**Al-Safwa University College**

**Department of Medical Laboratory Technique**

**1st Year Class**

# Analytical Chemistry
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**Professor Assistant**

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# concentration

## Molarity (M)

It is defined as the number of moles of solute in each liter of solution.

$$M = \frac{wt}{M.wt} \times \frac{1000}{V_{ml}}$$

$V_{ml}$ = Volume

$ml$ = mille liter

$= 1\ cm^3$

### Example

How many grams of $Na_2SO_4$ is required to prepare 500 ml of 0.1M solution?

Solution

$$M = \frac{wt}{M.wt} \times \frac{1000}{V_{ml}}$$

$$0.1 = \frac{wt}{142} \times \frac{1000}{500}$$

$$wt = 7.1\ g$$

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## Molality

number of moles of solute in 1 kg of pure solvent.

$$M = \frac{wt}{M.wt} \times \frac{1000}{1kg}$$

## Normality

$$N = \frac{wt}{eq.wt} \times \frac{1000}{V_L}$$

## Formality

$$F = \frac{spg \times \%^\circ \times 1000}{g.F.wt}$$

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## specific gravity (spg)

is defined as the ratio between the density of solution at $20^\circ c$ to that of water at $4^\circ c$

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$$M = \frac{spg \times \%^\circ \times 1000}{M.wt}$$

$$N = \frac{spg \times \%^\circ \times 1000}{eq.wt}$$

$$\frac{percent\ by\ weight}{} = \frac{weight\ of\ solute\ in\ (g)}{weight\ of\ solution\ in\ (g)} \times 100$$

## example

what is the percent by weight of Sugar in solution made by dissolving 10 g of sugar in 90 g water

$$percent\ by\ weight = \frac{10\ g \times 100}{10g + 90g} = 10\%$$

# Density and specific gravity

Density is the mass per unit volume at the temperature $20°c$, it is usually expressed $gm/ml$ or $gram/cm^3$, density of water is taken as $1.0$ $gm/cm^3$ at $4°c$ and $0.9982$ $gm/ml$ at $20°c$.

Specific gravity ( spg) is defined as the ratio between the density of solution at $20°c$ to that of water at $4°c$ hence it is dimension less quantity

$$Molarity \ (M) = \frac{spg \times \% \times 1000}{M.wt}$$

$$Normality \ (N) = \frac{spg \times \% \times 1000}{eq.wt}$$

**problem:** How can you prepare 100 ml of 0.3 F of $NaCl$ ( g. Fwt = 58.5 ) from the solid state ?

Answer:

$$Formality (F) = \frac{wt}{g.Fwt} \times \frac{1000}{V_{ml}}$$

$$0.3 = \frac{wt}{58.5} \times \frac{1000}{100}$$

$$wt = 0.3 \times 58.5 \times \frac{100}{1000}$$

wt = 1.755 g of $NaCl$ should be dissolved in 100 ml of distilled water to get the concentration

0.3 F

**problem** what is the formula concentration of solution that is 5% wt/wt of $K_2SO_4$ ( g.Fwt = 174) and specific gravity of 1.03

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Answer :  $F = \dfrac{spg \times \% \times 1000}{g \cdot F \cdot wt}$

$= \dfrac{1.03 \times 5/100 \times 1000}{174}$

$= 0.296$

problem:  How can you prepare 2 Liters of 0.15 F from 0.5 F AgNO₃ ?

answer   $F_1 \times V_1 = F_2 \times V_2$

$0.5 \times V_1 = 0.15 \times 2$

$\therefore V_1 = 0.6$ Liter or 600 ml
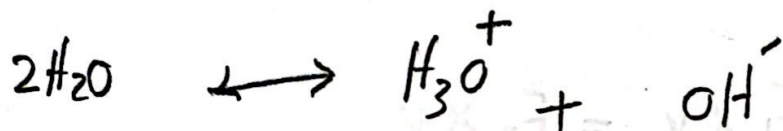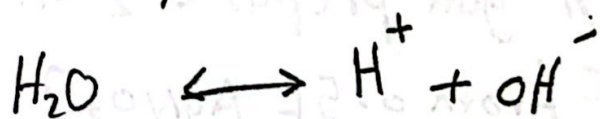
So we must take 600ml of 0.5 F of AgNO₃ solution and complet it to 2 Liter with distilled water.

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# Ion product of water

water is a very weak electrolyte, being ionized to the extent of only a few parts/billion. This ionization assume a considerable importance.

The ionization of water is represented by the equation

$$H_2O \longleftrightarrow H^+ + OH^-$$

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

The equilibrium constant is

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

in water and dilute aqueous solutions, conc

of $H_2O$ is constant and could be omitted in equilibrium constant formulations.

The mass action expression for equilibrium will be

$$* \quad K_w = [I^+][OH] = 1.01 \times 10^{-14}$$
$$(at\ 25\ ^\circ C)$$

$K_w$ is called the ion product constant of water.

in aqueous solutions to maintain $K_w$ at $1.0 \times 10^{-14}$.

An acidic solution is one in which $[H^+]$ is greater than $[OH^-]$ and the opposite is correct for alkaline solution for any given concentration of $H^+$ or $OH^-$ the corresponding concentration of $OH^-$ or $H^+$ is easily calculated from $K_w$.

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# The pH Scale

The very small quantities of $OH^-$ or $H^+$ cannot be easily represented.

In 1909 Sorenson introduced the term

pH, $pH = Log \dfrac{1}{[H^+]} = -Log[H^+]$

Thus if $[H^+] = 1 \times 10^{-5}$

$pH = -Log \, 1 \times 10^{-5} = -(-5.00) = 5$

if $[H^+] = 5.0 \times 10^{-4}$

$pH = -Log \, 5 \times 10^{-4} = -0.7 + 4 = 3.3$

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

$$\underline{pk_w = pH + pOH} \quad *$$

in $H_2O$ and neutral aqueous solutions

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \text{ and}$$

$$pH = pOH = 7 \therefore pH + pOH = 14$$

In acidic solution the $[H^+] > [OH^-]$ and pH is less than 7.0 and pOH > 7

In alkaline solution the $[OH^-] > [H^+]$ and pOH is < than 7.0 and pH ⟩7⟩

A 10 fold change in $[H^+]$ or $[OH^-]$ corresponds to

a change of one unit in pH or pOH because $\log 10 = 1.00$

Example
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In certain solution $[H^+] = 1.0 \times 10^{-6}$

calculate pH, pOH, $[OH^-]$

Solution !
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$$pH = -\log [H^+] = -(-6) = 6$$

$$pH + pOH = 14 \quad , \quad pOH = 14 - 6 = 8$$

$$[OH^-] = \frac{K_w}{[H^+]} = 1.0 \times 10^{-8}$$

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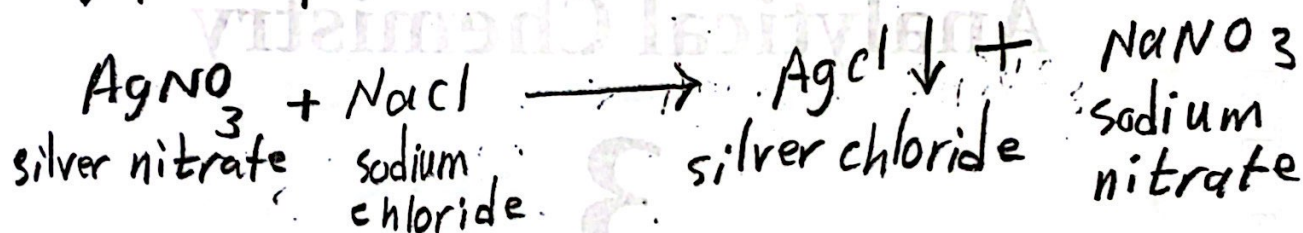1st Year Class

# Analytical Chemistry

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# Reaction type of inorganic compounds
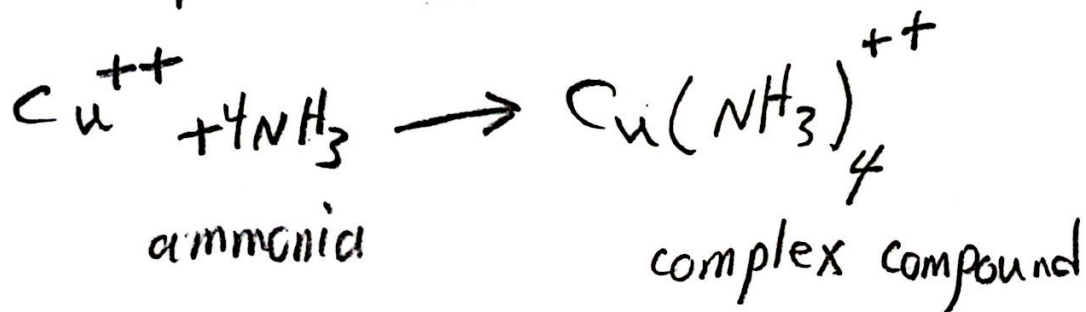
1) Neutralization or acid base reaction

$$\underset{\text{Base}}{NaOH} + \underset{\text{acid}}{HCl} \longrightarrow \underset{\text{salt}}{NaCl} + \underset{\text{water}}{H_2O}$$

2) precipitation reaction

$$\underset{\text{silver nitrate}}{AgNO_3} + \underset{\substack{\text{sodium} \\ \text{chloride}}}{NaCl} \longrightarrow \underset{\text{silver chloride}}{AgCl \downarrow} + \underset{\substack{\text{sodium} \\ \text{nitrate}}}{NaNO_3}$$

3) oxidation reduction reactions

4) complex formation reactions

$$Cu^{++} + \underset{\text{ammonia}}{4NH_3} \longrightarrow \underset{\text{complex compound}}{Cu(NH_3)_4^{++}}$$

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# Neutralization Titrations

Some terms used in volumetric titrimetry

* standard solution (or standard titrant) is reagent of known concentration that is used to carry out a titrimetric analysis

* Titration: is performed by slowly adding a standard solution from a buret or other liquid dispensing device to a solution of the analyte until the reaction between the two is judged complete.

the volume or mass of reagent needed to complete the titration is determined from the difference between the initial and final reading.

* Equivalent point and End point

The equivalence point in a titration is a theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample.

* The end point: is the point in a titration when a physical change occurs that is associated with the condition of chemical equivalence.

* The difference in volume or mass between the equivalence point and end point is the titration error.

* Indicators are often added to the analyte solution to produce an observable physical change (the end) at or near

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near the equivalence point,

Typical indicator changes include the appearance or disappearance of a color

\* A primary standard solution it is "an ultra pure compound that serves the reference material for a titrimetric method of analysis.

— The neutralization of hydronium or hydroxide ion to form water is widly used as the basis for volumetric determinations, of acids, bases and salt.

The reaction is characterised by a rapid change in pH near the equivalence point, a change that is

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readily detected by an acid – base
indicator or that can be followed
electrically by use of a pH meter

## * Calculation of pH

In considering the feasibility titrations
and in selecting the proper indicator
for a given titration, analyst often

need to calculate the pH of solution.
under various conditions.

### pH of strong acids and strong bases

Since strong acids and strong bases are
highly dissociated, the calculation of pH
or pOH is a simple process as the

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$[OH^-]$ or $[H^+]$ is directly related to the concentration of the substance.

## problems

1-) calculate the pH value of a solution of a completely ionized 1.0 M solution of acid or base?

$[H^+] = 1 M \quad pH = -Log\, 1 = 0$

similarly in a completely ionized 1.0 M of base

$[OH^-] = 1 M \quad pOH = -Log\, 1 = 0$

$pH = 14 - 0 = 14$

2-) calculate the $[H^+]$ and pH of

0.009 N Hydrochloric acid

$[H^+] = 0.009 N \qquad pH = -Log(9.0 \times 10^{-3})$

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$pH = -Log\ 9.0 - Log\ 10^{-3}$

$pH = -0.95 + 3 = 2.05$

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3) Calculate the pH value of a solution of sodium hydroxide whose $[OH^-]$ is $1.05 \times 10^{-3}$

$pOH = -(Log\ 1.05 + Log\ 10^{-3})$

$pOH = -(0.02 - 3) = 2.98$

$pH = 14.00 - 2.08 = 11.92$

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4) Calculate the hydrogen ion concentration of a solution of pH 5.3

$pH = -Log[H^+]$,   $5.3 = -Log[H^+]$

$[H^+]$ = the antilog of 5.3

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

$$[H^+] = 5.01 \times 10^{-6} M$$

$$pOH = 14 - 5.3 = 8.7$$

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5-) calculate the $[OH^-]$ concentration of

pH 10.75 , $pOH = 14 - 10.75 = 3.25$

$[OH^-]$ = the antilog of 3.25

$$[OH^-] = 10^{-pOH} = 10^{-3.25}$$

$$[OH^-] = 5.62 \times 10^{-4} M$$

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# pH of solutions of weak acids and bases

Since weak acids and bases are only partially ionized in solution, the $[H^+]$ and $[OH^-]$ in such solutions are Less than the molar concentration of the reagent.

calculation of pH or pOH requires a knowledge of the concentration of the substance, as well as the magnitude of its ionization constant.

A) calculation of pH of solutions of weak monoprotic acids

The ionization of weak monoprotic acid may be represented by :

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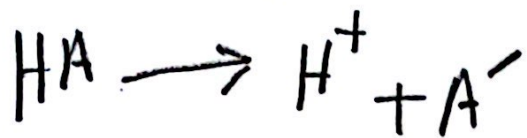
$$HA \longrightarrow H^+ + A^-$$

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

If the acid is pure itis ionization gives equal concentrations of $H^+$ and $A^-$ ions and since their activities may

be assumed equal in dilute solutions, therefore:   $[H^+] = [A^-]$

if the total acid concentration is $C_a$. moles/Liter, then the moles of the unionized acid $[HA]$ must be numerically equal to   $C_a - [H^+]$

$$K_a = \frac{[H^+]^2}{C_a - [H^+]}$$

the acid is weak and slightly ionized thus $[H^+]$ is very small compared to $C_a$ and can be neglected and the equation will be

$$K_a = \frac{[H^+]^2}{C_a}$$

and $[H^+]^2 = K_a \, C_a$

there for

$$\ast \quad pH = \tfrac{1}{2}\left(pK_a + p\,C_a\right)$$

Example    calculate the pH and $[H^+]$ of $0.1\,N$ acetic acid $\left(pK_a = 4.76\right)$
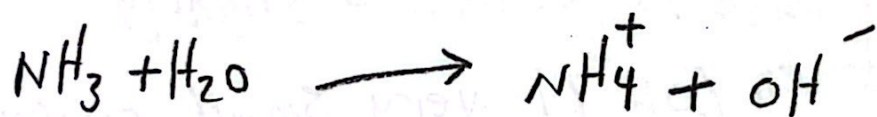
$$pH = \tfrac{1}{2}\left(4.76 + 1.00\right) = 2.88$$

$$[H^+] = 1.31 \times 10^{-3} M = 10^{-pH}$$

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## B) Calculation of pH of solutions of weak monoequivalent bases:

Aqueous solution of ammonia are basic due to the following reaction

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

and the ionization constant of the base $K_b$ is :

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

if the base is pure, its ionization gives equal concentrations of $[NH_4^+]$ and $[OH^-]$ ions, therefor $[NH_4^+] = [OH^-]$ if the total concentration of the base is $C_b$ moles/Liter, then the moles of the

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unionized base $[NH_3]$ must be numerically equal to $C_b - [OH^-]$ and the above equation becomes

$$K_b = \frac{[OH^-]^2}{C_b - [OH^-]}$$

Since the base is weak and slightly ionized then $[OH^-]$ is very small compared to $C_b$ so the $[OH^-]$ can be neglected and the equation will be

$$K_b = \frac{[OH^-]^2}{C_b} \quad \text{and} \quad [OH^-]^2 = K_b C_b$$

* $pOH = \frac{1}{2}(pK_b + pC_b)$

* $pH = pK_w - \frac{1}{2}(pK_b + pC_b)$

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## problem

calculate the pH and the $[H^+]$ of 0.13 N ammonia solution $(pk_b = 4.76)$

$$pH = 14.00 - \frac{1}{2}(4.76 + 0.89)$$

$$pH = 11.18 \quad \longrightarrow \quad [H^+] = 10^{-11.18}$$

$$[H^+] = 6.6 \times 10^{-12} M \qquad \text{anti Log of } pH$$

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# Calculions of pH of solutions of salts of weak acids and bases

Salts of weak acids or bases react with water to give basic or acidic Solutions respectively. This phenomenon known as

* hydrolysis. A hydrolytic reaction proceeds because ions of salts of weak acids or bases tend to react with the $H^+$ or $OH^-$ of water to form slightly ionized acids or bases. The reaction of these salts with water not proceed to completion but reaches to an equilibrium point that has an equilibrium constant known as

* hydrolysis constant $K_h$.

The extent to which thy hydrolytic reactions proceed is related to the ionization constants of the formed acids or bases. The Lower the ionization constant the Larger is the degree of hydrolysis.

Ⓐ Salts of weak acids and strong bases: $(CH_3COONa)$  salt

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The hydrolysis of Sodium acetate in water may be represented as follows:

$$H_2O + CH_3COO^- \longrightarrow CH_3COOH + OH^-$$

the acetate ion reacts with water to form the slighly ionized acetic acid. This require that some of the water molecules ionize to maintain the ion product of water

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of water $K_w$ constant and producing more hydroxyl ions and the medium will be alkaline. The hydrolysis constant $K_h$ o the above reaction can be repersented as follows

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad (1)$$

The hydrolysis constat $K_h$ can be calculated as follows: we have $K_w = [H^+][OH^-]$

$[OH^-] = K_w / [H^+]$ substitution of the value in equation (1) yield:

$$K_h = \frac{[CH_3COGH] K_w}{[H^+][CH_3COO^-]} \quad (2)$$

since $\quad \dfrac{1}{K_a} = \dfrac{[CH_3COOH]}{[CH_3COO^-][H^+]}$

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substitution in equation 2 we get

$$K_h = K_W / K_a \qquad (3)$$

since both-equations (1) and (3)
equal $K_h$, then

$$\frac{K_W}{K_a} = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = K_h \qquad (4)$$

The $CH_3^+$ and the pH of an aqueous
solution of a salt of a weak acid and
a strong base can be derived from equation
(4) as follows: By considering $C_S$ as
the initial concentration of the salt in
moles/Liter and Y as the ionized part.
Then $\dfrac{K_W}{K_a} = \dfrac{Y^2}{C_S - Y} \qquad (5)$

where $(C_s - Y)$ is the concentration of the the salt remaining at equilibrium.

Since $Y$ is small in relation to $C_s$ so it can be neglected, accordingly equation (5) will be modified to:

$$\frac{K_w}{K_a} = \frac{Y^2}{C_s}$$

then $Y = [OH^-] = \sqrt{K_w C_s / K_a}$

$$[OH^-] = (K_w C_s / K_a)^{1/2}$$

$$* pOH = \frac{1}{2}(pk_w + pC_s - pk_a) \quad (6)$$

$$pH = pk_w - \frac{1}{2}(pk_w + pC_s - pk_a) \quad (7)$$

$$* pH = \frac{1}{2}(pk_w - pC_s + pk_a) \quad (8)$$

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The degree of hydrolysis, $h$, of a salt analogous to the degree of ionization of a weak acid or base, is the fraction of the salt hydrolyzed at equilibrium thus:

$$h = Y/C_s \qquad *$$

Example  calculate the pH, $[H^+]$, $[OH^-]$ and the degree of hydrolysis of a $0.1M$ sodium acetate solution, $(pK_a = 4.76)$

Solution  From equation 8

$$pH = \tfrac{1}{2}(14.0 - 1.00 + 4.76) = 8.88$$

$[H^+] =$ the antilog of $8.88 = 1.3 \times 10^{-9} M$

$$[OH^-] = 10^{-14}/1.3 \times 10^{-9} = 7.5 \times 10^{-6} M$$

$$h = \frac{7.5 \times 10^{-6}}{0.10} = 7.5 \times 10^{-5}$$