States of Matter

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PHAR 201

1st semester

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Outline

1. **States in which matter exists**
2. **Real an ideal gases.**
3. **The change in the state of matter**
4. ***Phase rule***
5. ***Latent heat***
6. ***Vapor pressure***
7. ***Eutectic mixtures***

Objectives

1. Understand the nature of the intra- and intermolecular forces that are involved in stabilizing molecular and physical structures.
2. Understand the differences in these forces and their relevance to different types molecules.
3. Appreciate the differences in the strengths of the intermolecular forces that are responsible for the stability of structures in the different states of matter.
4. Perform calculations involving the ideal gas law, molecular weights, vapor pressure, boiling points, kinetic molecular theory, van der Waals real gases.

Matter exists in one of the three states:

1) **Solids**
2) **liquids**
3) **Gases**

- Tow factors usually determine the state in which the matter exists

1. the intensity of intermolecular forces.
2. Temperature.

Solids have the strongest intermolecular forces and the gases have the weakest .

The gaseous state:

The physical behavior of gases is independent of the chemical nature of the molecules, therefore almost all gases respond in an identical way to the variations in pressure, temp. and volume .

Since the molecules in a gas are always in a state of vigorous motion, these travel in a random paths, colloid with one another and with the wall of the container in which they are confined.

These tend to occupy completely all the space available in the container and exert a pressure on the wall of the container .

So the general behavior of gases with the variation of pressure, volume and temp. can be given by the ideal gas equation

$$P\,V = n\,R\,T$$

P: pressure

V: volume

n: no. of moles of gas

R: gas constant 0.821 lit. atm. $mole^{-1} deg.^{-1}$

T: absolute temp.

From this equation volume of gas is directly proportional to the no. of moles and absolute temp. and inversely proportional to the pressure.

If we have 2 cases the equation will be

$$\frac{P1V1}{T1} = \frac{P2V2}{T2}$$

- For the real gases we have

Vander waals' equation

$$\left(P + \frac{a}{v^2} \right) (v - b) = R T$$

(for 1 mole)

a and b is the vander waals constant for each gas

$\frac{a}{v}$ is the internal pressure/mol resulting from the intermolecular forces of attraction between molecules.

- Real and actual gases deviate from ideal gases as the molecules tend to attract one another .this deviation become significant when? ....and explain?
- So in what condition the real and actual gases behave as an ideal gas ?

- **The liquid state;**
- The liquid state can be considered as an intermediate state as matter goes from the solid state to the gaseous state

- So the liquid can be considered as highly compressed gas or slightly released solids.

The molecules in the gas have a constant motion owing to their kinetic energy which is proportional to the absolute temp. of the gas.

- When the gas is cooled its kinetic energy is decreased, as the temp. being decreased a stage is reached where the molecules almost loose their kinetic energy and are not able to overcome the forces of attraction at this stage the gas converted to liquid.
- Liquification of gases also can be achieved by increasing the pressure on the gas, however pressure is effective only below a certain temp. this temp. is called ***critical temp*****.**

- **Critical temperature** :
- Is the temperature above which the gas cannot be liquefied even if very high pressure is applied .

Critical pressure : the pressure required to liquefy the gas at its critical temperature.

- The critical temperature of water is

374 C°

and its critical pressure is

218 atmosphere.

- **Aerosols**

- Liqiufication of gas can be achieved by applying a pressure on it and keeping the temperature below the critical temperature.

Why ?

- In pharmaceutical aerosols , a drug is dissolved or suspended in a **propellant .**
- **Propellant:** materials which exist as a liquid under pressure conditions and converted to a gas under normal atmospheric conditions .
- Example on propellant ; fluorinated hydrocarbons , nitrogen and carbon dioxide .

How the aerosols container are filled ?

- 1. Cooling of propellants and drug to a low temp. within the container which is then sealed with the valve.

- 2. The drug is sealed in the container at room temp. and the required quantity of propellant is forced into the container under pressure.

- **The solid state:**

  The most important property of the solid state is the high degree of order in which the solid substances exist.

- The molecules of solids are held together by strong bonds

  1.ionic bonds .

  2.metallic bonds.

  3.Valence bonds.

  4.Molecular bonds

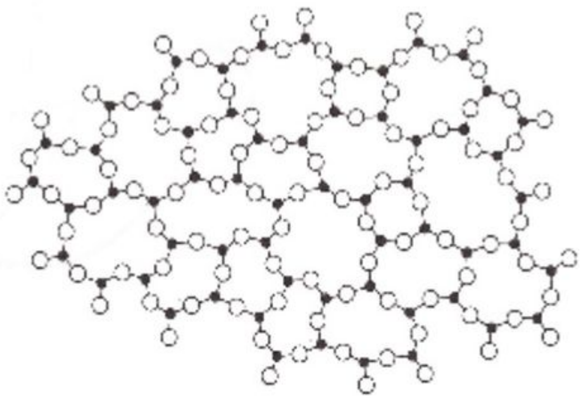
- **Crystalline solids :**The structural units of crystalline solids are arranged in fixed geometric patterns or lattices, these generally exhibit a definite shape and an orderly arrangement of units.
- These generally have a sharp melting point.
- Example minerals , metals and rocks .

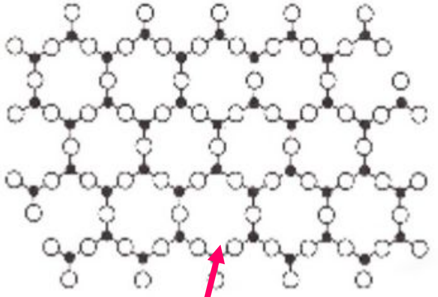
- **Amorphous solids:**

  The structural unites are arranged in a random manner, these amorphous solids can be considered as a super cooled liquids.

  amorphous solids do not have a sharp melting point and melt within some narrow range of temps. These are in general more soluble than crystalline solids.

- Example glass , woods and plastics





- Schematic representation of a random-network glassy form (top) and ordered crystalline lattice (bottom) of identical chemical composition

- ***Polymorphism:***

This is a phenomenon where compounds exist in more than one crystal and /or amorphous forms.

Different polymorphic forms of a substance usually exhibit different melting point , X-Ray diffraction patterns, solubility, dissolution behavior , stability , biological activity .

- **Example :** chloramphenicol , novobiocin , barbiturates , steroids such as cortisone and testosterone .

- ***Liquid crystals (mesophase)***

possess some of the properties of liquid and some of solids for example it possess the property of mobility and rotation and thus can considered to have the flow properties of liquids.

on the other hand it posses the property of

Birefringence *:*

is a property in that the light passing through a material is divided into two components with different velocities and hence different refractive index .

- Liquid crystalline states is found in nerve , brain tissue and blood vessels.

Atherosclerosis is thought to result from deposition of lipid in the liquid crystal state on the wall of the blood vessels.

The three components of bile (bile salts, cholesterol, and water) when present in a definite proportion can result in the formation of smectic crystals and these may be involved in the formation of gall stones.

- The Glassy state
- Although glass is considered to be a non conducting transparent solid, it is actually a type of solid matter.
- The atoms and molecules in most solids are arranged in an orderly manner whereas in glassy materials these are highly disordered .
- Glassy materials do not have a specific melting point but these slowly and gradually liquefy on heating

- **The change in the state of matter**

The molecules, atoms or ions are strongly held in close proximity by intermolecular, interatomic, or ionic forces respectively.

As the temperature of the substance increase, the particles acquire sufficient energy to disrupt the ordered arrangement and pass into the gaseous state in which the intermolecular forces are decreased to almost negligible

- ***Sublimation*** *:* a change of solid state to the gaseous state directly with out passing the liquid state .

when the solid converted to liquid and then to gaseous state the heat is absorbed and the Enthalpy (heat content) of the material increased and the Entropy (degree of randomness) also increased

- ***Phase rule*** **:** is a useful devise for relating the effect of different variables

(temperature, pressure, and conc.) upon the various phases in an equilibrium system containing a given number of components.

Gibbs̉ rule

$$F = C - P + 2$$

F: is the no. of degrees of freedom in the

system(temp, pressure, conc.)

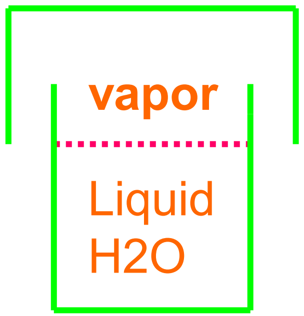
C: no. of components

P: no. of phases

- **Examples :**

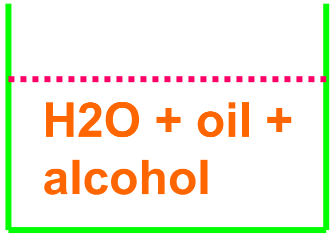
$$F = C - P + 2$$

- liquid water + vapor
- liquid water + liquid ethyl alcohol + vapor mixture (ethyl alcohol and water are completely miscible)
- liquid water and liquid benzyl alcohol and vapor mixture (benzyl alcohol and water are completely immiscible)

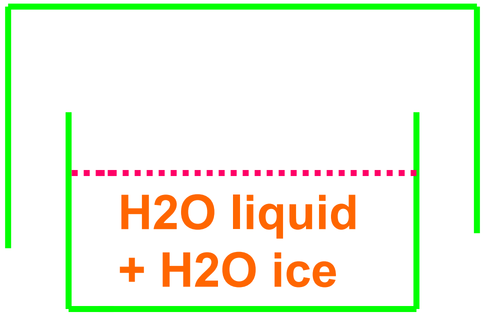


closed

Miscible , opened



opened



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Latent heat :

when a change in the state of material occurs the temperature usually remains constant but heat is absorbed, this heat which results in the change of matter without increasing the temp. is called the latent heat

Latent heat of fusion:

heat results in the change of state from

solid to liquid.

Example heat required to change ice to water at zero c°

Latent heat of vaporization :

is the quantity of heat absorbed to change liquid to vapor at its boiling point without changing the temperature of material.

Example heat required to change water to vapor at 100 c°

Vapor pressure:

When a liquid is kept in a closed evacuated container, molecules from its surface continuously leave and go into the free space above it, this is known as the process of vaporization.

Some molecules however return to the surface depending on their conc. in the vapor, this is known as the process of condensation.

At equilibrium when the rate of escape of molecules becomes equal to the return, the vapor is said to be saturated and the pressure exerted by the vapor at equilibrium is known as the ***vapor pressure.***

- The vapor pressure of liquids depends on the temp. and not on the amount of liquid or vapor as long as both liquid and vapor are present and equilibrium is maintained.
- As the temp. increased, more of liquid converted to vapor and vapor pressure increased, as the temp increased more, the density of vapor increased and that of liquid decreased, eventually, the densities of both phases become equal and the two phases cannot be distinguished. The temp. at which this occur is known as ***Critical temp.*** above which there is no liquid phase

Boiling point :is the temperature at which the vapor pressure of a liquid equals the external or atmospheric pressure.

at the boiling point all the absorbed heat is used to change the liquid to the vapor state and their is no rise in the temp. of the liquid until it is completely vaporized.

if the pressure above the liquid increased or decreased the boiling point increased or decreased.

Melting point : the temp. at which solids passes into liquid under atmospheric pressure.

Freezing point : the temp. at which liquid passes into solid under atmospheric pressure.

Vapor pressure of mixture of liquids

In case of 2 miscible liquids

- $P = Pa + Pb = Pa^{\circ} Xa + Pb^{\circ} Xb$

P: total vp

Pa°: vp of pure a

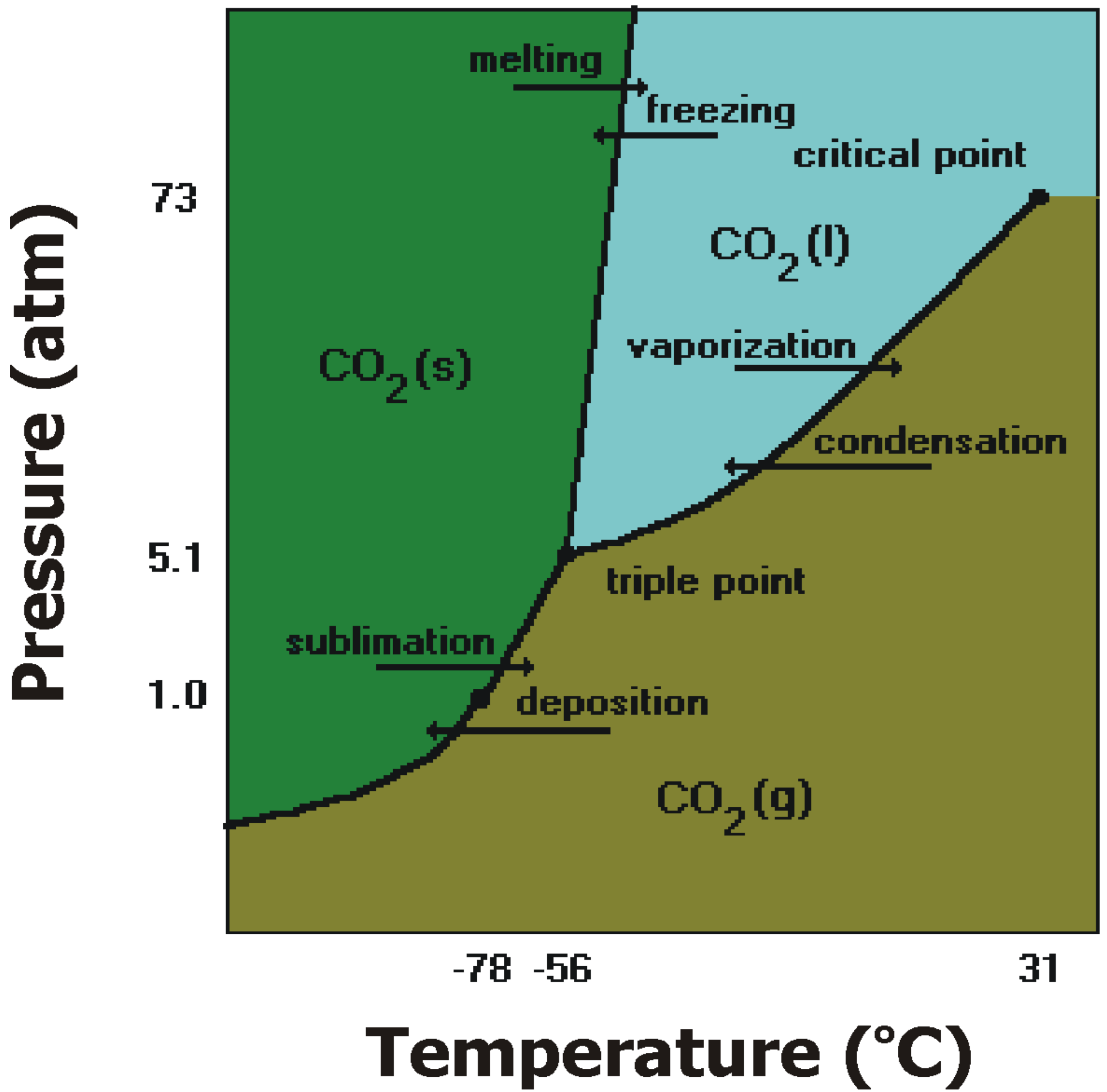
Xa: mole fraction of a

In case of 2 immiscible liquids

$$P = Pa^{\circ} + Pb^{\circ}$$

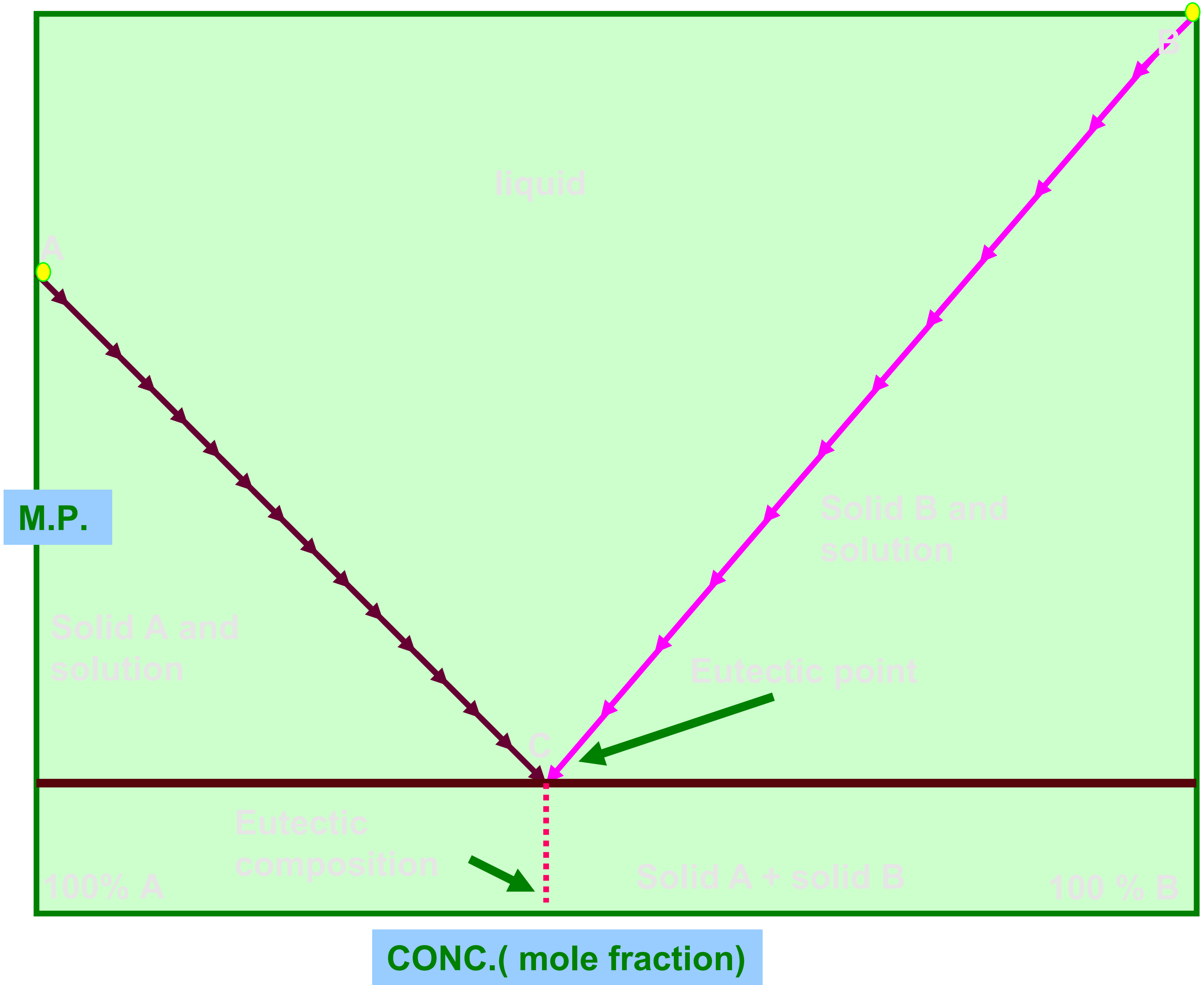
Sublimation: is the process of transportation of solids into the vapor without passing into the intermediate liquid phase .

Example on substance undergo sublimation : are camphor , menthol , naphthalene , other substances such as ice also can be forced to exhibit the phenomenon of sublimation by varying the temperature and pressure.


melting
freezing
critical point
73
CO_2(l)
vaporization
CO_2(s)
condensation
5.1
triple point
sublimation
1.0
deposition
CO_2(g)
-78
-56
31
Pressure (atm)
Temperature (°C)

Eutectic mixtures :

Certain substances such as menthol thymol , camphor , phenol , salol , when mixed in a particular proportion tend to liquefy due to redaction in their respective melting point , mixtures of such substances are known as eutectic mixtures .


liquid
A
B
M.P.
Solid B and solution
Solid A and solution
Eutectic point
C
Eutectic composition
100% A
Solid A + solid B
100 % B
CONC.(mole fraction)

In pharmaceutical practice , eutectic mixture is difficult to dispense in the form of powder so how we can incorporate such materials in a powder;

1) First mix each ingredient separately with an inert diluents such as light magnesium oxide , magnesium carbonate , starch , kaolin followed by gentle blending of the different portion.

2) The eutectic material can first be triturated together in order to force them to liquefy, the liquid can then be adsorbed on an inert diluents

The phenomenon of eutectic formation has been used in pharmaceutical practice to improve the dissolution behavior of certain drugs .

Example :

Aspirin 37% + acetaminophen 63%

Urea 46 % + acetaminophen 54%

Reference

MARTIN'S PHYSICAL PHARMACY AND PHARMACEUTICAL SCIENCES