## Atom:

The smallest portion of an element, that retain all of the properties of the element.
\{Diameter (1/100,000,000 cm.) \}
The number atoms in 1 gram - atom is $6.0235 \times 10^{23}$ (Avogadro number)

## Element:

Elements are the building blocks of all matter.
An element can be defined as a substance that cannot be broken down into any simpler substance by ordinary chemical means.
(E.g. oxygen, iron).

## Isotopes:

Atoms of an element having the same atomic number but different mass number.


Mass number 12


Mass number 13


Mass number 14

Three isotopes of carbon, atomic number 6 .

## Radioisotopes in medicine:

## Iodine - 131:

This isotope is used in the diagnosis and treatment of thyroid conditions.

## Technetium - 99m:

$\mathrm{Tc}{ }^{99 \mathrm{~m}}$ ( m for metastable) is one of the most widely used radioisotopes for various types of scans.

Cobalt - 60:

This radioisotope is employed in the treatment of many different types of cancer.

## Radioactivity:

Radioactivity is the property of emitting radiation from the nucleus of an atom.

The three types of radiation are:

1. Alpha particles are positively charged helium nuclei.
2. Beta particles are high speed electrons and are negatively charged.
3. Gamma rays are a high - energy from electromagnetic radiation and have no charge.

## Radio isomers pollution:

All of us come into contact with radiation through fallout from bomb tests. The levels, however, are very low and the effect is probably quite long term, if it is measurable at all. What about the more spectacular exposure to radiation that leads quickly to sickness and often death.

Of the many inorganic substances that interact negatively with physiological systems, mercury, lead, beryllium, and asbestos are potentially the most dangerous because they are stored in the body and have a cumulative effect.

## Debroglie equation:

Debroglie concluded that electrons might have wavelengths by first combining two relationships, one derived by Einstein, the other by Planck.

Einstein showed that the total energy E of any particle is proptional to its mass $M$, the proportionality constant being the square of the speed of light in a vacuum, c , or
$E=m c^{2}$ (energy of a particle of mass $m$ )
The plank relationship relating the energy of a wave to its frequency has already been mentioned.

$$
\begin{aligned}
& \mathrm{E}=\mathrm{h} v \text { (energy of a wave of frequency) } \\
& \mathrm{mc}^{2}=\mathrm{hv} \\
& v \lambda=\mathrm{c} \quad \lambda \text { : wave length } \\
& \mathrm{mc}^{2}=\mathrm{h}\left(\frac{\mathrm{c}}{\lambda}\right) \quad \text { and } \mathrm{m}=\frac{\mathrm{h}}{\lambda \mathrm{c}}
\end{aligned}
$$

## Matter:

Matter is any thing that occupies space and has weight. States of Matter are solid, liquid, and gas.

## Classification of Matter:



## Chemical Bonds: -

Chemical bonds can be divided into: -

1. Ionic bond: An ionic bond occurs when one or more electrons are transferred from one to another
e.g. $\mathrm{Li}\left(1 s^{2} 2 \mathrm{~s}^{1}\right)-\mathrm{e}^{-} \longrightarrow \mathrm{Li}^{+}\left(1 \mathrm{~s}^{2}\right)+\mathrm{e}^{-}$ $\mathrm{F}\left(\begin{array}{lll}1 \mathrm{~s}^{2} & 2 \mathrm{~s}^{2} & 2 \mathrm{p}^{5}\end{array}\right)+\mathrm{e}^{-} \longrightarrow \mathrm{F}^{-}\left(\begin{array}{cc}\mathrm{s}^{2} & 2 \mathrm{~s}^{2}\end{array} 2 \mathrm{p}^{6}\right)$

e.g. $\mathrm{CaCl}_{2}$
2. Covalent bond: A covalent bond results from sharing of a pair of electrons between atoms.

$$
\text { e.g. } \quad \mathrm{H}^{\bullet}+\mathrm{H}^{-} \longrightarrow \mathrm{H}_{2}
$$



$$
\begin{aligned}
& \text { e.g. } \quad \mathrm{CH}_{2}=\mathrm{CH}_{2} \\
& \mathrm{CH}=\mathrm{CH}
\end{aligned}
$$

3. Coordinate covalent band: Where a pair of electrons from one atom is shared by two atoms.

4. Hydrogen bonding: A particularly strong dipole - dipole attraction occurs when hydrogen is covalently bonded to a very small highly electronegative element such as fluorine, oxygen or nitrogen.


## Errors and statistics:

## Accuracy:

The accuracy of a determination may be defined as the concordance between it and the true or most probable value (relative error)

## Precision:

Precision may be defined as the concordance a series of measurements of the same quantity. The mean deviation or the relative mean deviation is a measure of precision.

Example: A substance was known to contain $49.06+\ldots .02$ percent of given constituents A. The result obtained by two observers using the same substance and the same general technique were:

Observe (1). 49.01; 49.21; 49.08 Mean 49.10 percent.
Relative mean error $=(49.10-49.06) / 49.06=0.08$ percent.
Relative mean deviation $=[(0.09+0.11+0.02) / 3 \times 100 / 49.10=$

$$
0.15 \text { percent. }
$$

Observe (2). 49.40; 49.44; 49.42 Mean $=49.42$ percent.
Relative mean error $=(49.42-49.06) / 49.06=0.73$ percent.
Relative mean deviation $=[(0.02+0.02+0.00) / 3 \times 100 / 49.42=$
0.03 percent.

## Classification of errors:

The errors may be divided into:
A) Determinate (systematic, constant) errors:

1. Instrumental errors:
(Impurities in reagents).
2. Methodic errors:
(Solubility of a precipitate, in complete reaction)
3. Operative errors
(Loss of precipitate during filtration)
4. Personal errors
(Color blindness)
B) Indeterminate errors:

Indeterminate errors are frequently called accidental or random, errors, such errors can be attributed to no known cause, nor can they be predicted as to magnitude or direction for any single measurement in a series or for any single measurement standing alone,

## Express of concentration

## The gram formula weight (gfw):

Is the summation of atomic weights, in grams, of all the atoms in the chemical formula of a substance. Thus, the gram formula weight for $\mathrm{H}_{2}$ is $2.016(2 \times 1.008) \mathrm{g}$; for NaCl it is $58.44(35.45+22.99) \mathrm{g}$.

## Formality:

Is defined as the number of gram-formula weights (gfw), of solute per liter of solution.

$$
\mathrm{F}=\frac{\mathrm{wt}}{\mathrm{gfw}} \times \frac{1000}{\mathrm{~V}(\mathrm{ml})}
$$

## Gram molecular weight (gmw):

Is employed rather than gram formula weight when we are concerned with a real chemical species. Thus, the gram molecular weight of $\mathrm{H}_{2}$ is its gram formula weight 2.016 g if we are dealing with the substance NaCl in water; we will not assign to it a gram molecular weight because this species is not found in aqueous media.

It is perfectly proper to assign gram molecular weights to $\mathrm{Na}^{+}(22.99 \mathrm{~g})$ and $\mathrm{Cl}^{-}(35.45 \mathrm{~g})$ since these are real chemical entities (strictly, these should be called gramionic weights rather than gram molecular weights, although this terminology is seldom encountered).

## Molarity or molar concentration:

Is defined as the number of molecular weights or moles of a solute per a liter of solution (or the number of millimoles per millimeter).

$$
\mathrm{M}=\frac{\mathrm{Wt}}{\mathrm{Gmw}} \times \frac{1000}{\mathrm{~V}(\mathrm{ml})}
$$

## Normality:

Is defined as the number of gram

* Equivalent weights (equivalents) of a substance dissolved in one liter of solution (or number of milliequivalents per millimeter).

The equivalent weight of a substance depends upon the type of reaction it undergoes.

Gram-equivalent weight $=\frac{\text { Molecular weight }}{\mathrm{n} \text { (equivalency) }}$
Example of equivalency

| Solute | n |
| :---: | :---: |
| Oxidation state |  |
| NaCl | 1 (where is of interest) |
| $\mathrm{BaCl}_{2}$ | 2 (where $\mathrm{Ba}^{2+}$ is of interest) |
| $\mathrm{ALCl}_{3}$ | 3 (where $\mathrm{Al}^{3+}$ is of interest) |
| $\mathrm{Na}_{2} \mathrm{SO}_{4}$ | 2 (where $\mathrm{SO}_{4}{ }^{2-}$ is of interest) |
| Replaceable Hydronium and Hydroxide Ions |  |
| HCl | 1 |
| $\mathrm{HNO}_{3}$ | 1 |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 1 (where product is $\mathrm{HSO}_{4}^{-}$) |
|  | 2 (where product is $\mathrm{SO}_{4}{ }^{2-}$ ) |
| NaOH | 1 |
| KOH | 1 |
| $\mathrm{Ba}(\mathrm{OH})_{2}$ | 2 |
|  | Change in oxidation state |
| $\mathrm{FeCl}_{3}$ | 1 (where product is $\mathrm{Fe}^{2+}$ ) |
| $\mathrm{MnO}_{4}{ }^{-}$ | 5 (where product is $\mathrm{Mn}^{+2}$ ) |
| $\mathrm{SnCl}_{4}$ | 2 (where product is $\mathrm{Sn}^{+2}$ ) |

[^0]Grams of solute
Gram - equivalent weight of solute

$$
\mathrm{N}=\frac{\mathrm{Wt}}{\mathrm{Eqw}} \mathrm{X} \frac{1000}{\mathrm{~V}\left(\mathrm{~m}_{1}\right)}
$$

## Parts per million; part per billion:

For very dilute solutions, it is convenient to express concentrations in term of:

$$
\begin{aligned}
& \text { Part per million }(\mathrm{PPM})=\frac{\text { Weight of solute }}{\text { Weight of solution }} \times 10^{6} \\
& \qquad \mathrm{PPM} \approx \frac{\mathrm{mg}}{\text { Liter solution }} \\
& \text { Part per billion }(\mathrm{ppb})=\frac{\text { Weight of solute }}{\text { Weight of solution }} \times 10^{9}
\end{aligned}
$$

## $\mathbf{P}$ - functions:

In some circumstances it is convenient to express the concentration of an ion in terms of the negative logarithm of its molar concentration. The most common p - function is:

$$
\mathrm{P}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]
$$

The term in brackets is the molar hydronium ion concentration.

## Density and specific Gravity:

The density of a substance measure its mass per unit volume and has units of $\mathrm{Kg} /$ liter or $\mathrm{g} / \mathrm{ml}$.

Specific gravity of a material is the ratio of its mass to that of an equal volume of water at $4 \mathrm{C}^{\circ}$. Specific gravity is unit less because water at $4 \mathrm{C}^{\circ}$ has a density of exactly $1 \mathrm{~g} / \mathrm{ml}$.

## Percentage concentration:

Weight percent $(W / W)=\frac{\text { Wt of solute }}{\text { Wt of solution }} \times 100$
Volume percent $(\mathrm{V} / \mathrm{V})=\frac{\text { Volume of solute }}{\substack{\text { Volume of solution } \\ 9}} \quad \mathrm{X} 100$

$$
\text { Weight percent }(\mathrm{W} / \mathrm{V})=\frac{\text { Wt of solute, } \mathrm{g}}{\text { Vol. of solution, } \mathrm{ml}} \quad \mathrm{X} 100
$$

## Solution - Diluent Volume Ratios:

The composition of a dilute solution is sometimes specified in terms of the volume of a more concentrated reagent and the volume of solvent to be used in diluting it. Thus a $1: 4 \mathrm{HCl}$ solution contains four volumes of water for each volume of concentrated Hydrochloric acid taken.

$$
\begin{aligned}
& \mathrm{V}_{1} \mathrm{C}_{1}=\mathrm{V}_{2} \mathrm{C}_{2} \\
& \mathrm{~N}=\frac{\mathrm{D} \mathrm{X} \mathrm{\%} \mathrm{X} 10}{\text { eq. wt }} \\
& \mathrm{M}=\frac{\mathrm{DX} \% \mathrm{X} \mathrm{10}}{\mathrm{M} \cdot \mathrm{Wt}}
\end{aligned}
$$

Molal solution contains a gram - molecular weight of solute dissolved in 1000 g of solvent.

## Chemical Equilibrium

In a solution of acetic acid, two reactions occurring simultaneously:

$$
\begin{equation*}
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}+\mathrm{CH}_{3} \mathrm{COOO}^{-} . \tag{I}
\end{equation*}
$$

And


When the rate which the ions are formed by reaction (I) is equal to the rate at which they disappear by reaction (II), there concentrations in the solution will no change with time. In fact, the concentrations of all the species will remain constant from this point on, this call equilibrium.

To indicate chemical equilibrium in a reacting system we use a set of double arrow $\longrightarrow$ in the chemical equation. Thus the equilibrium that we have been discussing is expressed as

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}+\mathrm{CH}_{3} \mathrm{COOO}^{-}
$$

The use of this notation implies that the forward reaction (the reaction going from to right) is occurring at the same rate as the reverse reaction (the reaction from right to left).

For strong electrolytes, the reverse reaction does not occare, for e.g. NaCl would write simply

$$
\mathrm{NaCl} \longrightarrow \mathrm{Na}^{+}{ }_{(\mathrm{aq)}}+\mathrm{Cl}^{-}{ }_{(\mathrm{aq})}
$$

## Equilibrium constant:

The generalized equation for a chemical equilibrium

$$
\mathrm{mM}+\mathrm{nN} \rightleftharpoons \mathrm{pP}+\mathrm{qQ}
$$

The equilibrium - constant expression for this reaction is

$$
K=\frac{[\mathrm{p}]^{\mathrm{p}}[\mathrm{Q}]^{\mathrm{q}}}{[\mathrm{M}]^{\mathrm{m}}[\mathrm{~N}]^{\mathrm{n}}}
$$

Where the letters in brackets represent the molar concentration of dissolved solutes or partial pressures (in atmospheres) if the reacting substances are gases.

## Common Types of Equilibrium - Constant Expressions:

1. Dissociation of water

Aqueous solutions always contain small amounts of hydronium and hydroxide ions as a consequence of the dissociation reaction

$$
2 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-}
$$

The equilibrium constant for this reaction.

$$
\mathrm{K}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}}
$$

[ $\mathrm{H}_{2} \mathrm{O}$ ] in the equation can be taken as constant

$$
\mathrm{K}\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}=\mathrm{Kw}=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]
$$

Where the new constant Kw is given the special name, the ion - product constant for water. ( $\approx 1 \times 10^{-14}$ at $25 \mathrm{C}^{\circ}$ )

$$
\begin{aligned}
\mathrm{pKw} & =-\log \mathrm{Kw} \\
& =-\log \left(1 \mathrm{X} 10^{-14}\right) \\
& =-(-14)=14 \\
\log \mathrm{Kw} & =\log \left[\mathrm{H}^{+}\right]+\log \left[\mathrm{OH}^{-}\right] \\
-\log \mathrm{Kw} & =\left(-\log \left[\mathrm{H}^{+}\right]\right)+\left(-\log \left[\mathrm{OH}^{-}\right]\right) \\
\mathrm{pKw} & =\mathrm{pH}+\mathrm{pOH} \\
& =\mathrm{pH}+\mathrm{pOH}
\end{aligned}
$$

## Example 1:

What is the ph of a 0.002 M HCl solution?

$$
\begin{aligned}
{\left[\mathrm{H}^{+}\right] } & =0.002 \mathrm{M}=2 \times 10^{-3} \mathrm{M} \\
\mathrm{pH} & =-\log \left[\mathrm{H}^{+}\right] \\
& =-\log \left[2 \times 10^{-3}\right] \\
& =-\left(\log 2+\log 10^{-3}\right) \\
& =-\{0.3+(-3)\} \\
& =-(-2.7) \\
& =2.7
\end{aligned}
$$

Example 2:
What is the pH of a $5 \times 10^{-4} \mathrm{M} \mathrm{NaOH}$ ?
Method 1

$$
\begin{aligned}
& \mathrm{Kw}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right] \\
& {\left[\mathrm{H}^{+}\right]=\frac{1 \times 10^{-14}}{5 \times 10^{-4}}=0.2 \times 10^{-10} \text { or } 2 \times 10^{-11} \mathrm{M}} \\
& \mathrm{pH}=-\log \left(2 \times 10^{-11}\right)=10.2
\end{aligned}
$$

Method 2

$$
\begin{aligned}
\mathrm{pOH} & =-\log \left[\mathrm{OH}^{-}\right] \\
\mathrm{pOH} & =-\log \left(5{\left.\mathrm{X} 10^{-4}\right)}\right. \\
& =3.3 \\
\mathrm{pH} & =\mathrm{pKw}-\mathrm{pOH} \\
& =14-3.3 \\
& =10.7
\end{aligned}
$$

2. Equilibrium involving slightly soluble ionic solids:

When an aqueous solution is saturated with a sparingly soluble salt (e.g. silver chloride) one or more equilibrium will be established:

$$
\begin{aligned}
& \mathrm{AgCl}_{(\mathrm{s})} \xlongequal[\sim]{\mathrm{AgCl}_{(\mathrm{aq})}} \mathrm{AgCl}_{(\mathrm{aq})} \\
& \mathrm{K}=\frac{[\mathrm{AgCl}]_{\mathrm{aq}}}{[\mathrm{AgCl}]_{\mathrm{s}}} \\
& \mathrm{Ag}^{+}+\mathrm{Cl}^{-} \\
& \mathrm{K}[\mathrm{AgCl}]_{\mathrm{s}}=\mathrm{K}_{1}=[\mathrm{AgCl}]_{\mathrm{aq}}
\end{aligned}
$$

The concentration of AgCl in a saturated solution is constant at any given temperature:

$$
\begin{aligned}
& \mathrm{K}_{2}=\frac{\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]}{[\mathrm{AgCl}]_{\mathrm{aq}}} \\
& \mathrm{~K}_{1} \mathrm{~K}_{2}=\mathrm{Ksp}-\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]
\end{aligned}
$$

The product of these two constants, Ksp , is called the solubility product constant.

## Buffer Solutions

Solutions containing both week acids and their salts or week bases and their salts. They have the capacity of resisting changes of pH when either acids or alkalies are added to them for example, suppose 1 ml of 0.1 M HCl is added to 99 ml of pure water $\mathrm{pH}_{7}$. The $\left[\mathrm{H}^{+}\right]$of the mixture will be about 0.001 M and its pH about 3 . Suppose, however, 1 ml of 0.1 M HCl is added to 99 ml of buffer solution containing 0.1 M acetic acid and 0.1 M sodium acetate. The pH of the buffer solution to begin with is 4.73 . When the HCl is added, the pH becomes about 4.72.

A similar condition exists when alkali is added to the buffer mixture. 1 ml of 0.1 M NaOH added to 99 ml of pure water gives a pH about 11 . Where as if it is added to 99 ml of the acetate buffer solution ( pH 4.73 ), the pH becomes 4.74 .

The chemical mechanism according to which buffers function may be illustrated by what happens when NaOH and HCl are added to an acetate buffer solution are as follows.


Upon addition of NaOH

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaOH} \longrightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}
$$

$$
\mathrm{CH}_{3} \mathrm{COONa}
$$

The addition of the alkali decreases the $\mathrm{CH}_{3} \mathrm{COOH}$ in the buffer and increases the $\mathrm{CH}_{3} \mathrm{COONa}$. The pH of the solution increases in proportion to the change in ratio of salt to acid in the buffer solution

## Upon addition of HCl

## $\mathrm{CH}_{3} \mathrm{COOH}$

$\mathrm{CH}_{3} \mathrm{COONa}+\mathrm{HCl} \longrightarrow \mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaCl}$
In this case the HCl reacts decrease $\mathrm{CH}_{3} \mathrm{COONa}$ and increase $\mathrm{CH}_{3} \mathrm{COOH}$ in the buffer. The pH of the solution falls in proportion to the change in ratio of salt to acid in the solution.

The Henderson - Hasselbalach equation for buffer solutions:
In the equilibrium reactions for the dissociation of HA and BA in a buffer solution, we have.
$\mathrm{HA} \rightleftharpoons \mathrm{H}^{+}+\mathrm{A}^{-}$, weakly dissociated

$$
\left\{\mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{CH}_{3} \mathrm{COO}^{-}\right\}
$$

$\mathrm{Ba} \longrightarrow \mathrm{B}^{+}+\mathrm{A}^{-}$, completely dissociated

$$
\left\{\mathrm{CH}_{3} \mathrm{COONa} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{Na}^{+}\right\}
$$

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

$$
\left[\mathrm{H}^{+}\right]=\mathrm{Ka} \frac{[\mathrm{HA}]}{\left[\mathrm{A}^{-}\right]} \quad \text { or }\left[\mathrm{H}^{+}\right]=\mathrm{Ka} \frac{[\mathrm{HA}]}{[\mathrm{BA}]} \text { or }\left[\mathrm{H}^{+}\right]=\mathrm{Ka} \frac{[\mathrm{Acid}]}{[\text { Salt }]}
$$

$$
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \mathrm{Ka} \frac{[\mathrm{HA}]}{[\mathrm{BA}]}
$$

$$
=-\left(\log \mathrm{Ka}+\log \frac{[\mathrm{HA}]}{[\mathrm{BA}]}\right)
$$

$$
=-\log \mathrm{Ka}-\log \frac{[\mathrm{HA}]}{[\mathrm{BA}]}
$$

$$
\begin{aligned}
& =-\log \mathrm{Ka}=\mathrm{pKa} \quad \text { and }-\log \quad \frac{[\mathrm{HA}]}{[\mathrm{BA}]} \log \frac{[\mathrm{BA}]}{[\mathrm{HA}]} \\
& \mathrm{pH}=\mathrm{pKa}+\log \quad \frac{[\mathrm{BA}]}{[\mathrm{HA}]} \text { or } \mathrm{pH}=\mathrm{pKa}+\log \frac{[\mathrm{salt}]}{[\mathrm{acid}]}
\end{aligned}
$$

A similar equation that would apply to a basic buffer is:

$$
\mathrm{pOH}=\mathrm{pK}_{\mathrm{b}}+\log \frac{[\text { salt }]}{[\text { base }]}
$$

Table $=$ salt - acid ratio and pH

| concentration |  |  | Percent |  |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{CH}_{3} \mathrm{COONa}$ | $\mathrm{CH}_{3} \mathrm{COOH}$ | ratio | dissociation |  |
| Molar | Normal | Salt / Acid | Of acid | pH |
| 0.00 | 0.2 | 0.00 | 1.00 | 2.7 |
| 0.01 | 0.2 | 0.05 | 0.20 | 3.4 |
| 0.05 | 0.2 | 0.25 | 0.04 | 4.1 |
| 0.10 | 0.25 | 0.50 | 0.02 | 4.4 |
| 0.15 | 0.2 | 0.75 | 0.012 | 4.6 |
| 0.20 | 0.2 | 1.00 | 0.01 | 4.7 |
| 0.30 | 0.2 | 1.50 | 0.006 | 4.9 |

## Capacity:

The larger the concentrations of the components of the buffer, the more effective it is at resisting changes in pH .

$$
\mathrm{pH}=\mathrm{pKa}+\log \frac{[\text { salt }]}{[\text { acid }]}
$$

Buffered solutions are very frequently used in (quantitative) analytical chemistry for example.

1. Ensure the proper progress of a reaction by removing $\mathrm{H}_{3} \mathrm{O}^{+}$or $\mathrm{OH}^{-}$reaction products as the save formed.
2. Control the level of pH during a precipitation process.
3. Maintain a required level of pH in order to guarantee the proper reaction of an indicator substance.
4. Are encountered at certain stages of titration processes.

Buffered solutions are of particular importance in most life processes. Many of the chemical mechanisms of body are pH - dependent; and as a case in point, the pH of human blood ranges about $\pm 0.05 \mathrm{pH}$ units around a value of 7.40 - Any marked change of a few tenths above or below this range can mean eventual death. Acid and base substances introduced into the system are usually carried by the blood as buffered form until the excesses (e.g., carbon dioxide and uric acid) can be removed by the lungs or kidneys. Changes in the normal level of the blood pH may provide for conditions, which prevent the buffering and transporting of such substances.

Analytical chemistry : deals with identification, characterization and measurement of the chemical species present in a sample.

Qualitative analysis : is to determine what the constituents are in the sample.

Quantitative analysis: is to determine how much of each of constituent is in the sample.

Thus the role of an analytical chemist is essential not only to chemical science but also to allied areas in biology, food science, medicine , biochemistry and engineering.

In pharmacology, accurate adjustment of a drug dose for an individual may necessitate the determination of its levels in the blood stream and in the pharmaceutical industry the quality of the manufactured drugs in tablet, solution, and emulsion form must be carefully controlled. Slight changes in composition or in purity of the drug itself can effect the therapeutic value.

## The analytical chemist and the analysis :-

The concept of measurement is basic to analytical chemistry. A simple measurement may involve properties such as mass, current, voltage, volume, or time. The measurement of such properties as absorption or emission of energy, optical rotation, over voltage, refractive index, equilibrium constant, rate constant, activation energy, or heat of reaction is more complex. Whether simple or complex, the reliability, utility, accuracy and specifity of these measurements are the responsibility of the analytical chemist. The analytical chemist is not only concerned with carrying out the analysis, but also with the how, why and where of using such measurements for analysis, separation, for the elucidation of the fundamental chemistry involved in problem.

## Volumetric Analysis:-

A quantitative analysis based upon the measurement of volume.

Titration:- Is the process by witch the quantity of analyte in a solution is determined from the amount of a standard reagent it consumes.

Standard solution:- The reagent of exactly known concentration that is used in a titration.

The concentration of a standard solution is established either directly or indirectly:-

1. By dissolving a carefully weighed quantity of the pure reagent and diluting to an exactly known volume.
2. By titrating a solution containing a weighed quantity of a pure compound with the reagent solution.

Standardization:- the process whereby the concentration of a standard solution is determined by titration of a primary standard is called a standardization.

Indicator:- is the chemical compound used to detect the end-point in volumetric analysis that exhibits a change in color as a result of concentration changes occurring near the equivalence point.

Primary standards:-
Good primary standards include the following:-

1. Highest purity.
2. Stability.
3. Absence of hydrate water.
4. Ready availability at reasonable cost.
5. Reasonably high equivalent weight.

## Standard solution:-

An ideal standard solution for titrimetric analysis would have the following properties:-

1. Its concentration should remain constant for months or years after preparation to eliminate the need for restandardization.
2. Its reaction with the analyte should be rapid, complete and can be described by balanced chemical equation.
3. A method must exist for detecting the equivalence point between the reagent and the analyte ; that is a satisfactory end point is required.

## End point in volumetric methods:-

End points are based upon a physical property which changes in characteristic way at or near the equivalence point in the titration. The most common end point involves as color changes due to the reagent, the analyte, or an indicator substance. Other physical properties, such as electrical potential, conductivity, temperature, and refractive index, have also been employed to locate the equivalence point in titrations.

It is convenient to classify volumetric methods according to four reaction types:-

1. Precipitation reactions:-
$\mathrm{AgNO}_{3}+\mathrm{NaBr} \longrightarrow \mathrm{AgBr}_{(\mathrm{s})}+\mathrm{NaNO}_{3}$
2. Neutralization reactions:-
$\mathrm{NaOH}+\mathrm{HCl} \longrightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{NaCl}$
3. Oxidation-reduction reaction:-
$\mathrm{Sn}^{+2}+\mathrm{Hg}^{2+}+\mathrm{Cl}^{-} \longrightarrow \mathrm{H}_{2} \mathrm{Cl}_{2}+\mathrm{Su}^{4+}$
4. Complex-formation reaction:-
$2 \mathrm{CN}^{-}+2 \mathrm{Ag}^{+} \longrightarrow \mathrm{Ag}\left[\mathrm{Ag}(\mathrm{CN})_{2}\right]_{(\mathrm{S})}$

## Theory of indicator:-

Acid-base indicators are generally organic compounds which behave as weak acids or bases. The dissociation or association reactions of indicators are accompanied by internal structural rearrangements that are responsible for the changes in color.

$$
\underset{\text { (acid color) }}{\mathrm{H}_{2} \mathrm{O}} \underset{\sim}{\mathrm{HIn}} \mathrm{H}_{3} \mathrm{O}^{+}+\underset{\text { (base color) }}{\mathrm{In}^{-}}
$$

Or


$$
\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]}
$$

And

$$
\mathrm{K}_{\mathrm{b}}=\frac{\left[\mathrm{InH}^{+}\right]\left[\mathrm{OH}^{-}\right]}{[\mathrm{In}]}
$$

The expressions can be rearranged to give :

$$
\frac{\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]}=\frac{\mathrm{Ka}}{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}
$$

And

$$
\frac{\left[\mathrm{InH}^{+}\right]}{[\mathrm{In}]}=\frac{\mathrm{K}_{\mathrm{b}}}{\left[\mathrm{OH}^{-}\right]}=\frac{\mathrm{K}_{\mathrm{b}}\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\mathrm{K}_{\mathrm{w}}}
$$

A solution containing an indicator will show a continuous change in the color with variations in pH . The human eye is not very sensitive to these changes, however typically, a five-to tenfold excess of one form is required before the color of that species appears predominant to the observer

$$
\begin{aligned}
& \frac{\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]} \leq \frac{1}{10} \\
& \frac{\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]} \geq \frac{10}{1}
\end{aligned}
$$

For the full acid color:

$$
\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{In}^{-}\right]}{[\mathrm{HIn}]}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] 1}{10}=\mathrm{Ka}
$$

$$
\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10 \mathrm{Ka}
$$

And similarly, for the full basic color:

$$
\begin{aligned}
& \frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] 10}{1}=\mathrm{Ka} \\
& {\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\frac{1}{10} \mathrm{Ka}}
\end{aligned}
$$

To obtain the indicator range, we take the negative logarithms of the two expressions. That is,

$$
\begin{aligned}
& \text { Indicator } \mathrm{pH} \text { range }=-\log 10 \mathrm{Ka} \text { to }-\log \frac{\mathrm{Ka}}{10} \\
& =-1+\mathrm{pKa} \text { to }-(-1)+\mathrm{pKa} \\
& =\mathrm{pKa} \pm 1 .
\end{aligned}
$$

## Spectrophotometric Method:

Many determinations made in the clinical laboratory are based upon measurements of radiant energy emitted, transmitted or absorbed.

## Components of Instruments for Absorption Measurements:

1. power supply.
2. a source of radiant energy, usually containing a large group of wave lengths, e.g., a tungsten lamp.
3. a monochromator e.g., a filter, prism, or diffraction gratting
4. a simple container to hold the sample and blank e.g., cuvette.
5. a detector system to detect the transmitted radiant energy and convert it into electrical energy so that it may be measured, e.g., a photocell.
6. a signal indicator, e.g., a meter reading percent T or absorbance.

major components of a single beam spectrophotometer


$$
\xrightarrow{\text { Io }}|\mathrm{Ia}| \xrightarrow{\text { It }}
$$

$$
\mathbf{I o}=\mathbf{I a}+\mathbf{I t}
$$

$$
\begin{array}{ll} 
& \begin{array}{l}
\text { Io }=\text { incident radiation power } \\
\mathrm{A}=\log \frac{\mathrm{It}}{\mathrm{Io}}
\end{array} \\
& \begin{array}{l}
\mathrm{It}=\text { transmitted radiation power } \\
\mathrm{A}=\text { absorbance }
\end{array} \\
\mathrm{T} \%=\frac{\mathrm{Io}}{\mathrm{It}} \times 100 & \mathrm{~T}=\text { Transmittance } \\
\mathrm{T} \%=\text { percent Transmittance } \\
\ell=\text { path length } \\
\mathrm{A} \alpha \ell & \varepsilon=\text { molar absorptivity } \\
\mathrm{A} \alpha \mathrm{C} & \mathrm{C}=\text { concentration } \\
\mathrm{A}=\varepsilon \ell \mathrm{C} & \\
\mathrm{~A}=\log \mathrm{T} &
\end{array}
$$


[^0]:    * gram - equivalents $=$

