PHASE EQUILIBRIUM
(Part 1)

DEFINITIONS

Most substances can exist in three basic aggregate states: gaseous, liquid and solid.

A solid substance can exist in two or more forms (modifications) of the solid state that differ in internal structure and properties, such as the white and black allotropes of phosphorus. This phenomenon is known as ***polymorphism.***

DEFINITIONS

- Transition from the liquid to the gaseous state is called **vaporization.**
- Transition from the solid to the gaseous is called **sublimation.**
- Transition from the gaseous to the liquid or solid is called **condensation.**
- Transition from the solid state to the liquid is called **melting**, or fusion, and the reverse process – **solidification or crystallization.**
- Transition from one modification of the solid state to another is called a **polymorphic transformation.**

DEFINITIONS

A **phase** is a homogeneous portion of a system that is uniform throughout in chemical composition and physical state and is separated from other parts of the system by a boundary surface.

Phase consisting of a single chemical substance is called simple (or pure) phase. A homogeneous system always consists of a single phase, while a heterogeneous one contains at least two phases.

DEFINITIONS

A **constituent of a system** is a chemical species that can be separated from it and is capable of exist in the isolated state for some time.

The constituents of an aqueous solution of sodium chloride are water and sodium chloride. The ions of sodium and of chlorine are not constituents, since they cannot exist as separate substances.

DEFINITIONS

A component is a chemically independent constituent of a system. The number of components is the minimum number of independent species that necessary to define the composition of all the phases present in the system. When no reactions take place in the system, the number of components is equal to the number of constituents.

DEFINITIONS

The number of **degrees of freedom (f) or variance** is defined as the number of parameters (temperature, pressure) that can be arbitrary varied (within certain limit) without changing the number or kind of phases in the system. In a one-component one-phase system the pressure and temperature may be changed independently without changing the number of phases, so f=2 (system is bivariant, or it has two degrees of freedom).

DEFINITIONS

Systems are classified according to the number of phases as

- one-phase,
- two-phase,
- three-phase

DEFINITIONS

Systems are classified according to the number of components as

- simple,
- binary,
- ternary, etc.

DEFINITIONS

Systems are classified according number of degrees of freedom or variance as

- invariant,
- monovariant,
- bivariant.

DEFINITIONS

A phase change or phase transition is a process in which at least one new phase appears in a system without the occurrence of a chemical reaction (for in-stance, ice melting, water freezing etc.). The reason of such transition justifies on the basis of thermodynamic tendency of a system to equality of the ***chemical potential***.

As a result, the difference between the chemical potentials of the component in both phases decrease, and when it becomes zero a state of **phase equilibrium** sets in.

GIBBS PHASE RULE

$$f = c - p + n$$

where :

f ***is a number of degrees of freedom or variance***

c ***is a number of components***

n ***is the external factors effects on the state of the system***

GIBBS PHASE RULE

Usually two factors, temperature and pressure, can effect on the state of the system and $n = 2$:

$$\mathbf{f = c - p + 2}$$

The number of degrees of freedom cannot be negative, hence the phase rule is sometimes written as follows:

$$\mathbf{p \leq c + 2}$$

THE CLAUSIUS – CLAPEYRON EQUATION

The Clapeiron equation gives the relative dT/dP in one-component and two-phase system, i.e., the pressure and temperature, in which two phases can coexist.

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H} \qquad or \qquad \frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

For vaporization process the equation can be written as

$$\frac{dT}{dP} = \frac{T\left(V_v - V_l\right)}{\Delta H}$$

THE CLAUSIUS – CLAPEYRON EQUATION

These two approximations turn the Clapeyron equation into

$$\frac{dT}{dP} = \frac{RT^2}{\Delta HP} \quad or \quad \frac{dP}{P} = \frac{\Delta H dT}{RT^2} \qquad \int_{P_1}^{P_2} d\ln P = \frac{\Delta H}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

This equation is applied not only for the heat calculation of the process but also it allows to calculate vapor pressure at any temperature if we know vapor pressure at a certain temperature.

ONE–COMPONENT SYSTEMS

For a one-component system, which is described by two intensive parameters (P and T) only one species is present and c=1, so the phase rule comes to form:

$$\mathbf{f = 3 - p}$$

If p = 1, then f = 2; if p = 2, then f = 1; if p = 3, then f = 0. Consequently, in one-component and two-phase system the maximum number of degrees of freedom is two, and the maximum number of phases in equilibrium is three.

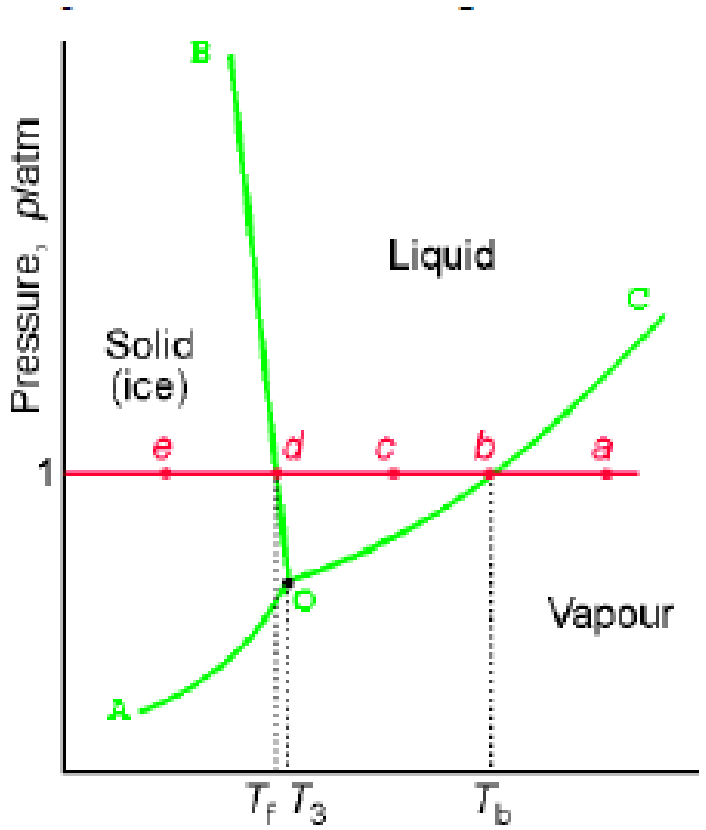
ONE–COMPONENT SYSTEMS

In physico-chemical analyses are widely applied phase diagrams to characterize various systems, which are usually plotted from experimental data. Such diagrams, showing dependence on the state of the system (and its phase equilibrium) on external conditions or on the composition of the system are called the **diagram of state or phase diagram.**

ONE–COMPONENT SYSTEMS

The diagram shows, how the number and the kind of the phases change, when pressure or (and) temperature change, as well as the relation of dP/dT. On phase diagram each phase is represented by an open area, two-phase equilibrium state by intersection lines of these areas, and three-phase equilibrium state by intersection point of these lines.

THE PHASE DIAGRAM OF WATER



Line OC (liquid-vapor line) shows the boiling point of water as a function of pressure. For all the points along this line f = 1

Line OB is the solid-liquid equilibrium line for water and gives the melting point of ice as a function of pressure

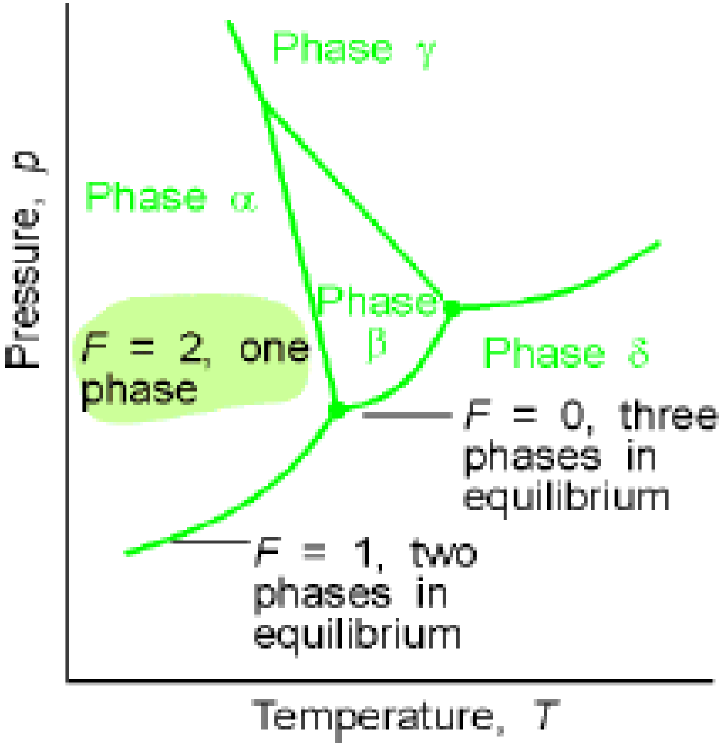
Line OA is the ice-vapor (sublimation) line and gives the values of pressure and temperature, in which ice and vapor are in equilibrium.

Point O, where three phases in equilibrium, is called the **triple point. In this case the system has zero degree of freedom (i.e., it is invariant).**

ONE–COMPONENT SYSTEMS

- **The boiling point** of a liquid at a given pressure is the temperature T at which its equilibrium vapor pressure equals to P. The normal boiling point is the temperature at which vapor pressure of a liquid equal to 1 atm (bar).
- **The melting point** of a solid at a given pressure P is the temperature at which solid and liquid are in equilibrium for pressure P. The normal melting point of a solid is the melting point at P=1atm. For a pure substance, the freezing point of the liquid at a given pressure equals the melting point of a solid.

THE PHASE DIA-GRAM OF SULFUR



The solid sulfur can exist in two modifications – orthorhombic and monoclinic forms under any conditions. We know that in one-component system four phases cannot be in equilibrium be-cause variance cannot be negative. Consequently, that on the phase diagram appear four regions of pure phases, six lines for two-phase equilibrium states, the existence of three triple points and there is no one point with four phases in equilibrium.