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Physical Pharmacy

The Liquid State

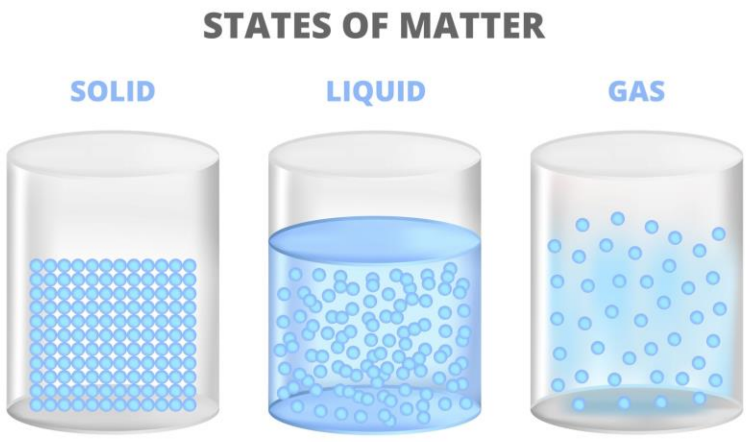
Contents

In this lecture you will learn:

- What is “**Liquid**” and what are the properties of Liquids ?
- What does “**Evaporation**” mean ?
- What is “**Vapor pressure**” and what are factors affecting it ?
- How to calculate **vapor pressure** ?
- What is “**Boiling point**” and what are factors affecting it ?

What is the Liquid State of Matter?

- Liquid is something without which we cannot assume our life.
- It is known to be one of the crucial components for the survival of living **organisms**.
- Liquids represent a compromise between order and disorder.
- In the liquid state, **the atoms or molecules are close to each other** and attractive forces between them are strong enough to hold them in close contact, but not strong enough to hold them in a fixed position like in a solid.



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What is the Liquid State of Matter?

General properties : Matter in liquid state has the following general properties:

- **Shape:**

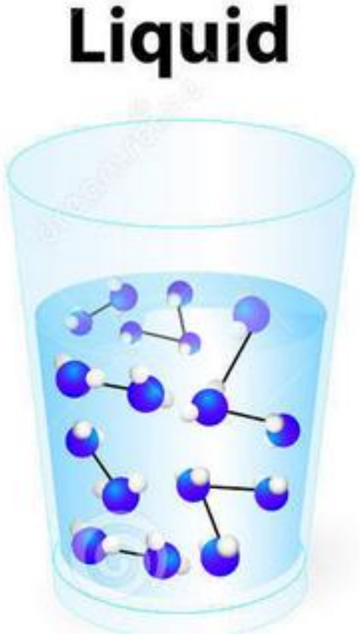
A liquid has no fixed shape but assumes the shape of the container in which it is placed

- **Volume**:

The volume of a given amount of a liquid remains unchanged irrespective of the shape or size of the vessel in which it is present

- **Density**:

a) liquids have densities higher than that of gaseous state under similar conditions.
b) The higher densities of liquids are due to the closer packing of the molecules in the liquid state.



What is the Liquid State of Matter?

General properties : Matter in liquid state has the following general properties:

- **Compressibility:**

a) Liquids are practically incompressible.
b) This is due to the very little free space available in the liquids.

- **Kinetic energy:**

Molecules in liquids also typically have lower kinetic energy compared to those in gases.

- **Diffusion:**

Rate of diffusion is much slower than in gases, and unlike gases, liquids do not disperse to all the space of the container.

- **Flowability:**

Liquids tend to flow readily in response to external forces.

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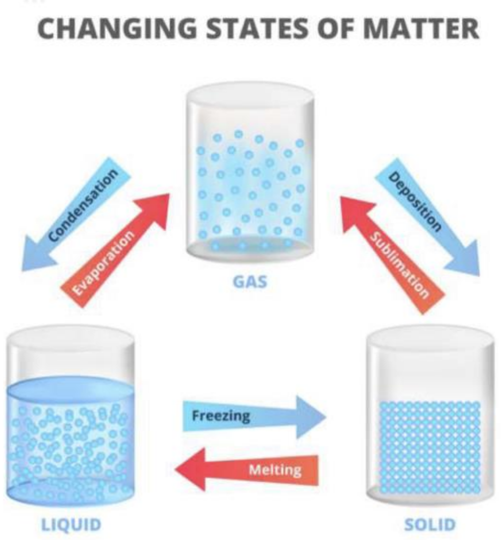
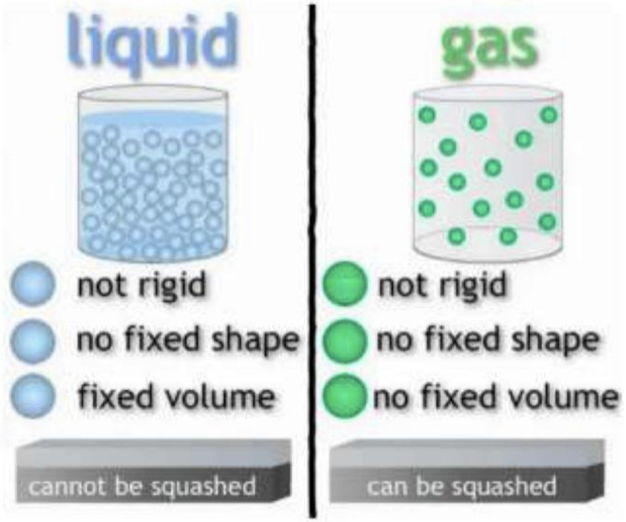
PHASE CHANGES :

- Evaporation: Liquid ⟶ Gas
- Condensation: Gas ⟶ Liquid
- Melting: Solid ⟶ Liquid
- Freezing: Liquid ⟶ Solid
- Sublimation: Solid ⟶ Gas





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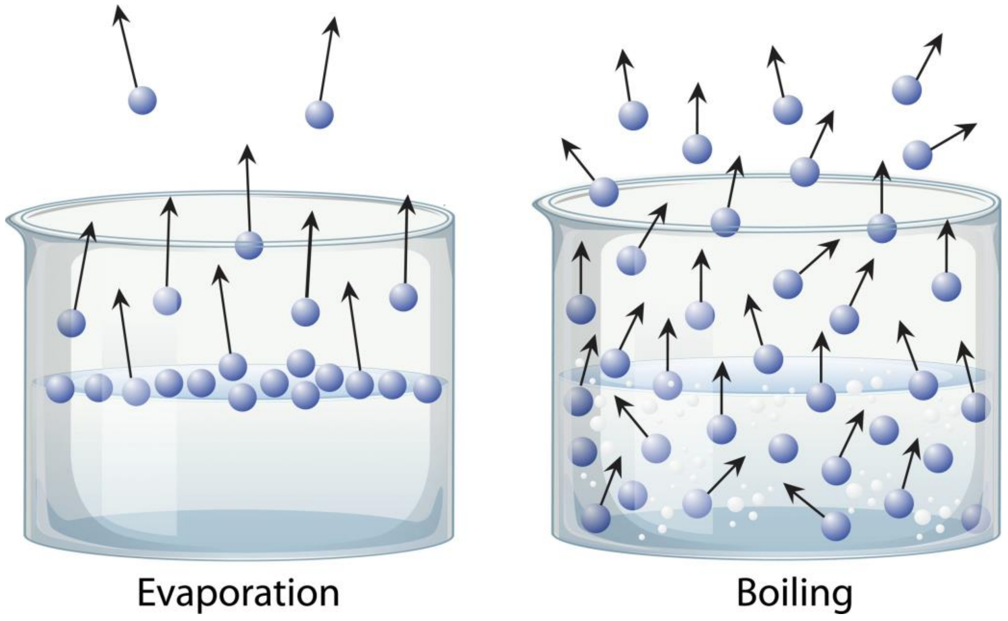
EVAPORATION

- **Evaporation**: is the process of escaping of molecules from liquid surface to vapour (or gaseous) state
- Does evaporation process differ when it occurs in a closed or open system ??



Evaporation which has reached equilibrium with the liquid surface is said to have reached saturation,

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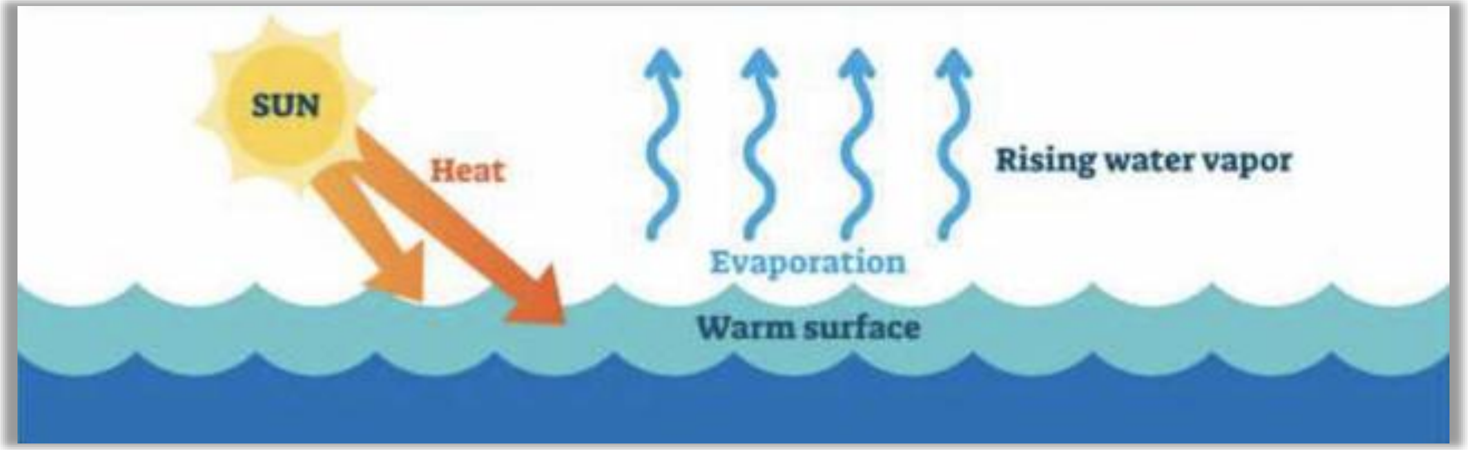
EVAPORATION



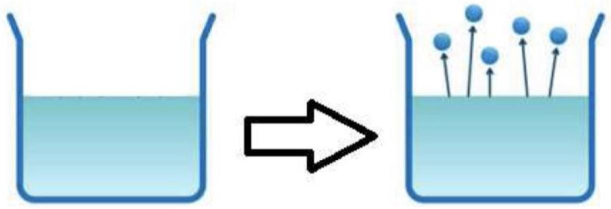
COHESIVE FORCES KEEP MOLECULES TOGETHER, EVAPORATION IS THE ESCAPE.

EVAPORATION

To explain the evaporation process:

- Assume you have a liquid in a container: **Initially** there will be no vapor or gas above that liquid.

- After some time, the molecules at the surface of the liquid (have higher kinetic energy than those in the bulk) will escape (leave) the liquid and form vapor **(evaporation takes place)**



Evaporation process in open system

- As the molecules with high kinetic energies keep on leaving the liquid phase by evaporation, the average kinetic energy of the remaining molecules continues to fall.

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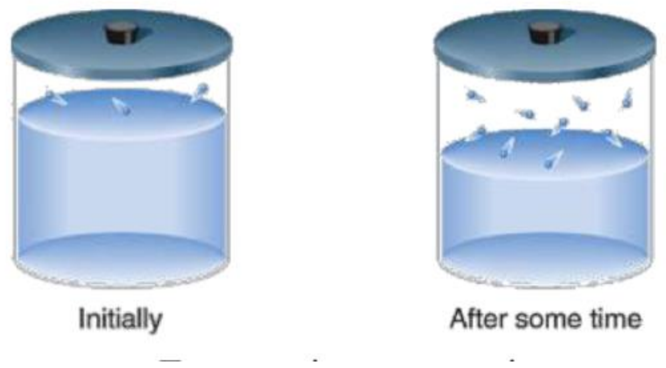
EVAPORATION

To explain the evaporation process:

- This is because each escaping molecule takes away with it more than the average amount of energy.

- Since the molecules left behind have lower average kinetic energy, the temperature of liquid falls .

- This is how evaporation causes cooling.



Evaporation process in open system

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EVAPORATION

Note:

- When evaporation takes place in a closed and limited space (closed evacuated vessel) at constant temperature, evaporation proceeds for some time and then seems to stop.
- This is due to the fact that an equilibrium is established.
- **This is explained as follows:**
- The molecules of the liquid which escape into the vapour phase exert a pressure on the liquid phase.
- Such pressure exerted by the vapor is called the vapor pressure (Vapor pressure is a physical property of pure liquids and solutions).
- At a particular temperature, the concentration of the vapor and the pressure that it exerts becomes constant.

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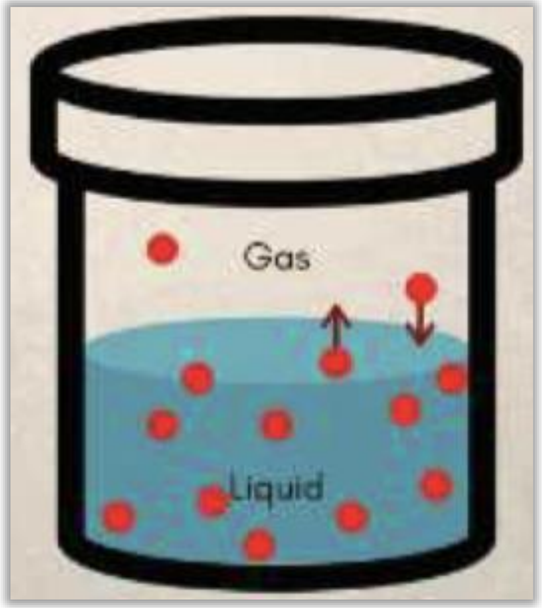
EVAPORATION

- When the **Rate of evaporation = Rate of condensation** we say the system is at dynamic equilibrium known as phase equilibrium in which the **liquid level will remain constant.**

- The vapor pressure at this point is known as **equilibrium vapor pressure.**

- **So:** Equilibrium vapor pressure is the pressure of a saturated vapor above its liquid state.



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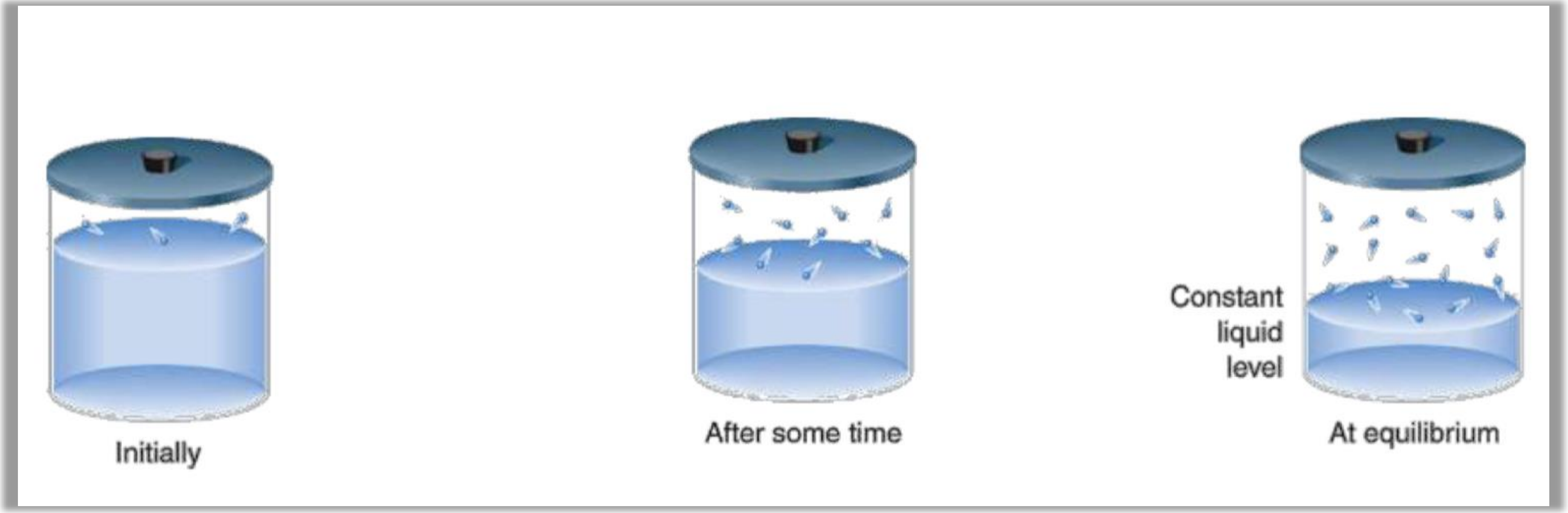
EVAPORATION



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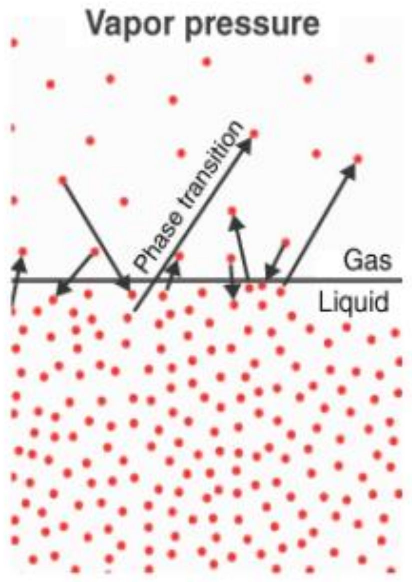
EVAPORATION

Factors affecting vapour pressure:

1. Nature of liquid (i.e, intermolecular forces)

- Each liquid has a **characteristic vapour pressure** at a given temperature.
- This is because each liquid has different magnitudes of intermolecular attractive forces and, therefore, different tendencies to evaporate.
- Those molecules that have strong **intermolecular attractive forces** have lower vapor pressures than expected.



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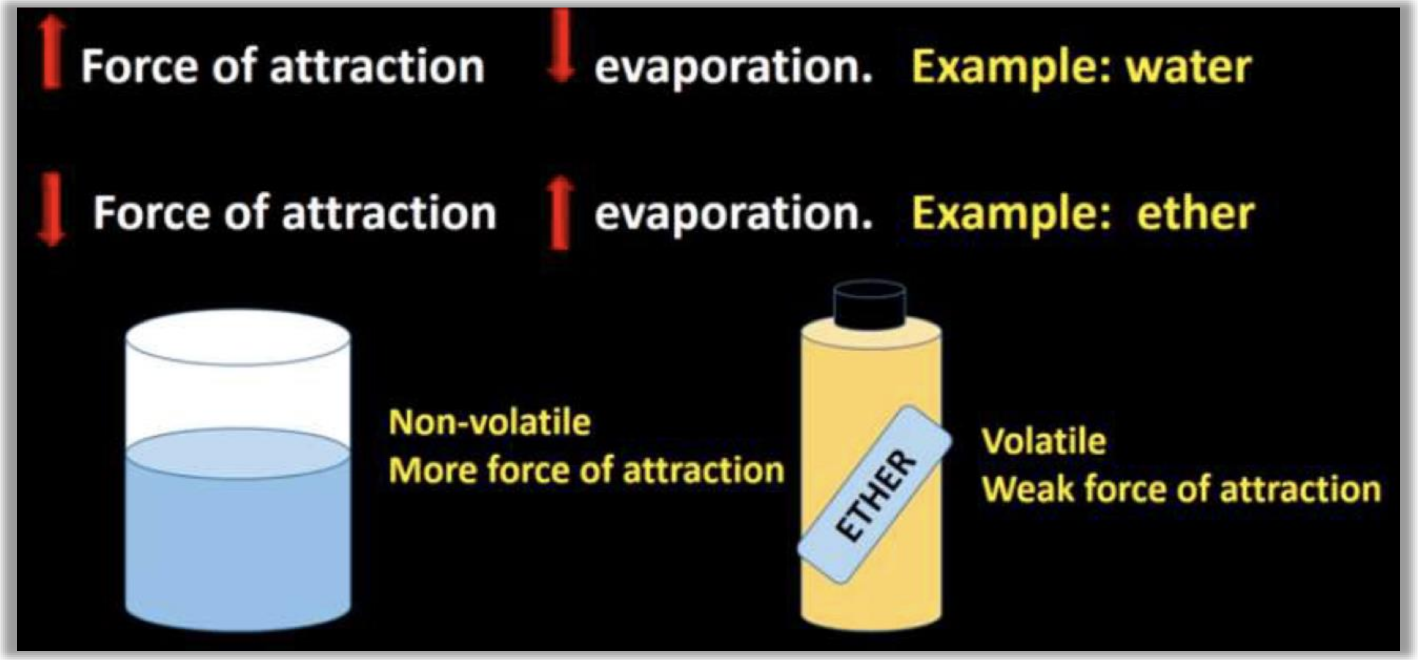
Factors affecting vapour pressure:

- **For example:** water contains strong hydrogen bonds, so it has a lower vapor pressure than ether, which has weaker intermolecular forces acting between its molecules.



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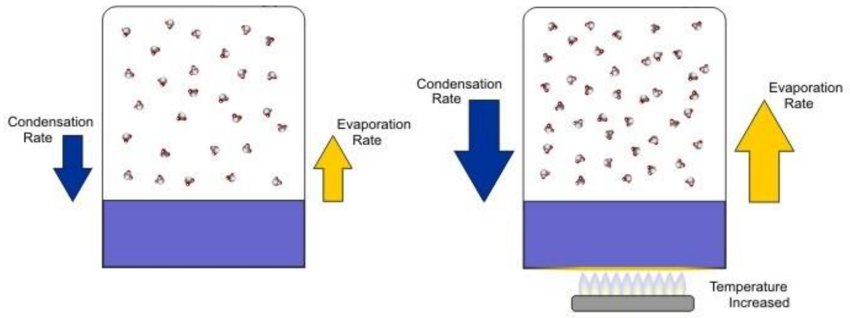
EVAPORATION

Factors affecting vapour pressure:

2. Temperature :

- The vaporization and condensation process is affected by the kinetic energy of molecules

- The **vapour pressure** of every liquid increases, as the **temperature of the liquid increases**



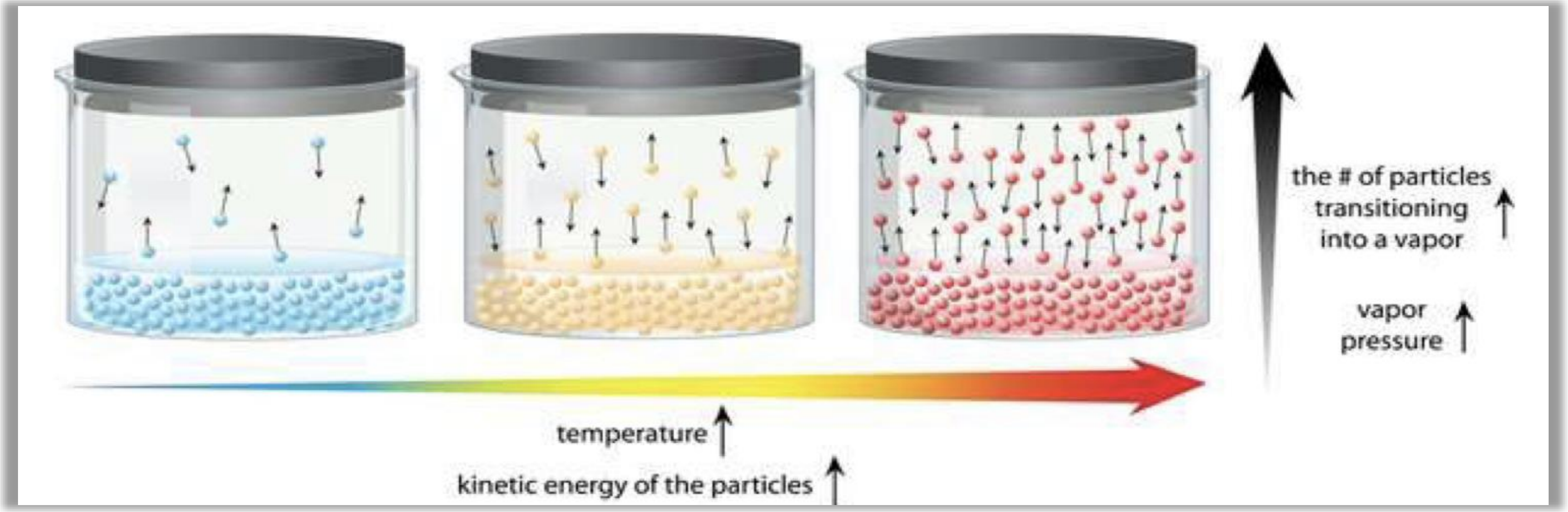
- **This is explained as follows:**

a) As the temperature of the liquids is increased, **the average kinetic energy** of the molecules of the liquid increases, with this the number of energetic molecules capable of escaping into the vapour phase also becomes large.

EVAPORATION

Factors affecting vapour pressure:

b. As a result, the rate of evaporation and the concentration of the molecules in the vapour phase increase.



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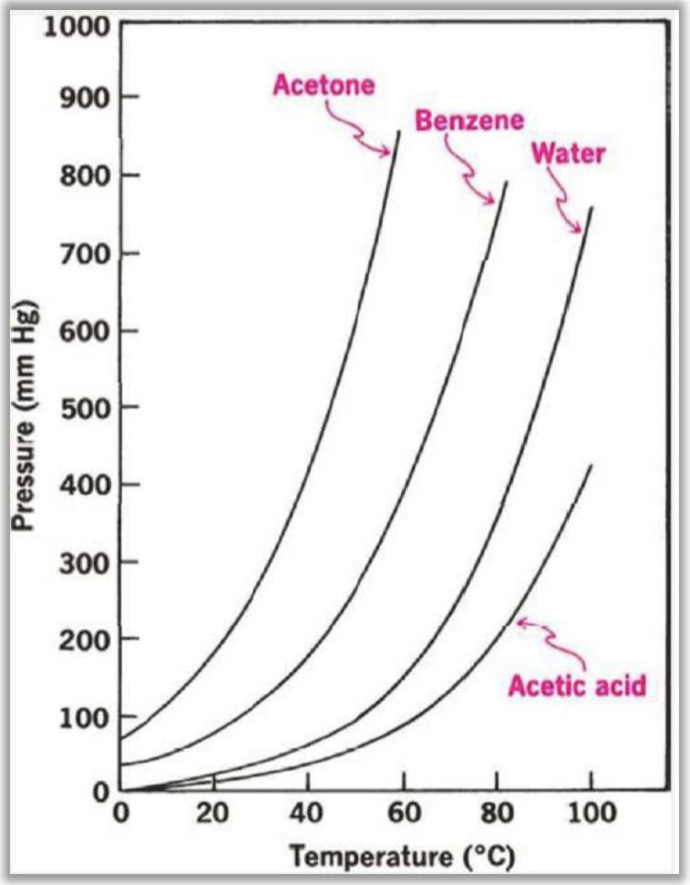
EVAPORATION

Factors affecting vapour pressure:

c. Any point on any one of the curves represents a condition in which the liquid and the vapor exist together in equilibrium

- **At constant temperature, increasing the pressure, the liquid will form a vapor**

- **At constant pressure, increasing the temperature, the liquid will form a vapor**



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EVAPORATION

Factors affecting vapour pressure:

substance	vapor pressure at 25°
diethyl ether ($CH3CH2OCH2CH3$)	0.7 atm
bromine	0.3 atm
ethyl alcohol ($CH3CH2oH$)	0.08 atm
water	0.03 atm

- **The relatively weak dipole-dipole forces and London forces between diethyl ether molecules results in a much higher vapor pressure compared to ethyl alcohol.**

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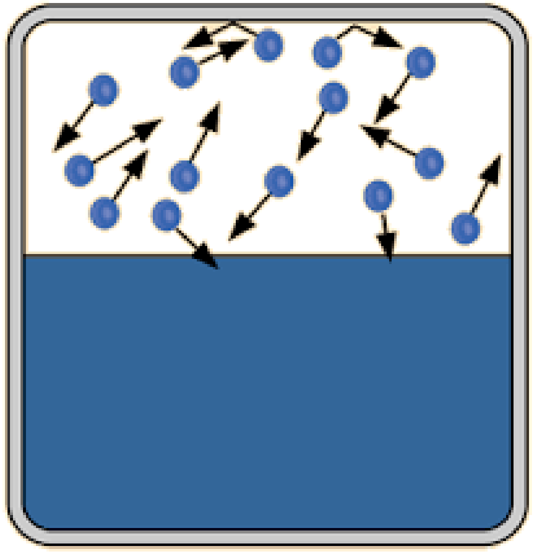
EVAPORATION

How to Calculate Vapor Pressure ?

- **Clausius-Clapeyron equation :** The relationship between the vapor pressure and the absolute temperature of a liquid is expressed by the"**Clausius-Clapeyron Equation“**

$$\log \frac{P2}{P1} \quad \frac{\Delta H_v(T2-T1)}{2.303RT1T2}$$

- where **p1** and **p2** are the vapor pressures at absolute temperatures **T1** and **T2**, and **ΔHv** is the molar heat of vaporization



EVAPORATION

How to Calculate Vapor Pressure ?

- **Molar heat of vaporization (ΔHv)** is the amount of heat necessary to vaporize one mole of the liquid at constant temperature.

- **Molar heat of vaporization** is a property of a substance which gives a measure of the intermolecular attractive forces characteristic of the liquid.

- **For example**: the heat of vaporization of water at **100 °C is 40.6 kJ per** mole while that of benzene at **80 °C is 31 kJ per mole**.

- Means attractive forces between **water molecules** are stronger than between **benzene molecules.**

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EVAPORATION

Clausius-Clapeyron equation: Example

Example: Compute the vapor pressure of water at 120°C, The vapor pressure of water at 100°C is 1 atm, and AHv is 9720 cal/mole.

Sol :

$$\log \frac{P2}{P1} = \frac{\Delta H(T2-T1)}{2.303RT1T2}$$

$$\log \frac{p2}{1} = \frac{9720(393-373)}{2.303x\ 1.987\ x\ 393x\ 373}$$

$$P2 = 1.9\ atm$$

P1 = 1 atm

P2 = ?

AH T2-Ti)

T1 = 100 + 273 = 373 K

T2 = 120 + 273 = 393 K

R = 1.987 cal/mol.kelvin

ΔHv = 9720

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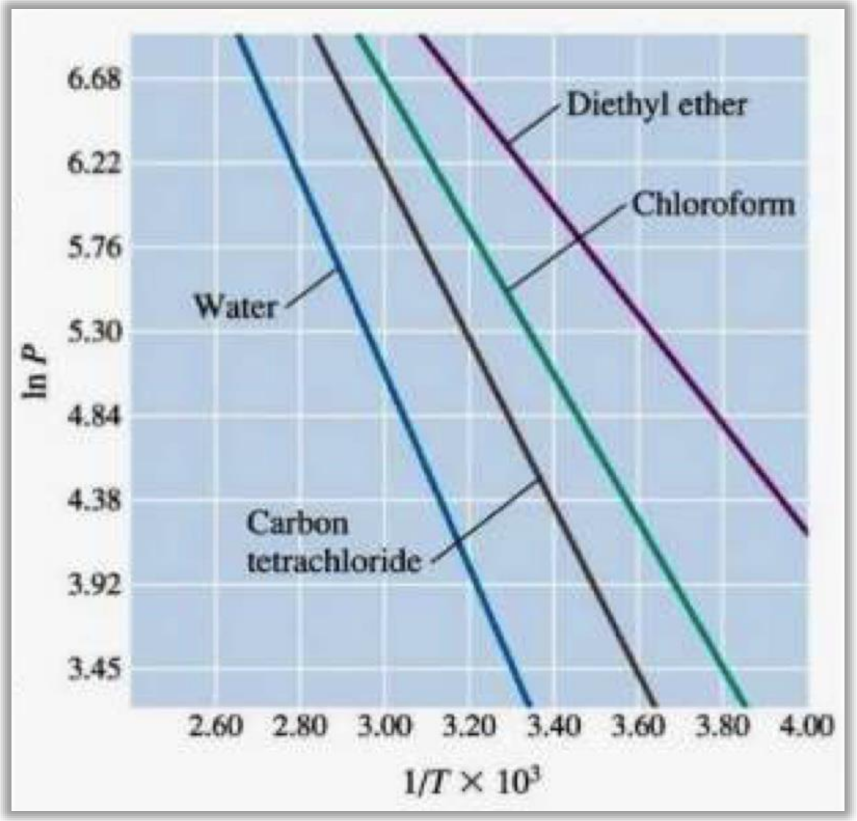
Evaporation

Clausius-Clapeyron equation

- **The Clausius Clapeyron equation can be written in a more general form:**

$$\log p = \frac{\Delta H_v}{2.303}\frac{1}{RT} + constant$$

- Aplot of logP against **1/T** results in a straight line.
- The heat of vaporization of the liquid can be calculated from the slope of the line.



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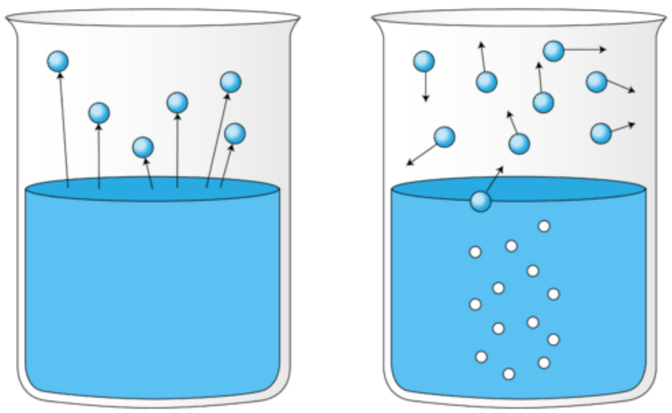
Boiling point

- When a liquid is heated in an open container, with the rise in temperature: its **vapour pressure** keeps on increasing till it becomes equal to the atmospheric pressure **(which is equal to 1 atm or 760 mm of Hg.)**

- At this point, molecules of the **liquid are readily converted to the vapour phase which form bubbles** that rise rapidly through the liquid and escape into gaseous state and the liquid is said to boil.

Evaporation | Boiling



Vapor Pressure < Atmospheric Pressure
Bubbles cannot form

Vapor Pressure = Atmospheric Pressure
Bubbles can form and rise

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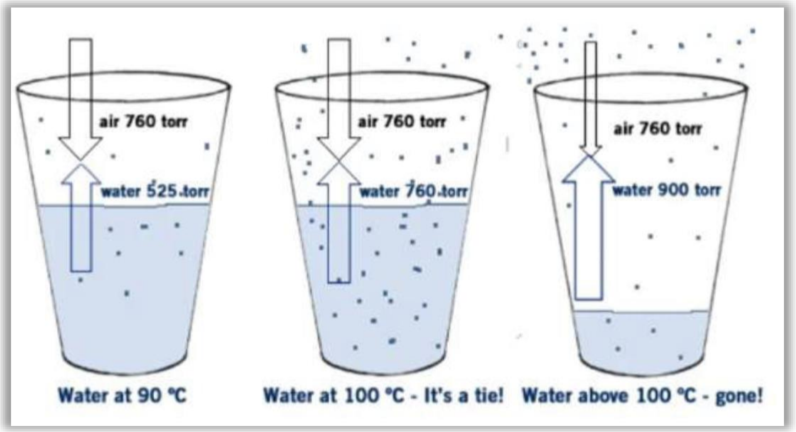
Boiling point

- The temperature at which **vapour pressure** of the liquid becomes equal to the atmospheric pressure is known as the **boiling point** of the liquid.

- The absorbed heat used to change the liguid to vapor (**at constant temperature i.e., boiling point**) is called the **latent heats of vaporization.**

- Liquids with **low vapor pressures** require considerably more energy to increase the vapor pressure to the point where it matches the applied pressure, thus, they **have relatively high boiling points**



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Boiling point

Factors that affect on boiling point :

1. Atmospheric pressure

- Changing altitude will cause a change in atmospheric pressure and therefore, a change in boiling point as follows:

a) **At** higher elevations, the atmospheric pressure decreases and the boiling point is lowered.

b) **At** a pressure of **700 mm Hg**, water boils at **97.7°C**; at **17.5** mm Hg, it boils at **20°C**.

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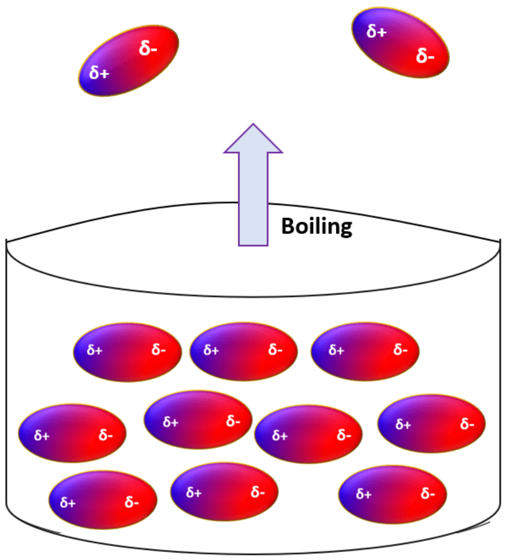
Boiling point

Factors that affect on boiling point :

2. Intermolecular Forces

- The boiling point may be considered the temperature at which thermal agitation can overcome the attractive forces between the molecules of a liquid.

- Therefore, the boiling point of a compound, like the heat of vaporization and the vapor pressure at a definite temperature, provides a rough indication of the magnitude of the attractive forces.



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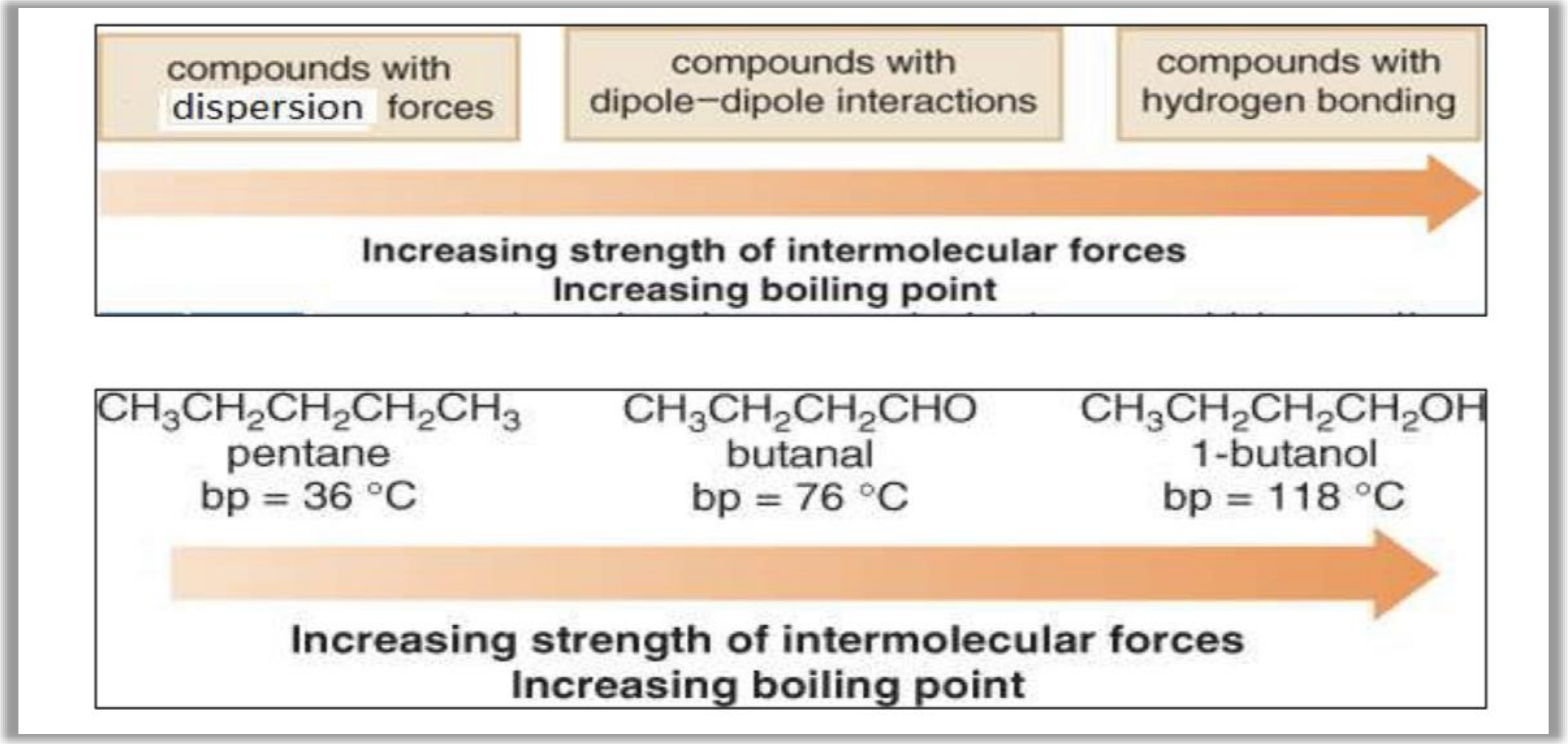
Boiling point

Factors that affect on boiling point :



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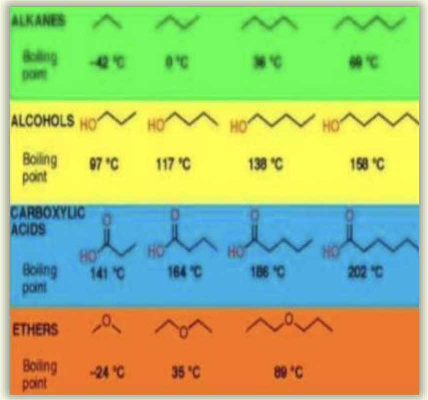
Boiling point

Factors that affect on boiling point :

Molecular weight

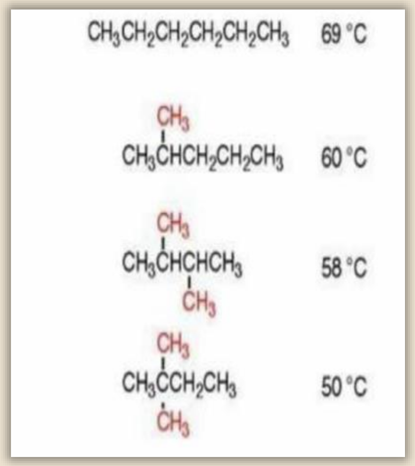
- The boiling points of normal hydrocarbons, simple alcohols, and carboxylic acids increase with molecular weight because van der Waals forces become greater with increasing numbers of atoms.



Larger surface (more electrons) → more sites of interaction →↑ B .p.

Molecular shape

- Branching of the chain produces a less compact molecule with reduced intermolecular attraction, and a decrease in the boiling point.



With the same molecular weight, boiling point of Linear > Branched

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Boiling point

Factors that affect on boiling point :

2. Intermolecular Forces

- Polar molecules (e.g water) exhibit high boiling points and high heats of vaporization because they are associated through hydrogen bonds.

- Non polar substances have low boiling points and low heats of vaporization because the molecules are held together predominantly by the weak London forces.

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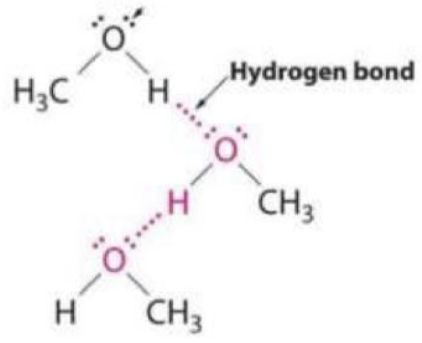
Boiling point

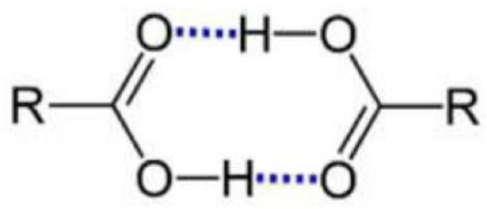
Factors that affect on boiling point :

2. Intermolecular Forces

- Alcohols boil at a much higher temperature than saturated hydrocarbons of the same molecular weight because of association of the alcohol molecules through hydrogen bonding.



- The boiling points of carboxylic acids are higher than that of alcohols because the acids form dimers through hydrogen bonding.



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Thank You !

https://t.me/Dr_Cube