

Phase Rule:

Phase rule was deduced by Willard Gibbs in 1876. It is applicable to all heterogenous systems and helps to know the effect of temperature , pressure and concentration on the system.

It can be stated as the sum of the number of phases and degrees of freedom of any system exceeds the number of components by 2.

$$P+F=C+2$$

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

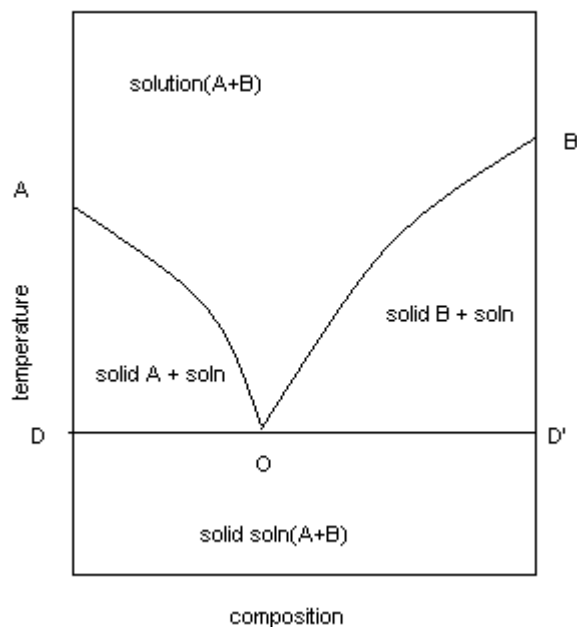
Terms involved in phase rule:

1. System: Part of the universe under study.
2. Homogeneous system: when system has same concentration throughout (All constituents in same state)
3. Heterogeneous system: system has different concentration in different regions of the system.
4. Phase: it is homogenous part of the system which is physically distinct and separated from other parts of the system by definite bounding surface.

Example:	Phases	P=
Air	Gases	1
Water in beaker	L+G	2
Water+benzene	L+L+G	3
$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	S+S+G	3
water		

5. Component: It is the minimum number of chemical entities which are essential to express the composition of every phase present in the system directly or in the form of a chemical equation.

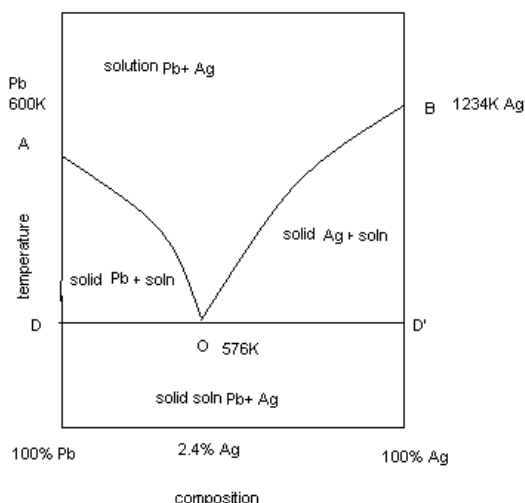
Two component system: Type I: Simple Eutectic system:



Simple eutectic system has $C=2$

Salient feature	Name	Phases	$P=$	$F'=C-P+1$	Variance
Points: A	F.P of pure A	Solid A + soln	2	1	monovariant
Point: B	F.P of pure B	Solid B+ soln	2	1	monovariant
Points: O	Eutectic point	Solid A + Solid B +soln	3	0	nonvariant
Curve AO	FP curve of A	Solid A + soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Curve BO	F.P curve of B	Solid B+ soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Solidus AD	i.e 100% A				
Solidus BD'	gives information about the composition of solid phase. i. e !00% B				
Solidus DD'	gives information about the composition of solid phase. i. e % of A and B				
Area above AOB	Solution of A and B with diff composition $P=1$, hence $F'=2$, bivariant				
Area Below DD'	Solid solution mixture of A and B with different composition , $P=1$, hence $F'=2$, bivariant				
Area within AOD	Solid A + soln, $P=2$, hence $F'=1$, monovariant				
Area within BOD'	Solid B + soln, $P=2$, hence $F'=1$, monovariant				

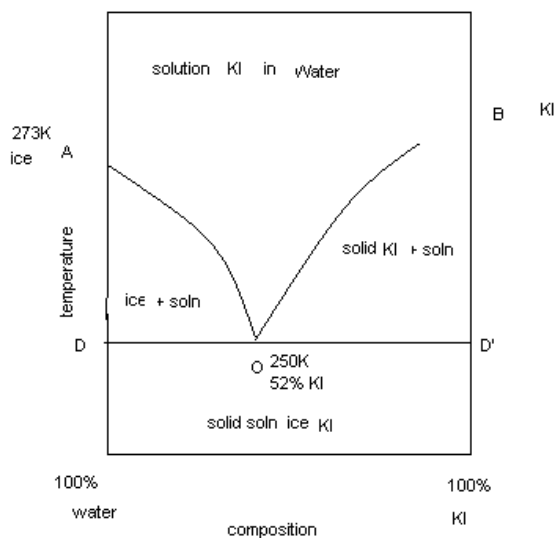
Simple Eutectic system: example Pb+ Ag



Simple eutectic system has $C=2$

Salient feature	Name	Phases	$P=$	$F'=C-P+1$	Variance
Points: A	F.P of pure Pb	Solid Pb+ soln	2	1	monovariant
Point: B	F.P of pure Ag	Solid Ag+ soln	2	1	monovariant
Points: O	Eutectic point	Solid Pb + Solid Ag +soln	3	0	nonvariant
Curve AO	F.P curve of Pb	Solid Pb + soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Curve BO	F.P curve of Ag	Solid Ag+ soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Solidus AD	gives information about the composition of solid phase. i. e 100% Pb				
Solidus BD'	gives information about the composition of solid phase. i. e 100% Ag				
Solidus DD'	gives information about the composition of solid phase. i. e % of Pb and Ag				
Area above AOB	Solution of Pb and Ag with diff composition $P=1$, hence $F'=2$, bivariant				
Area Below DD'	Solid solution mixture of Pb and Ag with different composition , $P=1$, hence $F'=2$, bivariant				
Area within AOD	Solid Pb+ soln, $P=2$, hence $F'=1$, monovariant				
Area within BOD'	Solid Ag+ soln, $P=2$, hence $F'=1$, monovariant				

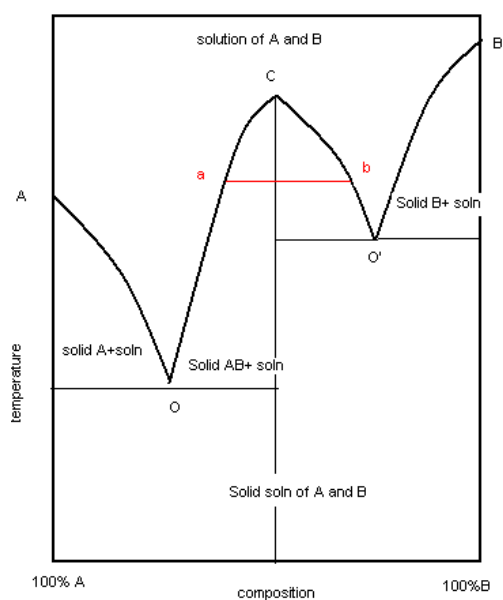
KI-water system:



Salient feature	Name	Phases	P=	F'=C-P+1	Variance
Points: A	F.P of pure water	Solid ice + soln	2	1	monovariant
Point: B	F.P of pure KI	Solid KI+ soln	2	1	monovariant
Points: O	Eutectic point	Solid ice + Solid KI + soln	3	0	nonvariant
Curve AO	FP curve of water	Solid ice+ soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Curve BO	Solubility curve of KI	Solid KI+ soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Solidus AD	Gives information about the composition of solid phase. i. e !00% H ₂ O				
Solidus BD'	Gives information about the composition of solid phase. i. e !00% KI				
Solidus DD'	Gives information about the composition of solid phase. i. e % of H ₂ O and KI				
Area above AOB	Solution of H ₂ O and KI with diff composition P=1, hence F'=2, bivariant				
Area Below DD'	Solid solution mixture of H ₂ O and KI with different composition , P=1, hence F'=2, bivariant				
Area within AOD	Solid Ice+ soln, P=2, hence F'=1, monovariant				
Area within BOD'	Solid KI + soln, P=2, hence F'=1, monovariant				

Two component system: Type II:

Formation of a compound with congruent MP: reduced phase rule: $F'=C-P+1$



new terms:

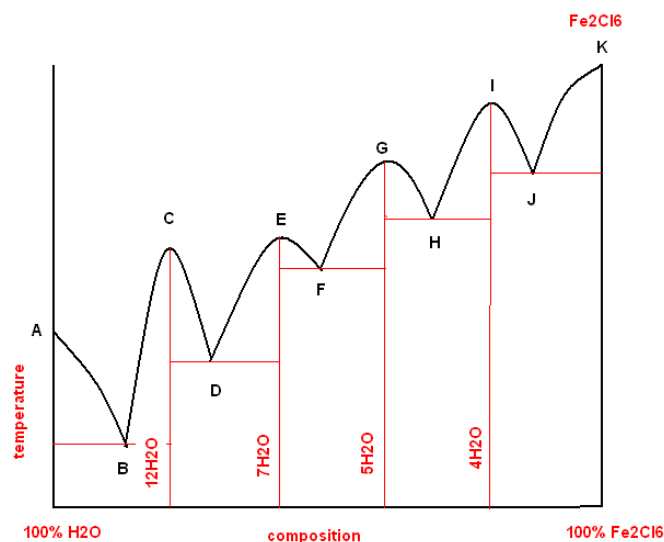
congruent MP: point where the composition of solid and soln is same hence $C=1$

Retroflex solubility: at a temperature the solid has two distinct solubilities a and b

Salient feature	Name	Phases	P=	C=	F'	Variance
Point A	FP of pure A					
Point B	FP of Pure B					
Point O	Eutectic point	Solid A+ solid AB + soln	3	2	0	nonvariant
Point C	Congruent MP of AB	Solution and solid AB with same composition	2	1	0	nonvariant
Point O'	Eutectic point	Solid B + solid AB + soln	3	2	0	nonvariant
Curve AO	FP curve of A in presence of B	Solid A + soln	2	2	1	mono variant
Curve OCO'	Solubility curve of AB	Soild AB and soln	2	2	1	mono variant
Curve O'B	FP curve of B in presence of A	Solid B + soln	2	2	1	mono variant
Area above AOB	Solution of A and B with diff composition		1	2	2	bivariant
Area within AOD	Solid A and soln		2	2	1	mono variant
Area below OC and CO'	Solid AB and soln		2	2	1	mono variant
Area below O'B	Solid B and soln		2	2	1	mono variant
Area below O and O'	Solid solution		1	2	2	bivariant
Point a and b: Retroflex solubilities of solid AB at temperature t						

FeCl₃-water system:

FeCl₃ forms four compounds with water as dodecahydrate [FeCl₃ 12H₂O], heptahydrate [FeCl₃ 7H₂O], pentahydrate [FeCl₃ 5H₂O], tetrahydrate [FeCl₃ 4H₂O]. so the phase diagram of the system consists of five simple eutectic diagrams as follows.



Salient feature	Name	Phases	P=	C=	F'	Variance
Point A [273K]	FP of water					
Curve AB	FP curve of water in pre of FeCl ₃	Solid ice+ soln	2	2	1	monovariant
Point B [218K]	Eutectic point	Ice+ 12H ₂ O+ soln	3	2	0	nonvariant
Curve BC	Solubility curve of 12H ₂ O	12H ₂ O + soln	2	2	1	monovariant
Point C [310K]	Congruent MP of 12 H ₂ O	12H ₂ O + soln	2	1	0	nonvariant
Curve CD	Solubility curve of 12H ₂ O	12H ₂ O + soln	2	2	1	monovariant
Point D [299K]	Eutectic point	12H ₂ O + 7H ₂ O+ soln	3	2	0	nonvariant
Curve DE	Solubility curve of 7H ₂ O	7H ₂ O + soln	2	2	1	monovariant
Point E [305.5K]	Congruent MP of 7H ₂ O	7H ₂ O + soln	2	1	0	nonvariant
Curve EF	Solubility curve of 7H ₂ O	7H ₂ O + soln	2	2	1	monovariant
Point F [303K]	Eutectic point	7H ₂ O + 5H ₂ O+ soln	3	2	0	nonvariant
Curve FG	Solubility curve of 5H ₂ O	5H ₂ O + soln	2	2	1	monovariant
Point G [329K]	Congruent MP of 5H ₂ O	5H ₂ O + soln	2	1	0	nonvariant
Curve GH	Solubility curve of 5H ₂ O	5H ₂ O + soln	2	2	1	monovariant

Point H [328K]	Eutectic point	5H ₂ O + 4H ₂ O+ soln	3	2	0	nonvariant
Curve HI	Solubility curve of 4H ₂ O	4H ₂ O + soln	2	2	1	monovariant
Point I [346.5K]	Congruent MP of 4H ₂ O	4H ₂ O + soln	2	1	0	nonvariant
Curve IJ	Solubility curve of 4H ₂ O	4H ₂ O + soln	2	2	1	monovariant
Point J [339K]	Eutectic point	4H ₂ O + Fe ₂ Cl ₆ + soln	3	2	0	nonvariant
Curve JK	Solubility curve of Fe ₂ Cl ₆	Fe ₂ Cl ₆ + soln	2	2	1	monovariant

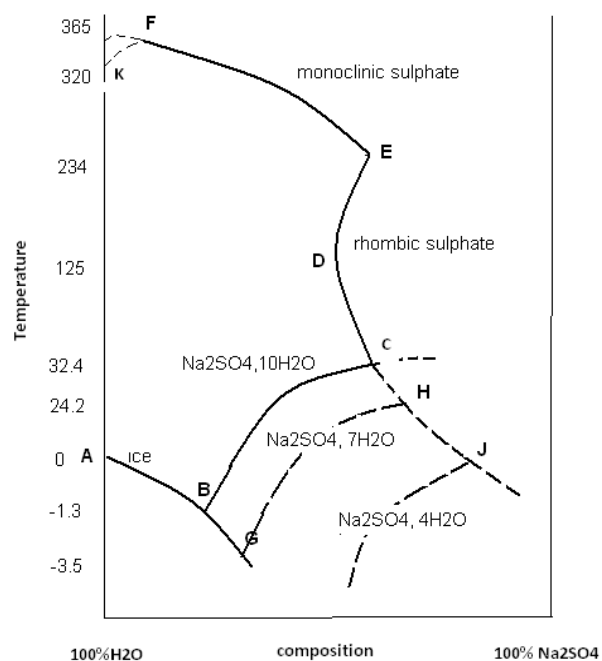
Two component system: Type III:

Formation of a compound with incongruent MP: reduced phase rule: $F' = C - P + 1$

Sodium sulphate-water System:

The system consists of seven phases as decahydrate [Na₂SO₄.10H₂O], heptahydrate[Na₂SO₄.7H₂O],,

Anhydrous Na₂SO₄ rhombic, anhydrous Na₂SO₄ monoclinic, ice and solution.



Salient feature	Name	Phases	P=	C=	F'	Variance
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Point A [0°C]	FP of water					
Curve AB	FP curve of water in pre of Na ₂ SO ₄	Solid ice+ soln	2	2	1	monovariant
Point B [-1.3°C]	Eutectic point	Ice+ 10H ₂ O+ soln	3	2	0	nonvariant
Curve BC	Solubility curve of 10H ₂ O	10H ₂ O + soln	2	2	1	monovariant
Point C [-3.5°C]	incongruent MP of 10 H ₂ O	10H ₂ O + soln + Rhombic sulphate	3	2	0	nonvariant
Curve CD	Solubility curve of Rhombic sulphate	Rhombic sulphate + soln	2	2	1	monovariant
Point D [125 °C]	Point of minimum solubility. above and below Point D, solubility increases					
Curve DE	Solubility curve of Rhombic sulphate	Rhombic sulphate + soln	2	2	1	monovariant
Point E [234 °C]	incongruent MP of	Rhombic sulphate + soln + Monoclinic sulphate	3	2	0	nonvariant
Curve EF	Solubility curve of Monoclinic sulphate	Monoclinic sulphate + soln	2	2	1	monovariant
Point F [365 °C]						
Curve BG	Metastable curve	Supercooled 10 H ₂ O + soln	2	2	1	monovariant
Point G[-3°C]	incongruent MP of 10H ₂ O	10H ₂ O + 7H ₂ O+ soln	3	2	0	nonvariant
Curve GH	Solubility curve of 7H ₂ O	7H ₂ O + soln	2	2	1	monovariant
Point H [24.2 °C]	incongruent MP of 7H ₂ O	7H ₂ O + Rhombic sulphate + soln	3	2	0	nonvariant
Curve HC	Metastable curve of Supercooled Rhombic sulphate	Rhombic sulphate + soln	2	2	1	monovariant
Point J	incongruent MP of supercooled 7H ₂ O	7H ₂ O + 4H ₂ O + soln	3	2	0	nonvariant
Curve IJ	Metastable curve of 4H ₂ O	4H ₂ O + soln	2	2	1	monovariant