Chapter 2

THERMODYNAMIC TERMINOLOGY

> There is nothing so strange in a strange land
> than the stranger that visits it.
>
> – Anonymous

Even though thermodynamics is a subject that is very easy to learn, some students find it difficult because they get confused with the meaning of the terms used in thermodynamics. In order to avoid such confusion, the thermodynamic meaning of the frequently used terms are clearly stated in this chapter. One can use this chapter as one uses a dictionary, coming back to it to refer to the thermodynamic meaning of a term, whenever there is a need for doing so.

2.1 System, Surroundings & Boundary

System	In thermodynamics, a system is either a quantity of matter or a region of space selected for study.
Surroundings	Everything that is outside the system is known as the surroundings.
Boundary	The closed surface that separates the system from its surroundings is known as the system boundary. Matter and/or energy are exchanged between the system and its surroundings across the boundary of the system.

Let us say we want to study the behaviour of air contained in a piston-cylinder device, the cross-section of which is shown in Figure 2.1. We consider the air within the piston-cylinder device as the system. Surroundings consists of the piston, the cylinder, and the environment outside the piston-cylinder device. The cross-section of the boundary is shown by the dashed line in Figure 2.1, and it is an imaginary surface that separates the air from the inner surfaces of the piston and the cylinder. Note that the shape and size of the boundary of the system are changed when the piston is moved by applying a force on the piston. Such a boundary is known as a **movable boundary**.

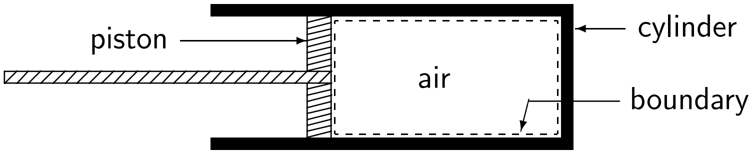


Figure 2.1 Cross-section of a piston-cylinder device containing air.

Another example of a system is the gas trapped in a closed tank shown in Figure 2.2. Its surroundings consists of the tank and the environment outside the tank. The boundary is shown by the dashed line in Figure 2.2.

If the tank is made up of rigid walls then the shape and size of the boundary cannot be changed when a force is applied on it. Such a boundary is known as a **rigid boundary**.

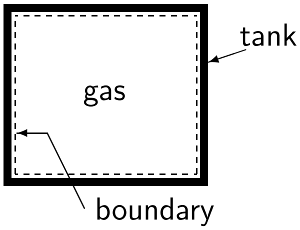


Figure 2.2 Cross-section of a closed tank containing gas.

Yet another example of a system is shown in Figure 2.3. We want to investigate the behaviour of the water contained in the tank. The problem here is that the mass of water within the tank does not remain the same throughout the investigation since water enters and leaves the tank through the inlet and outlet, respectively. Therefore, all what we could investigate is the behaviour of the mass of water within the tank at any given time. In such a situation, we choose the region in space that contains the mass of water within the tank as the system. The boundary of the system is marked by the dashed line shown in Figure 2.3. Everything outside the boundary is the surroundings.

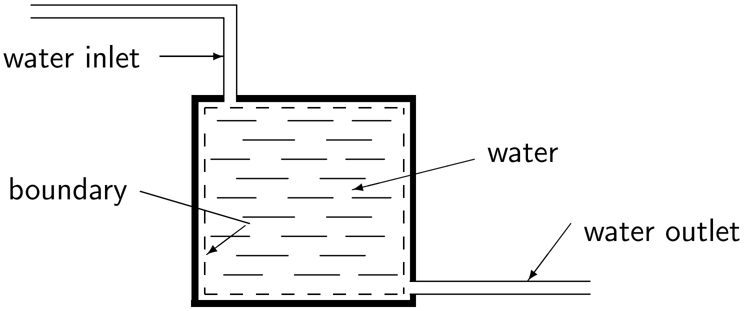


Figure 2.3 Cross-section of a tank containing water.

2.2 Closed, Open & Isolated Systems

A system can be a closed system, an open system or an isolated system depending on what can pass through its boundaries.

Closed System	A closed system contains the same matter within the system throughout the investigation. Therefore, no matter crosses the boundary of a closed system. However, energy can cross the boundary of a closed system.
Open System	An open system allows both matter and energy to enter or leave the system.
Isolated System	In an isolated system, neither matter nor energy enters or leaves the system.

Air trapped in the piston-cylinder device shown in Figure 2.1 is an example of a closed system since no air enters or leaves the system crossing the boundary. Another example of closed system is the gas contained in the tank shown in Figure 2.2 since the mass of gas remains the same throughout the investigation.

The system of Figure 2.1 has a movable boundary, and therefore work can be delivered to air by pushing the piston so as to decrease the volume of air. The system of Figure 2.2 has a rigid boundary, and therefore no work can be delivered to the gas contained within the rigid tank by moving the boundary. Heat could enter or leave the closed systems of Figure 2.1 and Figure 2.2 through the boundaries, provided the walls are made up of heat conducting materials.

The example of Figure 2.3 is an open system since matter, that is water, enters and leaves the system during the investigation. Heat can be supplied to the system through the walls of the container. Work, for example, can be provided to the system using a stirrer to stir water. An open system is also known as **control volume**, and its boundary known as **control surface**.

It should be borne in mind that one very seldom comes across an isolated system in real life. Nevertheless, in some cases, certain real systems are approximated to isolated systems when carrying out thermodynamic analyses.

2.3 Property

A **property** is any characteristic of a system which can be measured or calculated. Temperature and pressure are examples of properties that can be measured. Internal energy, enthalpy (see Chapter 4) and entropy (see Chapter 11) are examples of properties that can be calculated. Properties can be either intensive properties or extensive properties, the definitions of which are given below.

Extensive Property Any property that relates to the quantity of all matter present in the system is an extensive property.

Extensive properties can be added up. Volume and energy of the entire system are examples of extensive properties. We, in general, use upper case symbols to denote extensive properties, such as V for the total volume of the system, E for total energy, U for internal energy, H for enthalpy and S for entropy.

Intensive Property Any property that is definable at a point in the system is an intensive property, and its value may change from one point of a system to another.

Intensive properties cannot be added up. Temperature is an example of an intensive property, and we know that a thermometer inserted at different points in a system may register different temperatures. Pressure and density are also examples of intensive properties. We, in general, use lower case symbols to denote intensive properties. There are exceptions however, like the symbols T and P used for the intensive properties temperature and pressure, respectively.

Dividing an extensive property of a system by the total mass of the system, we get a property known as **specific property**. An example of specific property is specific volume, which is the total volume divided by the mass, and it takes the unit m^3/kg. Specific internal energy, specific enthalpy and specific entropy are all specific properties.

Dividing an extensive property of a system by the amount of substance present in a system, we get a property known as **molar property**. Molar volume, which is the total volume divided by the amount of substance, is an example of molar property. In this textbook, we use the unit $m^3/kmol$ for molar volume. Molar internal energy, molar enthalpy and molar entropy are all molar properties.

Both the specific and molar properties are intensive properties. In this textbook, we choose to denote them by the same lower case symbol. For example, v is used to denote both the specific and molar volumes, u for specific and molar internal energies, h for specific and molar enthalpies, and s for specific and molar entropies. Such a usage is acceptable since the respective units of v, u, h and s will clarify what the symbols represent.

`Student:` Teacher, what do you mean by amount of substance?

`Teacher:` You know that a quantity of matter can be measured by its mass. What you may not know is that the quantity of matter can also be measured in terms of the **amount of substance**. The unit of amount of substance is the mole, abbreviated 'mol'. The number of elementary entities in one mole of any substance is equal to the Avogadro's number, which is 6.022×10^{23}. Here elementary entities mean atoms, molecules, ions, electrons, etc.

`Student:` Teacher, you have not used the unit mol for the amount of substance. You have used kmol. What is kmol then?

`Teacher:` One kilomole is equivalent to 1000 moles, and therefore the number of elementary entities in one kilomole is equal to 6.022×10^{26}. When using kg as the unit for mass, it is convenient to use kilomole, abbreviated 'kmol', as the unit for the amount of substance.

`Student:` Teacher, now I know that the amount of substance is a way to quantify matter, and its unit is mole or kilomole. I also know that one kmol of matter contains 6.022×10^{26} elementary entities. In some textbooks, however, I have seen the unit kgmol. Is kgmol the same as kmol?

`Teacher:` Yes, it is. Consider a substance with molar mass M. We know that M grams of this substance is equivalent to one mole. If we take M kilograms of this substance then we have one kilogram-mole, abbreviated kgmol. Using these facts, let us work out the following:

$$1 \text{ kgmol} = M \text{ kg} = 1000\,M \text{ g} = 1000 \text{ mol} = 1 \text{ kmol}$$

`Student:` Okay. I see that one kgmol is the same as one kmol. Teacher, I want to know one more thing. What is molar mass?

`Teacher:` The ratio between the mass of a substance m and the amount of substance n is known as the **molar mass**, denoted by M. Therefore, $M = m/n$. For example, the molar mass of carbon^{12}, which is a particular form of carbon, is exactly 12 kg/kmol. The common unit for molar mass is g/mol, which is equivalent to kg/kmol, which is the unit used in this textbook.

`Student:` Thank you, Teacher. I have one more question. Is molar mass the same as molecular weight?

`Teacher:` The molecular weight is numerically equal to the molar mass taken in the unit g/mol or kg/kmol. However, unlike the molar mass, molecular weight is dimensionless. By the way, molecular weight is also known as **relative molecular mass**.

2.4 State

State The condition at which a system exists is called the state of a system. The state of a system is identified or described by its properties.

It is straight forward to describe the state of a system by its extensive properties such as the total volume of the systems. Describing a state of a system by its intensive properties, however, is a difficult task since intensive properties of a state may change from one point in the system to another. If we are to describe the state of a system by the intensive property temperature, for example, we need to measure the temperature at numerous points across the entire system using a very, very large number of thermometers. That would, of course, be an extremely difficult task to perform.

2.5 Equilibrium State

Equilibrium State An equilibrium state is a state at which all intensive properties remain uniform throughout the system.

When an intensive property remains uniform throughout the system, it has one and the same value at each and every point in the system.

For example, a thermometer would register identical values of temperatures at all points in a system at an equilibrium state. Therefore, a single value of temperature is enough to describe the entire system at an equilibrium state.

Similarly, pressure gauge would register the same value of pressure at any point in a system at an equilibrium state. Therefore, a single value of pressure is enough to describe the entire system at an equilibrium state.

In a system containing more than one component, chemical composition would be the same at any point in a system at an equilibrium state. Therefore, a single value of chemical composition is enough to describe the entire system at an equilibrium state.

It is the same with any other intensive property, such as specific volume, specific enthalpy or any other specific property, of a system at an equilibrium state. It is therefore an equilibrium state is a very convenient state to work with.

`ALL INTENSIVE PROPERTIES`
`REMAIN UNIFORM IN A SYSTEM`
`AT AN EQUILIBRIUM STATE.`

Let us now consider the ideal gas equation of state $PV = nRT$, where P is the pressure, V is the volume, n in the amount of substance, R is the universal gas constant, and T is the temperature. It is interesting to note that when we use the ideal gas equation of state, we use a single value of P and a single value of T to represent the state, which is justified only if the given state is an equilibrium state. It is important to note that properties of a system can be interrelated using the ideal gas equation of state, only if the state concerned is an equilibrium state.

2.6 Process

When a system changes from one state to another, it is said to execute a **process**. The continuous series of states that a system passes through during a process is called the **path of the process**. The following are a few processes that one frequently comes across in thermodynamics:

Constant Pressure Process: It is a process during which the pressure remains constant, while the other properties of the system may change.

Constant Volume Process: During a constant volume process, volume remains constant while the other properties may change from one state to another.

Isothermal Process: It is a constant temperature process. Even though the temperature remains constant in an isothermal process, heat may be transferred between the system and its surroundings. It is common to supply heat to a system to maintain its temperature constant.

Adiabatic Process: It is a process taking place while the system remains thermally insulated from its surroundings. That is, no heat is transferred between the system and its surroundings.

`Student:` Teacher, isn't an adiabatic process the same as an isothermal process.

`Teacher:` No, it is not. What makes you think that an adiabatic process is the same as an isothermal process?

`Student:` You said that no heat is transferred between the system and the surroundings of an adiabatic process. That means the temperature of the system could not change during the process. You also said that a process taking place at constant temperature is an isothermal process. Therefore, these two processes are the same. Aren't they?

`Teacher:` No, dear Student, they are not the same. I see that you are thinking that a temperature of a system must remain constant if the system does not exchange heat with its surroundings.

`Student:` Yes, Teacher. I think that.

`Teacher:` Dear Student, it is wrong to think that a temperature of a system does not change if the system does not exchange heat with its surroundings.

`Student:` Is it? Umm... Teacher, forgive me. I can't think of a system undergoing an adiabatic process where the temperature of the system changes. Could you please help me with an example of such a process?

`Teacher:` Yes, I could. Consider a gas contained in a piston-cylinder device. Let us take the gas as the system. Assume that the piston and the cylinder are made up of heat resistant material. As a result, no heat is exchanged between the system and the surroundings. Therefore, any process that this system undergoes is an adiabatic process. Could you agree with that?

`Student:` Yes, I could.

`Teacher:` Now, let us imagine that a force is applied on the outer face of the piston, as shown in Figure 2.4.

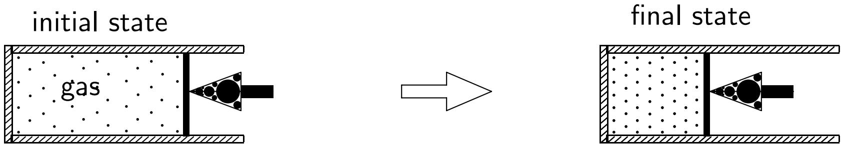


Figure 2.4 No heat is supplied, but a force is applied on the piston.

If the force applied is large enough for the piston to overcome friction, it would move such that the volume of the gas would be decreased. That is, the gas is compressed by applying a force. As you know, compressing a gas increases its pressure. Increasing the pressure increases its temperature. Therefore, we have just seen an example where the work done to compress the gas is responsible for increasing the temperature of the gas. So you see the temperature of the gas could be increased by compressing the gas during an adiabatic process.

`Student:` Teacher, I think that I am beginning to see the difference between an adiabatic process and an isothermal process.

`Teacher:` That is good. Let us then continue with the thermodynamic terminology.

2.7 Simple Compressible System

As absolute beginners in thermodynamics, let us restrict ourselves to studying the behaviour of **simple compressible systems**. These are systems comprising pure substances uninfluenced by surface tension effects, motion, and gravitational, electrical and magnetic fields.

`Student:` Teacher, what do you mean by pure substance?

`Teacher:` A pure substance is a substance with uniform chemical composition. Water is a pure substance since its chemical composition is the same everywhere.

`Student:` Water is one single chemical compound, and therefore it has uniform chemical composition. Air, which is a mixture of more than one chemical compound, is not a pure substance. Am I correct?

`Teacher:` Remember that **uniform chemical composition** is the keyword in defining a pure substance. Thus, air can be treated as a pure substance as far as the chemical composition of air remains uniform. For that matter, any mixture with a uniform chemical composition can be treated as a pure substance.

`Student:` I think I have got it. Any substance can be treated as a pure substance as far as its chemical composition remains uniform.

As we have seen above simple compressible systems are uninfluenced by surface tension effects and external force fields, and therefore work of changing surface area, electrical work, magnetic work, and the likes are absent in such systems. Thus, properties, such as surface tension, electrical charge, and magnetic dipole moment, have no significance when dealing with simple compressible systems.

The only form of work that we come across when working with simple compressible systems is **boundary work**, that is the work done to compress (or expand) the volume of the system. And, the properties used to characterize a state of a simple compressible system are pressure, volume, temperature, internal energy, enthalpy and entropy. We already have some idea about pressure, volume and temperature. Internal energy and enthalpy are introduced in Chapter 4, and entropy is introduced in Chapter 11.

It is common in the thermodynamic literature to refer to the simple compressible system as simple system.

2.8 State Postulate

Even though a state of a system can be characterized by a number of properties, repeated observations and experiments have shown that only two intensive properties of a simple compressible system can be independently chosen. That is to say the following:

> **Two independent, intensive properties are adequate to completely specify an equilibrium state of a simple compressible system**,

which is a simplified version of what is known as the **state postulate**. The above version of the state postulate is sometimes referred to as a **two-property rule**.

Once the two independent, intensive properties that specify the equilibrium state are chosen, any other intensive property at that equilibrium state is uniquely determined by these two properties.

Take, for example, air at 1 bar pressure and 27°C temperature. Assuming that air behaves as an ideal gas, the molar volume of air shall be calculated using the ideal gas equation of state as follows:

$$\begin{aligned} v &= \frac{V}{n} = \frac{RT}{P} = \frac{(8.314\ \mathsf{kJ/kmol\cdot K})\,(300\ \mathsf{K})}{100\ \mathsf{kPa}} \\ &= 24.94\ \mathsf{m^3/kmol} \end{aligned}$$

In this case, we take P and T as the independent intensive properties. Then, the third intensive property, molar volume v, is automatically fixed.

2.9 Property Diagram

Let us choose the independent, intensive properties as pressure P and specific volume v, and make a diagram of properties as in Figure 2.5. Consider point I in the property diagram, it has coordinates (P_o,v_o). Since, according to the state postulate, two independent, intensive properties are adequate to fix an equilibrium state of a simple compressible system, point I in the P-v diagram represents an equilibrium state of a simple compressible system.

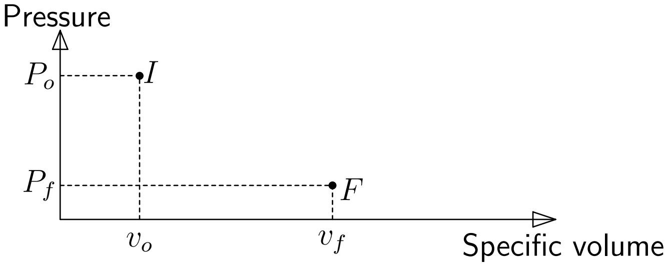


Figure 2.5 Equilibrium states I and F are shown on a property diagram.

Once (P_o,v_o) is specified, all the other intensive properties, such as T, u, h and s, at that equilibrium state are automatically fixed as functions of P_o and v_o. Therefore, the state represented by point I on a P-v diagram can as well be represented by a point on a h-s diagram, etc. That is to say an equilibrium state of a simple system is fixed by two of its intensive properties just in the same way as a point in space is fixed by its coordinates.

Let us now consider the equilibrium state represented by point F having the coordinate (P_f,v_f) in Figure 2.5. We know that all the other intensive properties at that equilibrium state are functions of P_f and v_f alone.

Let us consider a gas contained in a piston-cylinder device, say, at the equilibrium state I shown in Figure 2.5. Let us imagine that the gas undergoes a process, during which the gas expands and its pressure falls, until it reaches the equilibrium state F shown in Figure 2.5. It is important to note that whatever path is followed by the process to reach point F, the properties at F remain the same since they are functions only of P_f and v_f.

Suppose we need to determine the total change in the pressure of the system during the process considered. Since pressure is a property which depends on the state, and not on how the system reaches that state, the total change in pressure between the two equilibrium states I and F is given by

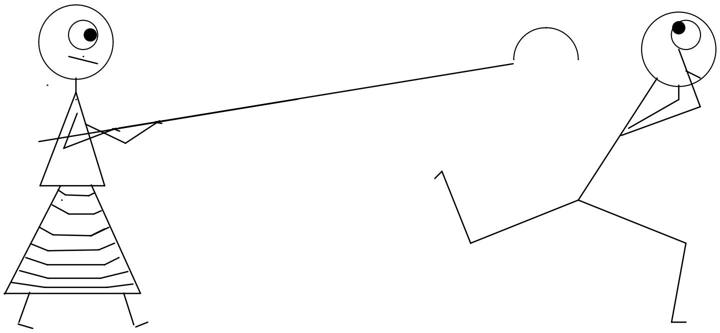
$$\int_{P_o}^{P_f} dP = P_f - P_o$$

where P_f and P_o represent the respective values of the property P at states F and I.

In general, for any one of the properties P, v, T, u, h or s, represented by the notation χ, say, we could write

$$\int_{\chi_o}^{\chi_f} d\chi = \chi_f - \chi_o$$

where χ_f and χ_o represent the respective values of the property χ at states F and I.



“don’t run away........., come back”