The thermodynamic state of a substance is specified by some of its properties like pressure, volume, temperature, internal energy and entropy. These properties undergo a change when the system passes from one state to another. These variables are known as thermodynamic variable co-ordinates. These are called macroscopic co-ordinates. They require the specification of few measurable properties of the system and do not require the knowledge of microscopic structure of matter composing the system.

Extensive and Intensive Variables

An extensive variable of a system is a macroscopic parameter which describes a system in equilibrium and which has a value equal to the sum of its values in each part of the system. The extensive variable depends upon the mass or the size of the substance present in the system.

Ex: Mass, Volume, internal energy, entropy, length, area, heat-capacity, electric charge, magnetisation etc.

* An intensive variable of ~~the~~ a substance is a macroscopic parameter which describes the system in equilibrium and has the same value in any part of the system. It is independent of mass or size of the system. It is a characteristic of the substance present in the system.

Ex: Pressure, temperature, viscosity, refractive index, density, specific volume, magnetic induction, surface tension, electromotive force etc.

Thermodynamic Potentials

The state of a system can be completely described by any two of the five state variables P, V, T, S and U. Out of these, U the internal energy state variable is determined by using the remaining four, as proved below. There are four thermodynamic potentials

(i) Internal energy, U

(ii) Helmholtz free energy, $F = U - TS$

(iii) Enthalpy, $H = U + PV$

(iv) Gibbs function, $G = U + PV - TS$

(1) Internal Energy U: The internal energy or the intrinsic energy is the total energy of a system. According to the 1st law of thermodynamics

$$dQ = dU + dW = dU + PdV$$
$$\therefore \quad dU = dQ - PdV$$

and from 2nd law of thermodynamics

$$dQ = TdS$$

Substituting for dQ, we get

$$\boxed{dU = TdS - PdV}$$

(a) for an adiabatic process

$$dQ = 0$$
$$dU = -PdV$$

i.e., the work done by the system in an adiabatic process is at the expense of its internal energy.

(b) for an isochoric adiabatic process:

$$dV = 0 \quad \text{and} \quad dQ = 0$$
$$dU = 0 \quad \text{or} \quad U = \text{a constant}$$

i.e., the internal energy of system remains constant in an isochoric adiabatic process.

(2) Helmholtz Free Energy, F: Helmholtz free energy is defined as

$$F = U - TS$$

As U, T and S are state variables, F is also a state variable. F has dimensions of energy. According to the 1st and 2nd law of thermodynamics

$$dU = TdS - dW$$

If the system is maintained at a constant temp. by exchanging heat continuously with the surroundings.

$$\text{then} \quad TdS = d(TS)$$
$$\therefore \quad dU = d(TS) - dW$$
$$\text{or} \quad d(U - TS) = -dW$$
$$dF = -dW$$

F is Helmholtz free energy or Helmholtz work function

$$\text{Now,} \quad dF = d(U - TS) = dU - TdS - SdT$$
$$\text{but} \quad dU = TdS - PdV$$
$$\therefore \quad dF = -PdV - SdT$$

This eqn gives the change in F during an infinitesimal reversible pro

(a) For reversible isothermal process

$$dT = 0$$

$$dF = -PdV \quad \text{or} \quad PdV = -dF$$

Thus the work done in a reversible isothermal process is equal to the decrease in Helmholtz free energy.

(b) For isothermal isochoric process

$$dT = 0 \quad \text{and} \quad dV = 0$$

$$dF = 0 \quad \text{or} \quad F = \text{a constant}$$

Thus Helmholtz free energy remains constant during isothermal isochoric process.

(3) Enthalpy, H This is known as total heat and is given by

$$H = U + PV$$

If a system undergoes infinitesimal reversible process change in enthalpy, $dH = dU + PdV + VdP$

But $dU = TdS - PdV$

$$dH = TdS + VdP$$

(a) For reversible isobaric process

$$dP = 0$$

$$dH = TdS = dQ$$

i.e., for an isobaric process, the change in enthalpy is equal to the heat absorbed.

(b) For an isobaric adiabatic process

$$dP = 0 \; ; \; dQ = 0$$

$$\therefore dH = 0 \quad \text{or} \quad H = \text{Constant}$$

i.e, enthalpy remains constant in a reversible isobaric adiabatic process.

(4) Gibbs Function G or Gibbs Free Energy: Gibbs function (G) is a thermodynamic potential at constant pressure. This is defined by the equation

$$G = U - TS + PV$$

as $F = U - TS$ $\therefore$, $G = F + PV$ $\quad G = H - TS$

Also $H = U + PV \Rightarrow H = G + TS$

∴ Enthalpy = Gibbs Free Energy + Latent heat

(a) For an isothermal process, $TdS = d(TS)$

(b) For an isobaric process, $dP = 0$

Hence if the process is isothermal and isobaric then

$$dH = d(TS)$$
$$d(H - TS) = 0$$
$$dG = 0 \quad \text{or} \quad G = \text{constant}$$

Where $G = H - TS$ is known as thermodynamic potential at constant pressure; or Gibbs function or Gibbs free energy

Significance of thermodynamic potentials

A mechanical system is said to be in stable equilibrium when the P.E of the system is minimum, and similar to this, in thermodynamics, the behaviours of internal energy (U), Helmholtz free energy (F), enthalpy (H) and Gibbs free energy (G) is similar to P.E in mechanics. As we have seen, the direction of isothermal - isochoric process is to make (F) minimum. In isothermal - isobaric process, 'G' tends to be minimum. In an isobaric - adiabatic process, 'H' tends to be minimum and in an isochoric adiabatic process 'U' tends to be minimum.

* Thermodynamic variables S, T, P and V can be derived from the differentiations of the four thermodynamic potentials w.r.t the independent variables associated with them. Let us derive them

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