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Physical Pharmacy

Phase Equilibrium And The Phase Rule

Contents

In this lecture you will learn:

- **Definition of phase and phase rule**
- **Definition supercritical fluid and its use**
- **Types of phase diagrams：**

a. Single component phase diagrams: water and CO2 phase diagrams as examples

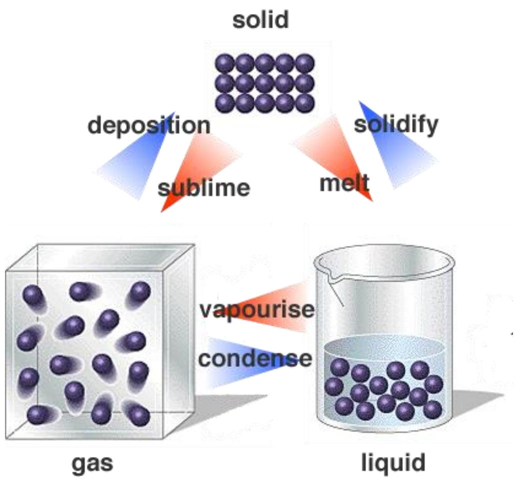
b. Two component phase diagrams

c. Three component phase diagrams

Definitions

- **Component**: is a substance in a system with a defined chemical structure.

- **State of matter:** is a form that matter can take at certain temperature and pressure.Examples are solid, liquid, gas.



- The states of matter can exist in different phases.
- **Phase :**

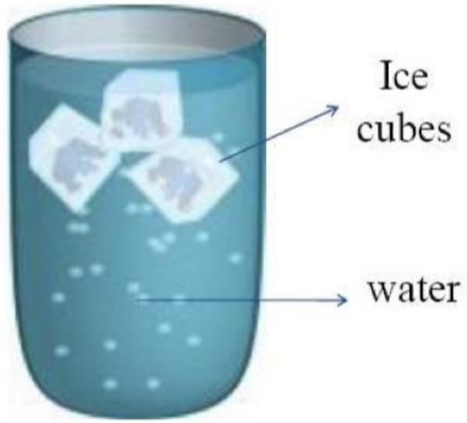
a. **is the form of matter that has uniform chemical and physical properties.**

b. **It is a homogenous, physically distinct and mechanically separable portion of the material with a given chemical composition and structure.**

c. **It is separated from other portions in the system by a boundary.**

Definitions

- When a phase in one form is altered to another form, a "**phase change**" is said to have occurred.
- When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties.
- **Each phase** can be defined by a series of independent variablesThus: to understand and define the state of each phase, knowledge of several variables is required



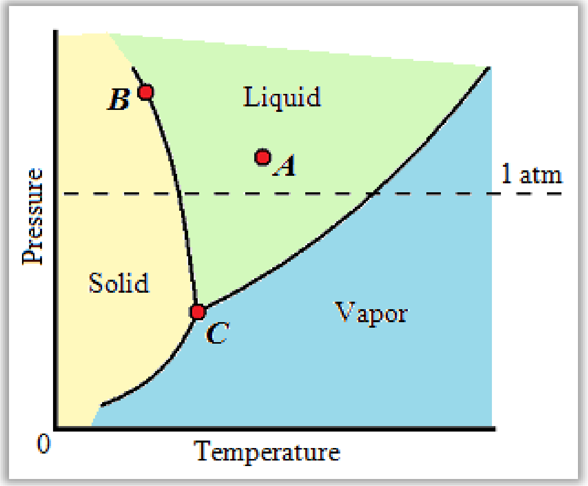
**Ice + water system is
One component
Two Phase system**

Phase rule

- Willard Gibbs formulated the phase rule, which is a relationship for determining the least number of variables (e.g., temperature, pressure, density, concentration, etc.) required to define the state of the system, or the number of variables which can be changed without changing the equilibrium state of the system.

- This critical number is called F, the number of degrees of freedom of the system, and the rule is expressed as follows:

$$F = C - P + 2$$



Phase rule

- **Where：C** is the number of components (the number of components is the smallest number of constituents by which the composition of each phase in the system at equilibrium can be expressed in the form of a chemical formula or equation)

- **P** is the number of phases present

- Thus: the number of degrees of freedom (**F**) is the least number of intensive variables that must be fixed/known to describe the system completely

- As the number of components increases (i.e, system becomes more complex), so do the required degrees of freedom needed to define the system (necessary to fix more variables to define the system).

Phase rule

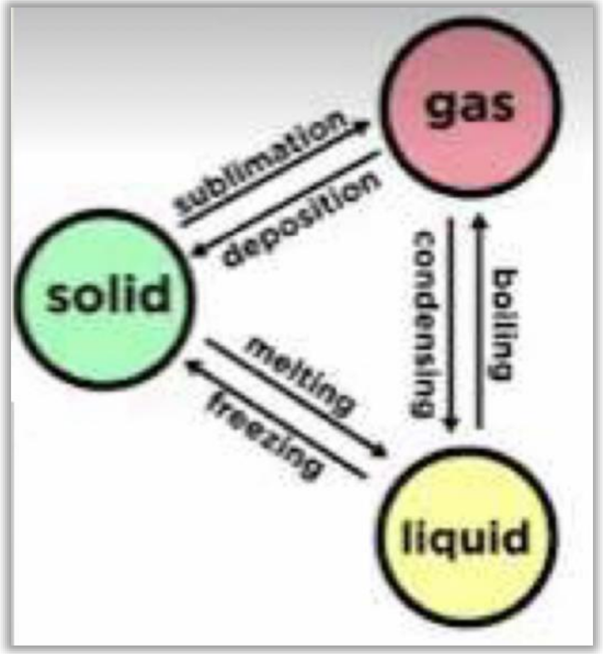
Phase Diagrams = phase equilibrium diagrams

- At most temperatures and pressures, a single pure substance at equilibrium exists entirely as a solid, liquid, or gas.

- BUT at certain temperatures and pressures, two and even all three phases may coexist.

- **Example**: **Pure water at**

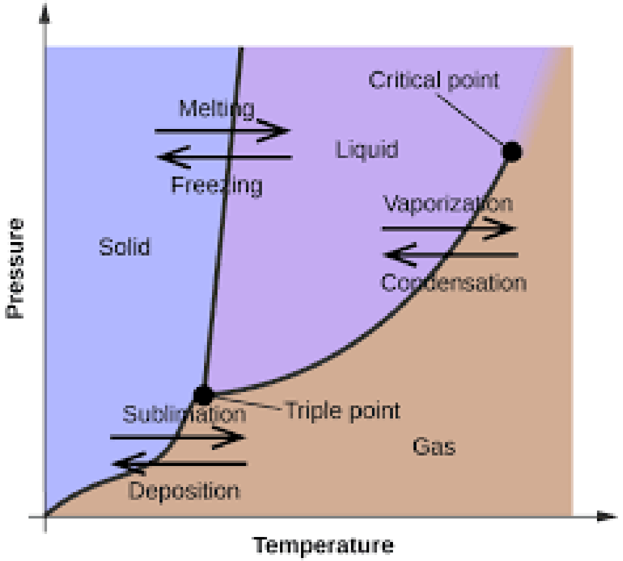
a. 130 C and 1 atm is **gas**
b. 40 C and 10 atm is **solid**
c. 100 C and 1 atm may be a **gas, Liquid,** or a **mixture of both**
d. 0.0098 C and 4.58 mm Hg may be a **solid**, a **gas**, a **liquid**, or a **mixture**



Phase rule

Phase Diagrams = phase equilibrium diagrams

- The phase diagram is a useful tool to **visualize** phase **behavior.**
- It is a chart or a graph of one system variable against another.
- (Relationship between composition of different phases and variables)
- It give details on conditions at which the substance phases exist as **solid, liquid or gas in equilibrium with each other.**



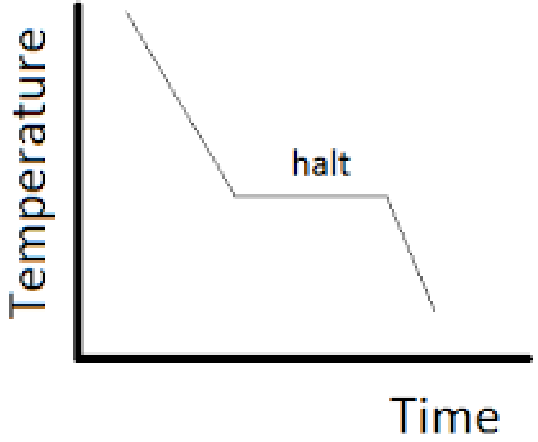
Phase rule

Phase diagram for a generic single-component system

- A typical phase diagram has pressure on the **y-axis** (typically in atmospheres) and temperature on the **x-axis** (typically in degrees **Celsius or Kelvin**).

- The diagram is divided into three areas, which represent the solid, liquid, and gaseous states of the substance.

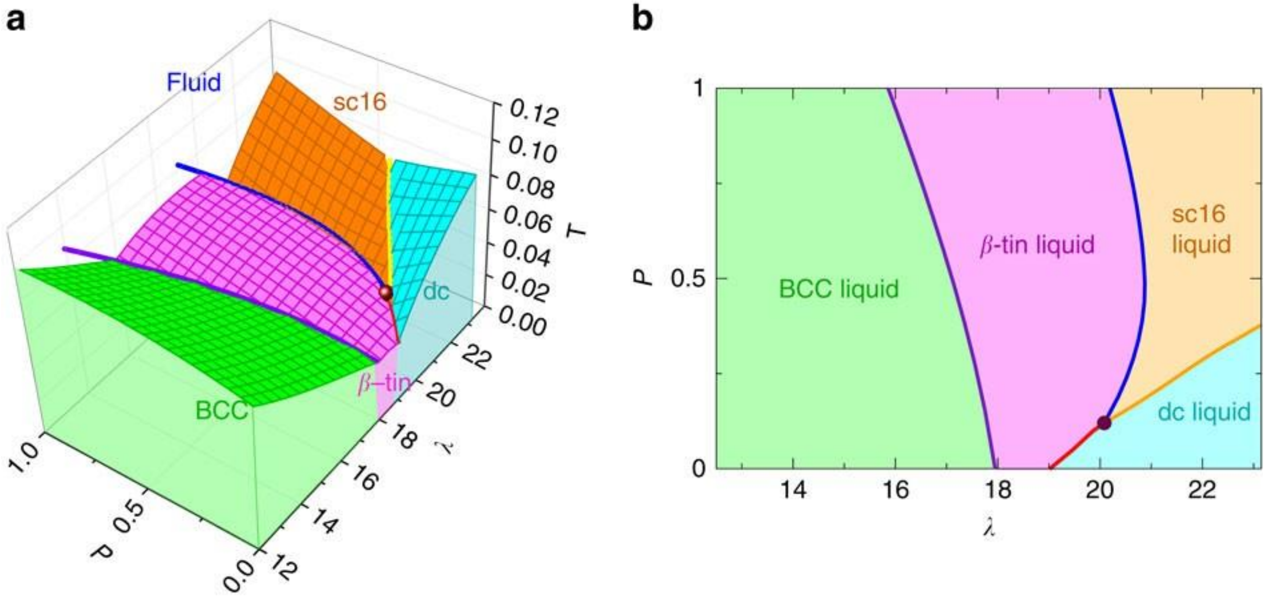
- The lines are known as "**equilibrium curves**": any point on these curves represent two phases which exist in equilibrium at certain temperature and pressure.



Phase rule

Phase diagram for a generic single-component system

- As we cross the lines or curves on the phase diagram, a phase change occurs.
- In other words, these lines define phase change points.



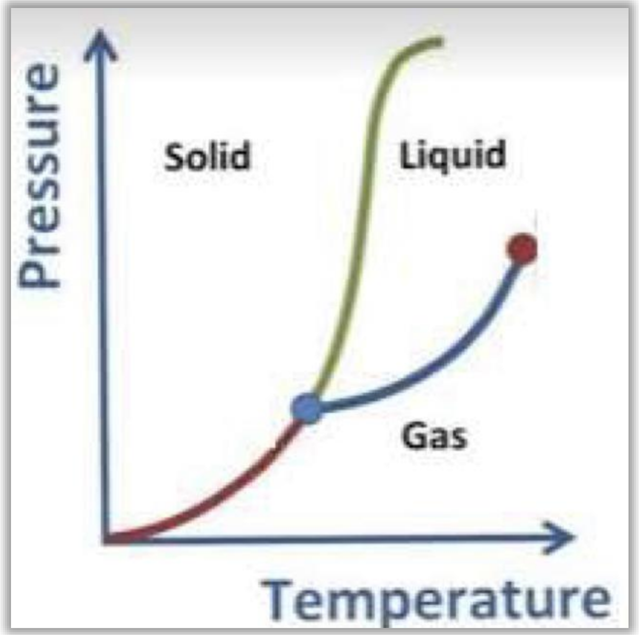
Phase rule

Phase diagram for a generic single-component system

- **The red** line divides the solid and gas phases, it represents sublimation (solid to gas) or deposition (gas to solid) curve: the transition between solid and gaseous states.

- **The green** line divides the solid and liquid phases, it represents melting or fusion (solid to liquid) and freezing (liquid to solid) curve: the transition between solid and liquid states.

- **The blue** line divides the liquid and gas phases, represents vaporization (liquid to gas) and condensation (gas to liquid) curve: the transition between gaseous and liquid states.



Phase rule

Phase diagram for a generic single-component system

- **There are also two important points on the diagram:**

1. The triple point:

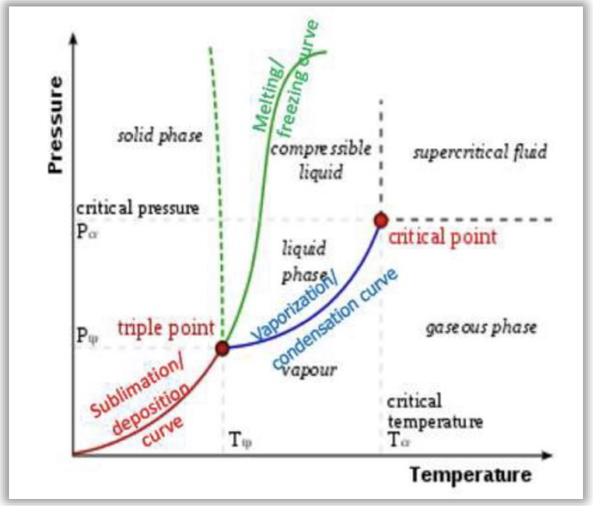
a. Is the point on a phase diagram at which the three states of matter: gas, liquid, and solid coexist.

b. It represents the combination of pressure and temperature that facilitates all phases of matter at equilibrium.

2. The critical point

a. Is the end point of a phase equilibrium curve.

b. It terminates the liquid/gas phase line and relates to the critical pressure.

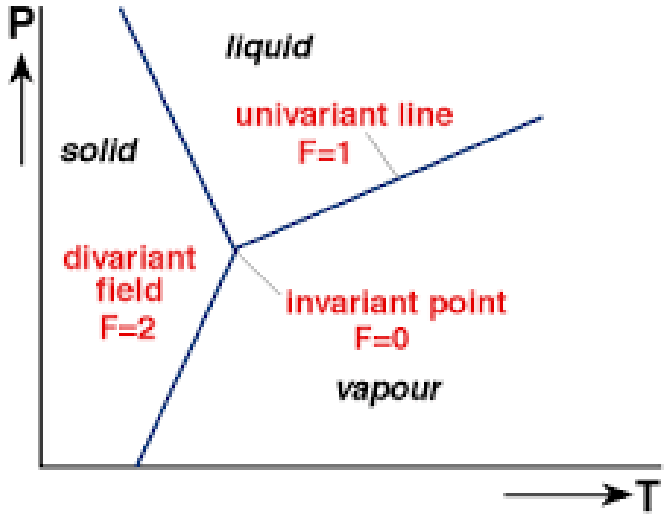


Phase rule

Phase diagram for a generic single-component system

- The higher the intermolecular forces of between the molecules, the higher the critical point will be.
- By knowing the critical point, we will be able to know the conditions at which we can change a gas into a liquid.
- At a pressure and temperature above the critical points a supercritical fluid forms (the point on a phase diagram at which the substance is indistinguishable between liquid and gaseous states)

One component phase diagram
C=1



The Supercritical Fluid State (SCFs)

- A supercritical fluid is a “**mesophase**” that combines the properties of gases and liquids.

- **How do you create a Supercritical Fluid?**

a. A supercritical fluid is a **highly compressed fluid**

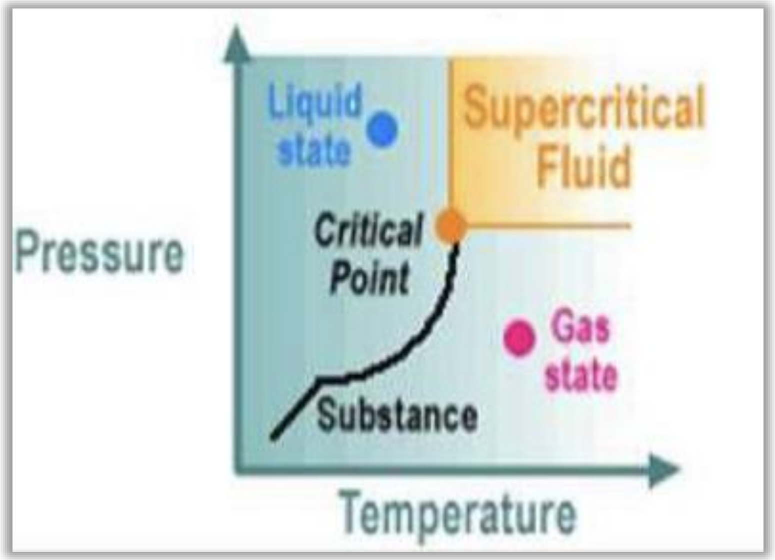
b. It is formed from the gaseous state by increasing the pressure above its critical points, at temperatures above the critical temperature.

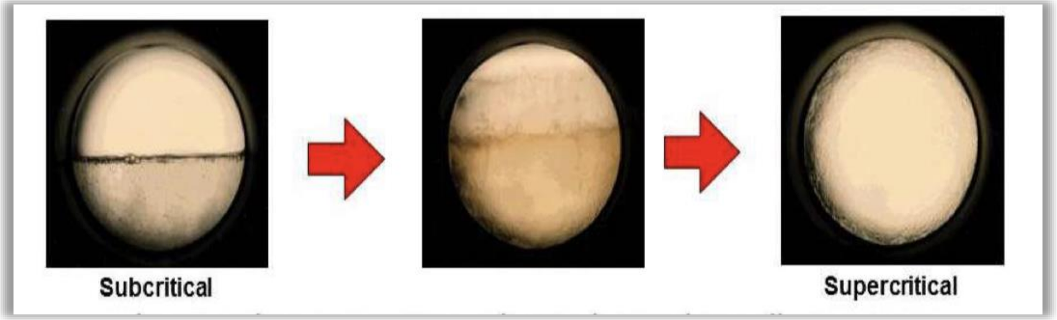
c. The critical pressure (P_c) is the minimum pressure required to liquefy a gas at a given temperature.

d. When the pressure is raised above the critical pressure, the density of the gas can increase without a significant increase in the viscosity.

The Supercritical Fluid State (SCFs)

- A substance becomes a supercritical fluid above its critical point of temperature and pressure
- Moves like a gas and dissolves things like a liquid
- Note: A gas that is brought above its critical temperature T_c will behave as a gas irrespective of the applied pressure.





Increasing pressure, phase boundary disappears

The Supercritical Fluid State (SCFs)

- The result of changes in pressure (at fixed temperature) or changes in temperature (at fixed pressure) becomes evident by referring to the phase diagram.

A → Vapour / Pressure → C → Liquid / Pressure → D → Heat / Pressure → End

Water at

T=20c

P=3mm Hg

Water at

T2=20c

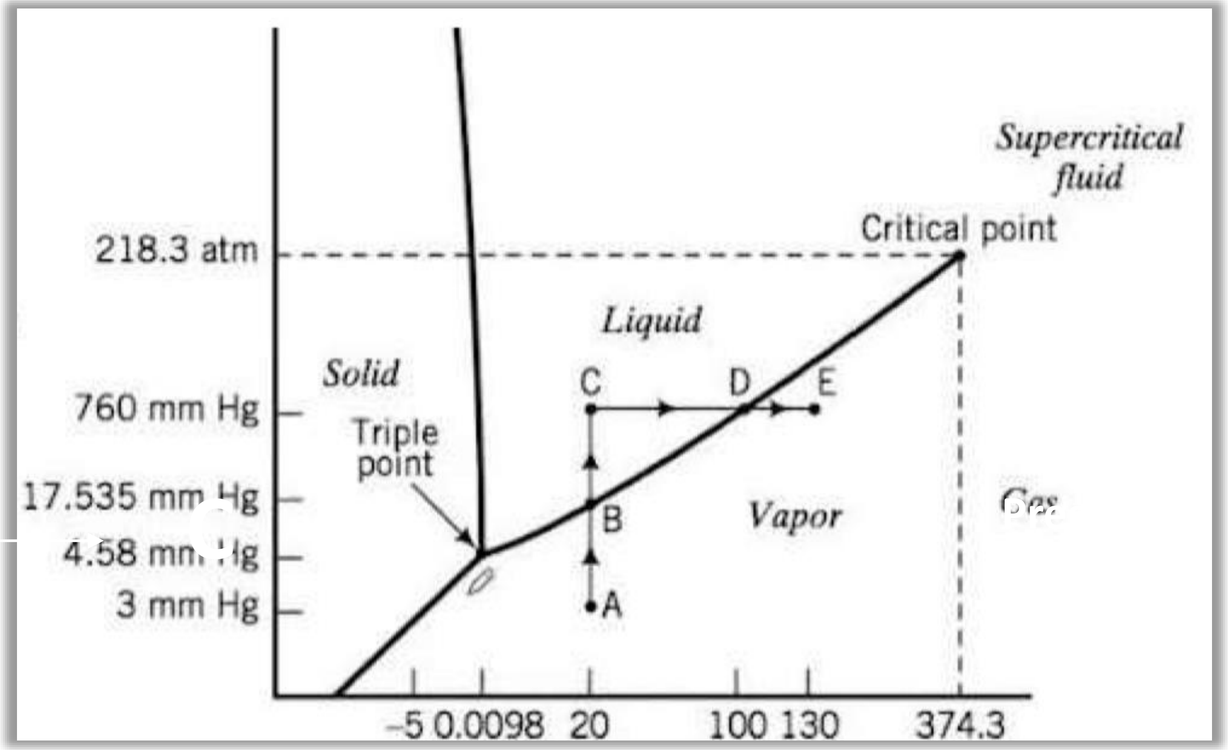
P2=760mm Hg

Water at

T3=130c

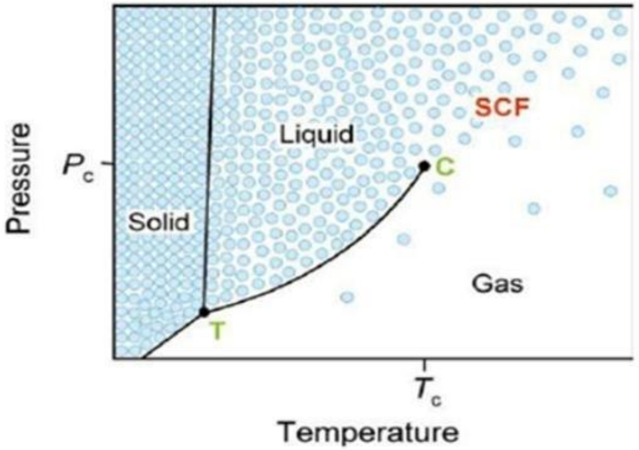
P3=760mm Hg

The Supercritical Fluid State (SCFs)



The Supercritical Fluid State (SCFs)

- With most substances, the temperature and pressure related to the triple point lie below standard atmospheric temperature and temperature and the pressure for the critical point lies above standard atmospheric pressure.
- Therefore at standard atmospheric pressure as temperature increases, most substances change from solid to liquid to gas, and at standard temperature as pressure increases, most substances change from gas to liquid to solid.
- An exception is water

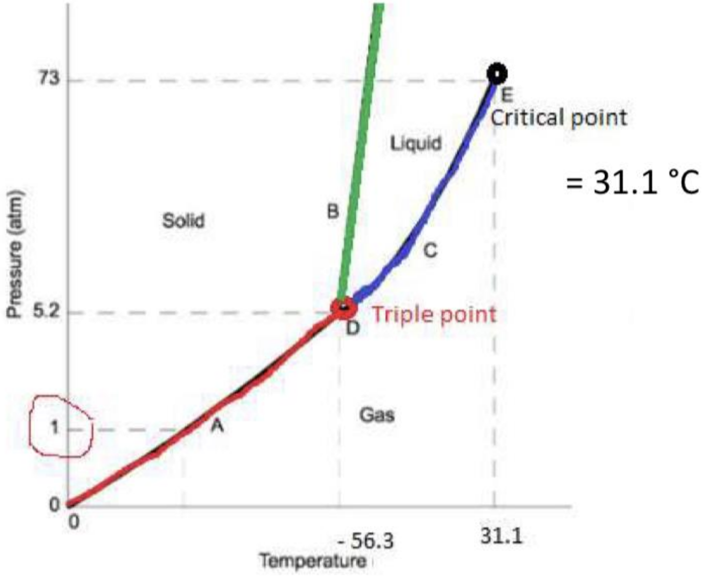


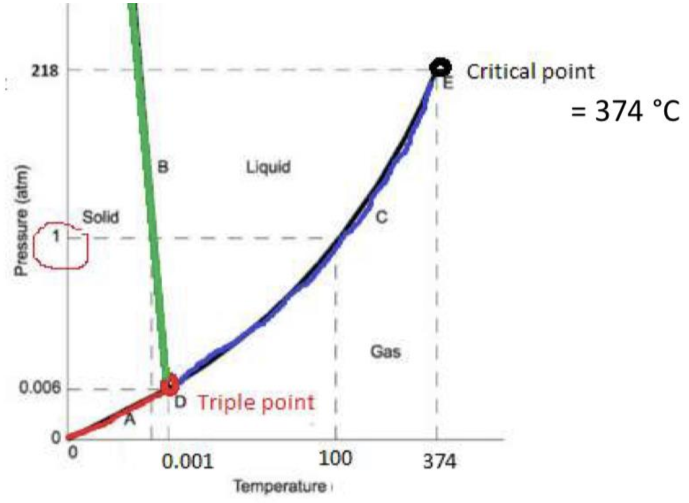
The Supercritical Fluid State (SCFs)

- For **CO2**, the atmospheric pressure (**1 atm**) lies below the triple point, therefore if we heat solid **CO2** (dry ice) it will sublime without changing into liquid.

- Supercritical **CO2** has the most accessible critical temperature at **31°C** and pressure of **72.8 atm**

- For Water, the atmospheric pressure (1 atm) lies above the triple point (as most of the materials) but unlike typical phase diagram of other materials, the solid/liquid phase line slopes negatively to the left (down the hill) which indicates that the liquid phase is more dense than the solid phase.





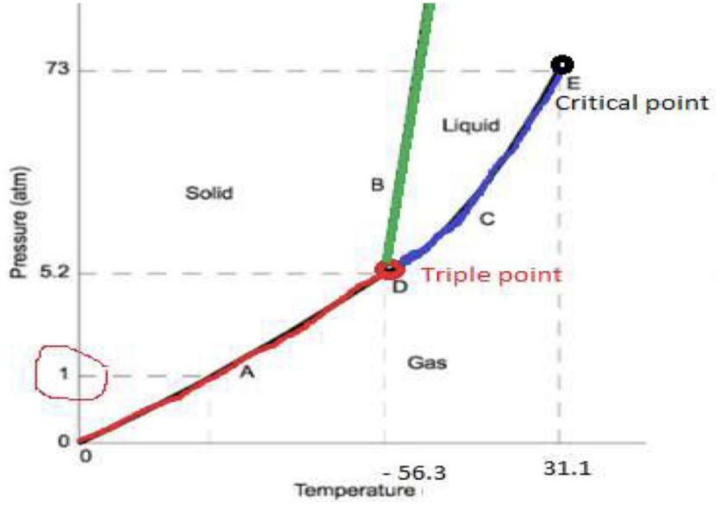
Phase diagrams for H_2O

The Supercritical Fluid State (SCFs)

Phase diagram of water Explanation

- If the temperature is held constant at t1, where water is in the gaseous state above the critical temperature, no matter how much the pressure is raised (vertically along the dashed line), the system remains as a gas.

- At a temperature t2 below the critical temperature, water vapor is converted into liquid water by an increase of pressure because the compression brings the molecules within the range of the attractive intermolecular forces.



Phase diagrams for CO_2

Critical temperature of water = 374.15°C
triple point of water = 0.0098°C

The Supercritical Fluid State (SCFs)

Phase diagram of water Explanation

- It is interesting to observe that at a temperature below the triple point, say t3, an increase of pressure on water in the vapor state converts the vapor first to ice and then at higher pressure into liquid water.

- This sequence, vapor → ice → liquid, is due to the fact that ice occupies a larger volume than liquid water below the triple point.

- 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°C** (or with respect to the phase rule, **F = 0).**

The Supercritical Fluid State (SCFs)

Application of the Phase Rule to Single-Component Systems

- **Water as an Example:**The number of components (C) in the equilibrium mixture of ice, liquid water, and water vapor is one because the composition of all

- **System is bivariant (F = 2).**

- **We must fix two variables, e.g., P and t, to define the system.**

- **Example: For certain volume of water vapor, if we want to duplicate its volume, we must know at least its temperature and pressure.**

System	Number or Phases	Degrees of Freedom
Gas, liquid, or solid	1	$F = C - P + 2$ $= 1 - 1 + 2 = 2$

The Supercritical Fluid State (SCFs)

Application of the Phase Rule to Single-Component Systems

- System is univariant (F = 1).
- We must fix one variable, e.g., either P or t, to define system
- Example: For G/L systems, by stating the temperature, we define the system completely because the pressure under which liquid and vapor can coexist is also defined.

System	Number or Phases	Degrees of Freedom
Gas-liquid, liquid-solid, or gas-solid	2	F = C- P + 2 = 1-2+ 2 = 1

The Supercritical Fluid State (SCFs)

Application of the Phase Rule to Single-Component Systems

- **System is invariant (F = 0) and can lie only at the point of intersectionof the lines bounding the three-phase regions,**

- **Example: S/L/G system: if we wish to prepare the three-phase system of ice-water-vapor, we have no choice as to the temperature or pressure at which we will work and if we attempt to vary the particular conditions we will lose any of the phases**

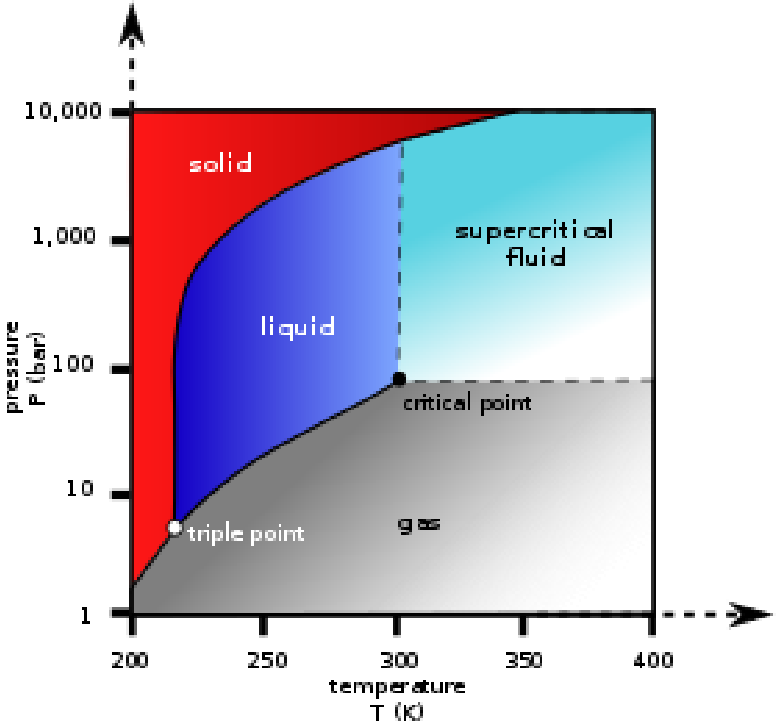
System	Number or Phases	Degrees of Freedom
Gas-liquid, solid	3	F = C- P + 2 = 1-3+ 2 =0

- **Note**: the greater the number of phases in equilibrium, the fewer are the degrees of freedom.

The Supercritical Fluid State (SCFs)

Phase diagram for a Two-component systems Containing Liquid Phases

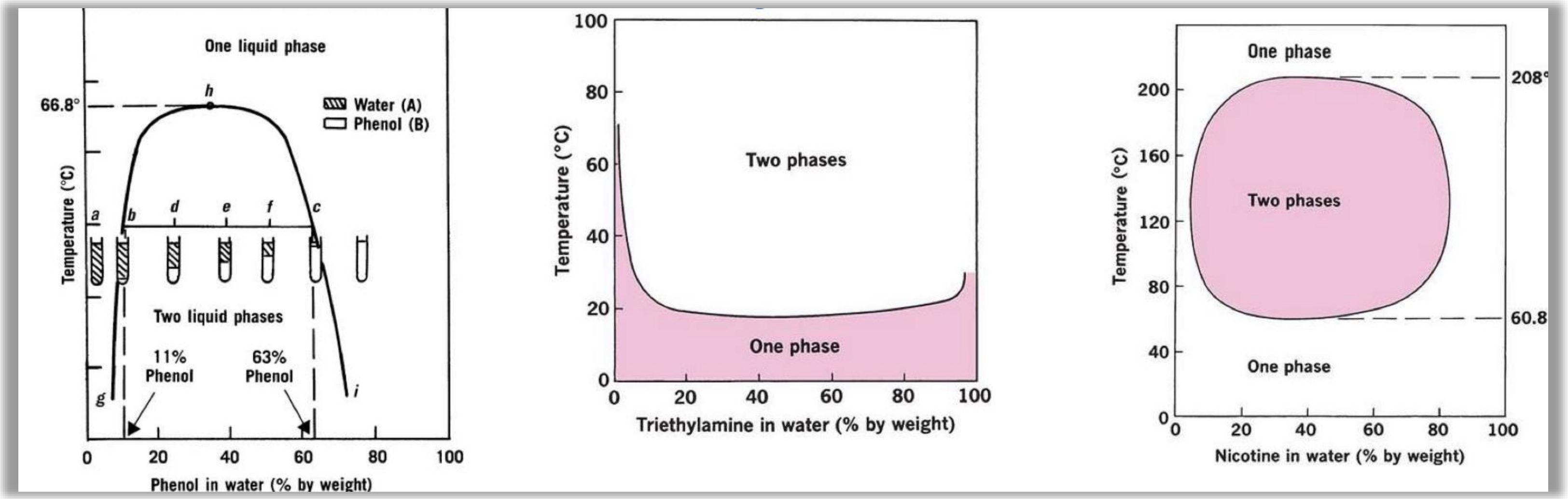
- The phase diagram is used in practice to formulate systems containing more than one component where it may be advantageous to achieve a single liquid-phase product



The Supercritical Fluid State (SCFs)

Phase diagram for a Two-component systems Containing Liquid Phases

- Phase diagram for the nicotine–water system, which has both a lower and an upper consolute temperature
- Phenol and water (partially miscible liquids): **F = C-P + 2 , F= 2-2+2 = 2**
- For two phase systems, we need to specify two variables: **temperature and concentration.**

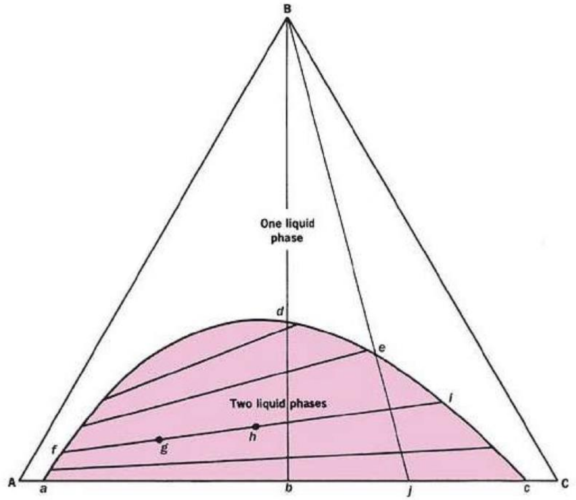


The Supercritical Fluid State (SCFs)

Phase Equilibria in Three-Component Systems

- In systems containing three components but only one phase:**F= C-P +2 , F= 3-1+2 = 4**

- We need to specify the temperature, pressure and concentration of two components of the 3-component system (only two concentrations are required because the concentration of the third component is obtained from the subtraction of the two concentrations from the total.



- If we regard the system as “condensed” and held the temperature constant, then, **F = 2** and we use a triangular graph paper for phase equilibria presentation.

Condensed Systems

- We have seen from the phase rule that in a single-component system the maximum number of degrees of freedom is two.

- This situation arises when only one phase is present

System	Number or Phases	Degrees of Freedom
Gas, liquid, or solid	1	$F = C - P + 2$ $= 1 - 1 + 2 = 2$

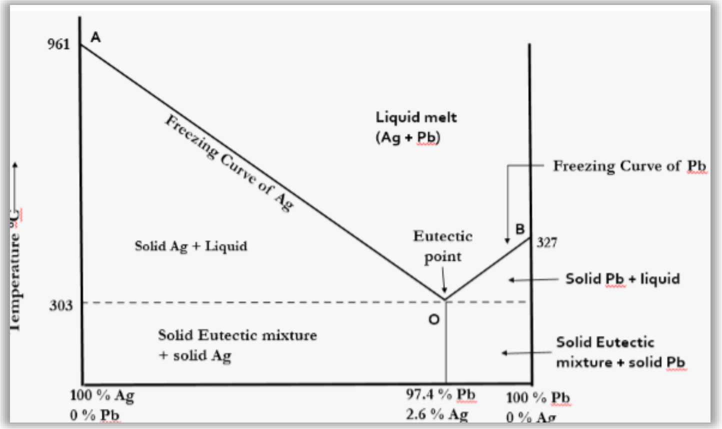
- In a two-component system, a maximum of three degrees of freedom is possible, for example, temperature, pressure, and concentration.

Condensed Systems

- Because in practice we are primarily concerned with liquid and/or solid phases in the particular system under examination, we frequently choose to disregard the vapor phase and work under normal conditions of **1 atm pressure.**

- In this manner, we reduce the number of degrees of freedom by one

- Only two variables (temperature and concentration) remain, and we are able to show the interaction of these variables using a rectangular-coordinate graph paper.



Condensed Systems

- Systems in which the vapor phase is ignored and only solid and/or liquid phases are considered (degree of freedom is reduced by one) are termed "condensed systems".
- For such cases to ignore the effect of vapor, we need to work under normal conditions of **1 atm pressure**
- Condensed systems are most appropriate for solid and liquid dosage forms, but in aerosol and gaseous systems, **vapor cannot be ignored**

Condensed Systems

- **Summary for the relationship between number of phases, number of components and degree of freedom**

Number of components	Number of phases	Degree of Freedom (F) F = C-P+2
1	1 2 3	F = 1-1+2 =2 F = 1-2+2 = 1 F = 1-3+2 = 0
2	1 2	F = 2-1+2 =3 (in practice, it is condensed to 2) F = 2-2+2 =2
3	1 2	F = 3-1+2 = 4 F = 3-2+2 =3

- As the number of phases increase, the degree of freedom decreases
- As the number of components increase, the degree of freedom increases

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Thank You !

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