PHASE RULE

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The Phase Rule:

- Introduction, Phase, Components, Degree of freedom, Derivation of Gibb's Phase, Three & Four Phase-One component system like water, sulphur systems, Two component -Eutectic systems like Silver-Lead, Zinc-Cadmium, Ferric Chloride-Water system

The Phase Rule

- It was first presented by ***Gibbs*** in 1875.
- It is very useful to understand the effect of intensive variables, such as temperature, pressure, or concentration, on the equilibrium between phases as well as between chemical constituents.
- It is used to deduce the number of degrees of freedom (*f*) for a system. Sometimes called: "*the variance of the system*".

- Homogenous Chemical Equilibrium

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2\,NH_{3(g)}$$

- Heterogonous Chemical Equilibrium

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

- Heterogonous Physical Equilibrium

Solid $\rightleftharpoons$ Liquid (Melting)

Liquid $\rightleftharpoons$ Vapour (Vaporisation)

Solid $\rightleftharpoons$ Vapour (Sublimation)

TERMS

Phase

- *A phase is defined as any homogeneous and physically distinct part of a system having all physical and chemical properties the same throughout the system.* ***A system may consist of one phase or more than one phase.***

Examples:-

- A system containing only liquid water is one-phase system
- A system containing liquid water and water vapour (gas) is a two phase system
- A system containing liquid water, water vapour and solid ice is a three phase system.
- Pure substances (solid, liquid, or gas) made of one chemical species only, is considered as one phase, thus, oxygen, benzene, and ice are all one phase.

Component:

- *The term component is defined as the* ***least number of independent chemical constituents*** *in terms of which the* ***composition of every phase can be expressed by means of a chemical equation.***

Examples:-

- **Water system has three phases,** ice, water and water vapour and the composition of all these phases is expressed in terms of one chemical individual water. **Thus water system has one component only.**
- **Similarly Sulphur system has four phases:** rhombic sulphur, monoclinic sulphur liquid sulphur and sulphur vapour and the composition of all these phases is expressed by one chemical individual sulphur. **Therefore Sulphur system is one component system.**
- **Thus, all the phases in one component system is expressed by only one chemical individual.**

- **A saturated solution of NaCl in contact with excess solid NaCl has two phases**. The composition of both the phases can be expressed in terms of two chemical individual NaCl and water. Hence a saturated solution of NaCl in water in contact with excess solid NaCl is a two component system.
- **DECOMPOSITION** OF CALCIUM CARBONATE

$$\mathbf{CaCO_3(s) = CaO(s) + CO_2(g)}$$

- It has three phases but the composition of the system can be expressed in terms of two of the three chemical substances in equilibrium. Hence it is a two component system

Dissociation of NH4Cl

$$\mathbf{NH_4Cl(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)}$$

- Ammonium chloride when heated in a closed vessel dissociates into ammonia and HCl gas. The system consists of two phases solid NH_4Cl and gaseous mixture containing NH_3 and HCl **However the constituents of the mixture are in the same proportion in which they are combined in solid NH4Cl.** The composition of the both the phases therefore be expressed in terms of the same chemical individual NH_4Cl. **Thus the dissociation of NH4Cl is one component system.**

DEGREES OF FREEDOM (F)

- ***It is defined as the least number of variable factors of a system which must be specified so that the remaining variables are fixed automatically and the system is completely defined***. E.g.
- **MONOVARIANT** or **UNIVARIANT SYSTEM**
- For Water = Water Vapour system, F=1, The system has two variables, P and T. At definite T, the vapour pressure of water can have only one fixed value. Thus if one variable is specified , the other is fixed automatically. Hence this system has one degree of freedom, it is **MONOVARIANT** or **UNIVARIANT.**
- **BIVARIANT SYSTEM**
- For a pure gas, PV=RT, if P and T values are specified there can have be only one definite value of V or that the volume is fixed automatically. Thus it has two degrees of freedom, the system is **BIVARIANT.**

TRIVARIANT SYSTEM

- A mixture of two or more gases is completely defined only when P, T and Composition are specified. If P and T be specified the third variable i.e. composition may be varied. Since it is necessary to specify three variables to define the system completely, it has three degrees. Thus it is **TRIVARIANT.**

NONVARIANT SYSTEM

- For ice, water, water vapour system, F=0, In this system, the three phases coexist at the freezing point of water. Since the freezing temperature of water has a definite value, the vapour pressure of water has also a fixed value. Since both the variables are already fixed, the system is defined automatically and there being no need to specify any variable. Hence this system has no degree of freedom.

Phase rule states that :

- When the equillibrium between any number of phases is influenced only by temperature, pressure and concentration but not influenced by gravity, or electrical or magnetic forces or by surface action then the number of Degrees of Freedom (F) of the system is related to the number of Components (C) and of Phases (P) by the phase rule equation:

$$\mathbf{F + P = C + 2}$$

Advantages of Phase Rule

- Phase rule is applicable to both Chemical and Physical equilibria.
- Phase rule is applicable to macroscopic systems and hence no information is required regarding molecular or micro structure.
- We can conveniently classify equilibrium states in terms of phases, components and degrees of freedom.
- The behaviour of system can be predicted under diff. conditions.
- According to phase rule, diff. systems behave similarly if they have same degrees of freedom.
- Phase rule helps in deciding under a giving set of conditions:

  1) Existence of equilibrium among various substances.

  2) Interconvergence of substance or

  3) Disappearance of some of the substances.

Limitations of Phase Rule

- Phase rule is applicable only for those systems which are in equilibrium. It is not much use for those systems which attain the equilibrium state very slowly.
- Only three degrees of freedom *viz,* temperature, pressure and components are allowed to influence the equilibrium systems.
- Under the same conditions of temperature and pressure, all the phases of the system must be present.
- It considers only the number of phases, rather than their amounts.

Derivation of Gibb's Phase Rule

- Consider a system in equillibrium consisting of C components distributed between P phases. Each component will be distributed between P phases.
- For thermal equillibrium between P phases, the temperature must be the Same for every phase, that is there will be only one value of temperature.
- For mechanical equillibrium between P phases, the pressure must be the Same for every phase, that is there will be only one value of pressure.
- For material equillibrium between P phases, the chemical potential μ of each component must have the Same for every phase.

- Let μ_{ij} be the chemical potential of ith component in jth phase. For the first component , chemical potential must be same in every phase:
- $\mu_{11} = \mu_{12} = \mu_{13} = \ldots\ldots\ldots\ldots \mu_{1p}$ (total P-1 equations)
- Similarly, for the second component the chemical potential must be same for every phase:
- $\mu_{21} = \mu_{22} = \mu_{23} = \ldots\ldots\ldots\ldots \mu_{2p}$ (total P-1 equations)
- Similarly, for the Cth component the chemical potential must have the same value in every phase:
- $\mu_{C1} = \mu_{C2} = \mu_{C3} = \ldots\ldots\ldots\ldots \mu_{Cp}$ (total P-1 equations)
- Therefore for the Cth component the total number of equations relating chemical potential = C(P-1).

- The given phase having C components at temperature T and pressure P, the chemical potential is determined by the mole fractions of all components present . However, for each phase, the sum of mole fractions of all components is unity, implying that at most C-1mole fractions can be independent. Therefore, for P Phases, there are at most P(C-1)independently variable mole fractions.
- In addition, the temperature and pressure are two other intensive variables of the system. Hence the total number of independently variable properties of the system = P(C-1) + 2. however, these P(C-1) + 2 variables are related to each other through P(C-1) equations.

- Hence,
- [Total number of independent intensive variable] = [Total number of variables] – [total number of equations connecting the variables]

$$F = P\,(C\text{-}1) + 2 - C\,(P - 1)$$

$$= PC - P + 2 - PC + C$$

$$F = C - P + 2$$

- This is Gibbs phase rule

Applying the phase rule to:

- One-component systems.
- Binary systems.
- Liquid-vapor equilibrium.
- Temperature-composition diagrams

Phase Rule in One-Component Systems

- The number of degrees of freedom seems to be related to the number of phases.

Phase Rule with Single Component Systems			
System	# of phases	Degrees of Freedom	Comments
Gas, liquid or solid	1	2	System is bivariant
Gas-liquid, liquid-solid, or gas-solid	2	1	System is univariant
Gas-liquid-solid	3	0	System is invariant

Examples: One component system like water, sulphur systems

The Water System

- We have only one component which is H_2O.

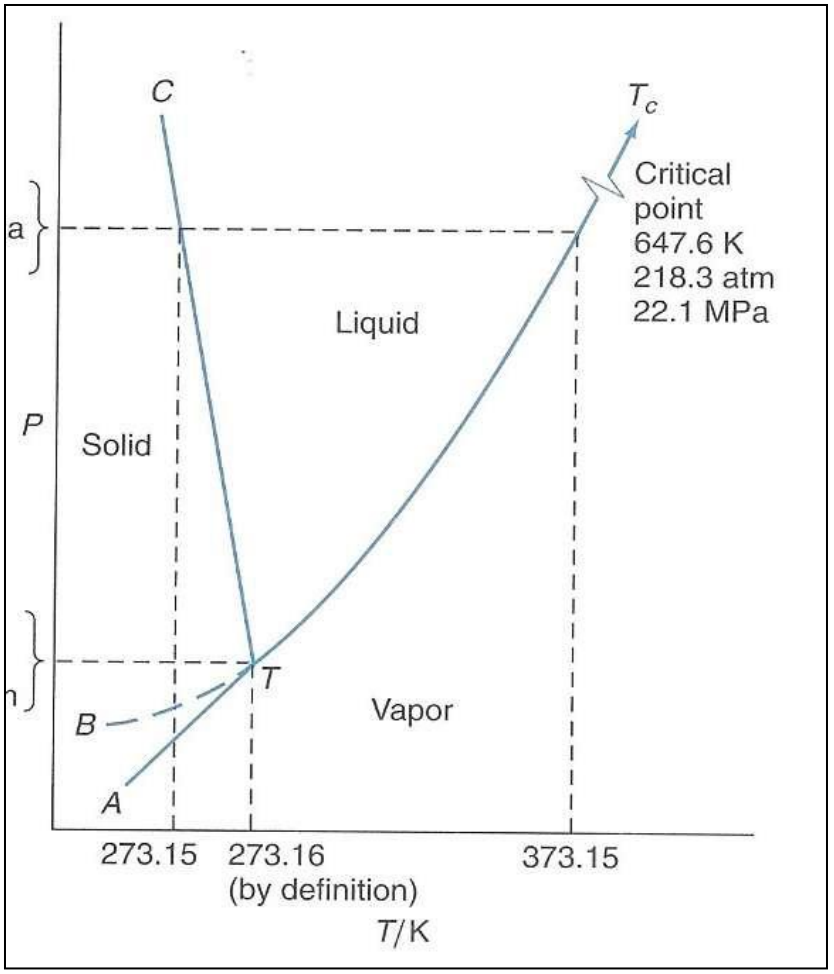
In the one-phase regions, one can vary either the temperature, or the pressure, or both (within limits) without crossing a phase line.

We say that in these regions:

$f = c - p + 2$

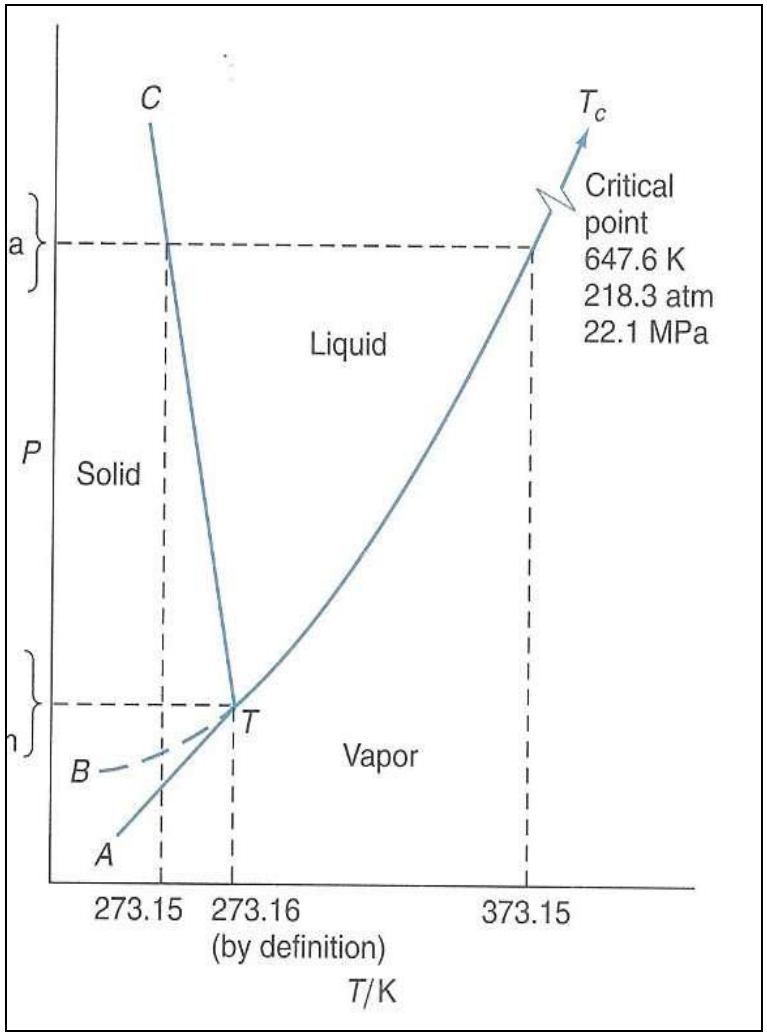
$= 1 - 1 + 2$

$= 2$ degrees of freedom.



Along a phase line we have two phases in equilibrium with each other, so on a phase line the number of phases is 2. If we want to stay on a phase line, we can't change the temperature and pressure independently. We say that along a phase line: $f = c - p + 2$

$= 1 - 2 + 2 = 1$ degree of freedom.



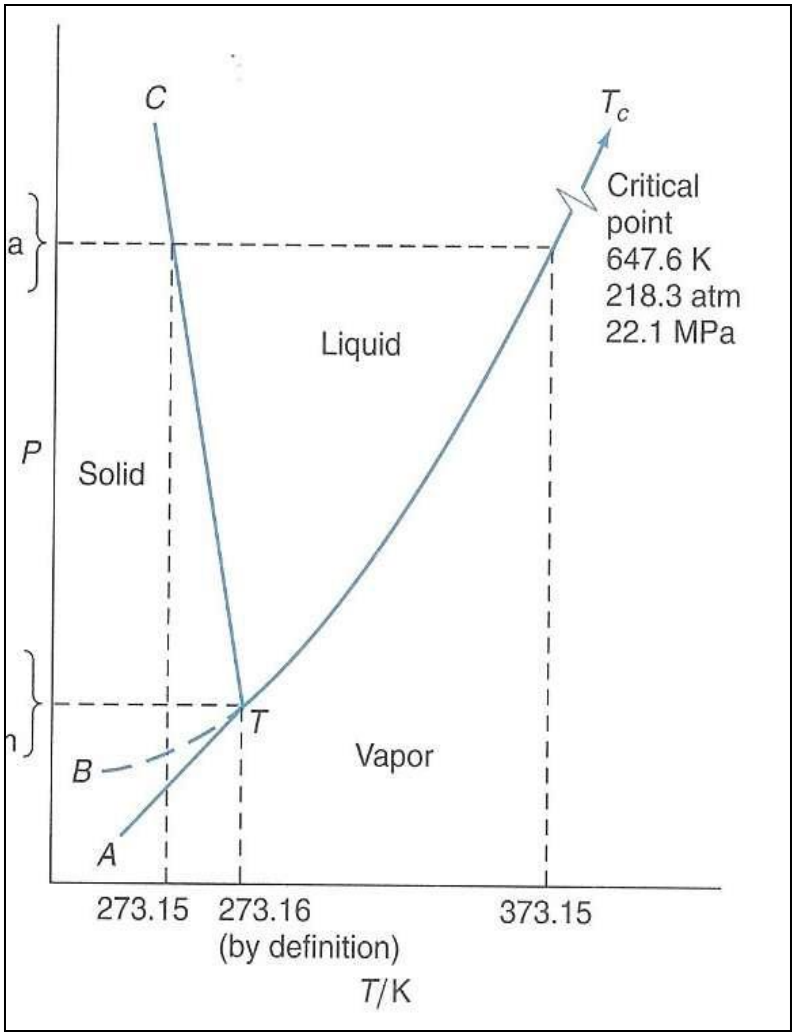
At the triple point there are three phases in equilibrium, but there is only one point on the diagram where we can have three phases in equilibrium with each other.

We say that at the triple point:

$$f = c - p + 2$$

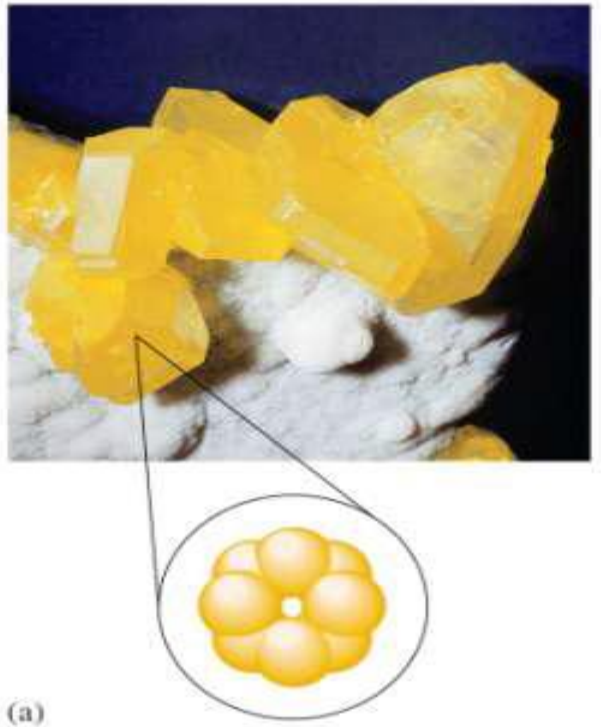
$= 1 - 3 + 2 = 0$ degrees of freedom.

The values of temp and pressure are 0.0075˚C and 4.58 mm respectively.



The Sulphur System

- Sulphur solid exists in two crystalline forms.
- Orthorhombic. S_8 or S(*rh*)
- Monoclinic. S_4 or S(*mo*)
- Yellow sulphur of the orthorhombic (or rhombic) crystalline form. It is the form that commonly exists under normal conditions.



Phase Diagram of Sulphur

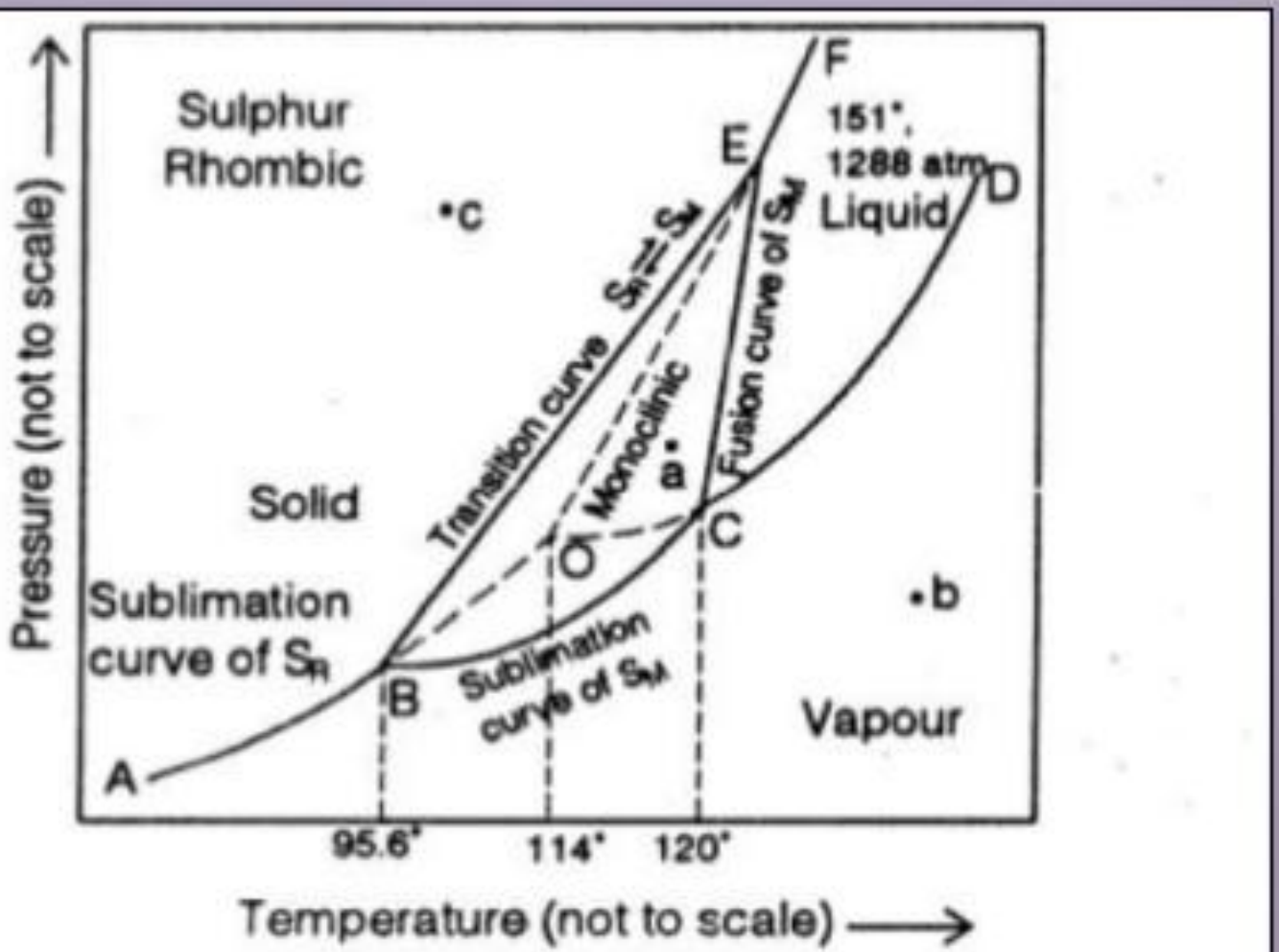
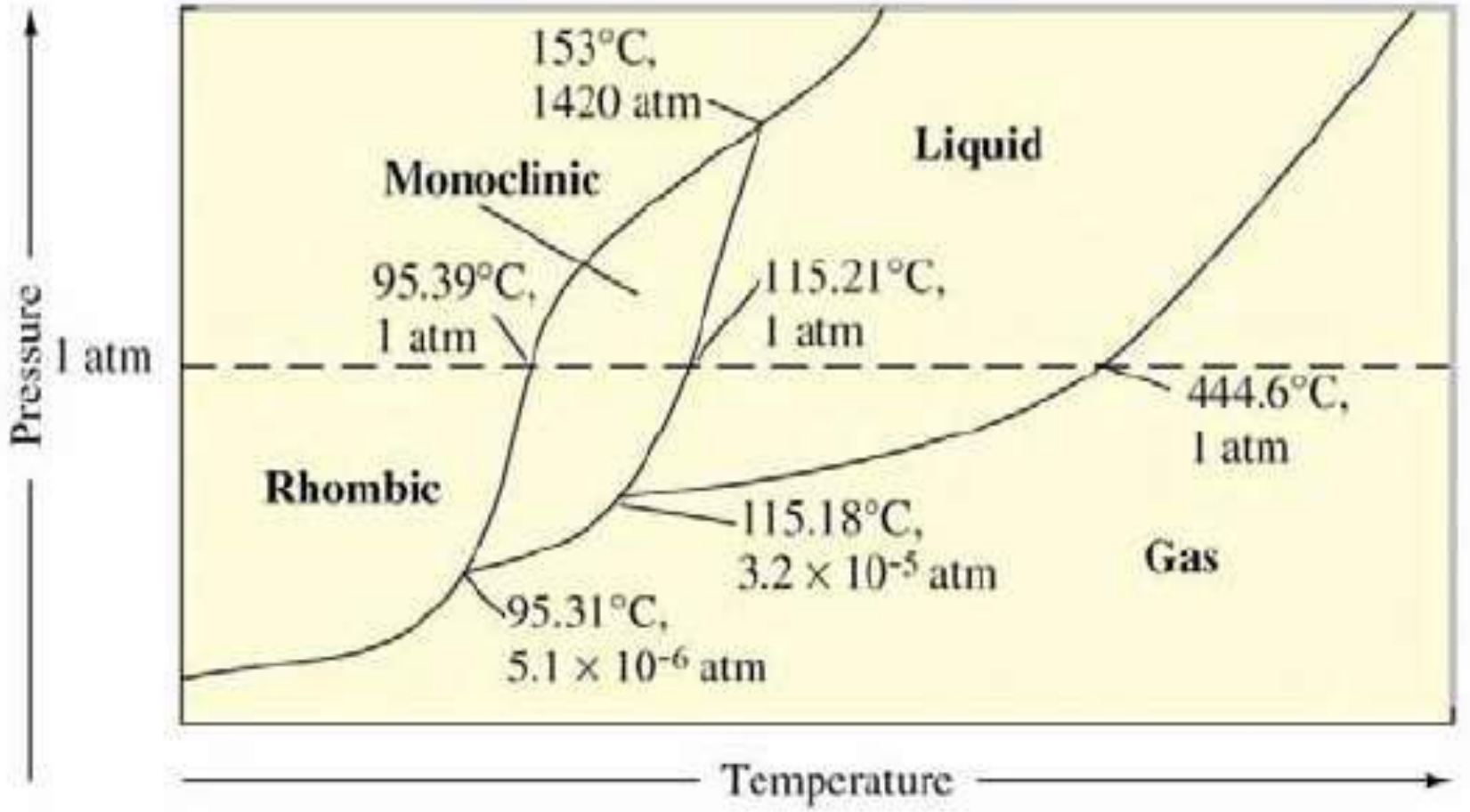


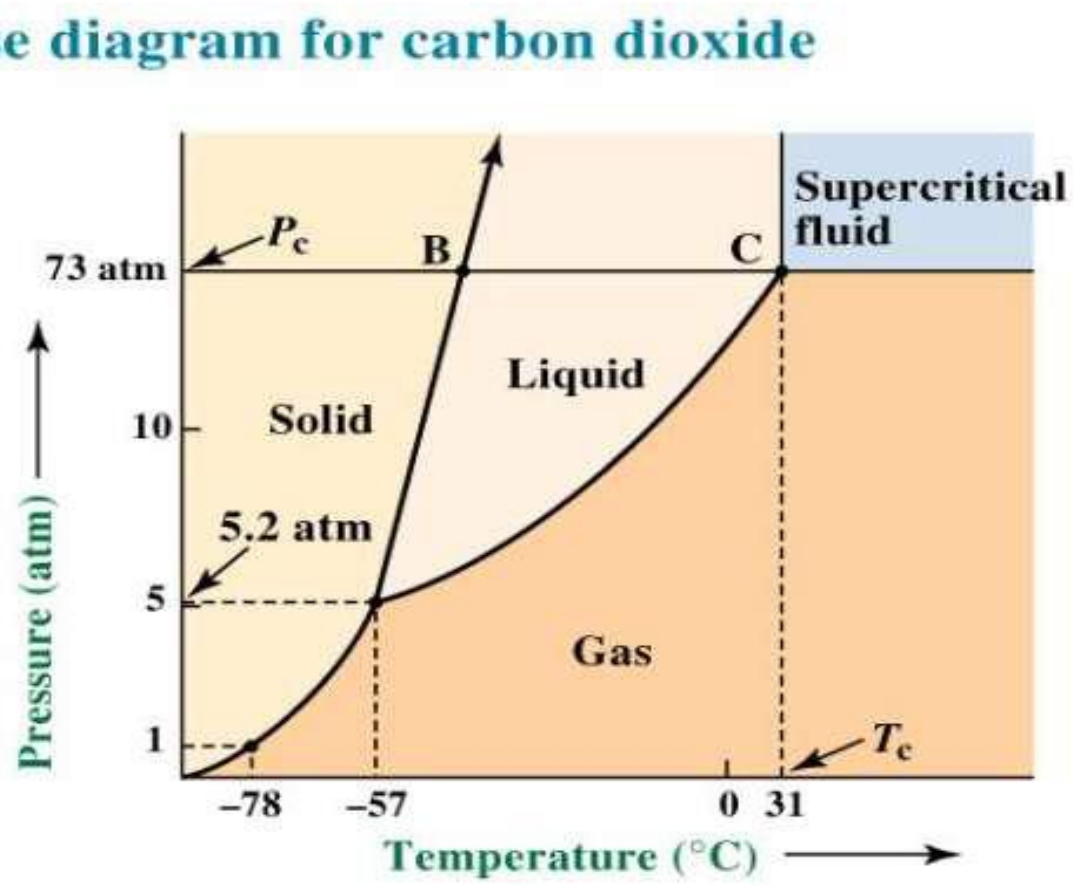
Fig. 2.17 Sulphur system

Phase Diagram of Sulphur

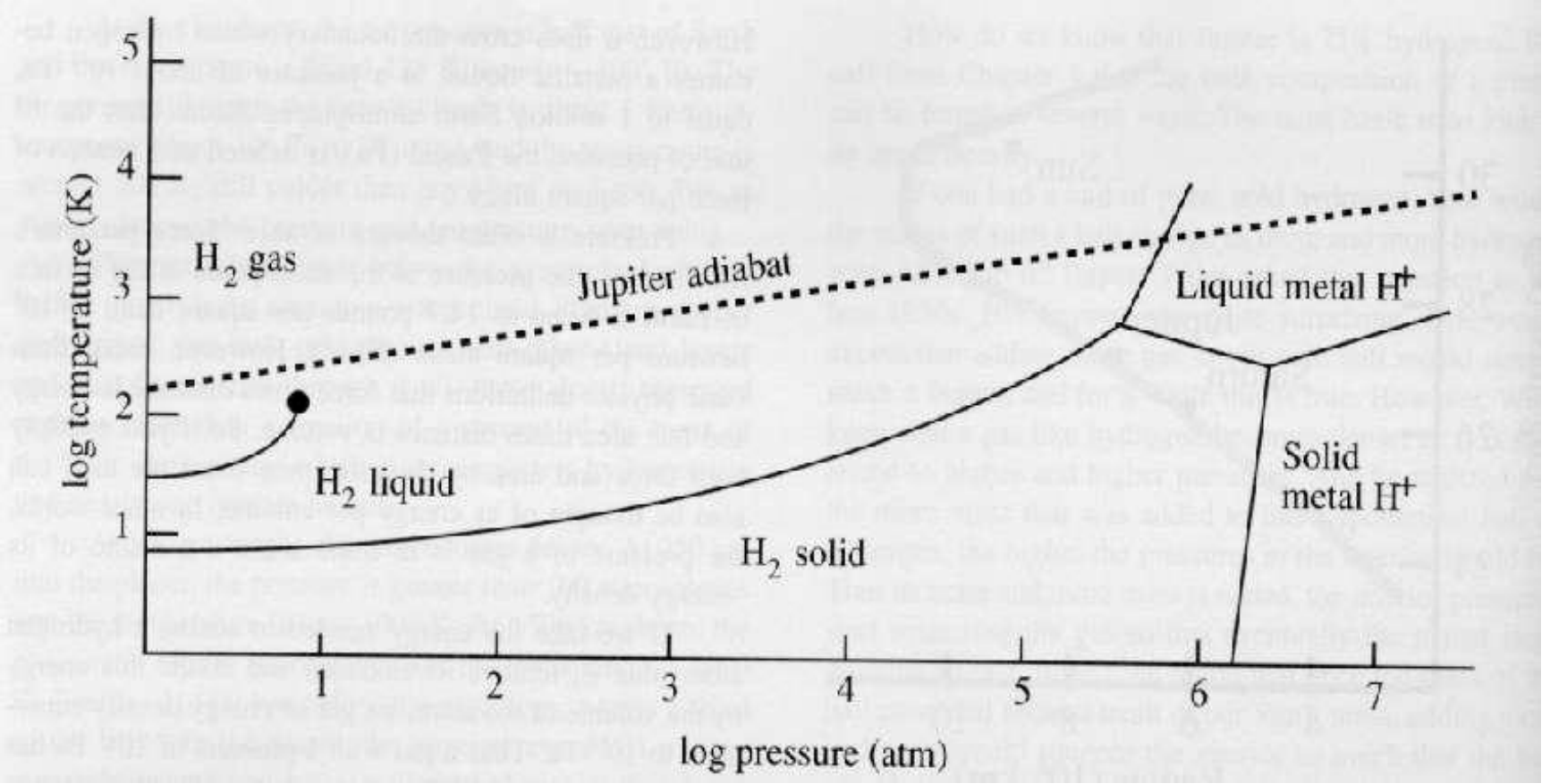


The Carbon Dioxide System

The phase rule should be applicable for any single component systems in general.

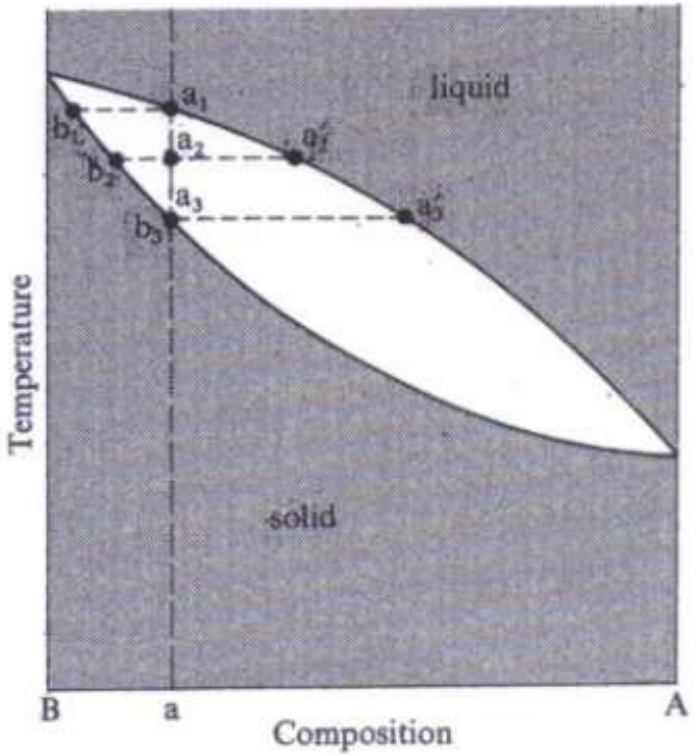


Phase Diagram of Hydrogen



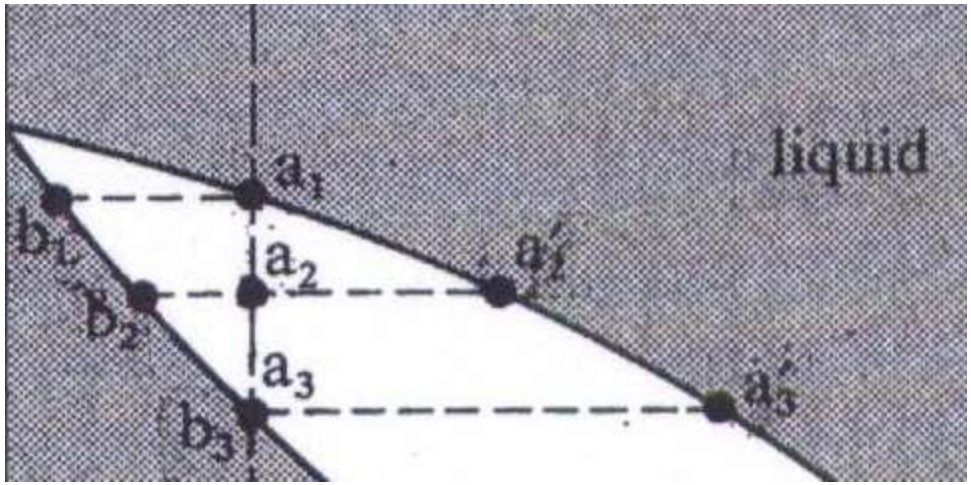
Binary Phase Diagram

- Phase diagram for two similar components; aka “Solid Solution”.
- Assume Pressure = 1 atm, so 2D rather than 3D plot.
- Two components, so F + P = 2 + 2 = 4
- Composition = mole fraction; 100% B to 100% A.
- *Tm(B)* = melting point of pure B.
- *Tm(A)* = melting point of pure A.
- *Liquidous* = boundary between liquid and mixed phase; gives liquid composition.
- *Solidous* = boundary between solid and mixed phase; gives solid composition.



- Heat mixture of A & B (at mole fraction indicated) to temperature 1. Then cool.
- At temperature 1, liquid phase has composition = mole fraction.
- At temperature 2, solid begins to ppt out; solid is mostly B mixed crystal (composition b1).
- At temperature 3, solid has composition b2 and liquid has composition a'2; note different mole fractions!

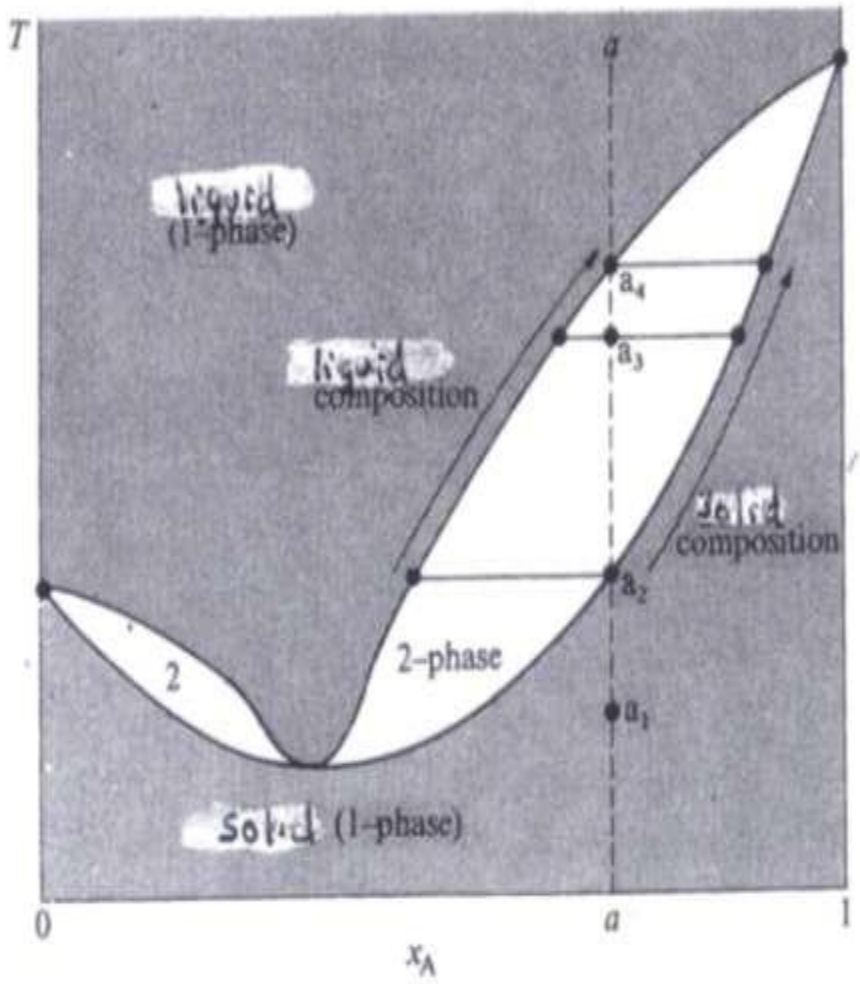
- at a given temperature, the liquid and solid that are in equilibrium with each other have different compositions.
- At temperature 4, solid formed has



- Note that on cooling, the solid will change composition from almost pure B to more and more A composition.
- Coring: freeze in tube from outside; core will have different composition.
- Heat & Beat: heat above liquidous, cool below solidous (but not too far), then beat (to make deformities), then reheat almost to solidous (increase diffusion), beat and repeat. Like? Blacksmith.

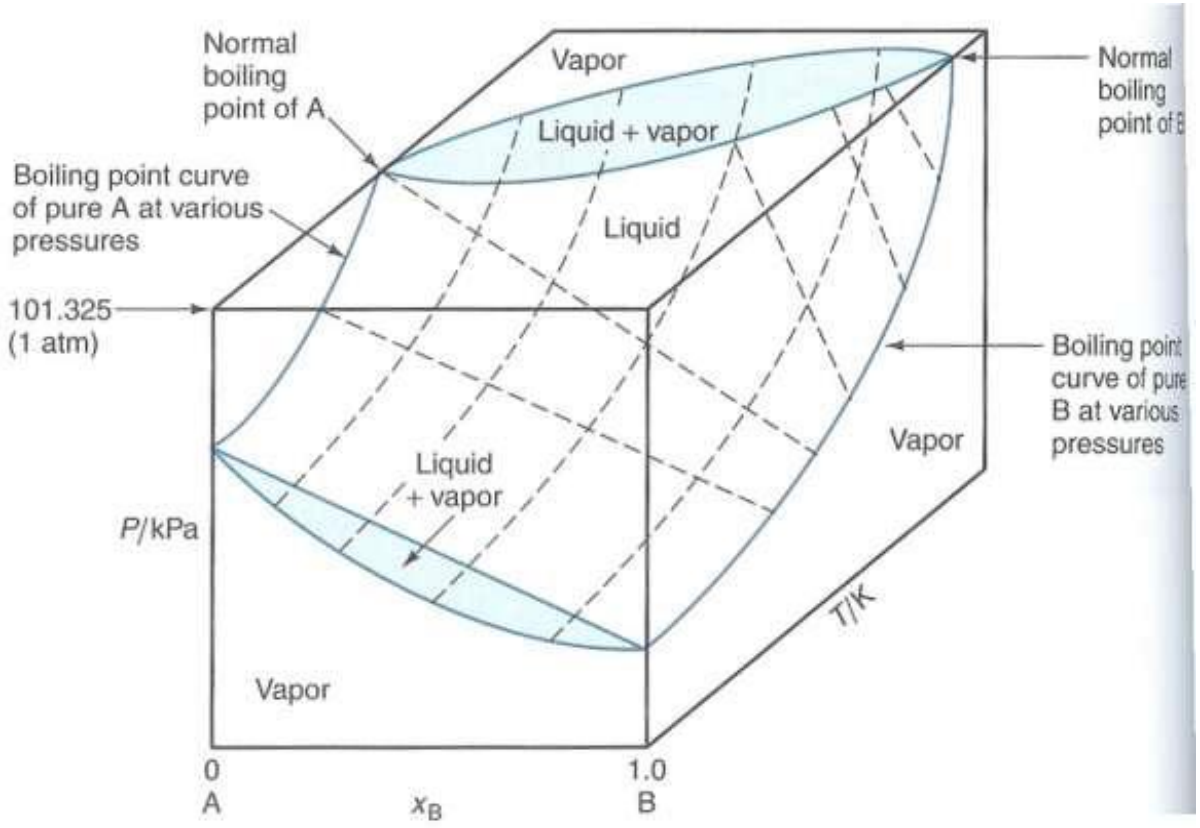
Example of a system involving the formation of mixed crystals with temperature minimum: *special point* for which the compositions of the solid and liquid are the same.

It is possible to have the special point at a temperature maximum.



Binary-System Phase Diagram with Three Variables: *P*, *T* and *x*

- The solid part of the surface represents the "liquid + vapor" region.
- Above it we have the liquid phase and below it we have the vapor phase.
- On the *T*-*P* planes we have pure liquid curves where the boiling point curves can be seen.



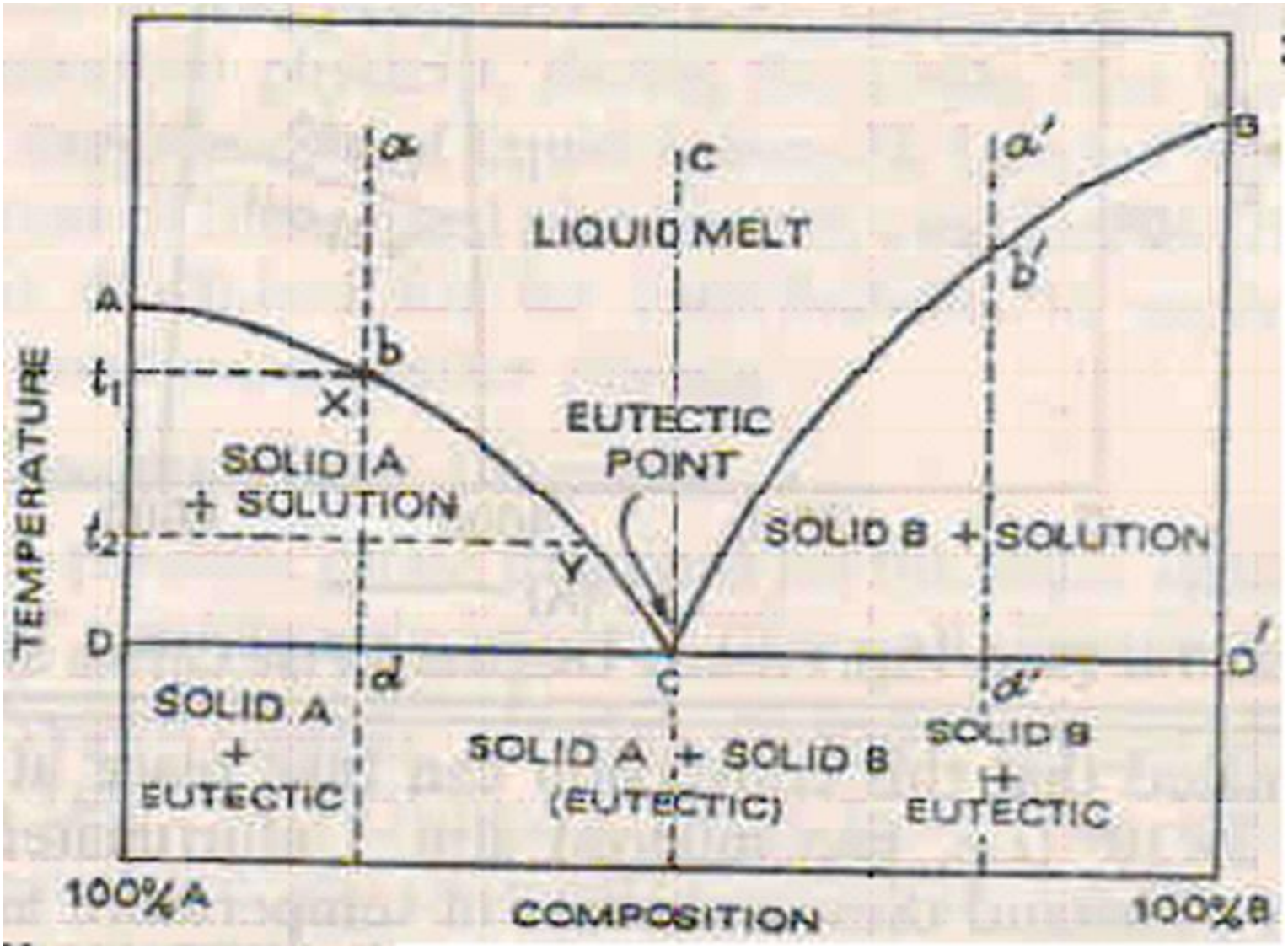
- On the *P*-*x* plane we have the normal pressure-composition phase diagram. It can be viewed at different temperatures.
- On the *T*-*x* plane we have the temperature composition Phase diagram, which is more commonly used in experimental work since it is more convenient to fix *P* rather than *T*.

Eutectic Phase Diagram

- A **eutectic system** is a homogeneous, solid mixture of two or more substances that form a super-lattice; the mixture either melts or solidifies at a lower temperature than the melting point of any of the individual substances.
- A eutectic system only forms when there is a specific ratio between the components.
- Sodium chloride and water form a eutectoid when the mixture is 23.3% salt by mass with a eutectic point at -21.2 degrees Celsius. The system is used to **make ice cream** and to melt ice and snow.

- The eutectic point of the mixture of ethanol and water is nearly pure ethanol. The value means there is a maximum proof or purity of alcohol that can be obtained using distillation.
- Eutectic alloys are often used for soldering. A typical composition is 63% tin and 37% lead by mass.
- Eutectoid glassy metals exhibit extreme corrosion resistance and strength.
- Inkjet printer ink is a eutectic mixture, permitting printing at a relatively low temperature.
- Galinstan is a liquid metal alloy (composed of gallium, indium, and tin) used as a low-toxicity replacement for mercury.

Simple eutectic system-General



Simple Eutectic(Lead-Silver System)

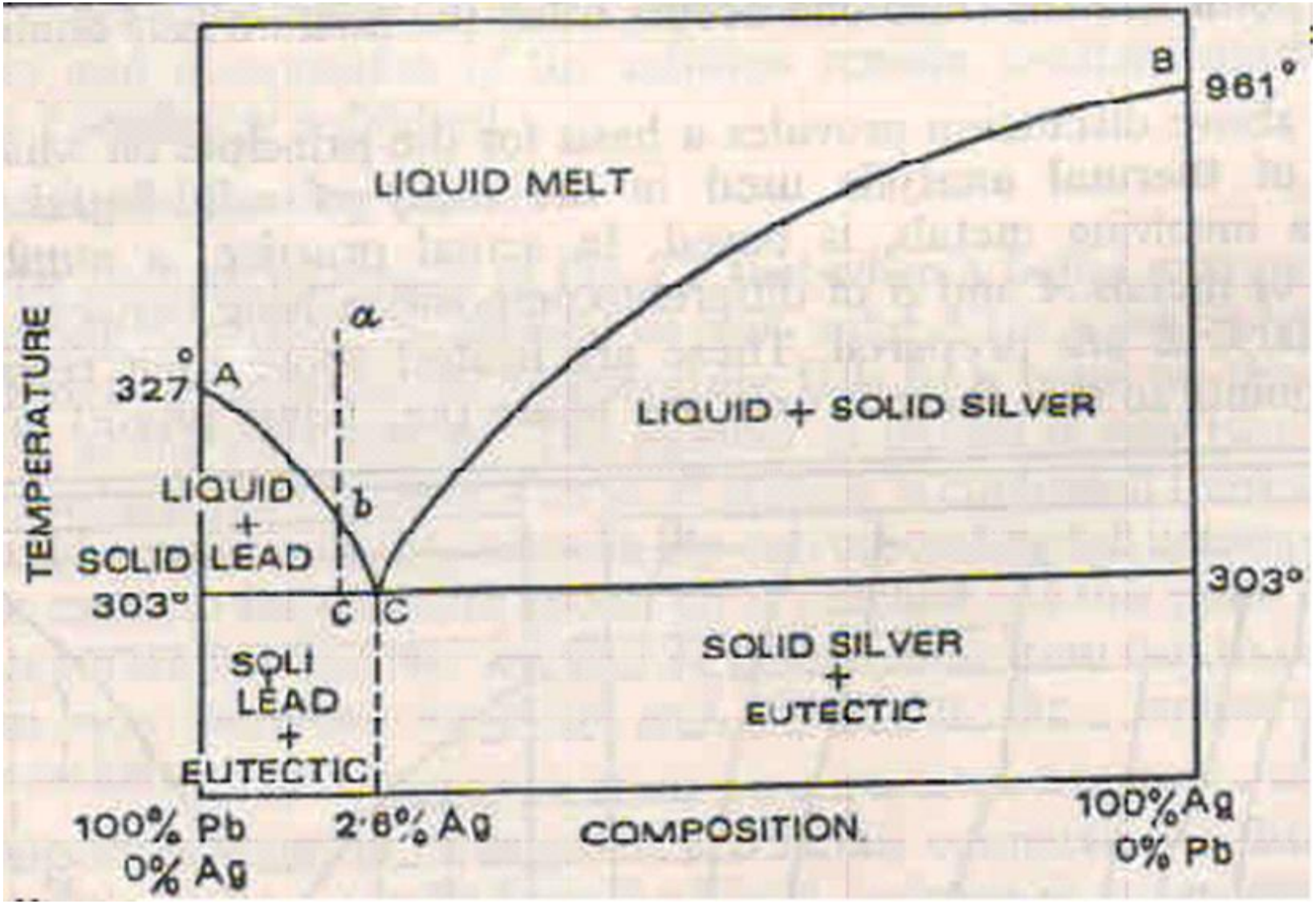
This system has two component and four phases.

- Solid silver
- Solid lead
- Solution of molten silver and lead
- Vapor

But the boiling point of Ag and Pb is completely high; the vapor phase is completely absent. Since the pressure has nearly no affected on equilibrium so the system can be conveniently represented by temp.-conc. diagram.

Such solid liquid system with the gas phase is absent is called condensed system.

Simple Eutectic(Lead-Silver System)



- The curve CB(freezing curve of Ag)
- The curve CA(freezing curve of Pb)
- The eutectic point ‘C'
- The Area ACB

Curve CB →→Freezing curve of Ag.

- It shows the effect on freezing point of Ag on addition of Pb in small quantities.
- The curve starts from (961)°C the M.P of Ag, where pure Ag coexists as solid and liquid(Vapors being neglected)

- The curve indicates that the meeting point of Ag falls gradually on adding Pb, along CB till the lowest point C (303)°C is reached where solution gets saturated with request to lead. At O more Pb can go in solution and consequently, the M.P. does not fall any further and if any Pb is added it separates as solid phase.
- Along this curve, solid Ag and solution (Vapors being negligible) coexist and hence, according to reduced phase rule equation $F = 2 - P + 1$ i.e. system is invariant. The point O(303)°C corresponds to a fixed composition of 2.62.6Ag and solution and 97.4 Pb and is known as eutectic composition.
- On cooling the whole mass crystallizes out as such.

- Curve CA→→Freezing curve of Pb
- It represents the effect on freezing point of Pb on gradual addition of small amount of Ag to it, point B is the M.P of pure Pb(−327)∘c.
- Along CA, the M.P gradually falls on addition of Ag till lowest point C is reached
- At this point solution gets saturated with respect to Ag and M.P of Pb does not fall any more. List item
- On cooling whole mass crystallizes out. Therefore the system is univariant like CA.

Point C → Eutectic point

- The two curve CA and CB meet at C, where three phases solid Ag, solid Pb and their solution coexist and according phase rule. The point of C represents a fixed composition of Ag −2.6 is called eutectic composition.
- At eutectic composition ^ temperature remains constant until the whole of melt solidifies in block to become solid of eutectic composition. However, further cooling results in simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point C.
- Bellow temperature line there are two regions.
- Eutectic solid + solid Ag in crystalline -stable
- Eutectic + solid Pb in crystalline-stable.

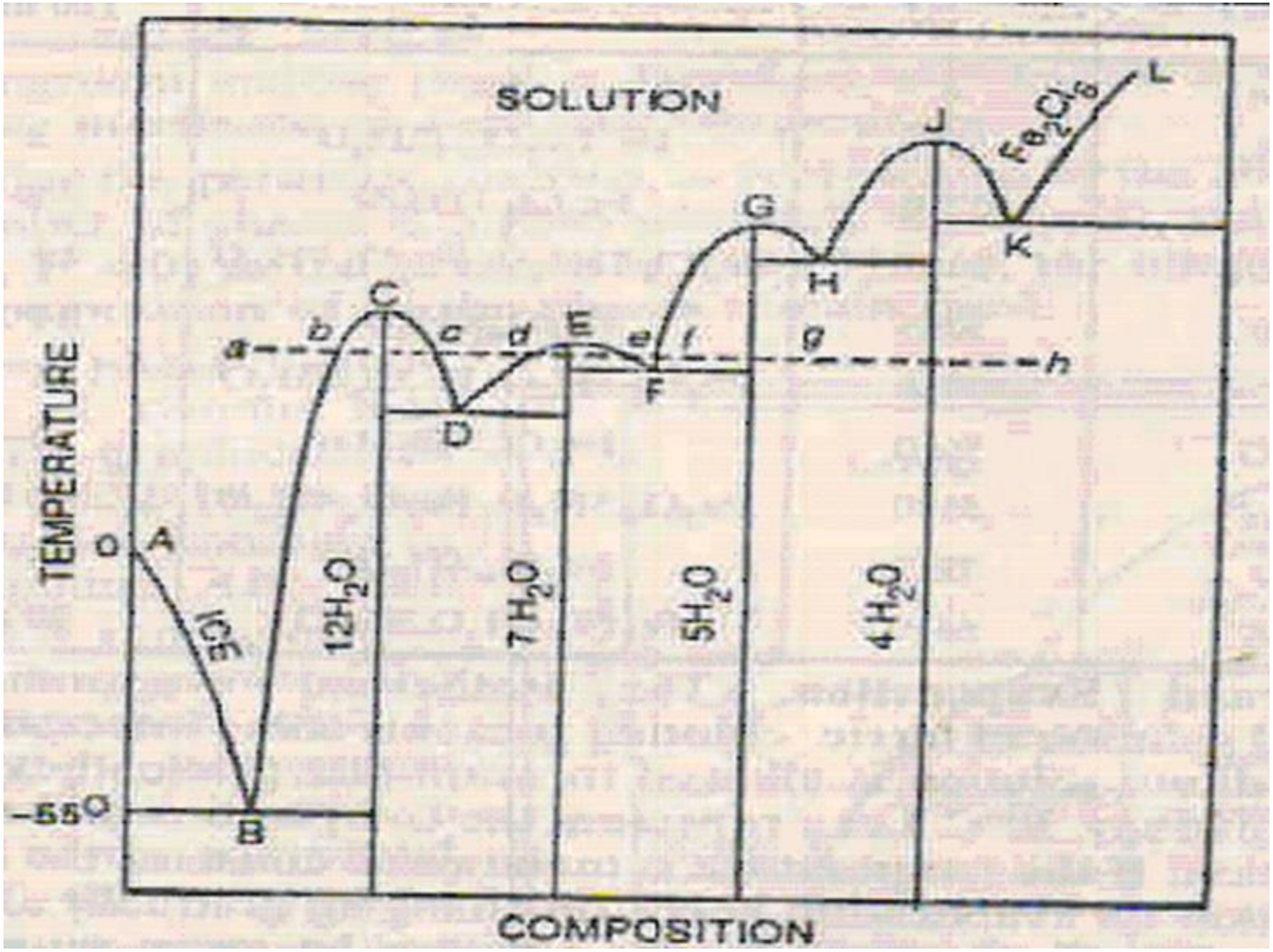
- It represents solution of Pb-Ag sample of Pb containing less than 2.6% Ag is taken at an arbitrary pt. on curve allowing mass cool temp gradually falls without any charge in composition till this point is reached to curve CB (M.pt. may be P).
- On lowering the temp lead begins to separate out of the composition varies along Pb till pt 0 is reached. On cooling whole mass solidifies into a block.

APPLICATIONS:-

- Used in Pattison's process of desilverization of Pb.
- If Pb is less than 2.6 Pb will separate out from solution,

If Pb is more than 2.6 Ag will separate out from solution

Ferric chloride-Water system



In this system four congruently melting compounds are formed which are,

- Dodecahydrate($Fe_2Cl_6.12H_2O$)
- Heptahydrate($Fe_2Cl_6.7H_2O$)
- Pentahydrate ($Fe_2Cl_6.5H_2O$)
- Tetrahydrate($Fe_2Cl_6.4H_2O$).

- The phase diagram consists of four maxima corresponding to the formation of these hydrates.
- Points C, E,G, J represents the congruent melting points of dodeca, hepta, penta and tetra hydrates respectively.
- The congruent melting point of a salt hydrate is also known as the dystectic point.

There are five cryohydric points at B, D, F, H and K.

- A is the melting point of ice.
- Addition of Fe_2Cl_6 lowers the melting point along AB.
- At the cryohydric point B the solution becomes saturated w.r.t dodecahydrate and represents the lowest temperature that can be attained with this system.
- Curves BCD, DEF, FGH and HJK represents the solubilities of dodeca, hepta, penta and tetra respectively while KL represents the solubility characteristic of the anhydrous salt.
- In the diagram the solubility of each hydrate increases with the rise of temperature.

- Now consider the phase changes that result when an unsaturated solution represented by point k is concentrated isothermally by adding anhydrous ferric chloride along KL.
- Firstly a saturated solution of dodecahydrate results at l.
- At m the whole mass solidifies to form dodecahydrate which melts when more of ferric chloride is added.
- Dodecahydrate disappears beyond n and between n and o an unsaturated solution exists.
- The solution becomes saturated with respect to heptahydrate at D.

- Further addition of ferric chloride increases the amount of solid heptahydrate in the solution and at p the whole solutions solidifies yielding heptahydrate.
- The heptahydrate persists upto q.
- Between q and r the solution remains unsaturated, at r the pentahydrate begins to crystallize out.
- At s solidification of whole mass into pentahydrate occurs.
- Between s and t a mixture of penta and tetrahydrate exists which is completely converted into tetrahydrate at t, beyond which tetrahydrate decomposes into anhydrous ferric chloride and at u only the anhydrous salt remains.

Fe_2Cl_6 –Water System : Details

POSITIONS	PHASE (S) at Equilibrium	C	P	Temp	F
A	$Ice_{(s)}$	1	2	0°C	0
Curve-AB	$Ice_{(s)}$ + **Solution** of Fe_2Cl_6	2	2		1
B	$Ice_{(s)}$ + **Solution** of Fe_2Cl_6 + $Fe_2Cl_6.12H_2O_{(s)}$	2	3	-55°C	0
Curve-BC	**Solution** of Fe_2Cl_6 + $Fe_2Cl_6.12H_2O_{(s)}$	2	2		1
C	$Fe_2Cl_6.12H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	1	2	37°C	0
Curve-CD	$Fe_2Cl_6.12H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	2	2		1
D	$Fe_2Cl_6.12H_2O_{(s)}$ + **Solution** of Fe_2Cl_6 + $Fe_2Cl_6.7H_2O_{(s)}$	2	3	26°C	0
Curve-DE	**Solution** of Fe_2Cl_6 + $Fe_2Cl_6.7H_2O_{(s)}$	2	2		1
E	$Fe_2Cl_6.7H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	1	2	32.5°C	0
Curve-EF	$Fe_2Cl_6.7H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	2	2		1

POSITIONS	PHASE (S) at Equilibrium	C	P	Temp	F
F	$Fe_2Cl_6.7H_2O_{(s)}$ + **Solution** of Fe_2Cl_6 + $Fe_2Cl_6.5H_2O_{(s)}$	2	3	30°C	0
Curve-FG	**Solution** of Fe_2Cl_6 + $Fe_2Cl_6.5H_2O_{(s)}$	2	2		1
G	$Fe_2Cl_6.5H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	1	2	56°C	0
Curve- GH	$Fe_2Cl_6.5H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	2	2		1
H	$Fe_2Cl_6.5H_2O_{(s)}$ + **Solution** of Fe_2Cl_6 + $Fe_2Cl_6.4H_2O_{(s)}$	2	3	55°C	0
Curve-HJ	**Solution** of Fe_2Cl_6 + $Fe_2Cl_6.4H_2O_{(s)}$	2	2		1
J	$Fe_2Cl_6.4H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	1	2	73.5°C	0
Curve-JK	$Fe_2Cl_6.4H_2O_{(s)}$ + **Solution** of Fe_2Cl_6	2	2		1
K	$Fe_2Cl_6.4H2O_{(s)}$ + **Solution** of Fe_2Cl_6 + $Fe_2Cl_{6(s)}$	2	3	66°C	0
Curve- KL	**Solution** of Fe_2Cl_6 + $Fe_2Cl_{6(s)}$	2	2		1

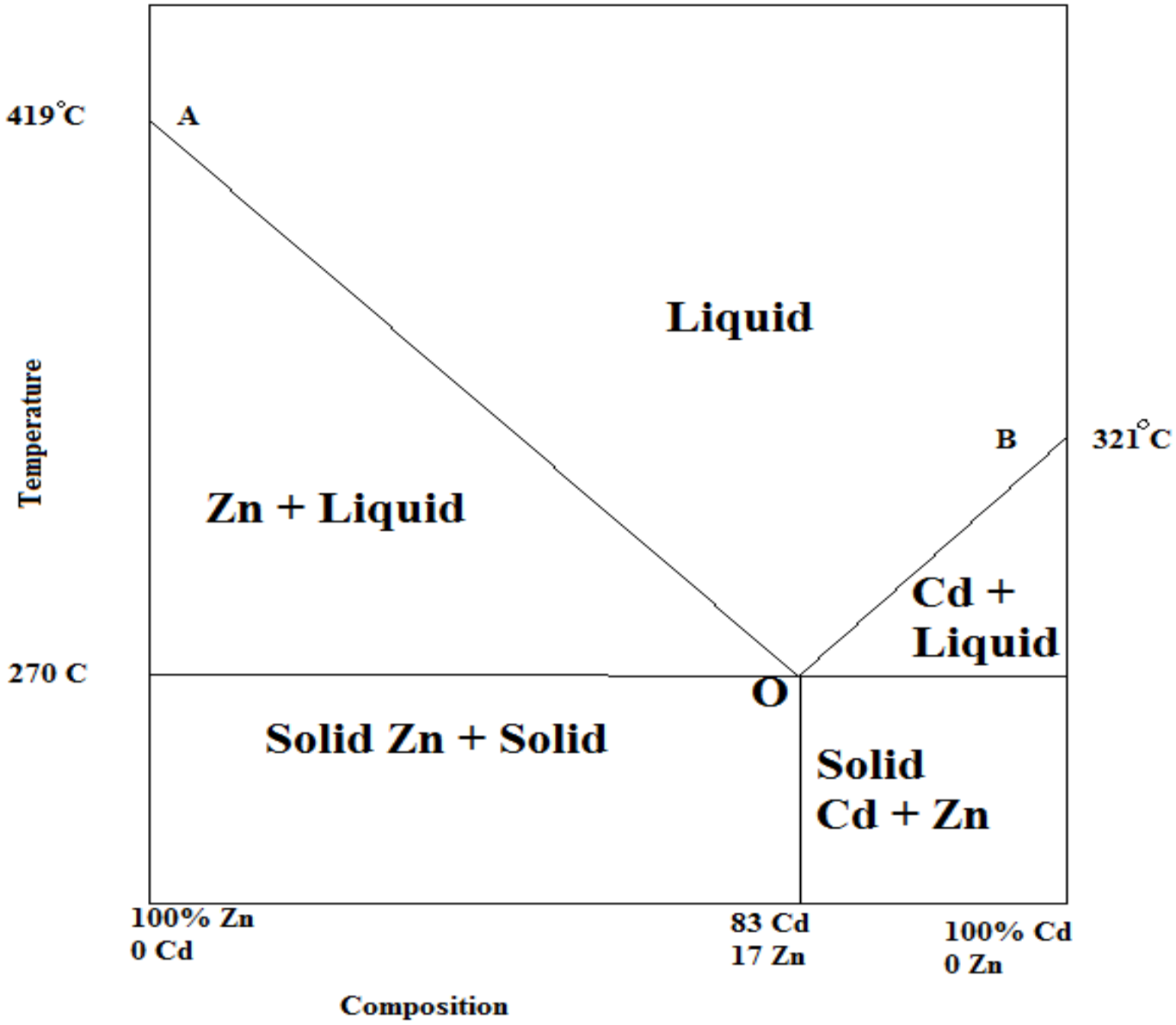
Uses of Eutectic Systems (Freezing mixtures)

System	% Salt in the Eutectic	Eutectic Temperature ºC
$NaCl.2H_2O$-Ice	23	-22
KI-Ice	52	-23
$CaCl_2.6H_2O$-Ice	15.2	-55.9
$NaNO_3$-Ice	33.3	-18.1
NH_4Cl-Ice	20.1	-16

Uses of Eutectic Systems (Low melting alloys)

- Wood metal:50% Bi ; 25% Pb; 12.5%Sn & 12.5% Cd-mp=65ºC
- Safety devices: Fuse wires ; Plugs

Zn- Cd System


419°C
A
Liquid
B
321°C
Temperature
Zn + Liquid
Cd +
Liquid
270 C
O
Solid Zn + Solid
Solid
Cd + Zn
100% Zn
0 Cd
83 Cd
17 Zn
100% Cd
0 Zn
Composition

- AO curve is the freezing curve of the Zinc.
- BO curve is the freezing curve of the Cd.
- O is the eutectic point.
- Above AO, F=2 bivariant
- Above BO, F=2 bivariant
- Point O is the eutectic point F-0, Non-variant.

Advantages of Phase Rule

- It provides a convenient method for classification of equilibrium states of system with the help of phase, component and degrees of freedom.
- It predicts the behaviour of system with changes in the intensive variables, such as temperature, pressure and composition.
- It indicates that different systems having the same number of degrees of freedom behave in the same manner.
- It is applicable to macroscopic system and therefore information about the molecular structure is not necessary .
- It takes no account of nature of the reactants or products in phase.
- It is applicable to physical as well as chemical equilibrium.

Applications of Phase rules

- Age- Hardening alloys
- Austenitic stainless steel
- Permanent magnets
- Development of new alloys
- Fabrication of these alloys into useful configurations.
- Design and control of heat treatment procedures for specific alloys that will produce the required mechanical, physical and chemical properties.
- Solving problems that arise with specific alloys in their performance in commercial applications.

Thank You