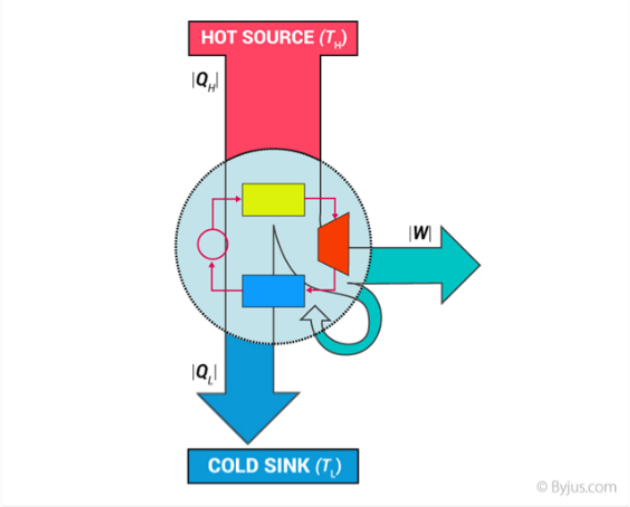
Thermodynamics

Introduction:

William Thomson coined the term thermodynamics in 1749. It is derived from two Greek words "thermes" meaning heat, and "dynamikos" meaning powerful. When we say the word dynamic we think of motion or movement and energy. Thus, the term thermodynamics means heat movement or heat flow.



What is Thermodynamics?

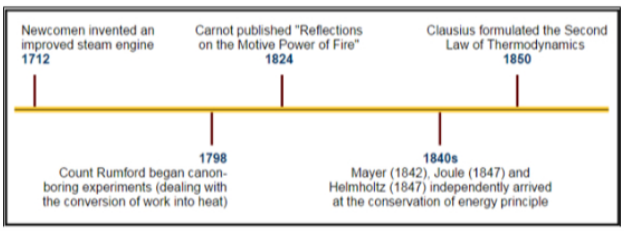
Thermodynamics is the branch of physics which is concerned with the relationship between other forms of energy and heat. To be specific, it explains how the thermal energy is converted to or from other forms of energy and how matter is affected by this process.

What is Thermal Energy?

Thermal energy is the energy that comes from heat. This heat is generated by the movement of tiny particles within an object. The faster these particles move, the more heat is generated.

Thermodynamics Timeline:

Thermodynamics has many sections under it and is considered as a broad subject because it deals with topics that exist all around us and thus classification becomes necessary.



- **Classical Thermodynamics** – In this section, the behavior of matter is analyzed with a macroscopic approach. Units such as temperature and pressure are taken into consideration which helps the individuals to calculate other properties and to predict the characteristics of the matter that is undergoing the process.
- **Statistical Thermodynamics** – In this section, every molecule is under the spotlight i.e. the properties of each and every molecule and ways in which they interact are taken into consideration to characterize the behavior of a group of molecules.
- **Pure Component Thermodynamics** – As the name itself states, this section tries to describe the behavior of a system that has an unadulterated or pure constituent.
- **Solution Thermodynamics** – This section attempts to describe the behavior of a system that contains more than one chemical in the mixture.

Here, we will focus on the Classical part of the thermodynamics in our curriculum.

Laws of Thermodynamics:

Zeroth Law:

The Zeroth Law is the basis for the measurement of temperature. It states that "two bodies which are in thermal equilibrium with a third body are in thermal equilibrium with each other."

First Law:

The first law of thermodynamics which is also known as the conservation of energy principle states that energy can neither be created nor destroyed, but it can be changed from one form to another.

Second Law:

The second law of thermodynamics states that Energy in the form of heat only flows from regions of higher temperature to that of lower temperature. Many individuals take this statement lightly and for granted, but it has an extensive impact and consequence. This is why it costs money to run an air conditioner.

Third Law:

The Third Law states, "The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K)." Entropy is sometimes called "waste energy," i.e., energy that is unable to do work, and since there is no heat energy whatsoever at absolute zero, there can be no waste energy.

What is Enthalpy?

Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy equals to the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure.

Mathematically, the enthalpy, H, equals to the sum of the internal energy, E, and the product of the pressure, P, and volume, V, of the system.

H = E + PV

What is Entropy?

Entropy is a thermodynamic quantity whose value depends on the physical state or condition of a system. In other words, it is a thermodynamic function used to measure the randomness or disorder of a system. For example, the entropy of a solid, where the particles are not free to move, is less than the entropy of a gas, where the particles will fill the container.

Different Measures of Energy:

Internal Energy:$U = \int TdS - PdV + \sum_i \mu_i dN_i$

Helmholtz free energy: F = U – TS

Enthalpy: H = U + PV

Gibbs Free Energy: G = U + PV – TS

Solved Examples:

Example 1: Calculate ΔG

at 290 K for the following reaction:

$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$

Given

ΔH = -120kJ

$\Delta S = -150JK^{-1}$

Solution: To make the unit of ΔS same as ΔH, we have to convert the unit of ΔS as follows,

Therefore, ΔG is -77kJ.