Subject ⇒ Chemistry
Chapter ⇒ Thermodynamics
Topic ⇒ Carnot theorem, Concept of Entropy.

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Carnot theorem

Carnot theorem is stated as-

The efficiency of a reversible heat engine depends only upon the temperatures of the source and the sink and is independent of the nature of the working substance.

In other words,

'All reversible heat engines working between the same two temperatures have the same efficiency.

We know that

$$w = q_2 - q_1$$

i.e. net work done by the system is equal to net heat absorbed by the system.

Putting the value of w in the following equation

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

Hence the efficiency of a heat engine may be given by any one of the following expressions -

$$\eta = \frac{w}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

This result deduced for a perfect gas depends upon the temperature limits between which the cycle operates.

obviously, the efficiency of the engine can be increased by widening the difference in the temperatures of the source and sink.

Definition of Entropy

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.

The symbol of entropy is S.

While the change in disorder accompanying a process from start to completion is represented by ΔS.

The entropy of a system is a state function and depends only on the initial and final states of the system.

The change in entropy (ΔS) for any process is given by the equation

$$\Delta S = S_{final} - S_{initial}$$

When $S_{final} > S_{initial}$, ΔS is positive.

A change in a system which is accompanied by an increase in entropy, tends to be spontaneous

Numerical definition

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For a reversible change taking place at a fixed temperature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided

by the temperature (T).

i.e. $$\Delta S = \frac{q}{T}$$

If heat is absorbed, then ΔS is positive and there will be increase in entropy.

If heat is evolved, then ΔS is negative and there is a decrease in entropy.

Units of entropy

Since, entropy is equal to heat energy divided by absolute temperature.

Therefore, it is measured in entropy unit (eu) which are Calories per degree per mole i.e. $Cal\,mol^{-1}K^{-1}$.

In the S.I system

Joules per mole per degree i.e. $J\,mol^{-1}K^{-1}$.

1 eu = 4.184

Entropy and Probability

Entropy ⇒ A measure of the disorder of a system.

A state of highly ordered, low entropy = Low probability.

A state is highly disordered, high entropy = High Probability.

In an irreversible process, the universe moves from a state of low probability to a state of higher probability.