(1.) Explain the Zeroth law of Thermodynamics:

Ans: The term zeroth law was coined by Ralph H. Fowler. The zeroth law of thermodynamics tells us the concept of temprature. The law states that if two bodies are each in thermal equilibrium with third one, then they are in thermal equilibrium with each other. Thermal equilibrium is a system whose maeroscopic properties like pressure, temprature, volume etc are not changing in time.

2. What is Phase rule or Gibbs phase rule.

Ans. In 1875 Josiah williard Gibbs published a general principle governing system in thermodynamic equillibrium called the Phase rule in a paper titled "On the Equillibrium of Heterogeneous substances.

It can mathematically represented as

$$P+F=C+2$$

where

P = The number of Phases of material

F = The number of degrees of freedom

C = The number of component of a system

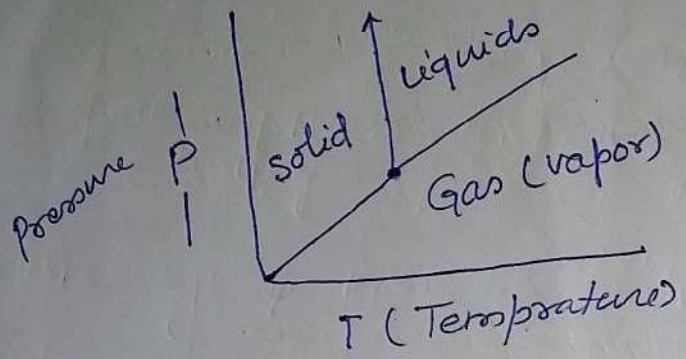
2 = represents two variables (Pressure & temprature)

Phase: A region of material that is chemically uniform, Physically distinct and mechanically seperable.

Componend: Minimum number of endependent species necesary to define the composition of all Phases of the system.

Degree of Freedom:

The number of intensive variables that are independant of each other or in other words the number of thermodynamics variables which can be specified independently without changing the phase in equillibrium.



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③ Define Hess's law

Ans: Hess's law of heat summation statis that for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation is the sum of enthalpy changes for the individual steps. or in other words the change in enthalpy in a chemical reaction, at a constant pressure is not dependent on the process, and only dependent on the initial and final statis of the chemical reaction. Hess's law can be seen as an application of the principle of conservation of energy

e.g consider the following two routes for preparation of methylene chloride (CH_2Cl_2) from the reaction between methane (CH_4) and chlorine (Cl_2)

Route I:

$$CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl_2(g) + 2HCl(g) \quad \Delta H^\circ_1 = -202.3 kJ$$

Route II

$CH_4(g) + 2Cl_2(g) \rightarrow CH_3Cl(g) + HCl \quad \Delta H_2^\circ = -98.3\,KJ$ — (i)

$CH_3Cl(g) + Cl_2(g) \rightarrow CH_2Cl_2(g) + HCl \quad \Delta H_3^\circ = -104.0\,KJ$ — (ii)

Adding change in enthalpy of both step

$$CH_4(g) + 2Cl_2(g) \rightarrow CH_2Cl_2(g) + 2HCl \quad \Delta H_3^\circ = -202.3\,KJ$$

Thus it can be clearly seen that no matter what path we follow, the total enthalpy change in the reaction is always the same

$$\Delta H_1^\circ = \Delta H_2^\circ + \Delta H_3^2 = -202.3\,KJ$$

Application of Hess's law

(1) Determination of heat of formation of substance which otherwise cannot be measured experimentaly:

Substances like methane, ~~CO_2~~ CO, benzene etc cannot be prepared by uniting their elements. Therefore it is not possible to measure the heats of formation of such compounds directly. These can be determined indirectly by using Hess's law.

(2) Determination of Heat Transition

The heat of transition of one allotropic form to another can also be calculated with the help of Hess's law. for example the enthalpy of transition from monoclinic sulfur to rhombic sulfur can be calculated for their heats of combustion which are

(i) $S_{rhombic} + O_2(g) \longrightarrow SO_2(g) \quad \Delta H = -291.4\,kJ$

(ii) $S_{monoclinic} + O_2(g) \rightarrow SO_2(g) \quad \Delta H = -295.4\,kJ$

Substracting eq. (ii) from (i) we get

$S_{rhombic} - S_{monoclinic} + O_2(g) - O_2(g) \rightarrow SO_2(g) + SO_2(g)$

$\Delta H = -291.4 - (-295.4)$

$\Delta H = 4.0\ kJ$

Thus heat of transition of rhombic sulfur to monoclinic sulfur is 4.0 kJ

(3.) Determination of heats of various reactions:

By using Hess's law we can calculate the heats or enthalpies of many reactions which otherwise cannot be measured directly. For example, from the following equations the enthalpy of dimerization of NO_2 can be calculated

(i) $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H = 67.9\ kJ$

(ii) $N_2(g) + 2O_2(g) \rightarrow 2N_2O_4(g)$ $\Delta H = 9.3\ kJ$

Substracting eq. (i) from eq. II we have

$2NO_2(g) \rightarrow N_2O_4(g)$ $\Delta H = (9.3 - 67.9)$

$= -58.6\ kJ$

Thus the heat of dimerization of NO_2 is $-58.6\ kJ$