Chapter 1 — Review of the Principles of Thermodynamics

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1 Review of Basic Concepts

1.1 Microscopic and Macroscopic Descriptions

The study of a thermodynamic system can be carried out according to two complementary scales of observation:

1.1.1 Microscopic Description

The microscopic (or statistical) description focuses on the individual behavior of the entities constituting the system: atoms, molecules, ions, or electrons. It relies on statistical and quantum mechanics.

- Variables: positions, velocities, energy levels, angular momenta.
- Objective: to determine macroscopic properties from the fundamental laws of microscopic physics.
- Example: the pressure of a gas is interpreted as the result of collisions of molecules with the walls of the container.

1.1.2 Macroscopic Description

The macroscopic (or phenomenological) description considers the system as a continuous medium, without concern for its atomic structure. It uses quantities measurable at our scale.

- Variables: pressure P, volume V, temperature T, mass m, etc.
- Objective: to establish relations between these quantities (equations of state) and to describe transformations.
- Example: the ideal gas law $PV = nRT$ relates macroscopic quantities.

2 Work, Heat, and Internal Energy

The energy of a system can be exchanged with the external environment in two main forms: work and heat.

2.1 Internal Energy (U)

Internal energy is the sum of all microscopic energies of the system (kinetic energy of molecules, potential interaction energy, vibrational energy, etc.).

- It is a state function: its variation depends only on the initial and final states, not on the path taken.
- For an ideal gas, U depends only on temperature: $dU = nC_v\,dT$, where C_v is the molar heat capacity at constant volume.

2.2 Work (W)

Work is an energy transfer due to the action of a macroscopic force on the system, causing displacement.

- For a quasi-static transformation, the elementary work of pressure forces is:

$$\delta W = -P_{\text{ext}}\, dV \qquad (1.1) \tag{1}$$

- The total work between two states is:

$$W = -\int_{V_1}^{V_2} P_{\text{ext}}\, dV \qquad (1.2) \tag{2}$$

- Sign convention: $W > 0$ if work is received by the system (compression), $W < 0$ if it is provided by the system (expansion).
- Work is not a state function: it depends on the path taken.

2.3 Heat (Q)

Heat is an energy transfer due to a temperature difference between the system and the external environment.

- For a transformation at constant heat capacity:

$$Q = mc\Delta T = nC\Delta T \qquad (1.3) \tag{3}$$

- Sign convention: $Q > 0$ if heat is received by the system (heating), $Q < 0$ if it is given off to the external environment.
- Heat is not a state function: it depends on the path taken (isothermal, isobaric, isochoric transformation, etc.).

3 Principle of Conservation of Energy

The principle of conservation of energy, or First Principle of Thermodynamics, states that energy can neither be created nor destroyed, but only transformed or transferred.

For a closed system at macroscopic rest, the variation of internal energy is equal to the sum of work and heat exchanged with the exterior:

$$\Delta U = W + Q \qquad (1.4) \tag{4}$$

or in differential form:

$$dU = \delta W + \delta Q \qquad (1.5) \tag{5}$$

3.1 Special Cases

- Isolated system: $W = 0$ and $Q = 0$, therefore $\Delta U = 0$. Internal energy is constant.
- Cyclic transformation: the final state is identical to the initial state, therefore $\Delta U = 0$, which implies $W = -Q$.
- Adiabatic transformation: $Q = 0$, therefore $\Delta U = W$. The work supplied serves to increase internal energy.
- Isochoric transformation: $W = 0$ (since $dV = 0$), therefore $\Delta U = Q_v$.

4 Definition of Thermal Equilibrium

Two systems are in thermal equilibrium when, placed in contact through a diathermic wall (permeable to heat), their respective temperatures no longer evolve and remain equal. There is then no net heat transfer between them.

4.1 Zeroth Principle of Thermodynamics

This fundamental principle, often called the Zeroth Principle, states that:

> If two systems A and B are each in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other.

This principle justifies the existence of a universal state quantity: **temperature**. It allows the construction of thermometers and the definition of temperature scales (Celsius, Kelvin, Fahrenheit).