

PHASE RULE:-

TO STUDY HETEROGENEOUS SYSTEMS CONSISTING OF TWO OR MORE PHASES IN EQUILIBRIUM J.W. GIBBS GAVE A VERY IMPORTANT GENERALIZATION CALLED GIBBS PHASE RULE.

GIBBS PHASE RULE:-

“FOR A HETEROGENEOUS SYSTEM IN EQUILIBRIUM AT A DEFINITE TEMPERATURE AND PRESSURE, THE NUMBER OF DEGREE OF FREEDOM IS GREATER THAN THE DIFFERENCE IN THE NUMBER OF COMPONENT AND THE NUMBER OF PHASES BY TWO PROVIDED THE EQUILIBRIUM IS NOT INFLUENCED BY EXTERNAL EFFECTS SUCH AS GRAVITY, ELECTRICAL OR MAGNETIC FORCES, SURFACE TENSION ETC.”

$$F = C - P + 2$$

WHERE

P = NUMBER OF PHASES

C = NUMBER OF COMPONENTS

F = DEGREE OF FREEDOM

TERMINOLOGY INVOLVED:-

PHASE (P) :-

“A PHASE IS DEFINED AS THE PART OF THE SYSTEM WHICH IS PHYSICALLY AND CHEMICALLY UNIFORM THROUGHOUT.”

OR

“ANY HOMOGENEOUS AND PHYSICALLY DISTINCT PART OF THE SYSTEM WHICH IS BOUNDED BY A SURFACE AND IS MECHANICALLY SEPARABLE FROM THE OTHER PART OF THE SYSTEM IS CALLED A PHASE.”



Examples:

1. $\text{NaCl} + \text{H}_2\text{O}$ forms homogeneous solution and hence it is one phase system.

(Liquid phase)

2. Gaseous mixture is a one phase system.

(Gas phase)

3. Water + alcohol forms one phase system.

(Liquid phase)

4. $\text{CCl}_4 + \text{H}_2\text{O}$ are immiscible and forms two phase system. (Two different liquid phases)

5. Mixture of graphite and diamond is a two phase system. (Two solid phases)

COMPONENTS (C):-

“IT IS DEFINED AS THE MINIMUM NUMBER OF INDEPENDENT CHEMICAL SPECIES NECESSARY TO DESCRIBE THE COMPOSITION OF EACH AND EVERY PHASE OF THE SYSTEM IN EQUILIBRIUM.”



EXAMPLES :

WATER VAPOUR (GAS)

ICE (SOLID)



As all these three phases contain only one chemical species that is H_2O so it is a one component three phase system.

NaCl + water forms completely miscible solution but contains two chemical species viz. H_2O and NaCl so it is a two component one phase system.

**IN CASE OF CHEMICALLY
REACTIVE SYSTEMS NUMBER OF
COMPONENTS ARE DETERMINED
BY USING THE RELATION.**

$$C = S - R$$

WHERE

C = NUMBER OF COMPONENTS

S = NUMBER OF CHEMICAL SPECIES PRESENT IN THE SYSTEM.

R = NUMBER OF INDEPENDENT CHEMICAL RELATIONS WHICH THE VARIOUS SPECIES UNDERGO.

Examples :

Consider a system consisting of following species.

PCl_5 , PCl_3 , Cl_2

following equilibrium exists between these species.



thus here $S = 3$ & $R = 1$

$$\text{C} = S - R$$

$$\text{C} = 3 - 1$$

$$\text{C} = 2$$

Consider thermal decomposition of CaCO_3 in a sealed tube.



$$\text{C} = S - R$$

$$\text{C} = 3 - 1$$

$$\text{C} = 2$$

Calculations of Number of Components in Ionic System:

Ionic System:

NaCl-KBr-H₂O



Therefore there are nine species in the above system undergoing four reactions as given above.

Species present : NaCl, KCl, NaBr, KBr, Na⁺, Cl⁻, K⁺, Br⁻ and H₂O

$$C = S - (R + 1)$$

$$C = 9 - (4 + 1) \quad C = 4$$

NUMBER OF DEGREE OF FREEDOM (F) OR VARIANCE:-

“THE DEGREE OF FREEDOM OF A SYSTEM IS DEFINED AS THE MINIMUM NUMBER OF INDEPENDENT VARIABLE SUCH AS TEMPERATURE, PRESSURE AND CONCENTRATION WHICH MUST BE SPECIFIED IN ORDER TO DEFINE THE SYSTEM COMPLETELY”

OR

“IT IS THE MINIMUM NUMBER OF INTENSIVE VARIABLE THAT MUST BE SPECIFIED TO KNOW THE VALUES OF ALL THE REMAINING INTENSIVE VARIABLES”



EXAMPLE:

CONSIDER A ONE COMPONENT ONE PHASE SYSTEM LIKE LIQUID WATER, IT WILL HAVE A NUMBER OF INTENSIVE PROPERTIES LIKE DENSITY, REFRACTIVE INDEX, SURFACE TENSION, VISCOSITY ETC. BUT IF TEMPERATURE AND PRESSURE ARE KNOWN THEN ALL OTHER PROPERTIES WILL HAVE FIX VALUES.

SAME FOLLOWS FROM THE GIBBS PHASE RULE EQUATION

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

TYPES OF SYSTEMS

1. NON-VARIANT OR INVARIANT

IF THE DEGREE OF FREEDOM FOR A SYSTEM IS ZERO THAN THE SYSTEM IS TERMED NON-VARIANT OR INVARIANT.

2. UNIVARIANT OR MONOVARIANT

A SYSTEM IS SAID TO BE UNIVARIANT OR MONOVARIANT IF ITS DEGREE OF FREEDOM IS ONE.

3. BIVARIANT

A SYSTEM IS SAID TO BE BIVARIANT IF ITS DEGREE OF FREEDOM IS TWO.



Phase Rule Derivation

Consider a heterogeneous system containing C components ($C_1, C_2, C_3, \dots, C_C$) distributed among P phases ($P_1, P_2, P_3, \dots, P_P$).

Number of degree of freedom (F) =

Total number of Variables – Number of variable Defined by the System because of its being in equilibrium.

Calculations of total number of variables:-

- Suppose a phase has two components then if the molar concentration of one of the components known then that of other can be calculated automatically since sum total of mole fraction of all the components is one. Therefore for C components if we know molar concentrations of (C-1) components then molar concentration of remaining one can be determined easily. For system consisting of P phases if concentrations P(C-1) components is known than that of other can be easily determined. Beside concentration variable other variables like temperature and pressure are same for all the phases in equilibrium. So total number of variable required to know properties of all the components are:

$$\text{Total Number of Variable} = P (C-1) + 2$$

Here factor two is added for temperature and pressure.

Calculations of number of variables defined by the system because of its being in equilibrium:-

Contribution of any component in a mixture towards the total free energy of the system of a constant composition at constant temperature and pressure is termed chemical potential and it is denoted by μ , further chemical potential of any component is same in all the phases if there is a multiphase equilibrium.

Thus for a system consisting of three phases in equilibrium

The chemical potential of a component can be represented as:


$$(\mu_1)P_1 = (\mu_1)P_2 = (\mu_1)P_3$$

Now if we know

$$(\mu_1)P_1 = (\mu_1)P_2$$

$$(\mu_1)P_2 = (\mu_1)P_3$$

Then $(\mu_1)P_1 = (\mu_1)P_3$ need not to be specified so for one component system in three phases two relations or variables are required so for P number of phases (P-1) relations or variables are required and for C components in P phases C(P-1) relations are required. Thus total number of degree of freedom can be calculated easily



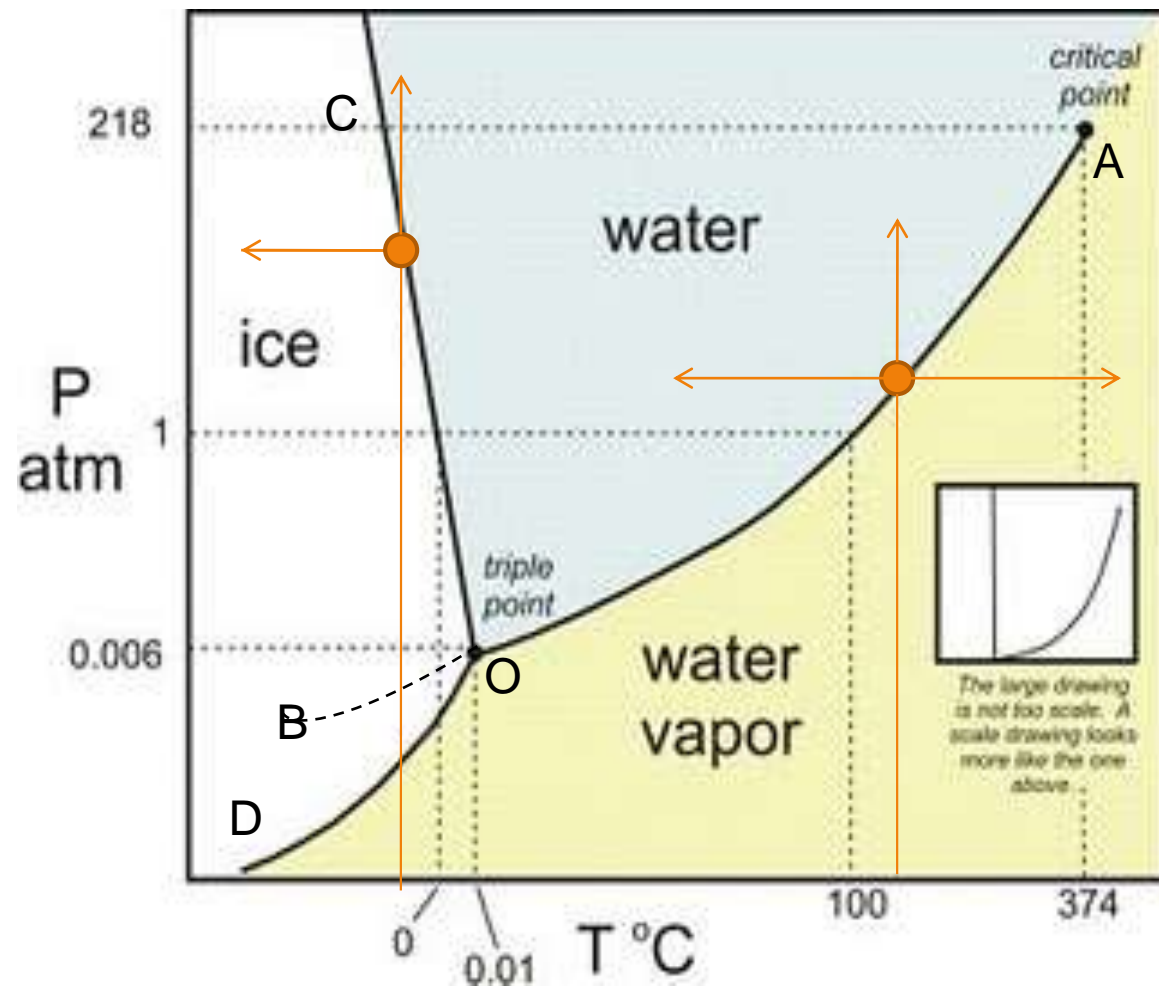
Number of degree of freedom (F) =
Total number of Variables – Number of
variable Defined by the System because
of its being in equilibrium.

$$F = P(C-1) + 2 - C(P-1)$$

$$F = C - P + 2$$

One component Systems

□ Phase Diagram of Water System

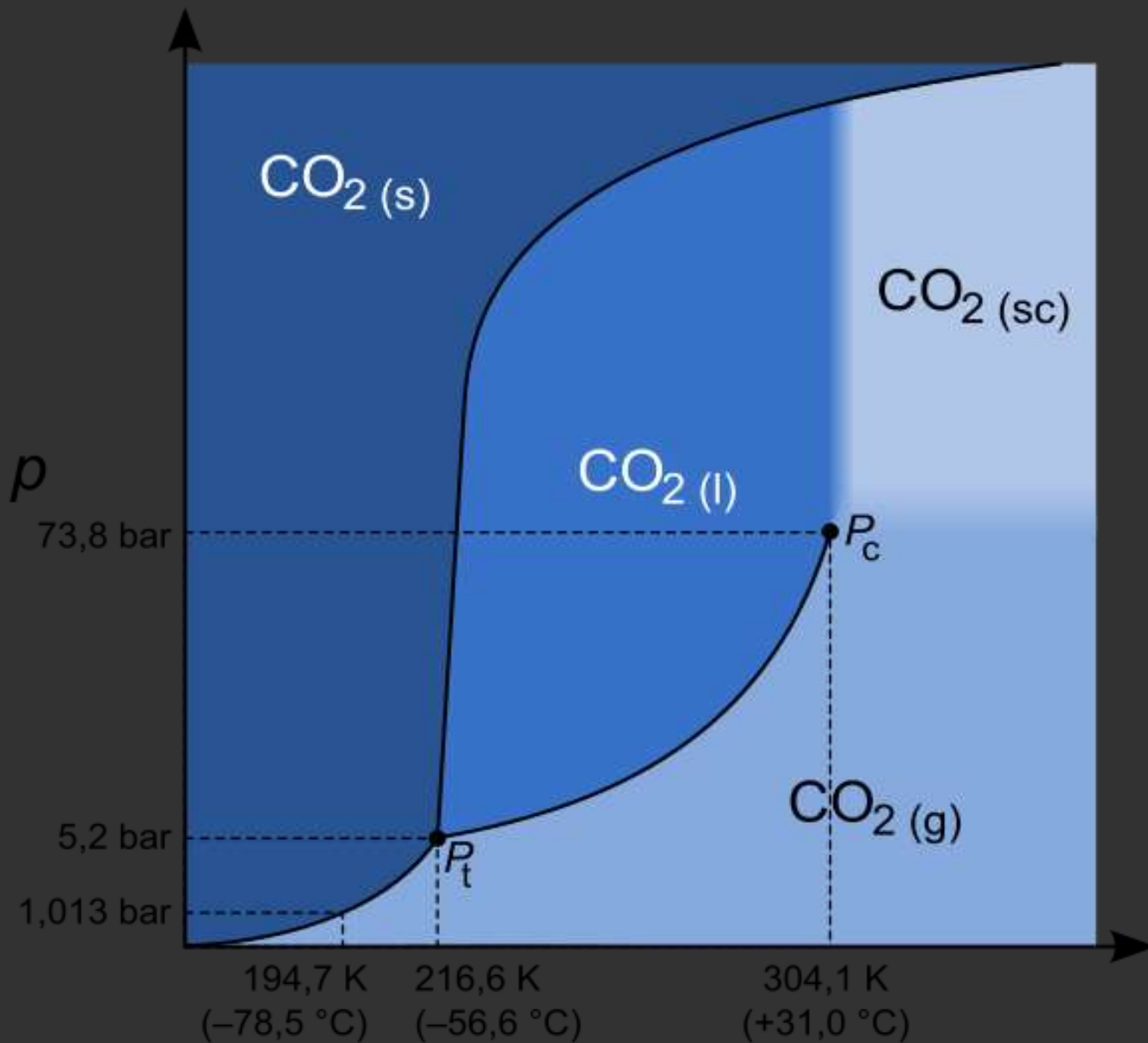


Super cooled Water





Ice skating & Flow of Glacier



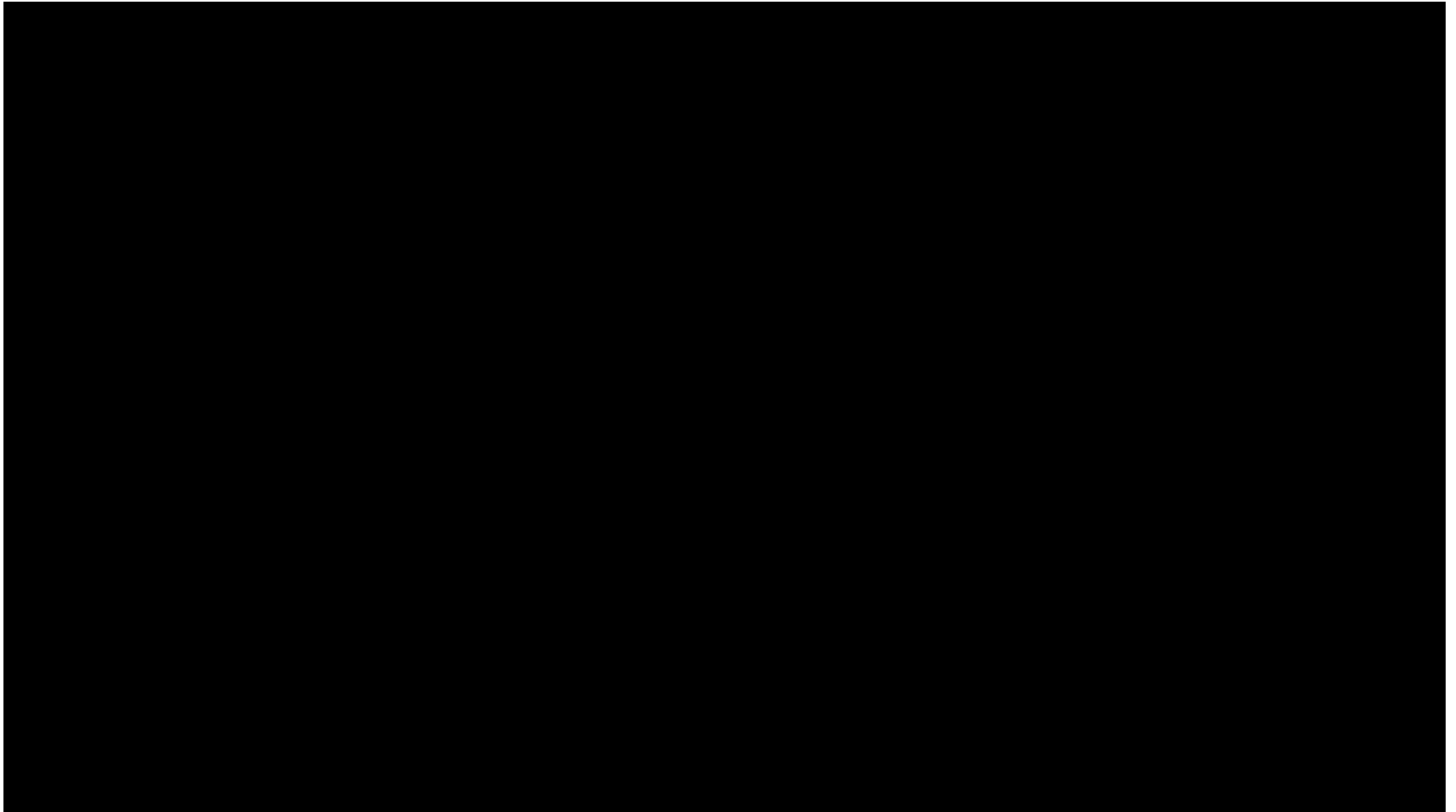
CO₂ System

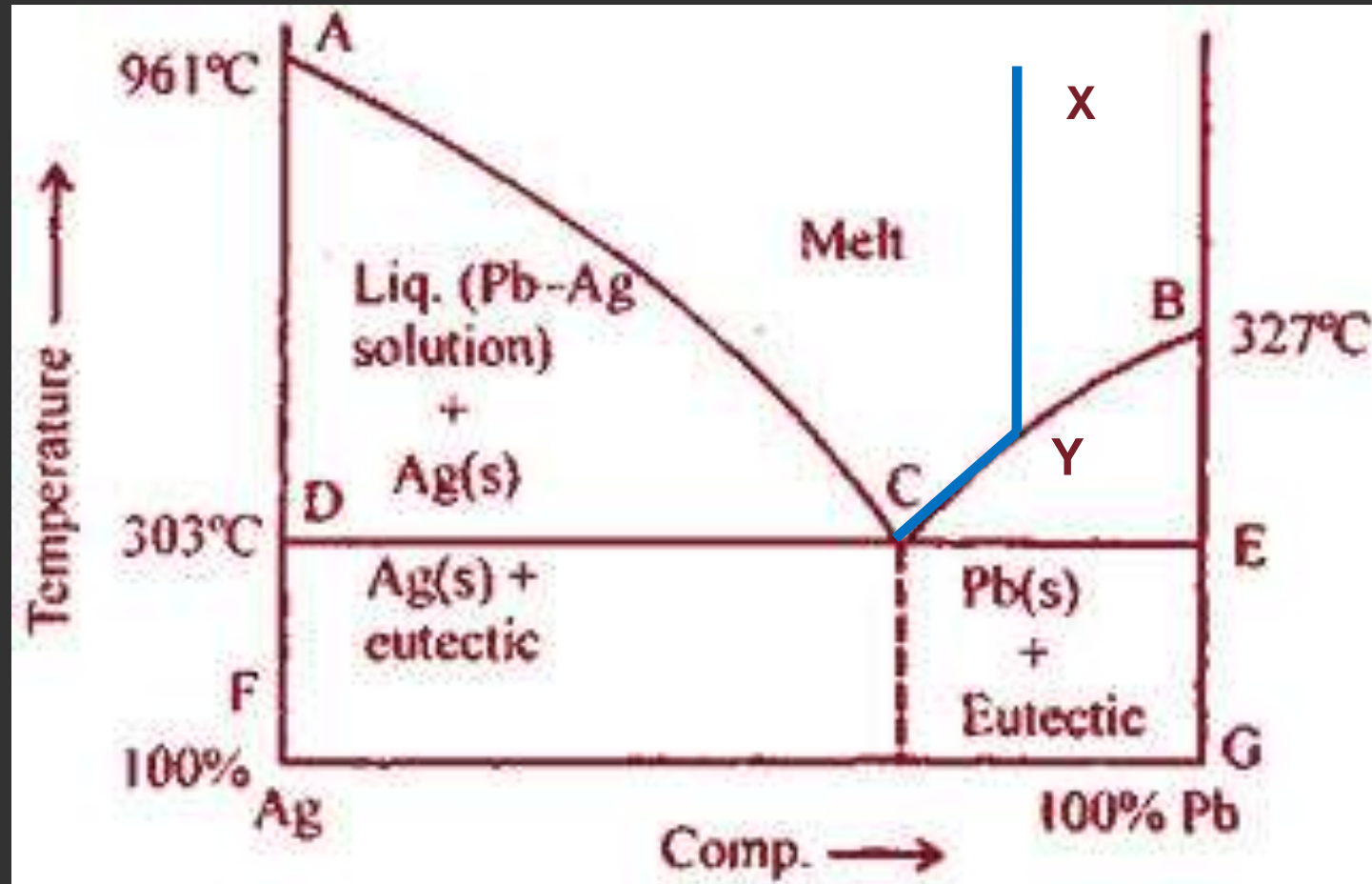
Though phase diagram of CO_2 resembles to water phase diagram but there are some point of difference.

- OC curve indicate +ve slop away from pressure axis indicating that m.pt of dry ice increases with increase in pressure this is because volume occupied by liquid CO_2 is greater than CO_2 solid.
- Solid CO_2 and liquid CO_2 can exist at a very high pressure of 5.11 atm. Hence, at ordinary pressure solid ice will be dry i.e. if temperature is raised at 5.11 atm it will directly vaporize to gaseous phase.
- At 1 atm CO_2 gas solidifies into dry ice without appearance of liquid phase by merely cooling to -78°C .

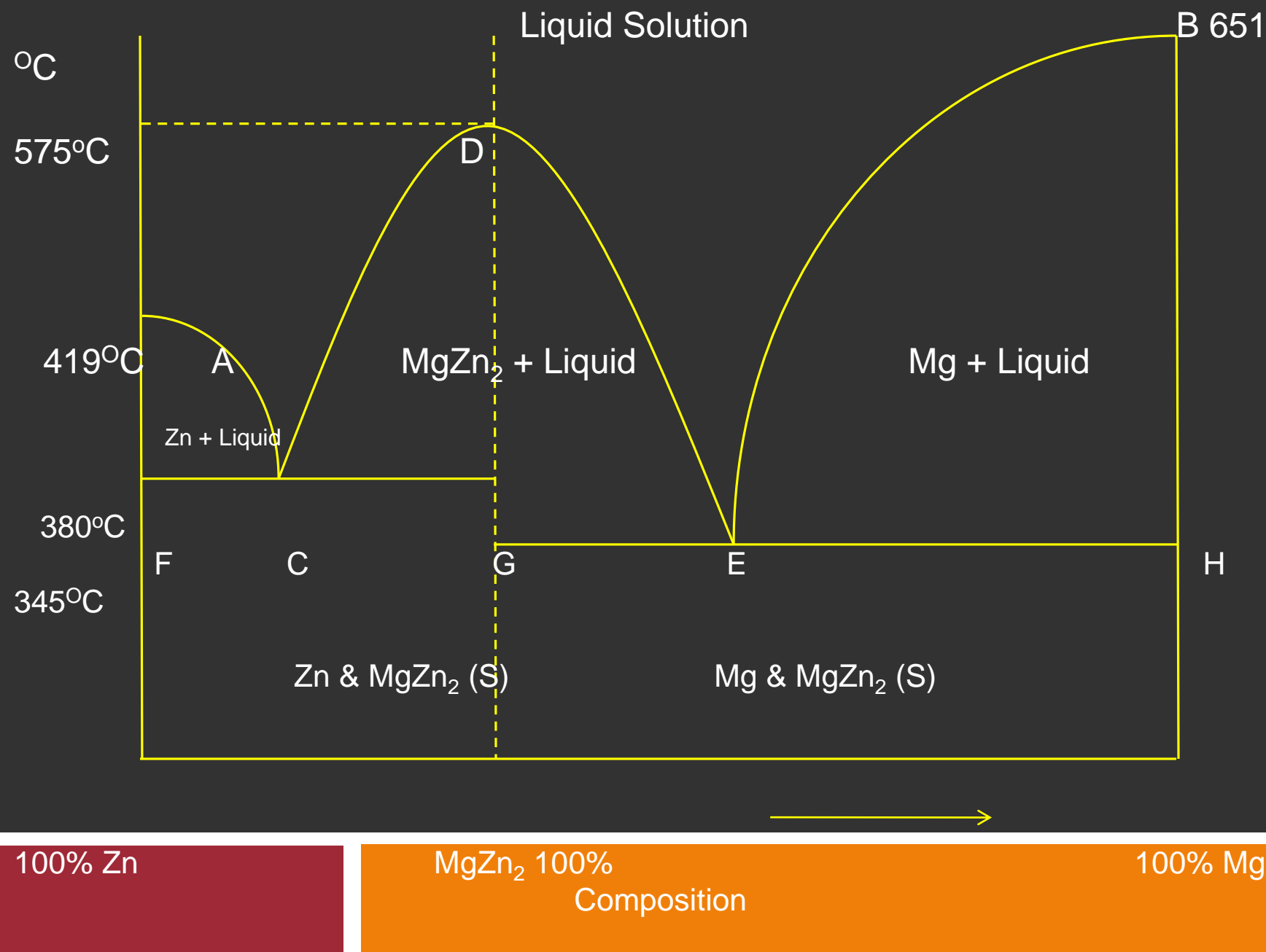
Point of difference between H_2O & CO_2 system

Dry Ice





Eutectic System: Pb-Ag System

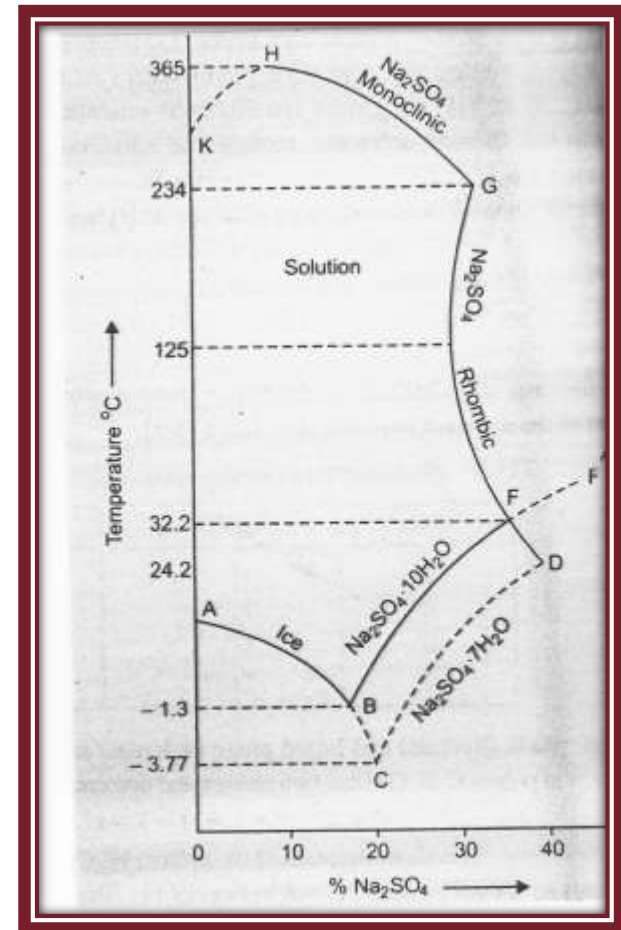


Incongruent Melting System

Sodium Sulphate -Water System

Phases Present:

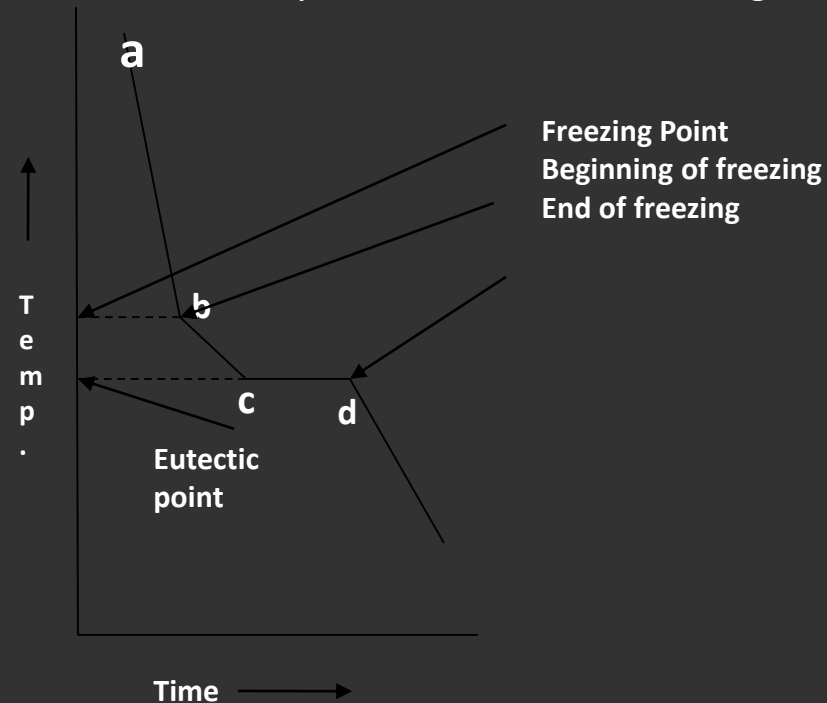
1. $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$
2. $\text{Na}_2\text{SO}_4 \cdot 7 \text{H}_2\text{O}$
3. Na_2SO_4 Rhombic
4. Na_2SO_4 Monoclinic
5. Ice
6. Liquid Solution
7. Vapour



Cooling Curves: The curve obtained on cooling the sample with respect to time is known as cooling curve. Cooling curves are helpful in constructing phase diagrams, determination of freezing point, eutectic point etc.

Determination of eutectic point:

To determine eutectic point of two component system the mixture of two components is fused/melted and allowed to cool slowly with time and a cooling curve as shown below is obtained.



Cooling Curve for two component system

When a solid phase begins to form, the rate of cooling abruptly alters and the cooling curve exhibits a break. However, the temperature does not remain constant, as in the case of pure substances. The temperature decreases continuously, but at a different rate and if the mixture forms an eutectic the fall of temperature continues, till the eutectic point is reached. The system now becomes invariant until the solidification is complete. Thereafter, the fall of temperature becomes uniform, but the rate of fall is quite different.

Following information can be obtained from the above cooling curve.

- Freezing point varies with the composition of the system, but the eutectic point remains same.
- As we are close to the eutectic composition the shorter is the bc and halt is more prolonged.
- If the mixture taken for determination coincides with eutectic composition, the curve shows no break corresponding to bc, but the break appears at C.

Freeze Drying – How does it work?

1. Fresh or cooked foods are flash frozen then placed in a vacuum chamber

2. About 90% of the food's moisture is drawn off by evaporating the ice at temperatures as low as -50°C

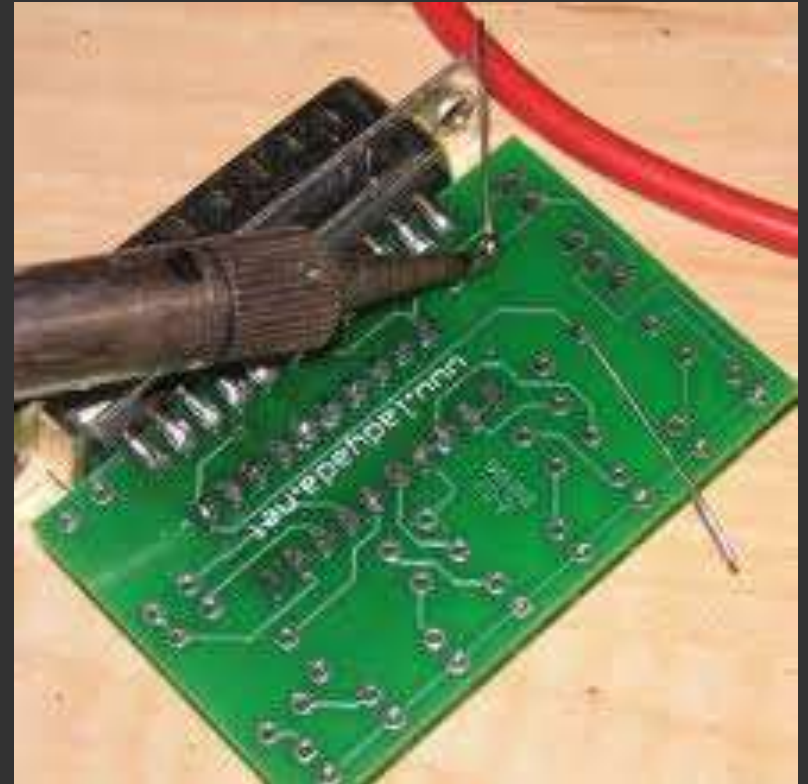
3. The freeze – dried food is sealed in moisture-and-oxygen proof packaging to ensure freshness until opened.

4. When the water is replaced the food regains it's original fresh flavour, aroma, texture and appearance.

Applications of Phase Rule: Lyophilization



Freeze Dried Strawberry and Tomotos



Solders



THANKS