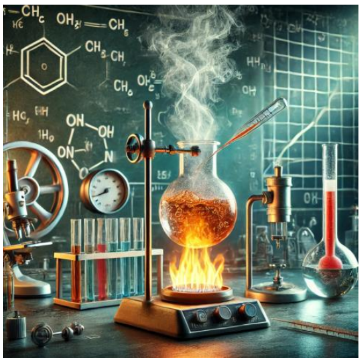
Thermodynamics



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1. Specific Objectives for Chapter II

Fundamental

- Define heat quantity (Q) and work as forms of energy transfer in thermodynamic systems.
- Classify methods of measuring heat, including the use of calorimetry for different types of substances and processes.
- Explain the relationship between heat and work in the context of thermodynamic transformations.
- Analyze thermodynamic processes to determine how heat and work contribute to energy changes within a system.

2. The Concept of Heat (Q)

2.1. Heat Quantity

Heat* refers to the energy transferred between systems or substances as a result of a temperature difference. Being a form of energy, heat adheres to the law of conservation, meaning it cannot be generated or annihilated but can move from one location to another and be transformed into other energy types.

When two objects at differing temperatures come into contact, energy moves from the warmer object (the one with the higher temperature) to the cooler one (the one with the lower temperature) until thermal equilibrium is reached. At equilibrium, there is no net heat* flow because the energy transferred in one direction is exactly balanced by the energy moving in the opposite direction.

A primary consequence of heat transfer is the alteration of temperature: adding heat increases temperature, while removing heat decreases it.

Experiments have demonstrated that the quantity of heat exchanged by a substance depends on three factors:

- The temperature change, ΔT, measured in degrees Celsius or Kelvin.
- The mass of the substance, m.
- Theintrinsic physical properties* of the substance, which are often related to its phase.
- The mathematical expression for heat transfer is given by:

$$dQ = C\,.\,dT \gg Q = \int_{T1}^{T2} C\,.\,dT$$

Here, the symbol C represents the heat capacity of the substance.

Extra

Furthermore, when a system absorbs a quantity of heat Q, its temperature increases by an amount ΔT in proportion to the absorbed heat, as described by the above relation.

$$Q = mc\Delta T$$

In the International System of Units (SI), heat is measured in calories (cal) or joules (J), where the conversion is:

1cal=4.18J

2.2. Heat Capacity

Definition

Heat capacity* refers to the quantity of heat required to raise the temperature of a given substance by 1.00°C. It is an extensive property, meaning it depends on both the mass and phase of the substance. The SI unit of heat capacity is J /K or Cal/K. It is expressed by the equation:

$$C = c\,.\,m$$

where:

- C is the heat capacity,
- c is the specific heat capacity,
- m is the mass of the substance.

2.3. Specific Heat Capacity

Definition

Specific heat capacity* (c) is an ***intensive property,**** meaning it does not depend on the amount of the substance. It represents the amount of heat needed to raise the temperature of 1.00 kg of a material by 1.00 °C (or 1.00 K).

The specific heat capacity is a characteristic property of a substance and is measured in SI units as J/(kg·K) or Cal/(kg·K).

There are two types of specific heats:

1. Specific heat at constant volume (Cv): The amount of energy needed to raise the temperature of a substance while keeping its volume constant.
2. Specific heat at constant pressure (Cp): The amount of energy required to raise the temperature of a substance while maintaining constant pressure.

The specific heat at constant pressure (Cp) is always greater than Cv because, under constant pressure, the system expands, requiring additional energy to facilitate this expansion.

For an ideal gas, the universal gas constant R is expressed as:

$$R = Cp - Cv$$

Specific heats for solids and liquids (incompressible substances):

$$R = Cv$$

Note

when heat is transferred from a system to its surroundings, the process is ***exothermic.***

when heat is transferred to a system from its surroundings, the process is ***endothermic***

$$Q_{Total} = \sum Q_{system} = Q_{S1} + Q_{S2}$$

2.4. Latent Heat

Definition

Latent heat refers to the energy ***absorbed*** or ***released*** by a substance during a phase change, occurring without a temperature change.

• The ***heat of fusion (Lf)*** is the energy required to melt a solid or freeze a liquid.

• The ***heat of vaporization (Lv)*** is the energy needed to vaporize a liquid or solid or condense a vapor.

Latent heat is typically measured in terms of energy per mole or unit mass of the substance undergoing a phase change. Common units include:

- Joules per mole (J/mol) or calories per mole (Cal/mol).
- Joules per kilogram (J/kg) or calories per kilogram (Cal/kg).

$$Q=nL$$

Or

$$Q=mL$$

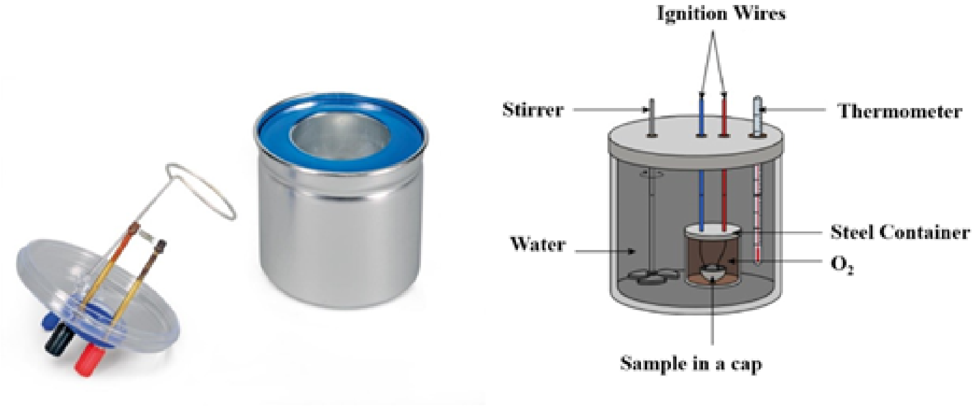
3. The Calorimetry and the work

3.1. Calorimetry

Definition

Calorimetry is the measurement of heat transfers. This process is carried out using devices called calorimeters.

A calorimeter is an isolated system, typically a thermally insulated chamber such as a thermos bottle or a calorimetric vessel, designed to prevent heat exchange with the surroundings. It is also tightly sealed with a lid to prevent any exchange of matter.



A simple calorimeter showing the main components

Calorimeters are used to determine the thermal properties of substances, particularly their heat capacity or the energy released during a reaction, by measuring temperature changes within the system. Heat transfer occurs solely inside the calorimetric container under atmospheric pressure.

In practice, to calculate the amount of heat, we use a calorimeter, which is based on the application of the zero principle in isolated system.

$$\sum Q_i = 0 \gg Q_{cal} + Q_1 + Q_2 = 0$$

$$Q_{cal} = C_{cal}(T_f - T_1)$$

$$Q_1 = m_1 c_1 (T_f - T_1)$$

$$Q_2 = m_2 c_2 (T_f - T_2)$$

$$C_{cal}(T_f - T_1) + m_1 c_1 (T_f - T_1) + m_2 c_2 (T_f - T_2) = 0$$

$$C_{cal} = \frac{-(m_1 c_1 (T_f - T_1) + m_2 c_2 (T_f - T_2))}{(T_f - T_2)}$$

When the specific heat of water is C = 1 cal /g.K, Ccal is equal to the water equivalent, which is the mass of water that absorbs the same amount of heat absorbed by the calorimeter.

3.2. Work in Thermodynamics

3.2.1. Definition and Fundamental Expression of Work

Definition

Thermodynamic work is conceptually related to mechanical work, but it specifically refers to the energy transfer that occurs when a system performs work on its surroundings (or vice versa). Unlike general mechanical work, the focus here is on the system and how it interacts with external forces.

In classical mechanics, the infinitesimal work dw done when a force F moves an object by a small displacement dh is expressed as:

$$dW = F \, . \, dh$$

In thermodynamics, pressure is defined as the external force applied per unit area on a movable boundary, such as a piston. This gives:

where Pext is the external pressure and A is the area of the movable surface. When this force causes a displacement, it leads to a change in volume dV, resulting in the thermodynamic expression for work:

and

$$F = P_{ext} \, . \, A$$

$$A \, . \, dh = -dV$$

So,

$$dW = -P_{ext} \, . \, dV$$

See "Illustration Video"

Glossary

Intrinsic Physical Properties

Properties that are independent of the amount of substance, also known as intensive properties, like pressure and temperature.

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