

# PHASE RULE

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$$F = C - P + 2$$

- The three primary phases of matter are often defined individually under different conditions.
- In practice we encounter states of matter in coexistence.
- The position of the equilibrium between these states is affected by the environment (temperature, pressure) and composition.

$$F = C - P + 2$$

- Phase
  - A consistent, physically distinct segment of a system that is separated from other segments of the system by binding surfaces.
- Phase Rule
  - A devise for determining of the least number of intensive variables (independent variables that do not depend on the phase volume or mass such as temperature, pressure, density or concentration) that can be changed without changing the equilibrium state of the system.
  - The least number required to define the state of the system.

$$F = C - P + 2$$

- Degrees of Freedom

- Intensive variables that must be known to describe the system completely. Ex. temperature, concentration, pressure, density, etc.

- The degrees of freedom of a system is expressed as follows:

$$F = C - P + 2$$

- Components or Chemical Entities

- Constituents by which the composition or make-up of each phase in the system can be expressed. Usually the chemical formula or chemical equation is used.

$$F = C - P + 2$$

- The phase rule is used to study and understand the way that temperature, pressure, concentration, etc. effect the phase of a substance.
- Application:
  - A gas, e.g. water vapour confined to a particular volume.
  - Apply phase rule:  $F = 1 - 1 + 2 = 2$ .
  - This means that two intensive variables (temperature and pressure, temperature and concentration) must be known to duplicate this system exactly.
  - Such a system is usually described as bivariant.

# $F = C - P + 2$

- Application:

- A liquid such as water in equilibrium with its vapor ( we have 2 phase system)
- $F = 1 - 2 + 2 = 1$ .
- By stating temperature, the system is completely defined because the pressure under which liquid and vapor can coexist is also fixed.
- If we decide to work under a particular pressure, then the temperature of the system is automatically defined:
- The system is described as univariant.

- Application:

- When we have a liquid water, vapor and ice
- Phase rule states that the degrees of freedom =  $1 - 3 + 2 = 0$
- There are no degrees of freedom, if we attempt to vary the conditions of temperature or pressure necessary to maintain the system, we will lose a phase.
- The combination is fixed and unique.
- The system is invariant.

# $F = C - P + 2$

- As the number of components increases, so do the required degrees of freedom needed to define the system. Consequently, as the system becomes more complex, it becomes necessary to fix more variables to define the system.
- As the number of phases in equilibrium increases, the number of the required degrees of freedom becomes less.
- Liquid water+vapor  $F=1-2+2=1$   
ethyl alcohol+vapor  $F=1-2+2=1$   
liquid water+liquid ethanol+vapor  $F=2-2+2=2$   
liquid water+liquid benzyl alcohol+vapor mixture  $\rightarrow$   
 $F=2-3+2=1 \rightarrow$  benzyl alcohol and water form two separate liquid phases and one vapor phase.

## Phase Rule with Single Component Systems

System	# of phases	Degrees of Freedom	Comments
Gas, liquid or solid	1	2	System is bivariant
Gas-liquid, liquid-solid, or gas-solid	2	1	System is univariant
Gas-liquid-solid	3	0	System is invariant



# One component systems

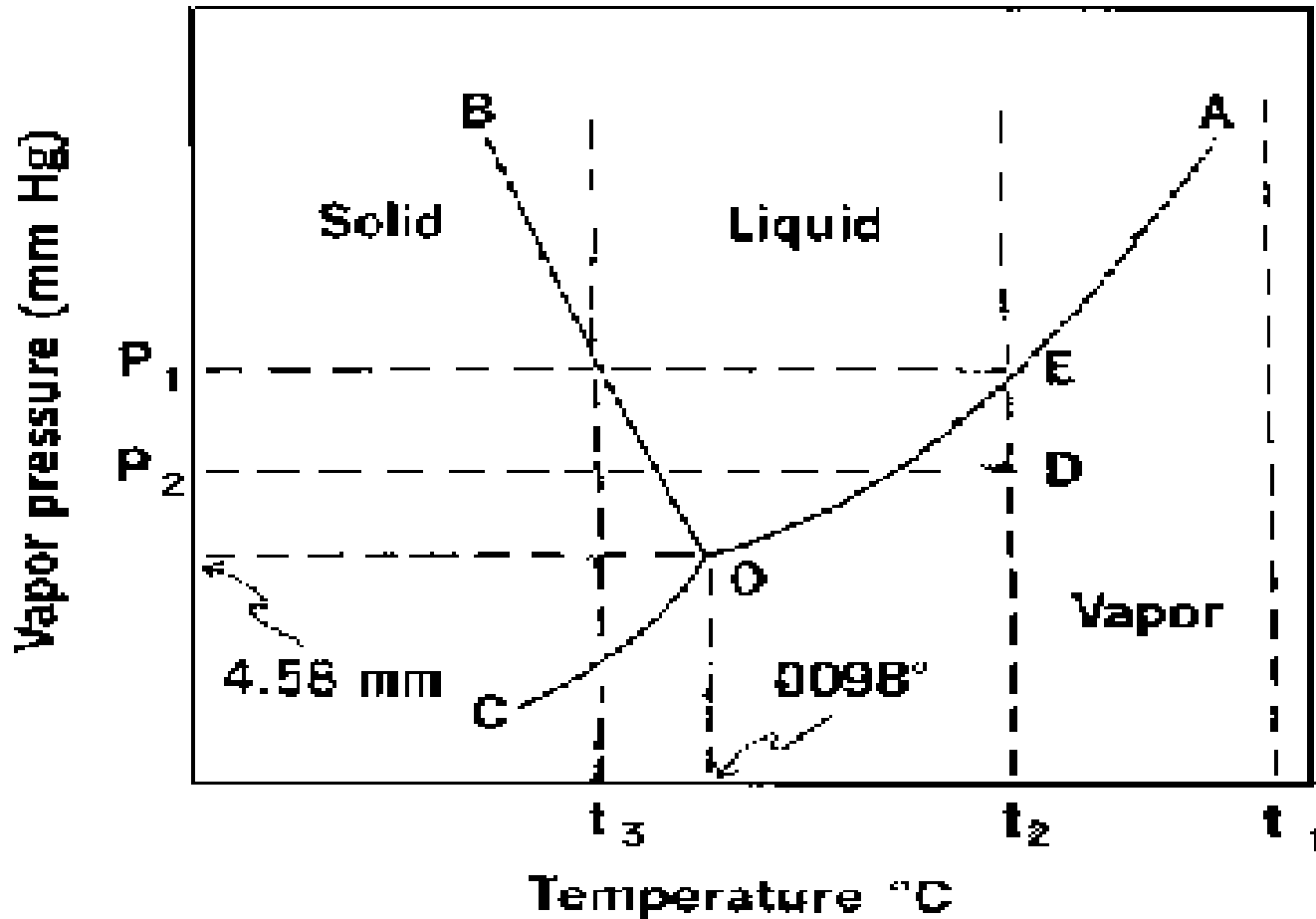


Figure – Phase diagram for water at moderate pressures

# One component systems

- The previous figure (phase diagram for water at moderate pressures), the curve OA is known as the vapor pressure curve; its upper limit is at the critical temperature,  $374^{\circ}\text{C}$  for water, and its lower end terminates at  $0.0098^{\circ}\text{C}$ , called the triple point. Along the vapor pressure curve, vapor and liquid coexist in equilibrium.
- Curve OC is the sublimation curve, and here vapor and solid exist together in equilibrium.
- Curve OB is the melting point curve at which liquid and solid are in equilibrium. The negative slope of OB shows that the freezing point of water decreases with increasing external pressure.

- If  $t_1$  is held constant, no matter how much the pressure is raised, the system remains a gas.
- At  $t_2$  below the critical temperature and above the triple point, water vapor is converted into liquid water by an increase in pressure.
- At temperature below the triple point e.g.  $t_3$ , an increase in pressure on water in the vapor state converts the vapor first to ice and then at higher pressure into liquid water.

# One component systems

- As mentioned in the table (phase rule with single component systems) and the figure (phase diagram for water at moderate pressures), in any one of the three regions in which pure solid, liquid, or vapor exists,  $F = 1 - 1 + 2 = 2$ , so two variables (e.g. temperature and pressure) are needed to describe the system. Along any of the three lines, where two phases exist,  $F = 1 - 2 + 2 = 1$ , hence, only one condition (either temperature or pressure) is needed to define the system. Finally, at the triple point where the three phases exist,  $F = 0$ .
- The triple point for air-free water is at  $0.0098^{\circ}\text{C}$  and  $4.58\text{mm Hg}$ .

# One component systems

- At the triple point, all three phases are in equilibrium, that is, the only equilibrium is at this pressure at this temperature of  $0.0098\text{ }^{\circ}\text{C}$ . The triple point for air-free water is at  $0.0098\text{ }^{\circ}\text{C}$  and  $4.58\text{ mm Hg}$ . Whereas the freezing point (the point at which liquid water is saturated with air is in equilibrium with ice at a total pressure of  $1\text{ atm}$ ) is  $0\text{ }^{\circ}\text{C}$ .
- In increasing the pressure from  $4.58\text{ mm Hg}$  to  $1\text{ atm}$ , the freezing point is lowered by  $0.0075\text{ }^{\circ}\text{C}$ . The freezing point is then lowered an additional  $0.0023\text{ }^{\circ}\text{C}$  by the presence of dissolved air in water at  $1\text{ atm}$ .

# Condensed Systems

- These are systems in which the vapor phase is ignored and only solid and/or liquid phases are considered.
- The vapor phase is disregarded and the pressure is considered to be 1 atm.
- The variables considered are: temperature and concentration.

# Two component systems containing liquid phases

- Miscible systems such as water and ethanol.
- Immiscible systems such as water and mercury.
- Partial miscibility (or immiscibility) such as phenol and water.
- *Critical solution temperature*: The maximum temperature at which the two – phase region exists.

# Two component systems containing liquid phases

- Phenol and water.
  - These liquids are partially miscible in each other.
  - At certain ratios the liquids are completely miscible and at others they are immiscible.
  - The 2 degrees of freedom of this mixture are temperature and concentration (condensed system).
  - The maximum temperature that these two liquids can exist in a 2 phase system is  $66.8^{\circ}\text{C}$ .
  - This is called the critical solution temperature or the upper consolute temperature.
  - In this system above  $66.8^{\circ}\text{C}$  all combinations of phenol and water will be completely miscible and will be one phase.



## Two component systems containing liquid phases

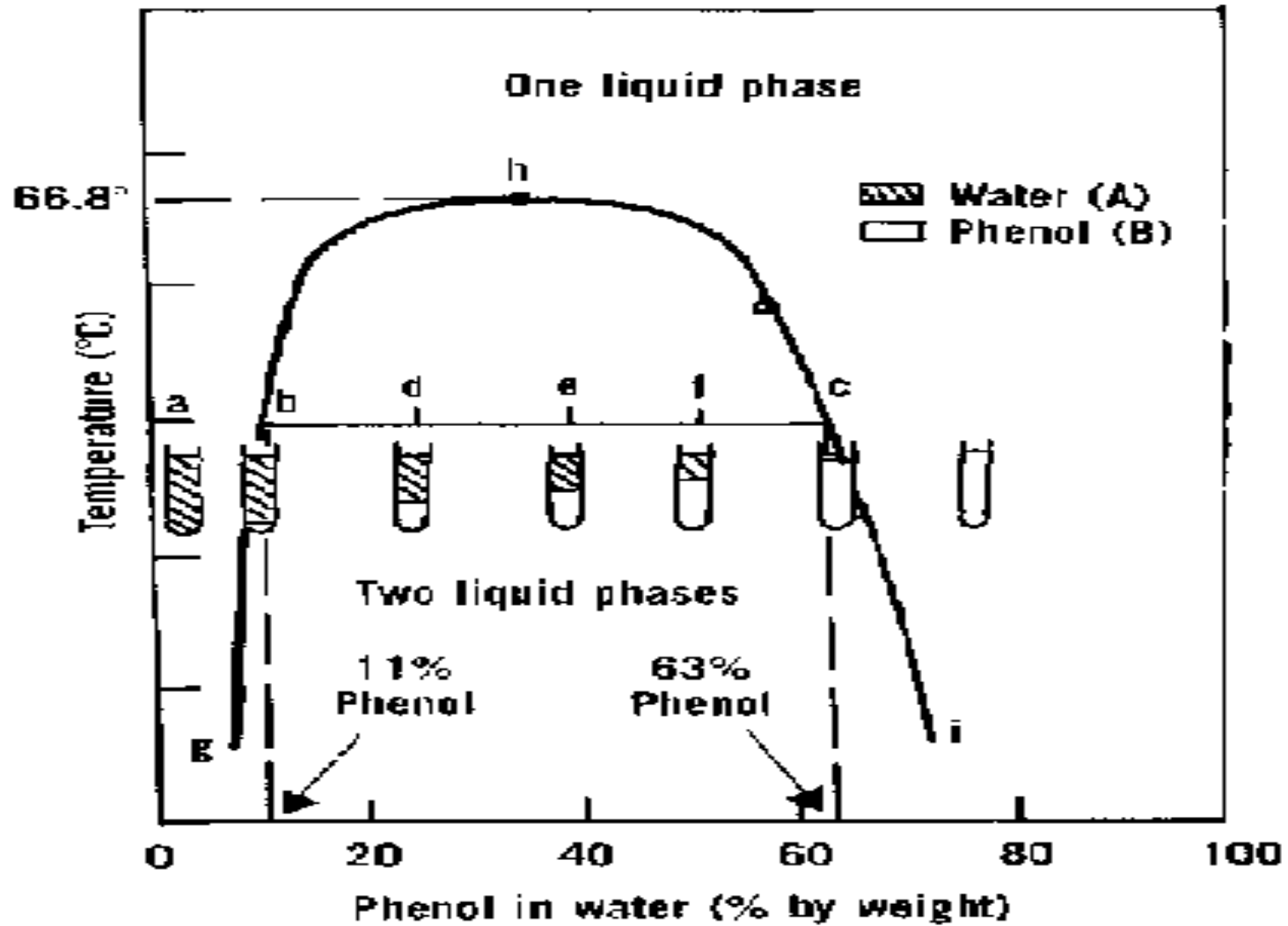


Figure – Temperature-composition diagram for the system consisting of water and phenol

# Two component systems containing liquid phases

- The curve gbhci shows the limits of temperature and concentration within which two liquid phases exist in equilibrium.
- The region outside this curve contain systems with only one liquid phase.

# Two component systems containing liquid phases

- Starting at the point a, a system with 100% water and adding known increments of phenol to a fixed weight of water while maintaining the system at 50°C will result in the formation of a single liquid phase (water with dissolved phenol).
- This continues until point b.
- At point b, a minute amount of a second phase appears.
- The concentration of phenol and water at which this occurs is 11% by weight of phenol in water.

## Two component systems containing liquid phases

- Analysis of the second phase, which separates out in the bottom, shows it to contain 63% by weight of phenol in water.
- This composition corresponds to point c in the diagram.
- As we prepare mixtures with increasing quantities of phenol (we proceed from point b to point c), the amount of the phenol-rich phase (B) increases and the amount of the water-rich phase (A) decreases.
- Once the total concentration of phenol exceeds 63% at 50°C, a single phenol-rich liquid phase is formed.

## Two component systems containing liquid phases

- The line *bc* drawn across the region containing two phases is termed the *tie line*.
- All systems prepared on a tie line, at equilibrium will separate into phases of constant composition, these phases are termed *conjugate phases*.
- Any system represented by a point on the line *bc* at 50°C separate to give a pair of conjugate phases whose compositions are *b* and *c*.

## Two component systems containing liquid phases

- The relative amounts of the two layers or phases vary.
- If we prepared a system containing 24% by weight of phenol and 76% by weight of water (point d), at equilibrium we will have two liquid phases.
- The upper one (A) has a composition of 11% phenol in water and the lower one (B) has a composition of 63% phenol in water.
- Phase B will lie below phase A because it is rich in phenol which has a higher density than water.

## Two component systems containing liquid phases

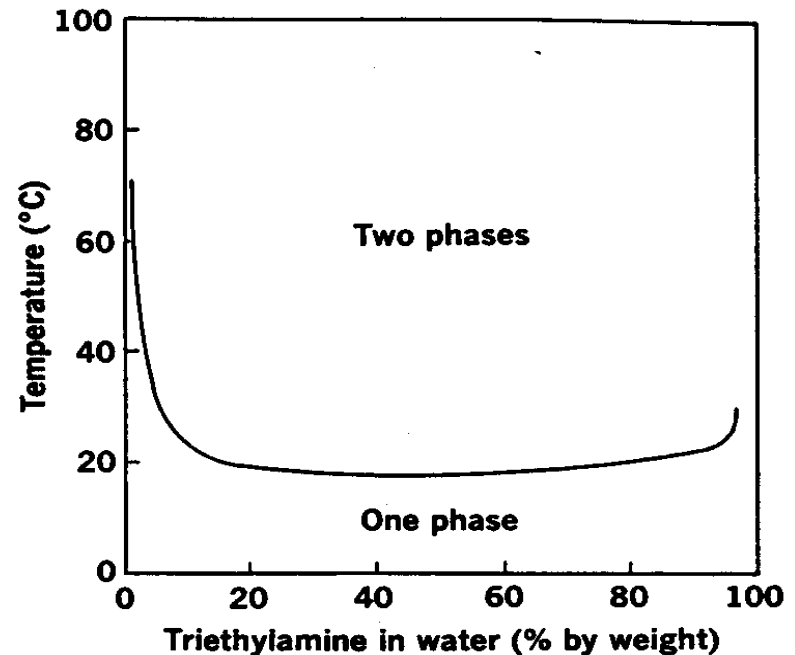
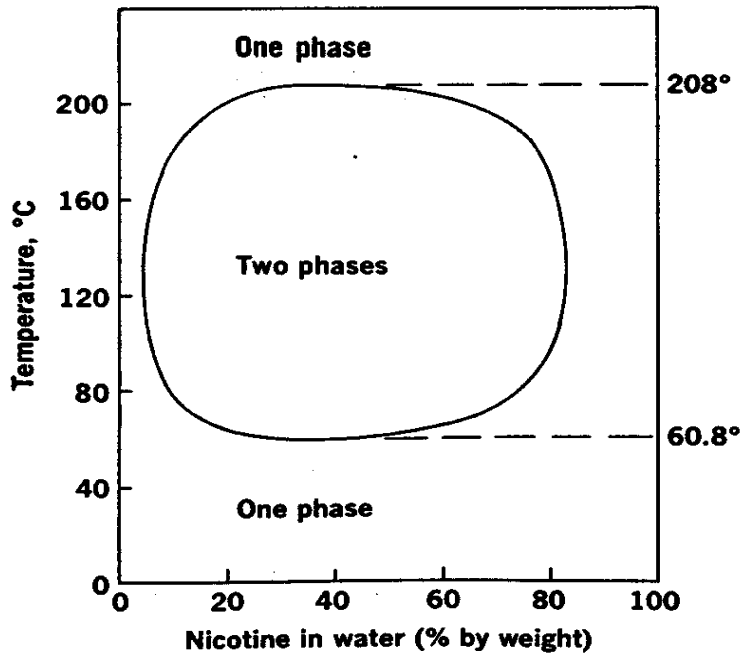
- The relative weights of the two phases can be calculated using the following formula:

$$\frac{\text{Weight of Phase A}}{\text{Weight of Phase B}} = \frac{\text{Length } dc}{\text{Length } bd}$$

- See example discussed page 40 in the fourth edition (page 51 in fifth edition, page 45 in sixth edition).
- See problem 2-21 page 52 in the fourth edition (2-21 page 687 in fifth edition, 2-14 in sixth edition).

# Two component systems containing liquid phases

- *Upper consolute temperature*: All combinations above this temperature are completely miscible (one phase).
- *Lower consolute temperature*: below which the components are miscible in all proportions.

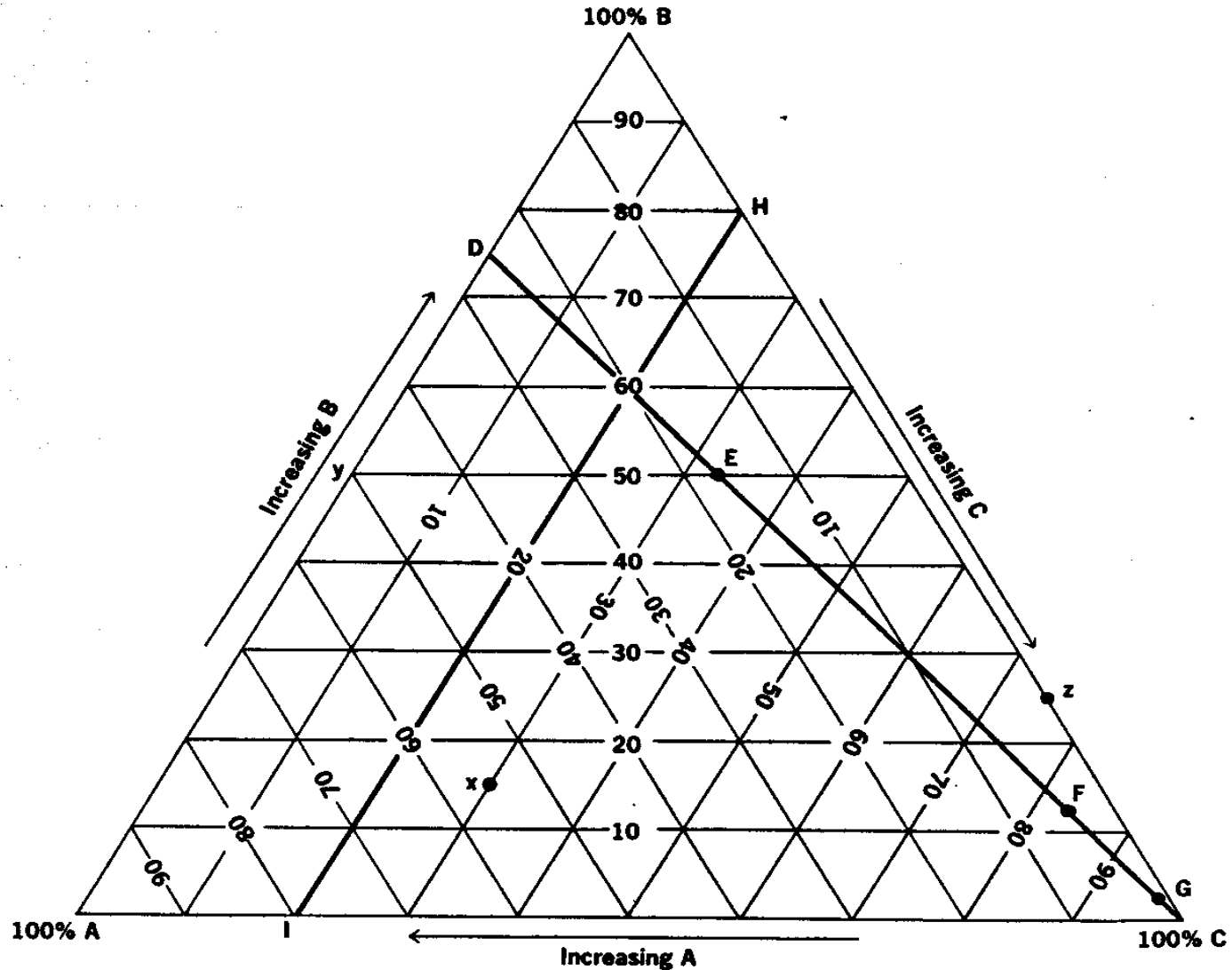




# Phase equilibrium in three component systems

- As one proceeds from binary systems to systems with three or more components, the phase diagrams become more complex.
- Each component adds another dimension to the representation of the phase equilibrium.
- Thus, for three components, two dimensions are required to represent the phase diagrams for a single temperature and pressure; these are conveniently depicted by a triangular diagram in which each vertex represents a pure component.

# Phase equilibrium in three component systems

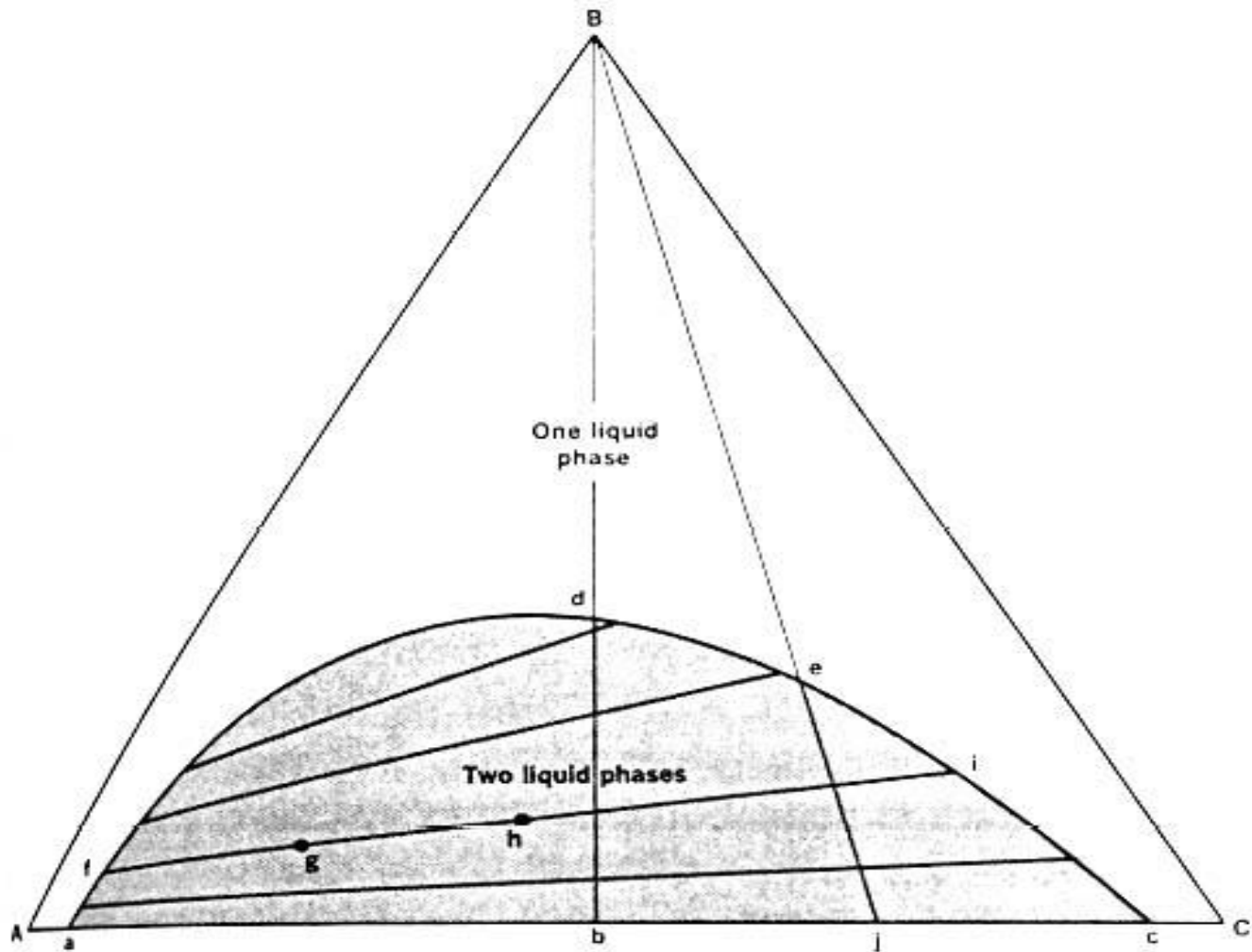


# Phase equilibrium in three component systems

- In a system containing three components, but only one phase there are 4 degrees of freedom. These are temperature, pressure, and the concentrations of 2 of the 3 components.
- This system is considered non-condensed. If we hold the temperature constant and the system is condensed where pressure is held at 1 atm then the degrees of freedom of the system are only 2.

# Ternary Systems with one pair of partially miscible liquids

- In a system in which there are 2 liquids which are partially miscible and then you add a liquid that is miscible with both original liquids there will be a phase in which all liquids are completely miscible or are one phase.
- An example of this is benzene and water which are partially miscible. Alcohol is completely miscible with both benzene and water. The addition of sufficient alcohol to a two-phase system of benzene and water would produce a single liquid phase in which all three components are miscible. Alcohol in this case is acting in a manner comparable to that of temperature in the binary phenol-water system. See figure on the next slide.
- The curve azeotropic, frequently termed the binodal curve, marks the extent of the two-phase region.



**Fig. 2-19.** A system of three liquids, one pair of which is partially miscible.

# Ternary Systems with one pair of partially miscible liquids

- In the previous figure (a system of three liquids, one pair of which is partially miscible),  $F=2$  in a single-phase region, so two concentrations must be defined to fix the particular region. Within the binodal curve,  $F=1$  so we need to know one concentration term, since this will allow the composition of one phase to be fixed on the binodal curve. From the tie line, we can then obtain the composition of the conjugate phase.
- The tie lines in this case are not parallel to the base of the triangle. It depends on the relative solubility of the third component (alcohol) in the other two components (water, benzene).