The Phase rule

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TERMS & Examples

- Homogenous Chemical Equilibrium

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

- Heterogonous Chemical Equilibrium

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

- Heterogonous Physical Equilibrium

  Solid → Liquid (Melting)

  Liquid → Vapour (Vaporisation)

  Solid → Vapour (Sublimation)

TERMS & Examples (Contd….)

- **PHASE , P** : Physically **distinct** & mechanically separable
- **COMPONENTS , C : Minimum** number of **chemical** species by means of which the composition each phase can be described

C = Number of chemical compounds – No of chemical and or physical (material or charge balance) relations existing with them

(i) WATER SYTEM: ice → water → vapor

P = 1, 2 or 3 ; C = 1 ; F = ?

TERMS & Examples(Contd.....)

(iii) Pb & Ag System

C= 2 ; P = 1, 2 or 3 ; F = 2 , 1 , 0

NB : There are no (chem or phys) relation between Pb & Ag

% **Pb = 100 - % Ag** is only a mathematical relation

DEGREES OF FREEDOM , F (Variables) **: Minimum** number of independent variables that must be fixed in order to understand the system fully.

- **The values of P & F depend on the condition**

PHASE RULE - Derivation

F = C-P+2 (Gibbs Phase Rule)

Degrees of freedom (F)

= Total No of variables – Total No of equations connecting them.

Total No of variables:

Conc.variables

C-1 for each phase

P(C-1) for all P phases + 2 (For P & T)

PHASE RULE – Derivation (Contd…)

Total No of equations

P-1 (For each component) ;

C(P-1) For all the ‘ C ’ components

Hence , F = {P(C-1)+2} – C(P-1)

= C-P + 2

PHASE CHANGES

$dG = VdP - SdT = 0$ (For equilibrium)

Clapeyron equation

$dp/dT = \Delta H/(T\Delta V)$

Solid Liquid (Fusion or Melting)

Clausius-Clapeyron equations (Vapors)

$d(\ln p)/dT = \Delta H/(RT^2)$

Liquid Vapour (Vaporisation)

Solid Vapour (Sublimation)

SYSTEMS TO BE STUDIED

PHASE DIAGRAM OF

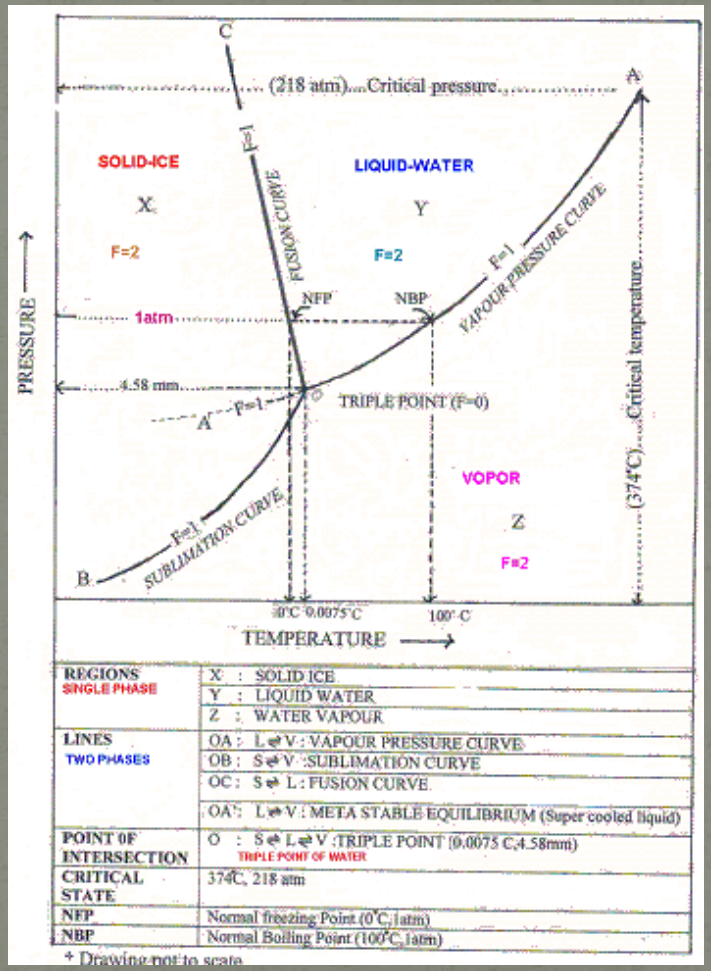
- One Component Systems
  - Water system
  - Sulphur system
- Two Component System

  Simple eutectic system - Lead-Silver system
- Compounds with congruent melting point.

  Ferric chloride-water system
- Compounds with incongruent melting point(SS).

  Sodium sulphate-water system

Water system



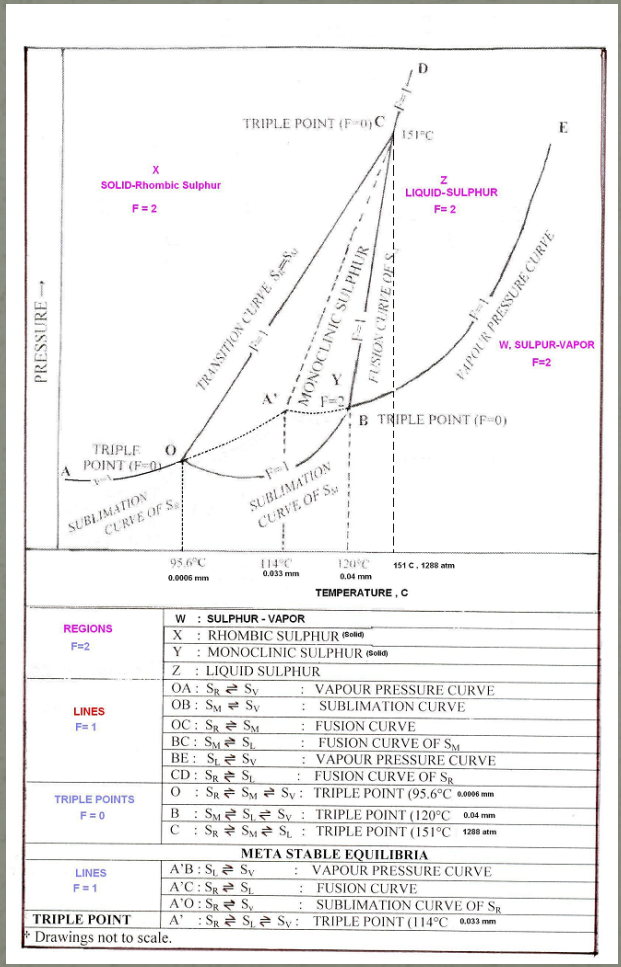
REGIONS SINGLE PHASE	X : SOLID ICE
	Y : LIQUID WATER
	Z : WATER VAPOUR
LINES TWO PHASES	OA : L ⇌ V : VAPOUR PRESSURE CURVE
	OB : S ⇌ V : SUBLIMATION CURVE
	OC : S ⇌ L : FUSION CURVE
	OA' : L ⇌ V : META STABLE EQUILIBRIUM (Super cooled liquid)
POINT OF INTERSECTION	O : S ⇌ L ⇌ V : TRIPLE POINT (0.0075 C,4.58mm) TRIPLE POINT OF WATER
CRITICAL STATE	374C, 218 atm
NFP	Normal freezing Point (0°C,1atm)
NBP	Normal Boiling Point (100°C,1atm)

* Drawing not to scale

Water System-Discussion

1. Curves-Sublimation, Vaporization, Fusion
2. Meta stable equilibrium curve
3. Ice Water curve has –ve slope
4. M.P of ice decreases with increase in p
5. Areas :F= 2 ; Lines :F= 1
6. Triple point:F = 0,0.0075ºC,4.58 mm Hg
7. Critical state 374ºC , 218 atm

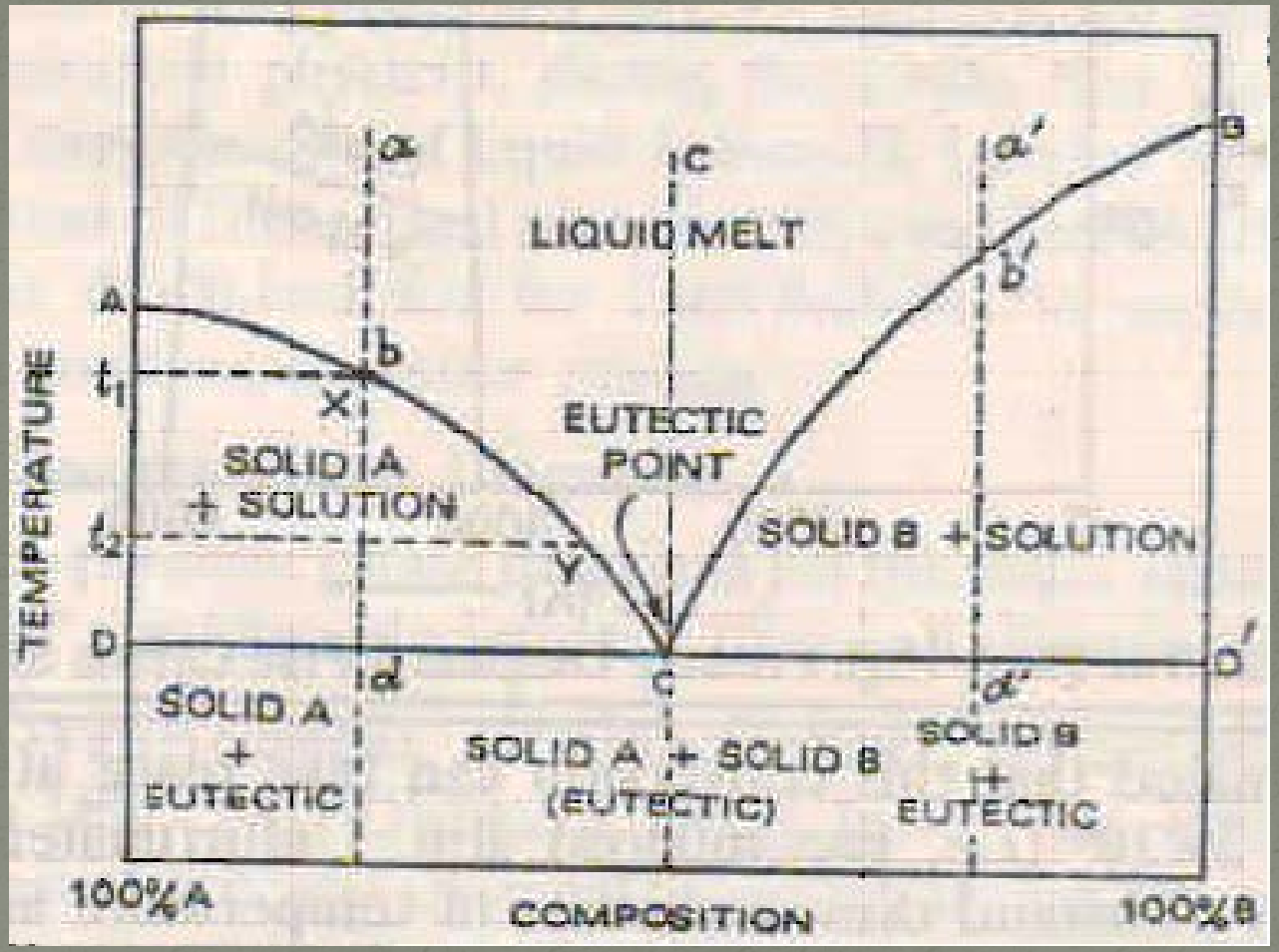
SULPHUR SYSTEM



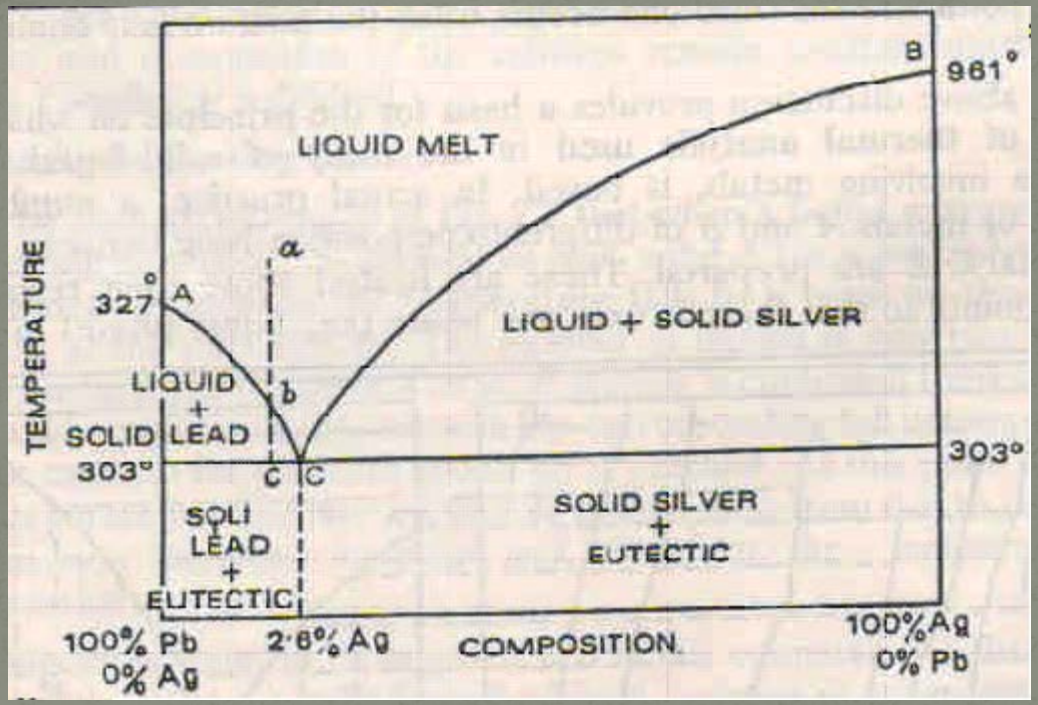
REGIONS F=2	W : SULPHUR - VAPOR	
	X : RHOMBIC SULPHUR (Solid)	
	Y : MONOCLINIC SULPHUR (Solid)	
	Z : LIQUID SULPHUR	
LINES F= 1	OA : $S_R \rightleftharpoons S_V$	: VAPOUR PRESSURE CURVE
	OB : $S_M \rightleftharpoons S_V$	: SUBLIMATION CURVE
	OC : $S_R \rightleftharpoons S_M$	: FUSION CURVE
	BC : $S_M \rightleftharpoons S_L$	: FUSION CURVE OF S_M
	BE : $S_L \rightleftharpoons S_V$	: VAPOUR PRESSURE CURVE
	CD : $S_R \rightleftharpoons S_L$	: FUSION CURVE OF S_R
TRIPLE POINTS F = 0	O : $S_R \rightleftharpoons S_M \rightleftharpoons S_V$	: TRIPLE POINT (95.6°C 0.0006 mm
	B : $S_M \rightleftharpoons S_L \rightleftharpoons S_V$	: TRIPLE POINT (120°C 0.04 mm
	C : $S_R \rightleftharpoons S_M \rightleftharpoons S_L$	: TRIPLE POINT (151°C 1288 atm
META STABLE EQUILIBRIA		
LINES F = 1	A'B : $S_L \rightleftharpoons S_V$	: VAPOUR PRESSURE CURVE
	A'C : $S_R \rightleftharpoons S_L$	: FUSION CURVE
	A'O : $S_R \rightleftharpoons S_V$	: SUBLIMATION CURVE OF S_R
TRIPLE POINT	A' : $S_R \rightleftharpoons S_L \rightleftharpoons S_V$	: TRIPLE POINT (114°C 0.033 mm

* Drawings not to scale.

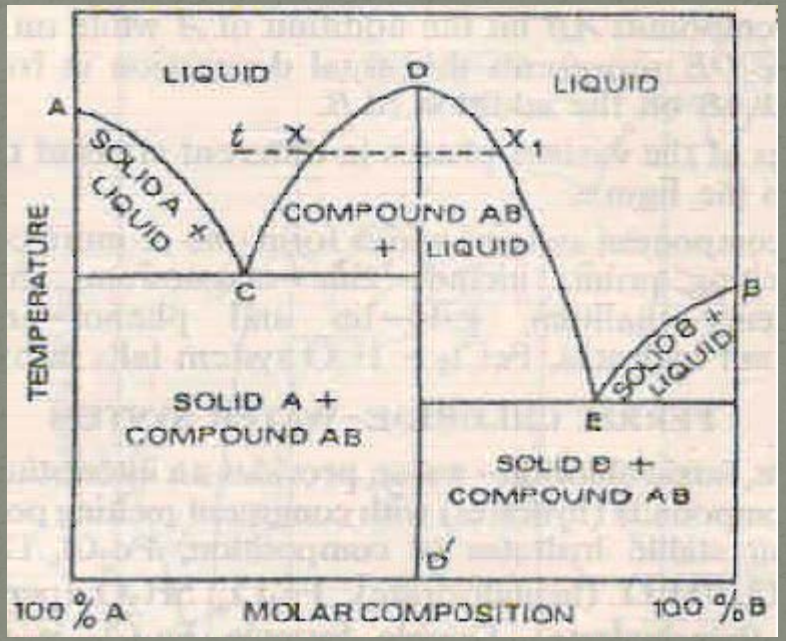
Simple eutectic system-General



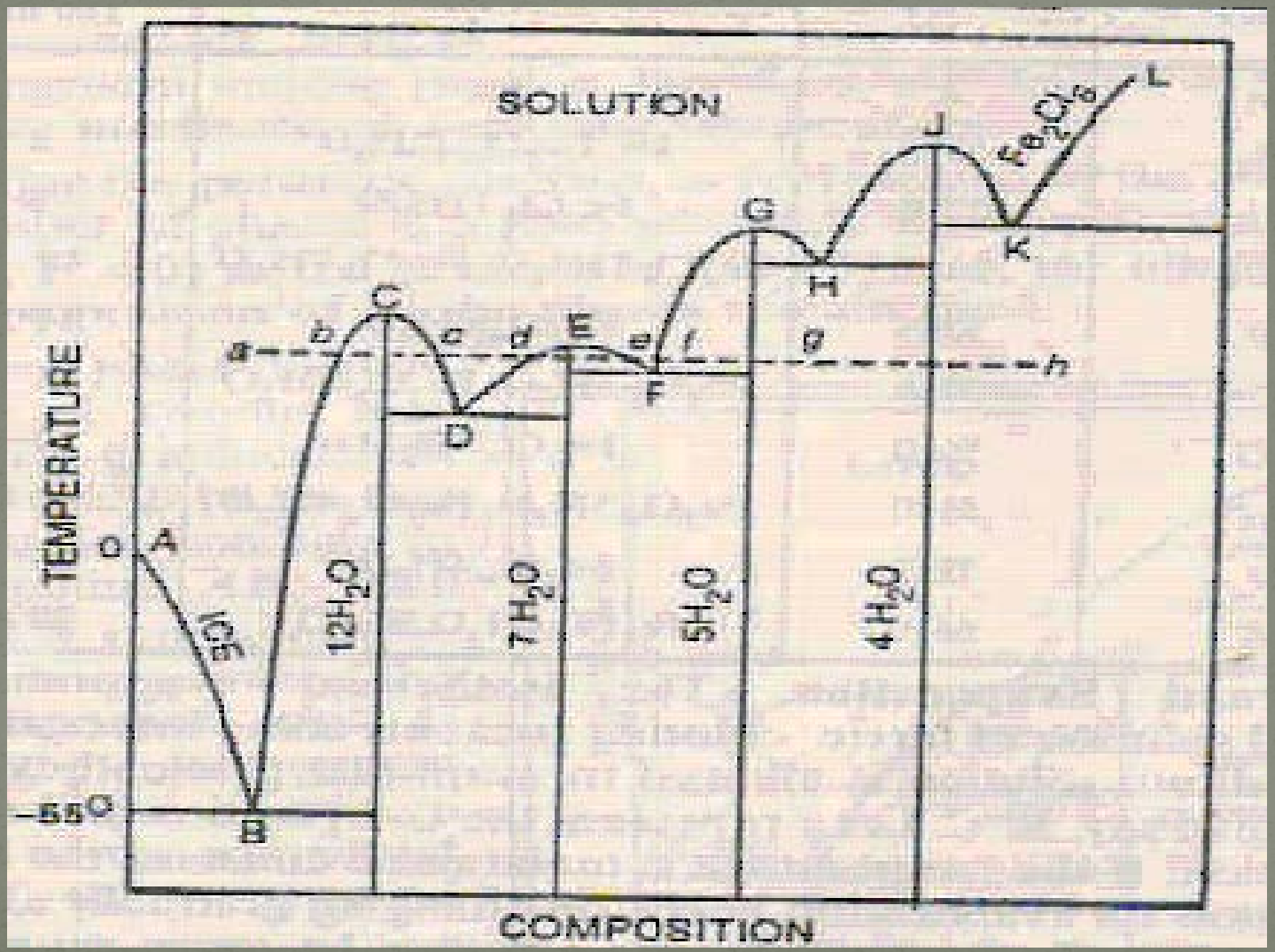
Simple Eutectic(Lead-Silver System)



Compounds formation with congruent melting point.



Ferric chloride-Water system

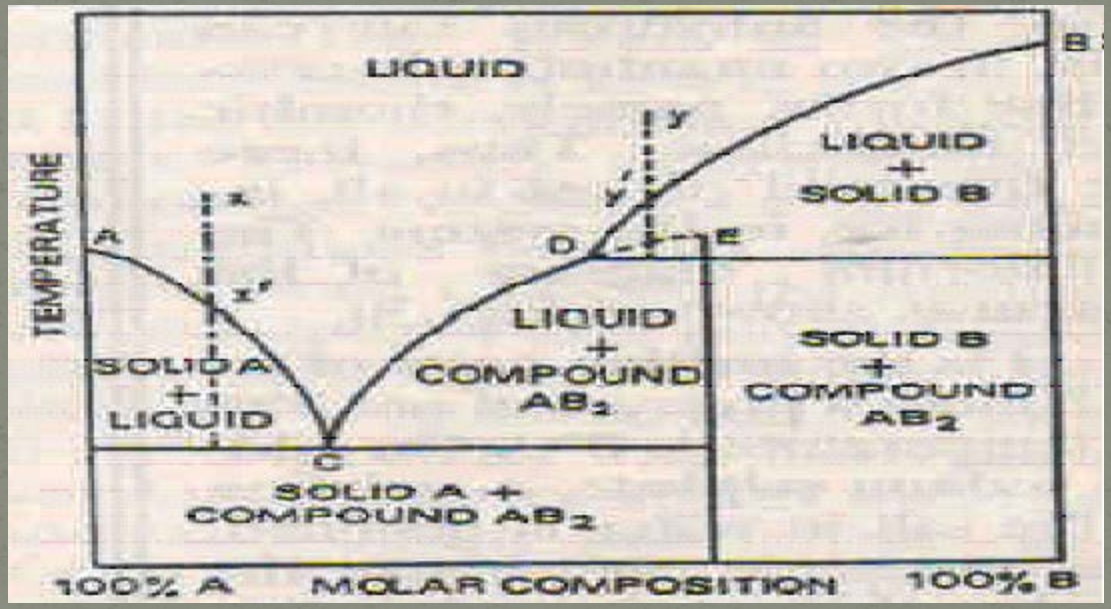


Fe_2Cl_6 –Water System : Details

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

Compound with incongruent melting point.

Peritectic Reaction(Change)-General

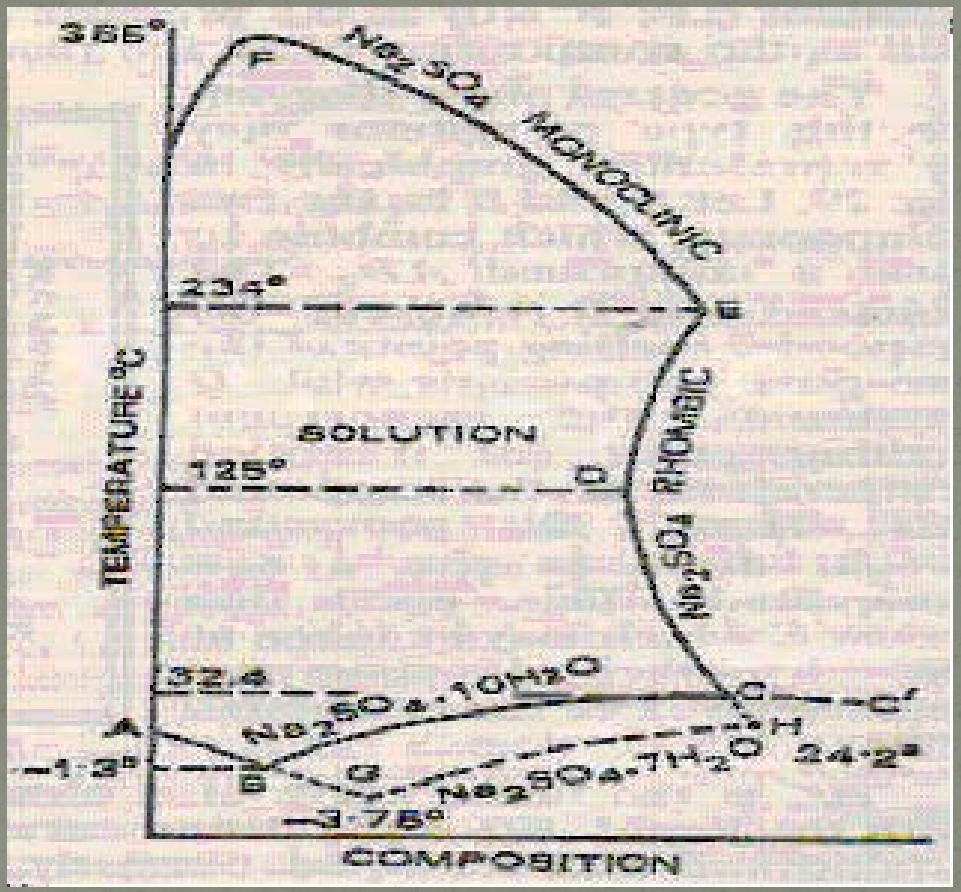


Compound formation with incongruentmelting point-Examples

- NaCl-Water ($NaCl.2H_2O$)
- $CaCl_2$-Water ($CaCl_2.6H_2O$)
- Na_2SO_4-Water
  ($Na_2SO_4.10H_2O$, $Na_2SO_4.7H_2O$ & $Na_2SO_4.4H_2O$)

Sodium sulphate-Water

Perttectic Change



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

Thank you