

Physical Significance of Entropy

1. Entropy as Measure of the Disorder of the System: —

It is obvious that all spontaneous processes like flow of heat from a hot end to cold end of a conductor; flow of electricity from a higher potential to a point at a lower potential, Expansion of gas in vacuum; diffusion of solute from concentrated to dilute solution.

Thus all these processes are accompanied by increase in the 'disorder' of the system.

So, all the spontaneous processes are accompanied by increase in entropy as well as increase in the disorder of the system.

It has also been shown that melting of a solid or evaporation of a liquid is accompanied by increase of entropy.

Thus, entropy is regarded as a measurement of the disorder of the system.

According to Gibbs, entropy is described as a measure of the "mixed-up-ness" of a system.

2. Entropy as a Measure of Probability: —

All spontaneous processes lead to increase in entropy and also to increase in disorder. A little condition will show that when a process is spontaneous it means that it is proceeding from a less probable to a more probable state.

It appears, therefore that there is a close relation between entropy S and the thermodynamic probability W of the state of the system both of which increase at the same time. This relationship was expressed by Boltzmann

as

$$S = k \ln W + \text{Constant} \quad \text{--- (1)}$$

where k is Boltzmann Constant, i.e. gas constant per single molecule ($= \frac{R}{N_A}$). Boltzmann defined thermodynamic probability of the system as the ratio of the probability of the actual state to the probability of the state in which there is complete order for the same energy and volume.

According to Planck, the const. in eqⁿ (1) is zero.

$$\text{So } S = k \ln W \quad \text{--- (2)}$$

This eqⁿ is known as Boltzmann entropy equation.

A solid at absolute zero temperature is considered to be in a most ordered state. In this case, evidently W is unity and hence $S_0 = 0$, the entropy of crystalline solid at absolute zero is therefore taken as zero.