

class 88  $\Rightarrow$  B.Sc.(Hons.) Part - IISubject  $\Rightarrow$  ChemistryChapter  $\Rightarrow$  ThermodynamicsTopic  $\Rightarrow$  Entropy change in a reversible and an irreversible processName  $\Rightarrow$  DR. Amarendra Kumar,  
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### Entropy change in a reversible process

If  $q_{rev.}$  is the heat absorbed by the system reversibly, then the heat lost by the surroundings will also be  $q_{rev.}$ . If the process takes place isothermally at the absolute temperature  $T$ . Then,

(i) Entropy change of the system is given by

$$\Delta S_{\text{system}} = \frac{q_{\text{rev.}}}{T}$$

(ii) Entropy change of the surroundings is given by

$$\Delta S_{\text{surroundings}} = -\frac{q_{\text{rev.}}}{T}$$

Thus the total entropy change for the combined system and the surroundings will be

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{q_{\text{rev.}}}{T} - \frac{q_{\text{rev.}}}{T}$$

$$\therefore \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

Thus in a reversible process, the net entropy change for the combined system and surroundings is zero.

## Entropy change for an irreversible process

If the total heat lost by the surroundings is  $q_{irrev}$ . This heat is absorbed by the system but the entropy change of the system does not depend upon the heat actually absorbed but it depends upon the heat absorbed reversibly i.e.  $q_{rev}$ .

Thus if the heat is absorbed isothermally by the system at the absolute temperature  $T$ , the entropy change of the system is given by

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T}$$

Let the loss of heat ( $q_{irrev}$ ) by the surroundings takes place infinitesimally slowly because the surroundings are much bigger in size and magnitude compared to the system (i.e. reversibly) and isothermally at temperature  $T$ . Then the entropy change of the surroundings is given by

$$\Delta S_{\text{surroundings}} = -\frac{q_{\text{irrev}}}{T}$$

The total entropy change for the combined system and the surroundings will become

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{irrev}}}{T}$$

We know that the work done in a reversible process is the maximum work i.e.

$$W_{\text{rev.}} > W_{\text{irrev.}} \quad \text{--- (1)}$$

further, as the internal energy ( $U$ ) is state function, the value of  $\Delta U$  is same whether the process is carried out reversibly or irreversibly. Therefore,

$$\Delta U = q_{\text{rev.}} - W_{\text{rev.}} = q_{\text{irrev.}} - W_{\text{irrev.}} \quad \text{--- (2)}$$

Combining results (1) and (2), we come to the conclusion.

(3)

$$\frac{q_{rev.}}{T} > \frac{q_{irrev.}}{T}$$

$$\therefore \frac{q_{rev.}}{T} > \frac{q_{irrev.}}{T}$$

$$\text{or, } \frac{q_{rev.}}{T} - \frac{q_{irrev.}}{T} > 0 \quad \text{--- (3)}$$

from result ( $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{q_{rev.}}{T} - \frac{q_{rev.}}{T} = 0$ )

and result (3) we have,

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Thus it may be concluded that in an irreversible process, the entropy change for the combined system and the surroundings is greater than zero i.e.

An irreversible process is accompanied by a net increase of entropy.

since all spontaneous processes are thermodynamically irreversible. It may be stated that

All spontaneous processes are accompanied by a net increase of entropy.

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