

## ENTROPY

The second law leads to a definition of a new thermodynamic property, called Entropy. Like internal energy ( $U$ )  $\rightarrow$  enthalpy ( $H$ ) entropy is a state function if it is denoted by  $S$ .

✓/✳  $dq$  is not perfect differential but  $dq/T$  is a perfect differential :

When a system changes from a given state to another state, the thermal charge ( $dq$ ), if any, depends on the way the change of the system is effected. i.e.  $dq$  depends on the path of the transformation. Hence  $dq$  is not a perfect differential (Mathematical approach given in page 15-16)

(1) Suppose, one mole of perfect gas undergoes a reversible expansion from  $V_1$  to  $V_2$  when temp. changes from  $T_1$  to  $T_2$ . Then from the first law,

$$dq = dU + PdV$$

$$\Rightarrow \int_I dq = \int_I dU + \int_I PdV$$

$$= \int_{T_1}^{T_2} C_v dT + \int_{V_1}^{V_2} RT d \ln V$$

$$= C_v (T_2 - T_1) + \int_{V_1}^{V_2} RT d \ln V \quad \rightarrow (1)$$

The integral value on the RHS,  $\int RT d \ln V$  can't be evaluated unless we know the relation bet<sup>n</sup>  $T$  &  $V$ . If  $T$  is constant (i.e. Isothermal Process) the integral will have one single value, and if  $T$  changes during the process, the integral have different values. Thus the magnitude of  $\int_I dq$  depends on the way the expansion is carried out.

Now dividing the eqn. (1) by  $T$  we have,

$$\int_I \frac{dq}{T} = \int_{T_1}^{T_2} C_v \frac{dT}{T} + \int_{V_1}^{V_2} R d \ln V$$

$$\Rightarrow \int_I^II \frac{dq}{T} = c_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

ie.  $\int_I^II \frac{dq}{T}$  for a given change from state I to state II can be evaluated without any reference to the path of transformation. Hence,  $\int \frac{dq}{T}$  is independent of the way the change is carried out. Though  $\int dq$  is not.

Such way it is concluded that  $\int \frac{dq}{T}$  is perfect differential but  $\int dq$  is not. #

✓ \* Definition of Entropy :- The heat change  $dq$  and the temp<sup>n</sup>  $T$  are thermodynamic quantities. The system has a thermodynamic function whose change measured by  $\frac{dq}{T}$ , it is independent of the path of transformation of the system. This function is called Entropy (named by Clausius) and denoted by  $S$ .

The change  $ds$  is measured by the ratio of the reversible heat change  $dq_r$  to the temp<sup>r</sup> at which the change occurs, i.e.

$$ds = \frac{dq_r}{T} ; \text{ suffix } r \text{ indicates reversibility.}$$

If the heat change takes place at different temp<sup>r</sup> then,

$$ds = \frac{dq_1}{T_1} + \frac{dq_2}{T_2} + \frac{dq_3}{T_3} + \dots$$

$$= \sum \frac{dq}{T}$$

$$\therefore \int ds = \int \frac{dq_r}{T}$$

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Comments :-

(i) Entropy  $S$  is a thermodynamic function whose magnitude depends only on the parameters of the system and can be expressed in terms of  $P, V, T$ .

(ii) The entropy change  $ds$  is a perfect differential. The entropy change is measured

by the reversible heat change of the system divided by the temp<sup>n</sup> in absolute scale.

ie.  $ds = \frac{dq}{T}$

(iii) Absorption of heat increases the entropy of the system. The rejection of heat by the system leads to a decrease in its entropy.

In a reversible adiabatic change ( $dq = 0$ ) the entropy change is zero. Such adiabatic changes are called iso-entropic changes.

\* Relation bet<sup>n</sup> Entropy & Internal Energy and Entropy & Enthalpy

We have,  $dU = dq - pdv$  |  $* dq = dU + pdv$   
 $\therefore dU = Tds - pdv$  |  $* \frac{dq}{T} = ds$   
 $\rightarrow (1)$  |  $\therefore dq = Tds$

And,  $dH = dU + pdv + vdp$  |  $\therefore H = U + pV$   
 $= Tds - pdv + pdv + vdp$   
 $\therefore dH = Tds + vdp \rightarrow (2) *$