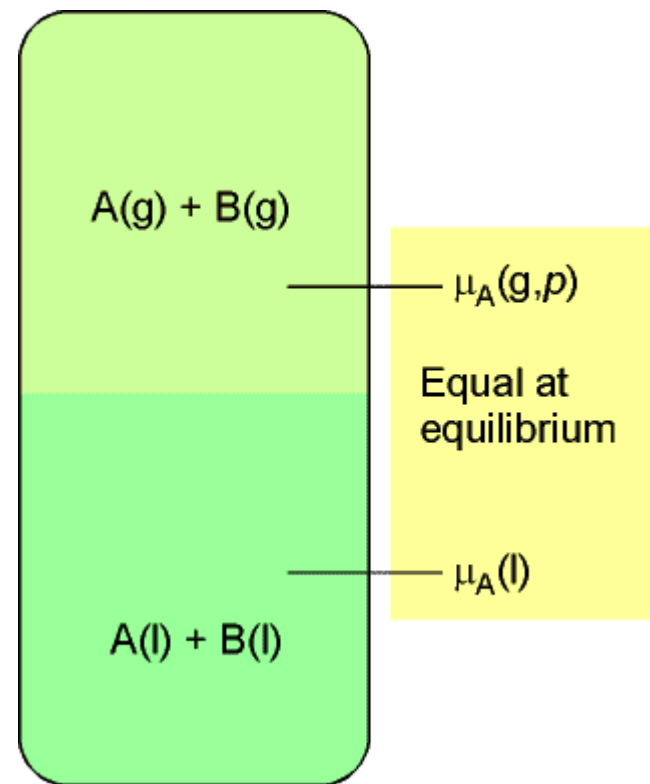


# Thermodynamic of Phase Stability

- 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.



# 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**

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

- Condensed System do not have gas phase and the effect of pressure is negligible.
- Only one variable is required to define the system completely then phase rule at constant pressure is defined as

$$F = C - P + 1$$

- It is also known as **Condensed or Reduced Phase Rule.**

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

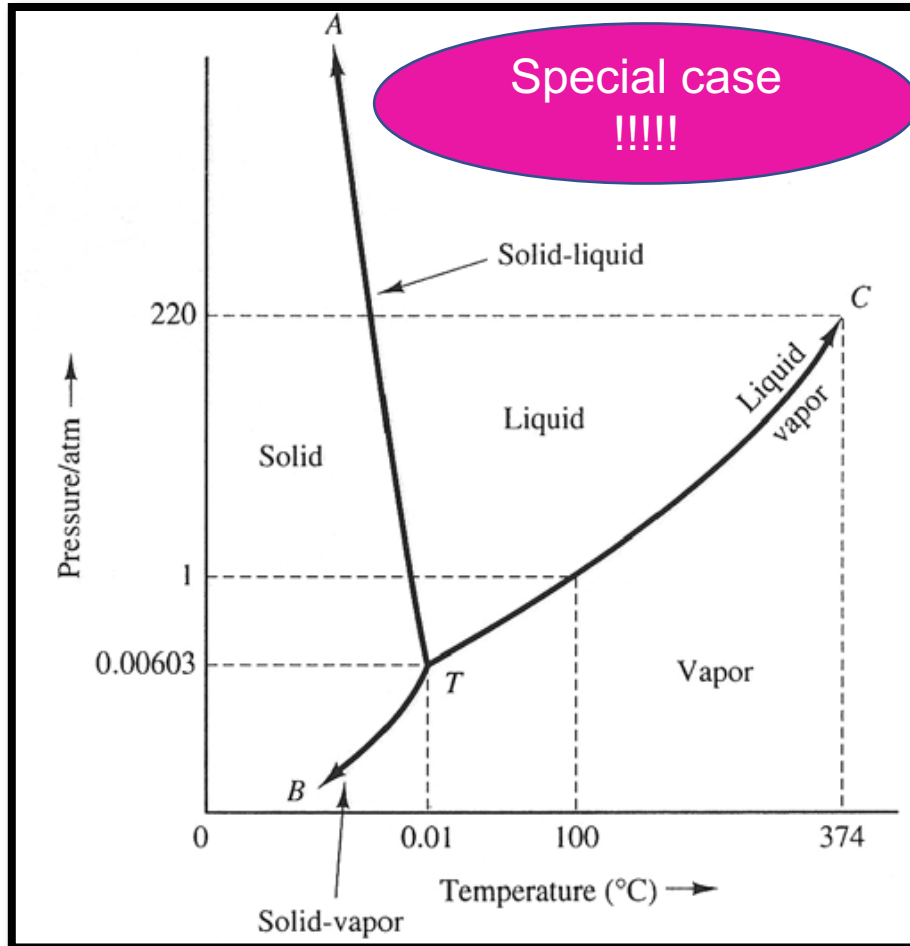


ONE COMPONENT  
SYSTEM



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

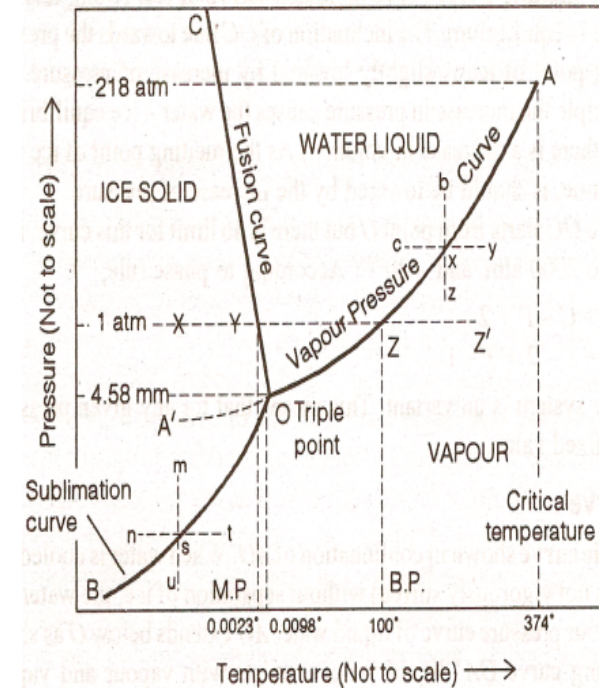
Water as the liquid is denser than the solid (ice floats on water).

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



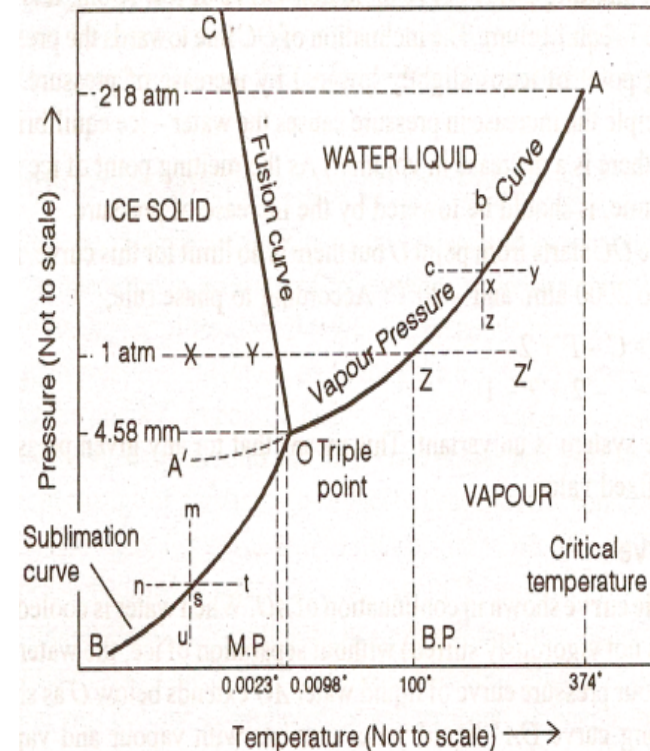
- ❑ **Vapour pressure curve** of water
- ❑ Divides liquid and vapour
- ❑ Represent the equilibrium between **liquid water and vapour**.
- ❑ It starts from the point 'O'
- ❑ Ends at critical temperature (374°C)
- ❑ Beyond A the two phases merge into each other.



### Along the Curve OA:

No. of Component = 1,                      No. of Phases = 2  
Degree of Freedom (F)                      =  $3 - P = 3 - 2 = 1$   
Hence the system is univariant.

- ✓ Sublimation curve of ice.
- ✓ Divides Ice and Vapour
- ✓ Represent the equilibrium between **Ice and vapour**
- ✓ This curve starts from point 'O'
- ✓ Extend upto absolute zero ( $-273^{\circ}\text{C}$ ).



### Along the Curve OB:

No. of Component = 1,

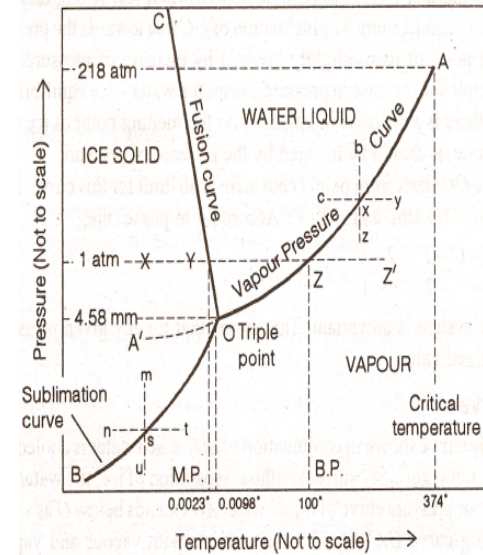
Degree of Freedom (F)

Hence the system is univariant.

No. of Phases = 2

$= 3 - P = 3 - 2 = 1$

- ✓ Freezing/melting curve.
- ✓ Divides Ice and water
- ✓ Represent equilibrium between **Ice and Water**
- ✓ This curve starts from point 'O'
- ✓ ends upto point 'C' (2000 atmospheres and -20°C).
- ✓ The Curve OC is inclined towards pressure axis.  
**melting point of Ice is lowered with the increase in pressure.**

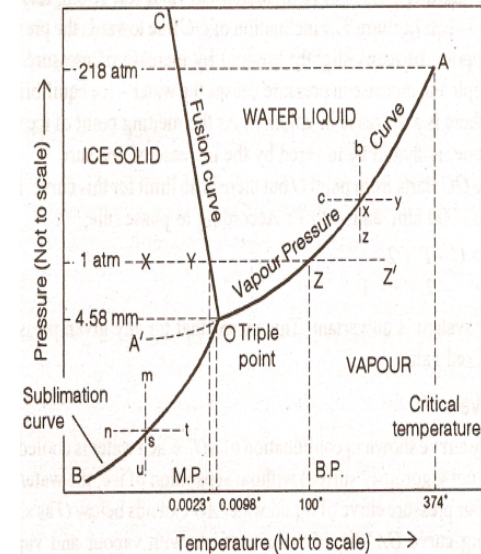


### Along the Curve OC:

No. of Component = 1,                      No. of Phases = 2  
Degree of Freedom (F)                      =  $3 - P = 3 - 2 = 1$   
Hence the system is univariant.

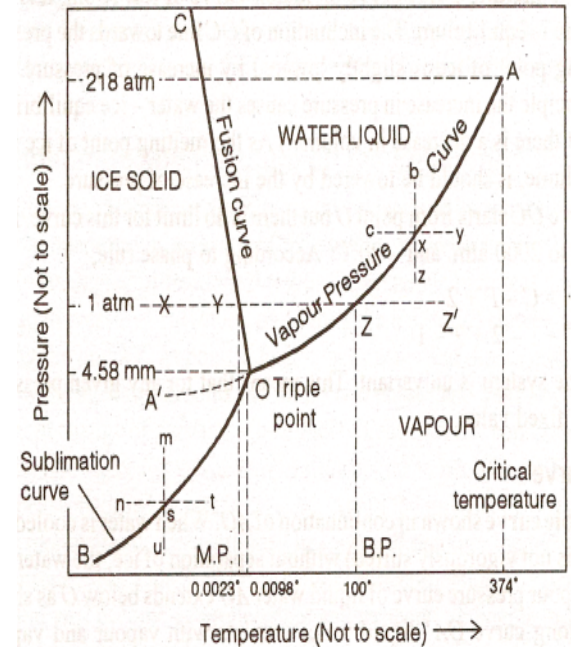
The areas represents Three phases of Water.

BOC (Solid),  
COA (Liquid) and  
AOB (Vapour) Three phases of Water.



No. of Component (C) = 1  
No. of Phases (P) = 1  
Degree of Freedom (F) =  $3 - P = 3 - 1 = 2$   
Hence the system is bivariant.

- ✓ At triple point all the **three phases** co-exist in **equilibrium**.
- ✓ curve OA, OB and OC meet.
- ✓ **0.0098°C** and 0.006 atm. or **4.58 mm Hg**



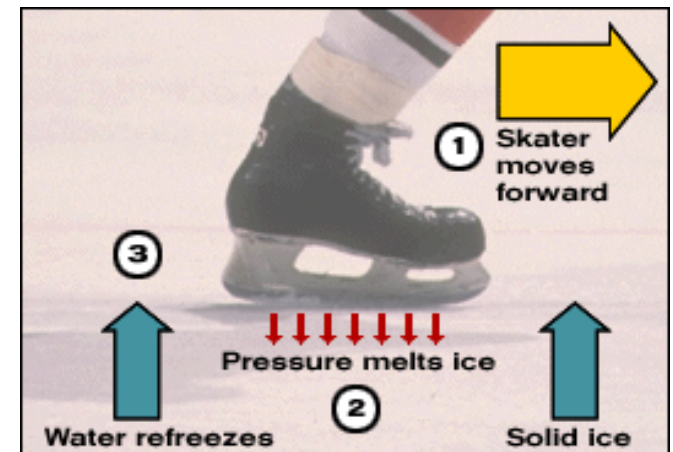
$$\begin{aligned} \text{No. of Component} &= 1 \\ \text{Degree of Freedom (F)} &= 3 - P = 3 - 3 = 0 \end{aligned}$$

Hence the system is invariant at the triple point 'O' (0.0098°C and 0.006 atm. or 4.58 mm Hg)

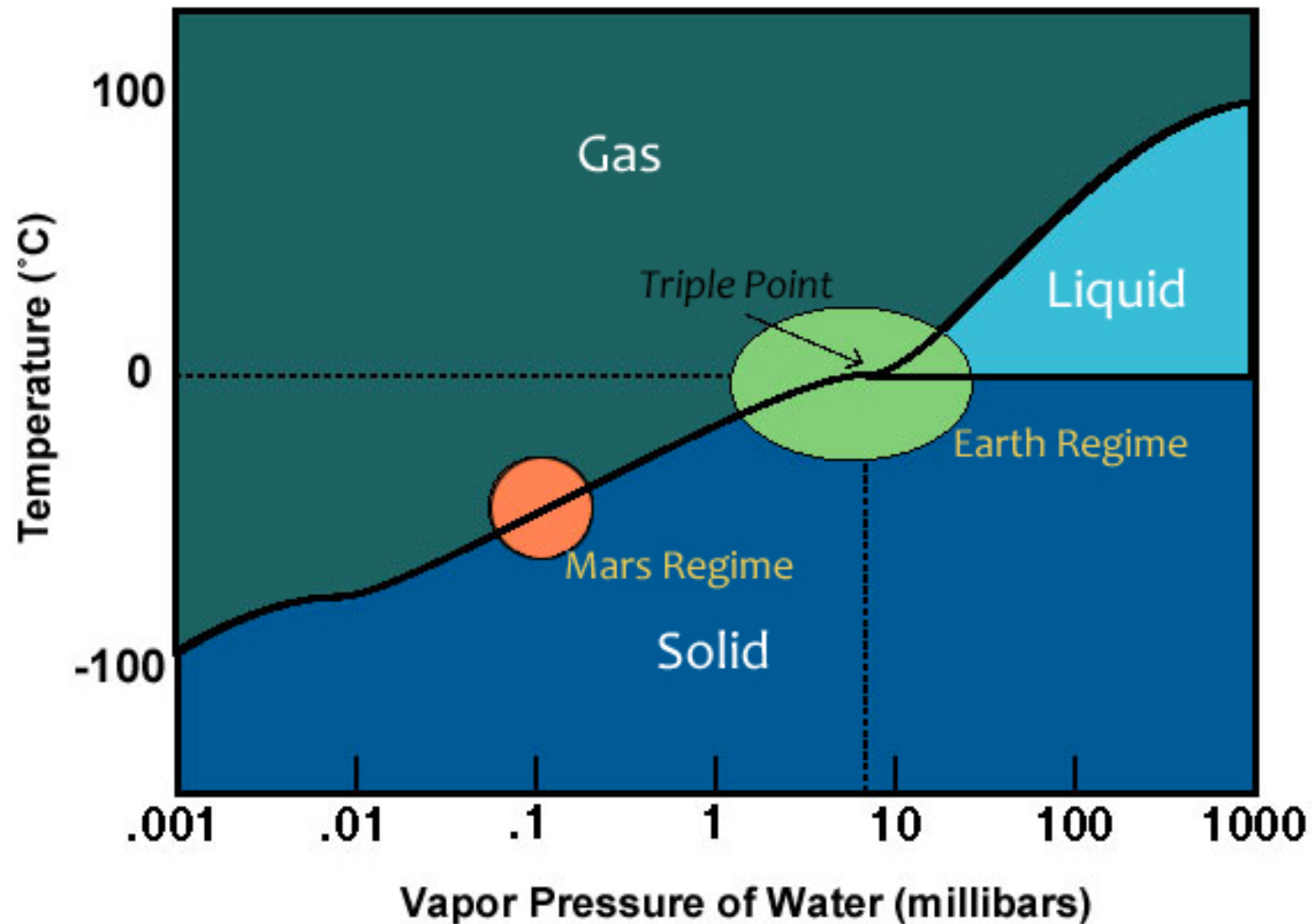




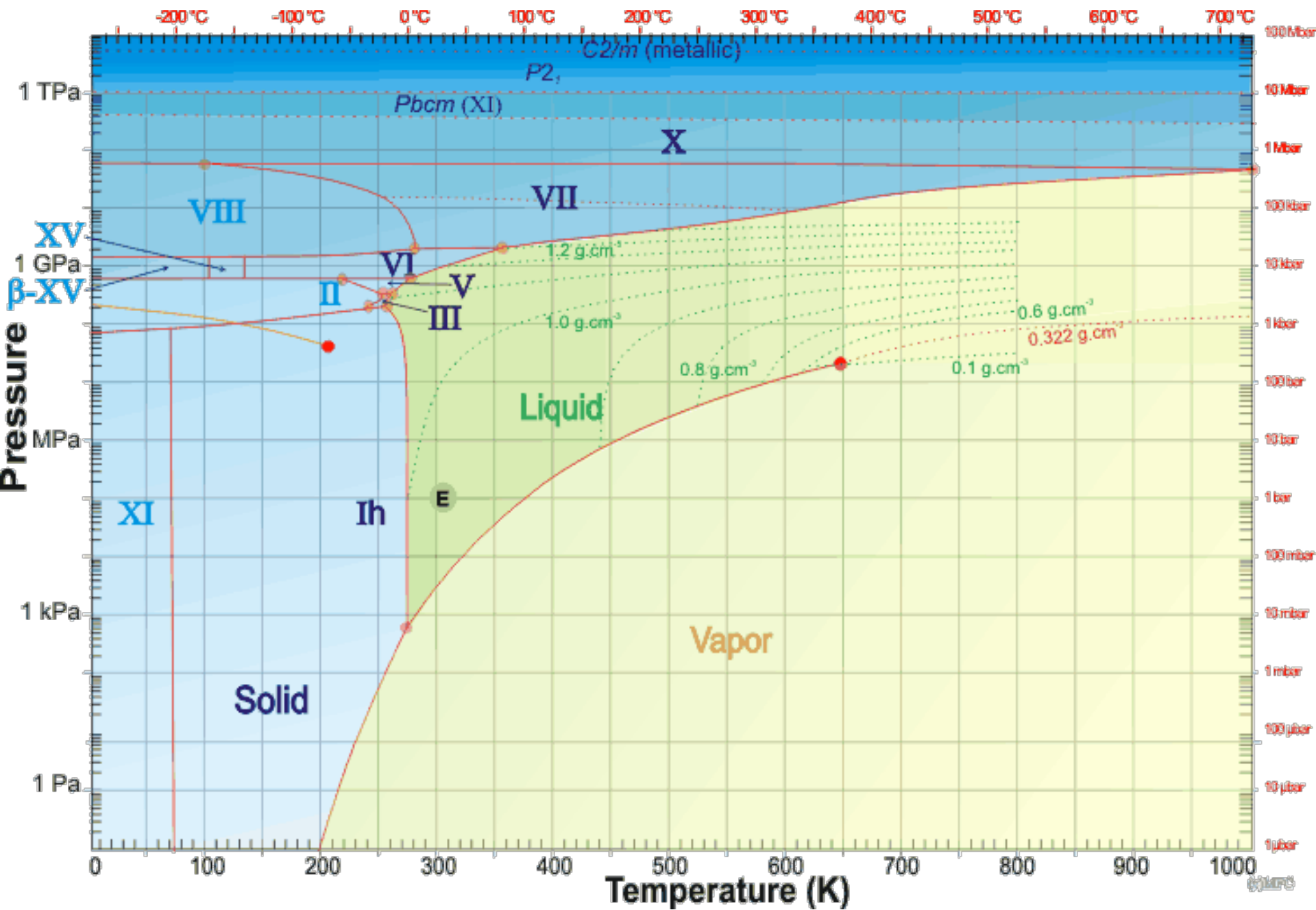
## Application of Water phase diagram



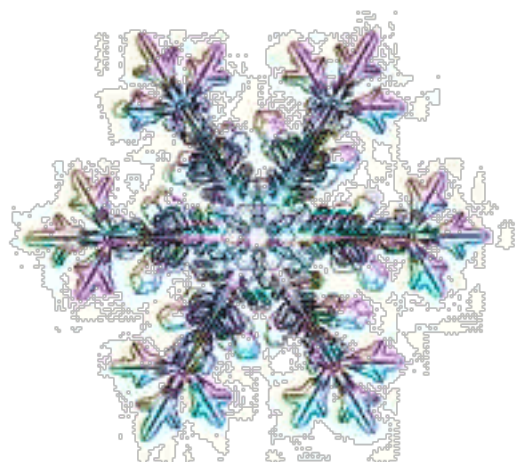
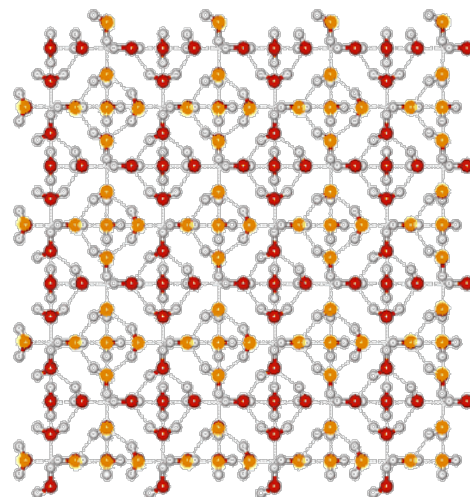
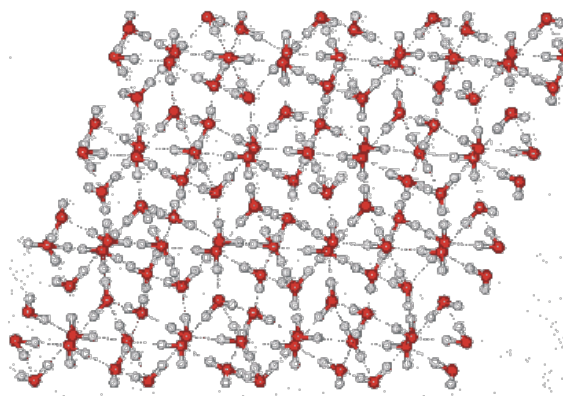
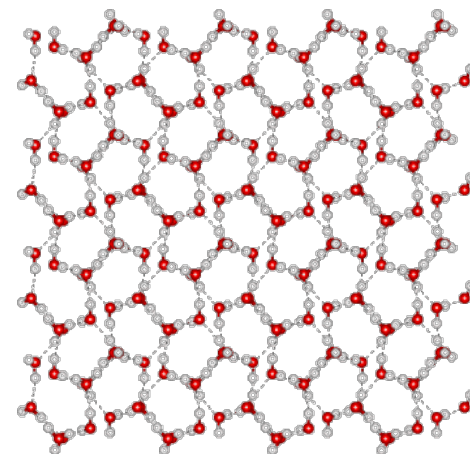
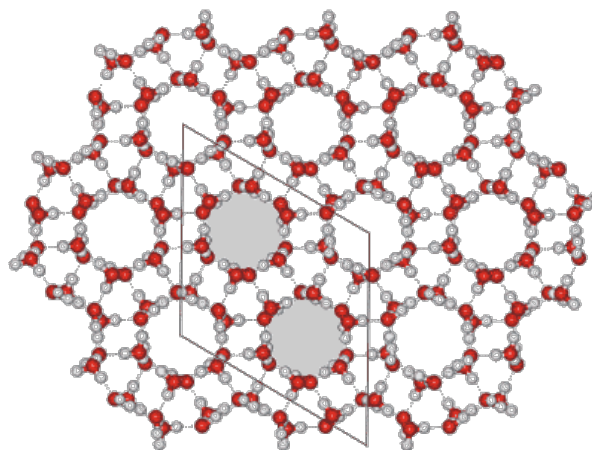
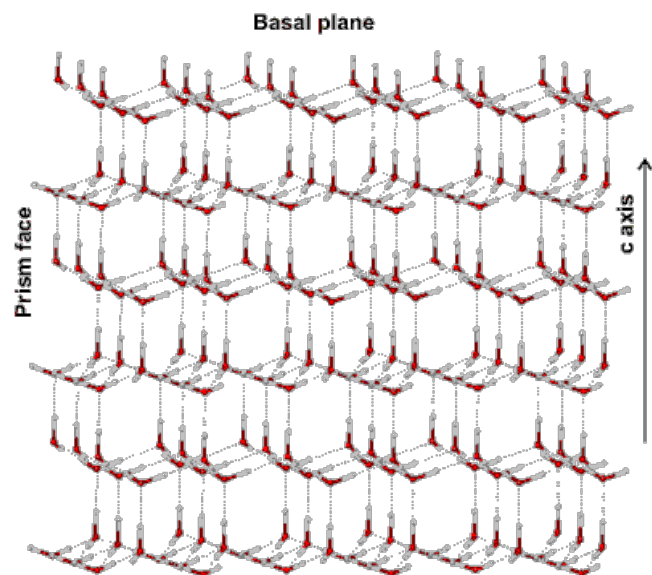
## Application of Water phase diagram



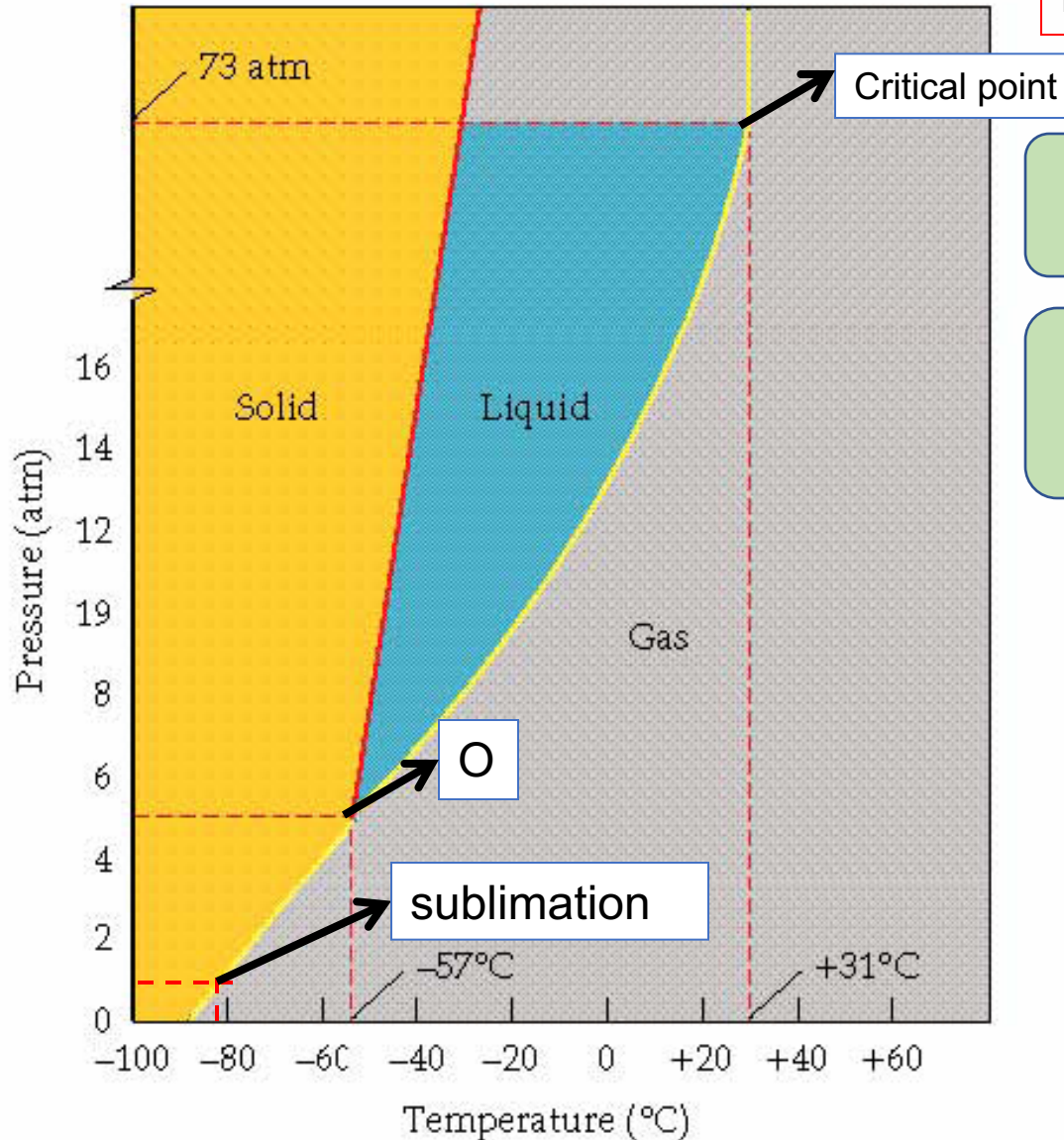
Water can exist on Mars as only a solid or a gas.







## 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

Curve AB

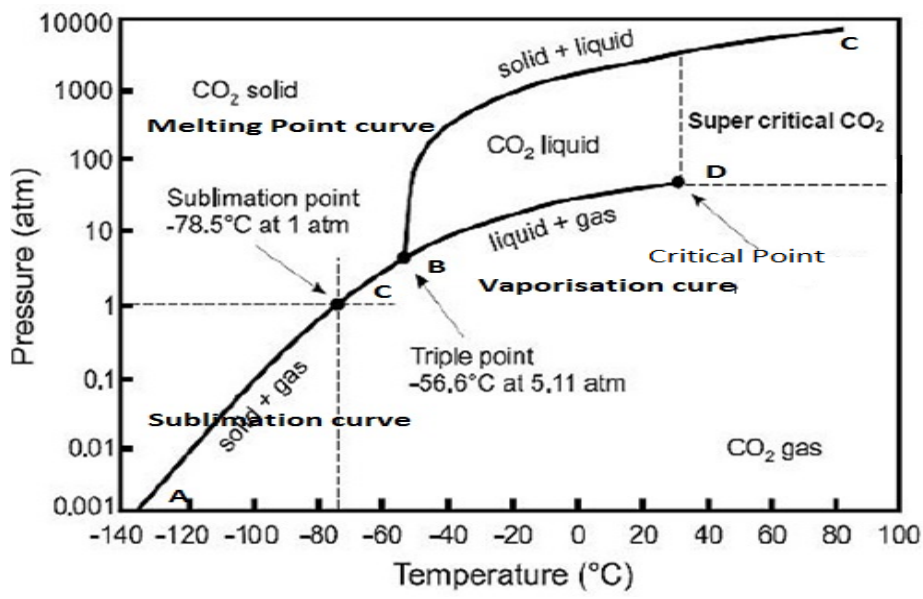
- ✓ Curve AB is the sublimation curve
- ✓ Solid CO<sub>2</sub> is in equilibrium with Gas CO<sub>2</sub>.
- ✓ Point 'C' is known as Sublimation point
- ✓ Temperature -78.5°C, Pressure 1 atm.

Curve BD

- ✓ Curve BD is the vaporisation curve
- ✓ Liquid CO<sub>2</sub> is in equilibrium with Gas CO<sub>2</sub>.
- ✓ This curve starts from Triple Point 'B'
- ✓ ends Critical point (Temperature 31.1°C, Pressure 72.8 atm.)

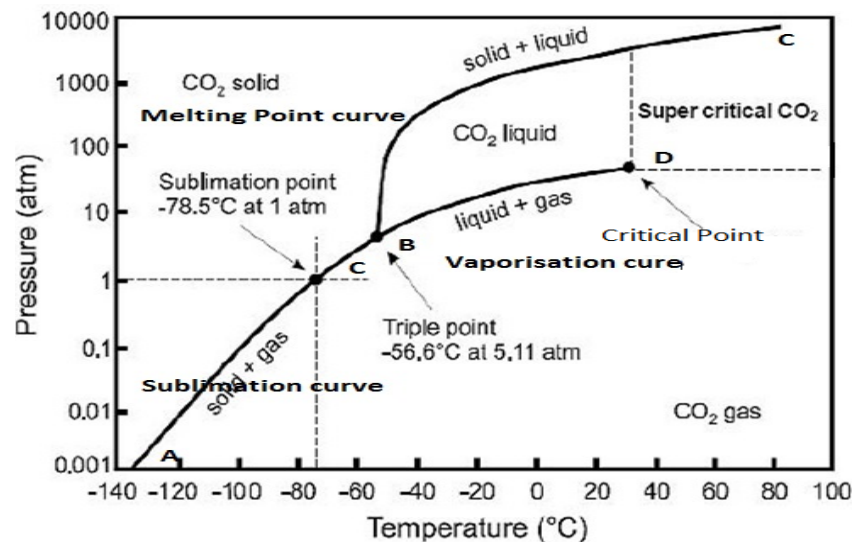
Curve BC

- ✓ Curve BC is the fusion curve
- ✓ Solid CO<sub>2</sub> is in equilibrium with Liquid CO<sub>2</sub>.
- ✓ This curve starts from Triple Point 'B' and ends at Point 'C'.



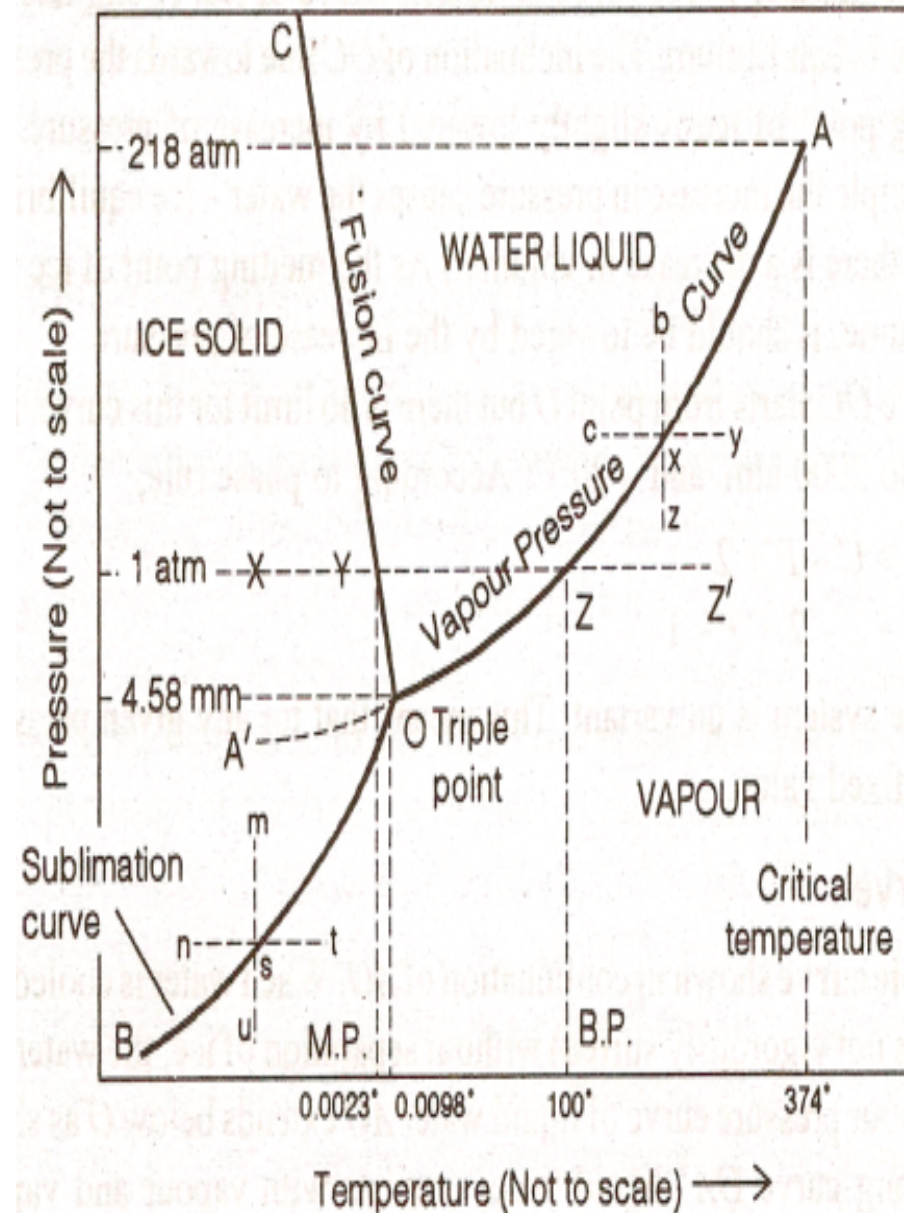
- ✓ At triple point 'B' all the three phases of CO<sub>2</sub> co-exist in equilibrium
- ✓ curve AB, BD and BC meet.
- ✓ Solid CO<sub>2</sub> = Liquid CO<sub>2</sub> = Gas CO<sub>2</sub>
- ✓ So, No. of Phases = 3

Hence the system is invariant at the triple point 'B' (-56.6°C and 5.11 atm.)

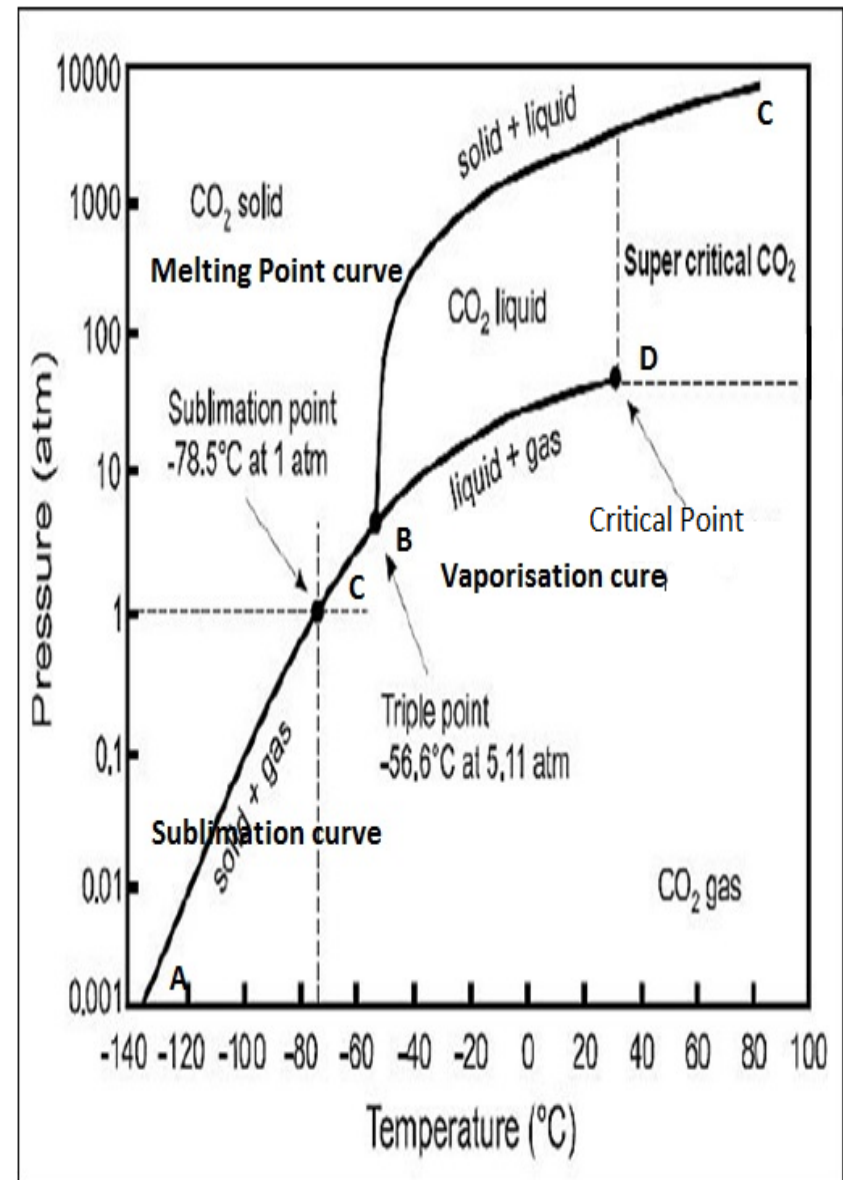




## Phase Diagram of H<sub>2</sub>O



## Phase Diagram of CO<sub>2</sub>



- ✓ In  $\text{CO}_2$  phase diagram the melting point curve slopes away from the pressure axis.
- ✓ Solid  $\text{CO}_2$  can exist in equilibrium with Liquid  $\text{CO}_2$  only at high pressure equal to 5.11 atm. While in  $\text{H}_2\text{O}$  system Ice and Water can exist in equilibrium at low pressure.
- ✓ Vapour pressure of Solid  $\text{CO}_2$  even at low temperature is very high and many time higher than that of Ice.
- ✓ At low atmospheric pressure  $\text{CO}_2$  gas can be directly solidify without attending the liquid phase just by cooling to  $-78.5^\circ\text{C}$ , this is why **the Solid  $\text{CO}_2$  is known as Dry Ice.**

# 1 - C Systems

## The system $\text{SiO}_2$

Two environmental variables: P and T

One component =  $\text{SiO}_2$

7 different phases

Point **A**:

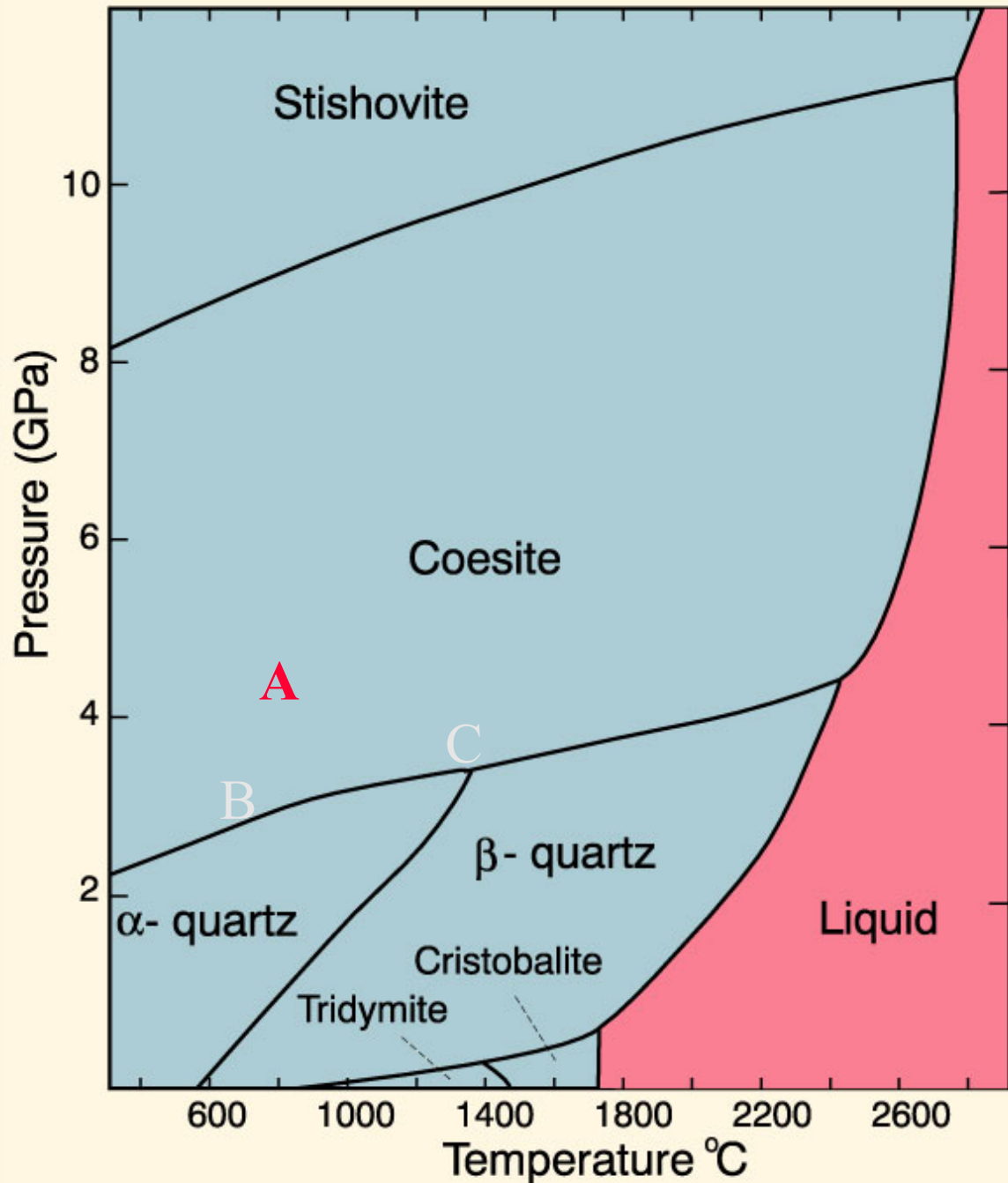
$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

Divariant area

= two variables to define a position in the coesite stability field



# 1 - C Systems

## 1. The system $\text{SiO}_2$

Two environmental variables: P and T

One component =  $\text{SiO}_2$

7 different phases

Point **B**:

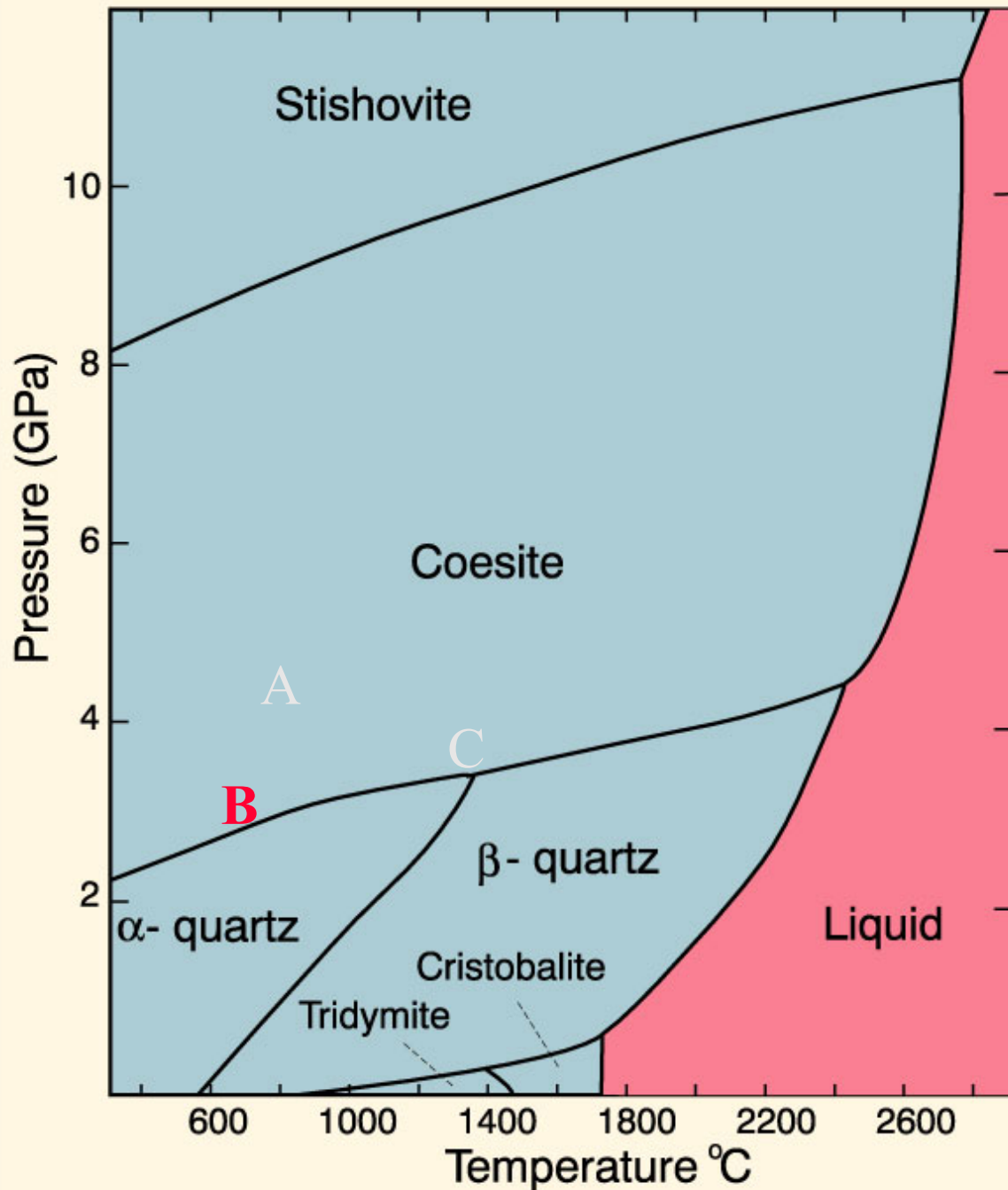
$$F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

Univariant area =

one variable to define a position on the coesite -  $\alpha$ -quartz phase boundary





# 1 - C Systems

## 1. The system $\text{SiO}_2$

Two environmental variables: P and T

One component =  $\text{SiO}_2$

7 different phases

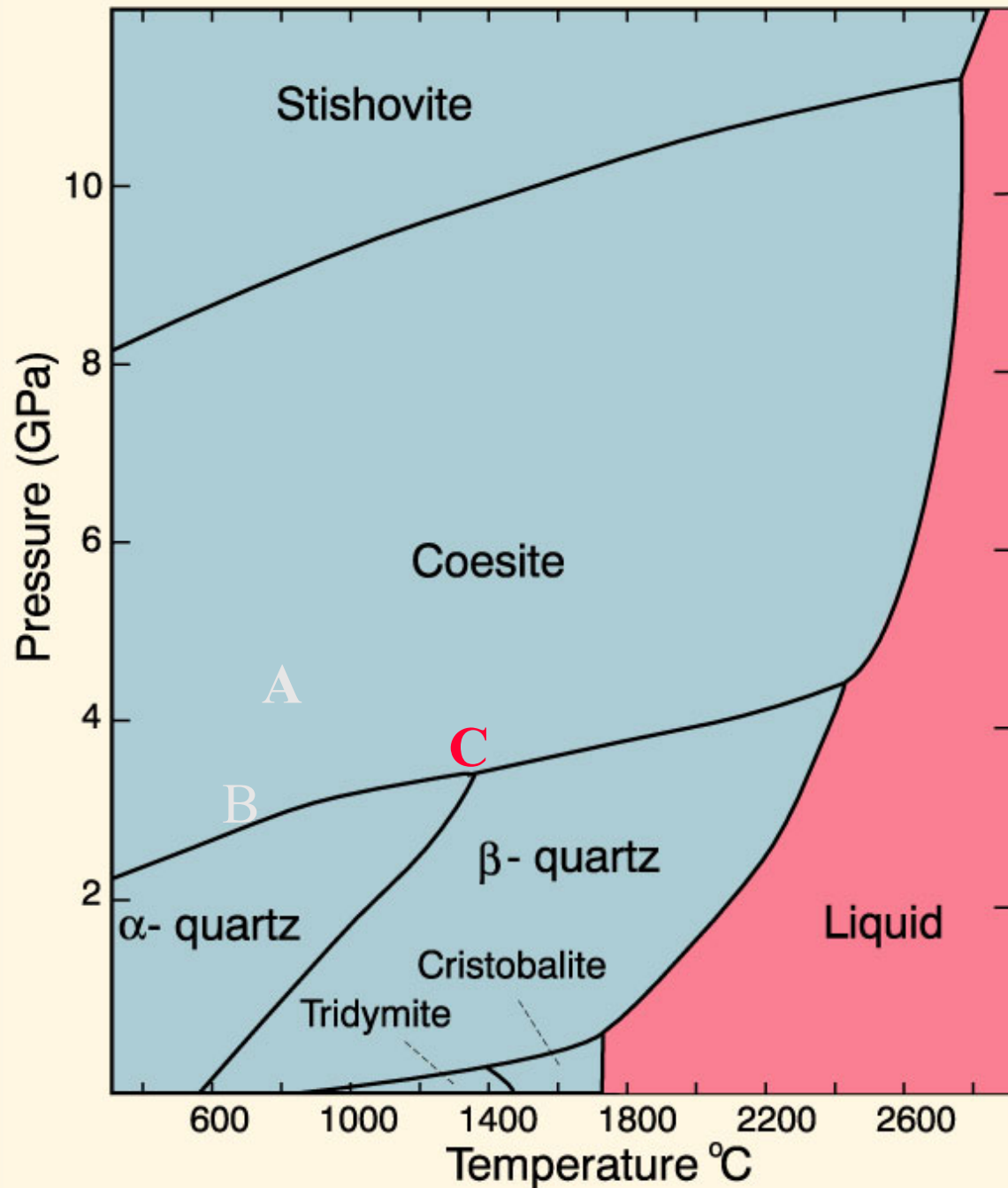
Point **C**:

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$F = 0$$

**invariant** = Triple point  
do not need any variable  
to define equilibrium  
between coesite,  
a- and b-quartz



A mixture of two gases is completely defined only when pressure, temperature and composition are specified. If pressure and temperature are specified then the third variable composition may be varied.

So it is necessary to specify all the three variables to define the system completely.

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

Hence the system is trivariant.