excess OH^- ions.

Step 4: Calculate $[OH^-]$(don't forget to combine volumes for overall volume of solution)

Step 5: Calculate pH.

Excess Weak Acid

The example we just completed had excess NaOH (strong base).

If the **weak acid is in excess**, then the resulting solution is a buffer solution.

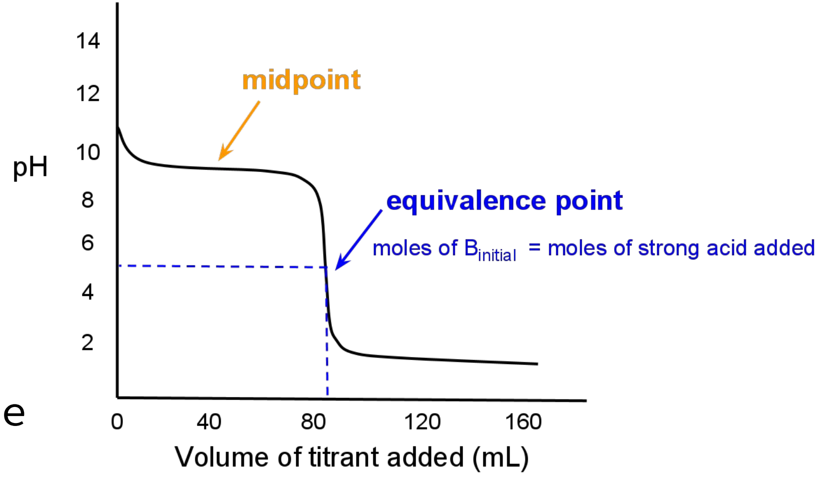
A buffer is a solution containing relatively high concentrations of a conjugate acid-base pair. If a small amount of a strong acid or base is added to a buffer solution, the buffer solution resists changes to the pH.

The Henderson-Hasselbalch equation can be used to determine the pH of the resulting solution. (Buffers are discussed further in 8.8 and the Henderson-Hasselbalch equation is discussed in 8.9)

WEAK BASE, STRONG ACID NEUTRALIZATION

Basically the opposite of weak acid/strong base neutralization.

- If the weak base is in excess - Henderson-Hasselbalch
- If the strong acid is in excess, then the pH of the resulting solution will be calculated from the molarity of the solution formed from the excess moles of the hydronium ion divided by the total volume of the solution (like our weak acid/strong base example)



Christine Chang

Weak/Strong Equimolar

If the weak base and strong acid (or weak acid and strong base) are equimolar the reaction is **at its equivalence point** (the moles of the acid and base are equal).

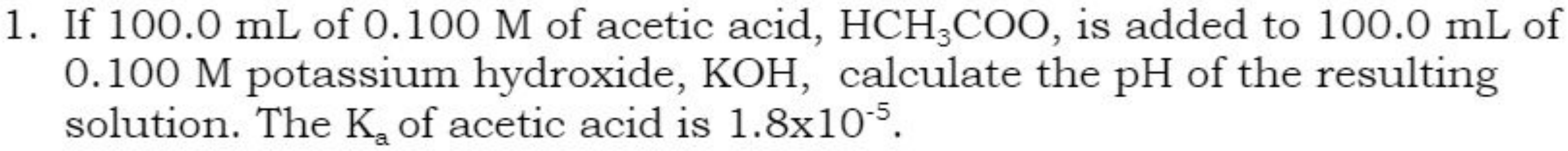
We will learn to calculate for both later in this Unit.

WEAK/WEAK NEUTRALIZATION

If weak acid and a weak base are combined the resulting solution will react to reach equilibrium. The reaction can be shown as:

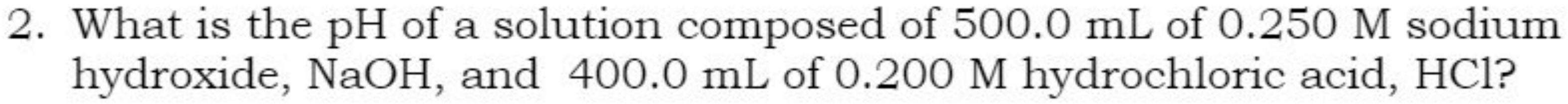
$$HA_{(aq)} + B_{(aq)} \rightleftharpoons A^{-}_{(aq)} + HB^{+}_{(aq)}$$

Together



1. If 100.0 mL of 0.100 M of acetic acid, HCH_3COO, is added to 100.0 mL of 0.100 M potassium hydroxide, KOH, calculate the pH of the resulting solution. The K_a of acetic acid is $1.8x10^{-5}$.

YOU DO, WE REVIEW



2. What is the pH of a solution composed of 500.0 mL of 0.250 M sodium hydroxide, NaOH, and 400.0 mL of 0.200 M hydrochloric acid, HCl?

If 100.0 mL of 0.100 M of acetic acid, HCH_3COO, is added to 100.0 mL of 0.100 M potassium hydroxide, KOH, calculate the pH of the resulting solution. The K_a of acetic acid is 1.8×10^{-5}.

Weak acid/Strong Base Neutralization Reaction:

$$HCH_3COO_{(aq)} + KOH_{(aq)} \rightarrow H_2O_{(l)} + KCH_3COO_{(aq)}$$

Net ionic equation:

$$HCH_3COO_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} + CH_3COO^-_{(aq)}$$

Since the moles of acid = moles of base, we know that the reaction will go to completion.

The reaction will then reestablish equilibrium with the weak conjugate base reacting with water. This is the basis for the ICE diagram.

$$H_2O_{(l)} + CH_3COO^-_{(aq)} \Leftrightarrow HCH_3COO_{(aq)} + OH^-_{(aq)}$$

$$\frac{0.0100 \text{ moles}}{0.200 \text{ L}}$$

	$H_2O_{(l)}$	$CH_3COO^-_{(aq)}$	$HCH_3COO_{(aq)}$	$OH^-_{(aq)}$
I		0.0500 M	0	0
C		-x	+x	+x
E		0.0500 -x	x	x

Since this is a base, we need to find the $K_b = K_w/K_a$.

$$\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b = \frac{[HCH_3COO][OH^-]}{[CH_3COO^-]}$$

$$5.6 \times 10^{-10} = \frac{[x][x]}{[0.0500 - x]}$$

$$x = 1.6 \times 10^{-3} M = [OH^-]$$

$$pOH = -\log(1.6 \times 10^{-3}) = 2.80$$

$$pH = 14 - 2.80 = 11.20$$

AGENDA

- Bellwork
- 8.5
- 8.6
- Card sort
- Lab

Bellwork

- List the 6 strong acids

ENDURING UNDERSTANDING:

SAP-9	The chemistry of acids and bases involves reversible proton-transfer reactions, with equilibrium concentrations being related to the strength of the acids and bases involved.

LEARNING OBJECTIVE:

SAP-9.E	Explain results from the titration of a mono- or polyprotic acid or base solution, in relation to the properties of the solution and its components.

Titrations

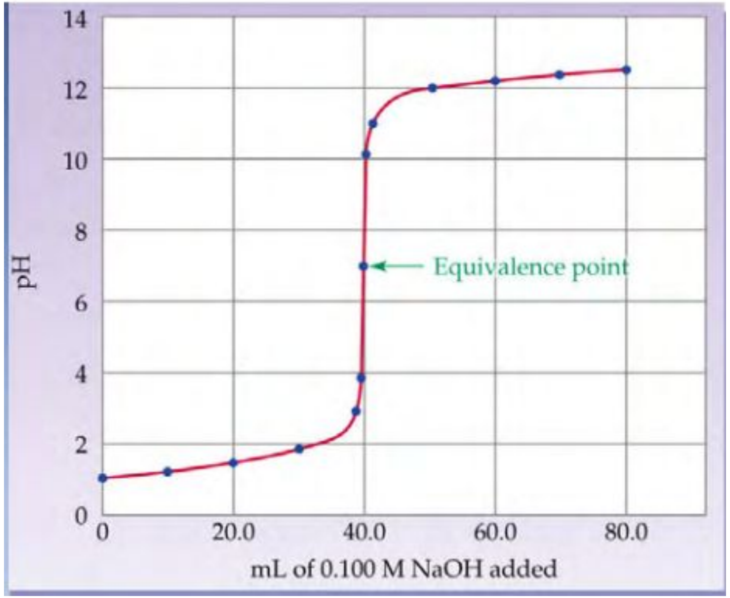
- Titrations are a quantitative way to analyze acid-base reactions.
- Typically, a known concentration of a base is added to an unknown concentration of an acid, or vice versa.
- The volume of both solutions is measured and used to calculate the unknown concentration.
- The solution with the known concentration is known as the **titrant**.
- The substance that you are trying to find out the about is called the **analyte**.

TITRATION OF STRONG ACID WITH STRONG BASE

- HCl being titrated with NaOH. When a strong acid and a strong base react the equivalence point will be at pH = 7.
- This is the point at which we have equal moles of the strong acid and strong base.
- The inflection point, (steepest portion/largest slope) corresponds to the equivalence point.
- The volume of sodium hydroxide, NaOH, needed to reach a pH of 7 can then be used to calculate the unknown molarity of the hydrochloric acid solution.

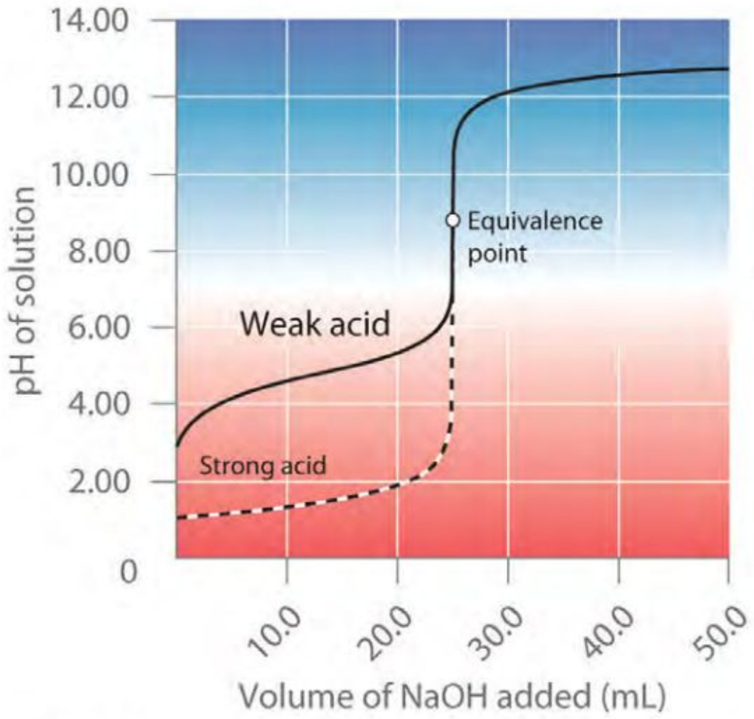
$$\text{Moles } H_3O^+ = \text{Moles } OH^-$$

$$M_{H3O+}V_{H3O+} = M_{OH-}V_{OH-}$$

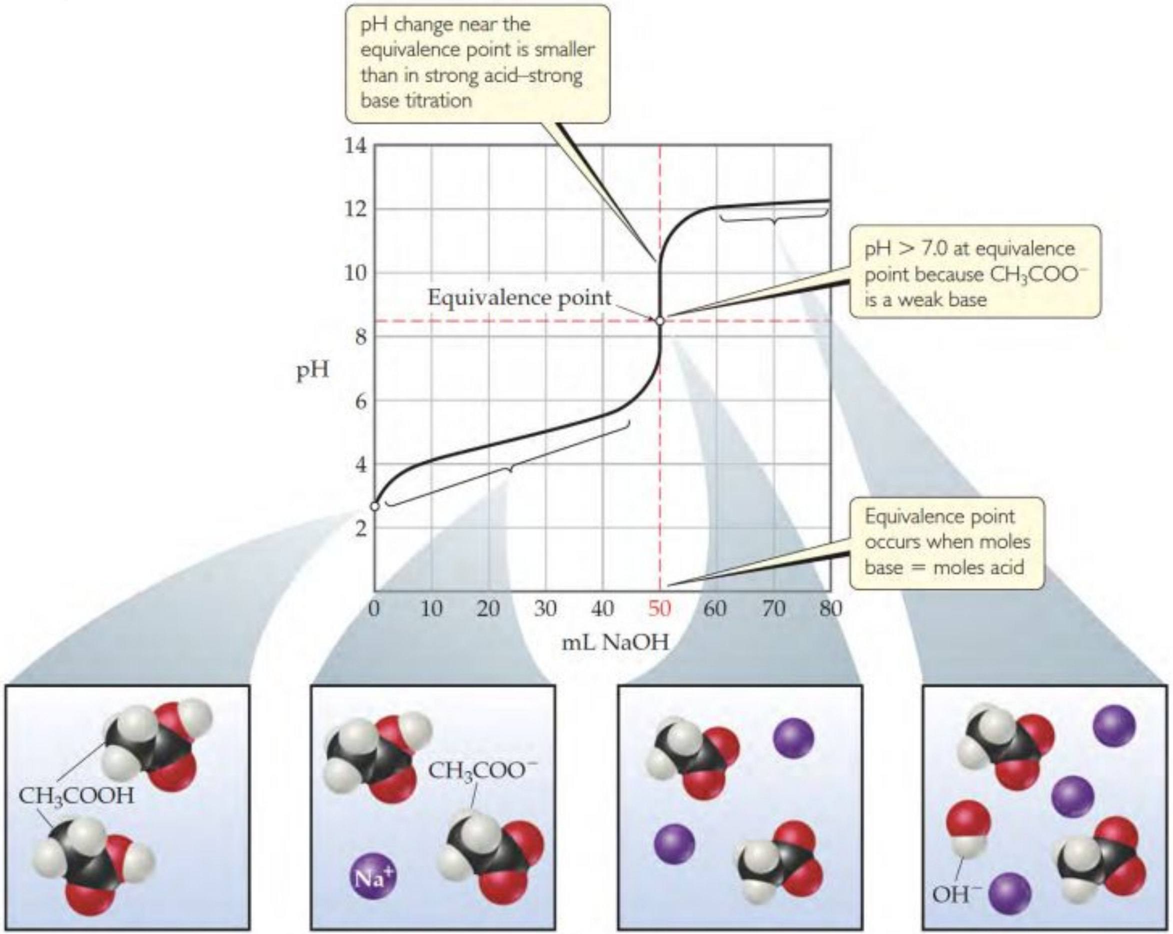


TITRATION OF WEAK ACID WITH STRONG BASE

- We are still going to determine the steepest part of our curve to determine the equivalence point (when the moles of acid and equal to the moles of base).
- When a strong base is added to a weak acid, the equivalence point will be occur at a pH>7, because the conjugate of a weak acid is a BASE - causing the solution to be basic.



Weak Acid/Strong Base Titration Curve Overview



pH change near the equivalence point is smaller than in strong acid–strong base titration

pH > 7.0 at equivalence point because CH_3COO^- is a weak base

Equivalence point occurs when moles base = moles acid

$CH_3COOH(aq)$ solution before titration

Added OH^- converts $CH_3COOH(aq)$ into $CH_3COO^-(aq)$, forming buffer solution

Acid completely neutralized by added base, $CH_3COONa(aq)$ salt solution results

No acid left to react with excess OH^-

MIDPOINT IMPORTANCE

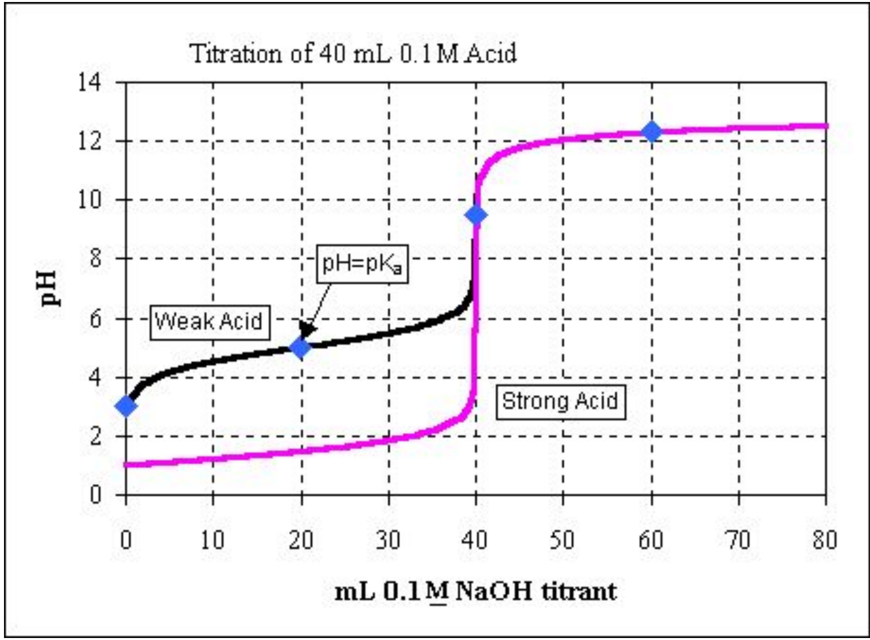
The **midpoint** of a weak acid or weak base titration is approximately halfway between the starting point and the equivalence point.

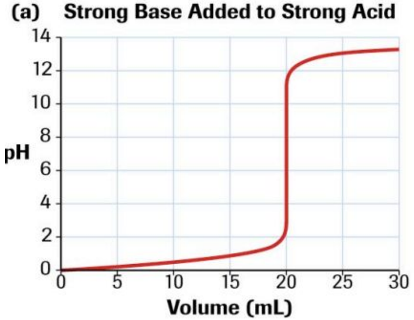
The **midpoint** (at 20 mL in curve right) is extremely significant as **half our acid has reacted**, to be replaced by our conjugate base, so [HA] = [A$^-$]

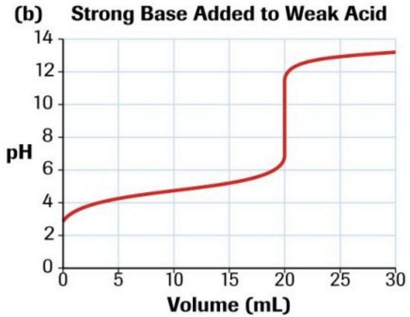
Later we will learn to use the Henderson-Hasselbalch equation:

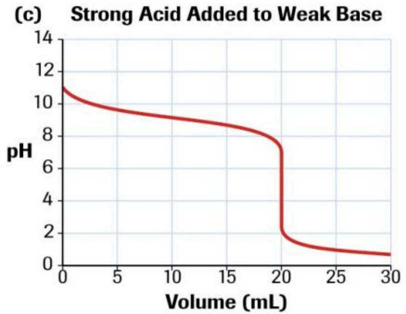
$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

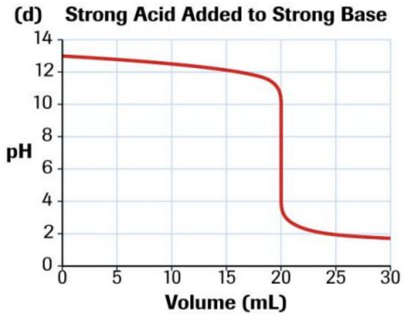
Learn today: **the pH at the midpoint tells us the pKa of the weak acid since [base]/[acid] = 1 and log 1 = 0**







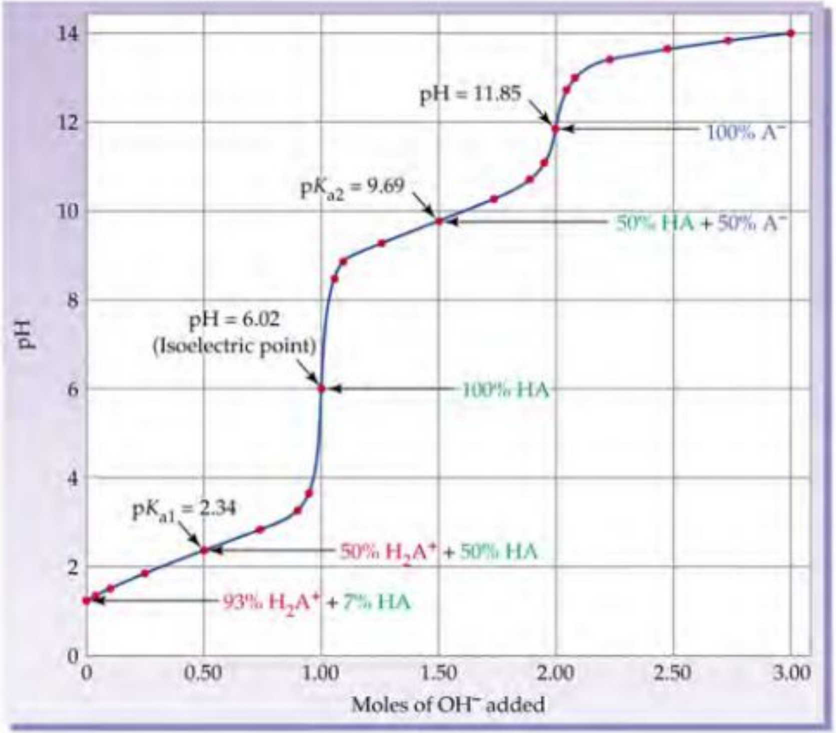




Strong Acid	*Weak Acid*	*Weak Base*	*Strong Base*
e.g 0.1M $HCl_{(aq)}$	e.g 0.1M $CH_3COOH_{(aq)}$	eg. 0.1M $NH_{3(aq)}$	e.g 0.1M $NaOH_{(aq)}$
starts at low pH = 1, due to 100% ionisation	*starts at higher pH* ≃ 3, due to lower ionisation <1%	*starts at lower pH* ≃ 11, due to lower ionisation <1%	*starts at high pH* = 13, due to 100% ionisation
pH changes slowly until very close to equivalence	*pH changes rapidly at first* but *then more slowly* until very close to equivalence	*pH changes rapidly at first* but *then more slowly* until very close to equivalence	*pH changes slowly* until very close to equivalence
large region of pH change around equivalence - about 8 pH units	*smaller region of pH change* around equivalence - about 4 pH units	*smaller region of pH change* around equivalence - about 4 pH units	*large region of pH change* around equivalence - about 8 pH units
At equivalence, ***pH = 7***	*At equivalence,* ***pH > 7***	*At equivalence,* ***pH < 7***	*At equivalence,* ***pH = 7***

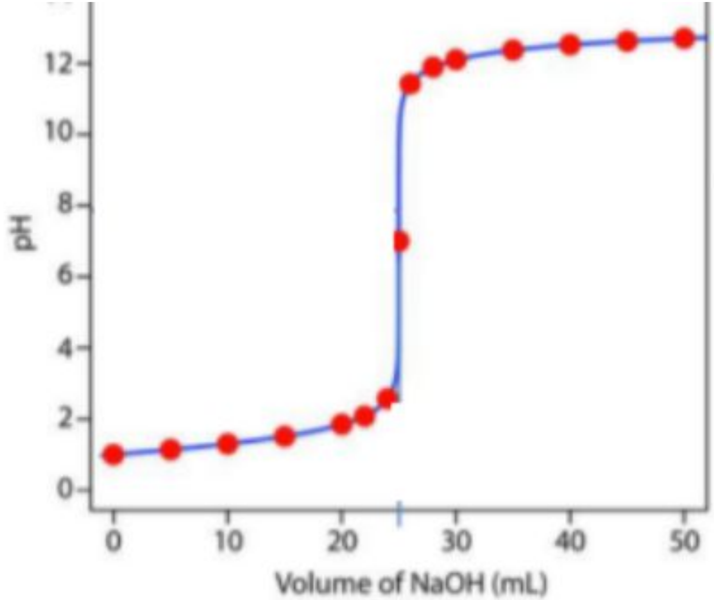
Titrations of Polyprotic Acids

- Diprotic acids, like H_2SO_3, titrated with a strong base are easily recognized by the two inflection points (regions of the curve where the slope appears to be at its steepest point).
- These two points correspond with the equivalence point for each of the protons being donated.
- diprotic acids have 2 different pKa values. The first proton donated is given pKa1 and the second pKa2.
- Graphically, pKa1 is the pH at ½ of the first equivalence point, while pKa2 corresponds to the second.



TOGETHER

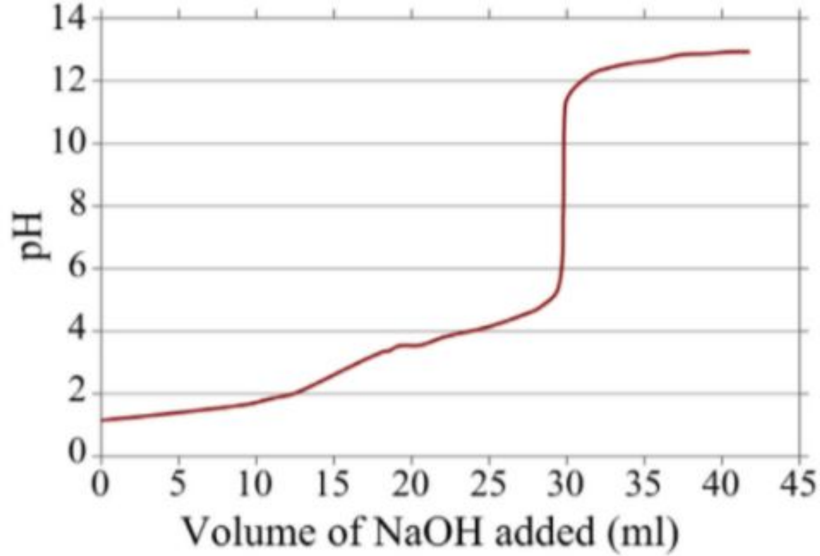
1. Given the Strong Acid/Strong Base titration curve shown, estimate the equivalence point, and determine the concentration of the HCl if you are titrating 20.0mL of HCl with 0.121M NaOH.



YOu Do We Review

2. The graph below shows the titration of oxalic acid, $C_2H_2O_4$, with sodium hydroxide, NaOH.

   Label the equivalence point, estimate the pH at the equivalence point, and estimate the pK_a of oxalic acid.



8.6 Molecular Structure of Acids and Bases

ENDURING UNDERSTANDING:	
SAP-9	The chemistry of acids and bases involves reversible proton-transfer reactions, with equilibrium concentrations being related to the strength of the acids and bases involved.

LEARNING OBJECTIVE:	
SAP-9.F	Explain the relationship between the strength of an acid or base and the structure of the molecule or ion.

ACID STRENGTH

We know that an acid is called STRONG when it ionizes completely.

But WHY are they able to ionize completely.

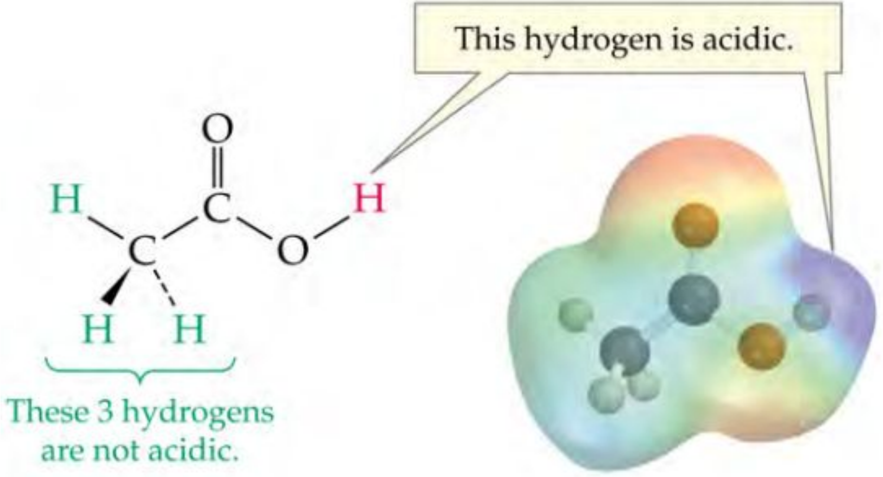
Why do weak acids only ionize some of their molecules?

Two considerations:

- The proton to be ionized
- The stability of the conjugate base

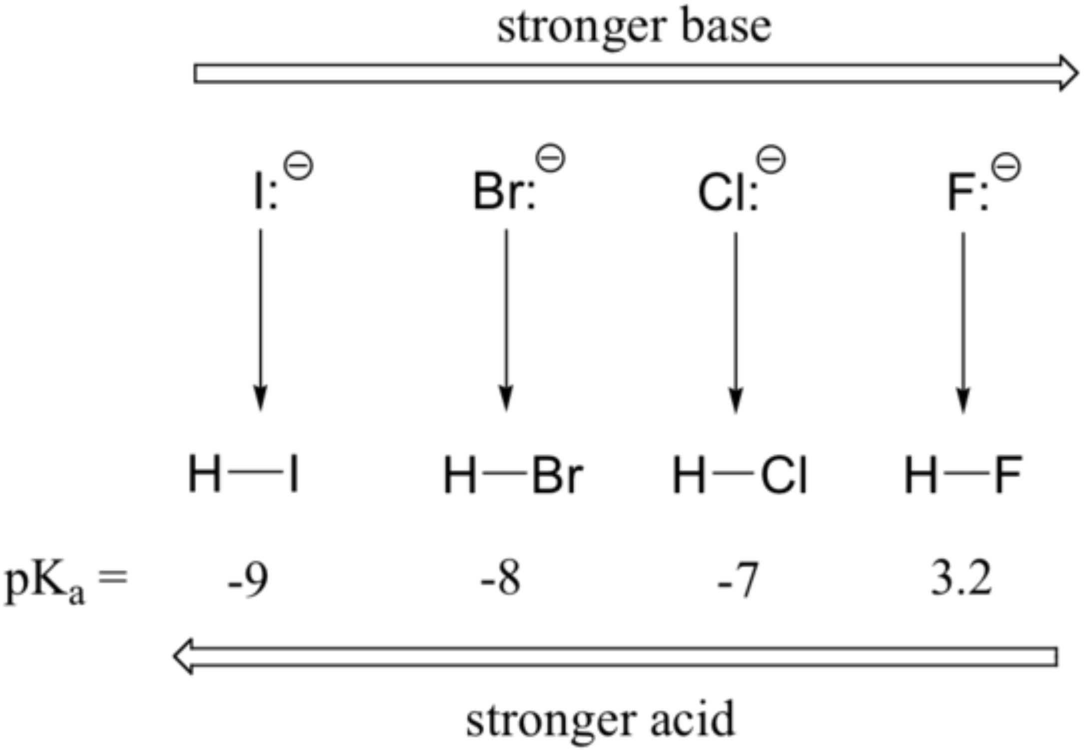
ACIDIC PROTONS

In general, only **hydrogens attached to atoms with a large electronegativity** are going to have a tendency to ionize when dissolved in water.

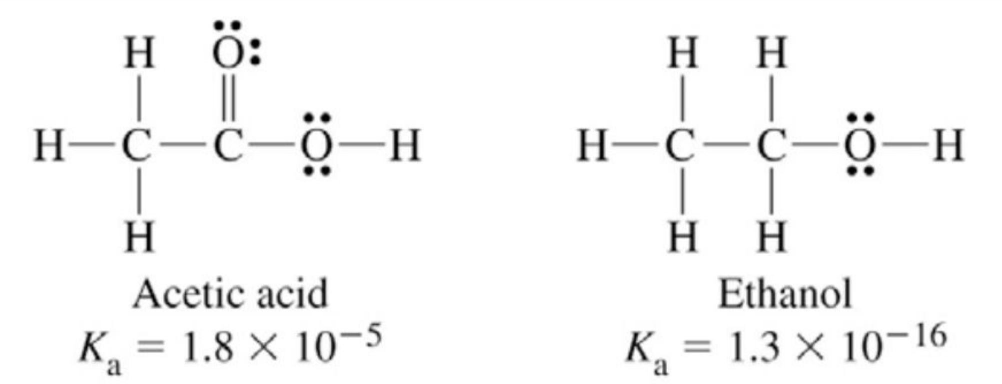


ACIDIC PROTONS

Why is HF a weaker acid than HI?



CONJUGATE STABILITY



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

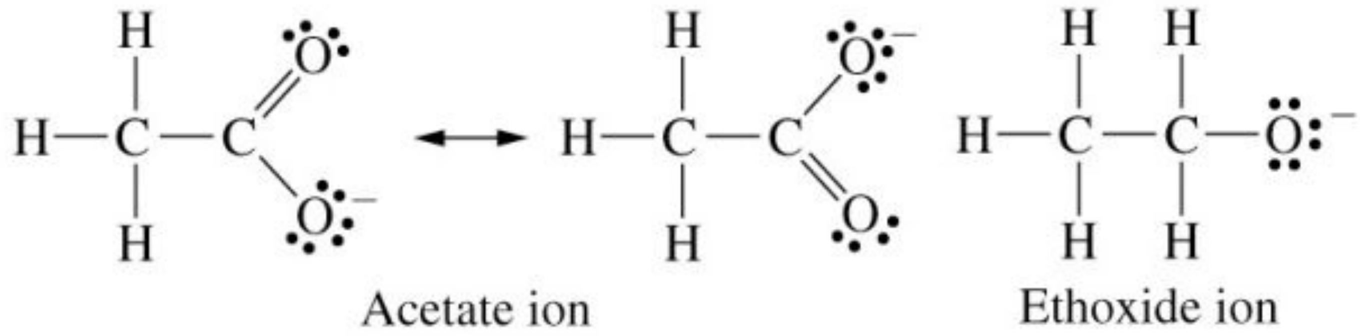
Ethanol
$K_a = 1.3 \times 10^{-16}$

Compare acetic acid and ethanol.

Both ethanol and ethanoic acid have a very polar H—O bond, but their acid properties are extremely different - in fact, ethanol is not usually considered an acid.

So why is acetic acid more acidic?

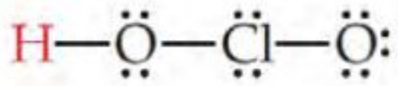
CONJUGATE STABILITY - RESONANCE!

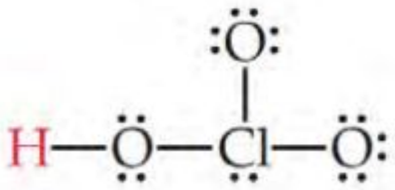


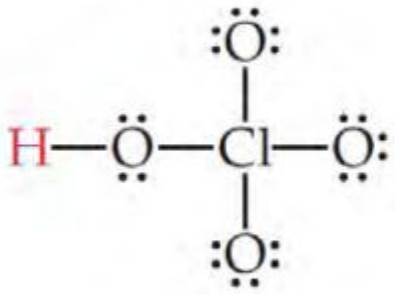
The difference is due to the ability of the ethanoate ion to be stabilized due to resonance structures which can effectively share the charge over a group of atoms.

QUICK CHECK

Which of the following is the STRONGEST acid?

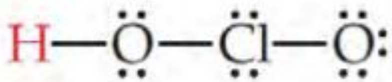
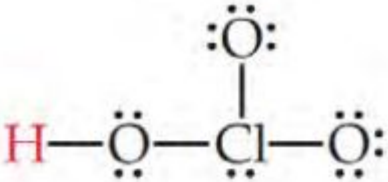
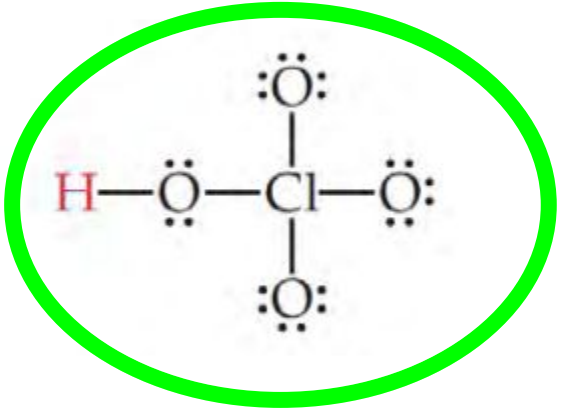






Quick Check

Which of the following is the STRONGEST acid?

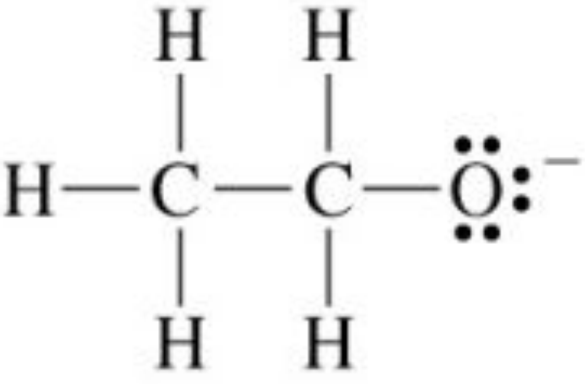
More resonance structures = more stabilized conjugate base = stronger acid!

The conjugate of a weak acid is a Stronger Base

The weakness of ethanol as an acid means that the conjugate base, the ethoxide ion, is a stronger base.

The negative charge is not stable! It really wants to ACCEPT A PROTON to stabilize.

The same qualities that make a molecule a weak acid help make its conjugate a strong base!

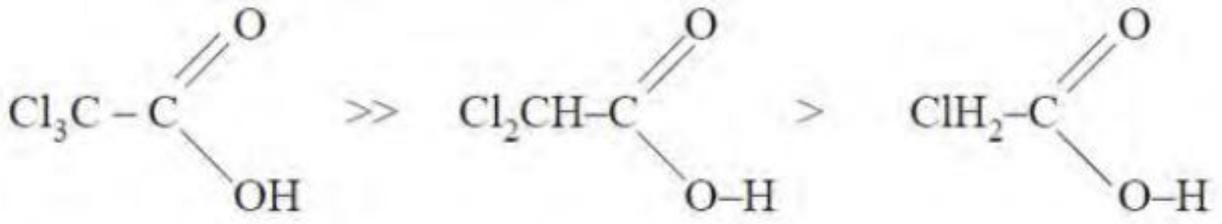


Ethoxide ion

Conjugate Stability - Inductive Effect

The presence of nearby electronegative atoms can also help to 'share' the negative charge, which increases the stability of the conjugate ion and makes it easier for the molecule to release the H^+ ion.

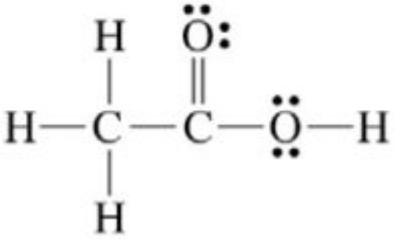
This is referred to as the **inductive effect** - where an electronegative atom draws electrical charge towards it.



trichloroacetic acid $K_a = 2.2 \times 10^{-1}$

dichloroacetic acid $K_a = 4.5 \times 10^{-2}$

monochloroacetic acid $K_a = 1.3 \times 10^{-3}$



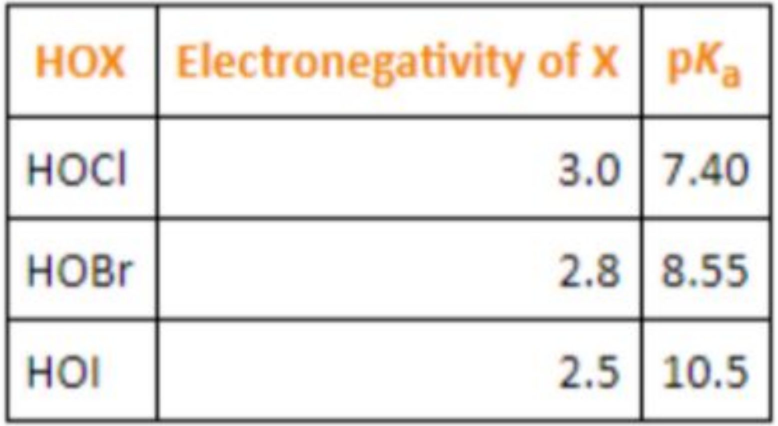
Acetic acid $K_a = 1.8 \times 10^{-5}$

DO NOT CONFUSE INDUCTIVE EFFECT WITH BOND LENGTH/STRENGTH TREND

General acid strength increases when more electronegative atoms are included in the structure.

For example, HOCl is more acidic than HOBr and HOI.

Because Cl is more electronegative than either Br or I, the H-O bond is more likely to give up the proton due to the strength of the inductive effect of the chlorine atom.

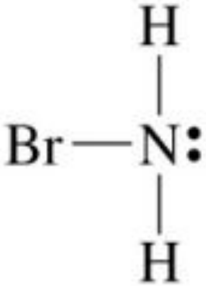


HOX	Electronegativity of X	pK_a
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

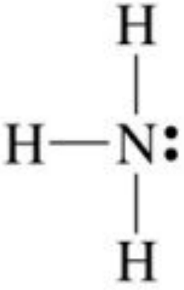
The inductive effect makes BASES weaker

While the inductive effect stabilizes conjugate acids, it makes bases less likely to accept a proton.

(Remember the higher the pK_b, the weaker the base)



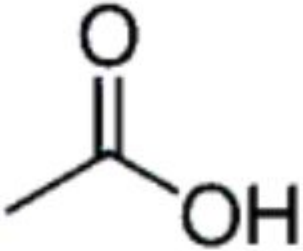
Bromamine, NH_2Br, pK_b = 7.61

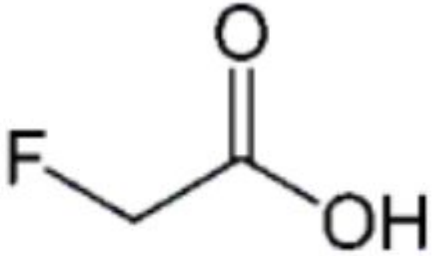


Ammonia, pK_b = 4.74

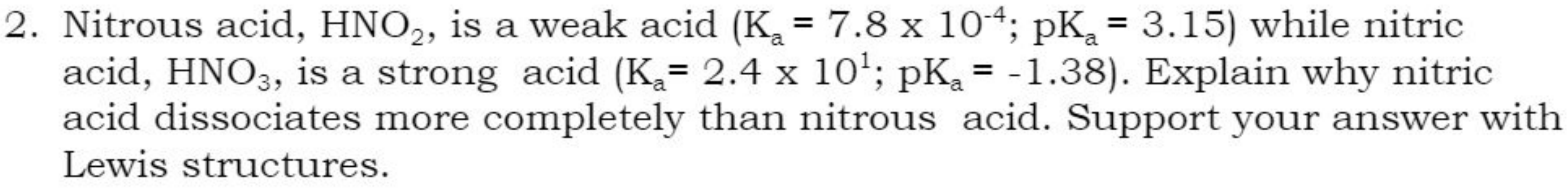
TOGETHER

1. How do you account for the difference in the pK_a of acetic acid (CH_3COOH, 4.76) and fluoroacetic acid (CH_2FCOOH, 2.59)?





You Do, We Review



2. Nitrous acid, HNO_2, is a weak acid ($K_a = 7.8 \times 10^{-4}$; $pK_a = 3.15$) while nitric acid, HNO_3, is a strong acid ($K_a = 2.4 \times 10^{1}$; $pK_a = -1.38$). Explain why nitric acid dissociates more completely than nitrous acid. Support your answer with Lewis structures.

Agenda

- Packet
- 8.7 and 8.8

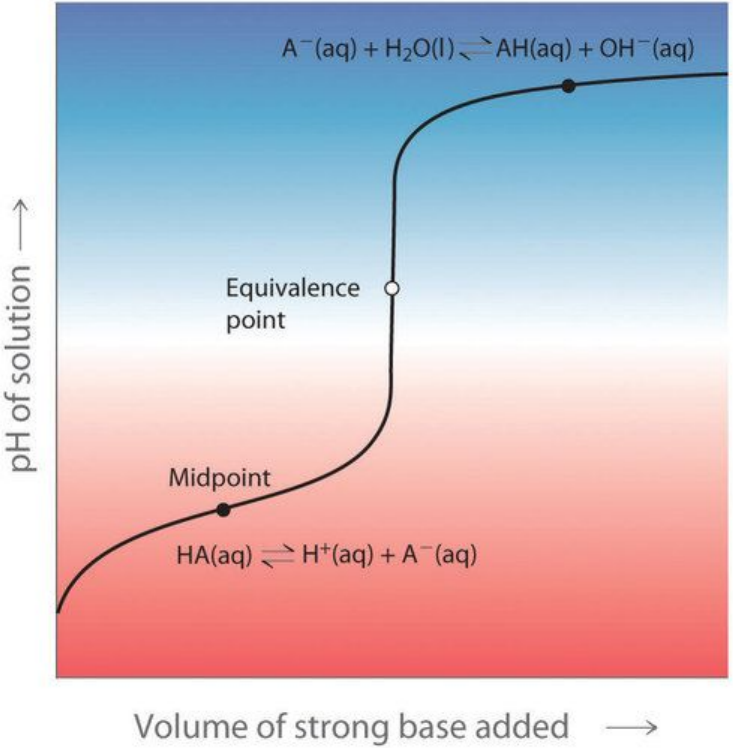
8.7 pH and pKa	
ENDURING UNDERSTANDING:	
SAP-10	A buffered solution resists changes to its pH when small amounts of acid or base are added
LEARNING OBJECTIVE:	
SAP-10.A	Explain the relationship between the predominant form of a weak acid or base in solution at a given pH and the pK_a of the conjugate acid or the pK_b of the conjugate base.

RELATIONSHIP BETWEEN PH AND PKA

$$HA_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

The equilibrium constant (or more specifically the acid dissociation constant) for the above reaction is:

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



RELATIONSHIP BETWEEN PH AND PKA

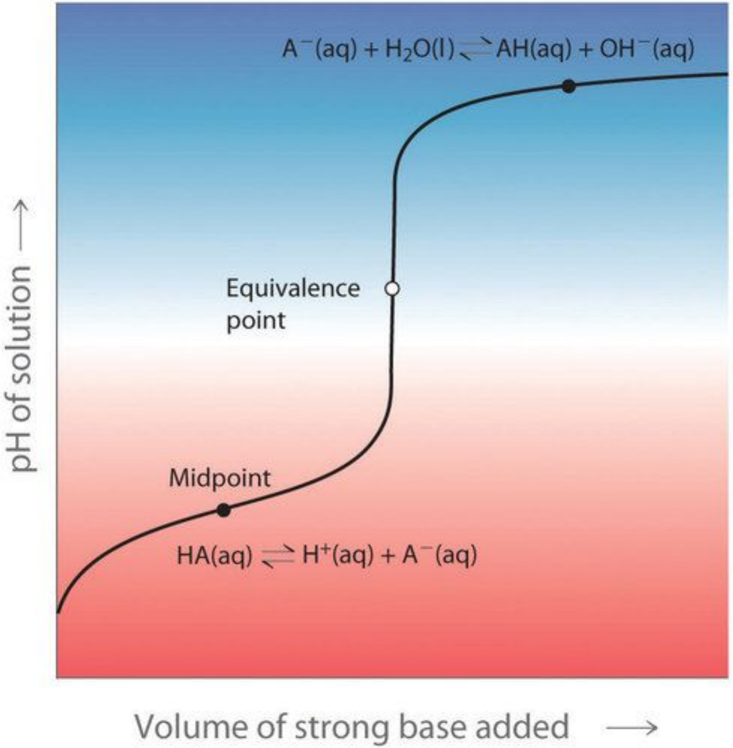
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

To see the relationship between pH and pKa we take the -log of both sides.

$\mathbf{pK_a = pH - log\ [A^-]/[HA]}$

Rearrange: $\mathbf{pH = pK_a + log[A^-]/[HA]}$

This is the Henderson-Hasselbalch equation!



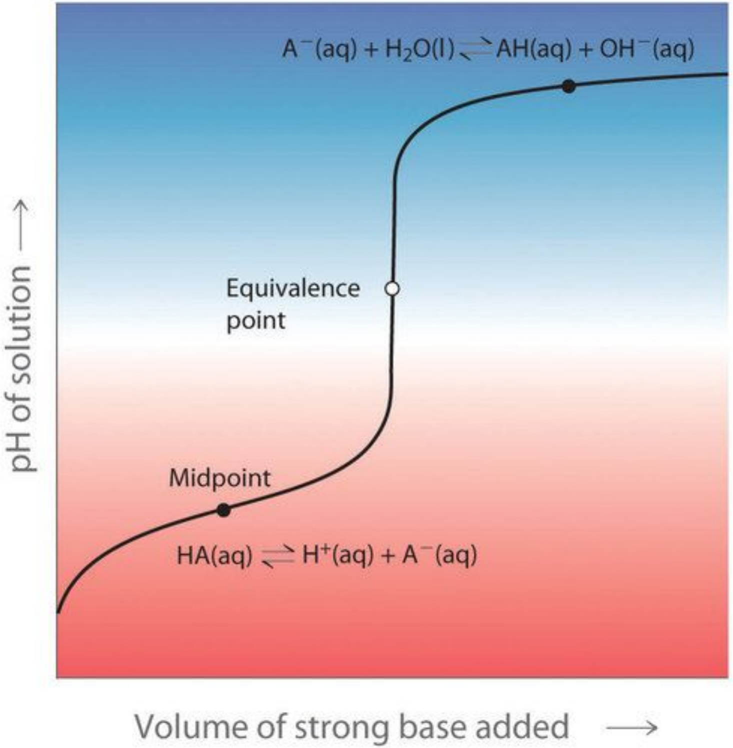
RELATIONSHIP BETWEEN pH AND pKa

REMEMBER: the **midpoint** had special significance as it identified the point at which

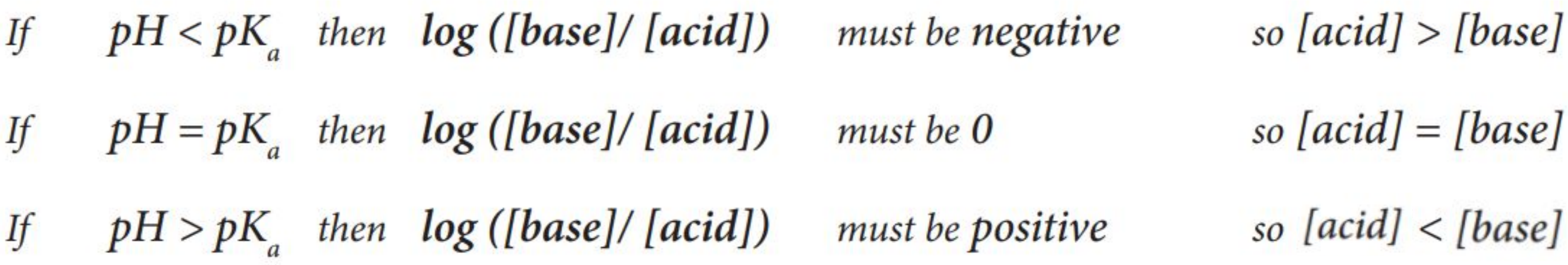
[acid] = [conjugate base]

and

pH = pK$_a$



RELATIONSHIP BETWEEN PH AND PKA



If $pH < pK_a$ then log ([base]/ [acid]) must be **negative** so [acid] > [base]

If $pH = pK_a$ then log ([base]/ [acid]) must be **0** so [acid] = [base]

If $pH > pK_a$ then log ([base]/ [acid]) must be **positive** so [acid] < [base]

$$pH = pK_a + \log[A^-]/[HA]$$

*log of a number < 1 is negative

*log of 1 = zero

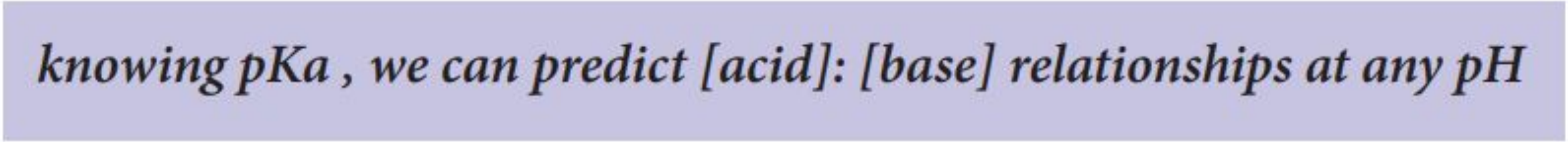
*log of a number > 1 is positive

$$HA_{(AQ)} + H_2O_{(L)} \leftrightharpoons H_3O^+_{(AQ)} + A^-_{(AQ)}$$

Thinking about Le Chatelier's Principle:

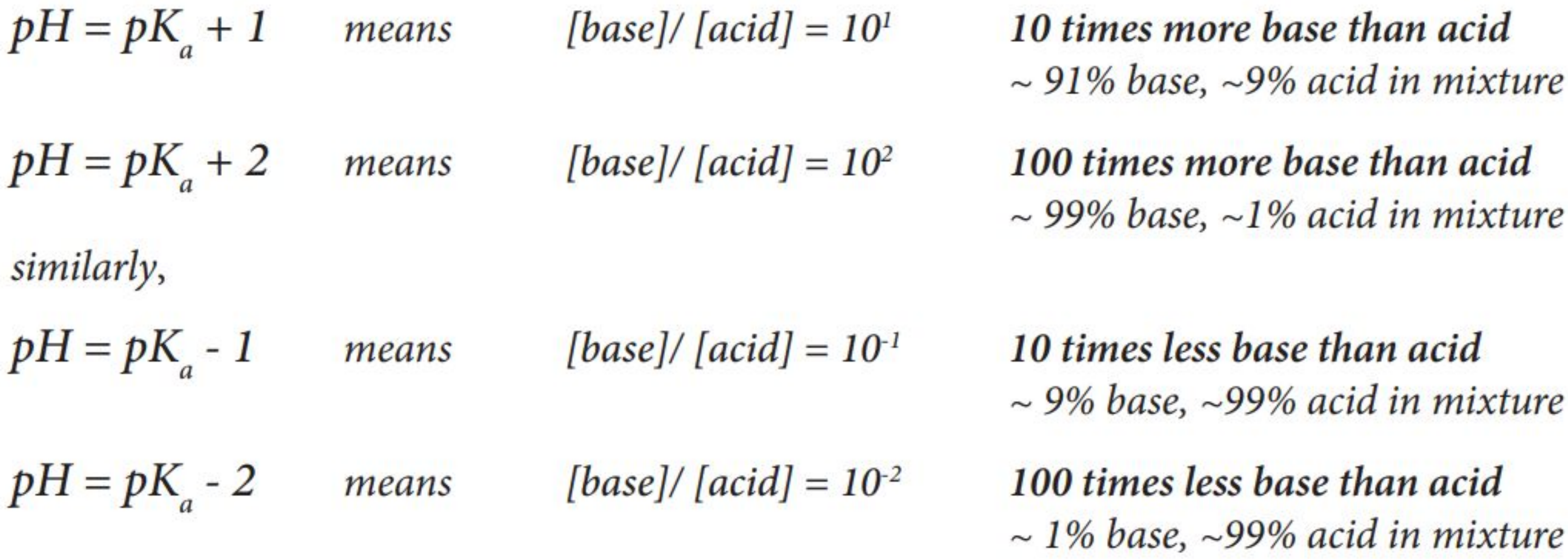
Lower pH mean increase $[H_3O^+]$, so the reverse rxn favored and we increase HA (acid)!

Higher pH means we decrease $[H_3O^+]$, so the forward rxn favored and we increase A^- (base)!



knowing pKa , we can predict [acid]: [base] relationships at any pH

THE DETAILS CAN BE HELPFUL!



$pH = pK_a + 1$	*means*	$[base]/[acid] = 10^1$	***10 times more base than acid*** *~ 91% base, ~9% acid in mixture*
$pH = pK_a + 2$	*means*	$[base]/[acid] = 10^2$	***100 times more base than acid*** *~ 99% base, ~1% acid in mixture*
similarly,			
$pH = pK_a - 1$	*means*	$[base]/[acid] = 10^{-1}$	***10 times less base than acid*** *~ 9% base, ~99% acid in mixture*
$pH = pK_a - 2$	*means*	$[base]/[acid] = 10^{-2}$	***100 times less base than acid*** *~ 1% base, ~99% acid in mixture*

INDICATORS

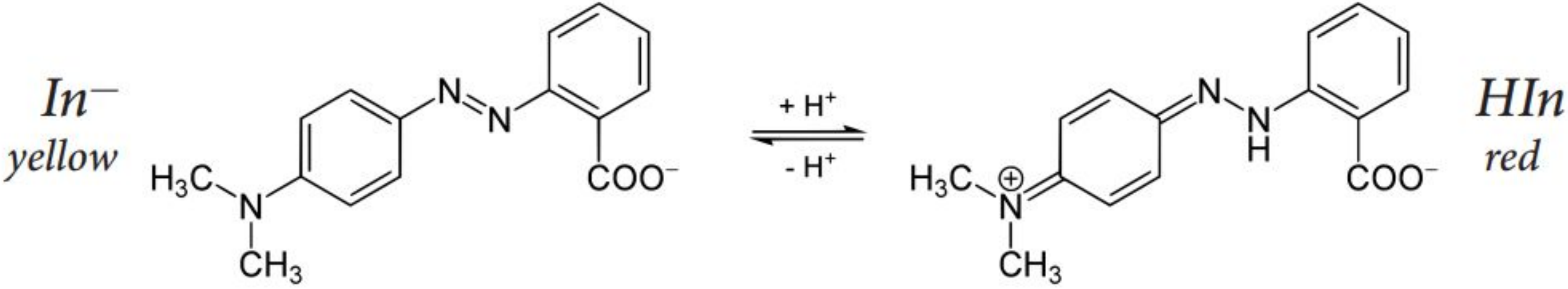
One way to see if a reaction has reached its equivalence point is to use an acid-base indicator that changes color at the pH of the equivalence point.

We call the pH where the color changes the “endpoint” of the titration.

Indicators are mixtures containing a conjugate pair of molecules - molecules whose structures differ by a H^+ ion.

One molecule is a weak acid (HA) while the other molecule is the conjugate base (normally A^-).

INDICATORS EXAMPLE: METHYL RED



While we can see the chemistry is slightly more complicated than the simple removal of a proton, we treat indicators exactly the same way we do weak acid/base conjugate pairs.

We use a new label:

$$\mathrm{HIn}_{(aq)} + \mathrm{H_2O}_{(l)} \leftrightharpoons \mathrm{H_3O^+}_{(aq)} + \mathrm{In^-}_{(aq)} \quad \text{and} \quad pH = pK_{In} + \log([In^-]/[HIn])$$

INDICATORS

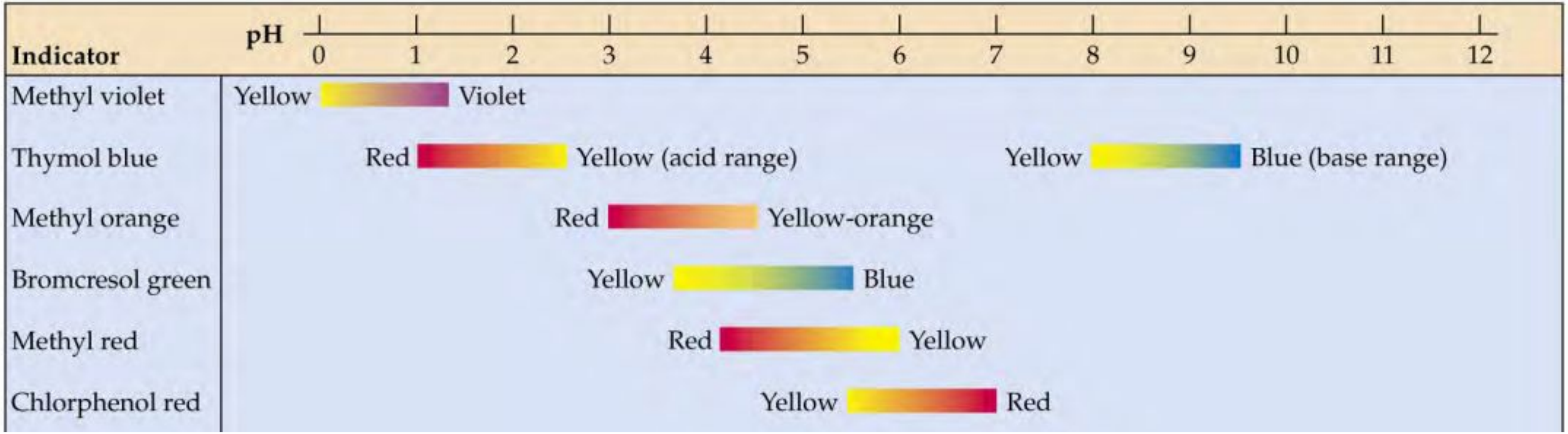
When choosing the correct indicator for a particular reaction it is important to find the indicator that has a color change at the equivalence point of the acid base neutralization.

- Strong acid + strong base = equivalence point pH =7
- Weak acid + strong base = equivalence point pH > 7 (because the conjugate base of the weak acid is in solution)
- Weak base + strong acid = equivalence point pH <7 (because the conjugate acid of the weak base is in solution)

Indicators

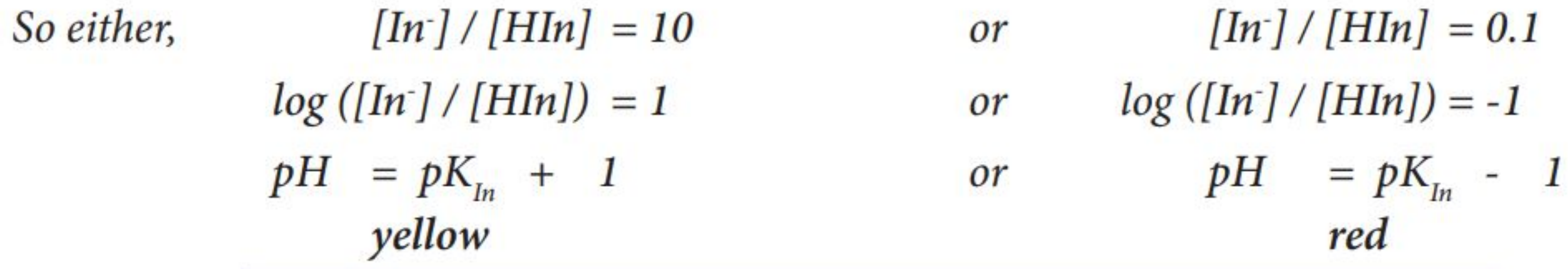
Notice that it is not strictly true to say that an indicator, for example - methyl red, is 'red in acid’ and 'yellow in base' since both colours are seen in solutions with pH < 7.

It is safer to say 'red at low pH's' and 'yellow at higher pH's'.



INDICATORS

In a mixture, if one color is ten times stronger than the other color then our eyes will only detect the dominant colour.



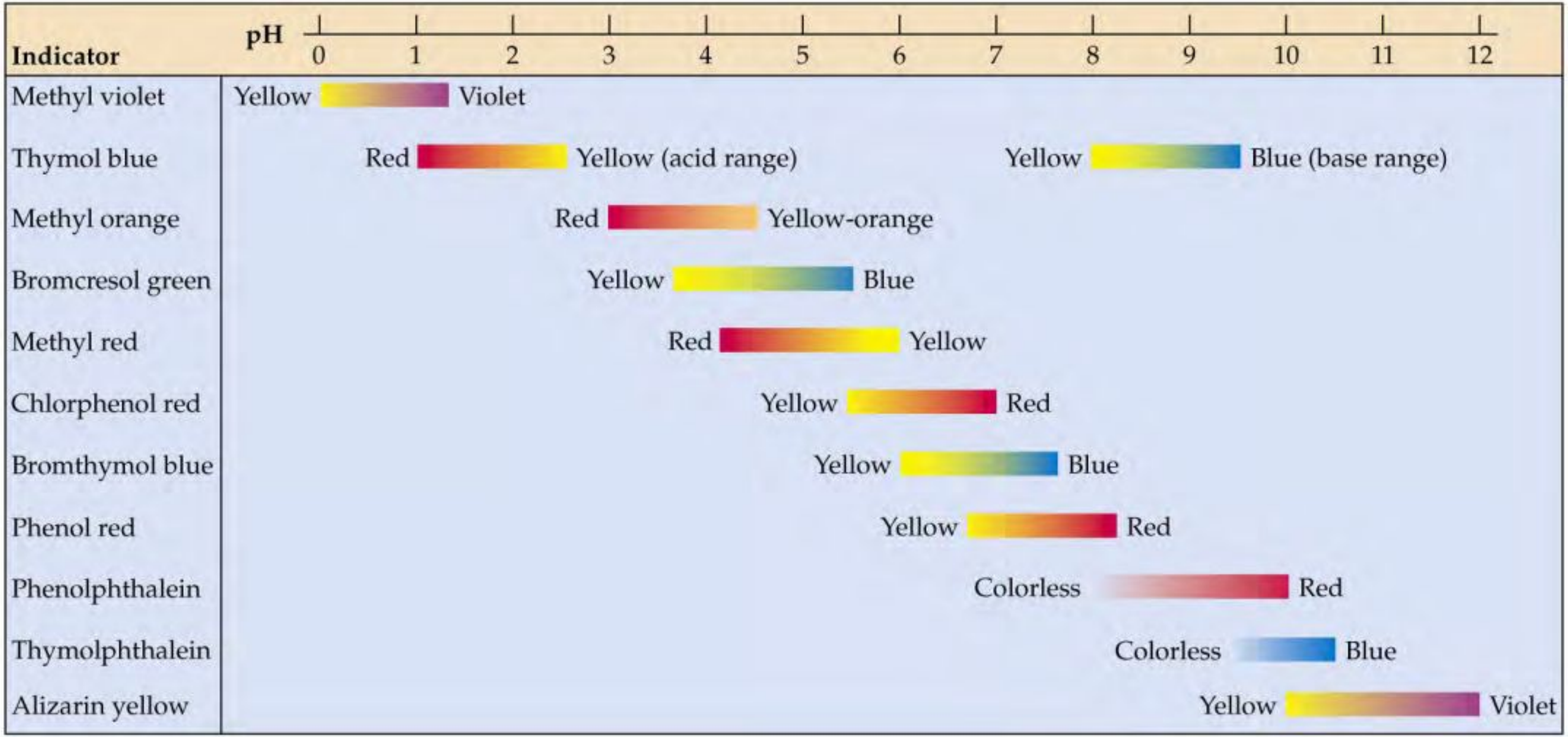
So either, $[In^-] / [HIn] = 10$ or $[In^-] / [HIn] = 0.1$

$\log([In^-] / [HIn]) = 1$ or $\log([In^-] / [HIn]) = -1$

$pH = pK_{In} + 1$ or $pH = pK_{In} - 1$

yellow **red**

Color changes typically occur 1 pH unit above or below the pK_a.

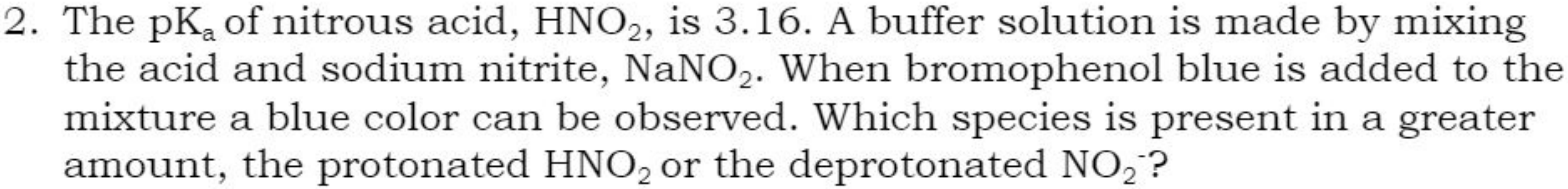

Indicator
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
Methyl violet
Yellow
Violet
Thymol blue
Red
Yellow (acid range)
Yellow
Blue (base range)
Methyl orange
Red
Yellow-orange
Bromcresol green
Yellow
Blue
Methyl red
Red
Yellow
Chlorphenol red
Yellow
Red
Bromthymol blue
Yellow
Blue
Phenol red
Yellow
Red
Phenolphthalein
Colorless
Red
Thymolphthalein
Colorless
Blue
Alizarin yellow
Yellow
Violet

TOGETHER

1. Alizarin Red S is an acid base indicator changes from red (pH 4) to yellow (pH 5.5). Remember that indicators are chemicals that have different colors when protonated and deprotonated.
    a. Would the protonated or the deprotonated form of alizarin red s be red? Explain your reasoning.

    b. Would this indicator be most effective for a titration (with sodium hydroxide, NaOH) of an acetic acid, HCH_3COO solution ($pK_a = 4.75$) or the titration of hydrochloric acid, HCl?

YOU DO, WE REVIEW



2. The pK_a of nitrous acid, HNO_2, is 3.16. A buffer solution is made by mixing the acid and sodium nitrite, $NaNO_2$. When bromophenol blue is added to the mixture a blue color can be observed. Which species is present in a greater amount, the protonated HNO_2 or the deprotonated NO_2^-?

8.8 Properties of Buffers

ENDURING UNDERSTANDING:

SAP-10	A buffered solution resists changes to its pH when small amounts of acid or base are added.

LEARNING OBJECTIVE:

SAP-10.B	Explain the relationship between the ability of a buffer to stabilize pH and the reactions that occur when an acid or a base is added to a buffered solution.

WHAT ARE BUFFERS?

- A buffer is a solution that contains a conjugate acid-base pair.
- Buffers are able to maintain the pH of a solution when small amounts of acids or bases are added to the solution.
- Buffers are frequently used in fish tanks, so that the pH of the water can be maintained.
- Another example of a buffer system is your blood, the buffering capacity of your blood means that your pH doesn’t fluctuate.

WEAK ACIDS AS BUFFERS

A solution of weak acid is mainly acid molecules with very few of the conjugate base ions present in the mixture.

Example: Ethanoic Acid

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

The addition of extra conjugate base ions (eg sodium ethanoate, $NaC_2H_3O_2$) or enough NaOH to react about half of the acid (mid-point) transforms the mixture into a **buffer solution**.

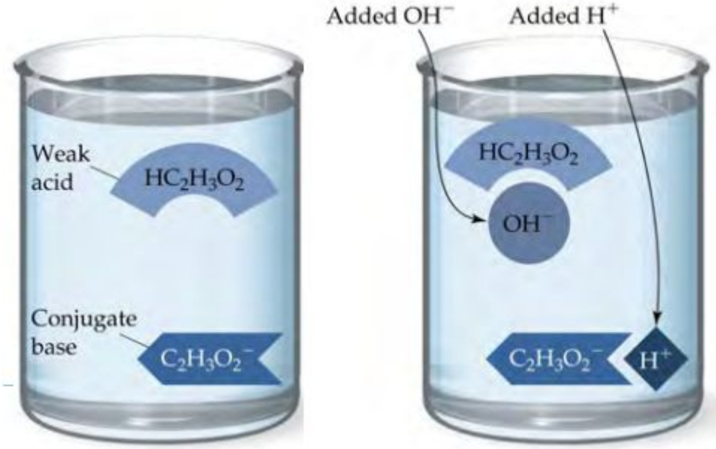
Weak Acids as Buffers

The large number of acid molecules will be able to respond to the addition of more OH⁻ ions:

$$HC_2H_3O_{2(aq)} + OH^-_{(aq)} \Longrightarrow H_2O_{(l)} + C_2H_3O_2^-{}_{(aq)}$$

The large number of conjugate base ions will be able to respond to the addition of more H+ ions:

$$C_2H_3O_2^-{}_{(aq)} + H_3O^+_{(aq)} \Longrightarrow H_2O_{(l)} + HC_2H_3O_{2(aq)}$$



Weak Bases as Buffers

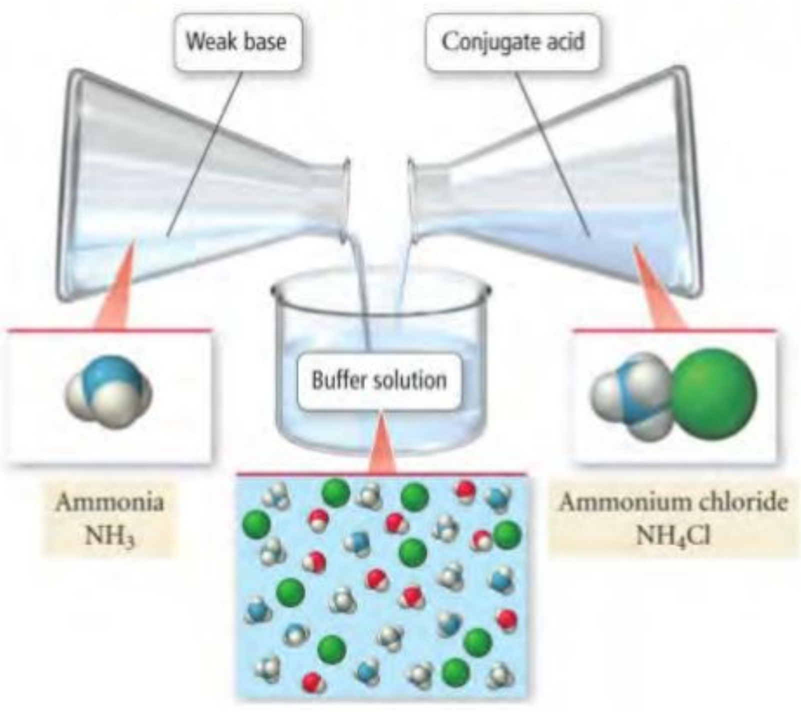
A solution of a weak base is mainly base molecules with very few of the conjugate acid ions present in the mixture.

Example: Dimethylamine

$$(CH_3)_2NH_{(aq)} + H_2O_{(l)} \rightleftarrows (CH_3)_2NH_2{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \qquad K_b = 5.4 \times 10^{-4} \text{ at } 25^{\circ}C$$

The addition of extra conjugate acid ions (dimethyl ammonium chloride, $(CH_3)_2NH_2Cl$) or enough HCl to react about half of the base (mid-point) transforms the mixture into a **buffer solution**.

WEAK BASES AS BUFFERS



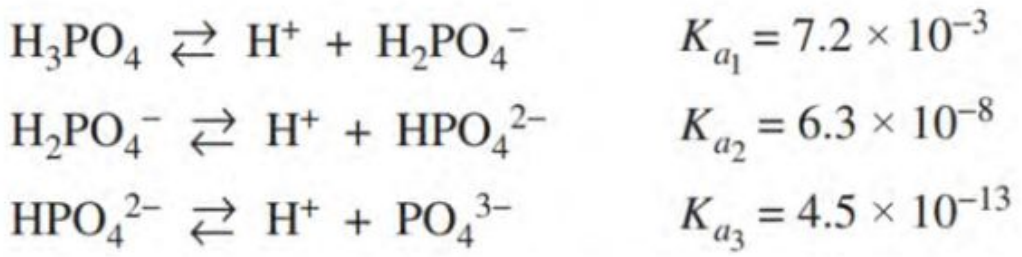
The large number of base molecules will be able to respond to the addition of more H^+ ions:

$$(CH_3)_2NH_{(aq)} + H^+_{(aq)} \Longrightarrow (CH_3)_2NH_2^+{}_{(aq)}$$

The large number of conjugate acid ions will be able to respond to the addition of more OH^- ions:

$$(CH_3)_2NH_2^+{}_{(aq)} + OH^-_{(aq)} \Longrightarrow H_2O_{(l)} + (CH_3)_2NH_{(aq)}$$

Polyprotic Buffers- amphoteric Buffers



$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \qquad K_{a_1} = 7.2 \times 10^{-3}$$

$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{2-} \qquad K_{a_2} = 6.3 \times 10^{-8}$$

$$HPO_4^{2-} \rightleftarrows H^+ + PO_4^{3-} \qquad K_{a_3} = 4.5 \times 10^{-13}$$

Polyprotic acids such as phosphoric acid, H_3PO_4, ionize to form the conjugate base $H_2PO_4^-$. However, this ion is also an acid and will go on to form its own conjugate base, HPO_4^{2-}.

A substance that can act as both an acid and a base is described as **amphoteric**. Water is another amphoteric molecule. (Al_2O_3 and some transition metal oxides are amphoteric - react with both acids and bases).

Polyprotic Buffers- amphoteric Buffers

A mixture with large quantities of an amphoteric molecule and conjugate can also act as a buffer.

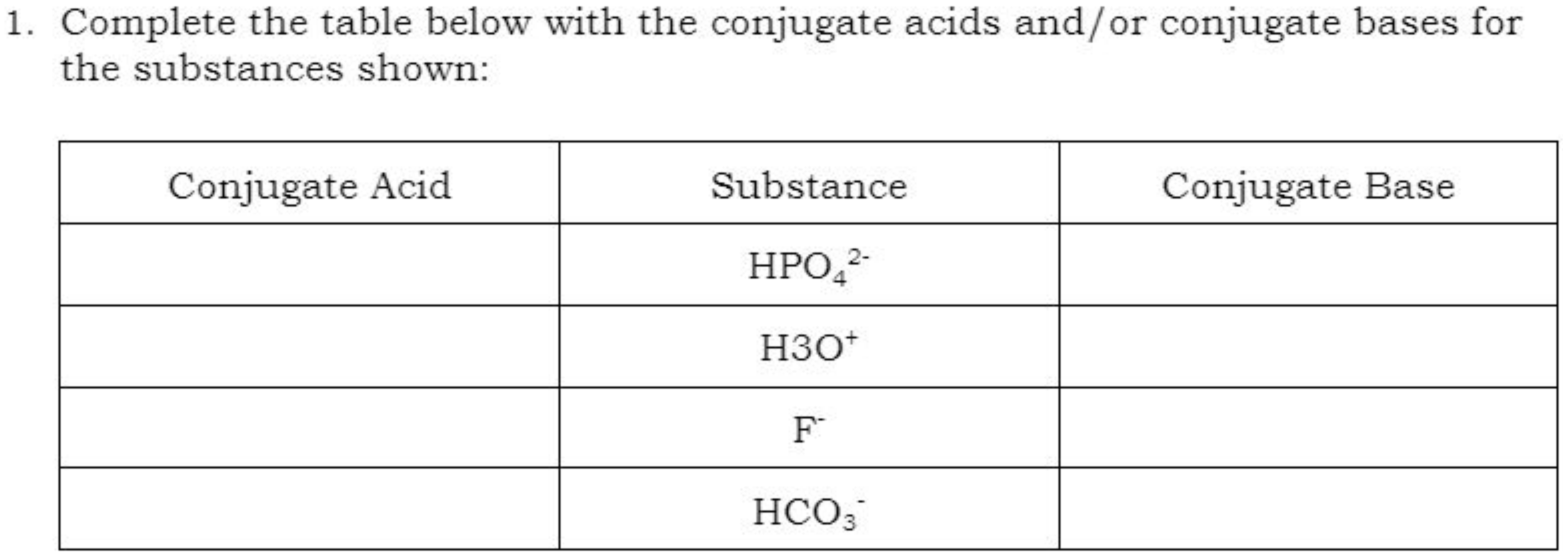
The large number of $H_2PO_4^-$ ions will be able to respond to the addition of more H^+ ions:

$$\mathbf{H_2PO_4^-{}_{(aq)} + H^+{}_{(aq)} \Longrightarrow H_3PO_{4(aq)}}$$

The large number of $H_2PO_4^-$ ions will be able to respond to the addition of more OH^- ions:

$$\mathbf{H_2PO_4^-{}_{(aq)} + OH^-{}_{(aq)} \Longrightarrow H_2O_{(l)} + HPO_4^{2-}{}_{(aq)}}$$

You Do, We Review



1. Complete the table below with the conjugate acids and/or conjugate bases for the substances shown:

Conjugate Acid	Substance	Conjugate Base
	HPO_4^{2-}	
	$H3O^+$	
	F^-	
	HCO_3^-	

8.9 Henderson-Hasselbalch Equation

ENDURING UNDERSTANDING:

SAP-10	A buffered solution resists changes to its pH when small amounts of acid or base are added.

LEARNING OBJECTIVE:

SAP-10.C	Identify the pH of a buffer solution based on the identity and concentrations of the conjugate acid-base pair used to create the buffer.

CALCULATING THE PH OF A BUFFER

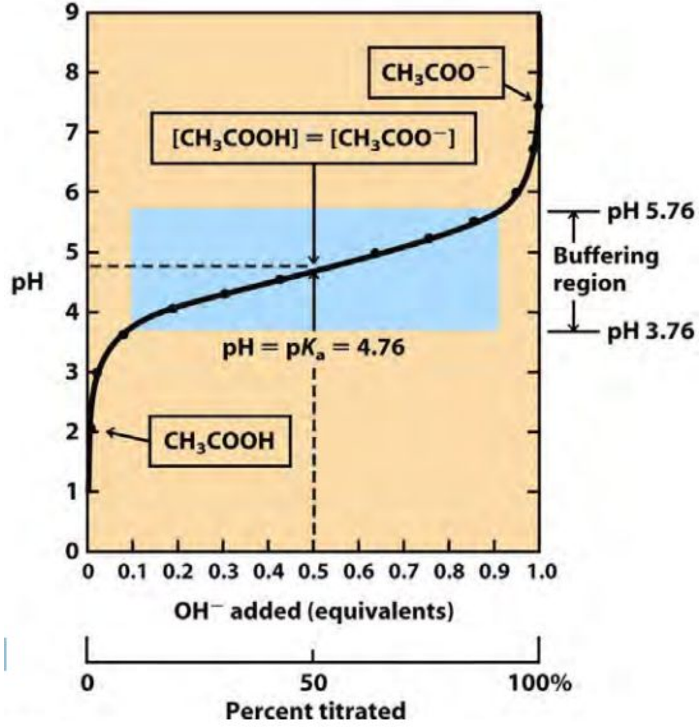
This is where we will utilise the Henderson-Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

When we prepare a buffer, usually [acid]=[base],
so log [base]/[acid] = 0, and pH = pKa.

CALCULATING pH OF A BUFFER

- If [acid] > [base] then pH < pKa
- If [base] > [acid] then pH > pKa
- Eventually, if [acid] >> [base] or [base] >> [acid] the mixture will lose its ability to function as a buffer.
- This usually corresponds with a tenfold difference will mean that the **Buffering region is effectively pKa ± 1**



EXAMPLE 1:

What is the pH of a buffer that is 0.12 M in lactic acid ($CH_3CH(OH)COOH$, or $HC_3H_5O_3$) and 0.10 M in sodium lactate ($CH_3CH(OH)COONa$, or $NaC_3H_5O_3$)? lactic acid Ka = 1.4×10^{-4}

Step 1: Convert Ka into pKa

Step 2: Substitute values into the Henderson-Hasselbalch equation.

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log \frac{[\text{base}]}{[\text{acid}]}$$

CALCULATING THE PH OF A WEAK BASE BUFFER

The Henderson-Hasselbalch equation can be easily modified to work for a buffer formed from a weak base and its conjugate acid, but, this time, we would be calculating **pOH using pKb**.

$$\mathrm{pOH} = \mathrm{p}K_\mathrm{b} + \log \frac{[\mathrm{acid}]}{[\mathrm{base}]}$$

Once pOH has been calculated, pH = 14 - pOH

Example 2

$$(CH_3)_2NH_{(aq)} + H_2O_{(l)} \rightleftarrows (CH_3)_2NH_2{}^+{}_{(aq)} + OH^-{}_{(aq)} \qquad K_b = 5.4 \times 10^{-4} \text{ at } 25°C$$

Calculate the pH of a solution at 25°C that is 0.100 M $(CH_3)_2NH_{(aq)}$ and 0.100 M $(CH_3)_2NH_2Cl_{(aq)}$?

Step 1: Convert Kb to pKb

Step2: Substitute values into the modified Henderson-Hasselbalch equation.

$$\mathrm{pOH} = \mathrm{p}K_\mathrm{b} + \log \frac{[\mathrm{acid}]}{[\mathrm{base}]}$$

Step3: Convert pOH to pH

EXAMPLE 3

1L solution of buffer: 0.10 M $HC_2H_3O_2$ and 0.10 M $NaC_2H_3O_2$.

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + C_2H_3O_2^{-}{}_{(aq)} \qquad K_a = 1.8 \text{ x } 10^{-5}$$

1. Find the starting pH
    a. Convert K_a to pK_a
    b. Use H-H

EXAMPLE 3

1L solution of buffer: 0.10 M $HC_2H_3O_2$ and 0.10 M $NaC_2H_3O_2$.

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)} \qquad K_a = 1.8 \times 10^{-5}$$

2. Find the pH after the addition of 0.01 mol H^+
   a. Use an ICE table to find new concentrations.

	$C_2H_3O_2^-$ +	H^+ →	$HC_2H_3O_2$
I	.1 mol	.01 mol	.1 mol
C		-.01	
E			

   b. Plug into H-H

EXAMPLE 3

1L solution of buffer: 0.10 M $HC_2H_3O_2$ and 0.10 M $NaC_2H_3O_2$.

$$HC_2H_3O_{2(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + C_2H_3O_2^-{}_{(aq)} \qquad K_a = 1.8 \text{ x } 10^{-5}$$

3. Find the pH after the addition of 0.01 mol OH^-
   a. Use an ICE table to find new concentrations.

	$C_2H_3O_2H$ +	OH^- →	$C_2H_3O_2^-$
I	.1 mol	.01 mol	.1 mol
C		-.01	
E			

   b. Plug into H-H

8.10 Buffering Capacity

ENDURING UNDERSTANDING:

SAP-10	A buffered solution resists changes to its pH when small amounts of acid or base are added.

LEARNING OBJECTIVE:

SAP-10.D	Explain the relationship between the buffer capacity of a solution and the relative concentrations of the conjugate acid and conjugate base components of the solution.

BUFFER SOLUTIONS

Buffer solutions are usually prepared from a weak acid and a salt of that acid or from a weak base and a salt of that base.

Two important characteristics of a buffered solution are its **buffer capacity** and its **pH range**.

Buffer Capacity is the term given to the amount of acid or base that can be added to a buffer system without the pH changing by more than a pH of 1.

The optimal pH of a buffer is equal to pKa (or pKb) of the acid (or base) used to prepare the buffer.

Changing the Concentrations of the Buffer mixture

The same pH (4.76) would be obtained from **any** ethanoic acid/ethanoate mixture where [acid] = [base].

Example:

- 1M ethanoic acid and 1M ethanoate
- .001 M ethanoic acid and .001 ethanoate

BOTH have a pH of 4.76 because [acid] = [base] and

pH = pKa + log ([base]/[acid])

However, 1M concentrations has the ability to respond to addition of MORE $H^+_{(aq)}$ or $OH^-_{(aq)}$ than the .001M concentrations. **Higher concentrations have a higher buffer capacity.**

***Increasing concentration of both acid and base equally means same pH and same pH range, but increases buffer capacity.**

EXAMPLE: Pka of acetic acid = 4.76

Buffer A:

0.100 M each of acetic acid, HCH_3COO, and sodium acetate, $NaCH_3COO$.

What will be the pH if 0.05 mols of NaOH is added to a 1L solution of the buffer?

Buffer B:

1.00 M each of acetic acid, HCH_3COO, and sodium acetate, $NaCH_3COO$.

What will be the pH if 0.05 mols of NaOH is added to a 1L solution of the buffer?

Changing the **Composition** of the Buffer Mixture

Different pH's (3.76 - 5.76) would be obtained from any ethanoic acid/ethanoate mixture where [acid] and[base] are not the same and their pH ranges would shift accordingly, though remain ± 1 of the new pH of the buffer.

Changing the **Composition** of the Buffer Mixture

- If [acid] > [base] then buffer has an increased capacity to deal with the addition of $OH^-_{(aq)}$ ions.
- Increasing concentration of acid over base means lower pH, lower pH range but increases buffer capacity to deal with $OH^-_{(aq)}$
- If [base] > [acid] then buffer has an increased capacity to deal with the addition of $H^+_{(aq)}$ ions.
- Increasing concentration of base over acid means higher pH, higher pH range but increases buffer capacity to deal with $H^+_{(aq)}$

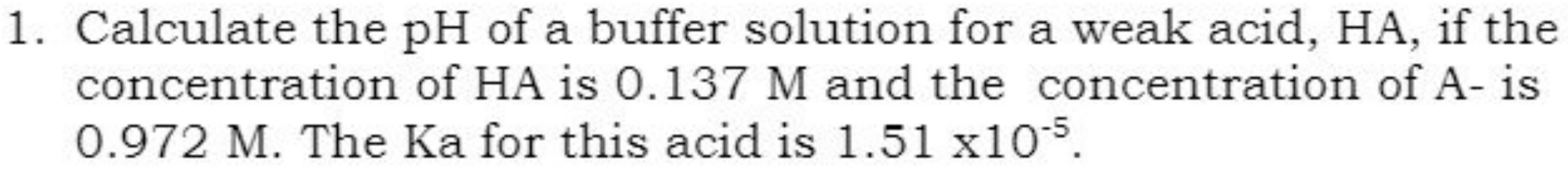
EXAMPLE:

Buffer C 0.100 M of acetic acid, HCH_3COO, and 1.00 M sodium acetate, $NaCH_3COO$. Pka of acetic acid = 4.76

What happens to the pH when 0.05 mols of HCl are added to 1L of the buffer solution?

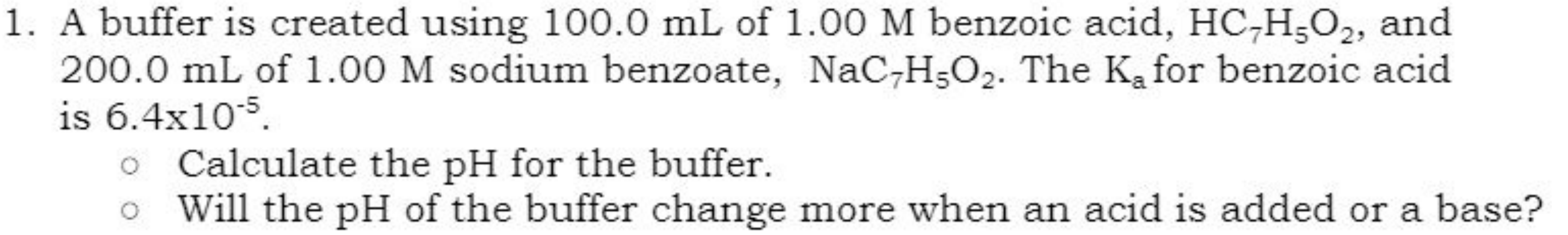
What happens to the pH when 0.05 mols of NaOH are added to 1L of the buffer solution?

TOGETHER (8.9)



1. Calculate the pH of a buffer solution for a weak acid, HA, if the concentration of HA is 0.137 M and the concentration of A- is 0.972 M. The Ka for this acid is 1.51 x10^{-5}.

TOGETHER (8.10)



1. A buffer is created using 100.0 mL of 1.00 M benzoic acid, $HC_7H_5O_2$, and 200.0 mL of 1.00 M sodium benzoate, $NaC_7H_5O_2$. The K_a for benzoic acid is $6.4x10^{-5}$.
   - Calculate the pH for the buffer.
   - Will the pH of the buffer change more when an acid is added or a base?