27th lecture

B.Sc (Chemistry Hons)

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Page 01

Phase Rule

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Phase Component and Degree of freedom

The Phase rule is a general principle in thermodynamic equilibrium. If F is the number of degree of freedom, C is the number of Components and P is the number of Phase then

$$F = C - P + 2$$

Phase is defined as any homogenous, physically distinct and mechanically separable portion of a system which is seperated from other such parts of the system by definite boundary surfaces in a system.

Component is defined as the smallest no. of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equilibrium.

Degree of freedom is defined as the minimum number of the independently variable factors such as the temperature, pressure and composition of the phases which must be arbitrarily specific in order to represent perfectly the condition of a system.

The rule assumes the components do not react with each other.

The number of degree of freedom is the no. of independent variables can be varied simultaneously and arbitrary without determining one another. An example of one component system is a system involving one pure chemical, while two component systems such as mixture of water and ethanol have two chemically independent components and so on. Typical phases are solid, liquid and gases.

The basis for the rule is that equilibrium between phases places a constraint on the intensive variables. More rigorously since the phases are in thermodynamic equilibrium with each other, the chemical potential of the phases must be equal. The number of equality influenced by gravitational, electrical or magnetic forces or by surface area and only by temperature, pressure and concentration.

For pure substances C=1, so that F = 3−P. In a single phase (P=1) condition of a pure component system, two variables (F=2), such as temperature and pressure can be chosen independently to be any pair of values consistent with the phase. However if the temperature and pressure ranges to a point where the pure component undergoes a seperation into two phases (P=2), F decreases from 2 to 1. When the system enters the two phases region, it becomes no longer possible to independently control temperature and pressure.

relationship determines the no. of degree of freedom.

For example:- If the chemical potentials of a liquid and of its vapour depend on temperature (T) and pressure (P), the equality of the chemical potentials will mean that each of those variables will be dependent on the other.

$\mu_{Liq}(T,P) = \mu_{vap}(T,P)$ where μ = Chemical potential defines temperature as a function of pressure or vice-versa.

To be more specific the composition of each phase is determined by C-1 intensive variables in each phase. The total no. of variables is (C-1)P+2 where the extra two are temp. T and Pressure P. The number of constraints is C(P-1), since the chemical potential of each component must be equal in all phases. Subtract the number of contraints ~~is C(P-1)~~ from the no. of variables to obtain the no. of degree of freedom as $F = (C-1)P+2-C(P-1) = C-P+2$

The rule is valid provided the equilibrium between phases is not