Reversible and irreversible process :→

(a) **Reversible process** → A reversible process is one which can be reversed in such a way that all changes taking place in the direct process are exactly repeated in the inverse order and opposite sense and no change are left in any of the body taking part in the process. Thus if a quantity of heat is supplied to a system and a quantity of work is obtained from it in the direct process, the same amount of heat should be obtained by doing the same amount of work as the system in the reverse process.

Examples: All isothermal and adiabatic changes are reversible when performed slowly. The process carried out is very slow, so no energy is distroyed on producing oscillation and eddy current and no heat is lost by conduction, convection & radiation.

If heat is suppplied to a given mass of gas at constant pressure, it expands and does some external work. If the same amount of work is done on the gas in compressing it the same amount of heat will be produced.

When certain amount of heat is supplied to the ice, it melts, if the same amount of heat is removed from it, the water so formed will be converted into ice.

slow elongation and contraction of a spring in such a way that the work done on the spring during stretching and the work done during contraction are equal, constitutes a reversible process.

→ **Irreversible process** → Any process that doesnot satisfy the condition of reversibility when it is reversed is said to be irreversible process. All natural process such as conduction, radiation, radio active decay are irreversible.

Examples :→ If a steel ball is made to fall on an inelastic lead sheet, its K.E. changes into heat energy by friction. This heat energy raises the temperature of lead sheet and no reverse transformation of this heat energy occures. Therefore this process can not reverse itself. There is no means by which the dissipated heat can be transformed back into mechanical K.E. to enable the ball to rise up again from the lead sheet. Hence it is an irreversible process.

Fast and sudden stretching of spring may produce vibration in it so that part of energy is there by dissipated. Hence the process becomes irreversible.

Heat produced by passing an electric current through the resistance is irreversible, because on reversible the direction of the current the same effect is observed.

→ Difference between reversible and irreversible process : →

Reversible process	Irreversible process
1. At the conclusion of the process and its reverse, the system is brought to the initial state without any change anywhere in the rest of the universe.	1. At the conclusion of the process and its reverse, the system is brought to the initial condition only at the cost of some change somewhere in the universe.
2. At the conclusion of the process and its reverse, the change in internal energy of the system is zero, i.e. $\Delta U = 0$.	2. At the conclusion of the process and its reverse, the change in internal energy of the system is zero. ie. $\Delta U = 0$.
3. This process takes place in an infinite time.	3. This process takes place in a short time.
4. This is an ideal concept.	4. This is the most practical concept.
5. This process must be free from dissipative forces.	5. This process takes place only when there is some dissipative force.

6. This process occurs only when the system passes quasistatically through small stage of virtual equilibrium, so that the change can be effected in either way.	6. This process occurs spontaneously and unidirectionally violently disturbing the equilibrium.
7. Net work done is zero.	7. Net workdone is not zero.
8. Net heat flow is zero.	8. Net heat flow is not zero.

→ Gibbs function (or potential) of a system :→

We know that Gibb's free energy $(G) = H - TS$

and Enthalpy $(H) = U + pV$

$$\therefore \quad G = U + pV - TS$$

$$\therefore \quad dG = dU + pdV + Vdp - Tds - sdT$$

$$= (Tds - pdV) + pdV + Vdp - Tds - sdT$$

$$\text{or,} \quad dG = Vdp - sdT$$

At constant pressure,

$$dG = -sdT$$

$$\text{or,} \quad S = -\left(\frac{\delta G}{\delta T}\right).$$

and similarly,

$$V = -\left(\frac{\delta G}{\delta p}\right)_T$$

Thus S and V are given by derivatives of G and this fact justifies its selection as a fourth thermodynamic potential.

Its significance is revealed when we consider reversible isothermal isobaric process.

$$dU = TdS - dW$$
$$= d(TS) - pdv - dA$$

Where dA is the work done by the system other than the mechanical work which is pdv.

or, $dU = d(TS) - d(pv) - dA$

or, $d(U + pv - TS) = -dA$

or, $dG = -dA$ $\quad (G = U + pV - TS$ by definition$)$

Thus the significance of G is that its decrease represents work available from the system in reversible isothermal - isobaric process.

Another significance is that in isothermal - isobaric process $dT = 0$ and $dp = 0$ and so $dG = 0$. Hence $G =$ constant in this process. This function is particularly important in connection with processes involving a change of phase. sublimation, fusion and vaporisation take place isothermally and isobarically and can be conceived as occuring reversibly. Hence, during such processes, the Gibbs function or Gibbs free energy of the system remains constant.