

# General Chemistry

## References:

- 1- General chemistry by Darrell D. Ebbing, 2007.
  - 2- fundamentals-of-chemistry by Romain Elsaid, 2012.
  - 3- Fundamentals of Analytical Chemistry by Skoog and West 2012.
  - 4- Basic concepts in biochemistry by Hiram F. Gilbert, 2000.
  - 5- Organic chemistry by Morrison and Boyd 7<sup>th</sup>, 2010.
  - 6- Instant Notes in General Chemistry by Mohammed Abdul Baset, Printed by Dar Alayam, Amman-Jordan, 2014, 299 p.
- 

## Lectures 1, 2

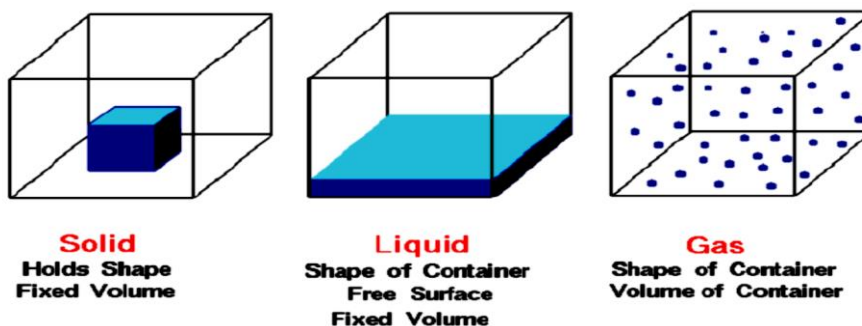
Dr. Mohammed Abdul Baset

### An introduction to chemistry

#### Matter

- Matter is anything which has mass and takes up space (volume)
- Examples of matter: Sand (a solid), Water (a liquid), Air (a mixture of gases)

**Solids** have shape and volume. **Liquids** have volume but adopt the shape of their container. **Gases** occupy the shape and volume of their container.



#### Substances

A substance is a form of matter that has constant chemical composition and characteristic properties. There are two kinds of substances—elements and compounds. Element is a pure chemical substance consisting of one type of atom. Compound is a pure chemical substance consisting of two or more different chemical elements.

#### Physical Properties

The properties related to the *state* (gas, liquid, or solid) or appearance of a sample are called *physical properties*. Some commonly known physical properties are density, state at room temperature, color, hardness, melting point, and boiling point.

#### Chemical Properties

A chemical property is a change in which at least one substance changes its composition and its set of properties. Examples: flammability, rust resistance, reactivity.

## Classification of matter (substance)

Therefore, matter is classified according to several different schemes. Matter may be classified as **organic** or **inorganic**. Other schemes are based on *chemical properties* of the various classes. For example, substances may be classified as **acids**, **bases**, or **salts**. In the method of classification of matter based on composition, a given specimen of material is regarded as either a *pure substance* or a *mixture*.

### Pure substance

Matter that has a constant composition and fixed properties.

### Mixture

A physical blend of matter that can theoretically be physically separated into two or more components.

### Homogeneous matter

Matter that has the same properties throughout the sample.

### Solutions

Homogeneous mixtures of two or more pure substances.

### Heterogeneous matter

Matter with properties that are not the same throughout the sample.

### Molecule

A **molecule** is comprised of two or more **chemically bonded** atoms. The atoms may be of the same type of element, or they may be different.

- **Molecular formulas** refer to the **actual** number of the different atoms which comprise a single molecule of a compound.
- **Empirical formulas** refer to the **smallest whole number ratios** of atoms in a particular compound.

Compound	Molecular Formula	Empirical Formula
Water	H <sub>2</sub> O	H <sub>2</sub> O
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	HO
Ethylene	C <sub>2</sub> H <sub>4</sub>	CH <sub>2</sub>
Ethane	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub>

### Ion

An ion is a particle (an atom or group of atoms) carrying positive or negative charge. Sometimes atoms gain or lose electrons. **Positive Ion (cation)** - Occurs when an atom **loses an electron**, it has more protons than electrons. **Negative Ion (anion)** - Occurs when an atom **gains an electron**, it will have more electrons than protons.

### Atoms

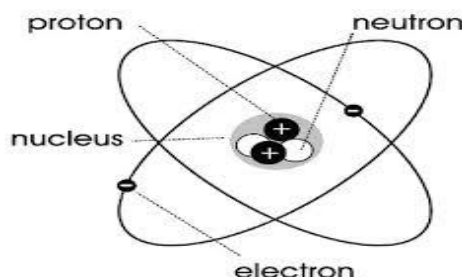
Atoms are the basic unit of chemistry. They consist of 3 smaller things:

**Protons** - these are positively charged (+)

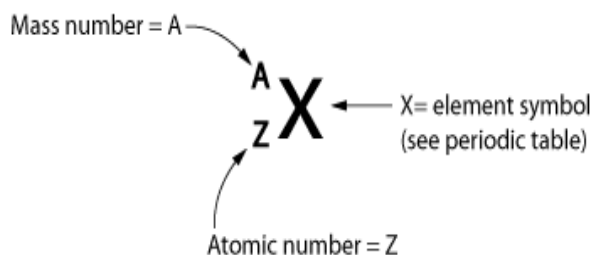
**Electrons** - these are negatively charged (-)

**Neutrons** - these have no charge

These 3 smaller particles are arranged in a particular way. In the center is the **Nucleus** where you find the positive Protons and neutral Neutrons. In orbit around the nucleus are the Electrons.



We use the following symbol to describe the atom:



### Atomic number of an atom

A number equal to the number of protons in the nucleus of an atom. Symbolically it is represented by **Z**.

$$Z = \text{Nuclear charge} = \text{number of protons}$$

### Mass number of an atom

A number equal to the sum of the number of protons and neutrons in the nucleus of an atom. Symbolically it is represented by **A**.

$$A = \text{Mass Number} = \text{Number of protons} + \text{Number of neutrons}$$

## Periodic Table of the Elements

### Periods and Groups

- The **periodic table** is a tabular arrangement of the chemical elements, organized on the basis of their atomic numbers, electron configurations (electron shell model), and recurring chemical properties.
- The first reasonably successful attempt was made by **Dimitri Mendeleev** in 1869. He had the idea of arranging elements in order of **increasing atomic mass**, and, most importantly, found that elements with similar chemical and physical properties occurred **periodically**. He placed these similar elements under each other in columns.
- In 1914, **Henry Moseley** determined that a better arrangement was in order of increasing atomic number, giving us the periodic table we have today.
- We can define the periodic table as an arrangement of elements in order of **increasing atomic number** placing those with similar chemical and physical properties in columns.
- The basic structure of the periodic table is its division into rows and columns, or periods and groups. A **period** consists of *the elements in any one horizontal row of the periodic table*. A **group** consists of *the elements in any one column of the periodic table*.

1 1A H																	18 8A He														
2 Li																	10 Ne														
3 3B Sc	4 4B Ti	5 5B V	6 6B Cr	7 7B Mn	8 8B Fe	9 8B Co	10 8B Ni	11 1B Cu	12 2B Zn	13 3A Al	14 4A Si	15 5A P	16 6A S	17 7A Cl	18 8A Ar																
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr														
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe														
55 Cs	56 Ba	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	113	114	115	116	117	118

- The groups are usually numbered. The numbering frequently seen in North America labels the groups with Roman numerals and A's and B's. In Europe, a similar convention has been used, but some columns have the A's and B's interchanged.
- To eliminate this confusion, the International Union of Pure and Applied Chemistry (IUPAC) suggested a convention in which the columns are numbered 1 to 18. When we refer to an element by its periodic group, we will use the traditional North American convention. The A groups are called main-group (or representative) elements; the B groups are called transition elements. The two rows of elements at the bottom of the table are called inner transition elements (the first row is referred to as the lanthanides; the second row, as the actinides).

### 1. Metals

- solids at room temperature (except Hg)
- metallic luster
- malleable and ductile
- good conductors of heat and electricity

### 2. Non-metals

- gases or solids at room temperature (except Br<sub>2</sub>)
- variety of color and appearance
- brittle solids
- insulators (poor conductors)

### 3. Metalloids (semimetal)

- intermediate in properties between metals and non-metals
- solids at room temperature
- many have more than one structure (one metallic, the other non-metallic)
- some are semi-conductors

## Main Group Elements (Vertical Groups)

**Group 1(IA) - Alkali Metals**

**Group 2(IIA) - Alkaline Earth Metals**

**Group 13(IIIA) - Boron Family**

**Group 14(IVA) - Carbon Family**

**Group 15(VA) - Nitrogen Family**

**Group 16(VIA) - Oxygen Family (Chalcogens)**

**Group 17(VIIA) - Halogens**

**Group 18(VIIIA) - Noble Gases**

## Other Groups ( Vertical and Horizontal Groups)

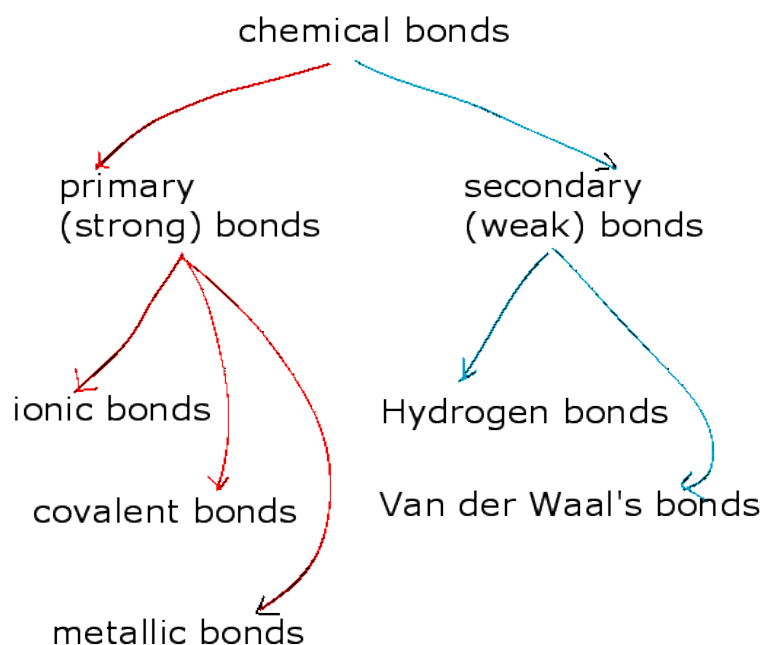
**Group 3-12(1B - 8B) - Transition Metals**

**Period 6 Group - Lanthanides (Rare Earth Elements)**

**Period 7 Group - Actinides**

## The Chemical Bond

A *chemical bond* is a strong force of attraction, which holds atoms together in molecules.



### The Classification of Chemical Bonds

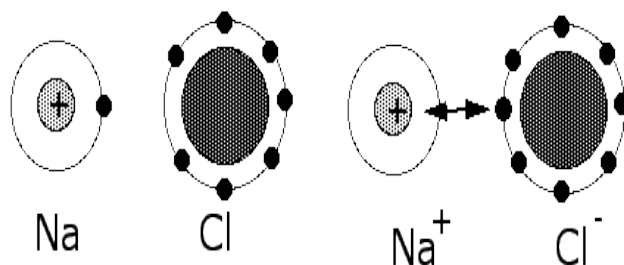
There are two major bond classifications, each with identifiable sub-groups:

#### Primary Bonds (Strong 100-1000 Kj/mol)

The three types of primary bonding reflect these ways in which atoms can group together by gaining or losing or sharing electrons, so they can get inert gas electron configurations.

#### 1. Ionic Bonds

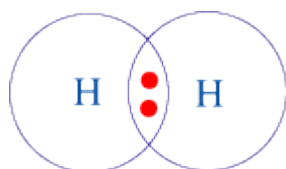
Atoms near the left or right sides of the periodic table can lose or gain 1 (or 2) electrons to form charged "ions". For example, a Sodium atom (row 3, column IA) can lose one electron to have 8 valence electrons and become a positively charged "cation". A Chlorine atom (row 3, column VIIA) can gain one electron to have 8 valence electrons and become a negatively charged "anion".



## 2. Covalent Bonds

In **covalent bonding** atoms share electrons.

Take for example the  $H_2$  molecule. Since each hydrogen has only one electron, when two hydrogens get together they can share their electrons.



Pure hydrogen exists as  $H_2$  molecules.

## 3. Metallic Bonds

The atoms are ionized, losing some electrons from the valence band. Those electrons form an electron sea, which binds the charged nuclei in place.

Metallic bonding occurs between the positive atom cores and the "nearly free" electrons.

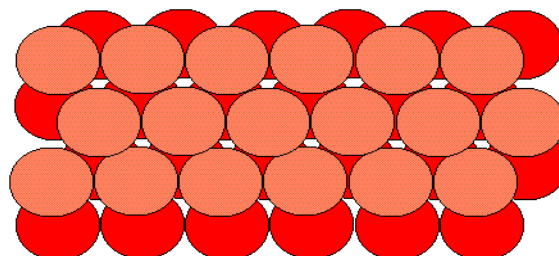
In metallic bonding:

- there are no charge requirements,
- there are no directional requirements, and
- there are long range effects.

This means that in metallic bonding the atoms pack together as closely as possible.

Metallic solids occur when large numbers of atoms bond together in close-packed structures.

They can be modelled as ping-pong balls glued together as shown in the diagram.



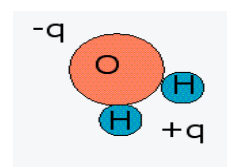
## Secondary Bonds (Weak <100 KJ/mol)

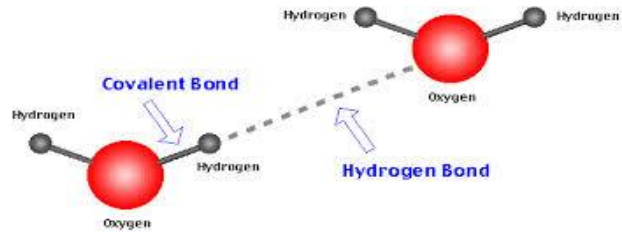
No electrons transferred or shared. Secondary or weak bonds are formed when there is effectively a partial and/or momentary charge.

### 1. Hydrogen bonding

Hydrogen bonding is the most common type of bonding between permanent dipoles. The situation that leads to Hydrogen bonding arises with a normal bond between a Hydrogen atom and a neighbor. Since any other atom will bind the electron from the Hydrogen atom more tightly, the electron will spend more time with the other atom. This creates a permanent dipole (a partially exposed proton) that can interact with other dipoles nearby.

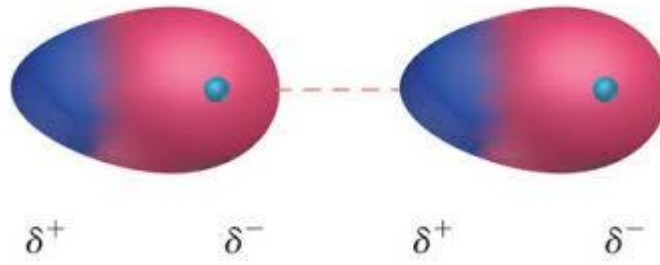
The water molecule ( $H_2O$ ) is the classic situation, where the Oxygen molecule binds electrons from both Hydrogen atoms more tightly than Hydrogen can. Hydrogen bonding between water molecules makes ice less dense than water so, in winter, rivers freeze down from the top and not up from the bottom, enabling life to survive.





## 2. Van der Waals Bonds

The dipoles involved in Van der Waals bonding come from fluctuations in the symmetry of the electron distribution surrounding the nucleus of an atom. Momentary electric dipoles are set up and give rise to weak, very short-range, non-directional attractive forces between molecules or atoms. Example: Ni atom



## Preparation of standard solution

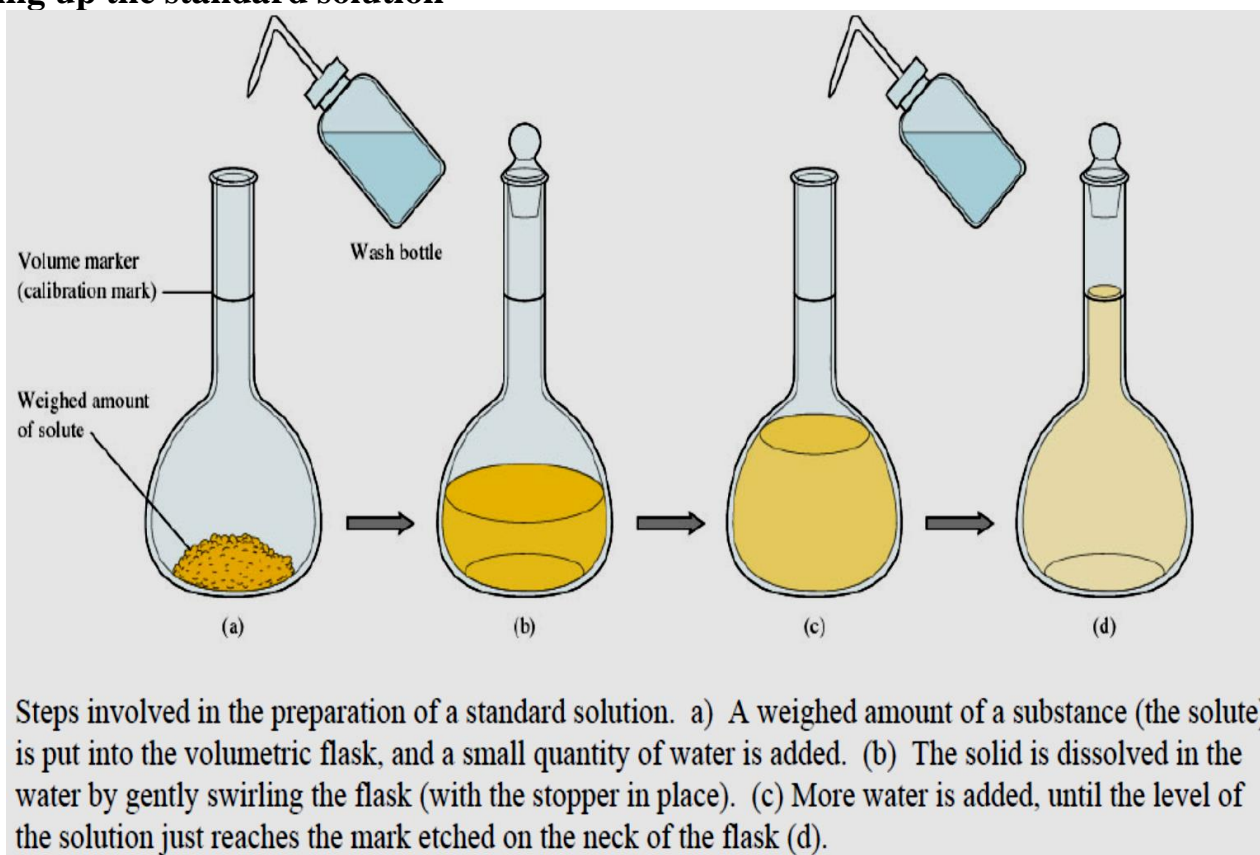
### What is a standard solution?

A standard solution is a solution whose concentration is known accurately. Its concentration is usually given in  $\text{mol dm}^{-3}$ .

$$\text{moles} = \text{concentration} \times \text{volume}$$

Concentration is in  $\text{mol dm}^{-3}$  ... and ... volume is in  $\text{dm}^3$ , so if the volume is given in  $\text{cm}^3$ , divide it by 1000 to get  $\text{dm}^3$

### Making up the standard solution



### Primary and secondary Standards solutions

A **primary standards** is a highly purified compound that serves as a reference material in titrations and in other analytical methods.

Important requirements for a primary standard are the following:

1. High purity.
2. Atmospheric stability (no sensitive to atmospheric oxygen)
3. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.
4. Modest cost.
5. They are powerful reactants
6. They have known formula and molecular weight
7. They are usually high molecular weight compounds

## Secondary standard solution:

A secondary standard solution is the one that must be standardized before use. This is because a secondary standard solution is not in its stable form. An example is the solution of NaOH.

## Secondary standards are

1. Influenced by atmosphere/environment
2. Concentration change over time
3. Usually powerful reactants
4. Usually cheap & easy to use

Chemists make two common types of "standard solutions":

- **Molar solutions**
- **Normal solutions**

A **Molar solution (M)** is a solution that contains 1 mole of solute in each litre of solution. A mole is the molecular weight (MW) expressed as grams (sometimes referred to as the 'gram molecular weight' (gMW)). Therefore, 1 M = 1 gMW of solute per litre of solution.

A **Normal solution (N)** is a solution that contains an equivalent weight of solute in one liter of solution. The preparation of a normal solution is based upon dissolving an equivalent weight of an equivalent single positive ionic species. Sometimes this is called the equivalent (molecular) weight.

## Important Units of Measurement

### 1- The Distinction between Mass and Weight

**Mass** is an invariant measure of the quantity of matter in an object. **Weight** is the force of attraction between an object and its surroundings, principally the earth.

Weight and mass are related by the familiar expression:

$$w = mg$$

Where  $w$  is the weight of an object,  $m$  is its mass, and  $g$  is the acceleration due to gravity.

### 2- Density

Density is defined as [mass](#) per unit volume.

$$\rho = \frac{m}{V}$$

density = mass / volume

The density of water is 1 gram/cm<sup>3</sup> since water was used as an early mass standard, one gram being informally defined as the mass of 1 cm<sup>3</sup> of water.

### 3- The Mole

A mole (also known as Avogadro's Number) is the amount of substance that contains as many elementary particles (atoms, ions, molecules) as there are in 12g of carbon-12 atoms.

**There are three definitions (equalities) of mole. They are:**

1 mole =  $6.02 \times 10^{23}$  particles

1 mole = molar mass (could be atomic mass from periodic table or molecular mass)

1 mole = 22.4 L of a gas

**Each definition can be written as a set of two conversion factors. They are:**

1 mole = molar mass (g) can be written as  $\left( \frac{1 \text{ mole}}{\text{molar mass (g)}} \right)$  OR  $\left( \frac{\text{molar mass (g)}}{1 \text{ mole}} \right)$

1 mole =  $6.02 \times 10^{23}$  particles can be written as  $\left( \frac{1 \text{ mole}}{6.02 \times 10^{23}} \right)$  OR  $\left( \frac{6.02 \times 10^{23}}{1 \text{ mole}} \right)$

## Units of Concentration

1) **Molarity: M** = moles of solute contained in one liter of solution.

$$\text{Molarity} = M = \frac{\text{moles of solute}}{\text{Volume of solution}} = \text{moles/L}$$

2) **Normality: N** = moles of reactive units per liter (equivalents per liter)

$$N = \frac{(1000)(\text{grams of solute})}{(\text{equivalent wt. of solute})(\text{ml of solution})}$$

$$N = n \times M$$

Where  $n$  is number of equivalents

### Example

5 grams of sodium hydroxide (NaOH) were dissolved in enough water to give 200 ml of solution. Calculate the normality of the solution.

### Solution

$$N = \frac{(1000)(5)}{(40)(200)} = .625$$

3) **Percent Composition by Mass (%) or weight Percent (% w/w)**

Use the following equation to calculate percent by mass:

$$\text{weight percent (w/w)} = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$$

4) **Volume Percent (% v/v)**

Volume percent or volume/volume percent most often is used when preparing solutions of liquids. Volume percent is defined as:

$$\text{volume percent (v/v)} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

5) **Weight/volume Percent (% w/v)**

$$\text{weight/volume percent (w/v)} = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$$

6) **Molality**

Molality,  $m$ , tells us the number of moles of solute dissolved in exactly one kilogram of solvent. (Note that molality is spelled with two "l"s and represented by a lower case  $m$ .)

We need two pieces of information to calculate the molality of a solute in a solution:

- The moles of solute present in the solution.
- The mass of solvent (in kilograms) in the solution.

To calculate molality we use the equation:

$$\text{Molality} = \frac{\text{moles of solute}}{\text{mass of solvent in kilograms}}$$

### 7) Mole Fraction

The mole fraction,  $X$ , of a component in a solution is the ratio of the number of moles of that component to the total number of moles of all components in the solution.

The mole fraction of A,  $X_A$ , in a solution consisting of A, B, C, ... is calculated using the equation:

$$X_A = \frac{\text{moles of A}}{\text{moles of A} + \text{moles of B} + \text{moles of C} + \dots}$$

To calculate the mole fraction of B,  $X_B$ , use:

$$X_B = \frac{\text{moles of B}}{\text{moles of A} + \text{moles of B} + \text{moles of C} + \dots}$$

### 8) Parts per notation

For very dilute solutions, part per million (ppm) is a convenient way to express concentration:

$$c_{\text{ppm}} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \text{ ppm}$$

Where  $C_{\text{ppm}}$  is the concentration in parts per millions.

ppm (parts-per-million,  $10^{-6}$ ), ppb (parts-per-billion,  $10^{-9}$ ), ppt (parts-per-trillion,  $10^{-12}$ ) and ppq (parts-per-quadrillion,  $10^{-15}$ ).

#### How to convert ppb to ppm?

$$1 \text{ ppm} = 1/10^6 = 10^{-6}$$

$$1 \text{ ppb} = 1/10^9 = 10^{-9}$$

So

$$1 \text{ ppm} = 1000 \text{ ppb}$$

#### How to convert grams/liter to ppm

$$C_{(\text{ppm})} = 1000 \times C_{(\text{g/kg})} = 10^6 \times C_{(\text{g/L})} / \rho_{(\text{kg/m}^3)}$$

#### How to convert moles/liter to ppm

$$C_{(\text{ppm})} = C_{(\text{mg/kg})} = 10^6 \times c_{(\text{mol/L})} \times M_{(\text{g/mol})} / \rho_{(\text{kg/m}^3)}$$

#### How to convert percent to ppm

The part P in percent (%) is equal to the part P in ppm divided by 10000:

$$P_{(\%)} = P_{(\text{ppm})} / 10000$$

## How to convert ppm to percent

The part P in ppm is equal to the part P in percent (%) times 10000

$$P_{(\text{ppm})} = P_{(\%) } \times 10000$$

## 9) Formality

Number of formula weight of a solute per litre of solution. It is represented by (F).

$$F = \frac{\text{Weight of solute in g / Formula weight}}{\text{Volume of solution in litre}}$$

Formal solutions generally show changes in formality where volume changes associated with temperature.

## 10) Diluting Solutions

Mathematically the relationship of diluting solution can be shown in the [equation](#):

$$M_1 V_1 = M_2 V_2$$

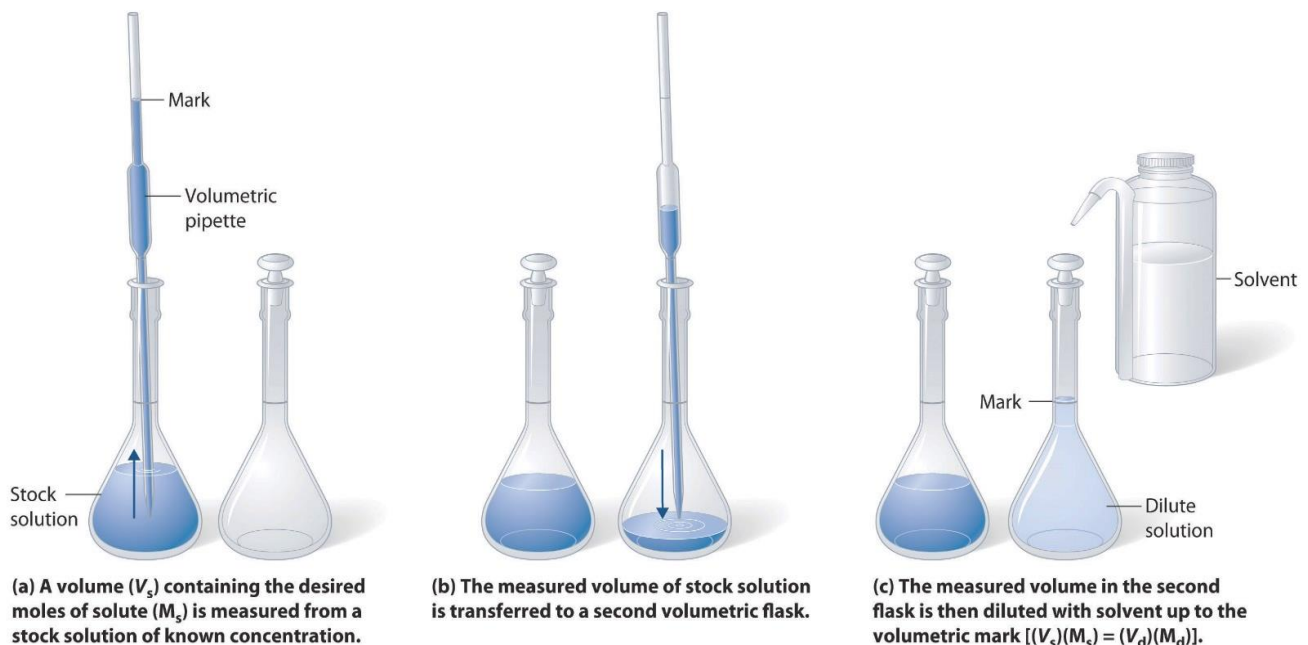
Where:

$C_1$  = Initial concentration or molarity.

$V_1$  = Initial volume.

$C_2$  = Final concentration or molarity.

$V_2$  = Final volume



## General dilution formula

$$M_c \times V_c = M_d \times V_d$$

concentrated

dilute

OR

$$M_f \times V_f = M_i \times V_i$$

final

initial

OR

$$M_1 \times V_1 = M_2 \times V_2$$

Solution 1

Solution 2

**Examples:**

1. 25.00 mL of a vinegar solution was diluted to 250.0 mL. The concentration of the diluted vinegar solution was determined to be 0.08527 M. What was the concentration of the original vinegar ?

<u>Conc'd Solution</u>	<u>Dilute Solution</u>
Vc = 25.00 mL	Vd = 250.0 mL
<b>Mc = ??????</b>	Md = 0.08527 M

Note: - The **volume increased 10 times**  
(10-fold dilution)  
- The **concentration must have decreased 10 times**  
(Mc = 0.8527 M)

Mathematically: **Mc x Vc = Md x Vd**

$$Mc = \frac{Md \times Vd}{Vc} = \frac{(0.08527 \text{ M})(250.0 \text{ mL})}{25.00 \text{ mL}} = \mathbf{0.8527 \text{ M}}$$

2. 1.00 mL of a solution of  $6.00 \times 10^{-4}$  M ferric chloride is diluted to 15.00 mL by addition of water. What is the concentration of the diluted solution ?

<u>Concentrated Solution</u>	<u>Dilute Solution</u>
V <sub>1</sub> = 1.00 mL	V <sub>2</sub> = 15.00 mL
M <sub>1</sub> = $6.00 \times 10^{-4}$ M	<b>M<sub>2</sub> = ???</b>

$$M_1 \times V_1 = M_2 \times V_2$$

$$M_2 = \frac{M_1 V_1}{V_2} = \frac{(6.00 \times 10^{-4} \text{ M})(1.00 \text{ mL})}{15.00 \text{ mL}} = 4.00 \times 10^{-5}$$

## Statistical treatment of analytical data

### 1. The Mean, the Median and the mode

The **mean** (or **average**) of a set of data values is the sum of all of the data values divided by the number of data values. That is:

$$\text{Mean} = \frac{\text{Sum of all data values}}{\text{Number of data values}}$$

Symbolically,

$$\bar{x} = \frac{\sum x}{n}$$

where  $\bar{x}$  (read as 'x bar') is the mean of the set of  $x$  values,  
 $\sum x$  is the sum of all the  $x$  values, and  
 $n$  is the number of  $x$  values.

#### Example 1:

The marks of seven students in a mathematics test with a maximum possible mark of 20 are given below 15 13 18 16 14 17 12.  
Find the mean of this set of data values.

Solution:

$$\begin{aligned}\text{Mean} &= \frac{\text{Sum of all data values}}{\text{Number of data values}} \\ &= \frac{15+13+18+16+14+17+12}{7} \\ &= \frac{105}{7} \\ &= 15\end{aligned}$$

So, the mean mark is **15**.

#### Example 2:

Find the mean of these numbers: 3, -7, 5, 13, -2  
The sum of these numbers is  $3 - 7 + 5 + 13 - 2 = 12$   
There are 5 numbers.

$$\text{Mean} = \frac{3 - 7 + 5 + 13 - 2}{5} = \frac{12}{5} = 2.4$$

The **median** of a set of data values is the middle value of the data set when it has been arranged in ascending order. That is, from the smallest value to the highest value.

**Example 1:**

The marks of nine students in a geography test that had a maximum possible mark of 50 are given below: 47 35 37 32 38 39 36 34 35.

Find the median of this set of data values.

Solution:

Arrange the data values in order from the lowest value to the highest value:

32 34 35 35 36 37 38 39 47

The fifth data value, 36, is the middle value in this arrangement.

Median = **36**

**In general:**

Median =  $\frac{1}{2}(n+1)$ th value, where  $n$  is the number of data values in the sample

If the number of values in the data set is even, then the **median** is the average of the two middle values.

**Example 2:**

Find the median of the following data set: 12 18 16 21 10 13 17 19

Solution:

Arrange the data values in order from the lowest value to the highest value:

10 12 13 16 17 18 19 21

The number of values in the data set is **8**, which is even. So, the median is the average of the two middle values.

$$\begin{aligned} \therefore \text{Median} &= \frac{4\text{th data value} + 5\text{th data value}}{2} \\ &= \frac{16+17}{2} \\ &= \frac{33}{2} \\ &= 16.5 \end{aligned}$$

The **mode** is the data value that appears the most in the set.

**Example:**

The following is a list of heights (in inches) of a high school basketball team:

67,66,70,74,72,68,71,75,68,72,71,68

To determine the **mode** all we need to do is determine which, if any, of the data values appear the most.

If you look carefully you will see that several of the values appear more than once, but only one of the values appears the most...

There are 2-71's, and 2-72's,  
 BUT, there are 3-68's!  
 So, the mode of this set is **68!**

## 5. Precision or accuracy

**Precision** is how close the measured values are to **each other**.

$$\text{precision} = \frac{\text{number of true positives}}{\text{number of true positives} + \text{false positives}}$$

Three terms are widely used to describe the precision of a set of replicate data: **standard deviation, variance, and coefficient of variation**.

The **Standard Deviation** is a measure of how spread out numbers are.  
 Its symbol is  $\sigma$  (the greek letter sigma)

The formula is easy: it is the square root of the **Variance**.

The **Variance** is defined as: The average of the **squared** differences from the Mean.

### Example:

You grow 5 crystals from a solution and measure the length of each crystal in millimeters. Here is your data: 600mm, 470mm, 170mm, 430mm and 300mm.  
 Find out the Mean, the Variance, and the Standard Deviation?

Solution:

$$\text{Mean} = \frac{600 + 470 + 170 + 430 + 300}{5} = \frac{1970}{5} = 394$$

To calculate the Variance, take each difference, square it, and then average the result:

$$\begin{aligned} \text{Variance: } \sigma^2 &= \frac{206^2 + 76^2 + (-224)^2 + 36^2 + (-94)^2}{5} \\ &= \frac{42,436 + 5,776 + 50,176 + 1,296 + 8,836}{5} \\ &= \frac{108,520}{5} = 21,704 \end{aligned}$$

So, the **Variance** is **21.704**.

And the Standard Deviation is just the square root of Variance, so:

**Standard Deviation:**  $\sigma = \sqrt{21.704} = 147.32... = 147$  (to the nearest mm)

The **coefficient of variation** (CV) as a percent is

$$\text{CV} = \frac{\text{Standard deviation}}{\text{mean}} \times 100$$

If the mean is 100 and the standard deviation is 5 then the coefficient of variation is 5%.

## 6. Random and Absolute Error

**Absolute error** is the amount of physical error in a measurement, period.

$$(\text{Absolute Error} = \text{Actual Value} - \text{Measured Value})$$

The **absolute error** (E) in the measurement of a quantity x is given by the equation:

$$E = x_i - x_t$$

where  $x_i$  is the true or accepted value of the quantity.

**Random errors** in experimental measurements are caused by unknown and unpredictable changes in the experiment. These changes may occur in the measuring instruments or in the environmental conditions.

## 7. Relative Error

**Relative error** gives an indication of how good a measurement is relative to the size of the thing being measured.

To calculate the relative error use the following way:

Observe the true value (x) and approximate measured value ( $x_o$ ). Then find the absolute deviation using formula:

$$\text{Absolute deviation } \Delta x = \text{True value} - \text{measured value} = x - x_o$$

Then substitute the absolute deviation value  $\Delta x$  in relative error formula given below:

$$\text{Relative error} = \frac{\Delta x}{x}$$

The relative error formula is given by

$$\text{Relative error} = \frac{\text{Absolute error}}{\text{Value of thing to be measured}} = \frac{\Delta x}{x}$$

In terms of percentage it is expressed as

$$\text{CV} = \frac{\Delta x}{x} \times 100 \%$$

Here  $\Delta x$  and x are absolute error and true value of the measurement.

### Example:

Student measures the size of metal ball as 3.97 cm but the actual size of it is 4 cm. Calculate the absolute error and relative error.

### Solution:

The measured value of metal ball  $x_o = 3.97$  cm

The true value of ball  $x = 4$  cm

$$\text{Absolute error } \Delta x = \text{True value} - \text{Measured value} = X - X_o = 4\text{cm} - 3.97\text{cm} = 0.03 \text{ cm}$$

$$\text{Relative error} = \frac{\Delta x}{x} = \frac{0.03}{4}$$

Relative error = *0.0075*.

## **8. Systematic errors**

The discrepancy between an accepted value of a parameter and an experimentally measured value results from deviations in the manner in which the measurement is carried out. No two measurements are exactly the same.

## Chemical Reactions

**Chemical reaction**, a process in which one or more substances, the reactants, are converted to one or more different substances, the products.

### Evidence for a chemical reactions

Rusting metal, candle burning, burning natural gas, bread making, automobile, fuel consumption, you hearing my voice, hand waving, burning of natural gas, blame, heat, smell, and moisture.

### Typical gross clues of chemical reactions

1. The color changes
2. Physical form changes
3. Bubbles form
4. Heat is produced or is absorbed

## 1. Balancing chemical Equation

### How to write and balance equations

1. Carefully read the description of the reaction. Know names of reactants from products.
2. Write the appropriate formulas for reactants and products.
3. Write a preliminary unbalanced equation that restates 1.
4. Balance the equation by inspection, starting with the most complicated molecule.

\*Do not change the identities of reactants and products.

\*An atom may be present as an element, a compound, or an ion.

\*Coefficients used must give the smallest integers to give a balanced equation.

### Examples:

#### 1-

Aluminum reacts with copper (II) chloride  $\text{CuCl}_2$  to form copper metal and aluminum chloride  $\text{AlCl}_3$ . Write the balanced equations for this reactions.

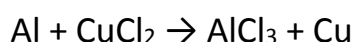
1. Identify the reactants and products.

Aluminum and copper (II) chloride are the reactants, and aluminum chloride and copper are the products.

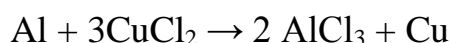
2. Write a word equation for the reaction.

aluminum + copper (II) chloride  $\rightarrow$  aluminum chloride + copper

3. Write the equation using formulas for the reactants and products.

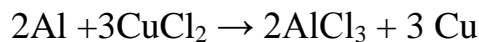


4. Balance the equation one element at a time. The same number of each type of atom must appear on both sides. To balance the number of chlorine atoms, you must multiply the amount of copper (II) chloride by 3 and multiply the amount of aluminum chloride by 2.



Atom	Reactants	Products	Balance
Al	2	2	✓
Cu	3	1	×
Cl	6	6	✓

To balance the equation, multiply the amount of copper produced by 3.



Atom	Reactants	Products	Balance
Al	2	2	✓
Cu	3	3	✓
Cl	6	6	✓

2-

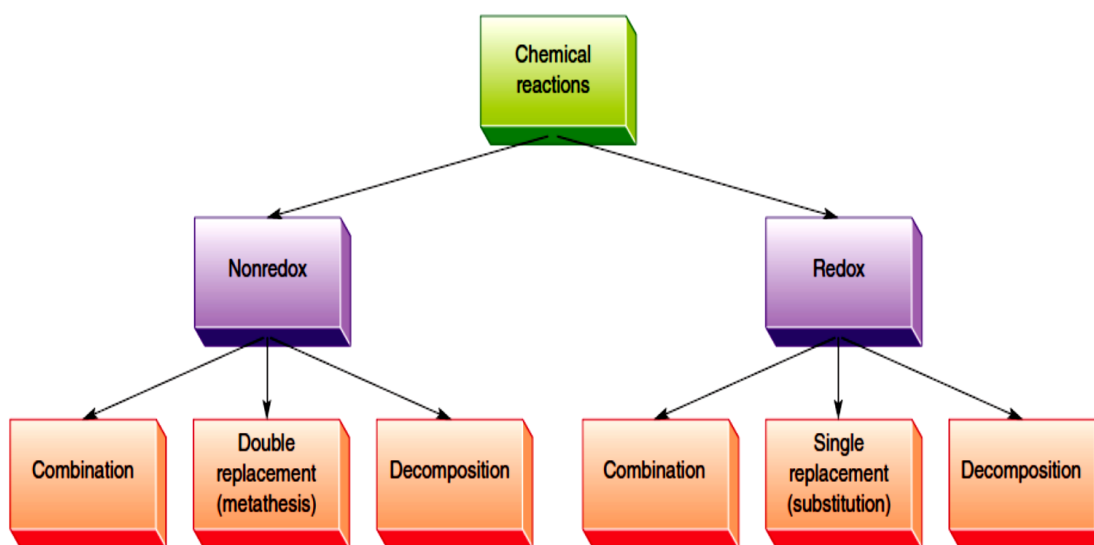


BALANCING A CHEMICAL EQUATION:



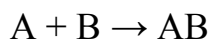
## 2. Types of chemical reactions

Most inorganic reactions can be classified into one of five general categories: direct union or combination, decomposition, displacement, metathesis or double displacement, and combustion reactions. Each of these will be discussed in more detail in the following:



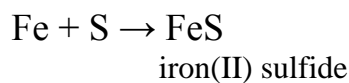
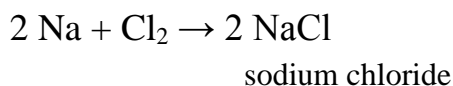
### 1. Direct Union or Combination Reactions

Any reaction in which two or more substances combine to form a single product is a *direct union* or *combination* reaction. The general form of a direct union reaction is

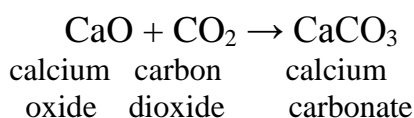
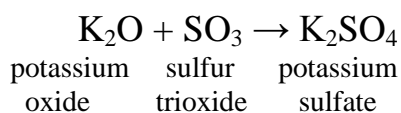


This type of reaction generally takes place between the following types of compounds:

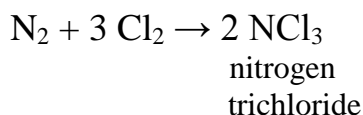
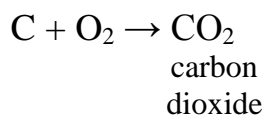
**a. A metal + non-metal**



**b. Metal oxide + non-metal oxide**



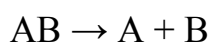
**c. Non-metal + non-metal**



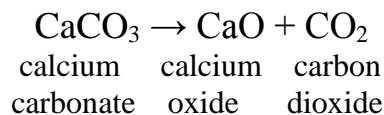
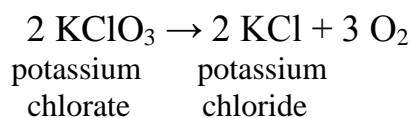
1 H																	2 He																														
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne																														
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar																														
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr																														
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe																														
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn																														
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo																														
<table border="1" style="width: 100%; text-align: center;"> <tr> <td>57 La</td><td>58 Ce</td><td>59 Pr</td><td>60 Nd</td><td>61 Pm</td><td>62 Sm</td><td>63 Eu</td><td>64 Gd</td><td>65 Tb</td><td>66 Dy</td><td>67 Ho</td><td>68 Er</td><td>69 Tm</td><td>70 Yb</td><td>71 Lu</td> </tr> <tr> <td>89 Ac</td><td>90 Th</td><td>91 Pa</td><td>92 U</td><td>93 Np</td><td>94 Pu</td><td>95 Am</td><td>96 Cm</td><td>97 Bk</td><td>98 Cf</td><td>99 Es</td><td>100 Fm</td><td>101 Md</td><td>102 No</td><td>103 Lr</td> </tr> </table>																		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr
57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu																																	
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr																																	

**2. Decomposition Reactions**

In a decomposition reaction a compound is broken down into smaller compounds or separate elements. A decomposition reaction is the reverse of a synthesis reaction. The general form for a decomposition reaction is:

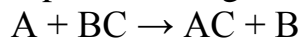


Some examples of decomposition reactions are:



### 3. Single Replacement Reactions (Substitution)

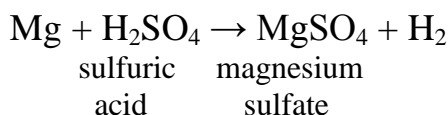
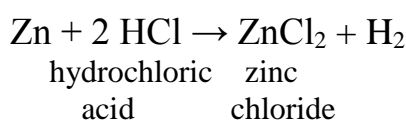
A single replacement involves an element reacting with a compound whereby the element displaces a second element from the compound. The general form of this type reaction is:



Single replacement reactions usually occur between the following combinations:

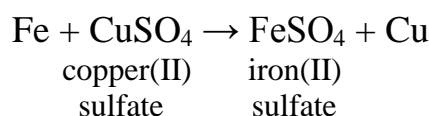
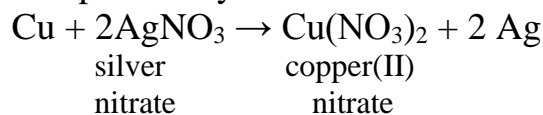
#### a. An active metal + an acid

When a metal which is above hydrogen in the activity series is reacted with an acid, hydrogen is liberated and a salt is formed.



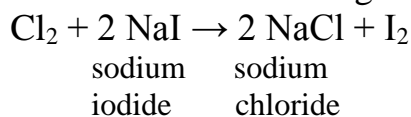
#### b. A metal + a salt

Each metal in the activity series displaces any metals below it to form a salt in solution.



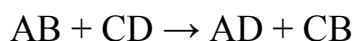
#### c. A Halogen + halide salt

A halogen (F, Cl, Br, I, At) will displace any less active halogen from a halide salt. The order of activity decreases going from top to bottom down the halogen family in the periodic table.



### 4. Metathesis or Double Replacement Reactions

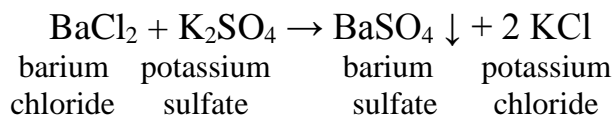
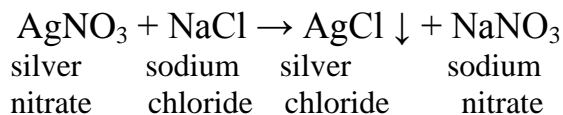
A metathesis is a double replacement reaction that usually occurs in water solution. The general form of a metathesis reaction is:



The principal conditions that favor the completion of these reactions are:

#### a. Precipitation Reactions

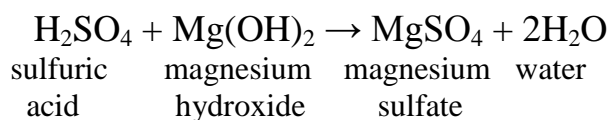
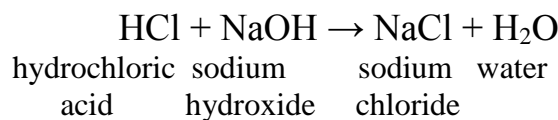
In this type of reaction, two compounds which are water soluble react to form two new compounds, one of which is a precipitate (i.e. insoluble in water). The precipitate is often indicated by an arrow pointing downward, ↓, written next to its formula.



## b. Neutralization Reactions (sometimes called acid-base reactions)

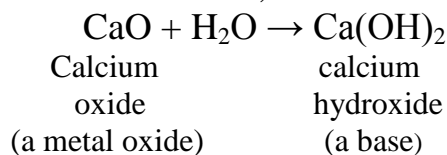
A neutralization reaction occurs between an acidic compound and a basic compound to form a chemical salt and water.

### 1. Reaction between an acid and a base

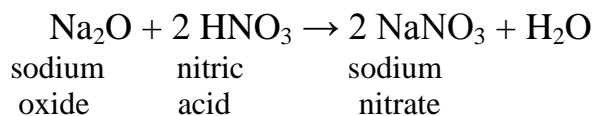
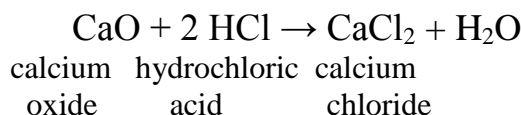


### 2. Reaction between a metal oxide and an acid.

When oxides of many metals are added to water, bases are formed.

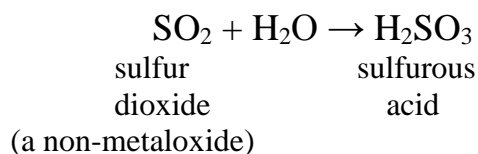


Generally, these metal oxides are called basic anhydrides and they act like bases when mixed with acids.

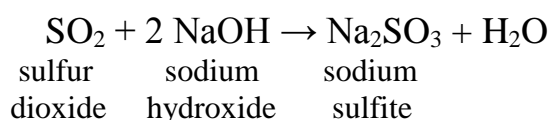


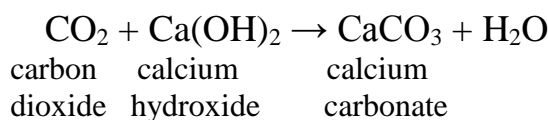
### 3. Reaction between a non-metal oxide and a base.

Many non-metal oxides are classified as acid anhydrides. These form acids when mixed with water.



Non-metal oxides act as acids when mixed with a base.

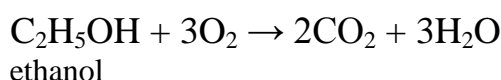
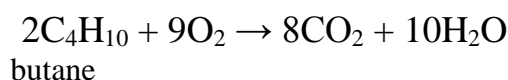
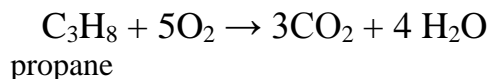




## 5. Combustion Reactions

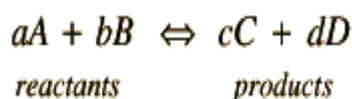
Combustion reactions generally apply to organic compounds, such as hydrocarbons, which are used as fuels. In these cases, the compound is being burned in air (or oxygen) and producing carbon dioxide and water as products. A general form for a combustion reaction is:

Some examples of combustion reactions are:

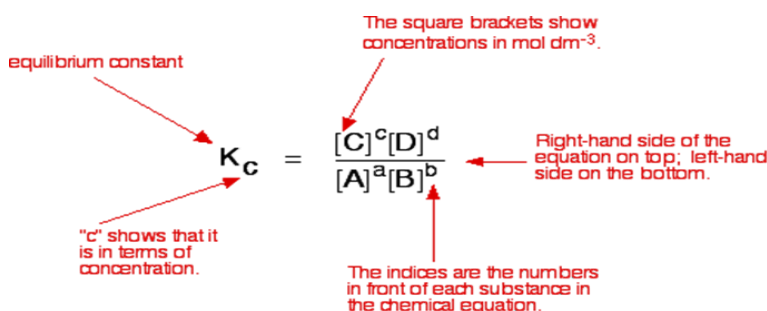


## 3. Equilibrium constant

To determine the equilibrium constant you must consider the chemical reaction written in the form:

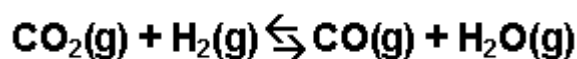


The equilibrium constant is defined as:



Where [C] represents the molar concentration.

**Example:** Calculate the value of the equilibrium constant,  $K_c$ , for the system shown, if 0.1908 moles of  $\text{CO}_2$ , 0.0908 moles of  $\text{H}_2$ , 0.0092 moles of  $\text{CO}$ , and 0.0092 moles of  $\text{H}_2\text{O}$  vapor were present in a 2.00 L reaction vessel were present at equilibrium.



- Write the equilibrium expression for the reaction system.

$$K_c = \frac{[\text{CO}][\text{H}_2\text{O}]}{[\text{CO}_2][\text{H}_2]}$$

- Since  $K_c$  is being determined, check to see if the given equilibrium amounts are expressed in moles per liter (molarity). In this example they are not; conversion of each is required.

$$[\text{CO}_2] = 0.1908 \text{ mol CO}_2 / 2.00 \text{ L} = 0.0954 \text{ M}$$

$$\begin{aligned}
 [\text{H}_2] &= 0.0454 \text{ M} \\
 [\text{CO}] &= 0.0046 \text{ M} \\
 [\text{H}_2\text{O}] &= 0.0046 \text{ M}
 \end{aligned}$$

- Substitute each concentration into the equilibrium expression and calculate the value of the equilibrium constant.

$$K_c = \frac{[0.0046][0.0046]}{[0.0954][0.0454]} = 0.0049 \text{ or } 4.9 \times 10^{-3}$$

For gaseous reactants it is more convenient to express the equilibrium condition in terms of the partial pressures of the reactants and products. For this case the equilibrium constant is defined by

$$K_P = \frac{P_C P_D}{P_A P_B}$$

Relationship between  $K_c$  and  $K_p$  is:

$$K_P = K_c (RT)^{\Delta n}$$

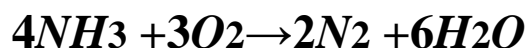
$K_c$ : is an equilibrium constant in terms of molar concentrations,  $K_p$ : is an equilibrium constant in terms of partial pressures, T: temperature, R: Ideal Gas Constant (0.0821 liter·atm/mol·K), n: is number of moles.

#### 4. Reaction rate

The rate of reaction,  $r$ , is defined to be the slope of the concentration-time plot for a species divided by the stoichiometric coefficient of that species. For the example shown

$$\text{rate of reaction} = r = - \frac{d[A]}{dt} = - \frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt}$$

For the oxidation of ammonia



it was found that the rate of formation of  $\text{N}_2$  was  $0.27 \text{ mol L}^{-1} \text{ s}^{-1}$ .

- At what rate was water being formed?
- At what rate was ammonia being consumed?

#### Solution

a) From the equation stoichiometry,  $\Delta[\text{H}_2\text{O}] = 6/2 \Delta[\text{N}_2]$ , so the rate of formation of  $\text{H}_2\text{O}$  is

$$3 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.81 \text{ mol L}^{-1} \text{ s}^{-1}$$

b) 4 moles of  $\text{NH}_3$  are consumed for every 2 moles of  $\text{N}_2$  formed, so the rate of disappearance of ammonia is

$$2 \times (0.27 \text{ mol L}^{-1} \text{ s}^{-1}) = 0.54 \text{ mol L}^{-1} \text{ s}^{-1}$$

## 5. Ionization and ionization energy

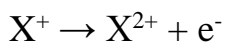
**Ionization** is the process by which an atom or a molecule acquires a negative or positive charge by gaining or losing electrons to form ions.

The  $n^{\text{th}}$  **ionization energy** refers to the amount of energy required to remove an electron from the species with a charge of  $(n-1)$ . For example, the first three ionization energies are defined as follows:

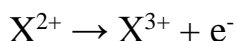
1<sup>st</sup> ionization energy



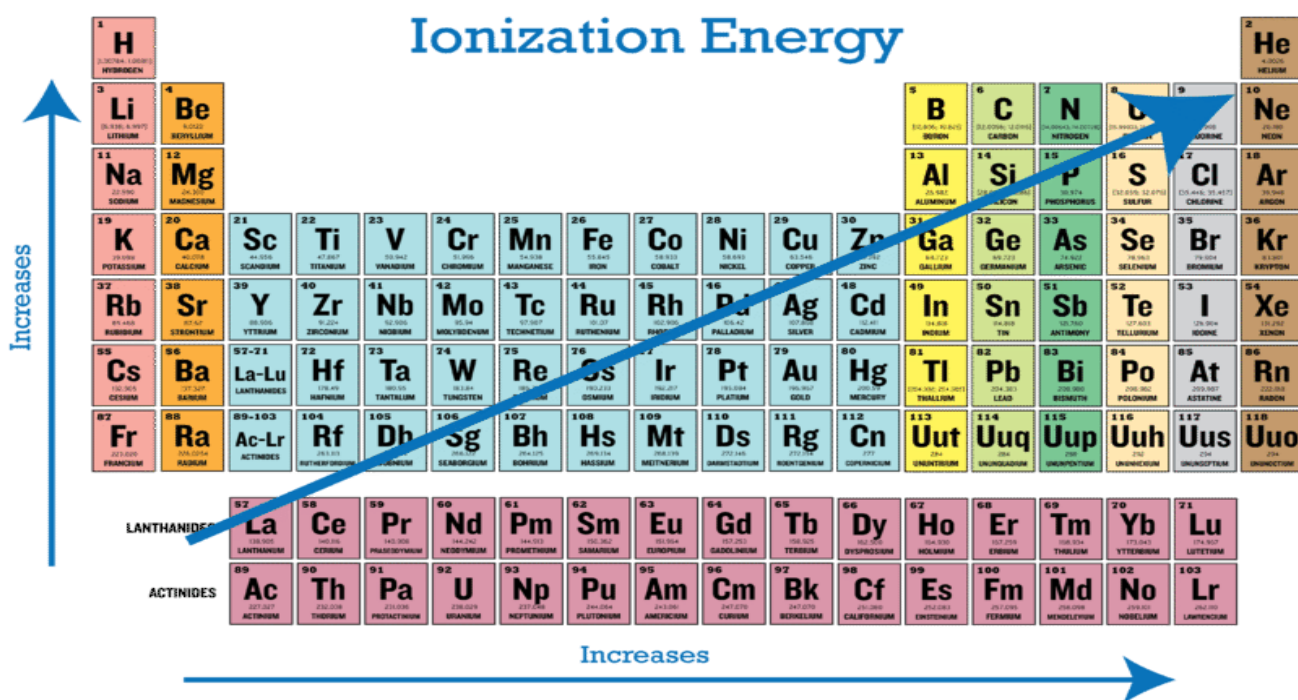
2<sup>nd</sup> ionization energy



3<sup>rd</sup> ionization energy



The amount of energy required to remove the outer electron is called **the first ionization energy**. Successive electron can be removed as well. The following equations show the first and second ionizations for the nitrogen atom.



## Acids and Bases

"**Acid**"--Latin word acidus, meaning sour. (Lemon)

"**Alkali**"--Arabic word for the ashes that come from burning certain plants; water solutions feel slippery and taste bitter. (Soap)

- **Lavoisier's oxygen theory of acids**

The first scientific concept of acids and bases was provided by *Lavoisier* circa 1776. Since Lavoisier's knowledge of strong acids was mainly restricted to oxoacids, such as HNO<sub>3</sub> (nitric acid) and H<sub>2</sub>SO<sub>4</sub> (sulphuric acid), which tend to contain central atoms in high oxidation states surrounded by oxygen. The *Lavoisier* definition was held as absolute truth for over 30 years, until the 1810 article and subsequent lectures by *Sir Humphry Davy* in which he proved the lack of oxygen in H<sub>2</sub>S, H<sub>2</sub>Te, and the hydrohalic acids.

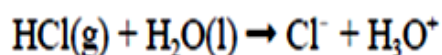
- **Liebig's hydrogen theory of acids**

This definition was proposed by Justus von Liebig circa 1838, based on his extensive works on the chemical composition of organic acids. This finished the doctrinal shift from oxygen-based acids to hydrogen-based acids, started by Davy. According to Liebig, an acid is a hydrogen-containing substance in which the hydrogen could be replaced by a metal.

- **Arrhenius Acids and Bases theory**

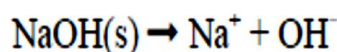
In 1884 *Svante Arrhenius* suggested that salts such as NaCl dissociate when they dissolve in water to give particles he called **ions**.

**Acid:** donates a hydrogen ion (H<sup>+</sup>) in water.



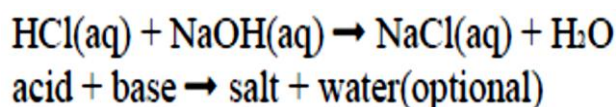
**Base:** donates a hydroxide ion in water (OH<sup>-</sup>).

For example, when NaOH(s) dissolves in water, the following reaction occurs.



The **Arrhenius acid-base** reaction yields as **salt**. In the Arrhenius definition, if one reacts an acid with a base, the product is a salt. The reaction may also produce water.

Example:

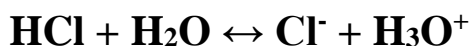


- **Brownsted-Lowry Acid-Base theory**

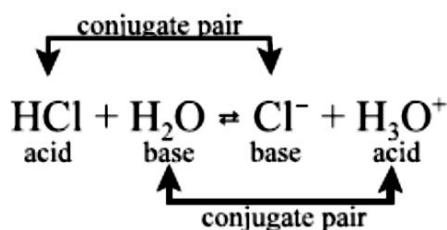
**Acid:** An acid is a proton donor in a reaction.

**Base:** A base is a proton acceptor in a reaction.

For example, for HCl dissolved in water, the following reaction exists.



Notice HCl is an acid because it transfers its proton to water, HCl and Cl<sup>-</sup> differ by an H<sup>+</sup> and H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> differ by an H<sup>+</sup>. These are called **conjugate acid-base pairs**. HCl is the conjugate of Cl<sup>-</sup> and H<sub>2</sub>O is the conjugate of H<sub>3</sub>O<sup>+</sup>. This is illustrated as follows:



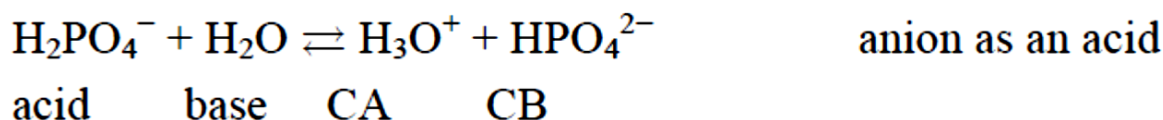
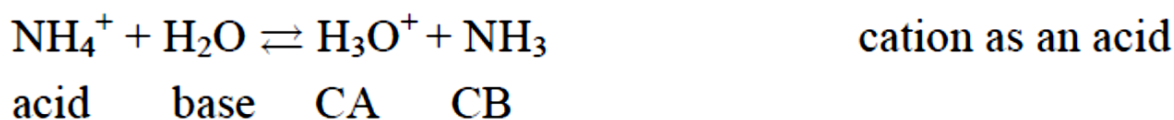
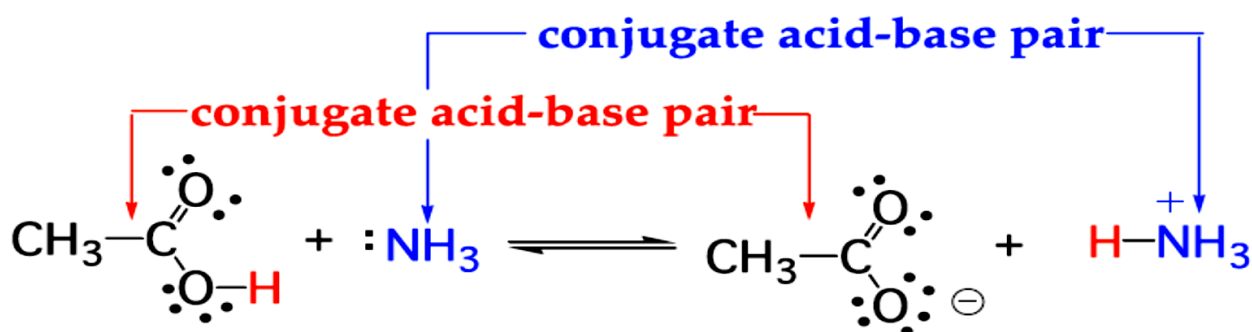
Summary for this reaction:

- 1) HCl and H<sub>3</sub>O<sup>+</sup> are the Brønsted-Lowry acids
- 2) H<sub>2</sub>O and Cl<sup>-</sup> are the Brønsted-Lowry bases
- 3) HCl and Cl<sup>-</sup> is a conjugate pair.
- 4) H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> is a conjugate pair.

Notice the only recognizable Arrhenius acid in this reaction is HCl. All the other species are defined by the reaction. (In water, H<sub>3</sub>O<sup>+</sup> is always a Brønsted-Lowry acid.)

**Conjugate acid-base pair**--A pair of compounds that differ by the presence of one H<sup>+</sup> unit.

**Examples:**



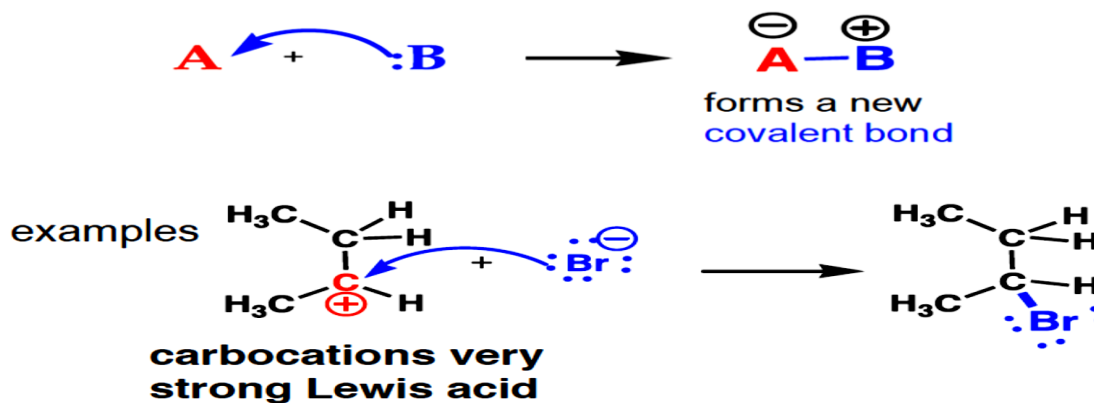
This theory is better; it explains ammonia as a base! This is the main theory that use for explain acid/base discussion.

- **Lewis Acid-Base theory**

**Acid:** accepts an electron pair for the formation of a compound or a complex ion.

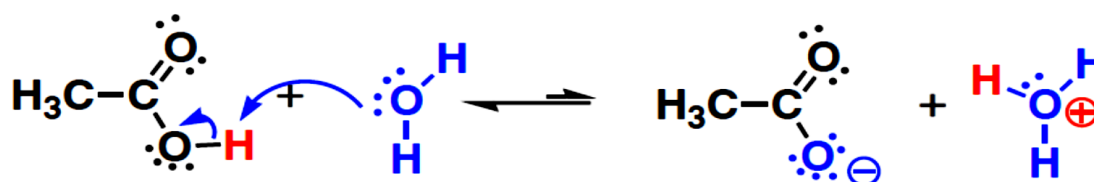
**Base:** donates an electron pair for the formation of a compound or a complex ion.

This theory explains all traditional acids and bases plus a host of coordination compounds and is used widely in organic chemistry. All Bronsted/Lowry acids are Lewis acids, not all Lewis acids are Bronsted acids.



### 1) Strengths of Acids and Bases

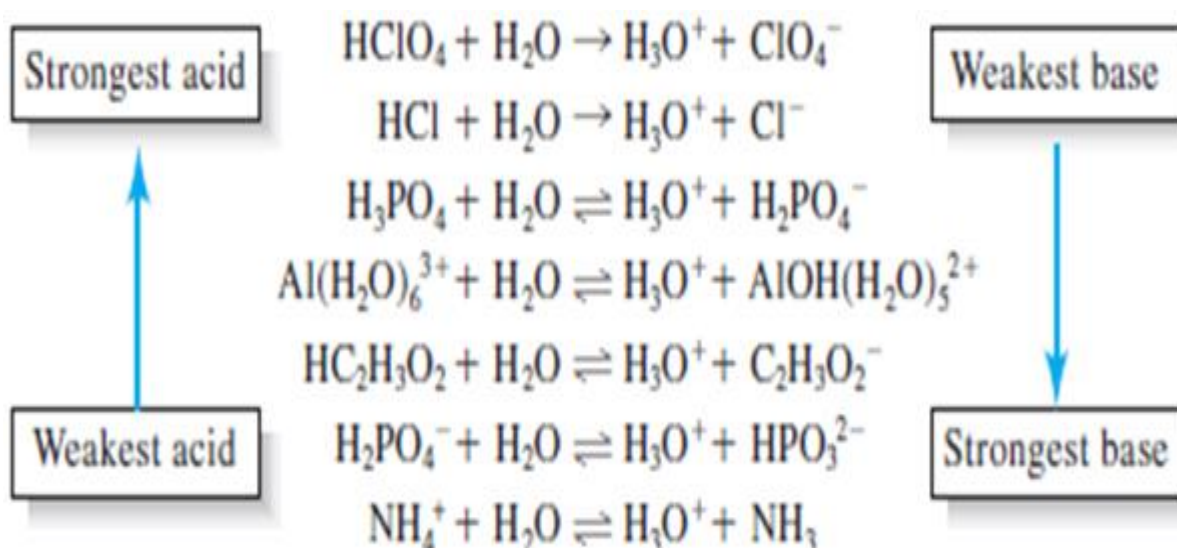
How is acid [base] strength expressed/compared? By **equilibrium constant**  
e.g.: dissociation (ionization) of acetic acid



$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

$$K_{\text{a}} = K_{\text{eq}}[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$pK_{\text{a}} = -\log K_{\text{a}}$$

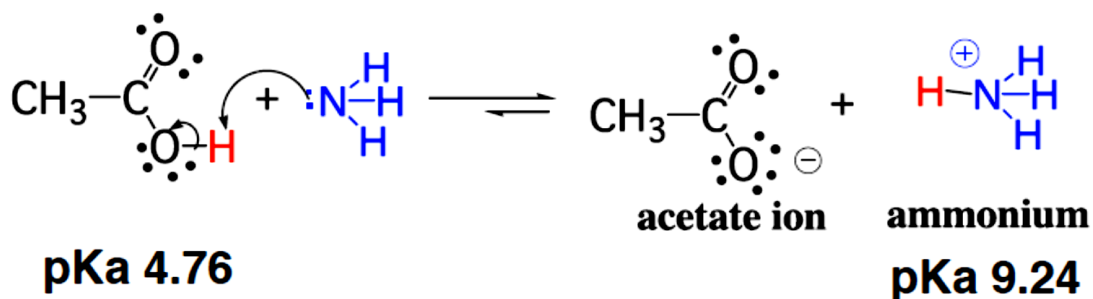


	Acid	Base	pKa	
Strong acid in water	HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	-10	Strong acid in ammonia
	HI	I <sup>-</sup>	-10	
	H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	-10	
	HBr	Br <sup>-</sup>	-9	
	HCl	Cl <sup>-</sup>	-7	
	HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	-2	
	H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	-1.74	
Weak acids in water	CCl <sub>3</sub> CO <sub>2</sub> H	CCl <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	0.52	
	HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	1.99	
	H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	2.12	
	CH <sub>2</sub> ClCO <sub>2</sub> H	CH <sub>2</sub> ClCO <sub>2</sub> <sup>-</sup>	2.85	
	HF	F <sup>-</sup>	3.17	
	HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>	3.3	
	CH <sub>3</sub> CO <sub>2</sub> H	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	4.75	
	C <sub>5</sub> H <sub>5</sub> NH <sup>+</sup>	C <sub>5</sub> H <sub>5</sub> N	5.25	
	H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	6.35	
	H <sub>2</sub> S	HS <sup>-</sup>	7.00	
	NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>	9.24	
	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>-2</sup>	10.33	
	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>2</sub>	10.56	
	H <sub>2</sub> O	OH <sup>-</sup>	15.74	
Not an acid in water	CH <sub>3</sub> OH	CH <sub>3</sub> O <sup>-</sup>	18	Weak acid in ammonia
	HCCH	HCC <sup>-</sup>	25	
	NH <sub>3</sub>	NH <sub>2</sub> <sup>-</sup>	34	
	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sup>-</sup>	36	Not an acid in ammonia
	CH <sub>3</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> <sup>-</sup>	42	

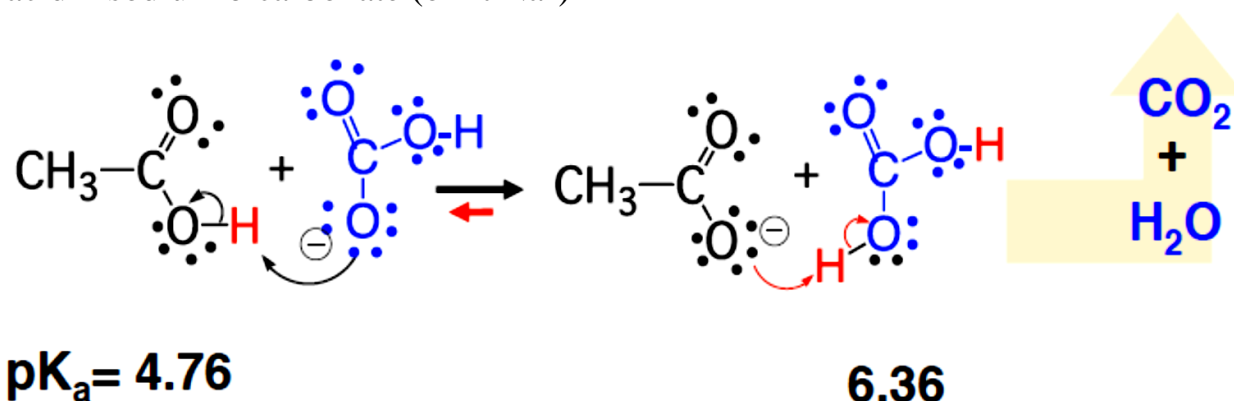
## 2) Acid-Base Equilibria

**Strong acid** - completely to product(s)

**Weak acid** - incomplete, gives an Equilibrium direction favors reaction of stronger acid-base pair



Acetic acid + sodium bicarbonate (omit Na<sup>+</sup>)



## pH, pOH and Kw calculation

**pH** is the measurement of the *hydrogen ion concentration*,  $[H^+]$ . Every aqueous solution can be measured to determine its pH value. This value ranges from 0 to 14 pH. Values below 7 pH exhibit acidic properties. Values above 7 pH exhibit basic properties. Since 7 pH is the center of the measurement scale, it is neither acidic nor basic and is, therefore, called "neutral."

Also, **pH** is defined as the *negative logarithm of the hydrogen ion* concentration. It is expressed mathematically as:

$$\text{pH} = -\log [H^+]$$

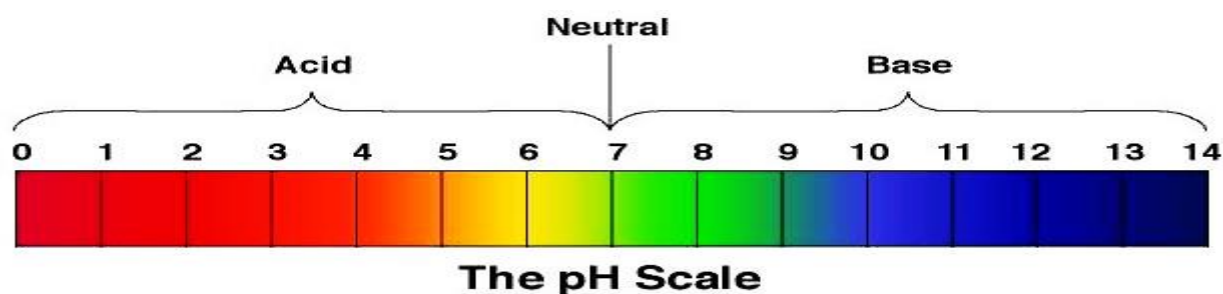
where:  $[H^+]$  is hydrogen ion concentration in mol/L

In a neutral solution, the  $[H^+] = 1 \times 10^{-7}$  mol/L. This represents a pH of 7.

$$\begin{aligned}\text{pH} &= -\log (1 \times 10^{-7}) \\ &= -(\log 1 + \log 10^{-7}) = -(0.0 + (-7)) = 7.0\end{aligned}$$

When determining the pH of a solution, the hydroxide ion concentration can be calculated:

$$[H^+][OH^-] = 10^{-14}$$



### The pOH scale

Base concentrations:

$$\text{pOH} = -\log_{10}[OH^-]$$

A neutral solution (25°C) has:

$$\text{pOH} = -\log_{10}[1.0 \times 10^{-7}] = -(-7.00) = 7.00$$

Since  $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

$$-\log(K_w) = -\log[H_3O^+] + (-\log[OH^-]) = -\log(1.0 \times 10^{-14})$$

$$\text{p}K_w = \text{pH} + \text{pOH} = 14.00$$

**Summary of Formulas**

Relating  $[H^+]$  and  $[OH^-]$ :

$$1.00 \times 10^{-14} = [H^+] \times [OH^-]$$

Relating pH to pOH:

$$14 = \text{pH} + \text{pOH}$$

Finding pH or pOH with concentration values:

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

Finding concentration values when given pH or pOH:

$$[H^+] = 10^{-\text{pH}}$$
$$[OH^-] = 10^{-\text{pOH}}$$

$$\text{pOH} = -\log[\text{OH}^-]$$

The negative log of the hydroxide ion molarity

$$\text{pK}_w = -\log K_w$$

The negative log of the water ion product,  $K_w$

$$\text{pK}_a = -\log K_a$$

The negative log of the acid dissociation constant,  $K_a$

$$\text{pK}_b = -\log K_b$$

The negative log of the base dissociation constant,  $K_b$

### Examples on pH and pOH:

#### Example 1: Calculating pH and pOH from $[\text{H}^+]$ $[\text{OH}^-]$

Calculate the pH and pOH of each solution based on their concentrations of  $\text{H}^+$  or  $\text{OH}^-$ .

a)  $[\text{H}^+] = 1.0 \times 10^{-2} \text{ M}$

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log(1.0 \times 10^{-2}) \text{ *plug into calculator}$$

$$\text{pH} = 2.0$$

$$14 = \text{pH} + \text{pOH}$$

$$14 = 2.0 + \text{pOH}$$

$$\text{pOH} = 12.0$$

b)  $[\text{OH}^-] = 8.2 \times 10^{-6} \text{ M}$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{pOH} = -\log(8.2 \times 10^{-6}) \text{ *plug into calculator}$$

$$\text{pOH} = 5.1$$

$$14 = \text{pH} + \text{pOH}$$

$$14 = \text{pH} + 5.1$$

$$\text{pH} = 8.9$$

#### Example 2: Calculating $[\text{H}^+]$ $[\text{OH}^-]$ from pH or pOH (going backwards is fun!)

a) What's the  $[\text{H}^+]$  of a solution with a pH of 3.41?

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

$$[\text{H}^+] = 10^{-3.41} \text{ *Plug into calculator}$$

$$[\text{H}^+] = 3.89 \times 10^{-4} \text{ M}$$

## pH

1. What is pH? *HINT: give me the definition, not the formula*

*The negative logarithm of the hydrogen ion concentration.*

2. Why do you think the pH scale is so useful?

*Scientists needed an easier way to notate the  $H^+$  ion concentration. The tiny numbers expressed in scientific notation could be more easily compared using a scale based on common logarithms.*

3. What is the equation for solving pH?

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

4. What does “[H<sup>+</sup>]” mean?

*The concentration of hydrogen ions.*

## pOH

5. What is pOH? *HINT: give me the definition, not the formula*

*The negative logarithm of the hydroxide ion concentration.*

6. In what way does the pOH scale “mirror the relationship between pH and [H<sup>+</sup>]”?

*The pOH scale is the exact opposite of the pH scale because it measures [OH] instead of [H<sup>+</sup>]. Notice 0-6.99 is acid on the pH scale, but basic on pOH scale. See Figure 18.15 on page 653 for a visual aid.*

7. What is the equation for pOH?

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

## Buffer solutions

- A **buffer** is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid.

### Buffers:

1. Resist changes in pH.
2. Are prepared by mixing a weak acid with its salt or by partly neutralizing a weak acid with strong base.
3. Allow living organisms to exist.
4. Are necessary for understanding acid base titrations.
5. Offer an unrivaled opportunity to use the Henderson-Hasselbalch equation.

### Acidic buffer solutions

- An acidic buffer solution is simply one which has a pH less than 7.
- Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt.
- In this case, if the solution contained equal molar concentrations of both the acid and the salt, it would have a pH of 4.76.
- An acid buffer is a mixture of weak acid and its salt with a strong base.
- Ex: 1. Acetic acid & sodium acetate ( $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ )  
2. Formic acid & potassium formate ( $\text{HCOOH} + \text{HCOOK}$ )  
3. Benzoic acid and & sodium benzoate ( $\text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{COONa}$ )  
4. Phosphoric acid & Sodium phosphate ( $\text{H}_3\text{PO}_4 + \text{Na}_3\text{PO}_4$ )

### Alkaline buffer solutions

- An alkaline buffer solution has a pH greater than 7.
- Alkaline buffer solutions are commonly made from a weak base and one of its salts.
- If these were mixed in equal molar proportions, the solution would have a pH of 9.25.
- Ex: ammonium hydroxide & ammonium chloride ( $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ )

### Requirements for buffer solution:

There are three requirements for buffer:

- Must be a mixture of weak acid and its salt or weak base and its salt
- A buffer must contain relatively large concentration of acid to react with added base ( $\text{OH}^-$ ) and also must contain similar concentration of base to reaction with added acid ( $\text{H}^+$ ).
- The acid and base components of the buffer must not consume each other in a neutralization reaction.

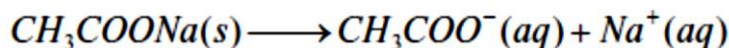
### Preparation of Buffer Solution

A buffer solution is prepared by mixing equal amount of weak acid and its salt, such as, acetic acid ( $\text{CH}_3\text{COOH}$ ) and sodium acetate ( $\text{CH}_3\text{COONa}$ ) or weak base and its salt, such as, ammonia ( $\text{NH}_3$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ).

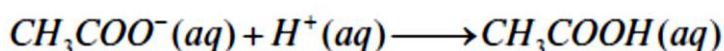
## Buffer Action

Let us see how the buffer reacts to the addition of small amount of acid or base. To illustrate this, consider the buffer containing acetic acid and sodium acetate.

Sodium acetate, a strong electrolyte, dissociates completely in water:



If an acid added, the  $\text{H}^+$  ions will react with conjugate base ( $\text{CH}_3\text{COO}^-$ ) in the buffer according to the equation:



The acid, thus regenerated, is a part of the buffer solution. On the other hand, if a base is added to the system, the  $\text{OH}^-$  ions will react with acid ( $\text{CH}_3\text{COOH}$ ) according the following equation.



## Types of buffers

A buffer solution is a solution the pH of which does not change significantly when a small amount of acid or base is added to it. There are four categories of buffers.

1. Strong acid buffers
2. Strong base buffers
3. Weak acid buffers
4. Weak base buffers

## Example:

Which of the following are buffer systems?

- (a) KF/HF
- (b) KBr/HBr
- (c)  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$
- (d)  $\text{NaClO}_4/\text{HClO}_4$
- (e)  $\text{NH}_3/\text{NH}_4\text{NO}_3$

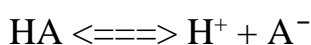
## Answer

- (a) HF is a weak acid and KF is its salt. Therefore, this is a buffer system.
- (b) HBr is a strong acid and hence this is not a buffer system.
- (c) NaHCO<sub>3</sub> contains a weak acid (HCO<sub>3</sub><sup>-</sup>) and Na<sub>2</sub>CO<sub>3</sub> is a salt of weak acid. Therefore, this is a buffer system.
- (d) HClO<sub>4</sub> is a strong acid and hence this is not a buffer system.
- (e) NH<sub>3</sub> is a weak base and NH<sub>4</sub>NO<sub>3</sub> is a salt of weak base, and therefore this is a buffer system.

## The pH of Buffer Solutions

The Henderson-Hasselbalch Equation is: (1) a rearrangement of the K<sub>a</sub> expression followed by (2) the use of negative logarithms. We will derive the HH equation using the generic weak acid HA.

Here is the dissociation equation for HA:



From which, we write the K<sub>a</sub> expression:

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

Next, we isolate the H<sup>+</sup> and put it on the left-hand side of the equation:

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

Now, we going to take the negative log of each of the three terms in the above equation. When I do that, they become:

- 1) -log [H<sup>+</sup>]
- 2) - log K<sub>a</sub>
- 3) -log ([HA] / [A<sup>-</sup>])

However,

- 1) this is the pH
- 2) this is the pK<sub>a</sub>
- 3) to get rid of the negative sign, we simply flip the log term to get this: + log ([A<sup>-</sup>] / [HA])

Inserting these last three items (the pH, the pK<sub>a</sub> and the rearranged log term), we arrive at the Henderson-Hasselbalch Equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

Here is a common way the HH equation is presented in a textbook explanation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt form}]}{[\text{acid form}]}$$

However, remember that the salt of a weak acid is a base (and the salt of a weak base is an acid).

Consequently, another common way to write the HH equation is to substitute "base" for "salt form". This is probably the most useful way to describe the interactions between the acidic form (the HA) and the basic form (the A<sup>-</sup>).

Here it is:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

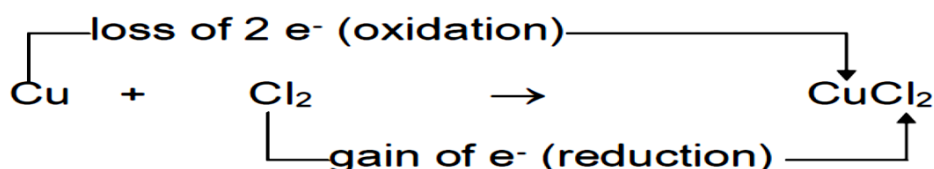
Remember this: the base is the one WITHOUT the proton and the acid is the one WITH the proton.

## Redox Reactions

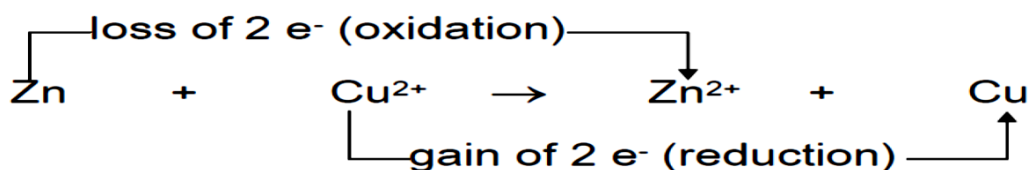
### 1. Redox reactions in terms of electron transfer

**Oxidation — loss of electron(s)**  
**Reduction — gain of electron(s)**

e.g. (1)

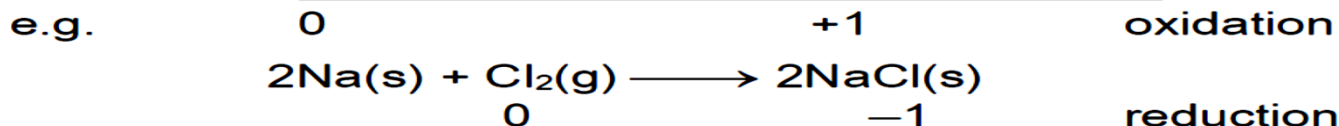


(2)



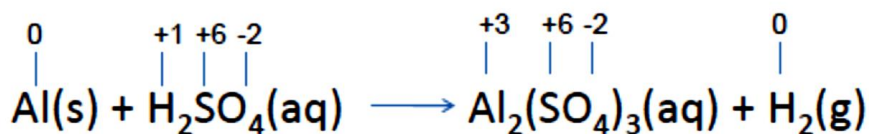
### 2. Redox reactions in terms of oxidation number

**Oxidation — increase in oxidation state**  
**Reduction — decrease in oxidation state**



Part a:

- Step 1. Assign oxidation numbers to all elements



- Step 2. Identify oxidized and reduced species

- Al was oxidized (O.N. of Al: 0 → +3)
- H<sub>2</sub>SO<sub>4</sub> was reduced (O.N. of H: +1 → 0)

- Step 3. Compute e<sup>-</sup> lost and e<sup>-</sup> gained

- In the oxidation: 3e<sup>-</sup> were lost from Al
- In the reduction: 1e<sup>-</sup> was gained by H

- Step 4. Multiply by factors to make e<sup>-</sup> lost equal to e<sup>-</sup> gained, and use the factors as coefficients

- Al lost 3e<sup>-</sup>, so the 1e<sup>-</sup> gained by H should be multiplied by 3. Put the coefficient 3 before H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>.

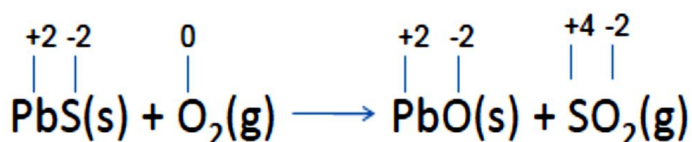


- Step 5. Complete the balancing by inspection



Part b:

- Step 1. Assign oxidation numbers to all elements



- Step 2. Identify oxidized and reduced species

- PbS was oxidized (O.N. of S: -2 → +4)
- O<sub>2</sub> was reduced (O.N. of O: 0 → -2)

- Step 3. Compute e<sup>-</sup> lost and e<sup>-</sup> gained

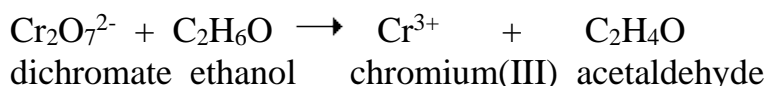
- In the oxidation: 6e<sup>-</sup> were lost from S
- In the reduction: 2e<sup>-</sup> were gained by each O

- **Step 4.** Multiply by factors to make  $e^-$  lost equal to  $e^-$  gained, and use the factors as coefficients
  - S lost  $6e^-$ , O gained  $4e^-$  ( $2e^-$  each O). Thus, put the coefficient  $3/2$  before  $O_2$ .
$$\text{PbS}(s) + 3/2\text{O}_2(g) \longrightarrow \text{PbO}(s) + \text{SO}_2(g)$$
- **Step 5.** Complete the balancing by inspection
 
$$2\text{PbS}(s) + 3\text{O}_2(g) \longrightarrow 2\text{PbO}(s) + 2\text{SO}_2(g)$$

## Balancing Redox Reactions Using the Half Reaction Method

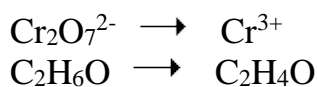
### Example -- Balancing Redox Reactions Which Occur in Acidic Solution

Organic compounds, called alcohols, are readily oxidized by acidic solutions of dichromate ions. The following reaction, written in net ionic form, records this change. The oxidation states of **each atom in each compound** is listed in order to identify the species that are oxidized and reduced, respectively.

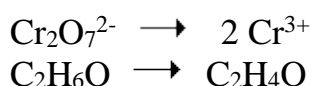


An examination of the oxidation states, indicates that carbon is being oxidized, and chromium, is being reduced. To balance the equation, use the following steps:

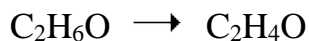
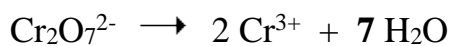
1. First, divide the equation into two halves; one will be an oxidation half-reaction and the other a reduction half- reaction, by grouping appropriate species. The nature of each will become evident in subsequent steps.



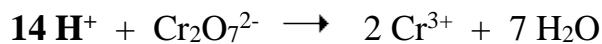
2. Second, if necessary, balance all elements except oxygen and hydrogen in both equations by inspection. In other words, balance the non-hydrogen and non-oxygen atoms only. By following this guideline in the example above, only the chromium reaction needs to be balanced by placing the coefficient, 2, in front of  $\text{Cr}^{3+}$  as shown below.



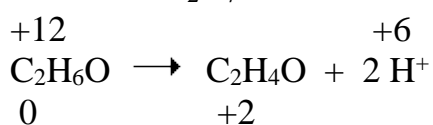
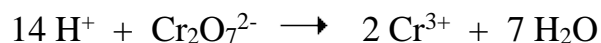
3. The third step involves balancing oxygen atoms. To do this, add water ( $\text{H}_2\text{O}$ ) molecules. Use 1 molecule of water for each oxygen atom that needs to be balanced. Add the appropriate number of water molecules to that side of the equation required to balance the oxygen atoms as shown below.



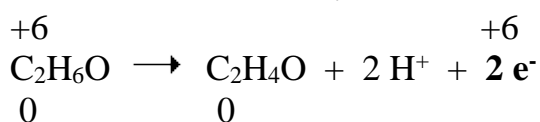
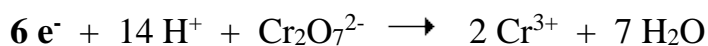
4. The fourth step involves balancing the hydrogen atoms. To do this one must use hydrogen ions ( $\text{H}^+$ ). Use one (1)  $\text{H}^+$  ion for every hydrogen atom that needs to balance. Add the appropriate number of hydrogen ions to that side of the equation required to balance the hydrogen atoms as shown below



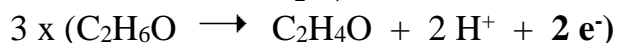
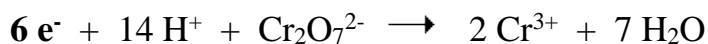
5. The fifth step involves the balancing charges. This is done by adding electrons ( $\text{e}^-$ ). Each electron has a charge equal to (-1). To determine the number of electrons required, find the net charge of each side the equation.



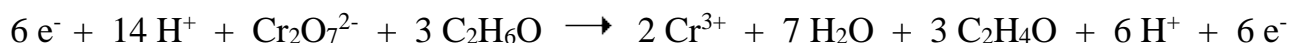
The electrons must always be added to that side which has the greater positive charge as shown below.



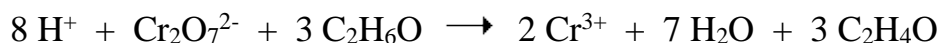
6. The sixth step involves multiplying each half-reaction by the smallest whole number that is required to equalize the number of electrons gained by reduction with the number of electrons produced by oxidation. Using this guideline, the oxidation half reaction must be multiplied by "3" to give the 6 electrons required by the reduction half-reaction.



7. The seventh and last step involves adding the two half reactions and reducing to the smallest whole number by cancelling species which on both sides of the arrow.



Note that the above equation can be further simplified by subtracting out 6  $\text{e}^-$  and 6  $\text{H}^+$  ions from both sides of the equation to give the final equation.



Note: the equation above is completely balanced in terms of having an **equal number of atoms as well as charges**.

## Titrimetric Methods

Titrimetric analysis consists in determining the number of moles of reagent (titrant), required to react quantitatively with the substance being determined. The titrant can be added (a) volumetrically, with a glass or automatic burette or with a low flow-rate pump or (b) coulometrically, with an electrochemical generation from a proper electrolyte.

➤ **Volumetric titrimetry**

– The volume of a standard reagent is the measured quantity

➤ **Gravimetric titrimetry**

– The mass of the reagent is measured quantity

➤ **Coulometric titrimetry**

– The quantity of charge in coulombs required to complete a reaction with the analyte is the measured quantity

– The “reagent” is a constant direct electrical current of known magnitude that consumes analyte. The time required (and thus the total charge) to complete the electrochemical reaction is measured

– When the analytical reactions involve electron transfer. These methods are often called redox titrations.

## Terms used in Volumetric Titrimetry

### **Titrant**

Titrant is a substance added from the burette. Titrant used and reaction that proceeds usually defines name of the titration - like acid-base (or alkalimetric) titration if we use strong acid (or strong base) as a titrant, or redox when the reaction that proceeds is of a redox type. Name can be also much more specific - like permanganometric titration (also known as manganometry or permanganometry) when titrant is potassium permanganate.

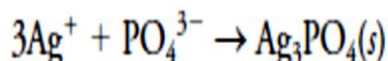
### **Titration**

A process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and the reagent is judge to be complete.

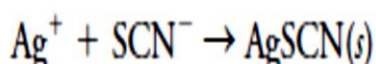
### **Back-titration**

A process in which the excess of a standard solution used to react with an analyte is determined by titration with a second standard solution.

For example, the amount of phosphate in a sample can be determined by adding a measured excess of standard silver nitrate to a solution of the sample, which leads to the formation of insoluble silver phosphate:



The excess silver nitrate is then back-titrated with a standard solution of potassium thiocyanate:



The amount of silver nitrate is chemically equivalent to the amount of phosphate ion plus the amount of thiocyanate used for the back-titration. The amount of phosphate is then the difference between the amount of silver nitrate and the amount of thiocyanate.

## Equivalence Points and End Points

### End point

The end point is expressed in range, the range should address to the equivalence point. End point is where the titration ends in practice. The closer the end point to the equivalence point the better, but it is often not easy to find a good method of equivalence point detection. However, very often, we can easily spot a point very close to the equivalence point - and that's where the end point will be.

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

In volumetric methods, the **titration error**,  $E_t$ , is given by

$$E_t = V_{ep} - V_{eq}$$

where  $V_{ep}$  is the actual volume of reagent required to reach the end point and  $V_{eq}$  is the theoretical volume necessary to reach the equivalence point.

### Different methods to determine the endpoint include:

- **pH indicator:**

A pH indicator is a substance that it changes its colour in response to a chemical change. An acid-base indicator changes its colour depending on the pH (e.g., phenolphthalein). Redox indicators are also frequently used. A drop of indicator solution is added to the titration at the start; at the endpoint has been reached the colour changes.

- **A potentiometer**

It is an instrument that measures the electrode potential of the solution. These are used for titrations based on a redox reaction; the potential of the working electrode will suddenly change as the endpoint is reached.

- **pH meter:**

It is a potentiometer that uses an electrode whose potential depends on the amount of  $H^+$  ion present in the solution. (It is an example of an ion-selective electrode.) This allows the pH of the solution to be measured throughout the titration. At the endpoint, there will be a sudden change in the measured pH. This method is more accurate than the indicator method and is very easily automated.

- **Conductance:**

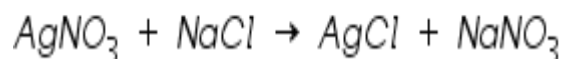
The conductivity of a solution depends on the ions present in it. During many titrations, the conductivity changes significantly. (i.e., during an acid-base titration, the  $H^+$  and  $OH^-$  ions react to form neutral  $H_2O$ , this changes the conductivity of the solution.) The total conductance of the solution also depends on the other ions present in the solution, such as counter ions. This also depends on the mobility of each ion and on the total concentration of ions that is the ionic strength.

- **Colour change:**

In some reactions, the solution changes colour without any added indicator. This is often seen in redox titrations, for instance, when the different oxidation states of the product and reactant produce different colours.

- **Precipitation:**

In this type of titration the strength of a solution is determined by its complete precipitation with a standard solution of another substance.



### **Equivalence point**

Equivalence point is where the titration should really end - titration fraction equals exactly 1, we have added stoichiometric amount of titrant to titrated substance. That's not necessarily where we end titration.

### **Indicators**

An **indicator** is a substance which is used to determine the end point in a titration. In acid-base **titrations**, organic substances (weak acids or weak bases) are generally used as **indicators**. They change their colour within a certain pH range.

### **Advantages of titration**

There are several reasons why titration is used in laboratories worldwide:

1. Titration is an established analytical technique
2. It is fast
3. It is a very accurate and precise technique
4. A high degree of automation can be implemented
5. Titration offers a good price/performance ratio compared to more sophisticated techniques
6. It can be used by low-skilled and low-trained operators
7. No need for highly specialized chemical knowledge

## **8.3. Types of titrations**

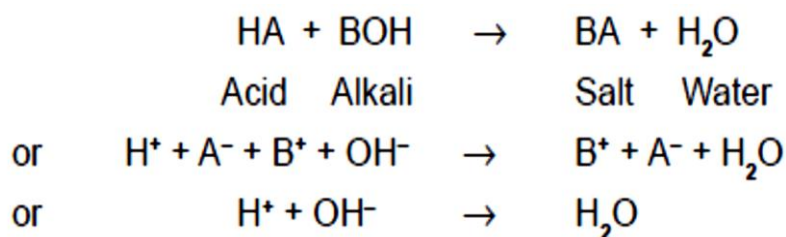
Titrations can be classified as:

- 1) Acid-base titrations or acidimetry and alkalimetry
- 2) Precipitation titrations
- 3) Complexometric titrations
- 4) Oxidation-reduction titrations or redox titrations

### **1) Acid-base titrations**

When the strength of an acid is determined with the help of a standard solution of base, it is known as acidimetry. Similarly, when the strength of a base (alkali) is determined with the help of a standard solution of an acid, it is known as acid, it is known as alkalimetry. Both these titrations

involve neutralisation of an alkali. In these titrations  $H^+$  ions of the acid combine with  $OH^-$  ions of the alkali to form unionised molecules of water.



The end point in these titrations is determined by the use of organic dyes which are either weak acids or weak bases. These change their colours within a limited range of hydrogen ion concentrations, i.e., pH of the solution. Phenolphthalein is a suitable indicator in the titrations of strong alkalis against strong acids or weak acids, Methyl orange is used as an indicator in the titrations of strong acids against strong and weak alkalis.

The (acid-base) neutralization reactions are of the following four types:

**1. A strong acid versus a strong base.**

pH curve of strong acid (eg. HCl) and strong base (eg. NaOH) is vertical over the pH range 4-10. So the indicators phenolphthalein (pH range 8.3-10.5), methyl red (pH range 4.4-6.5) and methyl orange (pH range 3.2-4.5) are suitable indicators for such a titration.

**2. A weak acid versus a strong base.**

pH curve of weak acid (eg.  $CH_3COOH$ ) and strong base (eg. NaOH) is vertical over the pH range 7-11. So phenolphthalein is suitable indicator for such a titration.

**3. A strong acid versus a weak base.**

pH curve of strong acid (eg. HCl,  $H_2SO_4$ ,  $HNO_3$ ) with a weak base (eg.  $NH_4OH$ ) is vertical over the pH range of 4-7. So methyl red and methyl orange are suitable indicators for such a titration.

**4. A weak acid versus a weak base.**

pH curve of weak acid and weak base indicators that there is no vertical part and hence, no suitable indicators can be used for such a titration.

**Calculation:**

$M_{\text{acid}}$  = Molarity of acid = \_\_\_\_\_ M

$V_{\text{acid}}$  = Volume of acid = \_\_\_\_\_ mL

$M_{\text{base}}$  = Molarity of base = \_\_\_\_\_ M

$V_{\text{base}}$  = Volume of base = \_\_\_\_\_ mL

moles = (moles/liter) x liters = MV

$$(M_1 \cdot V_1)_{\text{acid}} = (M_2 \cdot V_2)_{\text{base}}$$

## Examples of Titration Curves

General Type	Example	Typical Titration Curve	Features of Curve
Strong Acid and Strong Base	HCl added to NaOH	<p>0.10M HCl added to 10mL 0.10M NaOH</p> <p>The graph shows pH on the y-axis (0 to 14) and mL HCl added on the x-axis (0 to 20). The curve starts at a high pH of approximately 12.5 at 0 mL HCl. It remains relatively flat until about 8 mL, then drops sharply through a pH of 7 at 10 mL (the equivalence point), and continues to drop to a low pH of approximately 2.5 at 20 mL.</p>	<p>Curve begins at high pH typical of strong base and ends at low pH typical of strong acid.</p> <p>There is a large rapid change in pH near the equivalence point (pH = 7).</p>
Weak Acid and Strong Base	NaOH added to acetic acid ( $\text{CH}_3\text{COOH}$ )	<p>0.10M NaOH added to 10mL 0.10M acetic acid</p> <p>The graph shows pH on the y-axis (0 to 14) and mL NaOH added on the x-axis (0 to 20). The curve starts at a pH of approximately 4 at 0 mL NaOH. It rises gradually until about 8 mL, then rises sharply through a pH of approximately 8.5 at 10 mL (the equivalence point), and continues to rise to a high pH of approximately 12.5 at 20 mL.</p>	<p>Curve begins at a higher acidic pH and ends at high basic pH.</p> <p>The pH change at the equivalence point (pH &gt; 7) is not so great.</p>
Strong Acid and Weak Base	Ammonia ( $\text{NH}_3$ ) added to HCl	<p>0.10M ammonia added to 10mL 0.10M HCl</p> <p>The graph shows pH on the y-axis (0 to 14) and mL ammonia added on the x-axis (0 to 20). The curve starts at a low pH of approximately 2 at 0 mL ammonia. It rises gradually until about 8 mL, then rises sharply through a pH of approximately 6 at 10 mL (the equivalence point), and continues to rise to a pH of approximately 10 at 20 mL.</p>	<p>Curve begins at low pH and ends at a less high basic pH.</p> <p>The pH change at the equivalence point (pH &lt; 7) is similar to that for Strong Base and Weak Acid.</p>
Weak Acid and Weak Base	Ammonia ( $\text{NH}_3$ ) added to Acetic acid ( $\text{CH}_3\text{COOH}$ )	<p>0.10M ammonia added to 10mL 0.10M acetic acid</p> <p>The graph shows pH on the y-axis (0 to 14) and mL ammonia added on the x-axis (0 to 20). The curve starts at a pH of approximately 4 at 0 mL ammonia. It rises gradually until about 8 mL, then rises sharply through a pH of approximately 7 at 10 mL (the equivalence point), and continues to rise to a pH of approximately 10 at 20 mL.</p>	<p>Curve begins at higher acidic pH and ends at low basic pH.</p> <p>There is not a great pH change at the equivalence point (pH ~ 7) making this a very difficult titration to perform.</p>

## 2) Precipitometric (Precipitation) titrations

Analyte is titrated with a standard solution of a precipitating agent in accordance with defined reaction stoichiometry. Detection of the endpoint (at completion of the precipitation) is usually by either the appearance of excess titrant or the disappearance of the reactant.

## General Principles

The major precipitation reaction used is that of silver with a range of anions. These anions include:

- Chloride

- Bromide
- Iodide
- Thiocyanate

Titrations involving silver are termed argentometric, from the old name for silver, argentum. The reaction rates for the silver salt precipitation is rapid. The reaction ratio is 1:1 and silver salts formed are generally quite insoluble.

### Requirements

1. The precipitate formation is stoichiometric.
2. To allow the titrant to be added quickly, the equilibrium between the precipitate and its ions in solution must be attained rapidly. A slow attainment of equilibrium will cause over titration.
3. The precipitate must be of low solubility in the solution. This is indicated by small equilibrium constant ( $K_{sp}$ ).
4. A method to detect the stoichiometric point of the titration must be available. Although a number of indicators are available, in general, the best method for detecting the end point in precipitation titration is by an instrumental technique.

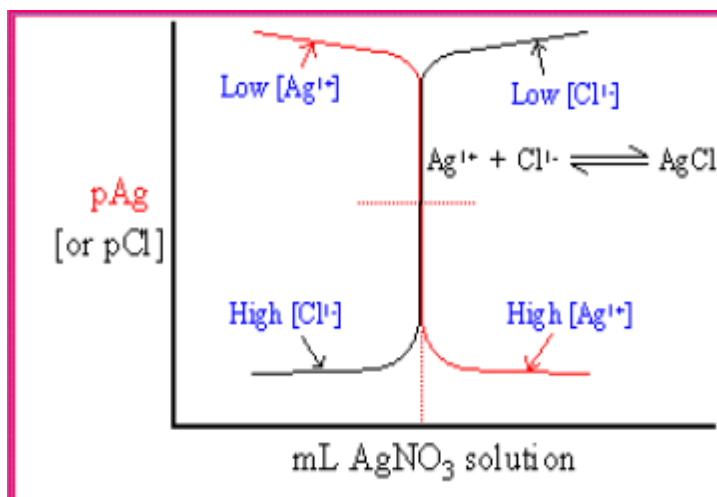
### Factors influencing the solubility

1. Temperature
2. Solvent properties
3. Common ions
4. Ionic activity
5. pH
6. Hydrolysis
7. Metal hydroxyde
8. Complex compound formation

### Titration Curves for Argentometric Methods

Plots of titration curves are normally sigmoidal curves consisting of pAg (or pAnalyte) versus volume of  $\text{AgNO}_3$  solution added. The points on the curve can be calculated, given the analyte concentration,  $\text{AgNO}_3$  concentration and the appropriate  $K_{sp}$ .

Example: Titration of chloride with silver.

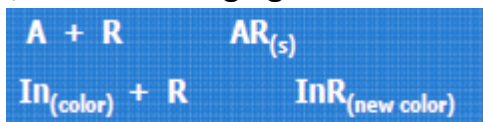


## Observations about Argentometric Titrations

High reagent concentrations give sharper, more dramatic equivalence point changes in pAg and better endpoints. The smaller the  $K_{sp}$ , the more complete the precipitation reaction and the sharper the equivalence region changes. Both  $K_{sp}$  and the reagent concentrations affect the choice and use of an endpoint indicator.

## Endpoint Indicators for Argentometric Titrations

- Indicators for argentometric titrations are selected to produce a color change at or near the equivalence point.
- Normally the indicator is selected to react with the added titrating agent, not the analyte. If A is the analyte, R the titrating agent and In is the indicator.



To make the indicator change color, excess R must be added. Obviously, the smaller the excess added to cause the color change, the smaller the end point error. This means that the indicator should give large color changes at very low concentrations.

## End Point Determination in Precipitation Titrations

Titrations with  $Ag^+$  are called argentometric titrations.

For argentometric titrations, three classical methods based on color indicator can be used for end point detection:

- Mohr titration—formation of colored precipitate at the endpoint.
- Volhard titration—formation of a soluble, colored complex at the endpoint.
- Fajans titration—adsorption of a colored indicator on the precipitate at the endpoint.

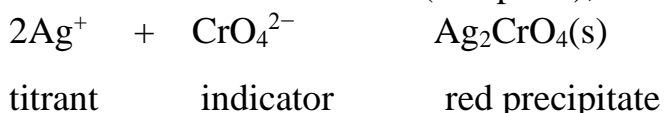
## The Mohr method

- The Mohr method was first published in 1855 as a method for chloride analysis.
- In the precipitation of chloride by silver ion, chromate ion ( $CrO_4^{2-}$ ) is used as an indicator in the formation of  $Ag_2CrO_4$ , a reddish-brown precipitate formed when excess  $Ag^+$  is present.



$$K_{sp} = 1.8 \times 10^{-10} (S = 1.34 \times 10^{-5} M)$$

- Mohr indicator reaction (end point),

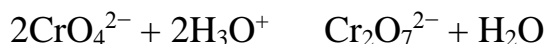


$$K_{sp} = 1.2 \times 10^{-12} (S = 6.7 \times 10^{-5} M)$$

- The concentration of titrant rises sharply near the equivalence point, and the solubility of  $Ag_2CrO_4$  is exceeded.
- The titrations are performed only in neutral or slightly basic medium to prevent silver hydroxide formation (at  $pH > 10$ ).



- Or the formation of chromic acid at pH < 7.



[CrO<sub>4</sub><sup>2-</sup>] become lower, more Ag<sup>+</sup> to be added to reach end point, which cause error.

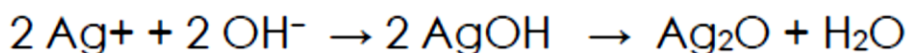
### Interferences and limitations of Mohr method:

- 1- The Mohr titration is applicable only **in neutral or faintly alkaline solution with pH values from about 6 to 10**. In acid solution, the CrO<sub>4</sub><sup>2-</sup> concentration is greatly decreased according to the following equilibrium:



and dichromate is formed whose silver salt is soluble. Therefore, no indicator precipitate forms.

If, on the other hand, the medium is alkaline, silver will precipitate as its oxide:



This interferes with the titration, the silver oxide may even precipitate before silver chromate especially where the solubility product of Ag<sub>2</sub>O is exceeded. If ammonium salts are present, the pH of the solution must not exceed pH 8 otherwise free ammonia will be produced and dissolve the silver chloride precipitate. Therefore, the halide solution should be neutralized before titration if necessary, by adding NaHCO<sub>3</sub> or dilute HNO<sub>3</sub>, as the case may be.

- 2- Cations that give insoluble chromate e.g. barium ions: They must be absent or removed before the titration.
- 3- The reverse titration of silver ion with chloride ion using chromate as indicator is not feasible, the flocculated Ag<sub>2</sub>CrO<sub>4</sub> formed initially, reacts slowly with chloride especially near the end point of the titration. However to determined silver by Mohr method, it is possible to add excess standard chloride solution and then back-titrate using the chromate indicator.
- 4- Titration of iodide; and of thiocyanate is not successful because silver iodide and silver thiocyanate adsorb chromate ions so strongly that a false and somewhat indistinct end point is obtained.

### Use of adsorption indications (Fajan method)

This method uses an adsorption indicator such of fluorescein and eosin. The indicator adsorb onto the surface of the silver salt precipitate at the endpoint. The adsorption process causes a change in the colour of the indicator.

- AgNO<sub>3</sub> added to a dilute solution of NaCl, the solution becomes turbid and if other electrolytes are absent, coagulation does not occur immediately.
- The colloidal sized AgCl particles adsorb Cl<sup>-</sup> and these attract sodium ions as shown in Fig below.
- Colloidal particles are electrically charged and repel each other preventing coagulation.

- As titration continues, the amount of chloride decreases but there is still some surface charge, which acts to repel the negatively charged indicator ion.

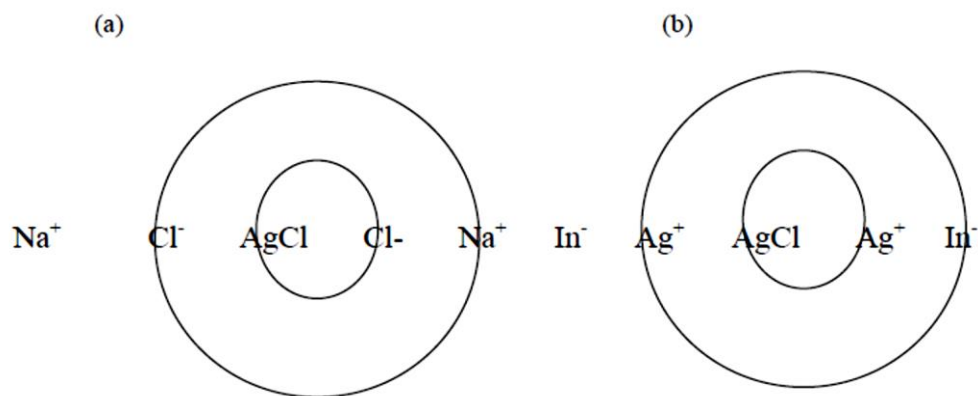


Figure. Colloidal silver salts (a) before endpoint and (b) after endpoint

- Immediately after endpoint there is an excess of silver ions which will adsorb onto the surface of the precipitate
- The charged surface has now changed polarity and attracts the negative indicator ion
- A colour change will be observed
- A blank titration is not required as the indicator does not react with the titrant

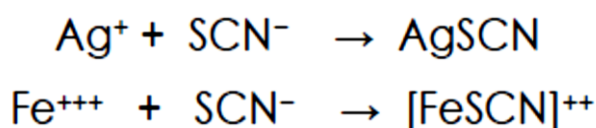
### Limitations of Fajan's method

- Low background levels of non-reacting ions to ensure that coagulation does not occur.
- Will not work with very low levels as there will not be enough precipitate to allow the colour change to be observed
- Method is pH dependent as the indicator must be in the ionised form

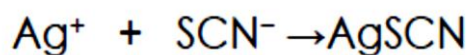
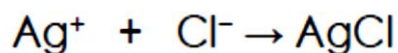
Fajan's method can be used to titrate silver with a standard chloride solution. This is not possible in Mohr's method since chromate added to a silver solution would immediately cause a precipitate.

### Formation of a soluble coloured compound (Potassium Thiocyanate as Titrant (Volhard method)):

This method uses a back titration with potassium thiocyanate and is suitable for the determination of chlorides, bromides and iodides in acidic solutions. A known excess of silver nitrate solution is added to the sample and the excess is back titrated with standard thiocyanate solution. The titration uses iron III as the indicator. The iron III indicator works by forming the coloured complex when an excess of thiocyanate occurs. The solution must be acidic, with a concentration of about 1 M in nitric to ensure the complex formed is stable. The method is suitable for the direct determination of silver or for the indirect determination of halide ions.



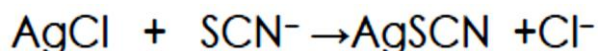
For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:



The two sparingly soluble salts will be in equilibrium with the solution hence:

$$\frac{[\text{Cl}^-]}{[\text{SCN}^-]} = \frac{S_{\text{AgCl}}}{S_{\text{AgSCN}}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 170$$

When the excess of silver has reacted, the thiocyanate may react with the silver chloride, since silver thiocyanate is the less soluble until the ratio  $[\text{Cl}^-] / [\text{SCN}^-]$  in the solution is 170.



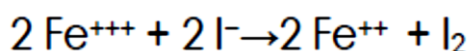
This will take place before reaction occurs with the ferric ions in the solution and there will consequently be a considerable titration error. It is therefore absolutely necessary to prevent the reaction between the thiocyanate, and the silver chloride. This may be effected in several ways, of which the first is probably the most reliable:

- a) The silver chloride is filtered off before back titration.
- b) After the addition of the silver nitrate, the suspension is boiled for about 3 minutes, cooled and then titrated immediately,
- c) An immiscible liquid is added to "coat" the silver chloride particles and thereby protect them from interaction with the thiocyanate. The most successful liquid is nitrobenzene.

With bromides, we have the equilibrium;

$$\frac{[\text{Br}^-]}{[\text{SCN}^-]} = \frac{S_{\text{AgBr}}}{S_{\text{AgSCN}}} = \frac{3.5 \times 10^{-13}}{7.1 \times 10^{-13}} = 0.5$$

The titration error is small, and no difficulties arise in the determination of the end point. Silver iodide (S.P.  $1.7 \times 10^{-16}$ ) is less soluble than the bromide, the titration error is negligible but the ferric ion indicator should not be added until excess of silver is present, since the dissolved iodide reacts with the ferric iron.



#### **Limitations of Argentometric titrations:**

- 1- Reducing agents, such as, sulphur dioxide interferes by reducing the silver ions, and must be removed by previous oxidation.
- 2- Coloured compounds of any sort obscure the end point, which is taken as the faintest ting of colour detectable on the precipitated silver halide, or in solution, as the case may be.
- 3- Silver halides are sensitive to photodecomposition, and the titration should be carried out in diffused daylight, or artificial light.
- 4- Most cations except the alkalies and alkaline earths interfere in several ways,

- a) Some, such as  $\text{Fe}^{3+}$  form insoluble coloured hydroxide in neutral or slightly acid medium;
- b) Some, such as  $\text{Al}^{3+}$ , hydrolyse to insoluble basic salts in neutral or slightly acid solution, showing a tendency to coprecipitate chloride;
- c)  $\text{Hg}^{2+}$  form soluble complexes with halides of the type  $[\text{HgI}_4]^{2-}$ .

### Comparison of silver titration methods

Method	Advantages	Disadvantages
<b>Mohr</b>	<ul style="list-style-type: none"> <li>• Simple</li> </ul>	<ul style="list-style-type: none"> <li>• Alkaline solutions only</li> <li>• Not suitable for iodide</li> <li>• Requires a blank</li> </ul>
<b>Fajans</b>	<ul style="list-style-type: none"> <li>• Capability for different pH ranges and selectivity with different indicators</li> </ul>	<ul style="list-style-type: none"> <li>• Difficulty with dilute solutions</li> <li>• Should not be a high background ionic level</li> </ul>
<b>Volhard</b>	<ul style="list-style-type: none"> <li>• Capable of direct silver and indirect halide analyses</li> <li>• Very clear colour change</li> </ul>	<ul style="list-style-type: none"> <li>• Must be 1M nitric acid solution</li> <li>• Some problems with specific anions</li> </ul>

### 3) Complexometric titrations

**Complexation Reaction:** A reaction between two species having a well-defined stoichiometry. The resulting bond is not permanent from a covalent standpoint.

**Complex:** The resulting structure formed during a complexation reaction.

**Coordination Center:** Metal ion in a complex (Lewis acid)

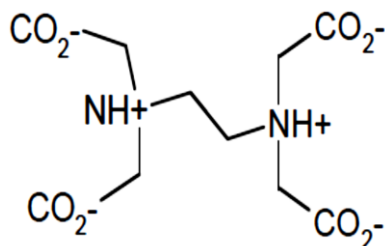
**Ligand:** The species that complexes the metal center. A single species can form one or more bonds with a single coordination center (Lewis base).

**Coordination Number:** Number of ligand bonds formed around the coordination center.

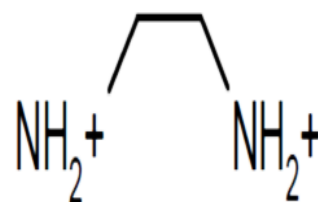
**Chelate:** Ligands that form multiple bonds (multidentate; bi, tri, tetra, penta).

#### Ethylenediaminetetraacetic acid

#### EDTA



#### Ethylenediamine

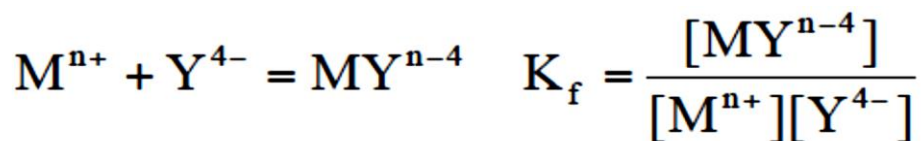


- EDTA is the most commonly used chelating agents as it can form complexes with a wide range of metals.
- The ability of EDTA to complex is dependent on its form. The most desirable state is the  $Y^{4-}$  form.
- As the pH increases, more EDTA becomes  $Y^{4-}$ .

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[H_6Y^{2+}] + [H_5Y^+] + [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}]}$$

$$\alpha_{Y^{4-}} = \frac{[Y^{4-}]}{[EDTA]}$$

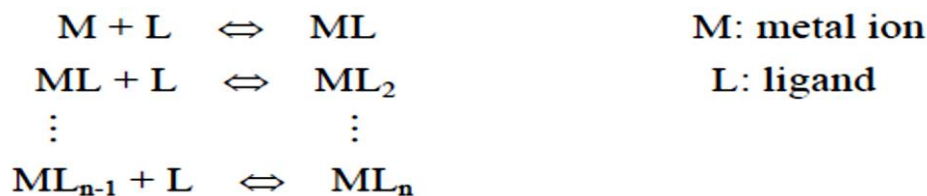
- The formation constant for metal-EDTA complexes is:



- It is important to note the requirement for the charge state of EDTA. Leads to a conditional (effective) formation constant

$$K'_f = \alpha_{Y^{4-}} K_f = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

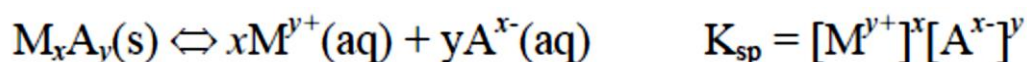
## Complexations Equilibria:



$$\begin{array}{lcl} \text{M} + \text{L} \rightleftharpoons \text{ML} & \beta_1 = \frac{[\text{ML}]}{[\text{M}][\text{L}]} = K_1 \\ \text{M} + 2\text{L} \rightleftharpoons \text{ML}_2 & \beta_2 = \frac{[\text{ML}_2]}{[\text{M}][\text{L}]^2} = K_1K_2 \\ \text{M} + 3\text{L} \rightleftharpoons \text{ML}_3 & \beta_3 = \frac{[\text{ML}_3]}{[\text{M}][\text{L}]^3} = K_1K_2K_3 \\ \vdots & & \\ \text{M} + n\text{L} \rightleftharpoons \text{ML}_n & \beta_n = \frac{[\text{ML}_n]}{[\text{M}][\text{L}]^n} = K_1K_2K_3 \cdots K_n \end{array}$$

$$\alpha_{\text{M}} = \frac{1}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \cdots + \beta_n[\text{L}]^n}$$
$$\alpha_{\text{ML}} = \frac{\beta_1[\text{L}]}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \cdots + \beta_n[\text{L}]^n}$$
$$\alpha_{\text{ML}_2} = \frac{\beta_2[\text{L}]^2}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \cdots + \beta_n[\text{L}]^n}$$
$$\alpha_{\text{ML}_n} = \frac{\beta_n[\text{L}]^n}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \cdots + \beta_n[\text{L}]^n}$$

## The Formation of Insoluble species



## EDTA titrations

1. Before the equivalence point there is excess M in solution.
2. At the equivalence point, treated as dissolving pure MY complex.
3. After equivalence there is excess EDTA.

## Indicators

To carry out metal cation titrations using EDTA, it is almost always necessary to use a complexometric indicator to determine when the end point has been reached. Common indicators are organic dyes such as Fast Sulphon Black, Eriochrome Black T. Color change shows that the indicator has been displaced (usually by EDTA) from the metal cations in solution when the endpoint has been reached.

## Metal ion indicators

The success of an EDTA titration depends upon the precise determination of the end point. The most common procedure utilizes metal ion indicators. The requisites of a metal ion indicator for use in the visual detection of end points include:

- (a) The colour reaction must be before the end point, when nearly all the metal ion is complexed with EDTA, the solution is strongly coloured.
- (b) The colour reaction should be specific or selective.
- (c) The metal-indicator complex must possess sufficient stability, otherwise, due to dissociation, a sharp colour change is not attained.
- (d) The colour contrast between the free indicator and the metal-indicator complex should be readily observed.
- (e) The indicator must be very sensitive to metal ions (i.e. to pM) so that the colour change occurs as near to equivalence point as possible.
- (f) The above requirements must be fulfilled within the pH range at which the titration is performed.

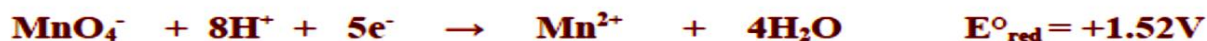
#### 4) Oxidation-reduction titrations or redox titrations

These titrations involve the titration of an **oxidizing agent (or oxidant)** with a **reducing agent (or reductant)** or vice versa. There must be a sufficiently large difference between the oxidizing and reducing capabilities of these agents for the reaction to undergo completion with a sharp end point.

Some of the commonly used oxidizing and reducing agents in the redox titrations are –

##### Oxidizing agents

- i. **KMnO<sub>4</sub>** in presence of dil H<sub>2</sub>SO<sub>4</sub>



- ii. **K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>** in dil. H<sub>2</sub>SO<sub>4</sub>

a moderately strong oxidizing agent; oxidizing ability depends strongly on pH, decreasing rapidly as solution becomes more neutral



- iii. **Iodine solution**



##### Reducing agents

- i. **Mohr's salt** **FeSO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O**



- ii. **Oxalic acid** **H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O**



- iii. **Sodium thiosulphate** **Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O**



## Precipitation methods (Gravimetry)

Gravimetric methods are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

### Classifications of gravimetric methods

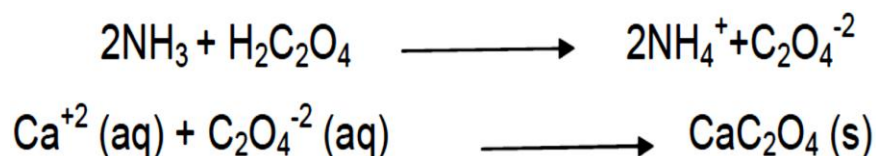
- 1- **Precipitation gravimetry**, the analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.
- 2- **Volatilization gravimetry**, the analyte is separated from other constituents of a sample by conversion to a gas of known chemical composition. The weight of this gas then serves as a measure of the analyte concentration.
- 3- **Electrogravimetry**, the analyte is separated by deposition on an electrode by an electrical current. The mass of this product then provides a measure of the analyte concentration.

### Features or properties of Gravimetric Analysis

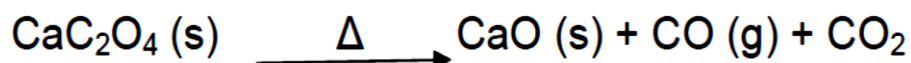
- Traditional Method.
- Cheap, easily available apparatus, simple to carry out.
- Slow, especially when accurate results are required.
- Wide range of sample concentrations (ng - kg).
- No calibration required (except for the balance).
- Accurate.

### Precipitation Gravimetry

- In precipitation gravimetry, the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, converted to a product of known composition by suitable heat treatment, and weighed. For example, a precipitation method for determining calcium in natural waters. The reactions are:



- The precipitate is filtered using a weighed filtering crucible, then dried and ignited. The process converts the precipitate entirely to calcium oxide. The reaction is:

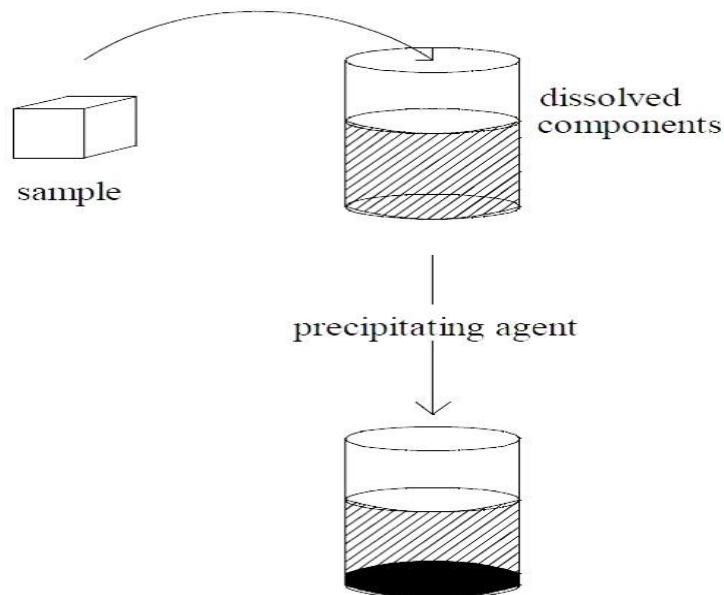


- After cooling, the crucible and precipitate are weighed, and the mass of calcium oxide is determined by subtracting the known mass of the crucible. The calcium content of the sample is then computed.

## Procedure for Precipitation gravimetry

The steps required in gravimetric analysis, after the sample has been dissolved, can be summarized as follows:

1. Preparation of the solution
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing
8. Calculation



## Properties precipitating reagents

- Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte.
- Specific reagents, which are rare, react only with a single chemical species. Selective reagents, which are more common, react with a limited number of species.

## Properties of good precipitates

1. Easily filtered and washed free of contaminants.
2. Of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing.
3. Unreactive with constituents of the atmosphere
4. Of known chemical composition after it is dried or, if necessary, ignited.

## Particle size and filterability of precipitates

- Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities.
- In addition, precipitates of this type are usually purer than are precipitates made up of fine particles.

## Factors that determine the particle size of precipitates

The particle size of solids formed by precipitation varies enormously.

### a- Colloidal suspensions,

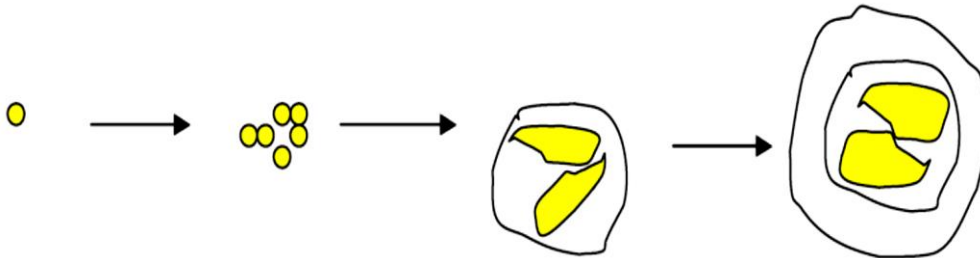
- Whose tiny particles are invisible to the naked eye ( $10^{-7}$ -  $10^{-4}$  cm in diameter).
- Colloidal particles show no tendency to settle from solution.
- Not easily filtered.

### b- Crystalline suspension

- Particles with dimensions on the order of tenths of a millimeter or greater.
- The temporary dispersion of such particles of tend to settle spontaneously.
- Easily filtered.

We can summarized the precipitation mechanism

- 1) Induction period.
- 2) Nucleation.
- 3) Particle growth to form larger crystal
- 4) Adsorption.
- 5) Electrostatic.



## Impurities in Precipitates

- Precipitates tend to carry down from the solution other constituents that are normally soluble, causing the precipitate to become contaminated.
- This process is called **coprecipitation**.
- In other words, coprecipitation is a phenomenon in which otherwise soluble compounds are removed from solution during precipitate formation.

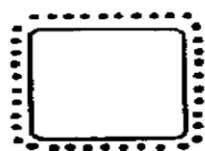
### Types of coprecipitation:

A: surface adsorption

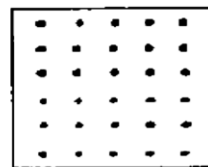
B: inclusion-isomorphous carrying (Mixed-crystal formation)

C: occlusion

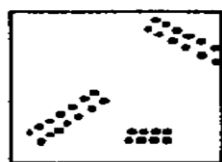
D: mechanical entrapment in colloidal.



A



B



C



D

## **Types of Precipitating Agents**

### **1- Inorganic Precipitating Agents**

These reagents typically form slightly soluble salts or hydrous oxides with the analyte. As you can see from the many entries for each reagent, few inorganic reagents are selective ( $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_4$ , etc.).

### **2- Reducing Agents**

This type of reagents convert an analyte to its elemental form for weighing ( $\text{SO}_2$ ,  $\text{SnCl}_2$ , etc.).

### **3- Organic Precipitating Agents**

- Numerous organic reagents have been developed for the gravimetric determination of inorganic species.
- Some of these reagents are significantly more selective in their reactions than the inorganic reagents (Dimethylglyoxime, cupron, etc.).
- We encounter two types of organic reagents. One forms slightly soluble non-ionic products called coordination compounds; the other forms products in which the bonding between the inorganic species and the reagent is largely ionic.

#### **Organic precipitating agents have the advantages of:**

- Some of organic precipitating agents are very selective, and others are very broad in the number of elements they will precipitate.
- Giving precipitates with very low solubility in water.
- Give a favorable gravimetric factor.