



# Why?

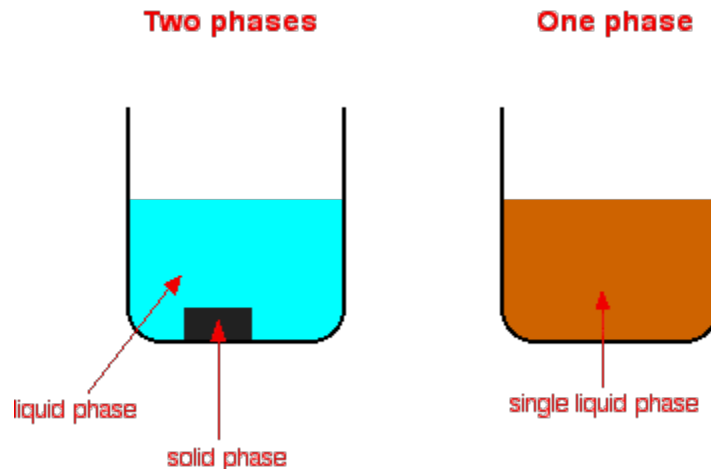
- Phase diagrams inform us about the behaviour of substances under different conditions.
- Important in the field of metallurgy, to tailor the mechanical properties of the materials for a specific application.

# Phase

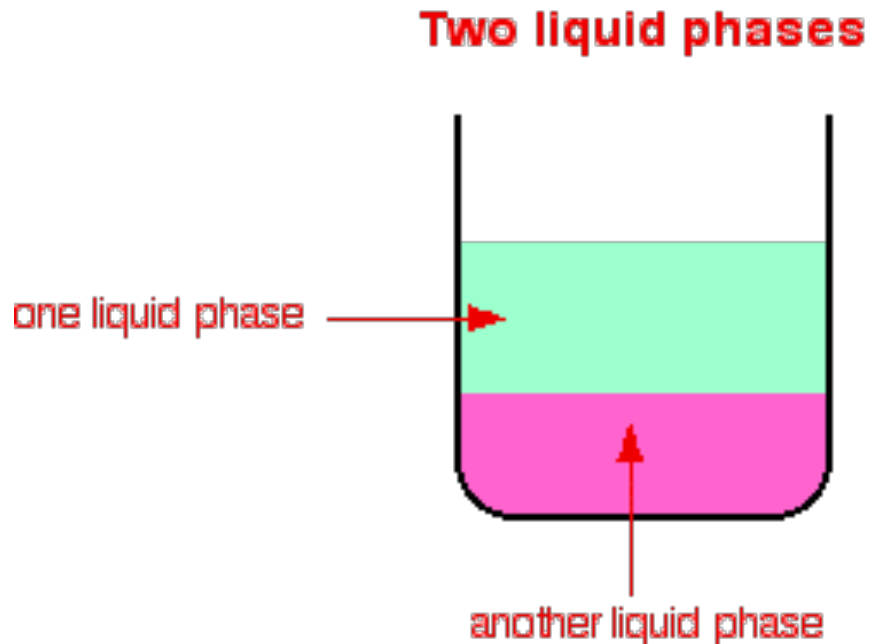
- A form of matter that is *uniform* throughout in chemical composition and physical state.
- Solid, liquid and gas phase of a substance.
- Various solid phases such as the white and black allotropes of phosphorous.
- The number of phases in system is denoted as  $P$ .
- A gas, or a mixture of gases is  $P = 1$ .
- Two fully miscible liquids also form a single phase.

# Phase

- If you look at a mixture and can see a boundary between two of the components, those substances are in different phases.
- A mixture containing a solid and a liquid consists of two phases.
- A mixture of various chemicals in a single solution consists of only one phase, because you can't see any boundary between them.



- **Phase** Vs the term **physical state** (solid, liquid or gas).
- **Phase** includes solids, liquids and gases, but is a bit more general. It can also apply to two liquids (oil and water, for example) which don't dissolve in each other. You could see the boundary between the two liquids.



# Examples of Phases



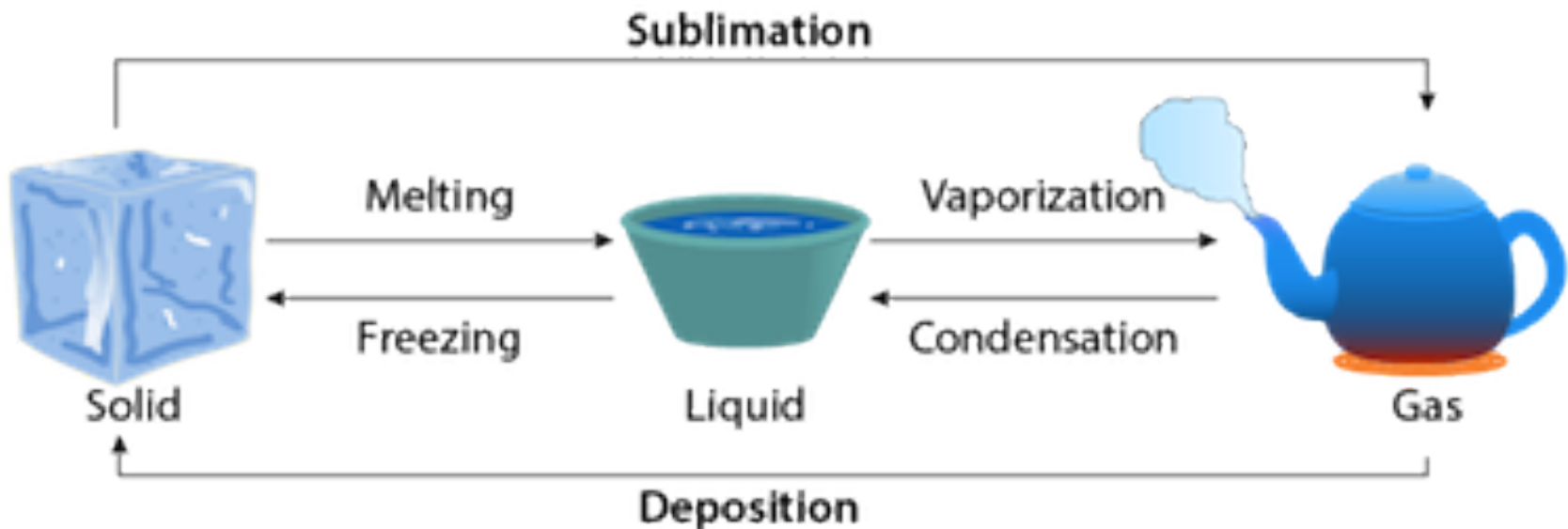
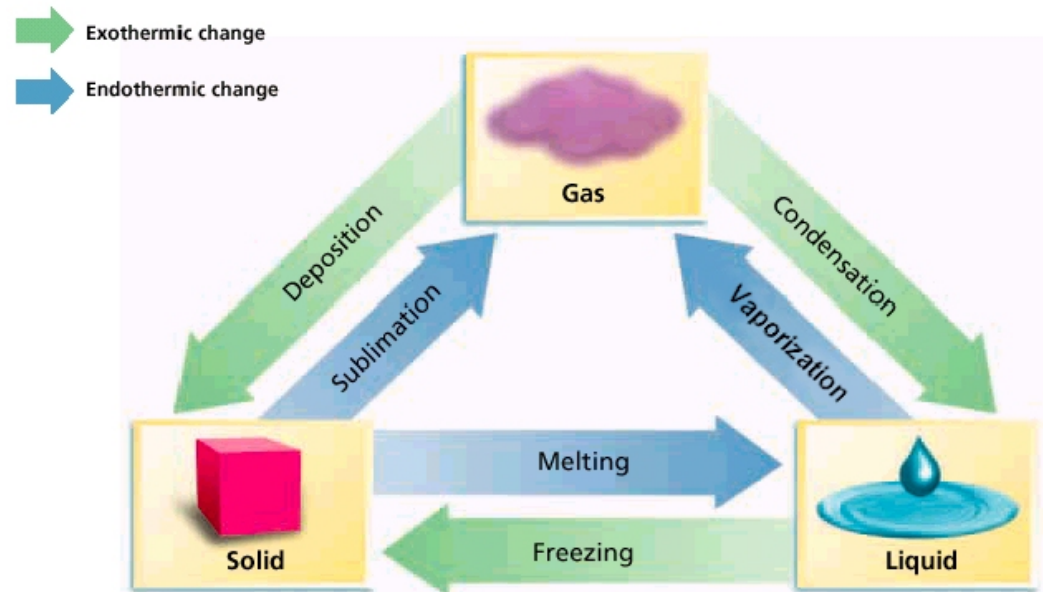
# Phase Transition



WEIGHT LOSS FOR SNOWMEN.

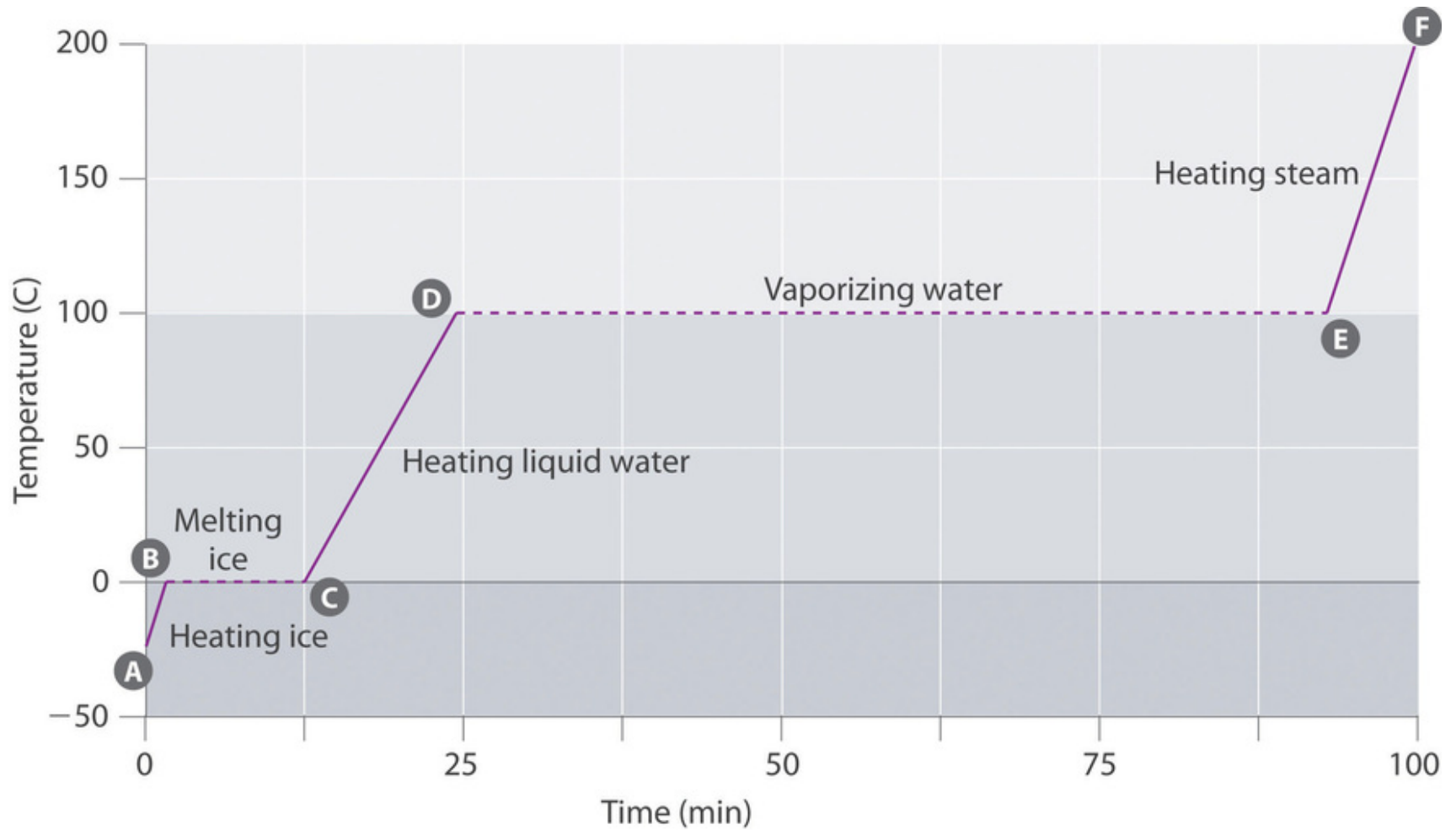
- The spontaneous conversion of one phase into another phase.
- Occurs at a characteristic temperature for a given pressure.
- Transition temperature,  $T_{\text{trs}}$ , is the temperature at which the two phases are in equilibrium.

- Vaporization
- Condensation
- Melting
- Freezing
- Sublimation
- Deposition





# Thermal Analysis

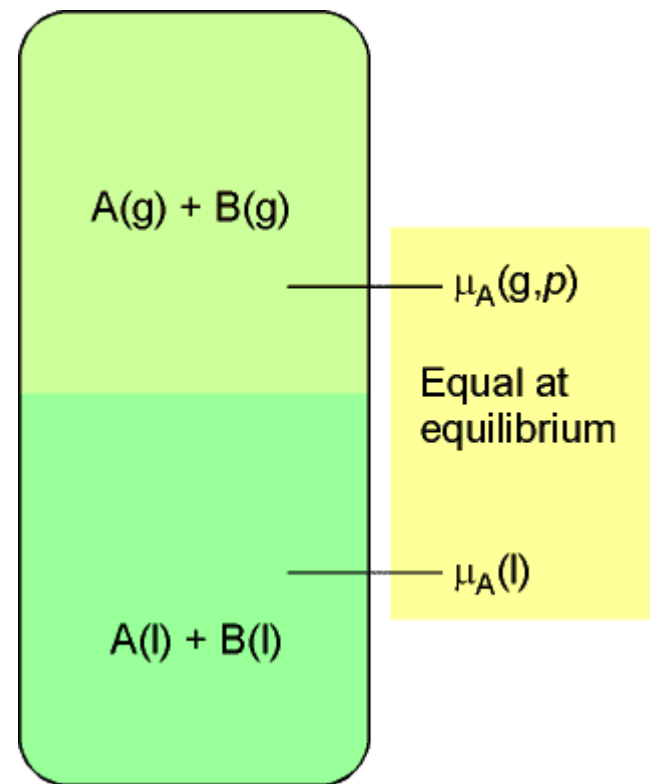




**And now, THERMODYNAMICS!**

# Thermodynamic of Phase Stability

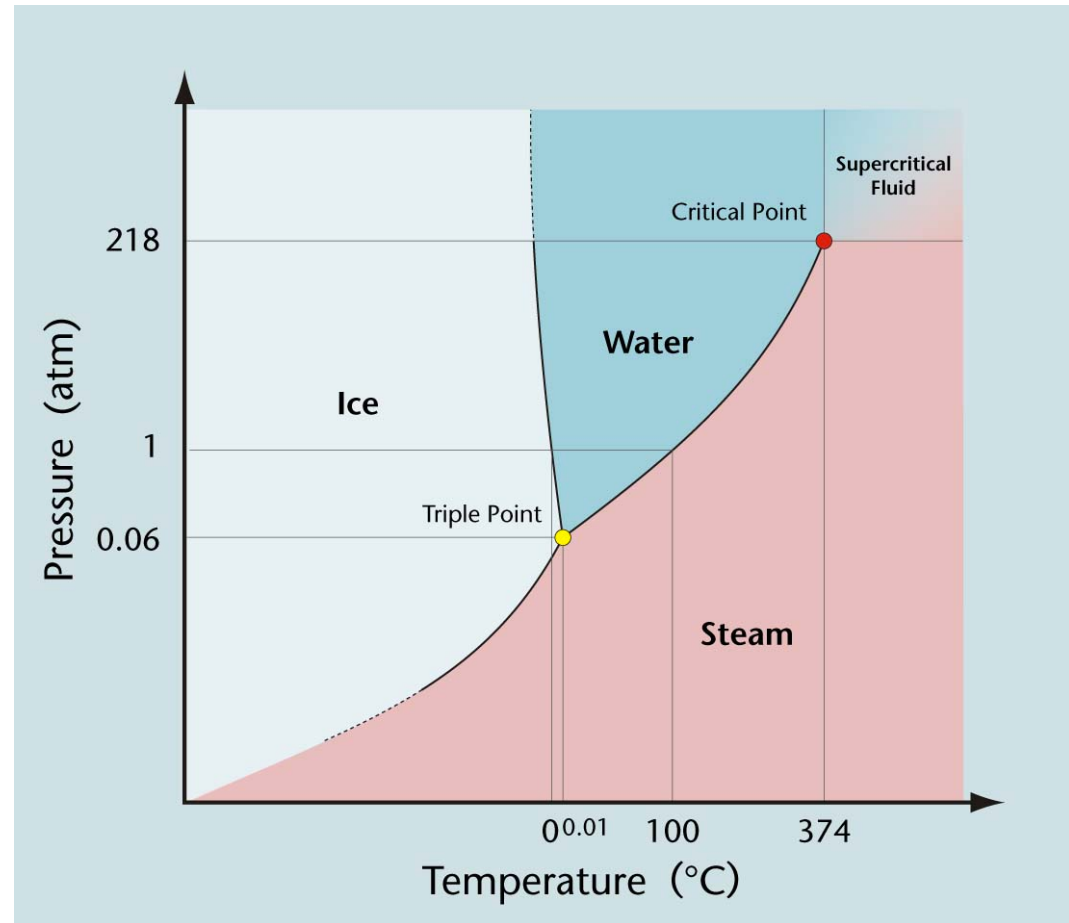
- When two or more phases are in equilibrium, the **chemical potential ( $\mu$ )** of a substance is the same in each phase and is the same at all points in each phase.
- $\mu$  is a measure of the potential that a substance has for undergoing a change in the system.
- is the rate of change of a free energy of a system with respect to the change in the number of atoms or molecules of the species that are added to the system.



# Phase Diagram

**Phase Diagram:** shows the regions of pressure and temperature at which its various phases are thermodynamically stable.

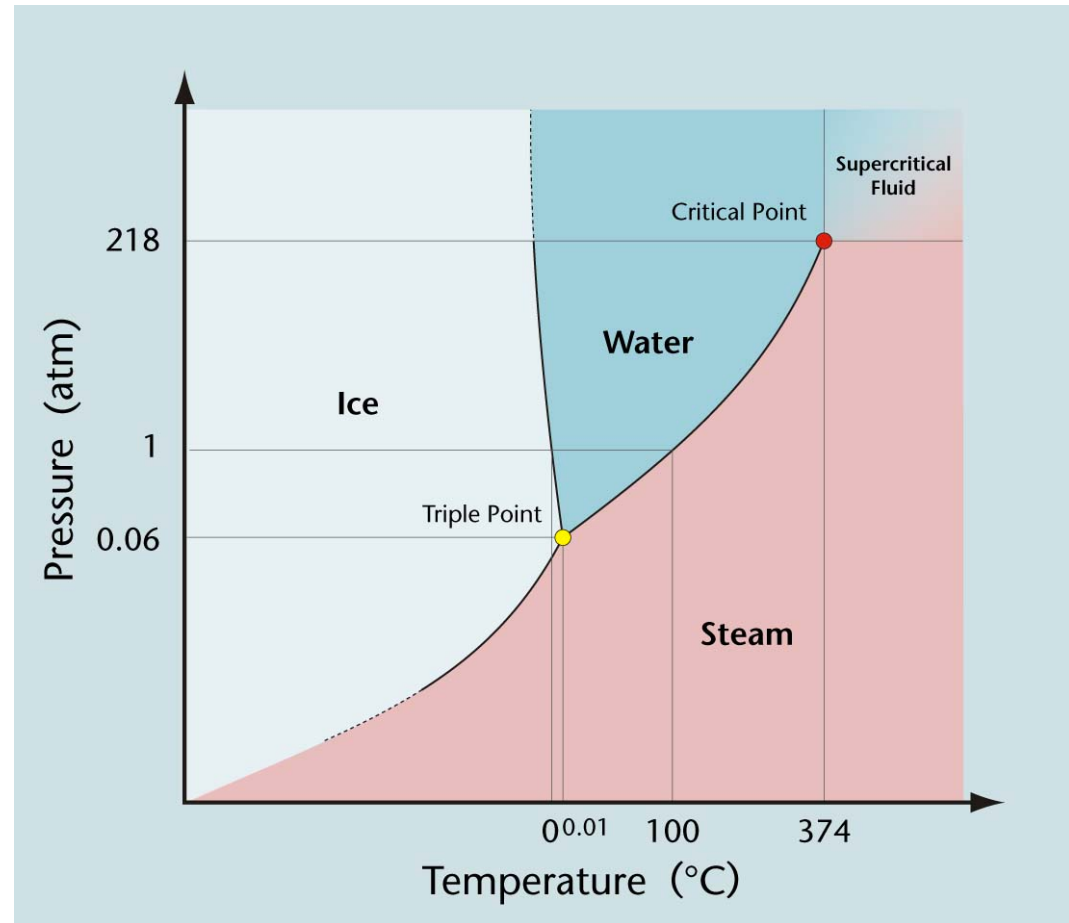
**Phase Boundary:** a boundary between regions, shows the values of P and T at which two phases coexist in equilibrium.



# Phase Diagram

Triple Point: all three phases can exist.

Critical Temperature: maximum temperature where a substance can exist as a liquid.



# PHASE RULES

Also known as Gibbs phase  
rule

$$F = C - P + 2$$

Degree of  
freedom or  
the number of  
independent  
variables

Number of  
component

The  
number of  
phase

2 variables  
(temperature  
and pressure)



COMPONENTS

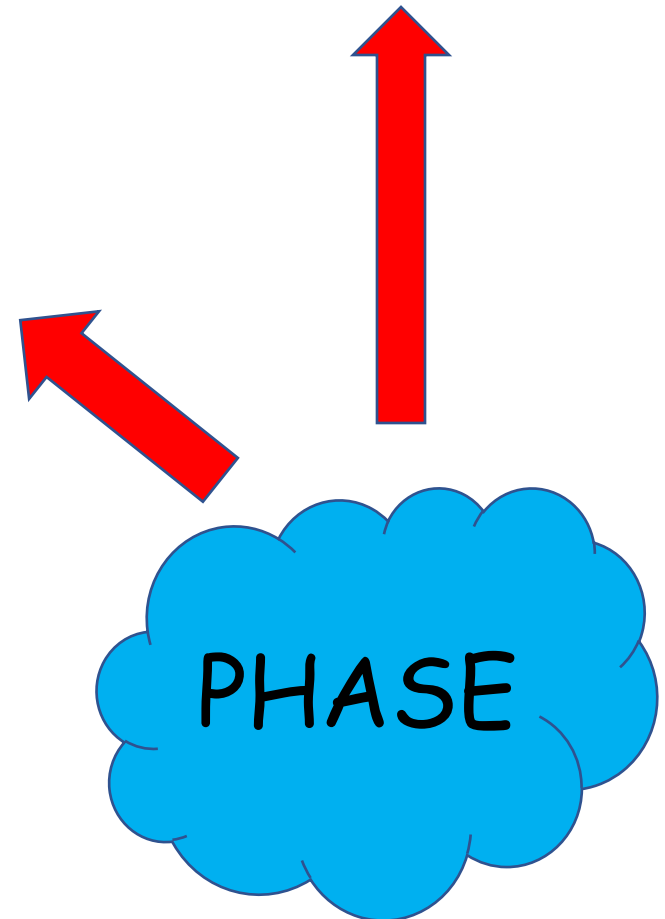
PHASE

DEFINITION

DEGREE OF FREEDOM

- 1) The mixture of ice and water = have two phase which is solid and liquid
- 2) The mixture of oxygen gas and nitrogen gas = have one phase which is gas phase (the system is homogen)
- 3) The mixture of oil and water = have 2 same phase(liquid). Oil and water are not homogen and have the boundaries to separate both phase
- 4)  $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$   
= 3 phase (2 solid, 1 gas)

- A chemically and structurally homogeneous portion of material
- Separated with other parts of the system





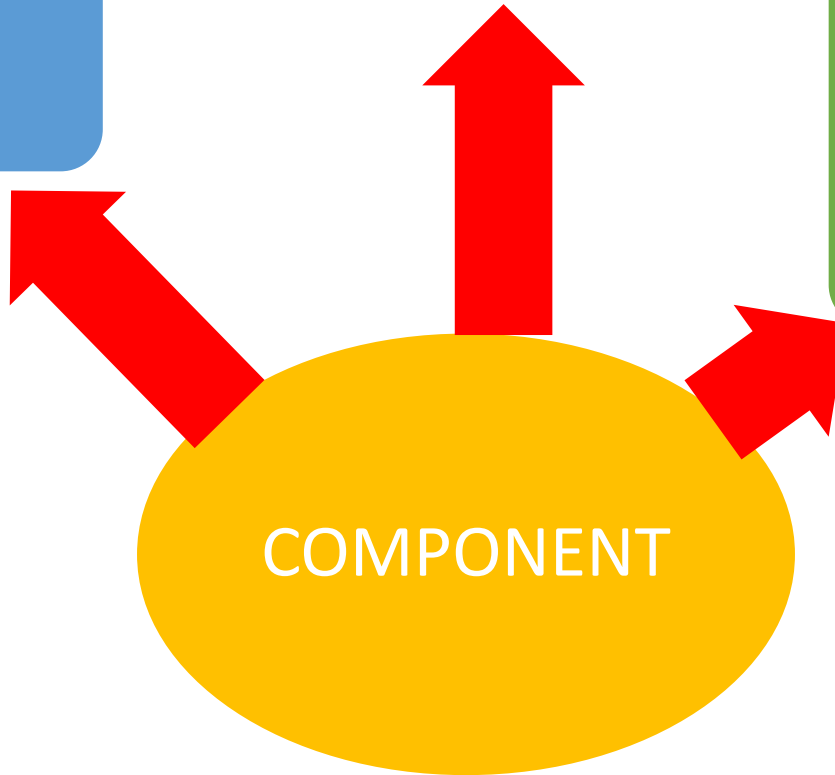
The number of chemical species that can explain the composition of all phase in a system

OR

The least number of different substances required to describe the composition of all phases in the system

- 1) water,  $\text{CO}_2$  = one component
- 2) Aqueous solution of potassium nitrate = 2 system component because have potassium nitrate salt and water.

COMPONENT



# DEGREE OF FREEDOM (F)

The number of variables that may be changed independently without causing the appearance of a new phase or disappearance of an existing phase

TYPES

UNIVARIANT

BIVARIANT

## EXAMPLES



Calculate the degree of freedom (F)

$$\begin{aligned} F &= C - P + 2 \\ &= 2 - 3 + 2 \\ &= 1 \text{ (univariant)} \end{aligned}$$

Means: only one variable, either temperature or pressure can be changed independently

The number of components is not always easy to determine at first glance, and it may require careful examination of the physical conditions of the system at equilibrium

# Derivation of Phase Rule

Balancing of **FIXED PARAMETERS** and **SYSTEM VARIABLES**

**HOW MANY VARIABLES ARE THERE IN A CHEMICAL SYSTEM?**

- Simplistically, “3”,  
    Pressure, Temperature, Composition,
- BUT, for more than one phase, what is the **TOTAL** number of variables?

# Assign C components between P phases

- For each Phase, composition is defined by  $(C-1)$  concentration terms.
- For ALL Phases in the system,  $P(C-1)$  = the number of concentration terms.
- Can also vary Pressure & Temperature, or  $P + T$ , which = 2 more variables.
- TOTAL NUMBER OF VARIABLES =  
 $P(C-1) + 2$

- Since the system is in equilibrium, BY DEFINITION, we have already implicitly defined some of the variables.
- So, if system is “in equilibrium”, and if there is NO NET CHANGE in the net “amounts” of chemicals moving between phases that are in dynamic equilibrium,
  - $A\mu_\alpha = A\mu_\beta = A\mu_\gamma \dots = A\mu_\infty$
  - $B\mu_\alpha = B\mu_\beta = B\mu_\gamma \dots = B\mu_\infty$
  - $B\mu_\alpha = B\mu_\beta = B\mu_\gamma \dots = B\mu_\infty$
- The chemical potential or the chemical flux of a given chemical must be the same in all phases coexisting at equilibrium-No NET Change!

For EACH Component, there are (P-1) independent equations relating the chemical potential,  $\mu$ , of that component in ALL of the Phases.

There are C(P-1) independent equations.

Thus, we “FIX” C(P-1) variables when we stipulate that the system is in equilibrium.

**F = number of “Freedom” factors**

$$\begin{array}{ccccccc} \mathbf{F} & = & \mathbf{[P(C-1) + 2]} & - & \mathbf{[C(P-1)]} & & = & \mathbf{C - P + 2} \\ & & \text{TOTAL} & & \text{AUTOMATICALLY FIXED} & & & \end{array}$$

Standard phase diagram for water (H<sub>2</sub>O)

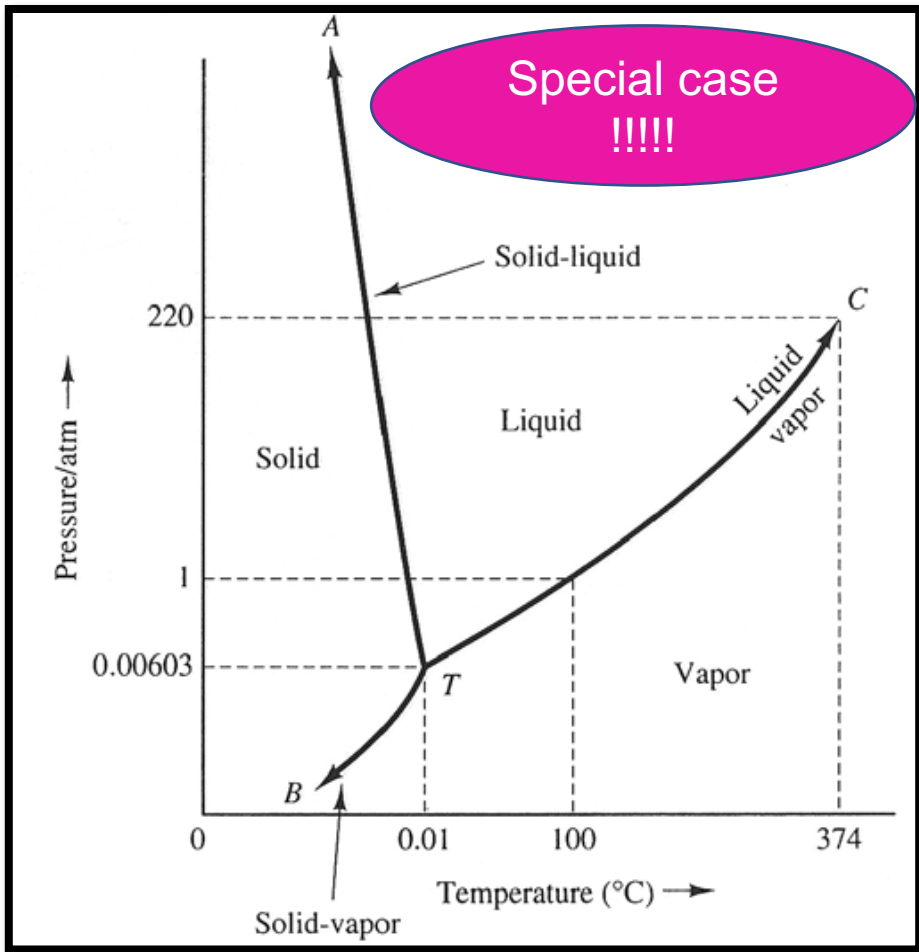


ONE COMPONENT  
SYSTEM



Standard phase diagram for carbon dioxide  
(CO<sub>2</sub>)

Standard phase diagram for water (H<sub>2</sub>O)



TA curve = known as melting point or freezing point

Represent the equilibrium between ice and liquid

Has a negative slope

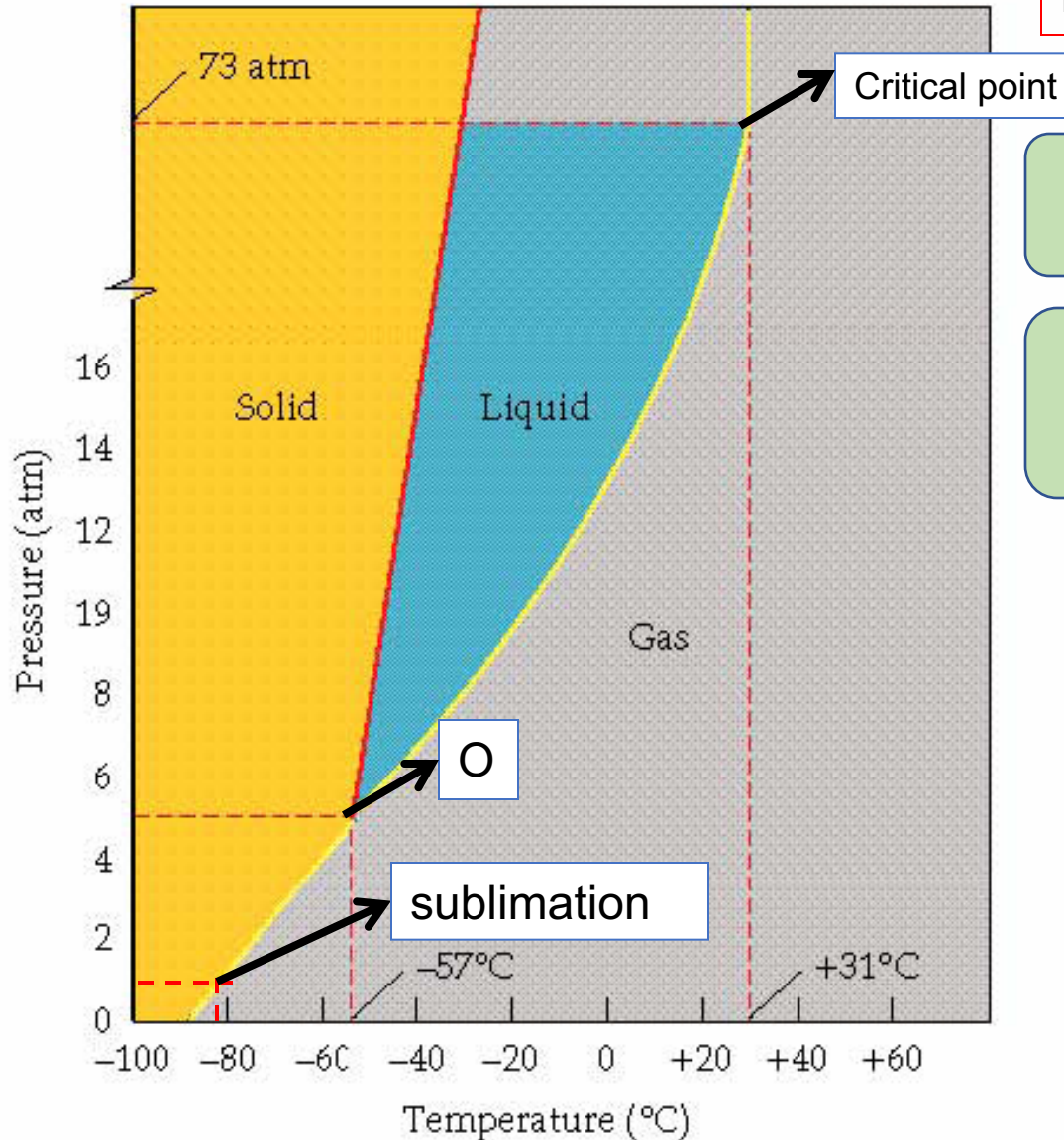
Water as the liquid is denser than the solid (ice floats on water).

That means that an increase of pressure favors the formation of liquid and that the melting point of water falls with increasing pressure.

This unique properties of water is due to the network of hydrogen bonding in ice is more extensive than in liquid



## Standard phase diagram for carbon dioxide (CO<sub>2</sub>)



The point O is the triple point for CO<sub>2</sub> (at 5.1 atm, -57° C). So, CO<sub>2</sub> solid can't be changed to liquid form at 1 atm.

Has a positive slope

So, it shows that the increase of pressure will increase the melting point for CO<sub>2</sub> solid