Thermodynamics

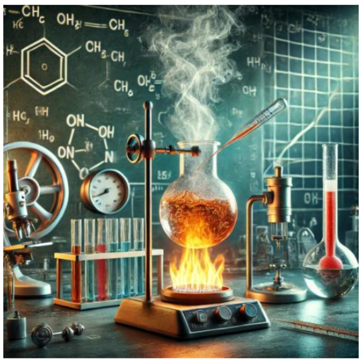

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Table of contents

I CHAPTER I: Generalities of thermodynamics

1. Specific Objectives For Chapter I

Fundamental

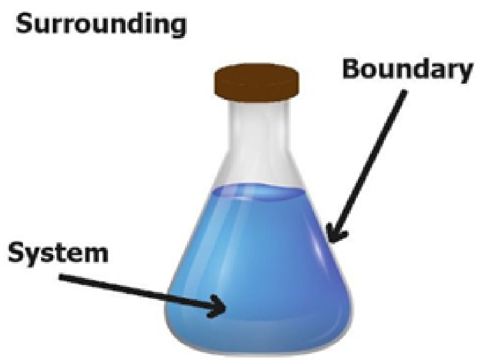
- Recall and define the basic principles and scope of thermodynamics.
- Identify and classify various forms of energy and illustrate how energy transforms during thermodynamic processes.
- Explain the mechanisms of energy exchange, including the concepts of heat and work.
- Analyze thermodynamic processes to determine system behavior under different equilibrium and non-equilibrium conditions.

2. Definitions in thermodynamics

2.1. System and Surroundings

Definition

Thermodynamics focuses on the study of ***macroscopic systems***, which may interact with other systems and their ***surroundings***. The surroundings also referred to as the environment, reservoir, or bath. Typically have an extremely large scale compared to the system. While a system may experience changes in its state due to this interaction, the state of the bath remains essentially unaffected due to its significantly larger size.



System illustration

Example

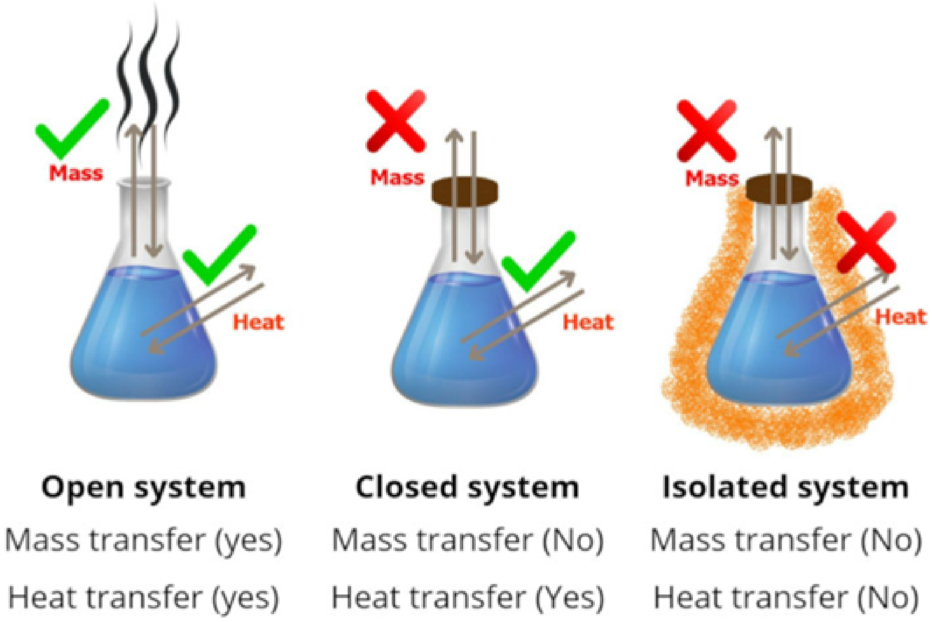
For example, a thermometer* (the system) measuring a body's temperature interacts with the body, which acts as ***the thermal reservoir***.

2.2. Types of Systems: Open, Closed, Adiabatic, and Isolated

Definition

Thermodynamic systems are categorized based on their ability to exchange matter and energy:

1. ***Open systems*** allow both matter and energy to pass between the system and its surroundings.
2. ***Closed systems*** can exchange energy but not mass with their environment. Heat transfer and work can occur, but no material crosses the boundary.
3. ***Adiabatic systems*** do not exchange heat with the environment due to thermal isolation. However, work can still be done on or by the system. Rapid processes are typically adiabatic because they occur too quickly for significant heat transfer to take place.
4. ***Isolated systems*** are completely insulated, allowing no exchange of either mass or energy with the surroundings.



THERMODYNAMIC SYSTEMS

2.3. Extensive, Intensive, and Specific Properties

Definition

Physical properties of macroscopic systems are classified as either intensive or extensive:

- ***Intensive properties*** (such as pressure and temperature) are independent of the system size.
- ***Extensive properties*** (like mass, volume, and energy) scale with the size of the system.

To clarify, if a system is divided into two equal parts, intensive properties remain unchanged in each part, while extensive properties are halved.

Additionally, specific properties are derived by dividing one extensive quantity by another, rendering them independent of system size. A common example is density

2.4. Quasi-Static, Reversible, and Irreversible Processes

Definition

Thermodynamics typically deals with systems in equilibrium states that do not change over time under steady conditions. However, real processes like heating or compression occur over time. This apparent contradiction is resolved by introducing

quasi-static processes*, which evolve so gradually that the system stays nearly in equilibrium throughout. The system's macroscopic variables such as pressure and volume can then be plotted continuously in what's known as state space or configuration space.

If external conditions change too quickly, the system may deviate from equilibrium, making variables like pressure and temperature undefined. For example, a rapid gas compression can generate shock waves that cause non-uniformities, resulting in a process that cannot be represented as a continuous line between equilibrium states.

Reversible processes are idealized, quasi-static paths that can proceed in either direction without any net change in the system or surroundings. Most quasi-static processes are reversible, but some exceptions exist, like the slow stirring of a fluid, which produces irreversible internal heating. Still, if the energy added by stirring is removed via thermal exchange with a bath, the system can be brought back along the same path in reverse, effectively inverting the process in the configurational space.

2.5. State of Matter

Definition

Matter is something that has mass and volume (takes up space). Matter can be found in several phases or states. The three most common phases of matter on Earth are solids, liquids and gases. Less commonly, we can also find matter as a plasma or Bose-Einstein (BE) condensate.

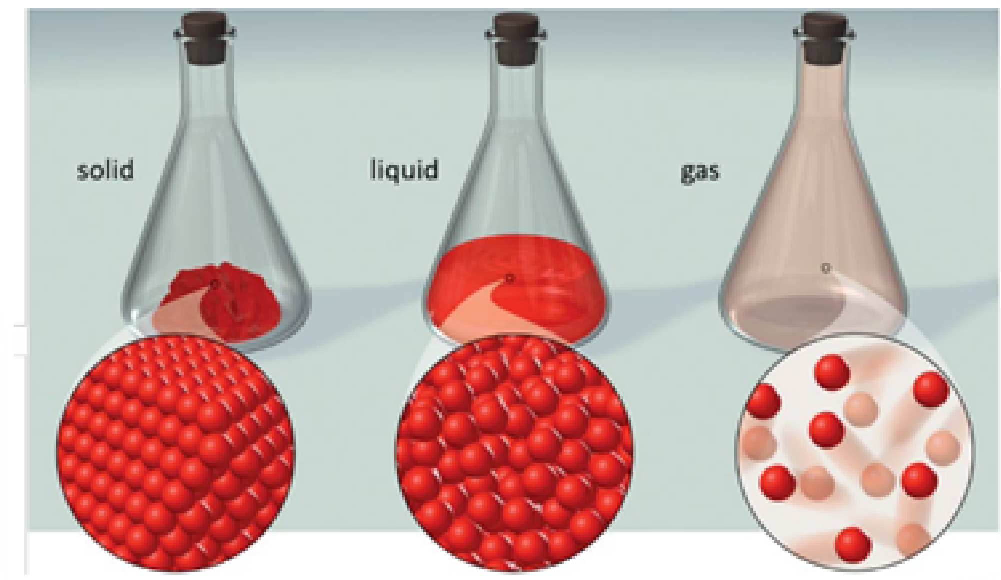
Solids have a fixed shape and volume. A solid's particles are packed closely together. There is not much space between the particles and there is little particle movement. A solid is not easily compressed.

Liquids have a fixed volume, but take the shape of the container in which they sit. There is not much space between the particles, but they can slide past each other and flow easily. A liquid is not easily compressed.

Gas fills the shape and volume of the container in which it sits. There is a lot of free space between its particles and they flow easily past each other. Gas can be compressed.

Plasma States of Matter

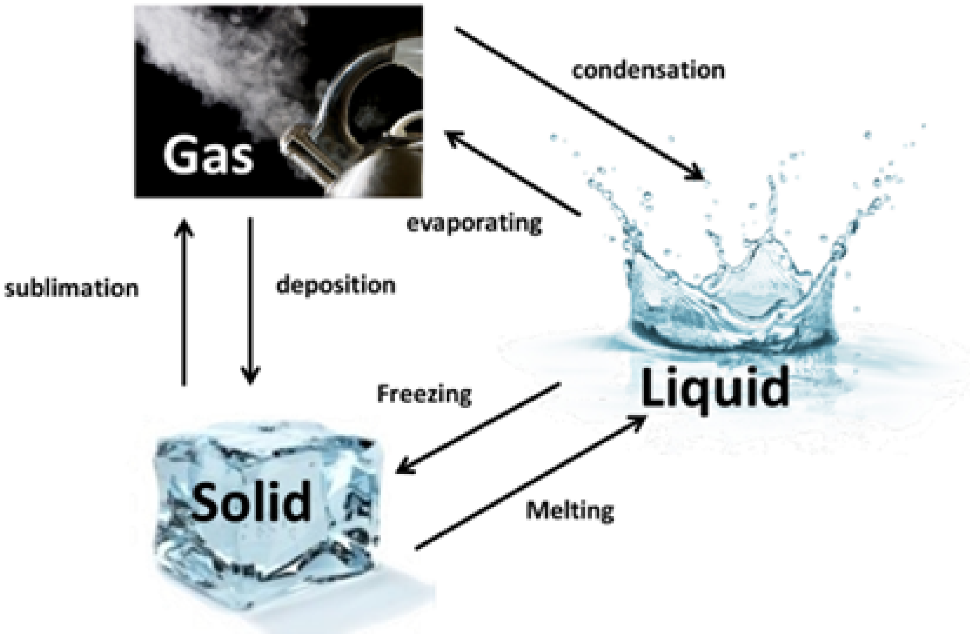
Plasma is one of four fundamental states of matter that contains a significant portion of charged particles in any combination of ions or electrons. Like gases, the plasma state has no fixed shape and volume and is less dense than the liquid or solid state. In modern science or technology, the plasma state of matter can be used for making television or many electronic devices.



Physical states

Molecules can shift from one physical state to another without changing their molecular structure (or chemical state). Water is still H20 when it is ice, steam or a liquid, even though its physical state has changed. Physical states can be changed by adding energy (i.e. increasing temperature or pressure) or releasing energy (i.e. cooling or lowering pressure). This does not change the matter's molecular structure. It is still the same matter or substance. When you heat a substance, you are adding energy to it. The movement of its molecules will increase until its physical state changes. The six ways to change the phase (state) of matter:

1. ***Melting*** changes a solid to a liquid. (i.e. dripping icicles)
2. ***Freezing*** changes a liquid to a solid. (i.e. lake freezing over)
3. ***Evaporation*** changes a liquid to a gas. (i.e. clothes drying on a clothesline)
4. ***Condensation*** changes a gas to liquid. (i.e. water forming on the outside of a cold glass)
5. ***Sublimation*** changes a solid to a gas. (i.e. ice cubes shrinking in the freezer)
6. ***Deposition*** changes a gas to a solid. (i.e. frost forming on the windows) These changes happen at precise temperatures for different substances. Scientists refer to these as melting point, freezing point, condensing point and boiling point. Water's melting point is 0°C, while its boiling point is 100°C.



Changes in state of matter

3. Description of a thermodynamic system

3.1. Thermodynamic Equilibrium

Definition

Thermodynamic Equilibrium is defined as a state of a macroscopic system in which all average properties do not change with time.

- ***Thermal equilibrium:**** Suppose you have some water at 60°C in a container. If this container is left to itself, it will gradually cool down to room temperature. This means that the container and water interact with the surroundings, and the water's temperature decreases with time. Once the system attains room (surroundings) temperature, no further change occurs. We then say that the container and water have attained thermal equilibrium with the surroundings
- ***Mechanical equilibrium:*** If within the system there are variations in pressure or elastic stress, its parts may move /expand/contract. When these movements cease, the system will be in mechanical equilibrium.
- ***Chemical equilibrium:**** when a system contains substances that can react chemically. After a sufficient time, when all chemical reactions show no tendency for a chemical change to occur, the system is said to be in chemical equilibrium.

4. Zeroth Law and First Law of Thermodynamics

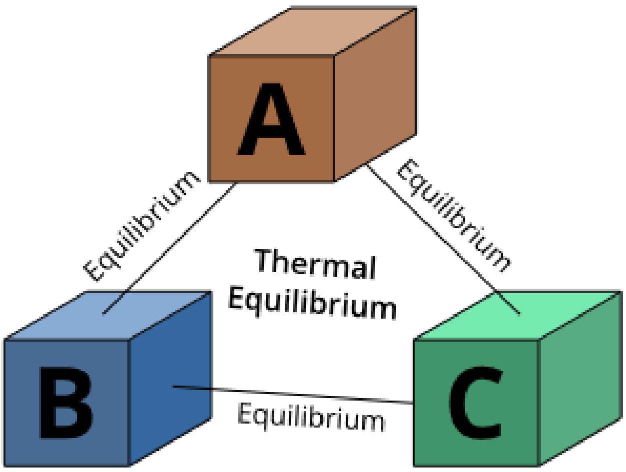
4.1. Definition of the zeroth Law of Thermodynamics

Definition

The zeroth law of thermodynamics states that if a system A is in ***thermal equilibrium*** with system B, and A is also in thermal equilibrium with a third system C, then B and C are in thermal equilibrium with each other. This fundamental principle forms the basis of how we define and measure temperature.

There are several ways to express the zeroth Law more simply:

- It tells us that any systems in thermal equilibrium share the same temperature.
- It confirms that temperature is a meaningful property, since it determines whether or not heat will transfer between systems.
- Heat can be exchanged even without direct contact, such as through radiation.
- However, if two systems are in thermal equilibrium, no net heat transfer occurs between them.



Zeroth law of thermodynamics

Example

A common real-life demonstration of the zeroth Law is ***the use of a thermometer***. For instance, in a traditional mercury thermometer, the ***mercury*** expands as the temperature rises. Because the cross-sectional area of the glass tube is constant, the expanding mercury moves upward. This increase in height corresponds to the rise in temperature, allowing us to measure how hot or cold something is thanks t***o thermal equilibrium*** between the thermometer and the object being measured.

4.2. Ideal Gas

4.2.1. Ideal Gas law

Definition

An ideal gas is a theoretical gas composed of many randomly moving point particles that interact only through elastic collisions and do not exert any intermolecular forces on each other.

In simpler terms, an ideal gas:

• Follows the ideal gas law:

$$PV = nRT$$

> P: pression (atm, Pa, 1 atm = 1,013 105 Pa, mmHg)
>
> V: volume (L, m^3, 1L = 10^3 m^3)
>
> n: number of moles (mol)
>
> R: ideal gas constant (R=0.0082 L am/mol K = 8.31 J/mol K = 2 cal/mol K)
>
> T: température (°C, K, T (K) = T (°C) +273)

Boyle's Law (Pressure-Volume Relationship)

$$P_1 V_1 = P_2 V_2$$

At constant temperature, the pressure of a gas is inversely proportional to its volume.

Charles' Law (Volume-Temperature Relationship)

$$V_1 / T_1 = V_2 / T_2$$

At constant pressure, the volume of a gas is directly proportional to its absolute temperature.

Gay-Lussac's Law (Pressure-Temperature Relationship)

$$P_1 / T_1 = P_2 / T_2$$

At constant volume, the pressure of a gas is directly proportional to its absolute temperature.

Avogadro's Law (Volume-Amount Relationship)

$$V_1 / n_1 = V_2 / n_2$$

At constant temperature and pressure, the volume of a gas is directly proportional to the number of moles.

4.2.2. State Function and Path function in thermodynamics

a) State Function

Definition

A ***state function*** (or point function) is a property of a system whose value depends only on the current state of the system, not on the way the system reached that state.

This means it is ***independent*** of the path taken to reach a particular condition.

b) Path Function

Definition

A ***path function*** is a property that ***does depend on the path*** or the specific process taken to move from one state to another.

Its value is not determined solely by the initial and final states, but also by the way in which the change occurre[*]d.

State function	Path function
pressure (P)	Heat (Q)
Temperature (T)	Work (W)
Volume (V)	
Mass (m)	
Density (D)	
Internal Energy (U)	
Enthalpy (H)	
Entropy (S)	

Example of a State and Path Function

Glossary

Quasi-Static Process

A process that happens so slowly that the system remains nearly in equilibrium at all times, allowing it to be represented clearly in state diagrams (configuration space).

Thermometer

A device used to measure temperature. It works by reaching thermal equilibrium with the object, allowing the system's temperature to be determined through expansion (e.g., of mercury).

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4

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