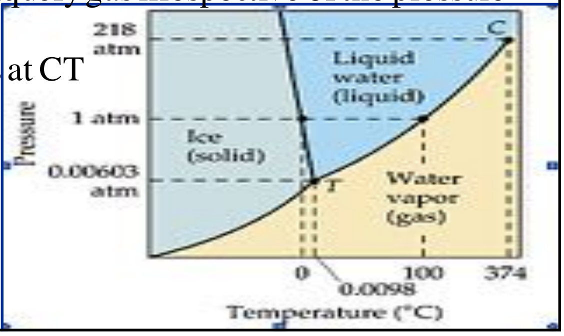
Liquid state

1) On cooling of gas a lose of **kinetic energy** (heat) and ↓ in the velocity of molecules.
2) On pressing molecules are brought within sphere of **VDW forces** and G pass to L state.
3) Liquids are considerably **denser** than gases and occupy a definite volume
4) Transition is depend on both **T** and **P**.
5) Critical temperature: above which impossible to liquefy gas irrespective of the pressure (liquid not exist).
6) Critical pressure : pressure required to liquefy gas at CT



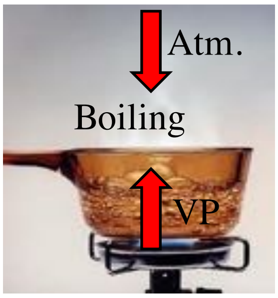
Methods of achieving liquefaction

- Use of freezing mixtures.
- **Adiabatic expansion** of ideal gases (no transfer or gain of heat), in which we have cooling occur due to collision frequency of gas within a flask.
- **Joule-Thomson effect** = Expansion of a highly compressed non-ideal gas into a region of low pressure, causes cooling? Due to expending of energy in overcoming the cohesive forces of attraction between molecules. Precooling the gas before expansion may enhance liquefaction.

Boiling point

When and where occur??

b.p. for water is 100° C at 760mmHg
b.p. for water is 97.7° C at 700mmHg
b.p. for water is 20° C at 17.5mmHg

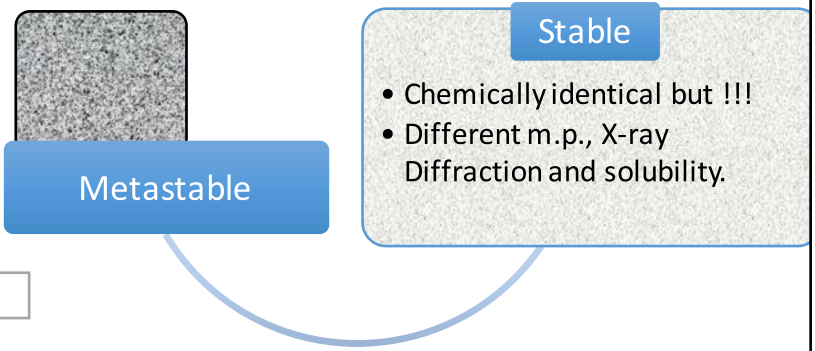


- Bp ⇧ with ⇧ in mwt of hydrocarbons, alcohols and carboxylic acids ???
- Branching cause a ↓, how???
- Ethanol shows higher Bp than corresponding hydrocarbons as a results of H-bond.
- Carboxylic acid have abnormal BP compare with HC of similar no of atoms ?

Solid and crystalline state:

- Definite shapes and an orderly arrangement of units.
- Unlike gases , uncompressible
- The structural units of crystalline solids arranged in fixed geometric patterns of lattices.
- Crystal have definite m.p.
- Crystallization as phenomenon may be occurred by precipitation of the compound out of solution and into an ordered array.
- Crystal habit (morphology) depend on the nature of the molecules and affected by temp, pressure, type of solvent, salt formation

Polymorphism:



Metastable

Stable

- Chemically identical but !!!
- Different m.p., X-ray Diffraction and solubility.

Ex: Diamonds and graphite

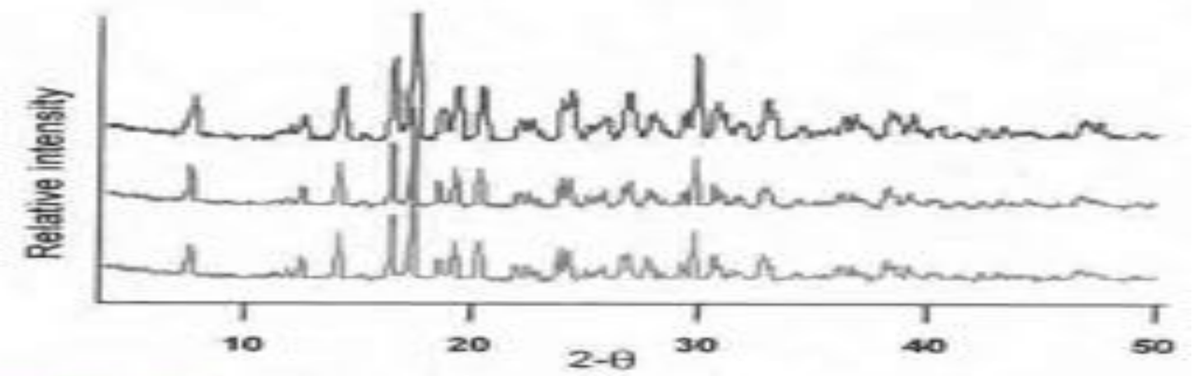
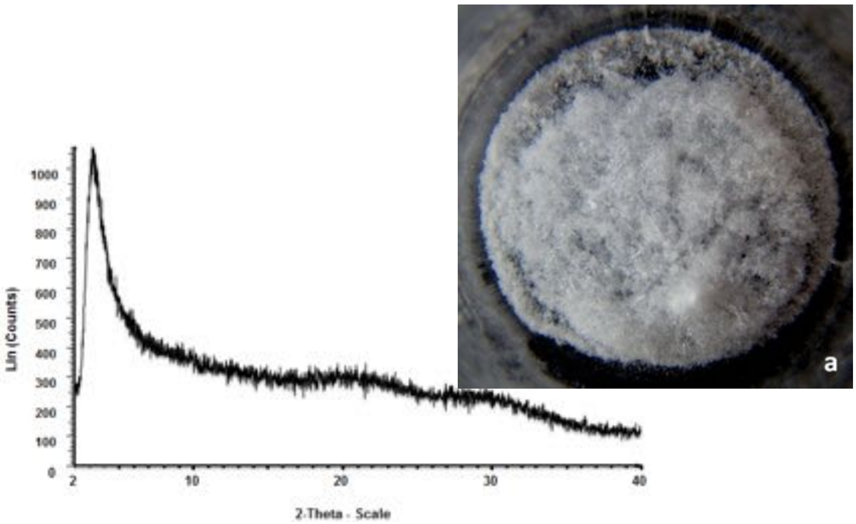


Fig. 2–12. Powder x-ray diffraction patterns for spirapril hydrochloride. The monohydrate (top) and the sample dehydrated at 75°C for 106 and 228 hr (middle and bottom, respectively) demonstrating that the structural motif is essentially unchanged in the "dehydrated hydrate." (From W. Xu, *Investigation of Solid State Stability of Selected Bioactive Compounds*, unpublished dissertation, Purdue University, Purdue, Ind., 1997. With permission.)



X-ray diffraction chromatogram of the amorphous solid (powder). No crystalline structure was observed.

Melting point and Heat of fusion

- The temperature at which a liquid passes into the solid state is known as the freezing point, it is also the melting point of a pure crystalline compound.
- Or the temperature at which the pure liquid and solid exist in equilibrium.
- The heat (energy) absorbed when 1 g of a solid melts or the heat liberated when it freezes is known as the latent heat of fusion.
- For water (ice) it is 0°C, Latent heat of fusion: = 80cal/gm
- It is affected by the pressure applied

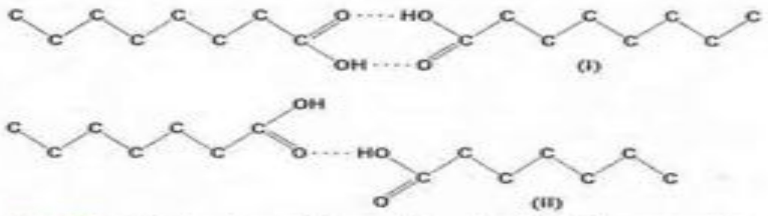


Fig. 2–14. Configuration of fatty acid molecules in the crystalline state. (Modified from A. E. Bailey, *Melting and Solidification of Fats*, Interscience, New York, 1950, p. 120.)

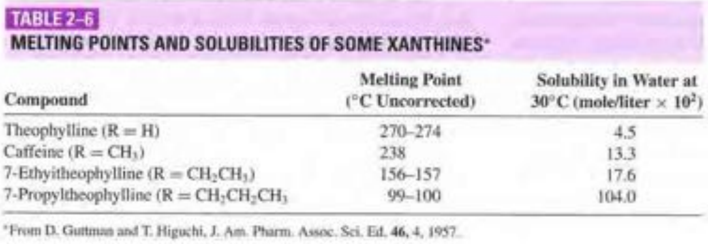
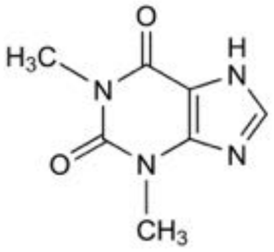


TABLE 2-6

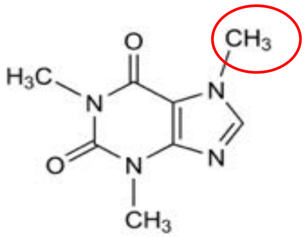
MELTING POINTS AND SOLUBILITIES OF SOME XANTHINES*

Compound	Melting Point (°C Uncorrected)	Solubility in Water at 30°C (mole/liter × 10^2)
Theophylline (R = H)	270–274	4.5
Caffeine (R = CH_3)	238	13.3
7-Ethyitheophylline (R = CH_2CH_3)	156–157	17.6
7-Propyltheophylline (R = $CH_2CH_2CH_3$	99–100	104.0

*From D. Guttman and T. Higuchi, J. Am. Pharm. Assoc. Sci. Ed. **46**, 4, 1957.



Soluble 1 in 120 of water



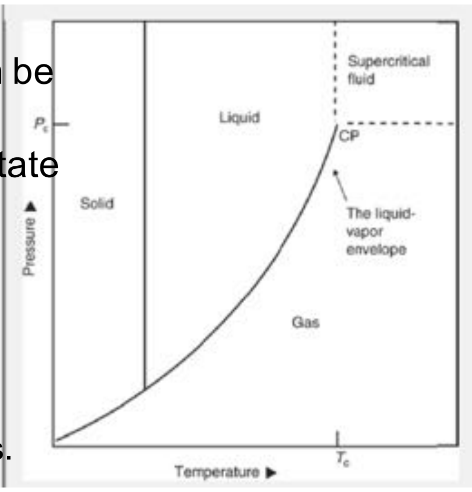
Soluble 1 in 46 of water,

Liquid crystalline state (**mesophase**):

- The name describe this state as intermediate bet **L** and **S** states.
- Liquid state: movement of molecules in three directions in addition to free rotation the three axes.
- Solid state: molecules are immobile and rotation is not readily possible.
- Types of liquid crystal according to movement and rotation:
  - Smectic.
  - Nemactic.

Supercritical fluid state

- intermediate between those of **L** and **G**, with better ability to **permeate solid substances** (gas-like) and having **high densities** that can be regulated by pressure (liquid-like).
- It is a mesophase formed from the gaseous state at certain conditions (**T** and **P**).
- **Applications**:
  - Extraction
  - Crystallization
  - Preparation of some polymer mixtures.
  - With advantages over liquid solvents like lower viscosity, more safe and lower energy requirements.
  - Decaffeination of coffee and tea



Thermal analysis

- Methods for characterizing the physical and chemicals changes of materials upon heating or cooling.
- The most commonly used are **DSC** (differential scanning calorimetry), **DTA** (differential thermal analysis), **TGA** (thermogravimetric analysis) and **DVS** (Dynamic vapor sorption).
- It is important for determination of purity, polymorphism, moisture content, amorphous content, stability and compatibility with additives.

Phase Rule

- It is a relationship for determining the least number of **intensive variables** that can be changed without changing the equilibrium state of the system, or, alternately, the least number required to define the state(s) of the system.
- **Intensive variable** : are independent variables that do not depend on the volume or size of the phase, such as: temperature, pressure, density, and concentration.

Phase Equilibrium and Phase Rule:

By J. Willard Gibbs

$$F = C - P + 2$$

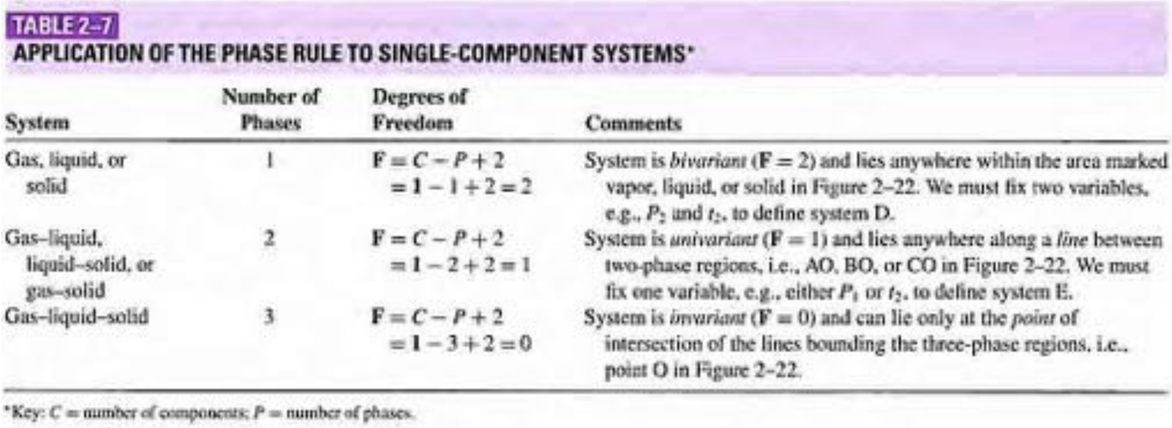


TABLE 2-7

APPLICATION OF THE PHASE RULE TO SINGLE-COMPONENT SYSTEMS*

System	Number of Phases	Degrees of Freedom	Comments
Gas, liquid, or solid	1	$F = C - P + 2$ $= 1 - 1 + 2 = 2$	System is *bivariant* (F = 2) and lies anywhere within the area marked vapor, liquid, or solid in Figure 2–22. We must fix two variables, e.g., P_2 and t_2, to define system D.
Gas–liquid, liquid–solid, or gas–solid	2	$F = C - P + 2$ $= 1 - 2 + 2 = 1$	System is *univariant* (F = 1) and lies anywhere along a *line* between two-phase regions, i.e., AO, BO, or CO in Figure 2–22. We must fix one variable, e.g., either P_1 or t_2, to define system E.
Gas–liquid–solid	3	$F = C - P + 2$ $= 1 - 3 + 2 = 0$	System is *invariant* (F = 0) and can lie only at the *point* of intersection of the lines bounding the three-phase regions, i.e., point O in Figure 2–22.

*Key: C = number of components; P = number of phases.

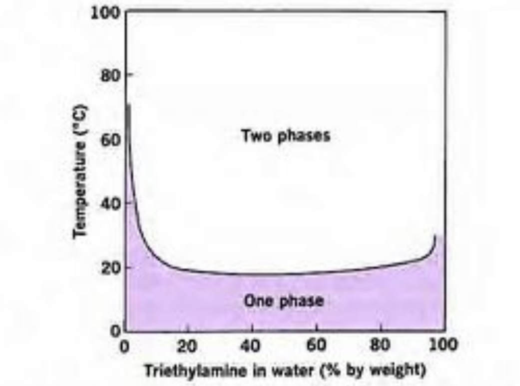


Fig. 2-24. Phase diagram for the system triethylamine–water showing lower consolute temperature.

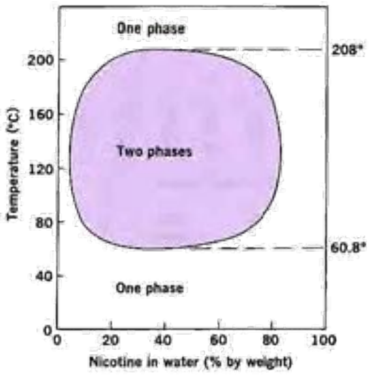
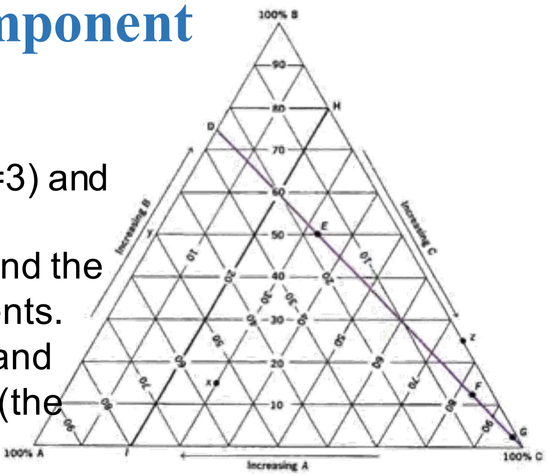


Fig. 2-25. Nicotine–water system showing upper and lower consolute temperatures.

Phase equilibria in three-component systems (ternary)



- Systems containing three components (C=3) and one phase (P=1), then F= 4.
- The variables are temperature, pressure and the concentrations of two of the three components.
- If the system is condensed (assumption), and the temperature is held constant, then F=2 (the concentrations are variables).
- For determination of the phase rule, we need triangular diagrams instead of planar ones.
- The miscibility between the liquid phases can affect these systems.

Thanks for your attention