

Notes

Programme : Bachelor of Science

Subject : Chemistry

Paper Code : CHC103

Paper Title : Physical Chemistry and Organic Chemistry.

Unit : 2

Module Name: Carbon dioxide system

Module No :13

Name of the Presenter: Fatima M Fernandes

Notes on CO₂ system

1) Number of Phases(P) : A phase is defined as a homogeneous, physically distinct and mechanically separable portion of system, which is separated from other parts of the system by definite boundary surfaces.

2) Number of Components(C): Component is defined as the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation.

3) Degree of Freedom(F) : Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.

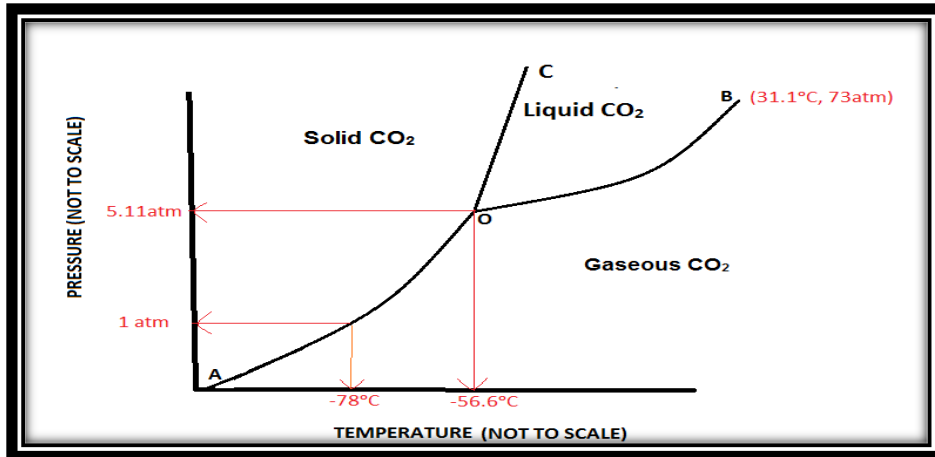
In the carbon dioxide system, P=3 that is, there are 3 phases, they are Solid CO₂, liquid CO₂ and gaseous CO₂.

In the carbon dioxide system, C=1 means Carbon dioxide is a one component system. The composition of every phase can be expressed in terms of one chemical constituent CO₂.

There are three types of equilibria in the carbon dioxide system.

- Solid CO₂ = liquid CO₂ Fusion
- Liquid CO₂ = Gaseous CO₂ Vapourisation
- Gaseous CO₂ = solid CO₂ Sublimation

Each equilibrium involves two phases.



In the phase Diagram, we have the following:

1) Curves

- OC: Freezing Point curve of solid CO₂; $\text{CO}_2(\text{s}) = \text{CO}_2(\text{l})$
- OB: Vapour Pressure curve of liquid CO₂; $\text{CO}_2(\text{l}) = \text{CO}_2(\text{g})$
- OA: Sublimation curve of solid CO₂; $\text{CO}_2(\text{s}) = \text{CO}_2(\text{g})$

On any curve $P=2$

2) Areas

- AOC: Solid CO₂
- COB: liquid CO₂
- AOB: Gaseous CO₂.

In any area $P=1$

3) Points

- Triple point O (-56.6 °C, 5.11atm)
- Critical point B (31.1°C, 73atm)

At the triple point $P=3$

Application of Phase Rule to carbon dioxide system (C) =1.

1. Along any curve

- Number of phases (P) =2

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$F=1$, that is Degree of Freedom is 1

Hence its a univariant system. It means that only one variable (either temperature or pressure) is sufficient to be fixed in order to define the system. System having only one degree of freedom

2. In any Area

- Number of phases (P) =1

Therefore,

$$F=C-P+2$$

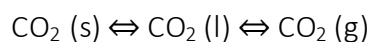
$$=1-1+2$$

$$=2$$

It's a bivariant system. Hence both temperature and pressure will have to be specified to describe a state in an area.

3. At the triple point:

At point O, all three phases solid ,liquid and gas coexist (P=3)



Applying the phase rule $F=C-P+2$.

$$F=1-3+2$$

$$=0$$

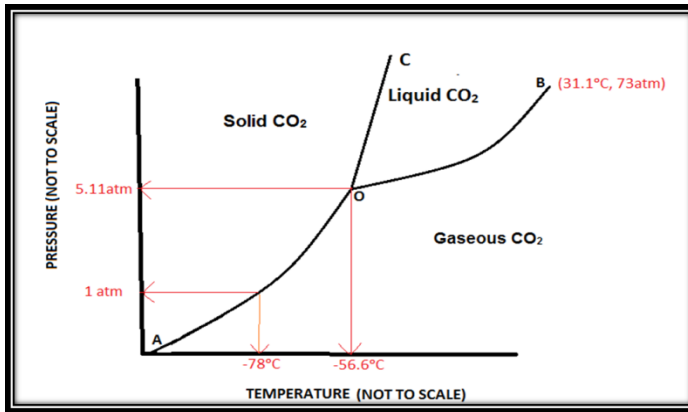
Hence at the triple point it is a non variant or invariant system. The triple point has rigid conditions. The temperature and pressure at the triple point are fixed. The pressure is 5.11 atm and temperature is -56.6°C.

At the supercritical point (B)

Liquid and gas phases have exactly the same density, and only a single phase exists. This single phase is called a supercritical fluid. The meniscus separating the liquid and gas phases disappears. Critical temperature is 31°C, a critical pressure is 73 atm

WHY CO₂ IS CALLED Dry ICE ?

Liquid CO₂ cannot exist at any pressure below 5.11 atm. So below this pressure solid CO₂ will directly pass into gaseous state without melting or liquid being formed that is the process of sublimation.



Difference between water system and carbon dioxide system

1. Solid – liquid boundary for water system has a negative slope whereas for carbon dioxide it has a positive slope.
2. Coordinates of the triple point in water system is (0.0098°C, 4.58 mm) whereas in carbon dioxide system (-56.6°C, 5.11 atm)
3. At 1 atmospheric pressure, water can exist in all 3 phases whereas liquid carbon dioxide does not exist in liquid phase. Solid CO₂ sublimates directly to a gas.