

CHAPTER 1: THERMODYNAMIC SYSTEMS: BASIC CONCEPTS

1.1 Introduction

The word “Thermodynamics” originates from its Greek roots (*therme*, heat; *dynamis*, force). As a subject it is concerned with quantification of *inter-relation* between energy and the *change of state* of any real world system. The extent of such change of state due to transfer of energy *to* or *from* the system is captured through the basic equations of thermodynamics which are derived starting from a set of fundamental observations known as “Laws of Thermodynamics”. The laws are essentially ‘postulates’ that govern the nature of interaction of real systems and energy. They are products of human experiential observations to which no exceptions have been found so far, and so are considered to be “laws”. The scope of application of the laws of thermodynamics ranges from the microscopic to the macroscopic order, and indeed to cosmological processes. Thus, all processes taking place in the universe, whether in non-living or living systems, are subject to the laws of thermodynamics.

Historically speaking, thermodynamics, is an extension of Newtonian mechanics which considered mechanical forces (or energy) as the agent of change of state of a body (anything possessing mass), the state being defined by its position and momentum with respect to a frame of reference. With the discovery steam power which propelled the so-called ‘Industrial Revolution’ of the 18th century, it became evident that not only the direct application of mechanical energy can change the state of a system, but that fluids themselves can act as reservoir of energy, which can be harnessed to effect changes in the real world to human advantage. It was this observation that laid the foundations of thermodynamics, which now constitutes a generalized way of understanding and quantifying *all* changes that occur during processes taking place in the universe as a result of application of energy in any form.

1.2 Thermodynamic System: Select Definitions

It may be evident from the foregoing introduction, that for the purpose of any thermodynamic analysis it is necessary to define a ‘system’. A *system*, in general, is any part of the universe which may be defined by a boundary which distinguishes it from the rest of the universe. Such a thermodynamic system is usually referred to as *control volume* as it would possess a volume and

would also contain a definite quantity of matter. The system boundary may be real or imaginary, and may change in shape as well as in size over time, i.e., increase or decrease.

A system can either be *closed* or *open*. A closed system does not allow any transfer of mass (material) across its boundary, while an open system is one which does. In either case energy transfer can occur across the system boundary in any of its various forms; for example, heat, work, electrical / magnetic energy, etc. However, for most real world systems of interest to chemical engineers the primary forms of energy that may transfer across boundaries are heat and work. In contrast to closed or open systems, a system which is enclosed by a boundary that allows neither mass nor energy transfer is an *isolated* system.

All matter *external* to the system constitutes the *surroundings*. The combination of the system and surroundings is called the *universe*. For all practical purposes, in any thermodynamic analysis of a system it is necessary to include only the immediate surroundings in which the effects are felt.

A very common and simple example of a thermodynamic system is a gas contained in a piston-and-cylinder arrangement derived from the idea of steam engines, which may typically

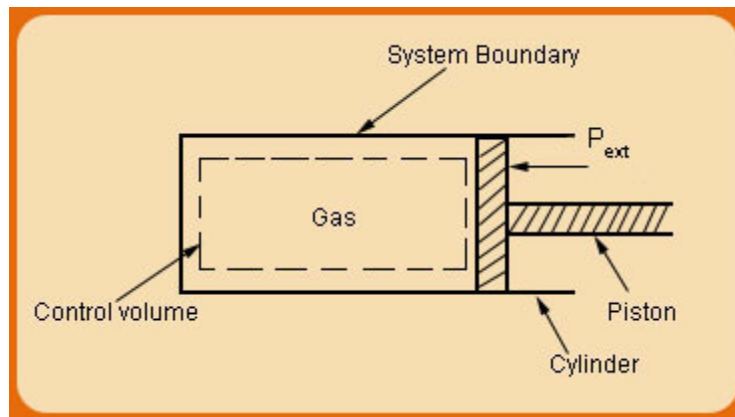


Fig. 1.1 Example of simple thermodynamic system

exchange heat or work with its surroundings. The dotted rectangle represents the 'control volume', which essentially encloses the mass of gas in the system, and walls (including that of the piston) form the boundary of the system. If the internal gas pressure and the external pressure (acting on the moveable piston) is the same, no net force operates on the system. If, however, there is a force imbalance, the piston would move until the internal and external pressures

equalize. In the process, some net work would be either delivered *to* or *by* the system, depending on whether the initial pressure of the gas is lower or higher than the externally applied pressure. In addition, if there is a temperature differential between the system and the surroundings the former may gain or lose energy through heat transfer across its boundary.

This brings us to a pertinent question: how does one characterize the changes that occur in the system during any thermodynamic process? Intuitively speaking, this may be most readily done if one could measure the change in terms of some properties of the system. A thermodynamic system is, thus, characterized by its *properties*, which essentially are *descriptors* of the *state* of the system. Change of state of a system is synonymous with change in the magnitude of its characteristic properties. The aim of the laws of thermodynamics is to establish a *quantitative* relationship between the energy applied during a process and the resulting *change* in the properties, and hence in the state of the system.

Thermodynamic properties are typically classified as *extensive* and *intensive*. A property which depends on the size (i.e., mass) of a system is an extensive property. The total volume of a system is an example of an extensive property. On the other hand, the properties which are independent of the size of a system are called intensive properties. Examples of intensive properties are *pressure* and *temperature*. The ratio of an extensive property to the mass or the property per unit mass (or mole) is called *specific* property. The ratio of an extensive property to the number of moles of the substance in the system, or the property per mole of the substance, is called the molar property.

$$\text{Specific volume (volume per mass or mole)} \quad V = V' / M \quad \dots(1.1)$$

$$\text{Molar Volume (volume per mole)} \quad V = V' / N$$

where,

$$V' = \text{total system volume (m}^3\text{)}$$

$$M = \text{total system mass (kg)}$$

$$N = \text{total moles in system (kg moles)}$$

1.3 Types of Energies associated with Thermodynamic Processes:

We know from the fundamentals of *Mechanics*, that the energy possessed by a body by virtue of its position or configuration is termed potential energy (PE). The potential energy of a body of mass m which is at an elevation z from the earth's surface (or any particular datum) is given by:

$$PE = mgz \quad \text{..(1.2)}$$

Where, g is the acceleration due to gravity ($= 9.81 \text{ m/s}^2$).

The energy possessed by a body by virtue of its motion is called the kinetic energy (KE). For a body of mass m moving with a velocity u , the kinetic energy of the body is given by:

$$KE = \frac{1}{2}mu^2 \quad \text{..(1.3)}$$

It follows that, like any mechanical body, a thermodynamic system containing a fluid, in principle may possess both PE and KE . It may be noted that both PE and KE are expressed in terms of macroscopic, directly measurable quantities; they, therefore, constitute macroscopic, mechanical forms of energy that a thermodynamic system may possess. As one may recall from the basic tenets of mechanics, PE and KE are inter-convertible in form.

It may also be noted that PE and KE are forms of energy possessed by a body as a whole by virtue of its *macroscopic* mass. However, matter is composed of atoms /molecules which have the capacity to translate, rotate and vibrate. Accordingly, one ascribes three forms intra-molecular energies: *translational*, *rotational* and *vibrational*. Further, energy is also associated with the motion of the electrons, spin of the electrons, intra-atomic (nucleus-electron, nucleus-nucleus) interactions, etc. Lastly, molecules are also subject to inter-molecular interactions which are electromagnetic in nature, especially at short intermolecular separation distances. All these forms of energy are *microscopic* in form and they cannot be readily estimated in terms of macroscopically measurable properties of matter. It needs to be emphasized that the microscopic form of energy is distinct from PE and KE of a body or a system, and are generally *independent* of the position or velocity of the body. Thus the energy possessed by matter due to the

microscopic modes of motion is referred to as the *internal energy* of the matter. The microscopic variety of energy forms the principal consideration in case of transformations that occur in a thermodynamic system. Indeed, as mentioned earlier, it is the realization that matter or fluids possessed useful form of microscopic energy (independent of macroscopic KE or PE) that formed the basis of the 18th century Industrial Revolution.

As we will see later, the majority of practical thermodynamic systems of interest are the ones that do not undergo change of state that entails significant change in its macroscopic potential and kinetic energies. Thus, it may be intuitively obvious that in a very general sense, when a thermodynamic system undergoes change of state, the attendant change in the internal energy is responsible for the energy leaving or entering the system. Such exchange of energy between a thermodynamic system and its surroundings may occur across the system boundary as either *heat* or *work* or both.

Thermodynamic Work:

Work can be of various forms: electrical, magnetic, gravitational, mechanical, etc. In general work refers to a form of energy transfer which results due to changes in the external *macroscopic* physical constraints on a thermodynamic system. For example, electrical work results when a charge moves against an externally applied electrical field. As we will see later, it is mechanical work that is most commonly encountered form in real thermodynamic systems, for example a typical chemical plant. In its simplest form, such work results from the energy applied to expand the volume of a system against an external pressure, or by driving a piston-head out of a cylinder against an external force. In both the last examples, work transfer takes place due to the application of a differential (or finite) force applied on the system boundary; the boundary either contracts or expands due to the application of such a force. In effect this results in the applied force acting over a distance, which results in mechanical energy transfer.

Consider the system in fig.1.2, where a force F acts on the piston and is given by pressure \times piston area. Work W is performed whenever this force translates through a distance.

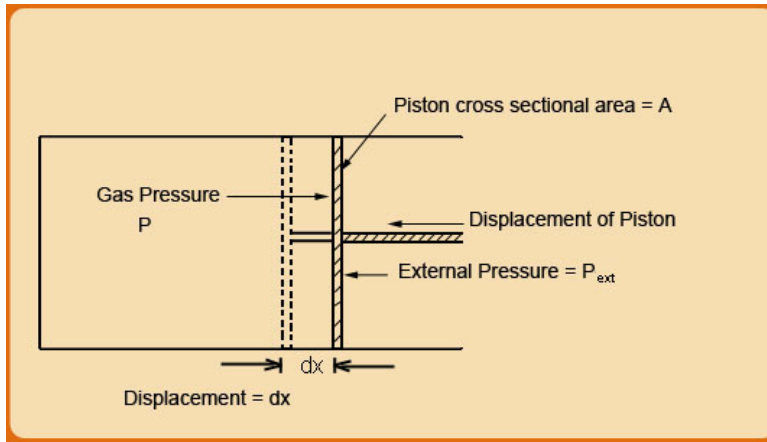


Fig. 1.2 Illustration of Thermodynamic Work

Thus for a differential displacement ' dx ' of the piston the quantity of work is given by the equation:

$$dW = Fdx \quad \text{..(1.4)}$$

Here F is the force acting along the line of the displacement x . If the movement takes place over a finite distance, the resulting work is obtained by integrating the above equation. By convention, work is regarded as *positive* when the displacement is in the same direction as the applied force and negative when they are in opposite directions. Thus, for the above example, the equation 1.4 may be rewritten as:

$$dW = -PA d(V' / A) \quad \text{..(1.5)}$$

If the piston area ' A ' is constant, then:

$$dW = -PdV' \quad \text{..(1.6)}$$

As may be evident from eqn. 1.6, when work is done on a system (say through compression) the volume decreases and hence the work term is positive. The reverse is true when the system performs work on the surroundings (through expansion of its boundary).

Heat

We invoke here the common observation that when a hot and a cold object are contacted, the hot one becomes cooler while the cold one becomes warmer. It is logical to argue that this need be due to transfer of ‘something’ between the two objects. The transferred entity is called *heat*. Thus, heat is that form of energy that is exchanged between system and its surrounding owing to a temperature differential between the two. More generally, heat is a form of energy that is transferred due to temperature *gradient* across space. Thus heat always flows down the gradient of temperature; i.e., from a higher to a lower temperature regions in space. In absence of such temperature differential there is no flow of heat energy between two points. Heat flow is regarded to be *positive* for a thermodynamic system, if it enters the latter and *negative* if it leaves.

Like work, heat is a form of energy that exists only in transit between a system and its surrounding. Neither work nor heat may be regarded as being possessed by a thermodynamic system. In a fundamental sense, the ultimate repositories of energy in matter are the atoms and molecules that comprise it. So after transit both work and heat can only transform into the kinetic and potential energy of the constituent atoms and molecules.

1.4 Thermodynamic Equilibrium

In general change of state of a thermodynamic system results from existence of gradients of various types *within* or *across* its boundary. Thus a gradient of pressure results in momentum or convective transport of mass. Temperature gradients result in heat transfer, while a gradient of concentration (more exactly, of *chemical potential*, as we shall see later) promotes diffusive mass transfer. Thus, as long as *internal* or *cross-boundary* gradients of any form as above exist with respect to a thermodynamic system it will undergo change of state in time. The result of all such changes is to annul the gradient that in the first place causes the changes. This process will continue till all types of gradients are nullified. In the ultimate limit one may then conceive of a state where all gradients (external or internal) are non-existent and the system exhibits no further changes. Under such a limiting condition, the system is said to be in a state of thermodynamic *equilibrium*. For a system to be thermodynamic equilibrium, it thus needs to also satisfy the criteria for mechanical, thermal and chemical equilibrium.

Types of Thermodynamic Equilibrium

A thermodynamic system may exist in various forms of equilibrium: *stable*, *unstable* and *metastable*. These diverse types of equilibrium states may be understood through analogy with a simple mechanical system as depicted in fig. 1.3 – a spherical body in a variety of gradients on a surface.

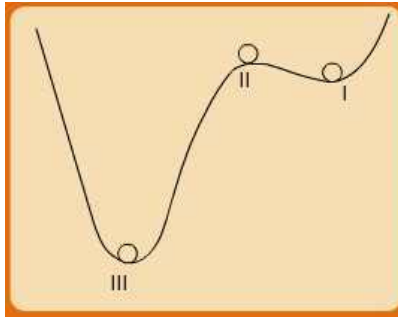


Fig. 1.3 Types of Mechanical Equilibrium

Consider the body to be initially in state 'I'. If disturbed by a mechanical force of a very small magnitude the body will return to its initial state. However, if the disturbance is of a large magnitude, the body is unlikely to return to its initial state. In this type of situation the body is said to be in *unstable* equilibrium. Consider next the state 'II'; even a very small disturbance will move the body to either positions 'I' or 'III'. This type of original equilibrium state is termed *metastable*. Lastly, if the body is initially in state 'III', it will tend to return to this state even under the influence of relatively larger disturbances. The body is then said to be in a *stable* equilibrium state. If 'E' is the potential energy of the body and 'x' is the effective displacement provided to the body in the vertical direction, the three equilibrium states may be described by the following equations:

$$\text{Stable Equilibrium: } \frac{\partial E}{\partial x} = 0; \quad \frac{\partial^2 E}{\partial x^2} > 0 \quad \dots(1.7)$$

$$\text{Unstable Equilibrium: } \frac{\partial E}{\partial x} = 0; \quad \frac{\partial^2 E}{\partial x^2} < 0 \quad \dots(1.8)$$

$$\text{Metastable Equilibrium: } \frac{\partial E}{\partial x} = 0; \quad \frac{\partial^2 E}{\partial x^2} = 0 \quad \dots(1.9)$$

The above arguments may well be extended to understand equilibrium states of thermodynamic systems, which are relatively more complex in configuration. The disturbances in such cases could be mechanical, thermal or chemical in nature. As we shall see later (section 6.3), for thermodynamic systems, the *equivalent* of (mechanical) potential energy is *Gibbs free energy*. The considerations of change of Gibbs free energy are required to understand various complex behaviour that a thermodynamic system containing multiple phases and components (either reactive or non-reactive) may display under the influence of changes brought about by exchange of energy across its boundary.

1.5 The Phase Rule

Originally formulated by the American scientist Josiah Willard Gibbs in the 1870's, the phase rule determines the number of independent variables that must be specified to establish the *intensive* state of *any* system at equilibrium. The derivation of the general phase rule is shown in chapter 6, but here we state it without proof:

$$F = 2 + N - \pi - r \quad \dots(1.10)$$

Here, F = degrees of freedom of the thermodynamic system in question; N = Number of components; π = number of co-existing phases, and r = number of independent reactions that may occur between the system components. For a non-reactive system, the phase rule simplifies to:

$$F = 2 + N - \pi \quad \dots(1.11)$$

In the most general sense a thermodynamic system may be multiphase and multi-component in nature. A phase is a form of matter that is homogeneous in chemical composition and physical state. Typical phases are solids, liquids and gases. For a multiphase system, interfaces typically demarcate the various phases, properties changing abruptly across such interfaces. Various phases can coexist, but they *must be in equilibrium* for the phase rule to apply. An example of a three-phase system at equilibrium is water at its triple point ($\sim 0^\circ\text{C}$, and 0.0061 bar), with ice, water and steam co-existing. A system involving one pure substance is an example of a single-component system. On the other hand mixtures of water and acetone have two chemically independent components.

The intensive state of a system at equilibrium is established when its temperature, pressure, and the compositions of all phases are fixed. These are therefore, regarded as phase-rule variables; but they are not all independent. The degrees of freedom derivable from the phase rule gives the number of variables which must be specified to fix all other remaining phase-rule variables. Thus, F means the number of intensive properties (such as temperature or pressure), which are independent of other intensive variables. For example, for a pure component gaseous system, phase rule yields *two* degrees of freedom. This implies that if one specifies temperature and pressure, all other intensive properties are then uniquely determined these two variables. Similarly for a biphasic system of a pure component – say water and steam – there is only one degree of freedom, i.e., either temperature or pressure may be specified to fix all other intensive properties of the system. At the triple point the degrees of freedom is zero, i.e., any change from such a state causes at least one of the phases to disappear.

1.6 Zeroth Law of Thermodynamics and Absolute Temperature

Thermometers with liquid working fluids are usually used for measurement of temperature. When such a device is brought in contact with a body whose temperature is to be measured, the liquid column inside the thermometer expands due to heat conducted from the body. The expanded length can be said to represent the degree of hotness in a somewhat *quantitative* manner.

The *Zeroth Law of Thermodynamics* states that if two bodies are in thermal equilibrium with a third body, then the two given bodies will be in thermal equilibrium with each other. The zeroth law of thermodynamics is used for measurement of temperature. In the Celsius temperature scale, two fixed points – ice point and steam point – are used to devise the scale. Thus, the freezing point of water (at standard atmospheric pressure) is assigned a value of zero, while the boiling point of pure water (at standard atmospheric pressure) denoted as 100. However for introducing detail, the distance between the two end points of the liquid column marks is arbitrarily divided into 100 equal spaces called *degrees*. This exercise can be extended both below zero and above 100 to expand the range of the thermometer.

The entire exercise can be carried out with any other substance as the thermometric fluid. However, for any specific measured temperature the extent of expansion of the liquid column

will vary with the thermometric fluid as each fluid would expand to different extent under the influence of temperature. To overcome this problem, the *ideal gas* (see next section) has been arbitrarily chosen as the thermometric fluid. Accordingly, the temperature scale of the SI system is then described by the Kelvin unit ($T^{\circ}K$). Its relation to the Celsius ($t^{\circ}C$) scale is given by:

$$T(^{\circ}K) = 273.15 + t(^{\circ}C)$$

Thus the lower limit of temperature, called absolute zero on the Kelvin scale, occurs at $-273.15^{\circ}C$.

1.7 The Ideal Gas

In the foregoing discussions we have pointed out that a thermodynamic system typically encloses a fluid (pure gas, liquid or solid or a mixture) within its boundary. The simplest of the intensive variables that can be used to define its state are temperature, pressure and molar volume (or density), and composition (in case of mixtures). Let us consider for example a pure gas in a vessel. As mentioned above, by phase rule the system has two degrees of freedom. It is an experimentally observed phenomenon that in an equilibrium state the intensive variables such as pressure, temperature and volume obey a definitive inter-relationship, which in its simplest form is expressed mathematically by the Boyle's and Charles's laws. These laws are compositely expressed in the form of the following equation that is said to represent a behaviour termed as *Ideal Gas Law*:

$$PV = RT \quad \text{..(1.12)}$$

Where, P = system pressure (say, Pa = N/m²), T = system temperature (in ⁰K), V = gas molar volume (mol/m³) and, R = universal gas constant (= 8.314J / mol⁰K). The above relation is said to represent an equation of state, and may alternately be written as:

$$PV^t = nRT \quad \text{..(1.13)}$$

Where, V^t = total system volume; n = total moles of gas in the system. Units of typical thermodynamic variables and that of the gas constant are provided in **Appendix I**.

The equations (1.10) and (1.11) are also termed *Equations of State* (EOS) as they relate the variables that represent the thermodynamic state of a system in the simplest possible manner. It is

obvious that the EOS indicates that if one fixes temperature and pressure the molar volume is automatically fixed as well, i.e., the latter is not an independent property in such a case.

The ideal gas law is a limiting law in the sense that it is valid primarily for gaseous systems at low pressure, strictly speaking at pressure far below the atmospheric. However, for practical purposes it is observed to remain valid at atmospheric pressures as well. As we shall see later, the ideal gas law serves as a very useful approximation as well as a datum for estimation of both the volumetric (chapter 2) as well as all other real fluid thermodynamic properties of practical interest (chapter 5, for example).

1.8 State and Path Dependent Thermodynamic Variables

Consider a gas at a certain temperature and a pressure within a piston-cylinder assembly (for example, fig. 1.2), which for arguments' sake we may assume to be isolated. If the piston position is held fixed at this point the gas state is said to be characterized by the temperature and the pressure and its corresponding volume. In its simplest form the relationship between these intensive variables may be described by (say) eqn. 1.12. Consider next that the gas is compressed by application of an extra force on the piston so that it moves inwards into the cylinder. This motion will continue till it reaches a point when the internal gas pressure equals the externally applied pressure on the piston. If there is no further increase in the force applied to the piston, the gas will also attain a new equilibrium state wherein the pressure and temperature would attain a new set of values. If, on the other hand the extra applied pressure is removed and the gas reverts to the earlier state the original temperature and pressure (and, of course volume) is restored. Extending this argument, in general, if the gas is heated or cooled, compressed or expanded, and then returned to its initial temperature and pressure, its intensive properties are restored to their initial values. It is evident, therefore, that such properties do not depend on the past history of the fluid or on the path by which it reaches a given state. They depend only on present state, irrespective of how they are attained. Such quantities are thus defined as *state variables*. Mathematically, this idea may be expressed as follows:

$$\int_{T_1}^{T_2} dT = T_2 - T_1 = \Delta T; \int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P; \int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V \quad \dots(1.14)$$

The changes in the above intensive properties depend only on the initial and final states of the system. They constitute point functions and their differentials are exact.

Let us next consider the case of thermodynamic work as defined by eqn. 1.6. It may be readily evident that if one can depict the exact variation of pressure and volume during a change of state of a system on a two-dimensional P-V graph, the area under the curve between the initial and final volumes equal the work associated with process. This is illustrated in fig. 1.4.

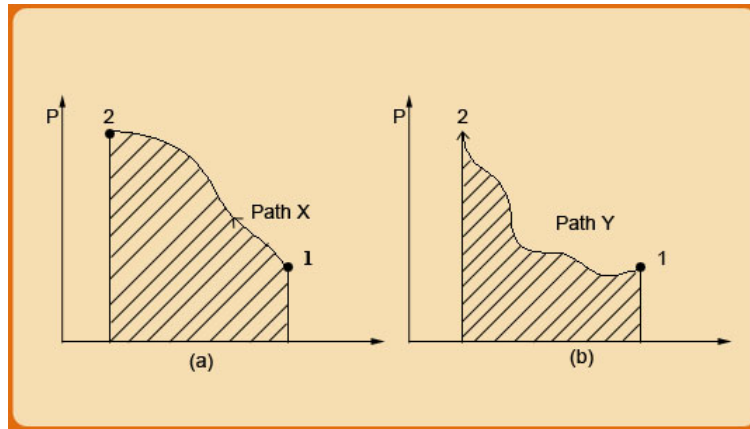


Fig. 1.4: Depiction of thermodynamic work on P-V plot

As shown in the above figure the work associated with a thermodynamic process clearly in dependent on the path followed in terms of P and V. It follows that if one were to go from state '1' to '2' by path X and then return to '1' by path Y the work in the two processes would differ and so one would not be giving and taking work out of the system in equal measure. An entity such as P-V work is, therefore, described as a *path variable*, and therefore is not directly dependent on the state of the system. This is obviously distinctive from the case of state variables such as P and V (and T). Thus, for quantifying work, one cannot write an equation of the same type as (1.12). The more appropriate relation for such variables may be written as:

$$\int_1^2 \delta W = W_{12} \quad \text{..(1.15)}$$

It may be pointed out that the notation δ is used to depict differential quantum of work in order to distinguish it from the differential quantity of a state variable as in eqn. 1.14. We demonstrate in chapter 3 that, like P-V work, heat transferred between a system and the surrounding is also a path variable and so one may also write:

$$\int_1^2 \delta Q = Q_{12} \quad \text{..(1.16)}$$

Heat and work are therefore quantities, and not properties; they account for the energy changes that occur in the system and surroundings and appear only when changes occur in a system. Although time is not a thermodynamic coordinate, the passage of time is inevitable whenever heat is transferred or work is accomplished.

1.9 Reversible and Irreversible Thermodynamic Processes

We have seen above that in absence of any gradients (or motive forces) a thermodynamic system continues to remain in a state of equilibrium. Obviously, if a disturbance (i.e., mechanical, thermal or chemical potential gradient) is impressed upon such a system it will transit from its initial state of equilibrium. However, as it moves away from its initial state the originally applied gradients will diminish progressively in time, and ultimately when they are reduced to infinitesimal levels the system will attain a new equilibrium state. A question arises here as to the nature of the process of change: if the initially impressed disturbances are reversed in direction (not magnitude) can the system return to its first equilibrium state back through the same intermediate states as it went through during the first phase of change? If that happens we depict the process as *reversible*, if not, then the process is termed *irreversible*.

It is necessary to understand the concept of *reversibility* of thermodynamic process more deeply as it is an *idealized* form of process of change and without that consideration it is not possible to represent or understand real thermodynamic processes, which are generally irreversible in nature.

What makes a thermodynamic process reversible? To answer the question let us again take the example of the simple gas-in-piston-and-cylinder system as shown in figure 1.5.

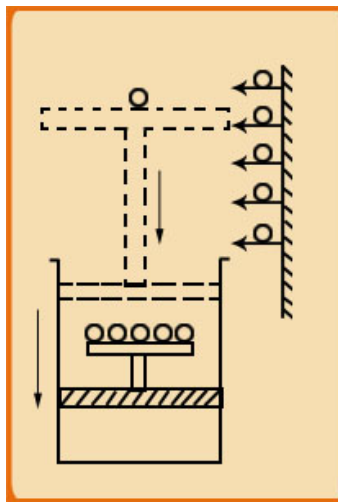


Fig. 1.5 Illustration of Reversibility of Thermodynamic Process

The system initially contains a pure gas whose pressure equals that exerted externally (due to piston weight), and its temperature is the same as that of the environment. Thus it is at equilibrium (say state 'A') as there are no mechanical, thermal or chemical concentration gradients in the system. Now a ball of a known weight is transferred on to the piston, whereupon the external pressure exceeds the gas pressure and the piston moves down to attain a new lower position at which point the gas has been compressed and its pressure once again equals that applied externally. At the same time if any differentials in temperature (within or across the system boundary) and internal concentration distribution of the gas molecules result due to the applied mechanical imbalance, heat and mass transfer will take place simultaneously until these gradients are also annulled and the system eventually comes to rest at a new equilibrium point (say, 'B'). We say that the system has undergone a process due to which its state has changed from A to B. Note that this process can be continued as long as desired by sequentially transferring more and more balls individually onto the piston and impelling the system to change in steps till say the end point state 'X'. The question that one may pose: is the process A-X reversible? That is, if one reversed all the initial steps of sequentially moving each ball off the piston so as to reach from state 'X' back to 'A' would all the interim states of the system as defined by temperature, pressure and volume at any point be identical to those obtained during the process of going from A to X?

To answer this question we need to understand the process occurring in the system a little more deeply. Consider first that a mass m_o is suddenly moved onto the piston from a shelf (at the same level). The piston assembly accelerates downwards, reaching its maximum velocity at the point where the downward force on the piston just balanced by the pressure exerted by the gas in the cylinder. However, the initial momentum of the plunging piston would carry it to a somewhat lower level, at which point it reverses direction. If the piston were held in this position of maximum depression brought about by transfer of the mass m_o , the decrease in its potential-energy would very nearly equal the work done on the gas during the downward movement. However, if unrestrained, the piston assembly would oscillate, with progressively decreasing amplitude, and would eventually come to rest at a new equilibrium position at a level below its initial position.

The oscillation of the piston assembly ceases because it is opposed by the viscosity of the gas, leading to a gradual conversion of the work initially done by the piston into heat, which in turn is converted to internal energy of the gas.

All processes carried out in finite time with real substances are accompanied in some degree by dissipative effects of one kind or another. However, one may conceive of processes that are free of dissipative effects. For the compression process depicted in Fig. 1.4, such effects issue from sudden addition of a finite mass to the piston. The resulting imbalance of forces acting on the piston causes its acceleration, and leads to its subsequent oscillation. The sudden addition of smaller mass increments may reduce but does not eliminate this dissipative effect. Even the addition of an infinitesimal mass leads to piston oscillations of infinitesimal amplitude and a consequent dissipative effect. However, one may *conceive* of an ideal process in which small mass increments are added one after another at a rate such that the piston movement downwards is continuous, with minute oscillation only at the end of the entire process.

This *idealized* case derives if one imagines of the masses added to the piston as being infinitesimally small. In such a situation the piston moves down at a uniform but infinitesimally slow rate. Since the disturbance each time is infinitesimal, the system is always infinitesimally displaced from the equilibrium state both internally as well with respect to external surroundings. Such a process which occurs very slowly and with infinitesimal driving forces is called a *quasi-static* process. To freeze ideas let us assume that the gas in the system follows the ideal gas law. Thus the pressure, temperature and volume at any point during the process are related by eqn. 1.12 (or 1.13). Now imagine that the process of gradual compression is reversed by removing each infinitesimal mass from the piston just as they were added during the forward process. Since during the expansion process also the system will always be differentially removed from equilibrium state at each point, the pressure, temperature and volume will also be governed by the relation 1.12. Since the latter is an equilibrium relationship and hence a unique one, each interim state of the system would exactly converge during both forward and backward progress of system states. Under such a condition the process of compression is said to be thermodynamically reversible. Both the system and its surroundings are ultimately restored to their initial conditions. In summary, therefore, if both the system and its surroundings can be restored to their respective

initial states by reversing the direction of the process, then the process is said to be reversible. If a process does not fulfill this criterion it is called an *irreversible* process.

It need be emphasized that a reversible process need be a quasi-static process, and that the origin of irreversibility lie in the existence of dissipative forces in real systems, such as viscosity, mechanical friction. These forces degrade *useful* work irreversibly into heat which is not re-convertible by simply reversing the direction of the process, since during a reverse process a fraction of useful work will again be lost in the form heat in overcoming the dissipative forces. Thus, in the above example system if there were no viscous or frictional forces opposing the motion of the piston the processes of compression and expansion would be reversible, provided of course all changes occur under infinitesimal gradients of force. The argument in the last sentence may be extended to state that if changes are brought about by finite gradients (in this case finite difference in force across the piston, associated with addition of finite mass to the piston), the process would necessarily be irreversible. This is because finite gradients will force the system to traverse through non-equilibrium interim states, during which the pressure, temperature and volume will not be constrained by a unique relationship such as eqn. 1.12, which holds for equilibrium states. Indeed, it would not be possible to define the non-equilibrium states in terms of a single temperature or pressure, as there would be internal gradients of these variables during processes induced by finite force imbalances across the system boundary. These very same considerations would apply for the reverse process of expansion as well, if it occurs under finite mechanical gradients. So in general during such processes it would not be possible to ascribe unique intensive properties to interim states during a change, and hence the forward and reverse “paths” would not coincide as they would if the process occurs under quasi-static conditions.

An additional point that obtains from the above considerations is that only under reversible conditions can one calculate the thermodynamic work by integrating eqn. 1.6, since at all points during the process the variables P, V and T are always uniquely related by the eqn. 1.12. Clearly if the process were occurring under irreversible conditions no such relation would hold and hence the calculation of the thermodynamic work would not be possible through a simple integration of eqn. 1.6.

The foregoing discussion has used the example of a single-phase closed-system, where compression and expansion processes are induced by gradients of mechanical force across the system boundary. There are, however, many processes which occur due to potential gradients other than mechanical forces. For example, heat flow is induced by temperature differences, electromotive force gradients lead to flow of electricity, and chemical reactions take place as there is a difference between the chemical potential of reactants and products. In general, it may be shown that all such processes brought about by potential gradients of various kinds would tend to reversibility if the gradients are themselves infinitesimal. For example, heat transfer across the boundary of a thermodynamic system would be reversible if the difference across it is of a differential amount ' dT ', and so on.

1.10 Significance of Chemical Engineering Thermodynamics: Process Plant Schema

Before we conclude the present chapter it would be appropriate to obtain a brief preview of the scope and utility of the principles of thermodynamics insofar as application to real world processes is concerned. Although based on relatively *abstract* principles, the laws of thermodynamics provide the fundamental *constraints* under which all *real* world processes take place. The ultimate application of the knowledge of the core principles of chemical engineering is in the design of a chemical process plant. Engineering thermodynamics constitutes one of the principal elements of such knowledge. Typically such a plant converts a set of raw materials to a desired product through a variety of steps that are schematically represented by Fig. 1.6.

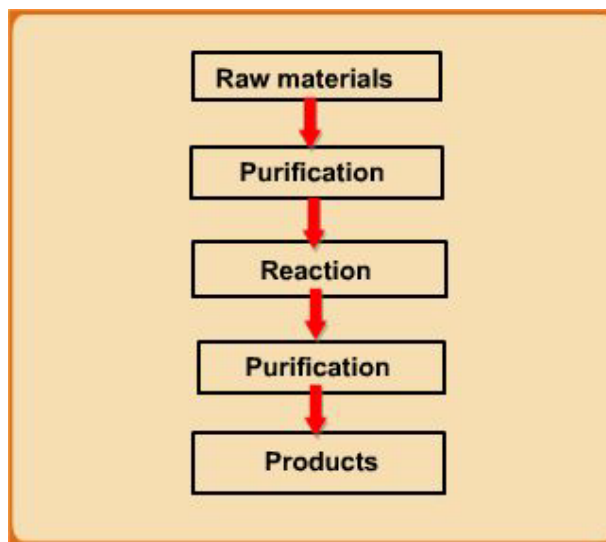


Fig. 1.6 Chemical Process Plant Schema

The raw materials most often are mixtures which need to be purified to obtain the right composition required for conversion to products. A wide variety of separation processes are available for carrying out such purification; examples include distillation, liquid-liquid extraction, precipitation from solutions, crystallization, etc. Practically all such separation processes involve generation of two or more phases, in one of which the desired raw material components are *preferentially* concentrated, which is then used to recover the substances in a relatively purer form. For a typical large scale chemical plant the separation process equipments may constitute more than half of the total capital investment.

The chemical reactor forms the “heart” of a chemical plant. It is here that once the feed materials are available in the right proportions (and compositions) they are reacted to yield the product. Obtaining the desired product requires an optimal choice of conditions under which the reactor may be operated. However, the product formed is very rarely obtained in a pure form. This is because typically the feed is never fully converted to product molecules and therefore the stream exiting the reactor is not a pure substance. In addition it is usually a common phenomenon that the intended chemical reaction is accompanied by often more than a single side reaction. The latter leads to the formation of side products, which results in “contamination” of the final product. Therefore, it is usually required to subject the reactor exit stream to another round of purification to obtain a product with the desired specifications of the product.

With regards to all such processes of purification and reaction, the laws of thermodynamics play a very fundamental role: they allow the calculation of the *principal* entities that form the basis of design and operation of process plants:

1. The *maximum degree of purification* that is possible under a given set of processing conditions
2. The *maximum degree of conversion* possible under the reaction conditions
3. The *optimal operating conditions* for separation and reaction processes
4. The *total energy required* to achieve the intended degree of separation and reaction, and therefore the plant energy load

The calculation of the above parameters tends to constitute 50-70% of the computational load encountered during the stage of basic process plant design. Thus, the principles of chemical

engineering thermodynamics is one of the mainstays of knowledge needed to realize the goal of plant design and operation.