Lecture 1 “Basic principles and formulations of thermodynamics”

Goal of the lecture: To study the fundamental laws and principles of thermodynamics, understand the meaning of basic terms such as system, surroundings, energy, work, and heat, and describe the main formulations of thermodynamic laws.

Thermodynamics is the branch of physics that studies the relationships between heat, work, temperature, and energy. It focuses on the conversion of energy from one form to another and its relation to the properties of matter, governed by four fundamental laws. The main concepts in thermodynamics include energy, heat, work, temperature, and entropy, which represents the degree of disorder in a system. This field has wide applications across science and engineering.

Heat is a form of energy that is transferred between objects of different temperatures, while work is the energy transferred when a force causes an object to move. Temperature measures how hot or cold something is, and energy is defined as the capacity to do work, which can exist in various forms such as kinetic, potential, chemical, or thermal energy. Entropy is a measure of the disorder or randomness in a system, reflecting the natural tendency of processes to move toward equilibrium.

The **Laws of Thermodynamics** describe fundamental principles governing energy and heat transfer. The **Zeroth Law** defines thermal equilibrium and temperature, stating that if two systems are each in thermal equilibrium with a third system, they are also in equilibrium with each other. The **First Law** asserts that energy cannot be created or destroyed, only transformed from one form to another, meaning the total energy of a system remains constant. The **Second Law** explains that the total entropy of an isolated system can only increase over time, indicating that natural processes move toward greater disorder. The **Third Law** states that as the temperature of a system approaches absolute zero, its entropy approaches a constant value.

Thermodynamics has many practical applications, such as improving the efficiency of engines, analyzing and designing power plants, refrigerators, and air conditioners, studying chemical reactions and biological processes, and predicting the behavior of physical systems, including weather patterns.

Thermodynamics is based on several key concepts:

1. **System and surroundings**

    - A system is the part of the universe chosen for study.
    - The surroundings include everything outside the system.

- The boundary separates the system from its surroundings.

Systems are classified as:

- **Open system:** exchanges both matter and energy (e.g., boiling water).
- **Closed system:** exchanges only energy (e.g., a sealed container of steam).
- **Isolated system:** exchanges neither matter nor energy (e.g., thermos bottle).

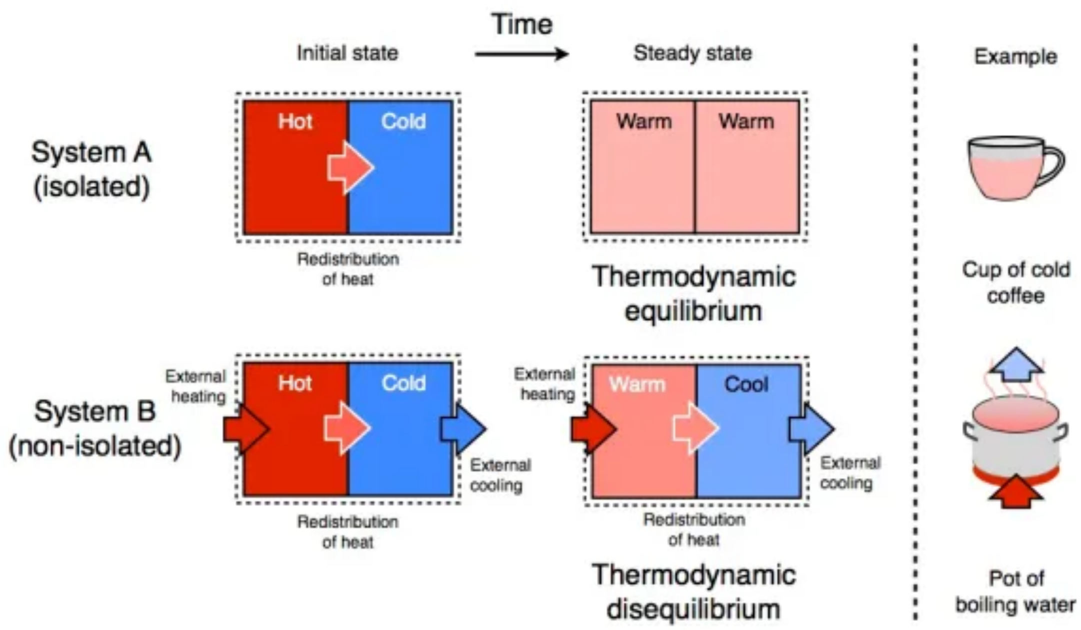

Figure 1. Schematic representation of thermodynamic systems (isolated – a), (non-isolated – b)

Main principles and formulations of thermodynamics

1. The Zeroth Law of Thermodynamics states that if two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other (Fig.2) . This principle establishes the concept of temperature and allows for the use of a single temperature scale to measure the thermal state of all systems. A practical example is using a thermometer: if a thermometer is in thermal equilibrium with two different objects, those two objects must also be in thermal equilibrium with each other. If two systems (A and B) are each in thermal equilibrium with a third system (C), then they are also in equilibrium with each other.
This law defines the concept of temperature.

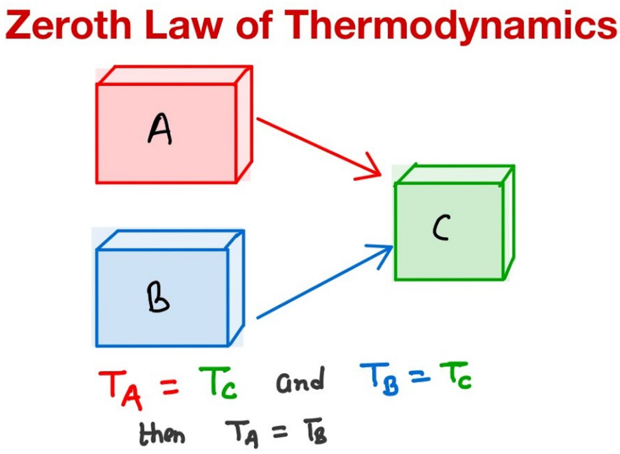

Figure – 2. Visual representation of the zero law of Thermodynamics.

2. First Law of Thermodynamics (Law of Energy Conservation): Energy cannot be created or destroyed — only transformed, only converted from one form to another.

$$\Delta U = Q - W \quad (1)$$

In a thermodynamic system, a change in internal energy (ΔU) is equal to the heat added to the system (Q) minus the work done by the system (W);

- $Q > 0$: heat absorbed by the system
- $W > 0$: work done by the system

Key aspects of the First Law of Thermodynamics

- **Energy conservation:** The total energy in an isolated system remains constant over time. It can change forms (e.g., from heat to work), but the total amount does not change.
- **Internal energy (ΔU):** This is the total energy contained within a system, including the kinetic and potential energy of its molecules. A change in internal energy is a result of heat and work being exchanged with the surroundings.
- **Heat (Q):** The transfer of thermal energy between systems due to a temperature difference.
- **Work (W):** Energy transferred to or from a system by a force acting over a distance.

3. Second Law of Thermodynamics

The second law of thermodynamics states that the total entropy (disorder) of an isolated system can only increase over time. A simpler way to understand this is that heat naturally flows from a hotter object to a colder one, but not the reverse, without external energy input. This law explains why systems tend toward disorder, like a room becoming messy over time, and why no energy conversion process can be 100% efficient, as some energy is always lost as waste heat.

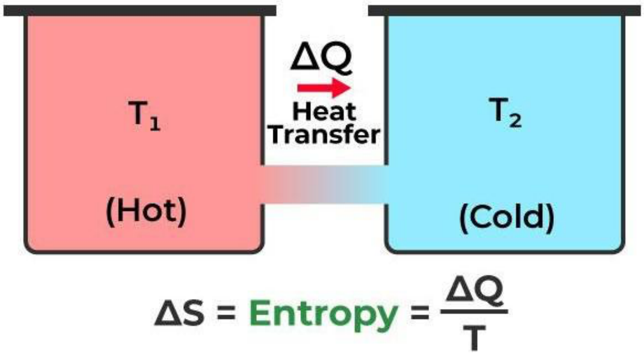

Figure – 3. Visual representation of the second law of Thermodynamics.

Natural processes occur in a direction that increases the total entropy (S) of the universe.
Entropy measures the degree of disorder or randomness.

$$\Delta Suniverse = \Delta Ssystem + \Delta Ssurroundings > 0$$

This law explains why heat flows spontaneously from hot to cold and not the other way around.

4. Third Law of Thermodynamics

The **Third Law of Thermodynamics** states that as the temperature of a perfect crystal approaches absolute zero (0 K), its entropy approaches zero. This is known as the Nernst heat theorem. At absolute zero, a perfect crystal has only one possible microstate, where every atom occupies its lowest-energy position in the crystal lattice. Since entropy is defined as (S = k \ln W), and when the number of microstates (W = 1), the entropy becomes zero ((\ln 1 = 0)).

The main consequence of this law is known as the **unattainability principle**, which states that it is impossible to reach absolute zero temperature in a finite number of steps. Although scientists can achieve temperatures extremely close to 0 K, the law dictates that absolute zero cannot be physically attained. As the temperature decreases, cooling processes become less efficient, and the amount of energy required to remove the remaining heat tends toward infinity.

Table 1 – Summary of the Laws of Thermodynamics

Law	Main statement	Key concept
Zero	Defines temperature and thermal equilibrium	Temperature
First	Energy is conversed	Internal energy
Second	Entropy always increases	Direction of processes
Third	Entropy -> 0 as T-> ; Absolute zero unattainable.	Absolute zero

The laws of thermodynamics govern energy and its transfer: the First Law states energy is conserved; the Second Law states that entropy (disorder) in an isolated system always increases; the Third Law states a system's entropy approaches a constant, minimum value at absolute zero temperature; and the Zeroth Law defines thermal equilibrium, where two systems in equilibrium with a third are in equilibrium with each other.

Questions for self-control:

1. What is a thermodynamic system and how is it classified?
2. State the Zeroth Law of Thermodynamics.
3. Write the mathematical expression of the First Law and explain each term.
4. What does entropy represent?
5. Explain the meaning of the unattainability principle in the Third Law.

Literature:

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