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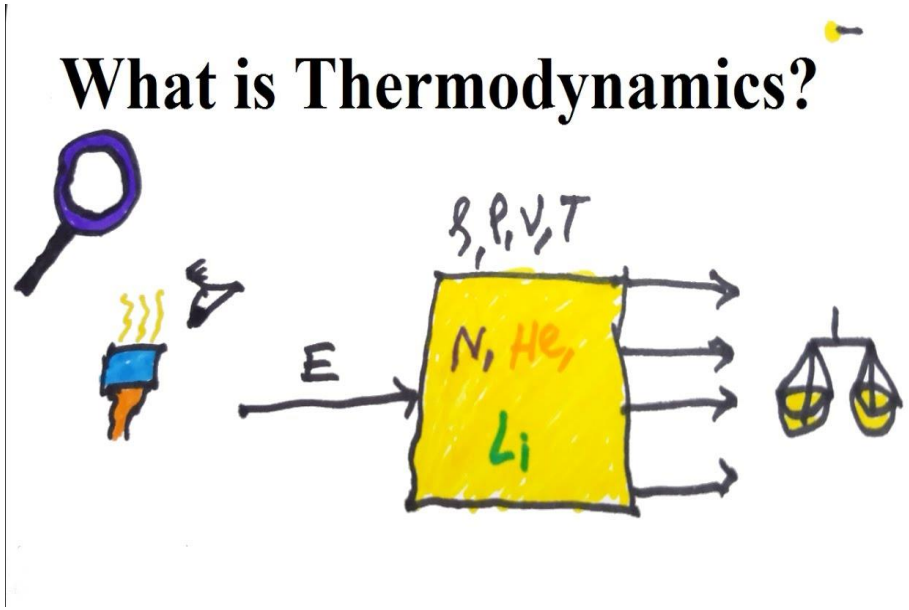
UNIT – 1 ENTROPY AND SECOND LAW OF THERMODYNAMICS

DEFINITION OF THERMODYNAMICS

- Thermodynamics is a Greek word which means flow of heat in physical and chemical reactions
- Thermodynamics is a branch of science which deals with study of different forms of energy and their interconversions
- It deals with energy changes in physical and chemical processes



FIRST LAW OF THERMODYNAMICS

- Energy of Universe is constant
- It law stated as;

> Energy can neither be created nor be destroyed,
> but it can only be converted from one form to another.

- Mathematically, it can be expressed as :

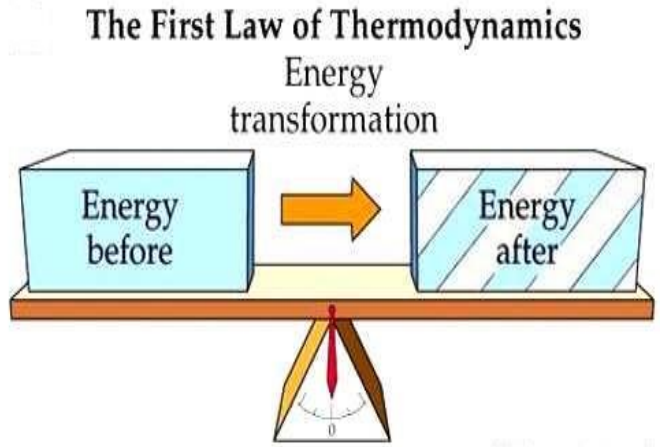
$$\Delta E = q - W$$

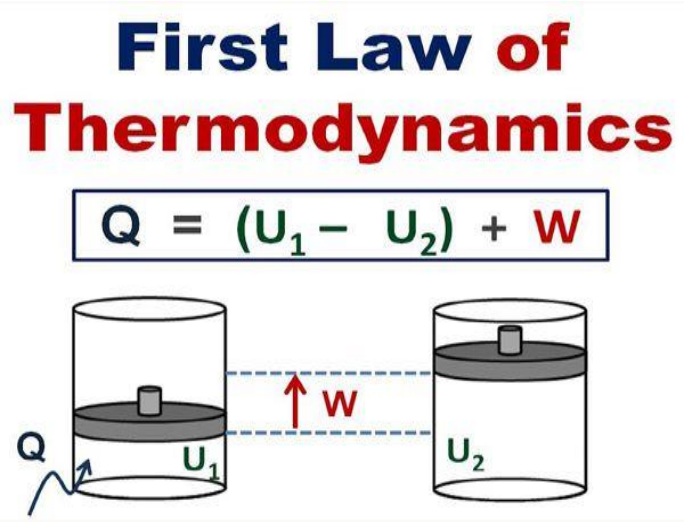
- Where, ΔE = Internal energy

  q = heat

  W = work done

- If the system changed its state without doing any work than W=0 and $\Delta E = q$. This means that absorbed or lost energy is stored as internal energy.
- If a system works without any transfer of energy then q=0, so, $\Delta E = W$. In general, $\Delta E = q - W$.



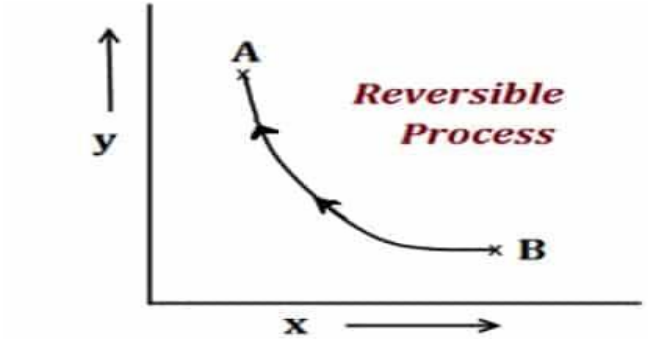


LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

- First law does not explain why chemical reactions do not proceed to completion and it also does not answer why spontaneous or natural processes are uni-directional. It also does not explain anything about the source of heat and direction of flow of heat.
- First law states that all forms of energy change into one another but does not define the extent of convertibility of one form of energy into another.
- First law cannot explain that while work can be completely converted into heat, heat cannot be completely converted into work without leaving permanent changes in the system or surroundings.
- First law cannot explain as to why all naturally occurring processes always tends to change spontaneously in a direction which leads to equilibrium.
- First law does not contradict the existence of heat engine of 100% efficiency or self- acting machines. But on the basis of human experiences we can say that such heat engines or machines are not attainable in actual practice.

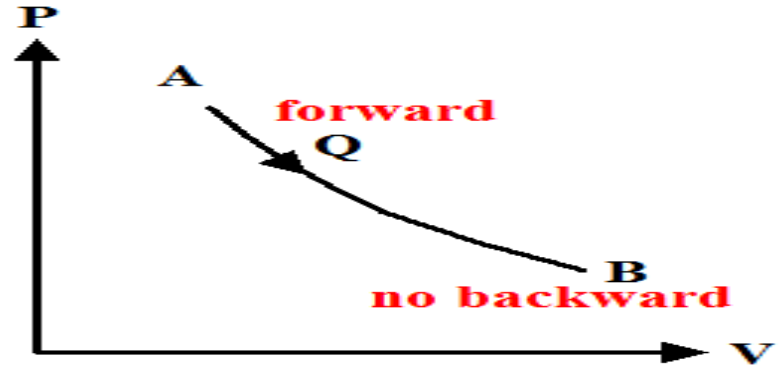
REVERSIBLE PROCESS

- A reversible process is a process that can be reversed in order to obtain the initial state of a system
- Can be reversed
- A reversible process can be made to proceed in forward or backward direction
- Work done in a reversible process is greater than the corresponding work done in irreversible process
- e.g. Working of a Galvanic cell which is made up of a zinc and a copper electrode



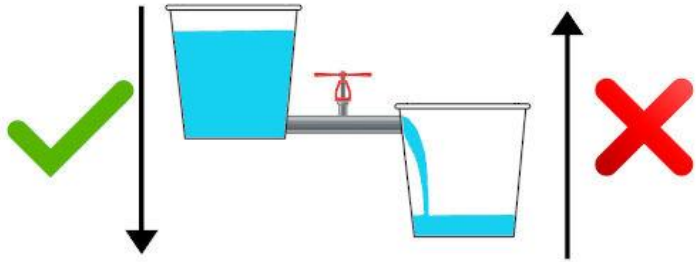
IRREVERSIBLE PROCESS

- An irreversible process is a thermodynamic process that cannot be reversed in order to obtain the initial state of a system
- Cannot be reversed
- Irreversible process can take place in one direction only
- Work done in a irreversible process is always lower than the same kind of work done in a reversible process
- e.g. Most of spontaneous processes are irreversible in nature like water flowing down a hill

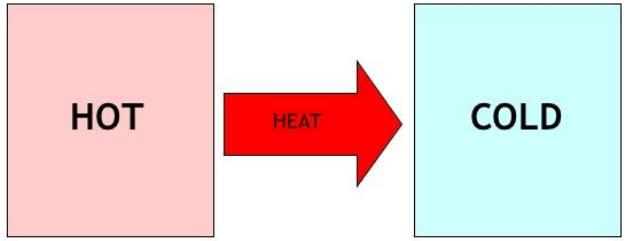


SPONTANEOUS PROCESS

- Those processes which actually occur in nature are known as natural or spontaneous processes.
- In such a process, a change takes place in a system without the aid of any external agency.
- For example;
  i) Liquid flows from a higher to a lower level
  ii) Gas spontaneously moves from a higher to lower pressure
  iii) Heat flows from a hotter body to a colder body
  iv) Dissolution of salt in water
  v) Evaporation of water in open vessel
- All this spontaneous reactions take place in one direction and are irreversible.



Water flows spontaneously from higher level to lower level



- Heat always moves from HOT to COLD.
  hot→cold

- Every system moves towards the state of equilibrium.
- Therefore, we may state that; **all spontaneous processes are irreversible or all spontaneous processes tend to a state of equilibrium.**

CRITERIA FOR SPONTANEOUS CHANGES

ΔG_{sys} < 0 (negative) , the process is spontaneous.

ΔG_{sys}= 0 (zero) , the process is at equilibrium.

ΔG_{sys}> 0 (positive) , the process is non-spontaneous.

CYCLIC PROCESS

- When a system completes a series of changes and ultimately returns to its original state, it is known to have completed one cycle. The entire process of changes is known as a cyclic process.
- Since the internal energy of a system depends only upon its state, it follows that in a cyclic process, the net change of internal energy is zero, i.e.,

According to First Law of Thermodynamics; $\Delta E = 0 = q - W$

$q = W$

- If a series of changes are conducted at a constant temperature, the cycle is known as an **isothermal cycle.**
- If the changes are carried out reversibly, then the cycle is known as a **reversible cycle.**
- The most well known cyclic process is **Carnot's Cycle.**

REFERENCE :

- Advance Physical Chemistry by Gurdeep Raj
- Textbook of Physical Chemistry by A.S. Negi
- Physical Chemistry by G.M. Barrow


Thank you