FACULTY OF SCIENCE, QENA
كلية العلوم بقنا

SOUTH VALLEY UNIVERSITY
جامعة جنوب الوادي

General Chemistry II

For 1st year Science students

Physical & Geological groups

Prepared by:

Dr. Ibrahim A. I. Hassan

Course of:

Chm 102: General Chemistry(II) - 3 Credit (Lecture 2h/w + Lab.3h/W) Prerequisite: Chm 101.

Contents: Organic Molecules: Structure, Bonding and Properties. Purification and Identification of Organic Compounds. Classification of Organic Compounds. Isomerism in Organic Compounds: Constitutional Isomers, Resonance versus Tautomerism. IUPAC Nomenclature of Organic Compounds, Functional Groups. Chemistry of Aliphatic Compounds (Alkanes and Cycloalkanes, Alkenes and Alkynes). **Physical Chemistry:** Explain the concept and types of chemical analysis - Identify the various volumetric analysis - identify the indicator concept and its work - acid and base - buffer solution - Identify the equilibrium system and factors effecting on equilibrium system – Le Chatelier principle - low of mass action - Explain the ionization of water - clarify the concept of pH Ostwald low for dilution – Hydrolysis - solubility product - common ion effect - salt formation - colloidal state and its preparation and characterization - low of gases.

Inorganic part.

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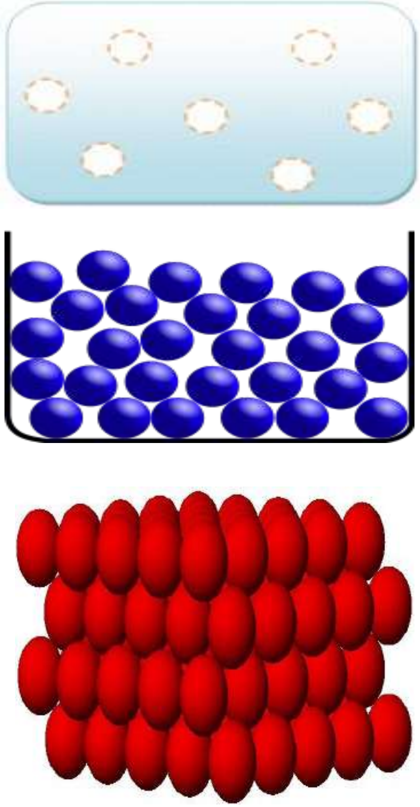
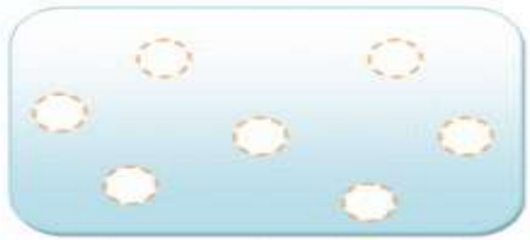
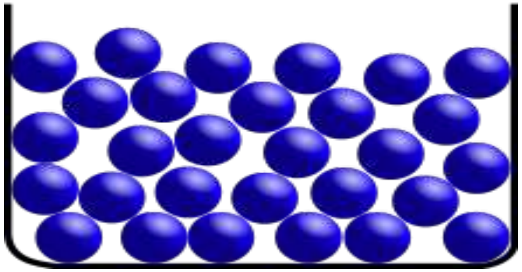


I. Matter States

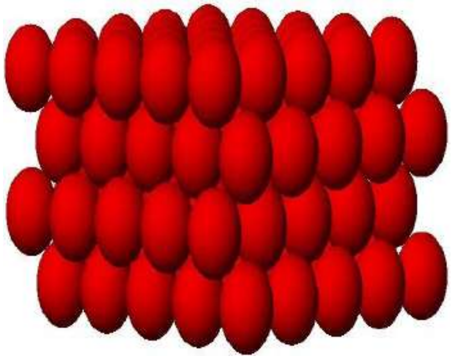
- Gas



- Liquid



- Solid state



- Plasma ???

Chemical Equilibrium

Factors affect on Chemical equilibrium

- Effect of Temperature.
- Effect of Concentration (Pressure in case of Gasses)
- Effect of Catalysts
- Types of Chemical Reactions:
  - ✓ Reversible
  - ✓ Irreversible

- **Le Chatleir's Principle**
- **Law of Mass Action**
- **Factors affect on Chemical equilibrium Constant.**
- **Applications on Law of Mass Action**

Ionic Equilibrium

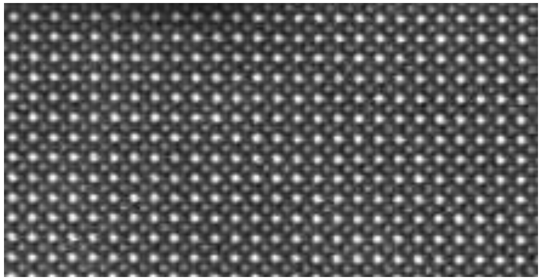
Application of Law of Mass Action on Ionic Equilibrium

- Ostwald dilution law
- Acid-Base Ionization
- Common ion Effect
- The ion Product of Water
- Hydrogen ion Exponent (pH)

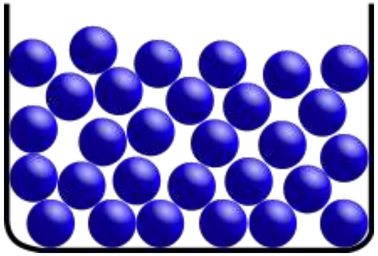
I. Matter States

Three states of matter are observable in everyday life:

- **Solid**



- **Liquid**



- **Gas**

Matter States

- **Solid state** maintains a fixed volume and shape, with component particles (atoms, molecules or ions) close together and fixed into place.

- **Liquid state** maintains a fixed volume, but has a variable shape that adapts to fit its container. Its particles are still close together but move freely.

- **Gaseous state** has both variable volume and shape, adapting both to fit its container. Its particles are neither close together nor fixed in place.

I. Gases

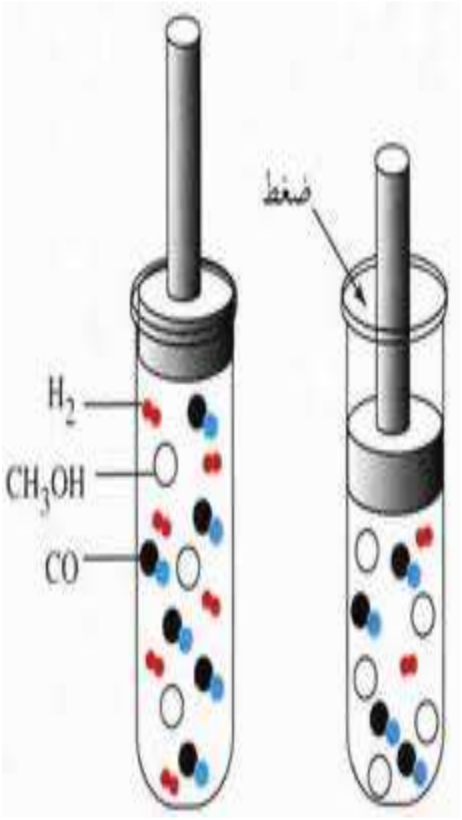
Physical Characteristics of Gases

Physical Characteristics	**Typical Units**
Volume, **V**	liters (**L**)
Pressure, **P**	atmosphere (1 **atm** = 1.015×10^5 N/m^2)*
Temperature, **T**	Kelvin (**K**)
Number of atoms or molecules, **n**	**mole** (1 mol = 6.022×10^{23} atoms or molecules)

$$*P = F_{(N)} / A_{(m^2)}$$

Gas Laws

- **Boyl's Law**
- **Charles & Gay Lussac's Law**
- **Law of Pressure**
- **The General Law of Gases**
- **Graham's Law for Diffusion.**
- **Dalton's Law for Partial Pressures.**
- **Diffraction gases laws**
- **Movement theory of gases**



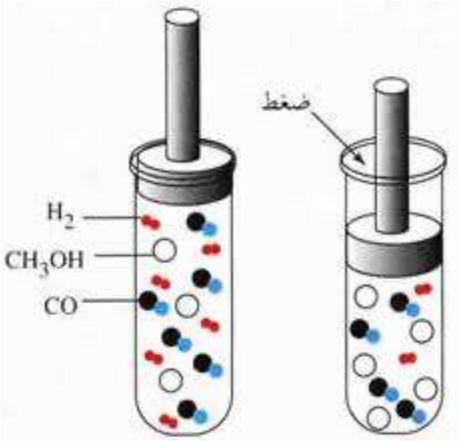
Gas' laws

- **Boyle's law:** or the pressure-volume law

States that the volume of a given amount of gas held at constant temperature varies inversely with the applied pressure.

$$P \ \alpha \ 1/V \quad \rightarrow \quad PV = \text{constant} \quad \text{or}$$

$$P_1V_1 = P_2V_2$$




Robert Boyle
1627-1691

Boyle's Law

"Father of Modern Chemistry"

Robert Boyle

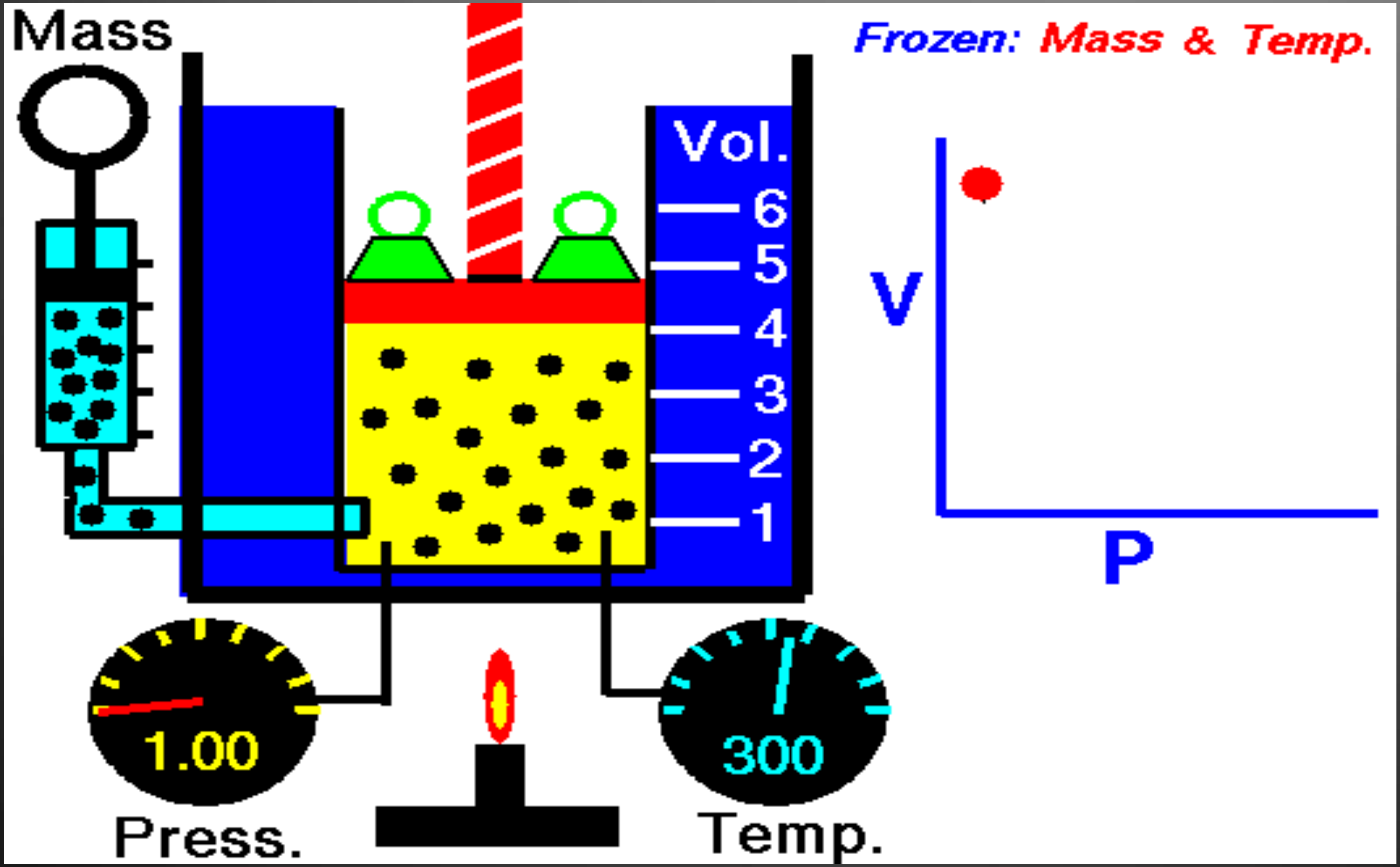
Chemist & Natural Philosopher

Listmore, Ireland

January 25, 1627 – December 30, 1690

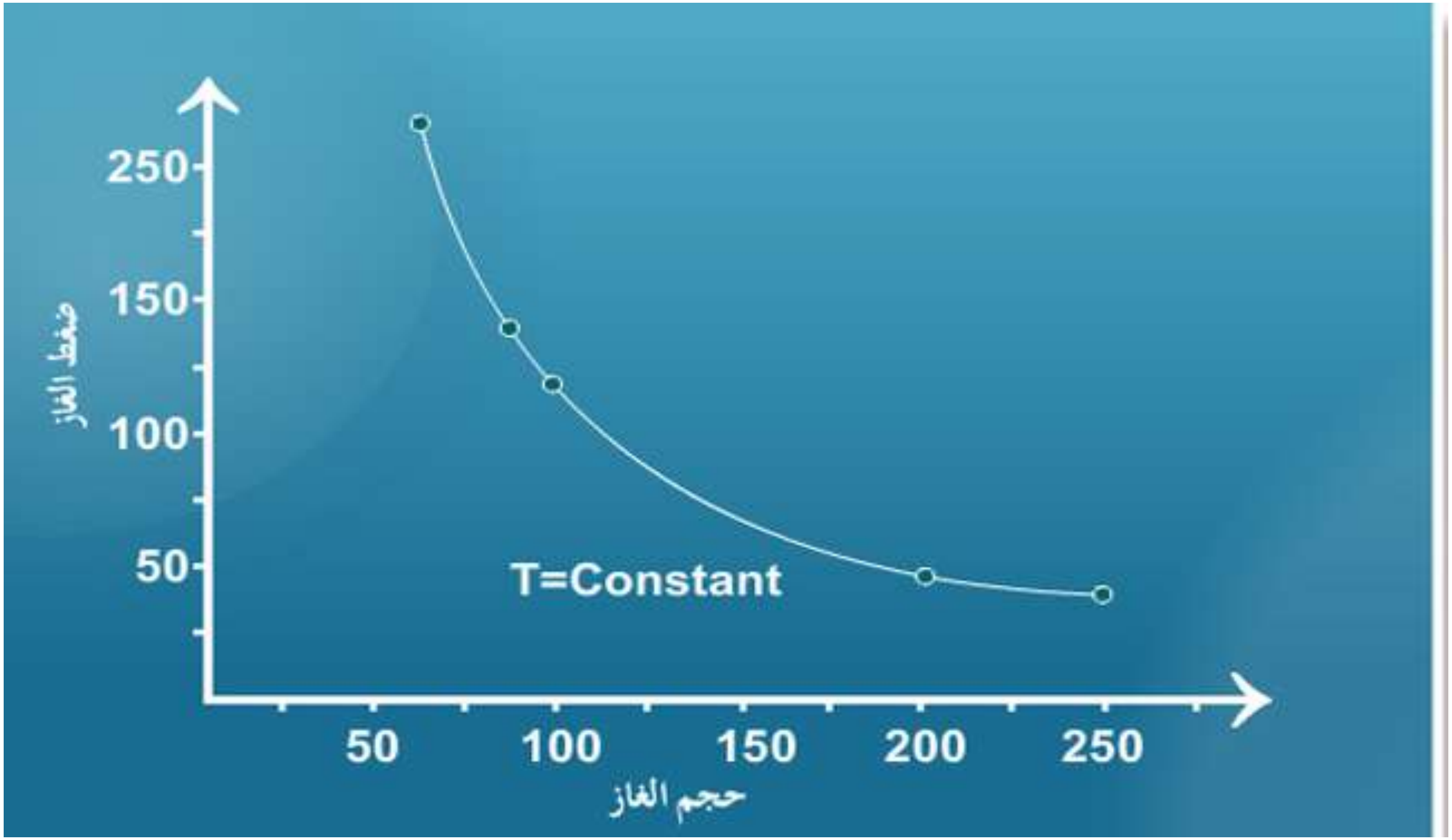
- **Pressure and volume are inversely related** at **constant temperature**.
- $PV = C$
- As one goes up, the other goes down.
- $P_1V_1 = P_2V_2$

Boyle's Law at Work…



Doubling the pressure reduces the volume by half. Conversely, when the volume doubles, the pressure decreases by half.

Boyle’s law


250
150
100
50
ضغط الغاز
T=Constant
50
100
150
200
250
حجم الغاز

- **Charles' Law**

The volume of a given amount of gas held at constant pressure is directly proportional to the Kelvin temperature.

or

The volume of a given amount of gas held at constant pressure increases by 1/273 of its volume at zero temperature if its temperature was increased by one Celsius.

- **Charles' Law**

$$V_t = V_0 + (t/273 \ \text{x}\ V_0)$$

$$V_t = V_0\,(1 + t/273) \qquad V_t` = V_0\,(1 + t`/273)$$

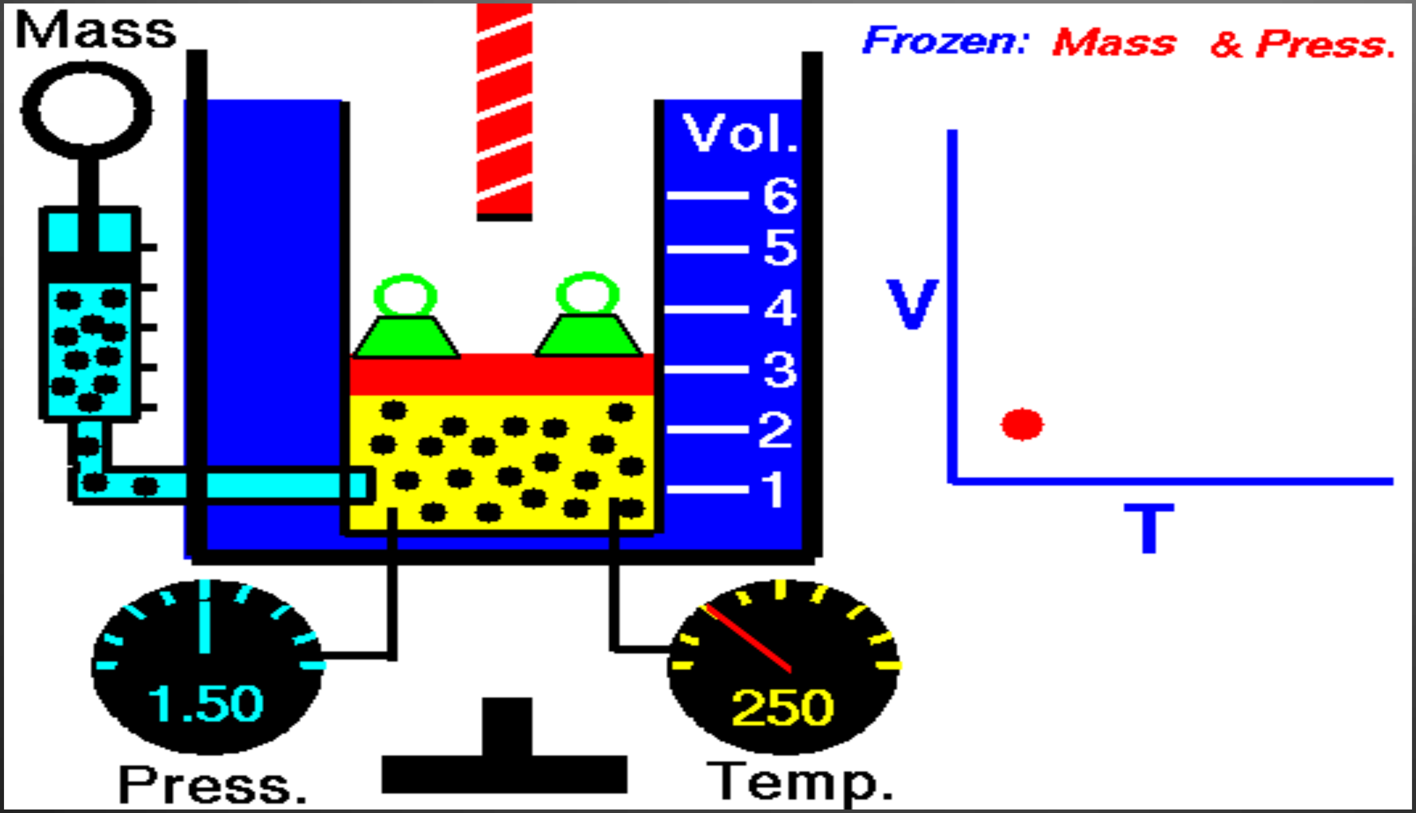
$$V_t \,/ V_t` = 273+t \ / \ 273+ t` = T/T`$$

Or $V \,\alpha\, T$ $V/T = \text{constant}$ or

$$V_1/T_1 = V_2/T_2$$

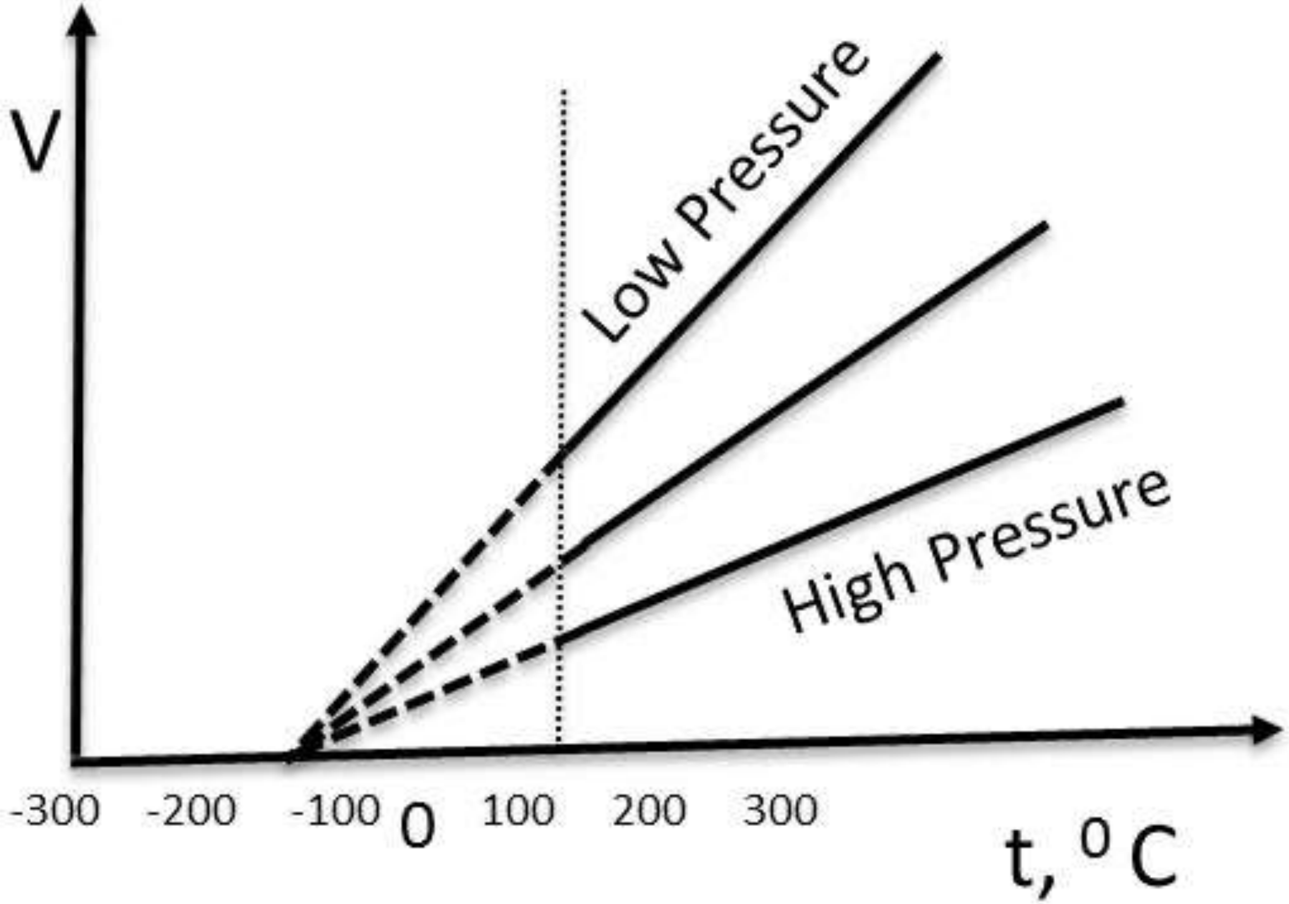
Jacques Alexandre César Charles
1746 - 1823

Charles’ Law at Work…



As the temperature increases, the volume increases. Conversely, when the temperature decreases, volume decreases.

- **Charles’ Law**



(Gay Lussac's Law

The pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature. Or

The pressure of a given amount of gas held at constant volume increases by 1/273 of its pressure at zero temperature if its temperature was increased by one Celsius.

Gay-Lussac Law

- At **constant volume**, **pressure** and **absolute temperature** are **directly related**.
- $P = k\,T$
- $P_1 / T_1 = P_2 / T_2$

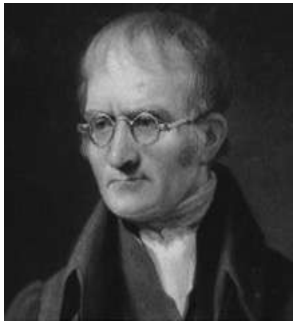
Joseph-Louis Gay-Lussac

Experimentalist

Limoges, France

December 6, 1778 – May 9, 1850

Dalton's Law of partial pressures



John Dalton

1766 - 1844

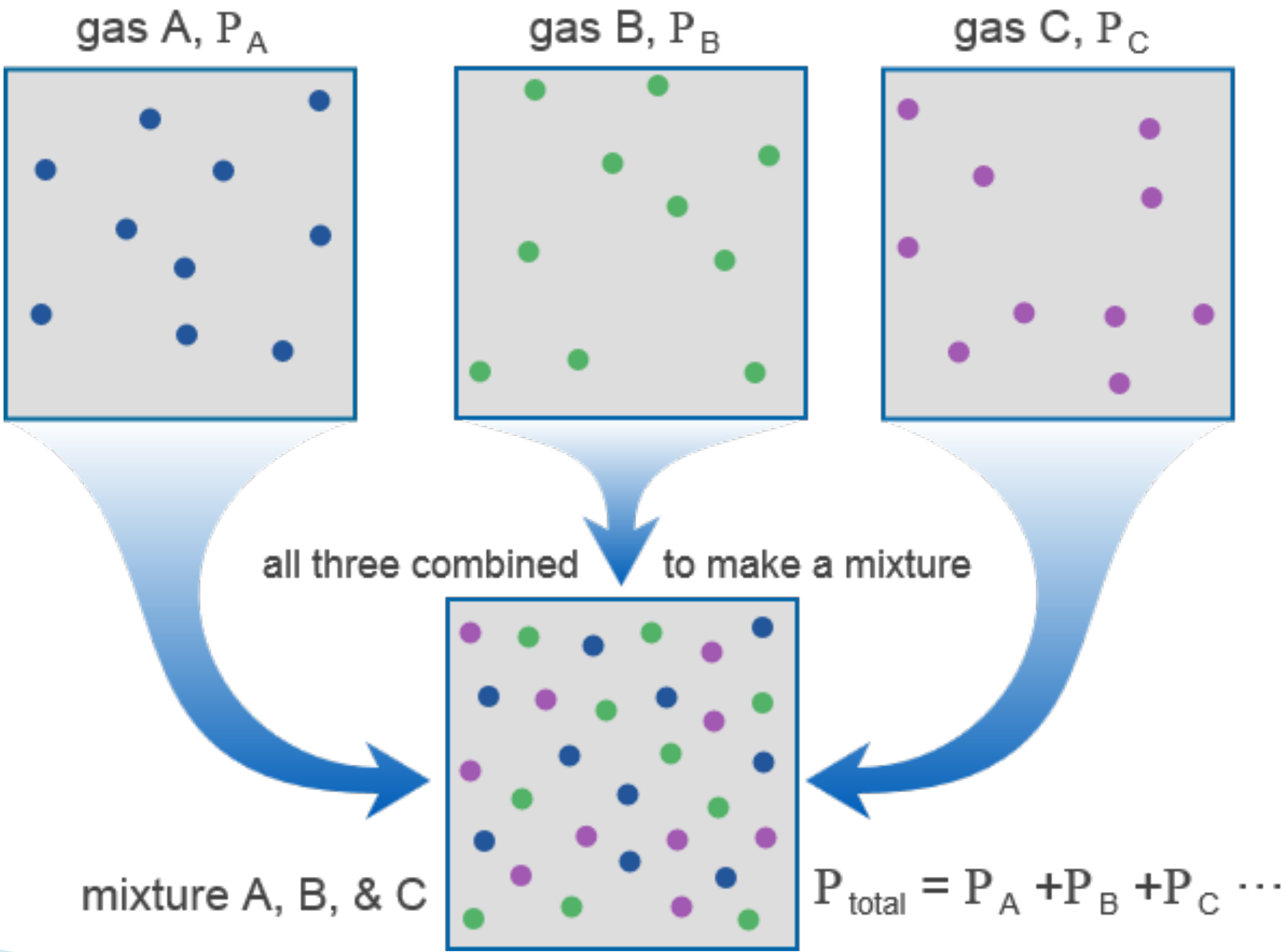
States that the total pressure exerted by a mixture of gases is the sum of partial pressure of each individual gas present. Each gas is assumed to be an ideal gas.

The total pressure of the gaseous mixture is equal to the sum of the partial pressures of gases.

Partial pressure is the pressure caused by the gas when it holds its own volume equal to the volume occupied by the whole mixture at the same temperature.

$$P_{total} = P_1 + P_2 + P_3 + \ldots$$

Dalton's Law of partial pressures



$$P_{total} = P_A + P_B + P_C \cdots$$

Dalton's Law of partial pressures

If the total pressure is P and its partial pressures are P_1,P_2,P_3,…..P_n , So:-

$$P = P_1 + P_2 + P_3 + \ldots\ldots P_n$$

If the number of moles of each gas are n_1, n_2, n_3 and its sum is n; the relationship between V, P, and n will be as:

$$P_1V = n_1RT \ldots\ldots\ldots\ldots1$$

$$P_2V = n_2 RT \ldots\ldots\ldots\ldots2$$

$$PV = nRT \quad \ldots\ldots\ldots\ldots3$$

Dalton's Law of partial pressures

By dividing equation 1 on 3:

$$P_1 = P \times (n_1/n)$$

This last equation makes it is possible to calculate the partial pressure, for any gas in gases mixture, by knowing the value of n_1/n.

Dalton's Law

- The **total pressure** in a container is the **sum of the pressure each gas** would exert if it were alone in the container.
- The total pressure is the sum of the partial pressures.
- $P_{Total} = P_1 + P_2 + P_3 + P_4 + P_5 \ldots$

(For each gas $P = nRT/V$)

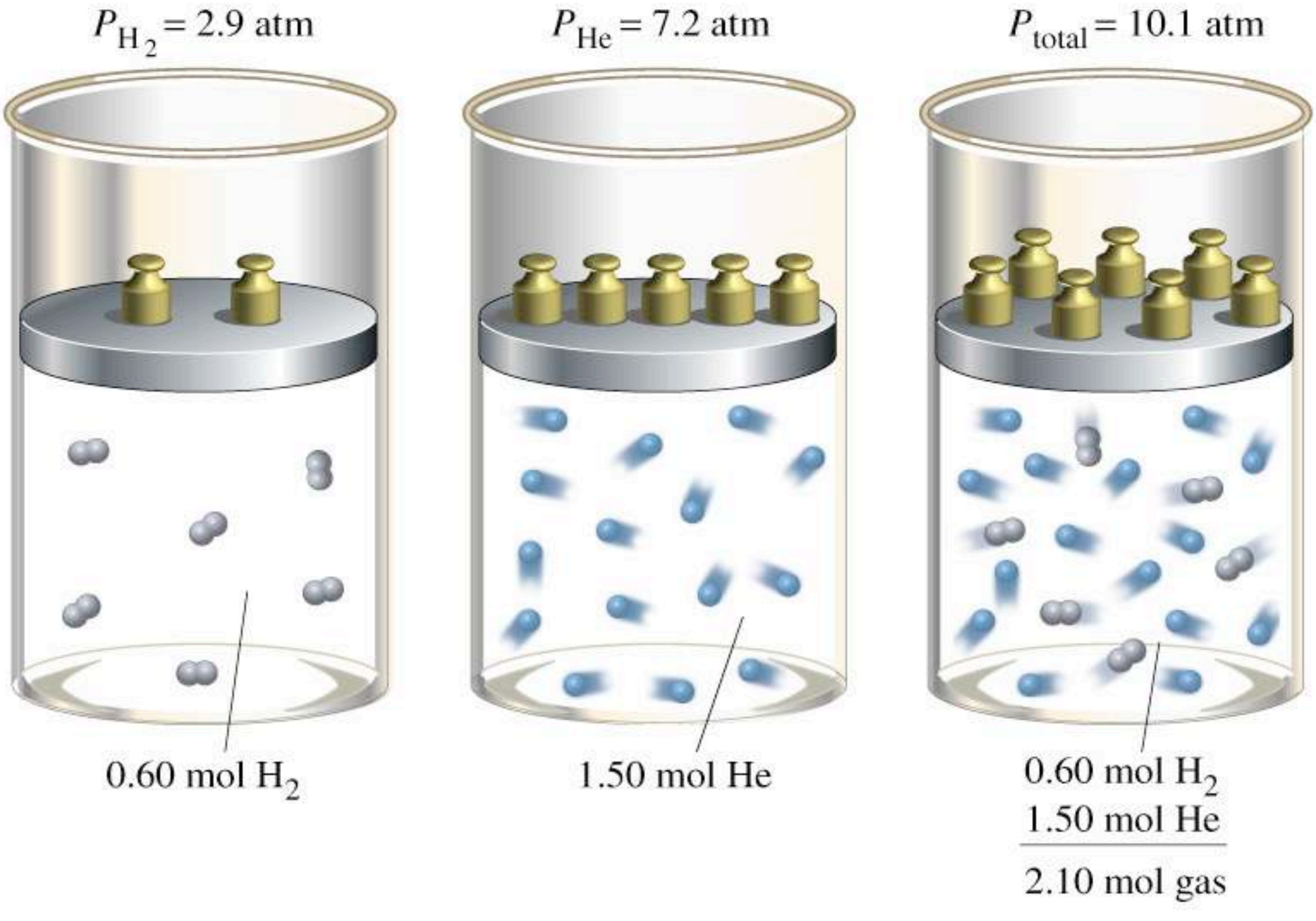
John Dalton

Chemist & Physicist

Eaglesfield, Cumberland, England

September 6, 1766 – July 27, 1844

Dalton's Law



(a) 5.0 L at 20 °C (b) 5.0 L at 20 °C (c) 5.0 L at 20 °C

Avogadro's Law

Amedeo Avogadro

Physicist

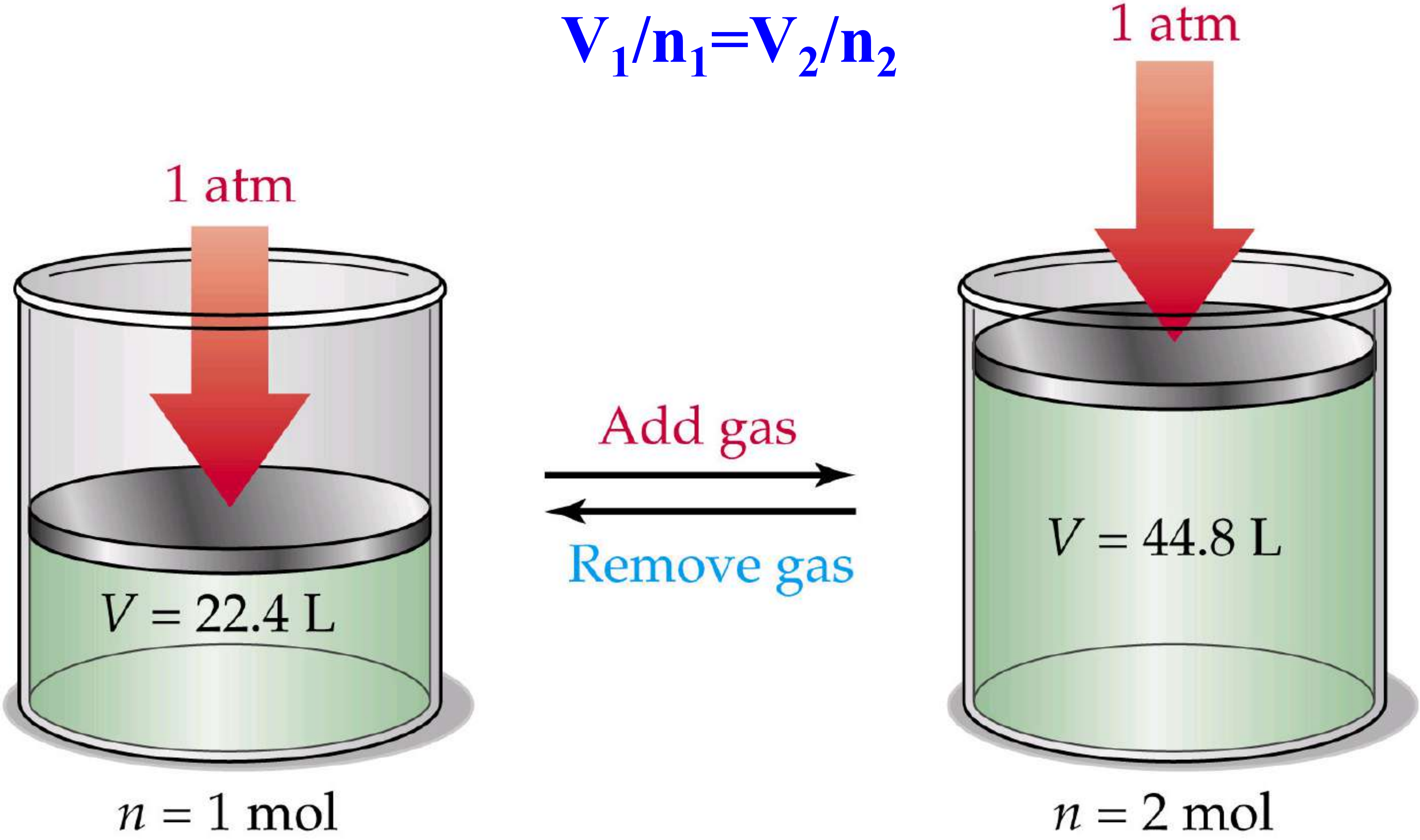
Turin, Italy

August 9, 1776 – July 9, 1856

- At **constant temperature and pressure**, the **volume** of a gas is **directly related to the number of moles**.
- $V = K n$
- $V_1 / n_1 = V_2 / n_2$

Avogadro's Law

$$V_1/n_1=V_2/n_2$$



Avogadro's Law

According to Avogadro's law; At constant temperature and pressure every mole of a gas, contained in a volume 22.4 L, contains 6.022 x 10^{23} molecules.

This is called <u>Avogadro's number (N)</u>

The Combined Gas Law

The volume of a given amount of gas is directly proportional to the ratio of its Kelvin temperature and inversely proportional to its pressure.

$$V \propto \frac{T}{P}$$

or

$$PV / T = C$$

or $P_1V_1 / T_1 = P_2V_2 / T_2 = P_3V_3 / T_3$ **etc.**

The Ideal Gas Law

$$PV = nRT$$

P = Pressure (in kPa)

V = Volume (in L)

T = Temperature (in K)

n = moles

R = *universal gas constant*

Ideal Gases

- An "ideal" gas exhibits certain theoretical properties:-

- Obeys all the gas laws under all conditions.
- Does not condense into a liquid when cooled.
- Shows perfectly straight lines when its V and T & P and T relationships are plotted on a graph.
- There are no gases that fit this definition perfectly. We assume that gases are ideal to simplify our calculations.
- Calculations have been done by using several gas laws (Boyle's Law, Charles's Law, Combined Gas Law).

GAS DIFFUSION AND EFFUSION

- **Diffusion** is the gradual mixing of molecules of different gases.

- **Effusion** is the movement of molecules through a small hole into an empty container.

GAS DIFFUSION AND EFFUSION

Graham’s law governs effusion and diffusion of gas molecules.

Graham has found that the gas diffusion speed is inversely proportional to the square root of the density of gas.

Thomas Graham, 1805-1869.
Professor in Glasgow and London.

GAS DIFFUSION AND EFFUSION

Molecules effuse through holes in a rubber balloon, for example, at a rate (= moles/time) that is proportional to T inversely proportional to M.

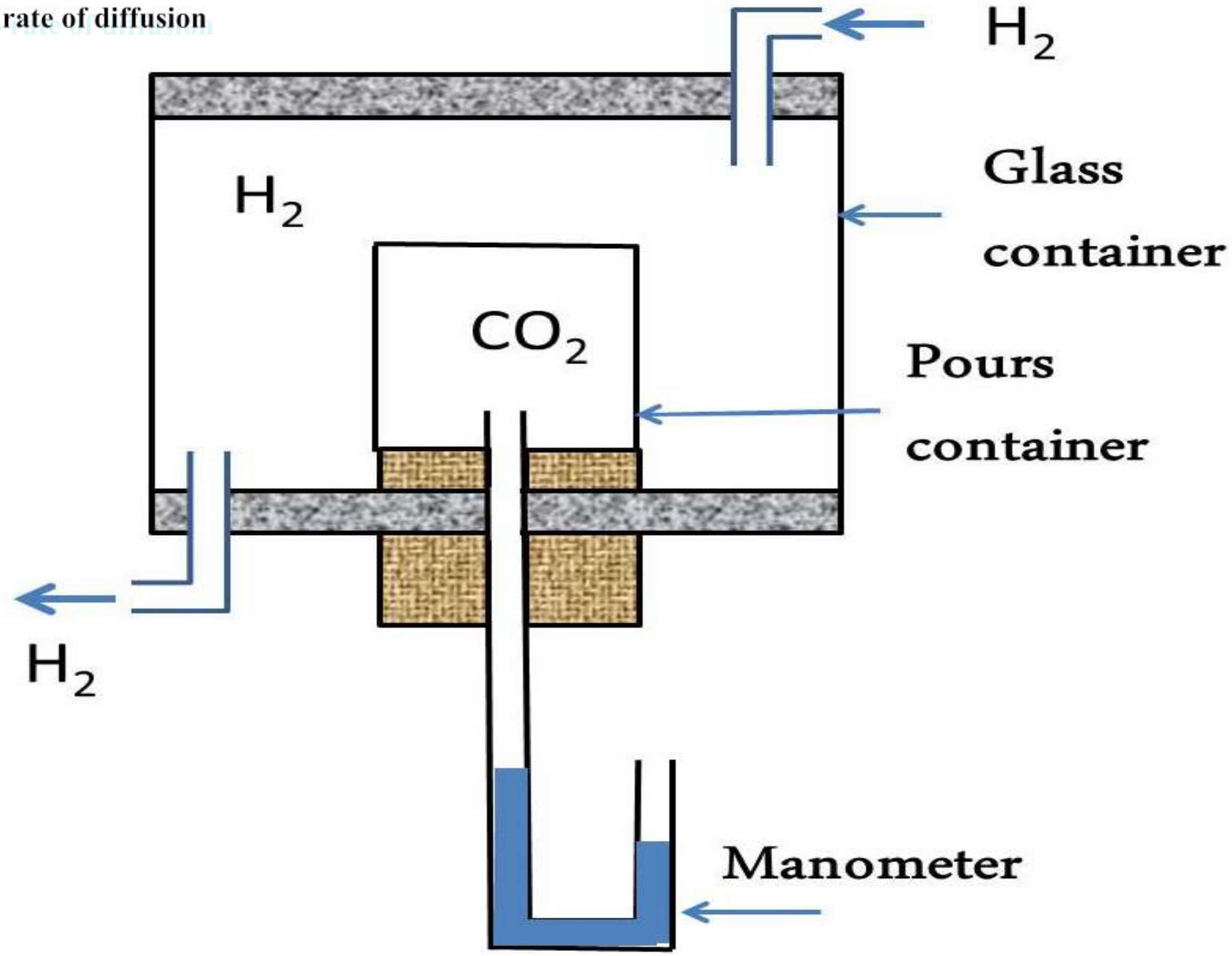
Therefore, (He) effuses more rapidly than O_2 at same T.

Relation of mass to rate of diffusion

- H_2 gas has a smaller particle size than that of CO_2 gas.
- H_2 diffuse into a porous container of CO_2 gas which leads to increase the pressure of CO_2 through the manometer.
- If H_2 was inside the porous container, and CO_2 was passed through, H_2 will diffuse out and the pressure decreases.

Gas Diffusion

relation of mass to rate of diffusion



Diffusion of Gasses

Gas deviation from Ideal behaviour:

Amagat found that Boyl’s law can't be applied on gasses under high pressure or low temperatures.

- **By plotting the relationship between P and PV it should give a straight line for an ideal gas, but that never happens.**
- **deviation decreases by increasing the temperature and decreasing of the pressure.**

Gas deviation from Ideal behaviour:

- **Gasses deviation depends on its type;**
- **Easily liquefied gasses such as CO_2 has much higher deviation ability than those gasses with difficult liquefaction such as N_2, (Fig 1).**

Gas deviation from Ideal behaviour:

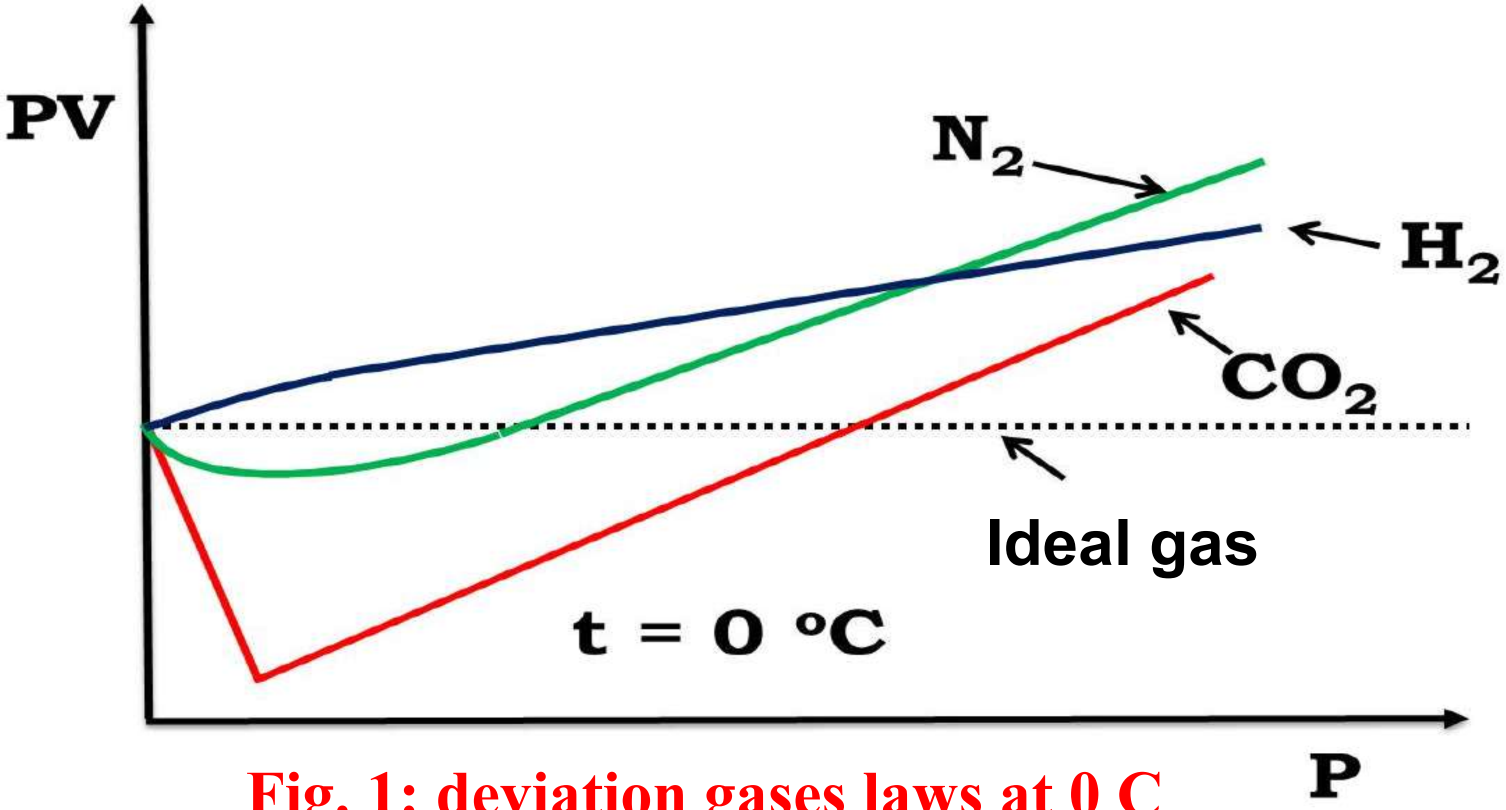


Fig. 1: deviation gases laws at 0 C

CO_2 gas deviation decreases with temperature

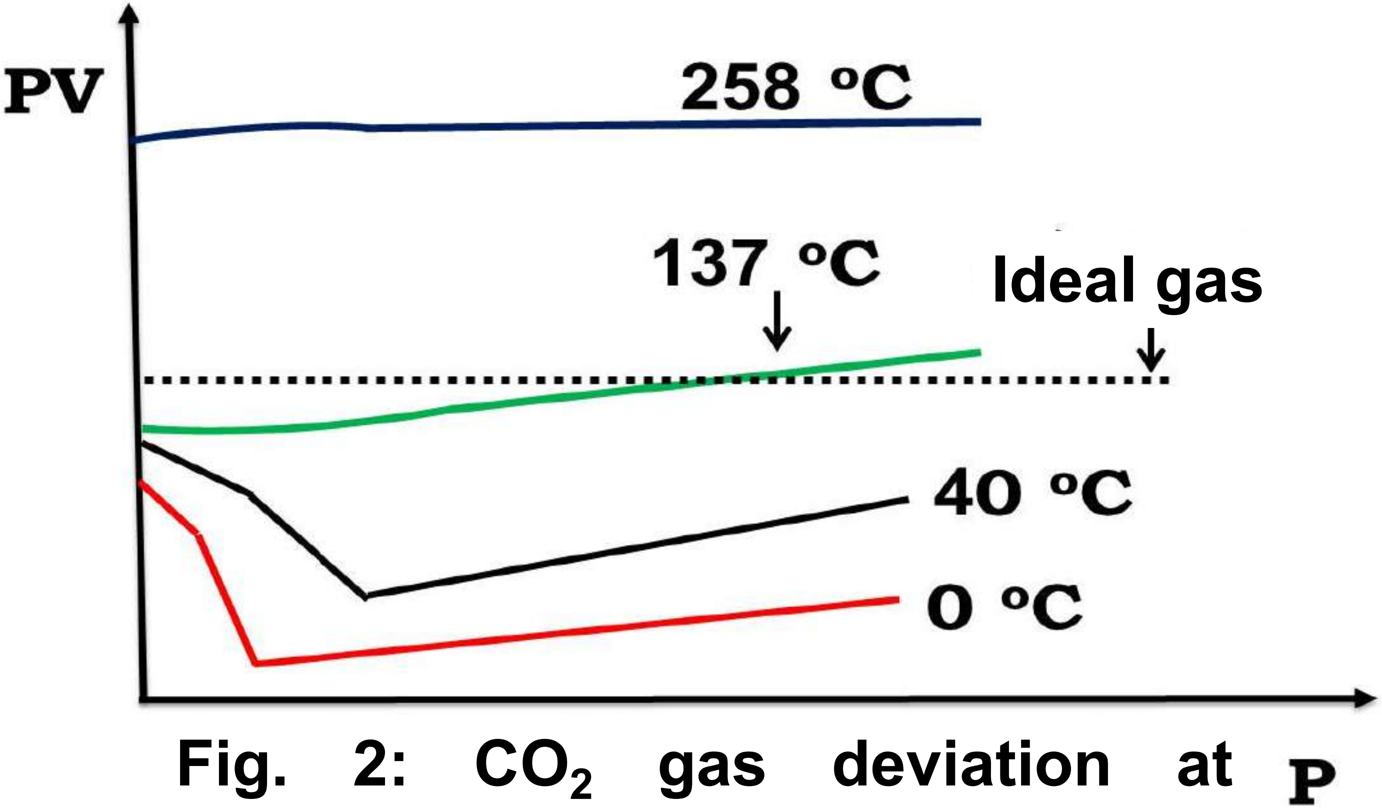


Fig. 2: CO_2 gas deviation at different Temperatures

Van der Waal equation


Van der Waal
1837 - 1923

- Deviation gases laws may be due to the existing attraction force between the particles and the volume they occupied.
- Gas laws represented by the general law of gases ($PV = nRT$) are not consistent with the behavior of gas except under low pressures and high temperatures.

Van der Waal equation

- At high pressure and low temperatures the volume of the particles and the force of the attraction increase.
- Dutch scientist, Van der Waal put a value representing the volume of the particles (b), which need to be withdrawn from the total gas volume (V-b)

Van der Waal equation

- The attraction force which affects on a moving particles towards the surface of the pot proportional with the concentration (C).
- At the same time the number of particles that collide with the surface of the pot also proportional with this value (C).
- So, the total attraction force proportional with C^2.

Van der Waal equation

- As the concentration is inversely proportional to the volume. So the attraction force will consequently inversely proportional with the Volume.

Attraction force α $1 / V^2$

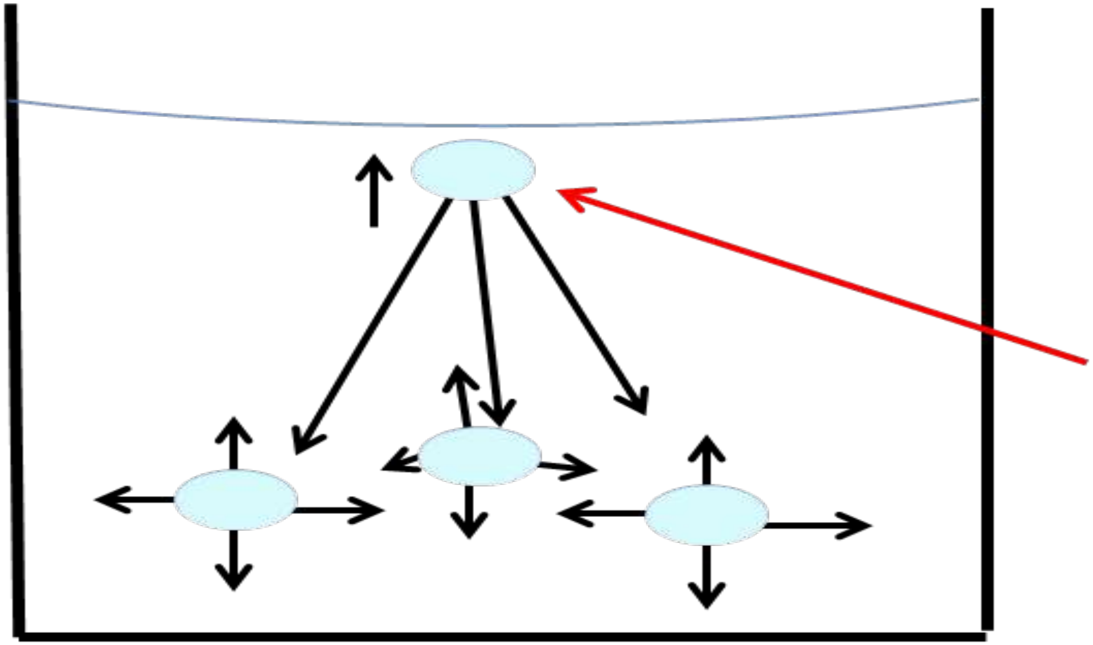
$= a / V^2$

This attraction force should be added to the pressure.

- So the real pressure should equal:

$$P = P + a/V^2$$

Van der Waal equation



Gas molecules moves towards the surface

Attraction force affect of gas molecules moves towards the surface

Van der Waal equation

So, the general equation of gases after the introduction of both the size of the particles and the attraction force between them is:

$$\boxed{(P + a/V^2)(V - b) = nRT}$$

Van der Waal equation

This is known as the equation of Van der Waal which consistent with the behavior of gas under higher pressures than that in the general equation of gases.

This equation does not solve the problem of deviation gases laws completely.

Van der Waal equation

- At low pressure; the value of (b) is extremely small in comparison to the total gas volume.
- $(P + a/V^2)\ (V) = nRT$

or $PV + a/V = nRT$

so, $PV = nRT - a/V$

Van der Waal equation

- **But if the pressure was very high, so the value of (a/V^2) will be tiny in comparison to the total pressure and can be neglected:**

$$P(V-b) = nRT$$

Or $$PV - Pb = nRT$$

so, $$PV = nRT + Pb$$

Movement theory of gases

Placed by Hook and Bernoulli in 1738 and completed by Krung, Clauzios and Maxwell in 1757, states:

1. **Gas is made up of small minutes (particles of small size).**
2. **Great distances between each other and the walls of its container**
3. **Gas particles move fast in straight lines and do not change direction unless they hit a wall or other molecules.**
4. **To illustrate this : cubic centimetre of oxygen containing at zero Celsius and under one atmosphere of pressure on 27×10^{18} molecules and is progressing quickly 460 m / s .**

Movement theory of gases

5. Gas molecules have complete flexibility which means that the speed of the particles as well as the amount of moves do not change after their collision with each other or with the wall of the pot .
6. Gas pressure is the result of collisions of molecules on the walls of the vessel containing it, and the high temperature increases the speed of molecules and thus increases the pressure.

Movement theory of gases

7. These molecules are spaced to such an extent that the attraction between them is almost non-existent and that it has no effect on the motion of molecules and the pressure on the surface of the pot . But at low temperature and high pressure the forces of attraction increases.

Gas Liquefaction

Michael Faraday
1791 - 1867

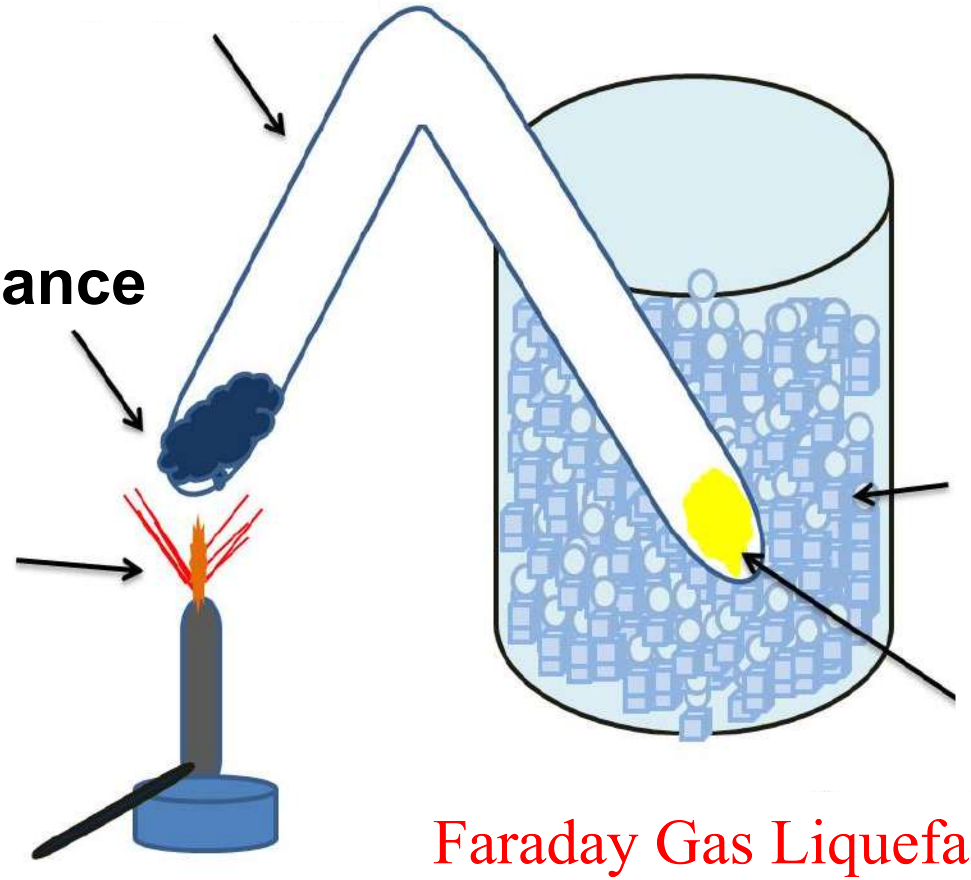
- **Faraday managed to liquefied a large number of liquefied gases using pressure and ice mixtures using twisted and locked tube.**
- **Gas material placed at one end and the gas is collected liquefied in the other end dipped in a cooled mixture.**

Gas Liquefaction

- **When the gas accumulates and increases pressure that will increase the attraction force between particles and turns the gas into a liquid.**

- **Faraday divided gases to : easily liquefied gases such as CO_2 & NH_3 and difficult or permanent , such as nitrogen and oxygen.**

Gas Liquefaction



Twisted and locked tube

Gas substance

Flame

Ice mixture

Liquefied gas

Faraday Gas Liquefaction Experiment

Gas Liquefaction

Faraday used different ice mixtures such as :

a) **A mixture of NaCl and ice - 23.6 ^{o}C.**

b) **A mixture of calcium chloride with ice - 51 ^{o}C.**

c) **A mixture of solid carbon dioxide and Either - 110 ^{o}C.**

d) **A mixture of solid carbon dioxide and acetone > - 110 ^{o}C.**

Gasses Laws

- Boyl's law $P_1V_1 = P_2V_2$
- Charles' Law $V_1/T_1 = V_2/T_2$
- Gay-Lussac's law $P_1/T_1 = P_2/T_2$
- Dalton Law $P_1/P = n_1/n$
- General law $P_1V_1/T_1 = P_2V_2/T_2$
- Or $PV = nRT$

Problems based on Gasses laws

- At 300 K the pressure of an amount of gas was 0.2 atm, how will be its pressure at 600 K?

Answer

From Gay-Lussac's law

$$P_1/T_1 = P_2/T_2$$

$$0.2/300 = P_2/600$$

$$P_2 = 0.4 \text{ atm.}$$

Problems based on Gasses laws

- At 300 K and a pressure of 1 atm.; a volume of an amount of gas was 200 cm^3, how much its volume will be if its pressure becomes 2 atm. and its temperature becomes 400K?

Answer

From combined law of gases

$$P_1V_1/T_1 = P_2V_2/T_2$$

$$V_2 = 400 \text{ x } 200/300 \text{ x } 2 = 133.3 \text{ Cm}^3$$

Chemical equilibrium

Chemical reaction:

- Spontaneous reaction such as precipitation and neutralization reactions.
- Slow reaction such as reaction of Hydrogen and Oxygen in the ordinary conditions.
- The majority of reactions are carried out in considerable speed.

Chemical equilibrium

Factors affecting on the reaction speed:

1- Temperature:

- Raising the temperature by 10 ^{o}C increases the reaction rate four times (Vant Huff)
- Heat activates the reaction and increases the collisions of molecules.

Factors affecting on the reaction speed:

2. Effect of concentration (pressure in the case of gases): increasing the concentration increases the number of collisions between reactants particles, so the reaction rate increases.

Factors affecting on the reaction speed:

2. **Effect of concentration (pressure in the case of gases):**

Precipitation of Sulphur increases with the increasing of the concentration of sodium thiosulfate.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + H_2O + S$$

The reaction rate decreases over time for the consumption of the reactants.

Factors affecting on the reaction speed:

3. **Stirring and increasing the exposed surface area to interact:**

Stirring and increasing the exposing surface area of the solute to solvent increasing the reaction rate.

Factors affecting on the reaction speed:

4. Effect of Catalyst:

It operates a small amount of motivation on the rate of reaction without being consumed or react. It increases the reaction rate.

Types of Chemical reactions:

1. **Irreversible reactions: (occur in an open system)**

Occur in one direction and the products can not find the opportunity to re-react again through losing it either through volatilization or precipitation.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2\uparrow$$

$$NaCl + AgNO_3 \longrightarrow NaNO_3 + AgCl\downarrow$$

In these reactions; the reactants are completely consumed, and the products total weights have the same as the total weight of the reactants.

Types of Chemical reactions:

1. **Reversible reactions: (occur in a closed system)**

Do not occur in only one direction , the outputs remain in space interact and combine to give the reactants. and the products total weights dont have the same as the total weight of the reactants.

$$CH_3COOH + C_2H_5OH \longleftrightarrow CH_3COOC_2H_5 + H_2O$$

Only 2/3 of acetic acid and ethyl alcohol reacts, one-third remains un-reacted.

Chemical equilibrium

Types of Chemical reactions:

1. Reversible reactions: (occur in a closed system)

At equilibrium, it would seem that the reaction has stopped, but what is really happening is that the combination of the reactants is happening on an ongoing basis to form products at the same time and at the same speed of combining the products to from the reactants, and this called as Dynamic Equilibrium.

Le Chatelier Principle:

When any system at equilibrium is subjected to change in concentration, temperature, volume, or pressure, then the system readjusts itself to (partially) counteract the effect of the applied change and a new equilibrium is established.

Le Chatelier Principle:

Factors affecting the equilibrium in the light of the Le Chatelier Principle:

1. **Effect of temperature:**

If a temperature of a balanced reaction at constant other variables is raised, the reaction is moving in the direction in which the absorption of heat occurs

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 + q \ (\text{Exothermic})$$

$$H_2O + C \rightleftharpoons CO + H_2 \ - q \ (\text{Endothermic})$$

Factors affecting the equilibrium in the light of the Le Chatelier Principle:

2. Effect of Pressure:

When a pressure is applied on a balanced system; it adjusts itself to the direction that tends to bring pressure to its original value, and this happens in the direction of less volume. Increasing the pressure helps on the completing of the gas reactions in which the products volume is less than that of reactants.

2. Effect of Pressure:

Increasing the pressure increase nitrogen tetra-oxide production

$$2NO_{2\,(gas)} \rightleftharpoons N_2O_{4\,(gas}$$

While is doesn't affect the balance of iron reaction cause there is no volume change.

$$3Fe_{\,(solid)} + 4H_2O_{\,(gas)} \rightleftharpoons Fe_3O_{4\,(solid)} + 4H_{2\,(gas)}$$

2. Effect of changing in Concentrations:

By adding an amount of a reactant to a balanced system, the system is moving in the forward direction and if the concentration of one of the reaction products added, the reaction will take the opposite direction.

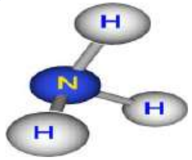
$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

- In this reaction, it was found that adding of water lead to increasing turbidity to form Bismuth Oxichloride.
- By adding of HCl turbidity disappears .

Applications on Le Chatelier Principle:

Chemical equilibrium

Exothermic reactions : formation of Ammonia



$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + q$$

- Reaction of N_2 with H_2 is exothermic reaction, it becomes on equilibrium at constant temperature.
- If pressure is added, it will increase the forward reaction (less volume).
- Heating increases the reverse reaction to reduce high temperature.
- Using catalyst or removing of Ammonia increases the forward reaction.

Applications on Le Chatelier Principle:

- **Exothermic reactions: Formation of Nitrous Oxide**

$$N_2 + O_2 \longleftrightarrow 2NO - \text{heat}$$

- **Reaction of Nitrogen and Oxygen is Exothermic reaction**
- **Heating increases the forward reaction while cooling does the opposite.**
- **Pressure doesn’t have any effect as the number of Reactant molecules equal those of products and the volume doesn’t change.**

Applications on Le Chatelier Principle:

2- Decomposition of Phosphorus pentachloride (Exothermic)

$$PCl_5 \longleftrightarrow PCl_3 + Cl_2 - \text{heat}$$

- Heating increases the forward reaction and cooling does the opposite.
- Pressure increase the reverse reaction to decrease the volume. So decreasing the pressure leads to increase the PCl5 decomposition.

Applications on Le Chatelier Principle:

Physical phenomena

- **Melting**

- **Solid is in equilibrium with its molten at constant melting temperature.**

- **Increasing the temperature increases the melting.**

$$\text{Solid} \longleftrightarrow \text{Liquid} - \text{heat}$$

- **Increasing pressure increases the solidification of molten except in case of ice, as ice volume is higher in volume than water.**

Applications on Le Chatelier Principle:

Boiling

- An equilibrium arises between liquid and its vapor at boiling point.

$$\text{Liquid} \longleftrightarrow \text{Vapor} - \text{heat}$$

- Increasing temp. increase the evaporation.
- Pressure increases the condensation of vapor into liquid.

Mass action law

Guldberg and Waage (1867)

"At constant temperature, the reaction rate is proportional with the active mass of reactants".

Active Mass = Moles/Liter = M

Mass action law

Deduction of the relationship between concentration of reactants and products.

Consider this reaction: $A + B \longleftrightarrow C + D$

If the Molecular concentrations:

Reactants= [A] [B]

Products= [C] [D].

Forward reaction spead = u_1

Backward (reverse) reaction rate = u_2

Mass action law

So,

$u_1 \alpha [A] x [B]$ $u_1 = K_1 [A] x [B]$

$u_2 \alpha [C] x [D]$ $u_2 = K_2 [C] x [D]$

K_1 and k_2 are the constants of forward and backward reactions.

Mass action law

At Equilibrium $u_1 = u_2$

$K_1 / K_2 = [C] \times [D] / [A] \times [B] = K_c$

Kc = equilibrium constant and known as:

“ the multiplication of products divided by that of reactants”

In case of more than one molecules or reactants or products:

$$\alpha A + \beta B \longleftrightarrow \gamma C + \delta D$$

Mass action law

$$u_1 = K_1 [A]^{\alpha} \times [B]^{\beta}$$

$$u_2 = K_2 [C]^{\gamma} \times [D]^{\delta}$$

At equilibrium $u_1 = u_2$

$$K_1 / K_2 = [C]^{\gamma} \times [D]^{\delta} / [A]^{\alpha} \times [B]^{\beta} = K_c$$

Mass action law

In gasses reactions; pressure replace the concentration:

If P_A, P_B, P_C, P_D are the partial pressures:

$$K_1/K_2 = P_C^{\gamma} \times P_D^{\delta} / P_A^{\alpha} \times P_B^{\beta} = K_P$$

K_p is the equilibrium constant.

The ion product of water

- Water reacts as acid with a base giving it a Hydrogen proton, while it reacts as a base with acid receiving a Hydrogen proton.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$K = a_{H3O+} \text{ x } a_{OH-}/(a_{H2O})^2$

The ionisation of water is very low, so its activity (unionised) can be considered as a constant.

$$K \text{ x } K^2 = a_{H3O+} \text{ x } a_{OH-}$$

$K_w = [H^+]\,[OH^-]$

The ion product of water

- **$K_w = 1 \times 10^{-14}$ at 25 °C**
- **in pure water**

$$[H^+] = [OH^-] = 1 \times 10^{-7}$$

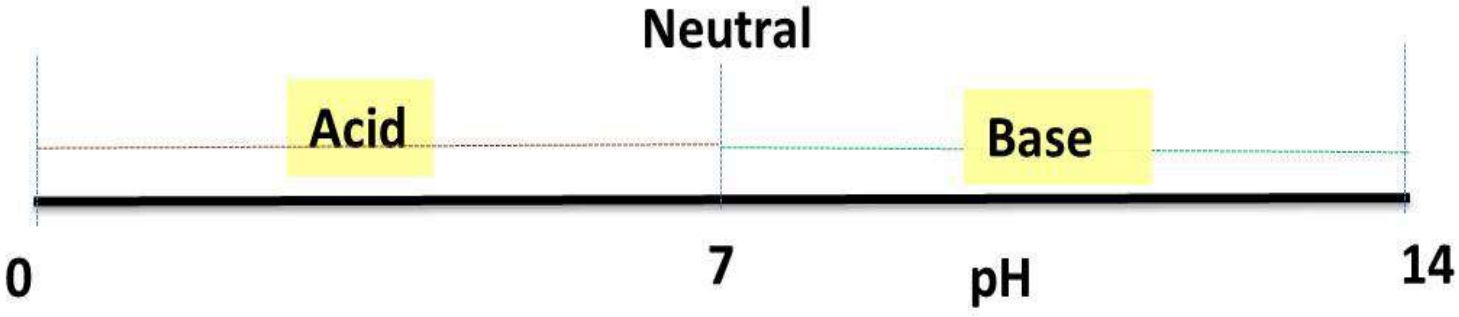
- **In aqueous solutions, the value of Kw $= 1 \times 10^{-14}$ is constant whatever the sources of H^+ and OH^-**
- **So, addition of Acid will lead to increase the H^+ concentration, consequently will lead to decrease the OH^- ions.**
- **If a base was added, OH^- will increase and H^+ will decrease.**

Hydrogen ion exponent (pH)

- **pH is a way of expression for Hydrogen concentration in solutions.**
- **Its value is between 0-14**
  - **$pH = - \log [H^+]$**
- **In neutral solution: $[H^+] = 10^{-7}$ …. $pH = - \log 10^{-7} = 7$**
- **For solution with hydrogen ions conc = 1 M $pH = -\log 1 =$ zero.**
- **For solution with hydroxel ions conc = 1 M**

$$[H^+] = K_w / [OH^-] = 10^{-14} / 1 = 10^{-14} \quad pH = 14$$

Hydrogen ion exponent (pH)



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

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

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

$$-\log [H^+] + (-\log [OH^-]) = -\log 10^{-14}$$

$$pH + pOH = 14$$

Buffer Solutions:

Are the solutions which prevent the changing in pH value when an acid or base is added.

It consists of a weak acid + its salt of strong base

Or

From a weak base + its salt of strong acid.

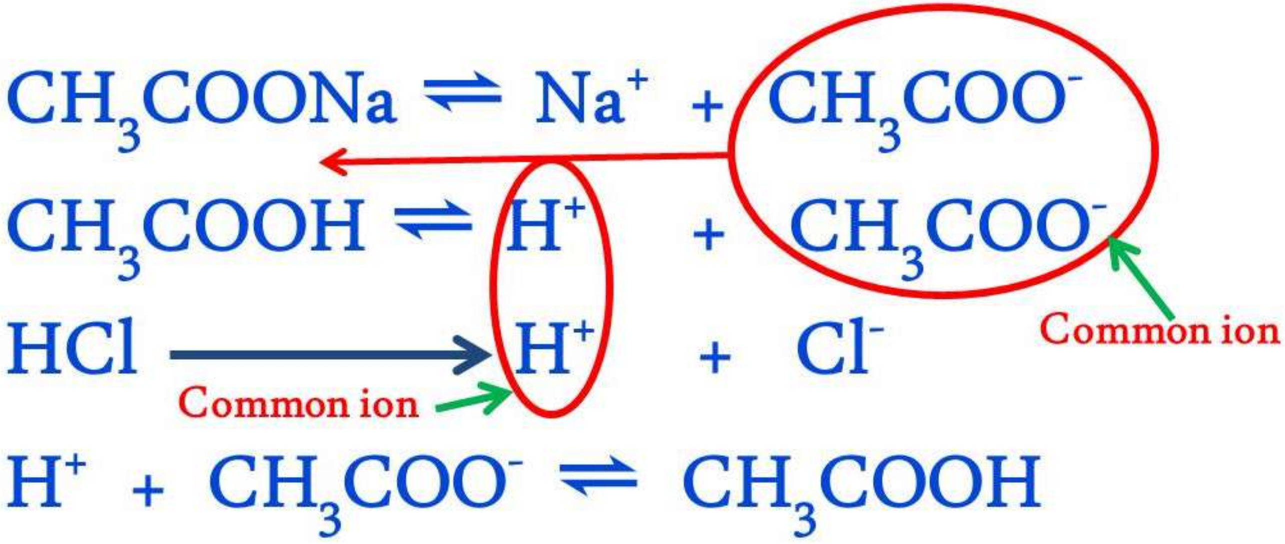
Examples:

Acetic acid + Sodium acetate pH = 3.7 – 5.6

$Na_2HPO_4 + Na_3PO_4$ pH = 11 - 12

Buffer solution mechanism

When HCl (strong) is added to acetic/acetate buffer soln., it reacts with the acetate forming Sod. Chloride and acetic acid(weak). That means the produced hydrogen from HCl are converted into weak ionised acetic acid.



$$CH_3COONa \rightleftharpoons Na^+ + CH_3COO^-$$

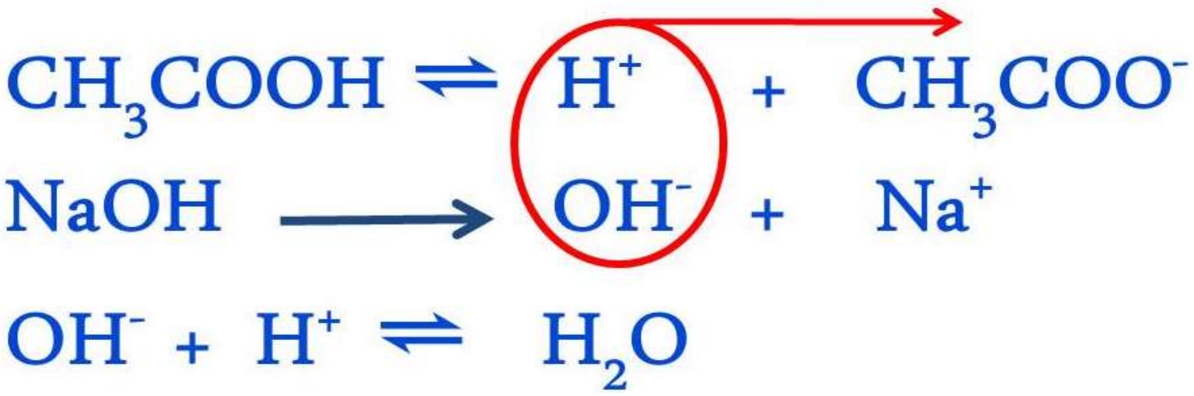
$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$HCl \longrightarrow H^+ + Cl^-$$

$$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$$

Buffer solution mechanism

If NaOH was added to the same buffer soln., so it reacts with hydrogen giving water, so acetic acid ionised to compensate the hydrogen ions.



$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

$$NaOH \longrightarrow OH^- + Na^+$$

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

Buffer solutions have a stock of acid and that of Base to face any external addition of base or acid.


Bronsted

Bronsted – Lowry Theory for acids and Bases


Lowry

- **Acid** is the substance which has tendency to give a Proton.
- **Base** is the substance which has tendency to gain a Proton.

$$\text{Base} + H^+ \rightleftharpoons \text{Acid}$$

- Acid get active in presence of Base and vice versa
- If an acid was added to water, water will react as a base receiving a hydrogen proton.

$$HCl\ (\text{acid}) + H_2O\ (\text{base}) \longrightarrow H_3O^+\ (\text{acid}) + Cl^-\ (\text{base})$$

Bronsted

Bronsted – Lowry Theory for acids and Bases

Lowry

- **If a base was added to water, water will act as an acid**

$$NH_3\text{(base)} + H_2O\text{ (acid)} \rightleftharpoons NH_4^+\text{ (acid)} + OH^-\text{ (base)}$$

Hydrolysis

- Solutions of simple salts have 4 possibilities:

1. **Neutral**: in which salt is sourced from strong acid and strong base.
2. **Acidic**: in which salt is sourced from strong acid and weak base.
3. **Basic**: in which salt is sourced from weak acid and strong base.
4. **Neutral or weak acidic or weak basic**: in which salt is sourced from weak acid and weak base. That depends on the ionisation constant of the acid and the base

Hydrolysis

- **Solutions of simple salts have 4 possibilities:**

1. **Neutral:**

$$NaCl \longrightarrow Na^{+} + Cl^{-}$$

$$H_2O \rightleftharpoons OH^{-} + H^{+}$$

Both of HCl and NaOH are strong, which means they are completely ionised, so the concentration of H^{+} and OH^{-} will remain as that in water (Neutral).

Hydrolysis

2. Acidic:

Such as soln. of NH_4Cl gives HCl which is completely ionised and NH_4OH which is weakly ionised.

Water molecules will ionised increasing the H^+ ions, so the net soln. will be acidic.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

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

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$NH_4^+ + Cl^- + OH^- + H^+ \rightleftharpoons NH_4OH + Cl^- + H^+$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

Hydrolysis

3. **Basic: such as CH_3COONa solution:**

gives NaOH which is completely ionised and CH_3COOH which is weakly ionised. Water molecules will ionised increasing the OH^- ions, so the net soln will be basic.

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

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

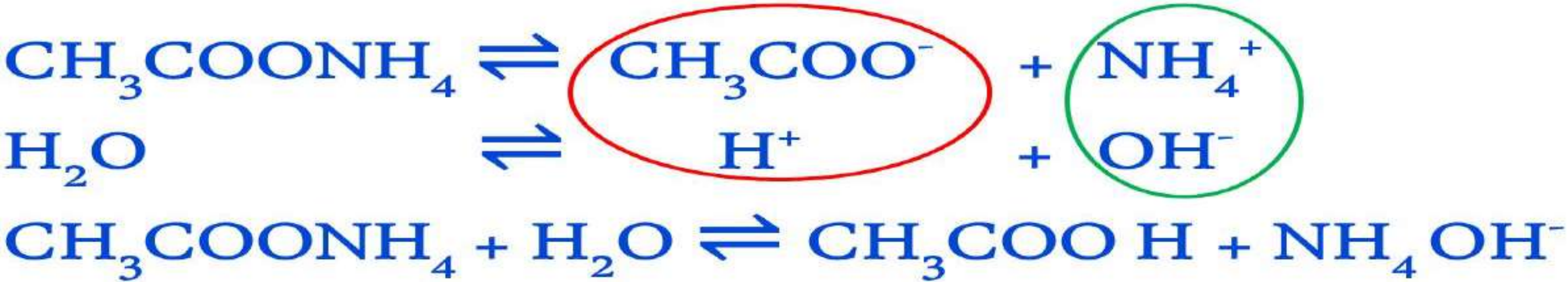
$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

Hydrolysis

4. **Neutral or weak acidic or weak basic : CH_3COONH_4**

This soln. will give CH_3COO^- and NH_4^+ ions which combine with H+ and OH- from water producing the weak acid (CH_3COOH) and the weak Base (NH_4OH).

The pH of the soln. depends on the strength of the weak acid and the weak base. It is usually neutral but in sometimes, it’s weak acidic or weak basic.



$$CH_3COONH_4 \rightleftharpoons CH_3COO^- + NH_4^+$$

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

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COO\,H + NH_4OH^-$$

Acid-Base Neutralisation

Acids and bases are neutralise through reaction producing water and salt. So according to the acid and base the produced salt can be one of 4 categories:

$$HA + BOH \rightleftharpoons AB + H_2O$$

1. **Reaction of Strong acid +Strong base:**

in which the reaction is Irreversible producing a salt soln. with pH = 7.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Acid-Base Neutralisation

2. **Reaction of Strong acid with weak base: reversable reaction giving an acidic salt solution.**

   e.g. NH_4Cl, pH = 5.

3. **Reaction of weak acid with strong base: giving a basic salt solution.**

   Such as

   CH_3COONa pH = 8.9

Acid-Base Neutralisation

4. **Reaction of weak acid with weak base:**

the produced salt is hydrolysed giving neutral, weak acidic, or weal basic soln.

Neutralisation reactions are important in titration processes from which unknown concentration can be calculated.

Acid-Base Neutralisation

Indicators: are weak organic acids or bases which used to detect the end or equivalent point in neutralisation titrations. they have different colours according to pH value.

Indictor examples:

- Phenolphthalein (ph.ph)
- Methyl Orange (M.O)

Indicator's Mechanism

ph.ph

$$\mathrm{HIn}\ (\text{Colorless}) \rightleftharpoons \mathrm{H^+} + \mathrm{In^-}\ (\text{Red})$$

$$\mathrm{NaOH} \longrightarrow \mathrm{OH^-} + \mathrm{Na^+}$$

$$\mathrm{HCl} \longrightarrow \mathrm{H^+} + \mathrm{Cl^-}$$

M.O

$$\mathrm{InOH}\ (\text{Yellow}) \rightleftharpoons \mathrm{OH^-} + \mathrm{In^-}\ (\text{Red})$$

Colloids

Solutions

- **Homogeneous mixtures**
- **Solvent = dissolving medium and presents in the larger amount**
  - **often liquid; frequently water**
  - **gas in air and other gas solutions**
  - **rarely a solid**
- **Solute(s) = dissolved material(s) and present in the smaller amount(s)**
  - **solids, liquids, or gases**
  - **often more than one solute**

Solutions

A saturated solution contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

An unsaturated solution contains less solute than the solvent has the capacity to dissolve at a specific temperature.

A supersaturated solution contains more solute than is present in a saturated solution at a specific temperature.

Solutions *vs* Colloids

- ❑ **Solution**
  - ❖ **Solute particle are of ionic or molecular size (a few nm across)**
  - ❖ **Transparent to ordinary light**
  - ❖ **Stable unless solvent evaporated**
- ❑ **Colloids**
  - ○ **Solute (called "dispersed phase") typically -1 nm to 100 nm**
  - ○ **Giant molecules (or "clumps" of smaller ones)**
  - ○ **Not totally transparent – Tyndall Effect**
  - ○ **Dispersed phase may separate out (similar to separation of mayonnaise).**

Suspensions and Colloids

Suspensions and colloids are NOT solutions.

Suspensions: The particles are so large that they settle out of the solvent if not constantly stirred.

Colloids: The particle is intermediate in size between those of a suspension and those of a solution.

Solutions	Colloidal Dispersions	Suspensions
Transparent (but often colored)	Often translucent or opaque, but may be transparent	Often opaque but, may appear translucent
No Tyndall effect	Tyndall effect	Not applicable
No Brownian movement	Brownian movement	Particles separate unless system is stirred
Cannot be separated by filtration	Cannot be separated by filtration	Can be separated by filtration

Colloids

- Colloids are everywhere:
  - In the human body
  - Washing powder, soup, toothpaste, etc.
  - Many foods (yogurt, butter, milk)
  - Nanotechnologies are based on chemistry of colloids

Types of Colloids

Examples	**Dispersed Substance**	**Dispersing Medium**	**Colloid Type**
Fog, aerosol sprays	Liquid	Gas	Aerosol
Smoke, airborne bacteria	Solid	Gas	Aerosol
Whipped cream, soap suds	Gas	Liquid	Foam
Milk, mayonnaise	Liquid	Liquid	Emulsion
Paint, clays, gelatin	Solid	Liquid	Sol
Marshmallow, Styrofoam	Gas	Solid	Solid foam

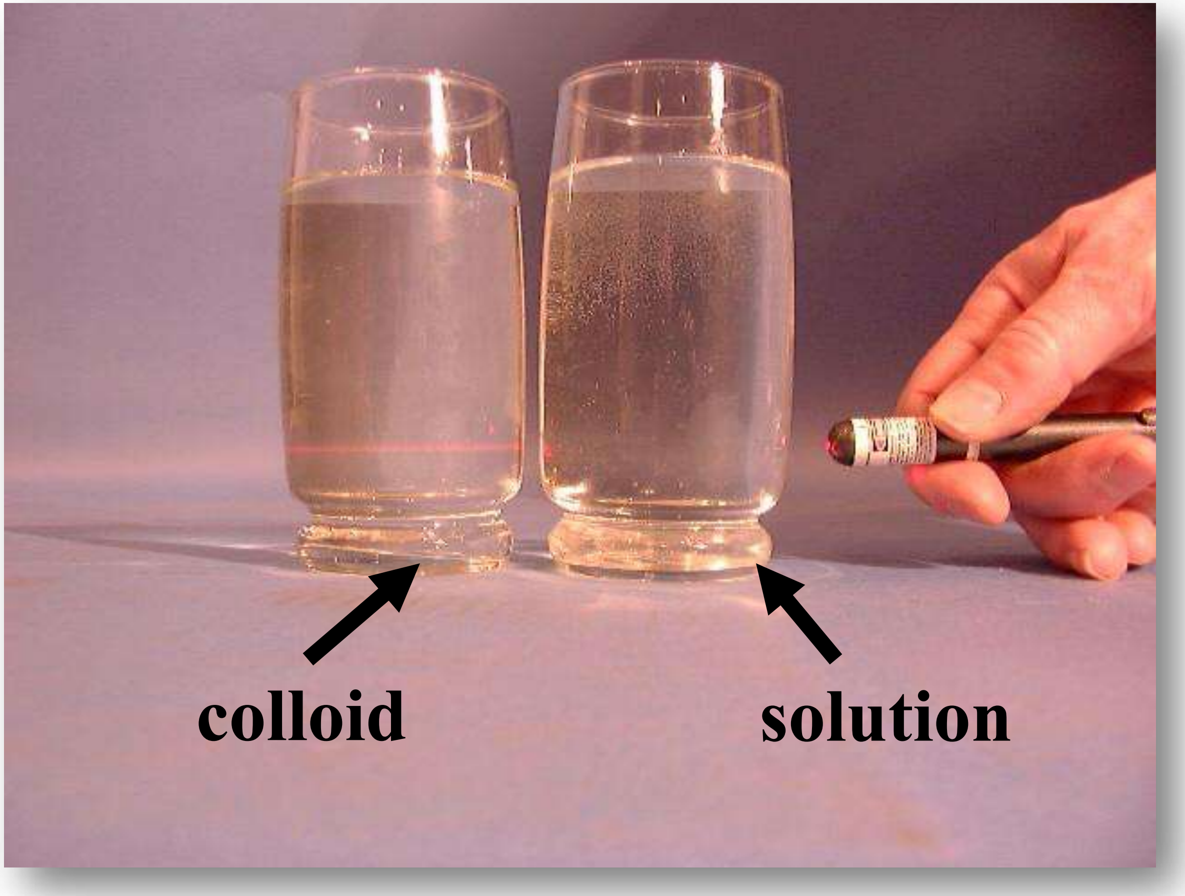
Some Colloidal Systems

System			
Dispersed phase	**Dispersion medium**	**Type**	**Example**
gas	liquid	foam	whipped cream
gas	solid	foam	marshmallow
liquid	liquid	emulsion	milk, mayonnaise
liquid	gas	aerosol	fog, aerosols
solid	gas	smoke	dust in air
solid	liquid	sols and gels	egg white, jellies, paint, blood, colloidal gold, starch in water, gelatin

The Tyndall Effect

Colloids scatter light, making a beam visible. Solutions do not scatter light.

Which glass contains a colloid?



Colloids

Particles in colloids and suspensions reflect or scatter light in all directions. Solutions do not scatter light.

The path of light is visible only when the light is scattered by particles.

a) Fog or mist is a colloid and thus exhibits the Tyndall effect.

b) Particles in colloids and suspensions reflect or scatter light in all directions.

c) Solutions do not scatter light.

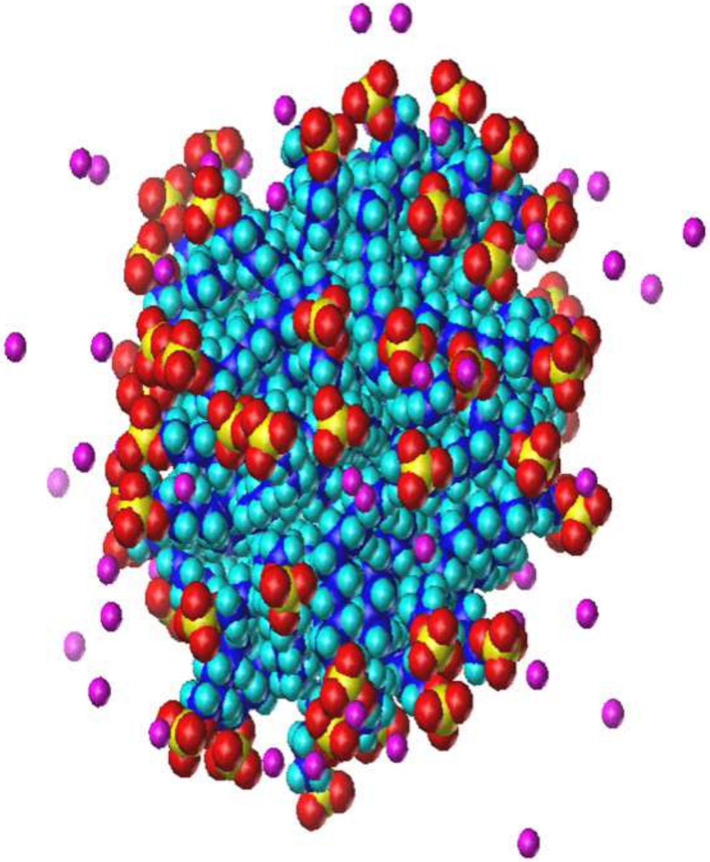
Colloids

Brownian Motion

- The chaotic movement of colloidal particles, which was first observed by the Scottish botanist Robert Brown (1773–1858), is called Brownian motion.
- Brownian motion is caused by collisions of the molecules of the dispersion medium with the small, dispersed colloidal particles.

Removal of Colloidal Particles

- Colloid particles are too small to be separated by physical means (e.g. filtration).
- Colloid particles are coagulated (enlarged) until they can be removed by filtration.



Removal of Colloidal Particles

Methods of coagulation:

- ☐ **Heating: (colloid particles move and are attracted to each other when they collide);**
- ☐ **Adding an electrolyte: (neutralize the surface charges on the colloid particles).**
- ☐ **Dialysis: using a semipermeable membranes separate ions from colloidal particles.**

Lyophilic & Lyophobic Colloids

If the colloids in water, it called ❑

Hydrophilic & Hydrophobic Colloids

- **“Water loving” colloids: hydrophilic.**
- **“Water hating” colloids: hydrophobic.**

Preparation methods of Colloids

There are two methods: Dispersion method and Condensation method.

I- Dispersion method :

- The substance is crushed into small particles until its diameter reaches between (1 : 100 nm), then added to the dispersed medium with stirring.
- For examples: starch in hot water, and cappuccino coffee .

I- Dispersion method :

1- Electrical Disintegration (Bredig's Arc Method):

- It is the combination of dispersion and condensation.
- This technique is most commonly used for the preparation of colloidal solutions of metals such as gold, silver, platinum, etc.
- It involves the use of two metal electrodes dipped in a dispersion medium.

I- Dispersion method :

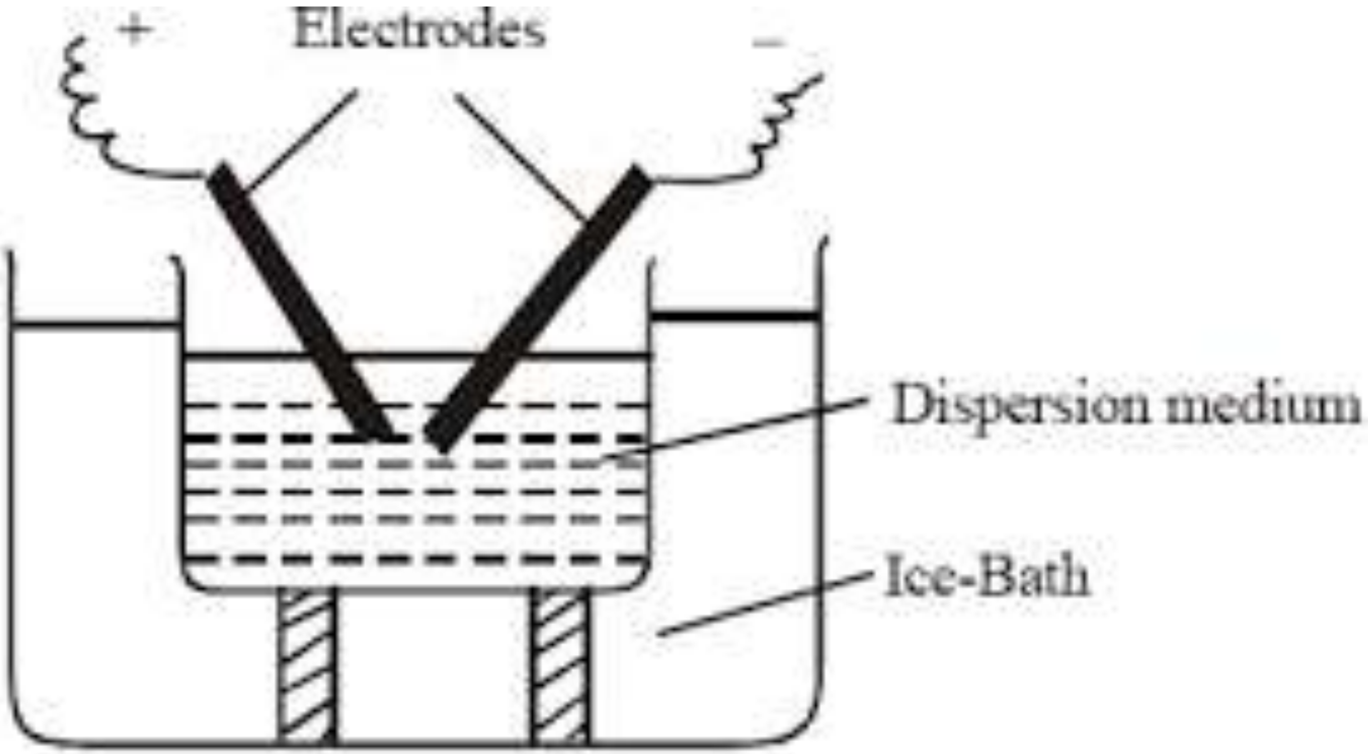
1- Electrical Disintegration (Bredig's Arc Method):

- An electrical arc of intense heat is produced, vaporizing some of the metal.
- The vapours condense to form precipitate in colloidal dimensions.

Preparation methods of Colloids

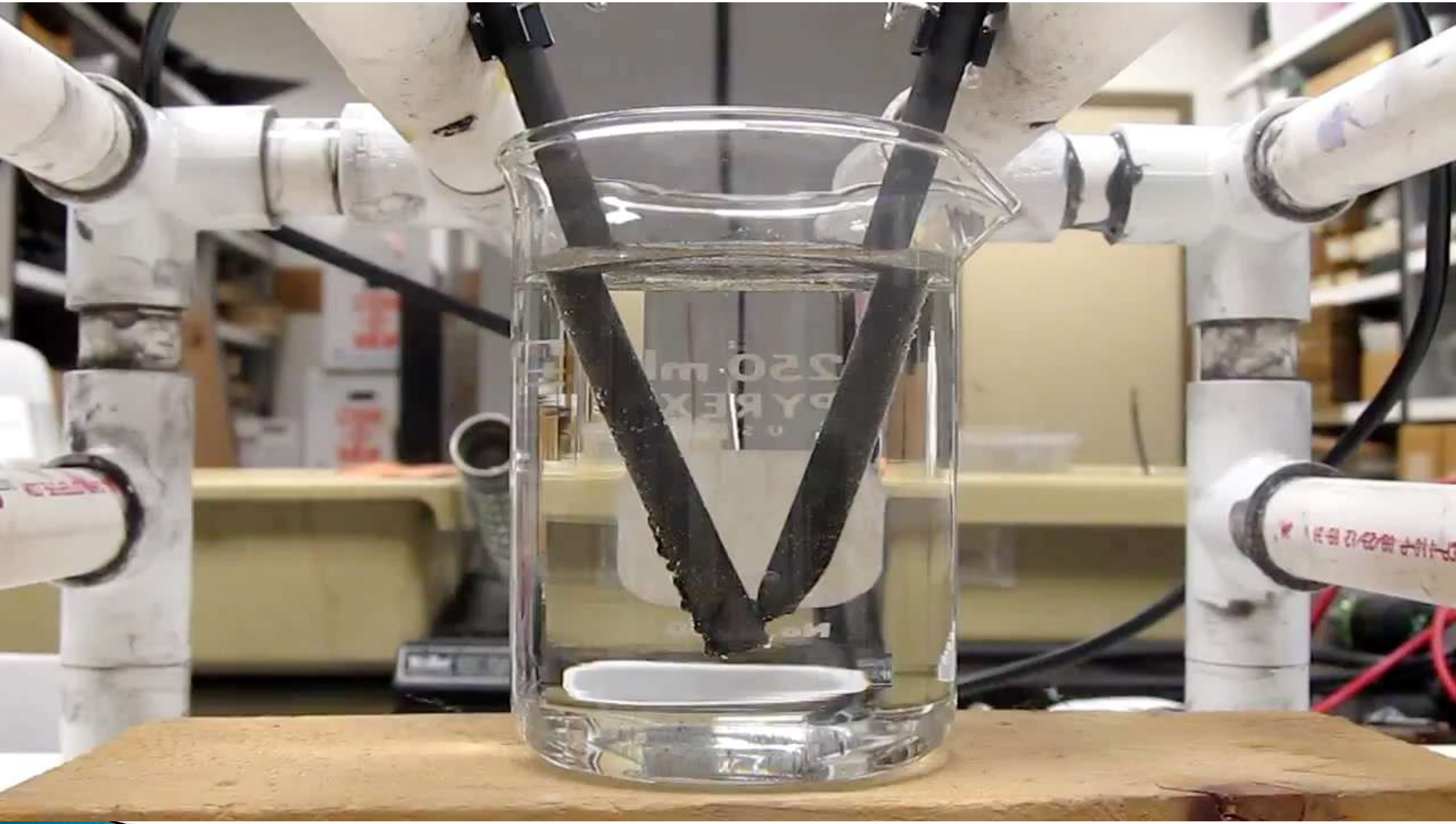
I- Dispersion method :

1- Electrical Disintegration (Bredig's Arc Method):



Preparation of colloidal solution by Bredig's Arc Method

Preparation methods of Colloids



I- Dispersion method :

2- Peptization:

Precipitate can be converted into colloidal form by shaking with dispersion medium in the presence of small amount of peptization agent (an electrolyte used to convert fresh precipitate into a colloidal solution).

For example: Adding Dilute HCl (as peptizing agent) to AgCl precipitate, so we can get a colloidal solution.

II- Condensation method:

The small particles are collected together into larger particles having the same volume of the colloid particles, by some processes like: Double Decomposition Technique, Oxidation, reduction, Hydrolysis, and Exchange of Solvent.

Preparation methods of Colloids

II- Condensation method:

a- Double Decomposition Technique:

When hydrogen sulphide is passed through a solution of arsenious oxide in distilled water, we get a colloidal solution of arsenious sulphide.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

Preparation methods of Colloids

II- Condensation method:

b- Oxidation Technique:

Such as; in the reaction of hydrogen supplied with Sulphur dioxide, where the atoms of Sulphur in water forms colloid.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

Or exploring H_2S to air for a long time.

$$H_2S + [O] \rightarrow H_2O + S$$

II- Condensation method:

c- Reduction Technique:

Another technique of preparing colloidal solutions of metals such as silver, gold as well as platinum involves the use of reducing agent for reduction of the salt solutions of these metals. Example of reducing agent include stannous chloride.

II- Condensation method:

d- Hydrolysis Technique:

It involves the use of boiling water to obtain colloidal solution of Ferric Hydroxide by adding drops of Conc. ferric chloride.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

Preparation methods of Colloids

II- Condensation method:

e- Exchange of Solvent

It involves the formation of a colloidal solution of an element by addition of its alcoholic solution to excess water. This colloidal formation can take place only when the element is more soluble in alcohol as compared to water.

Preparation methods of Colloids

II- Condensation method:

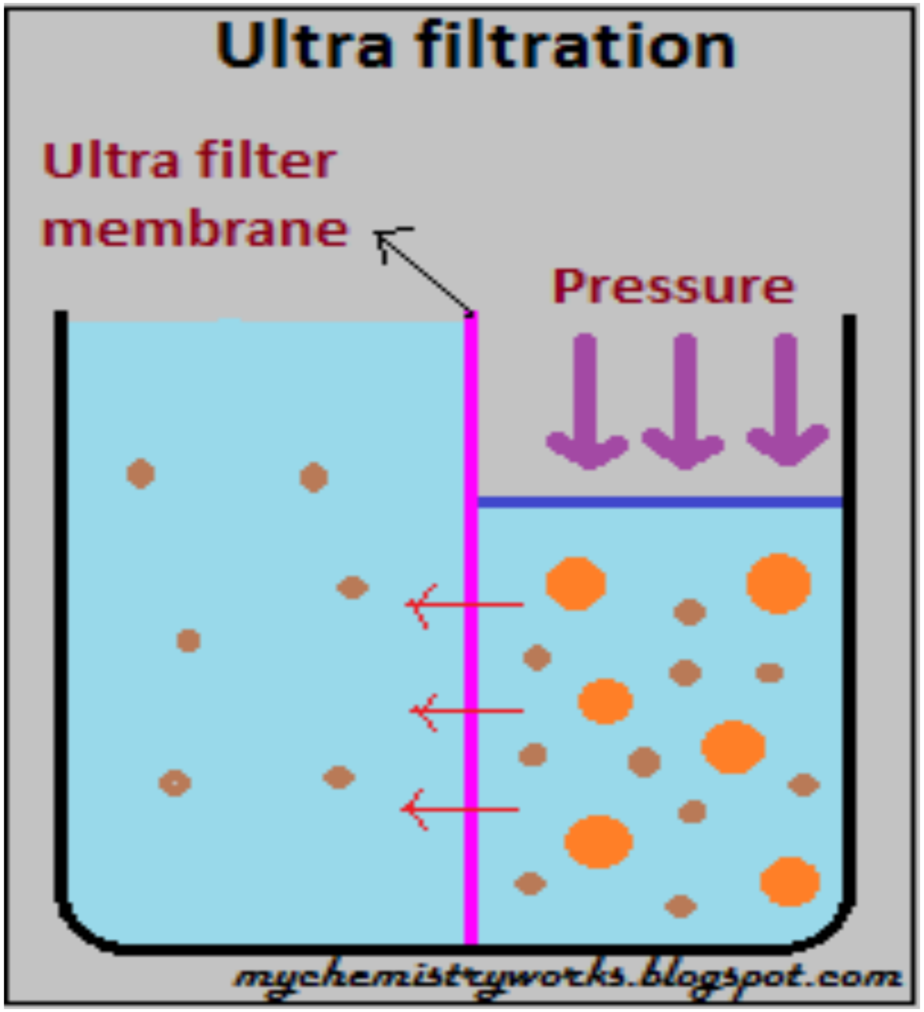
e- Exchange of Solvent

Example:

When an alcoholic solution of sulphur is made to pass through excess water it yields a colloidal solution of sulfur in water. This is because the solubility of sulphur is more in alcohol as compared to water.

Purification of Colloids:

1- Ultrafiltration:



Purification of Colloids:

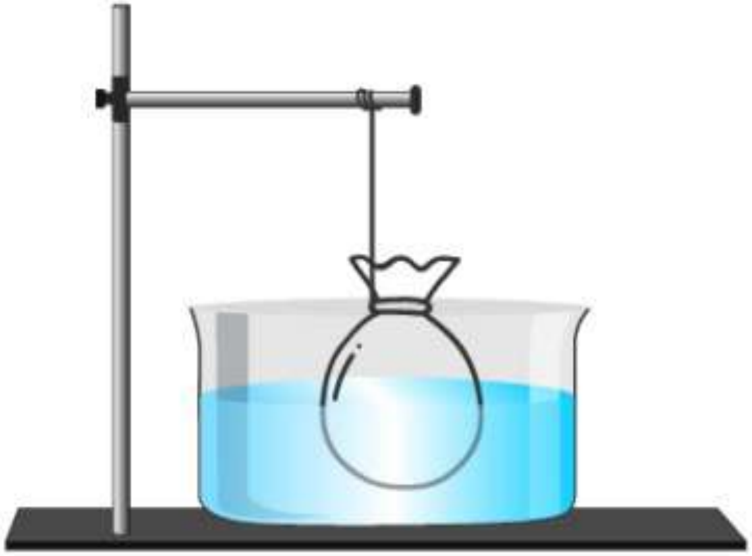
2- Dialysis and Electro-dialysis

After the preparation of the colloid, it becomes necessary to remove the excess electrolyte from the sol to impart stability to the sol. One could think of filtering the colloidal system, wash the colloid and re-disperse. But even the finest filter paper will retain little or none of the colloid.

Purification of Colloids:

2- Dialysis and Electro-dialysis

Electrolytes or other soluble materials in sols are removed by putting the sol in a membrane of cellophane or parchment surrounded by water.



Purification of a colloid

Purification of Colloids:

2- Dialysis and Electro-dialysis

The salts can pass through the membrane of parchment and are gradually washed away by running water whereas the colloid-is left inside the Vessel. This process of separation of colloid and Graham's `crystalloid' is called dialysis. Graham himself insisted on the importance of dialysis.

Purification of Colloids:

2- Dialysis and Electro-dialysis

The membrane through which dialysis is earned out serves as a sieve of extremely fine pore size so that only the small molecules or ions can pass, but not the relatively larger colloidal particles or large molecules of high polymers.

Purification of Colloids:

2- Dialysis and Electro-dialysis

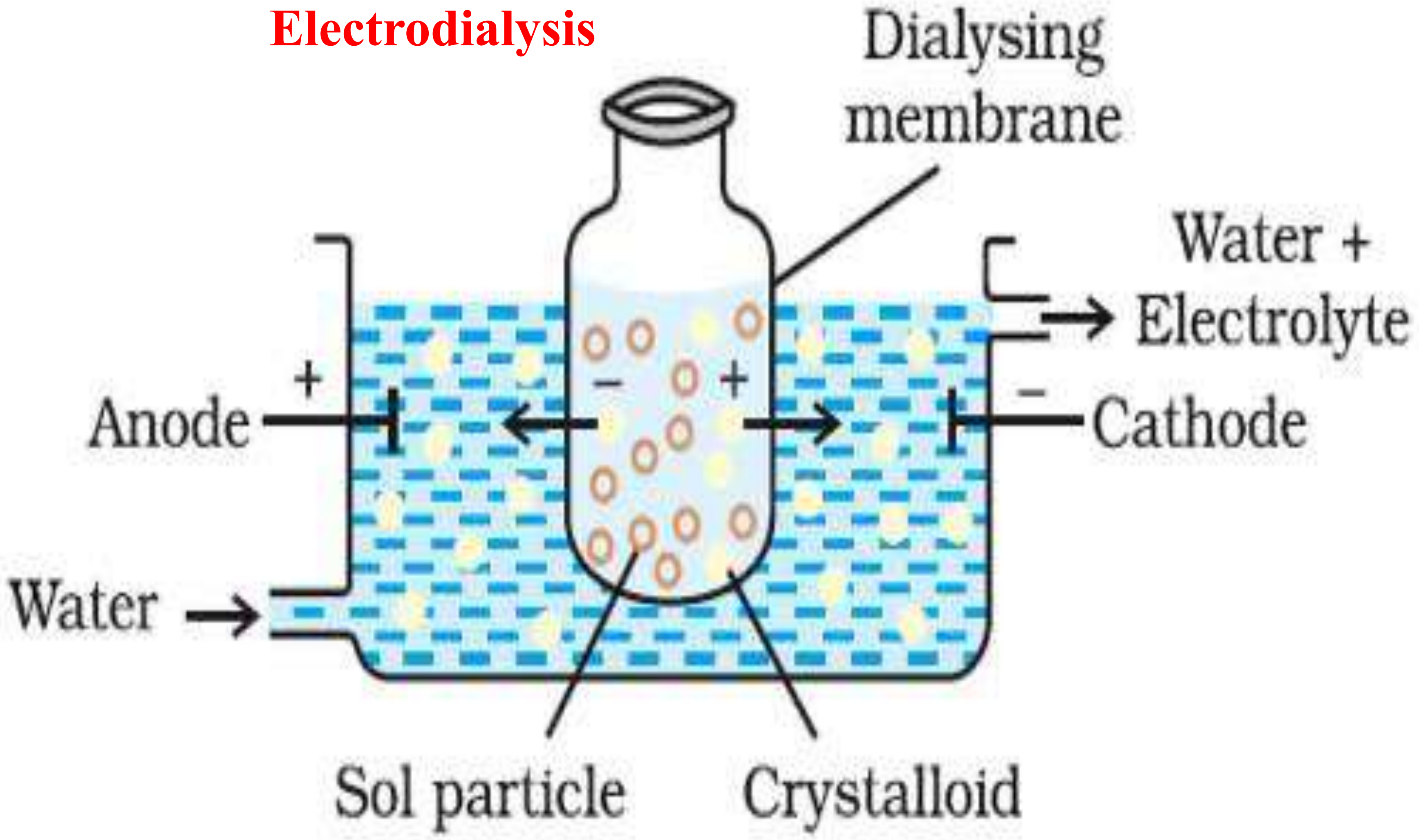
Electrodialysis

The dialysis can be improved and made faster if the assembly is subjected to a suitable electric field. The migration of the ion of the electrolytes through the membrane becomes fast in the electric field and makes the process rapid. This is known as electrodialysis.

Purification of Colloids:

2- Dialysis and Electro-dialysis

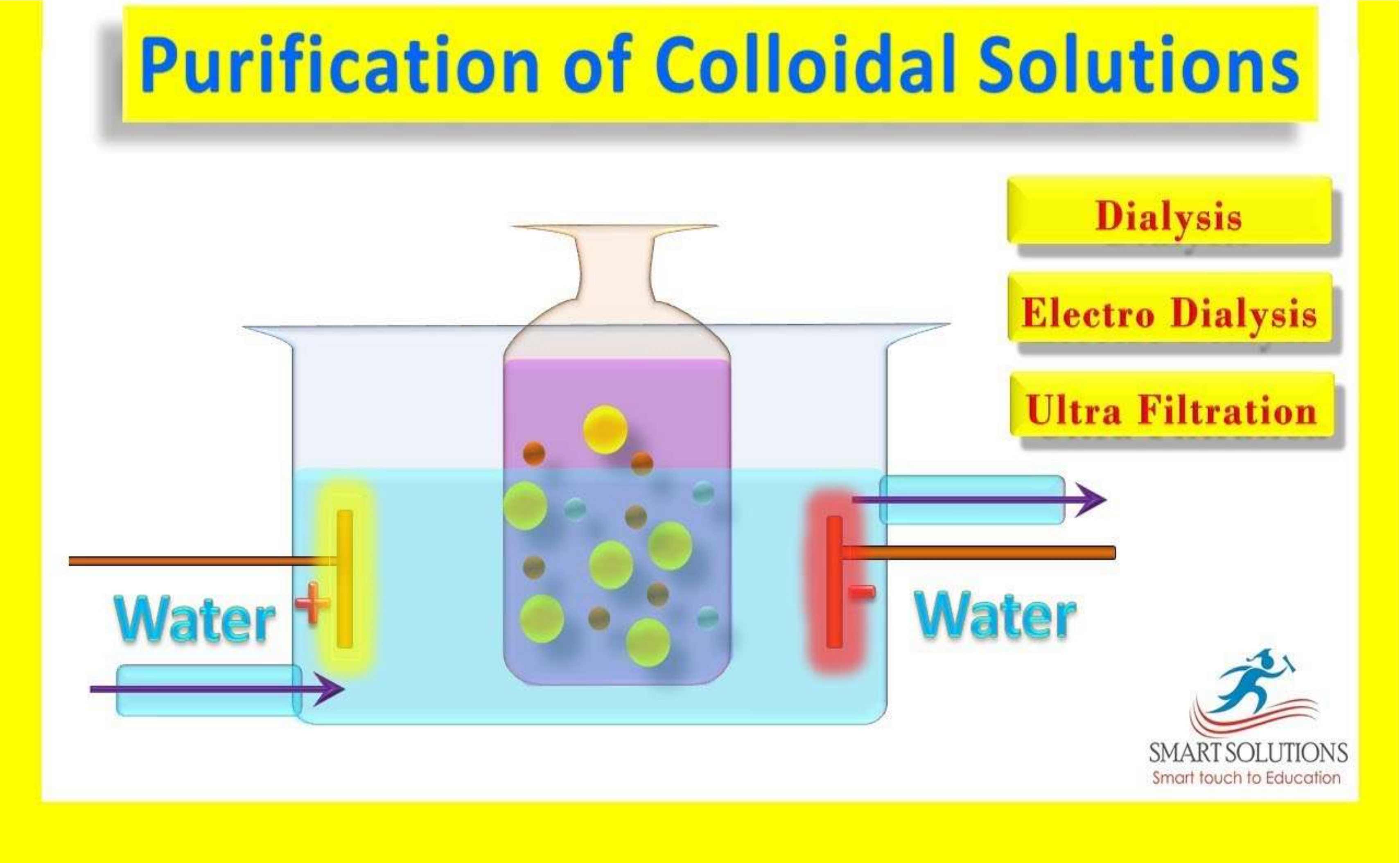
Electrodialysis

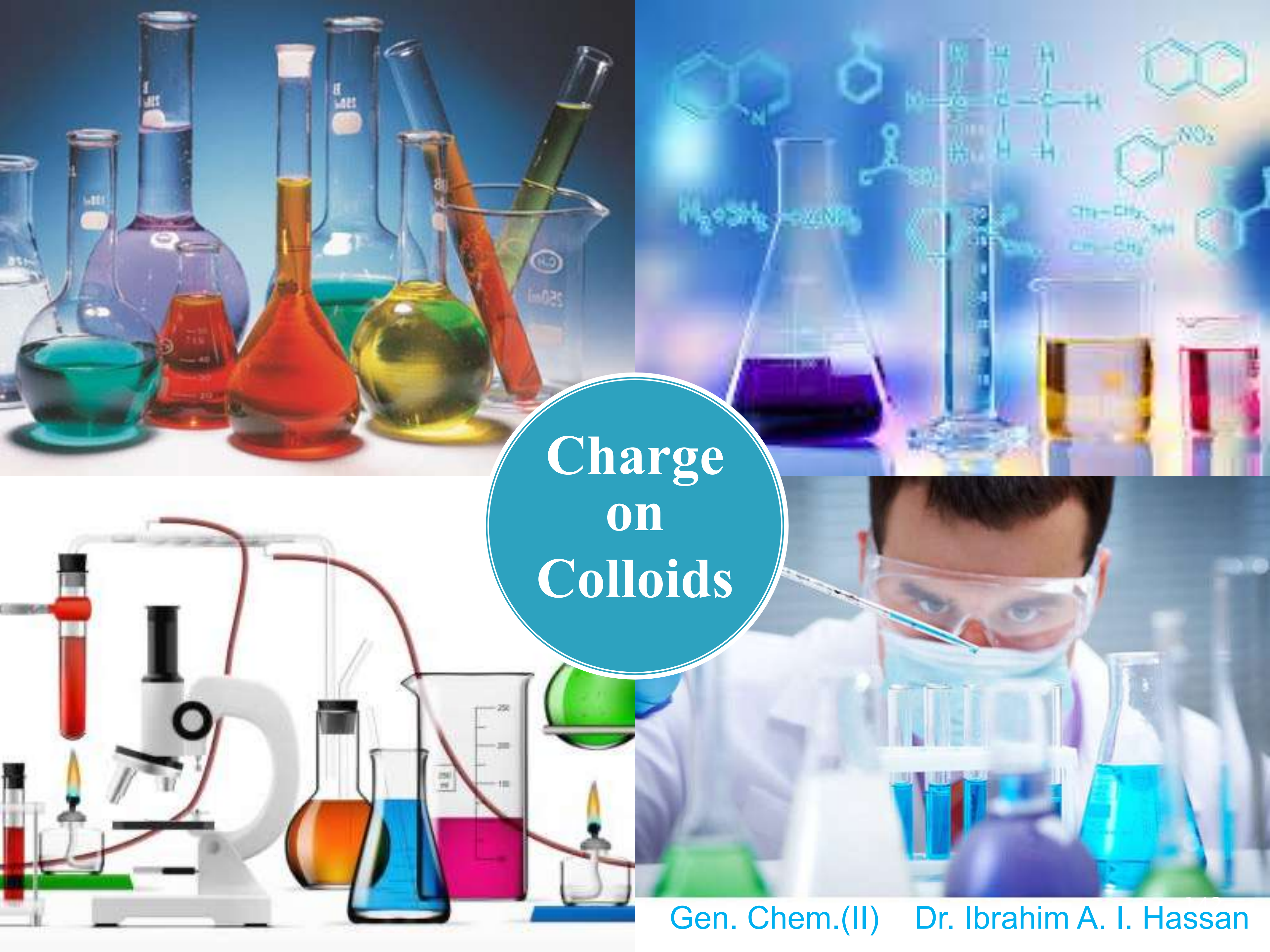


Purification of Colloids:

2- Dialysis and Electro-dialysis

Electrodialysis





Charge on Colloids

The source of the charge on the colloidal particles: -

Adsorption:

The source of the charge on the colloidal fines may be that the colloidal particles adsorb some of the charges present as impurities in the colloidal solution.

The source of the charge on the colloidal particles: -

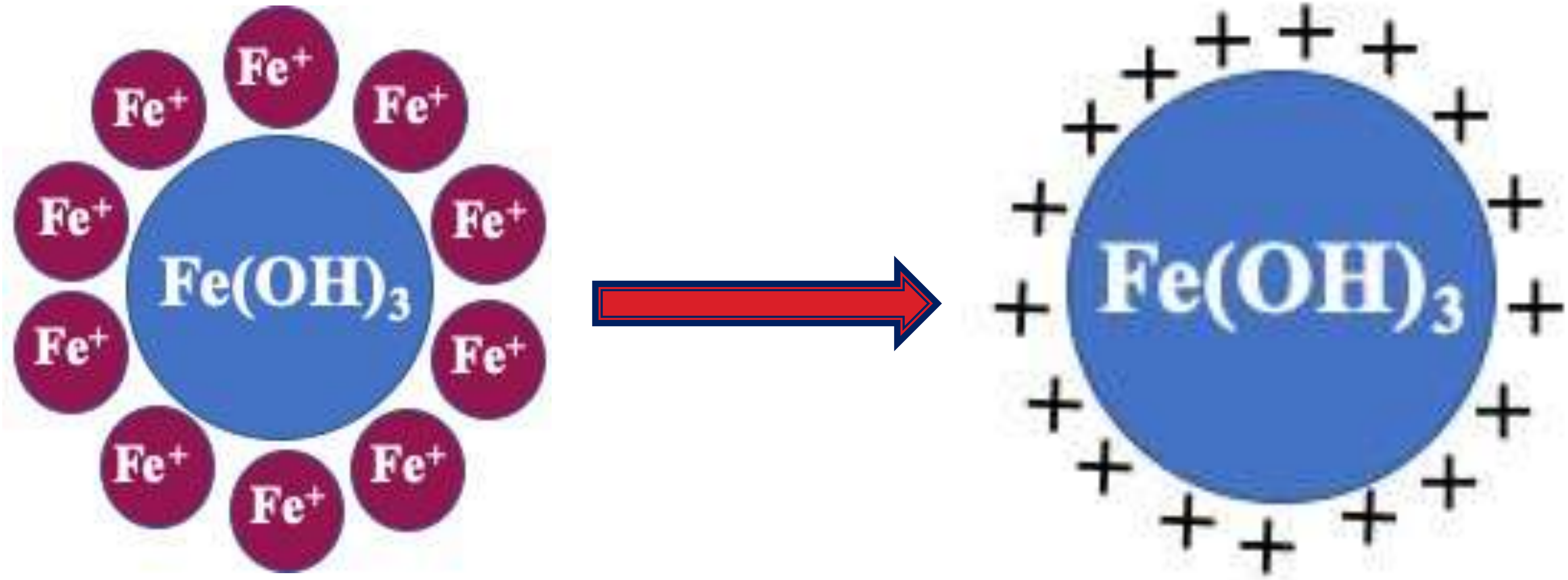
Adsorption:

Example:

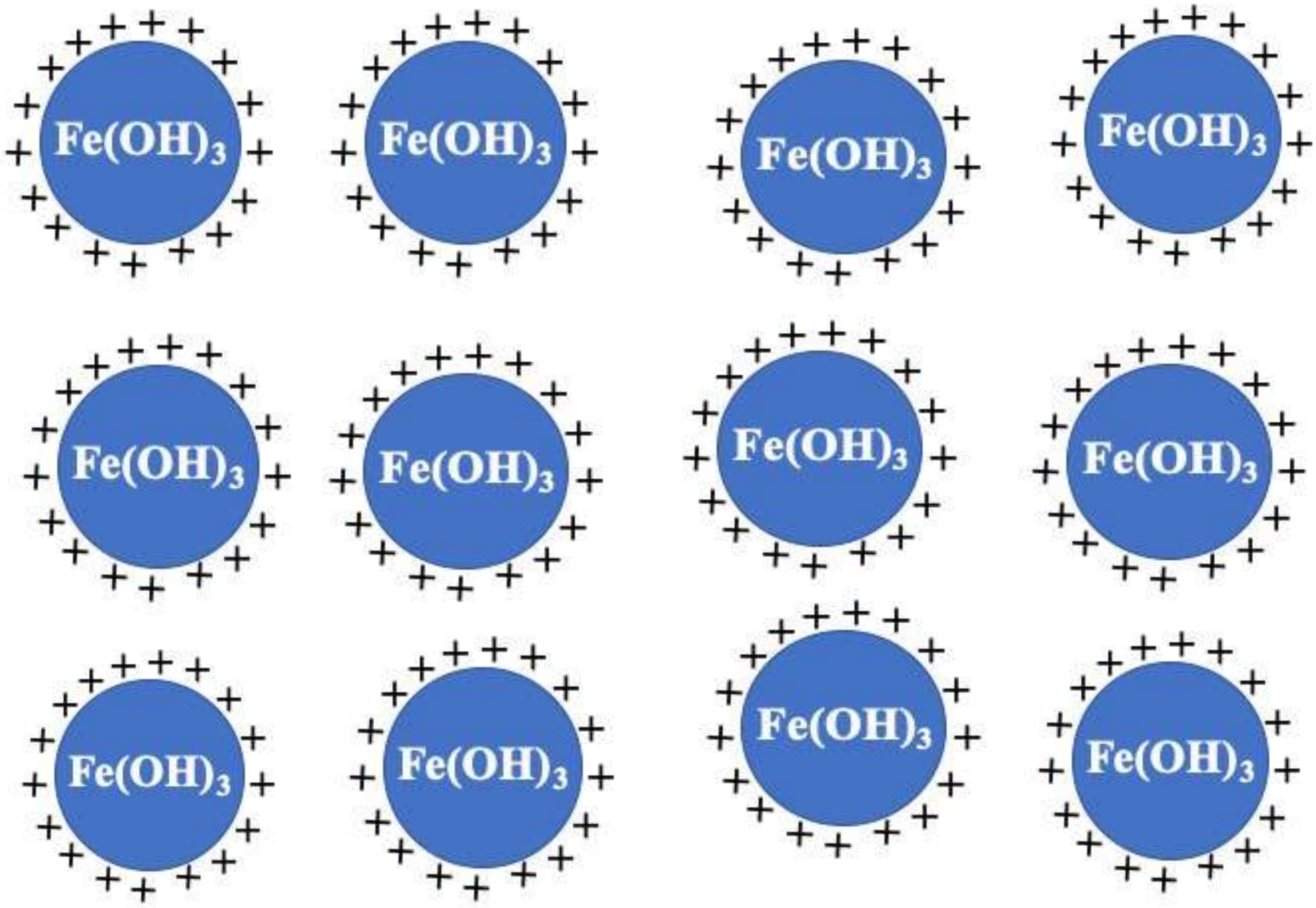
When preparing ferric hydroxide from hydrolysis of ferric chloride, by adding it to boiling water, there are leftover (positively charged) ferric ions (as impurities) and the colloidal particles adsorb them and acquire a positive charge.

The source of the charge on the colloidal particles: -

Adsorption



The dissonance between colloidal minutes leads to its stability



The source of the charge on the colloidal particles: -

- **The charge is formed on colloidal particles, depending on the medium in which they are found.**

Examples:

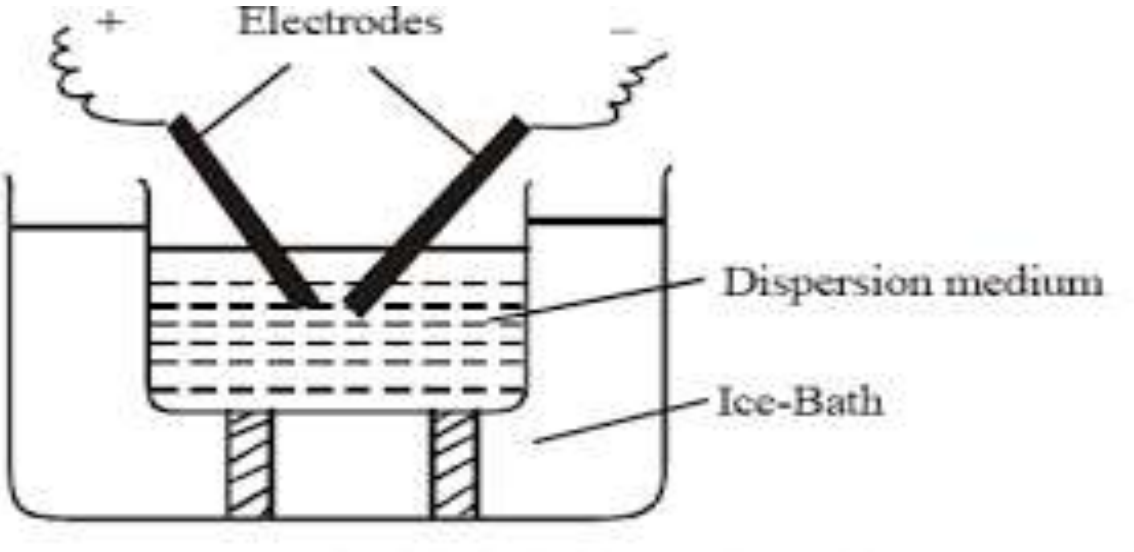
1. **Proteins: they are colloids. If they are present in an acidic medium, the colloidal particles become positively charged, but if the medium is basic then the colloidal particles have a negative charge.**

The source of the charge on the colloidal particles: -

Adsorption

Examples

2. **Gold**: **The colloidal solution of gold, prepared by the Bredig's arc method ,is not stable unless it contains a very small amount of alkali.**



2 : Preparation of colloidal solution by Bredig's Arc Method

The source of the charge on the colloidal particles: -

Adsorption

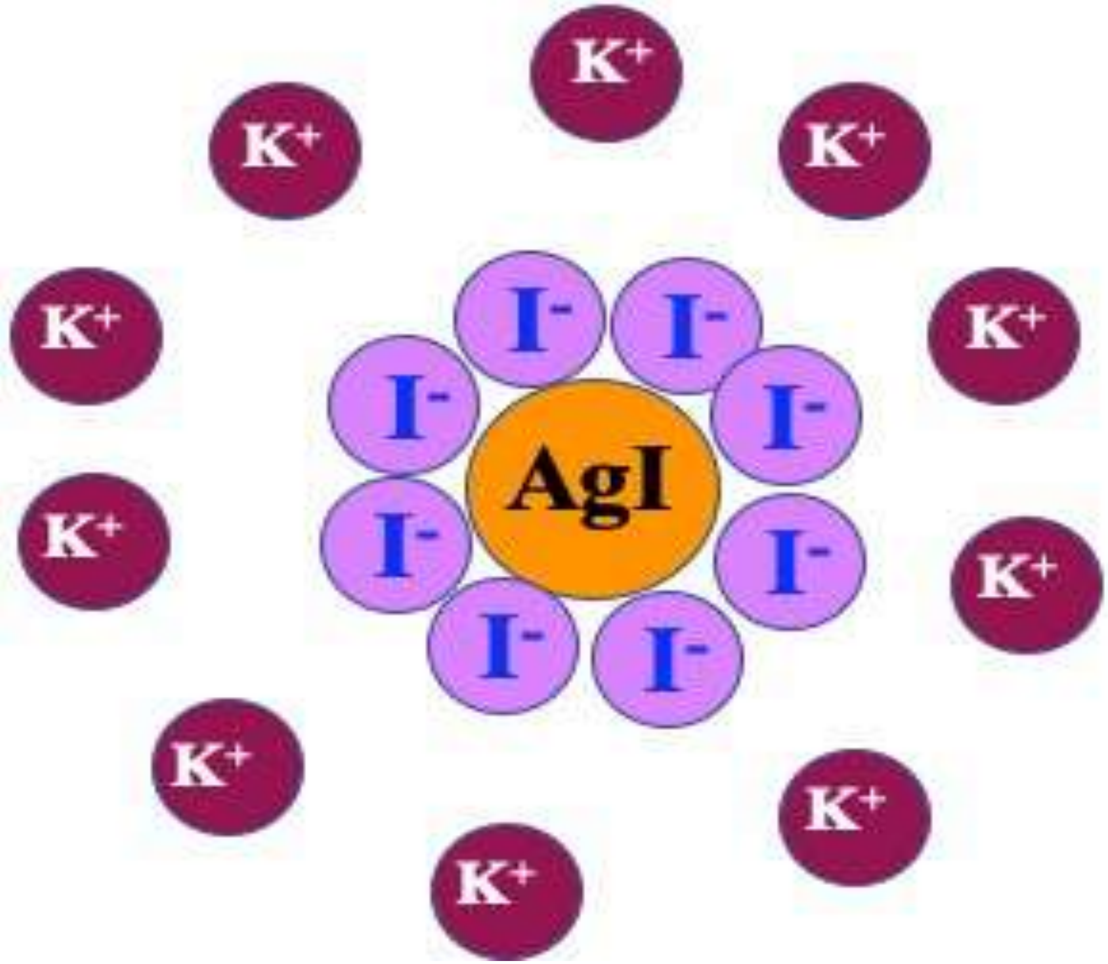
Examples

3. **When adding a dilute solution of $AgNO_3$ to an excess of KI solution; Negative Sol formed: This can be explained by the fact that colloidal particles adsorb negative iodide ions on their surface due to the presence of an increase of these ions, and potassium ions are arranged around them in the solution, and colloidal particles can be represented: $[AgI]\ I^-\ K^+$?**

The source of the charge on the colloidal particles: -

Adsorption

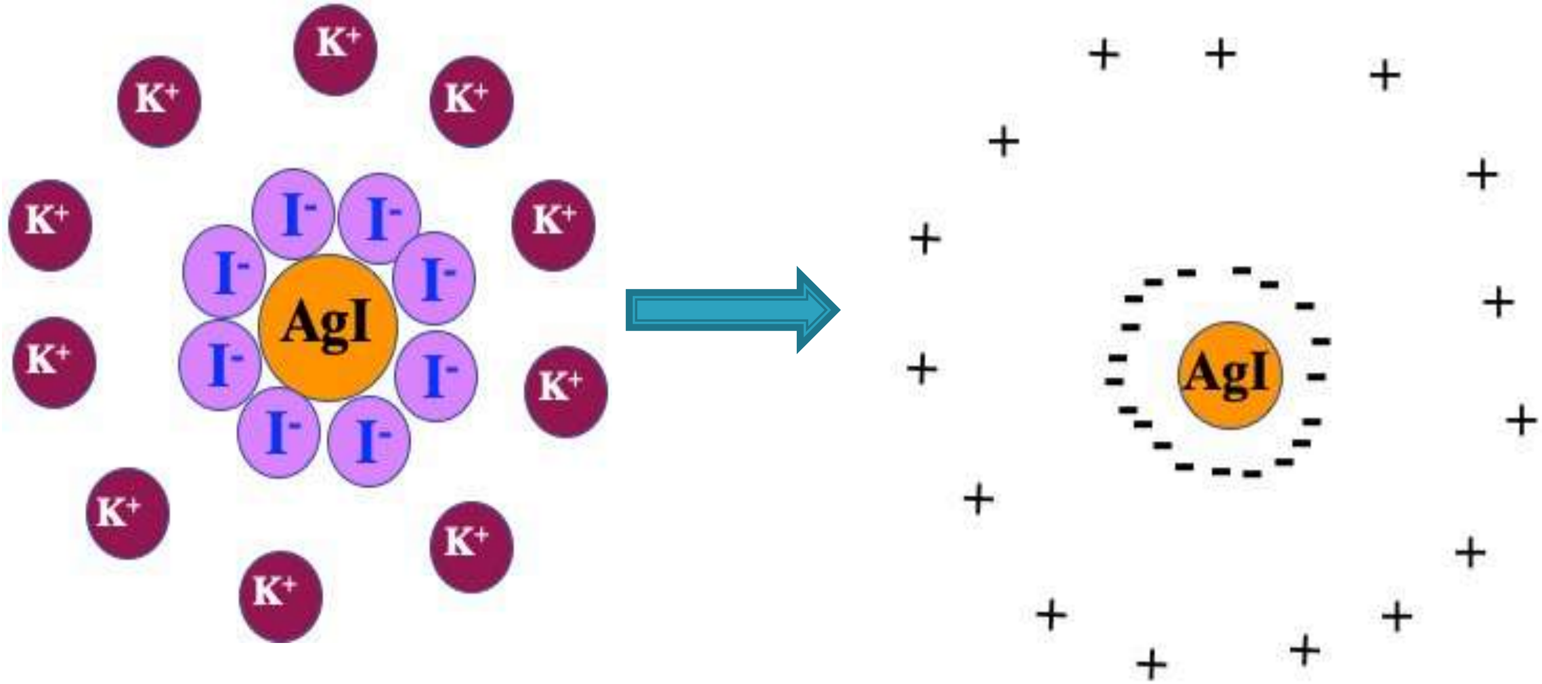
$[\mathrm{AgI}]\ \mathrm{I^-}\quad \mathrm{K^+}$



The source of the charge on the colloidal particles: -

Adsorption

$[\,\mathrm{AgI}\,]\ \mathrm{I}^{-}\quad \mathrm{K}^{+}\ ?$



The source of the charge on the colloidal particles: -

Adsorption

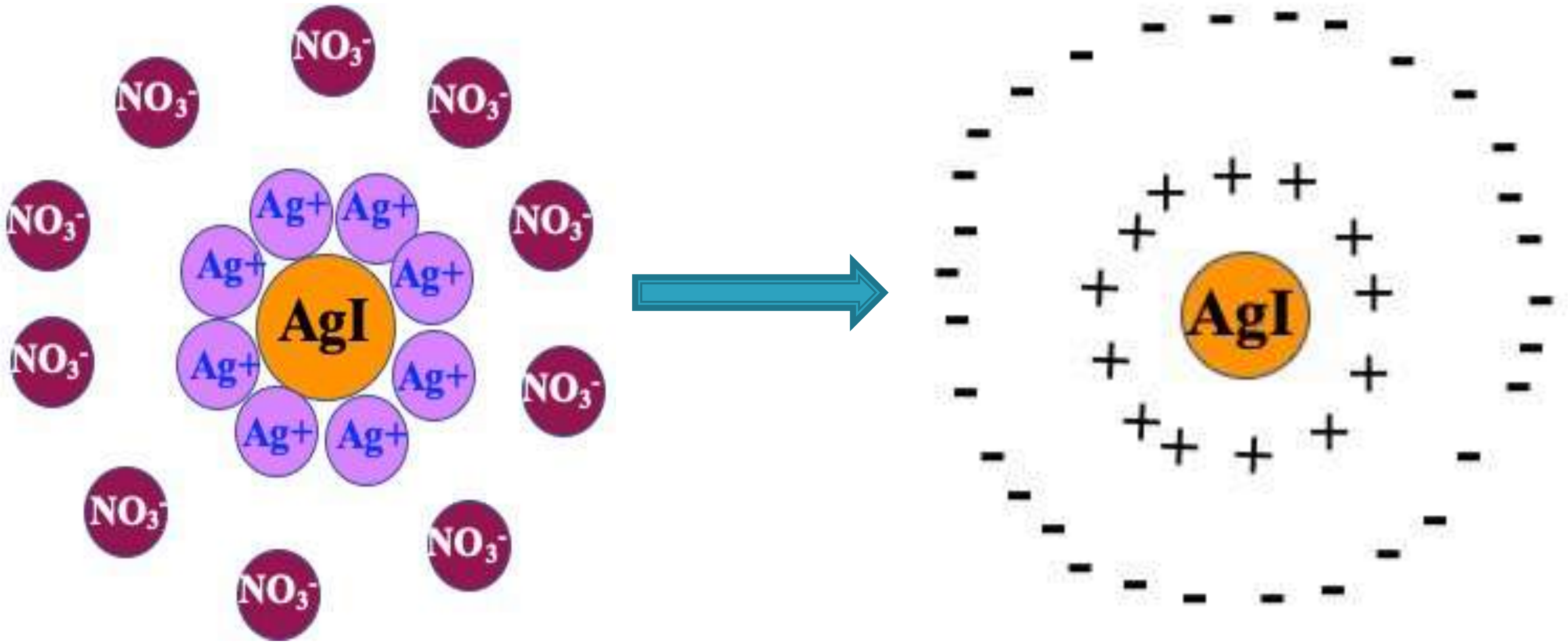
Excess of $AgNO_3$

$[AgI]Ag^+ \vdots NO_3^-$

The source of the charge on the colloidal particles: -

$[AgI]\,Ag^+ \vdots NO_3^-$

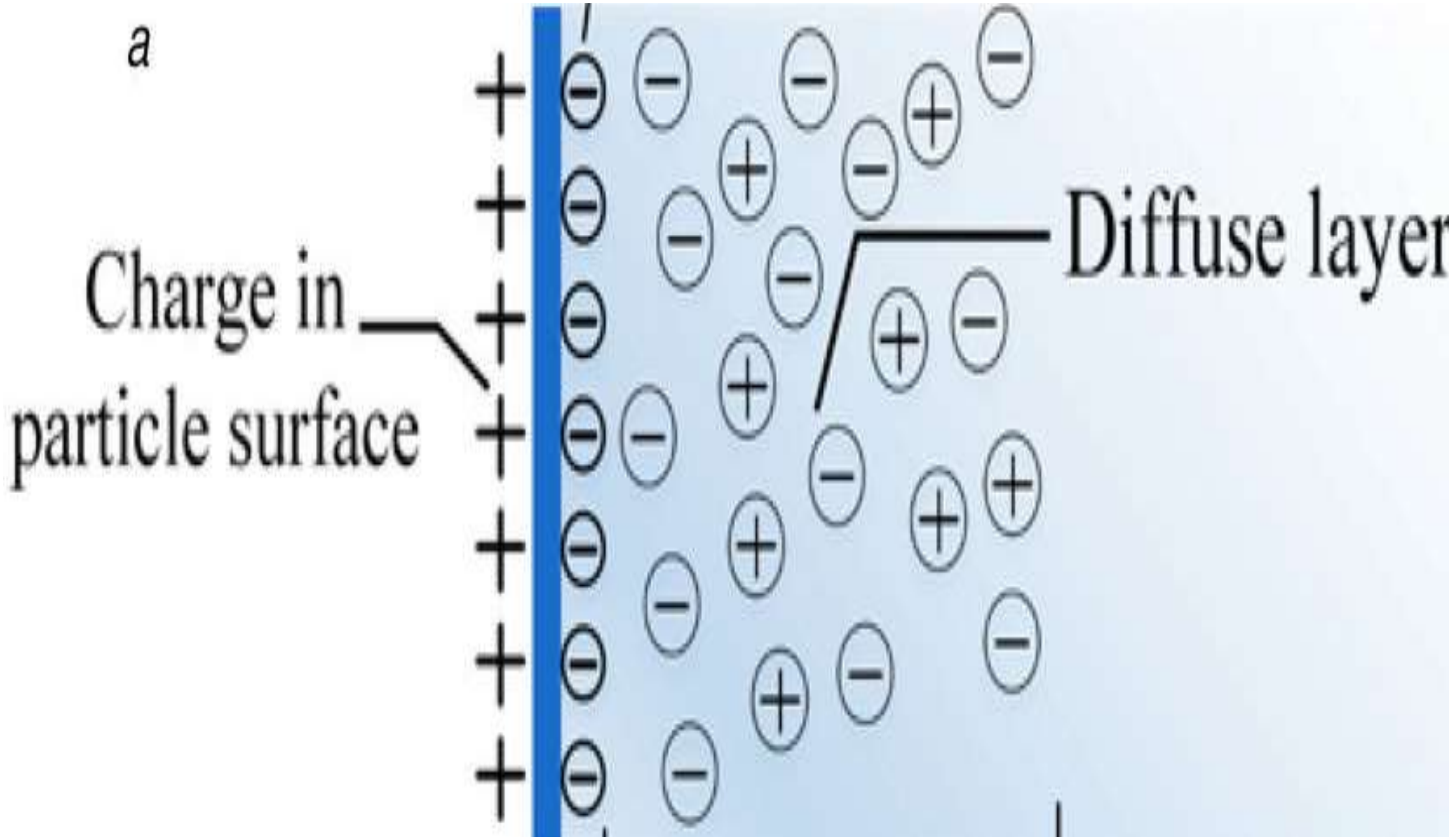
Adsorption



The source of the charge on the colloidal particles: -

Adsorption

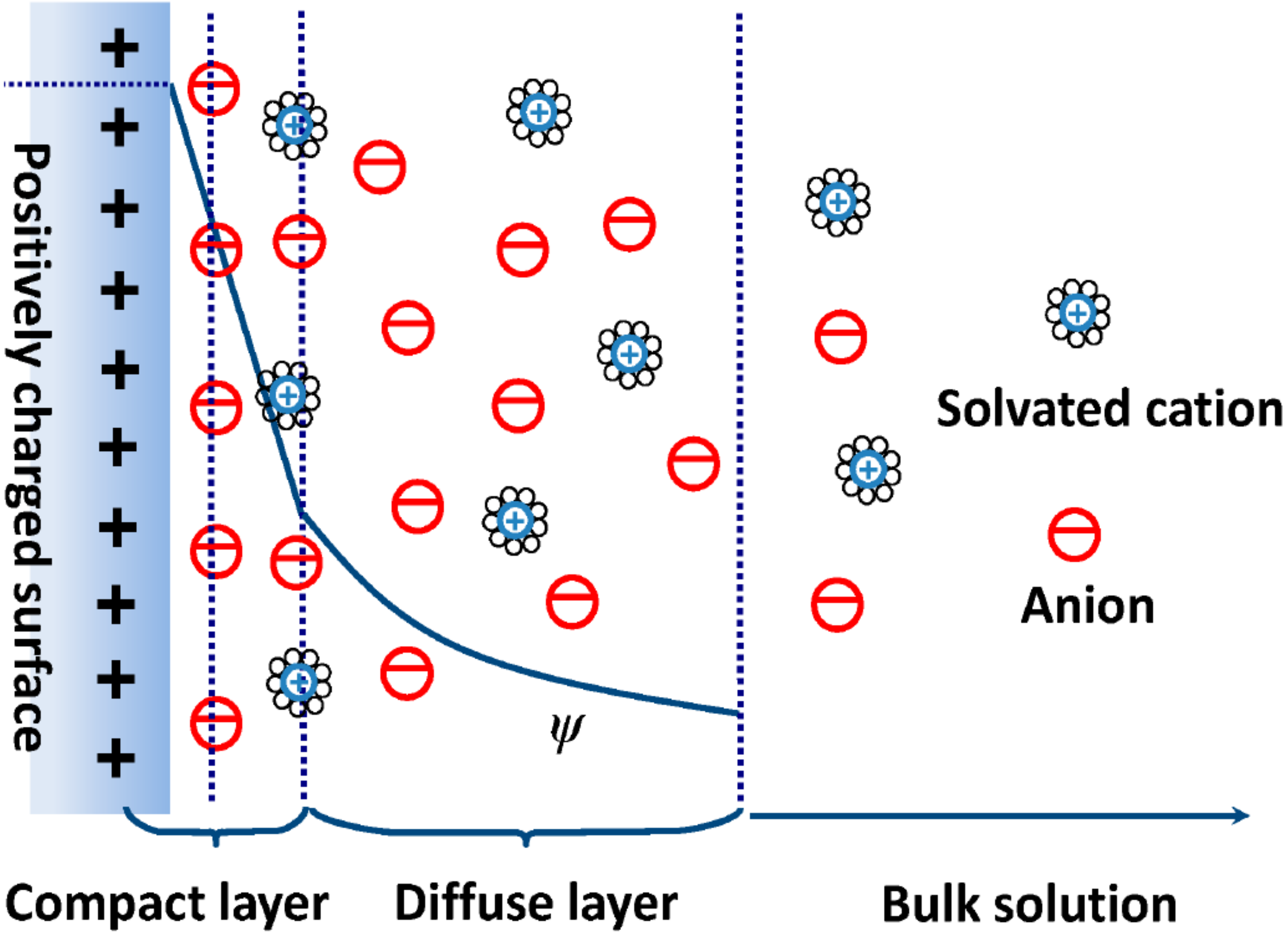
"Helmholtz Double Layer"



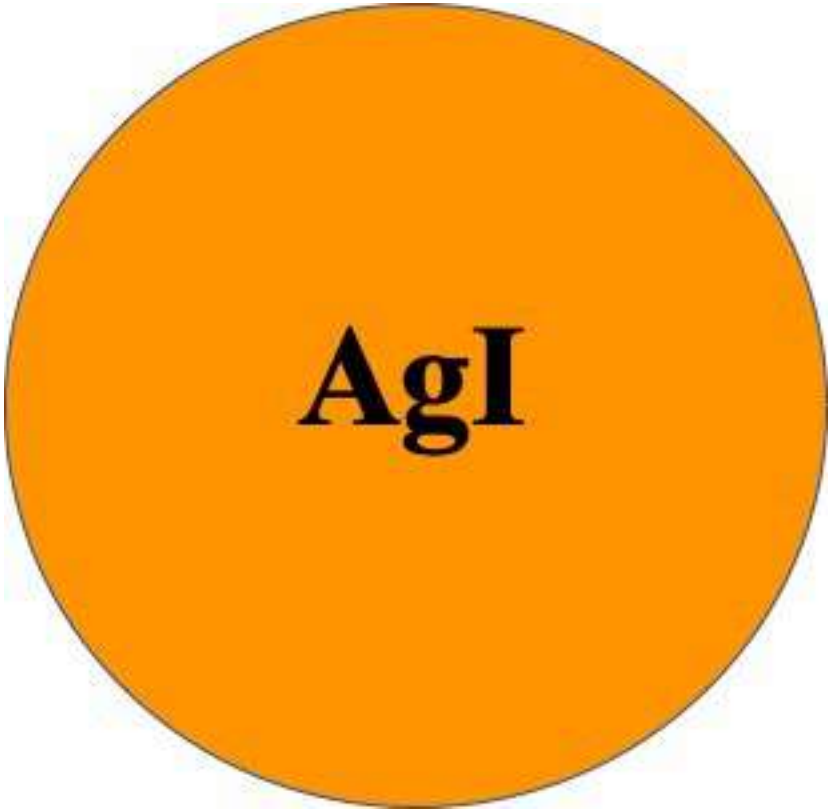
The source of the charge on the colloidal particles: -

Adsorption

"Helmholtz Double Layer"



- **When adding equal quantities of both KI and $AgNO_3$, AgI precipitates, no colloid formed?**



Solutions

True Solution

- It is a homogeneous mixture of two or more components.
- The particle diameter is < 1 nm.
- Examples: solutions of sugar, lactose, minerals, and vitamins.

- Solutions consists of two main components:

1. Solvent = dissolving medium and present in the larger amount.

Solutions

Solvent can be:

- ☐ often liquid; frequently water
- ☐ gas in air and other gas solutions
- ☐ rarely a solid

2. Solute(s) = dissolved material(s) and present in the smaller amount(s).

- ○ solids, liquids, and/or gases
- ○ often more than one solute

Solubility: It is the amount of solute required to prepare a saturated solution with a specific volume of solvent at a specific temperature.

According to the solubility, there are three types of solutions:

1. A saturated solution contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

2. **An unsaturated solution contains less solute than the solvent has the capacity to dissolve at a specific temperature.**

3. **A supersaturated solution contains more solute than is present in a saturated solution at a specific temperature.**

A supersaturated solution is clear before a seed crystal is added.

A supersaturated solution crystallizes rapidly when disturbed.

a) The solution is clear before a seed crystal is added.

b) Crystals begin to form in the solution immediately after the addition of a seed crystal.

c) Excess solute crystallizes rapidly. Applying Concepts *When the crystallization has ceased, will the solution be saturated or unsaturated?*

- Crystals begin to form in the solution immediately after the addition of a seed crystal.

- **Excess solute crystallizes rapidly.**

Solution Formation

The compositions of the solvent and the solute determine whether a substance will dissolve.

The factors that determine how fast a substance dissolves are:-

- **Nature of Solute / Solvent.**
- **Stirring (agitation).**
- **Temperature.**
- **The surface area of the dissolving particles.**

Factors Affecting Solubility

1. **Nature of Solute / Solvent.**

☐ **Like dissolves like.**

Organic solvents dissolve organic solute, and inorganic solvents dissolve inorganic solute.

Factors Affecting Solubility

1. **Nature of Solute / Solvent.**

2. Temperature :-

- **Solids/Liquids Solubility increases with temperature.**

Increasing Kinetic Energy (K.E.) increases motion and collision between solute / solvent, which leads to increasing the solubility.

Miscible vs. Immiscible

Miscible :- two liquids that dissolve in each other in all proportions.

Immiscible :- two liquids that are insoluble in one another.

The Chemical methods of expressing concentration

1. Percent (%w/v) - (Percentage weight in volume):

It expresses the number of grams of solute in 100 ml of solution.

2. g/L: Which means the number of grams of solute dissolved in one Liter of the solution.

3. Molarity (M):

Which is the number of moles (gram-molecular weights) of solute contained in1000 ml (1 Litre) of solution.

The Chemical methods of expressing concentration

4. **Molality (m):**

Is the number of moles of a solute contained in 1000 gm of a solvent.

5. **Normality (N):**

Is the number of equivalents (gram- equivalent weight) of the solute in one litre of solution.

The Chemical methods of expressing concentration

A. Equivalent weight of an acid

= Molecular weight of the acid / No. of replaceable hydrogen atoms.

= Molecular weight of the acid / Basicity of the acid

The Chemical methods of expressing concentration

A. Equivalent weight of an acid:-

For example, the basicity of Sulphuric acid is 2.

Equivalent weight of H_2SO_4 = Molecular weight of $H_2SO_4/2$ = 98/2 = 49 gm.

Equivalent weight of CH_3COOH = molecular weight of CH_3COOH /1 = 60/1 = 60 gm

The Chemical methods of expressing concentration

B. **Equivalent weight of a base** = **Molecular weight of the base/Number of replaceable hydroxide groups.**

= Molecular weight of the base/acidity of the base.

Equivalent weight of KOH = 56 /1 = 56

Equivalent weight of $Ca(OH)_2$ = 74 /2 = 37

The Chemical methods of expressing concentration

C. Equivalent weight of a Salt = Molecular weight of the Salt / Oxidation number of one of its halves multiplied in number of its ions.

Examples:

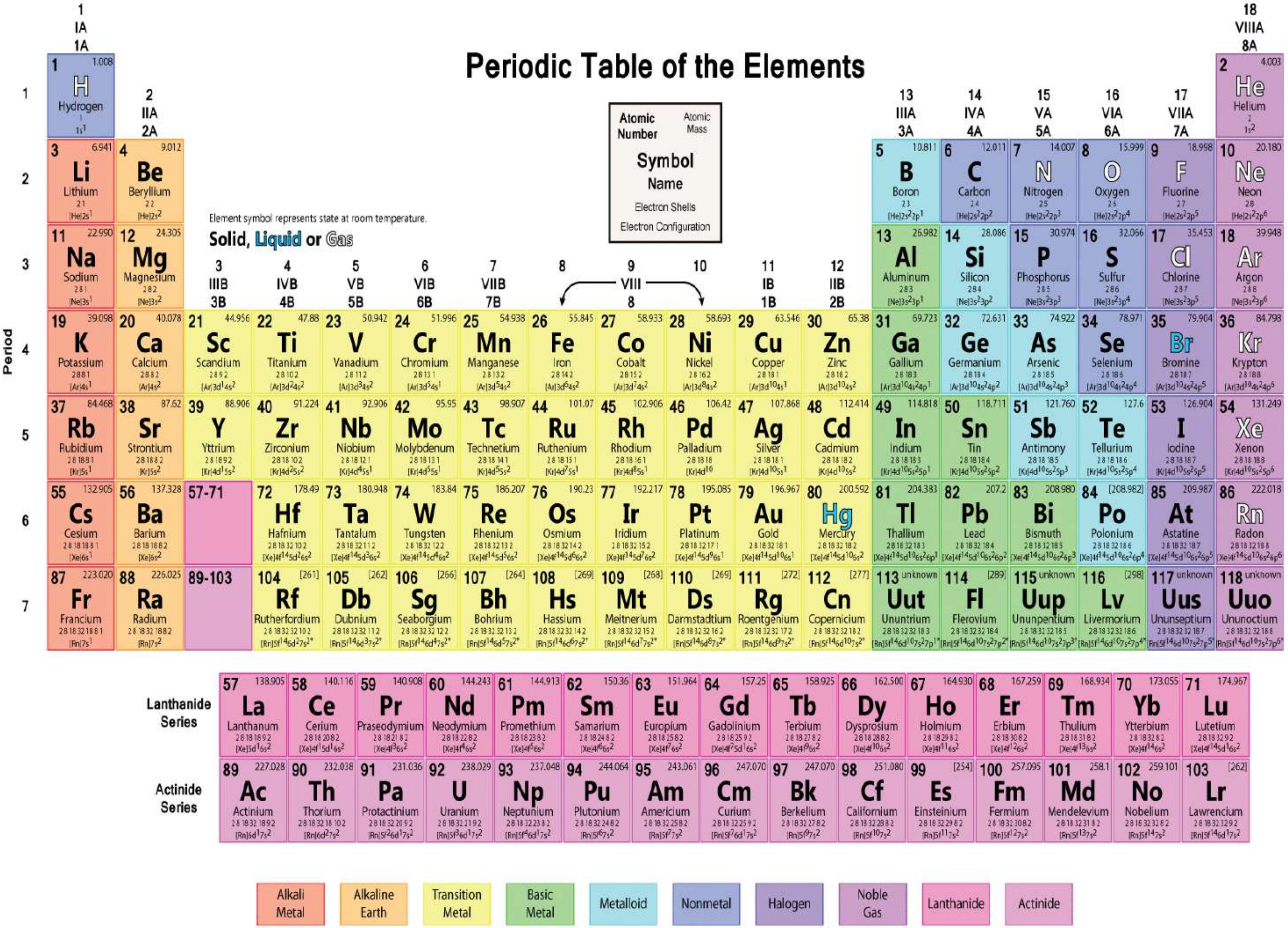
Equivalent weight of $Na^{+}Cl^{-}$ = 58.5 /1 = 58.5

Equivalent weight of $Ca^{+2}Cl_2^{-1}$ = 111 /2 = 55.5

By Using the periodic table, in the next slide, calculate the molecular and equivalent weights for the following substances?

1. $Al(OH)_3$
2. $SrBr_2$
3. Mn_2O_3
4. H_3PO_4
5. $Fe_2(SO_4)_3$

N.B. Each student should answer this question.



Periodic Table of the Elements

Atomic Number
Atomic Mass
Symbol
Name
Electron Shells
Electron Configuration

Element symbol represents state at room temperature.

Solid, Liquid or Gas

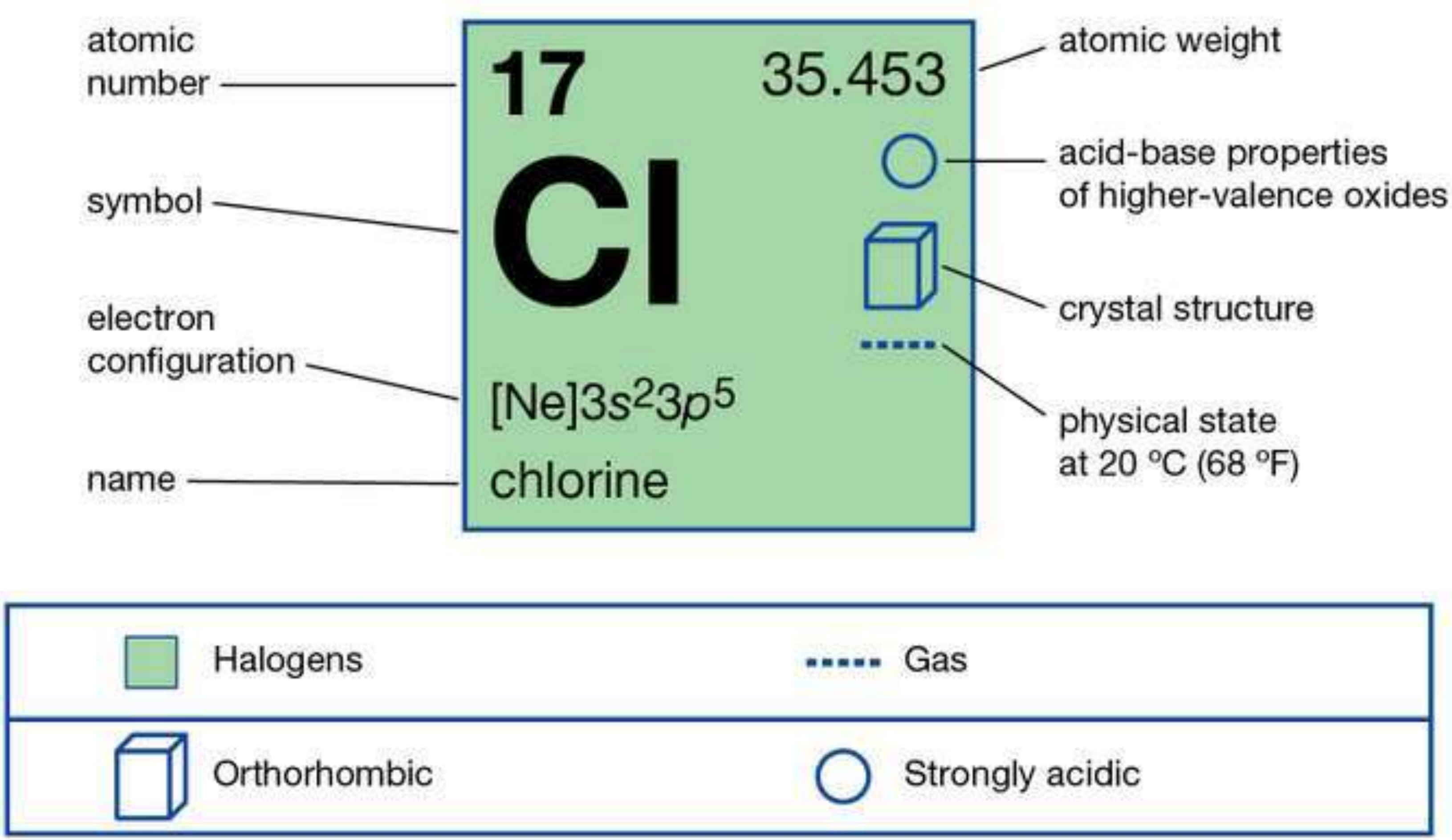
Period	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1	1 1.008 H Hydrogen 1 $1s^1$																	2 4.003 He Helium 2 $1s^2$
2	3 6.941 Li Lithium 2 1 $[He]2s^1$	4 9.012 Be Beryllium 2 2 $[He]2s^2$											5 10.811 B Boron 2 3 $[He]2s^2 2p^1$	6 12.011 C Carbon 2 4 $[He]2s^2 2p^2$	7 14.007 N Nitrogen 2 5 $[He]2s^2 2p^3$	8 15.999 O Oxygen 2 6 $[He]2s^2 2p^4$	9 18.998 F Fluorine 2 7 $[He]2s^2 2p^5$	10 20.180 Ne Neon 2 8 $[He]2s^2 2p^6$
3	11 22.990 Na Sodium 2 8 1 $[Ne]3s^1$	12 24.305 Mg Magnesium 2 8 2 $[Ne]3s^2$											13 26.982 Al Aluminum 2 8 3 $[Ne]3s^2 3p^1$	14 28.086 Si Silicon 2 8 4 $[Ne]3s^2 3p^2$	15 30.974 P Phosphorus 2 8 5 $[Ne]3s^2 3p^3$	16 32.066 S Sulfur 2 8 6 $[Ne]3s^2 3p^4$	17 35.453 Cl Chlorine 2 8 7 $[Ne]3s^2 3p^5$	18 39.948 Ar Argon 2 8 8 $[Ne]3s^2 3p^6$
4	19 39.098 K Potassium 2 8 8 1 $[Ar]4s^1$	20 40.078 Ca Calcium 2 8 8 2 $[Ar]4s^2$	21 44.956 Sc Scandium 2 8 9 2 $[Ar]3d^1 4s^2$	22 47.88 Ti Titanium 2 8 10 2 $[Ar]3d^2 4s^2$	23 50.942 V Vanadium 2 8 11 2 $[Ar]3d^3 4s^2$	24 51.996 Cr Chromium 2 8 13 1 $[Ar]3d^5 4s^1$	25 54.938 Mn Manganese 2 8 13 2 $[Ar]3d^5 4s^2$	26 55.845 Fe Iron 2 8 14 2 $[Ar]3d^6 4s^2$	27 58.933 Co Cobalt 2 8 15 2 $[Ar]3d^7 4s^2$	28 58.693 Ni Nickel 2 8 16 2 $[Ar]3d^8 4s^2$	29 63.546 Cu Copper 2 8 18 1 $[Ar]3d^{10} 4s^1$	30 65.38 Zn Zinc 2 8 18 2 $[Ar]3d^{10} 4s^2$	31 69.723 Ga Gallium 2 8 18 3 $[Ar]3d^{10} 4s^2 4p^1$	32 72.631 Ge Germanium 2 8 18 4 $[Ar]3d^{10} 4s^2 4p^2$	33 74.922 As Arsenic 2 8 18 5 $[Ar]3d^{10} 4s^2 4p^3$	34 78.971 Se Selenium 2 8 18 6 $[Ar]3d^{10} 4s^2 4p^4$	35 79.904 Br Bromine 2 8 18 7 $[Ar]3d^{10} 4s^2 4p^5$	36 84.798 Kr Krypton 2 8 18 8 $[Ar]3d^{10} 4s^2 4p^6$
5	37 84.468 Rb Rubidium 2 8 18 8 1 $[Kr]5s^1$	38 87.62 Sr Strontium 2 8 18 8 2 $[Kr]5s^2$	39 88.906 Y Yttrium 2 8 18 9 2 $[Kr]4d^1 5s^2$	40 91.224 Zr Zirconium 2 8 18 10 2 $[Kr]4d^2 5s^2$	41 92.906 Nb Niobium 2 8 18 12 1 $[Kr]4d^4 5s^1$	42 95.95 Mo Molybdenum 2 8 18 13 1 $[Kr]4d^5 5s^1$	43 98.907 Tc Technetium 2 8 18 14 1 $[Kr]4d^5 5s^2$	44 101.07 Ru Ruthenium 2 8 18 15 1 $[Kr]4d^7 5s^1$	45 102.906 Rh Rhodium 2 8 18 16 1 $[Kr]4d^8 5s^1$	46 106.42 Pd Palladium 2 8 18 18 $[Kr]4d^{10}$	47 107.868 Ag Silver 2 8 18 18 1 $[Kr]4d^{10} 5s^1$	48 112.414 Cd Cadmium 2 8 18 18 2 $[Kr]4d^{10} 5s^2$	49 114.818 In Indium 2 8 18 18 3 $[Kr]4d^{10} 5s^2 5p^1$	50 118.711 Sn Tin 2 8 18 18 4 $[Kr]4d^{10} 5s^2 5p^2$	51 121.760 Sb Antimony 2 8 18 18 5 $[Kr]4d^{10} 5s^2 5p^3$	52 127.6 Te Tellurium 2 8 18 18 6 $[Kr]4d^{10} 5s^2 5p^4$	53 126.904 I Iodine 2 8 18 18 7 $[Kr]4d^{10} 5s^2 5p^5$	54 131.249 Xe Xenon 2 8 18 18 8 $[Kr]4d^{10} 5s^2 5p^6$
6	55 132.905 Cs Cesium 2 8 18 18 8 1 $[Xe]6s^1$	56 137.328 Ba Barium 2 8 18 18 8 2 $[Xe]6s^2$	57-71	72 178.49 Hf Hafnium 2 8 18 32 10 2 $[Xe]4f^{14} 5d^2 6s^2$	73 180.948 Ta Tantalum 2 8 18 32 11 2 $[Xe]4f^{14} 5d^3 6s^2$	74 183.84 W Tungsten 2 8 18 32 12 2 $[Xe]4f^{14} 5d^4 6s^2$	75 186.207 Re Rhenium 2 8 18 32 13 2 $[Xe]4f^{14} 5d^5 6s^2$	76 190.23 Os Osmium 2 8 18 32 14 2 $[Xe]4f^{14} 5d^6 6s^2$	77 192.217 Ir Iridium 2 8 18 32 15 2 $[Xe]4f^{14} 5d^7 6s^2$	78 195.085 Pt Platinum 2 8 18 32 17 1 $[Xe]4f^{14} 5d^9 6s^1$	79 196.967 Au Gold 2 8 18 32 18 1 $[Xe]4f^{14} 5d^{10} 6s^1$	80 200.592 Hg Mercury 2 8 18 32 18 2 $[Xe]4f^{14} 5d^{10} 6s^2$	81 204.383 Tl Thallium 2 8 18 32 18 3 $[Xe]4f^{14} 5d^{10} 6s^2 6p^1$	82 207.2 Pb Lead 2 8 18 32 18 4 $[Xe]4f^{14} 5d^{10} 6s^2 6p^2$	83 208.980 Bi Bismuth 2 8 18 32 18 5 $[Xe]4f^{14} 5d^{10} 6s^2 6p^3$	84 [208.982] Po Polonium 2 8 18 32 18 6 $[Xe]4f^{14} 5d^{10} 6s^2 6p^4$	85 209.987 At Astatine 2 8 18 32 18 7 $[Xe]4f^{14} 5d^{10} 6s^2 6p^5$	86 222.018 Rn Radon 2 8 18 32 18 8 $[Xe]4f^{14} 5d^{10} 6s^2 6p^6$
7	87 223.020 Fr Francium 2 8 18 32 18 8 1 $[Rn]7s^1$	88 226.025 Ra Radium 2 8 18 32 18 8 2 $[Rn]7s^2$	89-103	104 [261] Rf Rutherfordium 2 8 18 32 32 10 2 $[Rn]5f^{14} 6d^2 7s^{2*}$	105 [262] Db Dubnium 2 8 18 32 32 11 2 $[Rn]5f^{14} 6d^3 7s^{2*}$	106 [266] Sg Seaborgium 2 8 18 32 32 12 2 $[Rn]5f^{14} 6d^4 7s^{2*}$	107 [264] Bh Bohrium 2 8 18 32 32 13 2 $[Rn]5f^{14} 6d^5 7s^{2*}$	108 [269] Hs Hassium 2 8 18 32 32 14 2 $[Rn]5f^{14} 6d^6 7s^{2*}$	109 [268] Mt Meitnerium 2 8 18 32 32 15 2 $[Rn]5f^{14} 6d^7 7s^{2*}$	110 [269] Ds Darmstadtium 2 8 18 32 32 16 2 $[Rn]5f^{14} 6d^8 7s^{2*}$	111 [272] Rg Roentgenium 2 8 18 32 32 17 2 $[Rn]5f^{14} 6d^9 7s^{2*}$	112 [277] Cn Copernicium 2 8 18 32 32 18 2 $[Rn]5f^{14} 6d^{10} 7s^{2*}$	113 unknown Uut Ununtrium 2 8 18 32 32 18 3 $[Rn]5f^{14} 6d^{10} 7s^2 7p^{1*}$	114 [289] Fl Flerovium 2 8 18 32 32 18 4 $[Rn]5f^{14} 6d^{10} 7s^2 7p^{2*}$	115 unknown Uup Ununpentium 2 8 18 32 32 18 5 $[Rn]5f^{14} 6d^{10} 7s^2 7p^{3*}$	116 [298] Lv Livermorium 2 8 18 32 32 18 6 $[Rn]5f^{14} 6d^{10} 7s^2 7p^{4*}$	117 unknown Uus Ununseptium 2 8 18 32 32 18 7 $[Rn]5f^{14} 6d^{10} 7s^2 7p^{5*}$	118 unknown Uuo Ununoctium 2 8 18 32 32 18 8 $[Rn]5f^{14} 6d^{10} 7s^2 7p^{6*}$

Lanthanide Series	57 138.905 La Lanthanum 2 8 18 18 9 2 $[Xe]5d^1 6s^2$	58 140.116 Ce Cerium 2 8 18 20 8 2 $[Xe]4f^1 5d^1 6s^2$	59 140.908 Pr Praseodymium 2 8 18 21 8 2 $[Xe]4f^3 6s^2$	60 144.243 Nd Neodymium 2 8 18 22 8 2 $[Xe]4f^4 6s^2$	61 144.913 Pm Promethium 2 8 18 23 8 2 $[Xe]4f^5 6s^2$	62 150.36 Sm Samarium 2 8 18 24 8 2 $[Xe]4f^6 6s^2$	63 151.964 Eu Europium 2 8 18 25 8 2 $[Xe]4f^7 6s^2$	64 157.25 Gd Gadolinium 2 8 18 25 9 2 $[Xe]4f^7 5d^1 6s^2$	65 158.925 Tb Terbium 2 8 18 27 8 2 $[Xe]4f^9 6s^2$	66 162.500 Dy Dysprosium 2 8 18 28 8 2 $[Xe]4f^{10} 6s^2$	67 164.930 Ho Holmium 2 8 18 29 8 2 $[Xe]4f^{11} 6s^2$	68 167.259 Er Erbium 2 8 18 30 8 2 $[Xe]4f^{12} 6s^2$	69 168.934 Tm Thulium 2 8 18 31 8 2 $[Xe]4f^{13} 6s^2$	70 173.055 Yb Ytterbium 2 8 18 32 8 2 $[Xe]4f^{14} 6s^2$	71 174.967 Lu Lutetium 2 8 18 32 9 2 $[Xe]4f^{14} 5d^1 6s^2$
Actinide Series	89 227.028 Ac Actinium 2 8 18 32 18 9 2 $[Rn]6d^1 7s^2$	90 232.038 Th Thorium 2 8 18 32 18 10 2 $[Rn]6d^2 7s^2$	91 231.036 Pa Protactinium 2 8 18 32 20 9 2 $[Rn]5f^2 6d^1 7s^2$	92 238.029 U Uranium 2 8 18 32 21 9 2 $[Rn]5f^3 6d^1 7s^2$	93 237.048 Np Neptunium 2 8 18 32 23 8 2 $[Rn]5f^4 6d^1 7s^2$	94 244.064 Pu Plutonium 2 8 18 32 24 8 2 $[Rn]5f^6 7s^2$	95 243.061 Am Americium 2 8 18 32 25 8 2 $[Rn]5f^7 7s^2$	96 247.070 Cm Curium 2 8 18 32 25 9 2 $[Rn]5f^7 6d^1 7s^2$	97 247.070 Bk Berkelium 2 8 18 32 27 8 2 $[Rn]5f^9 7s^2$	98 251.080 Cf Californium 2 8 18 32 28 8 2 $[Rn]5f^{10} 7s^2$	99 [254] Es Einsteinium 2 8 18 32 29 8 2 $[Rn]5f^{11} 7s^2$	100 257.095 Fm Fermium 2 8 18 32 30 8 2 $[Rn]5f^{12} 7s^2$	101 258.1 Md Mendelevium 2 8 18 32 31 8 2 $[Rn]5f^{13} 7s^2$	102 259.101 No Nobelium 2 8 18 32 32 8 2 $[Rn]5f^{14} 7s^2$	103 [262] Lr Lawrencium 2 8 18 32 32 9 2 $[Rn]5f^{14} 6d^1 7s^2$

Alkali Metal
Alkaline Earth
Transition Metal
Basic Metal
Metalloid
Nonmetal
Halogen
Noble Gas
Lanthanide
Actinide


8
2s² 2p⁴
O
Oxygen
15.999
VectorStock

Chlorine


atomic number
symbol
electron configuration
name
17
35.453
Cl
[Ne]3s²3p⁵
chlorine
atomic weight
acid-base properties of higher-valence oxides
crystal structure
physical state at 20 °C (68 °F)
Halogens
Gas
Orthorhombic
Strongly acidic

Types of Solutions according to the types of solvent and solute.

A. Gases in Gases: such as O_2 and N_2 in Air.

Gases mixed quickly in each other due to their quick distribution and the large interstitial distances among the gas particles.

Types of Solutions according to the types of solvent and solute.

B. Gases in Liquids solutions: such as ammonia and carbon dioxide in water.

$$NH_{3\,(g)} + H_2O_{\,(l)} = NH_4OH_{\,(aq)}$$

$$CO_{2\,(g)} + H_2O_{\,(l)} = H_2CO_{3\,(aq)}$$

Solubility of gas in liquid is defined as the gas volume which is required to prepare a saturated solution of 1 cm^3 of the solvent.

Factors affecting the suitability of gases in liquids.

1. The gas type.

- ✓ The much easy liquefying gases the much easy for them to soluble in liquids.

for example solubility of carbon dioxide and water is much higher than the solubility of oxygen in water.

- ✓ The solubility of gases increases if the gas tends to react with the liquid.

For example ammonia soluble in water forming NH_4OH.

Factors affecting the suitability of gases in liquids.

2. Liquid type:

- **The solubility of gas is different from liquid to liquid.**

For example the solubility of carbon dioxide in benzene is much more than its solubility in water.

3. Effect of temperature.

The solubility of gases in liquids is exothermic process, so these solubility decreases by increasing the temperature.

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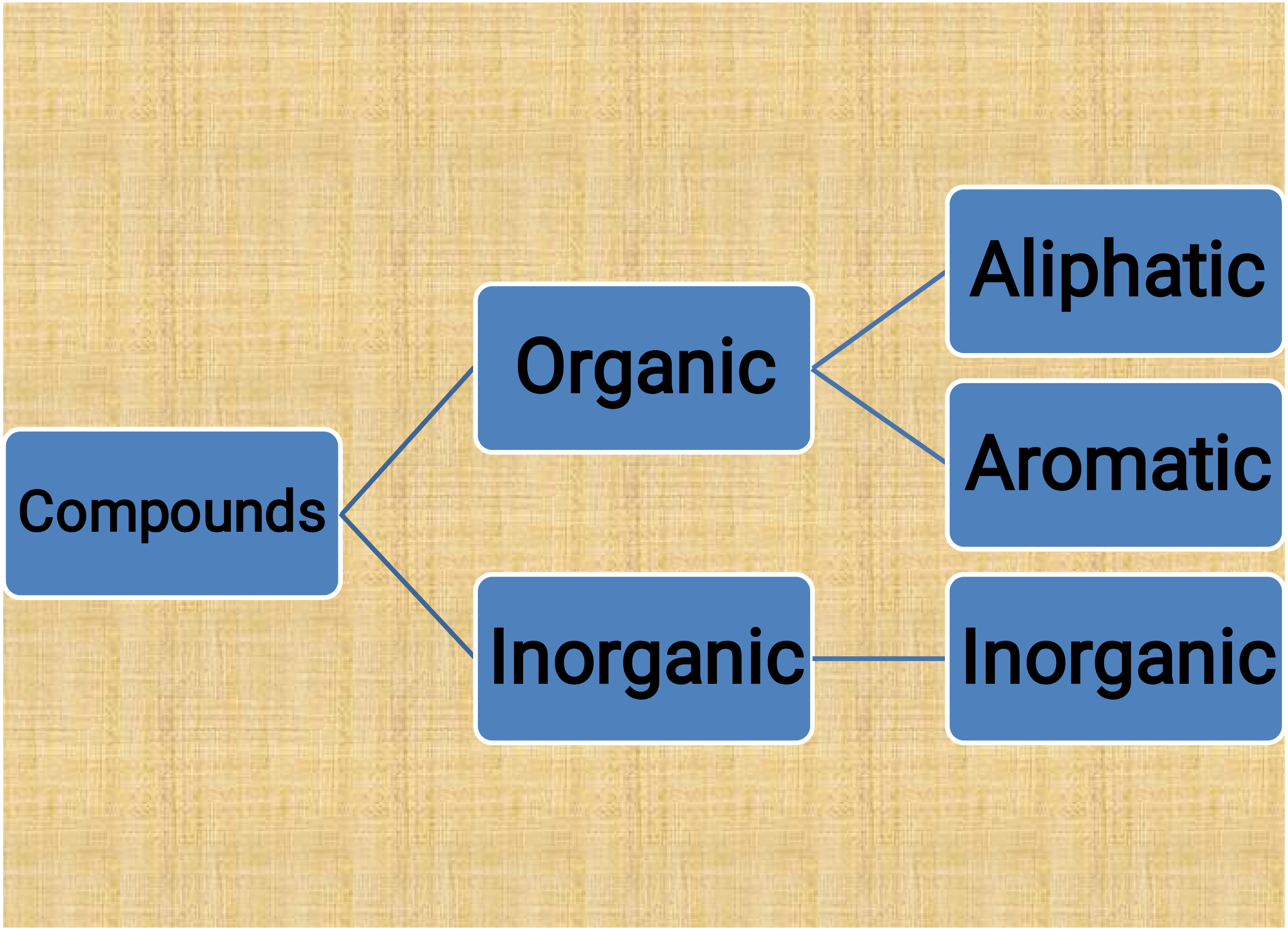
Part 2: Organic Chemistry

Dr. Abobakr Haridy

Organic Chemistry

Aliphatic Compounds

Classification of compounds



Compounds

Organic

Inorganic

Aliphatic

Aromatic

Inorganic

Introduction to Organic Chemistry

- ❑ Organic chemistry is the study of the structure, properties, composition, reactions, and preparation of carbon-containing compounds. Most organic compounds contain carbon and hydrogen, but they may also include any number of other elements (e.g., nitrogen, oxygen, halogens, phosphorus, silicon, sulfur).
- ❑ Organic chemistry plays an important part in our daily life because food, clothes, paper, ink, rubber, soap, perfumes, medicines etc. are indispensable to us for proper living. Organic compounds are important constituents of many products e.g., paint, food, plastic, explosive, medicine, petrochemical, pesticide etc.

* Classification of organic compounds

1- Hydrocarbons (C,H)

2- Alcohols (C,H,O)

3- Aldehydes (C,H,O)

4- Ketones (C,H,O)

5- carboxylic acids (C,H,O)

6-Esters (C,H,O)

7- Amines (C,H,N)

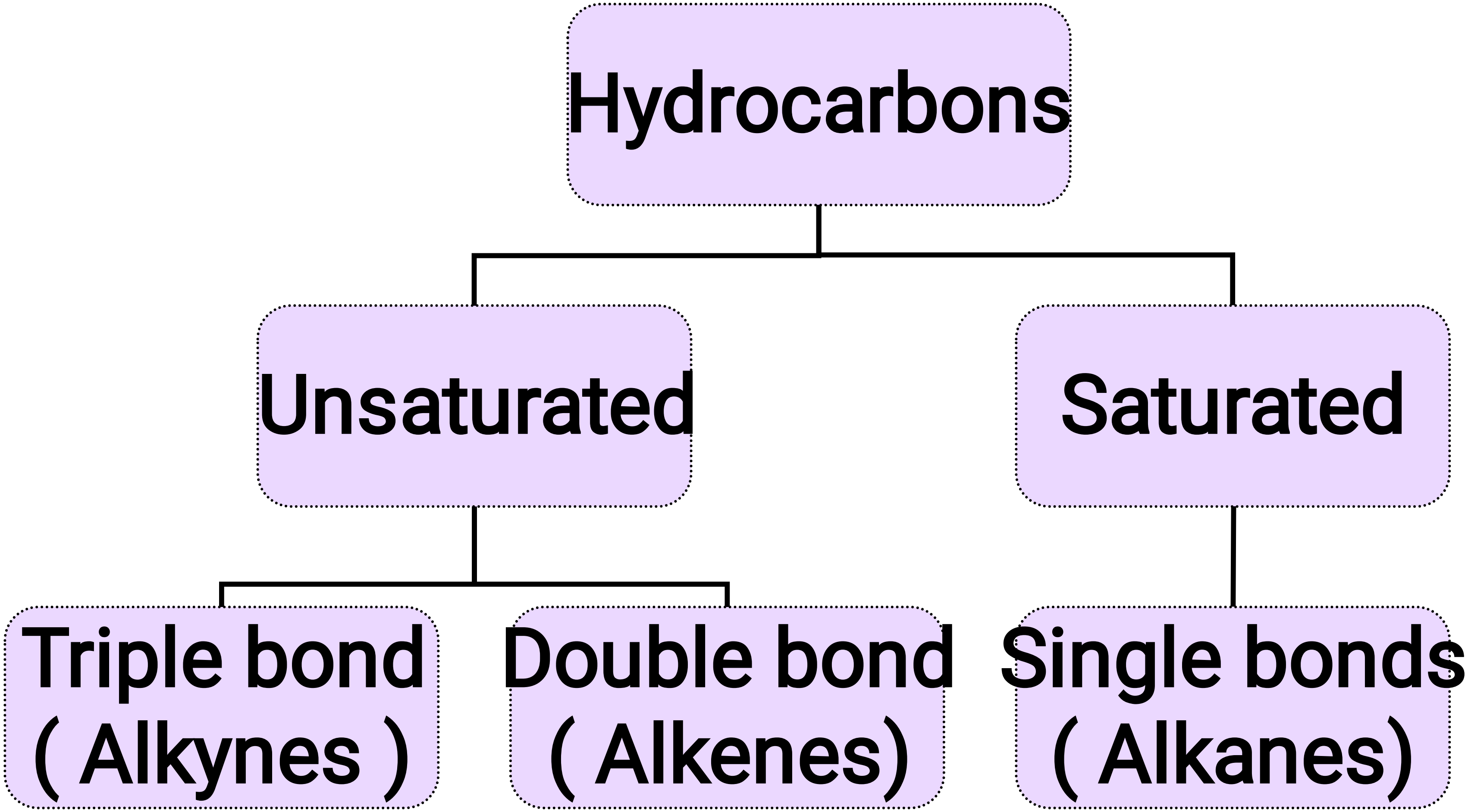
8- Amides (C,H,O,N)

9- Imides (C,H,O,N)

Hydrocarbons

What are hydrocarbons?

Hydrocarbons are compounds comprised exclusively of carbon and hydrogen.



Hydrocarbons

Unsaturated

Saturated

Triple bond (Alkynes)

Double bond (Alkenes)

Single bonds (Alkanes)

Alkanes C_nH_{2n+2}

What are Alkanes? Alkanes are organic compounds that consist of single-bonded carbon and hydrogen atoms. The formula for Alkanes is C_nH_{2n+2}, subdivided into three groups – chain alkanes, cycloalkanes, and the branched alkanes.

List of Alkanes

Methane (CH_4)

Ethane (C_2H_6)

Propane (C_3H_8)

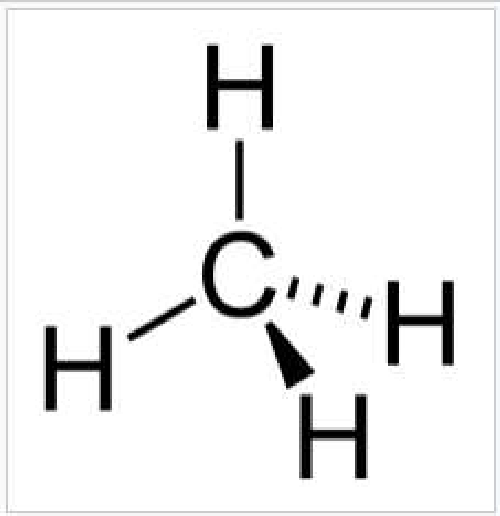
Butane (C_4H_{10})

Pentane (C_5H_{12})

Hexane (C_6H_{14})

Heptane (C_7H_{16})

Octane (C_8H_{18})

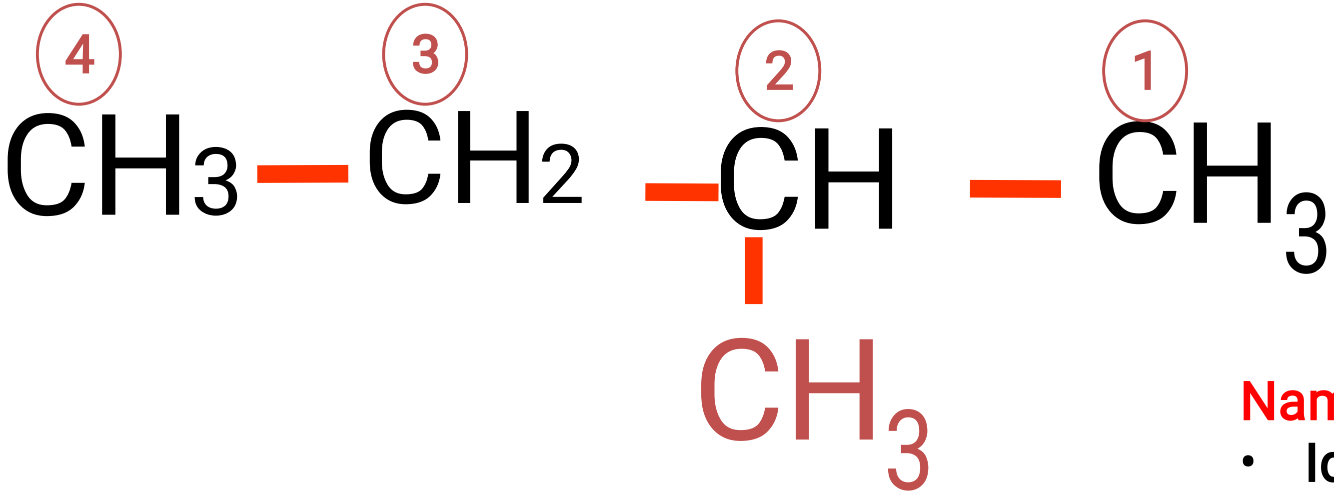


Chemical structure of methane, the simplest alkane

Tetrahedral shape with angles 109.5°

Alkane	Formula	Boiling point [°C]	Melting point [°C]	Density [kg/m³] (at 20 °C)	Isomers
Methane	CH_4	−162	−182	0.656 (gas)	1
Ethane	C_2H_6	−89	−183	1.26 (gas)	1
Propane	C_3H_8	−42	−188	2.01 (gas)	1
Butane	C_4H_{10}	0	−138	2.48 (gas)	2
Pentane	C_5H_{12}	36	−130	626 (liquid)	3
Hexane	C_6H_{14}	69	−95	659 (liquid)	5
Heptane	C_7H_{16}	98	−91	684 (liquid)	9
Octane	C_8H_{18}	126	−57	703 (liquid)	18
Nonane	C_9H_{20}	151	−54	718 (liquid)	35
Decane	$C_{10}H_{22}$	174	−30	730 (liquid)	75
Undecane	$C_{11}H_{24}$	196	−26	740 (liquid)	159
Dodecane	$C_{12}H_{26}$	216	−10	749 (liquid)	355
Tridecane	$C_{13}H_{28}$	235	−5.4	756 (liquid)	802
Tetradecane	$C_{14}H_{30}$	253	5.9	763 (liquid)	1858
Pentadecane	$C_{15}H_{32}$	270	10	769 (liquid)	4347
Hexadecane	$C_{16}H_{34}$	287	18	773 (liquid)	10,359
Heptadecane	$C_{17}H_{36}$	303	22	777 (solid)	24,894
Octadecane	$C_{18}H_{38}$	317	28	781 (solid)	60,523
Nonadecane	$C_{19}H_{40}$	330	32	785 (solid)	148,284
Icosane	$C_{20}H_{42}$	343	37	789 (solid)	366,319

Nomenclature of alkane



$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

Naming rule

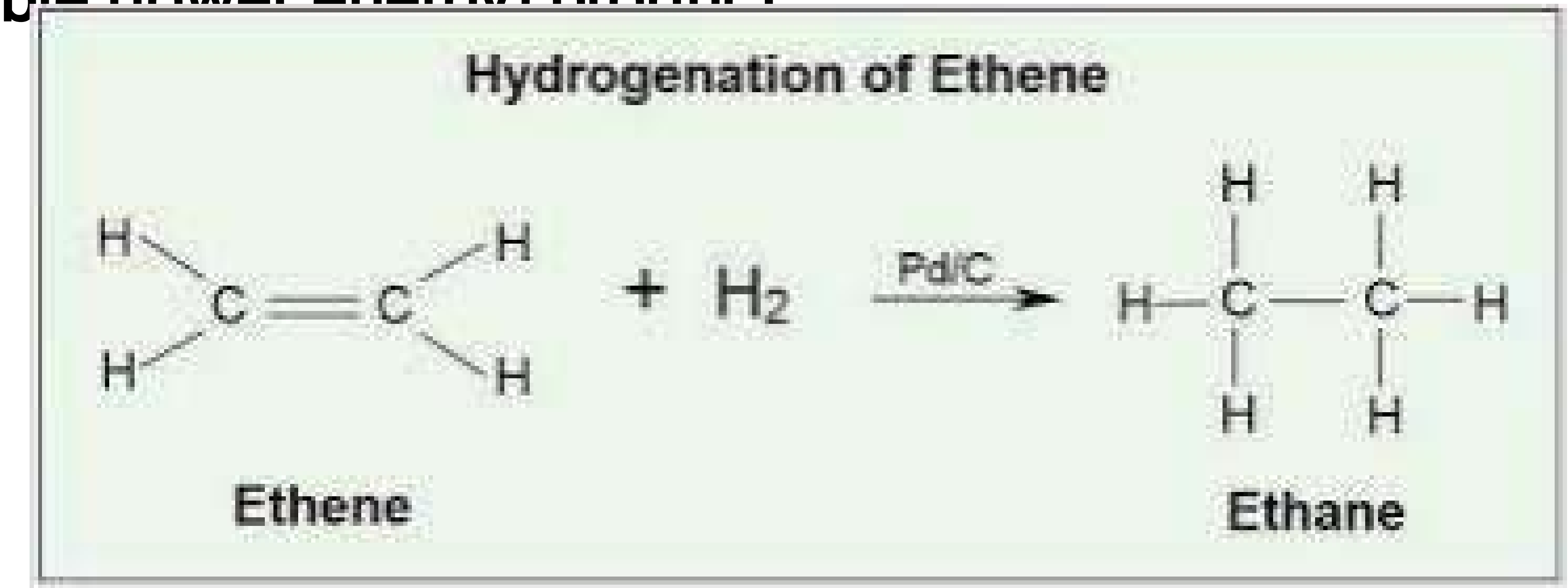
- Identify longest chain
- Branch will take the lowest numbe

2-methylbutane

Preparation of alkanes

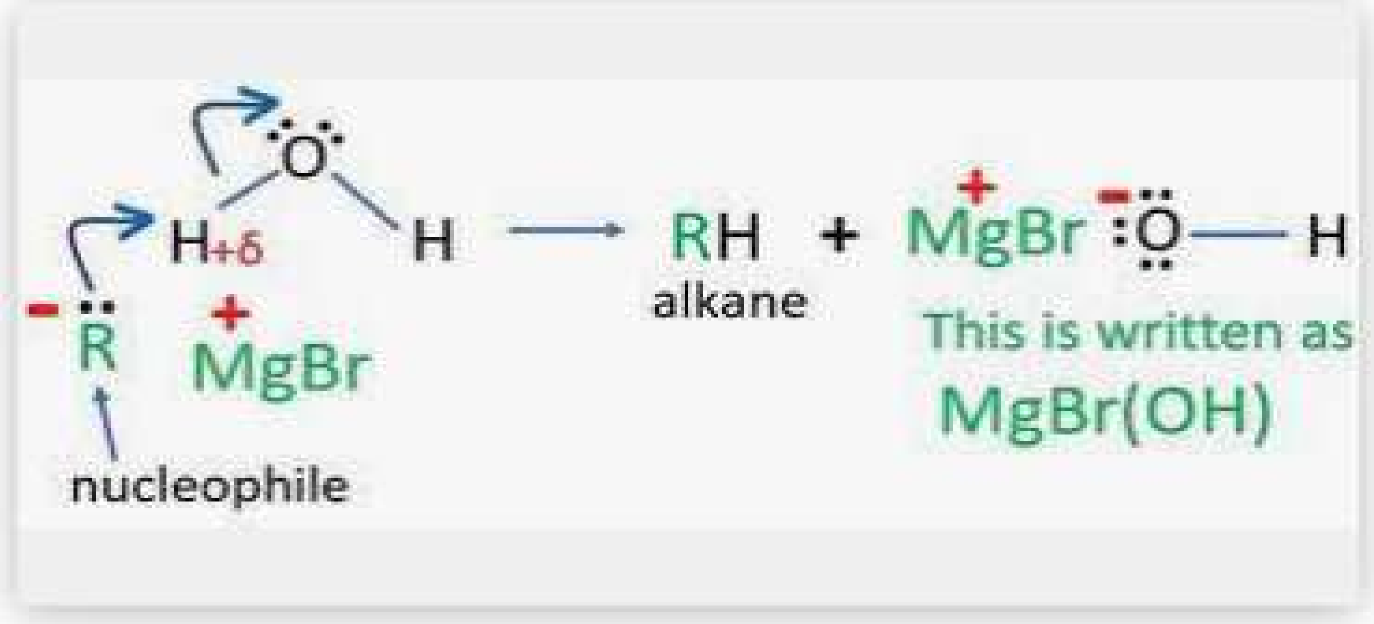
1- Hydrogenation of alkene

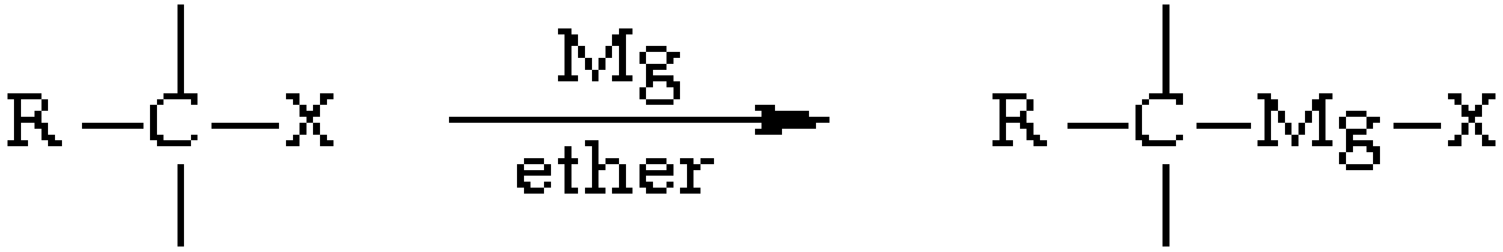
In a hydrogenation reaction, two hydrogen atoms are added across the double bond of an alkene, resulting in a saturated alkane. Hydrogenation of a double bond is a thermodynamically favorable reaction because it forms a more stable (lower energy) product



2- Hydrolysis of Grignard reagent

The Grignard reagent is very unstable in water and **hydrolyzes to create an alkane compound**. The Grignard reagent should be produced in dry media for this reason (without water or moisture). The alkane is used to preserve the number of carbon atoms in the Grignard reagent.

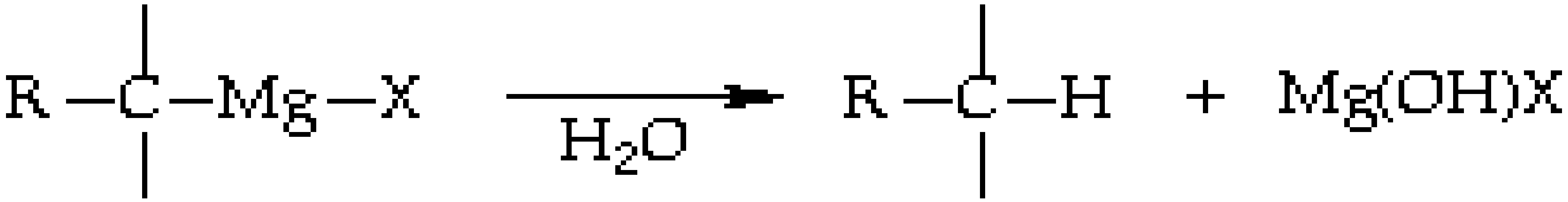




$$R-C-X \xrightarrow[\text{ether}]{\text{Mg}} R-C-Mg-X$$

an alkyl halide

a Grignard reagent

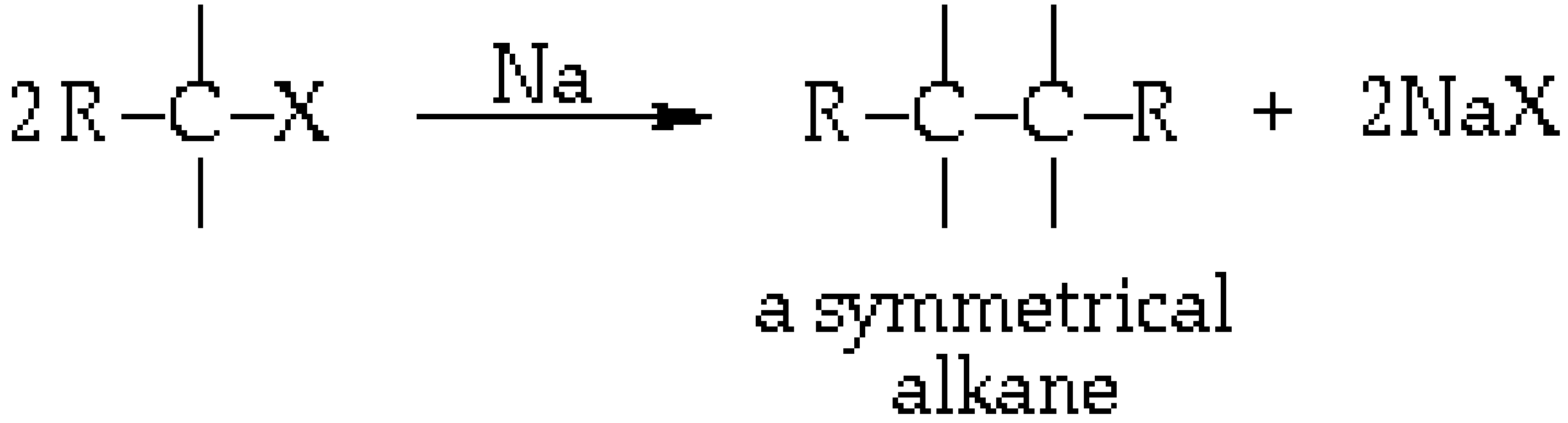


$$R-C-Mg-X \xrightarrow[H_2O]{} R-C-H + Mg(OH)X$$

alkane

3) Wurtz Reaction

It used for the synthesis of alkanes with even number of carbon atoms



$$2R-\overset{|}{\underset{|}{C}}-X \xrightarrow{Na} R-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-R + 2NaX$$

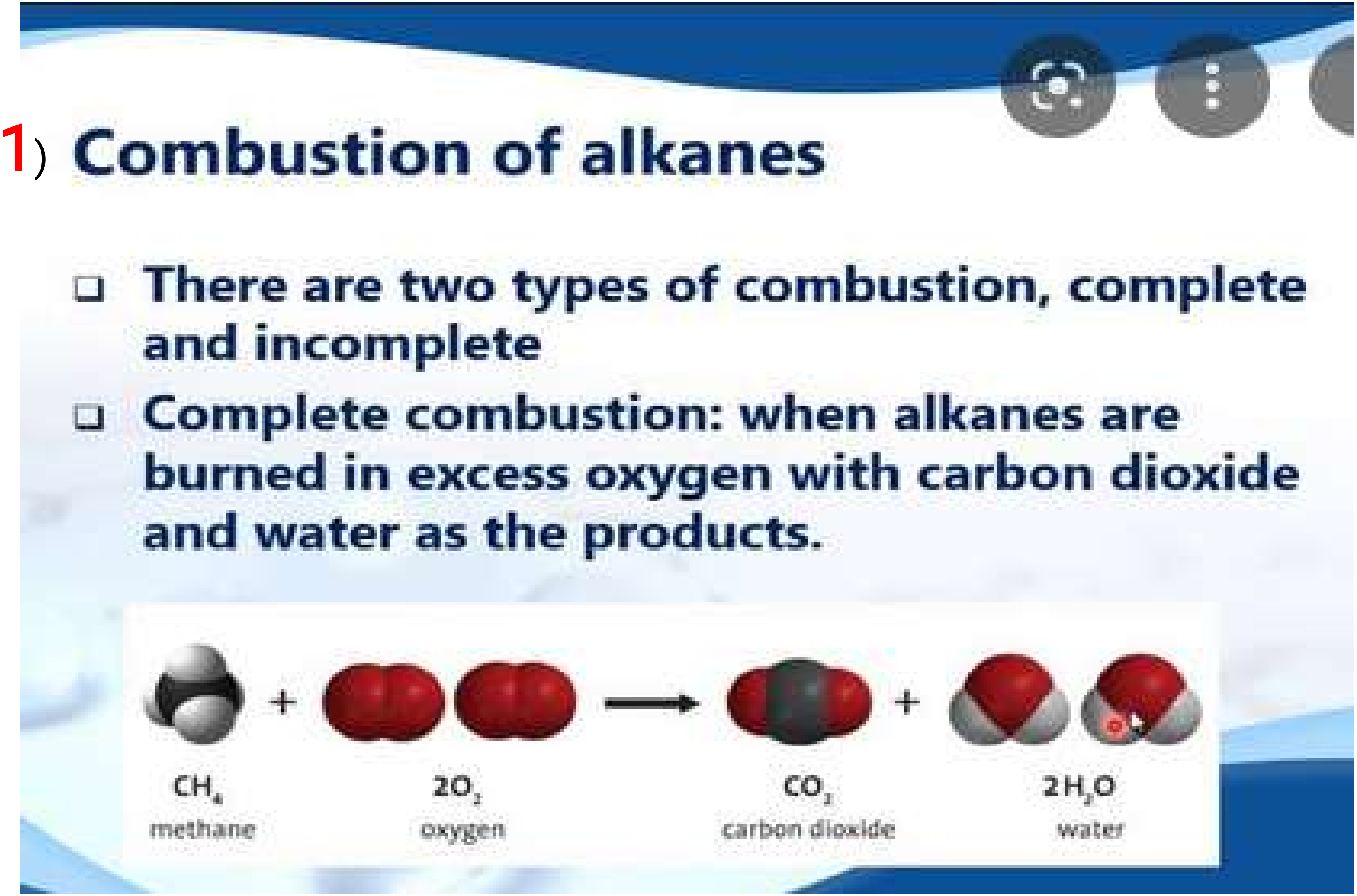
a symmetrical alkane

$$2\ CH_3-CH_2-CH_2-Br + 2\ Na \longrightarrow CH_3-CH_2-CH_2-CH_2-CH_2-CH_3 + 2\ NaBr$$

Propyl bromide

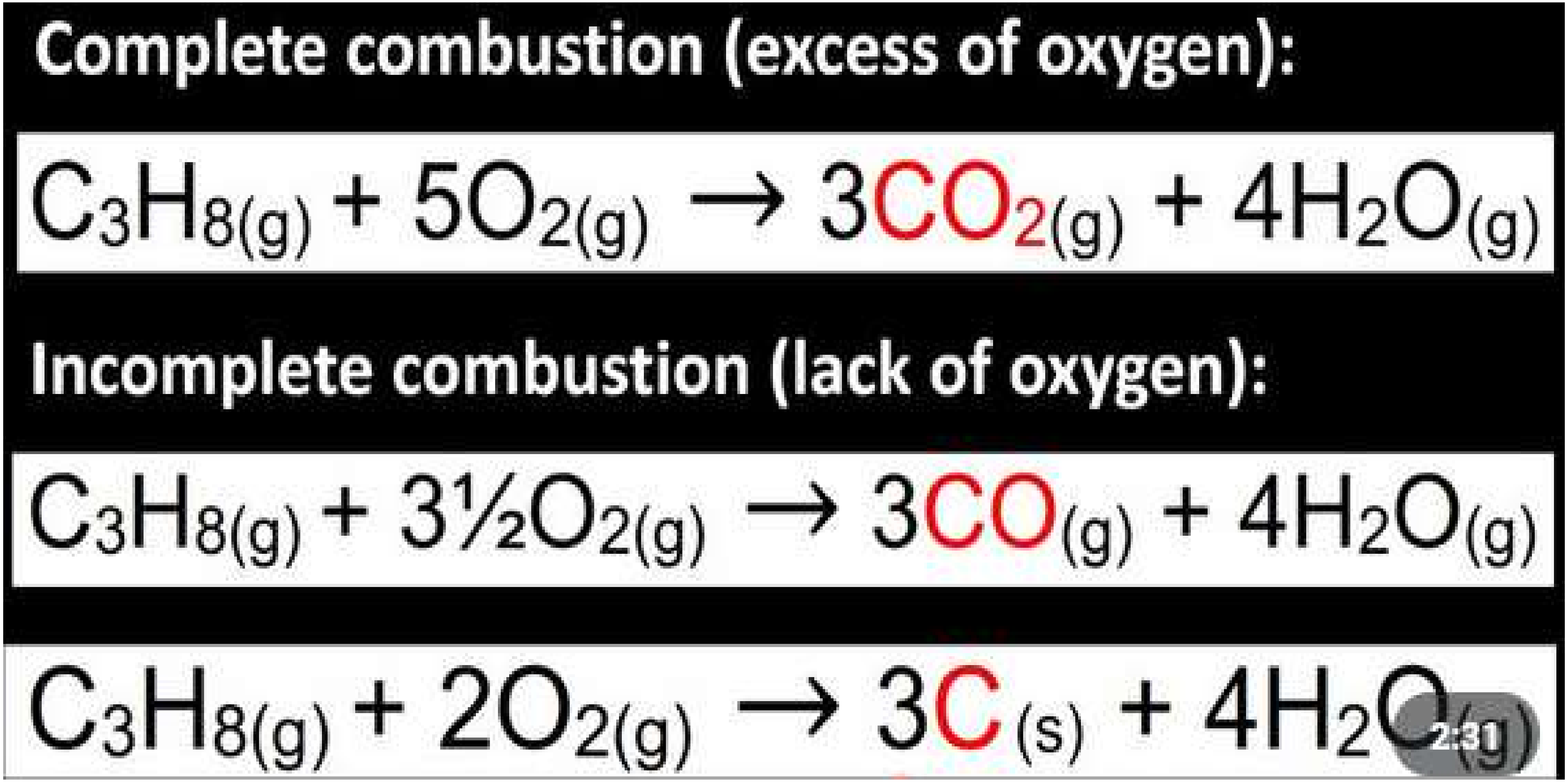
hexane

Reactions of alkanes



1) Combustion of alkanes

- ☐ There are two types of combustion, complete and incomplete
- ☐ Complete combustion: when alkanes are burned in excess oxygen with carbon dioxide and water as the products.



Complete combustion (excess of oxygen):

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

Incomplete combustion (lack of oxygen):

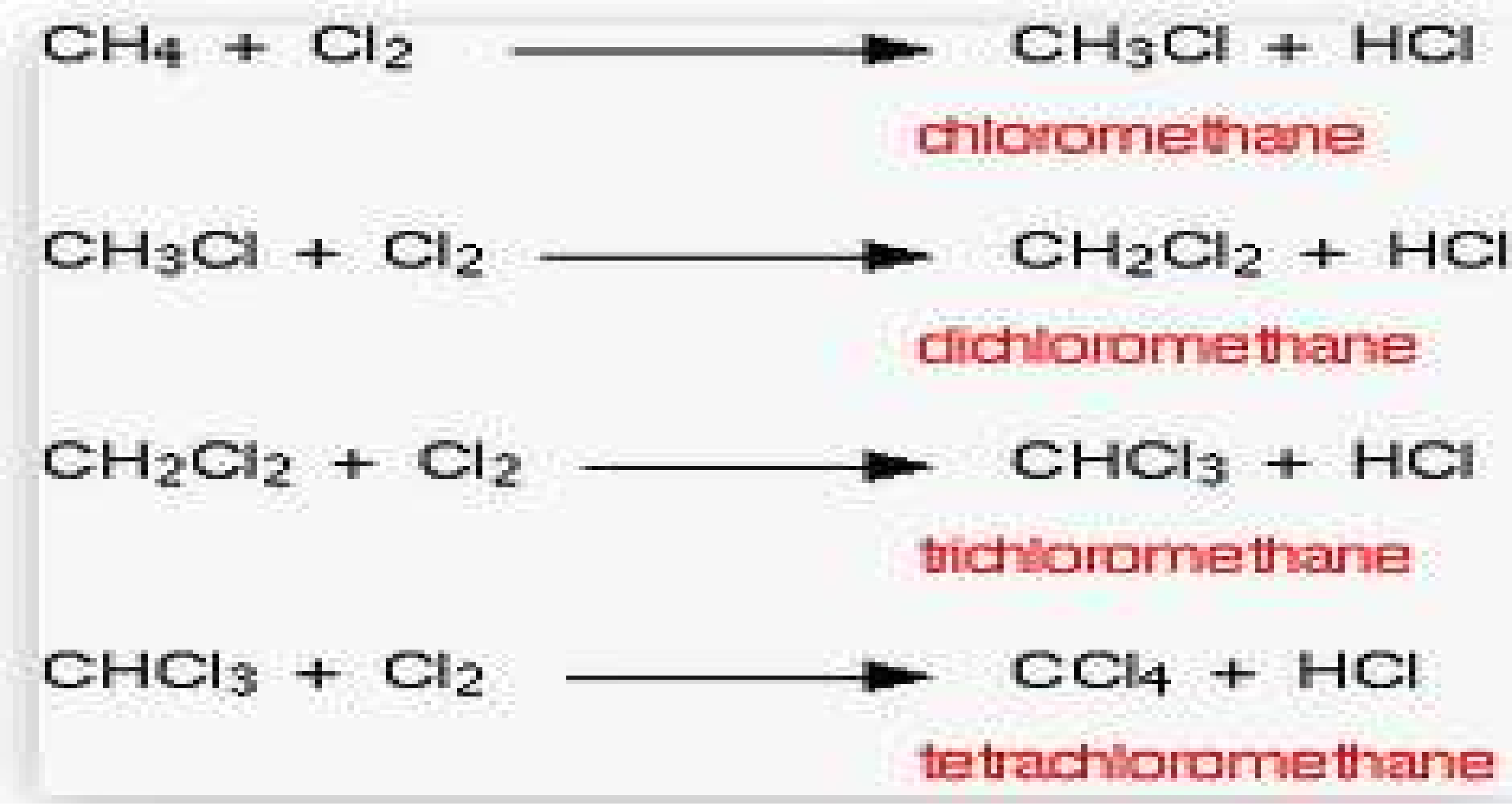
$$C_3H_{8(g)} + 3\tfrac{1}{2}O_{2(g)} \rightarrow 3CO_{(g)} + 4H_2O_{(g)}$$

$$C_3H_{8(g)} + 2O_{2(g)} \rightarrow 3C_{(s)} + 4H_2O_{(g)}$$

2- Replacement reaction

Halogenation

What is Halogenation of Alkanes? Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms. Alkanes are notoriously unreactive compounds because they are non-polar and lack functional groups at which reactions can take place.



$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

chloromethane

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

dichloromethane

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

trichloromethane

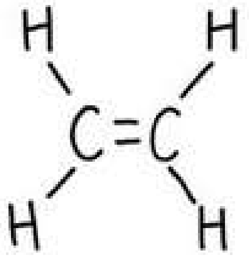
$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

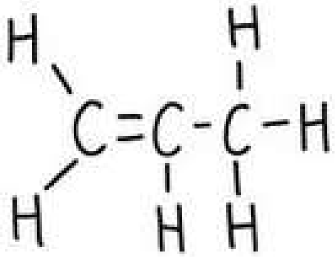
tetrachloromethane

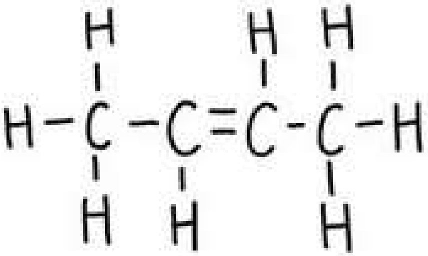
Alkenes
CnH2n

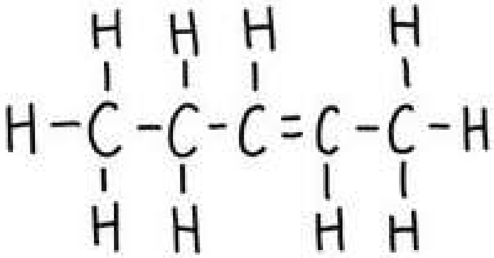
Alkenes are a class of hydrocarbons (e.g, containing only carbon and hydrogen) unsaturated compounds with at least one carbon-to-carbon double bond. Another term used to describe alkenes is olefins. Alkenes are more reactive than alkanes due to the presence of the double bond.

The first four members of the alkene homologous series are called **ethene, propene, butene and pentene.**


ETHENE

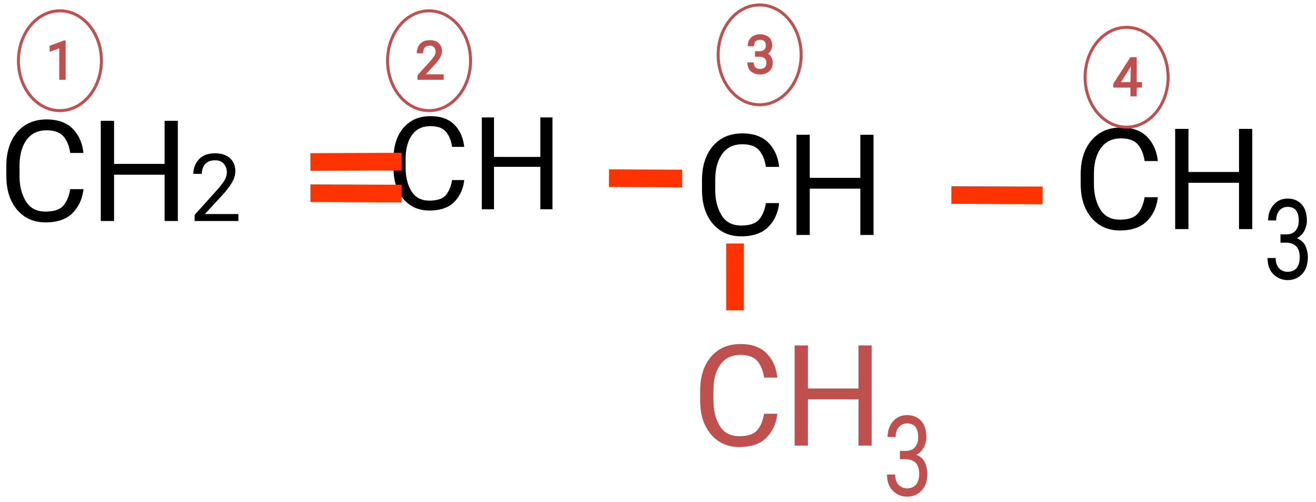

PROPENE


BUTENE


PENTENE

Angles 120°

Nomenclature of alkene



$$\overset{①}{CH_2}=\overset{②}{CH}-\underset{\underset{CH_3}{|}}{\overset{③}{CH}}-\overset{④}{CH_3}$$

3-methyl-1-butene

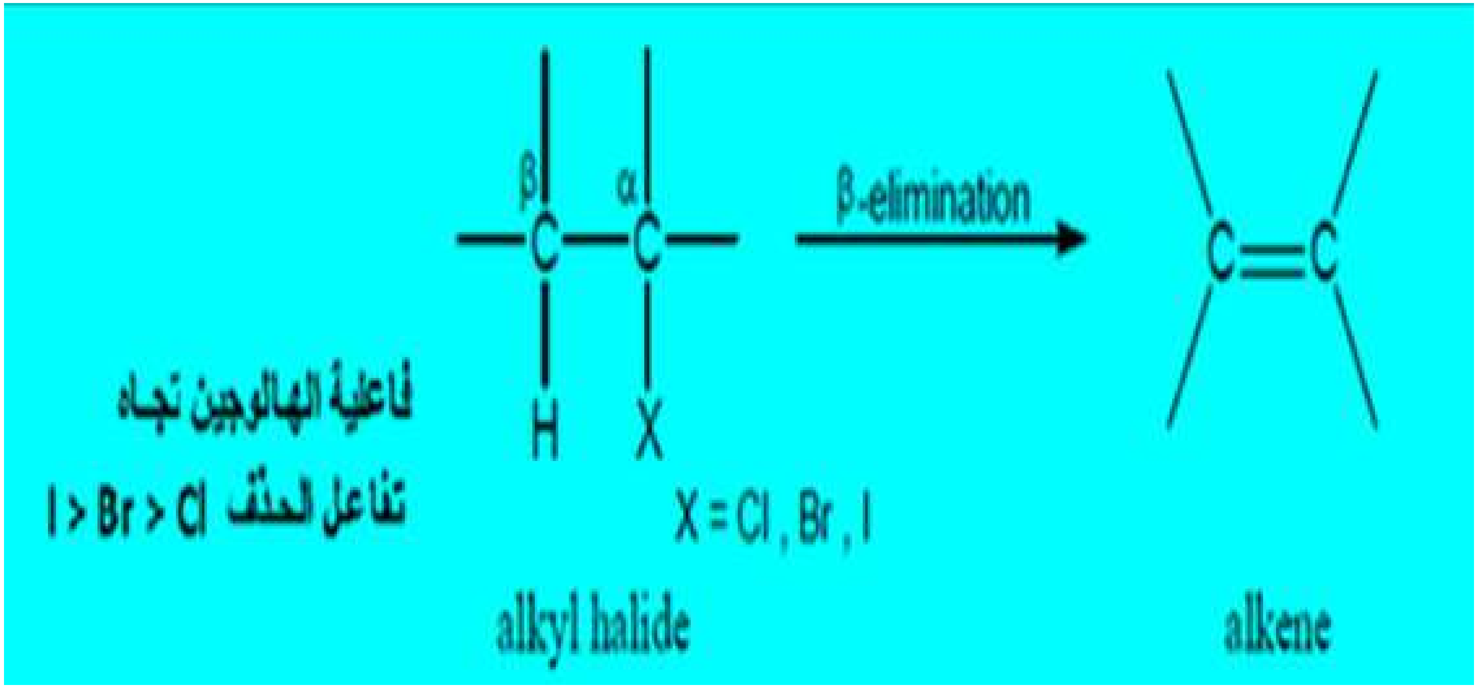
Naming rule

- Identify longest chain contains double bond
- Double bond will take the lowest number

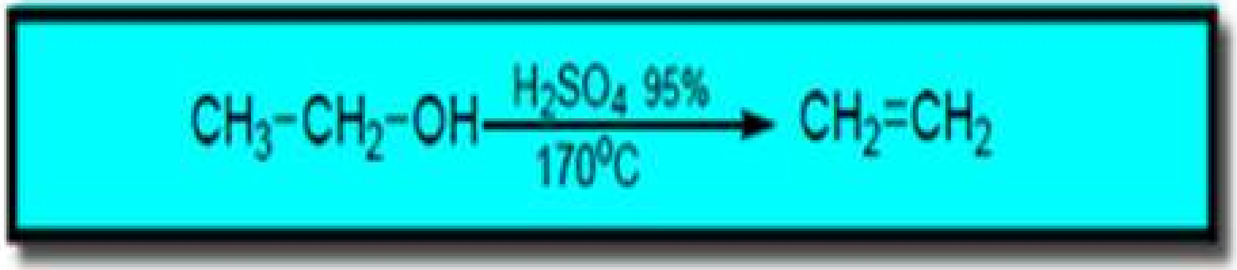
Preparation of Alkenes

(1) Dehydrohalogenation of alkyl halides

When an alkyl halide is heated with concentrated solution of KOH, a molecule of hydrogen halide eliminated and an alkene forms. This reaction is called dehydrohalogenation.

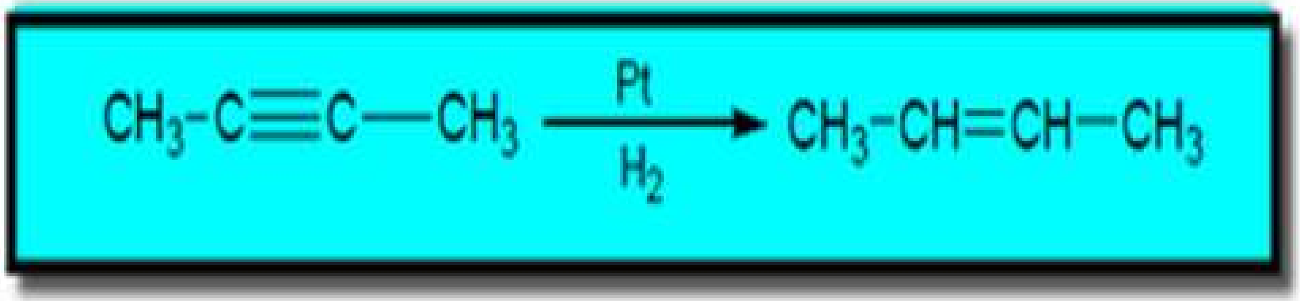


- من الكحول Dehydration of alcohols



$$CH_3-CH_2-OH \xrightarrow[170^{0}C]{H_2SO_4\ 95\%} CH_2=CH_2$$

- من الألكاينات Reduction of alkynes



$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2]{Pt} CH_3-CH=CH-CH_3$$

Chemical reactions of Alkenes

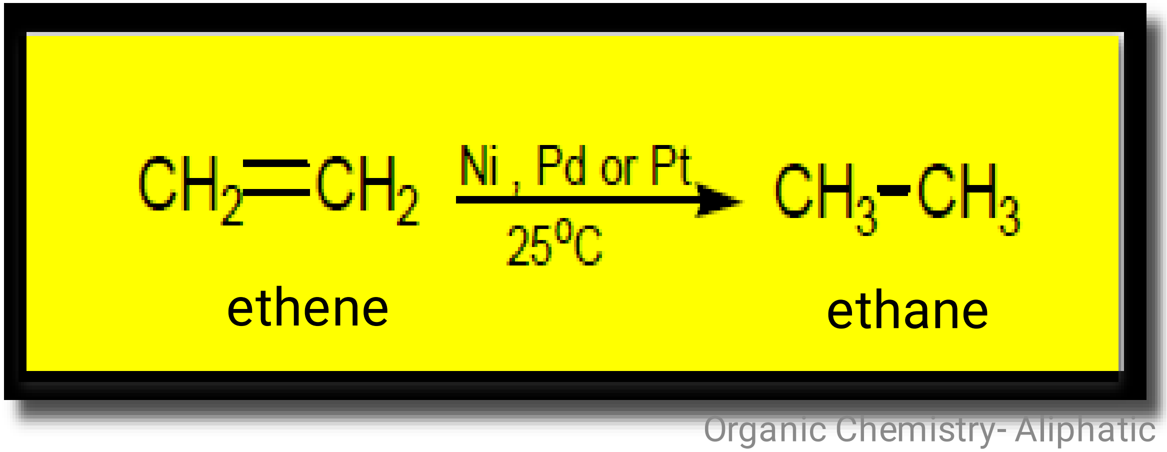
أولا / إضافة المتفاعلات المتماثلة

Addition of symmetric reactants such as H_2 or X_2

هي إضافة شقين متماثلين على الرابطة الزوجية .

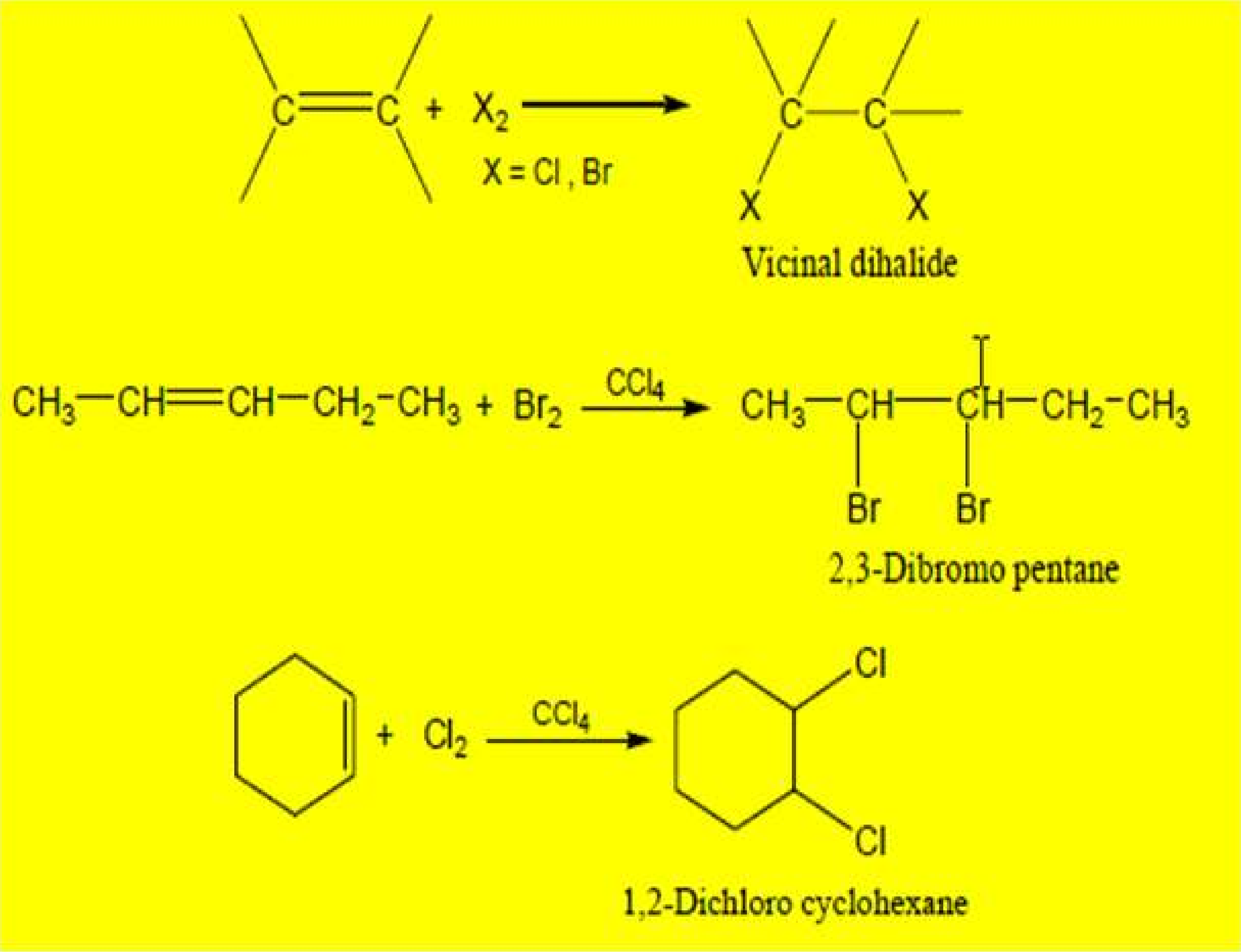
أ ـ إضافة الهيدروجين (الهدرجة Hydrogenation)

حيث يضاف الهيدروجين إلى الرابطة الثنائية في وجود عوامل حفازة وينتج الألكان المقابل .



$$CH_2{=}CH_2 \xrightarrow[25^0C]{Ni\ ,\ Pd\ or\ Pt} CH_3{-}CH_3$$

ب - إضافة الهالوجينات **Addition of halogen** (Halogenation الهلجنة)



Vicinal dihalide

2,3-Dibromo pentane

1,2-Dichloro cyclohexane

ثانيا / إضافة المتفاعلات غير المتماثلة

Addition of asymmetric reactants such as H_2O or HX

تعتمد إضافة متفاعل غير متماثل للألكين على تماثل أو عدم تماثل الألكين فإذا كان الألكين غير متماثل فأن إضافة الشقين غير المتماثلين تخضع لقاعدة ماركونيكوف .

What is Markovnikov's rule? Markovnikov's rule states that when an asymmetrical reagent is added to an asymmetrical alkene, then the negative half of the reagent will attach to the carbon atom containing fewer hydrogen atoms.

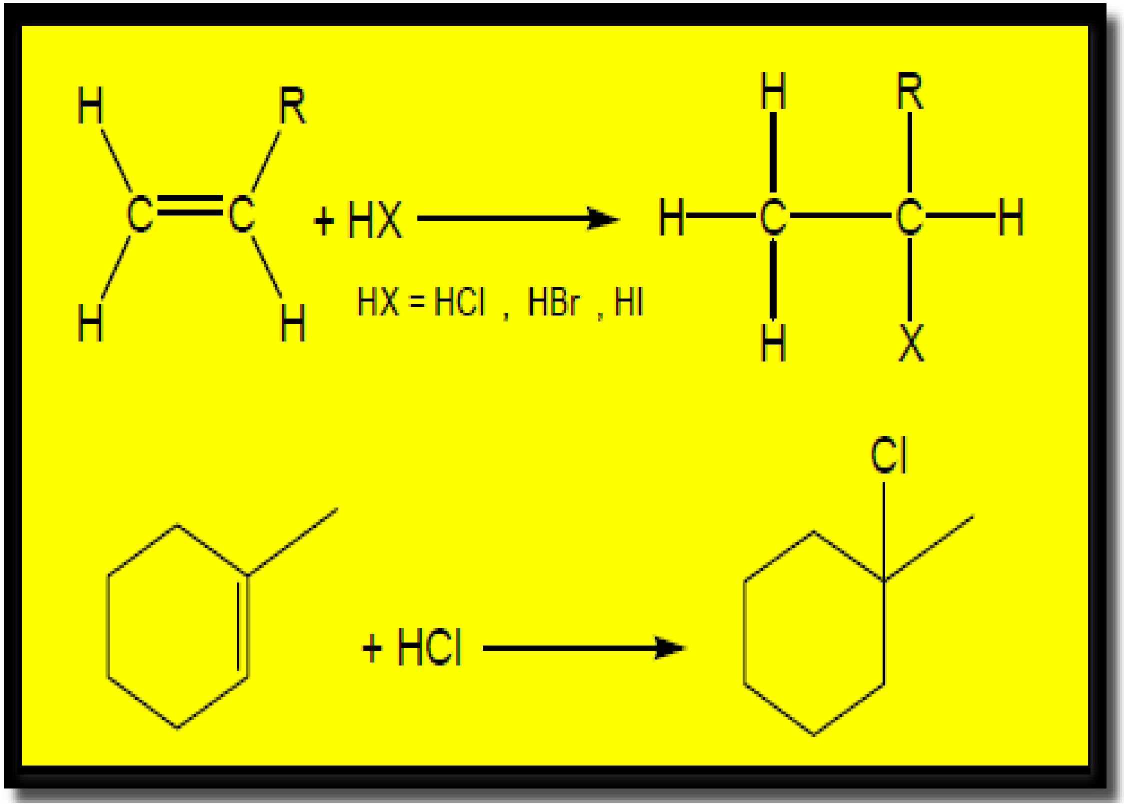
قاعدة ماركونيكوف Markovnikov,s rule

توصل العالم الروسي Vladimir V. Markovnikov سنة 1869م إلى آلية إضافة المتفاعل غير المتماثل للألكين غير المتماثل حيث تنص على : "عند الإضافة الأيونية لمتفاعل غير متماثل إلى ألكين غير متماثل فأن الشق الموجب يضاف إلى ذرة الكربون المتصلة بأعلى عدد من ذرات الهيدروجين بينما يتجه الشق السالب لذرة الكربون المتصلة بأقل عدد من ذرات الهيدروجين".

1- الإضافة حسب قاعدة ماركونيكوف Markovnikov addition

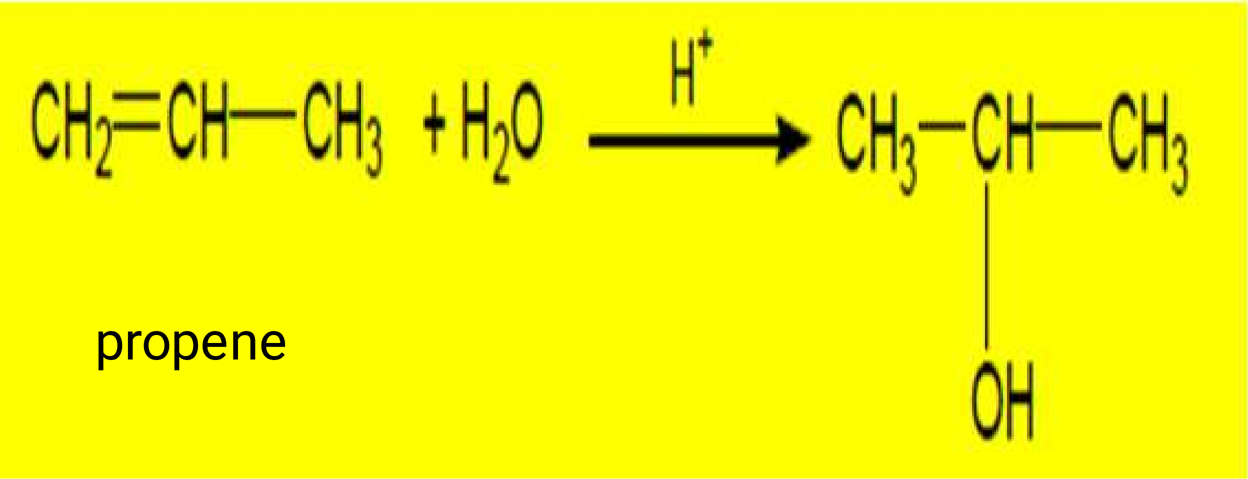
أ ـ إضافة هاليدات الهيدروجين Addition of hydrogen halides

لإجراء هذا التفاعل يستخدم الهاليد الغازي بإمراره مباشرة فى الألكين الذي يقوم بعمل المذيب أو عن طريق إذابة هاليد الهيدروجين فى حمض الخليك ثم يخلط مع الألكين .



b) Hydration (addition of H_2O)

Addition of water is carried out according to Markovnikov's rul



$$CH_2{=}CH{-}CH_3 + H_2O \xrightarrow{H^+} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

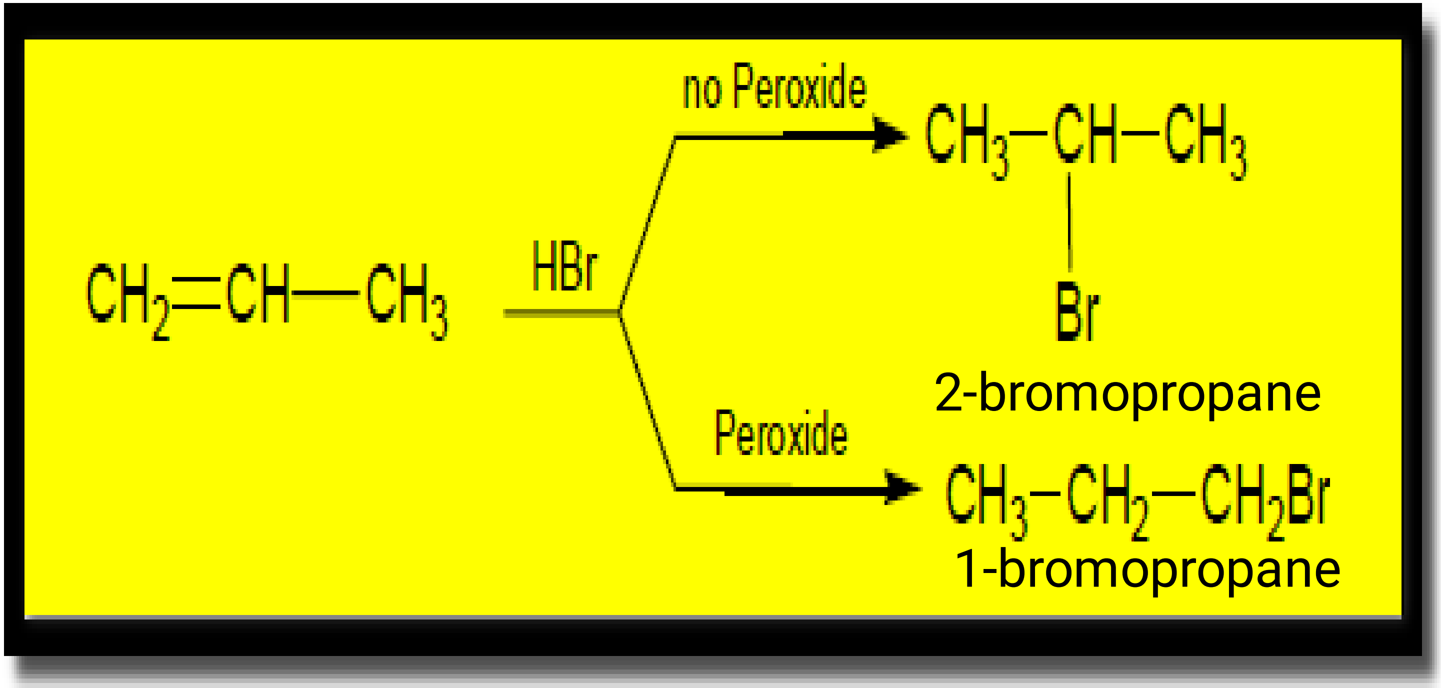
propene

2-propanol

2ـ الإضافة عكس قاعدة ماركونيكوف Anti-Markovnikov addition

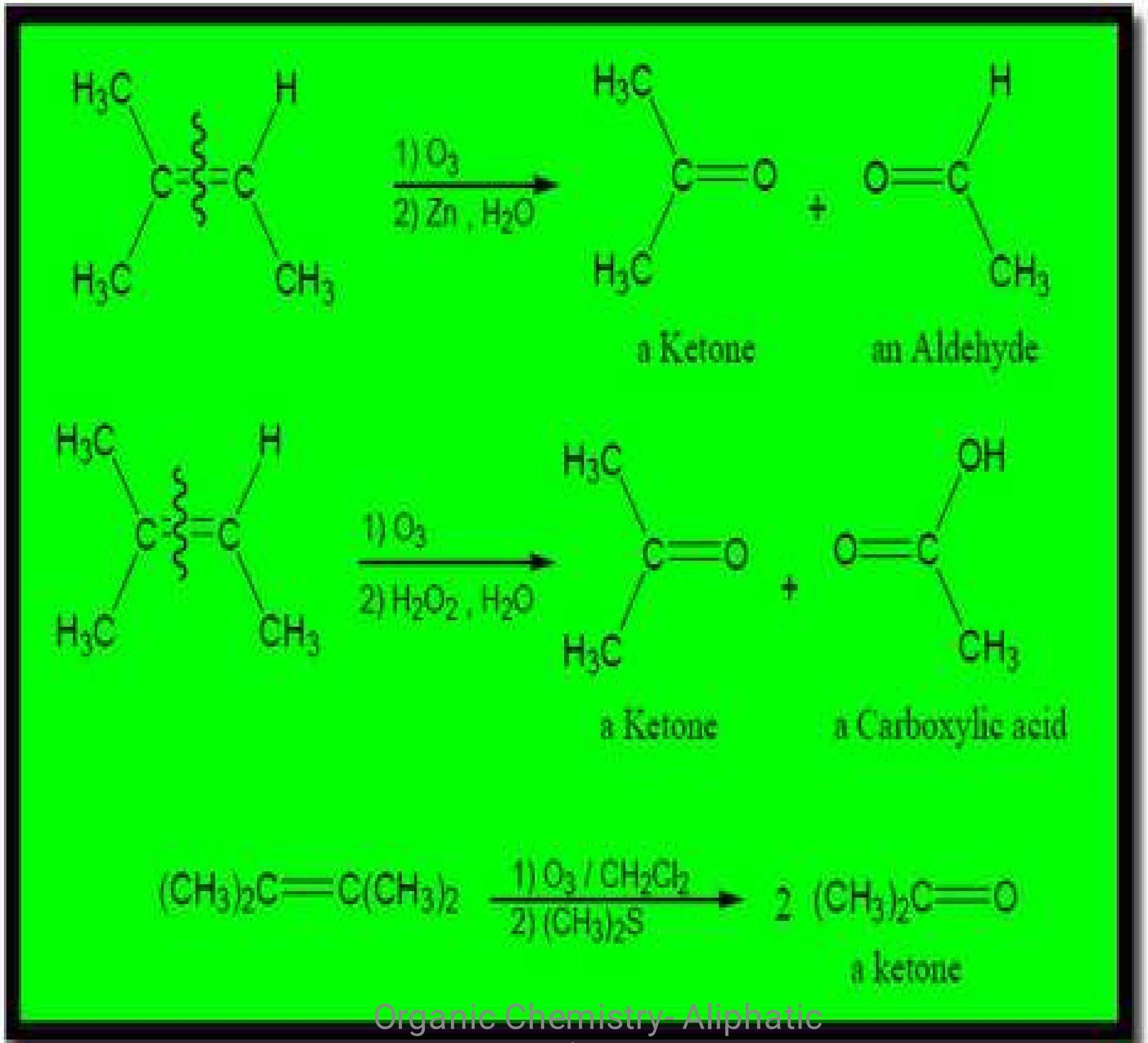
أ ـ إضافة هاليدات الهيدروجين Addition of hydrogen halides

عند إضافة هاليد الهيدروجين في وجود البيروكسيد فأن الإضافة تتم عكس قاعدة ماركونيكوف

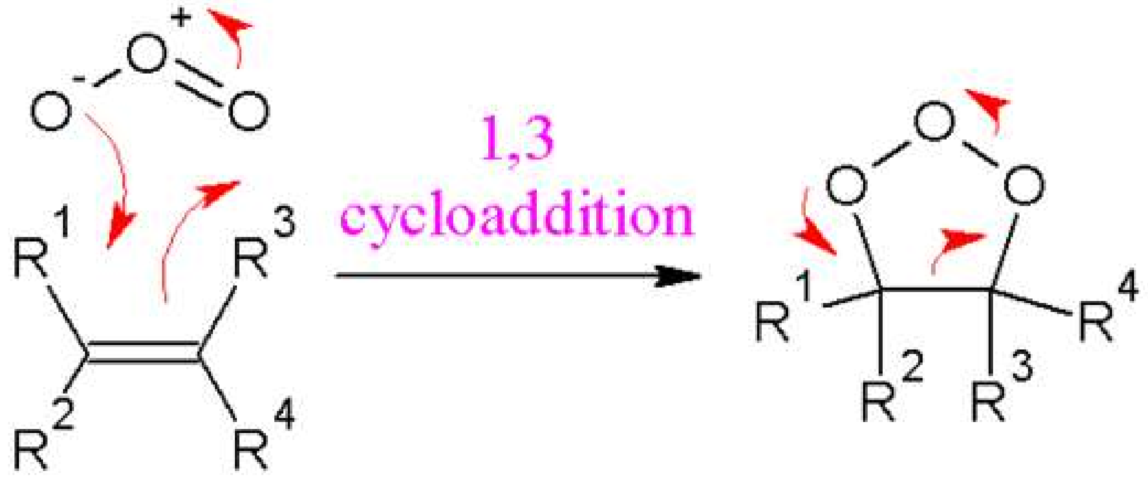


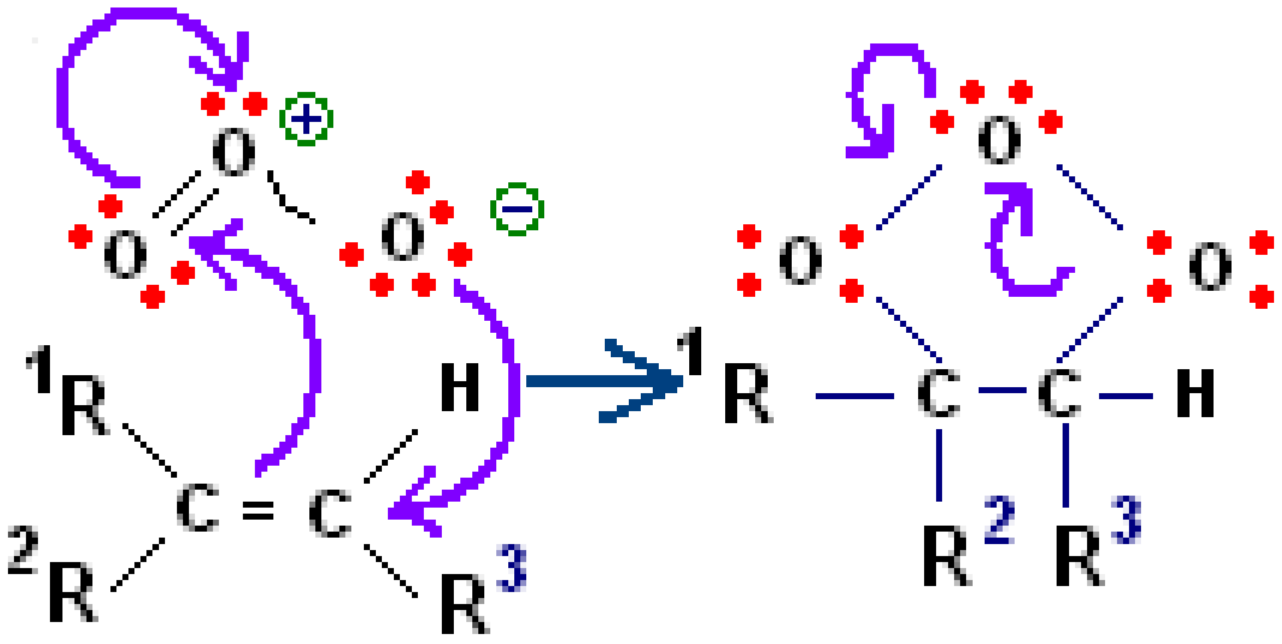
أ- التفاعل مع الأوزون Ozonization :

يتفاعل الأوزون بقوة مع الألكين ويعطي مركبات تسمى أوزونايد Ozonide التي يتم اختزالها بالخارصين Zn أو dimethyl sulfide $(CH_3)_2S$ إلى الدهيدات أو كيتونات وعند إعادة أكسدة مركبات الأوزونايد باستخدام H_2O_2 يتم تحويلها إلى أحماض كربوكسيلية وكيتونات.



Oxidation by Ozone





Alkynes CnH2n-2

Alkynes are hydrocarbons which contain carbon-carbon triple bonds. Their general formula is C_nH_{2n-2} for molecules with one triple bond (and no rings). Alkynes undergo many of the same reactions as alkenes, but can react twice because of the presence of the two p-bonds in the triple bond.

Alkynes are **hydrocarbons which contain carbon-carbon triple bonds.**

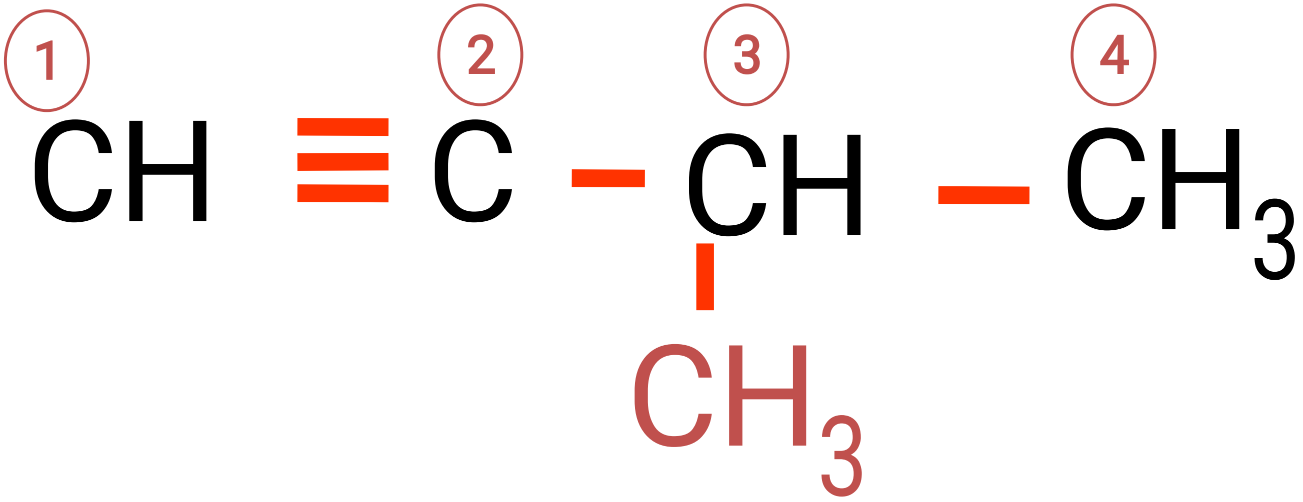
Simplest alkyne is Ethyne or Acetylene

$$H-C\equiv C-H$$

Angles 180°

General formula: C_nH_{2n-2}

Nomenclature of alkyne



$CH \equiv C - \underset{CH_3}{CH} - CH_3$

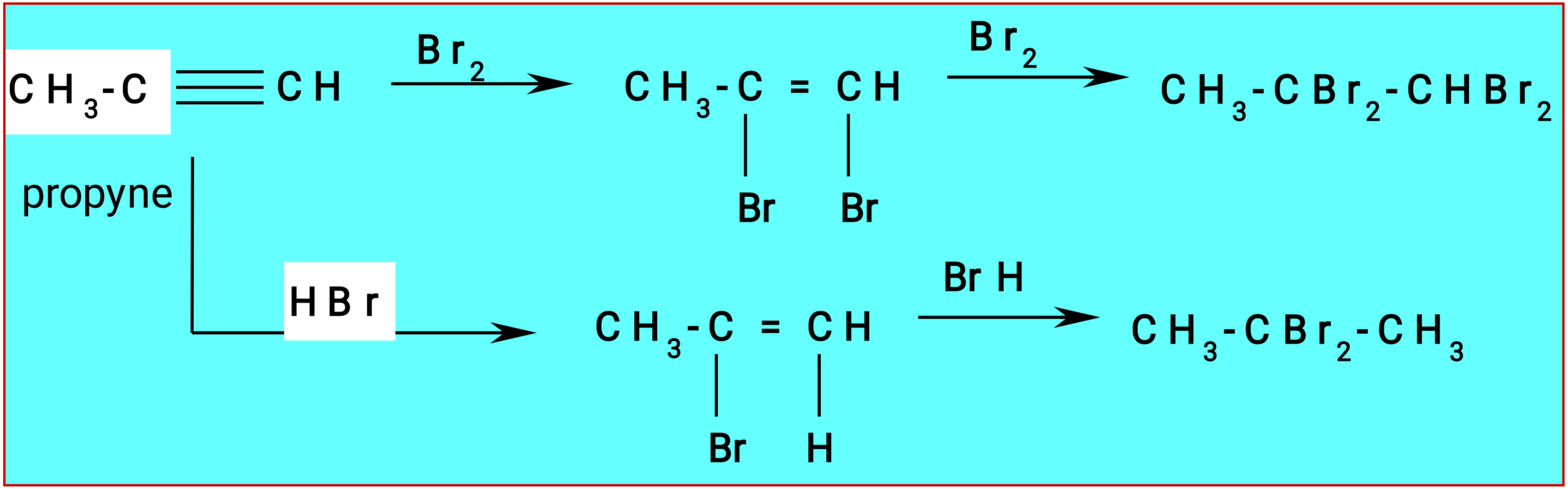
3-methyl-1-butyne

Naming rule

- Identify longest chain contains double bond
- Triple bond will take the lowest number

Reactions of Alkynes

Bromonation Br_2 / Addition of HBr



propyne

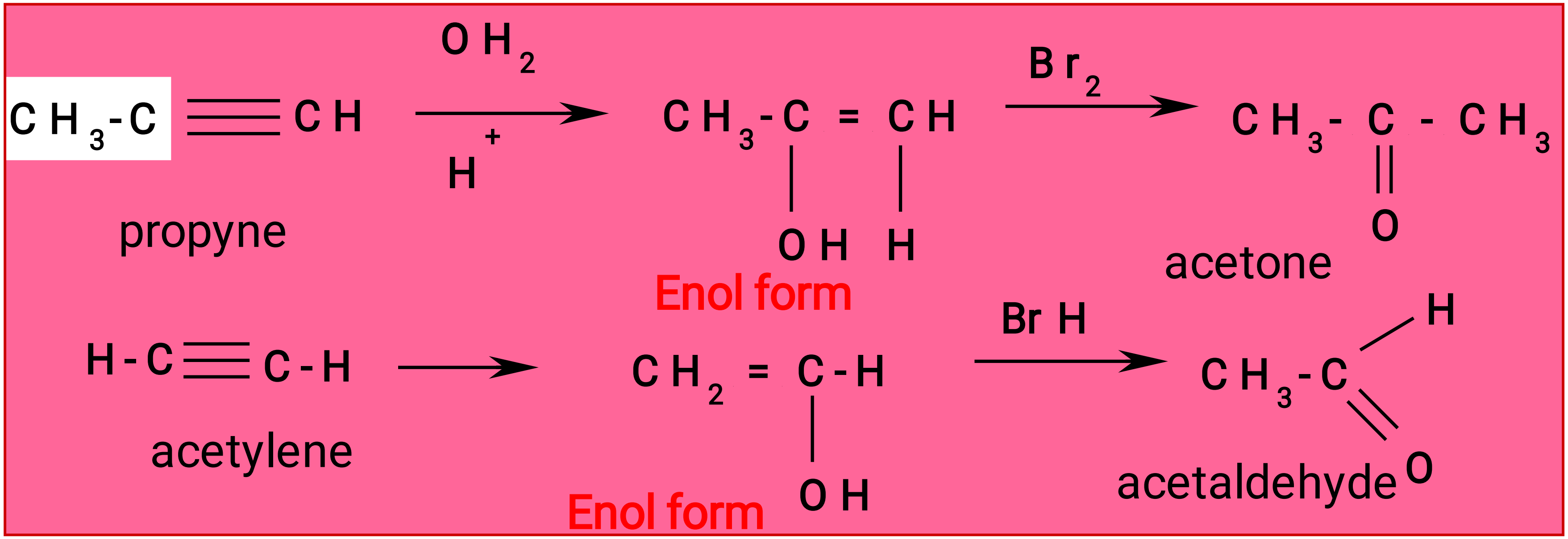
$CH_3-C\equiv CH \xrightarrow{Br_2} CH_3-C(Br)=CH(Br) \xrightarrow{Br_2} CH_3-CBr_2-CHBr_2$

$CH_3-C\equiv CH \xrightarrow{HBr} CH_3-C(Br)=CH(H) \xrightarrow{Br\,H} CH_3-CBr_2-CH_3$

Hydration (addition of H_2O) Markovnikov addition

Hydration of alkyne gives aldehyde or ketone

Firstly, it gives an enol form (unstable) which convert to a keto form (stable) via Tautomerizaton process.



Alcohols

Alcohols

- Types of Alcohols
- Nomenclature
- Synthesis
- Reactions

Types of Alcohols

According to number of –OH group

1- Mono-hydric
2- Di
3- Tri

According to position of –OH group

1- Primary
2- Secondary
3-Tertiary

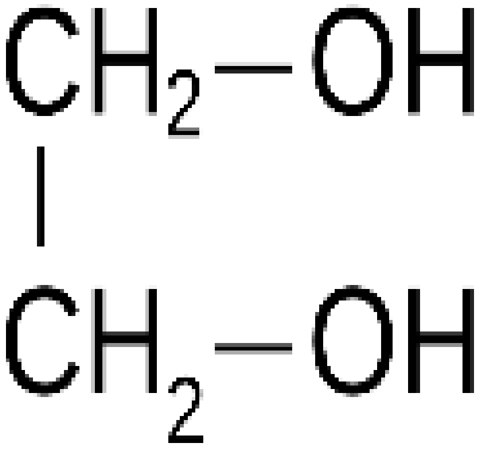
According to number of –OH group

CH_3OH

methanol

CH_3CH_2OH

ethanol

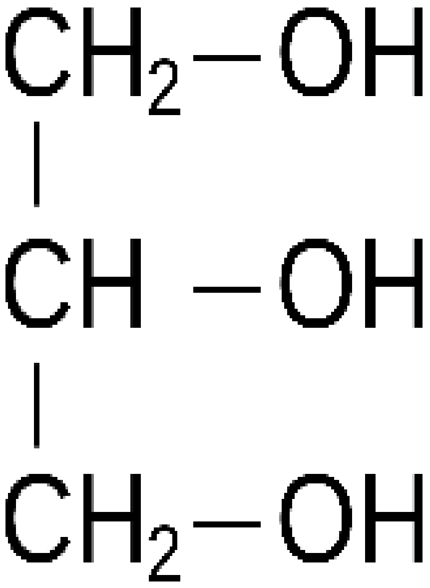


$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

Ethylene glycol

1,2-dihydroxyethane

Ethane-1,2-diol



$$\begin{array}{l} CH_2-OH \\ | \\ CH\ -OH \\ | \\ CH_2-OH \end{array}$$

Glycerol

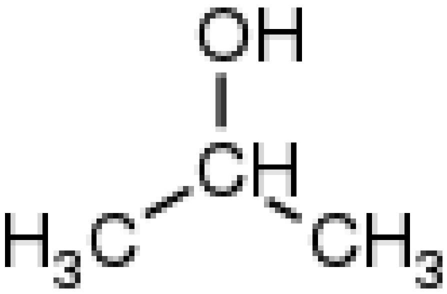
1,2,3-trihydroxypropan

propane-1,2,3-triol

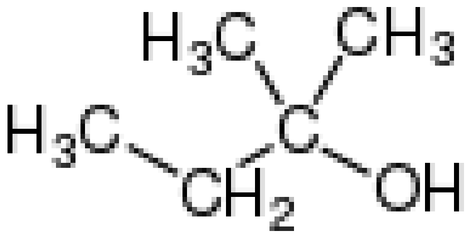
According to position of –OH group

$CH_3CH_2CH_2OH$

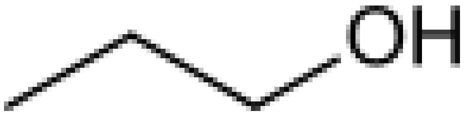
Primary

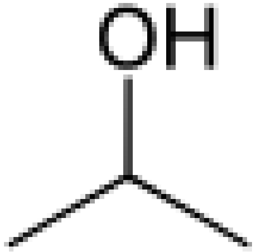


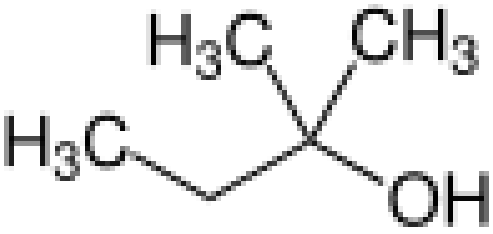
Secondary



Tertiary







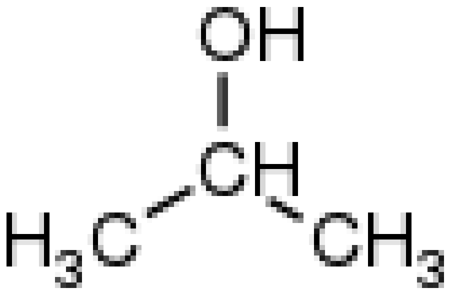
Nomenclature of alcohols

CH_3OH

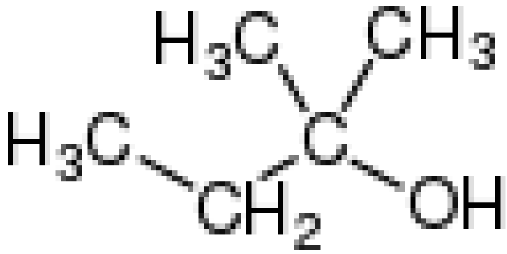
Methanol / Methyl alcohol

CH_3CH_2OH

Ethanol / Ethyl alcohol



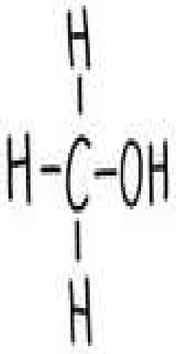
2-propanol/ Isopropanol



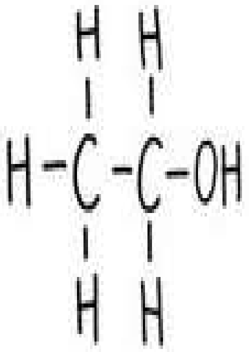
2-methyl-2-butanol

Naming rule

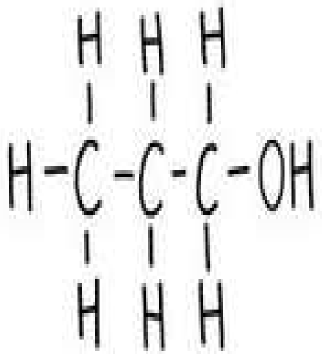
- Identify longest chain contains functional group
- Carbon of functional group will take the lowest number



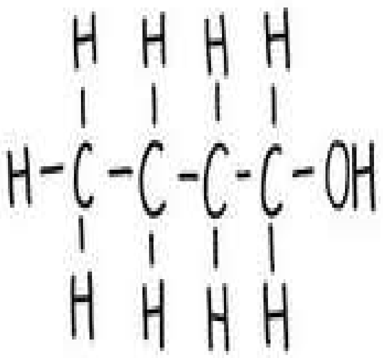
METHANOL



ETHANOL



PROPANOL



BUTANOL

Synthesis of alcohols

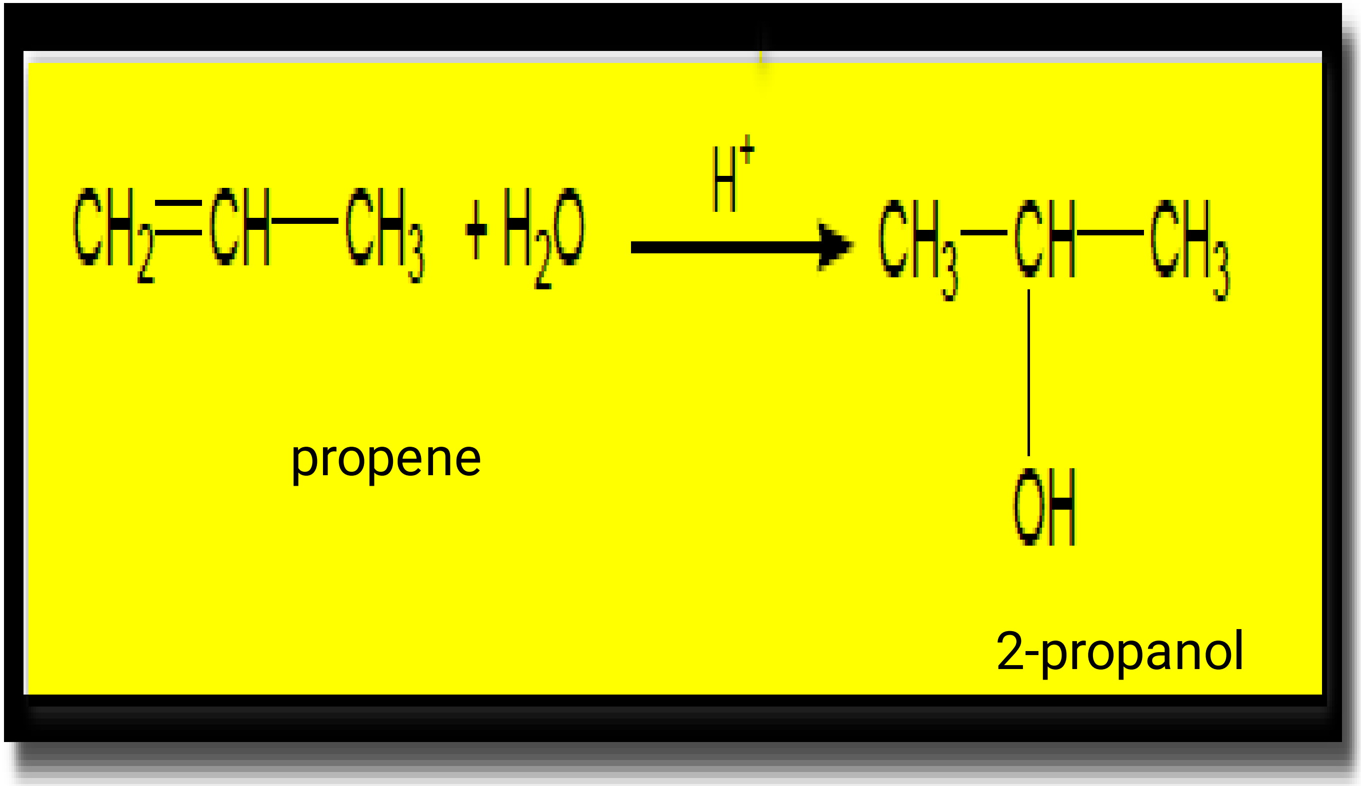
1) Hydrolysis of Alkyl Halides

This is a nucleophilic substitution reaction.

$$\text{R-X} + \text{KOH}_{aq} \rightarrow \text{R-OH}$$

2) Hydration - Addition of water (الإماهة) ب- إضافة الماء

Markincove's rule



$$CH_2{=}CH{-}CH_3 + H_2O \xrightarrow{H^+} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$$

propene

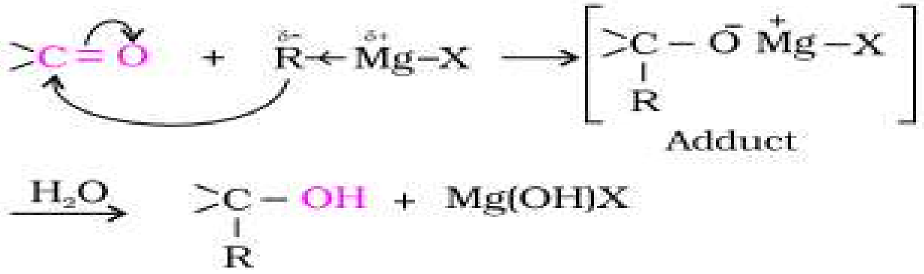
2-propanol

3) Preparation of Alcohols from Grignard Reagent

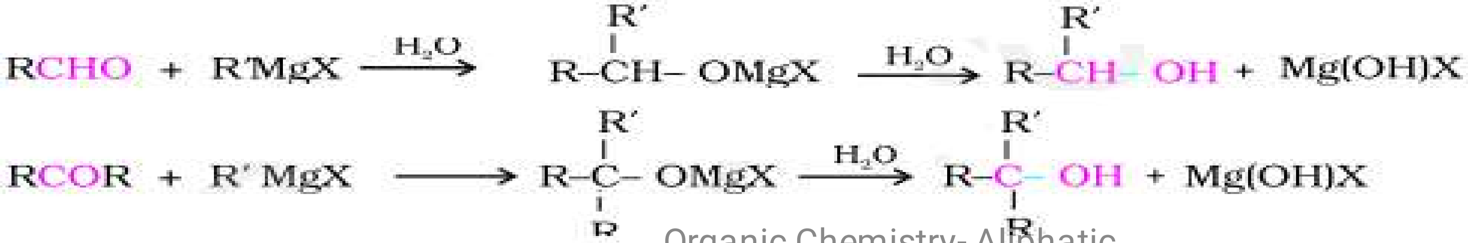
$$CH_3I + Mg \xrightarrow{Ether} CH_3MgI$$

$$CH_3CH_2Br + Mg \xrightarrow{Ether} CH_3CH_2MgBr$$

Ethyl bromide Ethylmagnesium bromide



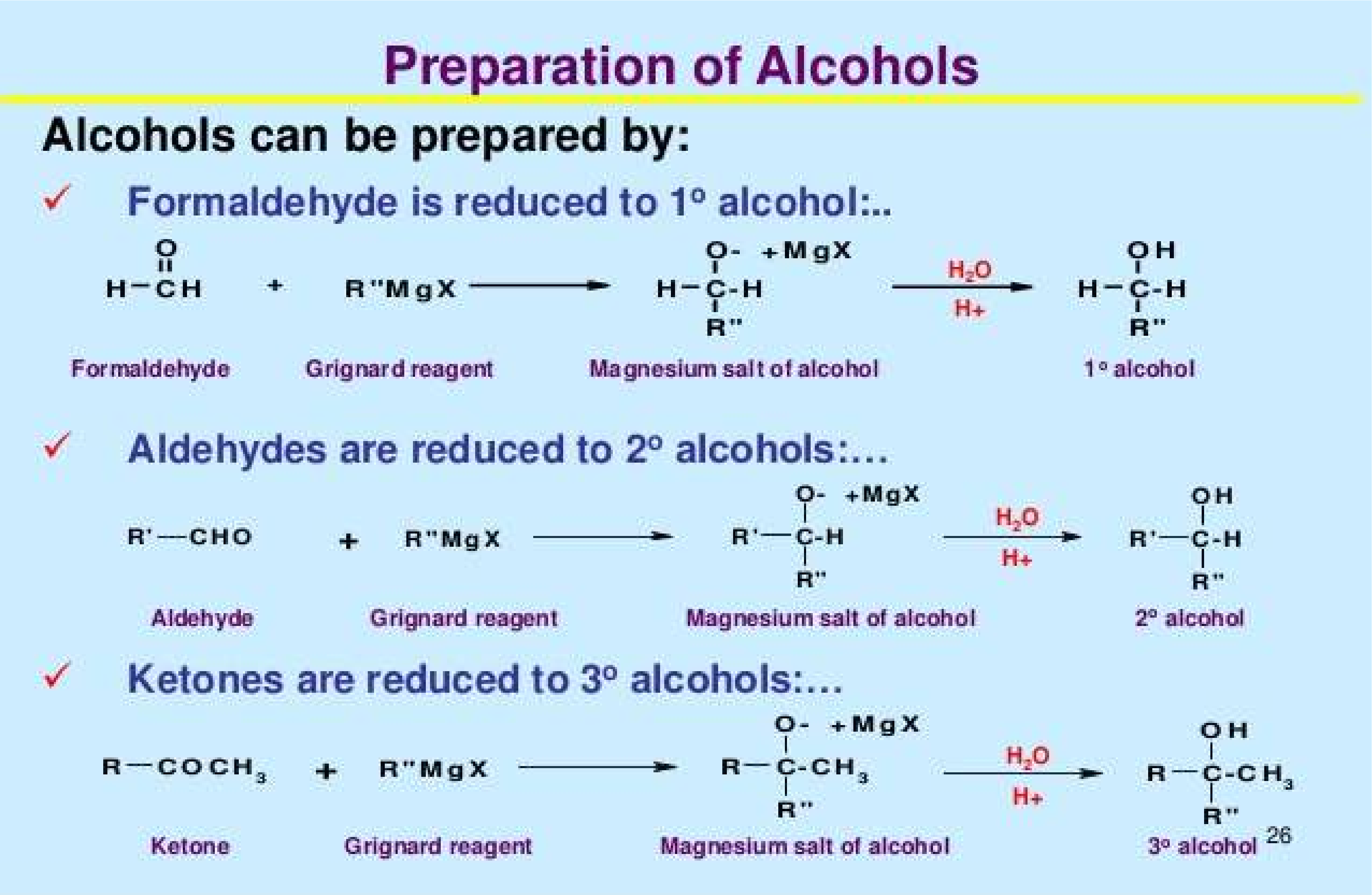
$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$



$$RCHO + R'MgX \xrightarrow{H_2O} R\text{–}\overset{R'}{\overset{|}{C}}H\text{–}OMgX \xrightarrow{H_2O} R\text{–}\overset{R'}{\overset{|}{C}}H\text{–}OH + Mg(OH)X$$

$$RCOR + R'MgX \longrightarrow R\text{–}\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\text{–}OMgX \xrightarrow{H_2O} R\text{–}\underset{R}{\underset{|}{\overset{R'}{\overset{|}{C}}}}\text{–}OH + Mg(OH)X$$

The Grignard reagent : an organometallic compound



Preparation of Alcohols

Alcohols can be prepared by:

- ✓ Formaldehyde is reduced to 1° alcohol:..

$$H-\overset{\overset{O}{\|}}{C}-H + R''MgX \longrightarrow H-\overset{O^- \; {}^+MgX}{\underset{R''}{C}}-H \xrightarrow[H+]{H_2O} H-\overset{OH}{\underset{R''}{C}}-H$$

Formaldehyde | Grignard reagent | Magnesium salt of alcohol | 1° alcohol

- ✓ Aldehydes are reduced to 2° alcohols:...

$$R'-CHO + R''MgX \longrightarrow R'-\overset{O^- \; {}^+MgX}{\underset{R''}{C}}-H \xrightarrow[H+]{H_2O} R'-\overset{OH}{\underset{R''}{C}}-H$$

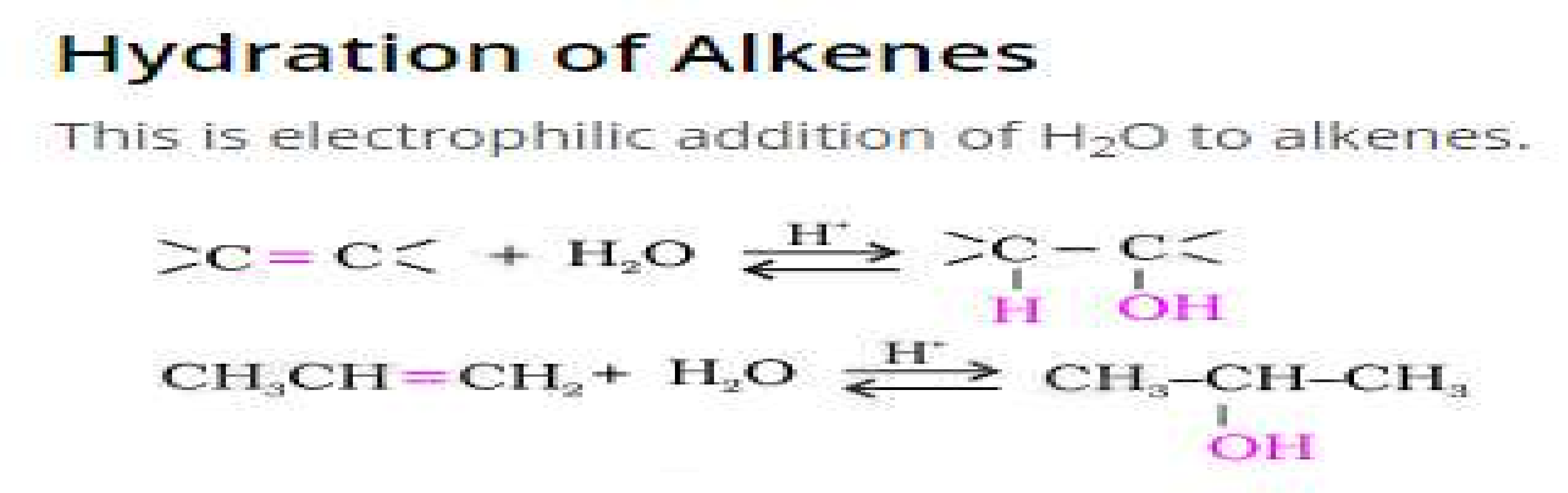
Aldehyde | Grignard reagent | Magnesium salt of alcohol | 2° alcohol

- ✓ Ketones are reduced to 3° alcohols:...

$$R-COCH_3 + R''MgX \longrightarrow R-\overset{O^- \; {}^+MgX}{\underset{R''}{C}}-CH_3 \xrightarrow[H+]{H_2O} R-\overset{OH}{\underset{R''}{C}}-CH_3$$

Ketone | Grignard reagent | Magnesium salt of alcohol | 3° alcohol

26



Hydration of Alkenes

This is electrophilic addition of H_2O to alkenes.

$$>C=C< \; + \; H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} >\underset{H}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}<$$

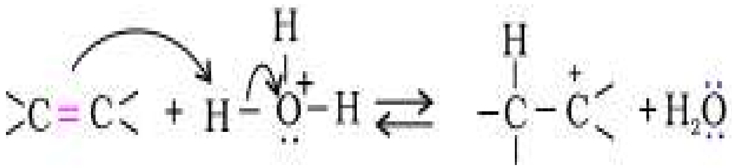
$$CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-\underset{OH}{\underset{|}{C}H}-CH_3$$

by application of Markincove's rule: 2-propanol

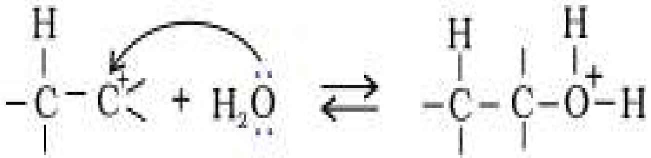
by application of anti- Markincove's rule: 1-propanol

Mechanism of Hydration of alkenes:

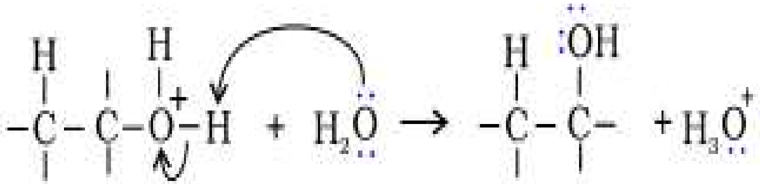
Protonation of alkene to form carbocation by electrophilic



Nucleophilic attack of water on carbocation.



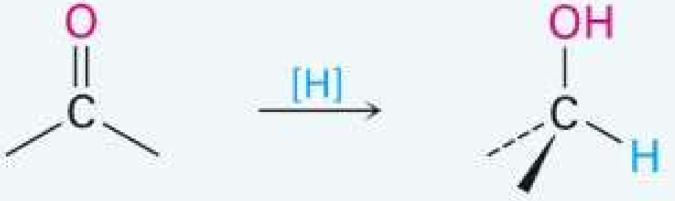
Deprotonation to form an alcohol.



Except ethyl alcohol no other primary alcohol can be obtained by this method, however hydroboration of terminal alkenes give primary alcohols.

Alcohols from Carbonyl Compounds: Reduction

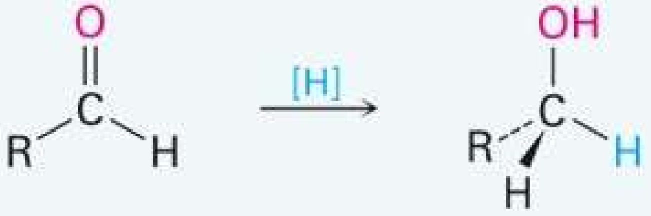
- Reduction of a carbonyl compound gives an alcohol
  - Addition of H to a C=O bond



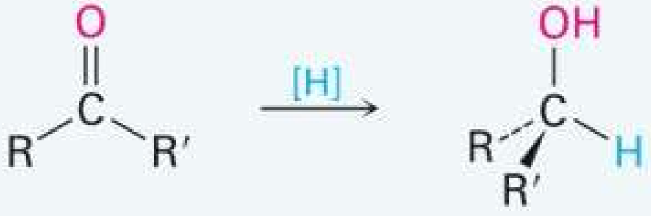
where [H] is a reducing agent

A carbonyl compound **An alcohol**

- Reduction of aldehydes gives primary alcohols
- Reduction of ketones gives secondary alcohols



An aldehyde **A primary alcohol**



A ketone **A secondary alcohol**

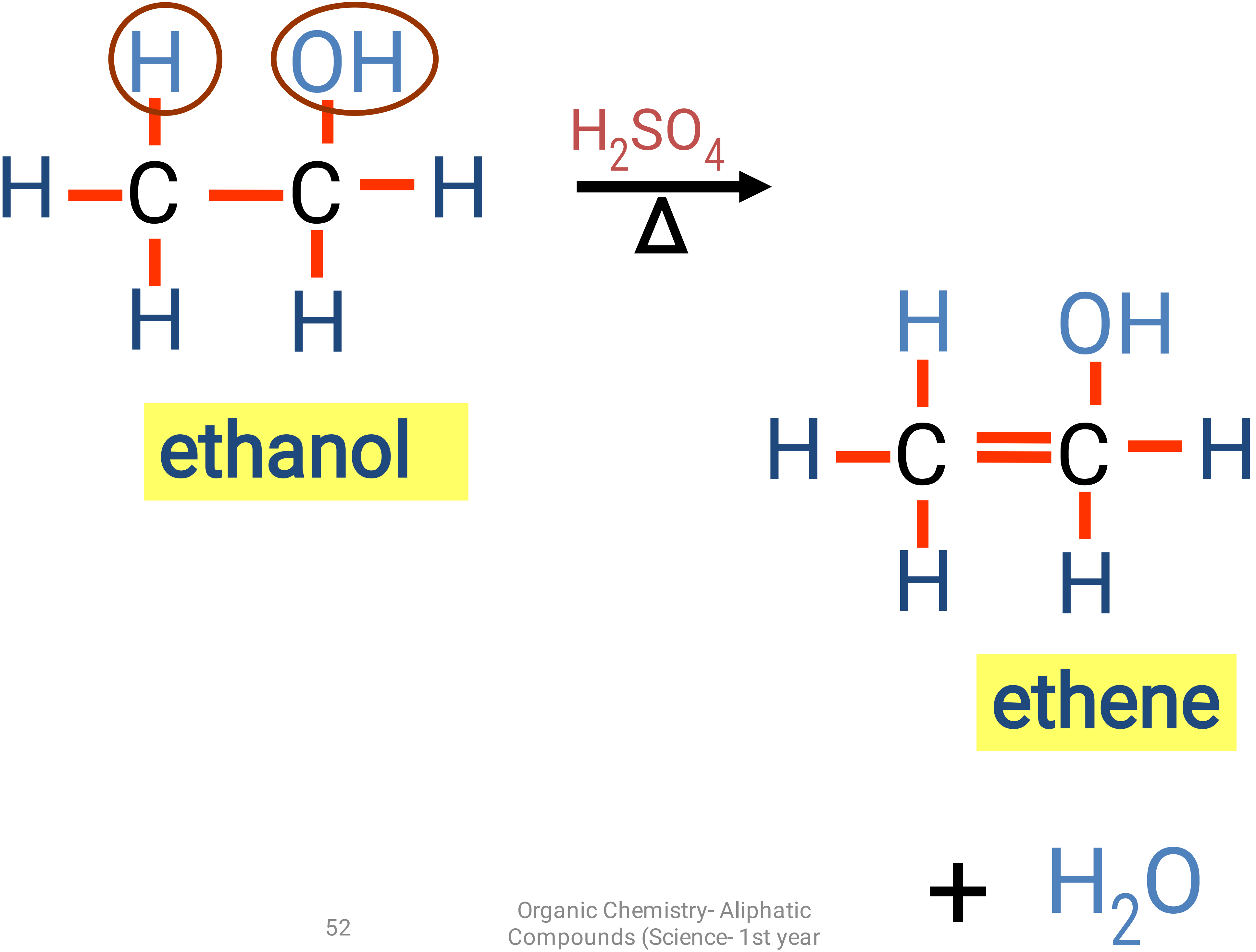
Reactions of alcohols

1- Elimination R. (Dehydration)

$$\underset{\text{alcohol}}{RCH_2-CH_2OH} \xrightarrow[-\ H_2O]{Al_2O_3,\ 623\ K} \underset{\text{alkene}}{RCH=CH_2}$$

For example,

$$\underset{\text{ethanol}}{C_2H_5OH} \xrightarrow[-\ H_2O]{Al_2O_3,\ 623\ K} \underset{\text{ethene}}{CH_2=CH_2}$$

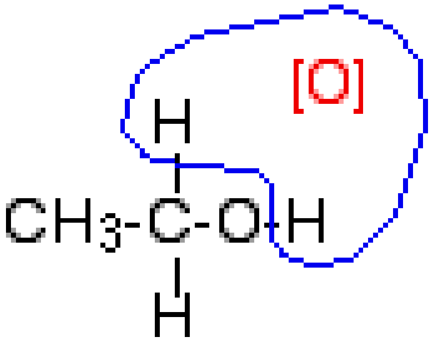
H
OH
H
C
C
H
H
H
H_2SO_4
Δ
ethanol
H
OH
H
C
C
H
H
H
ethene
+ H_2O

2- Oxidation

Primary alcohol $\xrightarrow{[O]}$ Aldehyde

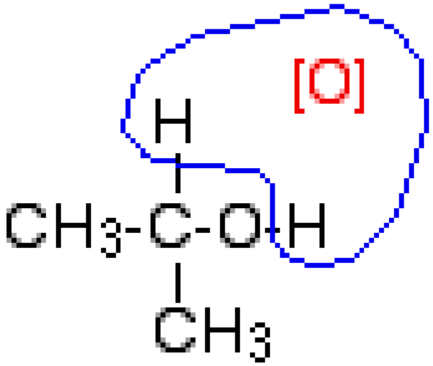
Secondary alcohol $\xrightarrow{[O]}$ Ketone

Tertiary alcohols $\xrightarrow{[O]}$ No oxidation primary



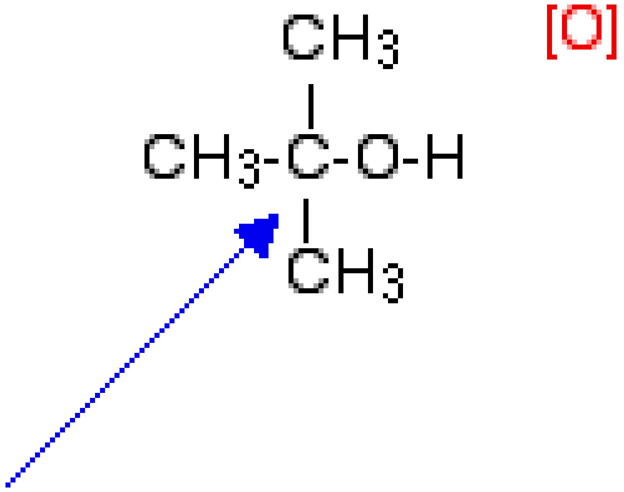
$$CH_3\text{-}\overset{H}{\underset{H}{C}}\text{-}O\text{-}H$$

secondary



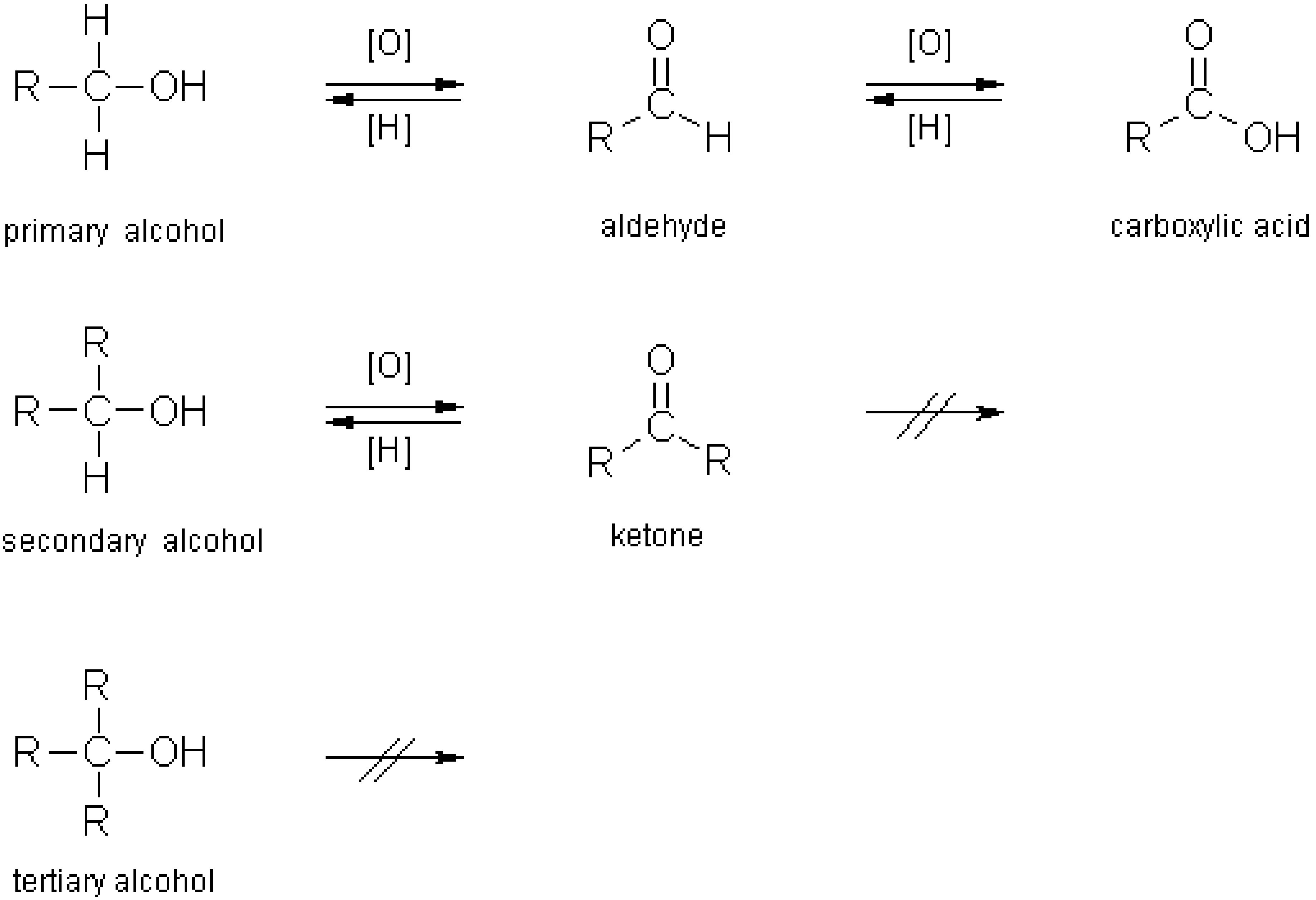
$$CH_3\text{-}\overset{H}{\underset{CH_3}{C}}\text{-}O\text{-}H$$

tertiary

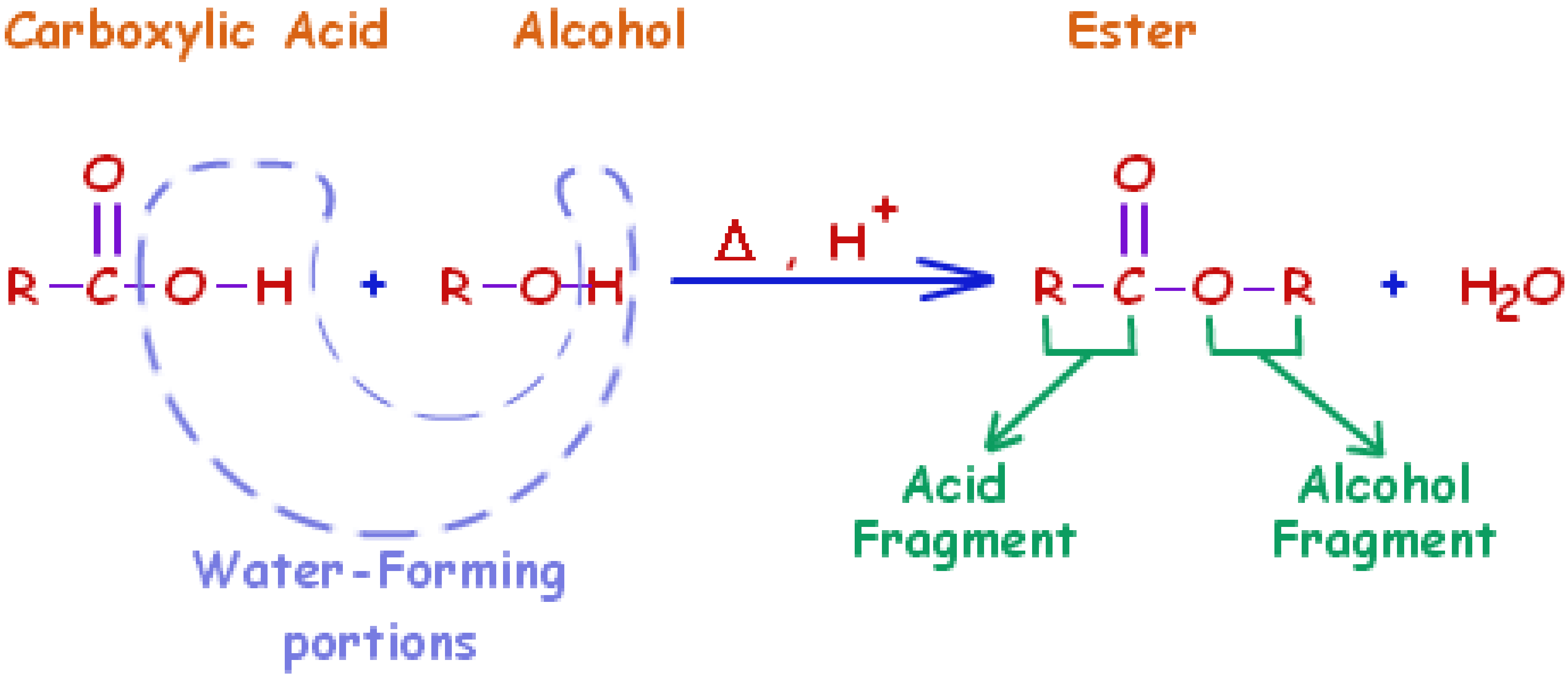


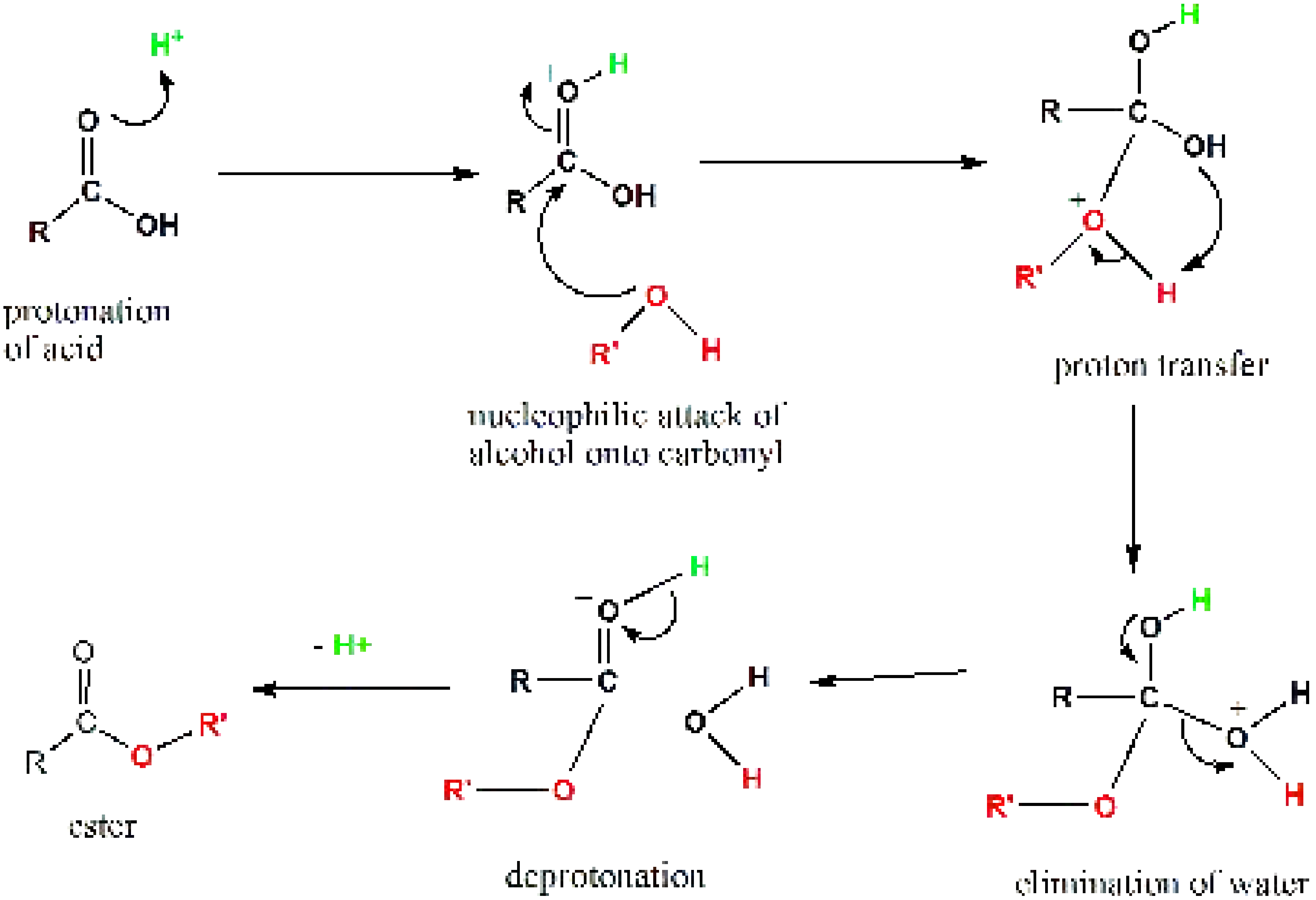
$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}O\text{-}H$$

There is no hydrogen attached to this carbon for the oxygen to remove.


[O]
[H]
[O]
[H]
primary alcohol
aldehyde
carboxylic acid
[O]
[H]
secondary alcohol
ketone
tertiary alcohol

3-Esterfication




H+
O
C
R
OH
protonation of acid
O
H
C
R
OH
O
R'
H
nucleophilic attack of alcohol onto carbonyl
O
H
R
C
OH
+
O
R'
H
proton transfer
O
H
R
C
+
O
H
R'
O
H
elimination of water
O
H
R
C
R'
O
H
O
H
deprotonation
- H+
O
C
R
O
R'
ester

Aldehydes and Ketones

ALDEHYDES & KETONES

(ALKANALS & ALKANONES)

Aldehydes and Ketones

Properties

Nomenclature

Preparation

Reactions

Carbonyl Functional Groups

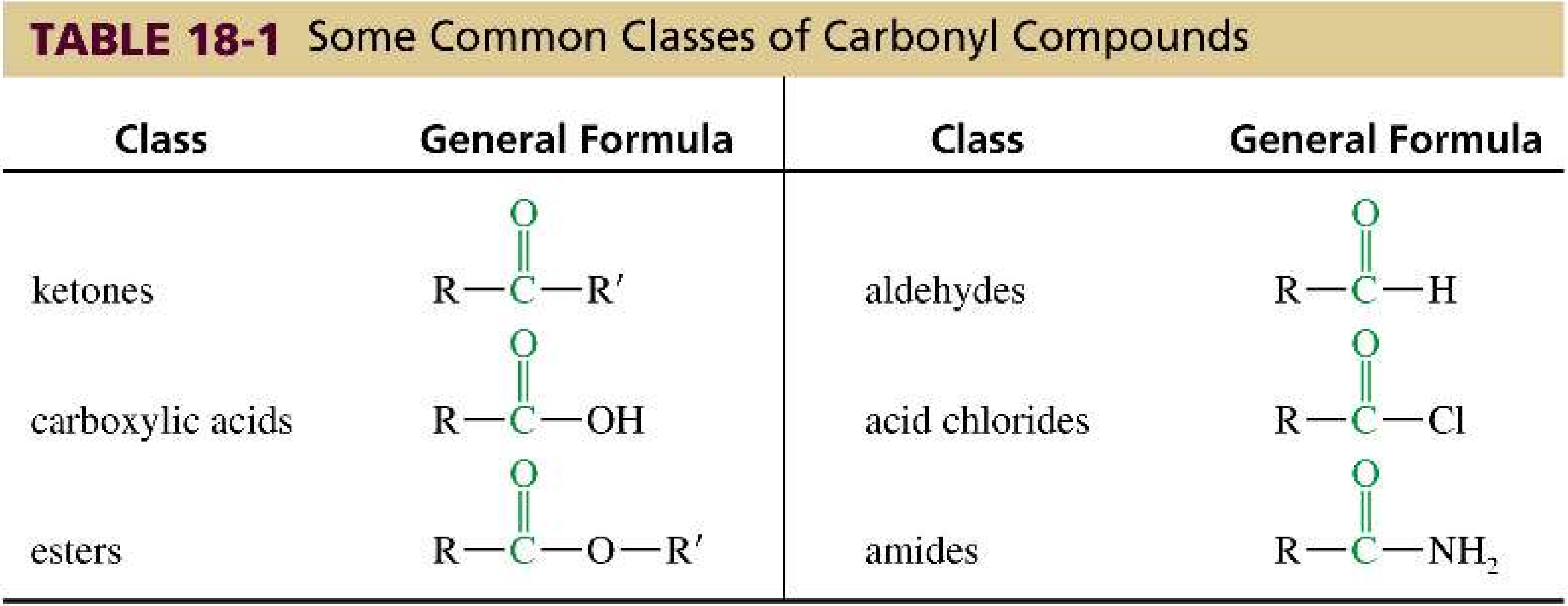
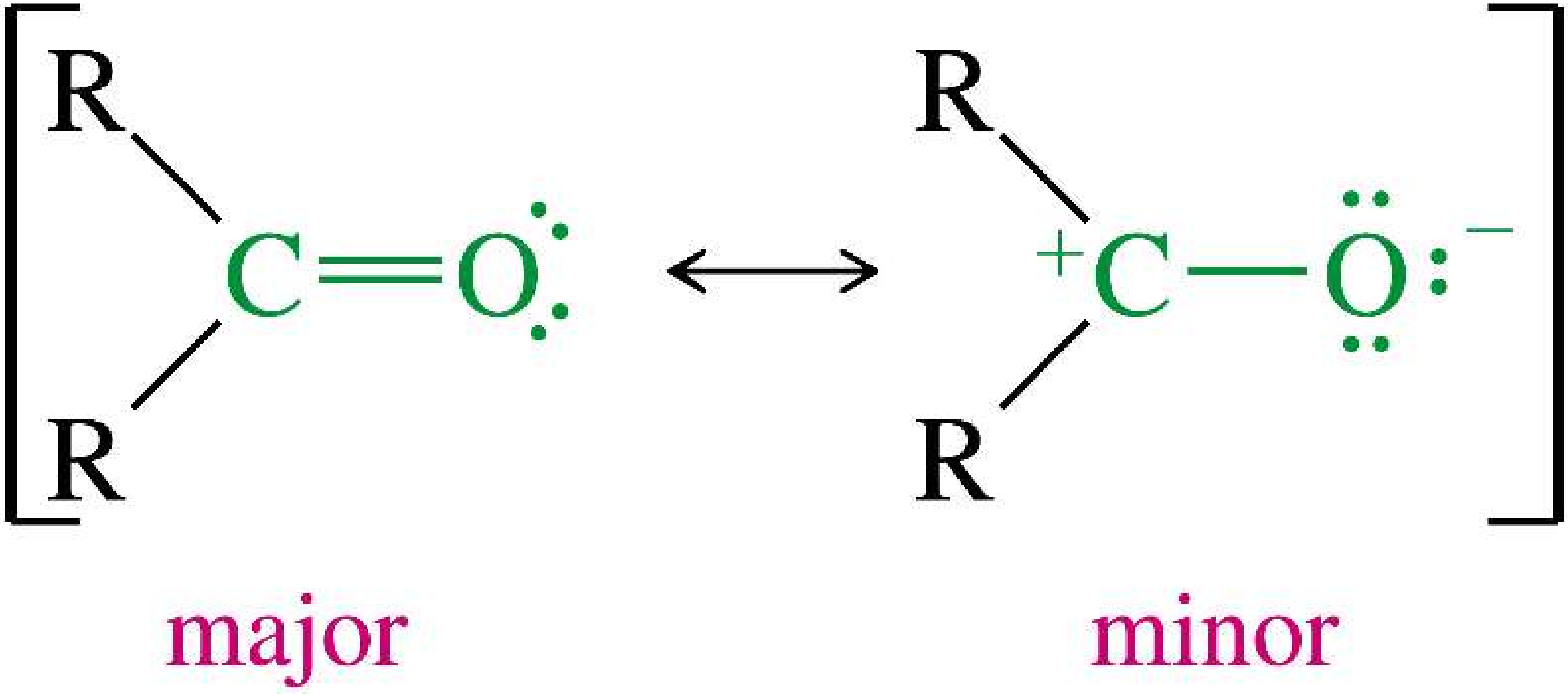


TABLE 18-1 Some Common Classes of Carbonyl Compounds

Class	General Formula	Class	General Formula
ketones	$R-\overset{\overset{\large O}{\|}}{C}-R'$	aldehydes	$R-\overset{\overset{\large O}{\|}}{C}-H$
carboxylic acids	$R-\overset{\overset{\large O}{\|}}{C}-OH$	acid chlorides	$R-\overset{\overset{\large O}{\|}}{C}-Cl$
esters	$R-\overset{\overset{\large O}{\|}}{C}-O-R'$	amides	$R-\overset{\overset{\large O}{\|}}{C}-NH_2$

Large Dipole Controls Properties and Reactivity



Boiling Points

Dipole-Dipole Interactions

$CH_3CH_2CH_2CH_3$

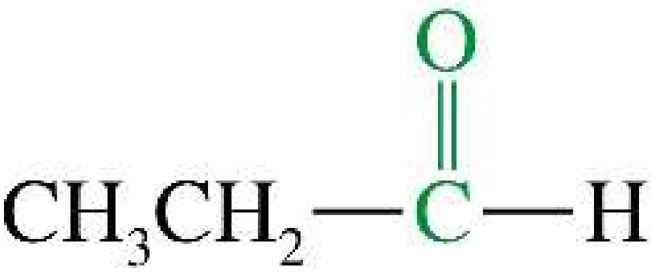
butane

bp 0°C

$CH_3—O—CH_2CH_3$

methoxyethane

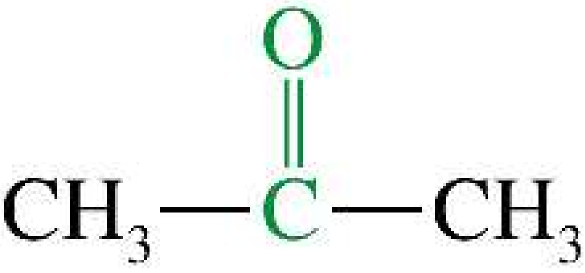
bp 8°C



$CH_3CH_2—\overset{\displaystyle O}{\overset{\|}{C}}—H$

propanal

bp 49°C



$CH_3—\overset{\displaystyle O}{\overset{\|}{C}}—CH_3$

acetone

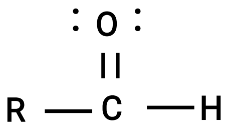
bp 56°C

$CH_3CH_2CH_2—OH$

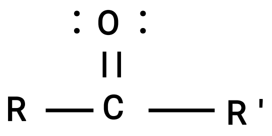
1-propanol

bp 97°C

ALDEHYDES & KETONES (ALKANALS & ALKANONES)

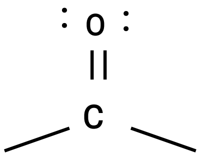


aldehyde



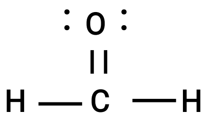
ketone

Aldehydes & ketones both contain the carbonyl group.



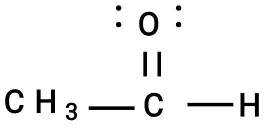
carbonyl group

- The simplest aldehyde is formaldehyde (CH_2O). It is the only aldehyde without an alkyl group attached to the carbonyl C.



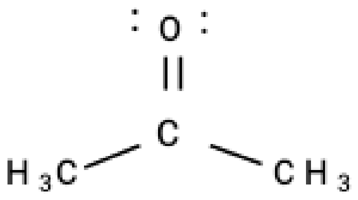
formaldehyde

All other aldehydes, such as acetaldehyde (CH_3CHO), have one alkyl group and one H attached to the carbonyl C.

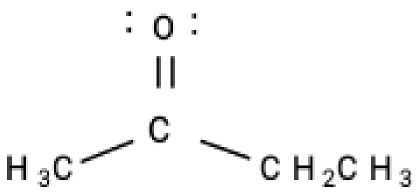


acetaldehyde

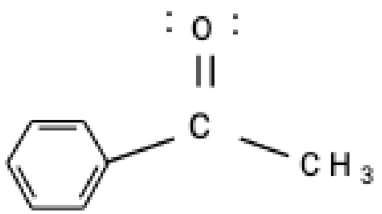
- All ketones have two alkyl groups attached to the carbonyl C.



dimethyl ketone
(acetone)



methyl ethyl ketone
(MEK)

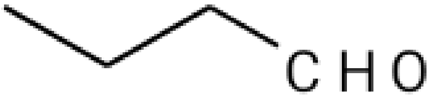


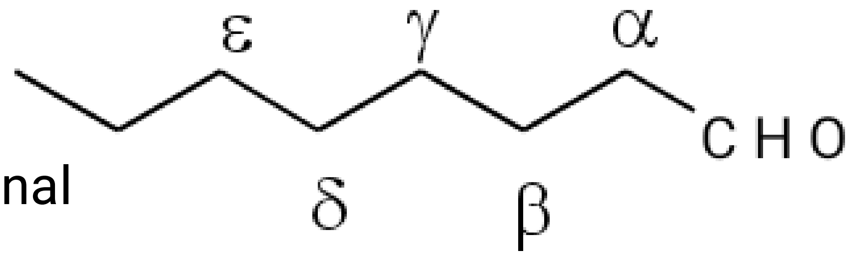
methyl phenyl ketone
(acetophenone)

Classical Aldehyde Nomenclature

Naming rule

- **Identify longest chain contains functional group**
- **Carbon of functional group will take the lowest number**

Prefix		
form	HCHO	Formaldehyde/ methanal
acet	CH_3CHO	Acetaldehyde/ ethanal
propion		propanal
butyr		
valer		

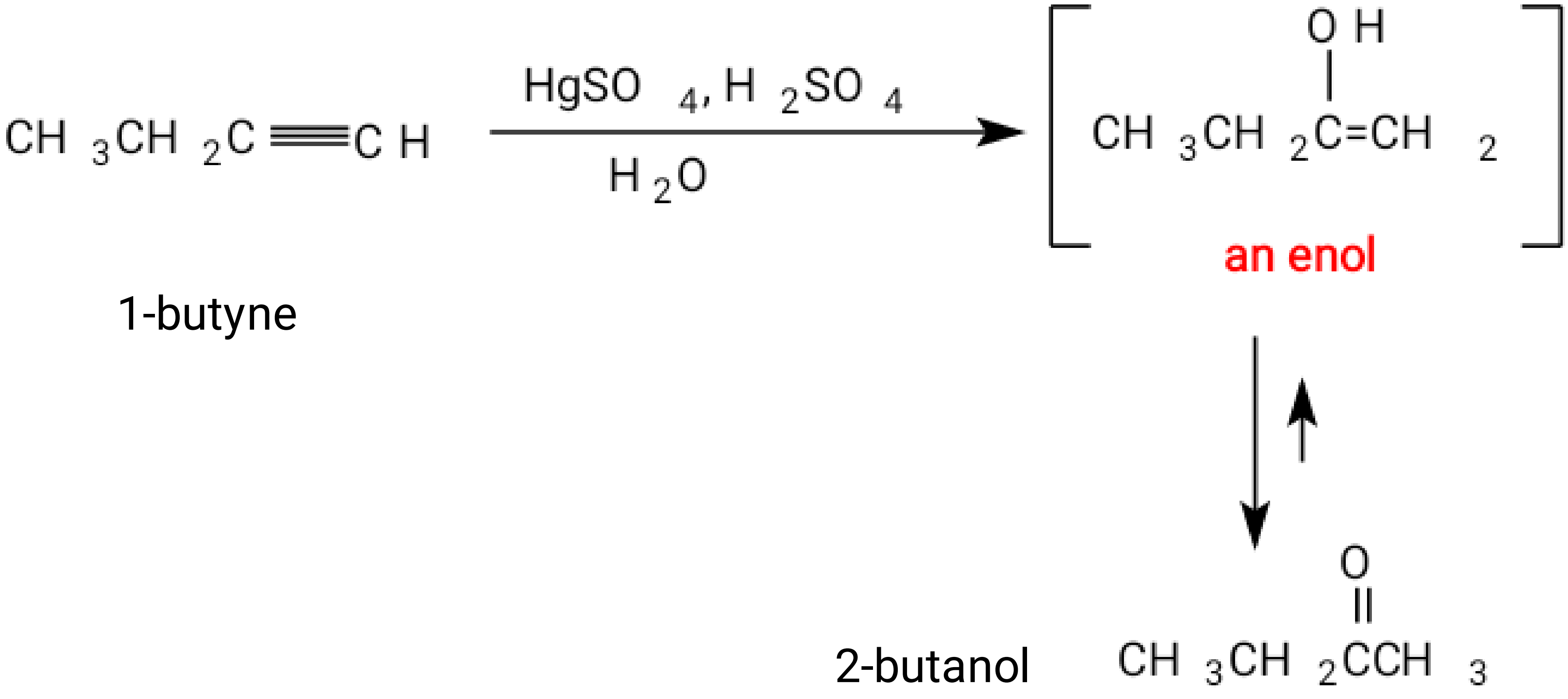


Preparation of Ketones and Aldehydes

1. Hydration of Alkynes (ketones with oxymercuration, aldehydes with hydroboration)
2. Ozonolysis of Alkenes (aldehydes and ketones depending on substitution)
3. Oxidation of alcohols
4. Reduction of acids

1- Hydration of alkyne

a) Markovnikov's rule



$$CH_3CH_2C\equiv CH \xrightarrow[H_2O]{HgSO_4,\ H_2SO_4} \left[CH_3CH_2\overset{OH}{\overset{|}{C}}{=}CH_2\right] \rightleftharpoons CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$$

1-butyne

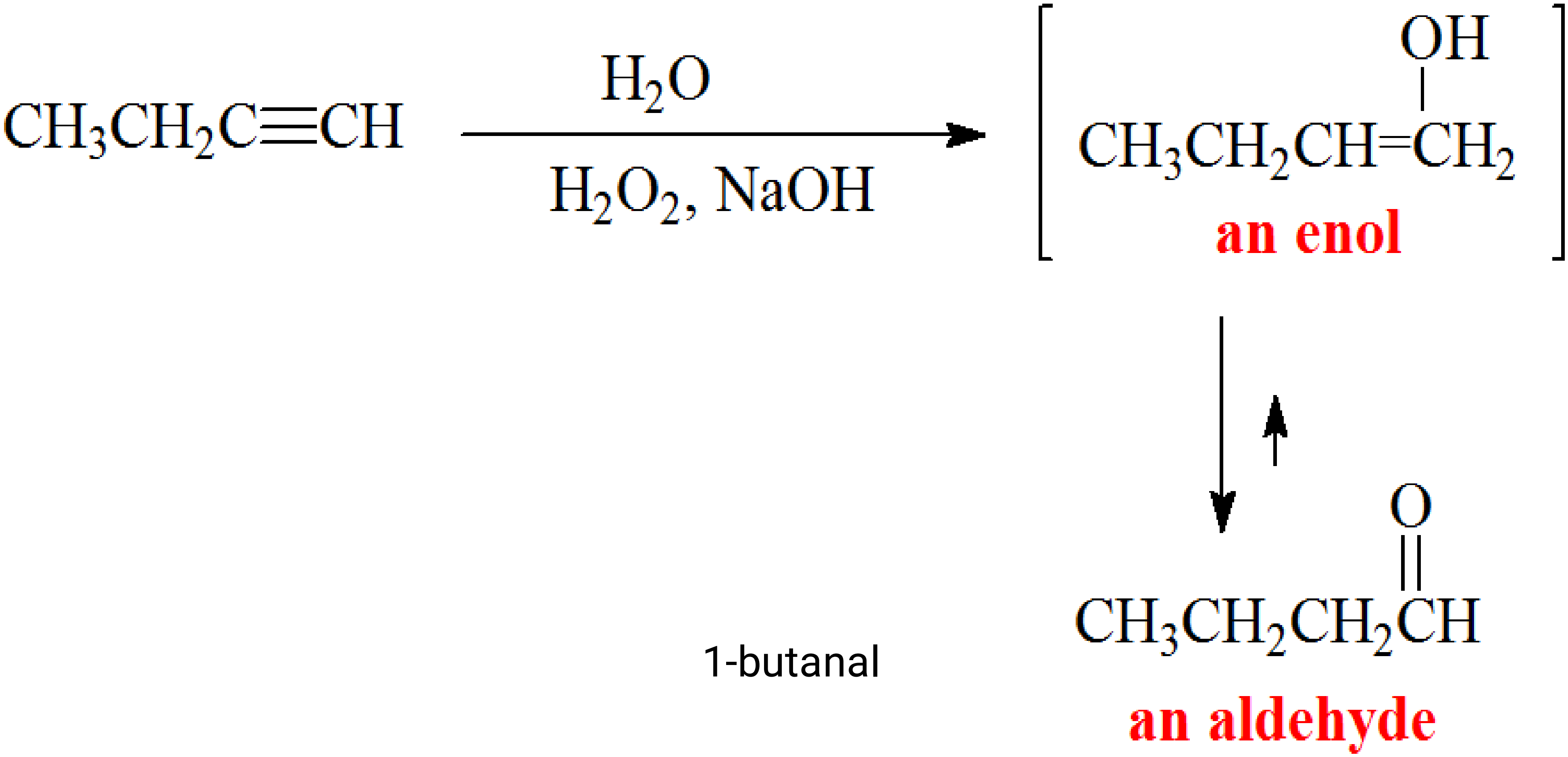
an enol

2-butanol

a ketone

Hydration

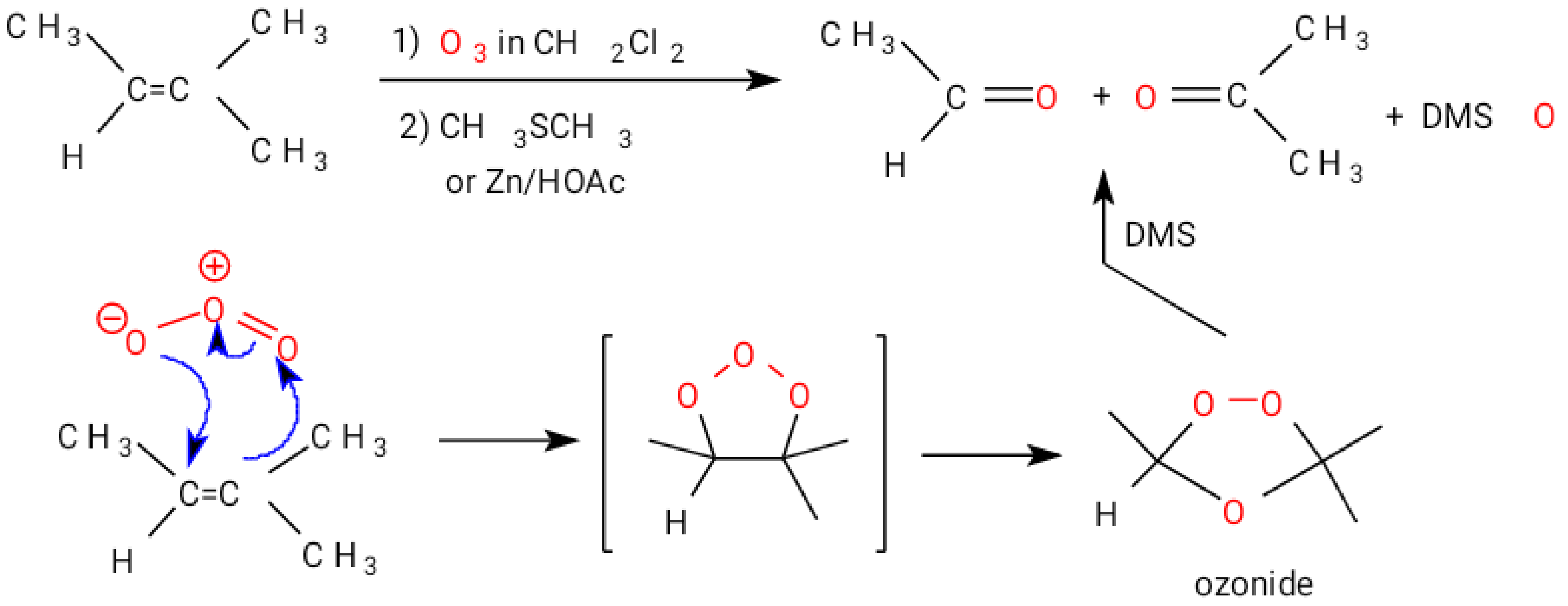
b) Anti- Markovnikov's rule



$$CH_3CH_2C\equiv CH \xrightarrow[H_2O_2,\ NaOH]{H_2O} \left[CH_3CH_2CH{=}\overset{OH}{\overset{|}{C}}H_2 \right] \rightleftharpoons CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$$

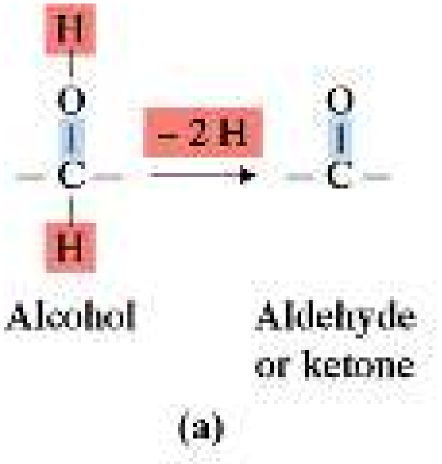
1-butanal

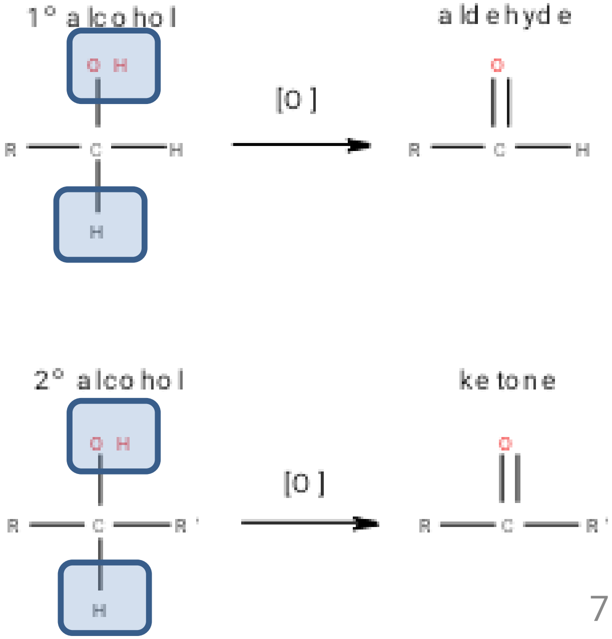
2- Ozonolysis
Alkene Cleavage



3- Oxidation of alcohols

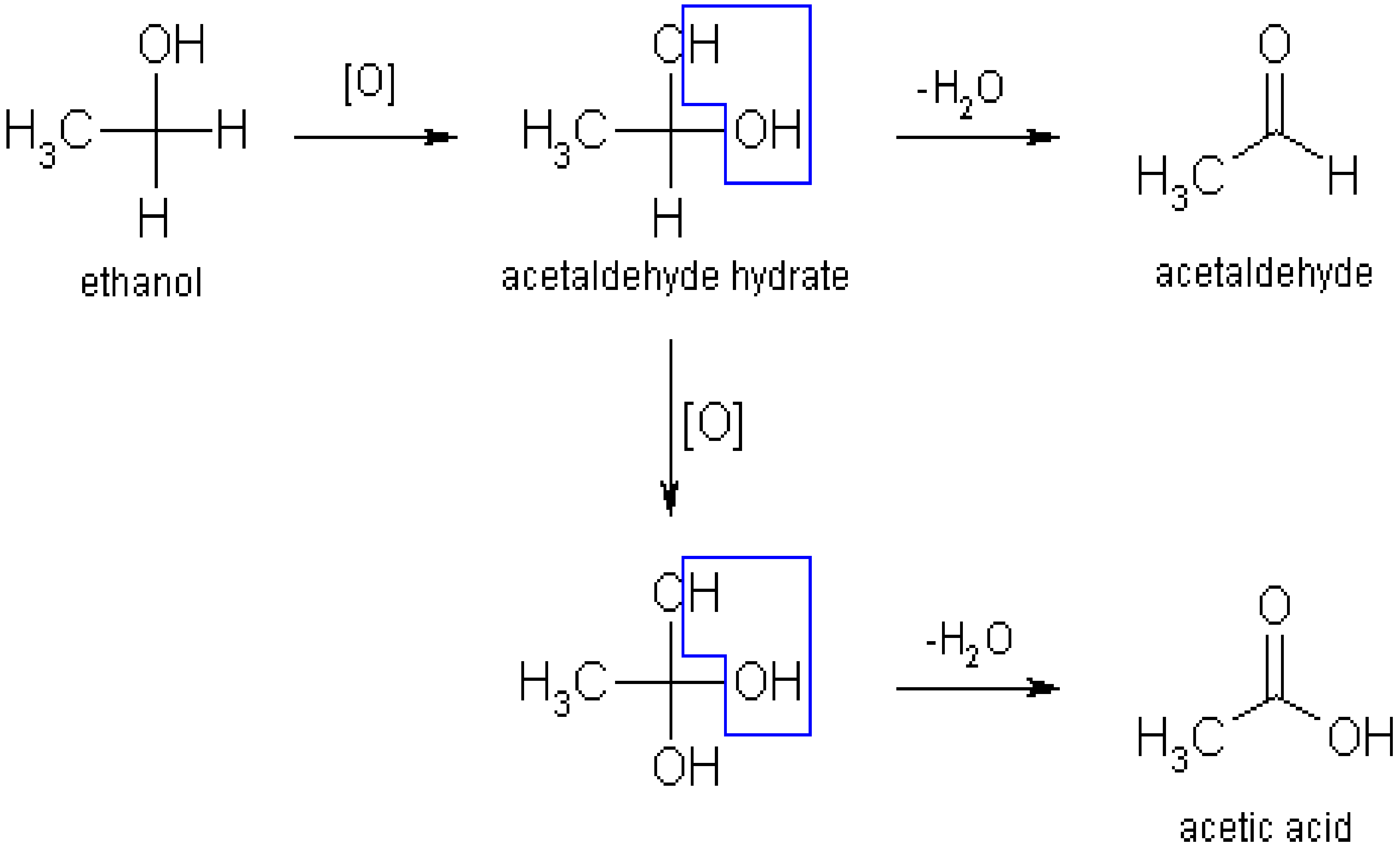
- alcohols can be oxidized to form aldehydes and ketones.
- Primary (1°) alcohols are oxidized to aldehydes (and subsequently to carboxylic acids)
- Secondary (2°) alcohols are oxidized to ketones





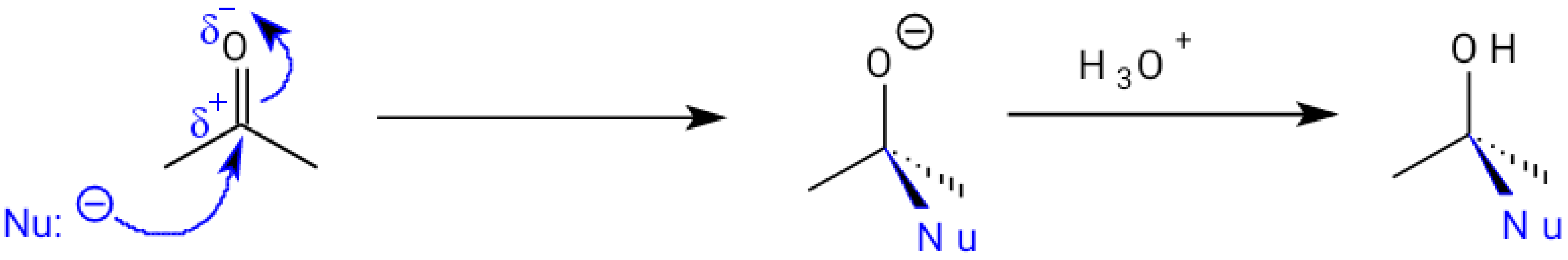
[O] = $KMnO_4$ or $K_2Cr_2O_7$

Contd. Oxidation of alcohols



Nucleophilic Addition Reactions:

Strong Nucleophiles

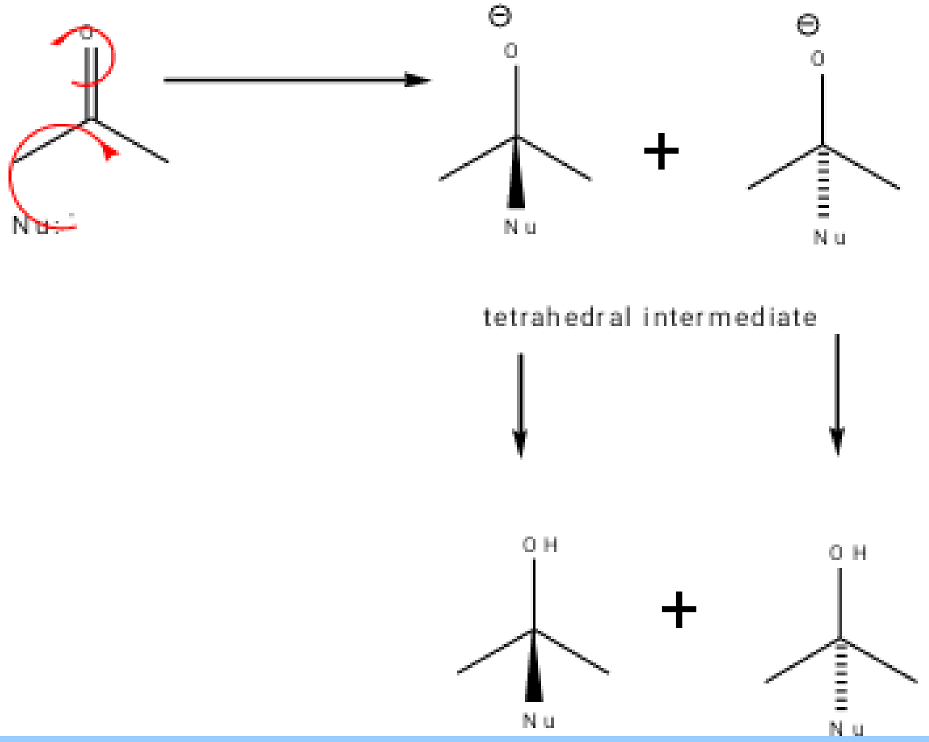


Basic nucleophiles: RMgX, RLi, $LiAlH_4$, $NaBH_4$, $RC{\equiv}CNa$

Nonbasic nucleophiles: CN^-

Addition of a nucleophile: Nucleophilic Addition

Good nucleophile, usually basic



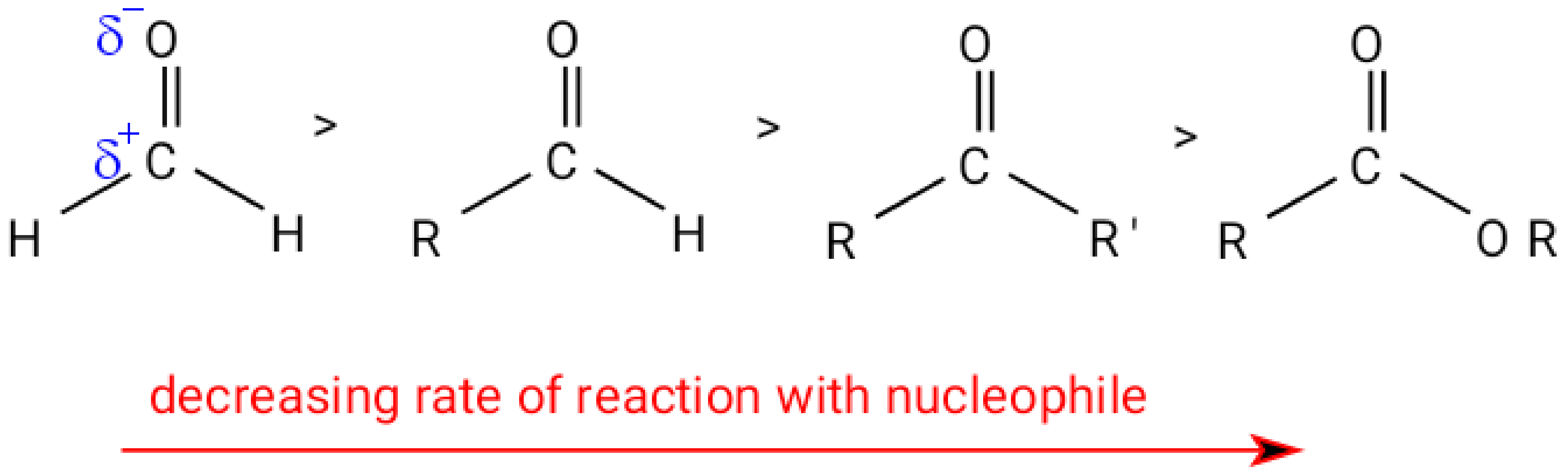
Attack of nucleophile occurs on both sides of carbonyl group.

Produces

Overall: H – Nu was added to carbonyl group double bond.

Notice that the CO bond order was reduced from 2 to 1. The addition reduced the bond order. We will use this idea later.

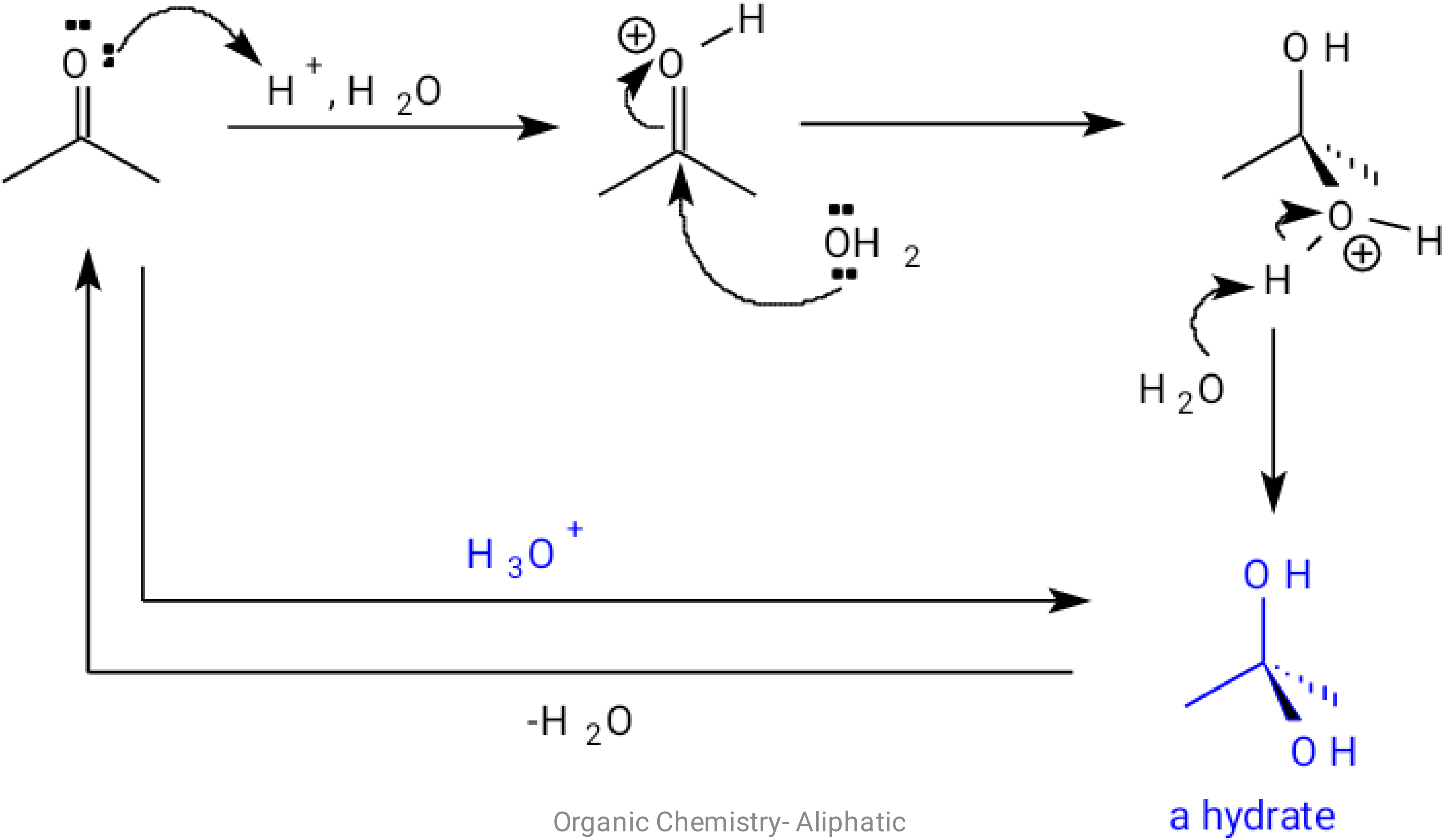
Carbonyl Compounds Reactivity



decreasing rate of reaction with nucleophile

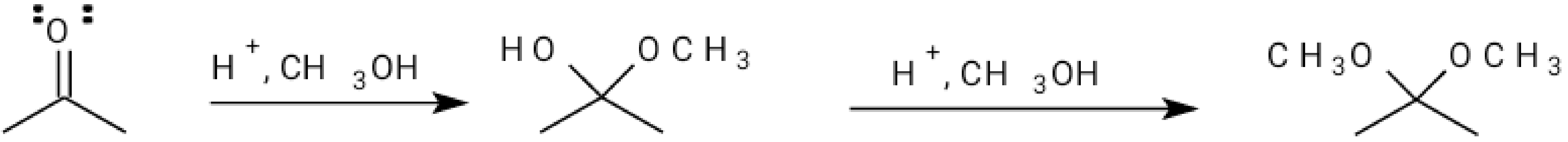
Nucleophilic Addition Reactions:

Weak Nucleophiles



Acetal Formation

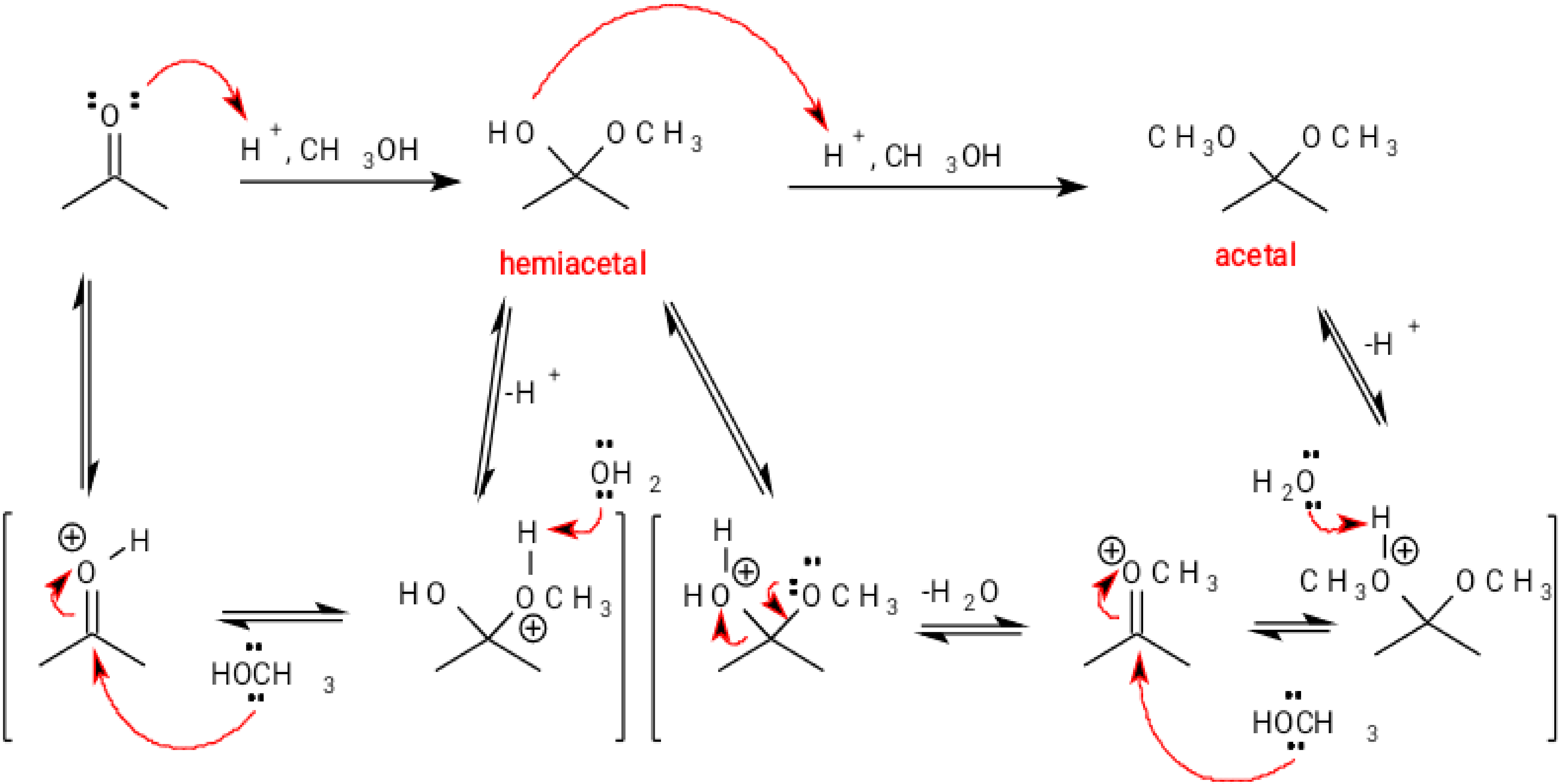
Carbonyl compound reacts with two molecules of alcohol to give a



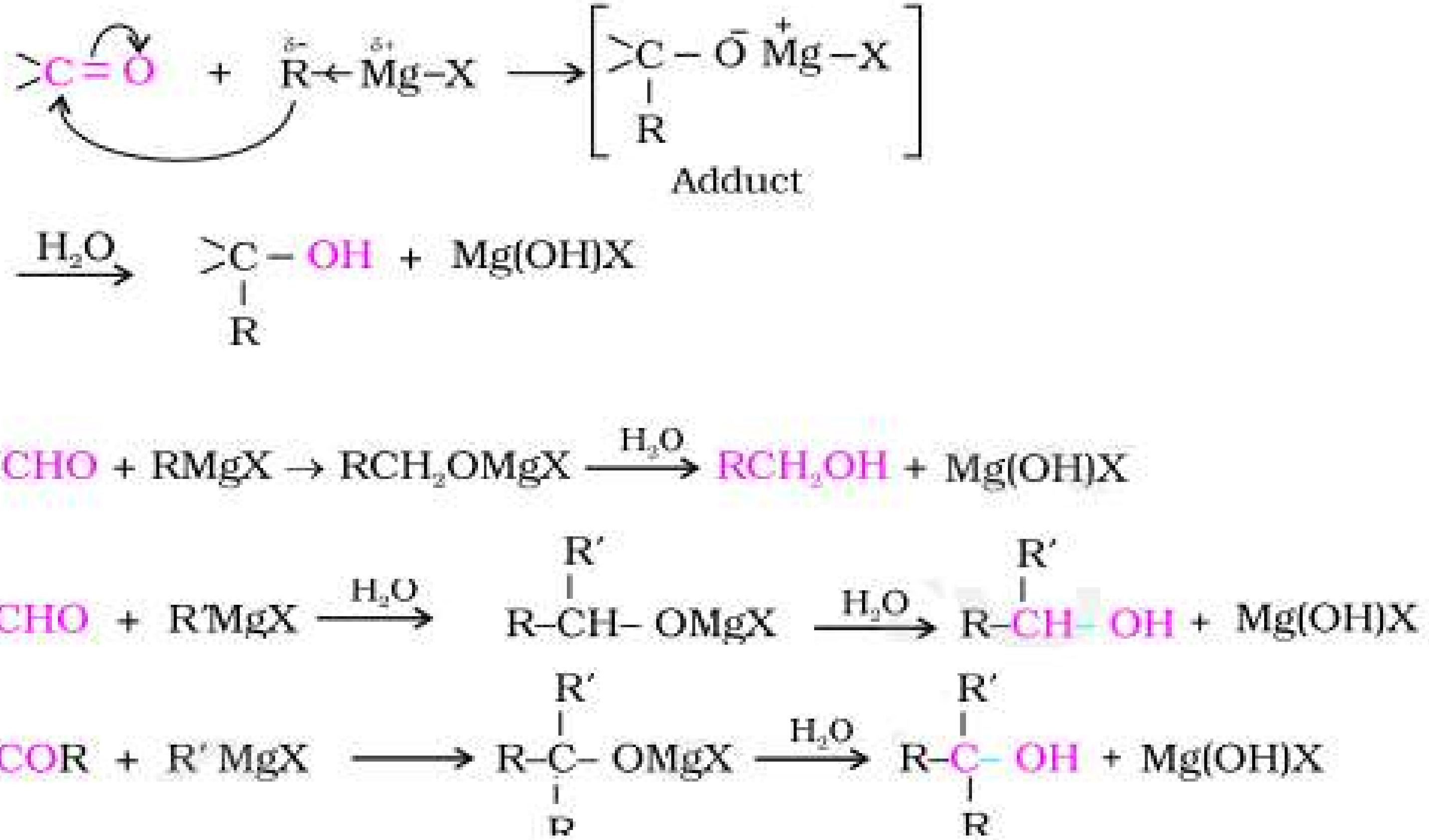
hemiacetal

acetal

Acetal mechanism



Preparation of alcohols from Grignard Reagent



$$>C=O \;+\; \overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}-X \longrightarrow \left[\, >\underset{\displaystyle R}{\underset{|}{C}}-\bar{O}\,\overset{+}{Mg}-X \,\right]$$

Adduct

$$\xrightarrow{H_2O} >\underset{\displaystyle R}{\underset{|}{C}}-OH \;+\; Mg(OH)X$$

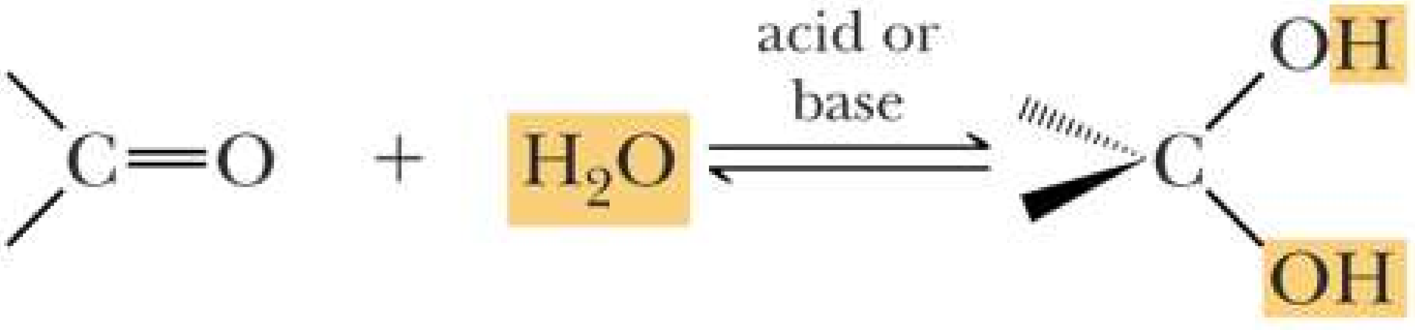
$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$

$$RCHO \;+\; R'MgX \xrightarrow{H_2O} R-\overset{\displaystyle R'}{\overset{|}{C}}H-OMgX \xrightarrow{H_2O} R-\overset{\displaystyle R'}{\overset{|}{C}}H-OH + Mg(OH)X$$

$$RCOR \;+\; R'MgX \longrightarrow R-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}-OMgX \xrightarrow{H_2O} R-\underset{\displaystyle R}{\underset{|}{\overset{\displaystyle R'}{\overset{|}{C}}}}-OH + Mg(OH)X$$

The Grignard reagent : an organometallic compound

Formation of Hydrates, carbonyls and water.



Carbonyl group of an aldehyde or ketone

A hydrate (a gem-diol)

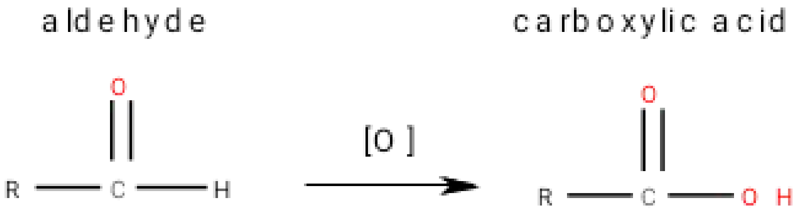
© 2006 Brooks/Cole - Thomson

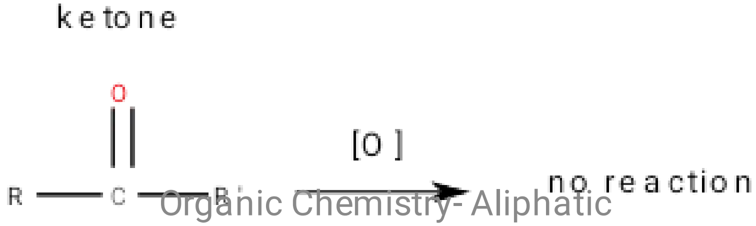
Carbonyl side of equilibrium is usually favored.

Oxidation and reduction of aldehydes and ketones

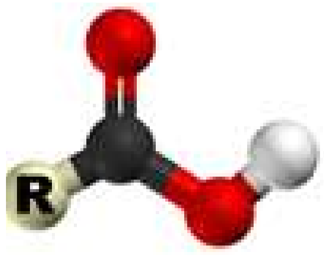
Oxidation reactions

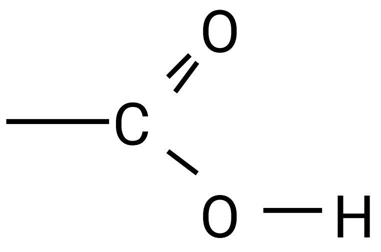
- Aldehydes can be oxidized easily to carboxylic acids
- Ketones are resistant to oxidation.





Carboxylic Acids





- Carboxylic acids are strong organic acids which contain the carboxyl group (-COOH, -CO_2H)

- Carboxylic acids are classified as aliphatic or aromatic depending on whether R or an Ar is attached to the carboxylic group
  R-COOH or Ar-COOH

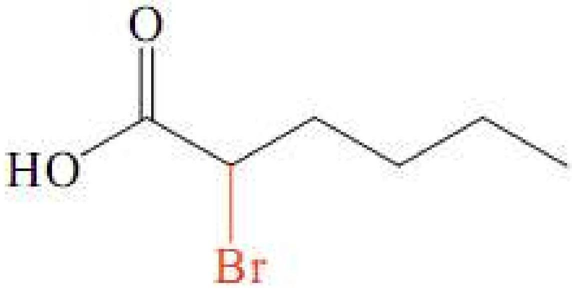
Nomenclature of carboxylic acids

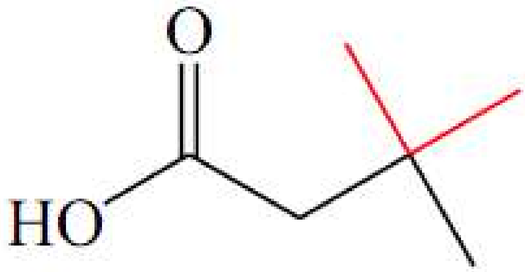
Formula	IUPAC	Common
	alkan -oic acid	prefix – ic acid
$HCOOH$	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid

Naming Rules

- Identify longest chain
- (IUPAC) Number carboxyl carbon as 1
- (Common) Assign α, β, γ, δ to carbon atoms adjacent to carboxyl carbon

Examples:



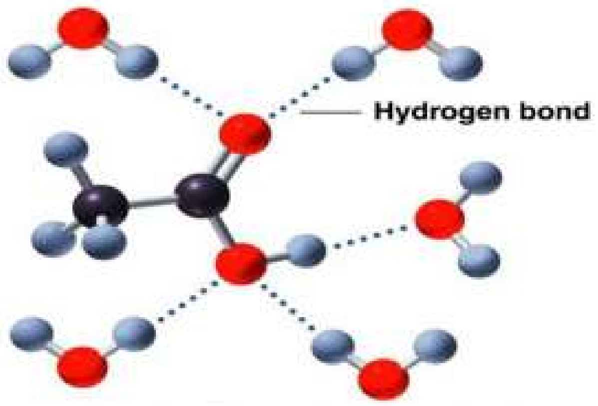


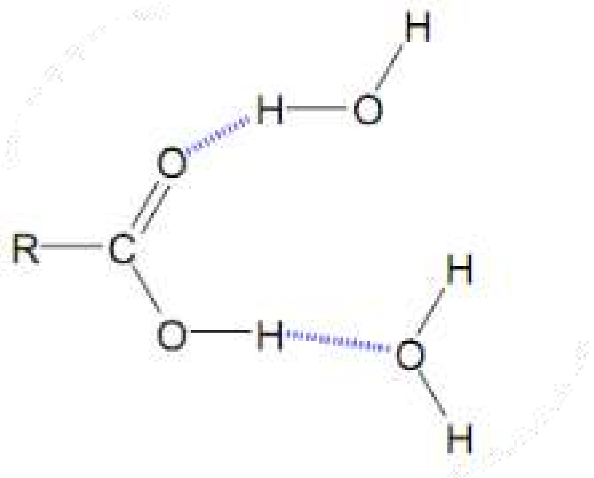
IUPAC:	2- bromohexanoic acid	3,3-dimethylbutanoic acid
Common:	α- bromohexanoic acid	β,β-dimethylbutyric acid

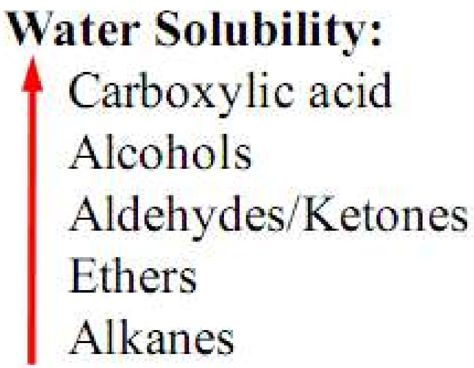
Physical Properties of Carboxylic Acids

1. Solubility

- The carboxylic acid are highly polar organic compounds.
- This polarity results from the presence of a strongly polarized carbonyl (C=O) group and hydroxyl (O-H) group.







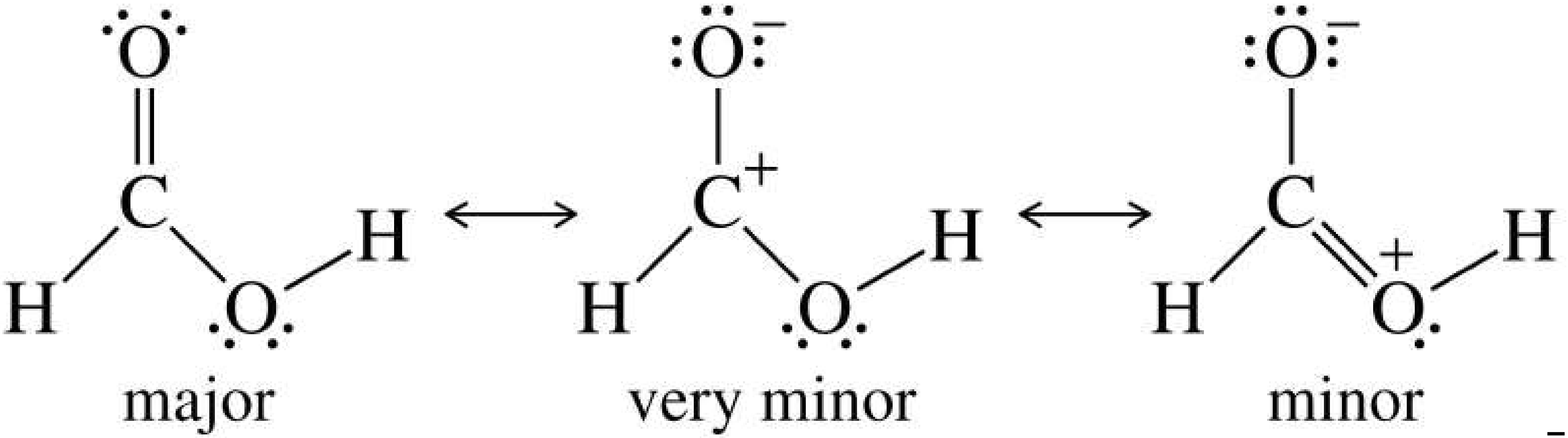
Water Solubility:

Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

- As the number of carbons in a carboxylic acid series becomes greater, the solubility in water decreases.
- Aromatic carboxylic acids are insoluble in water.

Structure of Carboxyl

- Carbon is *sp*^{2} hybridized.
- Bond angles are close to 120°.
- O-H eclipsed with C=O, to get overlap of π orbital with orbital of lone pair on oxygen.



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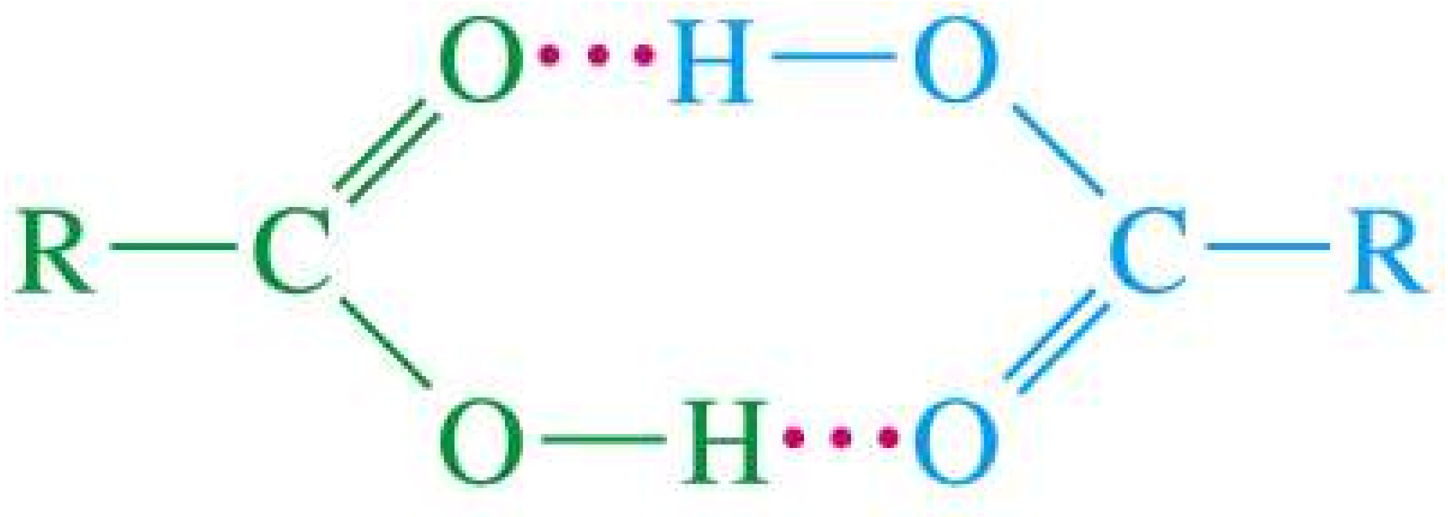
Boiling Points

Higher boiling points than similar alcohols, due to dimer formation.



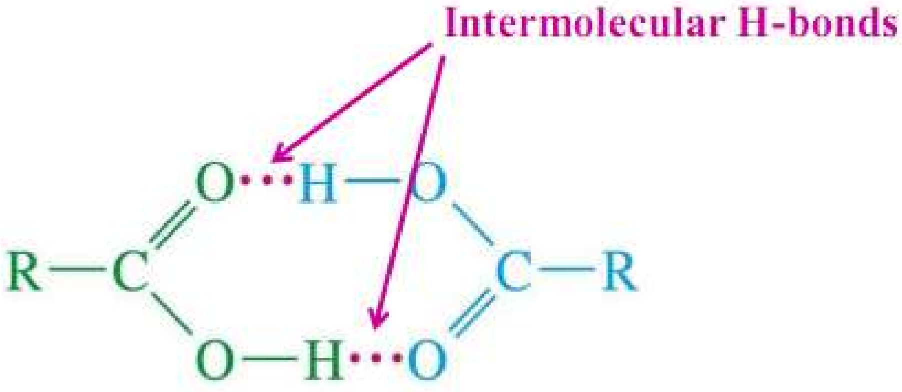
hydrogen-bonded acid dimer

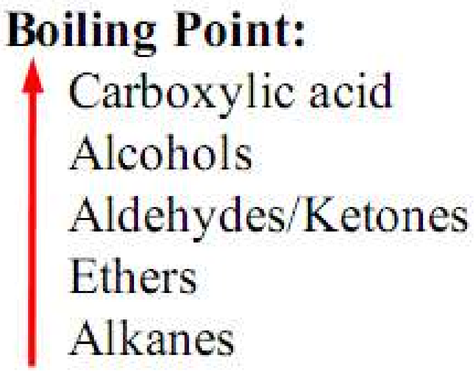
Acetic acid, b.p. 118°C

=>

2. Boiling Point

Carboxylic acids are polar compounds and form very strong intermolecular hydrogen bonds to form a dimer.





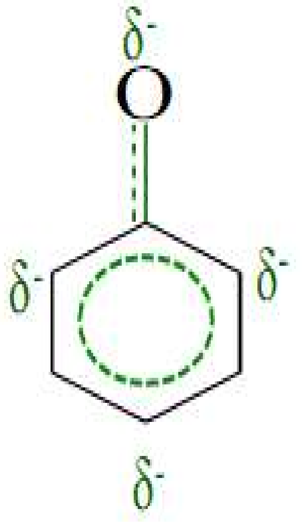
Boiling Point:

- Carboxylic acid
- Alcohols
- Aldehydes/Ketones
- Ethers
- Alkanes

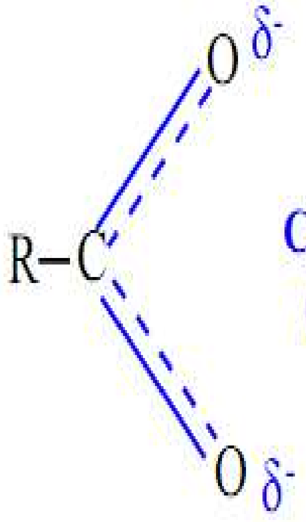
➢ As the number of carbons in a carboxylic acid series becomes greater, the boiling point increases.

Acidity and Acid Strength

- The most important chemical property of carboxylic acids chemistry is their acidic nature.
- The mineral acids (HCl, HBr, HI, H_2SO_4, H_3PO_4) are defined as "strong acids" because they undergo complete dissociation.
- Carboxylic acids are strong organic acids , they are much more acidic than alcohols.
- Carboxylic acids are stronger acids than phenols.



Phenoxide ion
(Less stable)



Carboxylate ion
(More stable)

Preparation of Carboxylic acids

1. Oxidation:

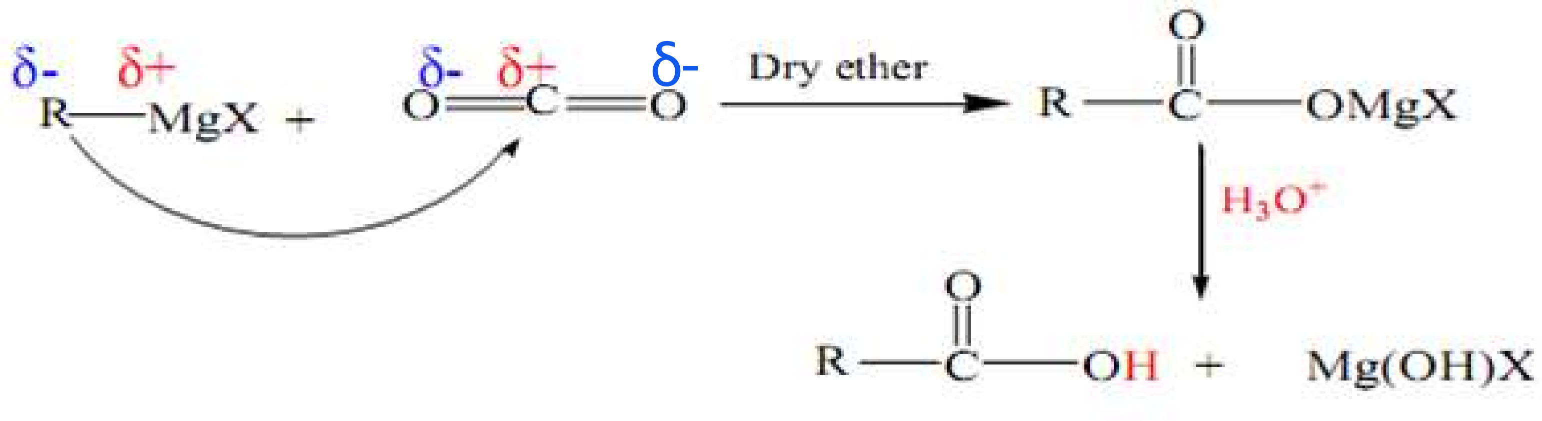
A. Oxidation of primary alcohols and aldehydes

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[\text{or} K_2Cr_2O_4 / H^+]{KMnO_4 / H^+ / \Delta} \underset{\text{Acetic acid}}{CH_3COOH}$$

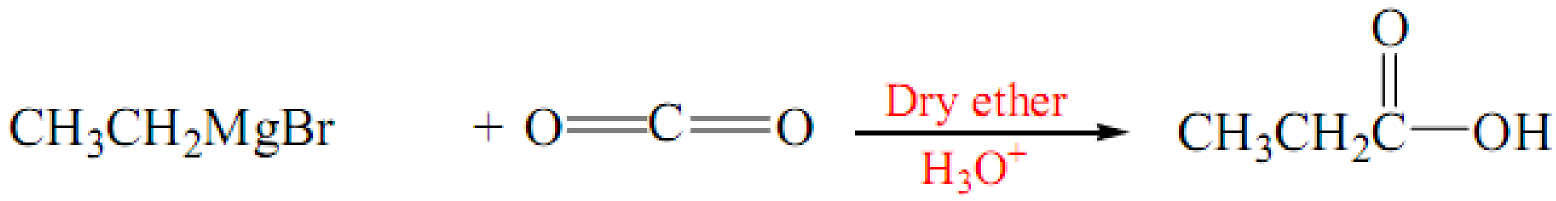
$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Acetic acid}}{CH_3COOH}$$

2. Carbonation of Grignard Reagents:

The addition of Grignard reagents to CO_2 in form of dry ice gives
an acid with one more carbon more than the original Grignard reagent.



Example:



$$CH_3CH_2MgBr + O{=}C{=}O \xrightarrow[H_3O^+]{\text{Dry ether}} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

3. Hydrolysis of Nitriles:

Nitriles:

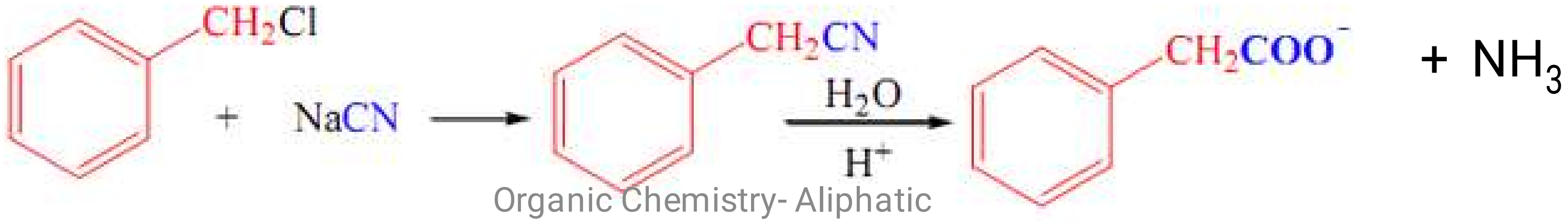
$$RC{\equiv}N \text{ or } ArC{\equiv}N$$

- They are prepared by reacting a 1° or 2° alkyl halide with cyanide
- Acid hydrolysis of a nitriles yields a carboxylic acids.

$$\underset{\text{Alkyl halide}}{RX} + \underset{\text{Cyanide salt}}{NaC{\equiv}N} \longrightarrow \underset{\text{Nitriles}}{RC{\equiv}N} \xrightarrow[H^+]{H_2O} \underset{\text{Carboxylic acids}}{RCOO^-} + NH_3$$

Examples:

$$CH_3CH_2Cl + NaCN \longrightarrow CH_3CH_2CN \xrightarrow[H^+]{H_2O} CH_3CH_2COO^- + NH_3$$



Reactions of Carboxylic acids

1. Reaction with Bases : Salt formation

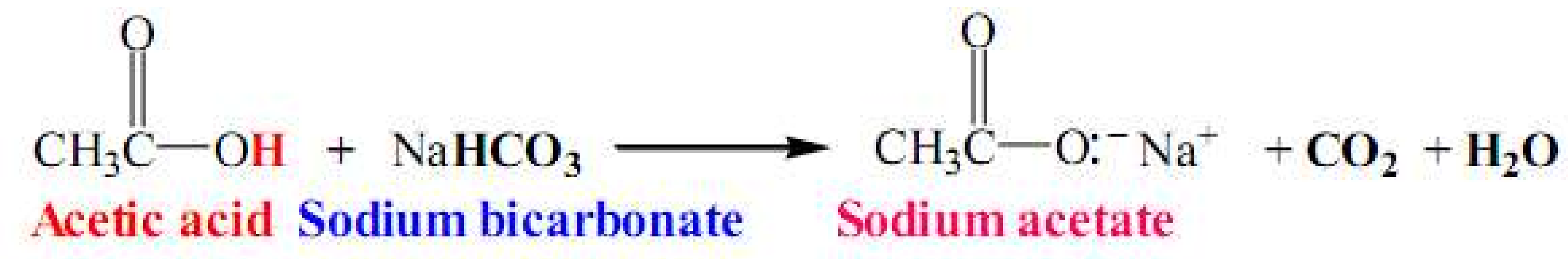
The carboxyl hydrogen is replaced by metal ion, M^+

A) With strong base:

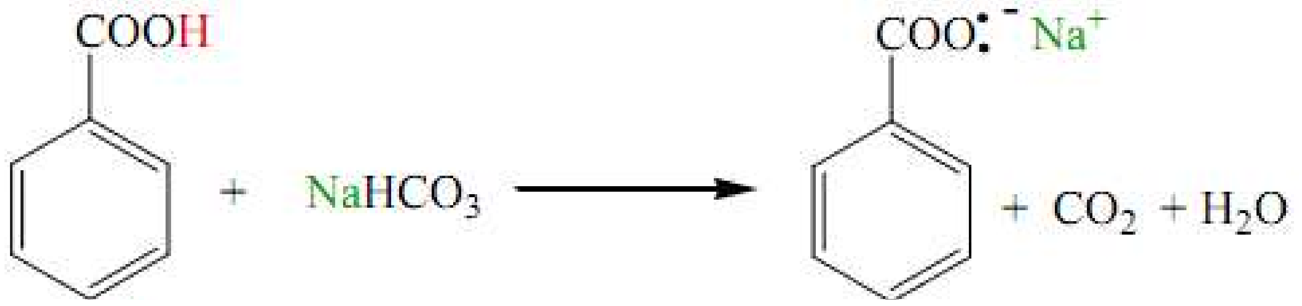
$$HCOOH + KOH \longrightarrow HCOO:^{-} K^{+} + H_2O$$

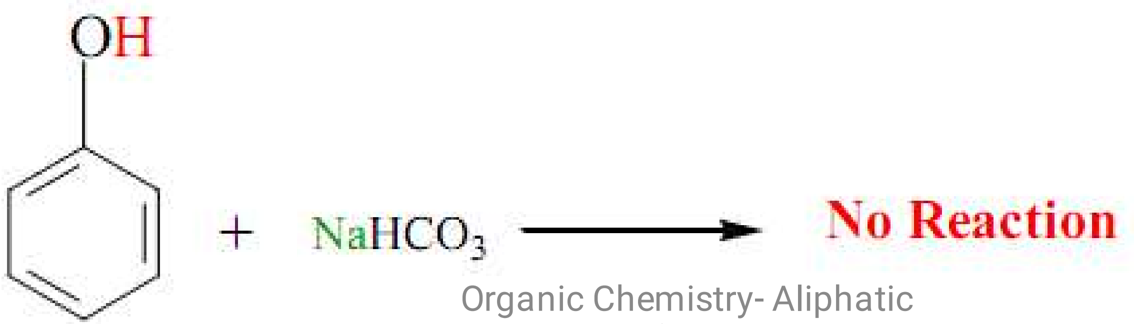
Formic acid **Potassium formate**

B) With weak base



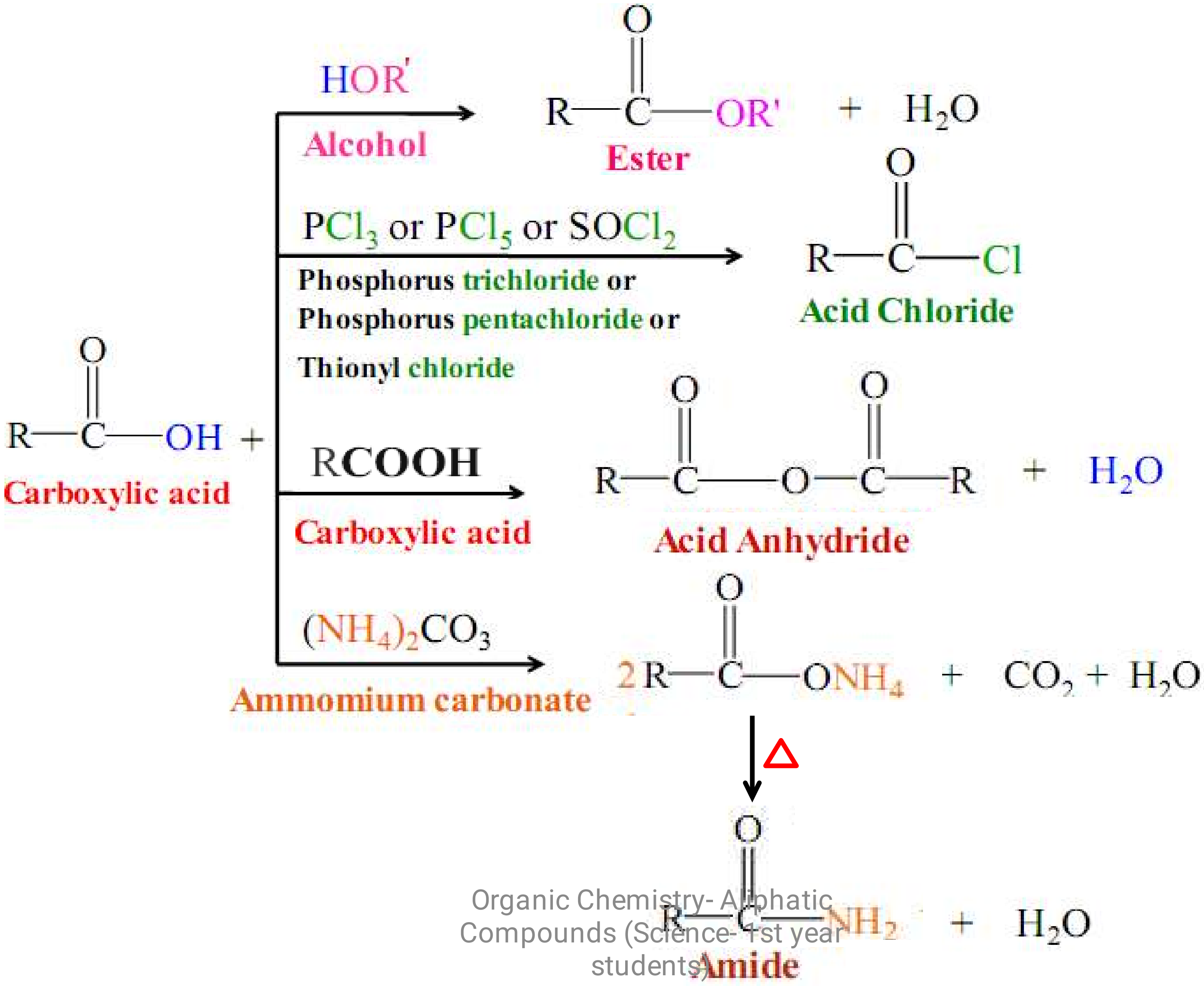
- Weaker acids like phenols react only with strong bases like (NaOH or KOH) and will not react with $NaHCO_3$





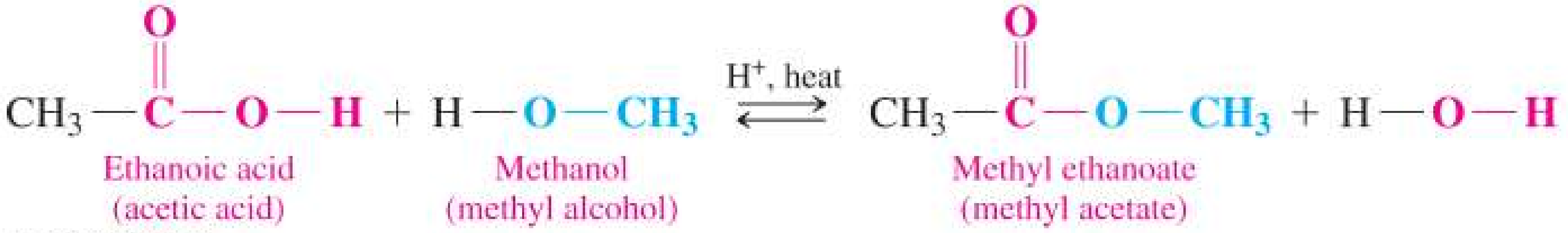
2. Reaction with Nucleophiles to form acid derivatives:

- When the OH of a carboxylic acid is replaced by a nucleophile, :Nu , a carboxylic acid derivative is produced.



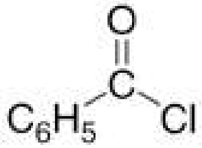
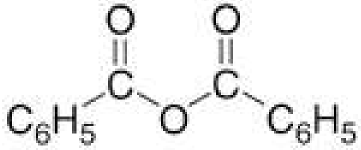
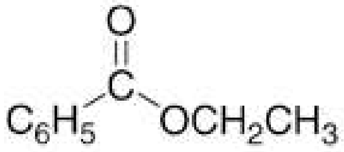
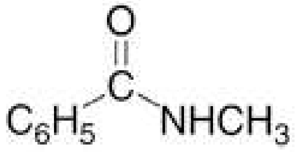
ESTERIFICATION

Esterification is the reaction of a carboxylic acid and alcohol in the presence of an acid catalyst to produce an ester.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-H + H-O-CH_3 \overset{H^+,\ heat}{\rightleftharpoons} CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3 + H-O-H$$

Derivatives of Carboxylic acids

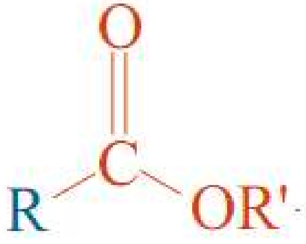
Compound	Name ending	Example	Name
acid chloride	**-yl chloride** or **-carbonyl chloride**	 $C_6H_5C(=O)Cl$	benzoyl chloride
anhydride	**anhydride**	 $C_6H_5C(=O)OC(=O)C_6H_5$	benzoic anhydride
ester	**-ate**	 $C_6H_5C(=O)OCH_2CH_3$	ethyl benzoate
amide	**-amide**	 $C_6H_5C(=O)NHCH_3$	*N*-methylbenzamide

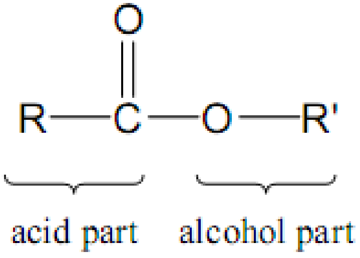
Nomenclature

Nomenclature: the functional derivatives' names are derived from the common or IUPAC names of the corresponding carboxylic acids.

1. Esters:

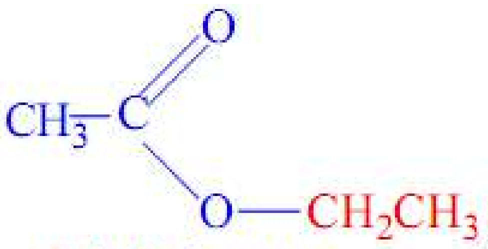
alkyl alkanoate



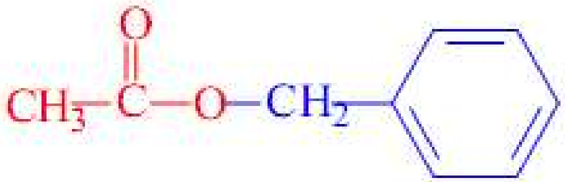


Change –ic acid to –ate preceded by the alkyl is derived from the alcohol, R'OH.

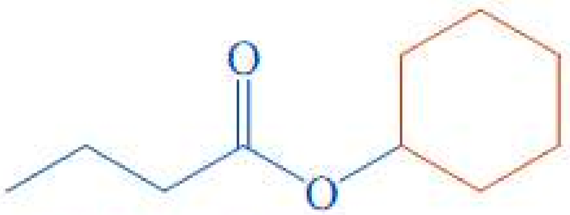
Examples:



Ethylethanoate

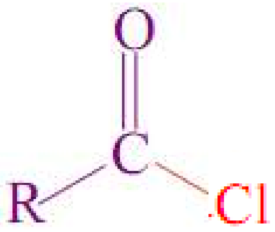


Benzyl ethanoate



Cyclohexyl butanoate

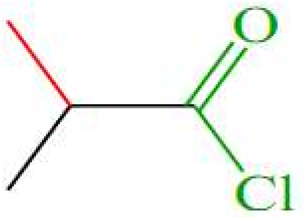
2. Acid Chlorides:



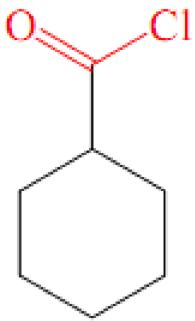
Change −ic acid to −yl chloride

Alkanoyl chloride

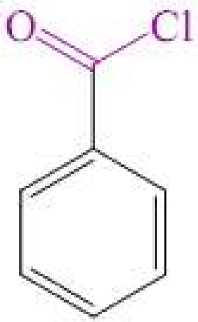
Examples:



2-methylpropanoyl chloride

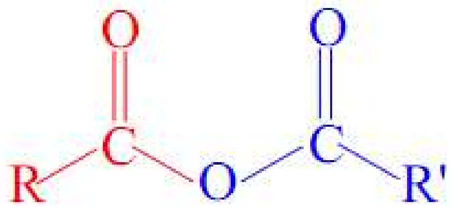


cyclohexanoyl chloride



Benzoyl chloride

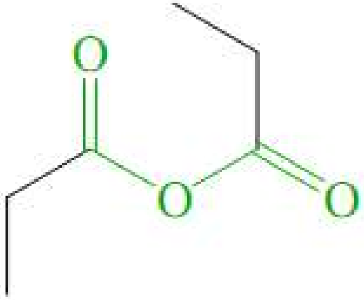
3. Acid Anhydride:



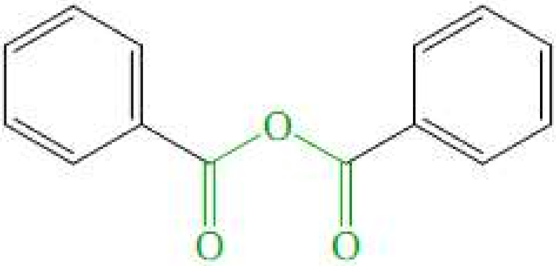
Change acid to anhydride

Examples:

alkanoic
anhydrides

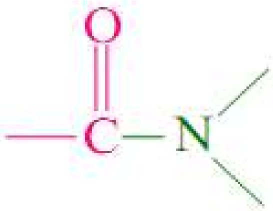


Propanoic anhydride



Benzoic anhydride

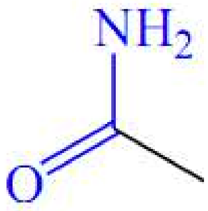
4. Amides:



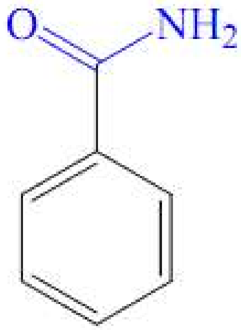
Change -oic acid to –amide

alkanamide

Examples:



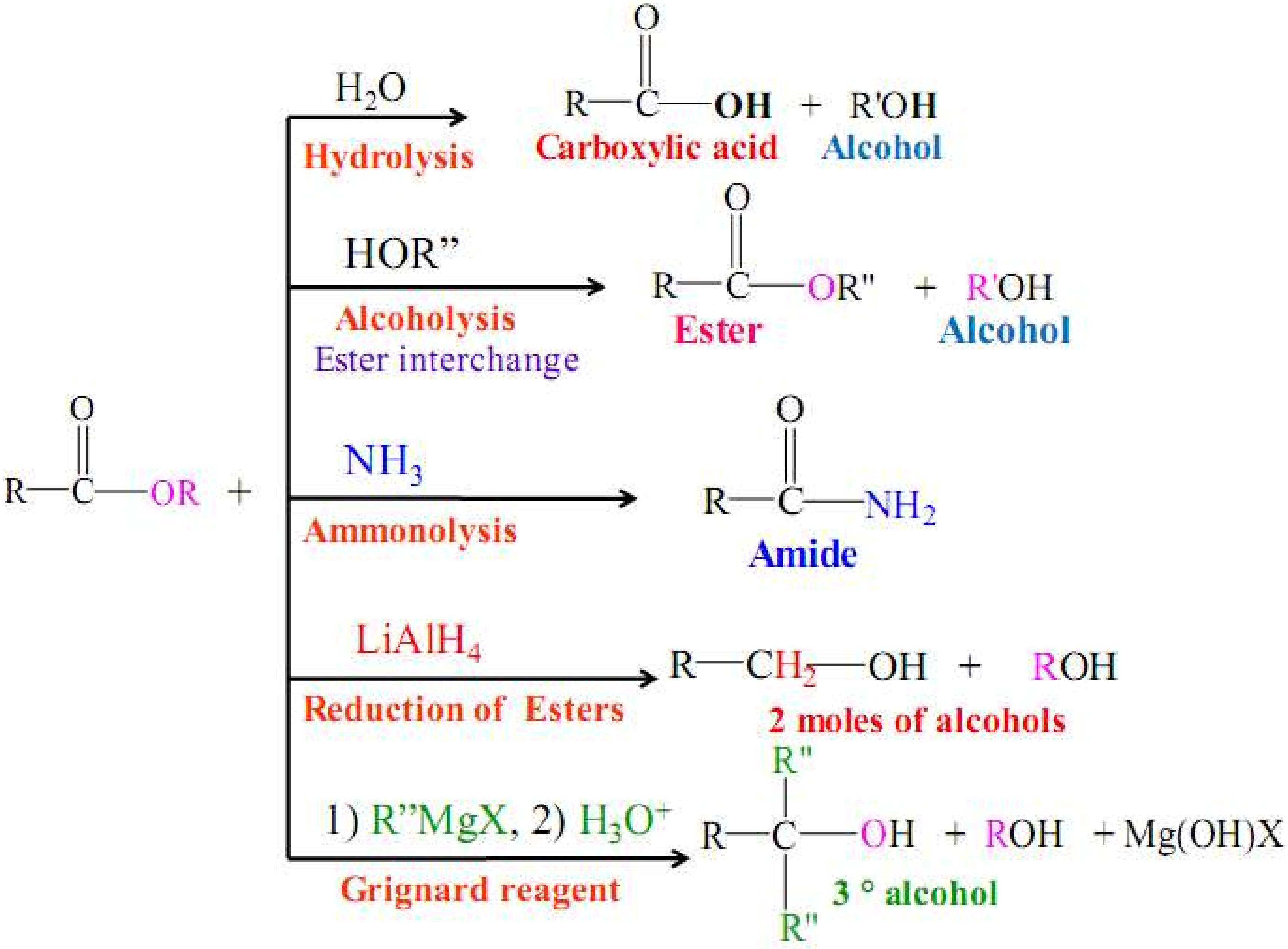
Acetamide
Ethanamide



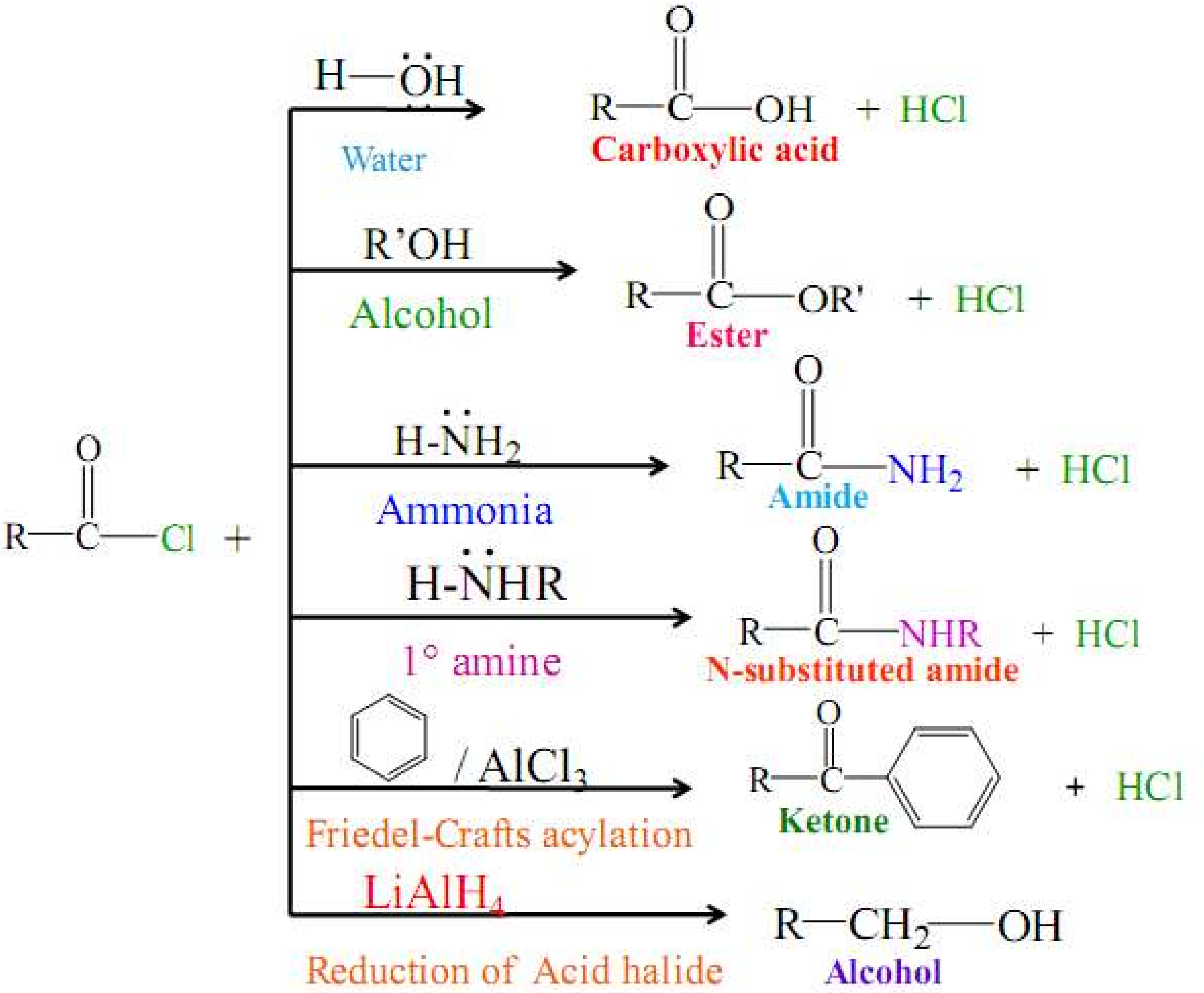
Benzamide

Acetanilide
N-phenylethanamide

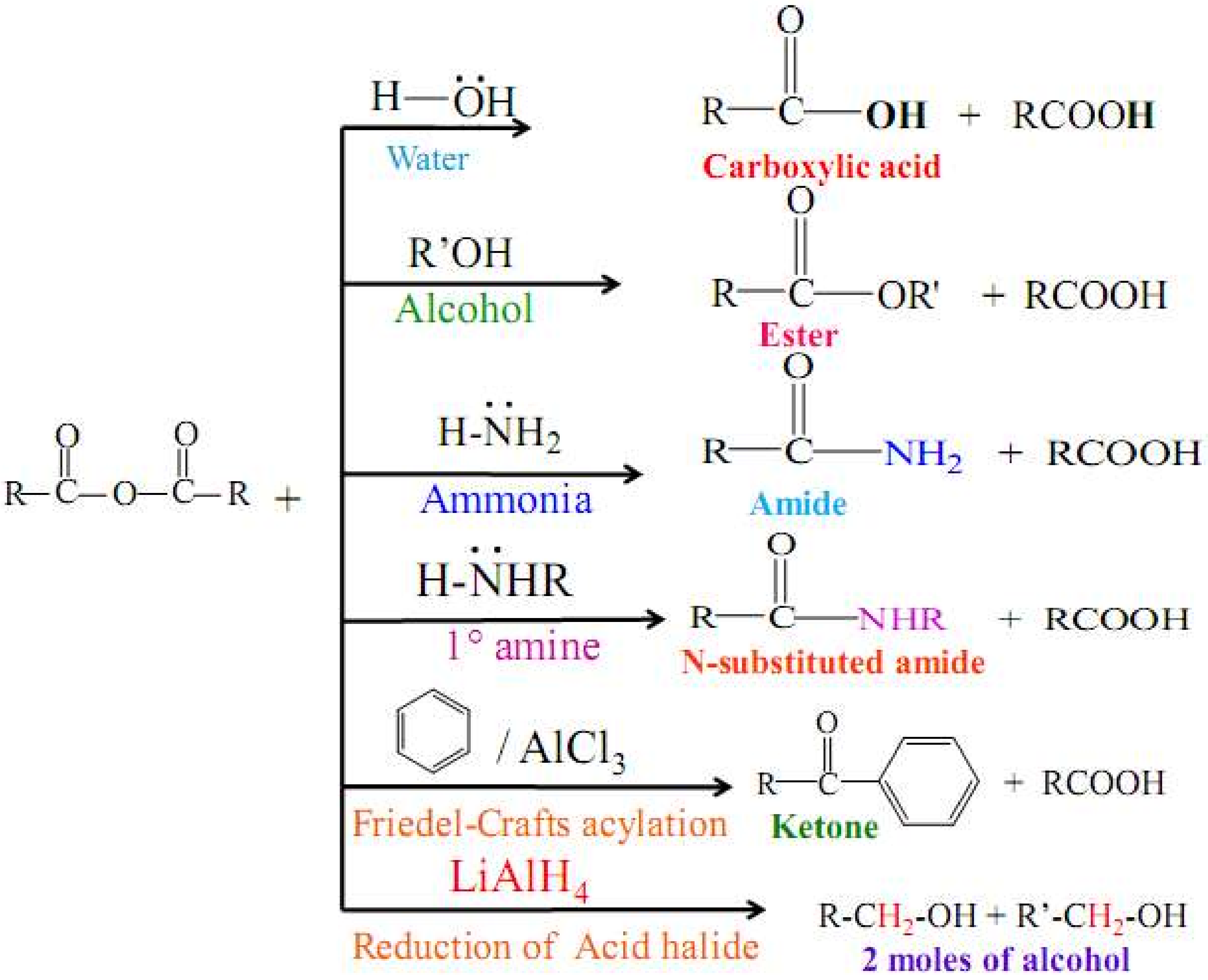
Esters Reactions:



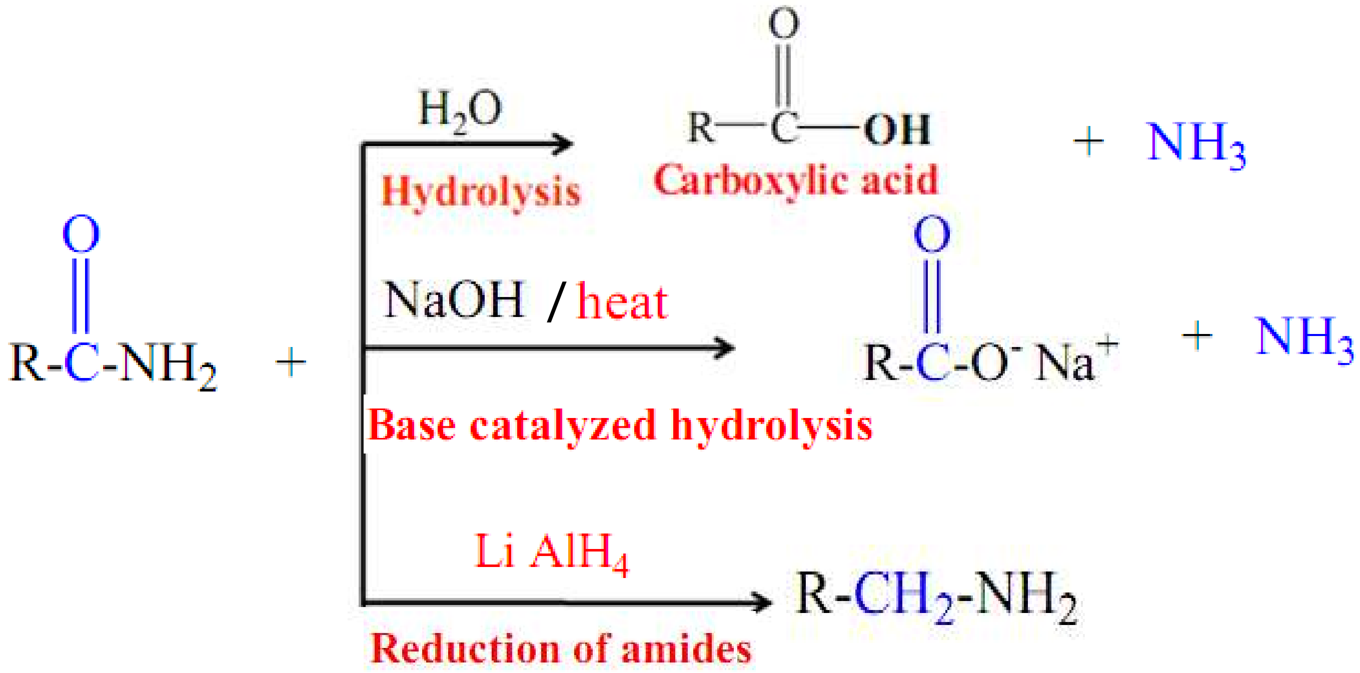
Acid Chlorides Reactions:



Acid Anhydride Reactions:

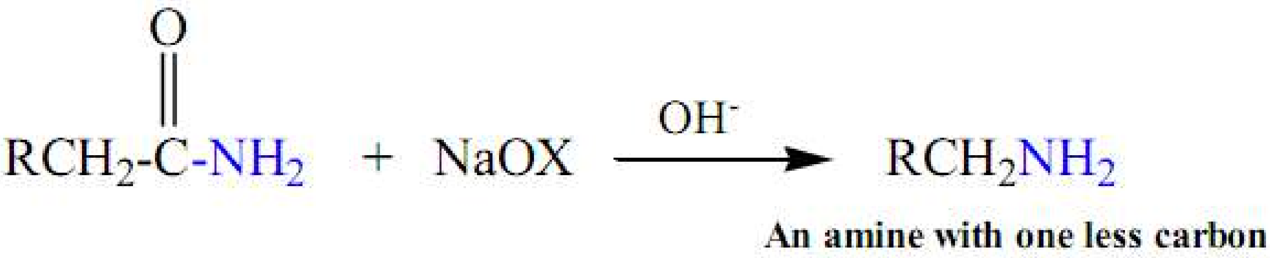


Amides Reactions:



4- Reaction of amides with alkaline hypohalite solution:

Reduced to amines containing one less carbon atom



$$RCH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}NH_2 + NaOX \xrightarrow{OH^-} RCH_2NH_2$$

An amine with one less carbon

Amines

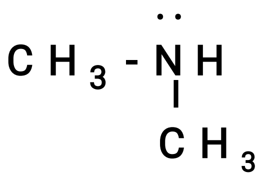
The organic bases

Structure & Classification

- Amines are classified as:
  - 1°, 2°, or , 3° amines: Amines in which there are 1, 2, or 3 alkyl or aryl groups.

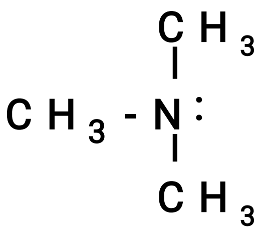
$CH_3-\ddot{N}H_2$

Methylamine (a 1° amine)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\ddot{N}}}H$

Dimethylamine (a 2° amine)



$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{N}}}}\!:$

Trimethylamine (a 3° amine)

Categorizing Amines

- **Amines are categorized by the number of alkyl groups attached to nitrogen:**

1º (primary amine) RNH_2

2º (secondary amine) R_2NH

3º (tertiary amine) R_3N

4º (quaternary amine salt) R_4N^+

Naming simple amines

- Simple 1° amines are named as “alkylamine”
  - Examples:
    - methylamine CH_3NH_2
    - ethylamine $CH_3CH_2NH_2$
    - butylamine $CH_3CH_2CH_2CH_2NH_2$

- Symmetrical 2° or 3° amines are named as “dialkylamine” or “trialkyamine”
  - Examples:
    - diethylamine $(CH_3CH_2)_2NH$; trimethylamine $(CH_3)_3N$

Naming more complex amines

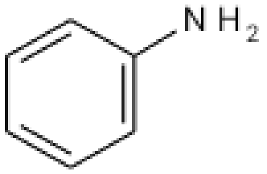
- Amines with more than one type of alkyl group may be named as N-substituted primary amines. The longer alkyl chain determines the base name.
  - Examples
    - N-methylpropylamine $CH_3NHCH_2CH_2CH_3$
    - N,N-dimethylethylamine $(CH_3)_2NCH_2CH_3$

Naming more complex amines

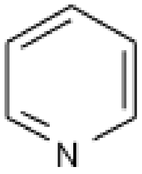
- Amines that have more than one functional group may be named using “amino” as a substituent on the parent molecule.
  - Examples:
    - 2-aminoethanol $H_2NCH_2CH_2OH$
    - 4-aminobutanoic acid $H_2NCH_2CH_2CH_2CO_2H$

Heterocyclic amines

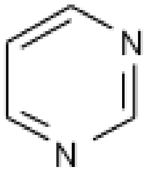
- Some amines have a nitrogen as part of a ring. These generally have common (non-systematic) names, which should be memorized:



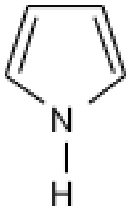
aniline



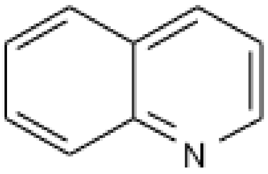
pyridine



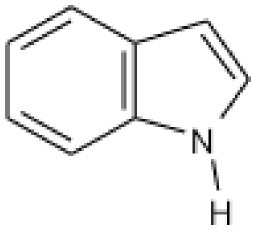
pyrimidine



pyrrole

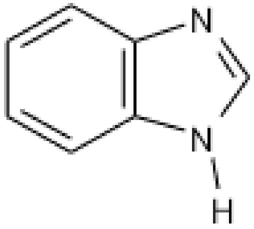


quinoline



indole

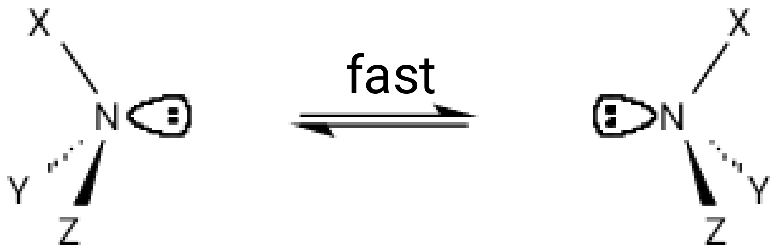
imidazole



benzimidazole

Structure of amines

- Amines have an sp^3 hybridized nitrogen
- In principle, tertiary amines with three different R groups should be chiral (i.e., have a stereocenter).
- However, rapid **pyramidal inversion** of the amine nitrogen prevents isolation of the enantiomers except where the nitrogen is part of a ring or has other geometrical constraint.



Properties of amines

- Amines are moderately polar and are capable of hydrogen bonding.
- Low MW amines (up to about C_5) are soluble in water; higher MW amines will dissolve in acidic solution (as their conjugate acid).
- Amines are weak bases.

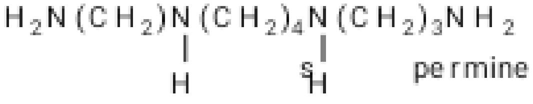
Example of biologically active amines

$H_2NCH_2CH_2CH_2CH_2NH_2$ putrescine

$H_2NCH_2CH_2CH_2CH_2CH_2NH_2$ cadaverine

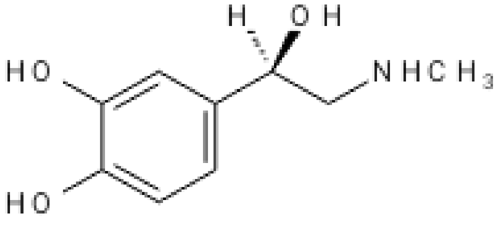
$$H_2NCH_2CH_2CH_2CH_2\underset{H}{\underset{|}{N}}CH_2CH_2CH_2CH_2NH_2$$

spermidine

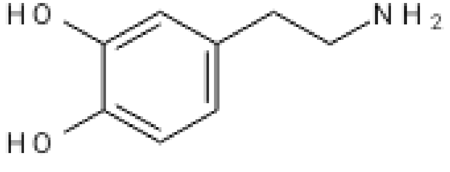


$$H_2N(CH_2)\underset{H}{\underset{|}{N}}(CH_2)_4\underset{H}{\underset{|}{N}}(CH_2)_3NH_2$$

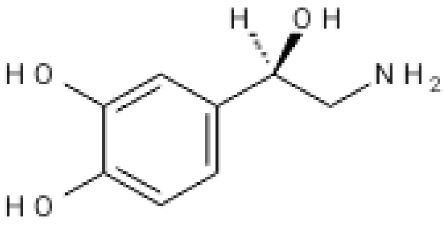
spermine



epinephrine
(adrenaline)



dopamine



norepinephrine
(noradrenaline)

Basicity of amines

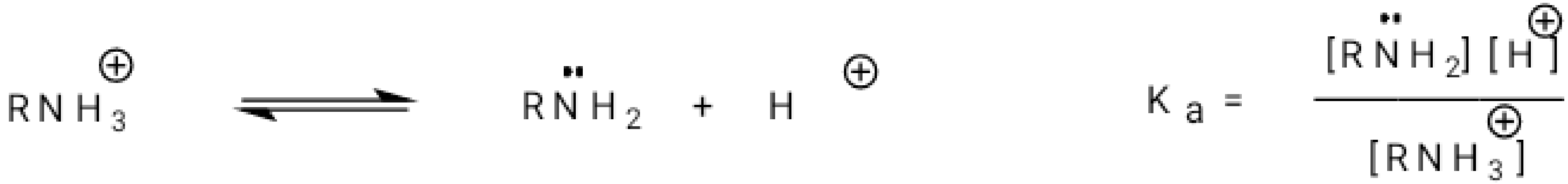
- Amines are slightly basic. This because they have a lone pair of electrons to donate to a proton. This same feature makes them nucleophiles.

$$K_b = \frac{[RNH_3^{\oplus}][OH^{\ominus}]}{[RNH_2]}$$

- Typical amines have K_b values = 10^{-3} to 10^{-4}

Basicity of amines…

- However, instead of measuring an amine’s basicity using the above equilibrium, chemists usually refer to the acidity of the conjugate acid of the amine. The weaker the conjugate acid, the stronger the base strength of the amine.

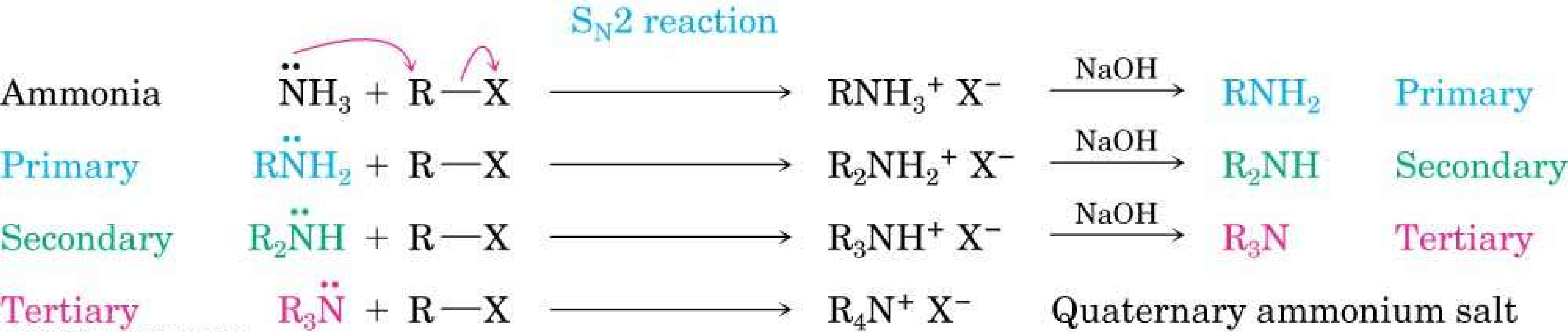


$$RNH_3^{\oplus} \rightleftharpoons R\ddot{N}H_2 + H^{\oplus} \qquad K_a = \frac{[R\ddot{N}H_2][H^{\oplus}]}{[RNH_3^{\oplus}]}$$

- Typical amines have K_a values (of their conjugate acids) of 10^{-10} to 10^{-11} (pK_a values of 10 to 11.)

SN2 Reactions of Alkyl Halides

- Ammonia and other amines are good nucleophiles



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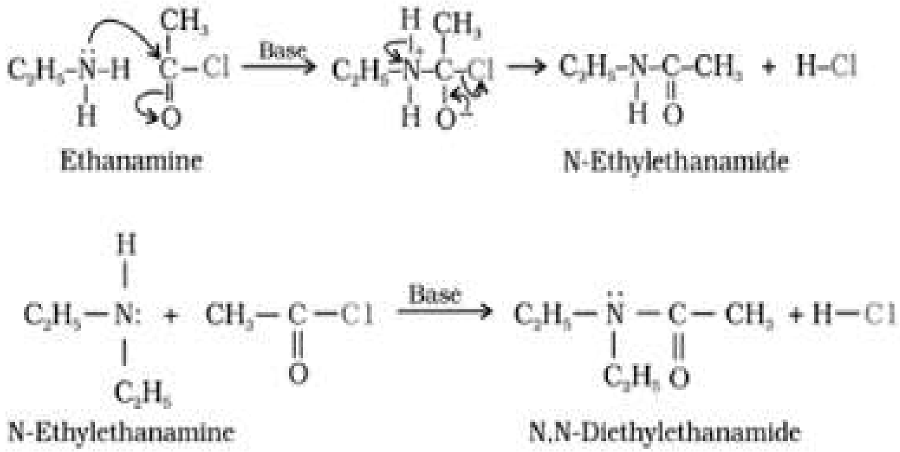
1) Alkylation

Alkylation of 1^0 amine generates 2^0 amine, 3^0 amine and finally the quaternary salts.

$$RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$$

2) Acylation

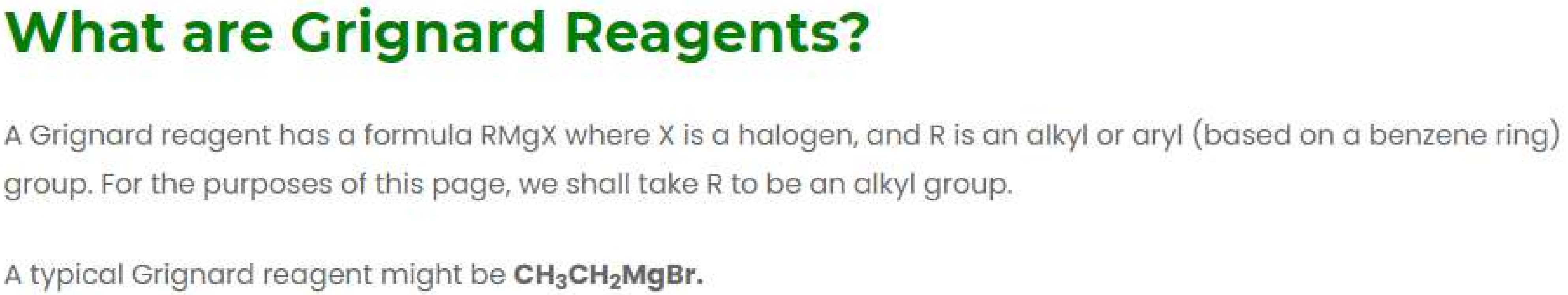
Acylation is the reaction with acid chlorides, anhydrides and esters. These occur by nucleophilic substitution reactions. The reaction is proceeded by the replacement of hydrogen atom of $-NH_2$ or >N–H group by the acyl group (RCOX).



We cannot acylate Tertiary (3°) amine. This is because there is no Hydrogen bonded to nitrogen.

Grignard’s reagent

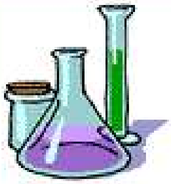
Grignard Reagent



What are Grignard Reagents?

A Grignard reagent has a formula RMgX where X is a halogen, and R is an alkyl or aryl (based on a benzene ring) group. For the purposes of this page, we shall take R to be an alkyl group.

A typical Grignard reagent might be **CH_3CH_2MgBr.**

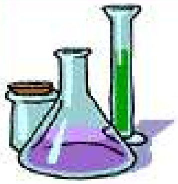


Background

- **<u>Grignard reagents</u>** are highly reactive organometallic reagents generated by treating alkyl or aryl halides with magnesium metal in the presence of an anhydrous ether.
- The reaction proceeds like a strong base reaction.

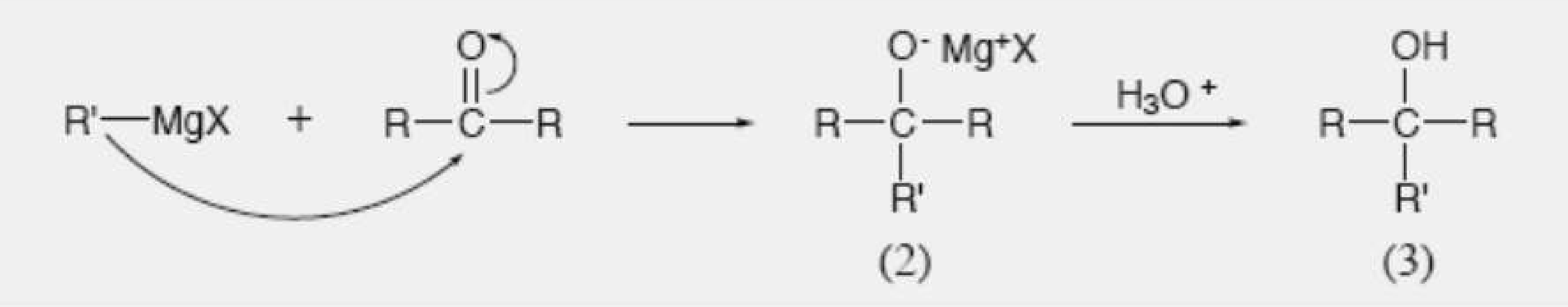
$$R'\text{-}X + Mg \longrightarrow [R'\text{-}X]^{-} + Mg^{+} \longrightarrow \overset{\delta-}{R'} - \overset{\delta+}{MgX}$$

- This reagent was discovered by ***Victor Grignard*** around 1900.



Background

- A Grignard reagent is capable of reacting with many different substrates such as carbonyl compounds, alkyl halides and other organometallic reagents.
- The addition of **Grignard reagents to carbonyl compounds** such as aldehydes, ketones, and esters yields the corresponding **secondary and tertiary alcohols**.



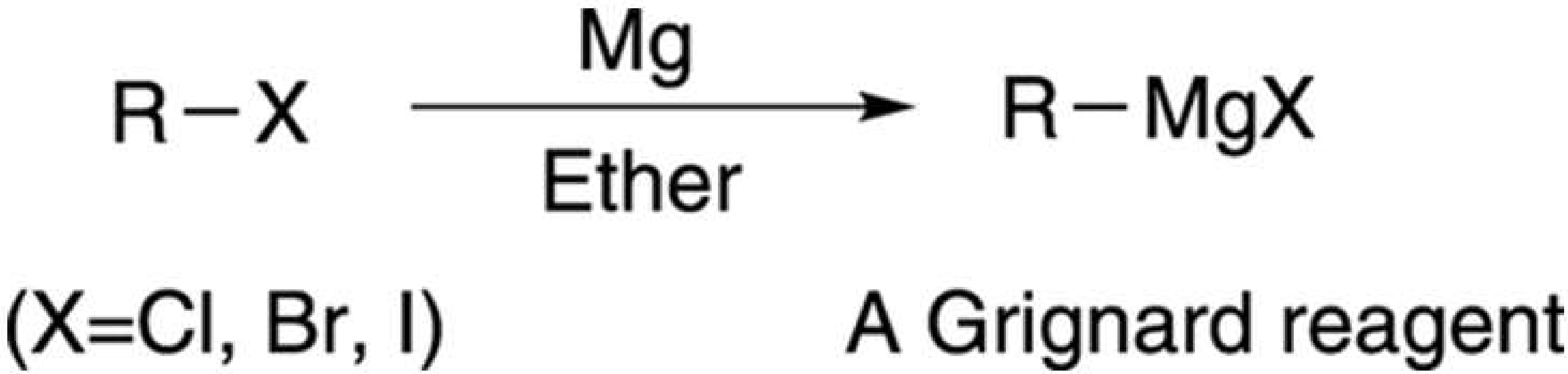
(2)

(3)

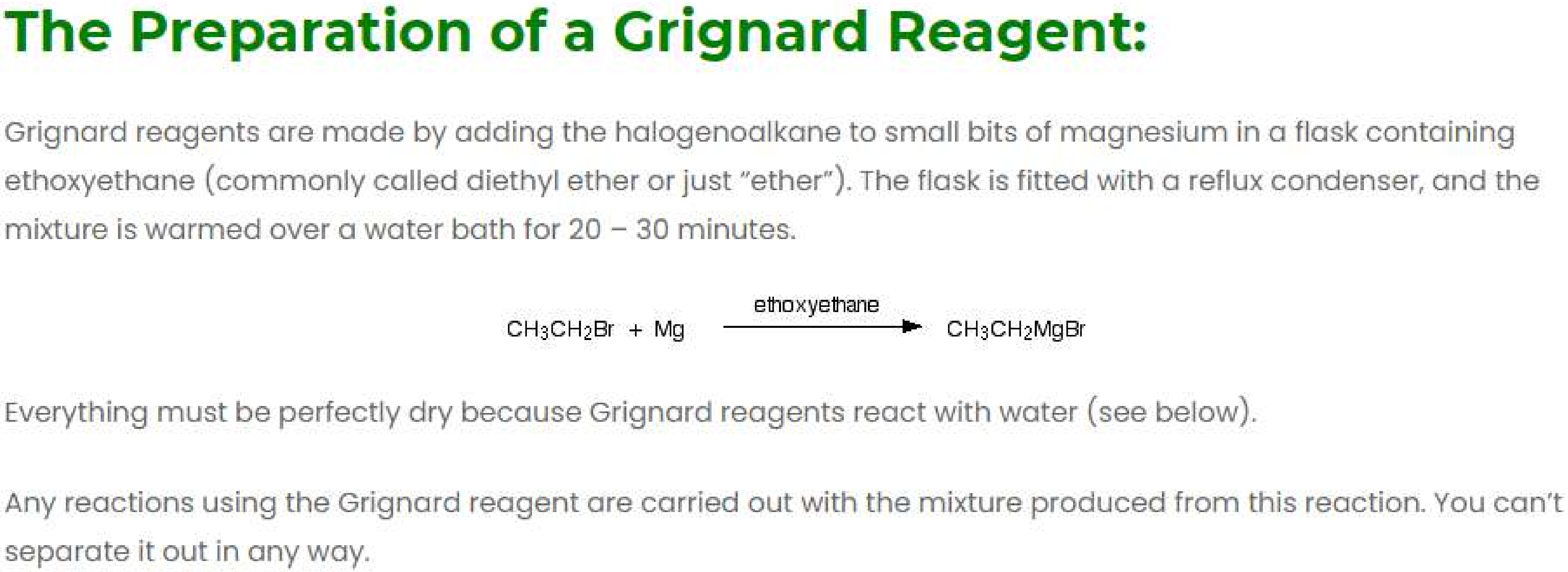
- The **Grignard reaction** results in the formation of a ***carbon-carbon bond***.
- **Grignard reagents** are extremely strong bases that can react violently with hydroxylic compounds such as water or alcohols:

$$R{-}MgBr + H{-}OH \longrightarrow R{-}H + HOMgBr$$

The Preparation of a Grignard Reagent:



$$R-X \xrightarrow[\text{Ether}]{\text{Mg}} R-MgX$$



The Preparation of a Grignard Reagent:

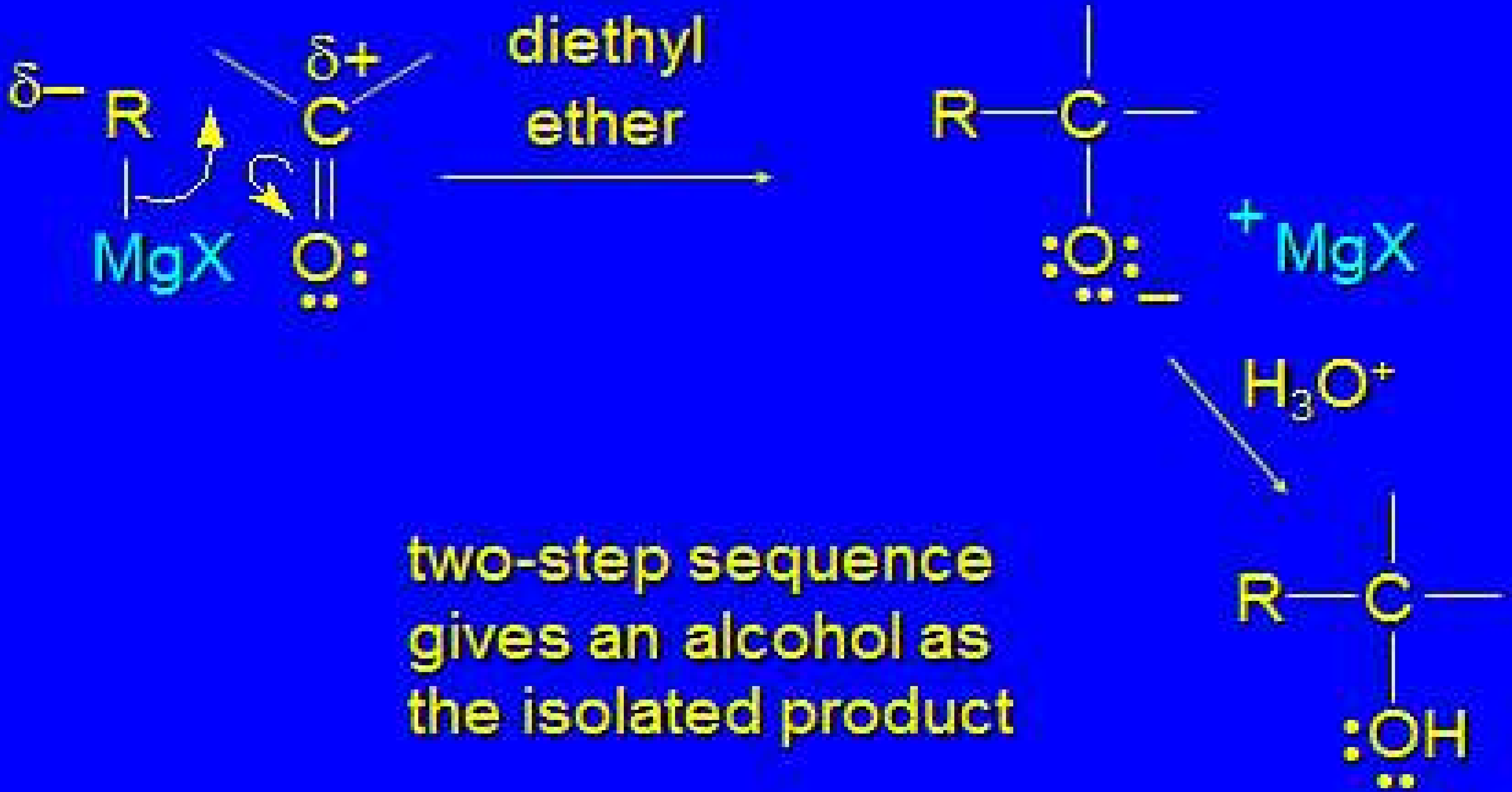
Grignard reagents are made by adding the halogenoalkane to small bits of magnesium in a flask containing ethoxyethane (commonly called diethyl ether or just "ether"). The flask is fitted with a reflux condenser, and the mixture is warmed over a water bath for 20 – 30 minutes.

$$CH_3CH_2Br + Mg \xrightarrow{\text{ethoxyethane}} CH_3CH_2MgBr$$

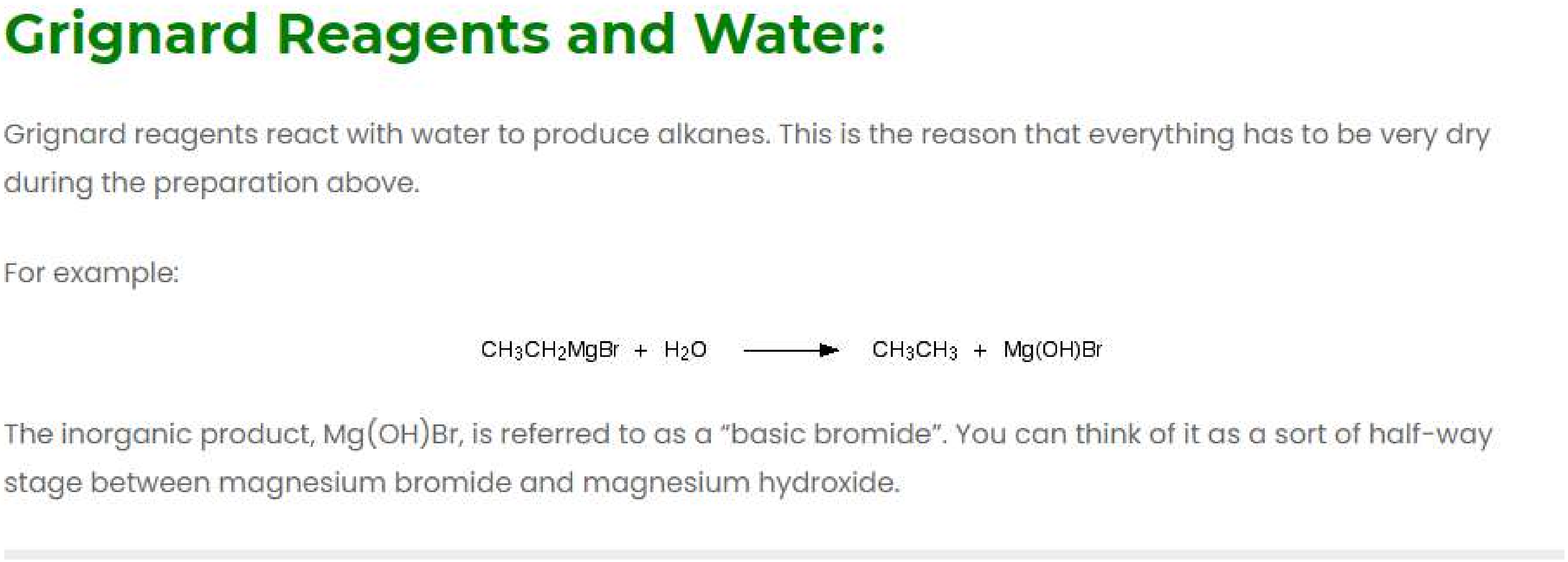
Everything must be perfectly dry because Grignard reagents react with water (see below).

Any reactions using the Grignard reagent are carried out with the mixture produced from this reaction. You can't separate it out in any way.

Grignard reagents act as nucleophiles toward the carbonyl group



two-step sequence gives an alcohol as the isolated product



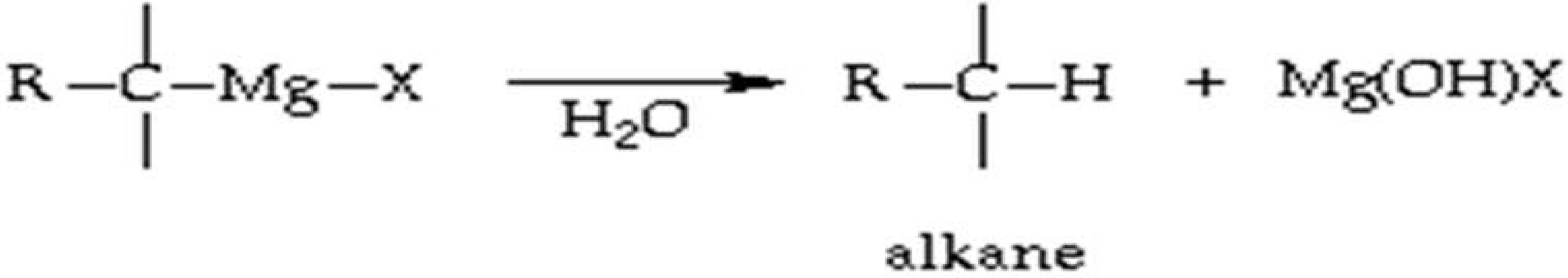
Grignard Reagents and Water:

Grignard reagents react with water to produce alkanes. This is the reason that everything has to be very dry during the preparation above.

For example:

$$CH_3CH_2MgBr + H_2O \longrightarrow CH_3CH_3 + Mg(OH)Br$$

The inorganic product, Mg(OH)Br, is referred to as a "basic bromide". You can think of it as a sort of half-way stage between magnesium bromide and magnesium hydroxide.



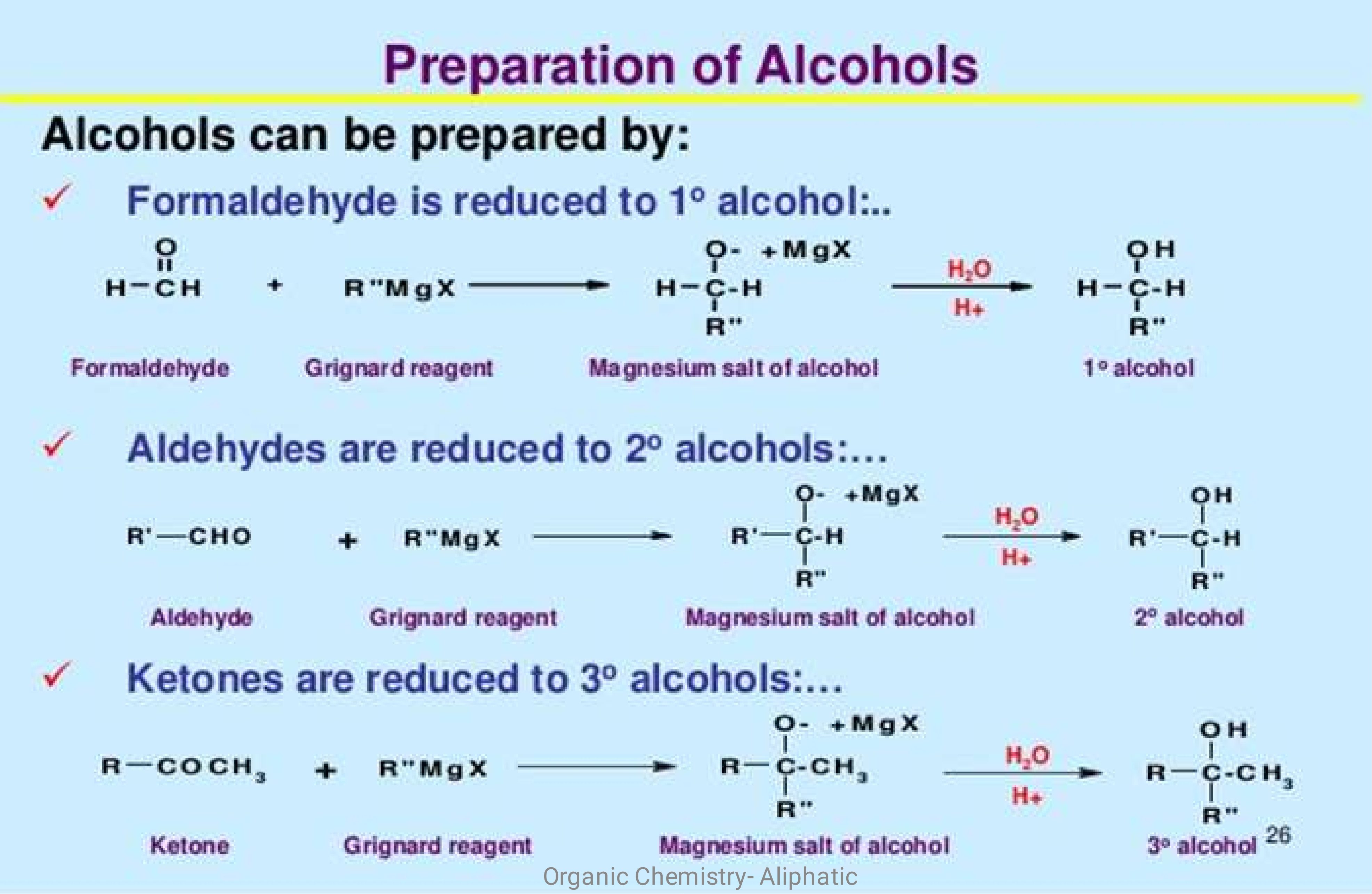
Grignard reagents react with:

formaldehyde to give primary alcohols

aldehydes to give secondary alcohols

ketones to give tertiary alcohols

esters to give tertiary alcohols



Preparation of Alcohols

Alcohols can be prepared by:

- ✓ Formaldehyde is reduced to 1° alcohol:..

$$H-\overset{O}{\overset{\|}{C}}H + R''MgX \longrightarrow H-\underset{R''}{\overset{O^- \quad {}^+MgX}{C}}-H \xrightarrow[H+]{H_2O} H-\underset{R''}{\overset{OH}{C}}-H$$

Formaldehyde · Grignard reagent · Magnesium salt of alcohol · 1° alcohol

- ✓ Aldehydes are reduced to 2° alcohols:...

$$R'-CHO + R''MgX \longrightarrow R'-\underset{R''}{\overset{O^- \quad {}^+MgX}{C}}-H \xrightarrow[H+]{H_2O} R'-\underset{R''}{\overset{OH}{C}}-H$$

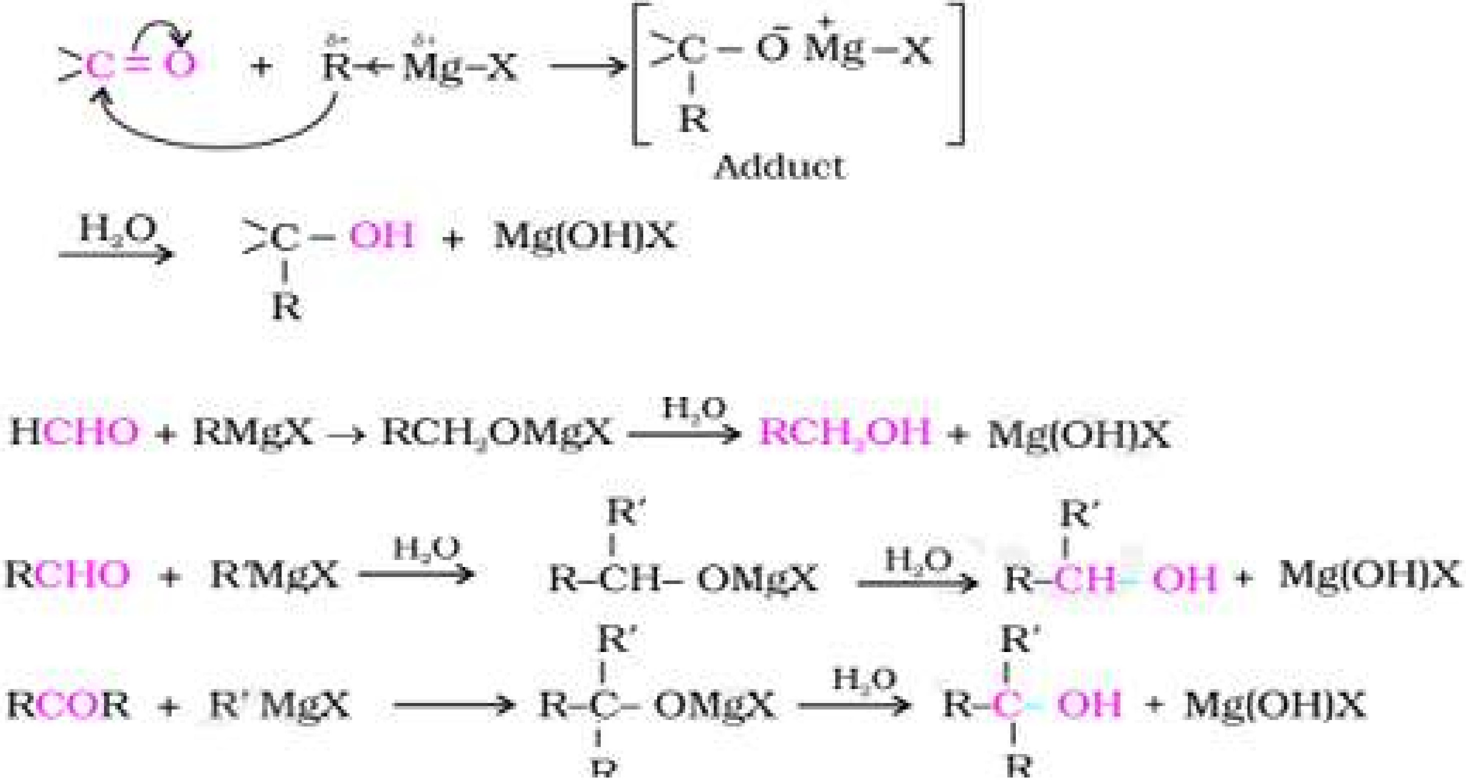
Aldehyde · Grignard reagent · Magnesium salt of alcohol · 2° alcohol

- ✓ Ketones are reduced to 3° alcohols:...

$$R-COCH_3 + R''MgX \longrightarrow R-\underset{R''}{\overset{O^- \quad {}^+MgX}{C}}-CH_3 \xrightarrow[H+]{H_2O} R-\underset{R''}{\overset{OH}{C}}-CH_3$$

Ketone · Grignard reagent · Magnesium salt of alcohol · 3° alcohol

Mechanism



$$>C=O + \overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}-X \longrightarrow \left[>\underset{R}{C}-\bar{O}\,\overset{+}{Mg}-X\right]$$

$$\xrightarrow{H_2O} >\underset{R}{C}-OH + Mg(OH)X$$

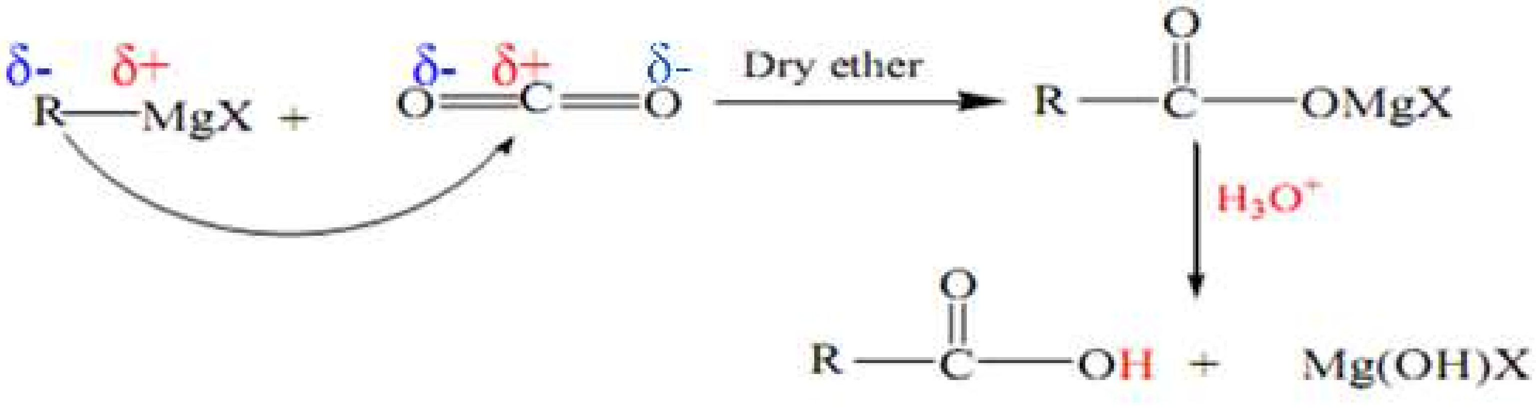
$$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH + Mg(OH)X$$

$$RCHO + R'MgX \xrightarrow{H_2O} R-\overset{R'}{CH}-OMgX \xrightarrow{H_2O} R-\overset{R'}{CH}-OH + Mg(OH)X$$

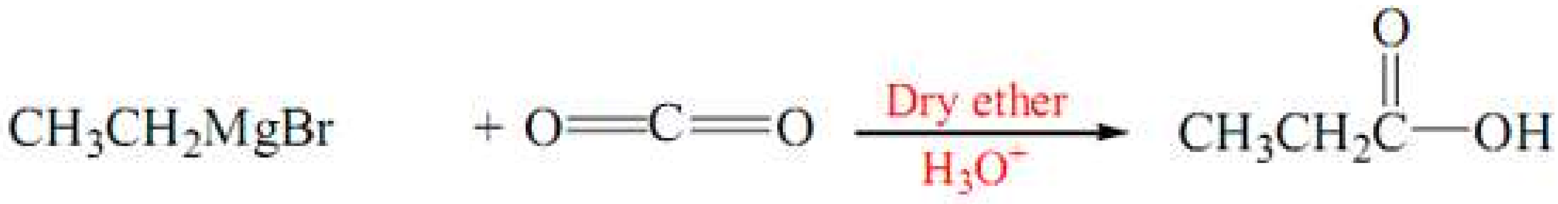
$$RCOR + R'MgX \longrightarrow R-\overset{R'}{\underset{R}{C}}-OMgX \xrightarrow{H_2O} R-\overset{R'}{\underset{R}{C}}-OH + Mg(OH)X$$

The Grignard reagent : an organometallic compound

Grignard Reagents and Carbon Dioxide:



Example



$$CH_3CH_2MgBr + O{=}C{=}O \xrightarrow[H_3O^+]{\text{Dry ether}} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

Chemical Reactions

Chemical Reaction

parts are mixed together to make something new.

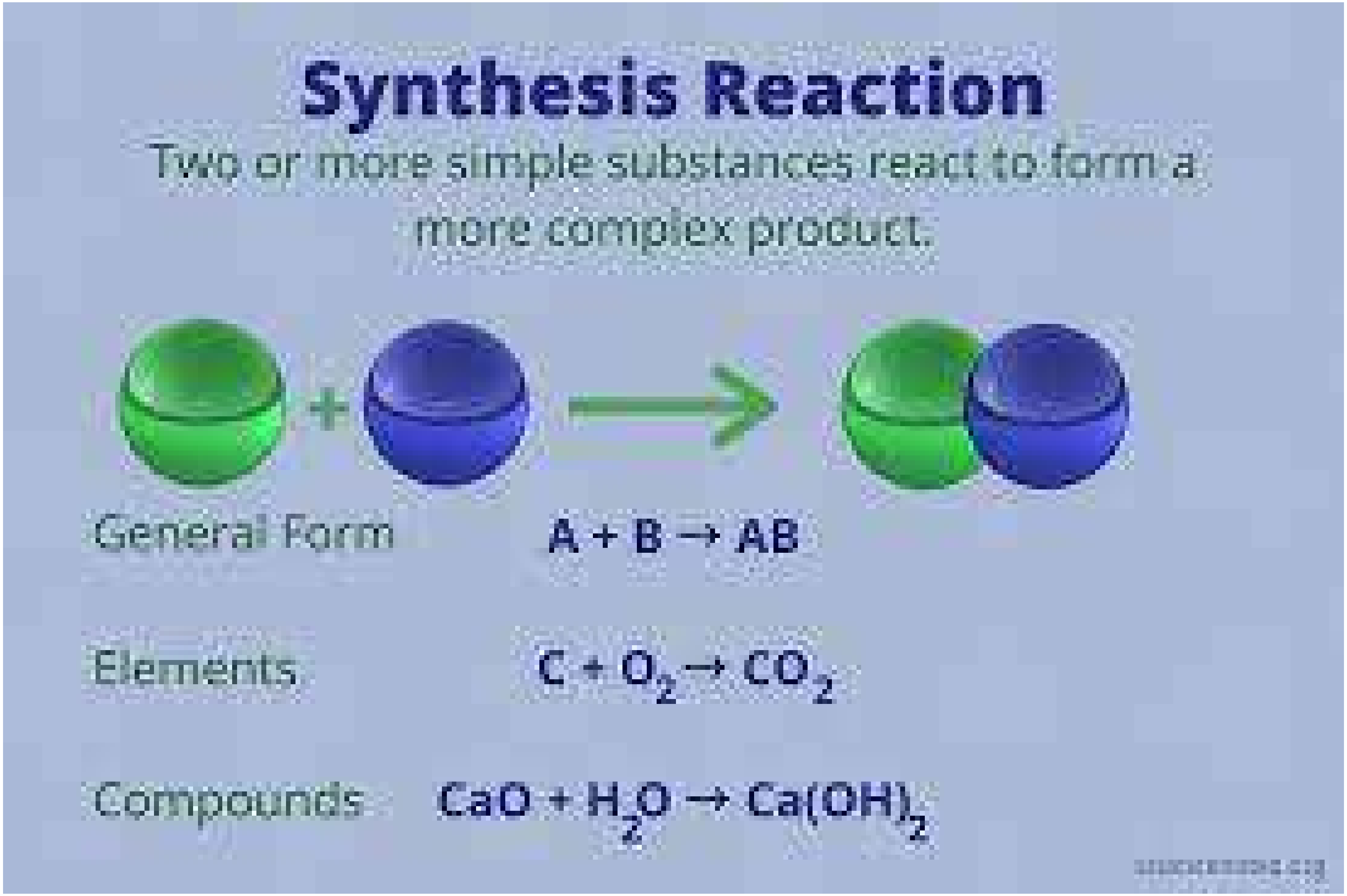
General: $A + B \rightarrow AB$

Types of Reactions

1. Synthesis reactions
2. Decomposition reactions
3. Substitution reactions
4. Addition reactions
5. Elimination reactions

You need to be able to identify each type.

1. Synthesis



Synthesis Reaction

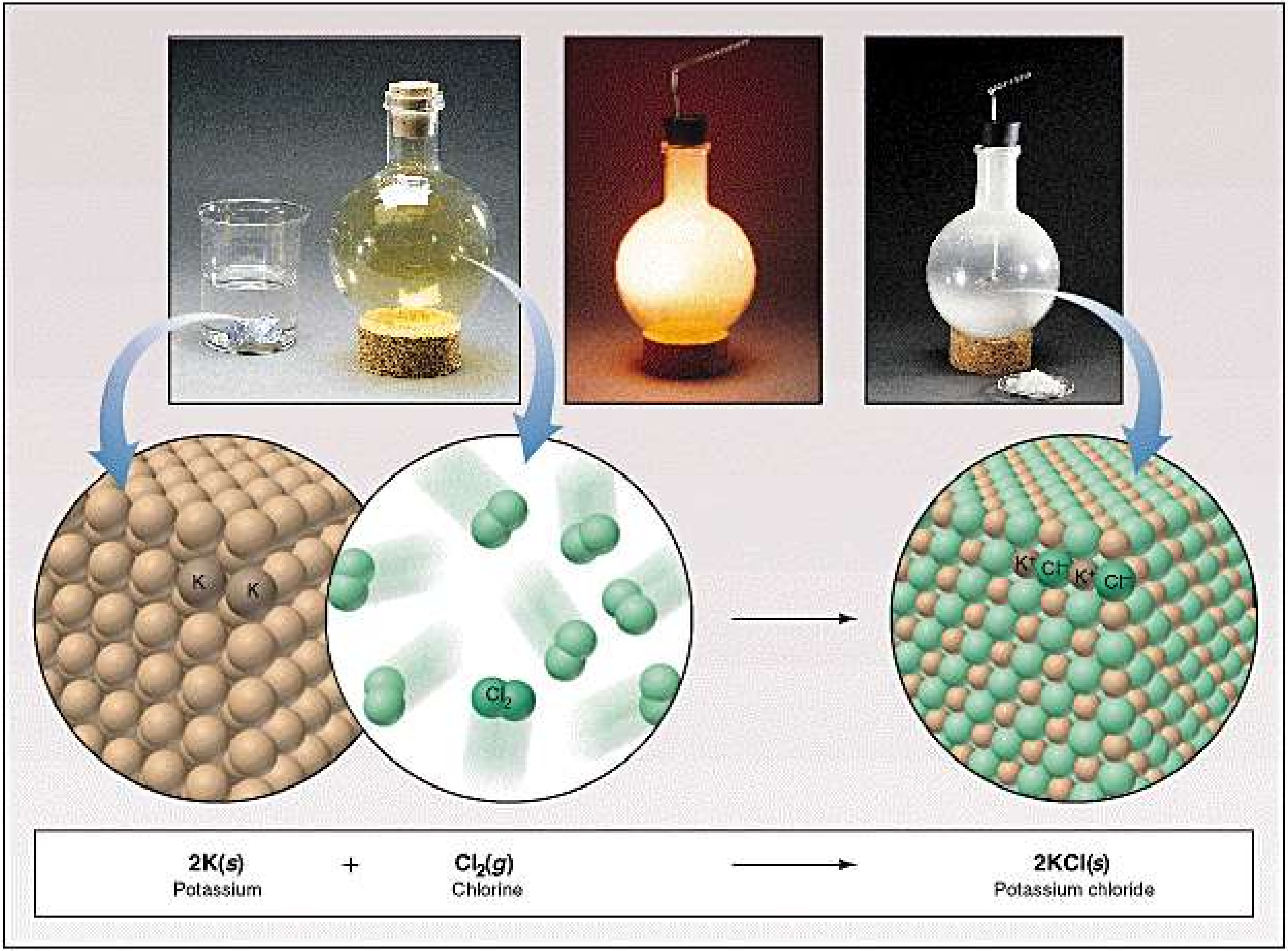
Two or more simple substances react to form a more complex product.

General Form $A + B \rightarrow AB$

Elements $C + O_2 \rightarrow CO_2$

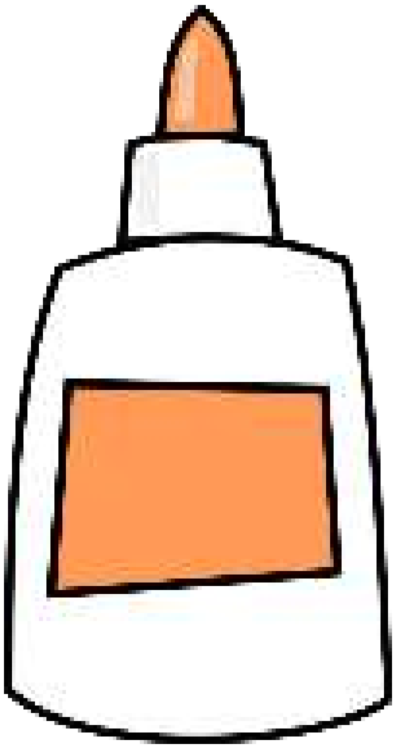
Compounds $CaO + H_2O \rightarrow Ca(OH)_2$

Ex. Synthesis Reaction



$$2K(s) + Cl_2(g) \longrightarrow 2KCl(s)$$

Synthesis



- Predict the products.

$2Na_{(s)} + Cl_{2(g)} \rightarrow$ $2\ NaCl_{(s)}$

$Mg_{(s)}$ 🖃 $F_{2(g)} \rightarrow$ $MgF_{2(s)}$

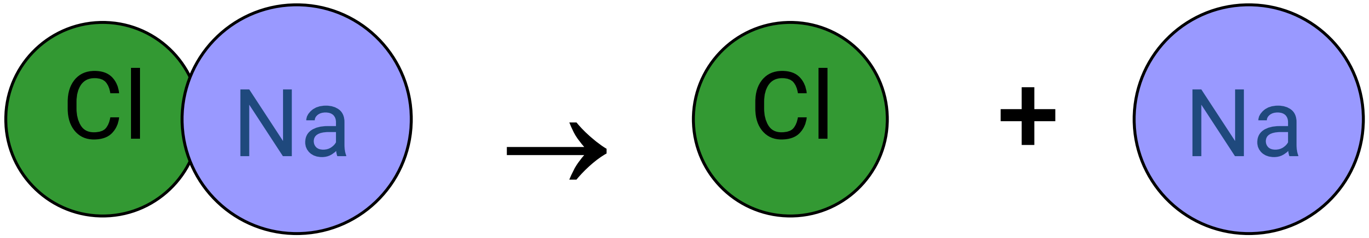
2 3

$Al_{(s)}$ 🖃 $F_{2(g)} \rightarrow$ $2\ AlF_{3(s)}$

Synthesis = join together

2. Decomposition

Example: NaCl



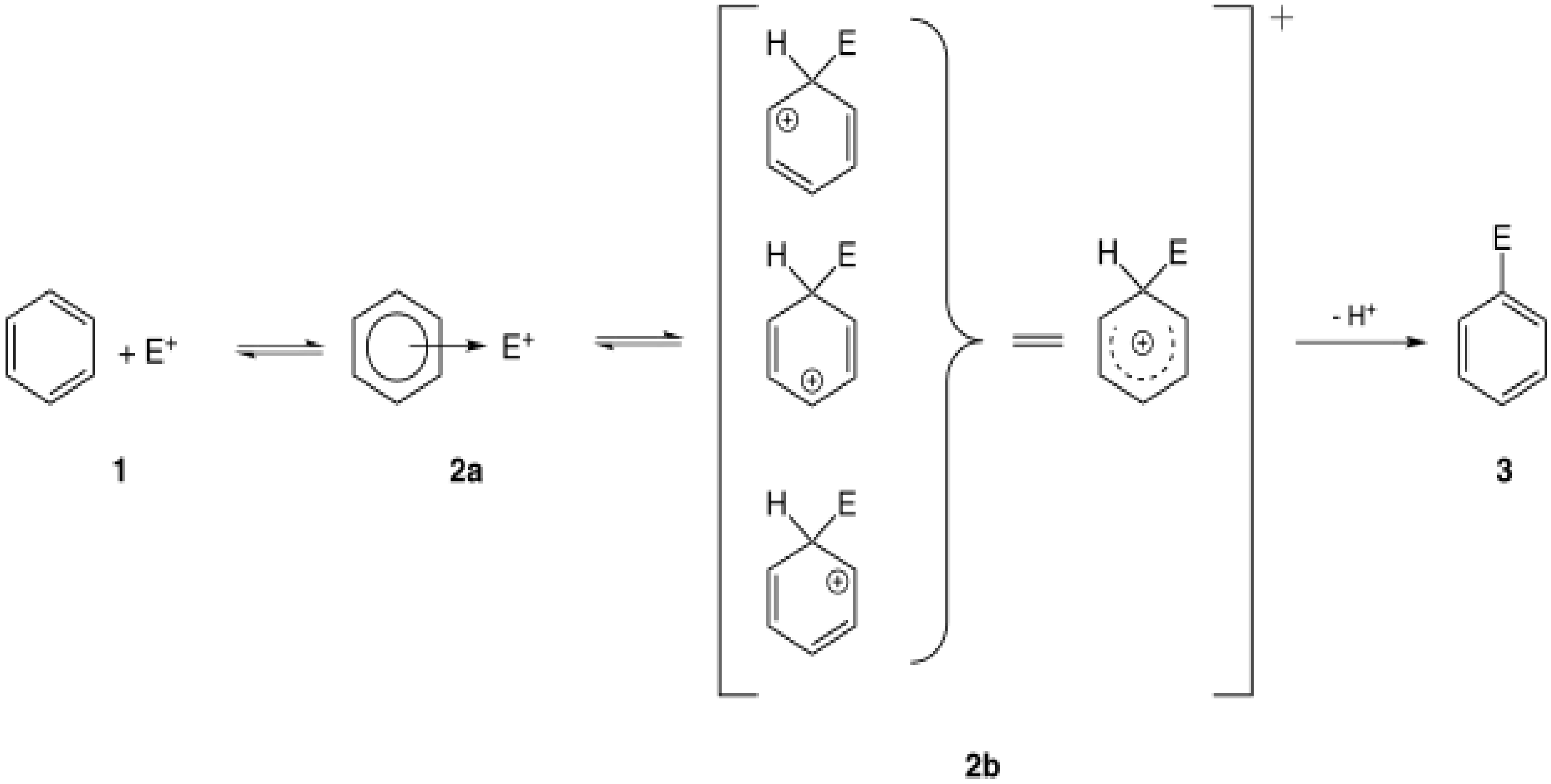
General: $AB \rightarrow A + B$

3. Substitution reaction

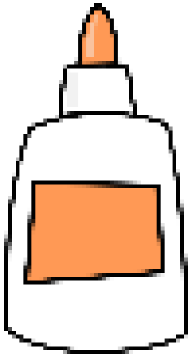
a- Nucleophilic reaction

b- Electrophilic reaction

$$R\text{-}Br + OH^{-} \rightarrow R\text{-}OH + Br^{-}$$


+ E⁺
E⁺
H
E
- H⁺
1
2a
2b
3

Synthesis



join together

A + B → AB

Decomposition

split apart

AB → A 🖃 B

Single Replacement

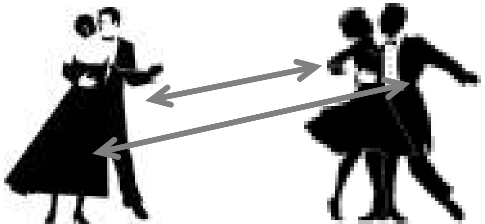
trade 1 place

AB + C → AC 🖃 B

Double Replacement

trade 2 places

AB + CD → AC 🖃 BD



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3- *Smith, Michael B.; March, Jerry (2007), Advanced Organic Chemistry Reactions, Mechanisms, and Structure (6th ed.), New York: Wiley-Interscience, ISBN 978-0-471-72091-1*

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