

ENTROPY

The entropy of a system is a thermodynamics state parameter and can be defined by number of ways as

DEFINITION 1

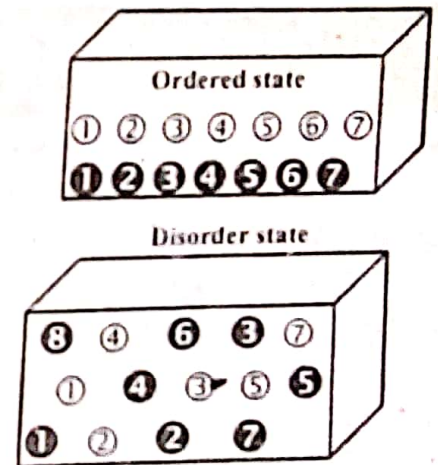
The measure of disorderness or randomness of the system is called entropy.

EXAMPLE

Consider a box having rows of black and white balls arranged neatly upon each other. It is called ordered state of the system as shown in fig.

Now shake the box gently. The balls will get mixed together and ordered state will be lost. This state is now called disordered state.

The measure of disorderness or randomness of the system is called entropy. The entropy once increased in natural way can never be restored by that natural way. It means no amount of shake can restore original state.



DEFINITION 2

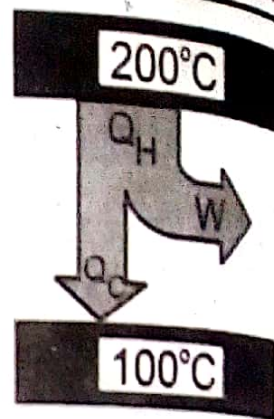
The measure of the amount of energy of the system that is unavailable to do work is called entropy.

EXAMPLE

Consider two heat reservoirs such that one is at temperature 100°C called LTR and other is at temperature 200°C called HTR. Now make their thermal contact. It will behave as heat engine and energy is available for doing work.

After some time thermal equilibrium is attained and system will be at 150°C . The system has heat energy but unavailable for doing work because this arrangement is now becomes single reservoir and no more a heat engine.

The measure of the amount of energy of the system that is unavailable to do work is called entropy.



DEFINITION 3

The thermal property of a system that remains constant during adiabatic process is called entropy.

EXPLANATION

The entropy of a system increases when heat flows into a system at constant temperature because by addition of heat in a system produces disorderness in its molecules. The entropy in this case is taken as positive. The entropy of a system decreases when heat leaves the system at constant temperature because molecules get arranged. The entropy in this case is taken as negative.

The entropy of a system depends upon initial and final states of the system, hence we can measure only change in entropy of the system.

The adiabatic process is that in which no heat enters or leaves the system, therefore entropy of the system remains constant.

Finally, it may be concluded that increase in entropy means transition from more ordered state to less ordered state or from more available energy to less available energy or from more probable state to less probable state of the system.

REVERSIBLE PROCESS

The process that can be retraced after differential changes in the environment is called reversible process.

The Carnot cycle is a reversible process that operates between HTR having heat Q_H and LTR having heat Q_L . The respective temperatures of HTR and LTR are T_H and T_L . The efficiency of Carnot heat engine in terms of heats is

$$e = 1 - \frac{Q_L}{Q_H} \quad \text{-----(1)}$$

The efficiency of Carnot heat engine in terms of temperatures is

$$e = 1 - \frac{T_L}{T_H} \quad \text{-----(2)}$$

Comparing eq(1) and eq(2)

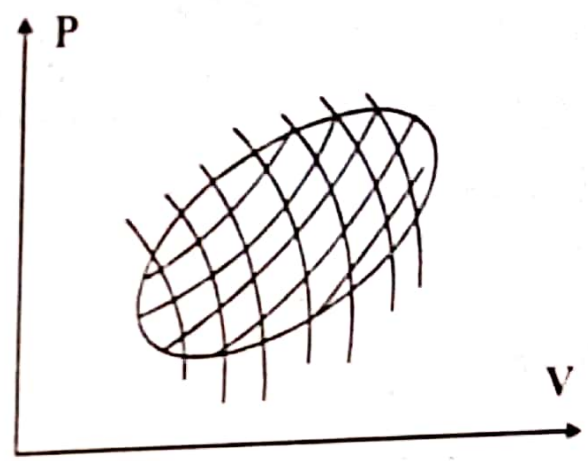
$$1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$
$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

The heat Q_H enters into system and taken as positive whereas heat Q_L leaves the system and taken as negative when cycle of Carnot heat engine operates. Now remove the absolute values, we can write as

$$\frac{Q_H}{T_H} = \frac{-Q_L}{T_L}$$

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$

This equation shows algebraic sum of $\frac{Q}{T}$ is zero for Carnot cycle. This statement can be generalized for any reversible process and stated as any reversible process is assembly of Carnot cycles that consists of isotherms and adiabats.



Under these conditions we can write as

$$\sum \frac{Q}{T} = 0$$

In limiting case \sum changes to \int . Therefore, for reversible process we can write as

$$\oint \frac{dQ}{T} = 0$$

Where circle on integral indicates that integral is evaluated for a complete cycle. The heat dQ is a quantity of heat that leaves or enters the system. For any part (a to b) of the cycle of heat engine, this can be used to define a change in entropy S for the system and written as

$$\Delta S = S(b) - S(a) = \int_a^b \frac{dQ}{T}$$

The quantity $\frac{dQ}{T}$ is differential change in state variable and called entropy change. It is denoted by dS

$$dS = \frac{dQ}{T}$$

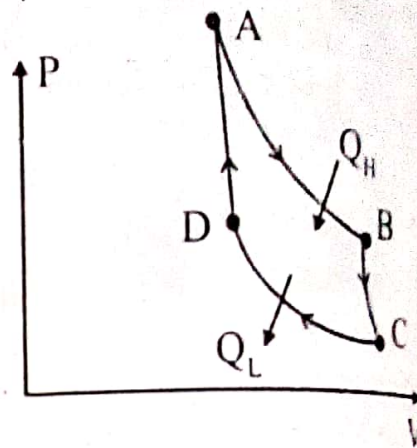
The process having entropy change zero is called reversible. This is called Clausius theorem. The SI unit of entropy is called J/K. The entropy change is negative when heat leaves the system and entropy change is positive when heat enters into system.

CLAUSIUS THEOREM

The Clausius theorem states that process will be reversible if its net change in entropy is zero. Conversely if net change in entropy is zero that process will be reversible.

PROOF

Consider a Carnot cycle that is reversible process. It operates between two isotherms and two adiabats as shown in fig.



Now calculate change in entropy for Carnot cycle

$$\Delta S = \int_B^A \frac{dQ}{T} + \int_A^B \frac{dQ}{T} + \int_B^C \frac{dQ}{T} + \int_C^D \frac{dQ}{T}$$

The process along B to C is adiabatic where no heat dQ enters or leaves the system so $\int_B^C \frac{dQ}{T} = 0$. Similarly process along D to A is adiabatic where no heat dQ enters or

leaves the system so $\int_D^A \frac{dQ}{T} = 0$. The above eq becomes

$$\Delta S = \int_A^B \frac{dQ}{T} + 0 + \int_C^D \frac{dQ}{T} + 0$$

The process along A to B is isothermal expansion in which heat Q_H enters into system at temperature T_H and taken as positive. The process along C to D is isothermal compression in which heat Q_L leaves the system at temperature T_L and taken as negative

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_L}{T_L}$$

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_H}{T_H} = 0$$

$$\Delta S = 0$$

The Clausius theorem is proved

Q.8 Discuss entropy change in irreversible process and calculate entropy change in different irreversible processes?

IRREVERSIBLE PROCESS

The process that cannot be retraced by differential changes in the environment is called irreversible process.

The efficiency is less than that of the Carnot cycle in any irreversible process. The formula of entropy change is called Clausius inequality and written as

$$\oint \frac{dQ}{T} \leq 0$$

The equality in above result represents the Clausius Theorem and applies only to the ideal or Carnot cycle. Since the integral represents the net change in entropy in one complete cycle. The Clausius Inequality applies to any real engine cycle and implies a negative change in entropy on the cycle. That is, the entropy given to the environment during the cycle is larger than the entropy transferred to the engine by heat from the hot reservoir.

Any real engine cycle will result in more entropy given to the environment as compared to taken from it leading to an overall net increase in entropy.

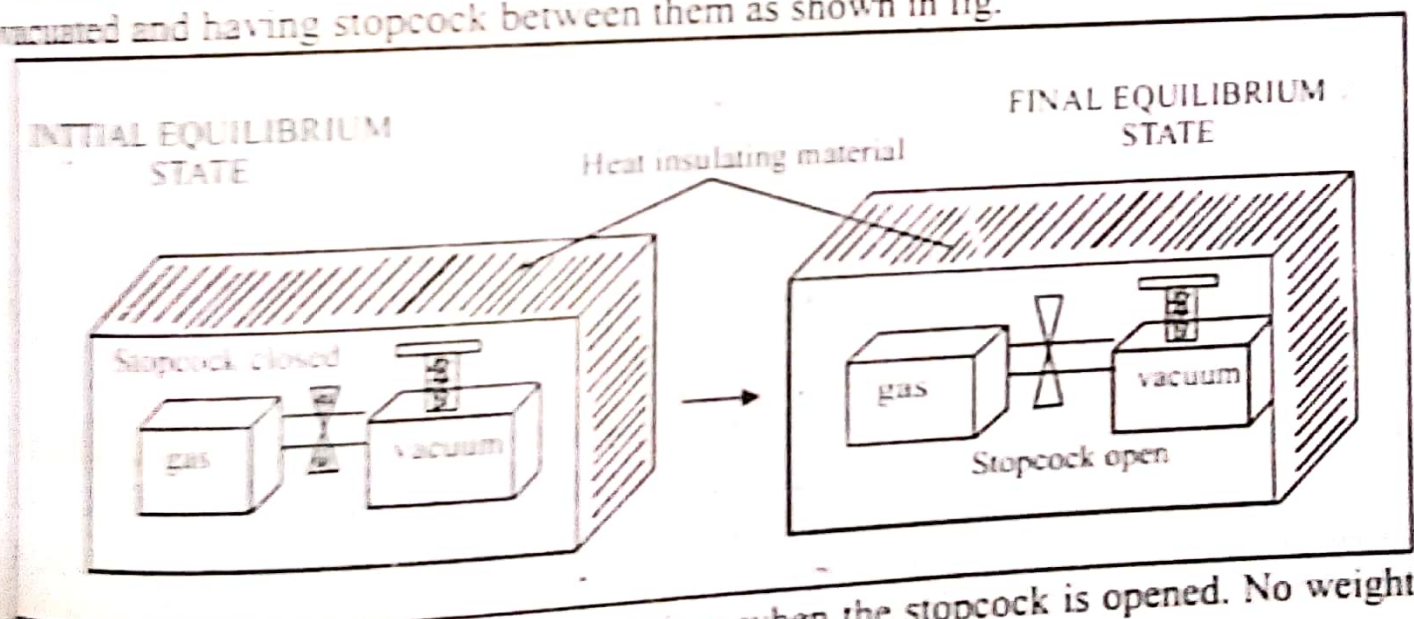
To find entropy change for irreversible process, first connect the path between two equilibrium states with reversible process and then calculate the entropy change by using formula.

$$\Delta S = \int_i^f \frac{dQ}{T}$$

This method of calculation of entropy change for irreversible process becomes more clear with following examples

FREE EXPANSION

The free expansion of a gas is an example of irreversible process. Consider two containers which are insulated such that one has n moles of ideal gas and other is evacuated and having stopcock between them as shown in fig.



The gas rushes into evacuate container when the stopcock is opened. No weight is done and no work is done in this process.

To find the entropy change choose a reversible path in the form of isothermal expansion from initial equilibrium state (P_i, V_i, T) to final equilibrium state (P_f, V_f, T) . Although procedure is different from free expansion but it is used to connect these two states.

The formula of entropy of reversible process is

$$\Delta S = \int_i^f \frac{dQ}{T} \quad \text{--- (1)}$$

For isothermal process $dE_{int} = 0$

The first law of thermodynamics under these conditions becomes

$$dE_{int} = dQ + dW$$

$$0 = dQ + (-PdV)$$

$$dQ = PdV$$

$$dQ = \frac{nRT}{V} dV \quad [PV = nRT]$$

Put value of dQ in eq (1)

$$\Delta S = \int_{V_i}^{V_f} \frac{nR T dV}{V T}$$

$$\Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$

This is the entropy change for irreversible free expansion process. Its value is positive because V_f is greater than V_i .

ISOCHORIC PROCESS

The process in which volume remains constant is called isochoric process. It is irreversible process. The work done at constant volume is zero. The amount of heat transfer at constant volume is $dQ_V = C_V n dT$

The entropy change for this isochoric irreversible process is given as

$$\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{dQ_V}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V n dT}{T} = n C_V \ln\left(\frac{T_f}{T_i}\right)$$

The entropy change is positive because T_f is greater than T_i for isochoric process.

ISOBARIC PROCESS

The process is called isobaric process when gas is heated at constant pressure. It is irreversible process. The work is done because piston moves when heat is transferred in system. The amount of heat transferred is $dQ_P = C_P n dT$

The entropy change for this isobaric irreversible process is given as

$$\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{dQ_P}{T}$$

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P n dT}{T} = n C_P \ln\left(\frac{T_f}{T_i}\right)$$

The entropy change is positive for isobaric process because T_f is greater than T_i .