# Phase Rule

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1

The *phase rule* is a generalization given by *Willard Gibbs* (1874),which seeks to explain the equilibrium existing in the heterogeneous system. It may be stated as: "*Provided the equilibrium between any number of phases is not influenced by gravity electrical or magnetic forces or by surface action and only by temperature, pressures and concentration, then the number of degrees of freedom(F) of the system is related to the number of components (C) and phases (P) by the phase rule equation*

$$F = C - P + 2$$

for any system at equilibrium at a definite temperature and pressure."

# Phase

A phase is defined as "an homogenous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces.

For example:

(1) At triple point, water consists of three phases:

Ice (s) ⇌ Water (l) ⇌ Water vapour (g)

(2) A gaseous mixture, being thoroughly miscible in all proportions, will constitute one phase only. Thus, a mixture of $N_2$ and $H_2$ forms ***one phase*** only.

(3) If two liquids are immiscible (e.g. benzene and water), they will form ***two*** separate phases.

(4) If two liquids are miscible (e.g. ethanol and water), they will form ***one liquid*** phase only.

(5) A *solution* of a substance in a solvent consists of *one* phase only, e.g. glucose solution in water.

(6) Each *solid* makes up a *separate* phase, except in the case of solid solutions, e.g. many forms of sulphur can exist together, but these are all separate phases.

(7) A *heterogeneous mixture* like

$$CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$

Consists of *three phases* (i.e., two solids and one gaseous)

Similarly, in the equilibrium reaction,

$$Fe\ (s) + H_2O\ (g) \rightleftharpoons FeO\ (s) + H_2(g)$$
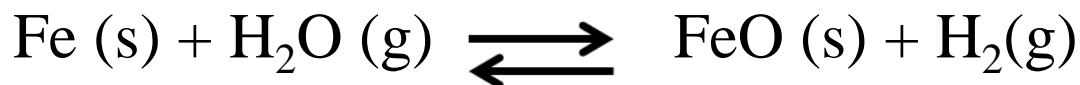
There are two sold phases, Fe and FeO and one gaseous phase consisting $H_2O$ (g) and $H_2$ (g). Thus *three phases* exist in equilibrium.

(8) A homogenous solid solution of a salt constitutes a single phase. Thas Mohr's salt [$FesO_4.(NH_4)_2SO_4.6H_2O$] solution constitutes a single phase.

4

# Component

By the term component is meant " **the smallest number of independent variable constituents**, taking part in the state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation"  For example":

(1) In water system

Ice (s) ⇌ Water (l) ⇌ Vapour(g)
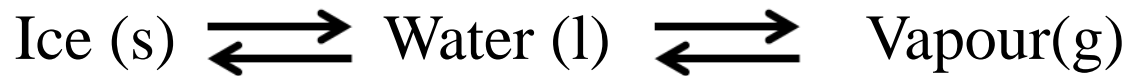
The chemical composition of all the three phases is $H_2O$. Hence it is one component system.

(2) The sulphur system consists of four phases, rhombic, monoclinic, liquid and vapour, the chemical composition of all phases is S. Hence, it is one component system.

*Minimum no. of constituents, sufficient for determining the composition of all phases of system.*

5

(3) The thermal decomposition of $CaCO_3$

$$CaCO_3 (s) \rightleftharpoons CaO(s) + CO_2(g)$$

The composition of each of the three phases can be expressed in terms of at least any two of the independently variable constituents, $CaCO_3$, $CaO$ and $CO_2$. Suppose CaCO3 and CaO are chosen as the two components, then the composition of different phases is represented as follows:

$$CaCO_3 = CaCO_3 + 0\ CaO$$
$$CaO = 0\ CaCO_3 + CaO$$
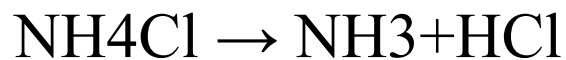$$CO_2 = CaCO_3 - CaO$$

Thus it is a ***two*** component system.

**A system in which ammonium chloride undergoes thermal** composition.

$NH_4Cl\ (s) \rightleftharpoons NH_3(g) + HCl\ (g)$

There are two phases, one solid-NH4Cl and the other gas – a mixture of NH3 and HCl. There are three constituents. Since NH3 and HCl can be prepared in the correct stoichiometric proportions by the reaction:

$NH_4Cl \rightarrow NH_3 + HCl$

The composition of both the solid and gaseous phase can be expressed in terms of

NH4Cl. Hence the number of components is one.

If additional HCl (or NH3) were added to the system, then the decomposition of NH4Cl would not give the correct composition of the gas phase. A second component, HCl (or NH3) would be needed to describe the gas phase.

**Degrees of freedom (or variance)**

The degrees of freedom or variance of a system is defined as the minimum number of variables such as temperature, pressure, concentration, which must be arbitrarily fixed in order to define the system completely.

e.g. the state of system explained by T,P and V (three variable)

But only two variable is sufficient to determine the state of system

If T and P are known for a system, we can calculate V, by using PV=nRT

Thus a pure gas has two degree of freedom.

**F (degrees of freedom; variance):**

number of attributes of a system ($T$, $P$, phase composition) that can be changed independently without creating or destroying a phase, or ...
number of parameters ($T$, $P$, system composition) that need to be described to completely define the composition and identity of each phase.
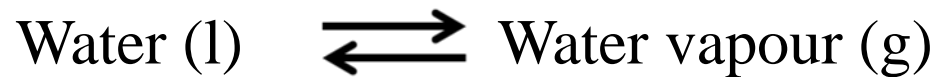
F = 3 : trivariant
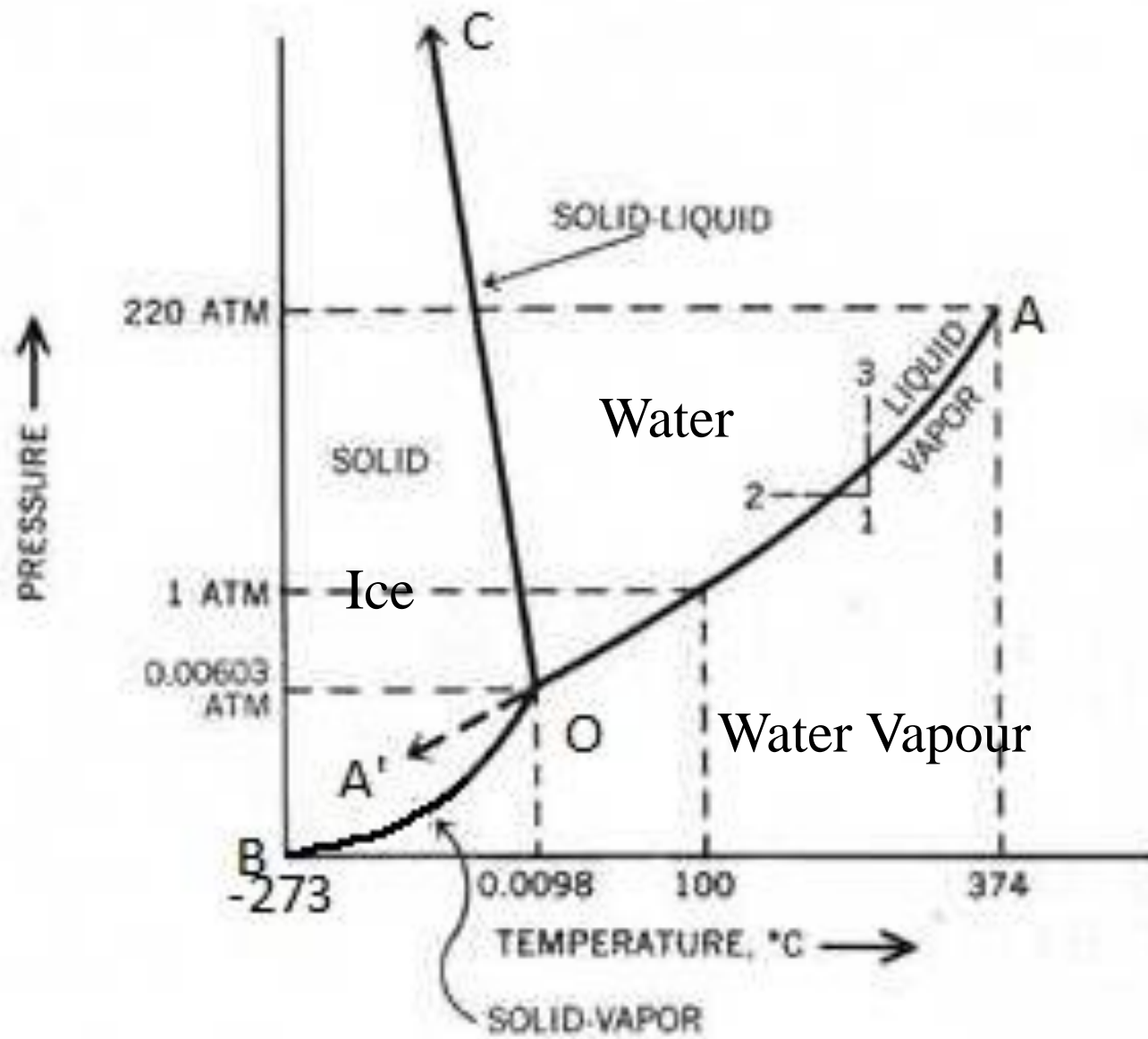F = 2 : divariant
F = 1 : univariant
F = 0 : invariant

if F < 0 then there must be disequilibrium.

Ice (s) $\rightleftharpoons$ Water (l) $\rightleftharpoons$ Water vapour (g)

F=?

Water (l) $\rightleftharpoons$ Water vapour (g)

F=?

Water System

Phase diagram of water consists the following three curves

1 Curve OA: It gives the equilibrium between liquid water and water vapours .it is called vapour pressure curve of water. The degree of freedom for this curve is given by:

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

2 Curve OB: It is the curve which represents the equilibrium between the ice and water vapours. This is sublimation curve of ice. The degree of freedom for this curve is given by:

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

3 Curve OC: It is the curve which represents the equilibrium between ice and liquid water. This is the melting point curve of ice. Degree of freedom for this curve is given by:

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

4 Curve OA' : This is the metastable curve for supercooled liquid. It is seen in the phase diagram curve OA' lies above the curve OB. Hence ,vapour pressure of metastable system is higher than of the stable system at same temperature.

- Along any three of the curves where two phases exist in equilibrium, **F** = 1 .

- Hence, only one condition need be given to define the system.

- If we state that the system contains both liquid water and water vapor in equilibrium at 100°C, we need not specify the pressure, for the vapor pressure can have no other value than 760 mm Hg at 100°C under these conditions.

- Similarly, only one variable is required to define the system along line OB or OC.

**Areas**

(i) The areas give the conditions of temperature and pressure under which single phase of water such as **water solid(ice), liquid water and water vapour** can exist.

(ii) It is necessary to specify both temperature and pressure to define a system within this area.

(iii) In this area , the curves $BOC, AOC$ and AOB are exist as ice, water (liquid) and water vapour respectively.
In these areas F=2. It is **Bivariant**

# Triple point O

➢ The point O at which the curves *AO, BO* and *CO* meet is called the "T**riple point"**.

➢ At this point all the three phases *viz ,* ice, water and vapour co-exist. Thus, **P =3.**

$$\mathbf{F = C - P + 2,} \quad = 1\text{-}3\text{+}2 , \quad \mathbf{F = 0}$$

➢ It indicates that there is **only one set of variables P and T** at which all
   the three phases coexist.

➢ If any of the variables is changed, then the **number of phases decreases.**

15

The **melting curve** or **fusion curve** of ice/water is very special. It has a negative slope (or tilted towards pressure axis) due to the fact that when ice melts, the molar volume decreases. Ice actually melt at lower temperature at higher pressure.
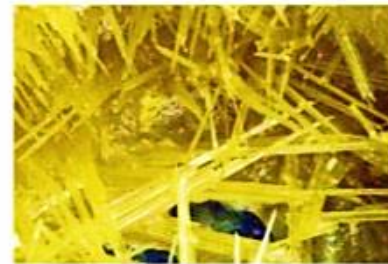
Example:
*The liquid formed between the skate and ice act as a lubricate so that the skater moves gracefully across the ice. The skate apply a very high pressure on to the ice.*

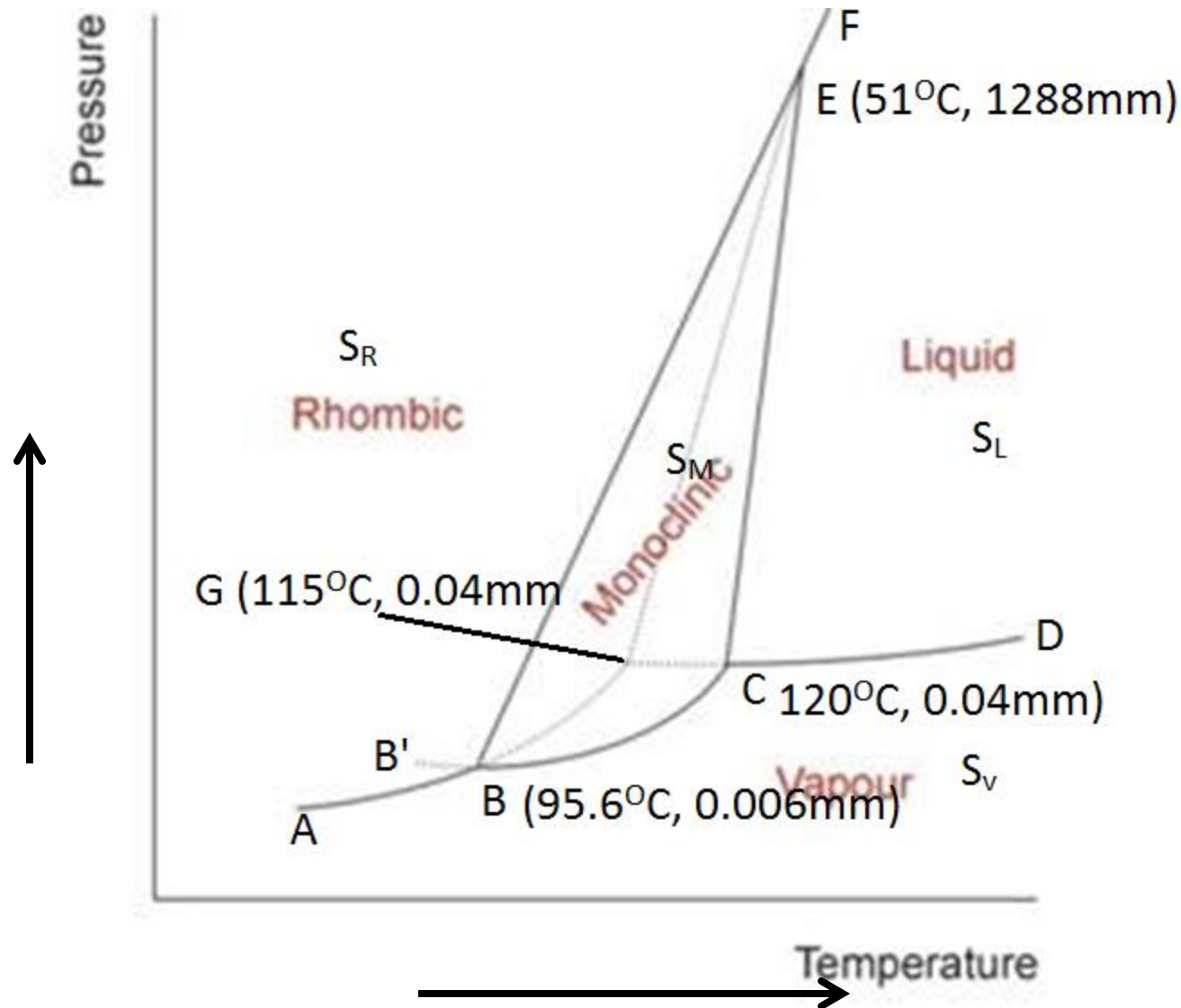# Phase Diagram of Sulphur

Sulphur Exist in four forms:

1. Rhombic Sulphur (SR) (m.p. 114°C)
2. Monoclinic Sulphur (SM) (m.p. 120°C)
3. Liquid sulphur ($S_L$)
4. Vapour Sulphur ($S_V$)



Monoclinic Sulphur



Rhombic Sulphur

Schematic phase diagram for sulphur showing existence
of rhombic and monoclinic allotropes
Dotted lines mark equilibria between metastable phases

# Curves In Phase Diagram

- Curve AB: Sublimation Curve of Rhombic Sulphur
- Curve BC: Sublimation Curve of Monoclinic Sulphur
- Curve CD: Vapor Pressure Curve of Liquid Sulphur
- Curve CE: Fusion Curve of Monoclinic Sulphur
- Curve BE: Transition Curve Solid Sulphur
- Curve EF Fusion Curve of Rhombic Sulphur

At any curve, phase rule becomes:

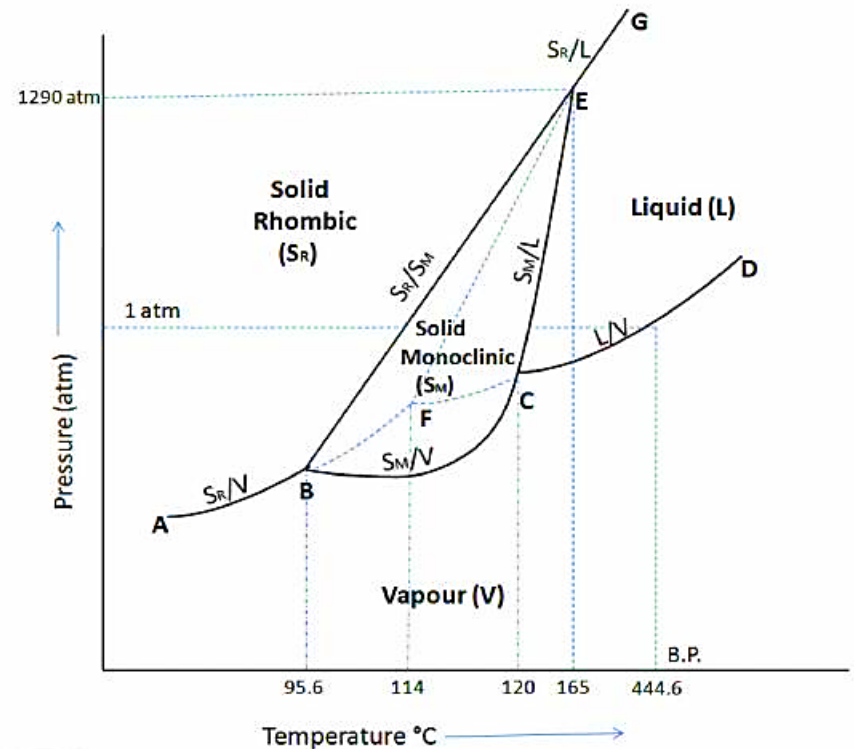$$F = 3-P = 3-2 = 1 \text{ (univarient)}$$

# Triple Points

- Triple Point **B**
- Triple Point **C**
- Triple Point **E**

- At any Triple Point,
  phase rule becomes:
  $F = 3-P = 3-3 = 0$
  (nonvarient)
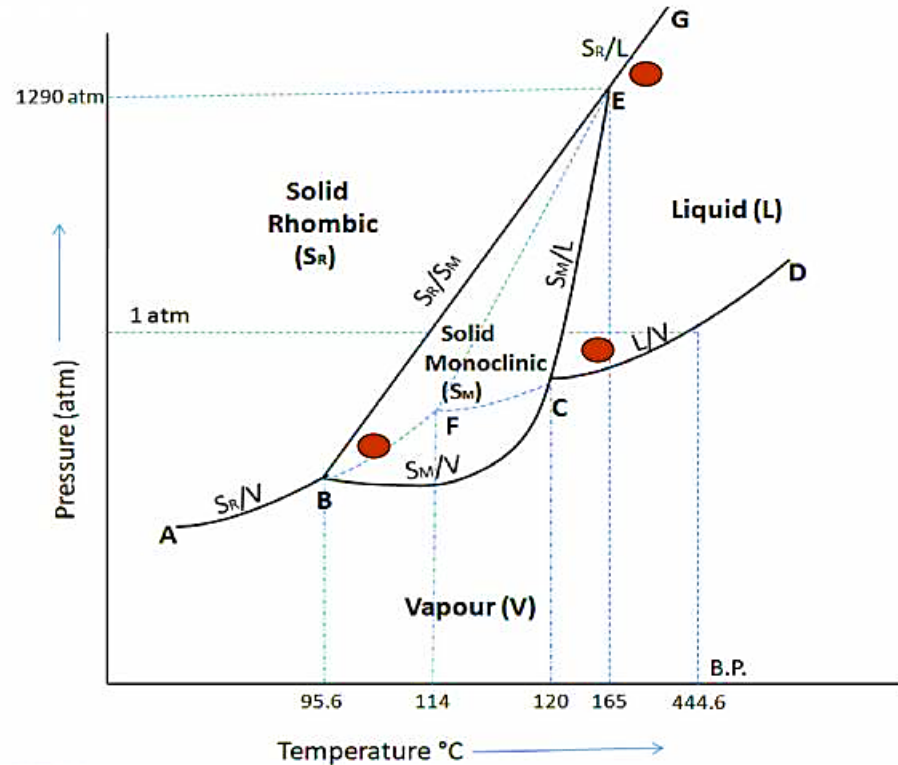
## Areas

- Area ABEG (Rhombic Sulphur)
- Area BCEB (Monoclinic Sulphur)
- Area DCEG (Sulphur Liquid)
- Area ABCD (Sulphur Vapors)

- In an area, Phase Rule becomes:
  $$F = 3-P = 3-1 = 2$$
  (bivariant)

# Reduced (or condensed) phase rule

In a *two-component* system, when P=1 degree of freedom (F) has the highest value**: F=C-P+2= 2-1+2=3**. Since the maximum number of degrees of freedom in a two component system is *three*, so the phase behavior of any binary system may be represented by a three dimensional diagram of *pressure*, *temperature* and *composition*.

A solid liquid equilibrium of an alloy has practically **no gas phase** and the effect of pressure is small on this type of equilibrium. Therefore, experiments are, usually, conducted under atmospheric pressure. Thus keeping the pressure constant of a system, in which vapour pressure is not considered, is known as condensed system. It will **reduce the degrees of freedom of the system by one** and for such a system, the phase rule becomes: **F=C-P+1**

**This is known as the reduced (or condensed) phase rule, having two variables, namely, temperature and concentration (or composition) of the constituents.**

# Eutectic system

A *eutectic system* is a mixture of chemical compounds or elements that have a single chemical composition that solidifies at a lower temperature than any other composition made up of the same ingredients. This composition is known as the **eutectic composition** and the temperature at which it solidifies is known as the **eutectic temperature**. On a phase diagram the intersection of the eutectic temperature and the eutectic composition gives the **eutectic point**. Non-eutectic mixtures will display solidification of one component of the mixture before the other.

## Eutectic System

- Two component system in which both the components are completely miscible in liquid phase but do not react chemically is called a eutectic system e.g. Ag-Pb System

- **Eutectic Temperature and composition:** for a pure substance A, the freezing point is higher and upon increasing the conc. of B freezing point decreases to lowest value. This is called eutectic temperature and composition at this state is called eutectic composition.

- **Eutectic Point:** (easily melted) is defined as the lowest melting point attained by the mixture

# Ag-Pb System

- It is a simple eutectic system in which silver and lead are completely soluble in liquid state.
- They do not react to form a any compound but on solidification they form an easy melting mixture.(eutectic system)
- Four phases that take part in equilibrium are:
  - 1. solid silver
  - 2. solid lead
  - 3. solution of Lead & silver
  - 4. Vapor
- Boiling point of Ag & Pb being high, so Gas phase is absent, so pressure has negligible effect.
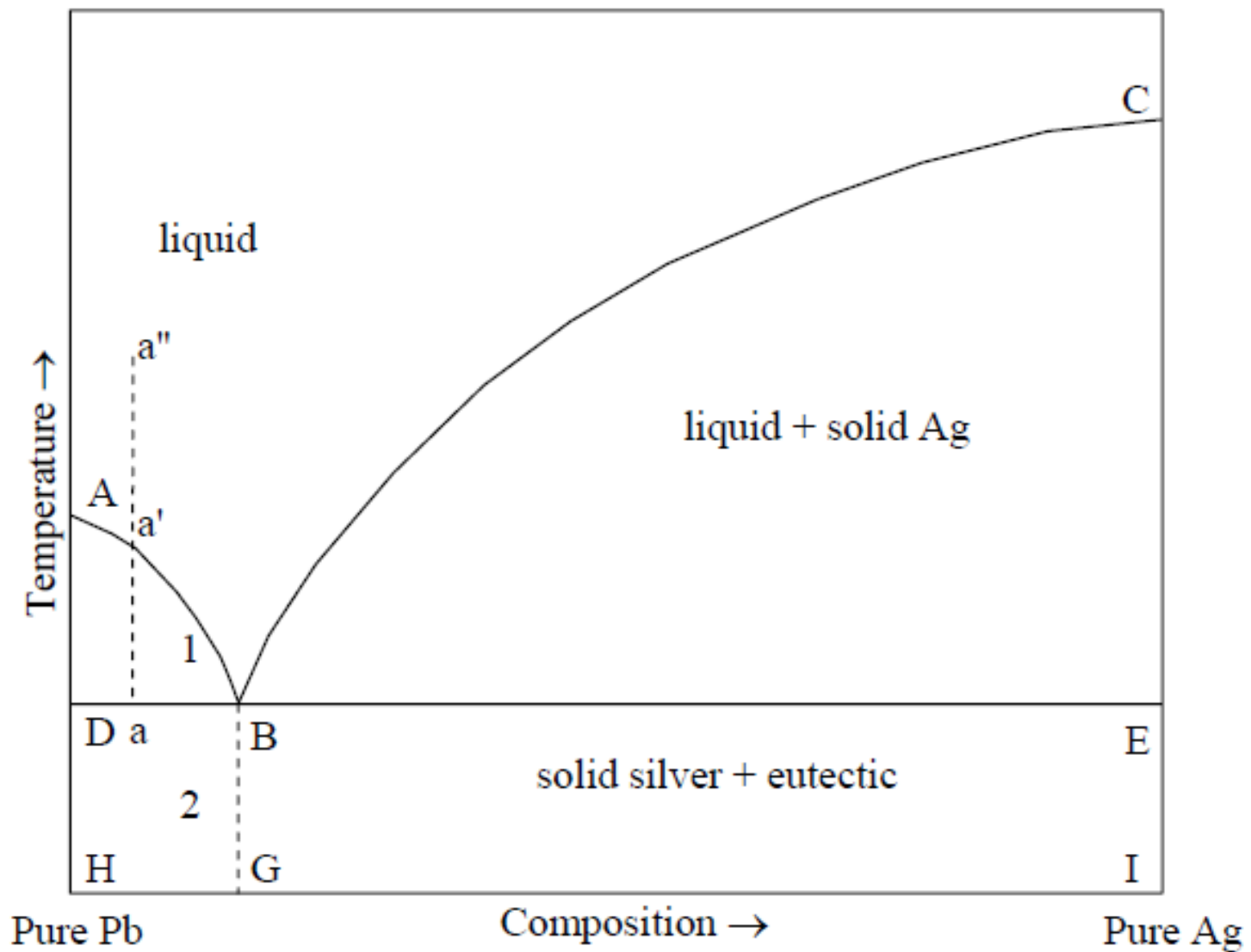- So S-L equilibrium without gas phase is known as condensed system.

Figure 10.3.5: The phase diagram for lead-silver system. 1. Liquid+solid Pb and 2. Solid Pb+eutectic

- AB and BC meets at point at B, B is common to both the curves, solid Pb, solid Ag and their liquid solution coexist.

- At this point degrees of freedom is zero and it is non- variant.
- Point B is lowest T of 303C at which liquid exist.

- If liquid cooled below this temperature both Ag & Pb separates in solid form as 2.6% Ag and 97.6 % Pb.

- In an alloy of Ag and Pb, Ag melts at 303C which is lower than melting point of Ag and Pb called eutectic mixture.

# *Description of the phase diagram for lead-silver system.*

| | | | |
|---|---|---|---|
| A (327°C) | Freezing point of lead | C=1, P=2, F=0 | Fixed T |
| C (961°C) | Freezing point of silver | C=1, P=2, F=0 | Fixed T |
| **B (303°C, 2.6 mass % Ag)** | **Eutectic point** | C=2, P=3, F=0 | **Fixed T and composition** |
| AB | Crystallization of lead begins | C=2, P=2, F=1 | T or composition |
| BC | Crystallization of silver begins | C=2, P=2, F=1 | T or composition |
| Area above ABC | Liquid phase | C=2, P=1, F=2 | T and composition |
| Area below DBE | Solid mixture | C=2, P=2, F=1 | T or composition |
| Area ADBA | Solid lead in equilibrium with liquid having composition given by the curve AB | C=2, P=2, F=1 | T or composition |

| Area CEBC | Solid silver in equilibrium with liquid having composition given by the curve BC | C=2, P=2, F=1 | T or composition |
|-----------|-----------------------------------------------------------------------------------|----------------|------------------|
| DBE | Both lead and silver separate from liquid of composition B | C=2, P=3, F=0 | Fixed T |

## System with congruent melting point

- **Congruent melting** : occurs during melting of a compound when the composition of the liquid that forms is the same as the composition of the solid.
- It can be contrasted with incongruent melting.

- A binary system is said to be possess a congruent melting point when it melts at sharp temperature to give a liquid of the same composition as that of solid.

- This generally happens in two-component systems.

- e.g. Zn-Mg System

## Pattinson's process for the desilverisation of argentiferous lead

The process of heating argentiferous lead containing a very small quantity of silver (~0.1 mass%) and cooling to get pure lead and liquid richer in silver is known as the Pattinson's process. This process can be understood by following the phase diagram of the lead-silver system. The argentiferous lead is melted and heated to a temperature above the melting point of pure lead. Let the point **a''** represent this system on the diagram. This system is then allowed to cool slowly and the temperature of the melt decreases along **a''-a'**. At **a'**, solid lead starts separating. As the system further cools, more and more lead separates and the liquid in equilibrium with the solid lead gets richer in silver. The lead that separates floats and is continuously removed by ladles. When the temperature of the liquid reaches 'a' on the line DBE, the eutectic temperature, solid lead is in equilibrium with the liquid having the composition B. After removing the lead that separates, the liquid is cooled further when it solidifies to give a mixture of lead and silver having the eutectic composition of 2.5 mass % of silver. This solid mixture of lead and silver is subjected to other processes for the recovery of silver.

**Limitations of Phase rule**

**(1)** It can be applied only for a system in equilibrium. Consequently it is of little value in case of very slow equilibrium state attaining system. **(2)** It applies only to a single equilibrium system; and provides no information regarding any other possible equilibria in the system. **(3)** It requires utmost care in deciding the number of phases existing in an equilibrium state, since it considers the number of phases, rather than their amounts. Thus, even if a trace of a phase is present, it accounts towards the total number of phases. **(4)** It conditions that all the phases of the system must be present simultaneously, under the identical conditions of temperature and pressure. **(5)** It conditions that solid and liquid phases must not be in finely-divided state; otherwise deviations occur.

# Remaining part of fuel (Combustion problems )

## COMBUSTION

Combustion is an exothermic chemical reaction, which is accompanied by evolution of heat and light and the temperature rises considerably. Eg.

$$C(s) \quad + \quad O_2 (g) \quad \longrightarrow \quad CO_2(g) \quad + \quad 97 \text{ kcal}$$

To ensure complete combustion of a fuel, it is essential that appropriate amount of oxygen and air is supplied. If the amount of oxygen and air supplied is insufficient, complete combustion will not takes place

Ignition temperature: the minimum temperature at which the substance ignites and burns without further addition of heat from outside.

**Calculation of Air Quantities**

To determine the amount of oxygen and hence the amount of air required for combustion for a unit quantity of fuel, the following chemical principles are applied.

(1) Substances always combine in definite proportions given by molecular mass.

$$C + O_2 \rightarrow CO_2$$
$$12 \quad 32 \quad 44$$
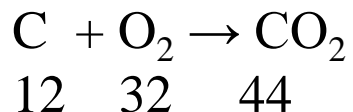
12 g of carbon requires 32 g of oxygen and 44 g of $CO_2$ is formed.
22.4 L of a gas at 0°C and 760 mm pressure has a mass equal to 1 mol.
That is, 22.4 L of oxygen has a mass of 32 g.

(3) Air contains 21% oxygen by volume and 23% oxygen by mass. From the amount of oxygen required by the fuel, the amount of air can be calculated.

1 kg oxygen is supplied by 1 x 100/23 = 4.35 kg of air
1 m³ of oxygen is supplied by 1x100/21= 4.76 m³ of air

(4) The molar mass of air is 28.94 g mol

(5) Minimum oxygen required for combustion is equal to the theoretical oxygen required minus the oxygen present in the fuel.

(6) Mass of any gas can be converted to volume at certain temperature and pressure by assuming that the gas behaves ideally.
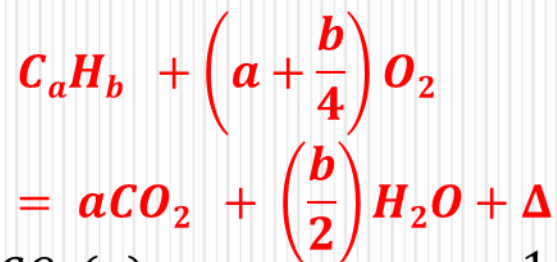$$(PV = nRT)$$

(7) The total amount of oxygen consumed is given by the sum of the amount of oxygen required by individual combustible constituents present in the fuel.
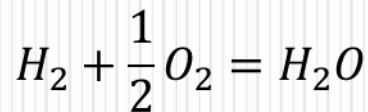
**Amount of oxygen required for combustion**

$$C_aH_b + \left(a + \frac{b}{4}\right)O_2$$

$$= aCO_2 + \left(\frac{b}{2}\right)H_2O + \Delta$$

$$C(s) + O_2(g) = CO_2(g)$$

$$\qquad 12g \qquad 32g \qquad 44g$$

$12$ g $C$ requires $32$ g $O_2$

$1$ g $C$ requires $\frac{32}{12}$ g $O_2$

$$H_2 + \frac{1}{2}O_2 = H_2O$$

$$2g \qquad 16g\,18g$$

$1$ g $H_2$ requires $\frac{16}{2}$ g $O_2$

**Procedure for combustion calculations:**

| Reaction | Weight of oxygen required (g) | Volume of oxygen required ($m^3$) |
|---|---|---|
| $C + O_2 \rightarrow CO_2$ <br> A gm or $m^3$ | $A \times 32/12$ | $A \times 1$ |
| $H_2 + 1/2\ O_2 \rightarrow H_2O$ <br> B gm or $m^3$ | $B \times 16/2$ | $B \times 1/2$ |
| $CO + 1/2\ O_2 \rightarrow CO_2$ <br> C gm or $m^3$ | $C \times 16/28$ | $C \times 1/2$ |
| $S + O_2 \rightarrow SO_2$ <br> D gm or $m^3$ | $D \times 1 \times 32/32$ | $D \times 1$ |
| $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ <br> E gm or $m^3$ | $E \times 2 \times 32/16$ | $E \times 2$ |
| $C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$ <br> F gm or $m^3$ | $F \times 3.5 \times 32/30$ | $F \times 3.5$ |
| $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ <br> G gm or $m^3$ | $G \times 3 \times 32/28$ | $G \times 3$ |
| $C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$ <br> H gm or $m^3$ | $H \times 6.5 \times 32/58$ | $H \times 6.5$ |
| Total | X | Y |
| Less $O_2$ in fuel | $= - w$ gm | $= - w\ m^3$ |

Let oxygen required = X – w (g) or Y –w (m$^3$)

Since air has 23% oxygen by weight and 21% oxygen by volume

   Weight of air required = Net oxygen × 100/23 kg

   Volume of air required = Net oxygen × 100/21 m$^3$

**Problem1**: A coal sample contains 87% carbon, 2% hydrogen, 1% oxygen, 1% Sulphur and ash. Calculate the theoretical weight and volume of air (NTP) required for complete combustion of 1kg of sample of coal.

Oxygen required for oxidizing a sample containing C% of carbon, H% of hydrogen and sulphur is
= 2489 g

Weight of the oxygen present = (1/100)1000
=10 gm

Actual amount of oxygen required = 2489 -10
= 2479 g

Therefore, air required = 2479 g x 100/23.2
=10780 g =10.78 kg
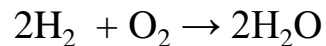
Volume of the oxygen required for combustion = (22400/32) 2479 =1735300cm$^3$

Volume of the air required for combustion = (100/21) 1735300cm$^3$
=826190 cm$^3$

$= \mathbf{8.27m^3}$

Problem2: A gaseous fuel is found to contains 22% $H_2$, 4% CO, 6%$CO_2$, 3% $O_2$ and 45% $N_2$. Calculate the volume of air required for complete combustion of 1m³ of fuel.

Reaction for combustion of hydrogen is

$$2H_2 + O_2 \rightarrow 2H_2O$$

2m³ of the hydrogen require 1 m³ of oxygen
Then 0.22m³ hydrogen require 0.11 m³ oxygen

$$CO + 1/2O_2 \rightarrow CO_2$$

1m³ of CO require 1/2 m³ of oxygen
Then 0.04m³ CO require 0.02 m³ oxygen
Total volume of oxygen required = 0.13 m3

Volume of oxygen already used = 0.03 m³
Actual volume of oxygen required =0.13-0.03 = 0.1 m³

Volume of air required =(100/21)0.1
$$= \mathbf{0.4762 \ m^3}$$

**Problem 4:** The percentage composition of a coal sample is :
C= 85%, H= 5%, O= 6%, N=4%,  S= 2% and ash = 5% and moisture = 3%

   a. Calculate the minimum amount of air needed in combustion of 1kg of coal
   b. Calculate the weight and volume of air required if it is supplied in 40 % excess.

1 kg of coal contains
C= 850g, H= 50, O= 60 g, N=40, S= 20 g and ash = 50g and water = 30 g

Weight of the carbon required = 850 x32/12 =2266.67 g

Weight of the hydrogen required = 16/2 x 50 = 400 g

Weight of the sulphur required 20x 32/32 -20 g

Total = 2686.67 g

Minimum quantity of air required =2686.67 x 100/23

$$= 11681.17 \text{ g}$$
$$=11.68 \text{ kg}$$

If supplied 40% excess, the weight = 11681.17 x140/100

$$= 1635.44 \text{ g}$$

Weight of air supplied =16.35kg

Minimum amount of $O_2$ required = 2686.67 g and at NTP 32 g of
$O_2$ occupies 22.4L

2686.67 g of $O_2$ occupies = 22.4x 2686.67/32   g
$$= 1880.67$$

Minimum amount of air required assuming it contains 23 % of O2 is

$$= 1880.67 \times 100 / 23$$
$$= 8176.82 \text{ of air}$$

If air to be supplied in 40% excess, the volume of air supplied $= 8176.82 \times 140 / 100$

$$=11447.55$$

Practice Question: Calculate the minimum amount (volume) of oxygen and air required for complete combustion of 1 m$^3$ of a gaseous fuel containing 30% methane, 30% ethane and 40% propane. Also calculate the total volume of $CO_2$ generated during combustion.

A gaseous fuel is found to contains 45% $H_2$, 15% CO, 36%$CH_4$, and 45% $N_2$. Calculate the volume of air required for complete combustion of 1m³ of fuel

Ans. 4.85

**Problem 4:** The percentage composition of a gaseous fuel sample is :
$CH_4$= 20%, CO= 10%, $CO_2$= 5%, $O_2$=2%, $C_2H_4$= 5% and $C_3H_8$ = 8% and rest $N_2$
Calculate volume of air supplied per m3 of fuel and %composition of dry flue gases

| constituents | O2 required | Volume of dry flue gases |
|---|---|---|
| CH4 | 0.20 x 2=0.40 | CO2= .20 x 1=0.20 |
| CO | 0.10 x 0.5=0.050 | CO2= .10 x 1=0.10 |
| CO2 | 0.05 | 0.05 |
| O2 | -0.02 | - |
| C2H4 | 0.05x 3=0.15 | 0.05x2= 0.10 |
| C3H8 | 0.08 x 5=0.40 | 0.08x3= 0.24 |
| N2 | 0.50 | N2=0.50 +79/100*VOLUME OF AIR |

The gases coming out after combustion CO2, SO2, N2, CO and O2 are called flue gases

Actual O2 required= 1-0.02=0.98 $m^3$

volume of air = 0.98*100/21 =4.67

Calculations of dry flue gases
$CO_2$= (0.20+0.10+0.05+0.10+0.24) = 0.69

$N_2$= N2 (in fuel) + N2 (from air)= 4.19

Total volume of dry pdt.=  0.69+4.19= 4.88

%CO2= 0.69/4.88* 100= 14.13%
%N2= 4.19/4.88*100= 85.86%

The percentage composition of a gaseous fuel sample is :
$CH_4$= 4%, CO= 26%, $CO_2$= 10%, $H_2$=10%, and rest $N_2$
Calculate volume of air supplied per m3 of fuel and
%composition of dry flue gases

# PHASE RULE

- It deals with the behaviour of heterogeneous system in the state of equilibrium.

- In general, phase rule help to predict quantitatively the effect of changing temp., pressure & concentration on a heterogeneous system in equilibrium.

- This heterogeneous system containing two or more phases at eq$^{m}$ is studied with the help of generalization called phase rule.