Fundamental Laws of Thermodynamics

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Contents

List of Figures

1 Introduction

In the realm of chemistry, thermodynamics plays a pivotal role in understanding the behavior of chemical systems and reactions.
It encompasses a set of fundamental laws that govern the behavior of energy and matter.
In this report, we will explore the foundational principles of thermodynamics, including the laws of thermodynamics, their significance, and their applications in various fields of science and engineering.
The fundamental laws of thermodynamics provide a framework for analyzing energy transformations and the spontaneity of chemical processes.
These laws govern the flow of heat, energy, and matter in chemical systems, shaping the directionality and feasibility of reactions.
The objective of this report is to provide an overview of the fundamental laws of thermodynamics and their implications in practical scenarios.

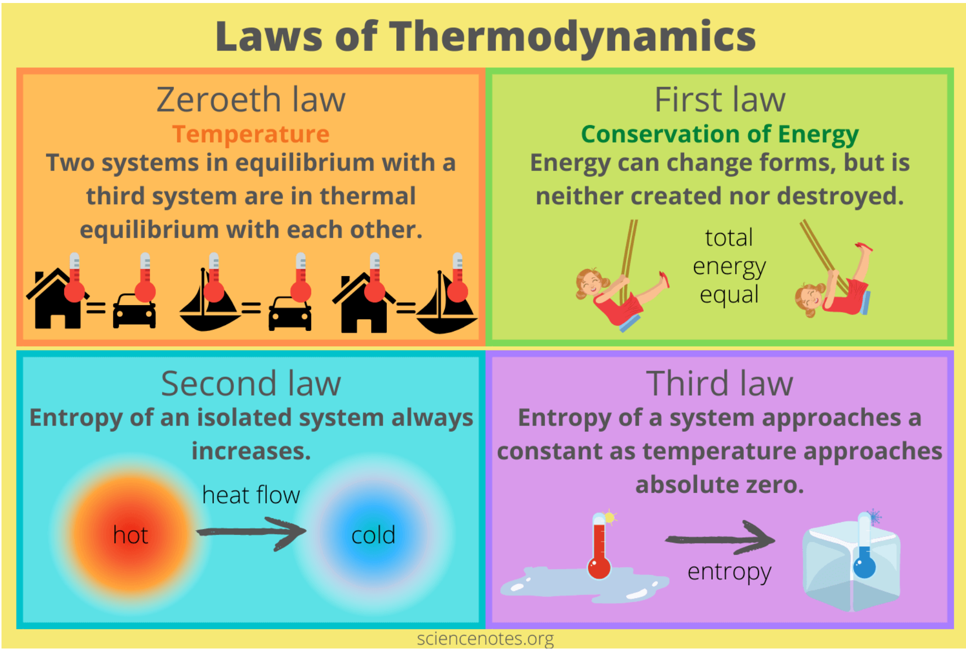

Figure 1: Laws of Thermodynamics

2 Zeroth Law of Thermodynamics

2.1 Definition

The Zeroth Law of Thermodynamics states that if two systems are in thermal equilibrium with a third system, then they are in thermal equilibrium with each other. In simpler terms, if objects A and C are at the same temperature, and objects B and C are also at the same temperature, then objects A and B must be at the same temperature, even if they are not in direct contact. This law implies that temperature is a measurable quantity that can be used to describe the thermal state of a system.

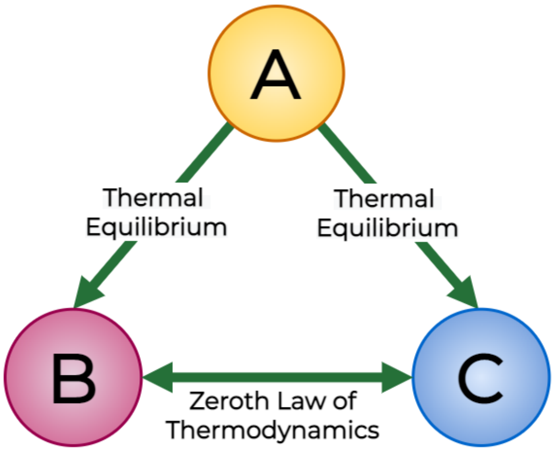

Figure 2: Zeroth Law of Thermodynamics

2.2 Explanation

This law introduces the concept of temperature as a measure of the thermal state of a system. If two systems have the same temperature, there is no net heat flow between them when they are in thermal contact. Thermal equilibrium is a state where there is no overall transfer of heat between two systems. The Zeroth Law is essential because it provides a foundation for defining and measuring temperature. It allows us to establish temperature scales and compare temperatures between different systems. For example, thermometers are devices based on the principles of the Zeroth Law, allowing us to measure temperature accurately.

2.3 Application

- The zeroth law of thermodynamics is important for the mathematical formulation of thermodynamics or, more precisely, to state the mathematical definition of temperature.
- This law is mostly used to compare the temperatures of different objects.
- Another example of the Zeroth law of thermodynamics is when you have two glasses of water. One glass contains hot water, and the other contains cold water.
- Now, if we leave them on the table for a few hours, they will attain thermal equilibrium with the temperature of the room.

3 First Law of Thermodynamics

3.1 Definition

The first law of thermodynamics, also known as the law of energy conservation, states that the total energy of an isolated system remains constant; energy can neither be created nor destroyed, only transformed from one form to another.

3.2 Equation

The mathematical expression of the first law of thermodynamics is:

$$\Delta U = Q - W$$

where
ΔU is the change in internal energy,
Q is the heat added to the system, and
W is the work done by the system.
Consider a closed system undergoing a thermodynamic process with no work done: $\Delta U = Q$
$dU = \delta Q$
$dU = T\,dS$ (from the definition of heat)
Now, let's consider a closed system undergoing a process where work is done: $\Delta U = Q - W$
$dU = \delta Q - \delta W$
$dU = T\,dS - P\,dV$ (from the definition of work)
For an open system, the first law of thermodynamics can be expressed as: $\Delta H = Q + W$
$dH = \delta Q + \delta W$
$dH = T\,dS + V\,dP$ (from enthalpy definition)

3.3 Explanation

The first law of thermodynamics is a statement of the principle of conservation of energy, which asserts that energy cannot be created or destroyed, only converted from one form to another. In the context of thermodynamics, this law implies that any heat added to a system must either increase its internal energy or perform work on the surroundings, and any work done by the system must either decrease its internal energy or transfer energy to the surroundings as heat.

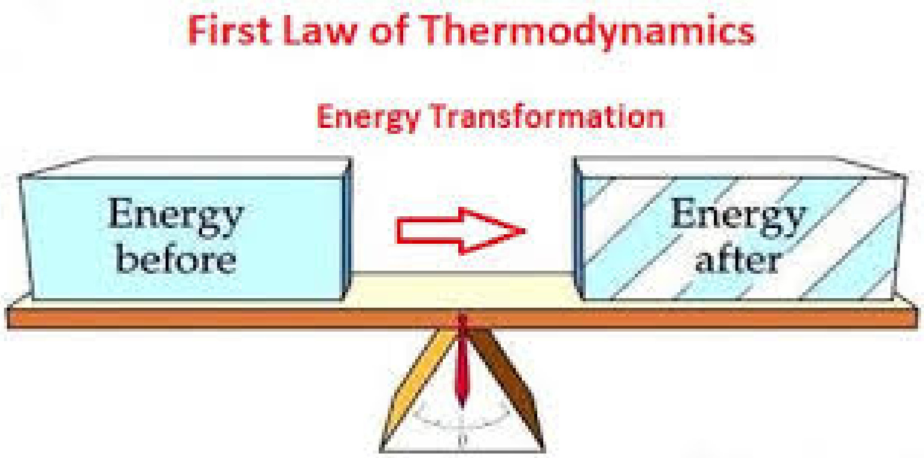

Figure 3: First Law of Thermodynamics

3.4 Application

- **Energy production and utilization:** The first law of thermodynamics is used to predict the efficiency of energy conversion processes, such as converting heat to mechanical work in a steam turbine or converting chemical energy to electrical energy in a battery.
- **Biological systems:** The first law of thermodynamics is used to understand the behavior of biological systems, such as the metabolism of living organisms. It is also used to design devices and technologies used in medicine, such as pacemakers and artificial organs.
- **Chemical reactions:** The first law of thermodynamics is used to understand the behavior of chemical reactions and predict the energy changes that will occur during a chemical reaction.

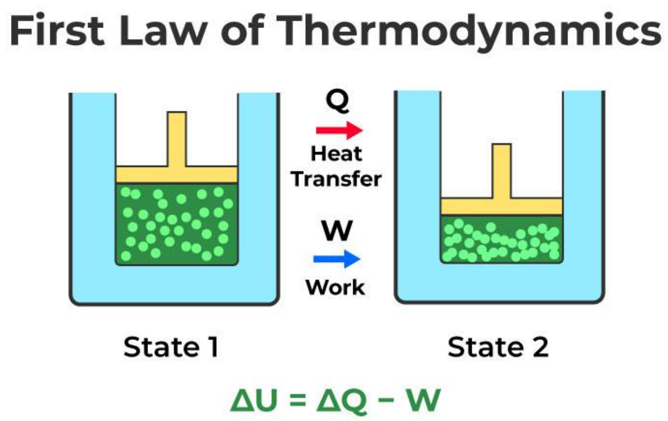

Figure 4: First Law of Thermodynamics

4 Second Law of Thermodynamics

4.1 Definition

The second law of thermodynamics states that in any cyclic process, the entropy of an isolated system tends to increase over time. This law implies that processes occur spontaneously in the direction of increasing entropy, and it provides a criterion for determining the feasibility of processes and the direction of heat transfer. In simple terms, the second law asserts that natural processes tend to move towards a state of greater disorder or randomness, and it places limitations on the efficiency of heat engines and other energy conversion devices.

4.2 Equation

The mathematical expression of the second law of thermodynamics is given by:

$$\Delta S \geq 0 \tag{1}$$

where ΔS is the change in entropy of the system.
The second law of thermodynamics can be derived from the Clausius inequality, which states that for any reversible process:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{2}$$

where δQ is the infinitesimal heat transfer and T is the temperature.

4.3 Explanation

The second law of thermodynamics implies that heat flows spontaneously from regions of higher temperature to regions of lower temperature, and it is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.
The second law of thermodynamics can be stated in various forms, but one common formulation is Kelvin-Planck statement:
Kelvin-Planck Statement: It is impossible to construct a device that operates in a cycle and produces no effect other than the extraction of heat from a single thermal reservoir and the performance of an equivalent amount of work.

Mathematically, this can be expressed as:

$$\oint \frac{\delta Q}{T} \leq 0$$

where δQ is the heat transfer and T is the temperature of the reservoir.
Another important statement of the second law is the Clausius statement:
Clausius Statement: It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a colder body to a hotter body.

Mathematically, this can be expressed as:

$$\oint \frac{\delta Q}{T} \geq 0$$

These statements are equivalent and provide the foundation for understanding the direction of heat transfer and the limitations of heat engines.

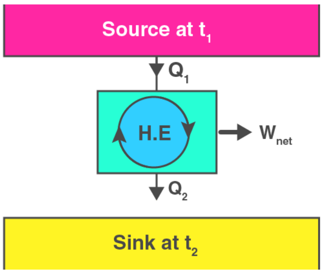

Figure 5: Kelvin-Planc's Statement

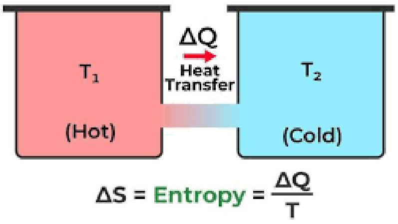

Figure 6: Clausius Statement

4.4 Application

- According to the law, heat always flows from a body at a higher temperature to a body at the lower temperature. This law is applicable to all types of heat engine cycles including Otto, Diesel, etc. for all types of working fluids used in the engines.
- Another application of this law is refrigerators and heat pumps based on the Reversed Carnot Cycle. If you want to move heat from a body at a lower temperature to a body at a higher temperature, then you have to supply external work.
- **Sweating in a crowded room:**In a crowded room, everybody (every person) starts sweating. The body starts cooling down by transferring the body heat to the sweat. Sweat evaporates adding heat to the room. Again, this happens due to the first and second law of thermodynamics in action.

5 Third Law of Thermodynamics

5.1 Definition

The third law of thermodynamics states that as the temperature of a system approaches absolute zero, the entropy of the system approaches a minimum value. The third law of thermodynamics states that the entropy of a perfect crystal at absolute zero temperature is exactly equal to zero. This law implies that it is impossible to reach absolute zero temperature through any finite series of processes. The third law has profound implications for the behavior of matter at extremely low temperatures and is often used to understand phenomena such as superconductivity and superfluidity.

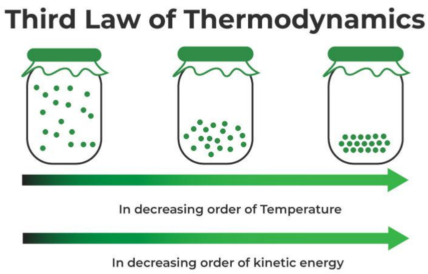

Figure 7: Third Law of Thermodynamics

5.2 Equation

The mathematical expression of the third law of thermodynamics is often stated as:

$$\lim_{T \to 0} S = 0 \tag{3}$$

where S is the entropy of the system and T is the temperature. The third law of thermodynamics can be derived from statistical mechanics, considering the behavior of the system at absolute zero temperature. It states that there is only one microstate available to the system, leading to zero entropy.

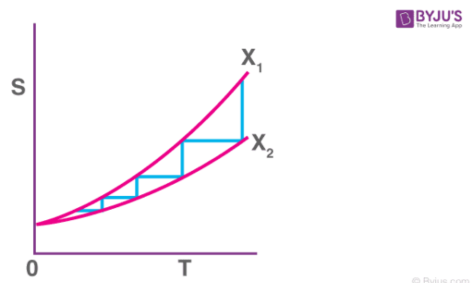

Figure 8: Third Law of Thermodynamics

5.3 Explanation

- A perfectly ordered system with only a single microstate available to it would have an entropy of zero.
- The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion

- S-$S_0 = K_B ln\Omega$

- S is the entropy of the system.

- S_0 *is the initial entropy*
- K_B *denotes the Boltzmann constant*
- Ω *refers to the total number of microstates that are consistent with the system's macroscopic configuration*

  - In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved

5.4 Application

- Absolute Zero: Scientists use the Third Law to study materials at extremely low temperatures, close to absolute zero. For example, in cryogenics research, where temperatures near absolute zero are used to study the behavior of materials, such as superconductors and quantum fluids.
- Preservation of Food: Freezing food items preserves them by slowing down the rate of chemical reactions and microbial growth. While not reaching absolute zero, the principles of the Third Law are at play as the temperature decreases, reducing the entropy and slowing down molecular motion, thereby extending the shelf life of the food.

6 Conclusion

In conclusion, the fundamental laws of thermodynamics form the cornerstone of our understanding of energy and its transformations in nature. The zeroth law establishes the concept of temperature and the thermal equilibrium between systems. The first law, also known as the law of conservation of energy, asserts that energy cannot be created or destroyed, only converted from one form to another. The second law introduces the concept of entropy, defining the direction of spontaneous processes and establishing the irreversibility of natural processes. Lastly, the third law provides insights into the behavior of matter at absolute zero temperature, offering fundamental constraints on the achievability of such conditions. Together, these laws provide a comprehensive framework for analyzing and predicting the behavior of physical systems, from the microscopic scale of molecules to the macroscopic scale of the universe.

7 References

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