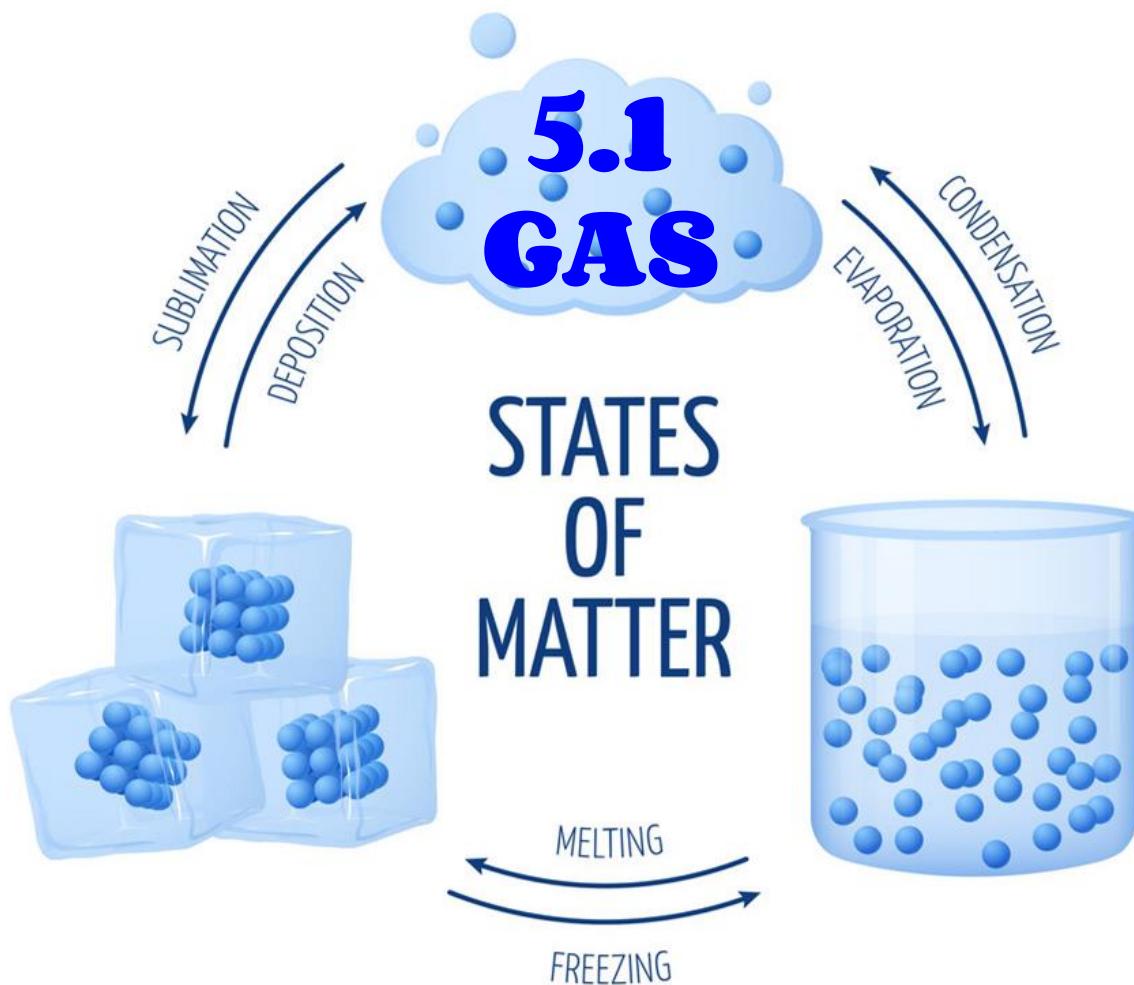


CHAPTER 5

STATES OF MATTER



KINETIC MOLECULAR THEORY OF GASES

Basic assumption (Postulates) :

1. The **size** of gas particles is extremely **small** compared with **volume** of container
 - ☞ **volume** of gas particles is **negligible**
2. Gas particles are in **constant** and **random** motion
 - ☞ they **frequently collide** with one another and with the walls of container

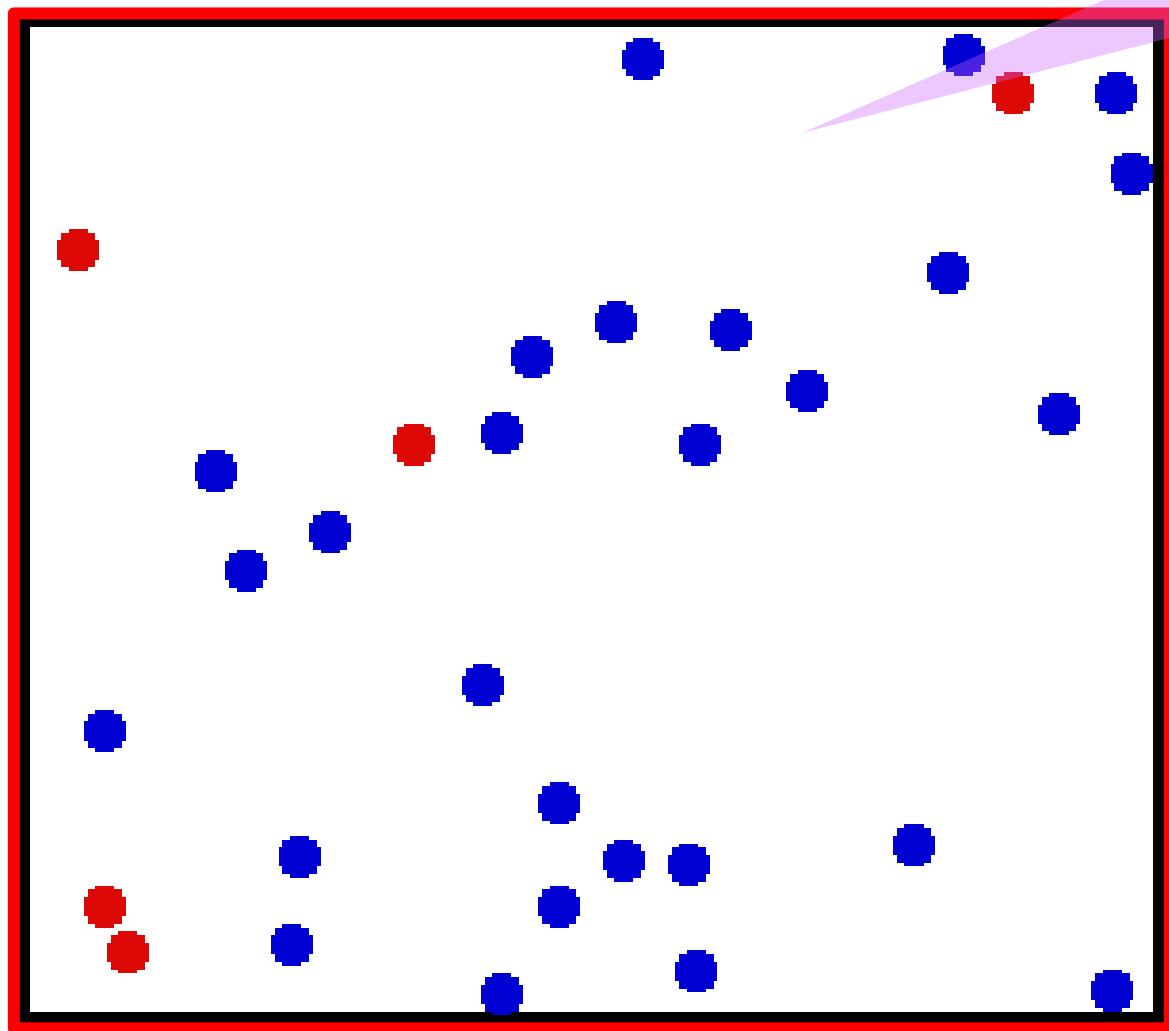
3. Collisions between gas particles are elastic

- ☞ no kinetic energy loss
- ☞ total kinetic energy is constant

4. Intermolecular forces (attractive and repulsive force) between gas particles are negligible.

5. The average kinetic energy of the particle is directly proportional to the absolute temperature.

Gas pressure is caused
by gas molecules colliding
container's walls



GAS LAW

@ The physical behavior of gas can be described by four variables:

Pressure (P)

Volume (V)

Temperature (T)

Amount
(number of moles) (n)

Boyle's law

Charles's law

Avogadro's law

BOYLE'S LAW

At constant temperature, the **volume** occupied by a fixed **amount** of gas is **inversely proportional** to the applied (external) **pressure**

$$V \propto 1/P \quad (\text{At constant } T \text{ and } n)$$

$$P V = \text{constant}$$

$$P_1 V_1 = P_2 V_2$$

Where P_1 = initial pressure

V_1 = initial volume

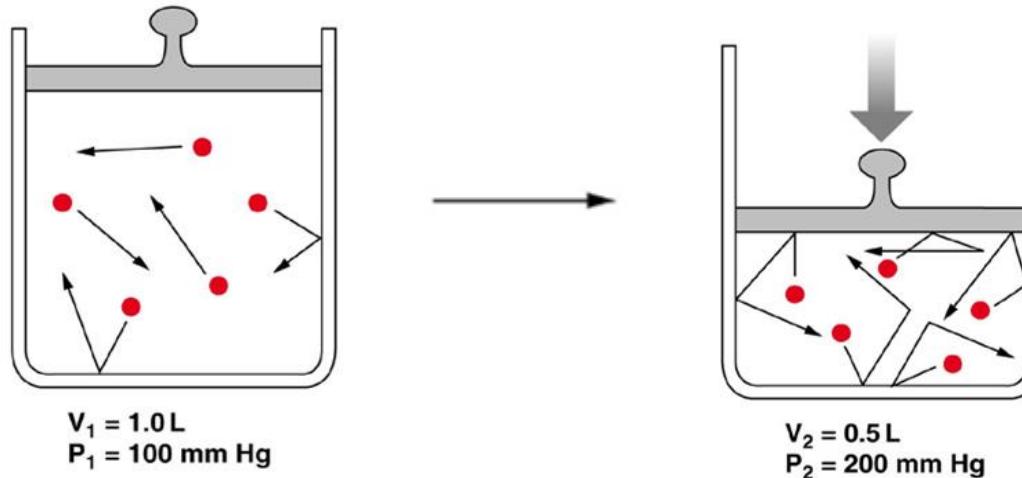
P_2 = final pressure

V_2 = final volume



Robert Boyle (1627-1691). British chemist and natural philosopher

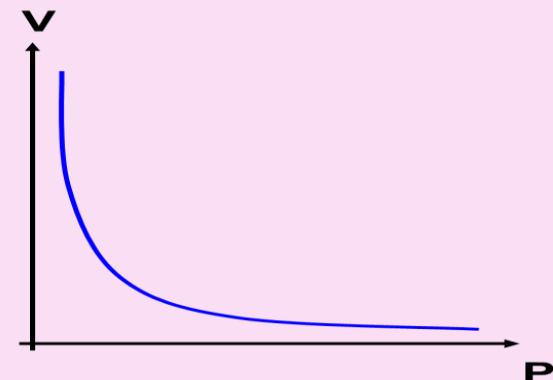
Boyle's law – $P \propto 1/V$ (at constant T and n)



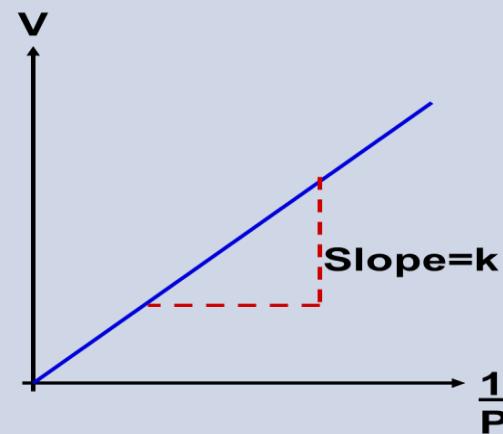
- When volume of container decrease, the average Kinetic Energy of the particles remain the same since temperature is constant.
- Therefore, no change in speed in which the particles move, but collision increase because the container is smaller.
- The increase in the frequency of collisions with the wall of container lead to an increase in the pressure of the gas.
- Boyle's law state that the volume of a fixed amount of gas is inversely proportional to the gas pressure at constant temperature.

GRAPH OF BOYLE'S LAW

Graph of V versus P

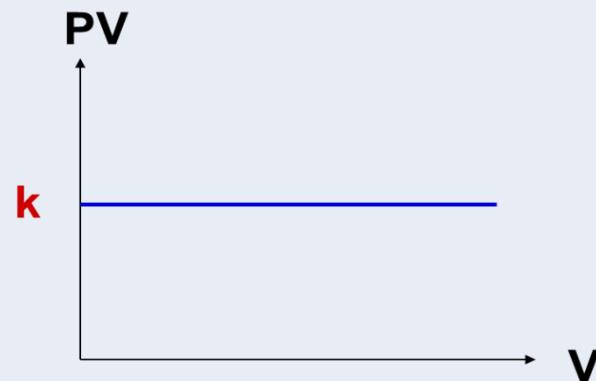


Graph of V versus 1/P



Graph of PV versus V

$$PV = \text{constant } (k)$$



EXERCISE 1

A sample of gas occupies 12.0 L under a pressure of 1.2 atm. What would its volume be if the pressure were increased to 2.4 atm?

ANSWER : $V_2 = 6.0\text{ L}$

CHARLES' LAW

At constant pressure, the **volume** occupied by a fixed **amount** of gas is **directly proportional** to its **absolute temperature (in Kelvin)**

$V \propto T$ (At constant P and n)

Where V_1 = initial volume

T_1 = initial temperature

V_2 = final volume

T_2 = final temperature

$$\frac{V}{T} = \text{constant}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

T in Kelvin (K)!

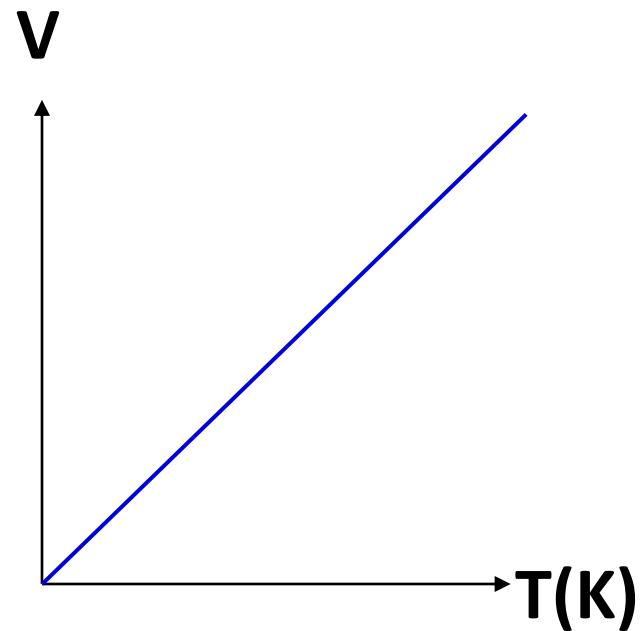
$$T(K) = T(^{\circ}\text{C}) + 273$$



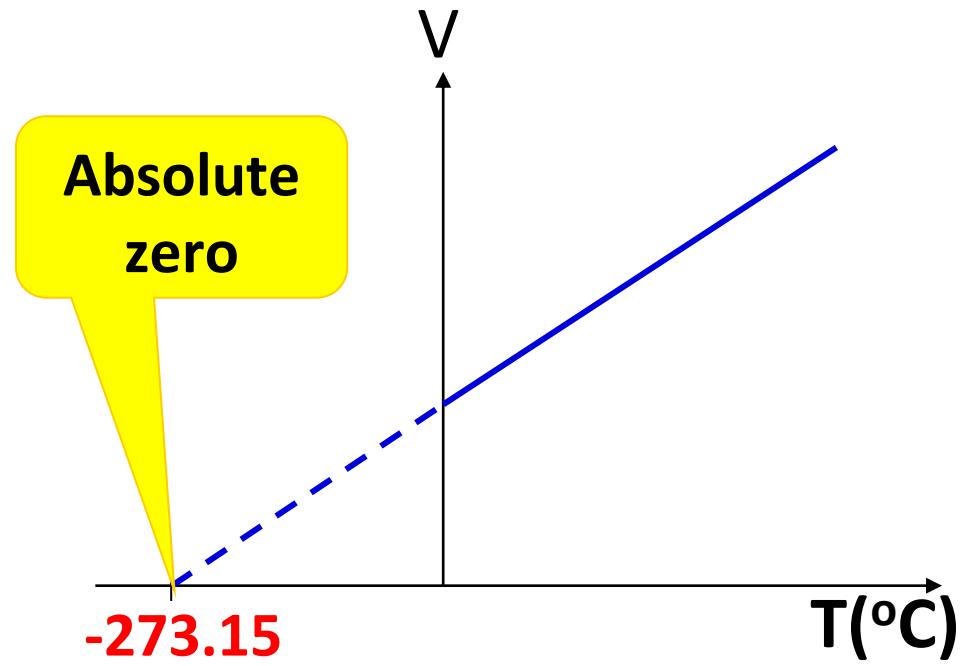
Jacques Alexandre Cesar Charles (1746-1823). French physicist.

Graphs based on Charles' Law

Graph of V versus T(K)



Graph of V versus T($^{\circ}$ C)



EXERCISE 2

A sample of carbon monoxide gas occupies 3.20 L at 125 °C. At what temperature will the gas occupy a volume of 1.54 L if the pressure remains constant?

ANSWER : $T_2 = 192\text{ K}$

AVOGADRO'S LAW

At constant pressure and temperature, the **volume** of a gas is **directly proportional** to the number of **moles** of the gas present

$$V \propto n$$

(At constant P and T)

$$\frac{V}{n} = \text{constant}$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Where V_1 = initial volume
 n_1 = initial number of mole
 V_2 = final volume
 n_2 = final number of mole

Lorenzo Romano Amedeo Carlo Avogadro di Quaregua e di Cerreto (1776-1856).



Italian mathematical physicist.

EXERCISE 3

A balloon has been filled to a volume of 1.90 L with 0.0920 mol of helium gas. If 0.0210 mol of additional helium is added to the balloon while the temperature and pressure are held constant, what is the new volume of the balloon?

ANSWER : V = 2.33 L

IDEAL GAS EQUATION



Boyle's Law

$$V \propto \frac{1}{P}$$

(At constant T and n)



Charles' Law

$$V \propto T$$

(At constant P and n)



Avogadro's Law

$$V \propto$$

(At constant P and T)
n

By combining the three gases laws

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

$$V = R \frac{Tn}{P}$$

or

$$PV = nRT$$

Where R : gas constant
 $= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ @
 $0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$

GAS CONSTANT, R

From ideal gas equation, we can write:

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{22.4 \text{ L} \times 1 \text{ atm}}{1 \text{ mol} \times 273 \text{ K}} \end{aligned}$$

$$= 0.08206 \frac{\text{L atm}}{\text{mol K}}$$

EXERCISE 4

What pressure, in atm, is exerted by 54.0 grams of Xe in a 1.00 liter flask at 20°C

ANSWER : $P = 9.89 \text{ atm}$

EXERCISE 5

What is the volume of a gas balloon filled with 4.00 moles of He when the atmospheric pressure is 748 torr and the temperature is 30°C?

ANSWER : $V= 101.07 \text{ L}$

EXERCISE 6

A steel tank has a volume of 438 L and is filled with 0.885 kg of O₂. Calculate the pressure (in atm) of O₂ at 21°C.

ANSWER : P = 1.53 atm

MOLAR MASS OF A VOLATILE LIQUID USING IDEAL GAS EQUATION

$$PV = nRT$$



Molar mass (M)

MOLAR MASS (M)

$$PV = nRT$$

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{PV}$$

$$\boxed{n = \frac{m}{M}}$$

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

$$M = \frac{mRT}{PV}$$

or

$$M = \frac{\rho RT}{P}$$

m : Mass of the gas in g

ρ : density of gas

M : Molar mass of the gas (Unit: g/mol)

EXERCISE 7

What is the density of oxygen gas (O_2) at 298 K and 0.987 atm?

ANSWER : $\rho = 1.29 \text{ g/L}$

EXERCISE 8

The density of phosphorus vapor at 310°C and 775 mmHg is 2.64 g/L. What is the molecular mass of phosphorus under these conditions?

ANSWER : Molecular mass = 124 amu

DALTON'S LAW OF PARTIAL PRESSURE

In a mixture of unreacting gases, the total pressure is the sum of the partial pressures of the individual gases

$$P_{\text{Total}} = P_A + P_B + P_C + \dots$$

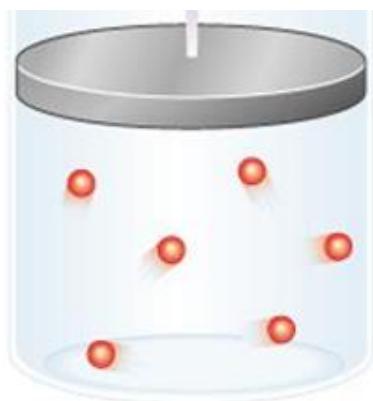
EXAMPLE:

$$P_{\text{Total}} = P_{\text{N}_2} + P_{\text{He}} + P_{\text{Ar}}$$

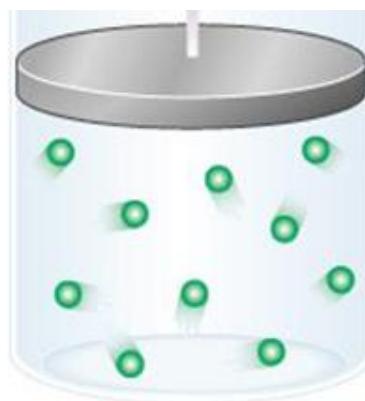
John Dalton (1766-1844). English chemist, mathematician, and philosopher

PARTIAL PRESSURE

Pressure that a gas would exert if it was present alone in the container

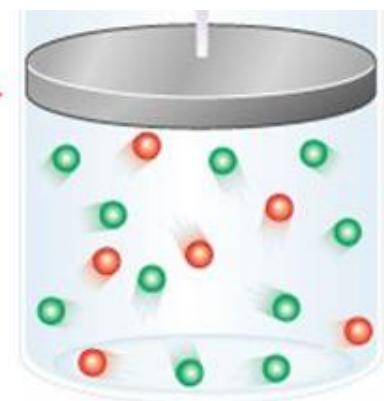


$$P_{N_2} = 1 \text{ atm}$$



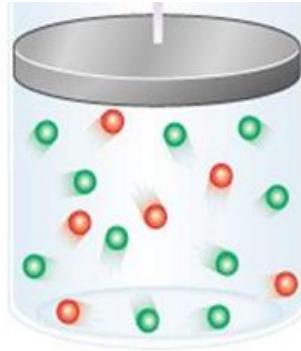
$$P_{Ar} = 2 \text{ atm}$$

Combining
the gases



$$\begin{aligned} P_{\text{Total}} &= P_{N_2} + P_{Ar} \\ &= 3 \text{ atm} \end{aligned}$$

Consider a case in which two gases, A and B, are in a container of fixed volume V:



The pressure exerted by gas A and gas B is:

$$P_A = \frac{n_A RT}{V}$$

n_A : moles of gas A

$$P_B = \frac{n_B RT}{V}$$

n_B : moles of gas B

According to Dalton's law:

$$P_{\text{Total}} = \text{Partial pressure of gas A} + \text{Partial pressure of gas B}$$

$$P_{\text{Total}} = P_A + P_B$$

$$= \frac{n_A RT}{V} + \frac{n_B RT}{V}$$

$$= (n_A + n_B) \frac{RT}{V}$$

$$= (n_{\text{Total}}) \frac{RT}{V}$$

Partial pressure of gases can be expressed in terms of mole fraction:

$$\text{Mole fraction } (X_A) = \frac{\text{moles of gas A}}{\text{Total number of moles of all gases}}$$

$$X_A = \frac{\left[\frac{P_A V}{R T} \right]}{\left[\frac{P_{Total} V}{R T} \right]}$$
$$= \frac{P_A}{P_{Total}}$$

$$P_A = X_A P_{Total}$$

EXERCISE 9

A gaseous mixture made from 6.00 g O₂ and 9.00g CH₄ is placed in a 15.0 L vessel at 0°C. What is the partial pressure of each gas, and what is the total pressure in the vessel?

ANSWER : P_{Total} = 1.12 atm

EXERCISE 10

A 4.00 L flask containing He at 6.00 atm is connected to a 2.00 L flask containing N₂ at 3.00 atm and the gases are allowed to mix.

- (a) Find the partial pressure of each gas after the gases are allowed to mix.

ANSWER : $P_{\text{He}} = 1.00 \text{ atm}$

- (b) Find the total pressure of the mixture.

ANSWER : $P_{\text{T}} = 5.00 \text{ atm}$

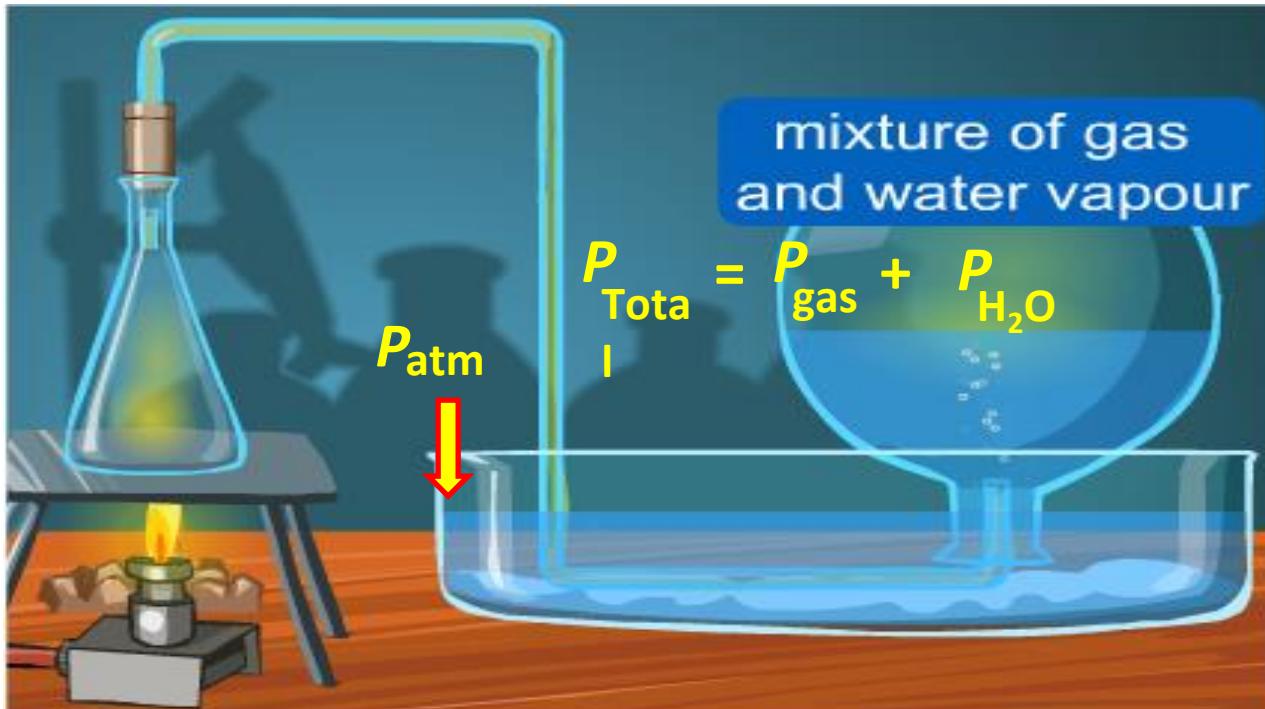
- (c) What is the mole fraction of helium?

ANSWER : $X_{\text{He}} = 0.800$

Application Of Dalton's Law In Collecting A Gas Over Water (Water Displacement Method)

- When a gas is collected “over water”, a mixture of the particular **gas** and **water vapour** is collected.
- By using Dalton's law:

$$P_{\text{Total}} = P_{\text{gas}} + P_{\text{H}_2\text{O}}$$





EXAMPLE:

When KClO_3 is heated, it decomposes to KCl and O_2 gas.



The O_2 gas produced is collected by water displacement method.



According to Dalton's law of partial pressure:

$$P_{\text{Total}} = P_{\text{O}_2} + P_{\text{H}_2\text{O}}$$

$$P_{\text{O}_2} = P_{\text{Total}} - P_{\text{H}_2\text{O}}$$

At 25°C , $P_{\text{H}_2\text{O}} = 23.8$ torr
(pressure of water vapor)



EXERCISE 11

Consider the reaction below:



A sample of 5.45 liters of oxygen is collected over water at a pressure of 735.5 torr and at a temperature of 25°C. How many grams of oxygen have been collected?

At 25°C, the vapor pressure of water = 23.8 torr

ANSWER : Mass of O₂= 6.69 g O₂

EXERCISE 12

When the certain amount of concentrated acid was added to a rock sample, a vigorous reaction occurred and an unknown gas was being released. An amount of 0.400g of a gas was collected in a 0.500 L bulb at a pressure of 0.655 atm and temperature of 27°C. Calculate the molar mass and density of the unknown gas.

ANSWER : Molar mass = 30.1 g mol^{-1}
Density = 0.800 g L^{-1} .

EXERCISE 13

A 500.0 mL vessel containing 1.35 g of chlorine gas has a pressure of 760 mmHg. When a certain amount of oxygen gas is added to the vessel, the gas pressure rises to 865 mmHg. Assume that the gases do not react with each other and the temperature remains constant, calculate the mass of oxygen gas added into the vessel.

ANSWER : Mass = 8.38×10^{-2} g

IDEAL GAS VS REAL GAS

Ideal gas

Any gas that **obeys the ideal gas equation** and has the properties as outlined by the **Kinetic Molecular Theory**

Real gas

Any gas that **disobey ideal gas law** also known as non-ideal gas

Does an ideal gas exist ?

IDEAL vs NON-IDEAL BEHAVIOURS OF GASES

Ideal gas (Ideal behaviour)

- ❖ **Volume** of gas particles is too small compared to the volume of container. Therefore, **volume of gas particle is negligible**
- ❖ **Intermolecular forces** between gas particles are **negligible**.
- ❖ **obeys** the ideal gas equation

$$PV = nRT$$

Real gas (Non-ideal behaviour)

- ❖ Gas particles have a certain **volume** & do **occupy some space**.
- ❖ There is **intermolecular forces** between gas particles
- ❖ **obeys** the Van der Waals equation

$$\left[P + \frac{n^2a}{V^2} \right] (V - nb) = nRT$$

van der Waals EQUATION

- ① Since **real gas does not exhibit ideal gas behaviour at high pressure and low temperature the ideal gas equation need to be adjusted :**
- ② van der Waals adjusted the ideal gas equation by correcting two parameters:
 - i) The **volume of** gas particles occupied in the container.
 - ii) The **intermolecular forces** acting between gas particles.

Ideal Gas equation : $PV = nRT$

Van Der Waals equation :

$$\left[P + \frac{n^2a}{V^2} \right] (V - nb) = nRT$$

Correction for
molecular attraction

Correction for molecular volume

Where, P = Pressure of gas (real)
 V = Volume of container
 n = Mole of gas
 a, b = Van der Waals constant

$$P_{ideal} > P_{real}$$

$$P = P + \frac{n^2a}{V^2}$$

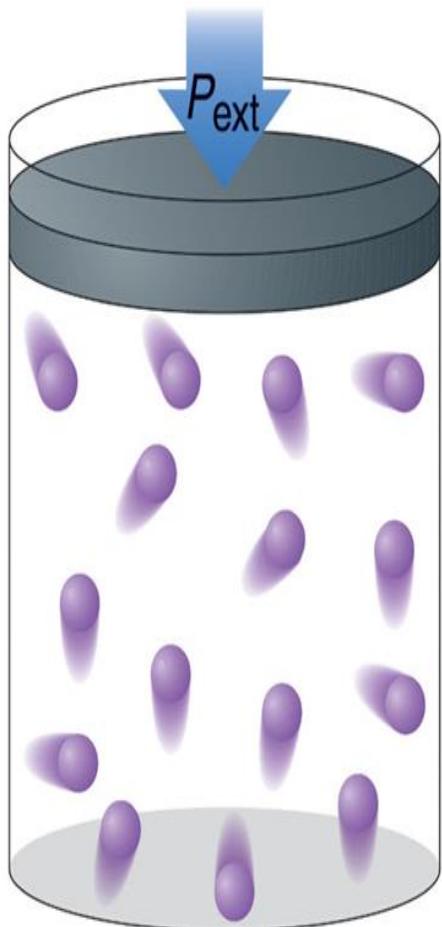
$$V = V_{\text{container}}$$

$$\begin{aligned} V &= V_{\text{container}} - V_{\text{gas}} \\ &= V_{\text{container}} - nb \end{aligned}$$

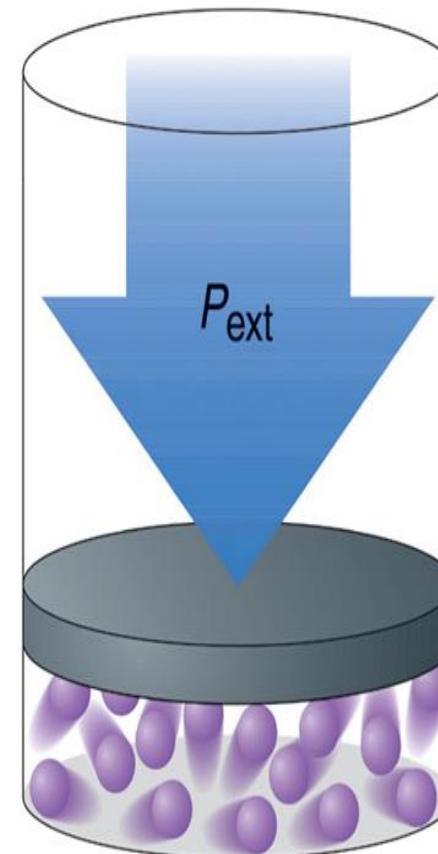
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The effect of molecular volume on measured gas volume

Ordinary P_{ext} :
free volume \approx
container volume



P_{ext} increases
→

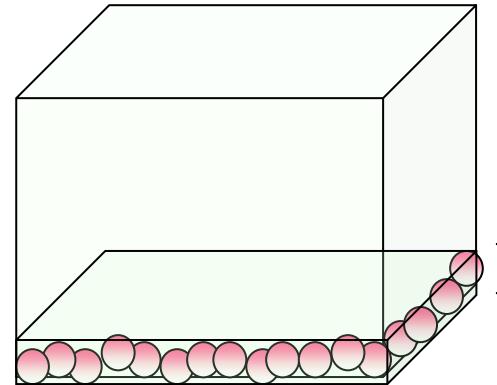
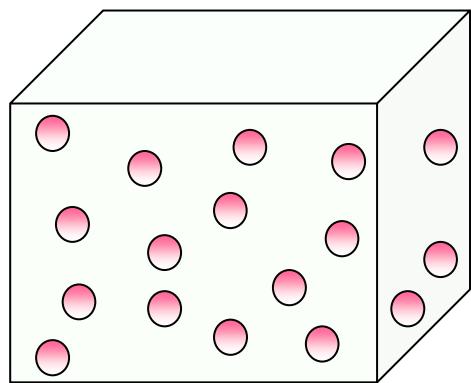


Very high P_{ext} :
free volume $<$
container volume

Volume of gas molecules



- In **real situation**, the gas molecules **occupy sizable portion of the container** :
 - **space occupied by the gas molecules have to be taken into consideration**
 - **the space restrict the movement of the gas molecules**
 - **the volume occupied by of the gas molecules must be subtracted from the total volume**



nb

☞ The volume is decreased by the factor of ***nb***, which accounts for the **finite volume** occupied by the gas particles.

$$\begin{aligned}\therefore V &= V_{\text{container}} - V_{\text{gas}} \\ &= V_{\text{container}} - nb\end{aligned}$$

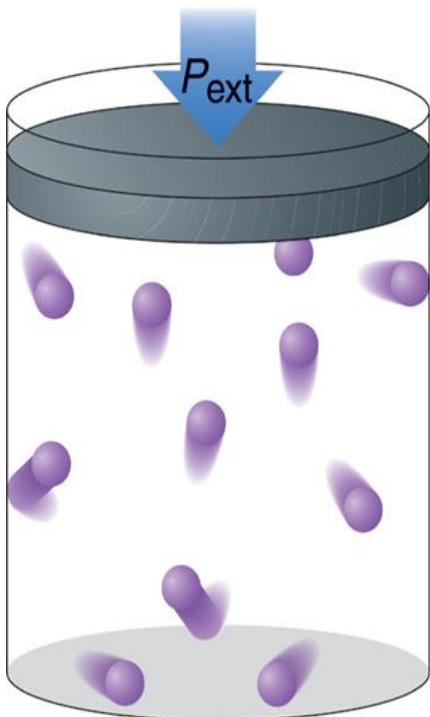
n : moles of molecules

b : constant representing the volume occupied by the gas particles

Molecule size bigger , greater value of *b*

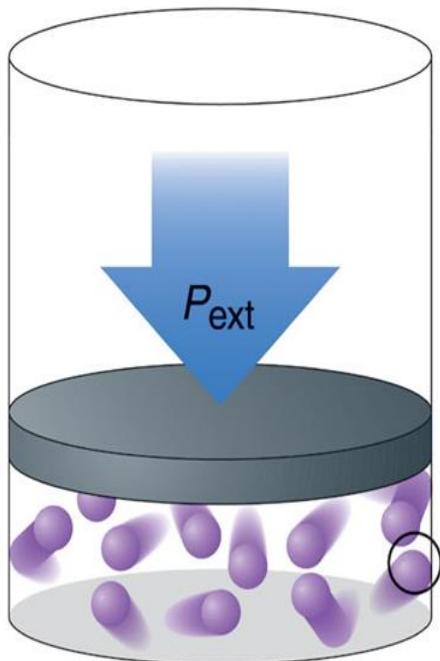
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The effect of intermolecular forces on measured gas pressure

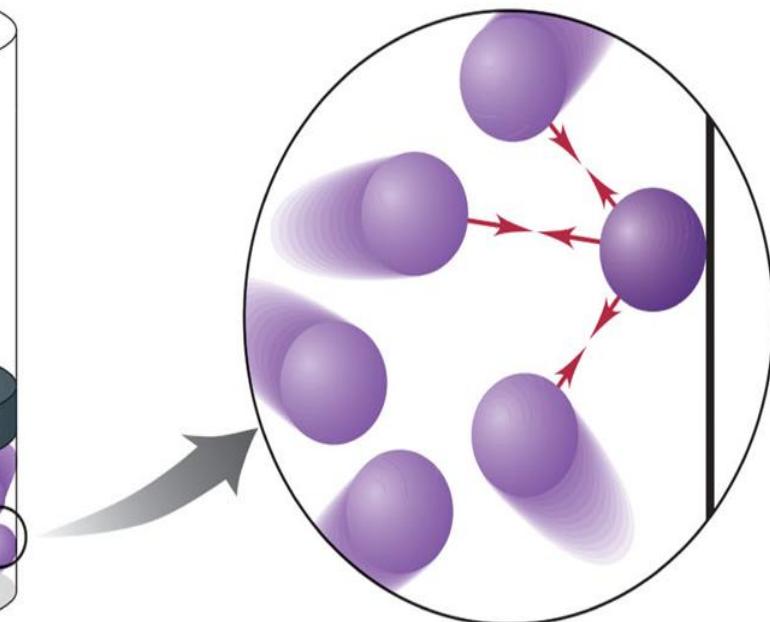


Ordinary P_{ext} :
molecules too far
apart to interact

P_{ext}
increases
→



Moderately high P_{ext} :
molecules close
enough to interact



Attractions lower
force of collision
with wall



The **intermolecular forces** have an effect on the **speed** of the moving gas particles.



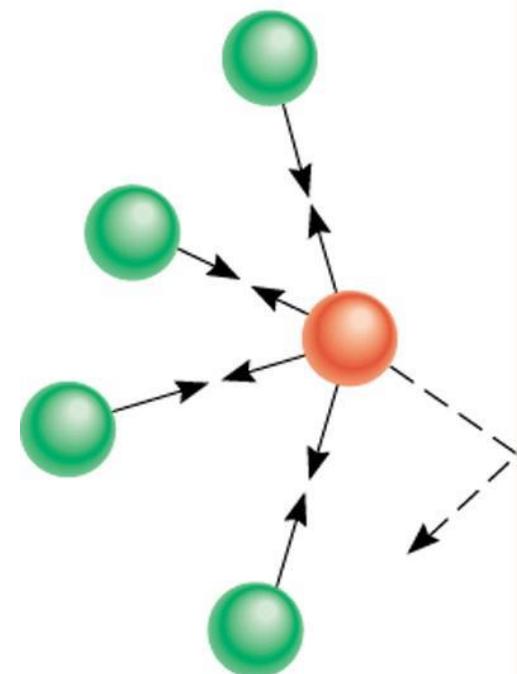
Gas particles that experience this force will **move slowly**.



The **collision** of gas particles with the wall of container become **less**.



lower pressure exert compare to ideal gas situation



$$\therefore P_{\text{real}} < P_{\text{ideal}}$$

 The pressure is decreased by the factor $\frac{n^2a}{V^2}$ which accounts for the **intermolecular forces** between the gas particles.

 The **term pressure** need to be corrected by adding coefficient $\frac{n^2a}{V^2}$

$$\therefore P = P_{\text{real}} + \frac{n^2a}{V^2}$$

n : moles of particles

a : constant relates to intermolecular forces between gas particles

intermolecular forces stronger , greater value of a

CONDITIONS AT WHICH REAL GASES APPROACH THE IDEAL BEHAVIOUR

① At very low pressure (Constant Temperature)

- Volume of container is increased
- The gas particles are far apart from each other in a large volume
- Volume of gas molecules is too small compared to volume of the container, thus volume of gas molecules are negligible
- There is no intermolecular forces between gas particles, so intermolecular forces are negligible

Hence, it obey kinetic–molecular theory, the gas behave ideally.

② At high temperature (At constant volume)

- Gas particles have **high kinetic energy** and move at high speed
- There is no intermolecular forces between gas particles
 - intermolecular forces are **negligible**

Hence, it **obey kinetic–molecular theory, the gas behave ideally.**

EXERCISE 14

The van der Waals equation for real gas is given as:

$$\left[P + \frac{n^2a}{V^2} \right] (V - nb) = nRT$$

- a) There are two factors that cause real gas to deviate from ideal behaviour. Relate these two factors with the constant a and b in van der Waals equation.
- b) Both constant a and b have different unit. Drive the unit for constant a and b .

5.0 STATES OF MATTER

5.2 Liquid

Liquid

Properties

- Shape & Volume
- Surface Tension
- Viscosity
- Compressibility
- Diffusion

Vapourization &
Condensation

Processes

Vapour Pressure

Boiling Point

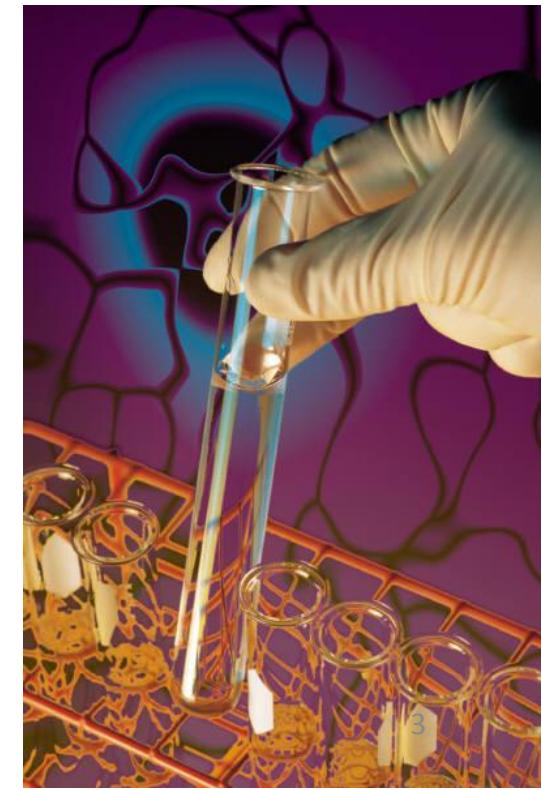
→ Normal Boiling Point

Relationship between:

1. Intermolecular Forces & Vapor Pressure
2. Vapor pressure & Boiling point

PROPERTIES OF LIQUID

- ④ Conforms to **shape of container**
- ④ Volume limited by **surface**
- ④ Only **slightly compressible**
- ④ Moderate ability to **flow**
- ④ Molecules **slide past one another freely**



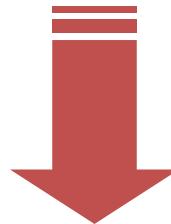
SHAPE AND FLUIDITY

- ④ Liquid has a **definite volume** but **not a definite shape**
- ④ Molecules arranged **closely** but **not rigidly**
- ④ Molecules held together by **intermolecular force**, but they able to **move freely**
- ④ Moderately highly **fluidity** and take the **shape of container**
- ④ Liquid conforms to **shape** and **volume** of container

DIFFUSION



Liquid **diffuse slower**



Stronger **intermolecular force** and **close arrangement**

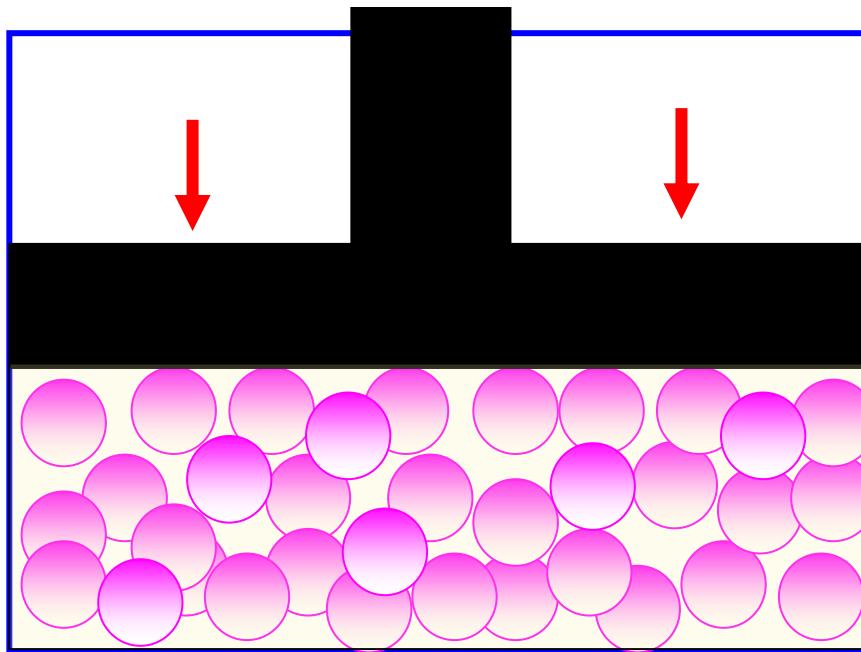


COMPRESSIBILITY

⌚ Very little free space between molecules



⌚ Compress only slightly



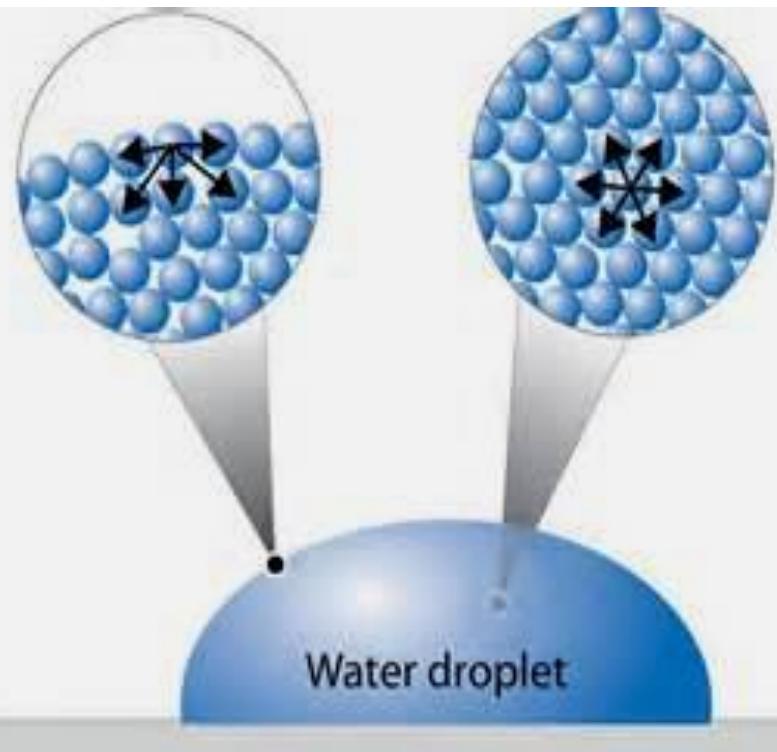
SURFACE TENSION

Surface tension is **energy** required to **increase surface area** by a unit area



A paper clip will float on water if it is carefully placed on the surface of the water. It is held up by surface tension

It is caused by the difference in intermolecular forces experienced by molecules at the surface of a liquid and those experienced by molecules in the interior



Molecules in the interior are surrounded and are pulled equally in all directions.

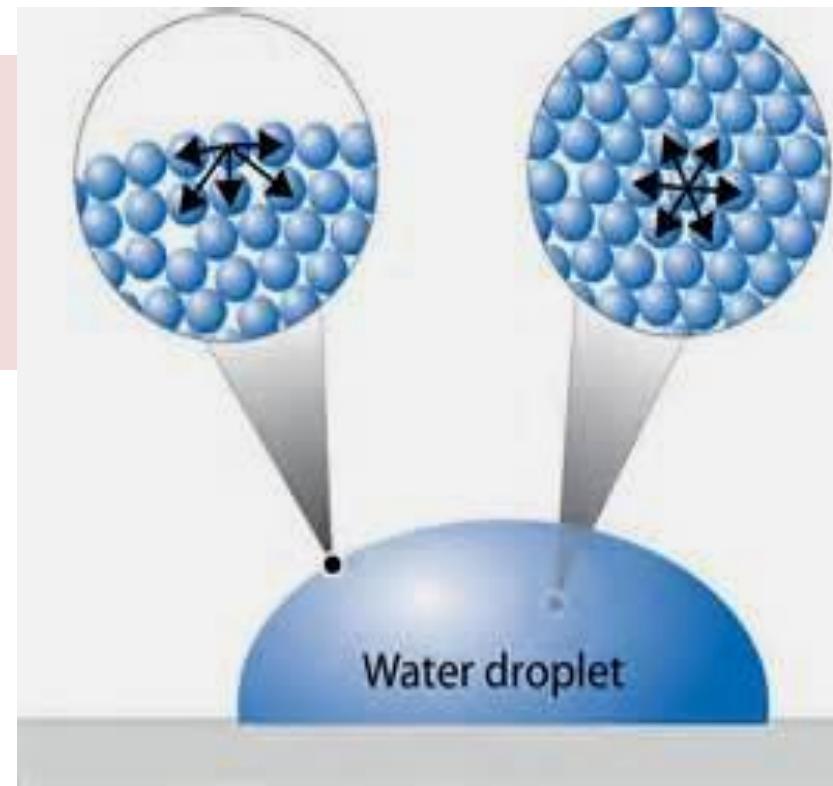
Molecules at the surface feel attractive forces from below and sideways and are thus pulled in toward the liquid.

Therefore, a liquid surface tends to have the smallest possible area.

To increase the surface area, molecules must move to the surface by breaking some attractions in interior, which requires energy and cause the surface tighten like an elastic film

Factor affecting surface area :

Intermolecular forces ↑
surface tension ↑



The stronger the forces are between molecules in a liquid, the greater the surface tension

VISCOSITY

Viscosity = **resistance to flow due to intermolecular forces**

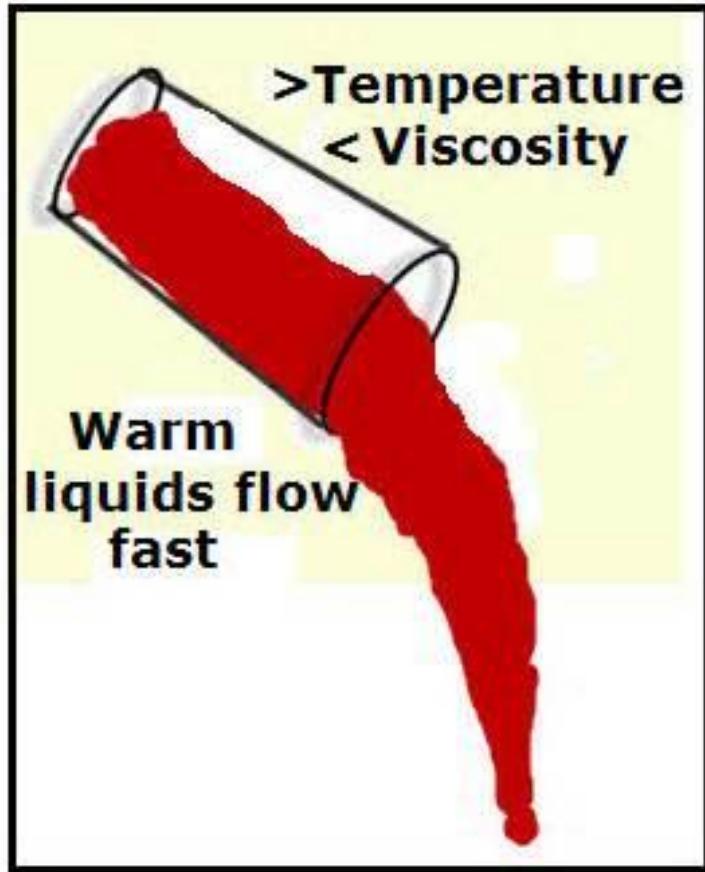




Factor affecting viscosity:

- Size and shape of molecules
- Intermolecular forces
- Temperature

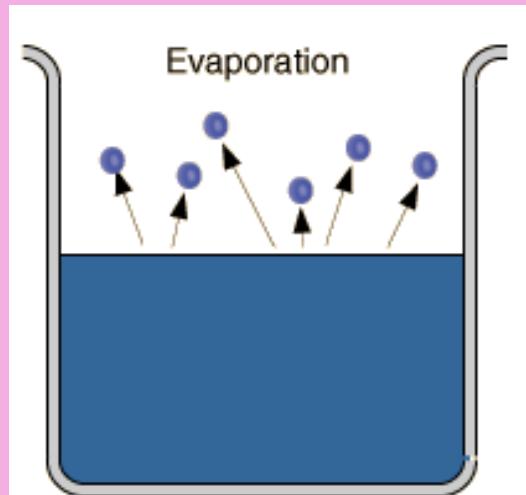




Small and spherical molecules are easy to flow
(weaker intermolecular forces)
→ viscosity decrease

Temperature ↑
Viscosity ↓

VAPORISATION AND CONDENSATION



VAPORIZATION

CONDENSATION

- Process in which a liquid is changed into a gas
- When the kinetic energy of liquid molecules increases,
 - molecules will move faster.
 - more molecules possess sufficient kinetic energy to overcome the intermolecular forces
 - & escape from the surface as vapour molecules.

- Process in which a gas is changed into a liquid
- When the vapor molecules are cooled and lose kinetic energy,
 - molecules will move slower.
 - they do not have sufficient kinetic energy to remain as vapour molecules.
 - ∴ Molecules come closer, attract one another and return as liquid molecules.

FACTORS AFFECTING RATE OF VAPORIZATION

Surface area

Surface area ↑, vaporization rate ↑

- number of molecules with high energy have chance to **escape from surface** ↑

Temperature

Temperature ↑, vaporization rate ↑

- more molecules have **higher kinetic energy**
- number of molecules **escape from surface** ↑

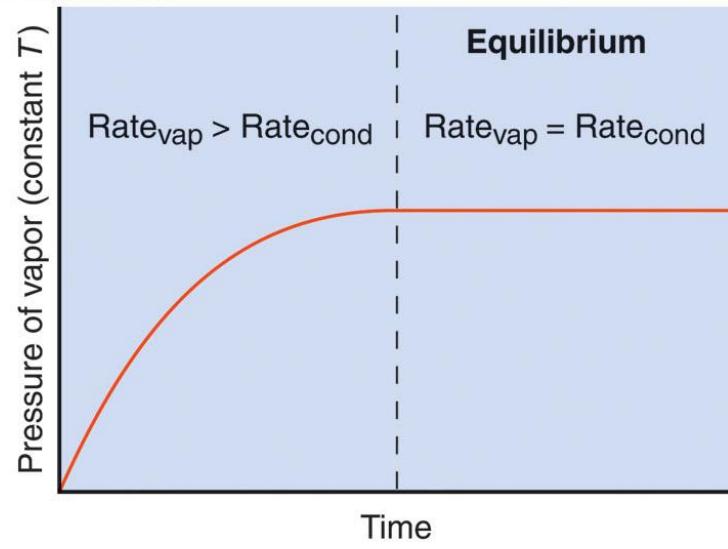
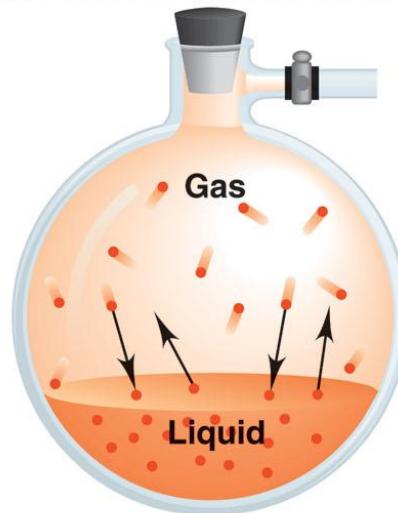
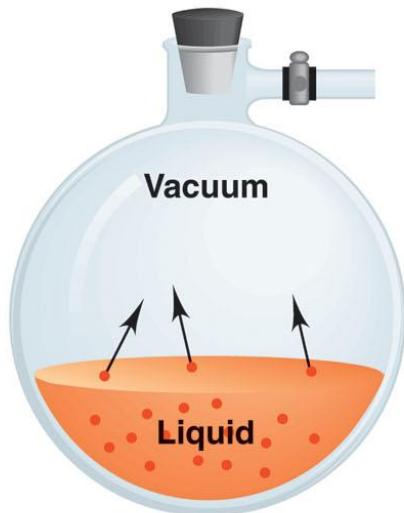
Strength of intermolecular forces

Strength ↓ , vaporization rate ↑

VAPOUR PRESSURE

The pressure exerted by vapour in equilibrium with its liquid in a closed container.

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VOLATILITY OF LIQUID



Volatile liquids

- **High vapor pressures at room temperature**



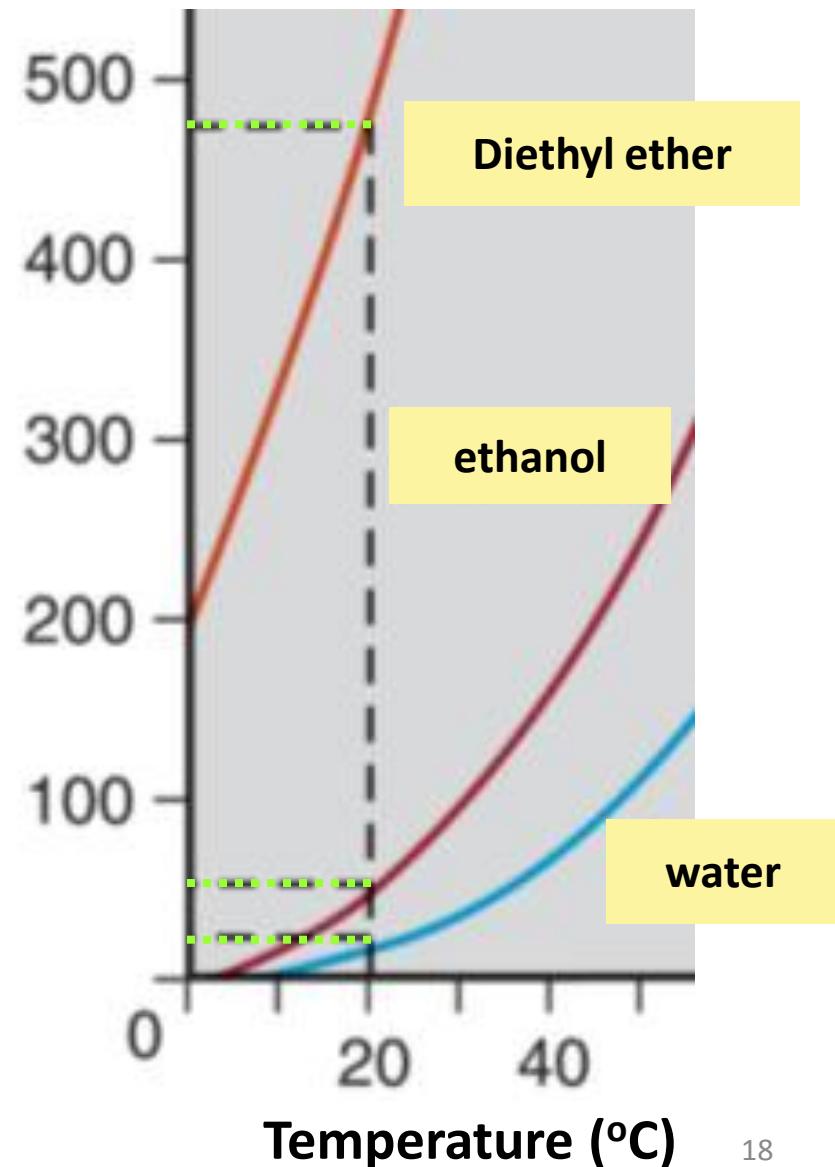
Nonvolatile liquids

- **Very low vapor pressures at room temperature**

EXAMPLE:

- At any given temperature, (example: 20°C) diethyl ether has the highest vapor pressure and water the lowest
- Diethyl ether has the weakest intermolecular forces and water the strongest

Vapor pressure (torr)



BOILING POINT



The **temperature** at which the **vapour pressure** of a liquid is **equal** to the **external (atmospheric) pressure**

EXAMPLE: boiling point of water

100°C at 760 torr (sea level)

94°C at 610 torr (Boulder, Colorado)

72°C at 270 torr (Mt. Everest)

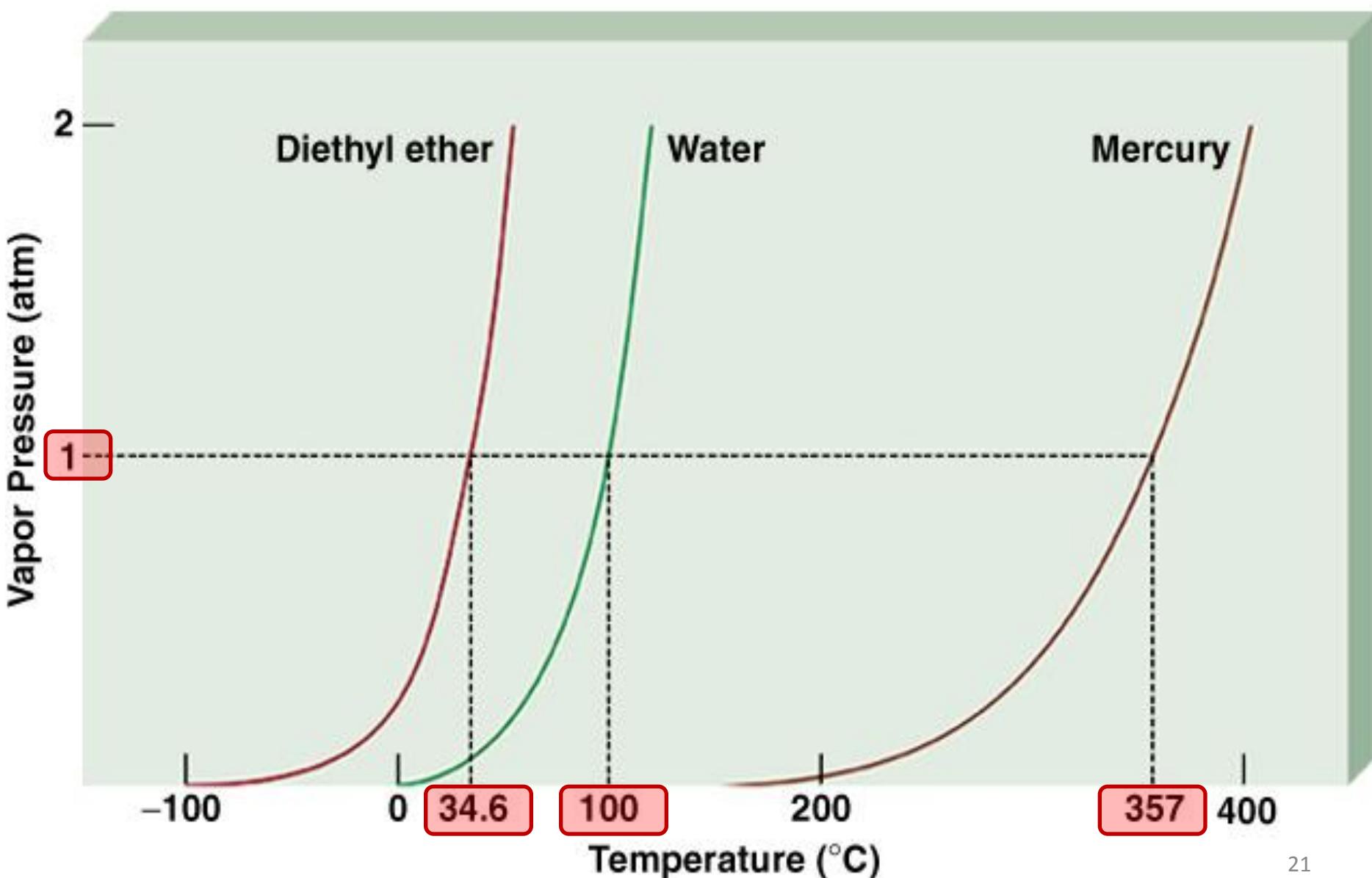
NORMAL BOILING POINT



The temperature at which a liquid boils when the external pressure is 1 atm



Vapor Pressure vs. Temperature



KEEP IN MIND



If the **pressure** is not mentioned when the boiling point is measured, we **assume** it as **normal boiling point (at 1 atm)** .



FACTOR AFFECTING VAPOUR PRESSURE

Temperature

Temperature ↑

- molecules move **faster**,
- **easy** to escape to form vapour molecules.

∴ vapour pressure is **high**

Strength of
intermolecular
forces

Weak intermolecular forces,

- liquid molecules **easy** to escape to form vapour.

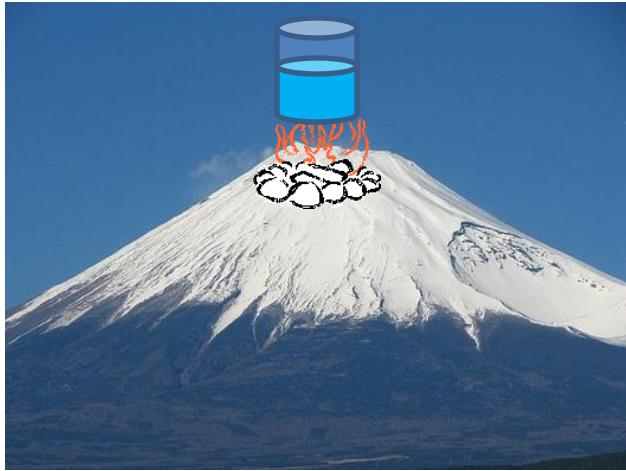
∴ vapour pressure is **high**

FACTOR AFFECTING BOILING POINT

1) Atmospheric pressure

- When atmospheric pressure ↓
- Heat needed to make **vapour pressure equals** to atmospheric pressure ↓
- Boiling point ↓

Boiling point of water



Mt. Fuji
(3776 m)
Bp = 87°C



Mt. Everest
(8848 m)
Bp = 71°C



2) Intermolecular forces

- Strength ↑ , boiling point ↑

Substance	Boiling Point* (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	–186	6.3
Benzene (C_6H_6)	80.1	31.0
Ethanol (C_2H_5OH)	78.3	39.3
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Mercury (Hg)	357	59.0
Methane (CH_4)	–164	9.2
Water (H_2O)	100	40.79

* Measured at 1 atm.

KEEP IN MIND

Strength of intermolecular forces depend on:

- Types of forces

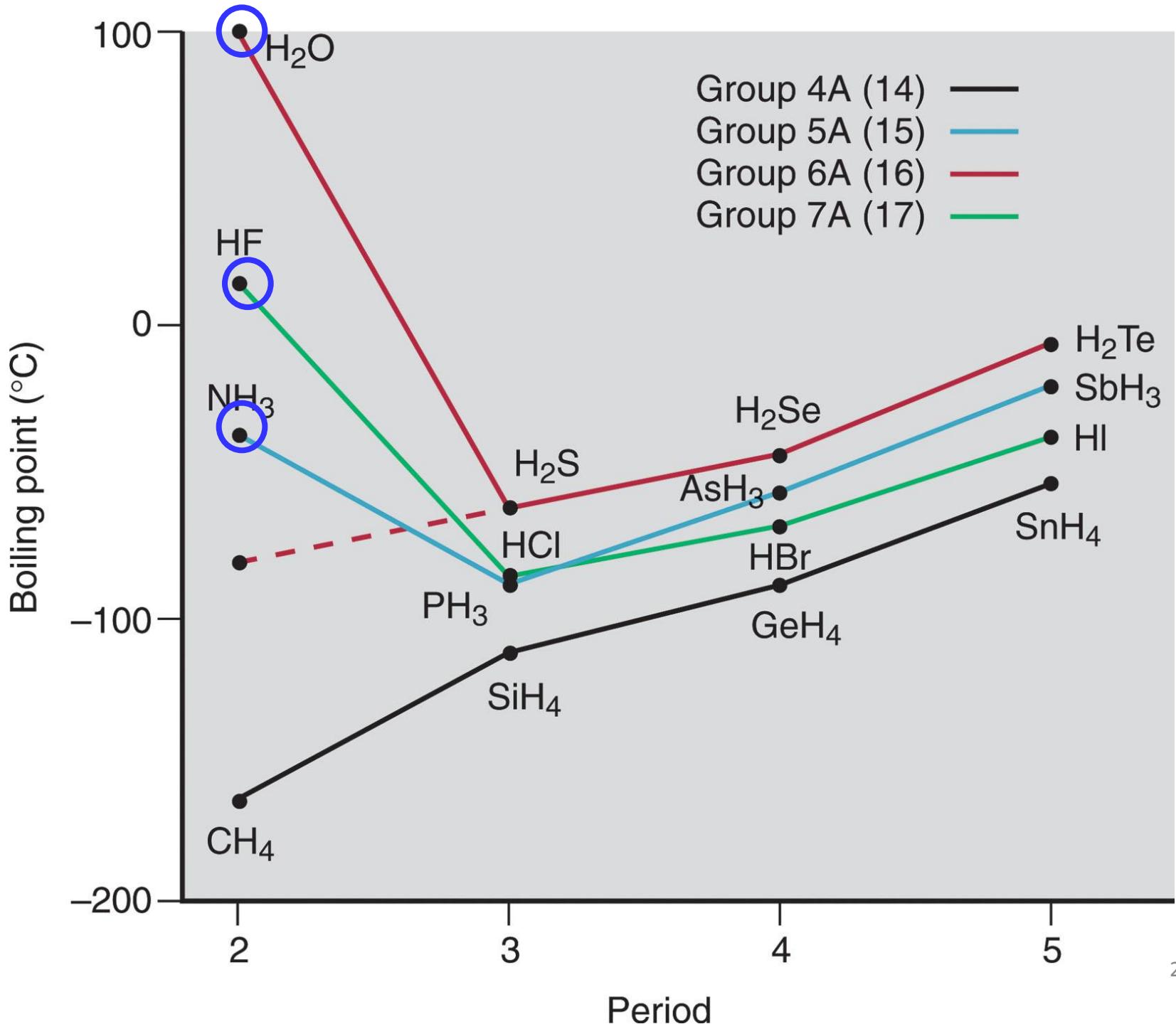
EXAMPLE:

Hydrogen bond is much **stronger** than Van der Waals force

- Molar mass

EXAMPLE:

Cl_2 (molar mass = 70.91 g/mol) has a **higher** boiling point than F_2 (molar mass = 38.00 g/mol)



7A (17)	8A (18)
Substance Model <i>Molar mass</i> <i>Boiling point (K)</i>	He 4.003 4.22
F₂ 38.00 85.0	Ne 20.18 27.1
Cl₂ 70.91 239	Ar 39.95 87.3
Br₂ 159.8 333	Kr 83.80 120
I₂ 253.8 458	Xe 131.3 165

- ⌚ Size of atom / molecule ↑
- ⌚ Intermolecular forces ↑
- ⌚ Vapour pressure ↓
- ⌚ Boiling point ↑

Increasing strength of dispersion forces

SUMMARY

weaker
attractive
force

higher
vapor
pressure

Lower
boiling point

Liquid that have weaker attractive forces will have higher vapor pressure and lower boiling point.

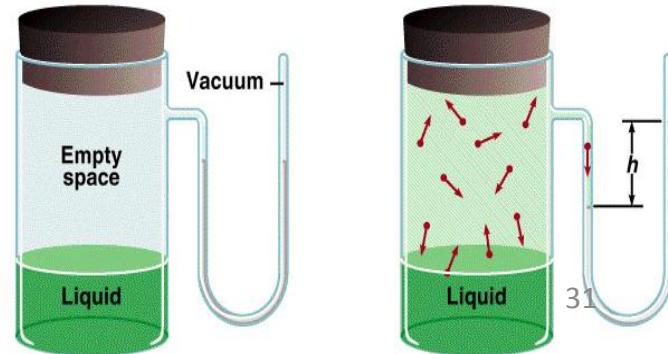


EXAMPLE 1 :

A beaker of water is placed in closed container.
Predict the effect on the vapor pressure of the
water when

- (a) its temperature is lowered
- (b) the volume of container is double
- (c) more water is added to the beaker

Apparatus for Measuring
the Vapor Pressure of a Liquid





EXAMPLE 2 :

Which of the following statement is true?

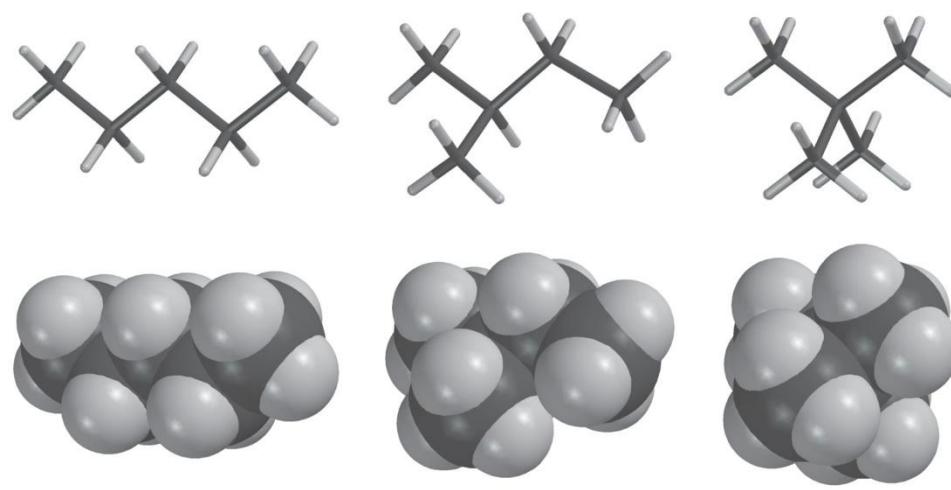
- (a) Liquid A boils at a lower temperature than liquid B. This fact indicates that liquid A has weaker intermolecular forces than B.**
- (b) Liquid M boils at a higher temperature than liquid N. This indicates that M has a higher vapor pressure than N at any temperature.**



EXAMPLE 3:

Explain the following statement:

- (a) Liquid with long molecules has higher viscosity than with spherical ones.
- (b) Liquid molecules with higher molar mass are more viscous than that of a lower molar mass



(a) Pentane: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

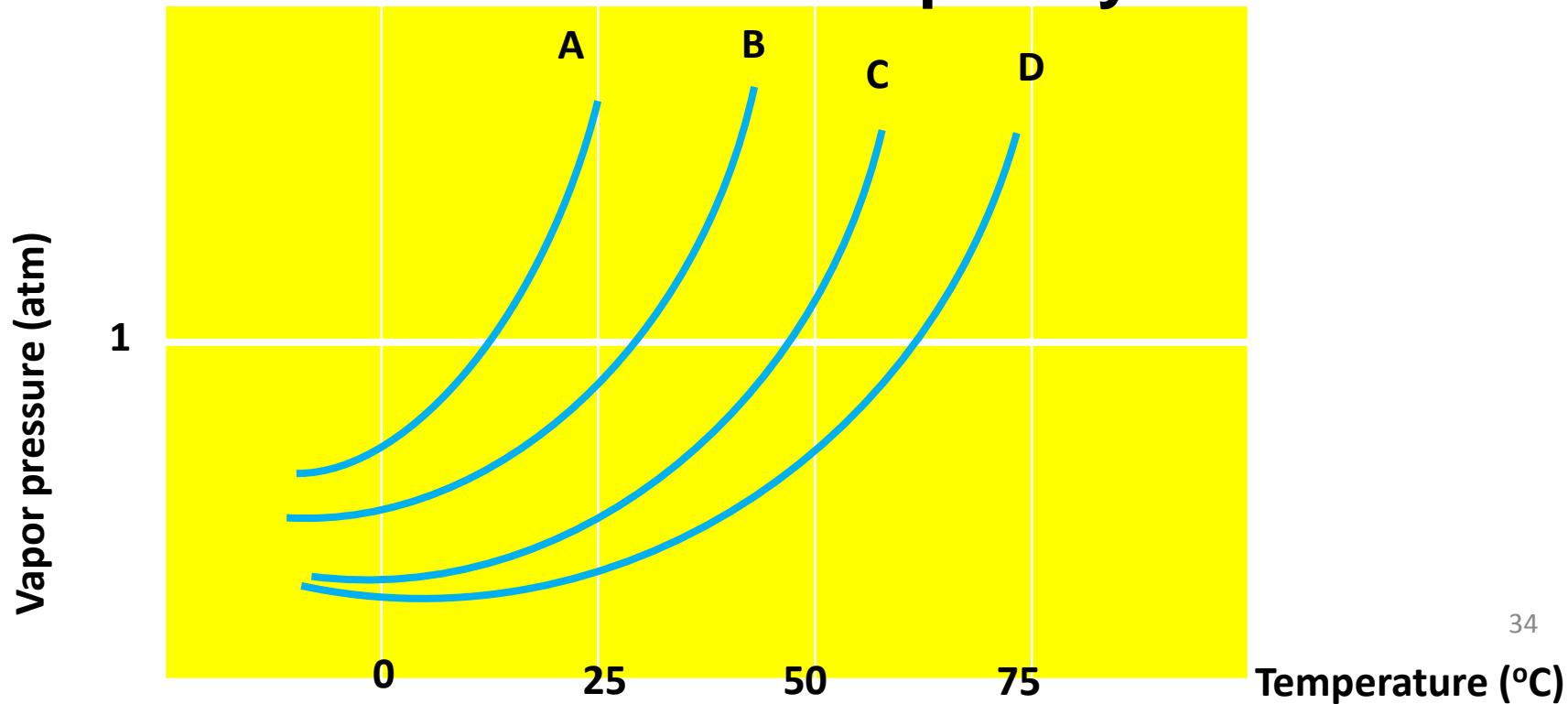
(b) 2-Methylbutane:
 $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$

(c) 2,2-Dimethylpropane:
 $(\text{CH}_3)_4\text{C}$



EXAMPLE 4 :

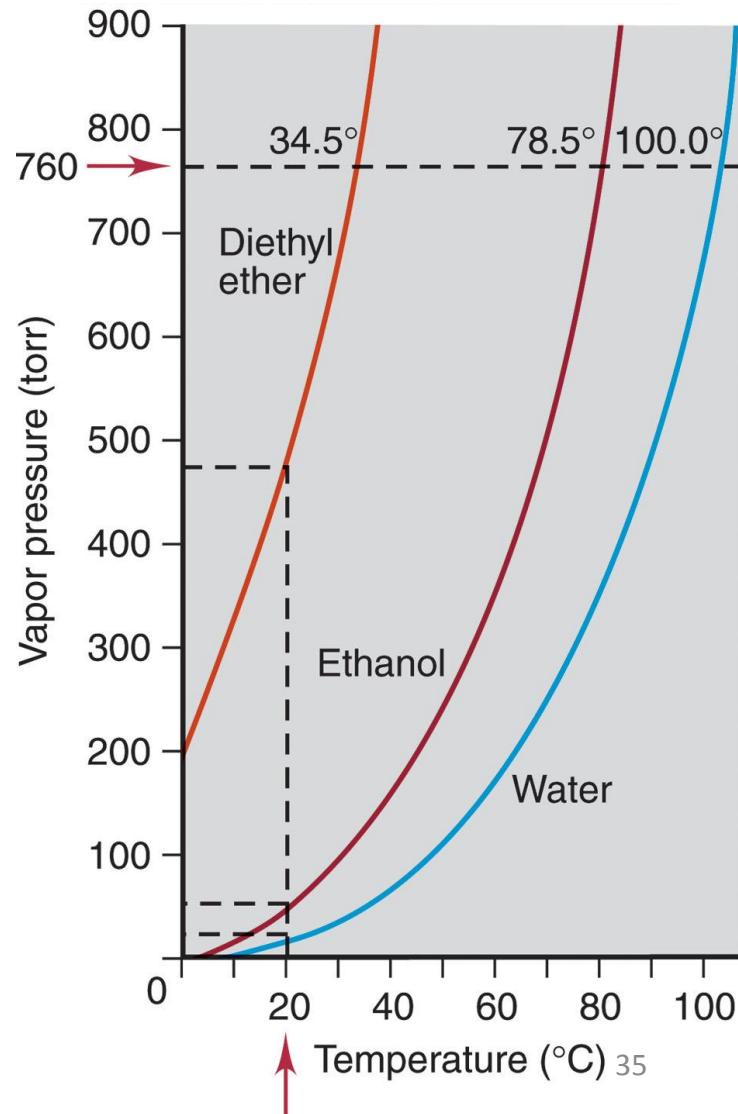
The vapor pressure curves for four substances are shown in the plot. Which one of these four substances will have the greatest intermolecular attractive forces at 25°C? Explain your answer.





EXAMPLE 5 :

By referring to the graph shown, what is the boiling point of water when the external pressure is 187.5 mmHg?



5.0 STATES OF MATTER

5.3 Solid



Fixed-shape of solid

Explain the process of:

Freezing (solidification)

Melting (fusion)

sublimation

deposition

Differentiate between amorphous and crystalline solids

Types of crystalline solids with appropriate examples.

metallic
ionic
Molecular covalent
Giant covalent

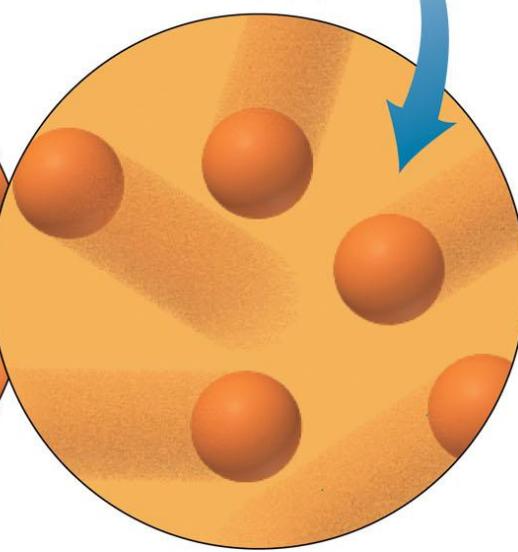
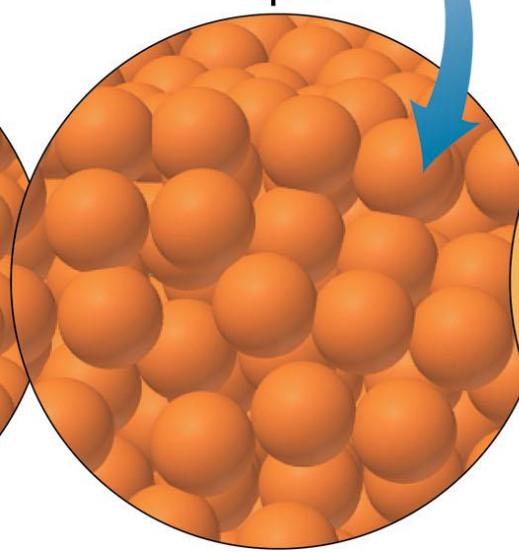
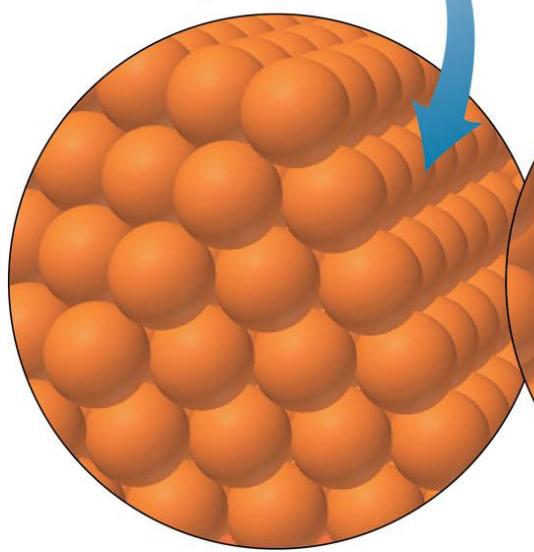
Compare the properties of solid with liquid and gas



Solid

Liquid

Gas



PROPERTIES OF SOLID

Why solid are in fixed-shape ??

- ④ Atoms / molecules in solids are **arranged closely** together & definite order.
- ④ They can only **vibrate** and **rotate** about **fixed position**.
- ④ They have **rigid arrangement** & cannot **move freely**

PROPERTIES OF SOLID

④ Shape and volume

- **Maintain its own shape and size**

④ Compressibility

- **Almost none**

④ Ability to flow

- **Almost none**

④ Density

- **High**

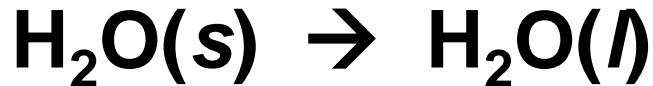
④ Motion of molecules

- **Vibrate about fixed positions**

MELTING (FUSION)

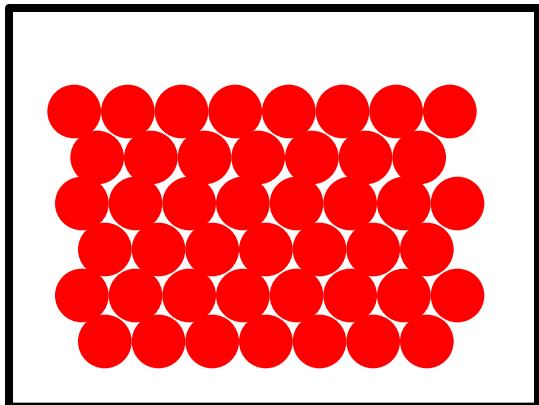
- ⦿ Solid changes to liquid

EXAMPLE:



- ⦿ When solid heated, the particles gain kinetic energy and vibrate faster
- ⦿ At certain temperature, the particles have enough kinetic energy to break free of their fixed position

(i)

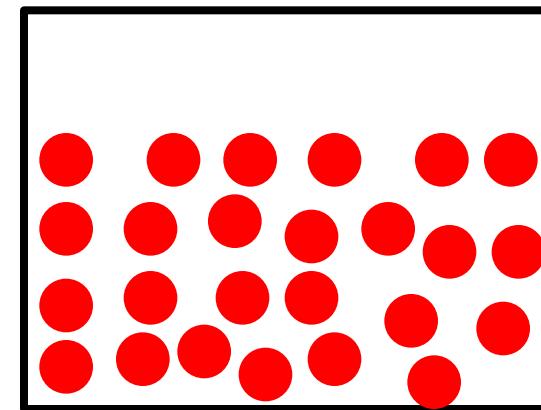


solid



heated

(iii)



liquid

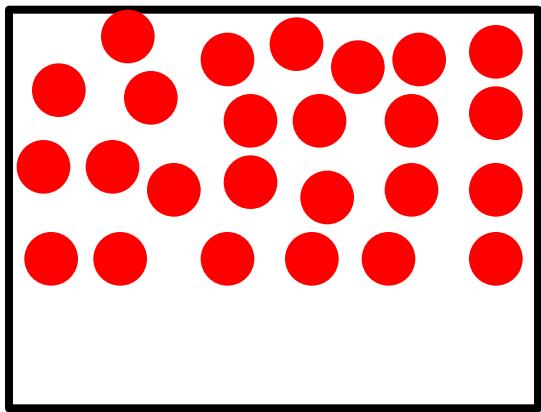
FREEZING (SOLIDIFICATION)

☞ Liquid changes to solid

EXAMPLE:

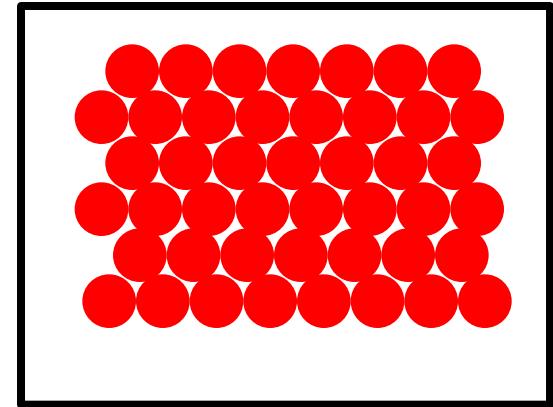


- ☞ When liquid cooled, the particles **lose kinetic energy** and move more **slowly**.
- ☞ ∴ Intermolecular forces become **stronger** and particles become **fixed** in position.



liquid

→
Cooled
(temperature decreased)



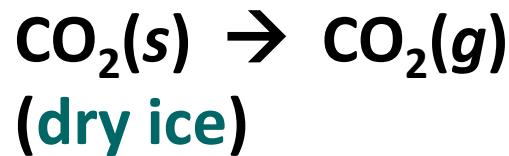
solid

As the temperature drops, fewer particles have enough kinetic energy to overcome neighbouring attractions, and the particles lock into place. As more and more of the particles settle into a relatively fixed position, the substance gains a shape of its own and becomes a solid.

SUBLIMATION

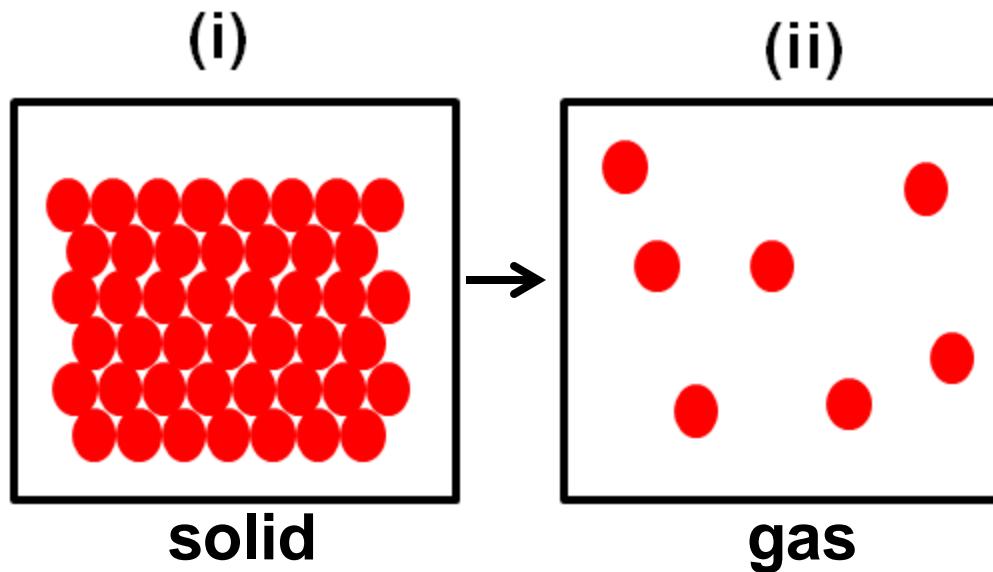
- Solid changes directly to gas without becoming a liquid

EXAMPLE:



When a substance sublimes, molecules leave the surface of the solid, where they are held by less tightly than the interior

The combination of **intermolecular attractions** and **atmospheric pressure** is **not great enough** to keep the particles near to one another when they leave solid state.



DEPOSITION



Gas changes directly to solid without becoming a liquid

EXAMPLE: $I_2(g) \rightarrow I_2(s)$

When iodine vapor comes in contact with a **cold surface**, it **deposits** iodine crystals
 $I_2(g) \rightarrow I_2(s)$

At ordinary atmospheric pressure, solid iodine **sublimes**: $I_2(s) \rightarrow I_2(g)$

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STRUCTURAL FEATURES



**Two broad categories based the
orderliness of their particles:**

- Crystalline
- Amorphous

8



13

Differentiate Between Amorphous & Crystalline solid

CRYSTALLINE SOLID

- Well-defined shape
- Particles (atom, molecules or ions) are in **orderly arrangement**

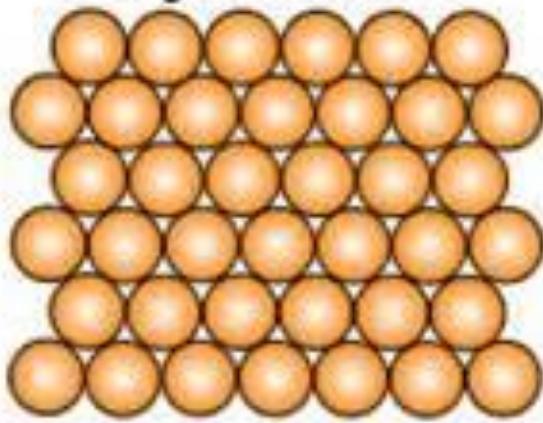
AMORPHOUS SOLID (Noncrystalline)

- **Poorly** defined shape
- **Lack** in orderly arrangement of their particles

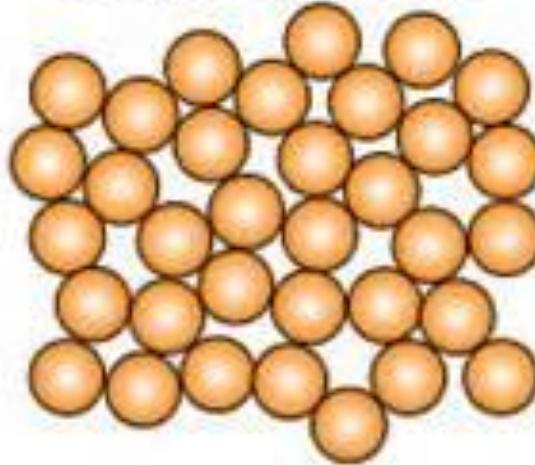
EXAMPLE:
metal, salt and diamond

EXAMPLE:
charcoal, rubber , glass

Crystalline



Amorphous



**Arrangement of particles in crystalline and
amorphous solid**

TYPES OF CRYSTALLINE SOLIDS



Defined by **type of **particles** in the crystal**

👉 determine the **forces between them:**

- Metallic (Na, Fe)
- Ionic (NaCl, CaF₂)
- Molecular covalent (O₂, H₂O)
- Giant covalent (diamond, SiO₂)

METALLIC SOLID

- ④ **Lattice points** occupied by metal atoms
- ④ Held together by **strong metallic bond**
- ④ Soft to hard, low to very high melting point
- ④ **Good conductor of heat and electricity**
- ④ **Malleable, ductile**

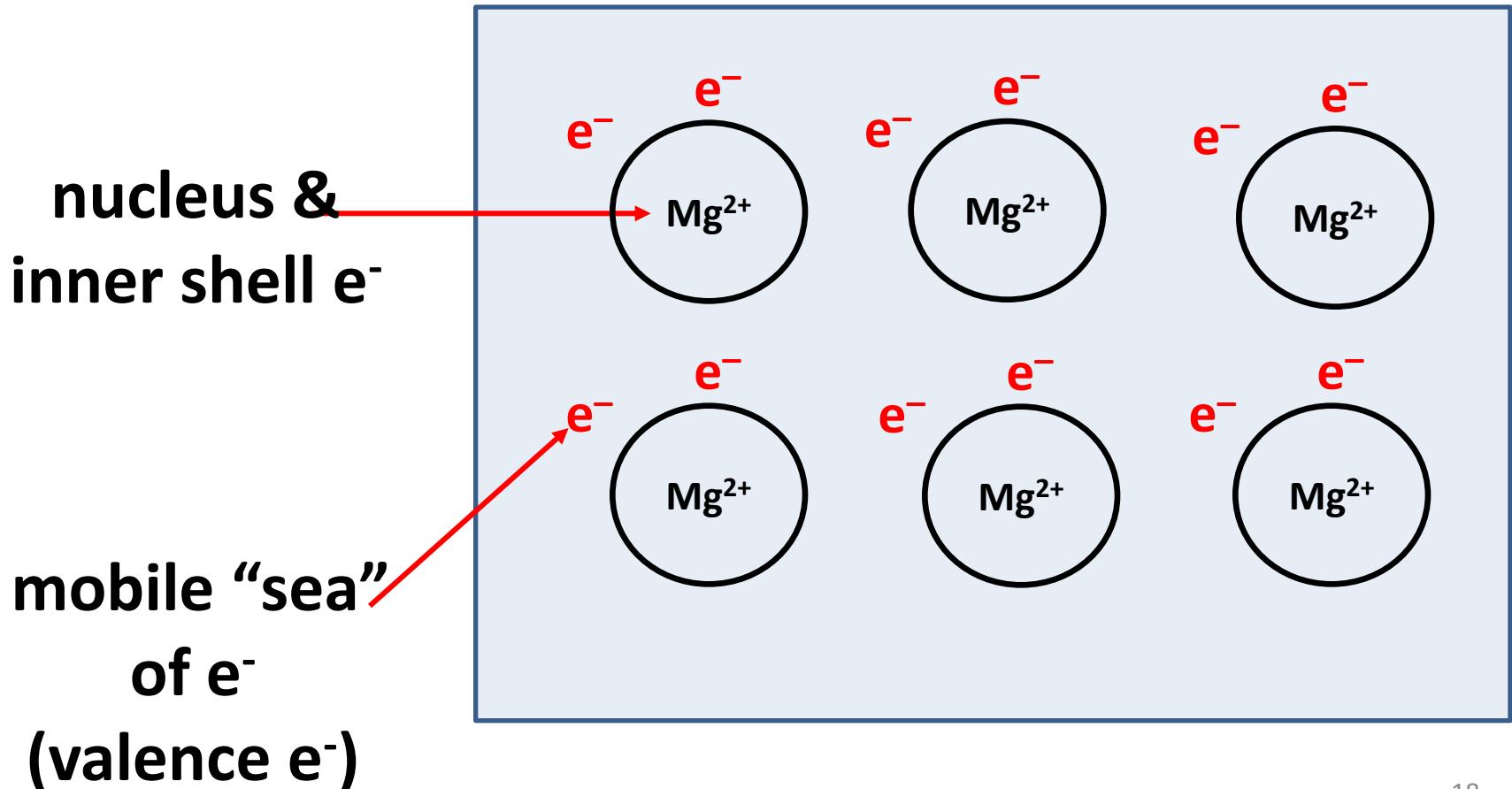
EXAMPLE:

Na, Zn, Fe



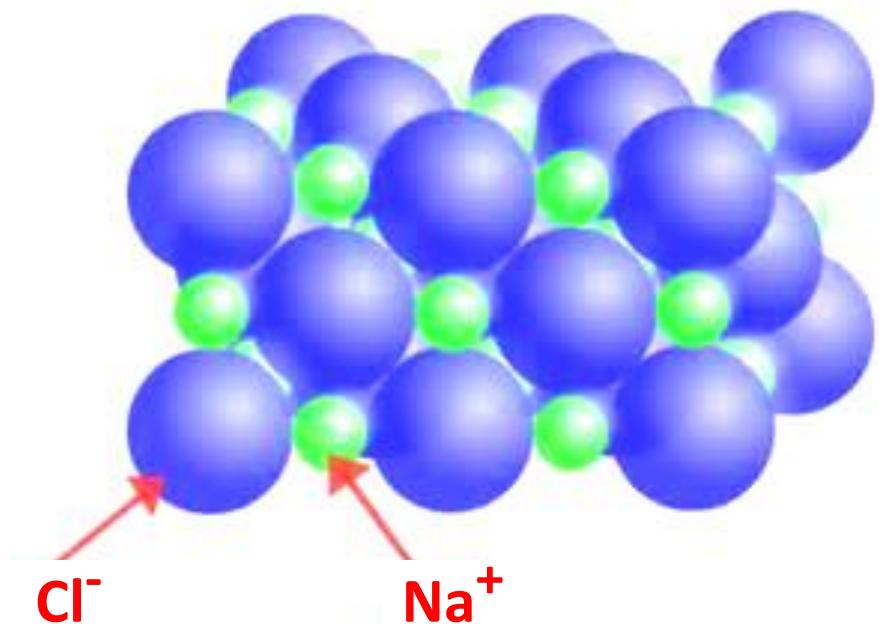
ELECTRON SEA MODEL

EXAMPLE : Magnesium metal



IONIC SOLID

- ⌚ Lattice points occupied by **cations** and **anions**
- ⌚ Held together by **strong electrostatic attraction**
- ⌚ **Hard, brittle, high melting point**
- ⌚ Poor conductor of heat and electricity
(in solid state) but does so in **molten state** or in **aqueous solution** due to the **free moving ions**



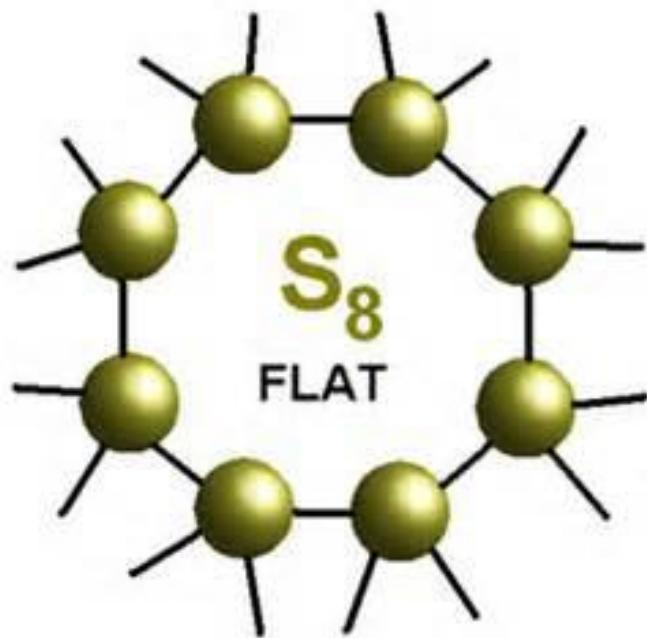
Example of ionic solid : NaCl

MOLECULAR COVALENT

- 🕒 Lattice points occupied by molecules
- 🕒 Held together by intermolecular force
- 🕒 Fairly soft, low to moderate melting point
- 🕒 Poor conductor of heat and electricity

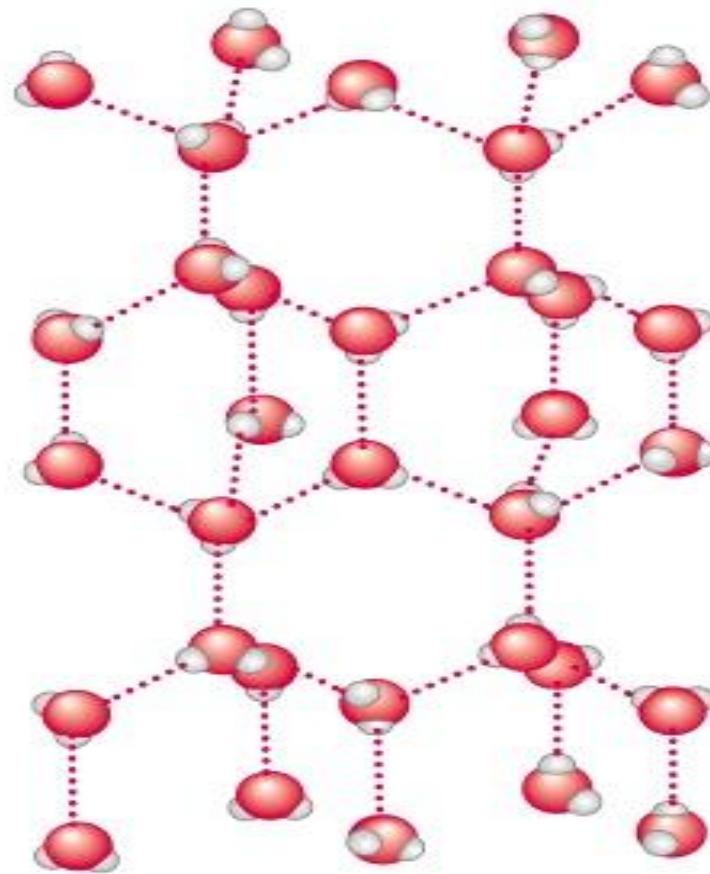
EXAMPLE: Nonpolar molecule : P_4 , S_8

Polar molecule : H_2O (ice)



ICE

(a) **Solid water (ice)**



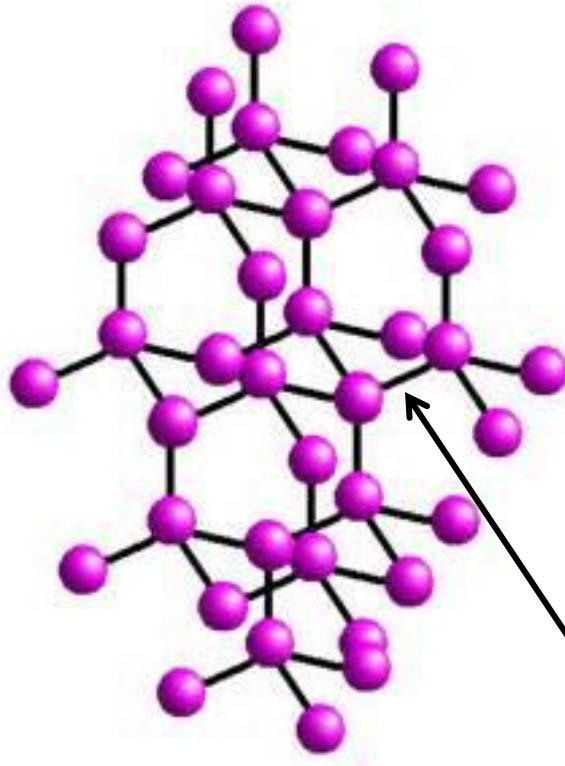
NETWORK SOLID

(GIANT COVALENT)

- Ⓐ Also called **giant covalent**
- Ⓑ Held together by strong **covalent link** and forms **network**
- Ⓒ **Very hard**, very **high** melting point
- Ⓓ Usually **poor** conductor of heat and electricity

EXAMPLE: C allotrope (diamond)
 SiO_2





**C allotrope
(diamond)**



Covalent bond

SiO_2

Comparison the properties of solid, liquid & gas

TERM	SOLID	LIQUID	GAS
Shape and volume	Maintain its own shape and size.	Conforms to shape of container. Has fixed (definite) volume	Conforms to shape & volume of container.
Viscosity	High	Moderate	Low
Compressibility	Almost none	Very low	High
Diffusion	Very slow	Slow	Fast/rapidly
Density	High	High	Low

5.0 STATES OF MATTER

5.4 Phase diagram

Phase
Diagram

Define

Phase

Triple point

Critical point

Phase Diagram

Positive Slope – CO_2

Negative Slope – H_2O

Triple Point & Critical Point on the
phase diagram

Anomalous behaviour of H_2O

Changes
in Phase

Temperature(constant P) @ ISOBARIC

Pressure (constant T) @ ISOTHERMAL

PHASE

- 🌀 A homogenous part of a system in contact with other parts of the system but separated from by well-defined boundary
- 🌀 A phase is **homogeneous part**
- 🌀 Phase consist of :
 - Solid
 - Liquid
 - Gas

EXAMPLE :



two phases

Solid phase : ice

Liquid phase : water

three-phase system

gas

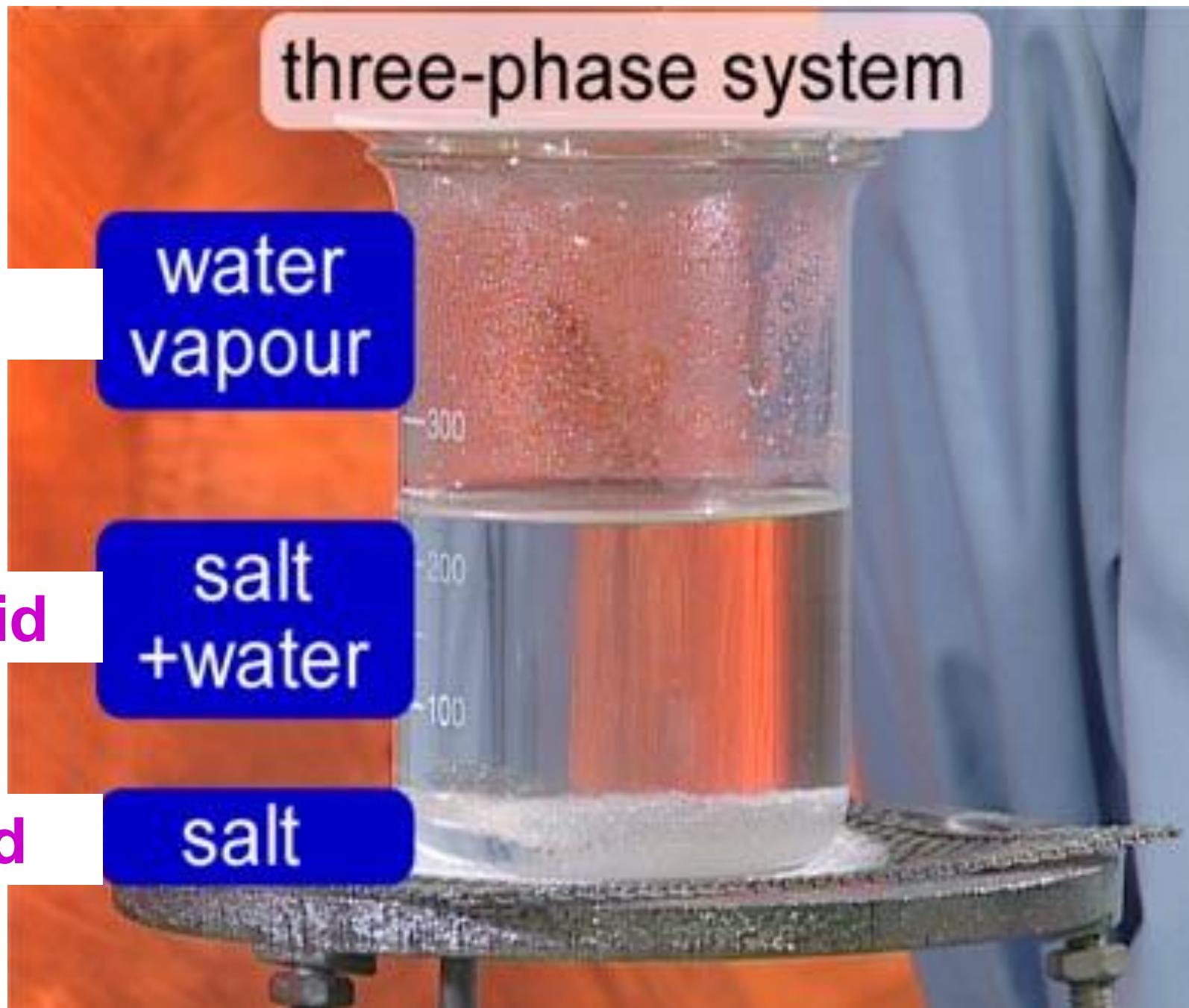
water
vapour

liquid

salt
+water

solid

salt



How many phase?



one phase (liquid)



Oil + water

two phase (liquid)
(but heterogenous)

How many phase?



**One gas only
one phase (gas)**



**Mixture of gases
one phase (gas)**

System	Phase	Description
Mixture of gases	1	Gases are well mixed. We cannot see the boundary between the gases.
Two liquids Do not mix (oil-water)	2	We can see the boundary between the two liquids.
Two liquids well mixed (alcohol-water)	1	We cannot see the boundary of the solution.

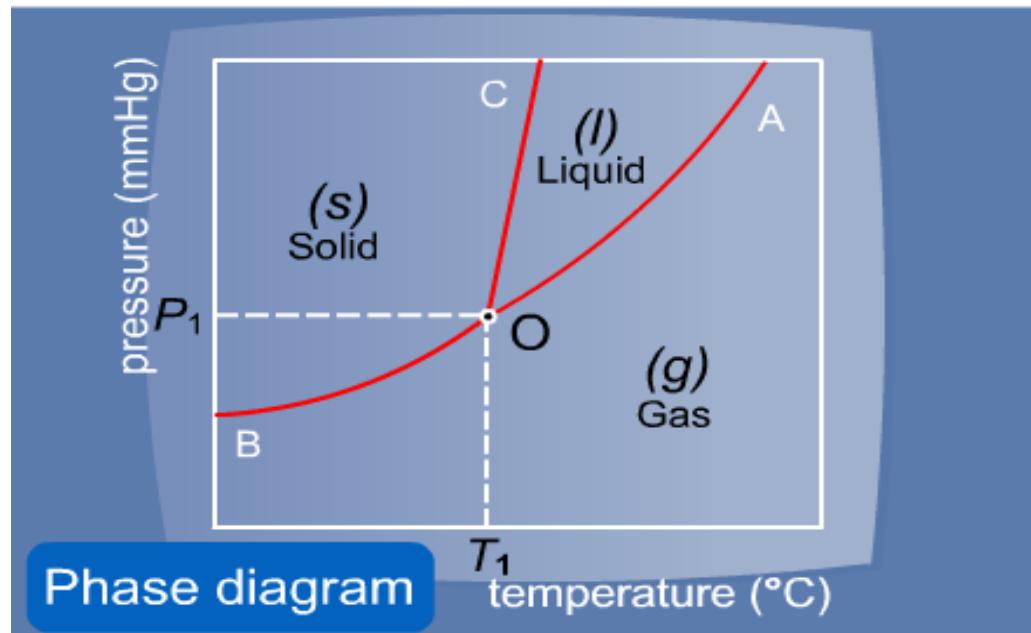
EXAMPLE :

Identify the phases of the following under normal conditions.

- (a) Steel
- (b) Mercury
- (c) Aqueous ethanol
- (d) A saturated solution of copper sulphate stored in a closed bottle

PHASE DIAGRAM

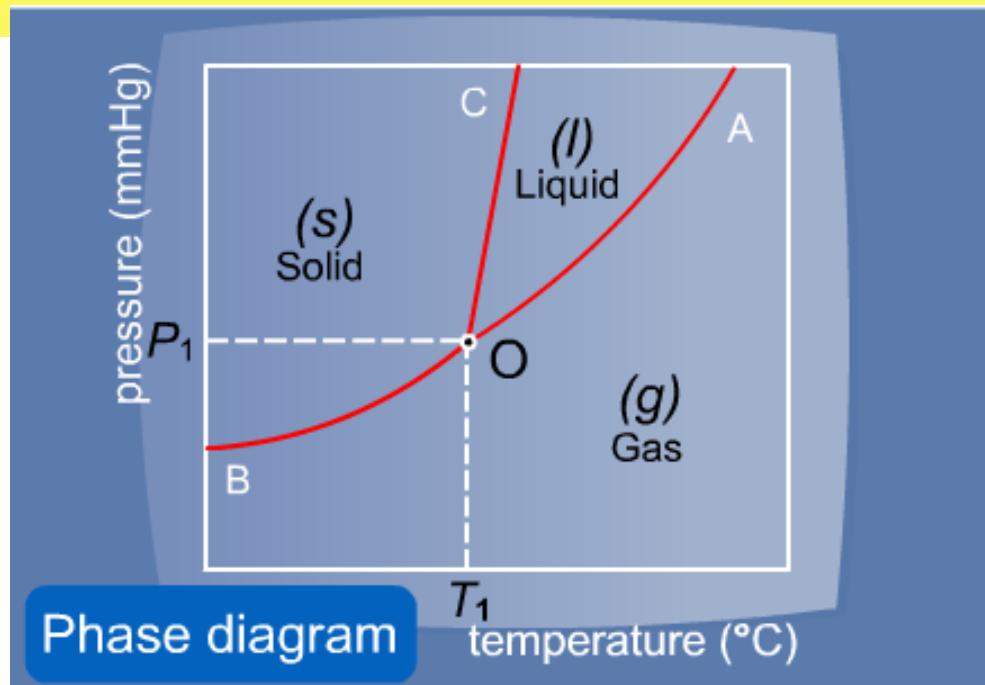
⌚ A diagram showing the **regions** of **pressure** and **temperature** at which a substance exists as a solid, liquid or vapor phases are **thermodynamically stable**.





It combines equilibrium curves of:

- liquid \rightleftharpoons gas : Line OA
- solid \rightleftharpoons liquid : Line OC
- solid \rightleftharpoons gas : Line OB

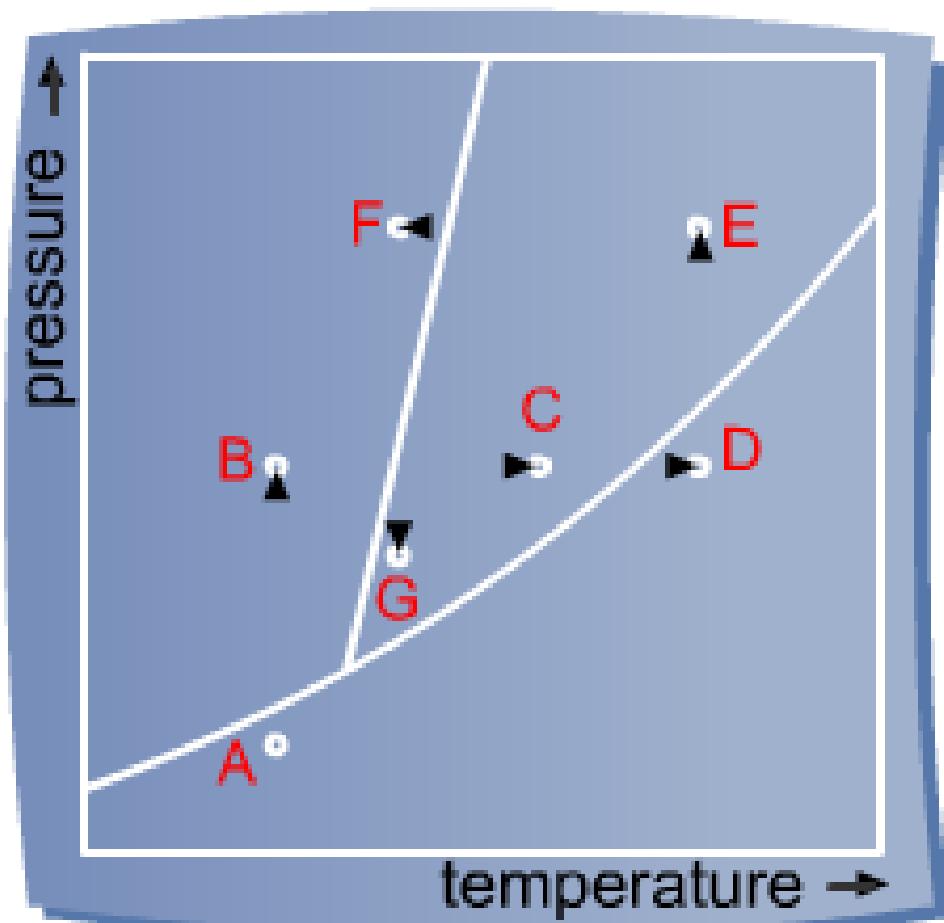




EXAMPLE 1 :

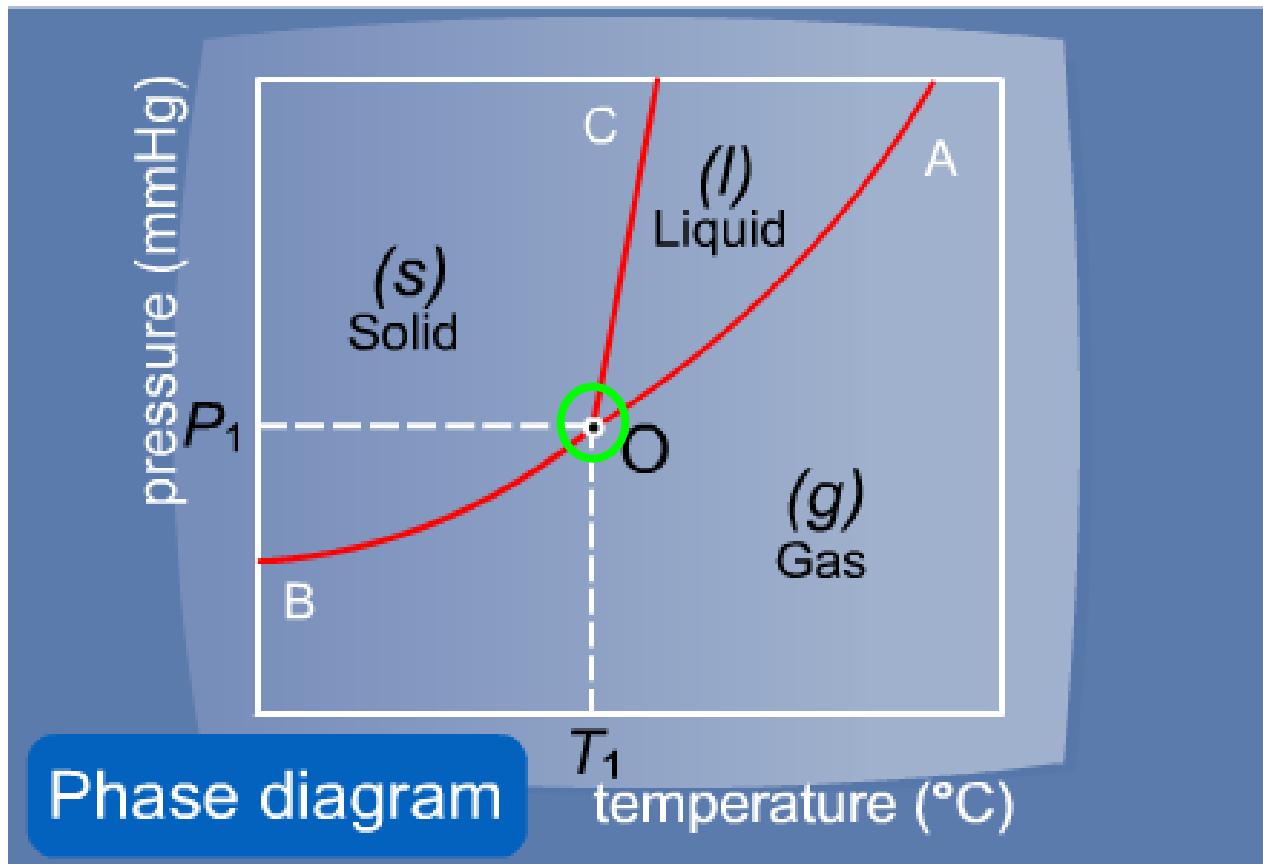
Predict the phase changes.

- (a) A-B
- (b) B-C
- (c) C-D
- (d) D-E
- (e) E-F
- (f) F-G



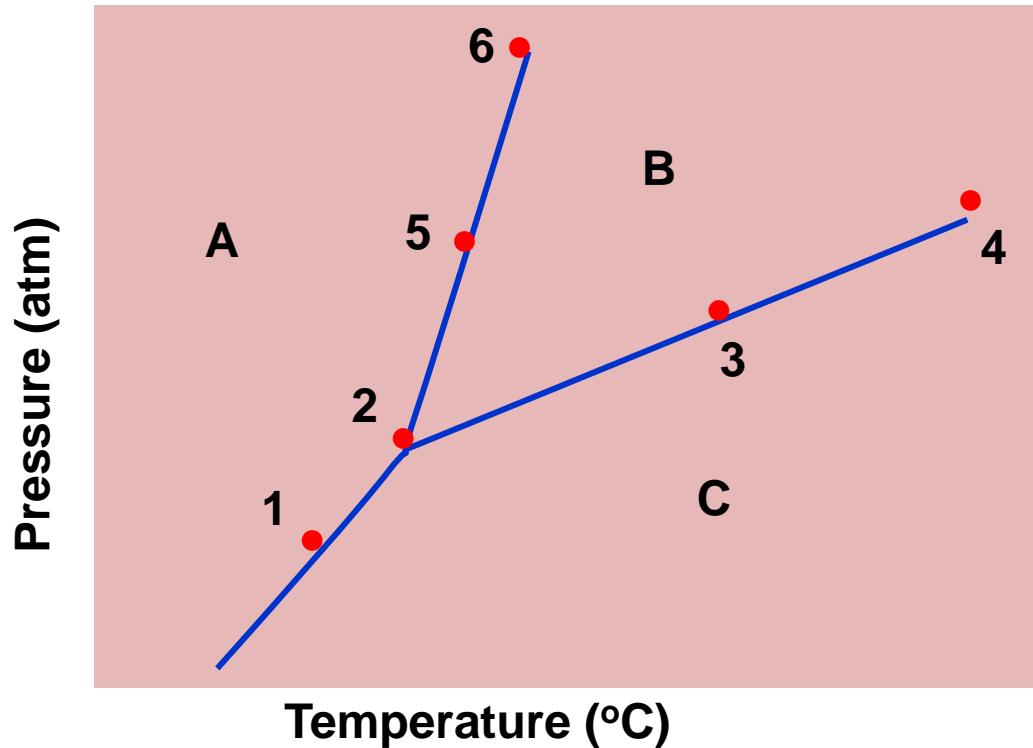
TRIPLE POINT

Solid, liquid and vapor simultaneously exist in equilibrium





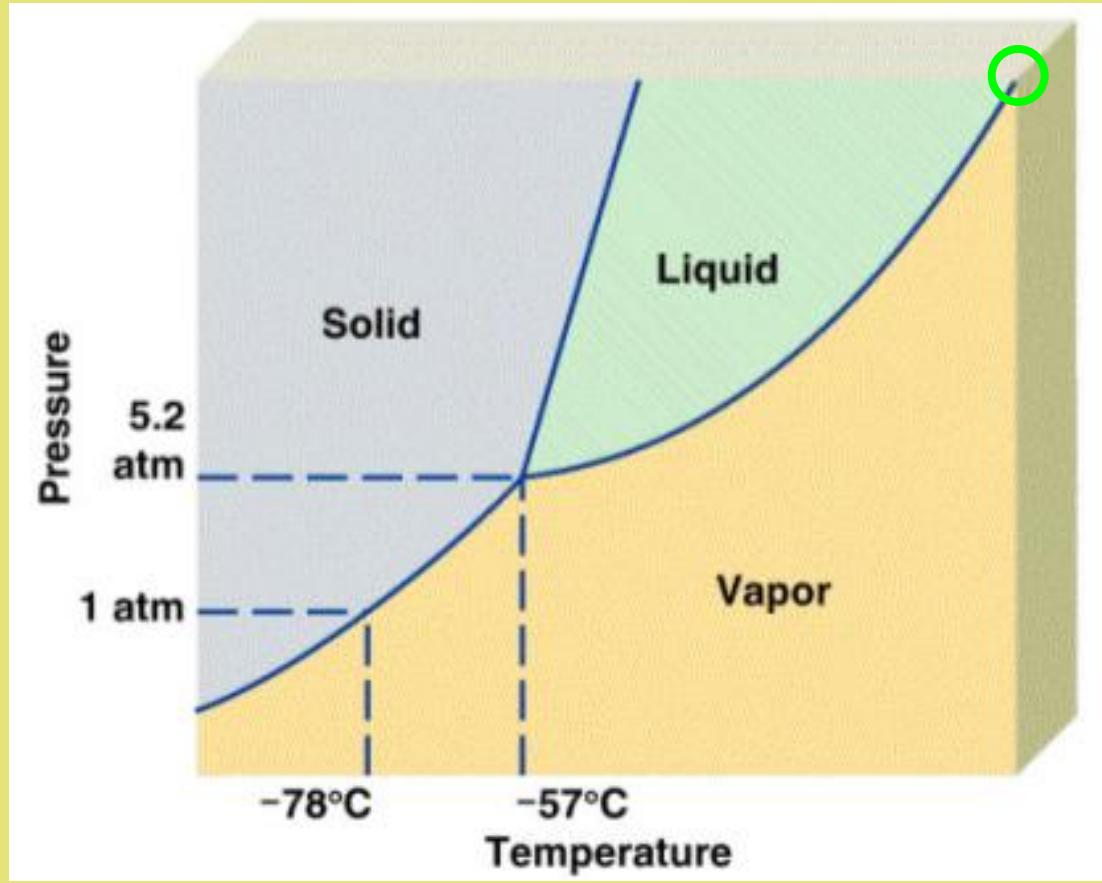
EXAMPLE 2:



- (a) What phase is present in region A? Region B?
Region C?
- (b) What phases are in equilibrium at point 1?
Point 2? Point 3? Point 5?

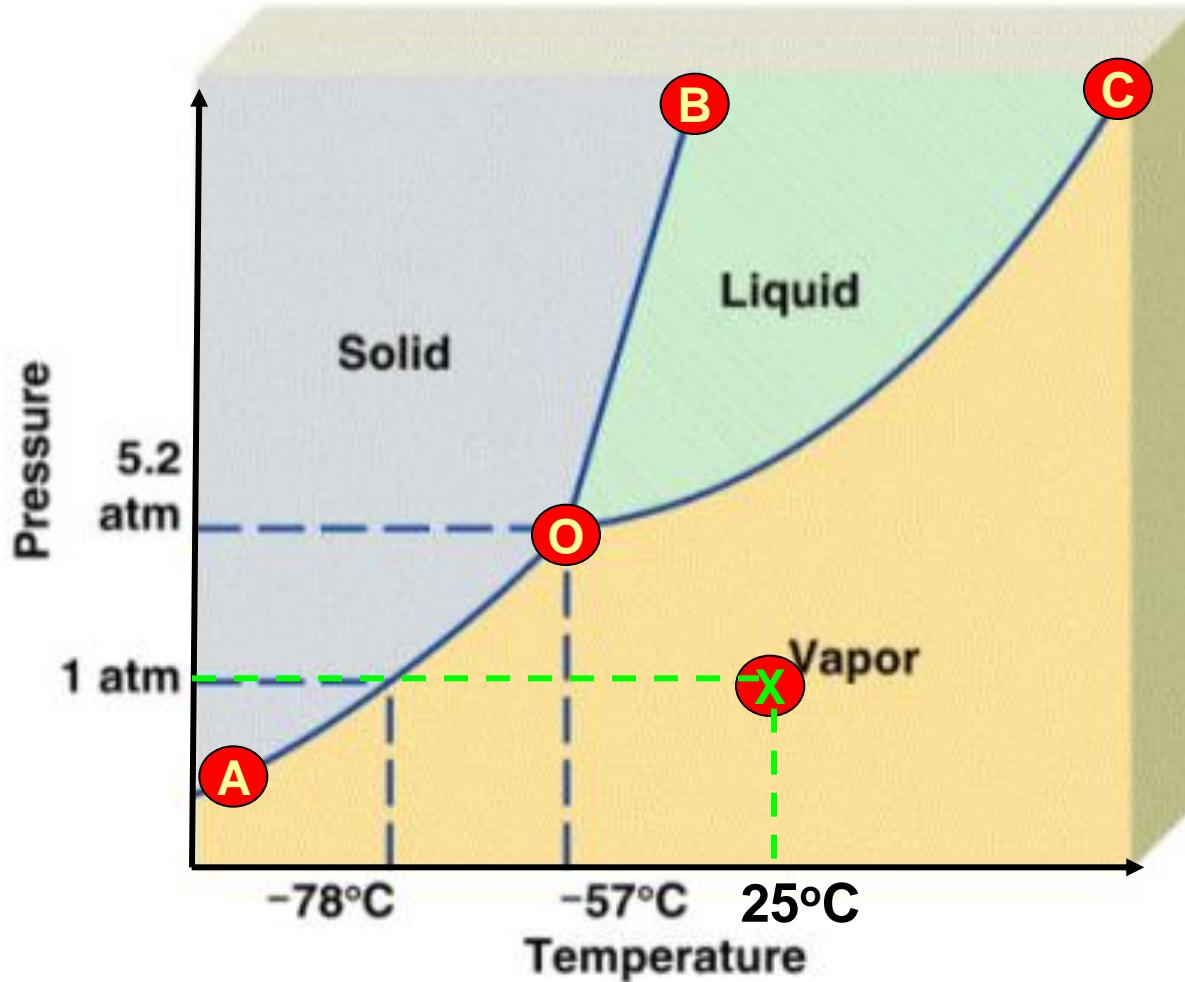
CRITICAL POINT

- 🕒 The **end of liquid–gas line**
- 🕒 The **highest temperature at which a gas can be liquefied**
- 🕒 **Density of liquid equal to density of gas**
- 🕒 Above the critical point, the **liquid phase cannot exist**, regardless the pressure
 - Phase **boundaries disappears**
 - Separate liquid and gas phase **no longer exist**

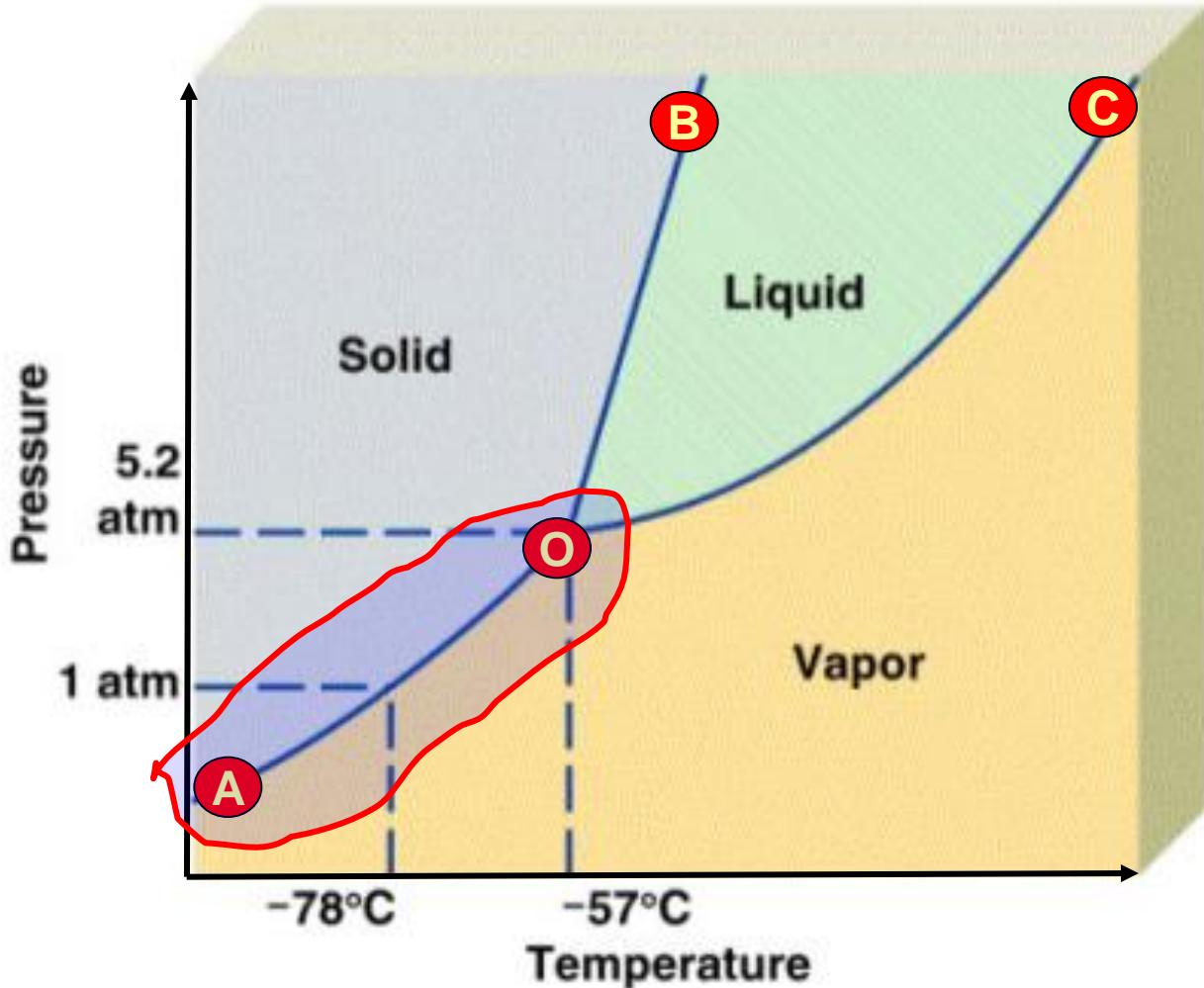


- At this point, the average **kinetic energy** of the molecules is so **high** that the vapor **cannot be condensed** no matter how much **pressure is applied**

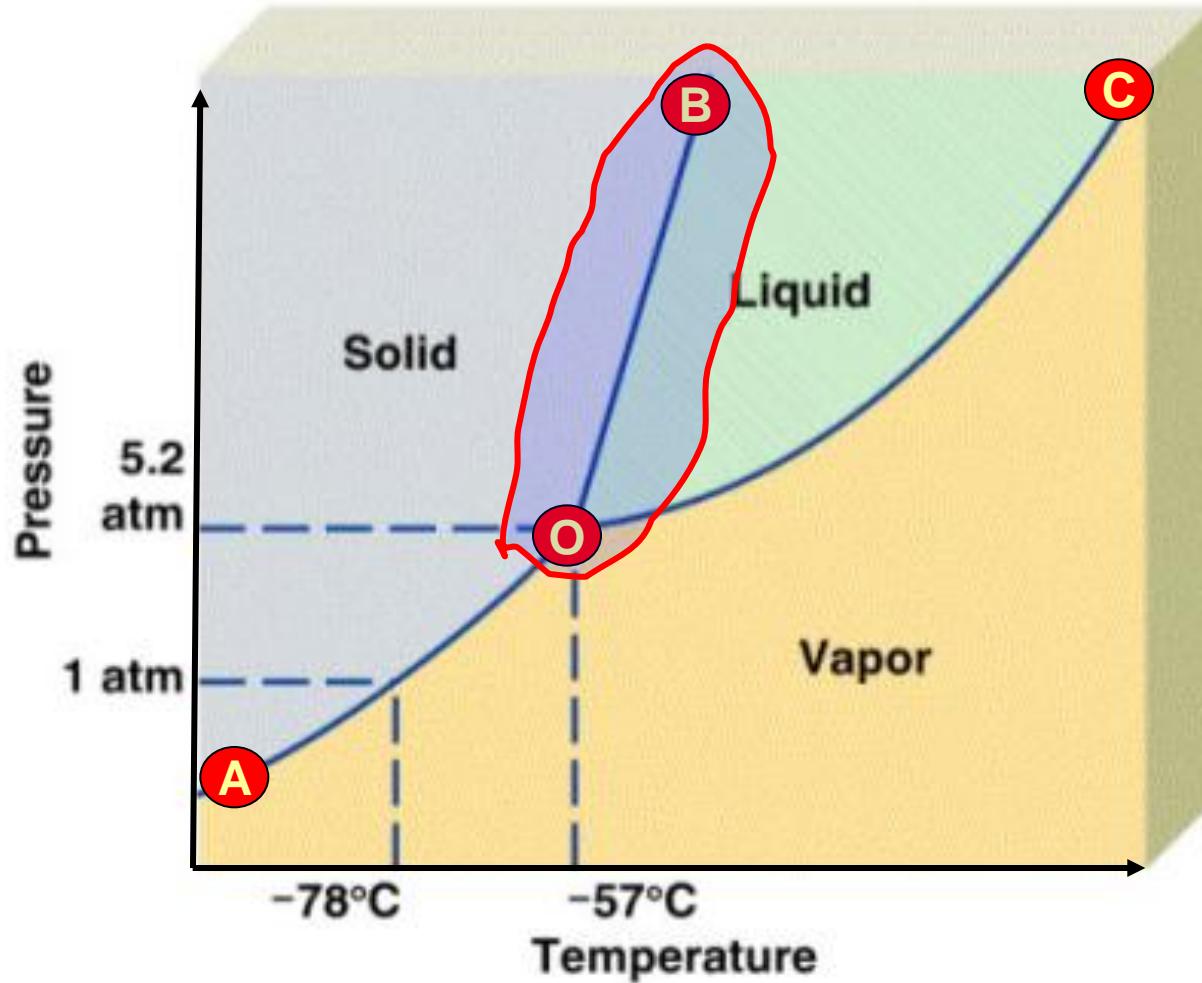
PHASE DIAGRAM OF CO₂



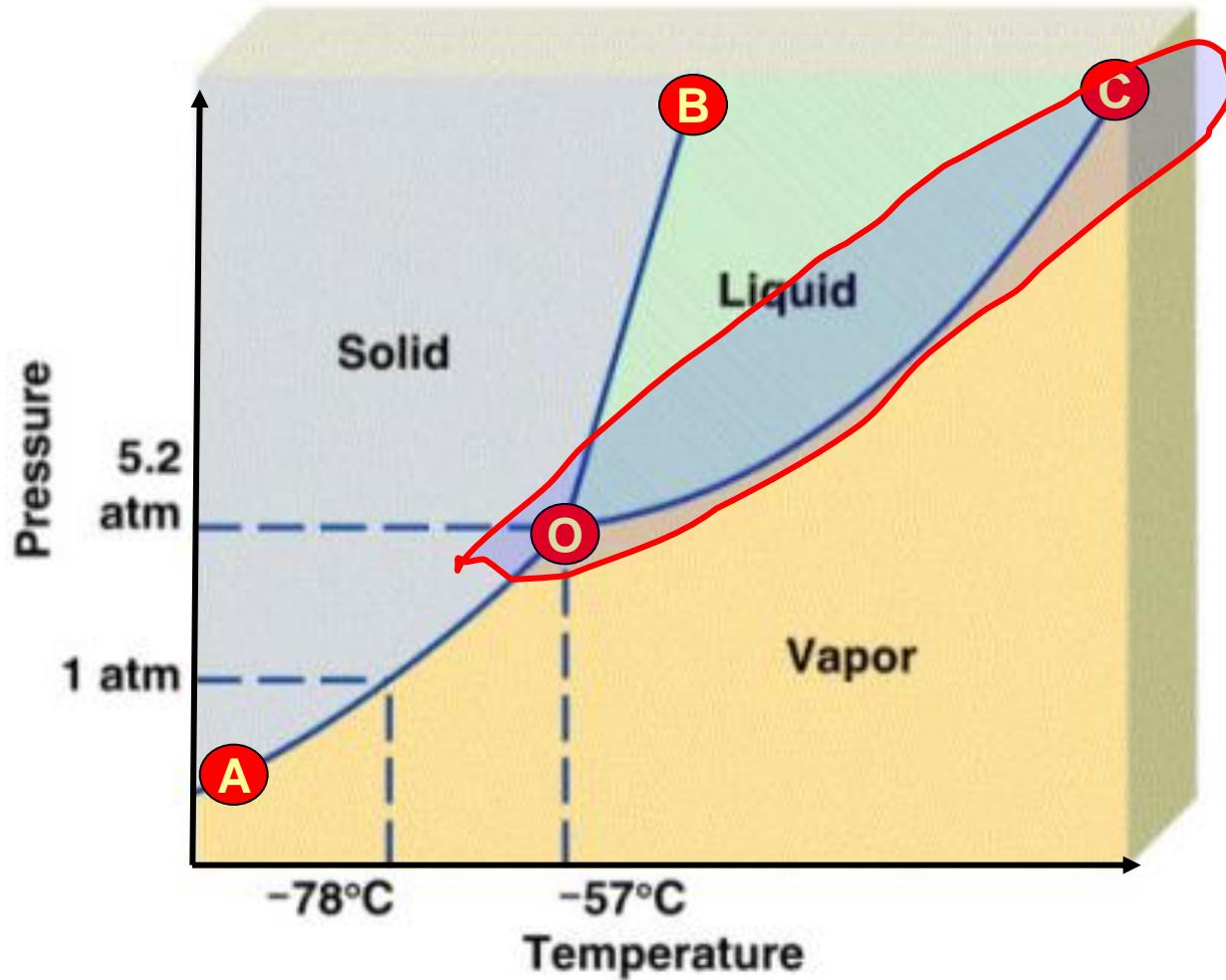
- CO₂ is a gas under normal conditions (25°C, 1 atm)



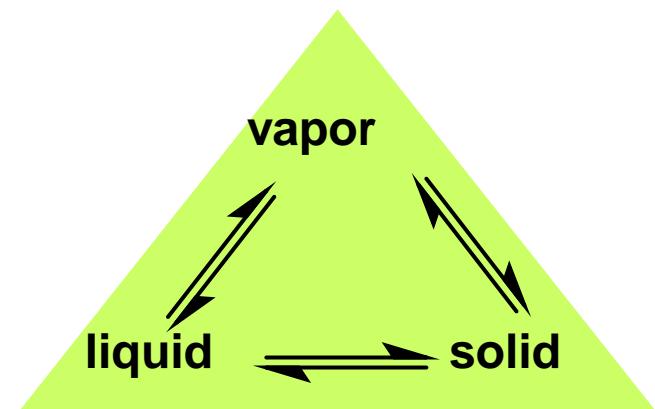
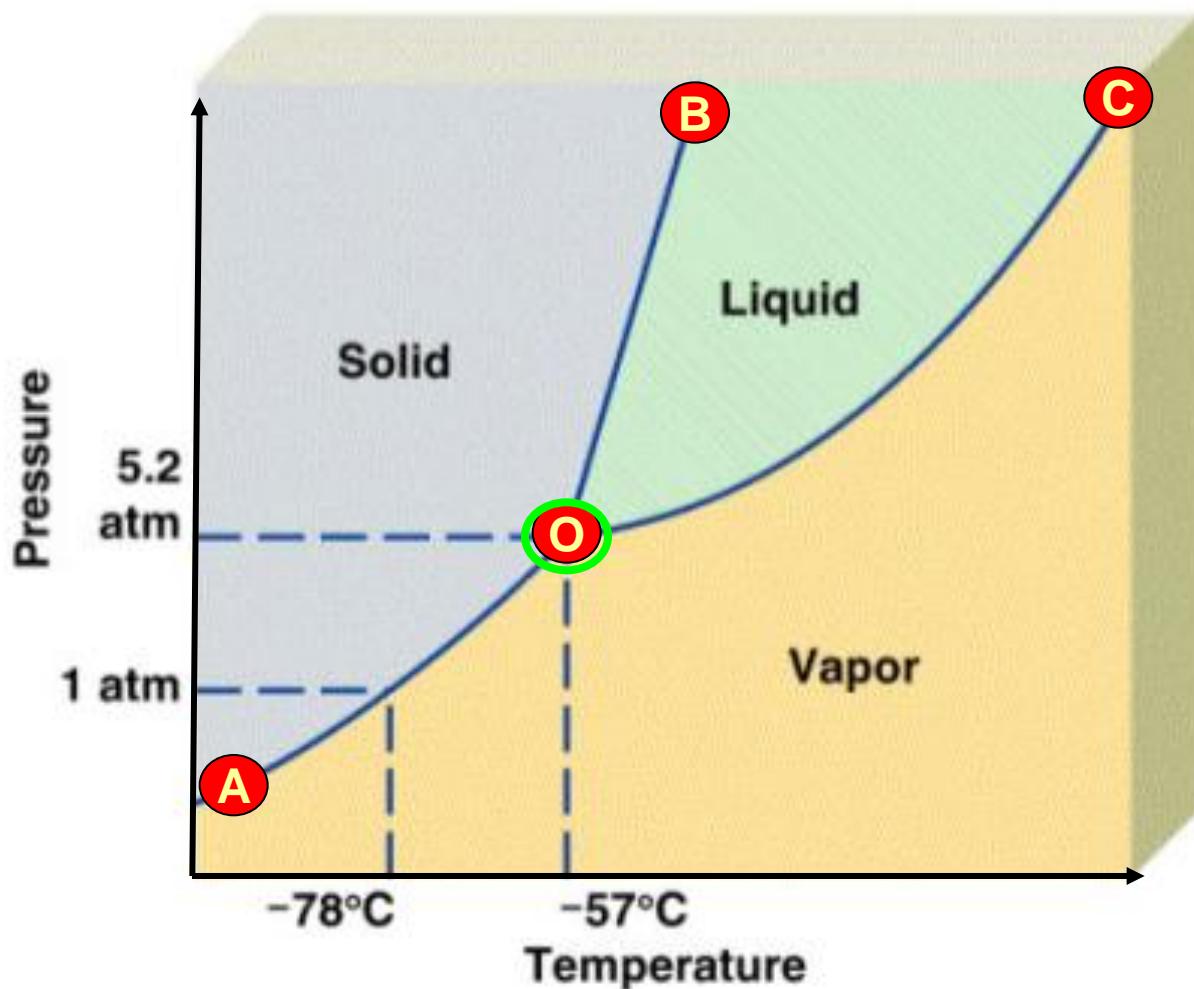
- Line OA: $\text{CO}_2(s) \rightleftharpoons \text{CO}_2(g)$
- Solid and gas exist in **equilibrium**



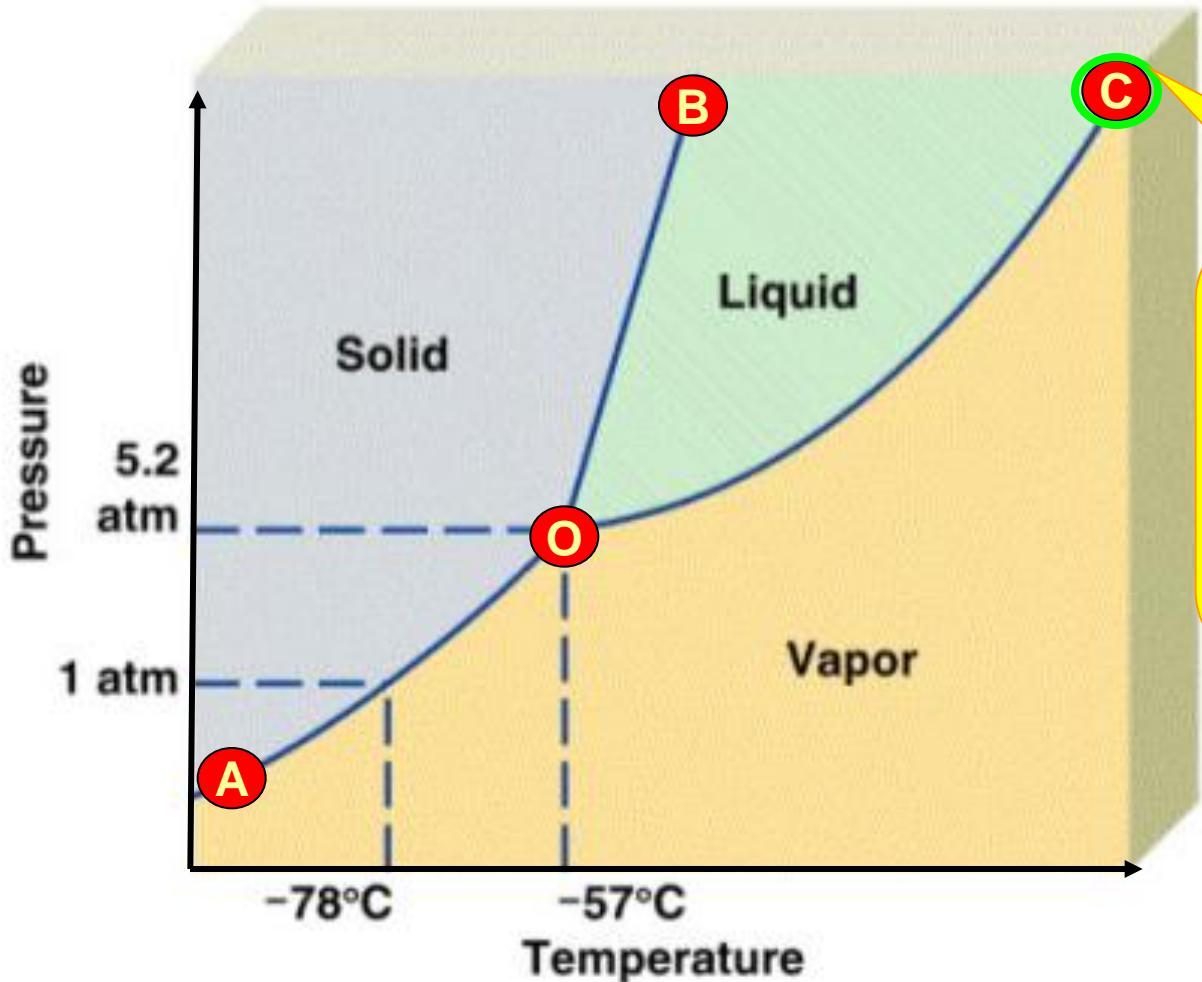
- Line OB: $\text{CO}_2(\text{s}) \rightleftharpoons \text{CO}_2(\text{l})$ (melting / freezing line)
 - ☞ solid and liquid exist in equilibrium



- Line OC: $\text{CO}_2(l) \rightleftharpoons \text{CO}_2(g)$ (boiling curve)
☞ liquid and gas exist in equilibrium

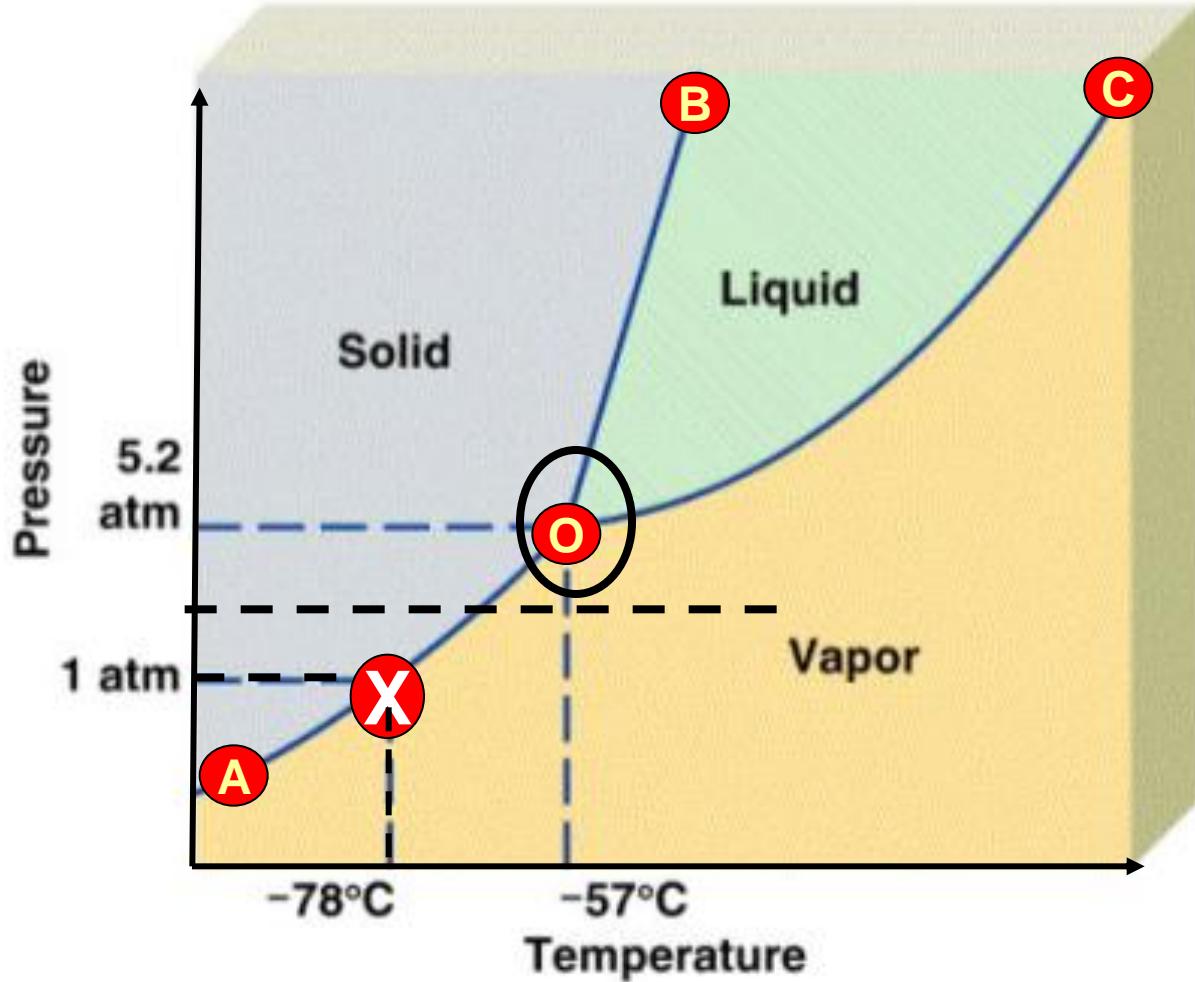


- Point O = **Triple Point** (-56.4°C , 5.2 atm)
- Solid, liquid and vapor exist in **equilibrium**

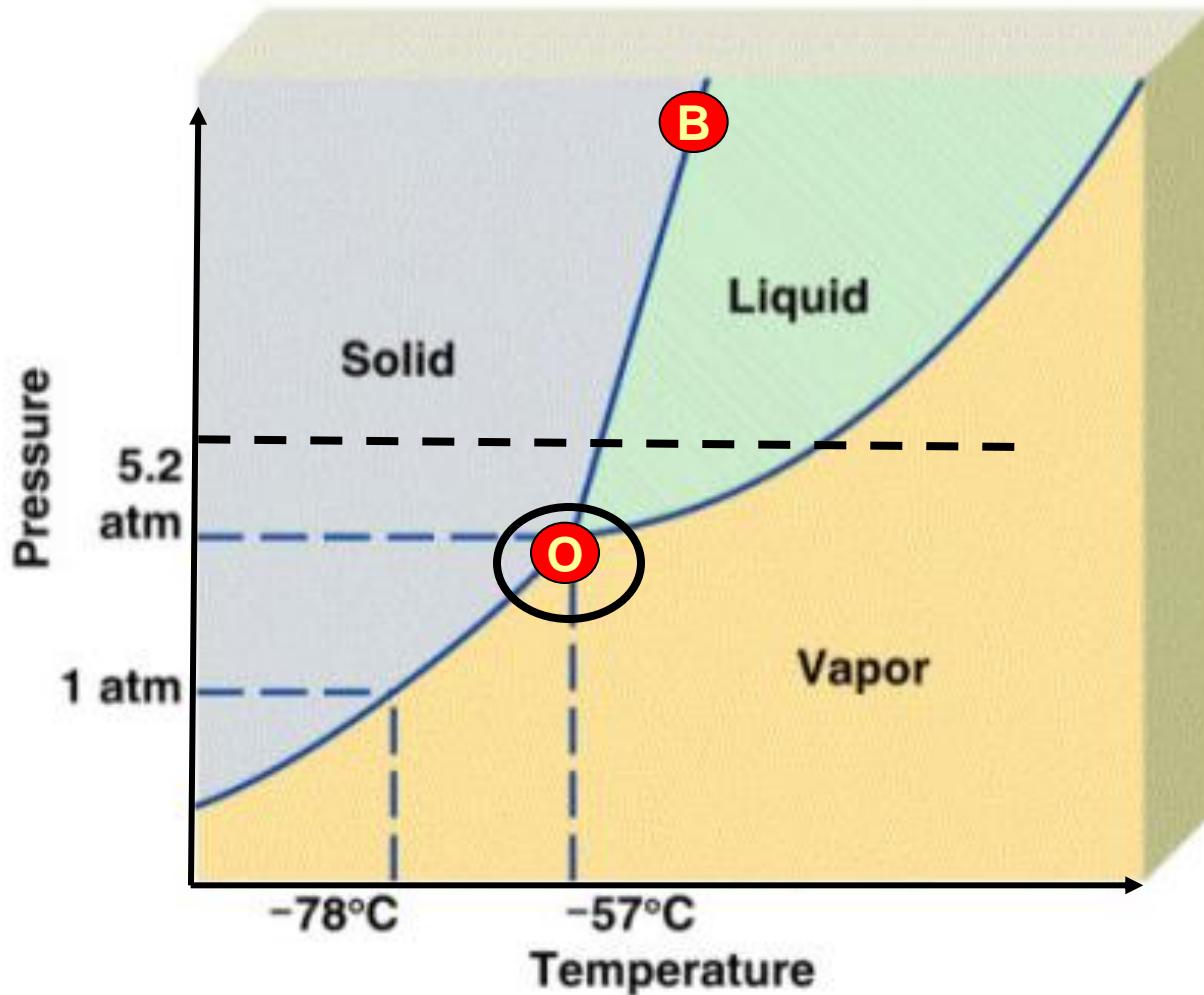


Above the critical point, the liquid phase cannot exist, regardless the pressure

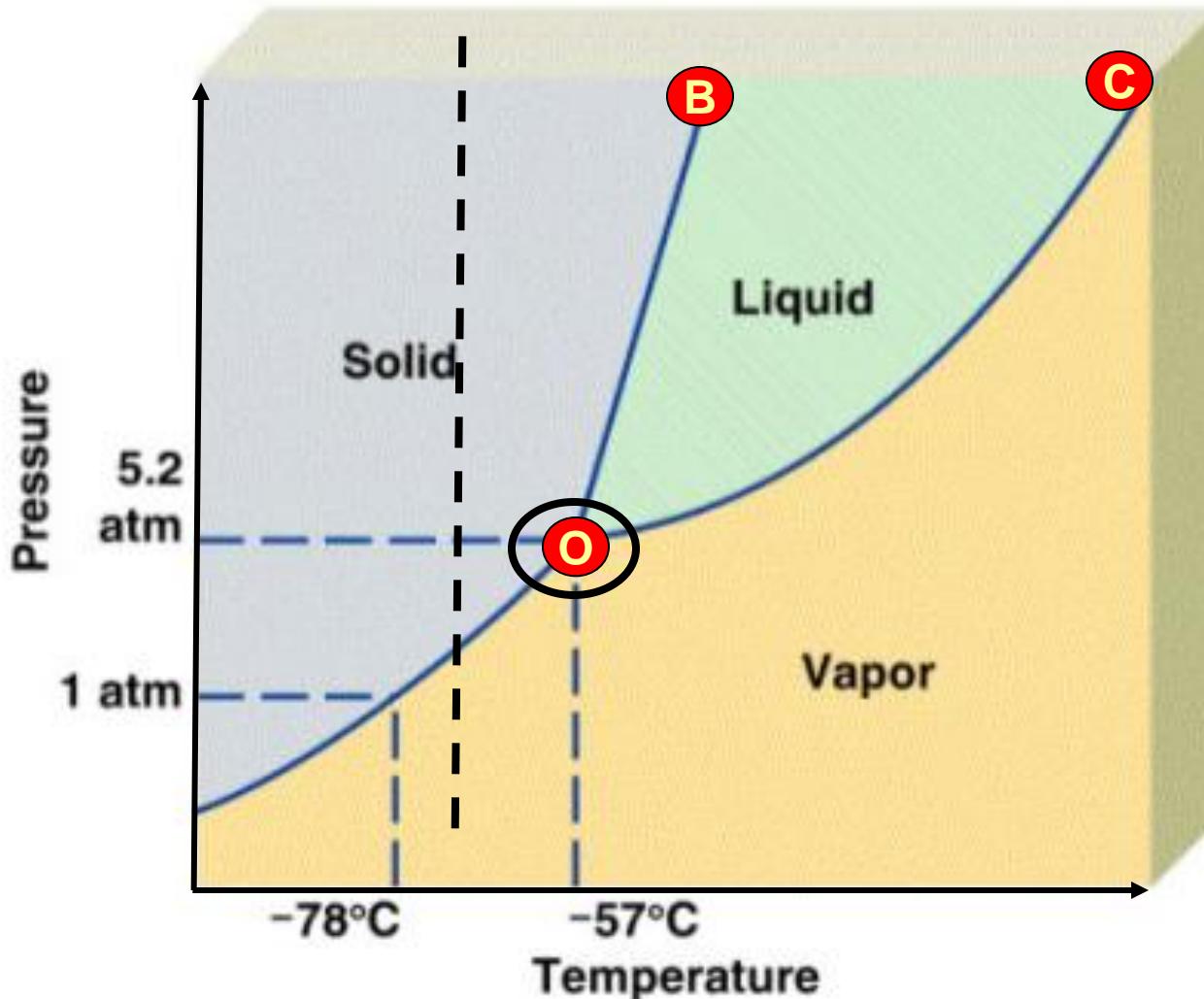
- Point C: Critical Point (31°C , 73 atm)



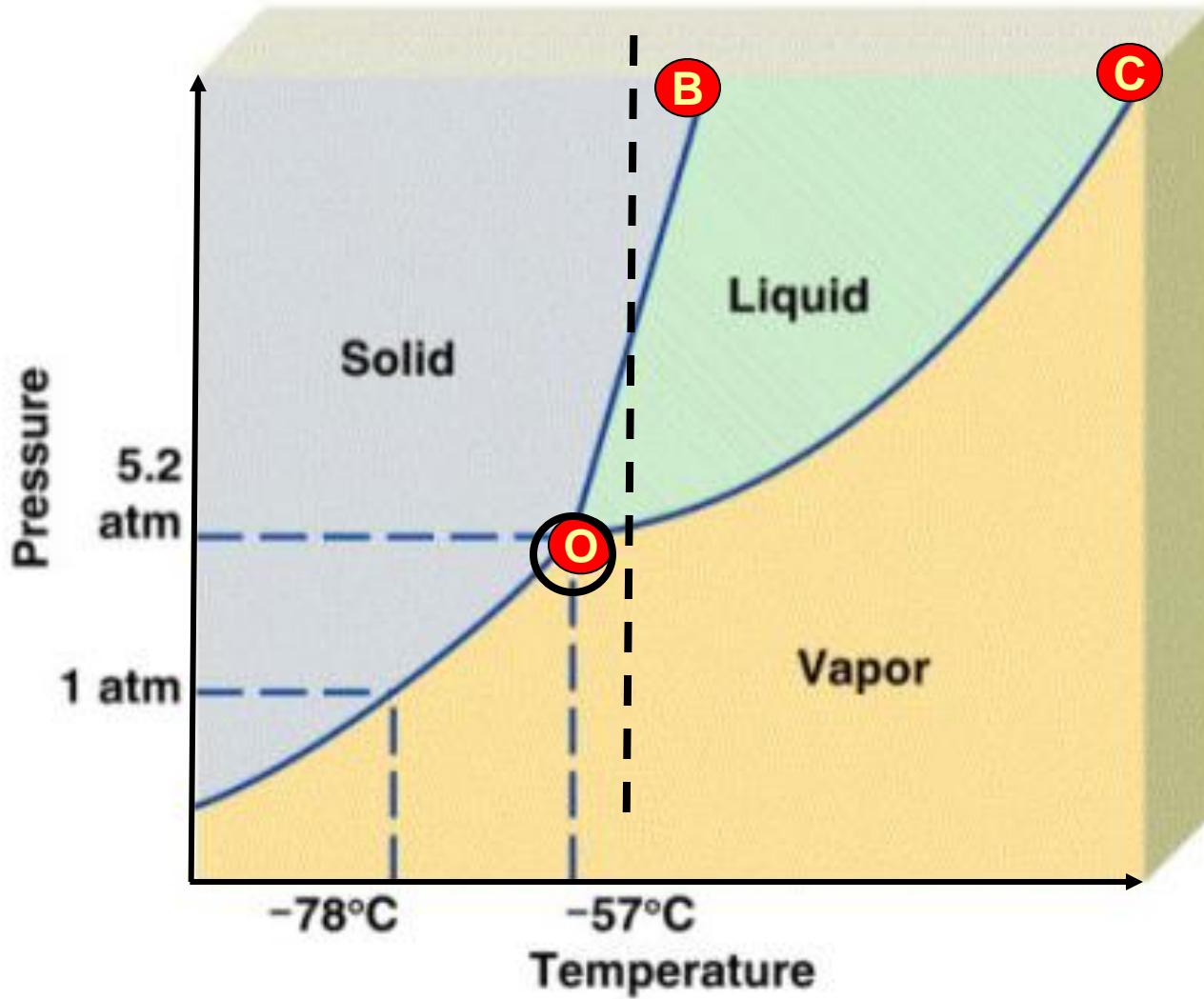
- At pressure < 5.2 atm:
- Phase change from **solid → gas or vice versa**
- When solid CO₂ heated at 1 atm, it **sublimes** at -78°C



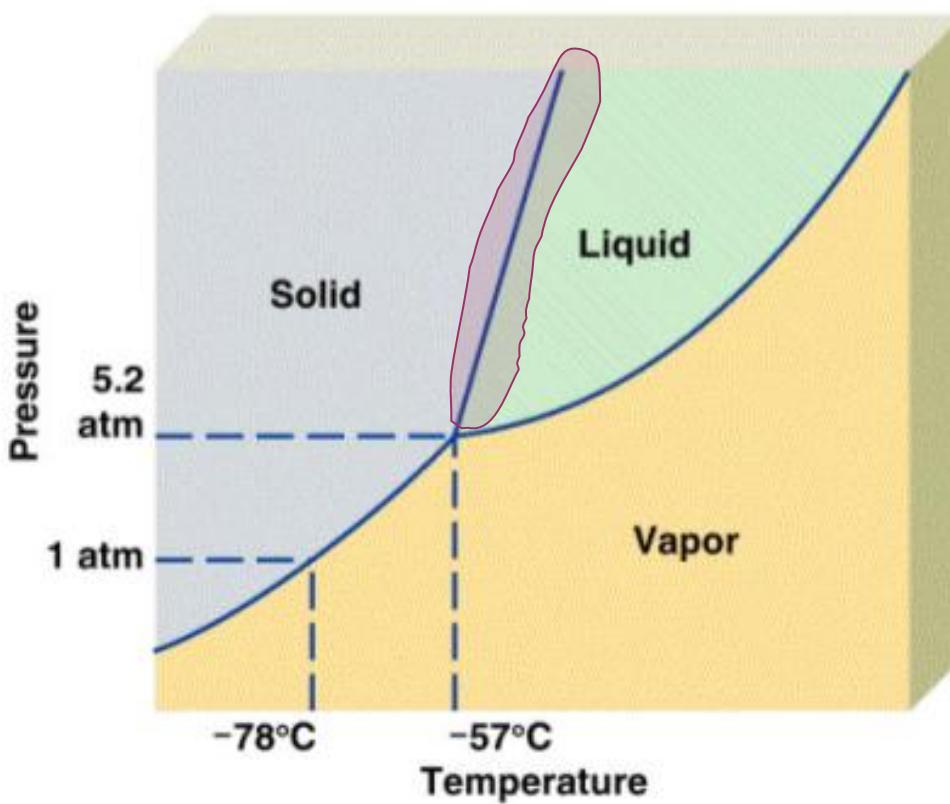
- At pressure > 5.2 atm:
- Phase change from solid \rightarrow liquid \rightarrow gas or vice versa



- At temperature $< -57^{\circ}\text{C}$:
- Phase change from gas \rightarrow solid or vice versa
(low P) (high P)



- At temperature $> -57^{\circ}\text{C}$:
- Phase change from gas \rightarrow liquid \rightarrow solid or vice versa
(low P) (high P)



The phase diagram for CO₂ is typical of most substances in that solid–liquid line slopes to the right (positive slope)
It means melting point (or freezing point) increase when the pressure increase



POSITIVE SLOPE

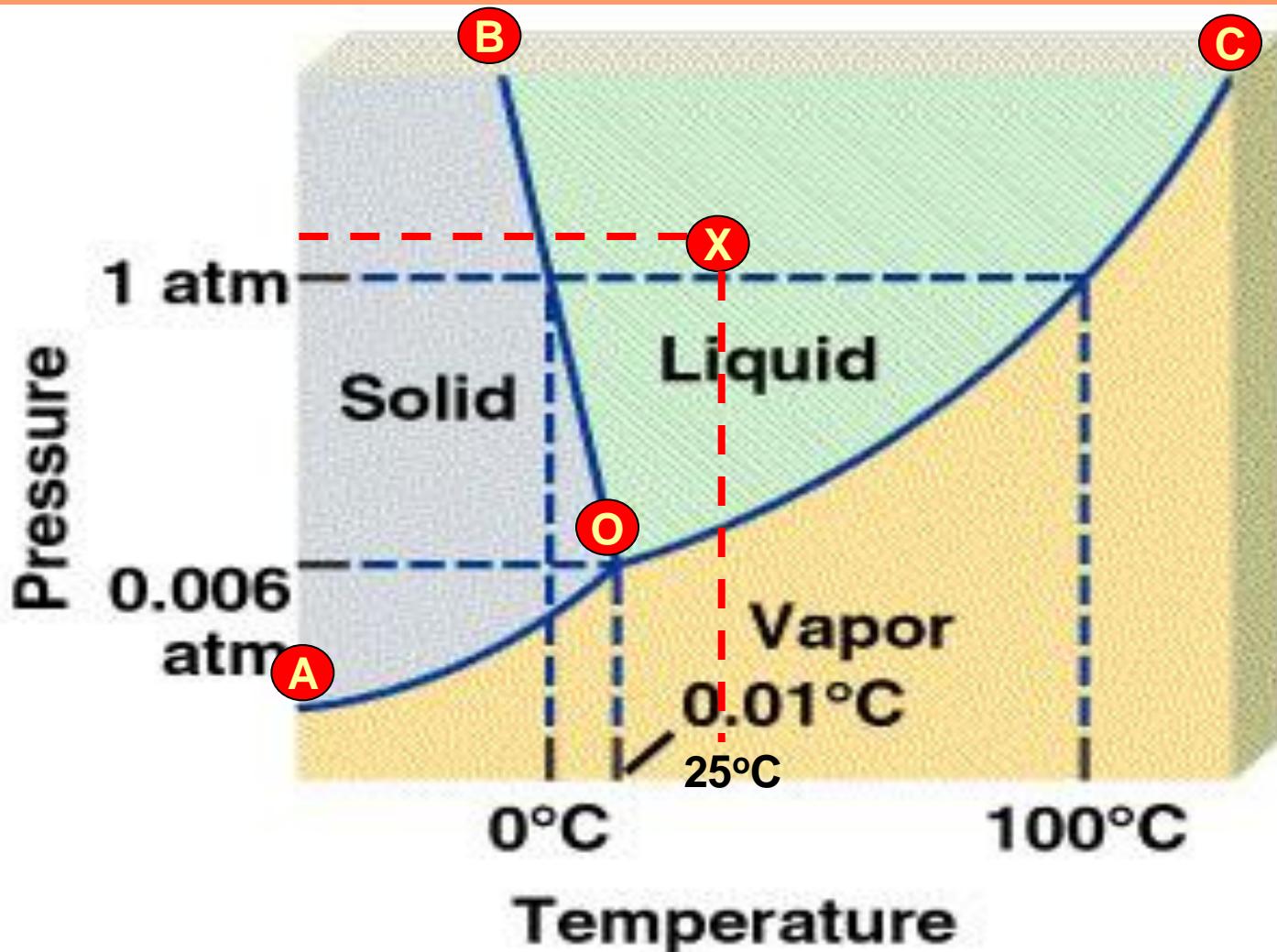
(Melting point increase when pressure increase)



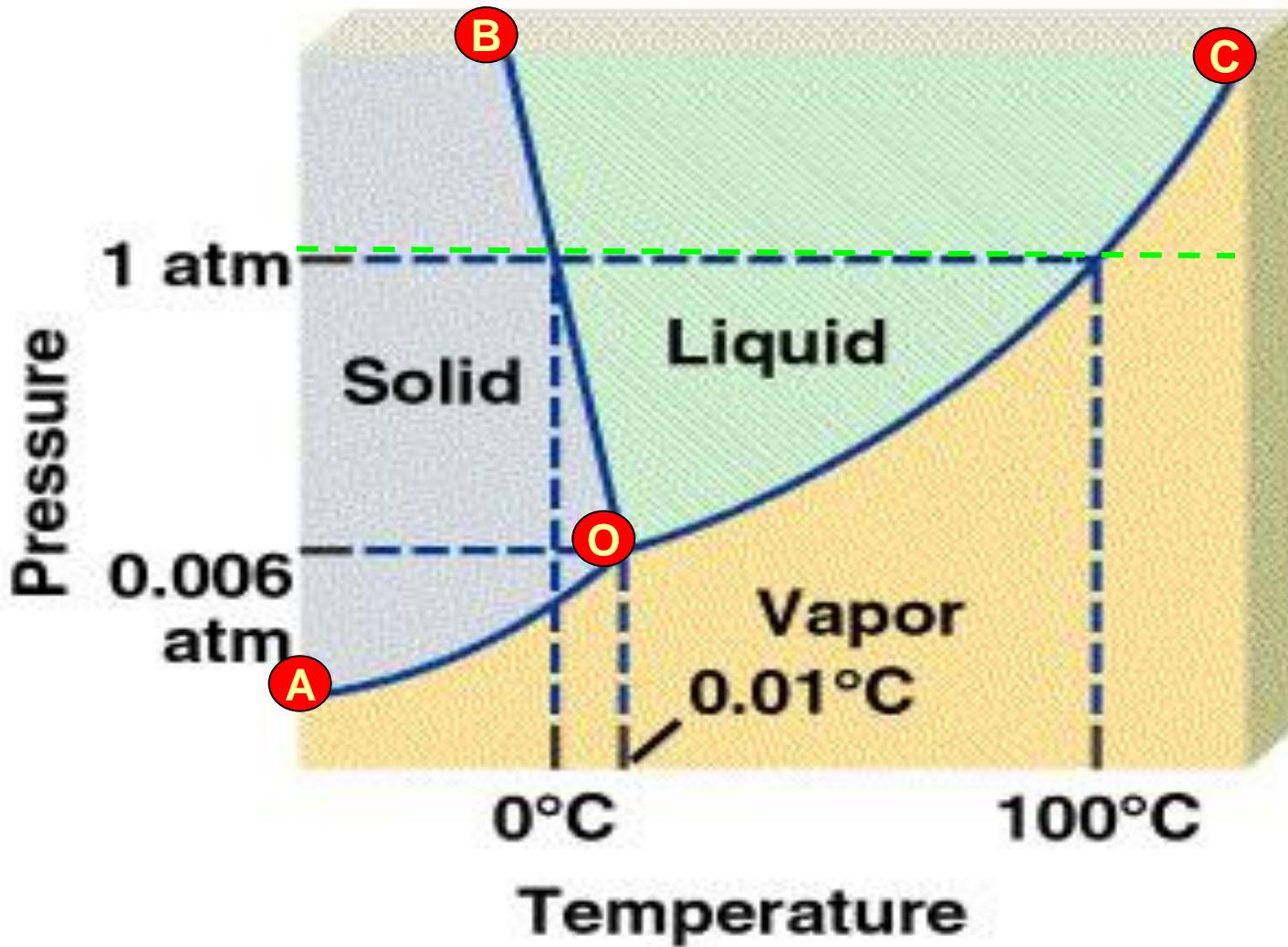
Reason:

- Solid CO₂ is more dense (occupy smaller volume) than liquid CO₂.
- At high pressure, it favours the formation of solid CO₂ which has smaller volume.
- More heat is needed to melt the solid CO₂.
∴ solid CO₂ melts at higher temperature at high pressure.

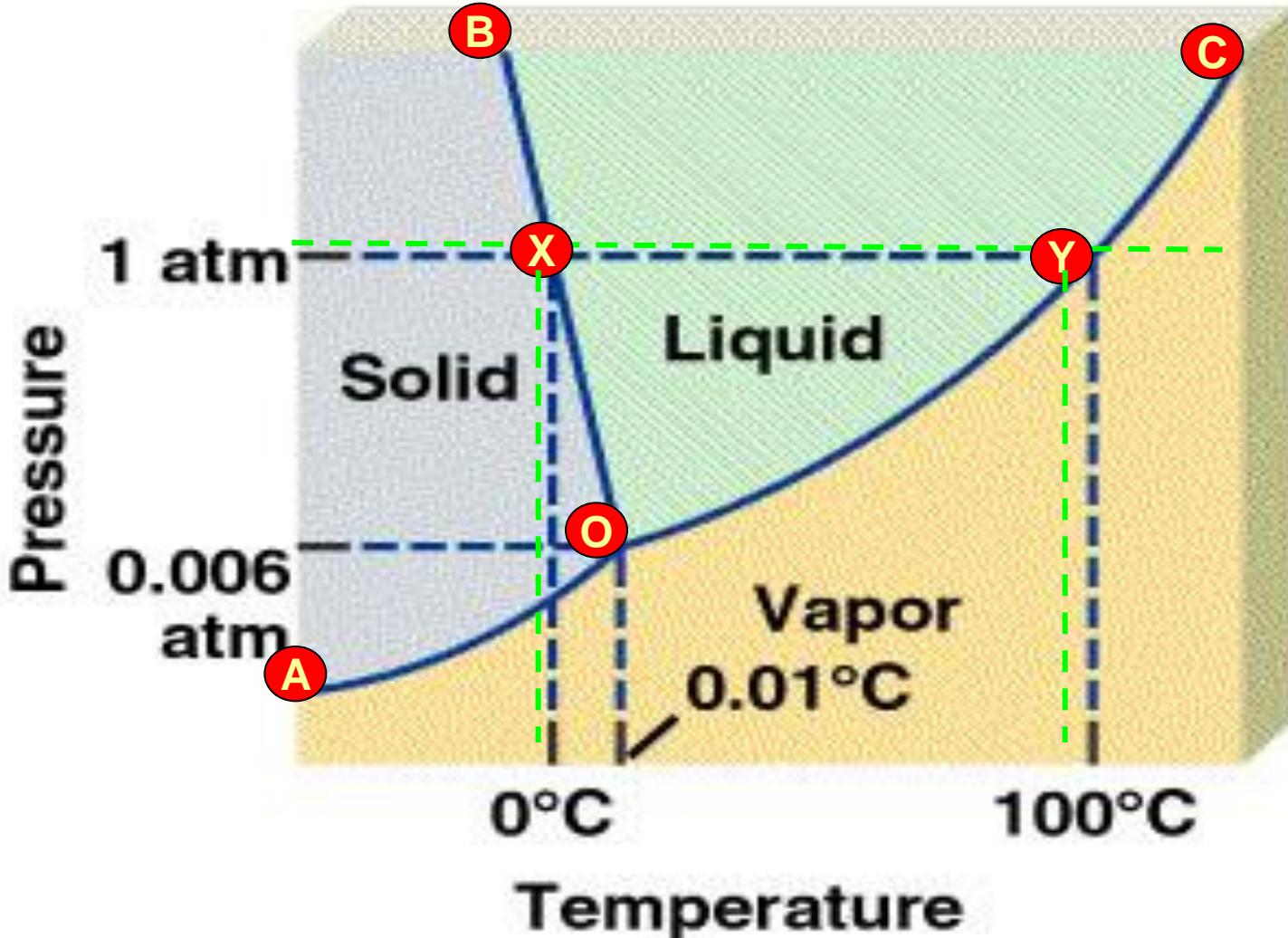
PHASE DIAGRAM OF H₂O



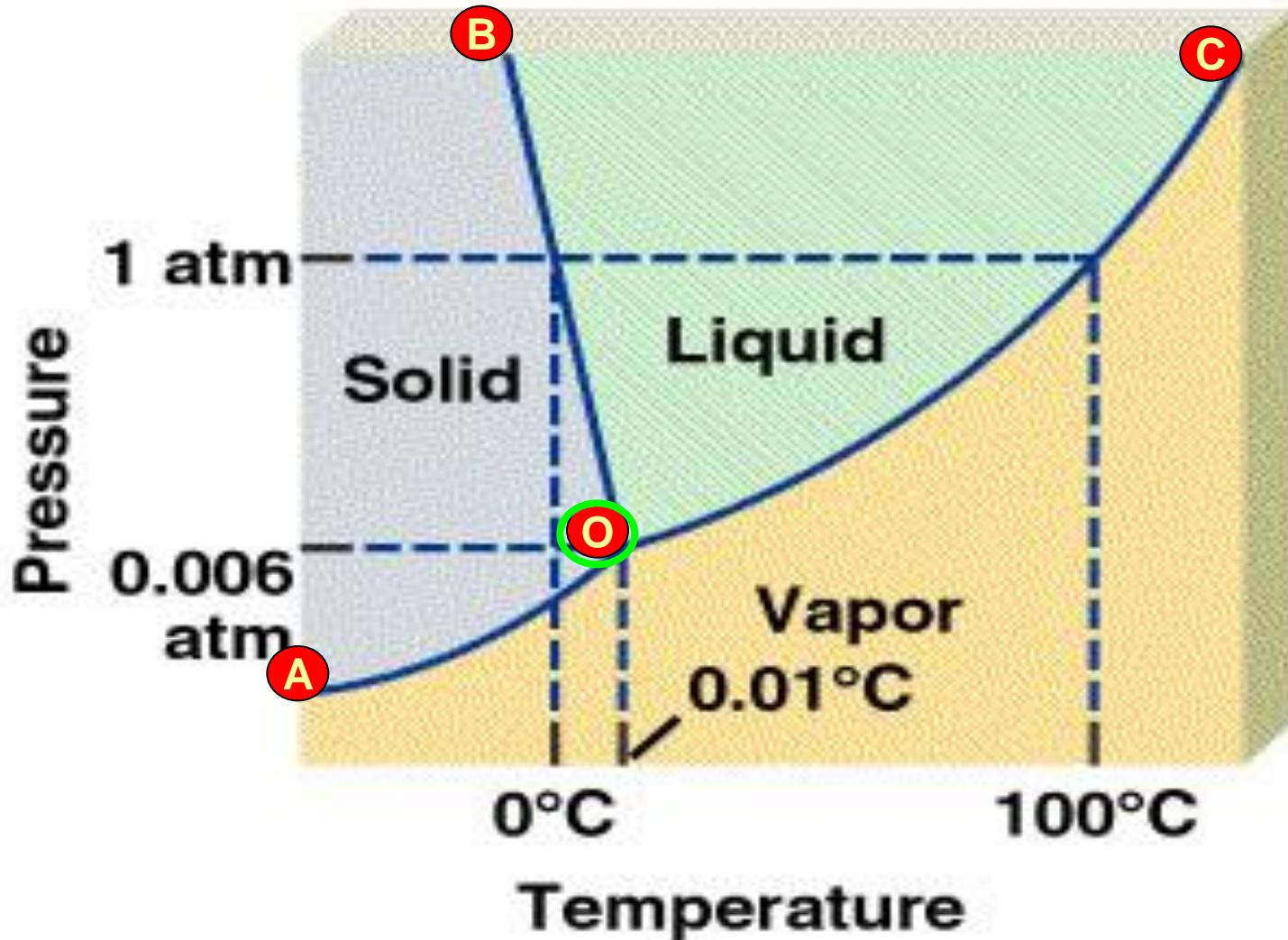
- H₂O is a liquid under normal conditions (25°C, 1 atm)



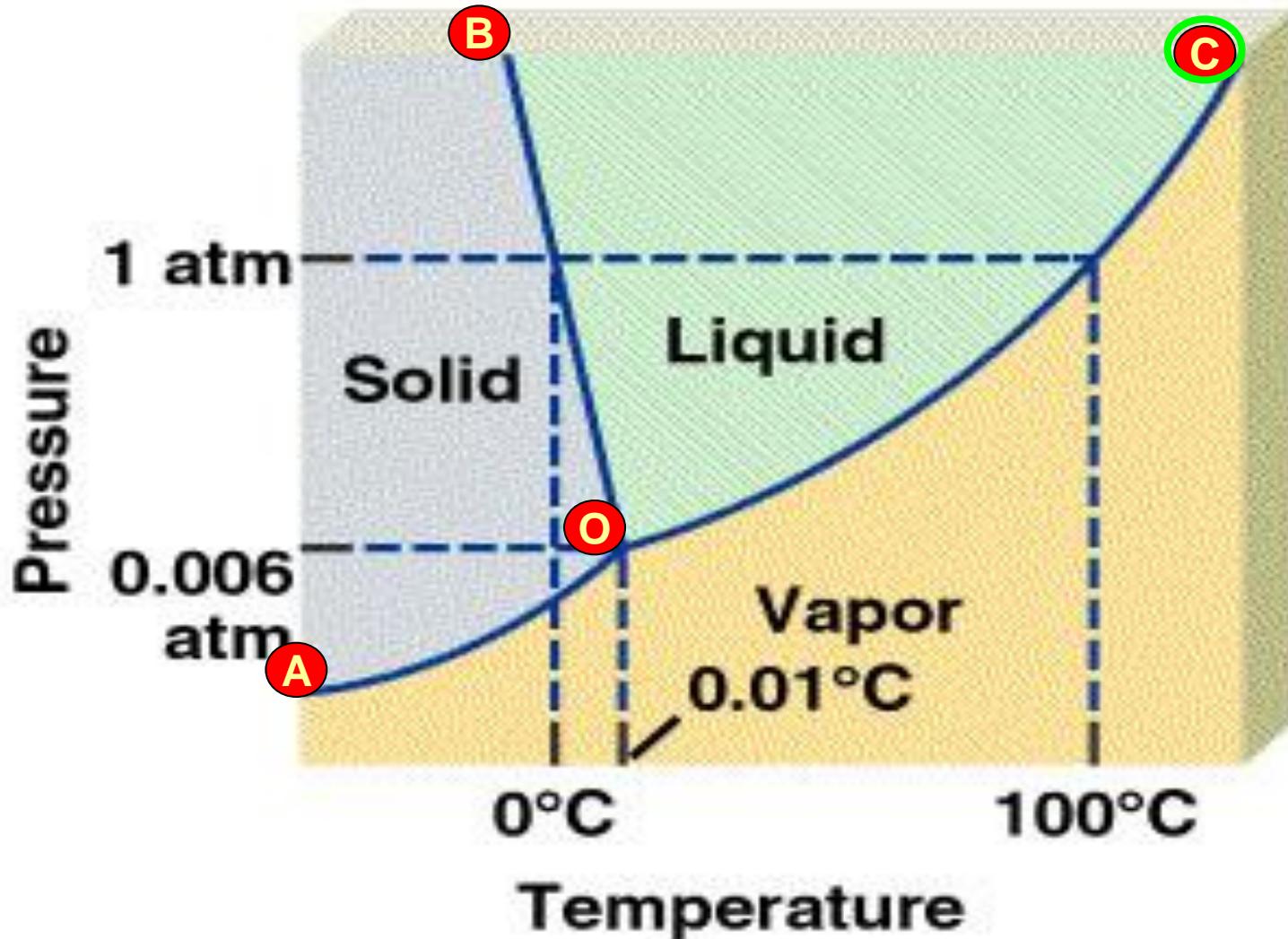
- At 1 atm, phase change from solid → liquid → gas or vice versa



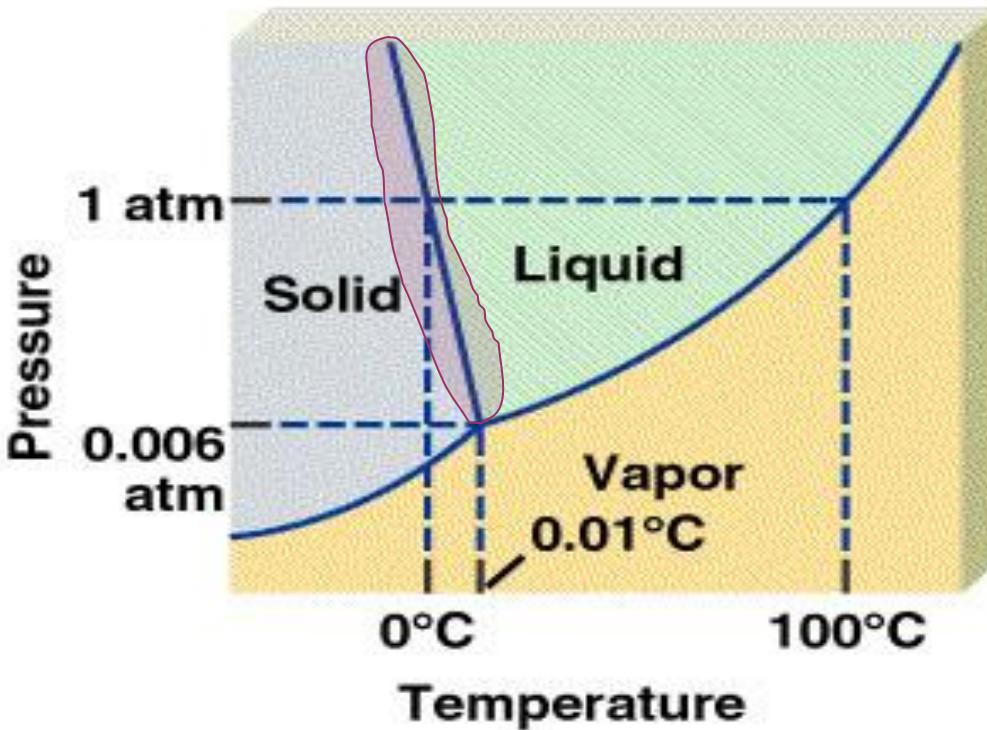
- At **1 atm**, melting point / freezing point = **0°C**
boiling point = **100°C**



- Point O = Triple Point (0.01°C , 0.006 atm)



- Point **C** = Critical Point (374°C , 218 atm)



The phase diagram for H_2O is one of few substances in that solid–liquid line slopes to the left (negative slope).

It means melting point decrease when pressure increase.

NEGATIVE SLOPE (Anomalous behavior of H₂O)

- Melting point decrease when pressure increase

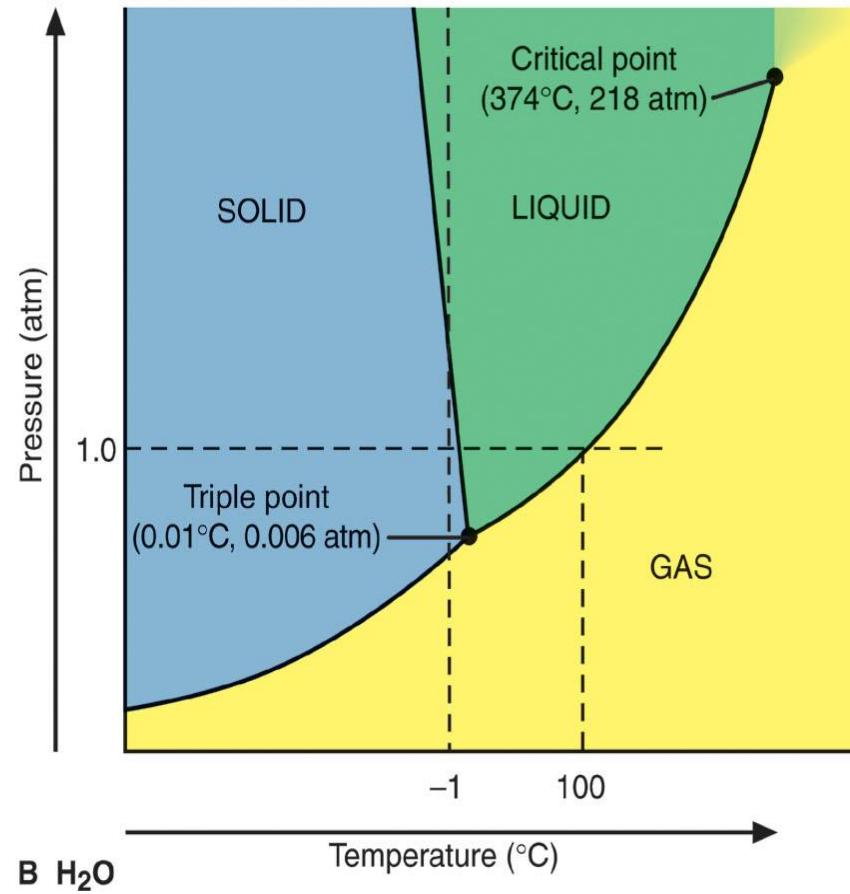
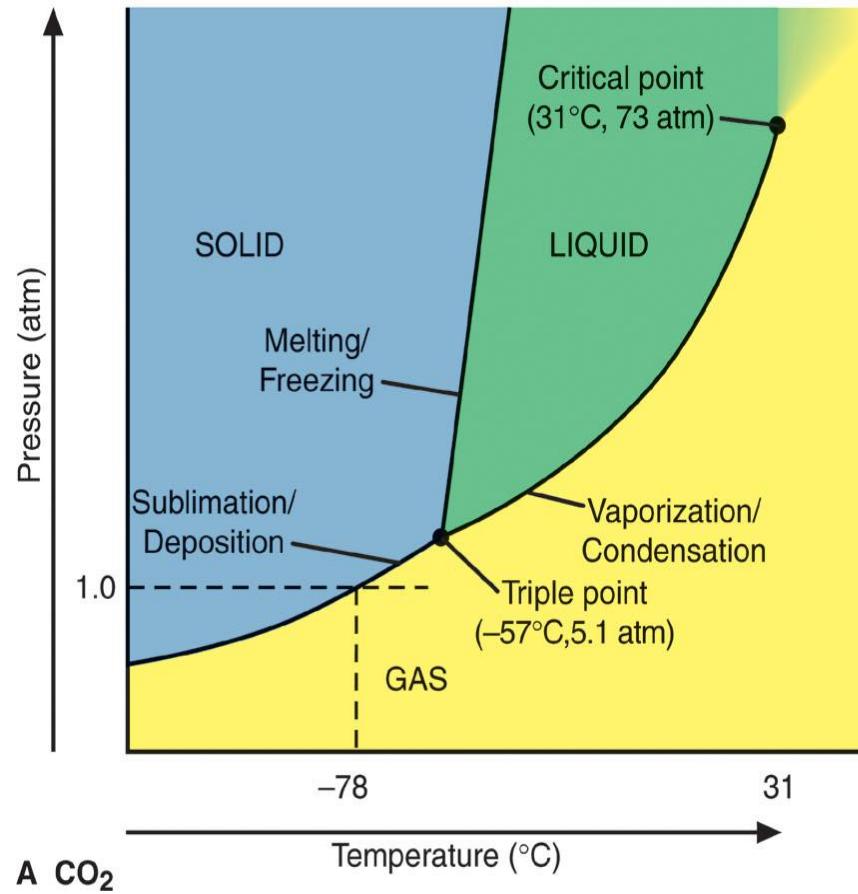


Reason:

- Solid H₂O (ice) is less dense (occupy larger volume) than liquid H₂O (water).
- At high pressure, it favours the formation of liquid H₂O which has smaller volume.
- Less heat is needed to melt the solid H₂O.
∴ solid H₂O melts at lower temperature at high pressure.

Phase diagram CO_2 Vs H_2O

The phase diagram for CO_2 has a solid–liquid curve with a positive slope, and the one for H_2O has a solid–liquid line with a negative slope. What macroscopic property can distinguish CO_2 from H_2O ?



- If the solid is more dense than the liquid, the solid–liquid line slopes to the right; if less dense, to the left.



EXAMPLE 3 :

Predict what would happen as a result of the following changes: (State the phase changes)

- (a) Starting at A, we raise the temperature at constant pressure.
- (b) Starting at C, we lower the temperature at constant pressure.
- (c) Starting at B, we lower the pressure at constant temperature.

