Chapter 3

Principles of Thermodynamics and the First Law of thermodynamics

4.1 Basic terms in thermodynamics

There are two terms: thermodynamic system and environment. Each of them is defined as follows:

- **System:** The space in the world where the physical or chemical process takes place. It is a relative system that can be very large or very small.

- **Environment:** The part that surrounds the system. It is a relative part that can be real or imaginary.

4.1.1 Systems that separate the system from the environment in thermodynamics

(1) Isolated system: This system is completely isolated by a real barrier, which is an insulating material, and does not allow the exchange of temperature and matter.

(2) Open system: This system is open, allowing the exchange of temperature and matter.

(3) Closed system: This is a system that does not allow the exchange of matter, but only allows the exchange of heat. This system is a middle ground between an isolated system and an open system.

4.1.2 Systems according to the processes that take place within them

(1) Isothermal system: This is a system in which an isothermal process takes place. In other words, this system and its surroundings are at the same temperature, i.e. they are thermally similar. This means that there is continuous heat exchange between the system and its surroundings, so that the temperature of the system equals the temperature of its surroundings. This system is similar to a closed system, as the substance is constant and the temperature of the system remains constant during the process because it exchanges heat with the environment. Therefore, temperature constancy is a distinctive feature of this system.

(2) Adibatic system: This is the system in which the 2diabatic process occurs. This system is an isolated system, meaning that its temperature does not leak to the outside, and it is called a closed system. This means that the temperature of the system is not equal to the temperature of the environment. In other words, this system neither absorbs nor loses heat.

4.2 The First Law of Thermodynamics

This law concerns energy. It describes the relationship between three fundamental variables:

(1) Work, symbolized by w.

(2) Heat, symbolized by q.

(3) Internal energy, symbolized by ΔE.

These three basic variables are defined as follows:

First: Work (W)

Work is an algebraic quantity (i.e., it has a value and a direction). For example, mechanical work is the simplest type of work. If the work is upward, the displacement is downward and the quantity is negative. If the work is downward and the displacement is upward, the quantity is positive. Since force has a direction, work also has a direction.

Mechanical work always represents the product of two quantities: the first is called the intensity coefficient, which represents force, and the second is the amplitude coefficient, which represents length (distance). From this, we conclude that

work = intensity coefficient × amplitude coefficient

There are several types of work, including:

(1) Extensional work

(2) Mechanical work

(3) Electrical work

(4) Surface work

(5) Attractive work

(6) Thermal work.

The following table shows the law and coefficients of intensity and amplitude for each type of work.

Table: Coefficients of intensity and amplitude for each type of work

Type of work	**Capacity coefficient**	**Intensity coefficient**	**Law**
Extensional work	(dv) Change in size	P	Pdv
Mechanical work	Distance (dl)	(Force) F	Fdl
Electrical work	QQ Electrical quantity = Time × Current Q=I×t	(Effort) E	EQ
Surface work	Area (dA)	Surface tension γ	γdA
Attractive work	Height (H)	mg (Mass × gravitational acceleration)	mgh
Thermal work.	(dt) The difference between temperature	(heat capacity) C	Cdt

Extensional work

$$dW = pdv$$
$$dv = v_2 - v_1$$

Example (1): (Expansion work) Reaction of iron with sulphuric acid

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \uparrow$$

During the reaction, 50 liters of hydrogen were released under standard conditions (T=0°C, P=1 atm).

Calculate the work (w) in units of (1) joule (J) and (2) (lit.atm).

$$\begin{aligned} dv &= v_2 - v_1 \\ &= 50 - 0 \\ &= 50\,\text{lit} \end{aligned}$$

1-

$$\begin{aligned} w &= pdv \\ &= 1\text{ atm} \times 50\text{ lit} \\ &= 50\text{ lit.atm} \end{aligned}$$

2-

$$\because\ 1\text{ atm} = 10^5\text{ Pa }(Nm^{-2}),\ 1\text{ joul} = 1Nm,\ 1M^3 = 1000\text{lit}$$
$$\therefore\ w = 1\times10^5 Nm^{-2} \times 50\times10^{-3} M^3$$
$$= 5\times10^3\text{ Joul }(Nm)$$

Or in other words:

$$R=0.082 \text{ lit.atm}$$
$$R=8.314 \text{ Joul}$$
$$W=50 \text{ lit.atm}$$
$$W=\frac{50 \text{ lit.atm}}{0.082 \text{ lit.atm}}\times 8.314 \text{ Joul}$$
$$=5069.5 \text{ Joul}$$

Example (2): (Work done by gravity) Calculate the work required to lift one kilogram a distance m against gravity.

$$m=1\text{Kg}, \quad h=\frac{1}{10}\text{m}$$

$$W = mgh \Rightarrow \text{Kg . m .S}^{-2}\text{.m}$$
$$=1.0\times 9.8\times \frac{1}{10}$$
$$=0.98 \simeq 1.0 \text{ Joul(1N.m } \Rightarrow \text{Kg . m .S}^{-2}\text{.m = 1Kg .m}^{2}\text{. S}^{-2}\text{)}$$

(The above example gives us the answer to the following question: What does work = 1 joule mean?)

- Positive work (w+): work done by the environment on the system

Negative work (w -): work done by the system on the environment

- Every expansion is negative work.

Every contraction is positive work.

- The units of measurement for work are the same as the main units of gas constant (R).

Second: Heat quantity (q)

It is considered an algebraic quantity (i.e., it has a value and direction) and can be positive or negative. There are some important characteristics, which are:

(1) In every exothermic reaction, the heat quantity (q) is negative because the system loses heat.

(2) In every heat-absorbing reaction, the heat quantity (q) is positive.

(3) In an isolated system, the heat quantity (q) is zero because there is no loss or gain of heat and only adiabatic processes (heat conservation) occur.

(4) If we have a system and no work is done within that system, the amount of heat in that system is gained (and when this system is heated, this energy (heat) is stored as kinetic energy within the system). Therefore, the internal energy.

Third: Internal energy (ΔE)

To understand the meaning of internal energy (ΔE), let us consider a simple experiment conducted by the scientist Joule. The experiment is as follows:

In this experiment, Joule observed that the amount of heat required to heat water does not depend on the type of work, whether electrical, thermal, or mechanical, nor does it depend on the path taken by the work, but rather depends only on the total work (i.e., the initial state and the final state). Joule therefore observed that the properties of the system depend on internal energy, which is kinetic energy + potential energy.

$$\Delta E = E_2 - E_1$$

If the experiment is conducted in an isolated system (q=0), the internal energy is converted into work. That is:

$$\Delta E = W$$