

'Heat cannot of itself flow from a colder to a hotter body, without the intervention of an outside agency.'

(5) The second law of thermodynamics can also be stated as, *'The energy of universe remains constant, but available energy is decreasing and entropy of universe is increasing to a condition of maximum entropy of randomness or chaos. When there is maximum chaos, the order will prevail itself.'*

The greatest value of the second law, so far as the chemist is concerned, lies in the fact that it forms the basis of predicting whether a particular reaction can occur, and if it occurs, then to what extent. In other words, the second law of thermodynamics gives us the conditions under which a portion of it may be converted into work. The second law of thermodynamics may be stated in a great variety of ways.

(1) **Kelvin-Planck Statement** - It is impossible to construct a cyclic process which converts heat completely into work.

CONCEPT OF ENTROPY.

Mathematically, it will be given by equation (20), when the change has been carried out reversibly. This is so because the said equation (20) has been derived from Carnot cycle in which all the changes are carried out reversibly.

It is difficult to define the actual entropy of the system. However, it is convenient to define the change of entropy during a change. Thus, **change of entropy** of a system is defined as the integral of all the terms involving heat absorbed (Q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly.

It is evident from equation (21) that the total amount of heat transferred in a reversible change is given by

$$q_{rev} = \int_A^B TdS$$

The integral can be interpreted graphically as the area under a curve, on a $T - S$ diagram (Figure 3) of a Carnot cycle.

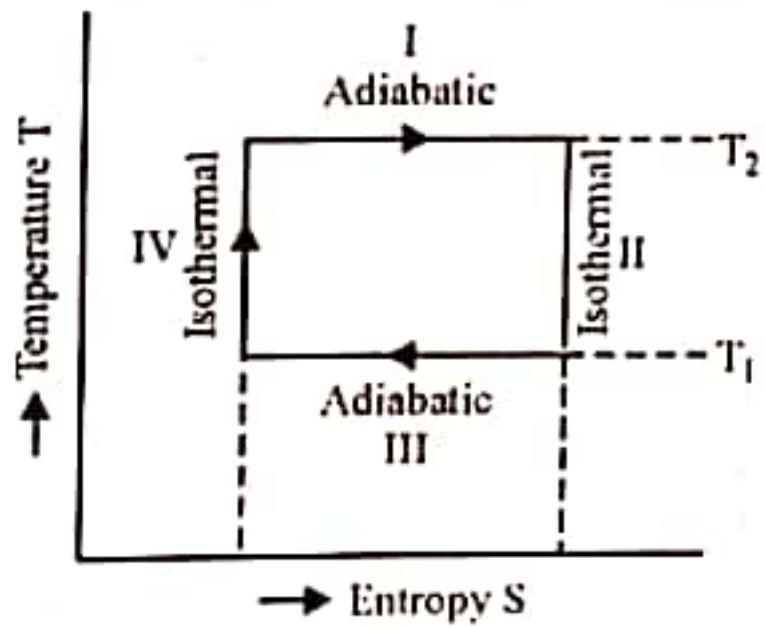


Fig. 3

[I] Physical Concept of Entropy

The definition of entropy changes according to expression $dS = \frac{dQ}{T}$ is very useful in making entropy calculations, but is almost meaningless as a definition. However, there are two other aspects which can provide a definite physical significance to entropy. These are as follows :

(a) Entropy is the degree of disorder or randomness of the molecules of a system: A characteristic property of a spontaneous process is that it is always accompanied by an increase in the 'disorder' or 'randomness' of the molecules of the system. In all such processes, there occurs an increase of entropy. Hence, entropy may be defined as a measure of disorder or random arrangement of the molecules in a system.

The concept of **disorder** and **randomness** can be explained as follows :

In the case of a gas at low pressure, the molecules are free to move in all possible directions or are free to move at random. Their motion is not confined to any particular direction. However, if the pressure is increased, the molecules of the gas occupy a comparatively smaller volume. It means that the chances of finding a molecule within a specified space have increased than before. In other words, the *degree of disorder has decreased* and there exists a greater order in the system. This orderliness increases as the pressure of the gas increases.

When the gaseous pressure is very high, then below the critical temperature of the gas, liquefaction of the gas occurs. The molecules come very close to each other than before. The molecules are thus in a very high ordered state as compared to that in the gas.

When the temperature falls below the freezing point of the solvent, the liquid changes into solid. In such a case, the molecules, ions or atoms are now held in a definite lattice. The molecules, ions or atoms are not allowed to move at all, but, however, vibration or rotation is possible. On further cooling this possibility also vanishes. It is observed that at 0°K, the disorder completely disappears or *absolute order* prevails. So, **at 0°K the entropy of a solid is regarded to be zero.**

[II] Entropy Unit

As indicated above, the *dimensions of entropy are energy \times temperature*. The energy is generally expressed in calories and hence the entropy is expressed as *calories per degree*. Calories per degree is sometimes referred to as entropy unit (e.u.).

As the entropy also depends upon the quantity of the substance involved, the mass must also be stated. We then have entropy units as *calories per degree per mole*.

[III] Measurement of Entropy

Since entropy is associated with a certain definite state, it may thus be measured from some arbitrary zero, corresponding to a particular state. This particular state in which entropy is assumed to be zero is called the *standard state*.

We must remember that zero value of entropy assigned to any particular state does not mean that its entropy is actually zero, because the arbitrary zero of the centigrade scale has nothing to do with the absolute zero. In fact, when we talk of entropy, we talk of change of entropy and not of its absolute value.

[IV] Entropy Change During Vaporisation of the Liquid

Since vaporisation takes place at constant temperature, the change in entropy of the liquid when it is converted into vapour at temperature T is given by,

$$\Delta S = \frac{Q_{rev}}{T} \quad (\text{cf. equation 22})$$

But $Q_{rev} = mL$, where m is the mass of the liquid that vaporises and L is the latent heat of vaporisation at T . Hence,

$$\Delta S = S_B - S_A = \frac{mL}{T} \quad \dots(24)$$

[V] Entropy Change When Liquid is Heated From T_1 to T_2

Consider that m grams of liquid is heated from a temperature T_1 to T_2 without any change in the state, occurring during heating. But for an elementary change, we have

$$dQ_{rev} = mSdT,$$

where

S = specific heat of the liquid.

Hence, change in entropy is given by,

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ_{rev}}{T} = \int_{T_1}^{T_2} \frac{mSdT}{T} \quad (\text{cf. equation 20})$$

$$= mS \int_{T_1}^{T_2} \frac{dT}{T} = mS \log_e \frac{T_2}{T_1} \quad \dots(25)$$