# الجامعة التكنولوجية

## قسم الهندسة الكيمياوية

## المرحلة الثانية

# الكيمياء الفيزياوية

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# Phase

A phase can be defined as a physically distinct and chemically homogeneous portion of a system that has a particular chemical composition and structure.

**gaseous state:**

seemingly only one phase occurs (gases always mix)

**liquid state:**

- often only one phase occurs (homogeneous solutions)e.g., salt water, molten $Na_2O$-$SiO_2$

-two immiscible liquids (or liquid mixtures) count as two phases

**solid state:**

• crystalline phases: e.g., ZnO and $SiO_2$ = two phases

• polymorphs: e g wurtzite ( zinc iron sulfide mineral ((Zn, Fe)S)) and sphaleriteZnS are different phases : e.g., wurtzite and sphaleriteZnS are different phases

• solid solutions = one phase (e.g., $Al_2O_3$-$Cr_2O_3$ mixtures)

## Gibbs Phase rule

The number of degrees of freedom, F (no. of independently variable factors), number of components, C, and number of phases in equilibrium, P, are related by Gibbs phase rule as

$$F = C - P + 2$$

- Number of external factors = 2 (pressure and temperature).

For metallurgical system pressure has no appreciable effect on phase equilibrium and hence, $F = C - P + 1$

P: number of phases present at equilibrium
C: number of components needed to describe the system
F: number of degrees of freedom, e.g. T, P, composition.
The number of components (C) is the minimum number of chemically independent constituents needed to describe the composition of the phases present in the system.
e. g , salt water. C = 2 (NaCl and water ) , solid magnesium silicates. C = 2(MgO and $SiO_2$), solid MgAl silicates. C = 3. (MgO, $Al_2O_3$, $SiO_2$ )

The degrees of freedom (F) is the number of independent variables that must be specified to define the system completely.

## Phase Equilibria and Phase Diagrams

Why it's important (*Some properties that might be difficult to predict using a "common sense" without the knowledge of the phase diagrams)*
example 1: Melting temperature of a mixture AB (solution) of two components A and B could be either lower or higher than the melting point of each component (!).

This could be a failure mechanism in electronic or mechanical components. But could also be used to your advantage.

• example 2: Upon cooling to a lower temperature a phase transformation of a material could cause expansion, which could cause internal stresses and failure (e.g. tin food cans will crumble at low T)

• example 3: No abrupt liquid-to-solid transformation when two components are present (solid + liquid in a temperature range

Example 4: Chip-Solder-Joint-Failure • example 4: Tmelt (Sn) = 232 C, Tmelt (Pb) = 327 C……

butTmelt ($Sn_{0.62}Pb_{0.38}$) = 183 C, so this is a common soldering alloy

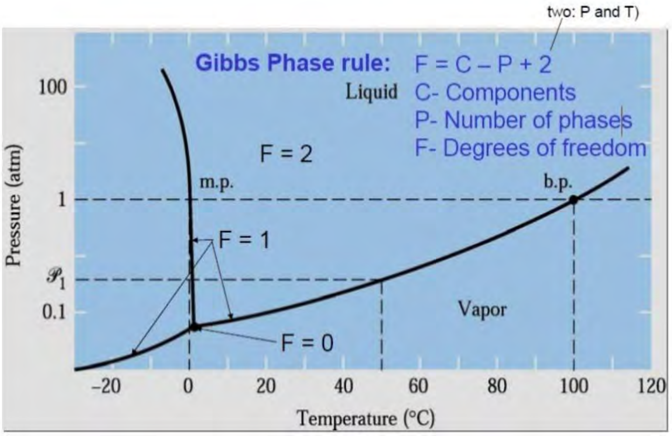
• example 5: Tmelt (Au) = 1064 C, Tmelt (Si) = 2550 C……

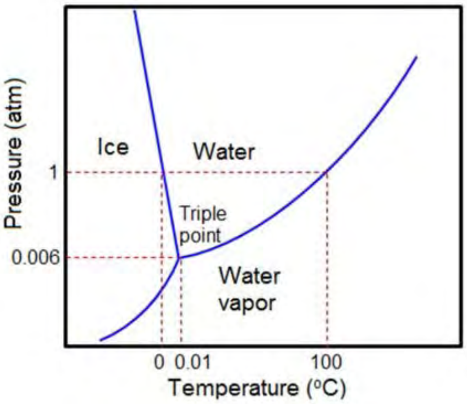
butTmelt ($Au_{0.97}Si_{0.03}$) = 363 C, so thin layer of gold is used to attach Si chip to a ceramic substrate (shock protection)

• example 6: Mechanical properties (hardness and tensile strength) of an alloy could be substantially higher than that of the individual components (e.g. hardness (AgCu) about twice the harness of Ag or Cu)

### One component system

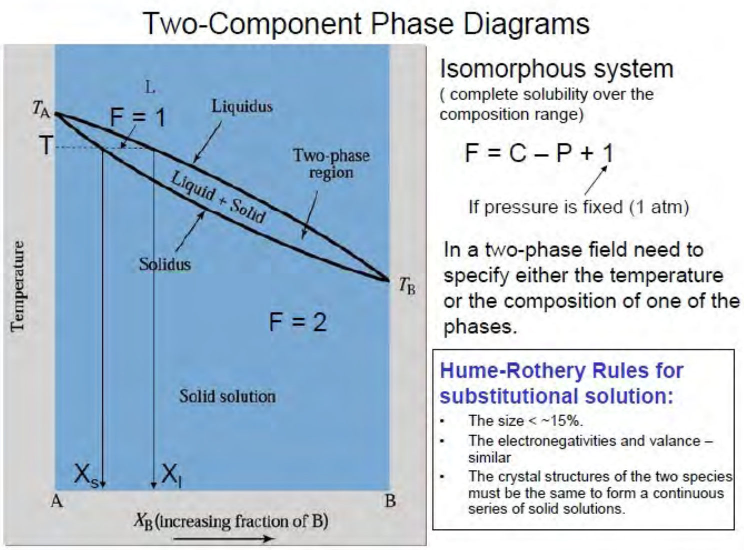
The simplest phase diagram is the water which is a one component system. It is also known as pressure-temperature or P-T diagram. Two phases exist along each of the three phase boundaries. At low pressure (0.006 atm) and temperature (0.01 °C) all the three phases coexist at a point called triple point.





## Binary Phase diagrams :

A binary phase is a two component system. Binary phase diagrams are most commonly used in alloy designing. The simplest binary system is the Cu-Ni which exhibits complete solubility in liquid and solid state



Two-Component Phase Diagrams

Isomorphous system

( complete solubility over the composition range)

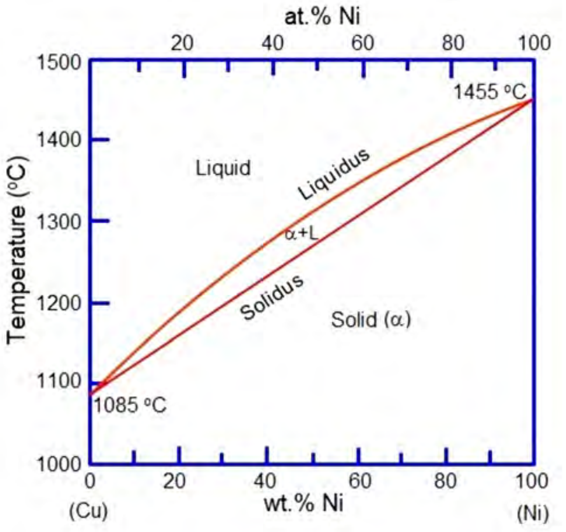
F = C – P + 1

If pressure is fixed (1 atm)

In a two-phase field need to specify either the temperature or the composition of one of the phases.

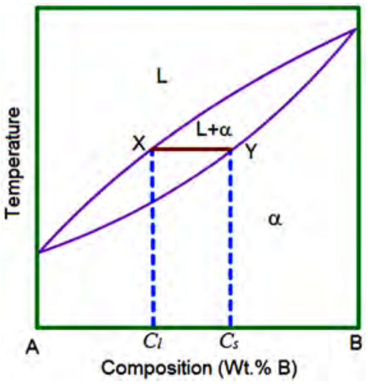
**Hume-Rothery Rules for substitutional solution:**

- The size < ~15%.
- The electronegativities and valance – similar
- The crystal structures of the two species must be the same to form a continuous series of solid solutions.



The line above which the alloy is liquid is called the liquidus line. At temperature just below this line crystals of α solid solution start forming. The line below which solidification completes is called solidus line. Hence, only α solid solution exists at any temperature below the solidus line.The intermediate region between liquidus and solidus lines is the two-phase region where liquid and solid coexist. It can be noted that the two metals are soluble in each other in the entire range of compositions in both liquid and solid state. This kind of system is known as ‘**Isomorphous**’ system.

The composition of phases in the two-phase region is not same. To find the composition of the individual phases in the two phase region, a horizontal line (XY), called tie line, is drawn andits intercepts on the liquidus and solidus lines, $C_l$ and $C_s$, are taken as the composition of the liquid and solid respectively.



We have previously looked at two-component boiling diagrams. These diagrams are descriptions of the state of the system on a graph of temperature versus composition (at constant pressure). At high temperatures the system is all in the gas (or vapor) phase. At the lower temperatures the system is in the liquid phase. In between these two situations there is a region where there are two phases (vapor and liquid) in equilibrium with each other.If we continue to cool the system we will eventually reach a temperature where one or both of the pure components will freeze. At temperatures at and below the melting points the phase diagram will look something like the following hypothetical phase diagram involving a substance "A" and a substance "B." In this diagram we are plotting temperature versus the mole fraction of substance B.

## Liquid-Vapor Equilibrium

For each component in a binary mixture, one could make a vapor–liquid equilibrium diagram. Such a diagram would graph liquid mole fraction on a horizontal axis and vapor mole fraction on a vertical axis. In such VLE diagrams, liquid mole fractions for components 1 and 2 can be represented as $x_1$ and $x_2$ respectively, and vapor mole fractions of the corresponding components are commonly represented as y1 and y2, Similarly for binary mixtures in these VLE diagrams:

$$x_1 + x_2 = 1 \text{ and } y_1 + y_2 = 1$$

Such VLE diagrams are square with a diagonal line running from the ($x_1 = 0$, $y_1 = 0$) corner to the ($x_1 = 1$, $y_1 = 1$)

Possible degrees of freedom: T, P, mole fraction of A

$x_A$ = mole fraction of A in the liquid

$y_A$ = mole fraction of A in the vapor

$z_A$ = overall mole fraction of A (for the entire system)

We can plot either T vs$z_A$ holding P constant, or P vs$z_A$ ,holding T constant.

Let A be the more volatile substance:

$P_A^* > P_B^*$ and $T_{b,A} < T_{b,B}$

**Pressure-composition diagrams**

Fix the temperature at some value, T.

Assume Raoult's Law:

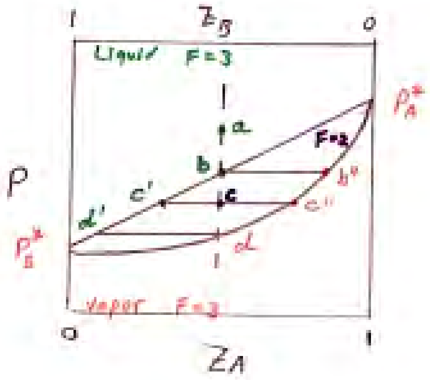
$P = P_A^* x_A + P_B^* x_B$

$P = P_A^* x_A + P_B^*(1 - x_A) = P_B^* + (P_A^* - P_B^*)x_A$

**Composition of the vapor**

$$y_A = \frac{P_A}{P} = \frac{x_A P_A^*}{P_B^* + (P_A^* - P_B^*)x_A} > x_A$$

$$y_B = \frac{P_B}{P} = \frac{x_B P_B^*}{P_B^* + (P_A^* - P_B^*)x_A} < x_B$$



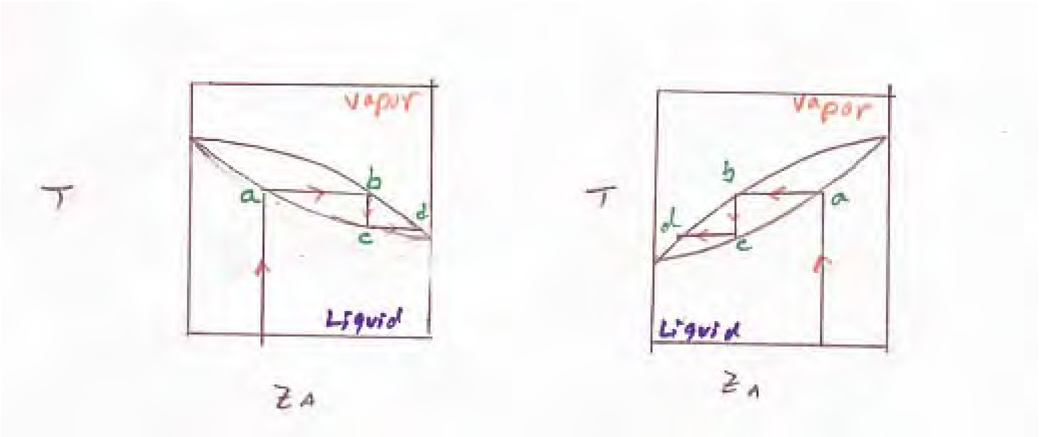
Point a: One phase, F = 3 (T, P, $x_A$)
Point b: Liquid starts to vaporize, F = 2 (T, P ;$x_A$ not free.)
$x_A$ = zb, $y_A$ = yb" Vapor is rich in A.
Point c: Liquid has lost so much A that its composition is $x_A$ = xc'. The vapor is now poorer in A, $y_A$ = yc"

Ratio of moles in the two phases is given by the lever rule:

$$\frac{n_{liq}}{n_{vap}} = \frac{cc''}{cc'}$$

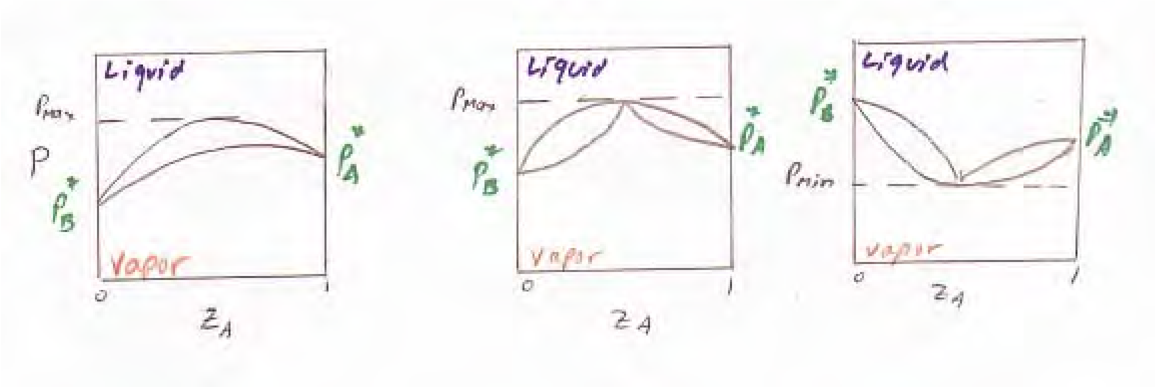
Point d: Liquid is almost all gone, $xA = xd'$, $yA = yd = zA$ .
For points below d, only the vapor is present (F=3).

## Distillation



Point a. Mixture starts to boil, with $x_A = z_A$, $y_A = z_b$
Points b-c. Vapor is condensed to form a liquid with $x_A = z_b = z_c$
Point c. The liquid that was collected in the previous step is boiled to form a vapor with $x_A = z_d$
Condensation of the last bit of vapor produces a liquid
very rich in either A (if $T_{b,A} < T_{b,B}$ on the left) or B (if $T_{b,A} > T_{b,B}$ on the right).

## Non-ideal solutions



Left: Impossible phase diagram, because at $P_{max}$, where the liquid of this composition just starts to boil, there is no corresponding point on the vapor curve. (There is no tie line.) The vapor should always lie below the liquid in a pressure-composition diagram. At an extremum they must touch.

Center: Vapor pressure reaches a maximum because of repulsion between A and B. This is an ***azeotrope***, where the liquid and vapor have the same composition. (Note an error in the drawing: The vapor curve does not have a cusp, but rather is tangent to the liquid curve.)
Right: Vapor pressure reaches a minimum because of attraction between A and B. This is also an ***azeotrope***