Physical Pharmacy Laboratory
2nd stage
College of Pharmacy

Lab.3 : Two component systems containing liquid phases

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Phase Equilibria

- **Matter** exists in **three phases**: solid, liquid, and gas.
- in real systems, these phases often **coexist**, e.g., **ice water** on a hot day contains **ice (solid), water (liquid), and vapor (gas)**.
- The coexistence and stability of phases depend on:
  - Temperature of the system and surroundings
  - Amount of each phase present
  - Whether the system is **open or sealed**
    - In **open systems**, water vapor escapes, preventing true equilibrium.
    - In **sealed systems**, equilibrium can be reached and maintained; changes in temperature affect phase presence (e.g., only ice in a freezer).

The Phase Rule

- Developed by **J. Willard Gibbs**.
- **Gibbs Phase Rule** describes how many **independent variables** can be changed without changing the number of phases in a system

The phase rule is given by:

$$F=C-P+2$$

Where:

F = **Degrees of freedom** (F) → number of independent variables (like temperature, pressure) that can be changed without altering the number of phases.

C = **Components** → minimum number of chemical substances needed to describe the system.

P = **Phases** → physically distinct parts of the system (solid, liquid, gas).

Examples

- **Pure water**

(C = 1), one phase (P = 1):

F=C–P+2

F = 1 – 1 + 2 = 2 → **temperature and pressure** can vary independently.

- **Ice + water**

(C = 1, P = 2)

F = 1 → only **one variable** can be changed independently.

- **Ethanol + water**

(C = 2), one liquid phase (P = 1):

  - Mixtures of Water and Alcohols
  - Completely miscible → One liquid phase + vapour
  - **F = 3** → temperature, pressure, and composition can vary.

The Phase Examples

How many phases in each of the following systems?

1. Liquid water, pieces of ice and water vapor are present together.
   - **Number of phases = 3**
2. A solution of NaCl in water
   - **Number of phases = 1**
3. Liquid water + water vapour
   - **Number of phases = 2**
4. Liquid water + water vapor + air
   - **Number of phases = 2**

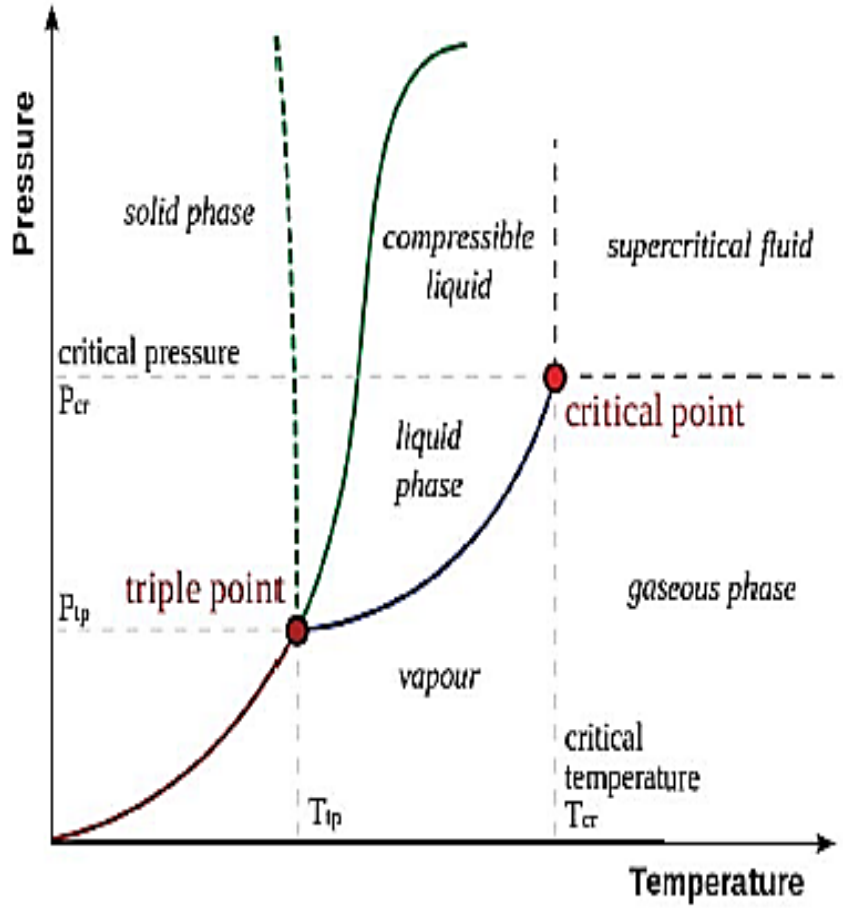
◆ **General Concepts**

- As the **number of components increases**, the degrees of freedom also increase.
- As the **number of phases increases**, degrees of freedom **decrease**.
- The **triple point** (e.g., ice-water-vapor) has **no** degrees of freedom.

One component system

- Consider a one component system composed of a liquid with a particular volume. Using the phase rule:
- **F = 1 - 1 + 2 = 2** (the maximum number of degree of freedom for one component system).
- Only **two independent variables** are required to define the system (temperature and pressure).
- For a one component system composed of a liquid and its vapor. Using the phase rule:

  F = 1 - 2 + 2 = 1
  - **Only one independent variable** is required to define this system (either temperature or pressure).



Two component systems containing liquid phases

- **Miscible systems** Two liquids are completely miscible when they mix in all proportions to form a single homogeneous phase.
- Examples:
  - Ethanol + water
  - Acetone + water
- The system contains only **one liquid phase**.
- **Immiscible systems** Two liquids are partially miscible when each liquid can dissolve some amount of the other, but complete mixing does not occur over all compositions.
- For example:
  - **Phenol + water**
- At certain compositions, the mixture separates into:
  - ✓ A water-rich phase
  - ✓ A phenol-rich phase

➢ This phenomenon is called **liquid–liquid phase separation**.

Two component systems containing liquid phases

- **For two component systems**:

  C = 2 F = C - P + 2 F = 4 - P

  P = 1 at least, so F is 3 at most

  ➢ Three variables are required: *temperature, pressure, and composition*.

  - If the pressure is fixed:

    Only *temperature and composition* are required.

Factors Affecting Miscibility

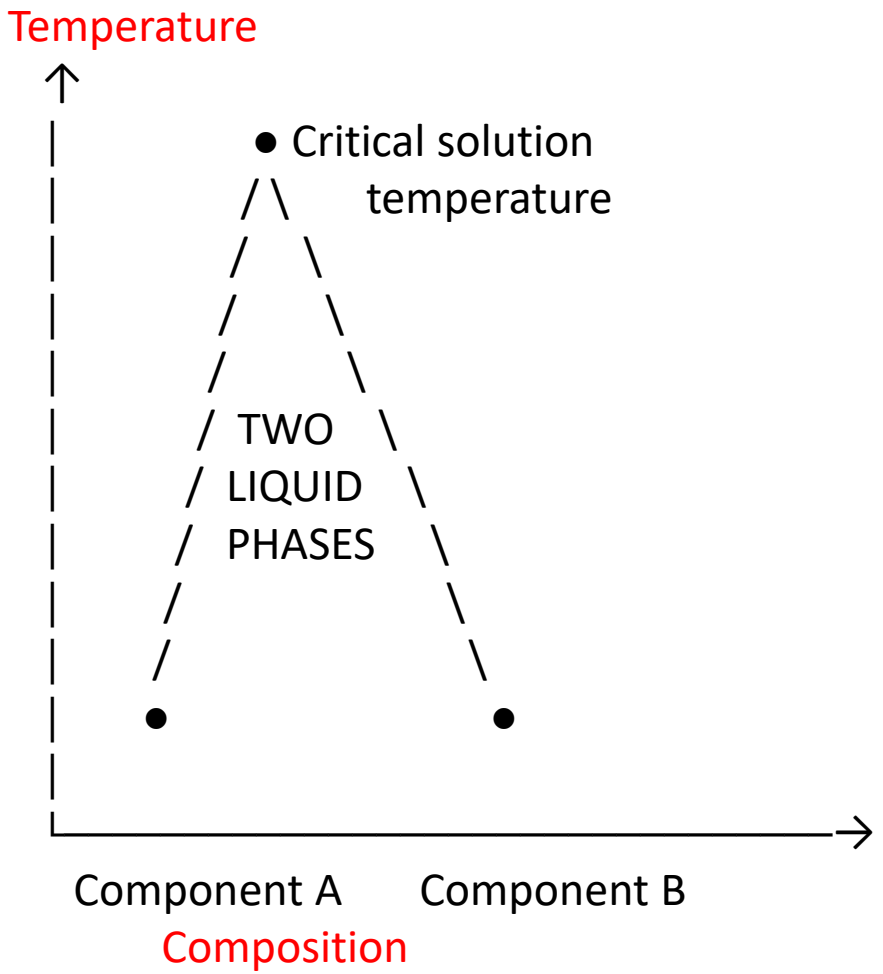
- The miscibility of two liquids depends on several factors:
  1. **Molecular structure**
     - Liquids with similar molecular interactions tend to be more miscible.
  2. **Polarity**
     - Polar liquids generally mix better with polar liquids, while nonpolar liquids tend to mix with nonpolar liquids.
  3. **Hydrogen bonding**
     - Hydrogen bonding can substantially affect mutual solubility.
  4. **Temperature**
     - Temperature can increase or decrease mutual solubility.
  5. **Composition**
     - The extent of miscibility depends on the relative amounts of the two components.

Liquid–Liquid Equilibrium

- When two partially miscible liquids are mixed and allowed to stand, the system may separate into two liquid phases.
- After sufficient time, equilibrium is established.
- At equilibrium: {Chemical potential of each component is equal in both phases}

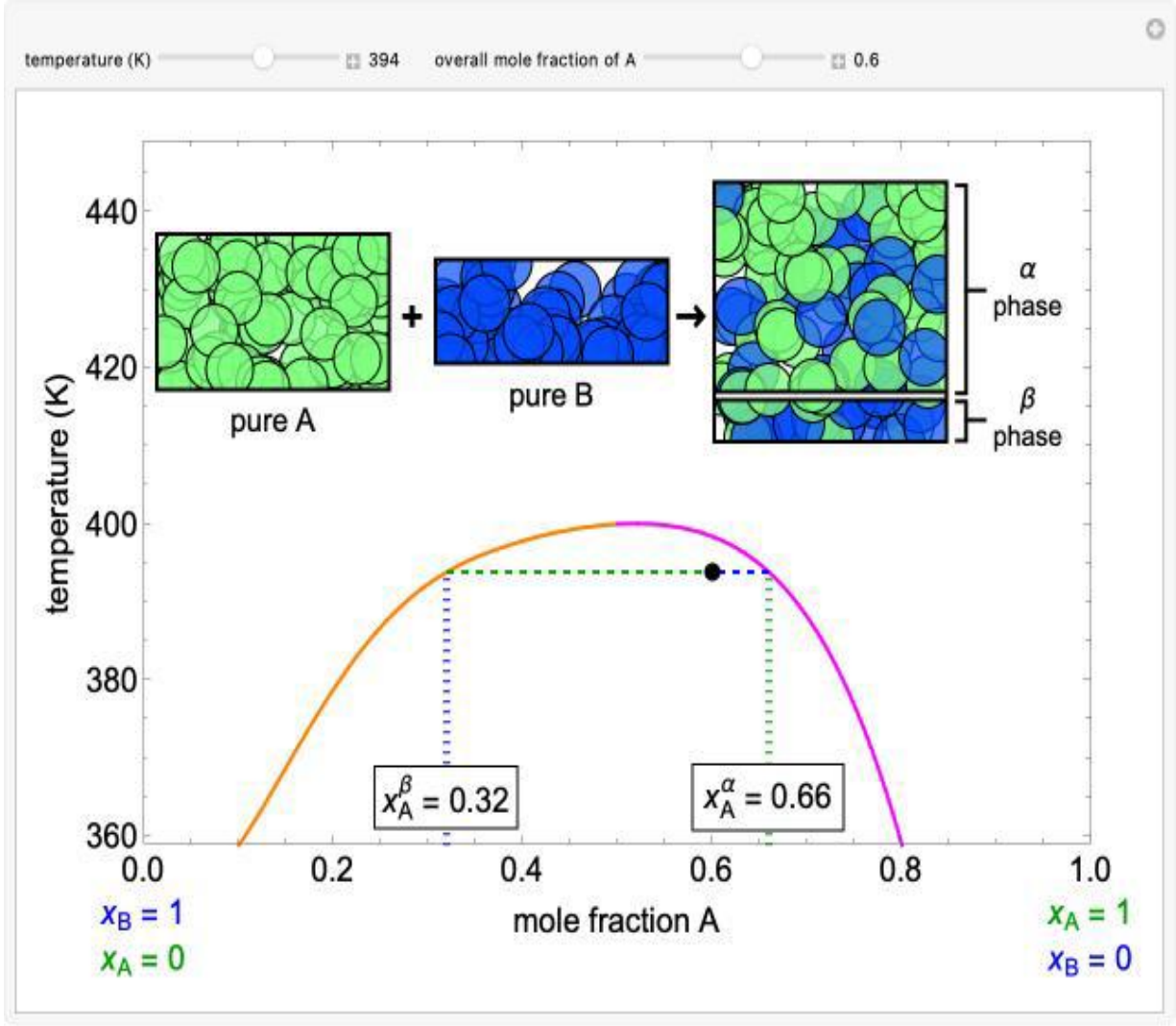
Binary Liquid Phase Diagram

- A phase diagram is used to show the relationship between:
  - Temperature
  - Composition
  - Number of phases
- For a typical partially miscible binary liquid system, the diagram can be represented as:
  - **Binary liquid phase diagram**: The **whole diagram** showing how two components behave as composition, temperature, or pressure changes. It can contain single-phase regions, two-phase regions, and boundaries.
- The enclosed region represents compositions where **two liquid phases coexist**.
- Outside this region, there is **one liquid phase**.



Phase Behavior of a Binary Liquid System

- Consider the **water–n-butanol system**.
  - At low concentration of butanol, the system can exist as a single water-rich phase.
  - As more butanol is added, a point is reached where the mixture becomes unstable and separates into:
  - ➢ **Water-rich phase + Butanol-rich phase**
    - The boundary between the one-phase and two-phase regions is called the: **Binodal curve / solubility curve**



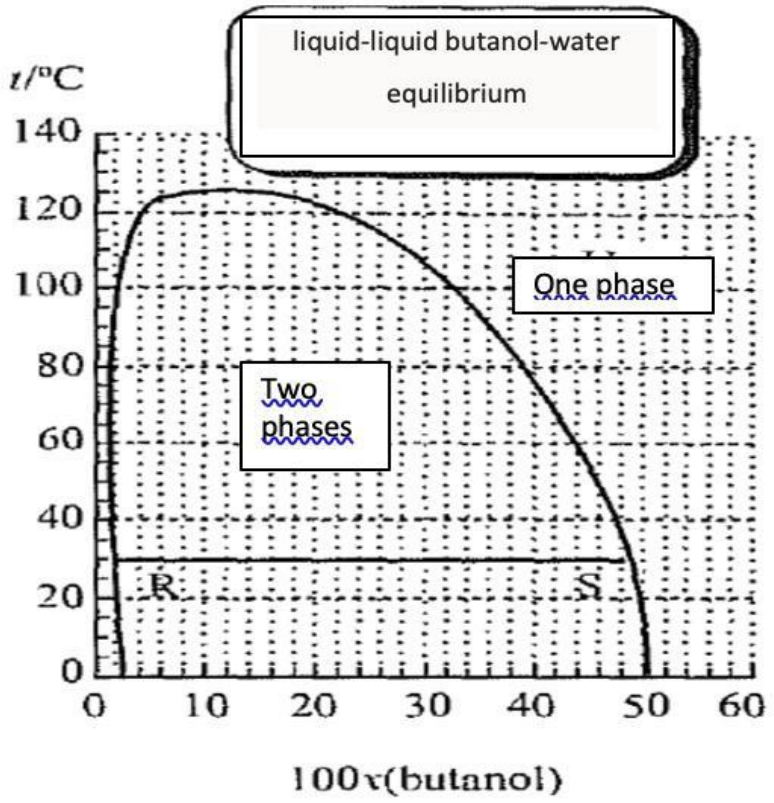
Binodal Curve

- The boundary separating the one-phase and two-phase regions is called the: **Binodal curve**
- **I**t represents the compositions of the two phases that coexist at equilibrium.

➢ Inside the binodal curve: **Two liquid phases exist.**

➢ Outside the binodal curve: **One liquid phase exists.**

This is the phase diagram of the liquid-liquid equilibrium of a butanol-water mixture at atmospheric pressure.



How are the moles of water and butanol divided into the different phases under the following conditions? :

a) $n_{butanol} = 3$, $n_{water} = 2$, room temperature

b) $n_{butanol} = 1$, $n_{water} = 4$, at 30Cº

c) $n_{butanol} = 0.5$, $n_{water} = 4.5$, at 100Cº

Critical Solution Temperature (CST)

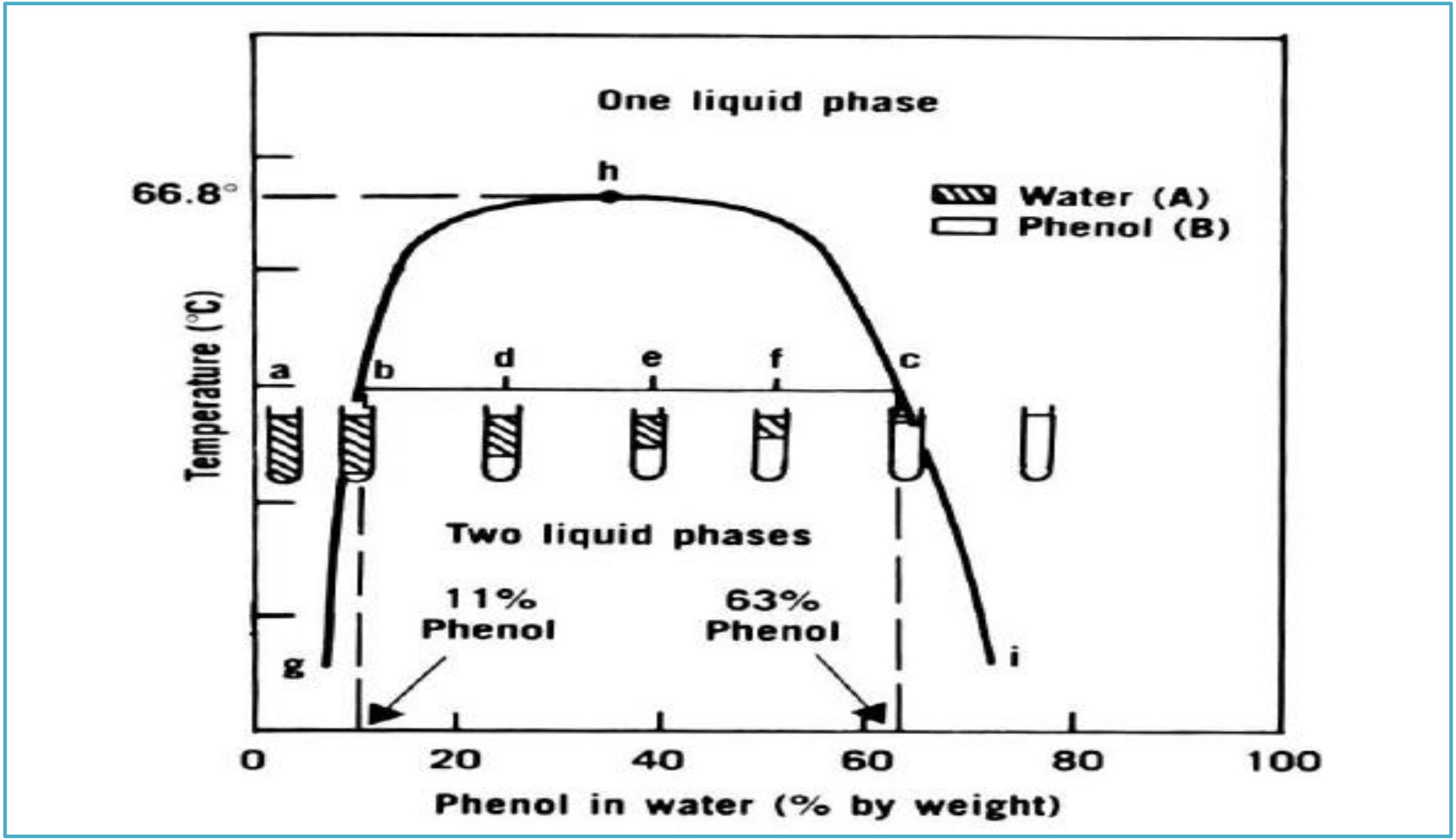
- The **Critical Solution Temperature (CST)** is the temperature at which **two partially miscible liquids become completely miscible in all proportions**.
- In a **binary liquid–liquid phase diagram**, the CST corresponds to the **critical point (plait point)** of the binodal curve.
- **Types of CST**
  - **Upper Critical Solution Temperature (UCST):**

    Above this temperature, the two liquids become completely miscible. *Example: phenol–water system.*
  - **Lower Critical Solution Temperature (LCST):**

    Below this temperature, the two liquids are completely miscible; above it, they separate into two phases. *Example: some polymer–solvent systems.*
  - At the CST: The compositions of the two liquid phases become identical.

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°C.
  - This is called the critical solution temperature or the upper consolute temperature.
  - In this system above 66.8°C all combinations *of phenol and water will be completely miscible and will be one phase.*


One liquid phase
66.8°
h
Water (A)
Phenol (B)
Temperature (°C)
a
b
d
e
f
c
Two liquid phases
11%
Phenol
63%
Phenol
g
i
0
20
40
60
80
100
Phenol in water (% by weight)


Thank You