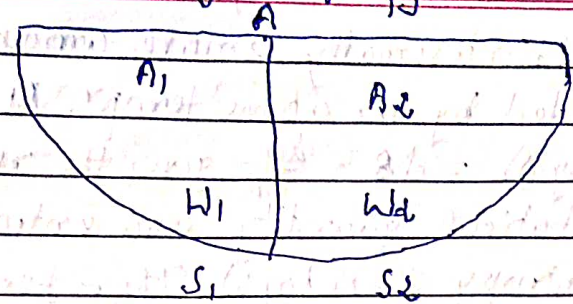


* Additive Nature of Entropy :-



System A \rightarrow Having entropy S corresponding to a thermodynamic probability W . Let us divide the system into two sub systems.

Subsystem $A_1 \rightarrow$ Entropy S_1 and thermodynamic probability W_1 .

Subsystem $A_2 \rightarrow$ Entropy S_2 and thermodynamic probability W_2 .

According to law of probability, combined probability for A_1 and A_2 $W = W_1 \times W_2$

Now $S = k \log W$, $S_1 = k \log W_1$, $S_2 = k \log W_2$

or, $S_1 + S_2 = k \log W_1 + k \log W_2$
 $= k \log (W_1 \times W_2) = k \log W = S$

$\therefore S = S_1 + S_2$

This argument can be extended to a system consisting of more than two subsystems in equilibrium, $S = S_1 + S_2 + \dots$

Hence the entropy of the system is equal to the sum of the entropies of its subsystems.

In other words entropy like volume, area and internal energy is an extensive parameter. An extensive parameter is a quantity the value of which in value of composite system is equal to the sum of its value in each of the subsystems. Quantities like temp., pressure, surface tension, etc. which remain unchanged if the system is subdivided are known as intensive parameter.

* Change of Entropy :- The entropy is change as defined as the ratio of the infinitesimally small amount of heat supplied to a system divided by the above temp. R and V constant. The relation $k d(\log w) = dS = \frac{dq}{T}$ gives the relation between probability, a statistical quantity and entropy a thermodynamic quantity. Now, entropy $S = k \log w$. Therefore entropy being proportional to w is also related to disorder in the system. Entropy is taken to measure of disorder. According to law of increase of entropy, the entropy of every natural system tends to increase. The same can be stated as follows:- Every system tends to proceed the state of max^m disorder.

* Principle of Increase of Entropy :-

Since when the system is in equilibrium entropy (S) has its max^m value. That is, ~~$\Delta S > 0$~~ $\Delta S = 0$ for the equilibrium state of the system. When the system moves from a state of lowest probability to the state of max^m probability, there is an increase in entropy. As this process is irreversible, we have $\Delta S > 0$. Thus the entropy of the isolated system remains constant or increases according as the changes it undergoes are reversible or irreversible.

* Entropy :-

Criterion for a physical, chemical change:- The result $\Delta \geq 0$ is of great significance. The process in which $\Delta S > 0$, that is, there is increase in entropy of the universe, is irreversible and the one in which $\Delta S = 0$ i.e. entropy remains constant, irreversible. This, too, gives basis for any process to occur. In this universe all natural processes are taking place irreversibly and hence by all processes going around as

the entropy of the universe is ever increasing. The natural direction of any physical or chemical change is therefore, towards irreversibility. The second law of thermodynamics in terms of Entropy can be stated as:-

A physical or chemical process will proceed in the direction that causes the entropy of the universe to increase. This is also called the principle of entropy of universe.

- * **Thermal Equilibrium:** - If all the parts of the system are at the same temp. - it is said to be in equilibrium therm. i.e. it is in the state of max^m thermodynamic probability.
- * **Order and disorder:** - When complete and definite information is known for all the particles of a system, it is said to be in perfect order.

- * **Entropy and Availability of Heat energy for work:** -

Unavailable work due to conduction = $T_0 \Delta S$. Hence the increase of unavailable energy is equal to the increase of entropy multiplied by lowest temp. available.

Thus entropy is a measure of the unavailability of energy and the law of entropy implies that the available energy in the world tends to zero. This is also known as the principle of degradation or running downhill of energy.

Thus unavailability of work from heat is decreasing since entropy increases in all processes. In other words, availability is decreasing, we are heading towards heat death.

- * **Change of Entropy in reversible and irreversible processes:** -

1.) Entropy of universe remains constant in Reversible processes.

2.) Entropy increases in Irreversible Processes.

Let us take the cycle of an irreversible engine which absorbs Q_1 amount of heat at temp. T_1 .

Then the efficiency of this engine will be $\frac{Q_1 - Q_2}{Q_1}$ and the efficiency of a reversible Carnot engine working between the same two temps. $1 - \frac{T_2}{T_1}$. Since the efficiency of an irreversible one working between the same two temps. We have for an irreversible cycle,

$$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1} \quad \text{or,} \quad \frac{Q_2}{Q_1} > \frac{T_2}{T_1}$$

$$\text{or,} \quad \frac{Q_1}{T_1} + \left(-\frac{Q_2}{T_2}\right) < 0 \quad \text{or,} \quad \sum \frac{Q}{T} < 0$$

Now any arbitrary irreversible cyclic process may be divided into large no. of infinitesimal small irreversible cyclic processes conceding the argument as above, we have for any irreversible cyclic process,

$$\oint \frac{dQ}{T} < 0.$$