State of Matter

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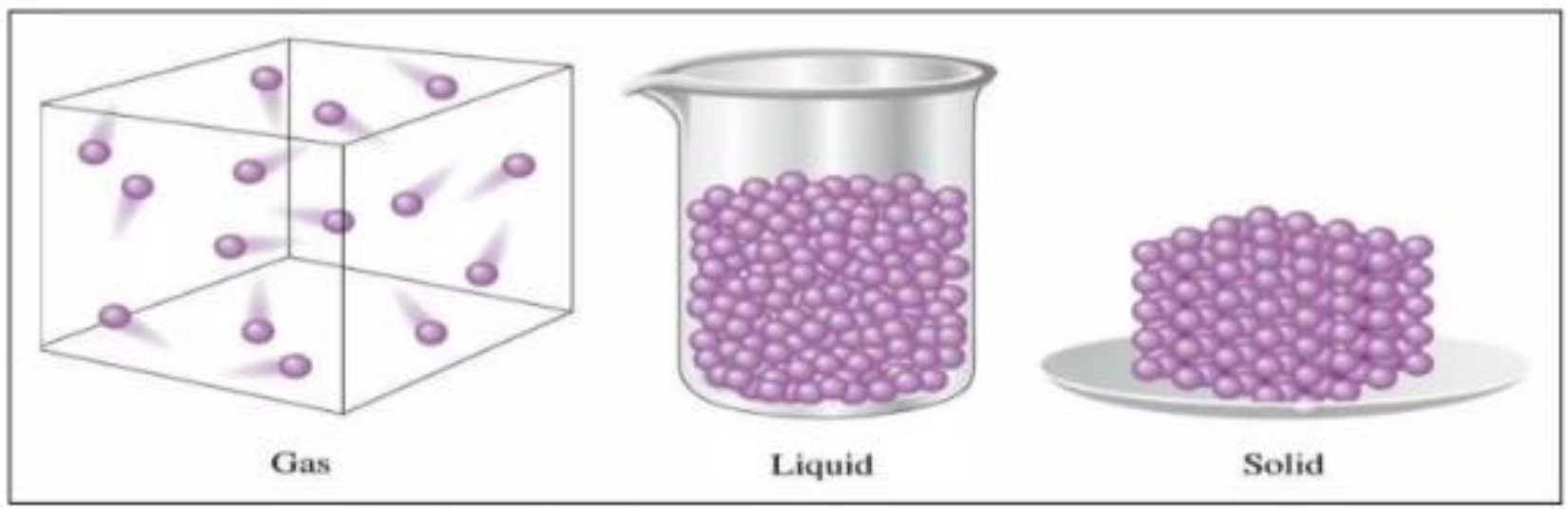
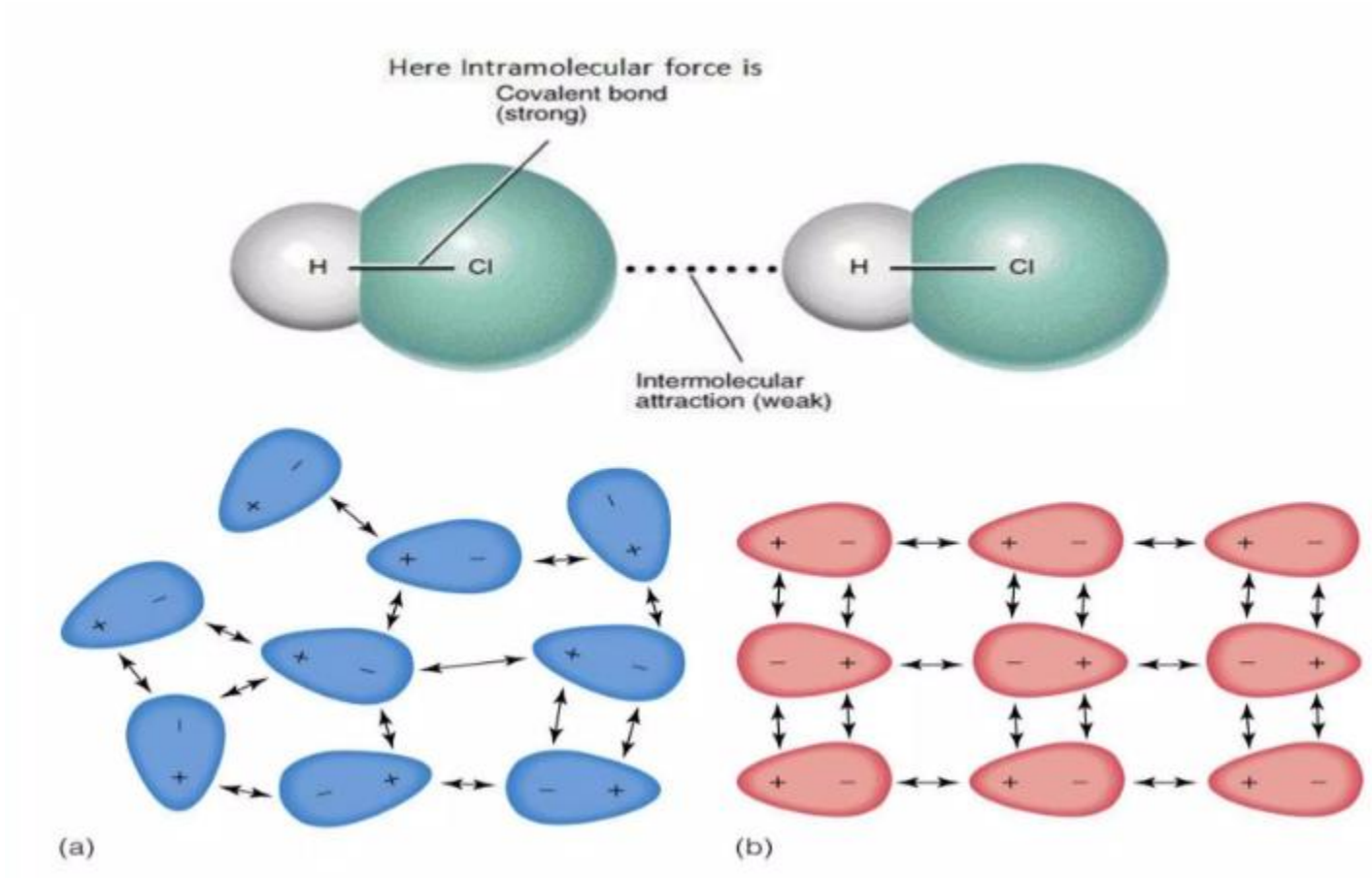
Comparison of Gases, Liquids and Solids

- **Gases** are compressible fluids. Their molecules are widely separated.
- **Liquids** are relatively incompressible fluids. Their molecules are more tightly packed.
- **Solids** are nearly incompressible and rigid. Their molecules or ions are in close contact and do not move.



In order for molecules to exist in aggregates in gases, liquids and solids Intermolecular forces must exist


Here Intramolecular force is
Covalent bond
(strong)
H
Cl
H
Cl
Intermolecular
attraction (weak)
(a)
(b)

Ideal Gas Equation

Boyle's law: $P \propto \frac{1}{V}$ (at constant n and T)

Charles' law: $V \propto T$ (at constant n and P)

Avogadro's law: $V \propto n$ (at constant P and T)

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$PV = nRT$$

R is the **gas constant**

Gaseous state

The Effect of Pressure Changes on the Volume of an Ideal Gas

In the assay of ethyl nitrite spirit, the nitric oxide gas that is liberated from a definite quantity of spirit and collected in a gas burette occupies a volume of 30.0 mL at a temperature of 20°C and a pressure of 740 mm Hg. Assuming the gas is ideal, what is the volume at 0°C and 760 mm Hg? Write

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{740 \times 30.0}{273 + 20} = \frac{760 \times V_2}{273}$$

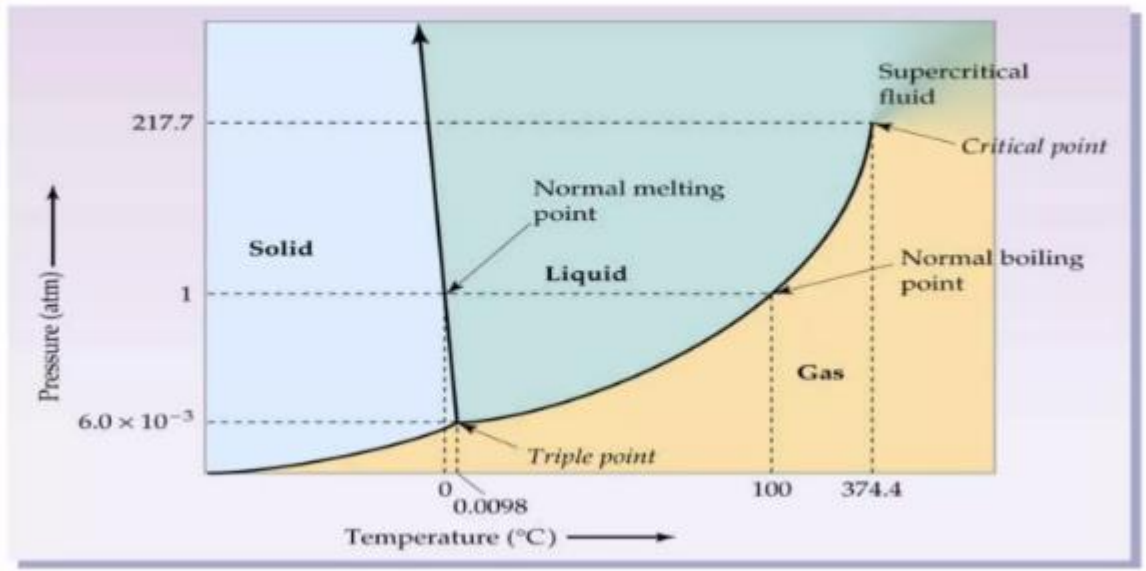
$$V_2 = 27.2\ \text{mL}$$

Liquefaction of Gases

- The ***critical temperature*** (T_c) is the temperature above which the gas cannot be made to liquefy, OR is the temperature above which the liquid cannot longer exist

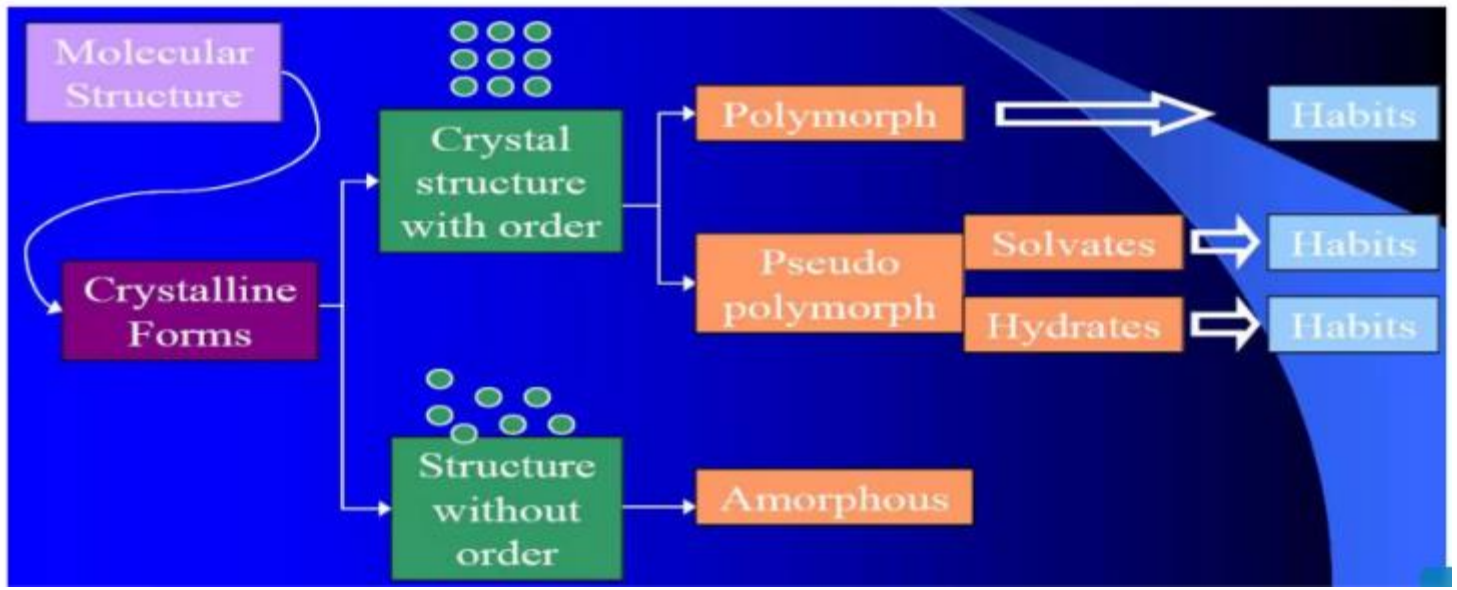
- The ***critical pressure*** (P_c) is the minimum pressure required to liquefy a gas at its critical temperature.

- ***critical temperature*** (T_c) of water is 374°C, or 647 K, and its critical pressure is 218 atm,


Supercritical fluid
217.7
Critical point
Normal melting point
Solid
Liquid
Normal boiling point
1
Gas
6.0×10^{-3}
Triple point
0
0.0098
100
374.4
Pressure (atm)
Temperature (°C)

SOLIDS & CRYSTALLINE STATE

Pharmaceutical Drugs: more than 80% are solid formulations

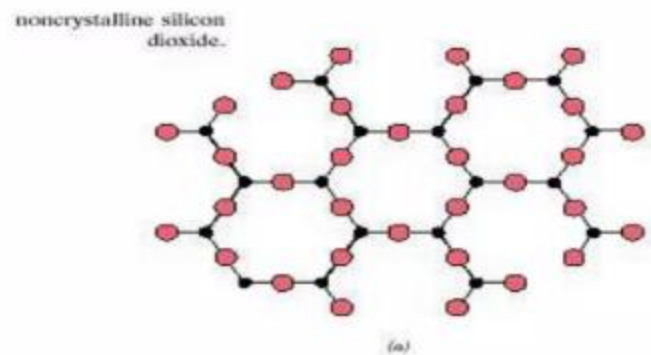


Solids and the crystalline state

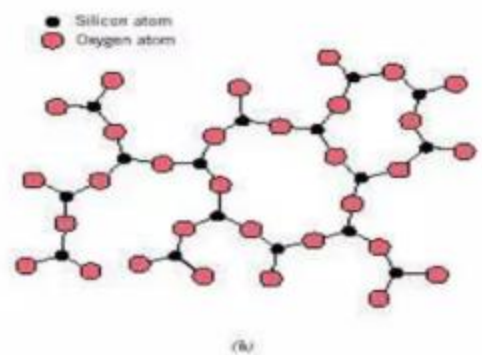
- A **crystalline solid** possesses rigid and long-range order.
- In a crystalline solid, atoms, molecules or ions occupy specific (predictable) positions.
- An **amorphous solid** does not possess a well-defined arrangement and long-range molecular order.

Classification of Solids

Crystalline

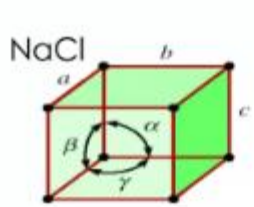


Amorphous

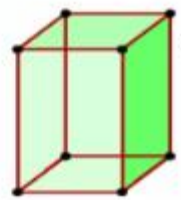


Crystal forms

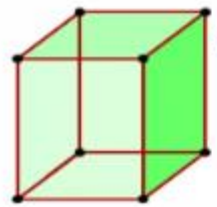
The various crystal forms are divide to basic 7 unit according to its symmetry



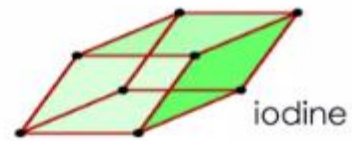
Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90°$



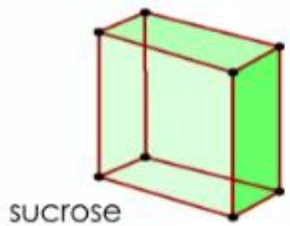
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90°$



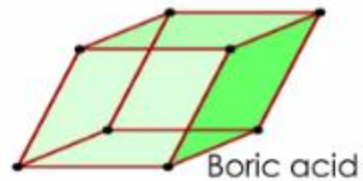
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$



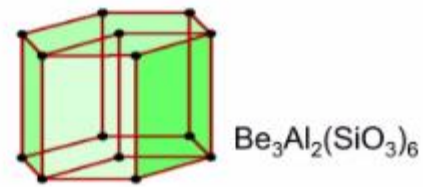
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90°$



Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90°$



Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$



Hexagonal
$a = b \neq c$
$\alpha = \beta = 90°,\ \gamma = 120°$

Polymorphism

- Some elemental substance such as C and S ,may exist in more than one crystalline form and are said to be allotropic, which is a special case of polymorphism

- Polymorphism is the ability of a substance to exist in more than one crystal structure

- ✓Polymorphism is the ability of a substance to exist in more than one crystal structure

- ✓Polymorphs: when two crystals have the same chemical composition but different internal structure (molecular packing –molecular conformation or / and inter or intra molecular interactions)modifications or polymorphs or forms

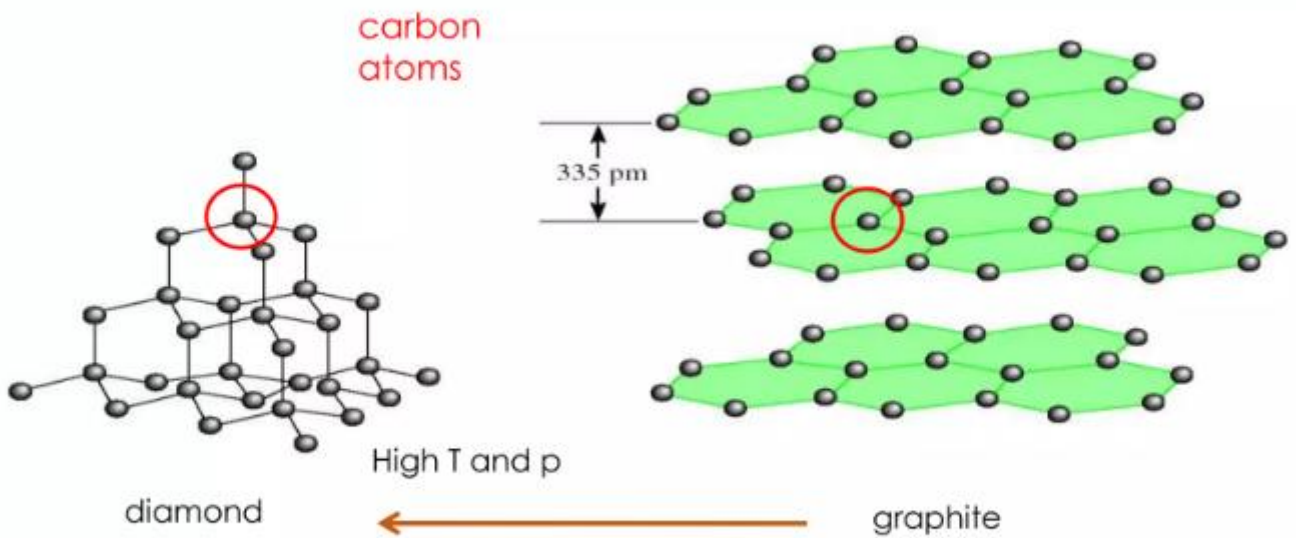
- ✓Pseudo polymorphs : different crystal forms have molecules of the same given substances and also contain molecules of solvent incorporated into a unique structure (solvates or hydrates (water))

Principle of polymorphism

- When the change from one form to another is reversible, it is said to be enantiotropic.

- When the transition takes place in one direction only—for example, from a metastable to a stable form—the change is said to be monotropic.

The most common example of polymorphism



Diamond is ***metastable*** and converts very slowly to graphite

Polymorphism

- Melting point
- Vapor pressure
- Hardness
- Optical, electrical magnetic properties
- Color
- IR spectra
- NMR spectra
- Photochemical reactivity
- Thermal stability
- Filtration and drying characteristics
- Dissolution rate
- Bioavailability
- Physical and chemical stability

Solubility and melting point are very important in pharmaceutical processes including dissolution and formulation.

Amorphous Solid

- An **amorphous solid** does not possess a well-defined arrangement and long-range molecular order.
- Amorphous substances, as well as cubic crystal, are **isotropic**, that is, they exhibit similar properties in all direction.

AMORPHOUS SOLIDS

Solids that don't have a definite geometrical shape are known as Amorphous Solids.

1. In these solids particles are randomly arranged in three dimension.
2. They don't have sharp melting points.
3. Amorphous solids are formed due to sudden cooling of liquid.
4. Amorphous solids melt over a wide range of temperature

Polymorphism and Industry/ Pharmaceutical

- Theobroma oil (cacao butter) is a polymorphic natural fat.

- Theobroma oil can exist in 4 different polymorphic forms of which only one is Stabile

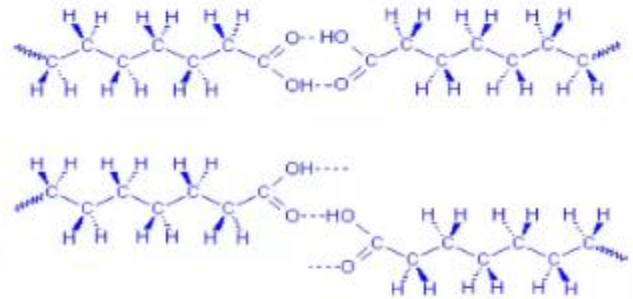
1. Unstable gamma form melting at 18°C
2. Alpha form melting at 22°C
3. Beta prime form melting at 28°C
4. Stable beta form melting at 34.5°C

- This is important in the preparation of theobroma suppositories.

- If the oil is heated to a point where it is completely liquified (about 35 C), the crystals of the stable polymorph are destroyed & the mass does not crystallize until it is cooled to 15 C.

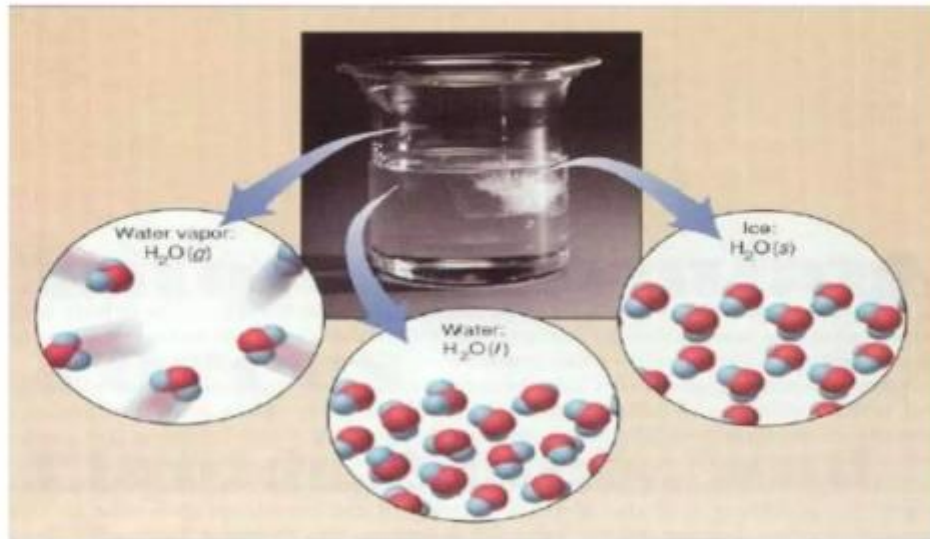
- The crystals that form are unstable & the suppositories melt at 24 C.

- Theobroma suppositories must be prepared below 33 C.

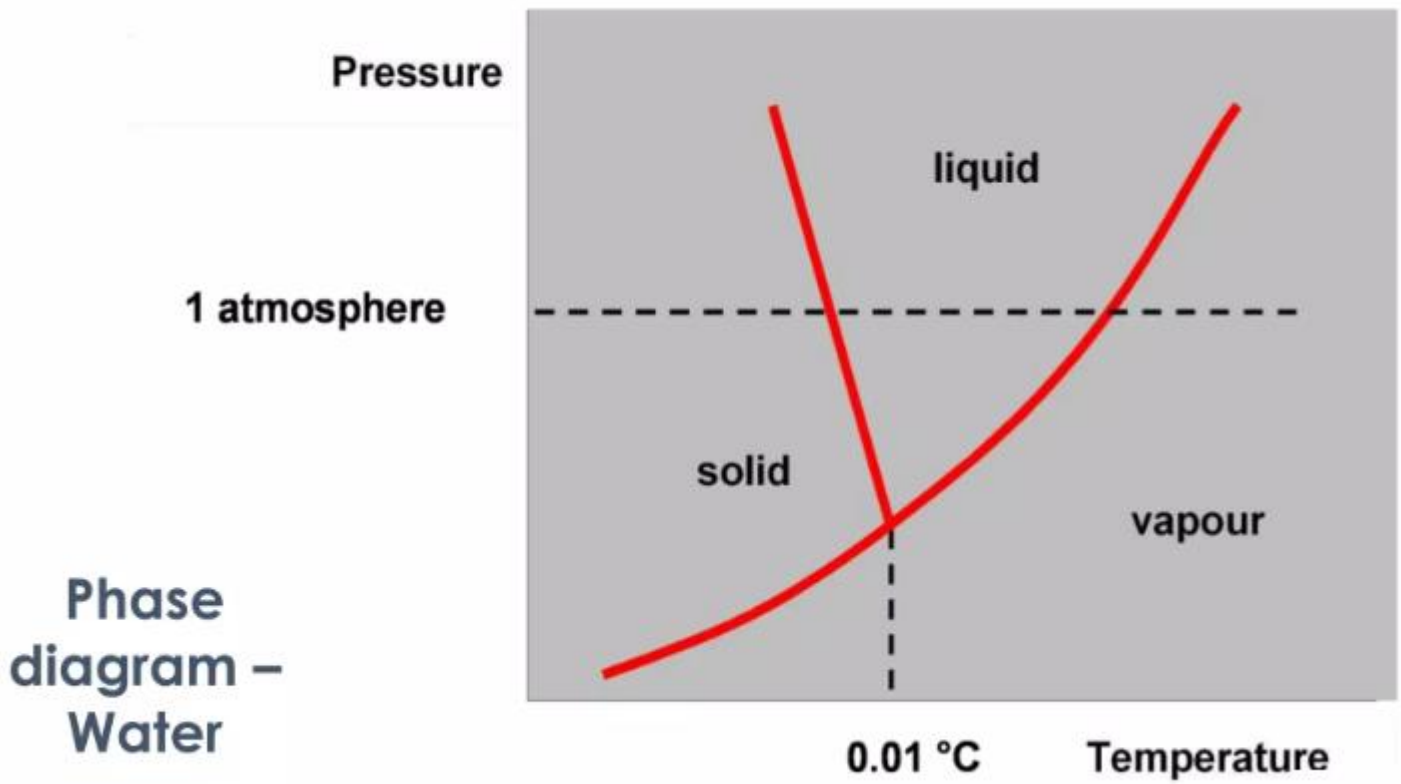


Configuration of fatty acid molecules in the crystallyne state. (Dashed lines indicate hydrogen bonding.)

Phase Equilibria & The Phase Rule



Phase diagram – Water



Phase Definition

- A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by interfaces.

- A part of a system is homogeneous if it has identical physical properties and chemical composition throughout the part.

✓ A phase may be gas, liquid or solid.
✓ A gas or a gaseous mixture is a single phase.
✓ Totally miscible liquids constitute a single phase.
✓ In an immiscible liquid system, each layer is counted as a separate phase.
✓ Every solid constitutes a single phase except when a solid solution is formed.
✓ A solid solution is considered as a single phase.
✓ Each polymorphic form constitutes a separate phase.

Examples

1. Liquid water, pieces of ice and water vapour are present together.

The number of phases is 3 as each form is a separate phase. Ice in the system is a single phase even if it is present as a number of pieces.

2. Calcium carbonate undergoes thermal decomposition.

The chemical reaction is: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

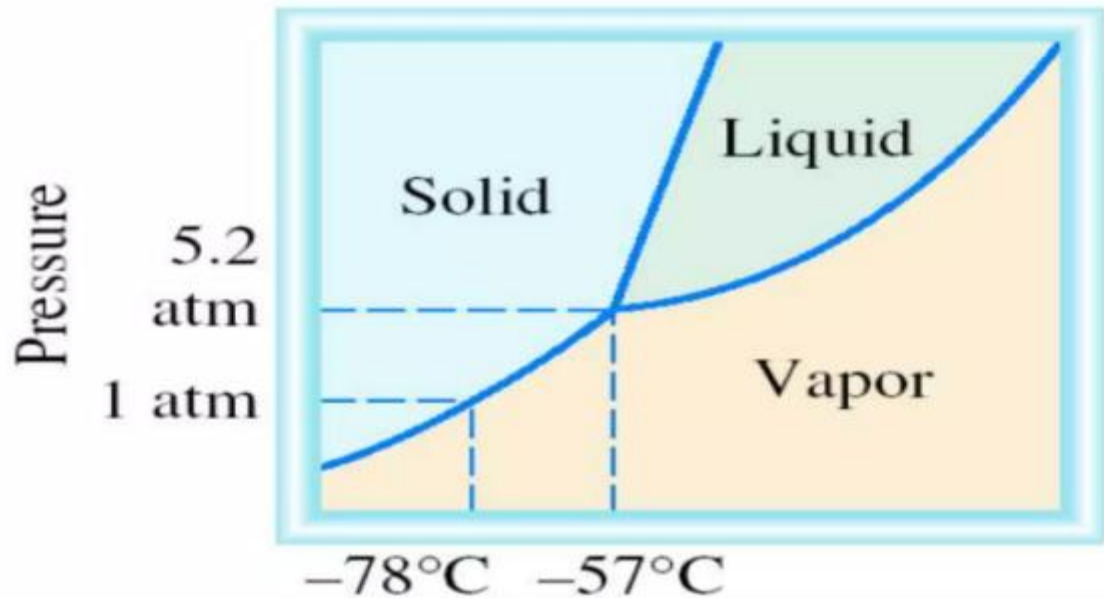
Number of phases = 3 : This system consists of 2 solid phases, CaCO3 and CaO and one gaseous phase, that of CO_2.

3. Ammonium chloride undergoes thermal decomposition. The chemical reaction is:

- NH4Cl(s)→ NH3 (g) + HCl (g) Number of phases = 2
- This system has two phases, one solid, NH_4Cl and one gaseous, a mixture of NH_3 and HCl.

4. A solution of NaCl in water Number of phases = 1

Phase Diagram of Carbon Dioxide



The Critical Solution Temperature: CST

- Is the maximum temperature at which the 2-phase region exists (or upper consolute temperature).
- In the case of the phenol-water system, this is 66.8°C (point h)
- All combinations of phenol and water > CST are completely miscible and yield 1-phase liquid systems.