CHAPTER TWO

The First Law and Other Basic Concepts

1. INTRODUCTION

A thermodynamic **system**, or simply system, is defined as a quantity of matter or a region in space chosen for study.

The region outside the system is called the **surroundings**.

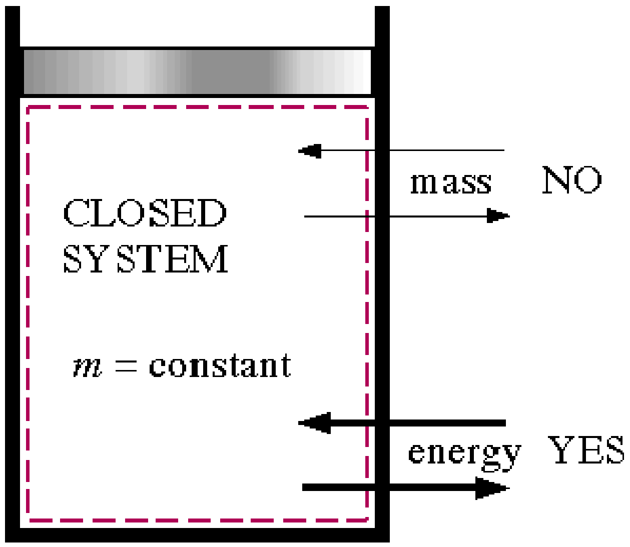
The real or imaginary surface that separates the system from its surroundings is called the **boundary**. The boundary of a system may be fixed or movable.

Surroundings are physical space outside the system boundary.

Systems may be considered to be closed or open, depending on whether a fixed mass or a fixed volume in space is chosen for study.

A closed system consists of a fixed amount of mass and no mass may cross the system boundary. The closed system boundary may move.

Examples of closed systems are sealed tanks and piston cylinder devices (note the volume does not have to be fixed). However, energy in the form of heat and work may cross the boundaries of a closed system.



An open system, or control volume, has mass as well as energy crossing the boundary, called a control surface. Examples of open systems are pumps, compressors, turbines, valves, and heat exchangers.

An isolated system is a general system of fixed mass where no heat or work may cross the boundaries.

An isolated system is a closed system with no energy crossing the boundaries and is normally a collection of a main system and its surroundings that are exchanging mass and energy among themselves and no other system.

2. INTERNAL ENERGY OF SYSTEM

The internal energy U of a system is the total of all kinds of energy possessed by the particles that make up the system.

Usually the internal energy consists of the sum of the potential and kinetic energies of the working gas molecules.

3. EXTENSIVE AND INTENSIVE PROPERTIES

Thermodynamic properties can be placed into two general classes: extensive and intensive.

A property of a system is called ***extensive*** if its value for the overall system is the sum of the values of the parts to which the system has been divided into

A property of a system is called *intensive* if its value is independent of the extent (size) of the system, and may vary from place to place and from moment to moment.
Some examples of intensive properties are: density, specific volume, pressure, and temperature.
An easy test for whether a property is extensive or intensive is to imagine a fixed amount of matter and ask if you cut the matter into two pieces would the property in question remain unchanged.

Example (extensive-intensive test)
Consider a fixed amount of gas in a closed insulated container. Assume the temperature, pressure, and density of the gas were uniform throughout the volume. If we cut the container in half by magically inserting an insulated impermeable wall that did not disturb the gas, then the temperature of the two halves would not change, the pressure would not change, and the density would not change; but the volume would be half that of the original volume, the total mass would also be cut in half, and the total energy would be cut in half as well.

Intensive properties may be functions of position and time; whereas extensive properties can only be functions of time

State function, function of state, state quantity, or state variable is a property of a system that depends only on the current state of the system, not on the way in which the system acquired that state (independent of path). A state function describes the equilibrium state of a system. For example, internal energy, enthalpy, and entropy are state quantities because they describe quantitatively an equilibrium state of a thermodynamic system, irrespective of how the system arrived in that state. In

contrast, mechanical work and heat are process quantities because their values depend on the specific transition (or path) between two equilibrium states.

Path function: A thermodynamic quantity whose value depends on the path of the process through the equilibrium state space of a thermodynamic system is termed a process function or, alternatively, a process quantity, or a **path function**. As an example, mechanical work and heat are process functions because they describe quantitatively the transition between equilibrium states of a thermodynamic system.

Path functions depend on the path taken to reach one state from another. Different routes give different quantities. Examples of path functions include work, heat and length. In contrast to path functions, state functions are independent of the path taken.

4. THE FIRST LAW OF THERMODYNAMICS

Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.

The first law applies to the system and surroundings, and not to the system alone. In its most basic form, the first law requires:

$$\Delta(\text{Energy of the system}) + \Delta(\text{Energy of surroundings}) = 0 \qquad (2.1)$$

5. ENERGY BALANCE FOR CLOSED SYSTEMS

Since no streams enter or leave a closed system, no internal energy is transported across the boundary of the system.

All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work. The second term of Eq. (2.1) may therefore be replaced by

$$\Delta(\text{Energy of surroundings}) = \pm Q \pm W$$

The choice of signs used with Q and W depends on which direction of transport is regarded as positive.

Heat Q and work W always refer to the system, and the modern sign convention makes the numerical values of both quantities positive for transfer into the system from the surroundings.

The corresponding quantities taken with reference to the surroundings, Qsur. and Wsur. have the opposite sign, i.e., Qsur. = - Q and Wsur. = - W. With this understanding:

$$\Delta(\text{Energy of surroundings}) = Q_{sur} + W_{sur.} = -Q - w$$

Equation (2.1) now become

$$\Delta(\text{Energy of the system}) = Q + W \qquad (2.2)$$

This equation means that the total energy change of a closed system equals the net energy transferred into it as heat and work.
Closed systems often undergo processes that cause no change in the system other than in its internal energy. For such processes, Eq. (2.2) reduces to:

$$\Delta U^t = Q + W \qquad (2.3)$$

where U^t is the total internal energy of the system. Equation (2.3) applies to processes involving finite changes in the internal energy of the system. For differential changes:

$$dU^t = dQ + dW \qquad (2.4)$$

Properties, such as volume Vt and internal energy U' depend on the quantity of material in a system. The principal thermodynamic coordinates for homogeneous fluids, are independent of the quantity of material, and are known as intensive properties. An alternative means of expression for the extensive properties of a homogeneous system, such as Vt and Ut, is:

$$V^t = mV \quad \text{or} \quad V^t = nV \qquad \text{and} \qquad U^t = mU \quad \text{or} \quad U^t = nU$$

For a closed system of n moles Eqs. (2.3) and (2.4) may now be written:

$$\boxed{\Delta(nU) = n\,\Delta U = Q + W} \qquad (2.5)$$

$$\boxed{d(nU) = n\,dU = dQ + dW} \qquad (2.6)$$

Thus for n = 1 Eqs. (2.5) and (2.6) become:

$$\Delta U = Q + W$$

$$dU = dQ + dW$$

Examples (2.1-2.4) from book

Example 2.1

Water flows over a waterfall 100 m in height. Take 1 kg of the water as the syste and assume that it does not exchange energy with its surroundings.

(*a*) What is the potential energy of the water at the top of the falls with respect the base of the falls?

(*b*) What is the kinetic energy of the water just before it strikes bottom?

(*c*) After the 1 kg of water enters the stream below the falls, what change h occurred in its state?

Solution 2.1

The 1 kg of water exchanges no energy with the surroundings. Thus, for each part of the process Eq. (2.1) reduces to:

$$\Delta(\text{Energy of the system}) = \Delta U + \Delta E_K + \Delta E_P = 0$$

(*a*) From Eq. (1.7), with g equal to its standard value,

$$E_P = mzg = 1\text{ kg} \times 100\text{ m} \times 9.8066\text{ m s}^{-2}$$

$$= 980.66\ \frac{\text{kg m}^2}{\text{s}^2} = 980.66\text{ N m} = 980.66\text{ J}$$

(*b*) During the free fall of the water no mechanism exists for conversion of potential or kinetic energy into internal energy. Thus ΔU must be zero:

$$\Delta E_K + \Delta E_P = E_{K_2} - E_{K_1} + E_{P_2} - E_{P_1} = 0$$

As an excellent approximation, let $E_{K_1} = E_{P_2} = 0$. Then,

$$E_{K_2} = E_{P_1} = 980.66\text{ J}$$

(*c*) As the 1 kg of water strikes bottom and mixes with other falling water to form a stream, the resulting turbulence has the effect of converting kinetic energy into internal energy. During this process, ΔE_P is essentially zero, and Eq. (2.1) becomes:

$$\Delta U + \Delta E_K = 0 \qquad \text{or} \qquad \Delta U = E_{K_2} - E_{K_3}$$

However, the stream velocity is assumed small, making E_{K_3} negligible. Thus,

$$\Delta U = E_{K_2} = 980.66\text{ J}$$

The overall result of the process is the conversion of potential energy of the water into internal energy of the water. This change in internal energy is manifested by a temperature rise of the water. Because energy in the amount of 4,184 J kg^{-1} is required for a temperature rise of 1°C in water, the temperature increase is 980.66/4,184 = 0.234°C, assuming no heat transfer with the surroundings.

Example 2.2

A gas is confined in a cylinder by a piston. The initial pressure of the gas is 7 bar, and the volume is 0.10 m^3. The piston is held in place by latches in the cylinder wall. The whole apparatus is placed in a total vacuum. What is the energy change of the apparatus if the restraining latches are removed so that the gas suddenly expands to double its initial volume, the piston striking other latches at the end of the process?

Solution 2.2

Because the question concerns the entire apparatus, the system is taken as the gas, piston, and cylinder. No work is done during the process, because no force external to the system moves, and no heat is transferred through the vacuum surrounding the apparatus. Hence Q and W are zero, and the total energy of the system does not change. Without further information we can say nothing about the distribution of energy among the parts of the system. This may well be different than the initial distribution.

Example 2.3

If the process described in Ex. 2.2 is repeated, not in a vacuum but in air at atmospheric pressure of 101.3 kPa, what is the energy change of the apparatus? Assume the rate of heat exchange between the apparatus and the surrounding air is slow compared with the rate at which the process occurs.

Solution 2.3

The system is chosen as before, but here work is done by the system in pushing back the atmosphere. It is evaluated as the product of the force of atmospheric pressure on the back side of the piston $F = P_{atm}A$ and the displacement of the piston $\Delta l = \Delta V^t/A$. Here, A is the area of the piston and ΔV^t is the volume change of the gas. This is work done by the system on the surroundings, and is a negative quantity; thus,

$$W = -F\,\Delta l = -P_{atm}\,\Delta V^t = -(101.3)(0.2 - 0.1)\text{ kPa m}^3 = -10.13\,\frac{\text{kN}}{\text{m}^2}\,\text{m}^3$$

or

$$W = -10.13\text{ kN m} = -10.13\text{ kJ}$$

Heat transfer between the system and surroundings is also possible in this case, but the problem is worked for the instant after the process has occurred and before appreciable heat transfer has had time to take place. Thus Q is assumed to be zero in Eq. (2.2), giving

$$\Delta(\text{Energy of the system}) = Q + W = 0 - 10.13 = -10.13\text{ kJ}$$

The total energy of the system has *decreased* by an amount equal to the work done on the surroundings.

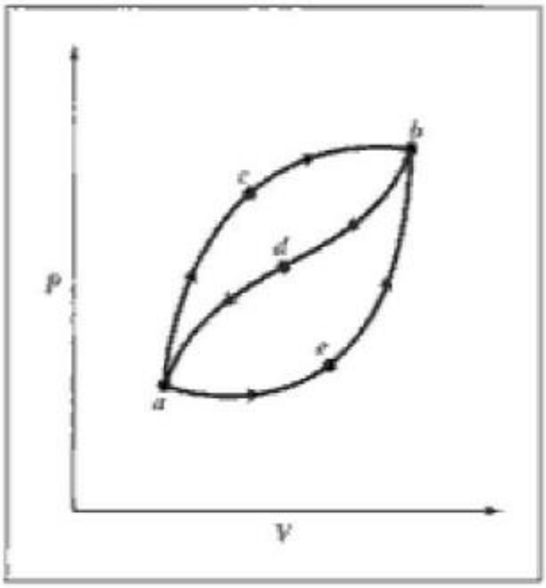
Example 2.4

When a system is taken from state *a* to state *b* in Fig. 2.1 along path *acb*, 100 J of heat flows into the system and the system does 40 J of work.

(*a*) How much heat flows into the system along path *aeb* if the work done by the system is 20 J?

(*b*) The system returns from *b* to *a* along path *bda*. If the work done on the system is 30 J, does the system absorb or liberate heat? How much?

Figure 2.1: Diagram for Ex. 2.4.



Solution 2.4

Assume that the system changes only in its internal energy and that Eq. (2.3) is applicable. For path *acb*, and thus for *any* path leading from *a* to *b*,

$$\Delta U^t_{ab} = Q_{acb} + W_{acb} = 100 - 40 = 60 \text{ J}$$

(*a*) For path *aeb*,

$$\Delta U^t_{ab} = 60 = Q_{aeb} + W_{aeb} = Q_{aeb} - 20 \qquad \text{whence} \qquad Q_{aeb} = 80 \text{ J}$$

(*b*) For path *bda*,

$$\Delta U^t_{ba} = -\Delta U^t_{ab} = -60 = Q_{bda} + W_{bda} = Q_{bda} + 30$$

and $$Q_{bda} = -60 - 30 = -90 \text{ J}$$

Heat is therefore transferred from the system to the surroundings.