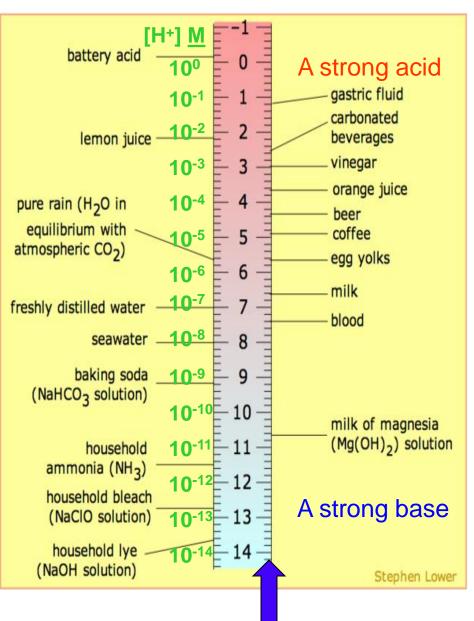
# pH (acidity) of solutions. Buffer Solutions. Hydrolysis

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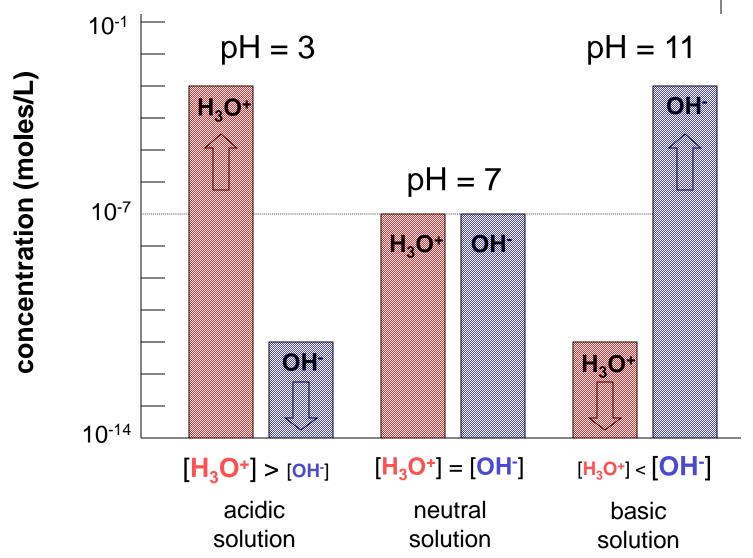


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- Most living cells have a *very* narrow range of tolerance for pH, i.e. [H<sup>+</sup>].
- The [H<sup>+</sup>] concentration will be important (either explicitly or implicitly) for many other topics in biology.
- [H<sup>+</sup>] is controlled in all biological organisms, and in virtually all biochemical experiments.
- Each pH unit represents a factor of 10 difference in [H<sup>+</sup>].

The pH scale goes from 0 to 14—because [H+][OH] = 10<sup>-14</sup>

# Acid – Base Concentrations



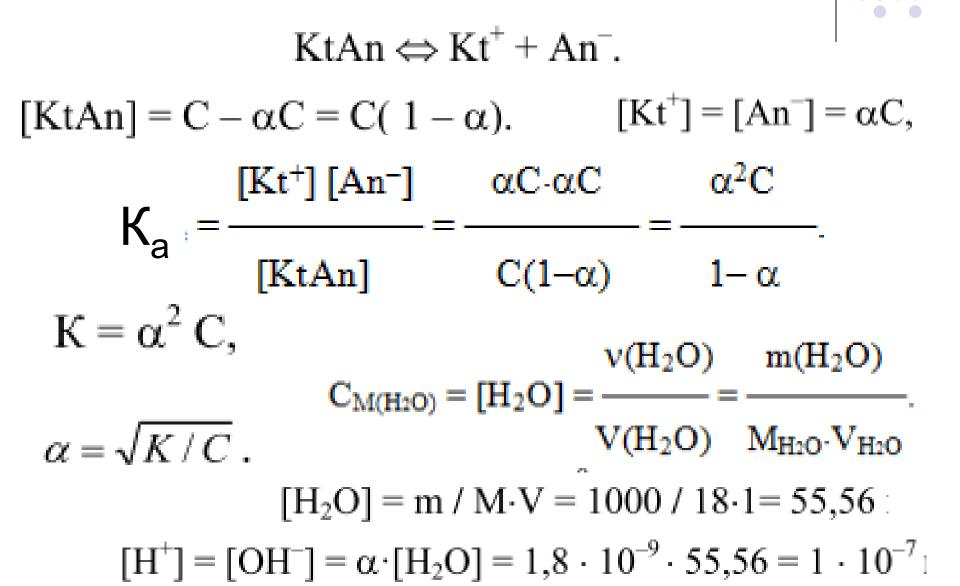




(a) Nonelectrolyte (b) Weak electrolyte (c) Strong electrolyte

Strong electrolytes completely dissociated on ions

## **Dissociation of weak electrolytes**



# **Equilibrium constant for water**

This equilibrium constant also has a special

name the <u>ion-product of water</u>, in pure

water at  $25^{\circ}C$ :  $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ 

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



We can write the equilibrium constant for

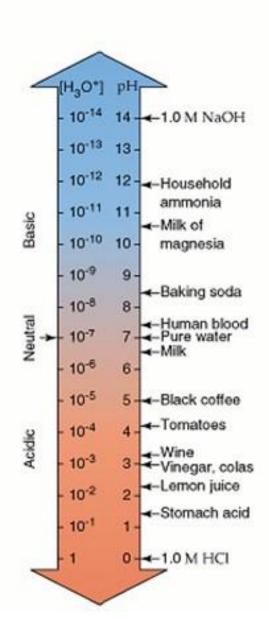
water in a new way:

$$-\log K_w = -\log[H^+] - \log[OH^-] = -\log[1 \cdot 10^{-14}]$$

$$pK_w = pH + pOH = 14$$

$$pH + pOH = 14$$





pH Scale  $[\mathbf{H}^+][\mathbf{OH}^-] = 1 \times 10^{-14}$  $pH = -log[H^+]$  $[H^+] = antilog(-pH)$  $pOH = -log[OH^-]$  $[OH^{-}] = antilog(-pOH)$ Acidic solution: pH < 7 Neutral solution: pH = 7 **Basic solution:** pH > 7

## **Ion concentration**

$$[H^+] = \alpha \cdot [acid] \quad [OH] = \alpha \cdot [base]$$

- For strong electrolytes α=1, so concentration of [H+] and [OH-] is equal concentration of base or concentration of acid respectively.
- For weak acids and bases we use degree of dissociation α. If we know Ka or Kb we use following formula

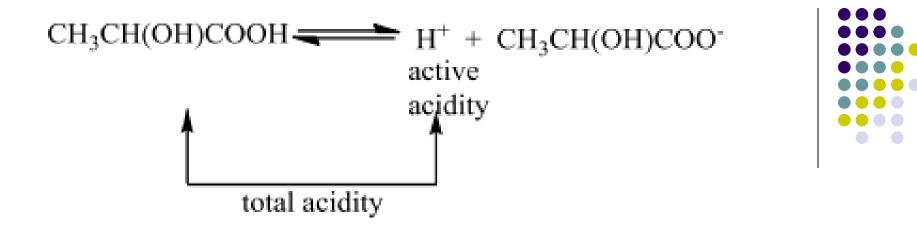
$$\alpha = \sqrt{K/C}.$$

The total acidity can be defined by titration. The active acidity is equal to the total acidity for strong electrolytes, because strong acid completely (100%) dissociated in solution to form  $H^+$ .

For example,  $HCl \rightleftharpoons H^+ + Cl^-$ .

The concentration of  $H^+$  is equal to the concentration of HCl.  $pH = -\log[H^+] = -\log C$ , where C is the molarity.

For the strong base solution:  $pOH = -log[OH^{-}] = -logC$ .



To calculate a pH of weak acid solution it is necessary to know besides the concentrations either the degree of the dissociation ( $\alpha$ ), or the dissociation constant (Ka):

 $pH = -logC \cdot \alpha$ , or

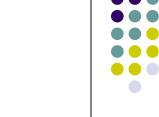
or : pH = 
$$-\log\sqrt{Ka \times C}$$
.

For the weak base solution:

$$pOH = -logC \times \alpha$$
, or  $= -log\sqrt{K_b \times C}$ ,

where α is the degree of dissociation (ionization) of the base; K<sub>b</sub> is the base dissociation (ionization) constant; C is the molarity.

# Calculation of the pH of Weak Acid Solutions



- **Problem:** What is the pH of a solution of 1.00 M nitrous acid,  $K_a = 4.0 \times 10^{-4}$
- Major species in solution: HNO<sub>2</sub> and H<sub>2</sub>O
- Which species can generate H<sup>+</sup> ions?
  - $HNO_2(aq) = H^+(aq) + NO_2^-(aq)$   $K_a = 4.0 \times 10^{-4}$
  - $H_2O(aq) = H^+(aq) + OH^-(aq)$   $K_w = 1.0 \times 10^{-14}$

• Ignore contribution from water,  $K_a >> K_w$ 

$$\left[H^{+}\right] = \sqrt{4.0 \cdot 10^{-4} \cdot 1.0} = 2 \cdot 10^{-2}$$

 $pH = -log [H^+] = -log 0.02 = 1.70$ 

### **Characteristics of Buffer Solutions**

- Contain weak acids or weak bases and their corresponding conjugate partners (common ions).
- Resist changes in pH.
- Buffering capacity depends on concentrations of weak acid or weak base and their common ions.
- Effective pH buffering range ~  $pK_a \pm 1$

Definition "Solutions which resist changes in pH when small quantities of acid or alkali are added."

Acidic Buffer (pH < 7) made from a weak acid + its sodium or potassium salt ethanoic acid sodium ethanoate

Alkaline Buffer (pH > 7) made from a weak base + its chloride ammonia ammonium chloride



## **Characteristics of Buffer Solutions**



- Buffers contain relatively large amounts of the weak acids (HA) and their conjugate base (A<sup>-</sup>), (or weak bases and their conjugate acids)
- 2. Buffer pH is determined by the  $pK_a$  of the acid HA and the molar ratio of the conjugate base to acid:  $[A^-]/[HA]$ .
- 3. Buffer pH changes very little because the ratio [A<sup>-</sup>]/[HA] changes very little when a small amount of strong acid or strong base is added.
- [H<sub>3</sub>O<sup>+</sup>] in buffer solutions remains more or less constant: Most of H<sup>+</sup> from strong acid is absorbed by the conjugate base A<sup>-</sup>; most of OH<sup>-</sup> added from strong base reacts with acid HA in the buffer to yield A<sup>-</sup> and H<sub>2</sub>O.

# **Buffering Capacity**

- How much H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup> the buffer can absorb without significantly changing its pH.
- Depends on the concentrations of HA and A<sup>-</sup>.
- High [HA] and [A<sup>-</sup>] lead to large buffering capacity.
- Optimal buffering occurs when [HA] = [A<sup>-</sup>];
- Ratio [A<sup>-</sup>] / [HA] ~ 1 strong resist to change when either H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup> is added.

**Buffer capacity** is a number of moles of a strong acid or a strong base that is needed to be added to 1 L of buffer solution in order to change its pH for 1 unit. The formula for calculating is: Buffer capacity for a acid =

 $\_$  normality of the adding acid  $\times$  volume of the adding acid

volume of buffer × changing of pH

Buffer capacity for a base =

\_normality of the adding base  $\times$  volume of the adding base

volume of buffer × changing of pH



### **Some Common Buffers**



Buffers	p <i>K</i>	pH Range
• HCOOH – HCOONa	3.74	2.74 - 4.74
• CH <sub>3</sub> COOH – CH <sub>3</sub> COONa	4.74	3.74 - 5.74
• $KH_2PO_4 - K_2HPO_4$	7.21	6.20 - 8.20
• $CO_2/H_2O - NaHCO_3$	6.37	5.40 - 7.40
• $NH_4Cl - NH_3$	9.25	8.25 - 10.25

# **Buffer solutions**

- Definition: a solution that resists change in pH
  - Typically a mixture of the acid and base form of a chemical
  - Can be adjusted to a particular pH value

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
  
Blood: pH = 7.35-7.45

- $[H+] = K_a \times [acid]/[base]$ Then take the log of both sides
- log<sub>10</sub>[H+] = log<sub>10</sub>K<sub>a</sub> + log<sub>10</sub> [acid]/[base]

Henderson-Hasselbach equation

pH = pKa - log<sub>10</sub> [acid]/[base]



# Weak acids, their conjugate bases, and buffers...



- Weak acids have only a modest tendency to shed their protons (definition of an acid).
- When they do, the corresponding negatively charged anion becomes a willing proton acceptor, and is called the *conjugate base*.
- The properties of a *buffer* rely on a balance between a weak acid and its conjugate base.
  - Henderson-Hasselbach equation

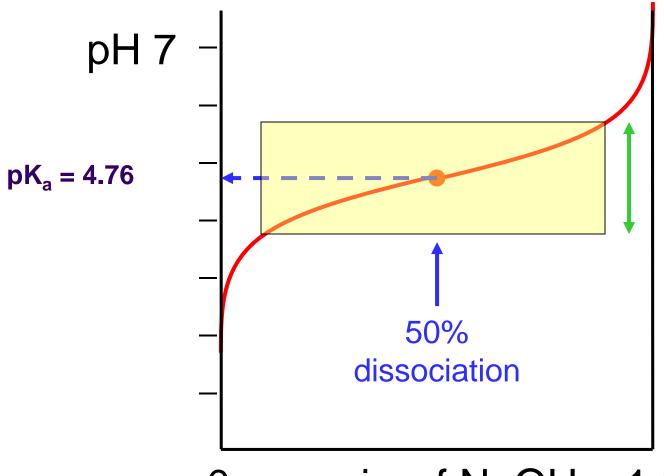
pH = pKa - log<sub>10</sub> [acid]/[base]

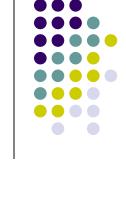
- Rearrange the equation to get
  - 10<sup>(pKa-pH)</sup> = [acid]/[base]

# **Chemistry of buffers**

- What happens when the concentration of the acid and base are equal?
  - Example: Prepare a buffer with 0.10M acetic acid and 0.10M acetate
    - pH = pKa log<sub>10</sub> [acid]/[base]
    - pH = pKa log<sub>10</sub> [0.10]/[0.10]
    - pH=pKa
    - Thus, the pH where equal concentrations of acid and base are present is defined as the pKa
- A buffer works most effectively at pH values that are <u>+</u> 1 pH unit from the pKa (the buffer range)

# Titration of acetic acid with sodium hydroxide

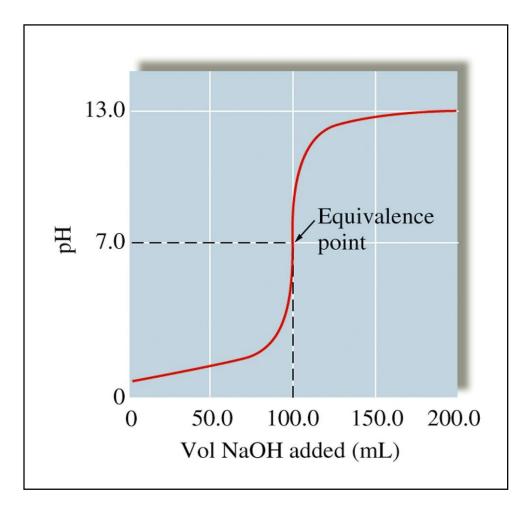




Buffering range: only small pH changes result from addition of base or acid

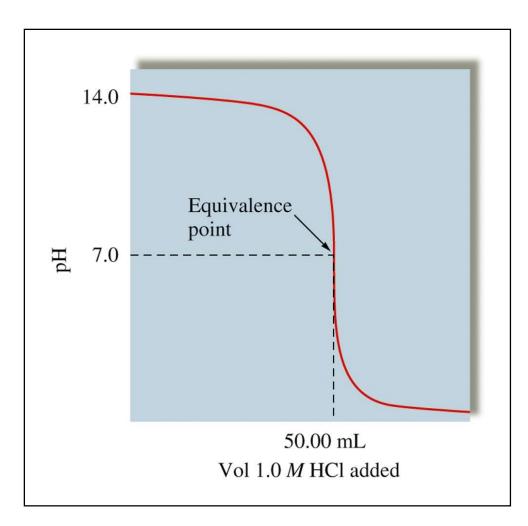
## 0 equiv. of NaOH 1.0 added

# The pH Curve for the Titration of 50.0 mL of 0.200 *M* HNO<sub>3</sub> with 0.100 *M* NaOH





# The pH Curve for the Titration of 100.0 mL of 0.50 *M* NaOH with 1.0 *M* HCI







# Ways to measure pH

- Indicator dyes and test strips
  - Less precise
  - Each indicator is only good for a small pH range (1-2 pH units)
  - But may be good for field usage, or measuring small volumes, or dealing with noxious samples.





### **Acid-Base Indicators**

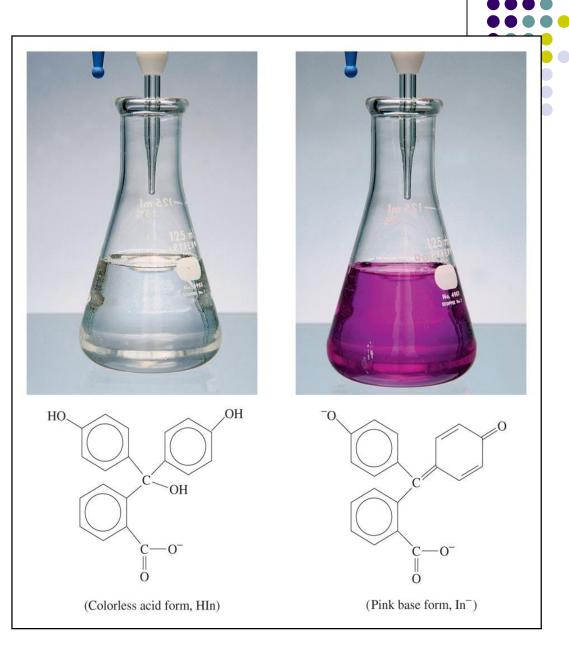


• An indicator is a substance added to acid or base solution to marks the *end point* of a titration by the change of its color.

For example, phenolphthalein changes from *colorless to pink* at the *end point* when an acid is titrated with a base.

• The *end point* of a titration should correspond to the *equivalence points* of the acid-base reaction.

### The Acid and Base Forms of the Indicator Phenolphthalein



### The Methyl Orange Indicator is Yellow in Basic Solution and Red in Acidic Solution





# **Choosing Indicators**



- 1. The pH range for color changes should occur within the sharp vertical rise (or drop) in the pH-titration curves.
- 2. An indicator changes color at  $pH = pK_a \pm 1$ , where  $pK_a$  is that of the indicator used.

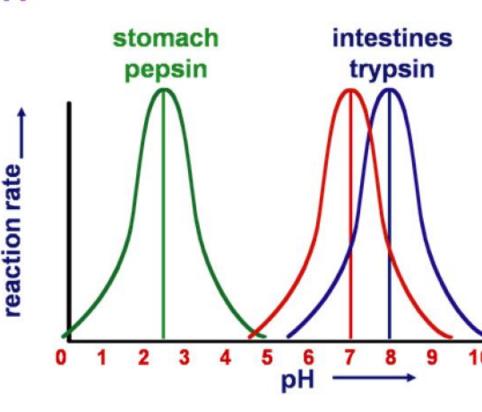
	Indicators:	Acid Color	Base Color	pH Range	Type of Titration
1.	Methyl orange	Orange	Yellow	3.2 – 4.5	strong acid-strong base strong acid-wea
	base				C
2.	Bromocresol green	Yellow	Blue	3.8-5.4	strong acid-strong base strong acid-weak base
3.	Methyl red	Red	Yellow	4.5 - 6.0	strong acid-strong base strong acid-weak base
4.	Bromothymol blue	Yellow	Blue	6.0-7.6	strong acid-strong base
5.	Phenol Red	Orange	Red	6.8 - 8.2	strong acid-strong base weak acid-strong base

## **pH Ranges for Indicators**

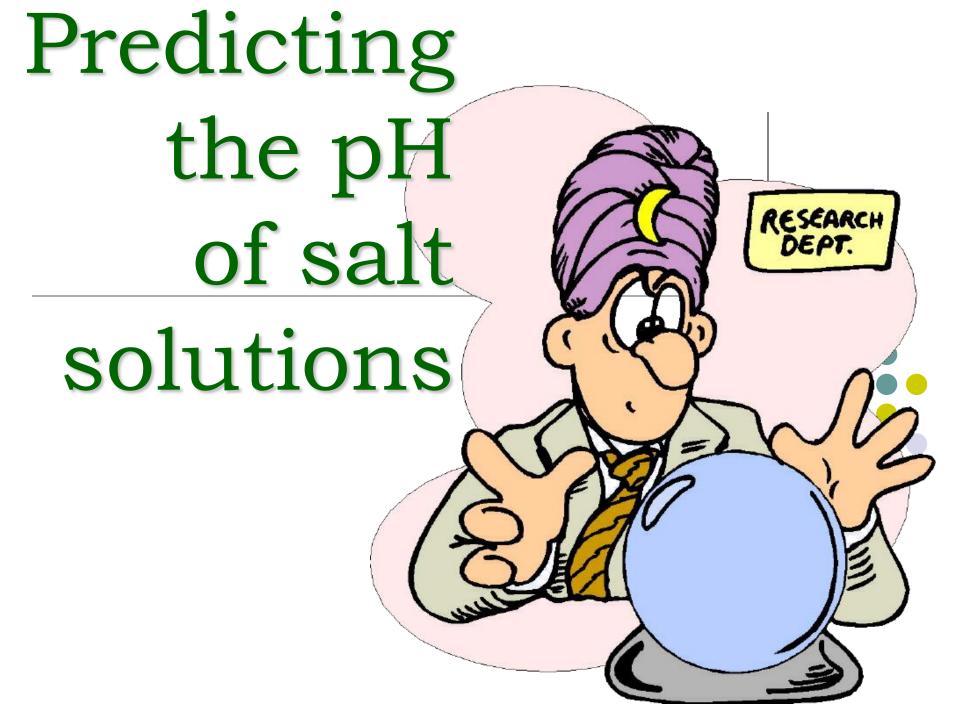
Indicator	Field of turn	pKa	Acid form	Basic form
Methyl purple	0.0 - 1.6	0.8	yellow	blue
Thymol blue	1.2 - 2.8	1.7	red	yellow
	8.0 - 9.6	8.9	yellow	blue
Helianthin	3.2 - 4.4	3.4	red	yellow
Bromophenol blue	3.0 - 4.6	3.9	yellow	blue
Bromocresol green	3.8 - 5.4	4.7	yellow	blue
Methyl red	4.8 - 6.0	5.0	red	yellow
Bromothymol blue	6.0 - 7.6	7.1	yellow	blue
Sunflower	5.0 - 8.0	6.5	red	blue
Phenol red	6.6 - 8.0	7.9	yellow	red
Phenolphthalein	8.0 - 10.0	9.4	colorless	crimson
Alizarin R yellow	10.1 - 12.0	11.2	yellow	red
Alizarin	11.0 - 12.4	11.7	red	purple

# Why is pH important in biology?

- pH affects solubility of many substances.
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- Many cells and organisms (esp. plants and aquatic animals) can only survive in a specific pH environment.







# Hydrolysis

## This reaction, in which water reacts with

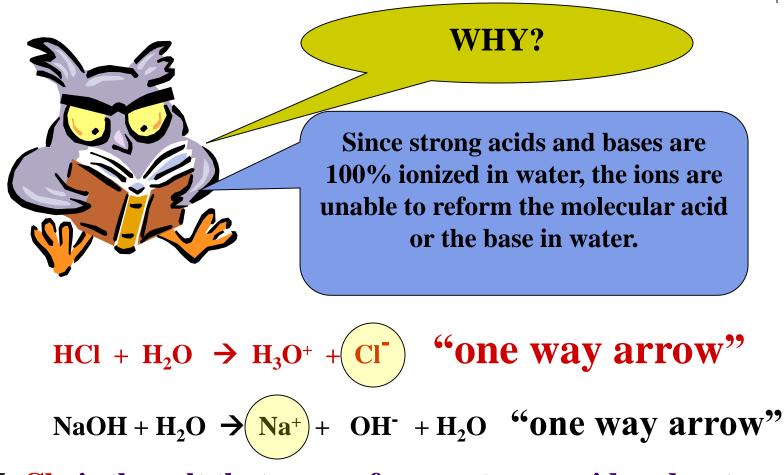
an ionic species in solution, is called

# hydrolysis.

Salts of strong acids and strong bases (for example, NaCl) do not hydrolyze: PH=7  $NaCl + H_2O = no \ reaction$ 

#### The ions of salts can have an influence on the pH of a solution.

#### Ions that come from a strong acid or base do not influence the pH.

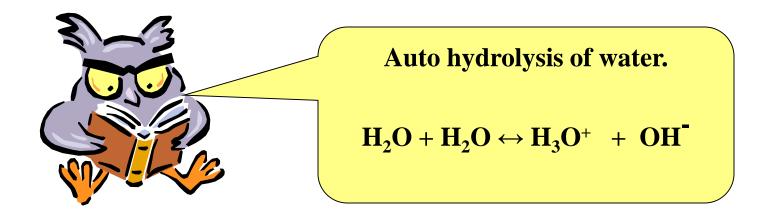


**NaCl** is the salt that comes from a strong acid and a strong base.

#### What would the pH of a sodium chloride solution (at 25°C)?

**pH** = 7

#### What gives rise to this pH?



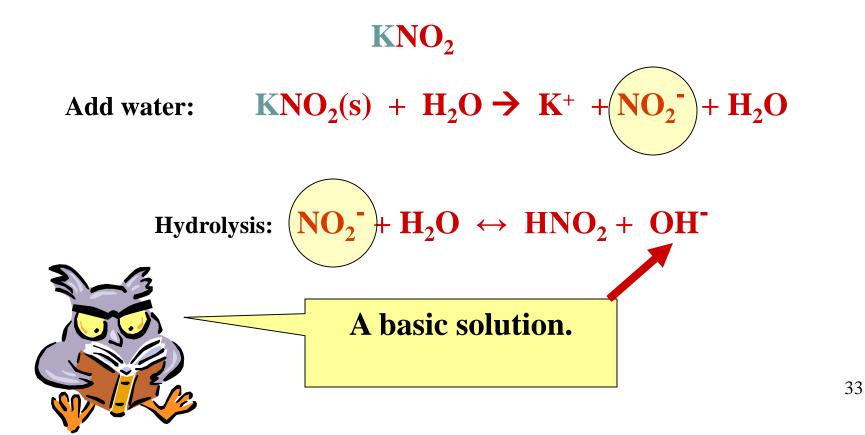


Salts that contain ions that come from a weak acid or base.



### weak acid: HNO<sub>2</sub>

A salt containing the anion of the weak acid and the cation from a strong base.



Calculate the pH of a 0.10 M KNO<sub>2</sub> solution.  $K_a(HNO_2) = 4.5 \ 10^{-4}$ .

**CHEMISTRY:**  $KNO_2(s) \rightarrow K^+ + NO_2^-$ More Chemistry:  $NO_2^- + H_2O \leftrightarrow HNO_2 + OH^-$ Equilibrium: I 0.10 N/A 0 () **C** -X N/A +X +X E 0.10-X N/A +X +X  $K_{b} = \frac{[HNO_{2}][OH]}{[NO_{2}]}$   $K_{a}K_{b} = 1.0 \times 10^{-14}$  $2.22 \times 10^{-11} = \frac{[x][x]}{[0.10 - x]}$  Try dropping  $pOH = -log[OH^{-}] = 5.83$  $x = 1.49 \times 10^{-6} = [OH^{-1}]$  pH = 14 - 5.83 = 8.17

Salts that contain ions that come from a weak acid or base.

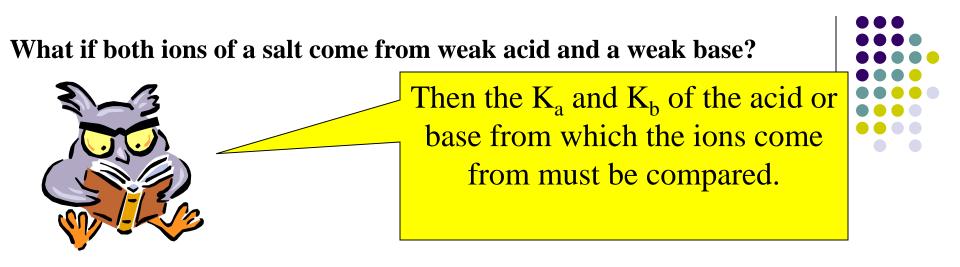
Weak Base: (CH<sub>3</sub>)<sub>3</sub>N trimethylamine



A salt containing the cation of the weak base and the anion from a strong acid. (CH<sub>3</sub>)<sub>3</sub>NHCl trimethylammonium chloride  $(CH_3)_3NHCl(s) + H_2O \rightarrow (CH_3)_3NH^+ + Cl^- + H_2O$ Add water:  $(CH_3)_3NH^+$  +  $H_2O \leftrightarrow (CH_3)_3NHQH + H^+$ **Hydrolysis:** An acidic solution.

Calculate the pH of a 0.10 (CH<sub>3</sub>)<sub>3</sub>NHCl solution.  $K_{h}((CH_{3})_{3}NHCl) = 7.4 \ 10^{-5}.$ CHEMISTRY:  $(CH_3)_3NHCl(s) + H_2O \rightarrow (CH_3)_3NH^+ + Cl_2$ More Chemistry:  $(CH_3)_3NH^+ + H_2O \leftrightarrow (CH_3)_3NHOH^- + H^+$ 0.10 N/A 0 0 Equilibrium: I C -x N/A **+X**  $+\mathbf{X}$ **E** 0.10-x N/A  $+\mathbf{X}$  $+\mathbf{X}$  $K_a = \frac{[(CH)_3 NHOH^-][H^+]}{[(CH)_3 NH^+]}$   $K_a K_b = 1.0 \times 10^{-14}$  $1.35 \times 10^{-10} = \frac{[x][x]}{50 \times 10^{-10}}$ [0.10 - x] $pH = -log[H^+] = 5.43$ 

 $x = 3.68 \times 10^{-6} = [H^+]$ 



# $$\begin{split} NH_4CN(aq) & K_a(NH_4^+) = \ 5.6 \ x \ 10^{-10} & K_b(CN^-) = 2.04 \ x \ 10^{-5} \end{split}$$ note: K<sub>a</sub> was calculated from K<sub>b</sub>(NH<sub>3</sub>) and K<sub>b</sub> from K<sub>a</sub> HCN

Since  $K_b(CN^-)$  is greater than  $K_a(NH_4^+)$ , the solution is basic.

Salts of weak acids and strong bases (for example CH<sub>3</sub>COONa) hydrolyze, producing a basic solution: pH>7.  $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$  $CH_3COO^- + Na^+ + HOH \rightleftharpoons CH_3COOH + Na^+ + OH^ Na^+ + HOH =$  no reaction Water reacts with a CH<sub>3</sub>COO<sup>-</sup> to produce OH<sup>-</sup>. A solution of  $CH_3COONa$  has a pH>7.

Salts of strong acids and weak bases (for example, NH<sub>4</sub>Cl) hydrolyze, producing a acidic solution: pH<7.

 $NH_4Cl \rightleftharpoons NH_4^+ + Cl^ Cl^- + H_2O \rightleftharpoons no \ reaction$  $NH_4^+ + H_2O \rightleftharpoons H^+ + NH_4OH$  $NH_4Cl + H_2O \rightleftharpoons NH_4OH + HCl$ 



Salts of weak acids and weak bases (for example, NH<sub>4</sub>CH<sub>3</sub>COO) hydrolyze, but whether the resulting solution is neutral, acidic, or basic depends on the relative values of K<sub>a</sub> and K<sub>b</sub>.

# **Steps in determining pH**

1. Write the ions that form: e.g.  $NH_4CN$  $\rightarrow NH_4^+ + CN^-$ 



- 2. Determine the reaction ions have with water:  $NH_4^++OH^-\leftrightarrow NH_3+H_2O, NH_3+H_2O\leftrightarrow NH_4^++OH^ CN^-+H^+ \rightarrow HCN, HCN \rightarrow CN^-+H^+$
- 3. Look up the Ka of the conjugate acid and the Kb of the conjugate base:

Kb = 
$$\frac{[NH_4^+][OH^-]}{[NH_3]}$$
 Ka =  $\frac{[CN^-][H^+]}{[HCN]}$   
= 1.8 x 10<sup>-5</sup> = 6.2 x 10<sup>-10</sup>

Determine if more H<sup>+</sup> or OH<sup>-</sup> is removed:
 More H<sup>+</sup> is removed, therefore BASIC

## Salt Hydrolysis



To determine whether a salt solution is acidic or basic, remember the following rules:

Strong acid + Strong base  $\longrightarrow$  Neutral solution Strong acid + Weak base  $\longrightarrow$  Acidic solution Weak acid + Strong base  $\longrightarrow$  Basic solution Weak acid + Weak base  $\longrightarrow$  Neutral solution

#### **Making Buffer Solution (example)**



A phosphate buffer with pH = 7.40 is prepared using  $KH_2PO_4$  and  $K_2HPO_4$ .

- (a) What is the molar ratio of  $[HPO_4^{2-}]$  to  $[H_2PO_4^{-}]$  in the buffered solution?
- (b) If  $[H_2PO_4^-]^= 0.20 M$ , what is  $[HPO_4^{2-}]$ ?

(c) How many grams of KH<sub>2</sub>PO<sub>4</sub> and K<sub>2</sub>HPO<sub>4</sub>, respectively, are needed to make 500. mL of this solution? (H<sub>2</sub>PO<sub>4</sub><sup>-</sup> has  $K_a = 6.2 \times 10^{-8}$ )

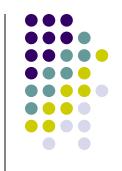
### **Solutions to Buffer**

(a) Use Henderson-Hasselbalch equation:

- $pH = pK_a + \log([HPO_4^{2-}]/[H_2PO_4^{-}])$
- $7.40 = 7.21 + \log([HPO_4^{2-}]/[H_2PO_4^{-}])$
- $\log([HPO_4^{2-}]/[H_2PO_4^{-}]) = 7.40 7.21 = 0.19$
- $[HPO_4^2]/[H_2PO_4] = 10^{0.19} = 1.55$

•  $[HPO_4^{2-}] = 1.55 \times 0.20 M = 0.31 M$ 

- (b) If  $[H_2PO_4^-] = 0.20 M$ ,



#### **Solutions to Buffer**



- (c) Moles of KH<sub>2</sub>PO<sub>4</sub> needed =
   500. mL x (1 L/1000 mL) x 0.20 mol/L = 0.10 mole
- Moles of K<sub>2</sub>HPO<sub>4</sub> needed = 500. mL x (1 L/1000 mL) x 0.31 mol/L = 0.155 mole
- Grams of  $KH_2PO_4$  needed =

0.10 mol x (136.086 g/mol) = 14 g

• Grams of  $K_2$ HPO<sub>4</sub> needed =

0.155 mol x (174.178 g/mol) = 27 g

### **Titration Problem**



Strong Acid-Weak Base Titration:

• A 20.0 mL aliquot of 0.100 M NH<sub>3</sub> is titrated with 0.100 M HCl. (a) What is the pH of the solution before titration? (b) What is the pH of the solution after 10.0 mL of HCl has been added? (c) What is the pH of the solution at equivalent point (after 20.0 mL of 0.100 M HCl is added)?

 $(K_{\rm b} \text{ of } \text{NH}_3 = 1.8 \text{ x } 10^{-5})$ 

#### **Solution to Titration Problem**



(a) Solving initial concentration of OH<sup>-</sup> by approximation method:

$$[OH^{-}] = \sqrt{[NH_{3}] \times K_{b}} =$$

$$= \sqrt{(0.100 \times 1.8 \times 10^{-5})} = 1.3 \times 10^{-3} M$$

$$[H_{3}O^{+}] = K_{w}/[OH^{-}] = (1.0 \times 10^{-14})/(1.3 \times 10^{-3})$$

$$= 7.5 \times 10^{-12} M$$

$$pH = -\log(7.5 \times 10^{-12} M) = 11.13$$

#### **Solution to Titration Problem**



(b) Concentration after 10.0 mL of HCl is added: Reaction:  $NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O$ 

 $[I]_{before rxn}$ :0.067 M0.033 M0.000 $[C]_{from rxn}$ :-0.033 M-0.033 M+0.033 M $[E]_{after rxn}$ :0.034 M0.0000.033 M

- $pH = pKa + log([NH_3]_f/[NH_4^+]_f)$
- $= -\log(5.6 \times 10^{-10}) + \log(0.034/0.033)$
- = 9.25 + (0.0) = 9.25

#### **Solution to Titration Problem**



(c) Calculating pH at equivalent point:

Reaction: $NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O$  $[I]_{before rxn}$ :0.050 M0.050 M $[C]_{from rxn}$ :-0.050 M-0.050 M $[E]_{after rxn}$ :0.000 M0.000

- At equivalent point,  $[NH_4^+] = 0.050 \text{ M}$
- $K_a$  for NH<sub>4</sub><sup>+</sup> =  $K_w/K_b = (1.0 \text{ x } 10^{-14})/(1.8 \text{ x } 10^{-5})$ = 5.6 x 10<sup>-10</sup>

#### **Solution to Titration Problem: example #3**

(c) Calculating pH at equivalent point (continue):

$$K_{\rm a} = x^2 / (0.050 - x) = 5.6 \text{ x } 10^{-10}$$

- $x = [H_3O^+],$
- Using approximation method,

$$[H_{3}O^{+}] = \sqrt{[NH_{4}^{+}] \times K_{a}}$$
$$= \sqrt{(0.050 \times (5.6 \times 10^{-10}))} = 5.3 \times 10^{-6} \text{ M}$$
$$\bullet \text{ pH} = -\log(5.3 \times 10^{-6} = 5.28)$$



#### **Solution to Titration Problem: example #3**

(c) Calculating pH at equivalent point (continue):

$$K_{\rm a} = x^2 / (0.050 - x) = 5.6 \text{ x } 10^{-10}$$

- $x = [H_3O^+],$
- Using approximation method,

$$[H_{3}O^{+}] = \sqrt{[NH_{4}^{+}] \times K_{a}}$$
$$= \sqrt{(0.050 \times (5.6 \times 10^{-10}))} = 5.3 \times 10^{-6} \text{ M}$$
$$\bullet \text{ pH} = -\log(5.3 \times 10^{-6} = 5.28)$$



### **pH of Buffer Solution**



- What is the pH of a buffer solution that is 0.45 *M* acetic acid (HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>) and 0.85 M sodium acetate (NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)? The  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .
- Solution:
- $pH = pK_a + log([C_2H_3O_2-]/[HC_2H_3O_2])$
- $pH = -log(1.8 \times 10^{-5}) + log(0.85/0.45)$
- pH = 4.74 + 0.28 = 5.02

## Thank you for your attention!

## Find more: http://www.chem.teset.sumdu.edu.ua

