

**FUNDAMENTALS  
OF  
CLASSICAL AND STATISTICAL  
THERMODYNAMICS  
SPRING 2005**

# 1. Basic Concepts of Thermodynamics

The basic concepts of thermodynamics such as system, energy, property, state, process, cycle, pressure, and temperature are explained.

*Thermodynamics* can be defined as the science of energy. *Energy* can be viewed as the ability to cause changes.

Thermodynamics is concerned with the *transfer of heat* and the appearance or disappearance of *work* attending various chemical and physical processes.

- The natural phenomena that occur about us;
- Controlled chemical reactions;
- The performance of engines
- Hypothetical processes such as chemical reactions that do not occur but can be imagined.

## **HISTORY:**

Thermodynamics emerged as a science with the construction of the first successful atmospheric steam engines in England by **Thomas Savery** in 1697 and **Thomas Newcomen** in 1712. These engines were very slow and inefficient, but they opened the way for the development of a new science.

The *first and second laws of thermodynamics* emerged

simultaneously in the 1850s primarily out of the works of **William Rankine, Rudolph Clausius, and Lord Kelvin** (formerly William Thomson). The term *thermodynamics* was first used in a publication by Lord Kelvin in 1849. The first thermodynamic textbook was written in 1859 by William Rankine, a professor at the University of Glasgow.

# Classical vs. Statistical Thermodynamics

Substances consist of large number of particles called *molecules*. The properties of the substance naturally depend on the behavior of these particles. For example, the pressure of a gas in a container is the result of momentum transfer between the molecules and the walls of the container. But one does not need to know the behavior of the gas particles to determine the pressure in the container. It would be sufficient to attach a pressure gage to the container.

This *macroscopic approach* to the study of thermodynamics which does not require knowledge of the behavior of individual particles is called *classical thermodynamics*. It provides a direct and easy way to the solution of engineering problems.

The only quantities and concepts which enter thermodynamics are the experimental properties of matter such as *pressure*, *volume*, *temperature* and *composition*. Such properties are the properties of matter in bulk rather than of individual isolated molecules and are, therefore, called *macroscopic properties* as opposed to *microscopic properties*.

A more elaborate approach, based on the *average behavior of large groups of individual particles*, is called *statistical thermodynamics*.

# The Usefulness of Thermodynamics

Thermodynamics is exceedingly general in its applicability, and this makes it a powerful tool for solving many kinds of important problem.

Every engineering activity involves an interaction between energy and matter; thus it is hard to imagine an area which does not relate to thermodynamics in some respect. Therefore, developing a good understanding of thermodynamic principles has long been an essential part of engineering education.

## Examples:

- Can predict if a particular chemical process can take place under any given conditions.
  - The amount of energy that must be put into the process and its maximum yield can also be determined.
  - The effect of changes in these conditions upon the equilibrium state can also be predicted.
- Equations may be written correlating physical and chemical properties of substances.
- The measurement of the heat evolved during the combustion of all kinds of fuel has obvious practical significance for the fuel technologists.

# Limitations of Thermodynamics

- Thermodynamics can often tell us, for example, that a process will occur but not how fast it will occur,
- It can often provide a quantitative description of an overall change in state without giving any indication of the character of the process by which the change might take place.
- Thermodynamics does not provide the deep insight into chemical and physical phenomena that is afforded by microscopic models and theories.
- The **weakness** is that thermodynamics does not provide the deep insight into chemical and physical phenomena that is afforded by microscopic models and theories.

# The Laws of Thermodynamics

Thermodynamics is the **science of heat and temperature** and, in particular, of the laws governing the conversion of heat into mechanical, electrical or other macroscopic forms of energy.

- It permits the derivation of relationships between different laws of nature, even though the laws themselves are not a consequence of thermodynamics.
- The relationships based upon it are completely **independent of any microscopic** explanation of chemical and physical phenomena.

Classical thermodynamics is based on the four laws of thermodynamics. In thermodynamics we are concerned with the behavior of vast quantities of particles in the substances that we study. The laws of thermodynamics are the laws of the generalized behavior of the particles. These laws are as follows:

1. The **zero<sup>th</sup> law** deals with **temperature** and **temperature scale**.
2. The **first law** deals with macroscopic properties, **work**, **energy**, **enthalpy**, etc.

One of the most fundamental laws of nature is the **conservation of energy principle**. It simply states that during an interaction, energy can change from one form to another but the total amount of energy remains constant. That is, energy cannot be created or destroyed. A rock falling off a cliff, for example,

picks up speed as a result of its potential energy being converted to kinetic energy.

The first law of thermodynamics, is simply an expression of the conservation of energy principle, and it asserts that *energy* is a thermodynamic property.

3. The second law mainly deals with *entropy*, a property most fundamentally responsible for the behavior of matter.

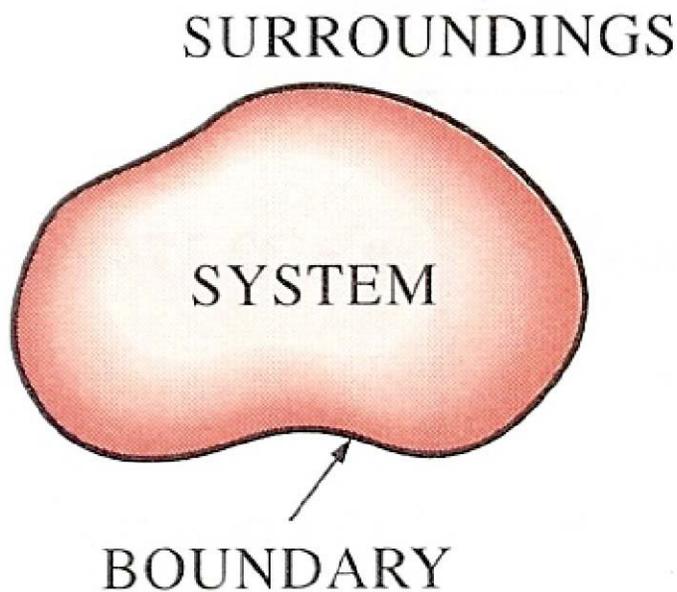
The second law of thermodynamics asserts that energy has *quality* as well as *quantity*, and actual processes occur in the direction of decreasing quality of energy.

Example: cooling of a cup of coffee is irreversible.

4. The third law deals with the *determination of entropy*.

# Thermodynamic System

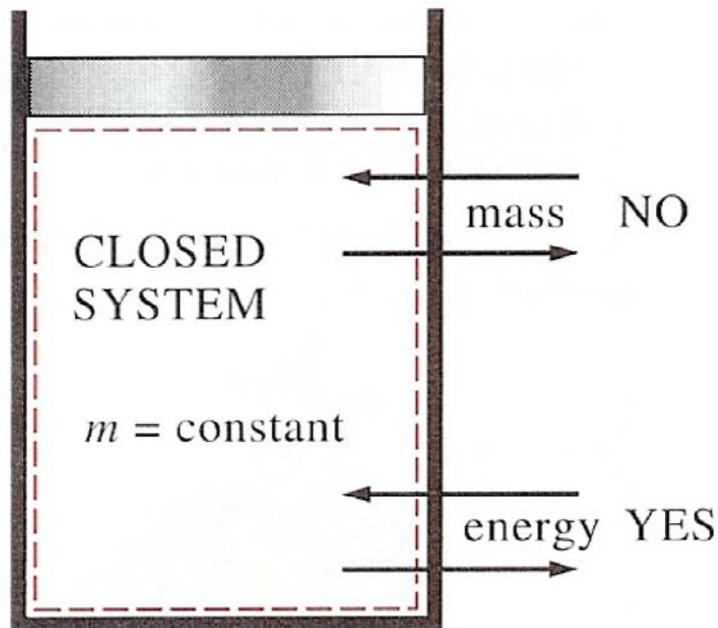
A thermodynamic system, or simply a system, is defined as a *quantity of matter or a region in space chosen for study*. The mass or region outside the system is called the *surroundings*. The real or imaginary surface that separates the system from its surrounding is called the *boundary*.



The **boundary** of a system can be *fixed or movable*. The boundary is the contact surface shared by both the system and the surroundings, and has zero thickness (does not contain any mass and does not occupy any volume in space).

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** (also known as a **control mass**) consists of a fixed amount of mass, and **no mass can cross its boundary**. That is, no mass can enter or leave a closed system.



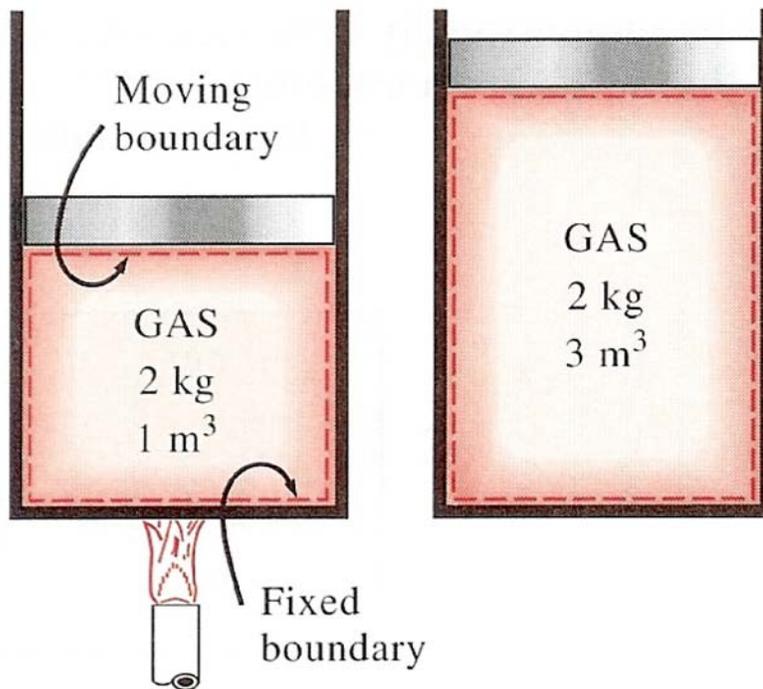
**Energy**, in the form of **heat or work**, can cross the boundary.

**Volume of a closed system does not have to be fixed.**

- As a special case, even **energy is not allowed to cross the boundary**, that system is called an **isolated system**.

## Example:

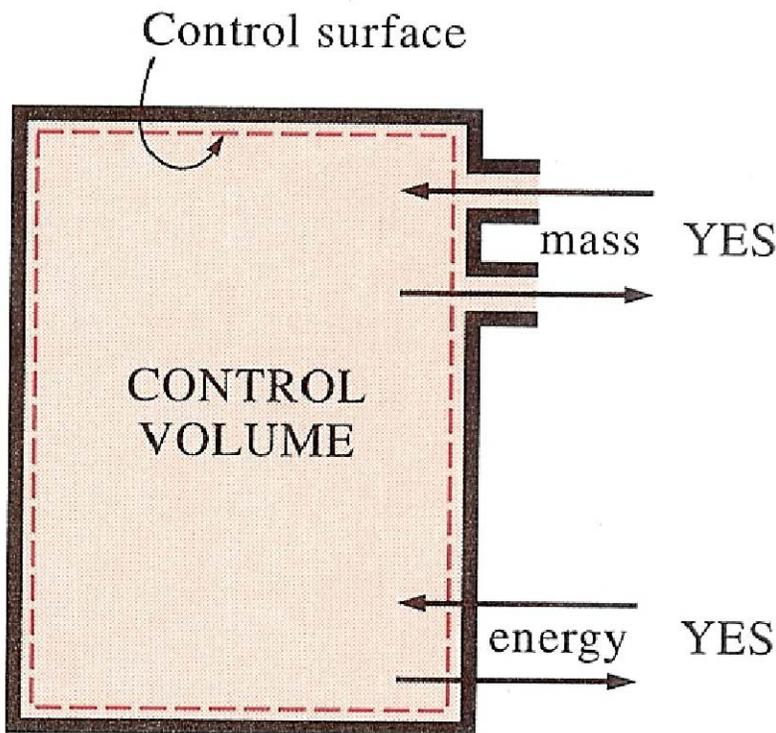
A piston-cylinder device:



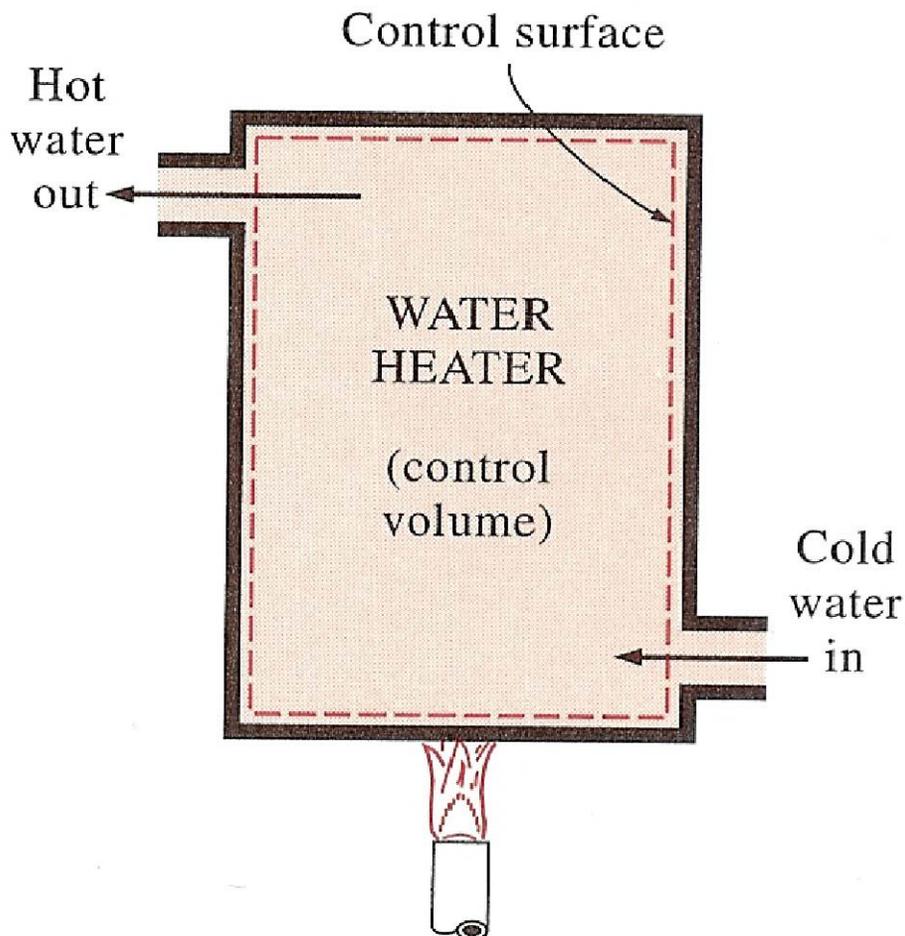
Inside the cylinder is a gas that is heated.

- The gas is **the system**.
- The inner surfaces of the piston and the cylinder form the **boundary**.
- Since no mass is crossing this boundary, it is a **closed system**.
- Energy may cross the boundary,
- Part of the boundary (the inner surface of the piston, in this case) may move.
- Everything outside the gas, including the piston and the cylinder, is the **surroundings**.

- An **open system** (or a **control volume**), is a **properly selected region in space**.
  - **Example:** It usually encloses a device that involves mass flow such as a compressor, turbine, or nozzle. Flow through these devices is best studied by selecting the region within the device as the control volume.
  - Both **mass and energy can cross the boundary of a control volume**, which is called a **control surface**.



**Example:** the water heater shown below. Let us say that we would like to determine how much heat we must transfer to the water in the tank in order to supply a steady stream of hot water.



Since hot water will leave the tank and be replaced by cold water, it is not convenient to choose a fixed mass as our system for the analysis. Instead, we can concentrate our attention on the volume formed by the interior surfaces of the tank and consider the hot and cold water streams as mass leaving and entering the control volume.

The interior surfaces of the tank form the **control surface** for this case, and mass are crossing the control surface at two locations.

*The thermodynamic relations that are applicable to closed and open systems are different. Therefore, it is extremely important that we recognize the type of system we have before we start analyzing it.*

In all thermodynamic analyses, the system under study *must* be defined carefully. In most cases, the system investigated is quite simple and obvious, and defining the system may seem like a tedious and unnecessary task. In other cases, however, the system under study may be rather involved, and a proper choice of the system may greatly simplify the analysis.

# Forms of Energy

Energy: thermal, mechanical, kinetic, potential, electric, magnetic, chemical, and nuclear, and their sum constitutes the **total energy  $E$  of a system**. The total energy of a system on a unit mass basis is denoted by  $e$  and is defined as:

$$e = \frac{E}{m}$$

The units are kJ/kg.

Thermodynamics only deals with the change of the total energy. Thus the total energy of a system can be assigned a value of zero ( $E = 0$ ) at some convenient reference point.

*The change in total energy of a system is independent of the reference point selected.*

The decrease in the potential energy of a falling rock, for example, depends on only the elevation difference and not the reference level chosen.

Forms of energy that make up the total energy of a system in two groups: **macroscopic** and **microscopic**.

- The **macroscopic forms of energy** are those a system possesses as a whole with respect to some outside reference frame, such as **kinetic** and **potential** energies.
  - The macroscopic energy of a system is related to **motion and the influence of some external effects**

such as gravity, magnetism, electricity, and surface tension.

- The energy that a system possesses as a result of its motion relative to some reference frame is called **kinetic energy  $KE$** . When all parts of a system move with the same velocity, the kinetic energy is expressed as:

$$KE = \frac{mV^2}{2}$$

where the script  $V$  denotes the velocity of the system relative to some fixed reference frame.

- The energy that a system possesses as a result of its elevation in a gravitational field is called **potential energy  $PE$**  and is expressed as

$$PE = mgz \text{ (kJ)}$$

where  $g$  is the gravitational acceleration and  $z$  is the elevation of the center of gravity of a system relative to some arbitrarily selected reference plane.

- The **microscopic forms of energy** are those related to the molecular structure of a system and the degree of the molecular activity, and they are independent of outside reference frames.
  - The sum of all the microscopic forms of energy is called the **internal energy** of a system and is

denoted by ***U***.

The term *energy* was coined in 1807 by Thomas Young, and its use in thermodynamics was proposed in 1852 by Lord Kelvin. The term *internal energy* and its symbol *U* first appeared in the works of Rudolph Clausius and William Rankine in the second half of the nineteenth century.

- The **magnetic, electric, and surface tension** effects are significant in some specialized cases only and are not considered in this course. In the absence of these effects, the total energy of a system consists of the **kinetic, potential, and internal energies** and is expressed as

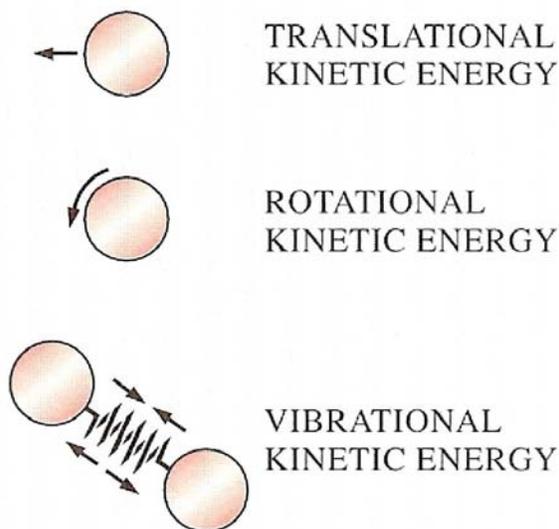
$$E = U + KE + PE$$

- Most closed systems remain stationary during a process and thus experience no change in their kinetic and potential energies. Closed systems whose velocity and elevation of center of gravity remain constant during a process are frequently referred to as **stationary systems**.
- The change in the total energy  $\Delta E$  of a stationary system is identical to the change in its internal energy  $\Delta U$ .
- *Here* a closed system is assumed to be stationary unless it is specifically stated otherwise.

## More about Internal Energy

Internal energy is defined as the sum of all the microscopic forms of energy of a system. It is related to the molecular structure and the degree of molecular activity.

The individual molecules of a system, in general, will move around with some **velocity**, **vibrate about each other**, and **rotate about an axis** during their random motion. Associated with these motions are translational, vibrational, and rotational kinetic energies.



The sum constitutes the **kinetic energy** of a molecule.

- The portion of the internal energy of a system associated with the kinetic energies of the molecules is called the sensible energy.

The average velocity and the degree of activity of the molecules are proportional to the [temperature of the gas](#). Thus, at higher temperatures, the molecules will possess higher kinetic energies, and as a result the system will have a higher internal energy.

- The internal energy is also associated with the intermolecular forces between the molecules of a system. These are the forces that bind the molecules to each other, and, as one would expect, they are strongest in solids and weakest in gases. If sufficient energy is added to the molecules of a solid or liquid, they will overcome these molecular forces and break away, turning the system to a gas. This is a [phase-change process](#). Because of this added energy, a system in the gas phase is at a higher internal energy level than it is in the solid or the liquid phase. [The internal energy associated with the phase of a system is called latent energy](#).
- The changes mentioned above can occur without a change in the chemical composition of a system. Most thermodynamic problems fall into this category, and one does not need to pay any attention to the forces binding the atoms in a molecule. [The internal energy associated with the atomic bonds in a molecule is called chemical \(or bond\) energy](#). During a chemical reaction, such as a combustion process, some chemical bonds are destroyed while others are formed. As a result, the internal energy changes.
- We should also mention the tremendous amount of internal energy associated with the bonds within the

nucleus of the atom itself. This energy is called **nuclear energy and is released during nuclear reactions**.

Obviously, we need not be concerned with nuclear energy in thermodynamics unless, of course, we have a fusion or fission reaction on our hands.

- The above forms of energy can be **contained** or **stored** in a system, and thus can be viewed as the **static forms of energy**.
- The forms of energy that are not stored in a system can be viewed as the **dynamic forms of energy**, or as **energy interactions**.

The dynamic forms of energy are recognized at the system boundary as they cross it, and they represent the energy gained or lost by a system during a process.

- The only two forms of energy interactions associated with a **closed system** are **heat transfer and work**.
  - An energy interaction is **heat transfer** if its driving force is a temperature difference.
  - Otherwise it is **work**.
- The **open systems** can also exchange energy via mass transfer, since any time mass is transferred into or out of a system, the energy contained in the mass is also transferred with it.

# Properties of a System

Any characteristic of a system is called a **property** such as

- pressure  $P$ ,
  - temperature  $T$ ,
  - volume  $V$ , and
  - mass  $m$ .
- 
- The list can be extended to include less familiar ones such as **viscosity**, **thermal conductivity**, **modulus of elasticity**, **thermal expansion coefficient**, **electric resistivity**, and even velocity and elevation.

Not all properties are independent. Some are defined in terms of other ones. For example, **density** is defined as **mass per unit volume**:

$$\rho = \frac{m}{V}$$

Sometimes the density of a substance is given relative to the density of a better known substance. Then it is called **specific gravity**, or **relative density**, and is defined as **the ratio of the density of a substance to the density of some standard substance at a specified temperature** (usually water at 4°C, for which  $\rho_{H2O} = 1000 \text{ kg/m}^3$ ). That is,

$$\rho_s = \frac{\rho}{\rho_{H2O}}$$

Note that specific gravity is a dimensionless quantity.

- A more frequently used property in thermodynamics is the **specific volume**. It is the reciprocal of density and is defined as *the volume per unit mass*:

$$v = \frac{V}{m} = \frac{1}{\rho}$$

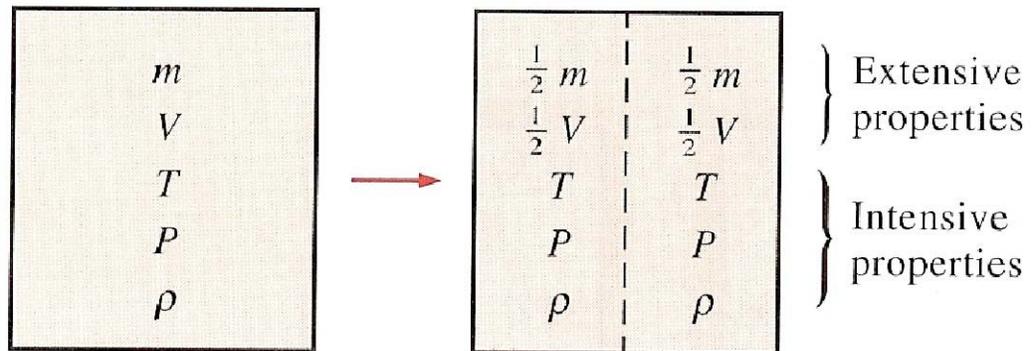
In **classical thermodynamics**, the atomic structure of a substance (thus, the spaces between and within the molecules) is disregarded, and **the substance is viewed to be a continuous, homogeneous matter with no microscopic holes, i.e., a continuum**.

This idealization is valid as long as we work with volumes, areas, and lengths that are large relative to the intermolecular spacing.

Properties are considered to be either **intensive** or **extensive**.

- **Intensive properties** are those that are independent of the size of a system, such as **temperature, pressure, and density**.
- **Extensive properties** are those whose values depend on the size-or extent-of the system. **Mass  $m$ , volume  $V$ , and total energy  $E$**  are some examples of extensive properties. As easy way to determine whether a property is intensive or

extensive is to divide the system into two equal parts with a partition.



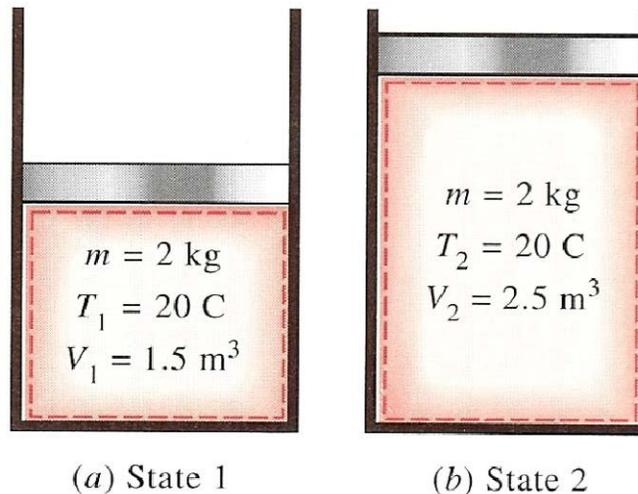
Each part will have the same value of intensive properties as the original system, but half the value of the extensive properties.

- **Extensive properties per unit mass** are called **specific properties**. Some examples of specific properties are
  - **specific volume** ( $v = V/m$ ),
  - **specific total energy** ( $e = E/m$ ), and
  - **specific internal energy** ( $u = U/m$ ).

# State and Equilibrium

Consider a system that is not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us **a set of properties that completely describe the condition, or the state**, of the system.

- At a given state, all the properties of a system have fixed values.
- If the value of even one property changes, the state will change to a different one.



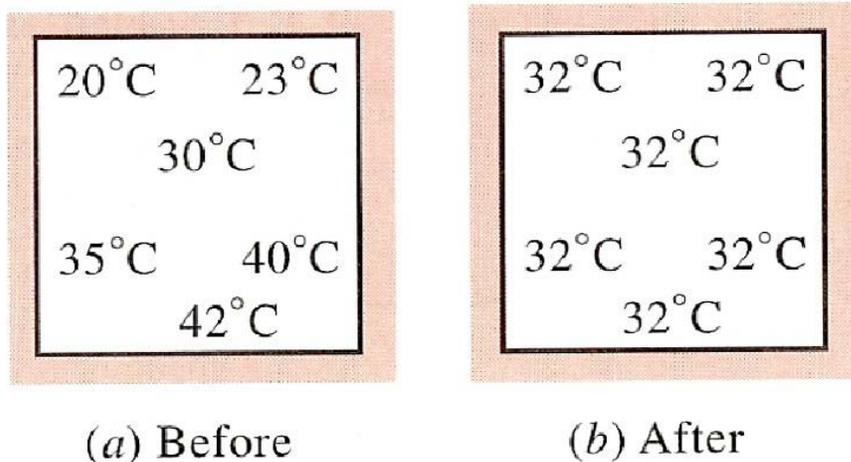
Thermodynamics deals with equilibrium states.

- The word **equilibrium** implies a state of balance.
- In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system.

- A system that is in equilibrium experiences no changes when it is isolated from its surroundings.

There are many types of equilibrium, and a system is not in thermodynamic equilibrium unless the conditions of all the relevant types of equilibrium are satisfied.

- A system is in **thermal equilibrium** if the temperature is the same throughout the entire system, as shown below.



The system involves no temperature differentials, which is the driving force for heat flow.

- **Mechanical equilibrium** is related to pressure, and a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time.

However, the pressure may vary within the system with elevation as a result of gravitational effects. But the higher pressure at a bottom layer is balanced by the extra weight it

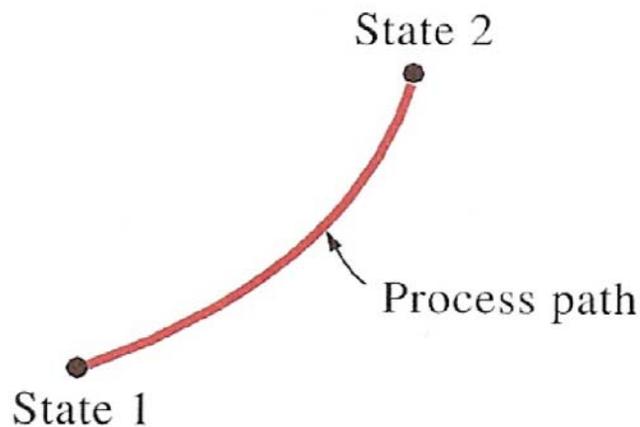
must carry, and, therefore, there is no imbalance of forces. The variation of pressure as a result of gravity in most thermodynamic systems is relatively small and usually disregarded.

- If a system involves two phases, it is **phase equilibrium** when the mass of each phase reaches an equilibrium level and stays there.
- Finally, a system is in **chemical equilibrium** if its chemical composition does not change with time, i.e., no chemical reactions occur.

# Processes and Cycles

Any change that a system undergoes from one equilibrium state to another is called a process.

The series of states through which a system passes during a process is called the path of the process.

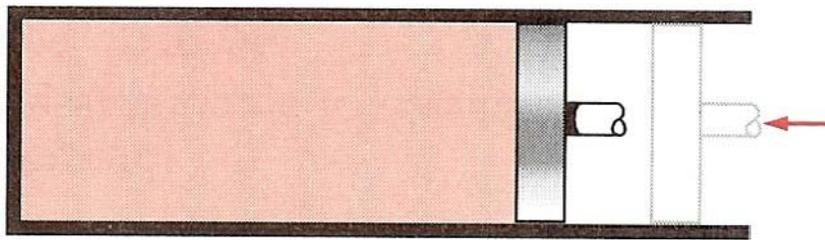


To describe a process completely, one should specify

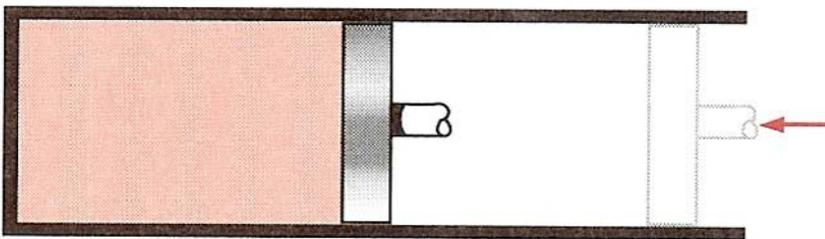
- the initial state and
- final state of the process, as well as
- the path it follows, and
- the interactions with the surroundings.

When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a quasi-static, or quasi-equilibrium, process.

- A quasi-equilibrium process can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.



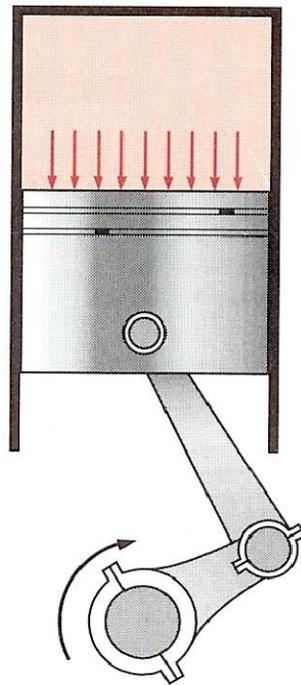
(a) Slow compression  
(quasi-equilibrium)



(b) Very fast compression  
(non-quasi-equilibrium)

- When a gas in a piston-cylinder device is compressed suddenly, the molecules near the face of the piston will not have enough time to escape and they will have to pile up in a small region in front of the piston, thus creating a high-pressure region there. Because of this pressure difference, the system can no longer be said to be in equilibrium, and this makes the entire process **non-quasi-equilibrium**.
- If the piston is moved slowly, the molecules will have sufficient time to redistribute and there will not be a molecule pileup in front of the piston. As a result, the pressure inside the cylinder will always be uniform and will rise at the same rate at all locations. Since equilibrium is maintained at all times, this is a **quasi-equilibrium process**.

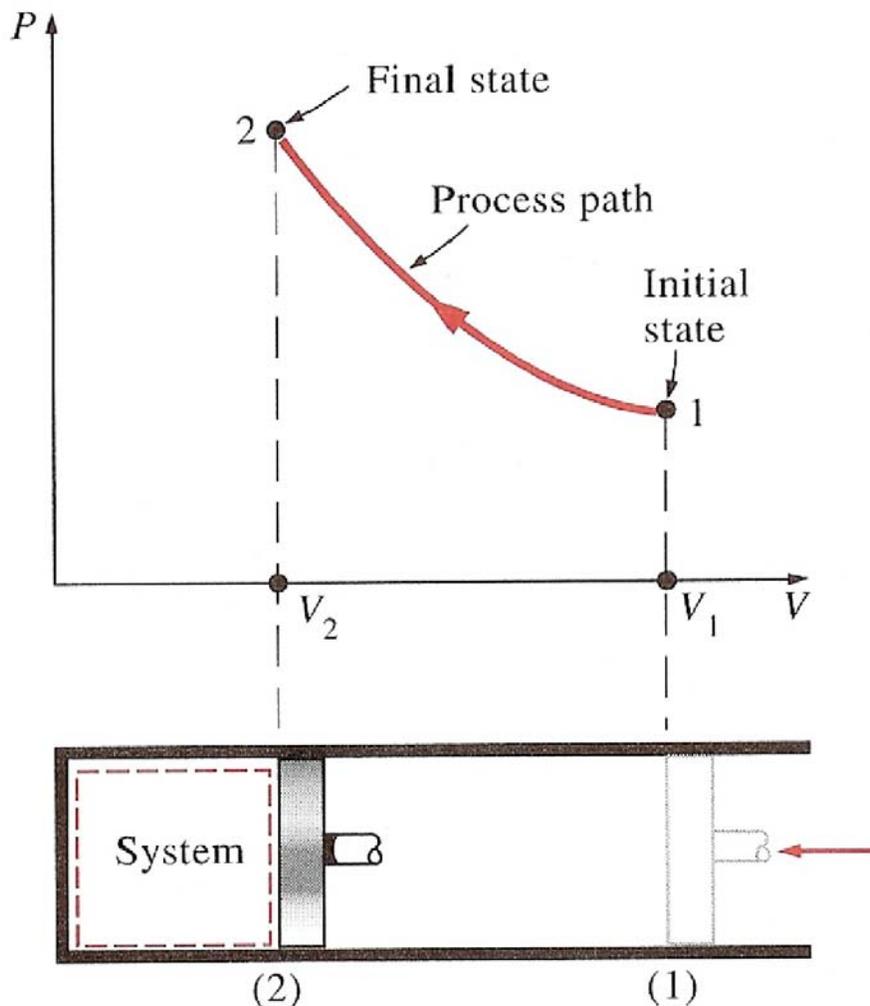
- A quasi-equilibrium process is an **idealized process** and is not a true representation of an actual process. But many actual processes closely approximate it, and they can be modeled as quasi-equilibrium with negligible error. Engineers are interested in quasi-equilibrium processes for two reasons. First, they are easy to analyze; second, work-producing devices deliver the most work when they operate on quasi-equilibrium processes.



Therefore, **quasi-equilibrium processes serve as standards to which actual processes can be compared.**

Process diagrams that are plotted by employing thermodynamic properties as coordinates are very useful in visualizing the processes. Some **common properties** that are used as coordinates are **temperature  $T$** , **pressure  $P$** , and **volume  $V$**  (or specific volume  $v$ ).

Figure below shows the  $P$ -  $V$  diagram of a compression process of a gas.



**Note:**

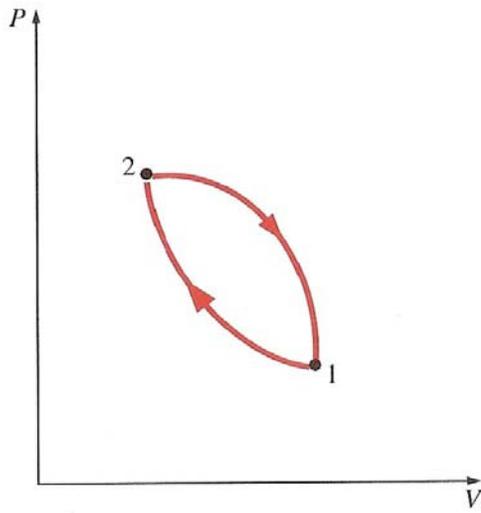
- The process path indicates a series of equilibrium states through which the system passes through during a process and has significance for quasi-equilibrium processes only.
- For non-quasiequilibrium processes, we are not able to specify the states through which the system passes during the process and so we cannot speak of a process path. A non-quasi-equilibrium process is denoted by a dashed line between the initial and final states instead of a solid line.

The prefix *iso-* is often used to designate a process for which a particular property remains constant.

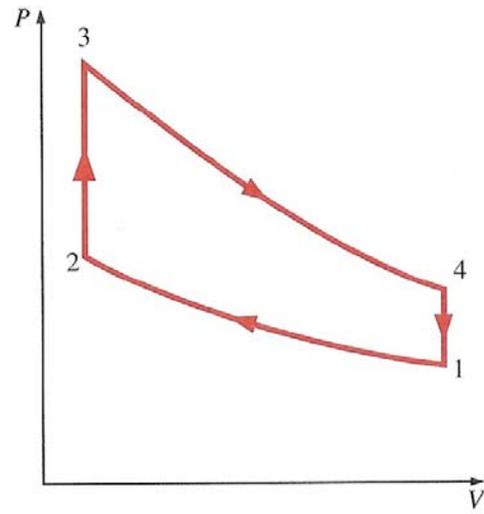
- An **isothermal process** is a process during which the temperature  $T$  remains constant,
- An **isobaric process** is a process during which the pressure  $P$  remains constant, and
- An **isochoric (or isometric) process** is a process during which the specific volume  $v$  remains constant.

A system is said to have undergone a **cycle** if it returns to its initial state at the end of the process. That is, **for a cycle the initial and final states are identical.**

Example of cycles:



(a) A two-process cycle



(b) A four-process cycle

# The state Postulate

The state of a system can be defined completely by the four observable macroscopic properties of matter known as the variables of state, namely pressure, volume, temperature and composition. How many properties are necessary to specify so that a state of a system is fully determined:

*The state of a simple compressible system is completely specified by two independent, intensive properties.*

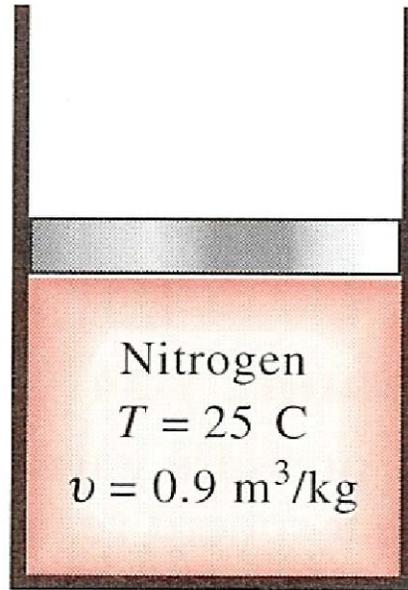
- A system is called a simple compressible system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects. These effects are due to external force fields and are negligible for most engineering problems.
- Otherwise, an additional property needs to be specified for each effect which is significant.

**Example:** If the gravitational effects are to be considered, for example, the elevation  $z$  needs to be specified in addition to the two properties necessary to fix the state.

The state postulate requires that the two properties specified be independent to fix the state.

- Two properties are independent if one property can be varied while the other one is held constant.

**Example:** Temperature and specific volume are always independent properties, and together they can fix the state of a simple compressible system.



**Note:** Temperature and pressure are independent properties for [single-phase systems](#), but are dependent properties for [multiphase systems](#). At sea level ( $P = 1\text{ atm}$ ), water boils at  $100^\circ\text{C}$ , but on a mountaintop where the pressure is lower, water boils at a lower temperature. That is,  $T = f(P)$  during a phase-change process; thus, temperature and pressure are not sufficient to fix the state of a two-phase system.

- The chosen independent variables are called the *state variables or variables of state* while the other properties which depend on them are called *state functions or functions of state*.
- There are two important properties of state functions or variables of state.
  1. Once we specify the state of a system by giving the values of all or a few of the state variables, e.g.  $P$ ,  $V$ ,  $T$ , and

composition, then all other properties such as mass  $m$ , density  $\rho$ , viscosity  $\eta$  and refractive index  $\mu$ , are fixed.

The relationship between the dependent and independent variables of state is known as **the equation of state**.

2. When the state of a system is altered, the change in any state function depends only on the initial and final state of the system, and not on how the change is brought about.

**Example:** When a gas is compressed from an initial pressure  $P_1$  to a final pressure  $P_2$  the change  $\Delta P$  in pressure is given by

$$\Delta P = P_2 - P_1.$$

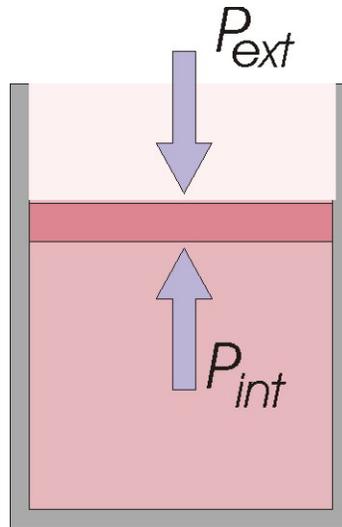
Only the initial and final values of the pressure determine  $\Delta P$ . Any intermediate values which  $\Delta P$  may have assumed in changing from  $P_1$  to  $P_2$  are immaterial.

# Reversible and Irreversible Paths

These two concepts are of fundamental importance in thermodynamics. Changes of state may be brought about along **reversible** or **irreversible paths**.

- A **reversible path** is one that may be followed in either direction. At any point the direction may be reversed by a small change in a variable such as the temperature or pressure.

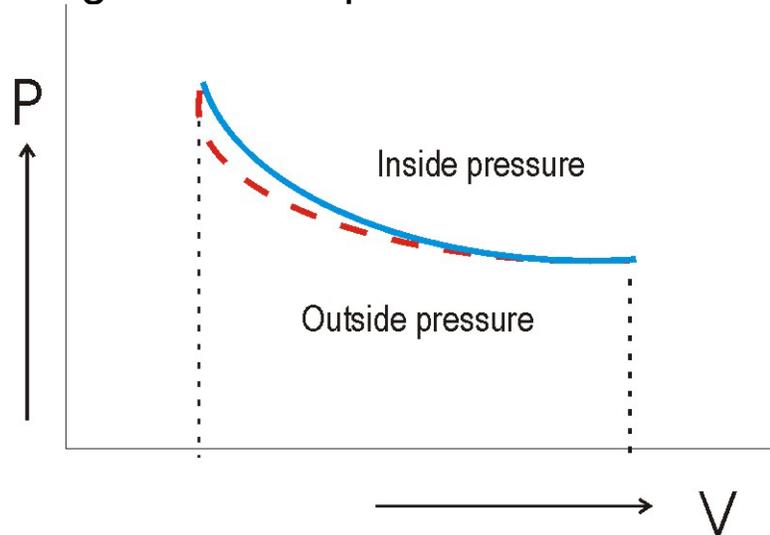
Example:



A cylinder containing a gas and that the cylinder has a piston that can move up or down exerting pressure on the gas.

- If the pressure exerted by the gas equals the external pressure, there is equilibrium. **At the equilibrium state, by a slight decrease in the piston pressure the gas can be made to expand; also by a slight increase of the piston pressure the gas can be made to contract.**
- Assume the gas is expanded by slowly decreasing the piston pressure so that **at all times it is very slightly smaller than the pressure exerted by the gas on the piston.**

A  $P$ -  $V$  diagram of this process is as shown below.



The smaller the difference between  $P_{int}$  and  $P_{ext}$ , the closer the red curve lies to the blue curve and the slower the rate at which the gas expands.

*In the idealized case where the two curves coincide, expansion takes an infinite time, because there is no pressure difference left to act on the piston.*

In this limiting case, expansion can be changed into compression by an infinitesimal increase in the outside pressure, and compression into expansion by an infinitesimal decrease in the outside pressure. Only under these circumstances is the expansion of the gas reversible.

Thus we can say that

- Reversible expansion of the gas is an idealized concept that can be carried out in theory only.
- Any actual expansion IS irreversible.
- A reversible process is generally an idealized concept

that represents the limit of a sequence of irreversible processes, for which the parameter changes required to reverse the direction become smaller and smaller. At the limit it proceeds infinitely slowly through a sequence of equilibrium states.