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Udai Pratap (Autonomous) College, Varanasi

E-learning Material

Module/ Lecture	05
Topic	Entropy and Its Physical Significance
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Entropy and Its Physical Significance

Entropy

Although Entropy is a real physical quantity but it is difficult to represent it and cannot be felt like pressure or temperature. It is visualized as a ghost quantity and can be understood only on the basis of its properties and its effect on other physical quantities. Entropy is the fundamental concept that sets thermodynamics apart from classical mechanics. It creates a distinction between the classical mechanics concept of energy and the thermodynamic concept of accessible energy.

Mathematically entropy is defined as

$$dS = \frac{\delta Q_{\text{rev}}}{T} \quad (1)$$

It is defined for reversible process. In adiabatic transformations,

$$\delta Q_{\text{rev}} = 0$$

$$dS=0$$

thus $S=\text{Constant.}$

Hence entropy is that thermal property of a substance (Physical Quantity) which remains constant during an adiabatic change.

Like energy entropy (s) is also an extensive property. It will have the units of J/K. The entropy of the system is not measured in absolute terms; rather it is measured in relative terms. The entropy of the system is measured in terms of the changes the system has undergone from the previous state to the final state. Thus the entropy is always measured as the change in entropy of the system denoted by dS and not merely S . If at all it is necessary to measure the value of the entropy at a

particular state of the system, then zero value of entropy is assigned to the previous chosen state of the system.

Entropy is a Point Function

Consider an arbitrary reversible cycle represented by closed curve $i \rightarrow f \rightarrow i$, then according to Clausius theorem,

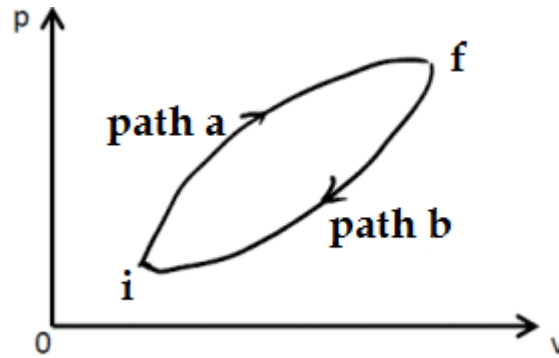


Fig. 1

$$\oint \frac{\delta Q}{T} = \int_{(a)}^f \frac{\delta Q}{T} + \int_{(b)}^i \frac{\delta Q}{T} = 0 \quad (1)$$

The cycle being reversible, if path b is traverse from f to i in opposite direction, then we have

$$\int_{(b)}^i \frac{\delta Q}{T} = - \int_{(b)}^f \frac{\delta Q}{T} \quad (2)$$

Thus from Eq. (1) and Eq. (2), we get

$$\int_{(a)}^f \frac{\delta Q}{T} - \int_{(b)}^f \frac{\delta Q}{T} = 0$$

i.e.
$$\int_{(a)}^f \frac{\delta Q}{T} = \int_{(b)}^f \frac{\delta Q}{T} \quad (3)$$

since path 'a' and path 'b' between the states I and f are chosen arbitrarily and represent any two reversible paths between I and f, hence we can say

$\int_i^f \frac{\delta Q}{T}$ is independent of path between I and f and depends only upon the coordinates of i and f.

Thus quantity $\frac{\delta Q}{T}$ can be expressed as a perfect differential of a point function; it is represented by dS, thus

$$dS = \frac{\delta Q}{T}$$

$$\int_i^f dS = \int_i^f \frac{\delta Q}{T}$$

$$S_f - S_i = \int_i^f \frac{\delta Q}{T}$$

The point function S was introduced by Clausius and is called entropy.

Principal of entropy increase

Consider a system that undergo the cycle as shown in the fig. 2.

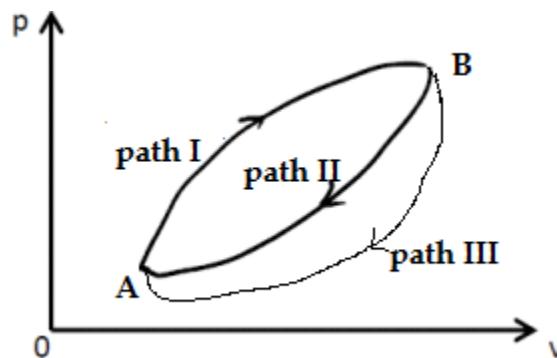


Fig. 2

The cycle $A \rightarrow I \rightarrow B \rightarrow II \rightarrow A$ made up of reversible processes I and II, from Clausius Theorem we can write

$$\oint \frac{\delta Q}{T} = \int_{(path I)}^B \frac{\delta Q_R}{T} + \int_{(path II)}^A \frac{\delta Q_R}{T} = 0 \quad (1)$$

Where suffix R denotes the reversible path. Now consider the irreversible cycle $A \rightarrow I \rightarrow B \rightarrow III \rightarrow A$ made of reversible process I and irreversible process III. For this cycle, from Clausius Inequality we have

$$\oint \frac{\delta Q}{T} = \int_{(path I)}^B \frac{\delta Q_R}{T} + \int_{(path II)}^A \frac{\delta Q_I}{T} < 0 \quad (2)$$

Where suffix I denotes the irreversible path. On combining Eq. (1) and Eq. (2), we get

$$\int_{(path II)}^A \frac{\delta Q_R}{T} > \int_{(path II)}^A \frac{\delta Q_I}{T} \quad (3)$$

Since path II is reversible and entropy is a function of state, we can write

$$S_A - S_B = \int_{(path II)}^A \frac{\delta Q_R}{T} = \int_B^A dS_{II} = \int_B^A dS_{III} \quad (4)$$

Therefore for an irreversible process

$$\int_B^A dS_{III} > \int_{(path III)}^A \frac{\delta Q_I}{T} \quad (5)$$

Thus for general case we may write

$$dS \geq \frac{\delta Q}{T} \quad (6)$$

The equality and greater than sign in Eq. (6) hold for reversible and irreversible processes respectively.

For an isolated system, there is no thermal interaction with the surrounding i.e. $\delta Q = 0$ and hence

$$dS \geq 0. \quad (7)$$

Thus the entropy of an isolated system cannot decrease; either remains constant or increases. This is known as principle of entropy increase.

Physical Significance of entropy

The entropy of a substance is real physical quantity and is a definite function of the state of the body like pressure, temperature, volume of internal energy. It is difficult to form a real conception of this quantity because it cannot be felt like temperature or pressure.

The known physical aspect of entropy is that it is a quantity which remains constant during a reversible adiabatic process and increases during an irreversible adiabatic process. But this is not sufficient to make the term entropy clear as far as physical significance is concerned. Physical significance can be understood from the following aspects:

1. Entropy and unavailable energy

The second law of thermodynamics tells us that whole amount of internal energy of any substance is not convertible into useful work. A portion of this energy which is used for doing useful work is called **available energy**. The remaining part of the energy which cannot be converted into useful work is called **unavailable energy**.

Entropy is a measure of this unavailable energy. In fact, the entropy may be defined as

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

or,

$$\text{Unavailable energy} = \text{Entropy} \times \text{Temperature}$$

An increment in the entropy implies a transition from more to less energy available for work.

2. Entropy and disorder

Entropy is a measure of the disorder or randomness in the system. At absolute zero the entropy tends to zero and the molecules of the system arrange themselves in perfect order. When a gas expands into vacuum, water flows out of a reservoir, spontaneous chain reaction takes place, an increase in the disorder occurs and therefore entropy increases. In the Gaseous state entropy is more than liquid and solid states. When the ice is converted into water and then into steam, entropy increases and also disorderly motion of molecule.

An increment in the entropy implies a transition from an ordered to a less ordered physical state.

3. Entropy and probability

Changes in order are expressed quantitatively in terms of entropy change, dS . Since a disordered state is more probable for systems than of order, the entropy and thermodynamic probabilities are closely related. An increment in entropy implies a transition from less probable to more probable physical state.