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ΔΙΕΡΓΑΣΙΕΣ ΔΙΑΧΩΡΙΣΜΟΥ

Μάθημα 3ο

Ακαδημαϊκό έτος 2017-2018

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Phase equilibria for crystallization from solutions

Solubility

- **Solution** : homogeneous mixture of two or more substances
- **Melt** : liquid at a temperature close to mp. Also :Liquid mixtures of two or more substances which solidify each separately upon cooling at room temperature
- **Example:** α -Naphthalene heated at temperature above its mp ($96\text{ }^{\circ}\text{C}$) is considered as a melt. The same holds for a liquid mixture of α -Naphthol and β -Naphthalene (mp $122\text{ }^{\circ}\text{C}$). However, the mixture of α -Naphthalene and methanol is a solution.

Thermodynamics??

- The macroscopic description of $\sim 10^{23}$ particles may be possibly done using only a few parameters!

“Simple systems”: Macroscopic, homogeneous, isotropic, uncharged, sufficiently large so that surface phenomena may be considered as negligible, unaffected by external factors including electric, magnetic or gravitational fields.

- Macroscopic observable properties are those derived from the combination of atomic co-ordinates and they are NOT time -dependent. Energy, momentum, angular momentum, etc.
- Besides those «mechanical» variables, in a system we have thermodynamic variables as well .

Thermodynamic Equilibrium

All systems tend to convert to a state the properties of which are determined from true properties independent on the history of the system (i.e. from the type of the externally applied interactions) .These states, which correspond to simple systems are by definition time independent and they are known as **equilibrium states**.

Thermodynamics describes these simple stationary states of equilibrium.

Axiom:

There are special states of simple systems (known as equilibrium states) which macroscopically are fully defined from functions such as the internal energy, U , volume V , and the number of moles N_1, \dots, N_r of the chemical components

Classical Thermodynamics: Fundamental concepts

Internal Energy, U

Entropy of the system, S

Volume of the system, V

Chemical composition, n_1, n_2, \dots, n_r moles
Of substances 1, 2, ..., r

The characteristic of the fundamental Concepts is that they are additive

The concepts having this, additive property:
Extensive properties or extensive parameters

The function relating the extensive parameters is:

$$U = f(S, V, n_1, n_2, \dots, n_r) \quad (1)$$



Independent Dependent
Variables

Consequence: Very small changes ΔS , ΔV , Δn_1 , ..., Δn_r results in the change ΔU of the dependent variable

$$\Delta U = T\Delta S - p\Delta V + \mu_1\Delta n_1 + \mu_2\Delta n_2 + \dots + \mu_r\Delta n_r \quad (2)$$

$\mu_1, \mu_2, \dots, \mu_r$: Chemical potentials

T, P, μ : **Intensive properties-parameters**

$$T, T', \quad T_{\Sigma} \neq T + T'$$

$$P, P', \quad P_{\Sigma_{\text{TOT}}} \neq P + P'$$

Equation (2) is the first law of thermodynamics

$$\Delta U = \underbrace{T\Delta S}_Q - \underbrace{p\Delta V}_W + \mu_1\Delta n_1 + \mu_2\Delta n_2 + \dots + \mu_r\Delta n_r$$

ΔG

U : **State function** (depends only on initial and final states of the system)

(assuming reversible addition into the system)

with

$$\Delta S=0, \Delta V=0, \Delta n_2=\Delta n_3=\dots \Delta n_r=0 \Rightarrow \Delta U=\mu_1\Delta n_1$$

or

$$\Delta S = \frac{Q}{T}$$

The differences of the intensive parameters T , P , μ are the **thermodynamic driving forces for physical changes**. Temperature differences \Rightarrow Heat flow (until thermal equilibrium is) **2nd law of thermodynamics**

$$\mu_1 = \frac{\Delta U}{\Delta n_1}$$

$$\mu_1 = \left(\frac{\partial U}{\partial n_1} \right)_{S, V, n_2, \dots, n_r}$$

$\Delta P \rightarrow$ pressure flow \rightarrow mechanical equilibrium

$\Delta \mu \rightarrow$ mass flow \rightarrow chemical equilibrium

At equilibrium the intensive parameters attain the same value at all parts of a composite system and every macroscopic change in the system ceases (T, P, μ).

The changes of the intensive parameters are related with the **Gibbs-Duhem equation**

$$S\Delta T - V\Delta P + n_1\Delta\mu_1 + n_2\Delta\mu_2 + \dots = 0$$

$r+1$ degrees of freedom ($r+2$ intensive parameters, one less may be changed independently)

Phase Equilibria

Classical
Thermodynamics

Equilibria

Physical

Chemical

Physical equilibria -> Phase equilibria

Phase: *part of a composite system, homogeneous separated with separating surfaces from the rest of the homogeneous parts of the composite system*

Water (Liquid) - Ice (Solid phase)

Water-Sugar -Vapour -> 2 phases (water+sugar 1 phase)

Water-Sand-> 2 phases

Composite system with 2 gas phases does not exist.

Two phases are in equilibrium when its intensive parameters (T, P, μ) become equal (when there are differences, changes occur)

The number of degrees of freedom, F , of a composite system, i.e. the number of intensive parameters which may be varied independently at equilibrium.

Composite system of φ phases

Each of the phases is defined by $C+2$ intensive parameters. ($C_{\text{chem.pot.}}, T, P$)

For each of the phases we write one Gibbs-Duhem equation which limits the degrees of freedom by one. We have therefore F equations of this type. In total the degrees of freedom are reduced by P , i.e.:

$$F = C + 2 - P$$

Instead of μ_i , the composition is used (mole fractions)

$$x_i = \frac{n_i}{\sum n}$$

$$\mu_i = \mu_i^0 + RT \ln x_i$$

Chemical potential and mole fraction

$f(T,P)$

Chemical potential of the pure component

Phase changes of a pure substance

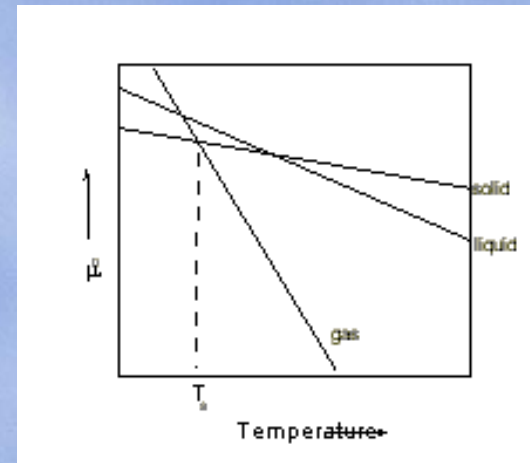
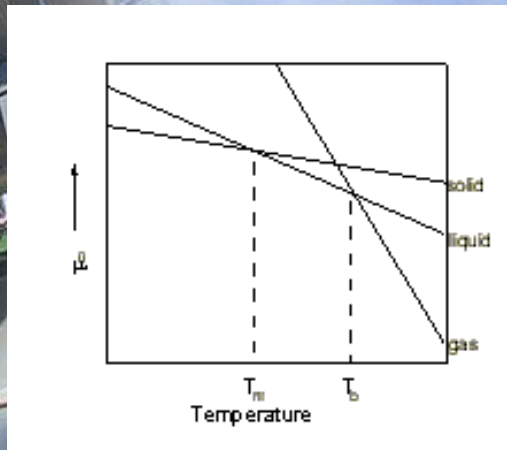
ice - water - vapor

Naphthalene (s) \rightarrow Naphthamene (g) - sublimation

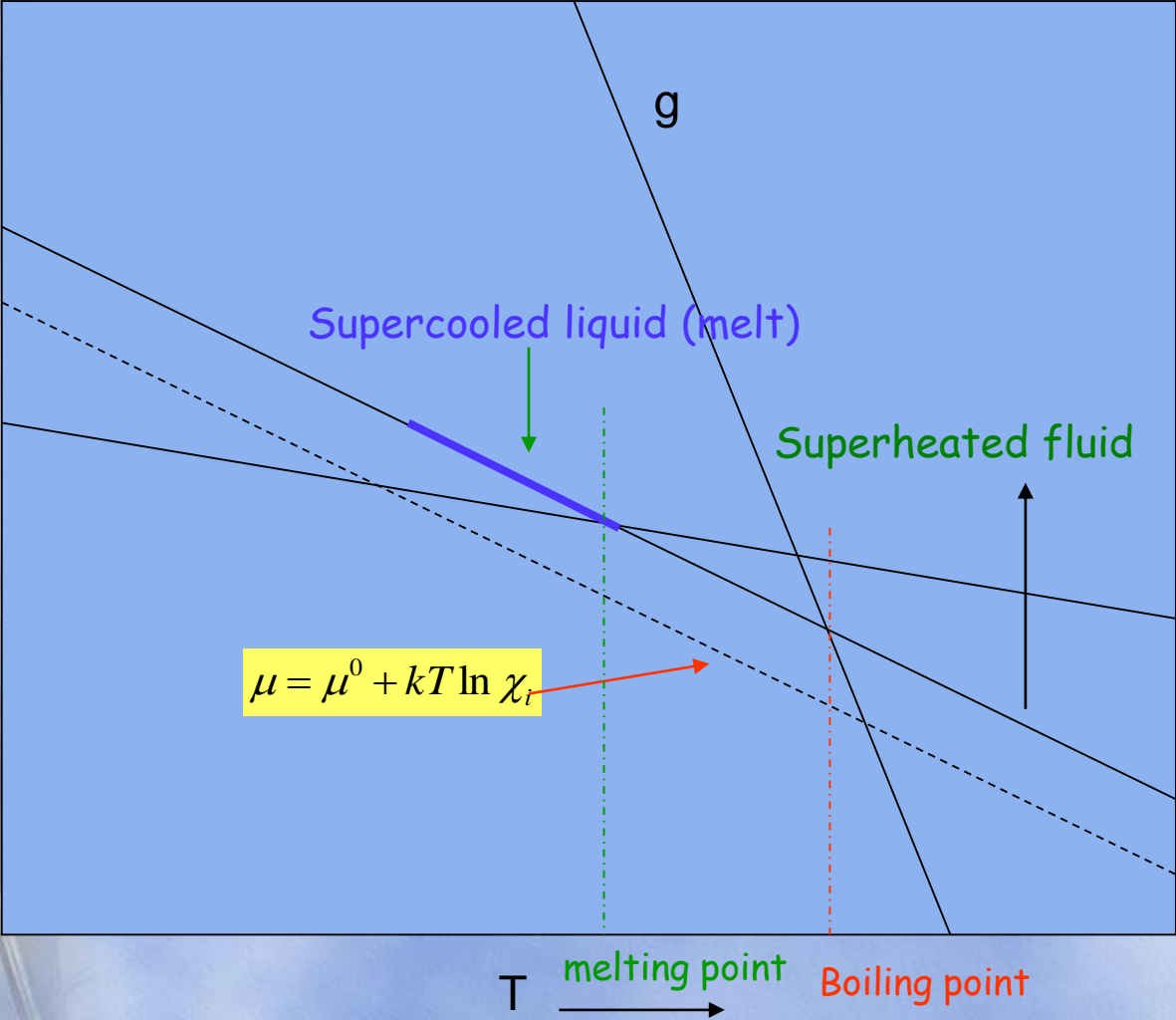
Definitions of classical thermodynamics.

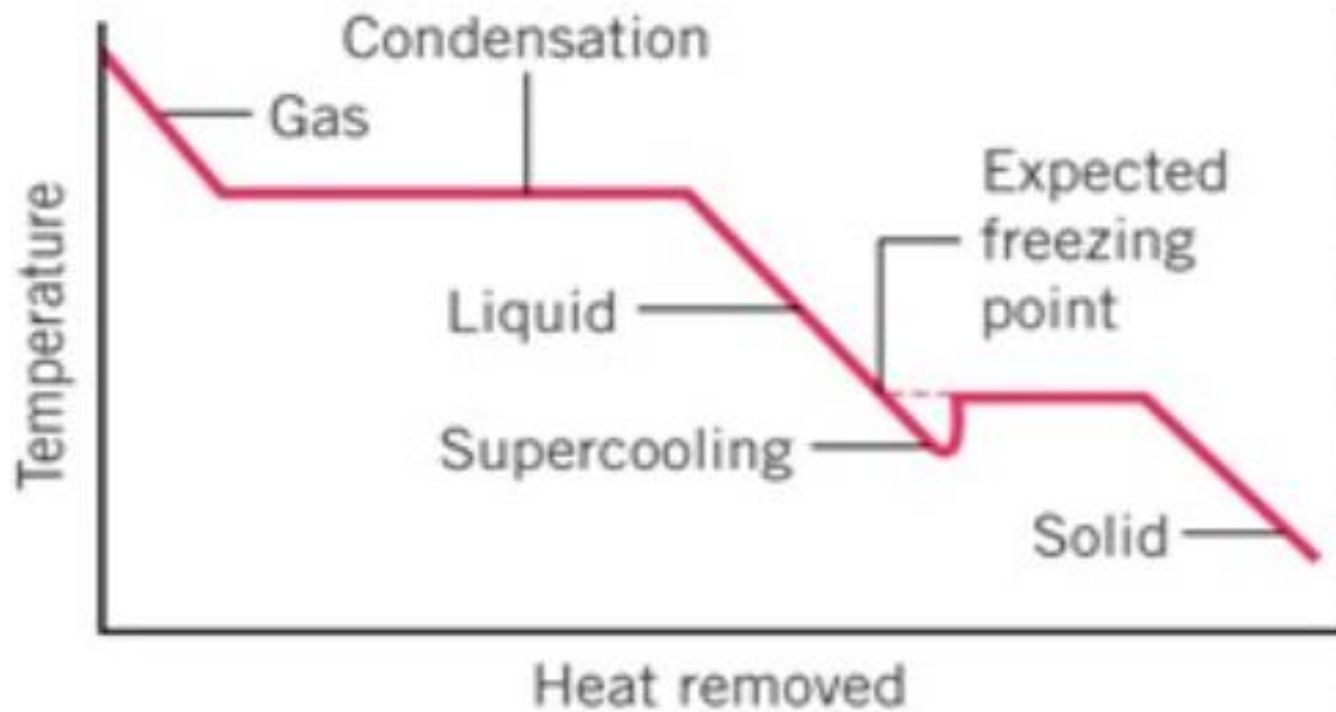
Phases and phase rule

- $SdT - VdP + n_1d\mu_1 + n_2d\mu_2 + \dots + n_r d\mu_r = 0$
- $f = r + 2 - \phi$
- $\mu_i = \mu_i^0 + RT \ln \chi_i$



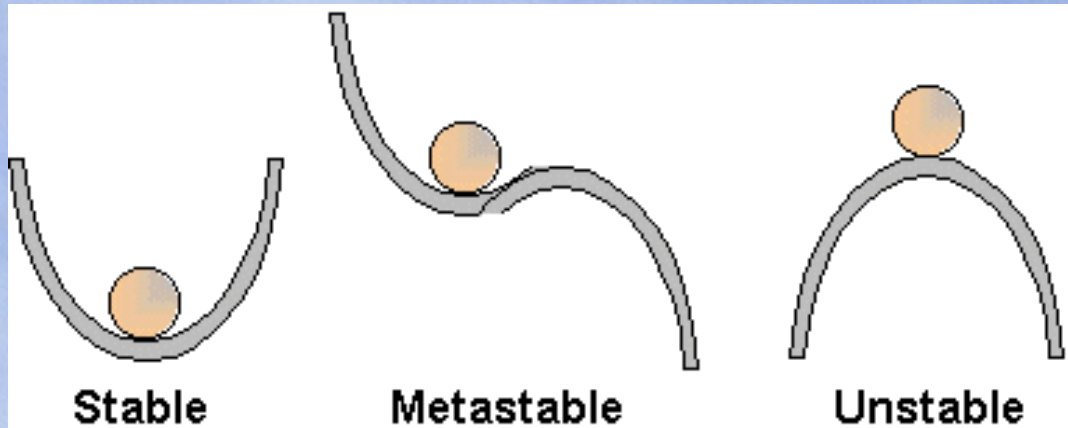
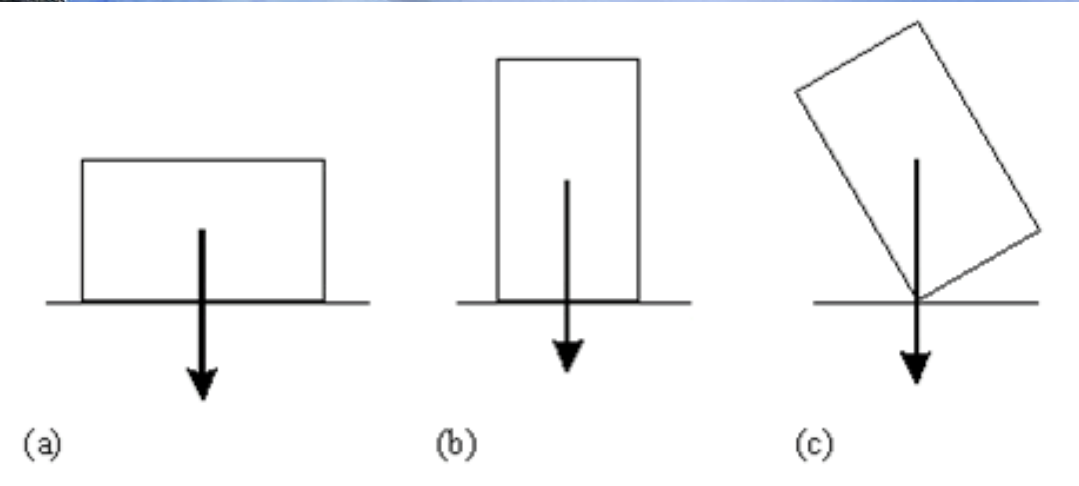
P=Constant

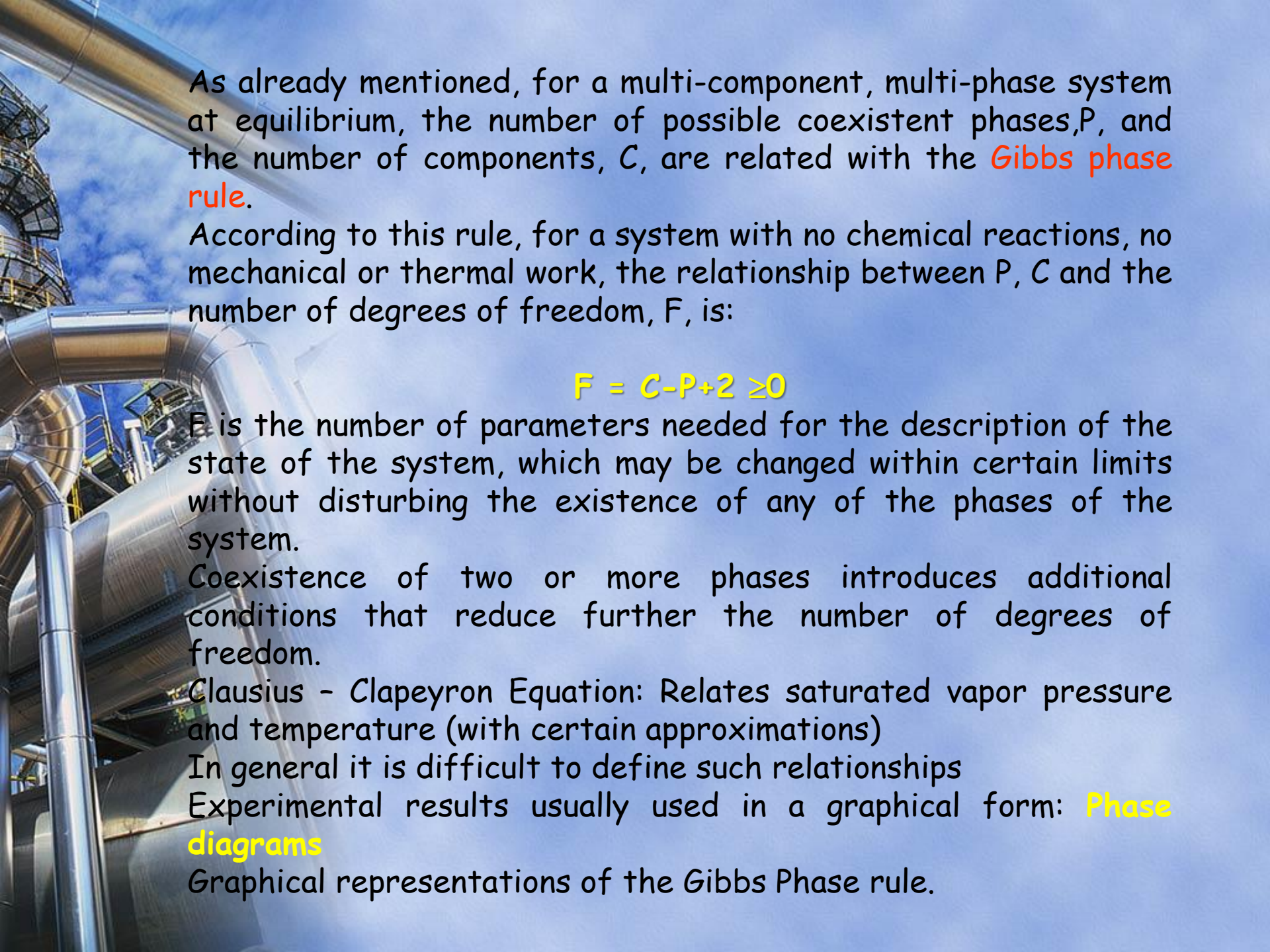




(b)

Metastable states





As already mentioned, for a multi-component, multi-phase system at equilibrium, the number of possible coexistent phases, P , and the number of components, C , are related with the **Gibbs phase rule**.

According to this rule, for a system with no chemical reactions, no mechanical or thermal work, the relationship between P , C and the number of degrees of freedom, F , is:

$$F = C - P + 2 \geq 0$$

F is the number of parameters needed for the description of the state of the system, which may be changed within certain limits without disturbing the existence of any of the phases of the system.

Coexistence of two or more phases introduces additional conditions that reduce further the number of degrees of freedom.

Clausius - Clapeyron Equation: Relates saturated vapor pressure and temperature (with certain approximations)

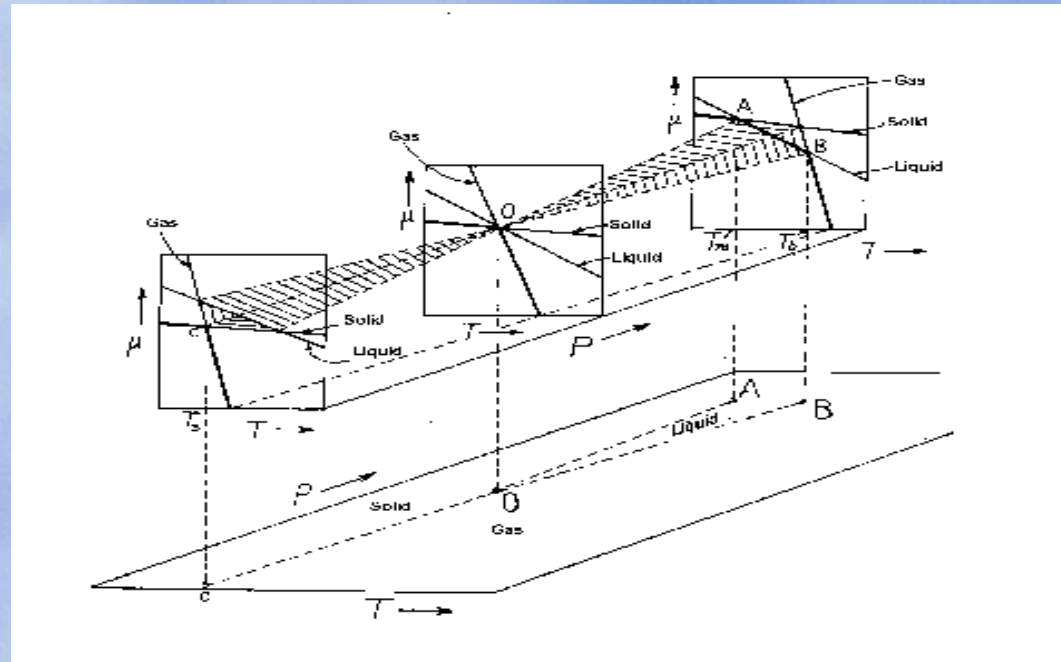
In general it is difficult to define such relationships

Experimental results usually used in a graphical form: **Phase diagrams**

Graphical representations of the Gibbs Phase rule.

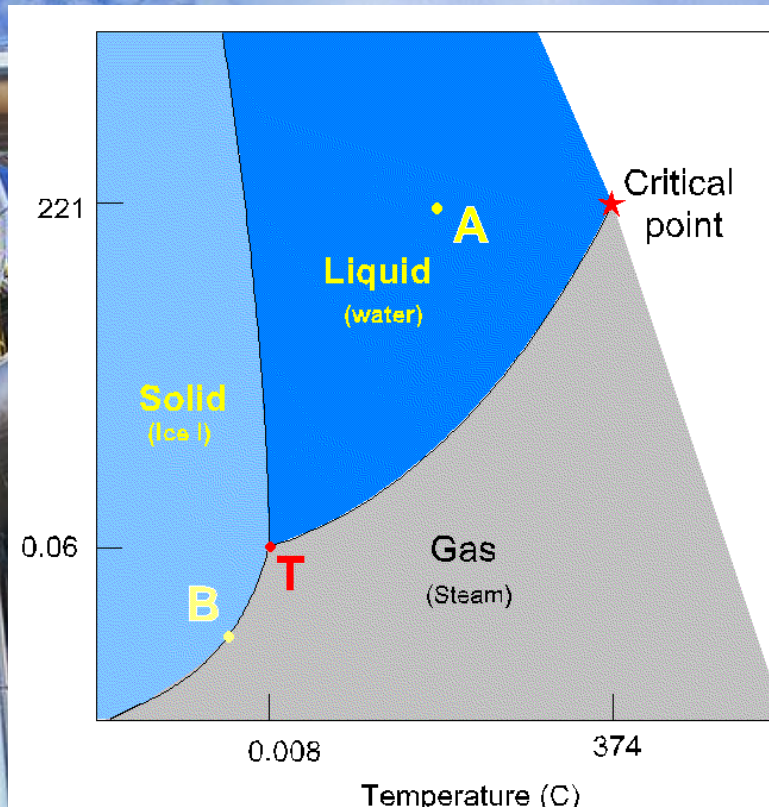
Pressure - Temperature diagrams for constant chemical potential

- Phase diagrams, P-T

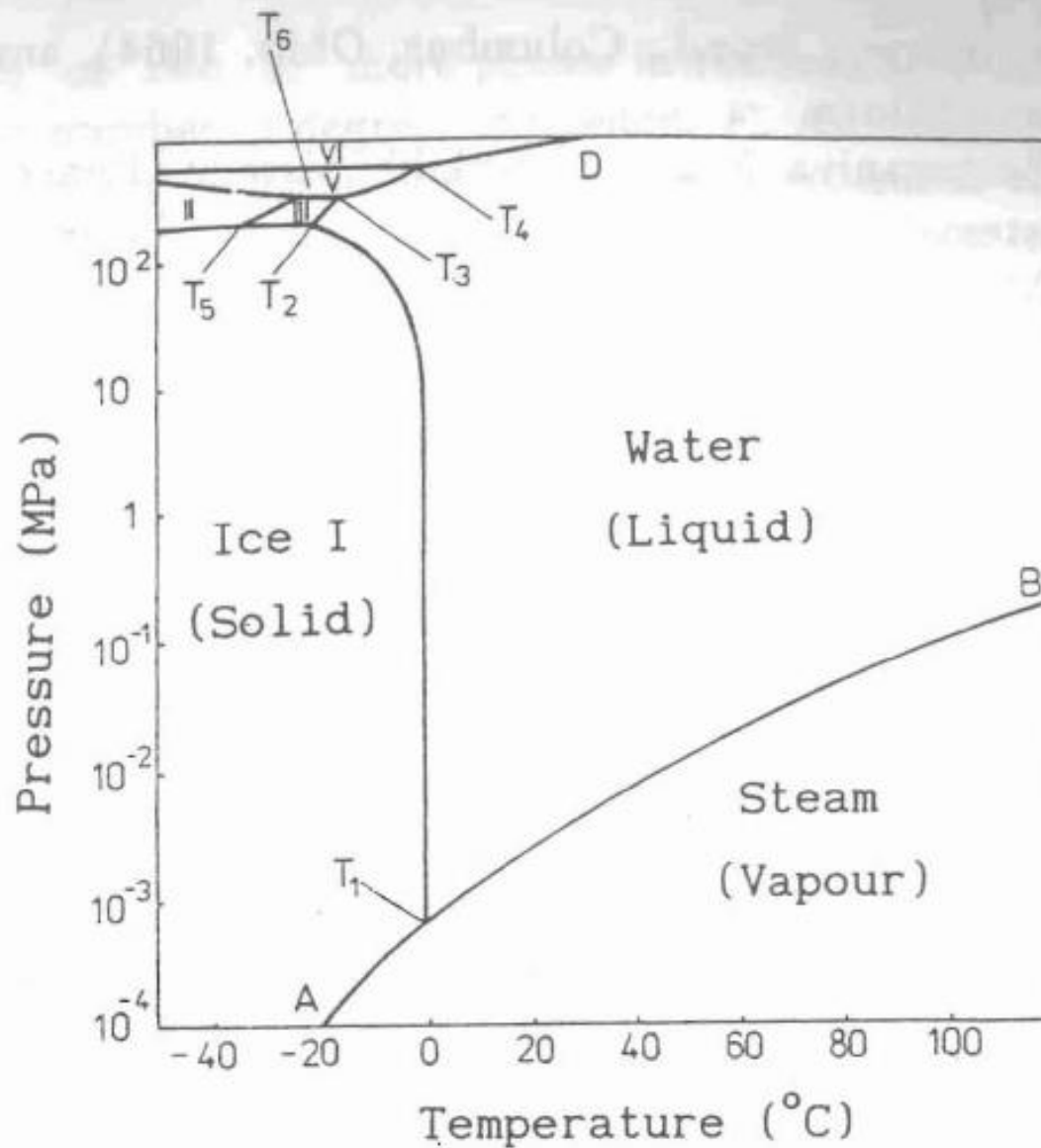


Water phase diagram

- Each of the three lines represents equilibrium between the respective phases. All lines intersect at the same point known as the triple point



Water phase diagram

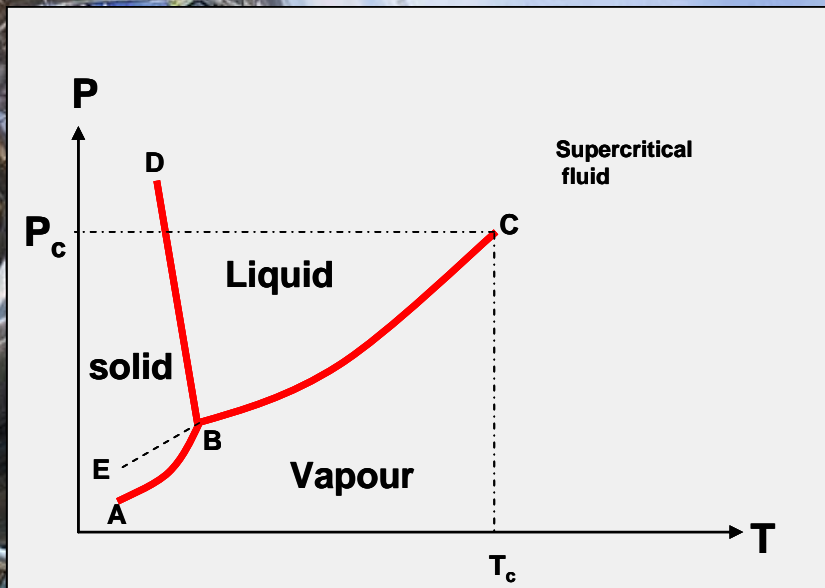


Phase Equilibria

Example: The Gibbs Phase Rule

Consider water in equilibrium with its vapour in a closed system

$$F = C - P + 2$$
$$= 1 - 2 + 2 = 1$$



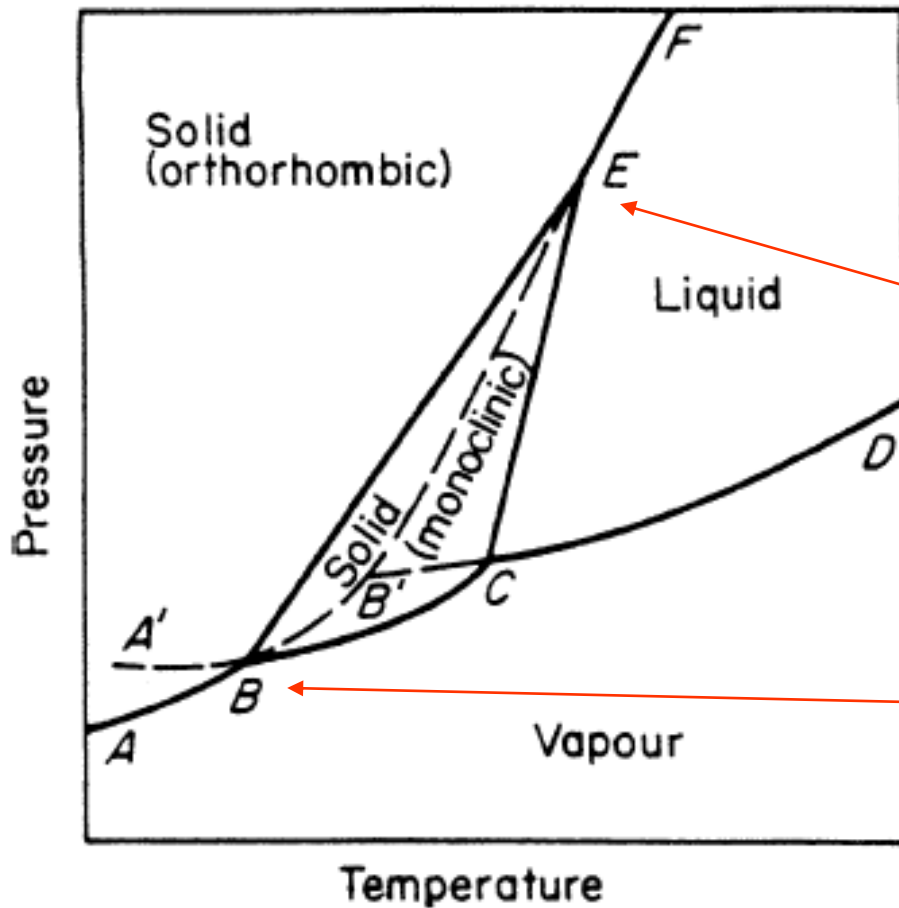
Schematic representation of the phase diagram for water

Specifying one intensive variable (eg. Temperature or pressure) will fully specify the system

For any given pressure, there is only one boiling temperature for pure water

How many degrees of freedom are there at the triple point?

The critical point and boiling, melting and freezing points of pure substances are invariant points

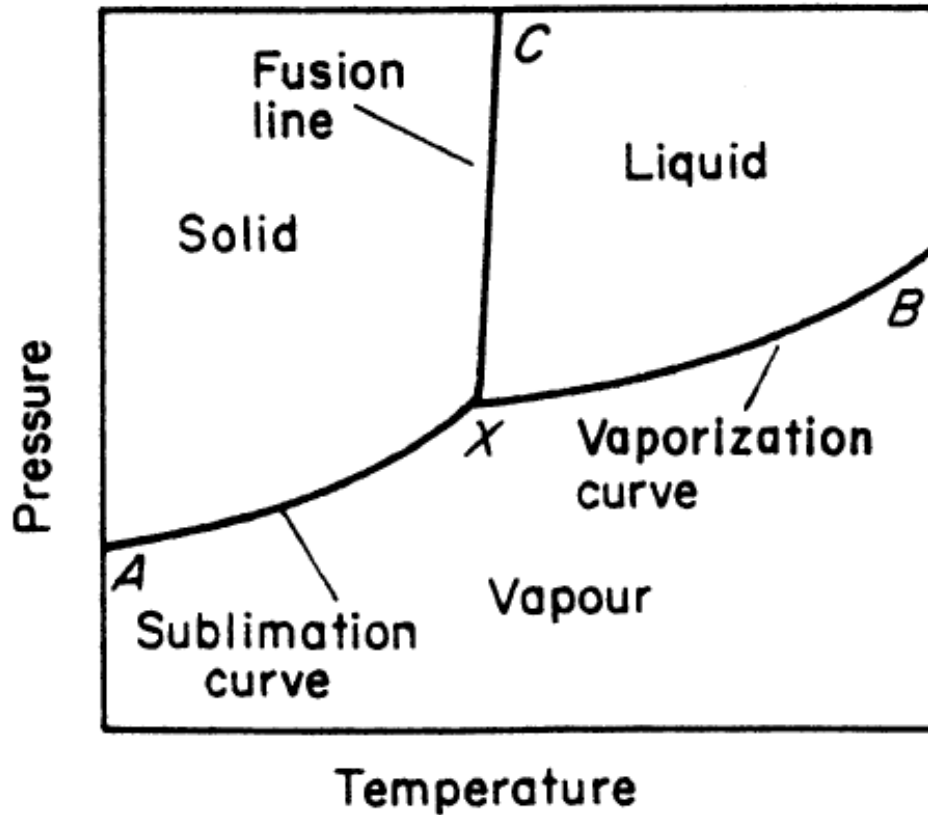


point E is a triple point representing the temperature and pressure (151°C and $1.31 \times 10^8 \text{ Nm}^{-2}$) at which orthorhombic and monoclinic sulphur and liquid sulphur are in stable equilibrium. Curve CD is the vapour pressure curve for

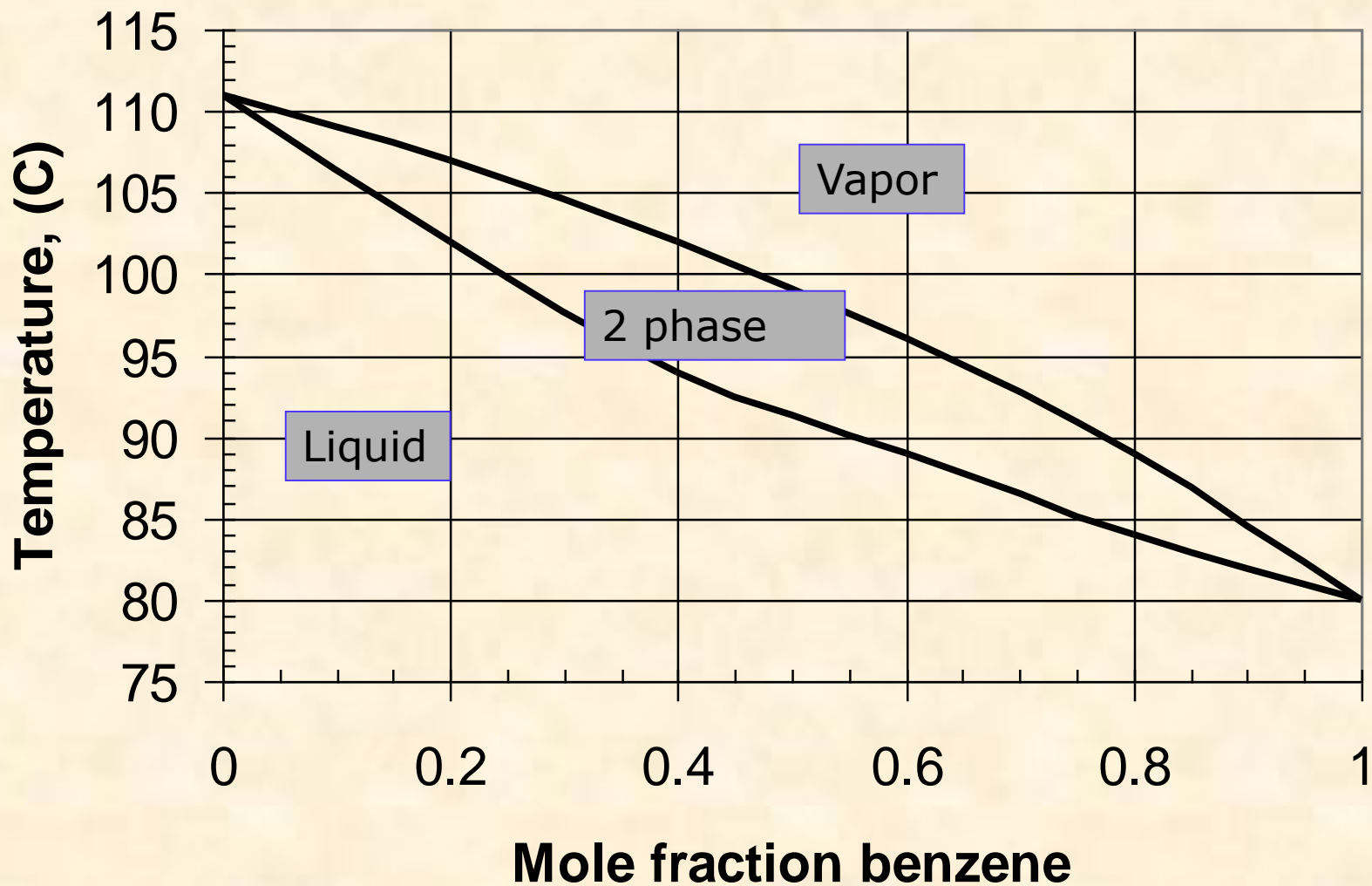
orthorhombic $\text{S} \rightleftharpoons$ monoclinic S . Point B , therefore, is a triple point representing the temperature and pressure (95.5°C and 0.51 Nm^{-2}) at which orthorhombic sulphur and sulphur vapour can coexist in stable equilibrium. Curve EF

Figure 4.2. Phase diagram for sulphur (not to scale)

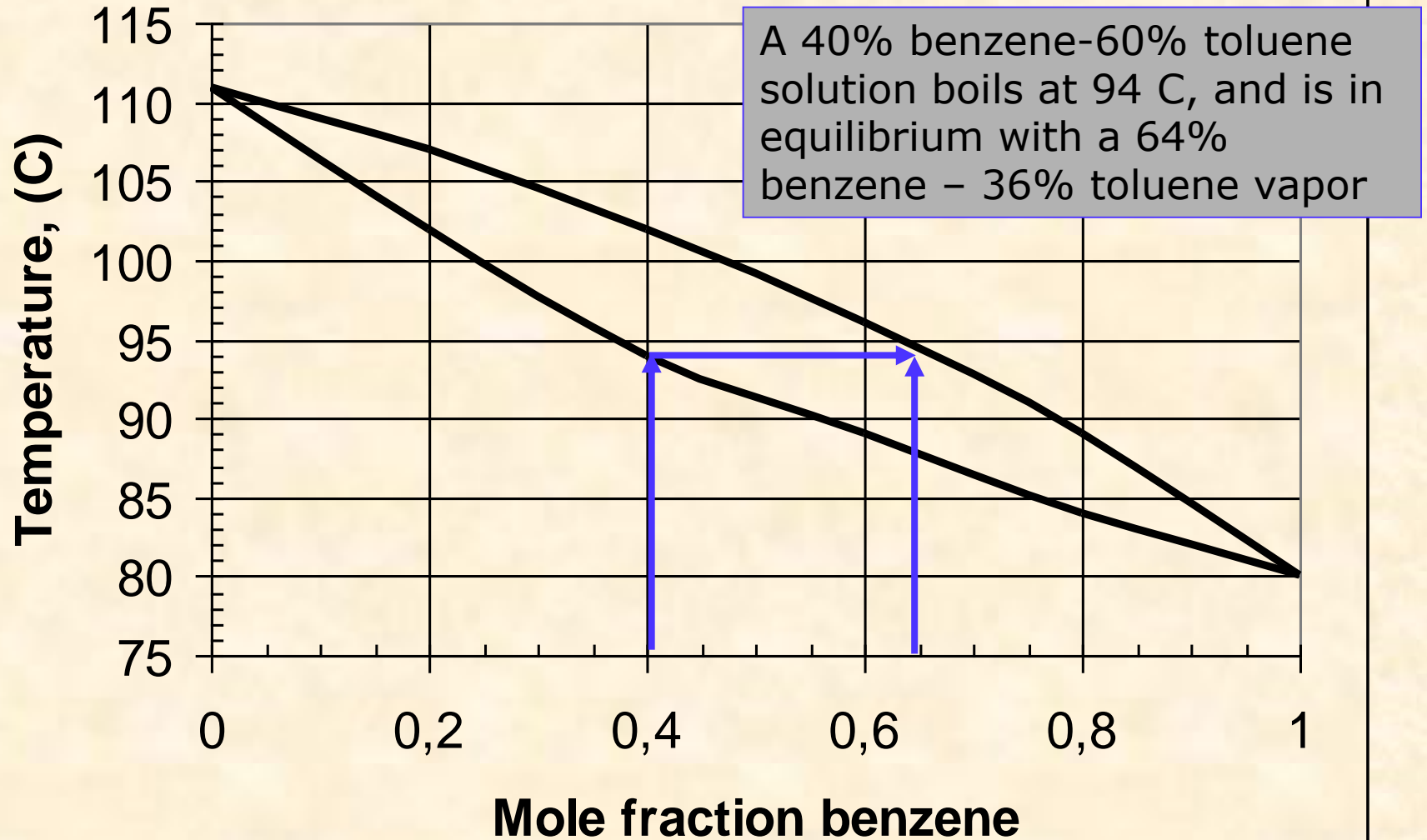
Temperature–pressure diagram for a single-component system



Liquid-Vapor Compositions of Benzene-Toluene at 1 atm

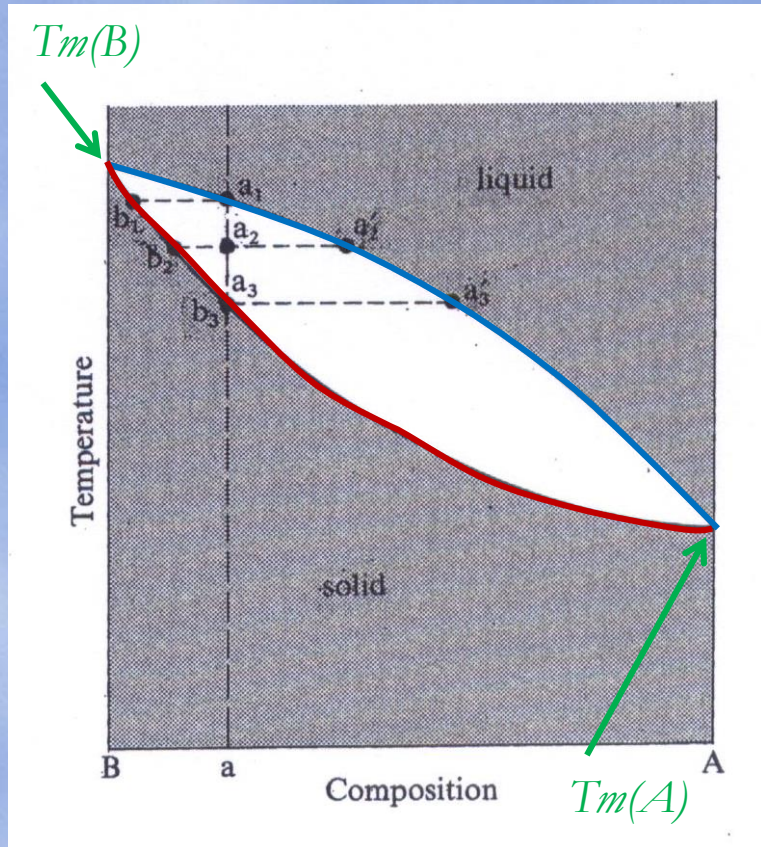


Liquid-Vapor Compositions of Benzene-Toluene at 1 atm



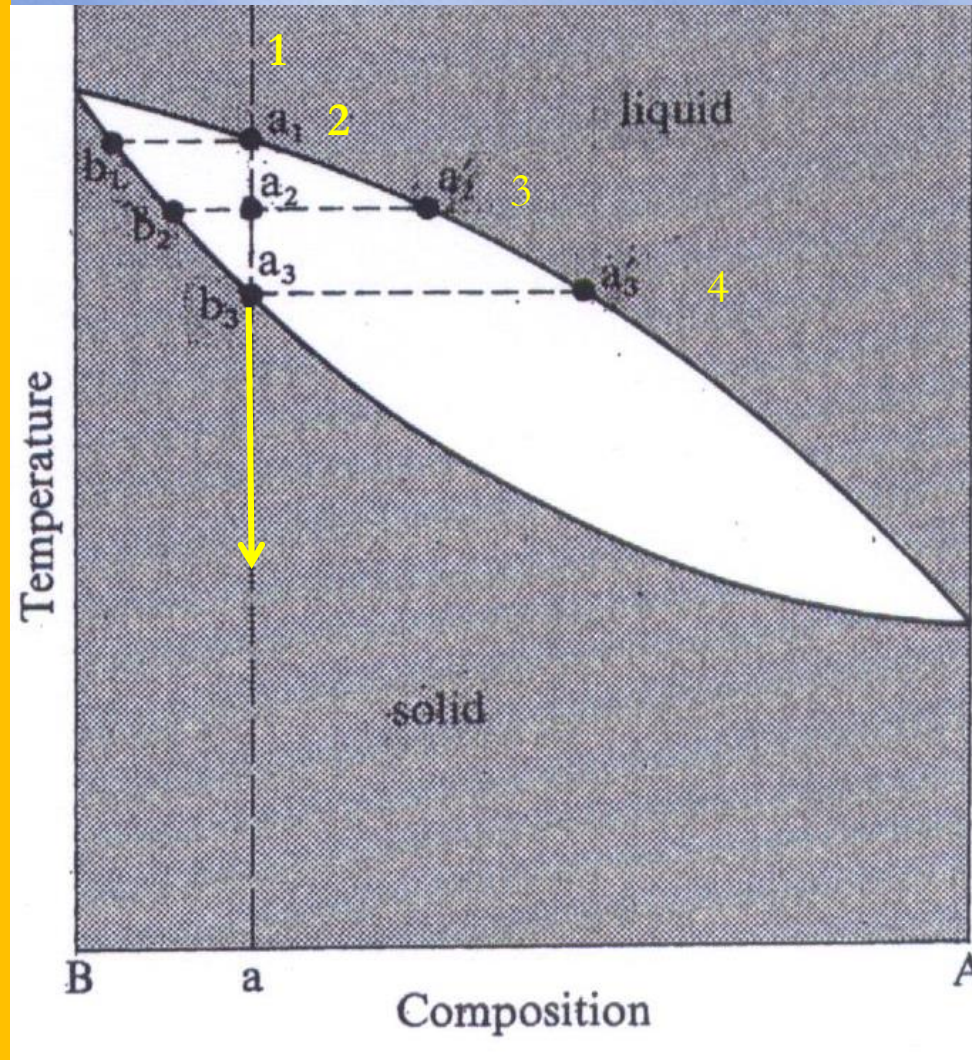
- Phase diagram for two similar components; "Solid Solution".
- Assume Pressure = 1 atm, so 2D rather than 3D plot.
- Two components, so $F + P = 2 + 2 = 4$
- Composition = mole fraction; 100% B to 100% A.
- $T_m(B)$ = melting point of pure B.
- $T_m(A)$ = melting point of pure A.
- *Liquidus* = boundary between liquid and mixed phase; gives liquid composition.
- *Solidus* = boundary between solid and mixed phase; gives solid composition.

Binary Phase Diagram



Binary Phase Diagram

- Heat mixture of A & B (at mole fraction indicated) to temperature 1. Then cool.
- At temperature 1, liquid phase has composition = mole fraction.
- At temperature 2, solid begins to ppt out; solid is mostly B mixed crystal (composition b_1).
- At temperature 3, solid has composition b_2 and liquid has composition a_2 ; note different mole fractions!
- at a given temperature, the liquid and solid that are in equilibrium with each other have different compositions.
- At temperature 4, solid formed has composition = b_3 = original mole fractions.



Solid-Liquid Equilibria

- When a solid and a liquid are at equilibrium, the respective chemical potential of each component in the two phases are equal
- For component A crystallizing:

$$\mu_{A,L} = \mu_{A,S}$$

- Neglecting effect of pressure but activities considered:

$$\mu_{A,L}^0(T) + RT \ln \alpha_{A,L} = \mu_{A,S}^0(T) + RT \ln \alpha_{A,S}$$

- Rearrangement of the equation yields

$$\ln \frac{\alpha_{A,L}}{\alpha_{A,S}} = \frac{\Delta H}{R} \left(\frac{1}{T_m} - \frac{1}{T} \right) + \frac{\Delta C_p}{R} \left(\ln \frac{T}{T_m} + \frac{T_m}{T} - 1 \right)$$

- ΔH_m : Enthalpy of melting
- ΔC_p : Difference in heat capacities of the pure solid and liquid phase at temperature T. When the melt behaves as ideal activities are equal to concentrations, $\alpha_{A,L} = X_{A,L}$. When the solid is pure $\alpha_{A,S} = 1$

A photograph of an industrial facility, likely a refinery or chemical plant, featuring large, shiny metal pipes and structures against a clear blue sky. The pipes are arranged in a complex network, with some curving upwards and others running horizontally. The background shows a bright, sunny sky with a few wispy clouds.

Phase Diagrams in Crystallization

- The behavior of a crystallizing mixture at equilibrium, as predicted by thermodynamics, can be depicted by a phase diagram
- Phase diagrams are graphic representations of regions of coexistence of phases as a function of state variables
- The description of the solid-liquid phase equilibria is usually limited to binary systems as the complexity of the diagrams increasing with increasing number of components

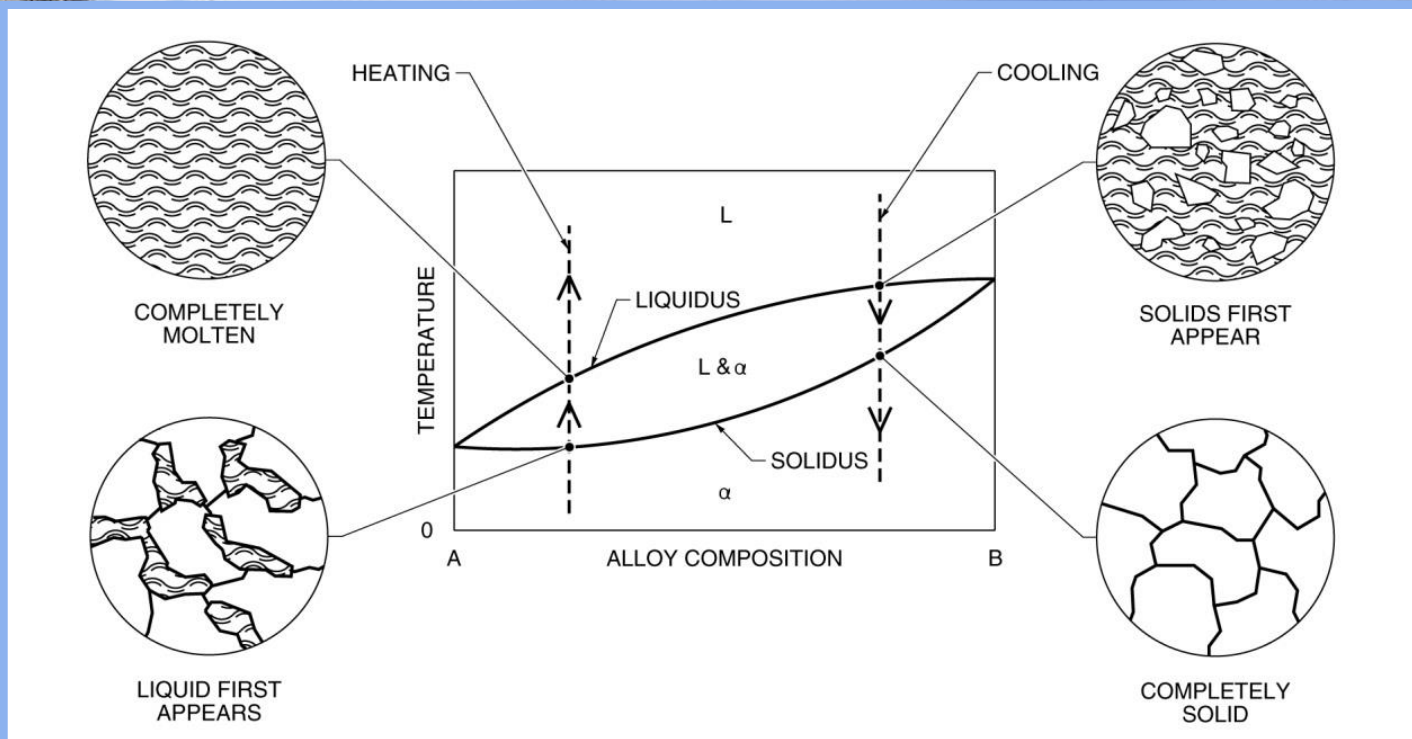
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Phase diagrams-crystallization

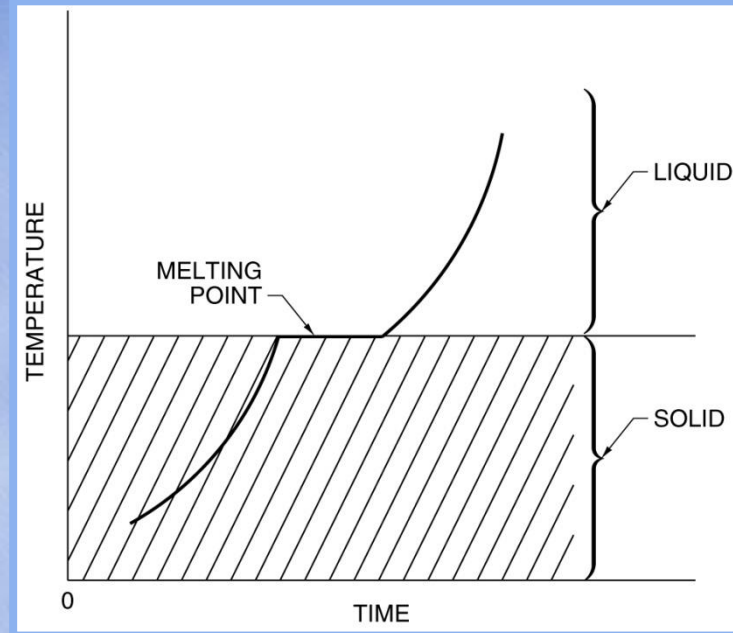
- Multicomponent systems are simplified and treated as combinations of binary systems
- The validity of this simplification, depends on the interaction between the components of the system
- The binary solid-liquid phase diagram represents usually the relation between temperature and composition. Two of the most common phase diagrams are those belonging to the eutectic and solid solution systems

Ni- Cu system

- The liquidus and solidus are the upper and lower boundaries between completely liquid and completely solid alloys.

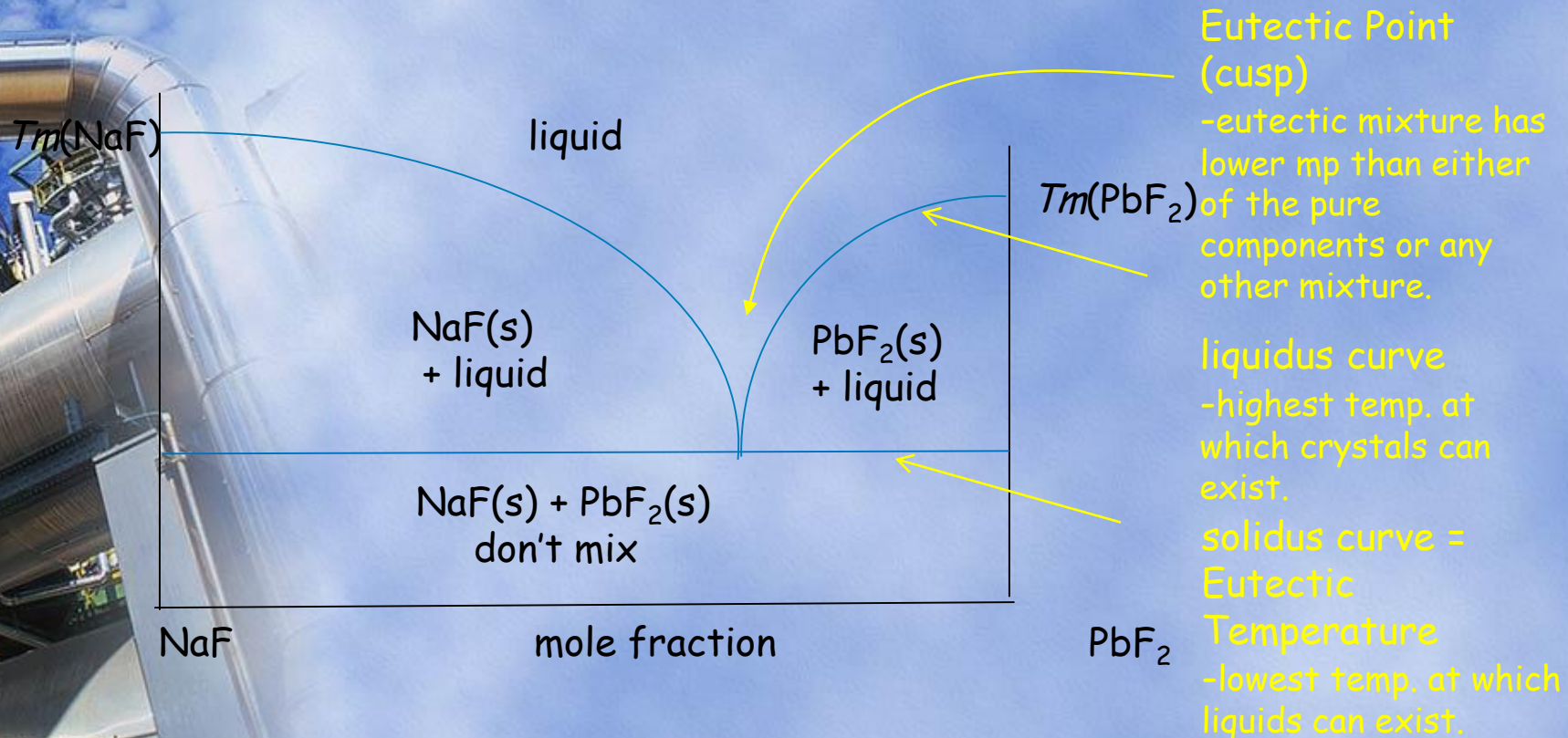


• The melting point of a pure metal is indicated by an isothermal transformation on the cooling curve.



Eutectic Phase Diagram

- What if two substances are NOT similar at all? They won't want to mix in the solid state, but will in the liquid; e.g. NaF & PbF₂.



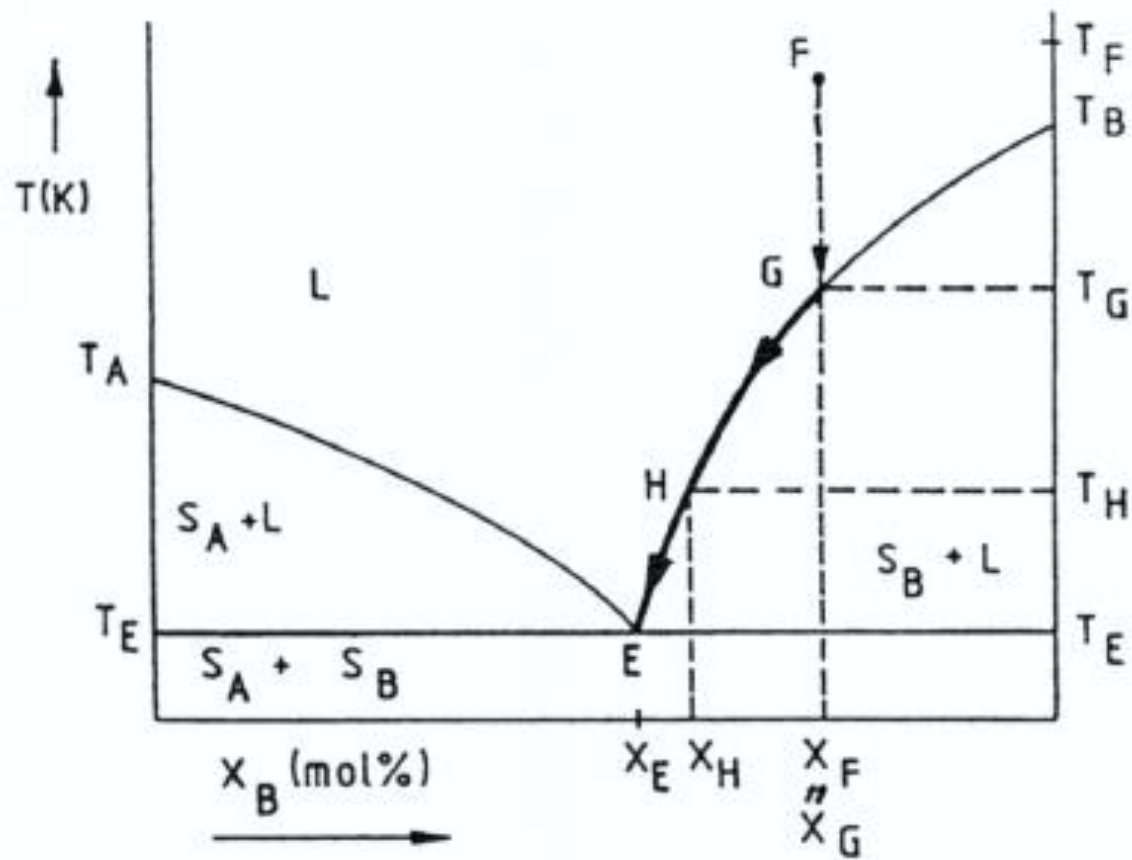


FIGURE 3.1. Simple binary eutectic solid-liquid equilibrium diagram. x = mol percentage of B.

Eutectic solid-liquid equilibrium

- T_A -E, T_B -E curves represent the crystallization temperatures of component A when containing impurity B and of component B when containing impurity A. The curves are known as the *liquidus* curves. Point E represents eutectic composition.
- Cooling from T_F to T_G pure B crystals appear in the mixture. Further cooling results in increasing crystal mass and depleting solution from component B. The liquid shifts to the composition of the eutectic, E

Prediction of Eutectic composition

$$\ln(\chi_{A,L}\gamma_{A,L}) = \frac{\Delta H_{A,m}}{RT} \left(\frac{T}{T_{A,m}} - 1 \right)$$

$$T = T_m \left[1 + \sum_{j=1}^n \alpha_j (\chi - \chi_m)^j \right]$$

T_m melting temperature of pure substance
 χ_m value of χ at T_m . For the binary system A-B, $\chi_m = 1$ for $T_{A,m}$ and 0 for $T_{B,m}$. Coefficients α are fitted by least squares

Accurate method but limited to 10 components systems