Chapter 4

INTERNAL ENERGY & ENTHALPY

> There the eye goes not, speech goes not, nor the mind.
> We know not, we understand not
> How one would teach it.
>
> – *Maitri Upanishad, 6.17*

This chapter gives a brief introduction to the properties internal energy and enthalpy, that are extensively used in the first law analyses of engines. Internal energy is a property used in the first law analyses of closed systems, and enthalpy is a property used in the first law analyses of open systems.

4.1 Internal Energy

Internal energy U represents the total of all the microscopic modes of energy associated with the random motion and the internal structure of molecules. By microscopic modes of energy, we mean, for example, the energy associated with the translational, rotational and vibrational motion of individual molecules and the energy associated with the intermolecular forces. The energy associated with the position, motion and spin of the electrons, with the nucleus-electrons interactions in an atom, and with the nucleus-nucleus interactions also contribute towards the microscopic modes of energy.

These different microscopic modes of energies are strongly related to macroscopic properties such as the temperature T, pressure P, volume V, electrical charge, magnetic dipole-moment, surface tension, etc. Internal energy U, which represents the total of all the microscopic modes of energy in a system, can therefore be taken as a function of all the macroscopic properties, and can be expressed as

$$U = U(P,\ T,\ V,\ \text{electrical charge},\ \text{magnetic dipole-moment, etc.})$$

When dealing with simple compressible systems, as we do here, there is no need for us to consider properties, such as electrical charge and magnetic dipole-moment. The properties that are relevant to simple compressible systems, apart from the internal energy, are pressure, temperature, volume, enthalpy, and entropy.

The state postulate says that an equilibrium state of a simple compressible system can be determined by specifying two independent, intensive properties alone (see Section 2.8). Let us choose these two intensive properties as specific (or molar) volume v and temperature T, then the specific (or molar) internal energy is described as

$$u = u(v, T) \quad \text{at an equilibrium state of a simple compressible system.}$$

`Student:` Teacher, I have a question. Property is any characteristic of a system which can be measured or calculated. We can measure the temperature of a system with a thermometer and the pressure by a barometer or by a pressure gauge. What is the meter that we use for measuring the internal energy?

`Teacher:` Internal energy cannot be measured, dear Student. For that matter, no energy can ever be measured by any meter. You know very well what kinetic energy is. Is there a meter to measure kinetic energy?

`Student:` Let me think about it. Hm..... No teacher, I have never used any meter to measure kinetic energy. Well..., there is no meter to measure potential energy, either. I have just calculated them from formulas describing these energies. Well...then there must be a formula to calculate the internal energy. What is that formula?

`Teacher:` Oh.. dear Student, we cannot give a formula for internal energy in classical thermodynamics.

`Student:` What is **classical thermodynamics**? Why cannot we give a formula for internal energy in classical thermodynamics?

`Teacher:` Classical thermodynamics deals only with **macroscopic properties** such as T, P and V. I say temperature is a macroscopic property since a thermometer inserted in a gas does not record the kinetic energy of each molecule, but the average kinetic energy of the molecules. Pressure, for example, results from the bombardment of molecules. Even though each molecule would bombard differently from the other, pressure probe measures only the local average value of all those bombardments. Therefore, pressure is a macroscopic property. Classical thermodynamics, which deals only with macroscopic properties, cannot provide a formula for internal energy that represents the total of all microscopic forms of energy. To have a formula for internal energy, one shall study **statistical thermodynamics** which deals with microscopic properties, such as the kinetic energy of an individual molecule, the spin of an electron in an atom, etc.

`Student:` Teacher, are you going to teach me statistical thermodynamics?

`Teacher:` No, I am not going to teach you statistical thermodynamics, because the first law analyses of most engineering systems can satisfactorily be carried out with what we will learn in classical thermodynamics.

`Student:` Teacher, there is no meter to measure the internal energy. There is no formula to calculate the internal energy in classical thermodynamics. How are we then going to know the value of internal energy at a given state of a system?

`Teacher:` Ah.. we are lucky there. We need not know the value of internal energy at a given state for the successful application of the first law of thermodynamics. Take a look at the first law applied to a closed system, which is $Q_{in} + W_{in} = \Delta U$, where ΔU is simply the internal energy difference between two given states of a system. Chapters 5 and 6 will show you how to evaluate the internal energy difference ΔU between two given states, without knowing the absolute value of U at either of the two states.

Internal energy U takes the unit of energy which, in SI units, is the joule, abbreviated J. We could also use multiples of this unit, such as kilojoule and megajoule, abbreviated kJ and MJ, respectively. Internal energy per unit mass is known as **specific internal energy**, and it is usually given the unit J/kg. Internal energy content of a substance divided by the amount of substance is known as **molar internal energy**, and it is usually given the unit J/mol. Note that, internal energy is an extensive property, whereas specific and molar internal energies are intensive properties.

In this textbook, we use the unit kJ for internal energy, kJ/kg for specific internal energy, and kJ/kmol for molar internal energy. We use U to denote the internal energy, and the notation u to denote both the specific and molar internal energies.

4.2 Enthalpy

Enthalpy, denoted by H, is defined as follows:

$$H \equiv U + PV \tag{4.1}$$

Since U, P and V are properties, H is also a property. The unit of enthalpy is the same as that of internal energy, which in general is the joules. The unit of PV, pressure multiplied by volume, is also joules provided P is in pascals (which is equivalent to N/m^2) and V is in m^3.

Dividing (4.1) by the mass of the substance, we get the **specific enthalpy** h as

$$h = u + Pv \tag{4.2}$$

where u is the specific internal energy and v is the specific volume. Common unit of specific enthalpy is J/kg.

Had we divided (4.1) by the amount of substance, we would have got the **molar enthalpy**. Then u would have been the molar internal energy and v the molar volume. Common unit of molar enthalpy is J/mol. Note that enthalpy is an extensive property. Specific and molar enthalpies are intensive properties.

In this textbook, we use the unit kJ for enthalpy, kJ/kg for specific enthalpy, and kJ/kmol for molar enthalpy. We use H to denote enthalpy, and the notation h to denote both the specific and molar enthalpies.

`Student:` Teacher, is enthalpy the same as heat?

`Teacher:` No. Enthalpy is very different from heat, and you will learn about the difference between enthalpy and heat in detail in Chapter 8. Now, let me tell you that the enthalpy of a system may be increased by supplying heat to the system.

`Student:` Teacher, forgive me for asking. What is enthalpy?

`Teacher:` My dear Student, there is only one answer for that question. Enthalpy is a property defined by $H = U + PV$.

`Student:` Teacher, I want the physical meaning of enthalpy.

`Teacher:` Forgive me, dear Student, I am unable to give you a physical meaning of enthalpy. All what I can tell you is we frequently encounter the combination of properties $U + PV$, particularly when applying the first law to open systems. For the sake of convenience, $U + PV$ is defined as a new property enthalpy. However, let me assure you that you will appreciate the significance of the property enthalpy when dealing with fluids in motion, as we will do with open systems in Chapters 9 and 10.

We know that a state of a simple compressible system can be described completely by two independent, intensive properties (see Section 2.8). If the properties are chosen as the specific (or molar) volume v and temperature T, then the specific (or molar) enthalpy can be written as

$$h = h(v, T) \quad \text{at an equilibrium state of a simple compressible system.}$$

`Student:` Teacher, you have chosen v and T as the independent, intensive properties, and expressed u and h as functions of v and T. Why don't we choose, for example, P and T as the independent, intensive properties, and express u and h as functions of P and T.

`Teacher:` Yes, we could also choose the independent, intensive properties to be P and T, which are in fact easier to measure and control. However, it is important to note that P and T can be independent of each other only when the substance is in a single phase. When a substance exists in two phases, like boiling water in a closed vessel, T cannot be changed without affecting P, or P without affecting T. Therefore, we can write $u = u(P, T)$ or $h = h(P, T)$ for an equilibrium state of a simple compressible system **only when the system remains in a single phase**.

4.3 Summary

- Internal energy is a property of a system that represents the sum of all microscopic modes of energy in the system.
- Enthalpy, H, is defined as

  $$H \equiv U + P\,V \tag{4.1}$$

  and the specific (or molar) enthalpy is therefore given by

  $$h = u + P\,v \tag{4.2}$$

- Specific (or molar) internal energy for a simple compressible system at an equilibrium state can be written as a function of temperature and specific (or molar) volume.
- Specific (or molar) enthalpy for a simple compressible system at an equilibrium state can be written as a function of temperature and specific (or molar) volume.
- For a simple compressible system at an equilibrium state u and h can also be written as functions of T and P provided the system remains in a single phase.