(ii) The cyclic integration involving a state function is zero. If ϕ is a state function

$$\oint d\phi = 0$$

(iii) The state function has an exact differential, i.e. if $\phi = f(x,y)$ is a state function ,

If a system is taken along a path (for example, by heating it), U changes from U_i to U_f, and the overall change is the sum (integral) of all the infinitesimal changes along the path :

$$\Delta U = \int_i^f dU$$

The value of ΔU depends on the initial and final states of the system but is independent of the path between them. This path independence of the integral is expressed by saying that dU is an 'exact differential'. In general, an exact differential is an infinitesimal quantity that, when integrated, gives a result that is independent of the path between the initial and final states.

State variables can be intensive or extensive. An intensive variable (eg. temperature, pressure, concentration) is one whose value is independent of the size of the system. An extensive variable (eg. volume , mass, surface area is one whose value is proportional to the size of the system.

✦ **Change in state function for example ΔP, ΔT, ΔV, ΔH are not state function.**

Extensive Properties (Depend upon quantity of Matter present and are additive)	**Intensive Properties (Do not depend upon quantity of Matter present and are non additive)**
Volume	Molar volume
Resistance	Molar conductivity
Number of moles	Density, Electromotive force
Mass	Refractive index
Free Energy (G)	Surface tension
Entropy (S)	Viscosity
Enthalpy (H)	molar free energy
Internal energy (E)	Specific heat
Heat capacity	Pressure
	Temperature
	Boiling point, freezing point etc

PATH FUNCTION

Function which depends on the path means how the process is carried out. heat & work are path functions

THERMODYNAMIC PROCESS :

A thermodynamic process involves change of a system from one state to another state.

TYPES OF PROCESS :

A process is called ***Isothermal***, if the temperature of the system remains constant during the change. It is carried out in a thermostat and in such a process the exchange of energy between the system and surroundings takes place. In such a process dT = 0 & dE = 0.

$\Delta H = \Delta U + \Delta(PV)$, at constant pressure $\Delta H = \Delta U + P\,\Delta V$

combining with first law.

$$\Delta H = q_p$$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

- The difference between ΔH & ΔU becomes significant only when gases are involved (insignificant in solids and liquids)

$$\Delta H = \Delta U + \Delta (PV) = \Delta U + nR\ \Delta T$$

$$\Delta H = \Delta U + (\Delta n_g)\, RT$$

- For a given system consider
  $H = f(T, P)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

- For isobaric process : $dP = 0$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT \text{ or } dH = C_P.\, dT,\ \Delta H = \int C_P.dT$$

- For an ideal gas $H = f(T)$ only

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 \text{ or } dH = C_P.\, dT,\ \Delta H = \int C_P.dT \text{ , for n moles of ideal gas } \Delta H = \int n\, C_p\, dT$$

- For Chemical reactions $\int d\,\Delta H = \int (\Delta\ C_p.dT$

$\Delta_r H_{T_2} - \Delta_r H_{T_1} = \Delta_r C_p\ (T_2 - T_1)$ **{Kirchoff's equation}**

similarly $\Delta_r U_{T_2} - \Delta_r U_{T_1} = \Delta_r C_v\ (T_2 - T_1)$

TYPES OF EQUILIBRIUM :

1.	Thermal equilibrium	:	Equality of temperature
2.	Mechanical equilibrium	:	Equality of pressure
3.	Material equilibrium	:	No change in composition

ZEROTH LAW OF THERMODYNAMICS

It states that, two systems in thermal equilibrium with a third system, are also in thermal equilibrium with each other.

FIRST LAW OF THERMODYNAMICS

It is law of conservation of energy. Mathematically for **closed system** at rest in absence of external fields this law is written as :

$$\Delta U = q + w$$

where ΔU is change in internal energy of the system q is the transfer of heat from surrounding to the system and w is the work involved (either done on the system or by the system) .

$-(dG_{system})_{T,P} = (dw_{non-PV})_{system}$

Non–PV work done by the system = decrease in gibbs free energy

- It can be shown that free energy change for a process is equal to the maximum possible work that can be derived from the process i.e.

$\Delta G^\circ = w_{max}$ (for a reversible change at constant pressure and temperature)

In case of a galvanic cell, free energy change, ΔG is related to the electrical work done in the cell.

$\Delta G = -nFE_{cell}$, where E_{cell} = e.m.f. of the cell ; F = Faraday constant and

n = number of electrons being transferred in the chemical process

So $\Delta G^\circ = -nF E^\circ_{cell}$, where E°_{cell} is the standard cell potential.

THIRD LAW OF THERMODYNAMICS :

"At absolute zero, the entropy of a perfectly crystalline substance is taken as zero", which means that at absolute zero every crystalline solid is in a state of perfect order and its entropy should be zero.

By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0k} = \int_0^T \frac{q_{rev}}{T}, \text{ since } S_{0K} = 0 \quad ; \quad S_T = \int_0^T \frac{q_{rev}}{T}$$

Absolute entropies of various substances have been tabulated and these value are used to calculate entropy changes for the reactions by the formula:

$$\Delta S^\circ = \sum \nu_P S^\circ \text{ (products)} - \sum \nu_R S^\circ \text{ (reactants)}$$

Variation of ΔS_r with temperature & pressure : $\int dS_r = \int \frac{\Delta_r C_{p,m} . dT}{T}$

$$\Delta_r S_{T_2} - \Delta_r S_{T_1} = \Delta_r C_{p,m} \ln \frac{T_2}{T_1}$$