ENTROPY AND SECOND LAW OF THERMODYNAMICS

The Second Law of Thermodynamics

Two distinct types of processes exist: reversible processes, also known as quasi-static processes, where the system remains in equilibrium with its surroundings throughout the entire procedure. However, reversible processes do not occur spontaneously; they are not natural. These processes do not contribute to the generation of disorder.

On the contrary, most of the processes occurring in our environment are instances of irreversible processes. Irreversible processes are also natural and spontaneous.

The second law of thermodynamics foretells the direction of natural transformations. It achieves this by utilizing a state function, 'S,' referred to as the system's entropy. However, to forecast the direction of natural changes, we also require another quantity, '$S_{surrounding}$,' known as the entropy of the surroundings. Notably, '$S_{surrounding}$' is a path-dependent quantity.

$$dS_{system} = \frac{dq\ rev}{T}$$

$$dS_{surr} = -\frac{dq}{T}$$

Since S_{system} is state function - If a system make transition from state A to state B - by infinite paths in few of them may be reversible and other may be irreversible. ΔS_{AB} will be same irrespective of path (A direct consequence of S_{system} being a state function).

However, if same transition from A to B is done by different irreversible path's, $\Delta S_{surrounding}$ will be different in all processes. However, if transition from A → B take place by many reversible path's, ΔS_{surer} along each path will be same because

$$-\sum_{A \circledast B}^{\text{path 1}} \frac{dq_{rev}}{T} = -\Delta S_{system} = -\sum_{AB}^{\text{path 2}} \frac{dq_{rev}}{T}$$

$$\Rightarrow \quad \underset{A\to B}{\Delta S_{surr}} \text{ (path 1)} = -\underset{A\to B}{\Delta S_{system}} = \underset{A\to B}{\Delta S_{surr}} \text{ (path 2)}$$

	ΔS_{system}	$\Delta S_{surrounding}$
Reversible process	$\int_A^B \frac{dq_{rev}}{T}$	$-\int_A^B \frac{dq_{rev}}{T}$
Irreversible process	$\int_A^B \frac{dq_{rev}}{T}$	$\int_A^B \frac{dq_{irrev}}{T} = -\left(\frac{q_{imev}}{T}\right)_{A\to B}$

Entropy changes of system and surrounding in reversible and irreversible process

Note that $$\Delta S_{sur} = -\frac{q_{actual}}{T}$$

Prediction of Spontaneity of Process:

If total entropy change in a process is positive the process must be spontaneous.

$$\Delta S_{system} + \Delta S_{surrounding} > 0 \text{ for spontaneous change.}$$

The formulation of the second law of thermodynamics emerged during the evolution of cyclic engines, particularly through the examination of the efficiency of steam engines. In 1824, a French engineer named Sadi Carnot highlighted a crucial concept. He emphasized that for a cyclic heat engine to sustain continuous mechanical work production, it must engage in heat exchange with two bodies at distinct temperatures, without a lower-temperature body to release heat to. Without this essential condition, the engine cannot operate continuously.

2^{nd} Law Statement

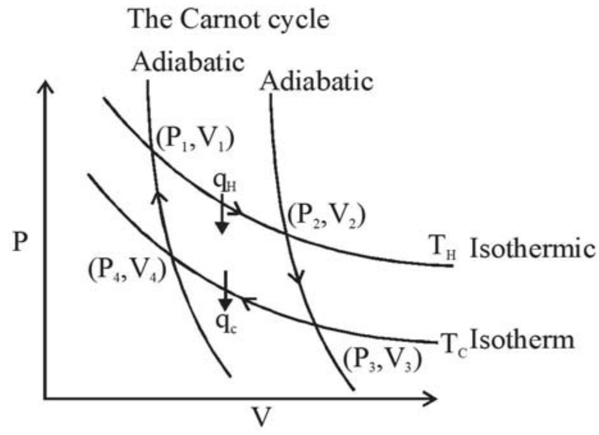
It's unattainable for a system to experience a cyclic process where the primary outcomes are the transfer of heat from a heat reservoir and the execution of an equal amount of work by the system on its surroundings.

The pivotal concept in the statement above revolves around a cyclic engine. In a cyclic engine, if the first phase involves work being performed and heat being absorbed, and the second phase involves expansion, the engine must ultimately return to its initial state. To contract, it necessitates the release of heat to a colder object (a heat sink).

In simpler terms, the energy acquired from a heat source in one cycle cannot be entirely transformed into work.

Efficiency of Carnot Engine.

Carnot conceived an engine that operates through reversible processes. The efficiency of the Carnot engine is at its peak because it operates according to a reversible cycle. The Carnot engine follows a four-step cycle.



Reversible isothermal expansion from P_1, V_1 to P_2, V_2 at temp T_H

Reversible adiabatic expansion from P_2, V_2 at temp T_H to P_3, V_3 at temp T_c

Reversible isothermal compression from P_3, V_3 to P_4, V_4 at temp T_H

Reversible isothermal compression from P_4, V_4 to P_1, V_1 at temp T_c

A Carnot engine releases the least amount of heat to its surroundings during its operation, ensuring that a maximum portion of the heat obtained from the heat source is transformed into work. As a result, the efficiency of a Carnot engine is expressed by the following equation:

$$\eta = \frac{\text{Net work done by engine in one cycle}}{\text{Net heat ab sorbed from source}}$$

$$\eta = \frac{-W_{net}}{q_H}$$

where w_{net} is network done on the engine(system) in one cycle.

It can be easily shown that – $w_{net} = q_H + q_C = w_{net}$

$$q_H + q_C = \frac{V_2}{V_1} + nRT_c \text{ In } \frac{V_2}{V_3} nRT_H \text{ ln also}$$

$$\left\{\begin{matrix} T_C V_4^{\gamma-1} = T_h V_1^{\gamma-1} \\ T_C V_3^{\gamma-1} = T_h V_2^{\gamma-1} \end{matrix}\right\} \Rightarrow \left\{\frac{V_4}{V_3} = \frac{V_1}{V_2}\right\}$$

because of reversible adiabatic process substituting these result's

$$\boxed{\eta = \frac{T_H - T_C}{T_H} = \frac{q_H + q_C}{q_H}}$$

The Efficiency of Carnot engine only depends upon temperature of source and sink and in dependent of choice of working substance.

Sum of the $\frac{q_{rev}}{T}$ in a cyclic process is zero.

For the Carnot cycle ⇒ for car not cycle

$$\frac{q_H}{T_H} + \frac{q_C}{T_C} = 0$$

$$\sum \frac{q_{rev}}{T} = 0$$

The result in previous article is valid for any reversible cyclic process. It can be very easily verified.

Hence $\int \frac{dq_{rev}}{T} = 0 \Rightarrow$ Sum of $\frac{dq_{rev}}{T}$ the over a cyclic path is zero.

now $\int dx = 0$ If $\Rightarrow dX$

is firetail of a state function and X being state function.

$\Rightarrow$ $dS = \frac{dq_{rev}}{T} =$ definite quantity

$\Rightarrow$ S_{system} is a state function.

Entropy Change in Various Thermodynamic Processes

1. Isothermal Reversible Process:

- In an isothermal reversible process where the temperature change (ΔT) is zero, the first law of thermodynamics ($dE = dq + dW$) can be expressed as $dE = 0$ when $\Delta T = 0$.
- Consequently, $dq = -dW$.
- The reversible heat transfer (ΔQ_{rev}) is given by $+2.303\ nRT \log\left(\frac{V_2}{V_1}\right)$.
- The change in entropy (ΔS) in this process is defined as $\Delta Qrev/T$, which further simplifies to $2.303n\ R \log\left(\frac{V_2}{V_1}\right)$ or $2.303n\ R \log\left(\frac{P_1}{P_2}\right)$.
- Importantly, the change in entropy is unaffected by the operating temperature.

2. Adiabatic Reversible Process:

- In an adiabatic reversible process, $\Delta S = \frac{q_{rev}}{T} = \Delta E + \frac{P\Delta V}{T} = 0$.
- For adiabatic processes, where $q_{rev} = 0$, the expression becomes $\Delta E = -P\Delta V$.
- However, in irreversible processes, ΔS is not equal to zero.

3. Isobaric Process (ΔP=0):

- For an isobaric process with constant pressure ($\Delta P = 0$), the heat transfer (dqP) is represented as $nCpdT$.
- The change in entropy (ΔS) can be determined through the integral

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{dq_p}{T}$$

- This integration leads to $S_2 - S_1 = nCp \ln \frac{T_2}{T_1}$.

- Alternatively, ΔS is expressed as 12.303nCp log $\frac{T_2}{T_1}$.

4. **Isochoric Process:**

- In an isochoric process, where the volume remains constant ($\Delta V = 0$), the heat transfer at constant volume (dq_v) is given by nC_vdT.
- The entropy change (ΔS) for such a process can be determined using the integral.

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{dq_v}{T} = \int_{T_1}^{T_2} \frac{nC_vdT}{T}$$

- This integration leads to $S_2 - S_1 = nCv \ln \frac{T_2}{T_1}$.
- Alternatively, ΔS is expressed as $2.303nC_v \log \frac{T_2}{T_1}$.
- This isochoric process is characterized by a constant volume, and the associated heat transfer and entropy changes are defined by the specific heat at constant volume (C_v). The expressions derived above provide a thermodynamic understanding of the behavior of a system undergoing an isochoric process.

Entropy Change in Phase Transformation:

During phase transformations, the change in entropy (ΔS) can be determined using the following expressions:

1. **Solid to Liquid Transformation:**

- For the process of a solid transforming into a liquid, the entropy change (ΔS_f) is given by the equation. $\Delta S_f = \frac{\Delta H_f}{T_f}$.
- Here, ΔH_f represents the enthalpy change for the solid-to-liquid transformation, and T_f is the final temperature.

2. **Liquid to Vapor Transformation:**

- When a liquid undergoes a transformation into a vapor, the entropy change (ΔS_v) is determined by.

$$\Delta Sv = \frac{\Delta H_v}{Tb}.$$

- In this context, ΔHv signifies the enthalpy change for the liquid-to-vapor transformation, and T_b is the boiling temperature.

  These equations provide a thermodynamic understanding of the entropy changes associated with the phase transformations from solid to liquid and from liquid to vapor.