# Phase equilibria and the phase rule

# The Phase

- A phase is a homogenous physically-distinct portion of a system that is separated from other parts of the system by boundary surfaces.
- A system containing water and its vapor is a two-phase system. An equilibrium mixture of ice, liquid water, and water vapor is a three phase system.
- A phase may be gas, liquid or solid.

# The Phase

- A gas or a gaseous mixture is a single phase.
- Completely miscible liquids constitute a single phase.
- In an immiscible liquid system, each layer is counted as a separate phase.
- Every solid constitutes a single phase except when a solid solution is formed.
- A solid solution is considered as a single phase.
- Each polymorphic form constitutes a separate phase.

# The Phase diagram

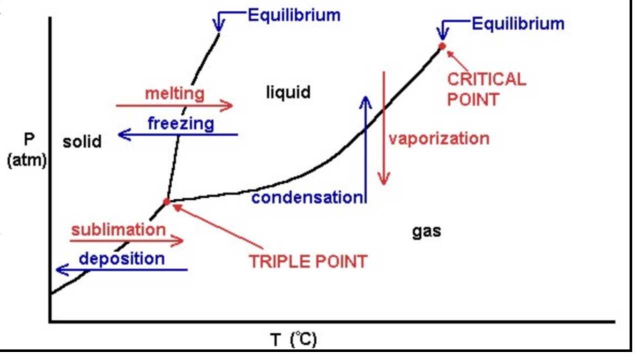
- Phase diagram shows the multisystem state changes with the temperature, pressure, composition and other intensive properties.

**Intensive properties** are properties that do not depend on size; e.g. pressure and temperature.

## The Phase diagram: One component system

- The simplest phase diagrams are pressure-temperature diagrams of a single simple substance.
- The axes correspond to the pressure and temperature.
- The lines in the phase diagram represent two phase systems, while the spaces between the lines represent one phase systems.

➢The triple point represents the temperature and pressure where all three physical states are in equilibrium (for water 0.01 $^{o}$C and 0.00603659 atm).



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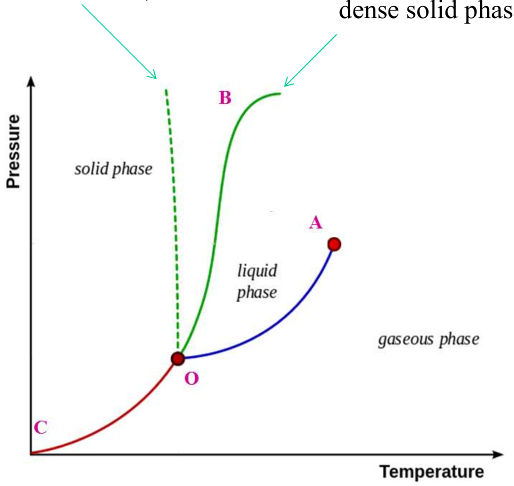
## The Phase diagram: One component system

The frozen state of water (ice) is actually less dense than the liquid state. Therefore; increasing pressure (which favors compactness of the molecules) will favor the liquid state.

For most substances the solid is denser than the liquid. Therefore; an increase in pressure usually favors the more dense solid phase.



Curve OA:
vapor pressure curve

Curve OB:
Melting point curve

Curve OC:
Sublimation curve

# The Phase diagram: One component system

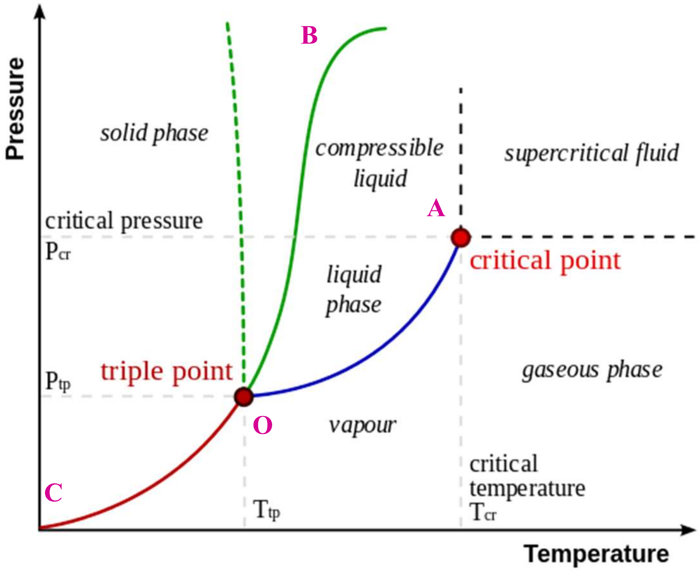
- The critical point is the point on a phase diagram that indicates the critical temperature and pressure.
- The critical temperature of a substance is the temperature above which that substance can no longer exist as a liquid, no matter how much the pressure is increased.
- In the same way, the critical pressure is the pressure above which the substance can no longer exist as a gas, no matter how high the temperature is.
- Supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist.

# The Phase diagram: One component system

Curve OA:
vapor pressure curve

Curve OB:
Melting point curve

Curve OC:
Sublimation curve



# The supercritical fluids

- In general terms, supercritical fluids have properties between those of a gas and a liquid.
- Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes.
- Supercritical fluids have the viscosity of a gas, but the densities and solvent power of a liquid, making SC fluids ideal for extraction.

# The Gibbs phase rule

- To understand and define the state of a phase, knowledge of several independent variables is required.
- Independent variables (also called intensive variables) are the variables that do not depend on the volume or size of the phase, e.g. temperature, pressure, density, boiling point and concentration.
- The Gibbs phase rule is expressed as follows:

$$F = C - P + 2$$

- **F**: is the number of degrees of freedom of the system which is the least number of intensive variables required to define the system completely (vary independently).
- **C**: number of components, **P**: number of phases present

# Application of phase rule to one component system

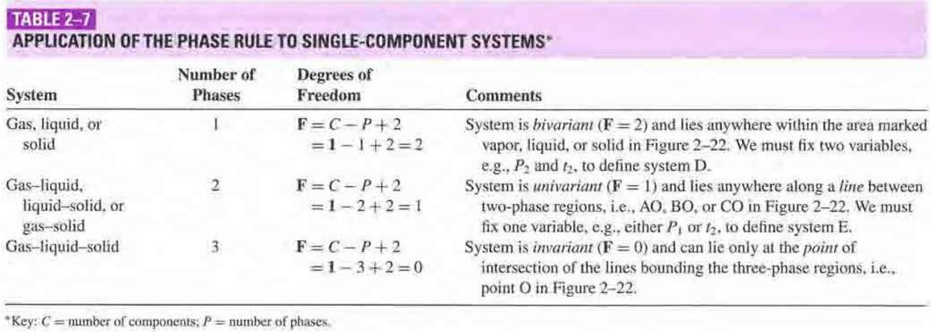


TABLE 2–7
APPLICATION OF THE PHASE RULE TO SINGLE-COMPONENT SYSTEMS*

| System | Number of Phases | Degrees of Freedom | Comments |
|---|---|---|---|
| Gas, liquid, or solid | 1 | $\mathbf{F} = C - P + 2$<br>$= 1 - 1 + 2 = 2$ | System is *bivariant* ($\mathbf{F} = 2$) 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 | $\mathbf{F} = C - P + 2$<br>$= 1 - 2 + 2 = 1$ | System is *univariant* ($\mathbf{F} = 1$) 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 | $\mathbf{F} = C - P + 2$<br>$= 1 - 3 + 2 = 0$ | System is *invariant* ($\mathbf{F} = 0$) 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.

# Two component system containing liquid phases

- Systems in which the vapor phase is ignored and only solid and liquid phases are considered are termed condensed systems.

- Systems containing liquids might be:

1. Completely immiscible (such as mercury and water)
2. Completely miscible in all proportions (e.g.ethanol and water)
3. Partially miscible (e.g. phenol and water)

# Two component system containing liquid phases

For two component systems:

**C=2 F = C – P + 2 ⟹ F = 4 – P**

**P ≥ 1 ⟹ F ≤ 3**

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

If the pressure is fixed, only temperature and composition are required.

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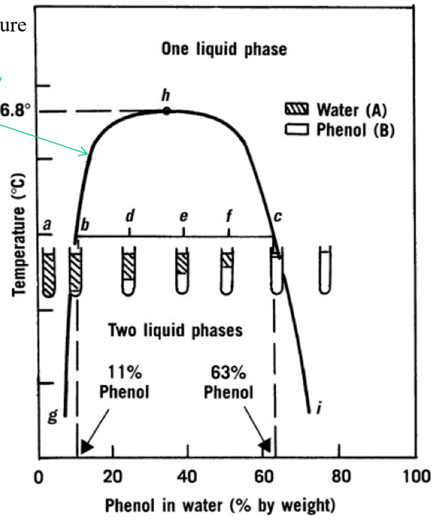
# Two component system containing liquid phases



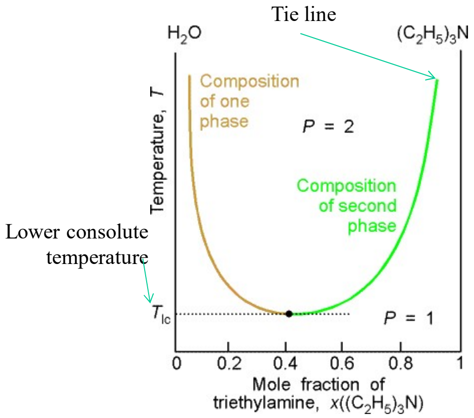
Upper consolute temperature = critical solution temperature

Binodal curve

Phase diagrams for two component systems are commonly constructed with temperature and composition as the coordinates.

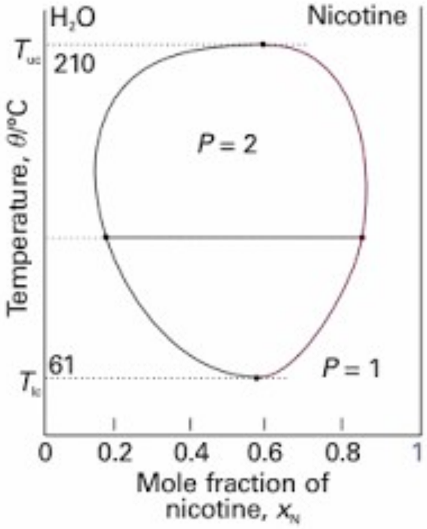
# Two component system containing liquid phases

Other liquid mixtures show no upper consolute temperature but lower consolute temperature.



# Two component system containing liquid phases

Other liquid mixtures show both upper and lower consolute temperatures.

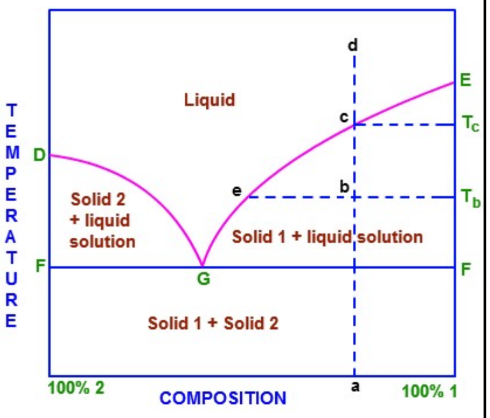


# Two component system containing solid and liquid phases

The points of **D** and **E** represent the melting points of **solids 2 and 1**.

Two component system consisting of two solids (**2 and 1**) when heated to a temperature above the melting points of both (**point d**), a one-phase system will form consisting of a liquid solution of **2 and 1**.

When the temperature fall to point c, pure solid 1 will form dispersed in a liquid solution of 1 and 2.



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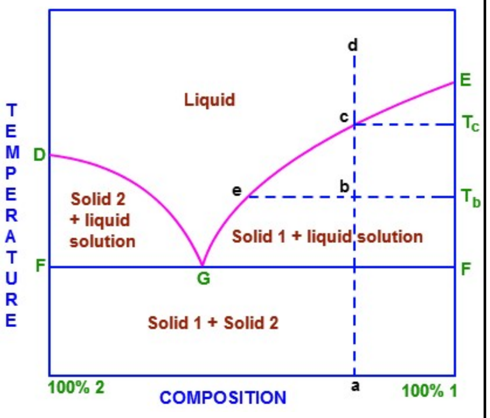
# Two component system containing solid and liquid phases

- At point **G** solid **1**, solid **2** and solution phase are in mutual equilibrium (exist together).
- The solid phase at this point is a finely divided two-phase dispersion of crystalline 1 and 2 called a eutectic, and G is the eutectic point. Eutectic melts at a lower temperature than either of its pure components.



# Phase equilibria in three-component systems

For three component systems:

**$C = 3 \quad F = C - P + 2 \Rightarrow F = 5 - P$**

**$P \geq 1 \Rightarrow F \leq 4$**

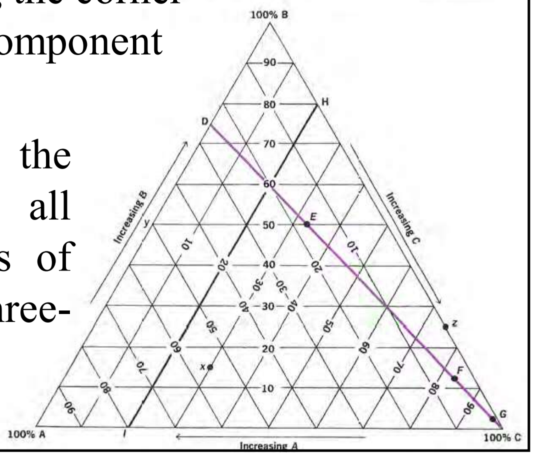
Four variables are required: temperature, pressure, and two compositions.

If the temperature and pressure are both fixed then, only two compositions are required

- Because we are dealing with a three-component system, it is more convenient to use triangular coordinate graphs

# Rules relating to triangular diagram

- Each of the three corners represent 100% by weight of one component.
- The three lines joining the corner points represent two component mixture.
- The area within the triangle represent all possible combinations of A, B , and C to give three-component system



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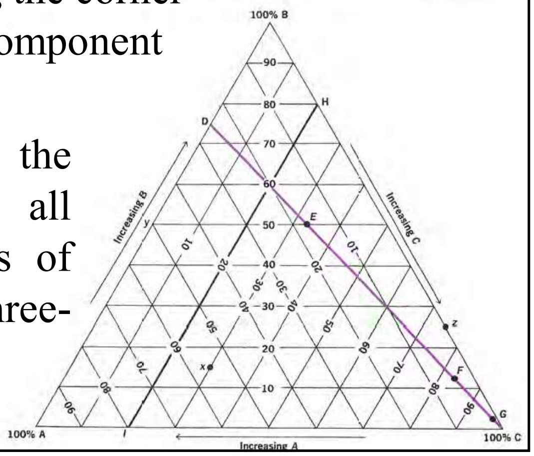

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# Ternary systems with one pair of partially miscible liquids

- E.g. Water, benzene and ethanol mixture
- Water and benzene are partially miscible
- Ethanol is miscible with both water and benzene

Binodal curve

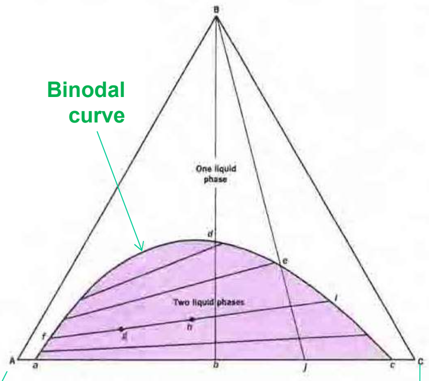

**Fig. 2-28.** A system of three liquids, one pair of which is partially miscible.

Partially miscible liquids

# Ternary systems with one pair of partially miscible liquids

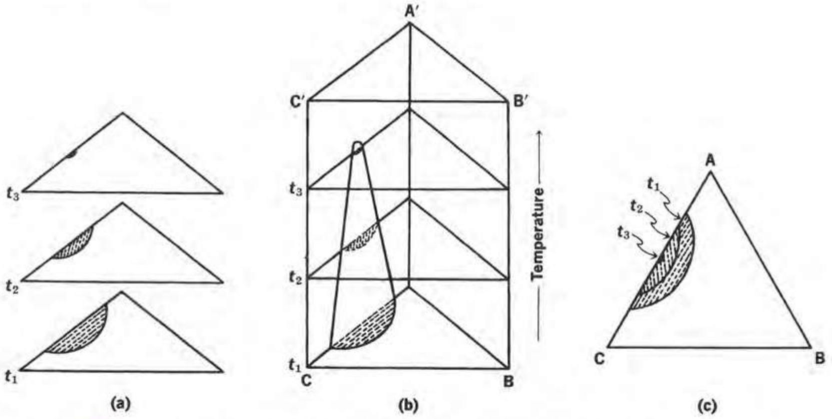

**Fig. 2–29.** Alterations of the binodal curves with changes in temperature. (*a*) Curves on the triangular diagrams at temperatures $t_1$, $t_2$, and $t_3$. (*b*) The three-dimensional arrangement of the diagrams in the order of increasing temperature. (*c*) The view one would obtain by looking down from the top of (*b*).

# Ternary systems with two or three pairs of partially miscible liquids

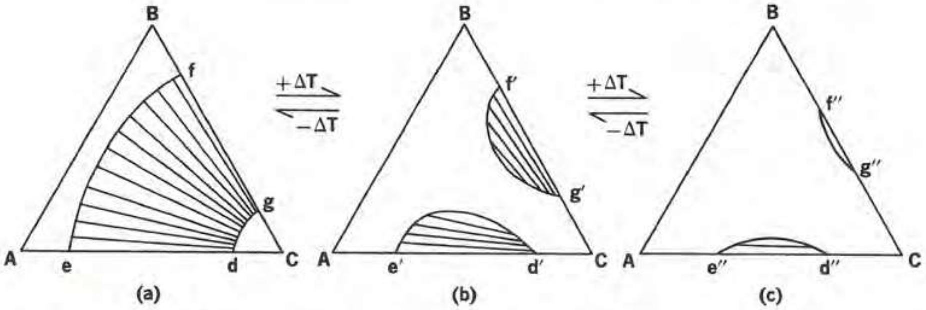

**Fig. 2–30.** Effect of temperature changes on the binodal curves representing a system of two pairs of partially miscible liquids.

# Ternary systems with two or three pairs of partially miscible liquids

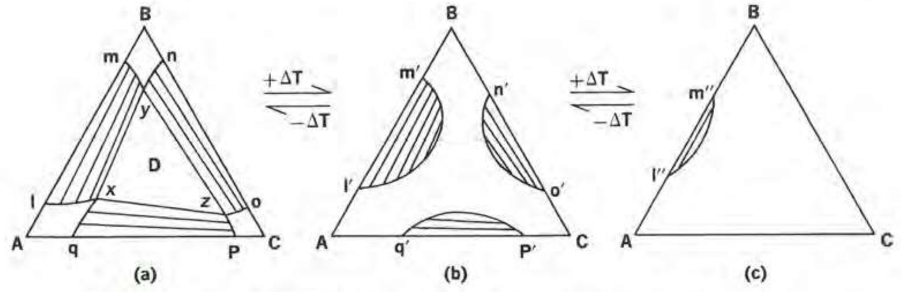

**Fig. 2–31.** Temperature effects on a system of three pairs of partially miscible liquids.