

Thermodynamics: 1st Law

Introduction

Thermodynamics is the study of energy transformations, particularly how heat energy and mechanical work are interconverted. It is essential for predicting the direction and extent of physical and chemical changes.

This module focuses on the First Law of Thermodynamics, which formalizes the principle of energy conservation in these processes:

- Understanding the First Law allows us to quantify energy changes, heat transfer, and work done in a system.
- It sets the foundation for understanding energy limits in all chemical and physical processes.

Learning Objectives

By the end of this module, you will be able to:

- **Define** a thermodynamic system and its surroundings, and differentiate between isolated, closed, and open systems.
- **Explain** the concepts of work (w) and heat (q) and their sign conventions in thermodynamic processes.
- **State and apply** the First Law of Thermodynamics to calculate changes in internal energy (ΔU).
- **Define** enthalpy (H) and understand its relationship to internal energy and pressure-volume work.

Key Concepts and Definitions

Term	Definition
System	The specific part of the universe under study (e.g., a reaction mixture).
Surroundings	Everything outside the system that can exchange energy with it.
Internal Energy (U)	The total energy contained within a thermodynamic system (kinetic and potential energy of particles).
State Function	A property whose value depends only on the current state of the system, not on how that state was reached (e.g., U, H, T, P, V).
Path Function	A property whose value depends on the path taken between states (e.g., Heat (q), Work (w)).
First Law of Thermodynamics	Energy cannot be created or destroyed, only converted from one form to another.

Detailed Discussion

1. System, Surroundings, and Energy Transfer

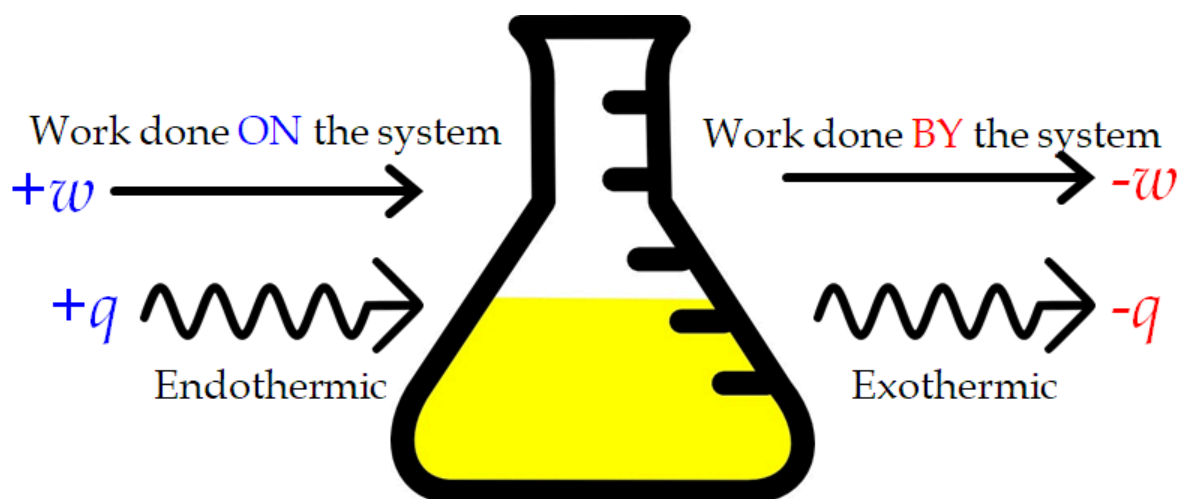
The crucial first step in any thermodynamic analysis is defining the system and its surroundings. The **boundary** between them can be real or imaginary, rigid or flexible. The classification of the system dictates which forms of energy transfer (mass, heat, or work) are possible:

- **Isolated System:** The most restricted system. No exchange of matter or energy (q or w) can occur across its boundaries. A perfectly insulated, rigid container (like an idealized Dewar flask) approximates this.
- **Closed System:** Energy can be exchanged with the surroundings, usually as heat or work, but mass cannot cross the boundary. A chemical reaction sealed in a flask is a closed system.
- **Open System:** The least restricted system, allowing the free exchange of both matter and energy. A common example is an open beaker of boiling water, where both heat and steam (mass) escape.

2. Work (w) and Heat (q)

Work and heat are dynamic quantities—energy in transit. They are **path functions**, meaning the total amount of energy transferred via heat or work depends entirely on the specific process pathway, unlike state functions which only consider the initial and final states.

The **Sign Conventions** are crucial for all calculations and must adhere to the perspective of the **system**:



- **Heat (q):** Positive when absorbed by the system (Endothermic, $q > 0$), and Negative when released by the system (Exothermic, $q < 0$).
- **Work (w):** Positive when done on the system (Compression, $w > 0$), and Negative when done by the system (Expansion, $w < 0$).

Pressure-Volume Work (PV Work): This is work associated with a change in volume (ΔV) against an opposing external pressure (P_{ext}), typical for gas phase reactions in cylinders or balloons.

- When the system expands ($\Delta V > 0$), the system does work, and w is negative, consistent with the sign convention.
- When compressed ($\Delta V < 0$), work is done on the system, and w is positive.

3. Internal Energy (U) and The First Law

Internal Energy (U) represents the sum of all microscopic energy forms within a system (translational, rotational, and vibrational kinetic energy of molecules, plus potential energy from chemical bonds and non-covalent interactions). Since U is a **state function**, its change (ΔU) is the same regardless of the path taken.

The **First Law of Thermodynamics** is the core principle of energy conservation applied to a system: the change in internal energy (ΔU) is determined only by the energy exchanged with the surroundings through heat (q) and work (w).

The First Law of Thermodynamics states that energy cannot be created or destroyed, only transferred. In chemistry, this is expressed mathematically as:

$$\Delta U = Q - W$$

Here:

- **q** = heat added to the system
- **w** = work done *by* the system

Heat added to the system increases its internal energy (**+q**), while work done by the system decreases it (**-w**), because the system uses up energy to do work on its surroundings.

In an **isolated system**, where **q = 0** and **w = 0**, the change in internal energy must also be zero: **$\Delta U = 0$**

This confirms that the total energy of the universe remains constant, reflecting the conservation of energy.

4. Enthalpy (H)

While internal energy (**U**) is a fundamental thermodynamic quantity, many chemical processes—especially reactions in open containers—occur under **constant pressure**, typically atmospheric pressure. Measuring heat flow (**q**) under constant pressure is much more convenient in a laboratory setting than directly determining **ΔU** .

To make heat measurements under constant pressure more meaningful, chemists defined a new state function called **enthalpy (H)**:

$$H = U + PV$$

This definition ensures that the heat absorbed or released at constant pressure corresponds directly to a property of the system. When pressure is constant, the change in enthalpy is equal to the heat exchanged:

$$\Delta H = q_p$$

This relationship arises from the First Law of Thermodynamics. For pressure-volume work ($w = P\Delta V$), the First Law becomes:

$$\Delta U = q - P\Delta V$$

Rearranging gives:

$$q_p = \Delta U + P\Delta V = \Delta H$$

Thus, enthalpy is designed so that **constant-pressure heat = ΔH** , making it the standard measure of reaction heat in chemistry.

Enthalpy is also a **state function**, meaning its value depends only on the initial and final states, not on the path taken. This makes ΔH consistent and simple to use for chemical reactions.

Interpreting ΔH

- $\Delta H > 0 \rightarrow$ Endothermic (heat absorbed; system feels cold)
- $\Delta H < 0 \rightarrow$ Exothermic (heat released; system feels warm)

Because most reactions in the lab are performed at constant atmospheric pressure, **enthalpy is the most practical thermodynamic quantity** for describing heat changes. It automatically accounts for expansion or compression work and directly reflects the energy changes that accompany chemical reactions.

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