States of Matter

Lecture 3
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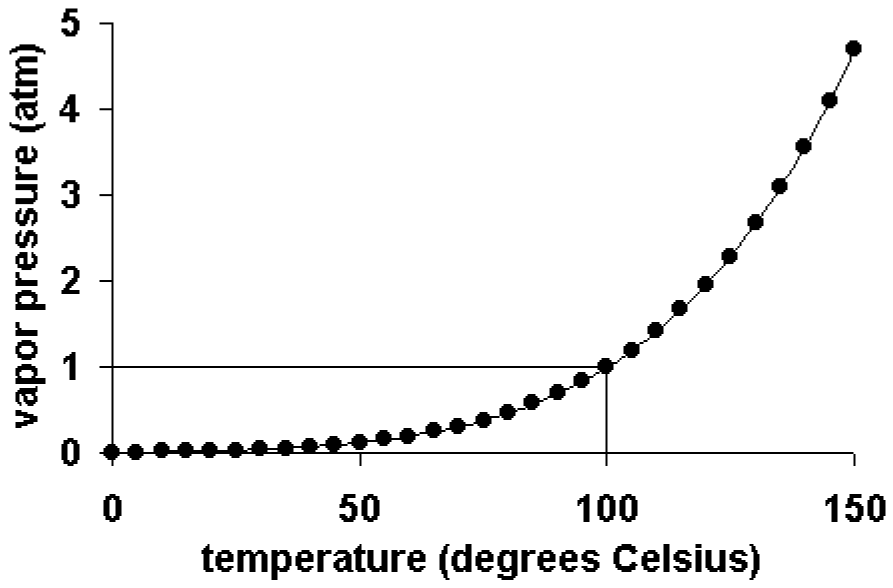
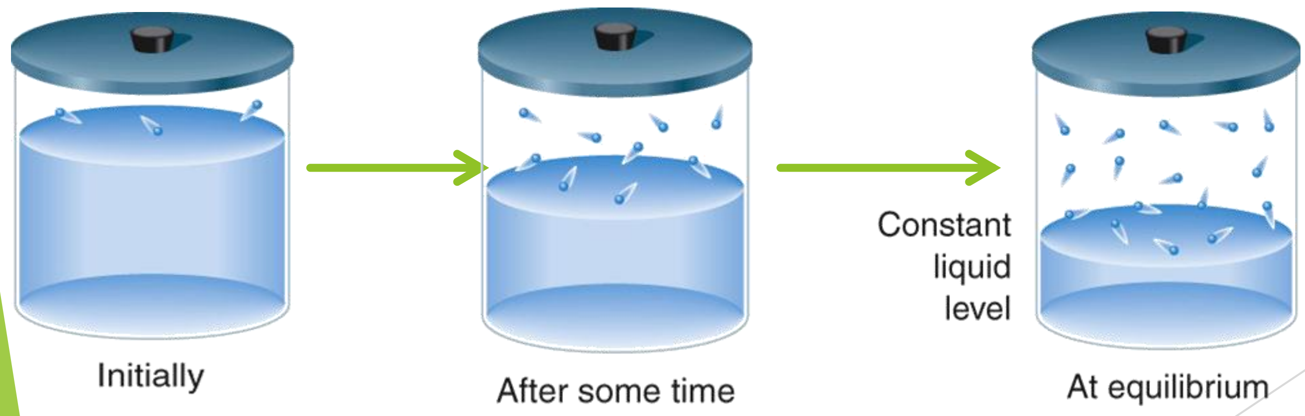
Physical Pharmacy

Vapor pressure of liquids

- **Evaporation** is the name of the process by which a liquid becomes a gas.
- Evaporation takes place from the surface of the liquid.
- The molecules on the surface of the liquid with sufficient energy will leave the liquid and enter the gas phase (forming a vapor above the liquid).

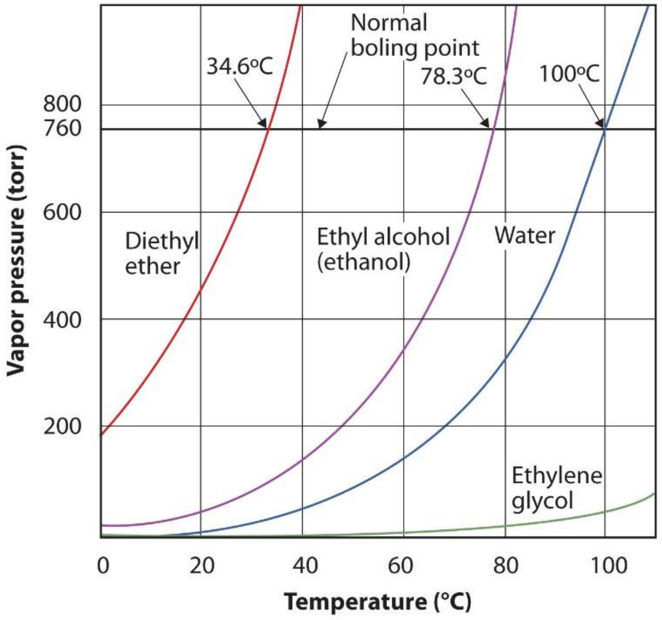


- This vapor exert a pressure on the surface of the liquid ,i.e., the **vapor pressure** at some molecules will return to the liquid state or condense.
- When the rate of condensation equal the rate of evaporization we say the system at equilibrium.
- The equilibrium vapor pressure is the vapor pressure measured when a dynamic equilibrium between condensation and evaporation.



The vapor pressure of a liquid **increases** with **temperature** because more molecules approach the velocity necessary for escape and pass into the gaseous state.

The vapor pressure of a liquid **depends** upon the chemical **nature** of the liquid.
Those molecules that have **strong intermolecular** attractive forces have **lower vapor pressures**



Clausius–Clapeyron equation It explains the effect of temperature on vapour pressure of a liquid and also the effect of pressure on the boiling point of a liquid.

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303\,R} \cdot \frac{(T_2 - T_1)}{(T_1 \cdot T_2)}$$

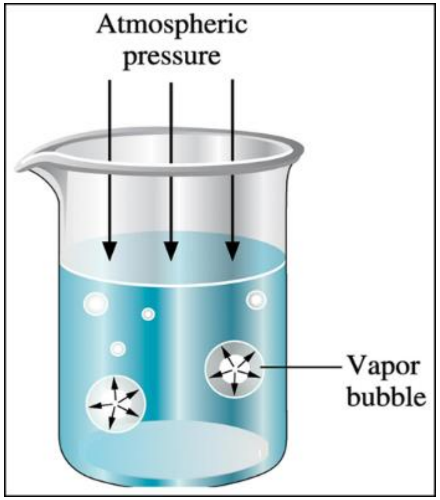
Compute the vapor pressure of water at 120 °C. the vapor pressure at 100 °C is 1 atm , may be taken as 9720 cal/mole for this temp.

$$\text{Log}\ \frac{p2}{1} = \frac{9720*\ (\ 393-373)}{2.303\ *1.978\ *393*373}$$

P2= 1.95 atm

Boiling point

- If a liquid is placed in open container and heated until the vapor pressure equals the atmospheric pressure, the vapor will form bubbles that rise rapidly through the liquid and escape into the gaseous state.
- The temperature at which the vapor pressure of a liquid equals the external pressure or the atmospheric pressure is called the **boiling point.**



Factors that affect the boiling point

- **Atmospheric pressure** : the boiling point of a liquid increases with the increase of atmospheric pressure. The atmospheric pressure at sea level is approximately 760 mmHg. At higher elevations, the atmospheric pressure decrease and the boiling point is lowered.
- **Intermolecular forces :**

1. London dispersion forces < dipole –dipole < Hydrogen bonding. The stronger the attractive forces, the higher the boiling point.
2. Number of sites for intermolecular interactions (surface area). Larger surface area means more sites for interactions causing increase boiling point.
3. Branching of the chain produce less compact molecules with reduced intermolecular attractions and decrease in the boiling point.

Boiling point of alcohol is higher than hydrocarbons of the same molecular weight because the presence of H-bonding. Boiling point of carboxylic acid is high because the presence of H bonding forming dimers.

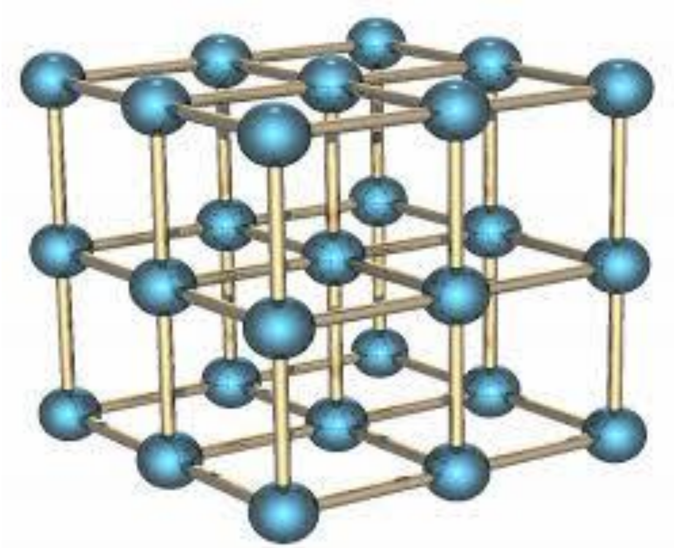
Solids

Crystalline solid

Amorphous solid

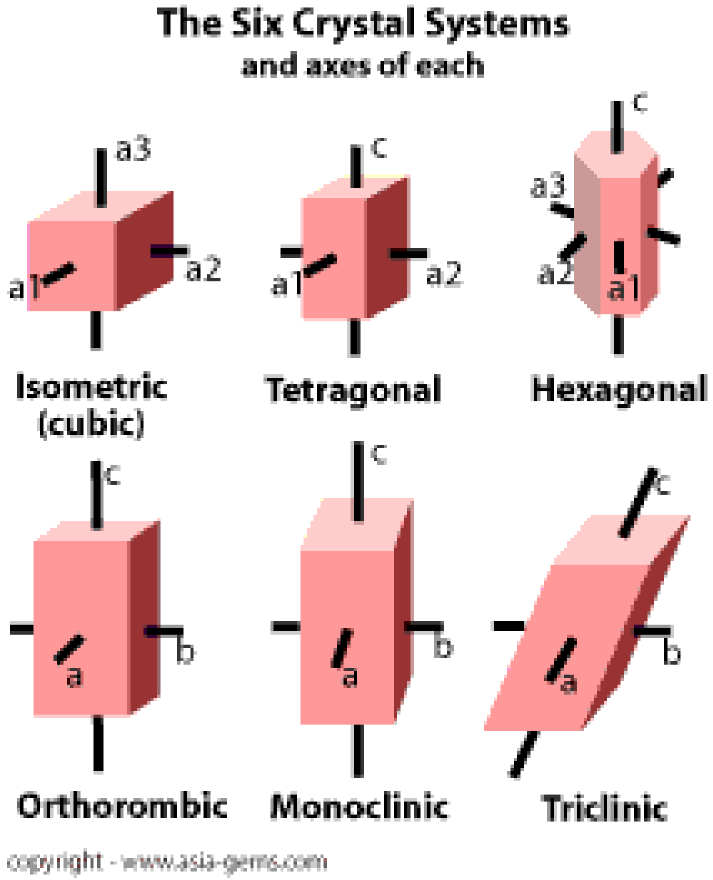
Crystalline Solids

- The structural units of crystalline solids, such as ice, sodium chloride, and menthol, are arranged **in fixed geometric patterns or lattices.** Crystalline solids, unlike liquids and gases, have definite shapes and an orderly arrangement of units.



- Gases are easily compressed, whereas solids, like liquids, are practically incompressible.
- Crystalline solids show definite **melting points**, passing rather sharply from the solid to the liquid.
- Crystalline structurer could be **atoms** like diamond and graphite, **molecules** such as carbon dioxide and naphthalene and **ions** like sodium cholrid.

Crystal forms



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.

- Polymorphs have different stabilities and may spontaneously convert from metastable to stable form.
- They exhibit different **melting points**, **x-ray diffraction** and **solubilities** even though they are identical chemically.
- Theobroma oil, or cacao butter, is a polymorphous natural fat. Theobroma oil is capable of existing in four polymorphic forms: the unstable gamma form, melting at 18°C; the alpha form, melting at 22°C; the beta prime form, melting at 28°C; and the stable beta form, melting at 34.5°C.

Variables affecting formation of polymorphism

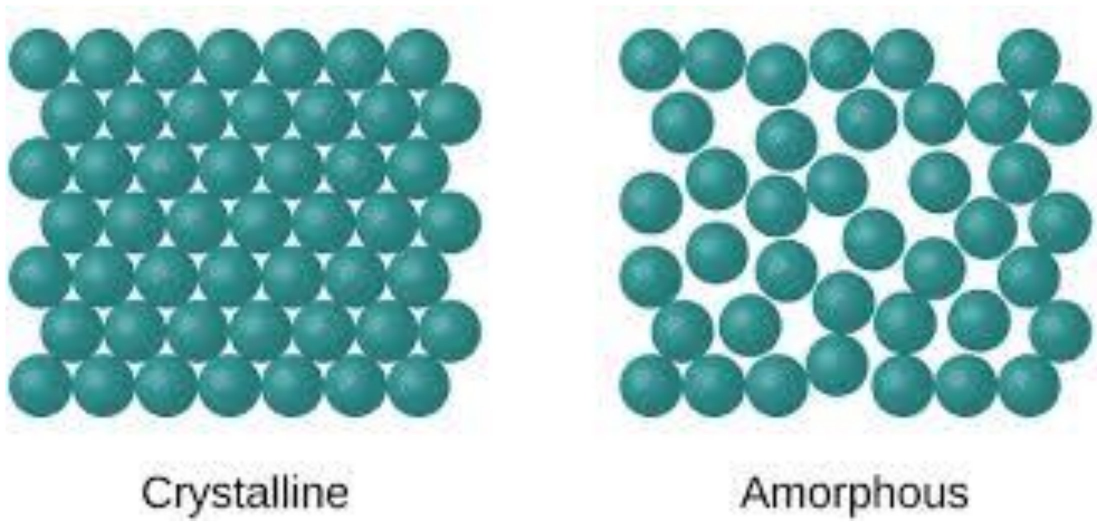
- Solvents differences.
- Impurities.
- Temperature.
- Geometry of covalent bond.
- The level of supersaturation.
- Attraction and repulsion of anion and cation.

The most common example of polymorphism is diamond and graphite. In this case, high temperature and pressure lead to the formation of diamond.

- In the case of slightly soluble drug, polymorphism may affect the rate of the drug dissolution. As results one polymorph may be more active therapeutically than another polymorph of the same drug.
- The polymorphic state of chloramphenicol palmiate is more active than other polymorphic form.
- SulfameterII is more active then form III.
- In suspension, cortisone acetate exists at least in five different forms, four of them are unstable in the presence of water and change to the stable form.

Amorphous Solid

- Solids that don’t have a definite geometrical shape are known as Amorphous Solids.
- Amorphous solid considers as supercooled liquid in which molecules are arranged in somewhat random manner as in liquid state. They don’t have a melting. points.



Crystalline
Amorphous