

# **Department of Chemical Engineering**

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**College of Engineering**

**KNUST**

**CHE 253**

## **CHEMICAL ENGINEERING THERMODYNAMICS I**

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**2. ENERGY AND THE FIRST LAW OF THERMODYNAMICS****Objectives**

- Understand the concept of energy conservation and transformation.
- Discuss the first law of thermodynamics.
- Explain the application of the first law of thermodynamics to open, closed systems and non-flow processes.

**2.0 INTRODUCTION**

Energy is simply defined as the capacity to do work. Energy is expended in agriculture for land clearing, planting, plant protection, harvesting and processing of produce; energy in the form of petrol and diesel oil is required for automobiles and farm tractors; energy in the form of sunshine is required to dry agricultural produce; nuclear energy is used to generate electricity. In whatever form of application, the essential practical characteristic of energy is that it can be transformed from one form to another and transferred between systems by work and heat transfer. Note that the total amount of energy is conserved in all transformations and transfers. The purpose of this chapter is to organize the above ideas into suitable forms for engineering analysis.

**2.1 ENERGY TRANSFER BY WORK**

The work  $W$  done by, or on, a system evaluated in terms of macroscopically observable forces and displacements is

$$W = \int_{s_1}^{s_2} F_s \cdot ds \quad (2.1)$$

A particular interaction is categorized as work interaction if it satisfies the following criterion:

Work is done by a system on its surroundings if the sole effect on everything external to the system could have been the raising of a weight. Note that the raising of a weight is, in effect, force acting through a distance. The test of whether a work interaction has taken place is not that the elevation

of a weight has actually taken place, or that a force has actually acted through a distance, but that the sole effect could have been an increase in the elevation of a weight.

Work is a means of transferring energy. Accordingly, the term work does not refer to what is being transferred between systems or what is stored within the system. Energy is transferred and stored when work is done.

### 2.1.1 Sign convention and notation

$W > 0$ : work is done on the system

$W < 0$ : work is done by the system

The value of  $W$  depends on the details of the interactions taking place between the system and surroundings during a process and not just the initial and the final states. Hence, work is not a property of a system and its differential is inexact and it is expressed as  $\delta W$ , but the differential of every property is exact and is represented by a total derivative.

### 2.1.2 Expansion or Compression Work

Let us evaluate the work done by the closed system shown in Fig 2.1 consisting of a gas (or liquid) contained in a piston-cylinder assembly as the gas expands. During the process the gas pressure exerts a normal force on the piston. Let  $p$  denote the pressure acting at the interface between the gas and the piston. The force exerted by the gas on the piston is simply the product  $pA$ , where  $A$  is the area of the piston face. The work done by the system as the piston is displaced a distance  $dx$  is

$$\delta W = - p A dx = - p dV \quad (2.2)$$

Since  $dV$  is positive when the volume increases, the work at the moving boundary is negative when the gas expands. For compression,  $dV$  is negative, and so the work done from Eq. 2.2 is positive. For a change in volume from  $V_1$  to  $V_2$ , the work is obtained by integrating Eq. 2.2.

$$W = - \int_{V_1}^{V_2} p dV \quad (2.3)$$

Although Eq. 2.3 is derived for the case of a gas (or liquid) in a piston-cylinder assembly, it is applicable to systems of any shape provided the pressure is uniform with position over the moving boundary.

### 2.1.3 Work in Quasi-equilibrium Expansion or Compression processes

The quasi-static work given by equation (2.3) can be obtained from a graph of the process on a  $p$ - $V$  diagram as shown in Fig. 2.1. The work done  $W$  is the area under the curve on the  $p$ - $V$  diagram.

The curve is obtained by plotting the variation of pressure with volume during the process and it depends on the details of the process as defined by the particular curve and not just on the end states hence work is not a property.

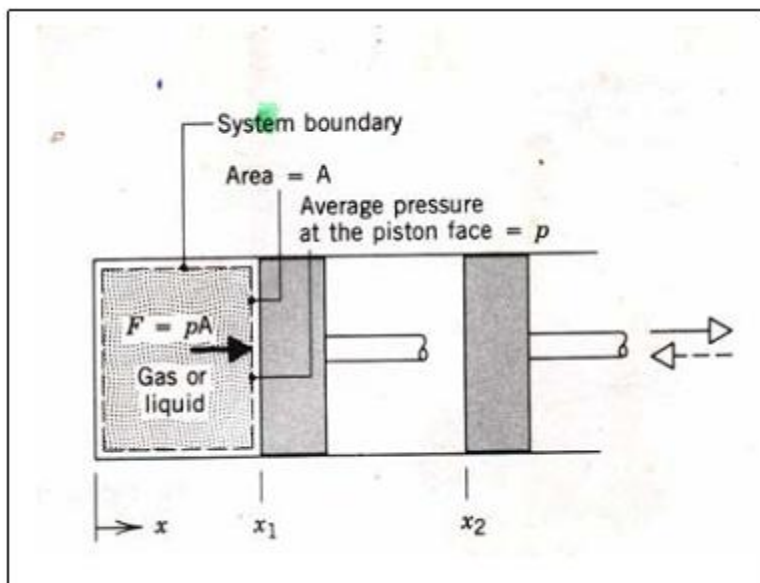


Fig.2.1 Expansion or compression of a gas or liquid

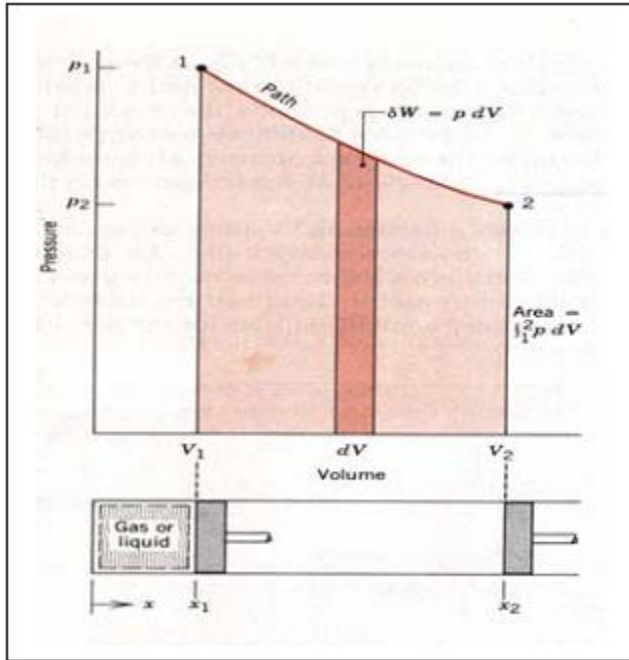


Fig. 2.2 Work of quasi-equilibrium process

The relationship between pressure and volume during an expansion or compression process also can be described analytically. An example is provided by the expression,  $pV^n = \text{constant}$  where the value of  $n$  is a constant for the particular process. A quasi-equilibrium process described by such an expression is called a polytropic process.

Note that

$$W = -\int_{V_1}^{V_2} p dV = -\int_{V_1}^{V_2} \frac{\text{constant}}{V^n} dV = -\text{constant} \left( \frac{V_2^{1-n} - V_1^{1-n}}{1-n} \right) \quad (2.4)$$

The constant in this expression can be evaluated at either end state: i.e.  $\text{constant} = p_1 V_1 = p_2 V_2$ .

The work expression then becomes

$$W = -\frac{(p_2 V_2^n) V_2^{1-n} - (p_1 V_1^n) V_1^{1-n}}{1-n} = \frac{p_2 V_2 - p_1 V_1}{n-1} \quad (2.5)$$

This expression is valid for all values of  $n$  except  $n=1$ . The case  $n=0$  is also treated under special cases.

#### 2.1.4 Special cases of the polytropic process

(a) The case of  $n=1$ : In this case, the pressure-volume relationship is constant.

The work done is

$$W = -\text{constant} \int_{V_1}^{V_2} \frac{dV}{V} = -(\text{constant}) \ln \frac{V_2}{V_1} = -(p_1 V_1) \ln \frac{V_2}{V_1} \quad (2.6)$$

(b) The case of  $n = 0$ : The pressure-volume relation reduces to  $\text{constant} = p$ , and the integral becomes

$$W = -p(V_2 - V_1) \quad (2.7)$$

(c) The pressure-volume relation for some processes may also be of the form  $p = aV + b$ .

The work expression, in this case, is given by

$$W = - \int_{V_1}^{V_2} p dV = - \int_{V_1}^{V_2} (aV + b) dV = - \left[ a \frac{V^2}{2} + bV \right]_{V_1}^{V_2} \quad (2.8)$$

By inserting the upper and lower limits into Eq. 2.8, the work done is evaluated. It can be shown that the expression for the work done reduces to

$$W = - \left( \frac{p_1 + p_2}{2} \right) (V_2 - V_1) \quad (2.9)$$

where the subscripts 1 and 2 refer to the initial and final states respectively. The latter expression is equivalent to the area under the p-V diagram for the process 1-2.

It must be noted that in whatever process, the work done can be evaluated as the area under the p-V diagram. The area interpretation of work in a quasi-equilibrium expansion or compression process allows for a simple demonstration of the idea that work depends on the process and therefore it is not a property. This can be confirmed with reference to Fig. 2.3.

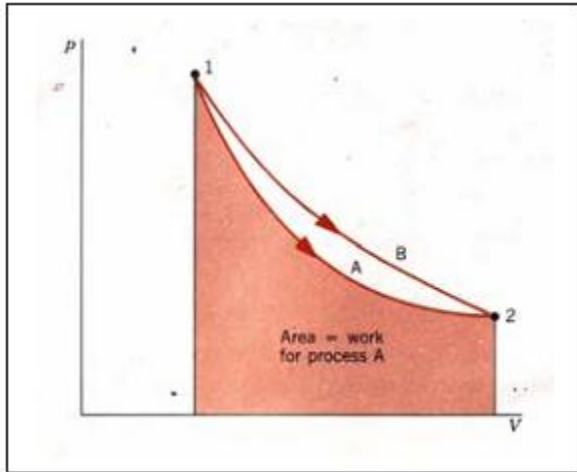


Fig. 2.3 Illustration that work depends of process

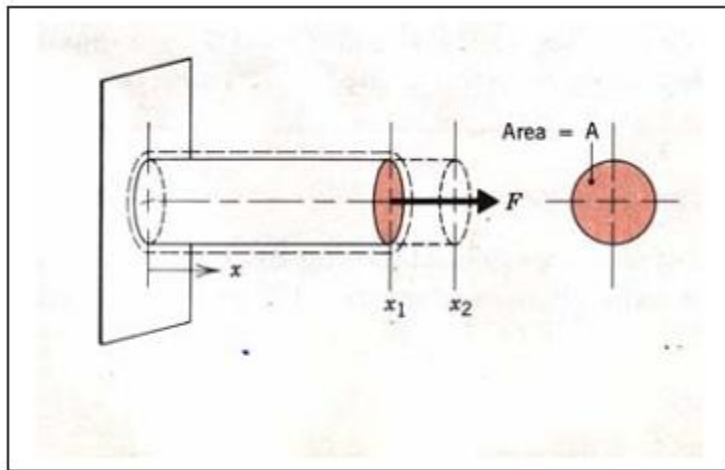


Fig. 2.4. Elongation of solid bar

**Extension of a Solid Bar:** Consider a system of a solid bar, as shown in Fig. 2.4. The bar is fixed at  $x = 0$ , and a force  $F$  is applied at the other end. The force  $F = \sigma A$ , where  $A$  is the cross-sectional area of the bar and  $\sigma$  the normal stress acting at the end of the bar. The work done as the end of the bar moves a distance  $dx$  is given by

$$\boxed{\delta W = +\sigma A dx} \quad (2.10)$$

The plus sign is required because work is done on the bar when  $dx$  is positive.

**Power Transmitted by a shaft:** Consider a shaft rotating with angular velocity  $\omega$  and exerting a torque  $\tau$  on its surroundings. The torque can be expressed in terms of a tangential force  $F_t$  and radius  $R$ :  $\tau = F_t R$ . The velocity at the point of application of the force is  $V = R\omega$ , where  $\omega$  is in radians per unit time.

The rate of energy transfer by work is called power and is denoted by  $\dot{W}$ . The rate of energy transfer by work is the product of the force and the velocity at the point of application of the force

$$\dot{W} = F \cdot V \quad (2.11)$$

Therefore, the expression for the power transmitted from the shaft to the surroundings is given by

$$\dot{W} = -F_t V = -(\tau / R)(R \omega) = -\tau \omega \quad (2.12)$$

A related case involving a gas stirred by a paddle wheel is shown in Fig. 2.5.

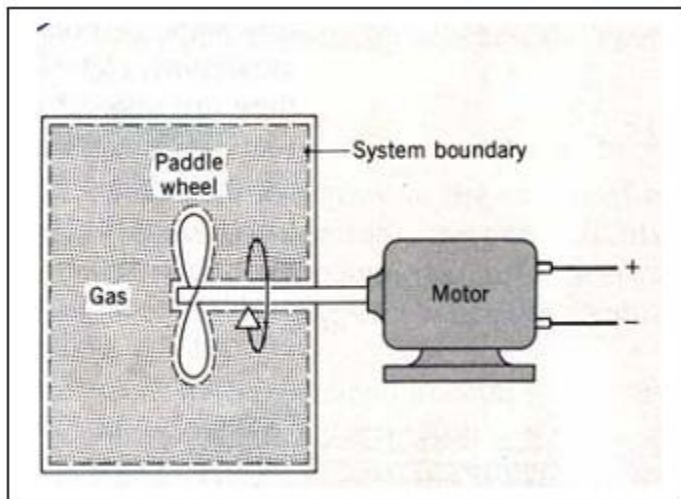


Fig. 2.5. Power transmitted to a gas by a paddle wheel

## 2.2 ENERGY TRANSFER BY HEAT

The quantity denoted by  $Q$  accounts for the amount of energy transferred to a system during a process by means other than work. Such an energy transfer is induced only as a result of a temperature difference between the system and its surroundings and occurs only in the direction of decreasing temperature. This means of energy transfer is called energy transfer by heat.

The symbol  $Q$  denotes an amount of energy transferred across the boundary of a system in a heat interaction with the system's surroundings. Heat transfer into a system is taken to be positive, and heat transfer from the system is taken as negative.

### 2.2.1 Sign convention for $Q$

$Q > 0$ : heat transfer to the system



$Q < 0$ : heat transfer from the system

Like work, heat is not a property and its differential is  $\delta Q$ . The amount of energy transfer by heat for a process is given by the integral

$$Q = \int_1^2 \delta Q = Q_{12} \quad (2.13)$$

## 2.3 JOULE'S EXPERIMENT

The present-day understanding of heat and its relation to work developed during the last half of the nineteenth century. Crucial to this understanding were the many experiments of James P. Joule (1818-1889), carried out in the cellar of his home near Manchester, England, during the decade following 1840.

In their essential elements Joule's experiments were simple enough, but he took elaborate precautions to insure accuracy. In the most famous series of measurements, he placed known amounts of water, oil, and mercury in an insulated container and agitated the fluid with a rotating stirrer. The amounts of work done on the fluid by the stirrer were accurately measured, and the temperature changes of the fluid were carefully noted. He found for each fluid that a fixed amount of work was required per unit mass for every degree of temperature rise caused by the stirring, and that the original temperature of the fluid could be restored by the transfer of heat through simple contact with a cooler object. Thus Joule was able to show conclusively that a quantitative relationship exists between work and heat and, therefore, that heat is a form of energy.

## 2.4 FIRST LAW OF THERMODYNAMICS

Under this section, the various forms of the First Law Thermodynamics (Non flow energy equation, steady flow energy equation and the general energy equation) will be studied and applied to solve thermodynamic problems.

In application of the first law to a given process, the sphere of influence of the process is divided into two parts, the *system* and its *surroundings*. *In its most basic form, the first law requires:*

$$\Delta(\text{Energy of System}) + \Delta(\text{Energy of Surroundings}) = 0 \quad (2.14)$$

where the difference operator " $\Delta$ " signifies finite changes in the quantities enclosed in parentheses. In the thermodynamic sense, heat and work refer to energy *in transit across the boundary* which divides the system from its surroundings. These forms of energy are not stored, and are never *contained in* a body or system. Energy is stored in its potential, kinetic, and internal forms; these reside with material objects and exist because of the position, configuration, and motion of matter.

#### 2.4.1 First Law of Thermodynamics for Closed Systems

Because of the historical association of the First Law with heat engine cycles, namely cycles producing a net amount of work on the surroundings, the law is usually stated in the form:

When any closed system is taken through a cycle, the net work delivered to the surroundings is proportional to the net heat taken from the surroundings.

However, the converse is also true, namely:

When a closed system is taken through a cycle, the work done on the system by its surroundings is proportional to the net heat delivered to the surroundings.

In its latter form, the statement refers to heat pump and refrigerator cycles.

#### **Corollary 1**

There exists a property of a closed system such that a change in its value is equal to the sum of the net heat and work transfers during any change of state. This property is the total energy,  $E$ , of the system. Thus, the First Law can be stated mathematically as

$$\sum_1^2 \delta Q + \sum_1^2 \delta W = \Delta E \quad (2.15)$$

However, in thermodynamics we are often concerned with stationary closed systems in which case the total energy,  $E$ , equals the internal energy,  $U$ , of the system. The First Law is, therefore, expressed mathematically in a form referred to as the non-flow energy equation (NFEE)

$$Q_{12} + W_{12} = \Delta U = U_2 - U_1, \quad (2.16)$$

where,

$$\sum_1^2 \delta Q = Q_{12} \text{ and } \sum_1^2 \delta W = W_{12} \quad (2.17)$$

Equation 2.17 may also be expressed in the differential form as

$$\delta Q + \delta W = dU \quad (2.18)$$

The first law of thermodynamics establishes the internal energy as a property of the system. As a property, the internal energy of a closed system in any given state would have only one value independent of the process through which the system arrived at the state.

For an isolated system the heat and work transfer are zero. It follows from equation (2.19), that the change in internal energy must be zero, which means that the internal energy of an isolated system is constant.

### **Corollary 2**

The internal energy of a closed system remains unchanged if the system is isolated from the surroundings.

That for isolated system  $W=0$ ,  $Q=0$  and it implies that  $U_1=U_2$ .

All what happens in this case is spontaneous redistribution of energy between parts of the system, which continues until a state of equilibrium is reached; there is no change in total quantity of energy within the system during the process. This corollary is the Principle of Conservation of Energy.

#### **2.4.2 First Law for a cyclic Process**

When a system undergoes a cycle all the thermodynamic properties, including internal energy; return to their initial values. The change in internal energy is, therefore, zero for the cyclic process. It follows from the First Law of Thermodynamics that

$$\sum \delta Q + \sum \delta W = 0 \quad \text{or} \quad \oint \delta Q = - \oint \delta W \quad (2.19)$$

That is the cyclic sum of the heat transfers and the work transfers should be zero. We can deduce from Eq. 2.19 that if a net amount of heat is not supplied by the surroundings during a cycle, no net amount of work can be delivered by the system. One can conclude from Equation (2.19) that

whenever a system operates in a cycle and the net heat transfer equals zero, then the net work transfer must also be zero.

## 2.5 APPLICATION OF FIRST LAW TO NON-FLOW PROCESSES (CLOSED SYSTEMS)

### 2.5.1 Constant Pressure Process

For a closed system undergoing a constant pressure process between states 1 and 2, the First Law can be written as

$$\int_1^2 \delta Q = U_2 - U_1 - \int_1^2 \delta W \quad (2.20)$$

Or

$$\int_1^2 \delta q = u_2 - u_1 + \int_1^2 p dv = u_2 - u_1 + p(v_2 - v_1) = (u_2 + p v_2) - (u_1 + p v_1) = h_2 - h_1 \quad (2.21)$$

i.e

$$\boxed{Q_{12} = H_2 - H_1} \quad (2.22)$$

Thus, for a closed system undergoing a constant pressure process the heat transferred is given by the change in the enthalpy of the system.

Hence,

$$h = u + pv \quad (2.23)$$

Enthalpy is particularly useful in the analysis of closed systems undergoing a constant pressure process and open systems undergoing all kinds of process because it includes the flow work given by the term “pv” as well as the internal energy of the system.

### 2.5.2 Polytropic Process

The relation between pressure and volume is given by  $pv^n = \text{constant}$ , where n is the polytropic index.

The energy transferred by heat between states 1 and 2 is given as  $Q_{12} + W_{12} = U_2 - U_1$ . When the relevant values of the work transfer and the internal energy are inserted the energy transferred by heat can be evaluated.

### 2.5.3 Adiabatic Process

This is the process undergone by a system thermally insulated from its surroundings. Work is done at the expense of its internal energy. For such a process since  $Q = 0$ , from the First Law

$$W_{12} = U_2 - U_1 \quad (2.24)$$

In adiabatic expansion, there is decrease in the internal of the system whereas in adiabatic compression there is increase in the internal energy of the system.

### 2.5.4 Isothermal process

This is a constant temperature process. From the First Law

$$\delta q + \delta w = du \quad (2.25)$$

But for a reversible process  $\delta q = Tds$  and since  $T$  is constant for an isothermal process it is possible to integrate this expression directly.

Thus, for a reversible isothermal process

$$q_{12} = T(s_2 - s_1)$$

Therefore,

$$w_{12} = u_2 - u_1 - q_{12} \text{ in general for an isothermal process.}$$

### 2.5.5 Constant Volume process

Applying the First Law and noting that  $W = 0$  since  $dV = 0$ , we have

$$Q_{12} = U_2 - U_1 \quad (2.26)$$

In the differential form,  $\delta Q = du$ . If the heat addition process is reversible then we write the differential for a constant volume process in the form

$$dQ = du$$

## 2.6 THERMODYNAMIC STATE AND STATE FUNCTIONS

A state function is a function that depends only on the current properties of the system and not on the history of the system. Examples of state functions include density, temperature and pressure.

For example, nitrogen gas at a temperature of 300 K and a pressure of 10kPa (1 bar) has a fixed specific volume or density and a fixed molar internal energy. Indeed, it has an established set of intensive thermodynamic properties. If this 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. Such properties do not depend on the past history of the substance nor on the means by which it reaches a given state. They depend only on present conditions, however reached. Such quantities are known as state functions.

A path function is a function that depends on the history of the system. Examples of path functions include work and heat.

$$\int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P \quad (2.27)$$

The differentials of heat and work are not changes, but are infinitesimal amounts. When integrated, these differentials give not finite changes, but finite amounts. Thus,

$$\int Q = Q \text{ and } \int W = W \quad (2.28)$$

## 2.6 EQUILIBRIUM

Equilibrium as a word denotes a static condition. In thermodynamics, it does not only mean the absence of change but the tendency toward change on a macroscopic scale. Thus a system at equilibrium exists under conditions such that no change in state can occur. Since any tendency toward change is caused by a driving force of one kind or another, the absence of such a tendency indicates also the absence of any driving force. Hence for a system at equilibrium all forces are in exact balance.

## 2.7 THE PHASE RULE

The state of a pure homogeneous fluid is fixed whenever two intensive thermodynamic properties are set at definite values. In contrast, when *two* phases are in equilibrium, the state of the system

is fixed when only a single property is specified. For example, a mixture of steam and liquid water in equilibrium at 101.325 kPa can exist only at 373.15 K (100°C). It is impossible to change the temperature without also changing the pressure if vapor and liquid are to continue to exist in equilibrium.

For *any* system at equilibrium, the number of independent variables that must be arbitrarily fixed to establish its *intensive* state is given by the celebrated phase rule of J. Willard Gibbs; who deduced it by theoretical reasoning in 1875. It is presented here without proof in the form applicable to nonreacting systems;

$$F = 2 - \pi + N \quad (2.29)$$

where  $\pi$  = the number of phases,  $N$  = the number of chemical species and  $F$  is the degrees of freedom of the system.

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 phase-rule variables, but they are not all independent. The phase rule gives the number of variables from this set which must be arbitrarily specified to fix all remaining phase-rule variables. A *phase* is a homogeneous region of matter. A gas or a mixture of gases, a liquid or a liquid solution, and a crystalline solid are examples of phases. A phase need not be continuous; examples of discontinuous phases are a gas dispersed as bubbles in a liquid, a liquid dispersed as droplets in another liquid with which it is immiscible, and solid crystals dispersed in either a gas or liquid. In each case a dispersed phase is distributed throughout a continuous phase.

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 a saturated aqueous salt solution at its boiling point with excess salt crystals present. The three phases ( $\pi = 3$ ) are crystalline salt, the saturated aqueous solution, and vapor generated at the boiling point. The two chemical species ( $N = 2$ ) are water and salt. For this system,  $F = 1$ . The phase-rule variables are *intensive* properties, which are independent of the extent of the system and of the individual phases. Thus the phase rule gives the same information for a large system as for a small one and for different relative amounts of the phases present.

The minimum number of degrees of freedom for any system is zero. When  $F = 0$ , the system is *invariant*; the equation becomes  $\pi = 2 + N$ . This value of  $N$  is the maximum number of phases which can coexist at equilibrium for a system containing  $N$  chemical species. When  $N = 1$ , this

number is 3, characteristic of a triple point. For example, the triple point of water, where liquid, vapor, and the common form of ice exist together in equilibrium, occurs at  $273.16\text{ K}$  ( $0.01^\circ\text{C}$ ) and  $0.0061\text{ bar}$ . Any change from these conditions causes at least one phase to disappear.

#### Example

How many degrees of freedom has:

(a) Liquid water in equilibrium with its vapor.

Answer

$$F = 2 - \pi + N; \quad (2.30)$$

where  $\pi = 2$ , system exists as two phases (liquid and vapor),  $N = 1$ , system contains a single chemical species.

This result is in agreement with the fact that for a given pressure water has but one boiling point. Temperature or pressure, but not both, may be specified for a system comprised of water in equilibrium with its vapor.

## 2.8 THE REVERSIBLE PROCESS

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions.

### 2.8.1 REVERSIBLE EXPANSION OF A GAS

The development of thermodynamics is facilitated by introduction of a special kind of closed system process characterized as reversible.

The nature of reversible processes is illustrated by the example of a simple expansion of gas in a piston-cylinder arrangement. The apparatus shown in Fig. 2.6 is imagined to exist in an evacuated space. The gas trapped inside the cylinder is chosen as the system; all else is the surroundings. Expansion processes result when mass is removed from the piston. For simplicity, assume that the piston slides within the cylinder without friction and that the piston and cylinder neither absorb nor transmit heat. Moreover, because the density of the gas in the cylinder is low and because the mass of gas is small, we ignore the effects of gravity on the contents of the cylinder. This means



that gravity-induced pressure gradients in the gas are very small relative to its pressure and that changes in potential energy of the gas are negligible in comparison with the potential-energy changes of the piston assembly.

The piston in Fig. 2.6 confines the gas at a pressure just sufficient to balance the weight of the piston and all that it supports. This is a condition of equilibrium, for the system has no tendency to change. Mass must be removed from the piston if it is to rise. Imagine first that a mass  $m$  is suddenly slid from the piston to a shelf (at the same level). The piston assembly accelerates upward, reaching its maximum velocity at the point where the upward force on the piston just balances its weight. Its momentum then carries it to a higher level, where it reverses direction. If the piston were held in this position of maximum elevation, its potential-energy increase would very nearly equal the work done by the gas during the initial stroke. However, when unconstrained, the piston assembly oscillates, with decreasing amplitude, ultimately coming to rest at a new equilibrium position at a level above its initial position.

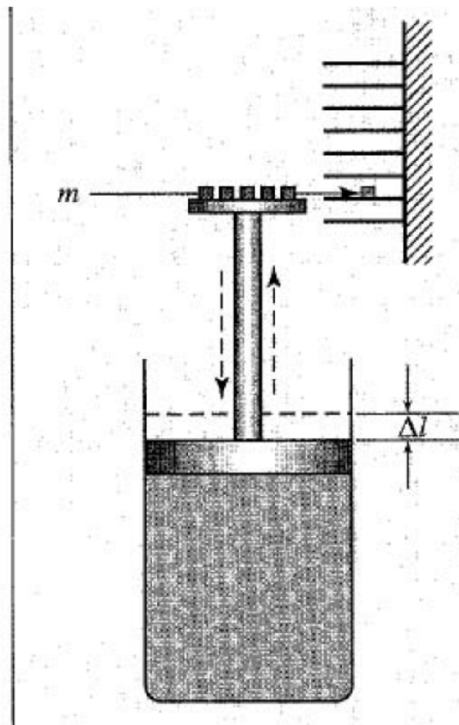


Figure 2.6 Expansion of a gas

Without the assumption of a frictionless piston, we cannot imagine a reversible process. If the piston sticks because of friction, a finite mass must be removed before the piston breaks free. Thus

the equilibrium condition necessary to reversibility is not maintained. Moreover, friction between two sliding parts is a mechanism for the dissipation of mechanical energy into internal energy.

This discussion has centered on a single closed-system process, the expansion of a gas in a cylinder. The opposite process, compression of a gas in a cylinder, is described in exactly the same way. There are, however, many processes which are driven by the imbalance of forces other than mechanical forces. For example, heat flow occurs when a temperature difference exists, electricity flows under the influence of an electromotive force, and chemical reactions occur because a chemical potential exists.

## 2.9 ENTHALPY

The usefulness of the enthalpy appears in energy balances for flow processes as applied to heat exchangers, evaporators, distillation columns, pumps, compressors, turbines, engines, etc., for calculation of heat and work.

The tabulation of values of  $Q$  and  $W$  for the infinite array of possible processes is impossible. The intensive state functions, however, such as specific volume, specific internal energy, and specific enthalpy, are intrinsic properties of matter. Once determined, their values can be tabulated as functions of temperature and pressure for each phase of a particular substance for future use in the calculation of  $Q$  and  $W$  for any process involving that substance. The determination of numerical values for these state functions and their correlation and use are treated in later chapters.

Since  $U$ ,  $P$ , and  $V$  are all state functions,  $H$  as defined by Eq. (2.23) is also a state function. Like  $U$  and  $V$ ,  $H$  is an intensive property of the system. The differential form of Eq. (2.23) is:

$$dH = dU + d(PV) \quad (2.31)$$

This equation applies whenever a differential change occurs in the system. Upon integration, it becomes an equation for a finite change in the system:

$$\Delta H = \Delta U + \Delta (PV) \quad (2.32)$$

## 2.9 HEAT CAPACITY

The smaller the temperature change in a body caused by the transfer of a given quantity of heat, the greater its capacity. Indeed, a heat capacity might be defined:

$$C \equiv \frac{dQ}{dT} \quad (2.33)$$

The difficulty with this is that it makes  $C$ , like  $Q$ , a process-dependent quantity rather than a state function.

### 2.9.1 Heat Capacity at Constant Volume

The constant-volume heat capacity is defined as:

$$C_V \equiv \left( \frac{\partial U}{\partial T} \right)_V \quad (2.34)$$

This definition accommodates both the molar heat capacity and the specific heat capacity (usually called specific heat), depending on whether  $U$  is the molar or specific internal energy. This relates in a simple way to a constant-volume process in a closed system, for which Eq. (2.34) may be written:

$$dU = C_V dT \quad (\text{const } V) \quad (2.35)$$

For a mechanically reversible, constant-volume process:

$$Q = n \Delta U = n \int_{T_1}^{T_2} C_V dT \quad (\text{const } V) \quad (2.36)$$

For the calculation of property changes, an actual process may be replaced by any other process which accomplishes the same change in state.

Such an alternative process may be selected, for example, because of its simplicity.

### 2.9.2 Heat Capacity at Constant Pressure

The constant-pressure heat capacity is defined as:

$$C_P \equiv \left( \frac{\partial H}{\partial T} \right)_P \quad (2.37)$$

This heat capacity relates in an especially simple way to a constant-pressure, closed-system process,

$$dH = C_P dT \quad (\text{const } P) \quad (2.38)$$

whence

$$\Delta H = \int_{T_1}^{T_2} C_P dT \quad (\text{const } P) \quad (2.39)$$

For a mechanically reversible, constant-pressure process,

$$Q = n \Delta H = n \int_{T_1}^{T_2} C_P dT \quad (\text{const } P) \quad (2.40)$$

Since H,  $C_P$ , and T are all state functions, Eq. (2.39) applies to any process for which  $P_2 = P_1$  whether or not it is actually carried out at constant pressure.

## 2.10 FIRST LAW OF THERMODYNAMICS FOR OPEN SYSTEMS

### 2.10.1 General Energy Equation

Figure 2.7 is the sketch of a typical open system. In practice an open system may have several inlets and outlets but it is usual to have one inlet and one outlet. It is also possible for the actual system boundaries to move but for most engineering applications the boundaries may be fixed. Considering an open system with fixed boundaries we pursue the analysis. We consider the events that take place over a short time interval  $dt$ . At the beginning of the time interval (i.e. at the time  $t$ ) the mass of the fluid in the open system is  $m_{s,t}$  and a small mass of fluid is just about to enter the system. During this time interval, the small mass of fluid,  $dm_i$ , enters the system and another small mass of fluid  $dm_o$ , leaves the system such that the mass of fluid at the end of the interval is  $m_{s,t+dt}$ . During this time interval, small amounts of heat and work,  $\delta Q$  and  $\delta W$  and cross the system boundaries and the properties of the fluid inside the system may change such that the energy of the system also changes from  $E_{x,t}$  to  $E_{x,t+dt}$ . Figure 2.7 shows the imaginary closed system at the beginning and end of the time interval. It is assumed that all properties are uniform at the inlet and outlet portions of the system. From the First Law we can write

$$\delta Q + \delta W = E_{x,t+dt} - E_{x,t}, \quad (2.41)$$

where, the subscript x refers to the imaginary closed system.

At the time the total energy of the imaginary closed system is given by

$$E_{x,t} = E_{s,t} + dm_i(u_i + \frac{1}{2}C_i^2 + g z_i) \quad (2.42)$$

and at the time  $t+dt$  the total energy is

$$E_{x,t+dt} = E_{s,t+dt} + dm_o(u_o + \frac{1}{2}C_o^2 + g z_o) \quad (2.43)$$

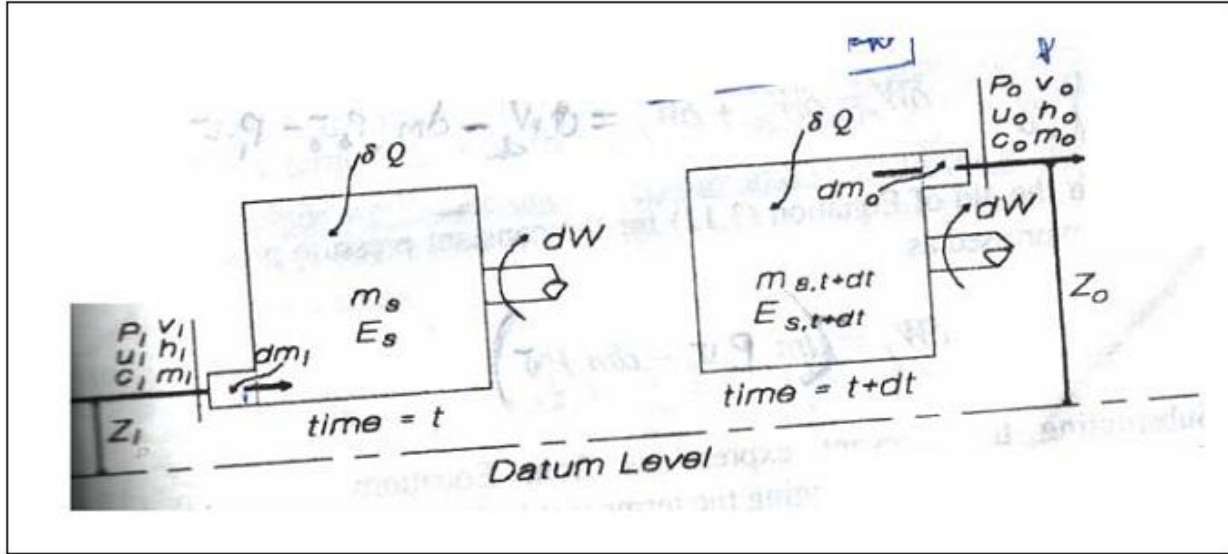


Fig. 2.7 Diagram showing an imaginary closed system at the beginning and end of a differential change of state.

The work done during the time interval is the sum of the shaft work and the flow work, which is the work, required to push the small mass  $dm_i$  into the original system and push  $dm_i$  out. The work transfer term in equation 2.41 is therefore given by

$$\delta W = \delta W_{sh} + \delta W_f = \delta W_{sh} - dm(p_o v_o - p_i v_i) \quad (2.44)$$

Substituting Eqs. 2.42 – 2.44 into Eq. 2.31 yields

$$\delta Q + \delta W_{sh} = (E_{s,t+dt} - E_{s,t}) + dm_o(u_o + p_o v_o + \frac{1}{2}C_o^2 + g z_o) - dm_i(u_i + p_i v_i + \frac{1}{2}C_i^2 + g z_i) \quad (2.45)$$

Substituting for enthalpy and dividing by  $dt$  yields

$$\frac{\delta Q}{dt} + \frac{\delta W_{sh}}{dt} = \frac{(E_{s,t+dt} - E_{s,t})}{dt} + \frac{dm_o}{dt}(h_o + \frac{1}{2}C_o^2 + g z_o) - \frac{dm_i}{dt}(h_i + \frac{1}{2}C_i^2 + g z_i) \quad (2.46)$$

In the limit as dt approaches zero, Eq. 2.46 becomes

$$\dot{Q} + \dot{W}_{sh} = \frac{dE_s}{dt} + \sum_{outlets} \dot{m}_o \left( h_o + \frac{1}{2} C_o^2 + g z_o \right) - \sum_{inlets} \dot{m}_i \left( h_i + \frac{1}{2} C_i^2 + g z_i \right) \quad (2.47)$$

Finally, it is necessary to account for the possibility of moving boundaries which may be rotating or undergoing a displacement. Since when the boundary moves more work terms may be considered and the shaft work in equation (2.47) is replaced by a more general work term W. With this substitution, Eq. 2.47 becomes

$$\dot{Q} + \dot{W} = \frac{dE_s}{dt} + \sum_{outlets} \dot{m}_o \left( h_o + \frac{1}{2} C_o^2 + g z_o \right) - \sum_{inlets} \dot{m}_i \left( h_i + \frac{1}{2} C_i^2 + g z_i \right) \quad (2.48)$$

### 2.10.2 Steady-Flow Energy Equation (SFEE)

The assumptions for the SFEE may be summarized as follows:

1. The boundaries of the system are fixed
2. The mass flow rate of the fluid is constant and is the same at inlet and outlet of the system  
( $\dot{m}_o = \dot{m}_i = \dot{m}$ )
3. The properties of the fluid at any point in the system remain constant with time ( $\frac{dE_s}{dt} = 0$ )
4. Heat and work transfer cross the boundaries of the system at uniform rates.

Following the above assumptions, the SFEE becomes

$$\dot{Q} + \dot{W} = \dot{m} (h_o - h_i) + \frac{1}{2} \dot{m} (C_o^2 - C_i^2) + \dot{m} g (z_o - z_i) \quad (2.49)$$

Note when the flow is one-dimensional, the mass flow rate becomes

$$\dot{Q} + \dot{W} = \dot{m} (h_o - h_i) + \frac{1}{2} \dot{m} (C_o^2 - C_i^2) + \dot{m} g (z_o - z_i) \quad (2.50)$$

Note when the flow is one-dimensional, the mass flow rate becomes  $\dot{m} = \rho A V$  (2.51)

and in terms of specific volume, v, the relation is

$$\dot{m} = \frac{A V}{v} \quad (2.52)$$

### 2.10.3 Practical applications of the SFEE

#### 2.10.3.1 Nozzles and diffusers

A nozzle is a flow passage of varying cross-sectional area in which the velocity of the gas or liquid increases in the direction of flow. In a diffuser, the liquid decelerates in the direction of flow. Figure 2.14 shows a nozzle in which the cross-sectional area decreases in the direction of flow and a diffuser in which the walls of the flow passage diverge. For nozzles and diffusers, the only work is the flow work at locations where the mass enters and exits the control volume and so the term  $W$  drops out of the energy rate equation for these devices. The change in the potential energy from the inlet to exit is negligible under most conditions. By combining these into a single expression and dropping the potential energy change from inlet to exit

$$\dot{Q}_{12} = \dot{m} (h_2 - h_1) + \dot{m} \frac{C_2^2 - C_1^2}{2} \quad (2.53)$$

The subscripts 1 and 2 denote the inlet and exit, respectively.

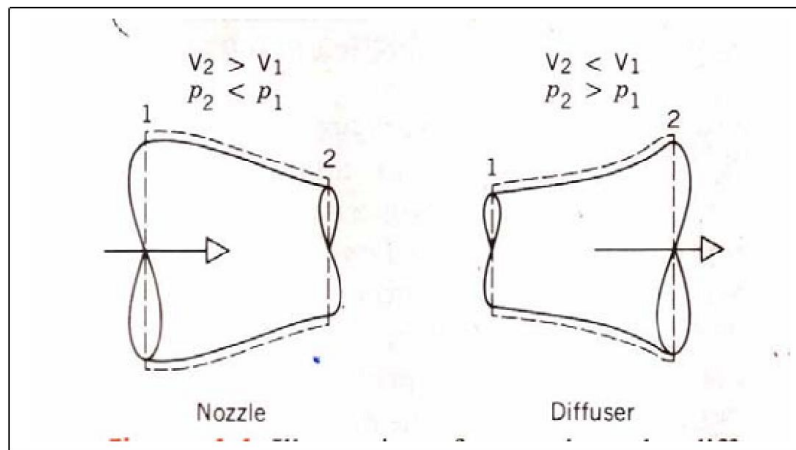


Fig 2.8 Illustration of a nozzle and a diffuser

#### 2.10.3.2 Turbines, compressors, fans and pumps

A turbine is a device in which work is developed as a result of a gas or liquid passing through a set of blades attached to a shaft free to rotate. A schematic of an axial-flow steam or gas turbine is shown in Figure 2.9. Turbines are widely used in vapour power plants, gas turbines power plants, and aircraft engines. In these applications, superheated steam or gas enters the turbine and expands to a lower exit pressure as work is developed. Water turbines are used in electric power plants.

Compressors, fans and pumps, on the other hand, are devices that require mechanical power to compress fluid or, simply put, to move a fluid from a low pressure to a relatively high-pressure zone. The processes that take place inside turbines, compressors, fans and pumps are usually assumed to be adiabatic and therefore  $Q = 0$ . Secondly, kinetic and potential energy terms are assumed to be negligible compared to the other terms in the SFEE. The resulting equation for this class of thermodynamic application is

$$\dot{W}_{12} = \dot{m} (h_2 - h_1) \quad (2.54)$$

Note that turbines are work-producing devices, while compressors, fans, and pumps are work requiring devices.

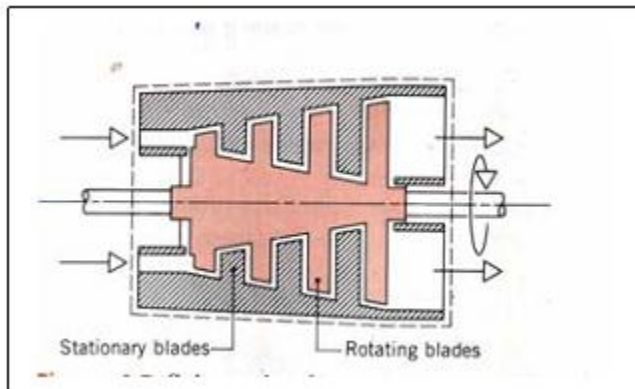


Fig. 2.9 Schematic of an axial flow turbine

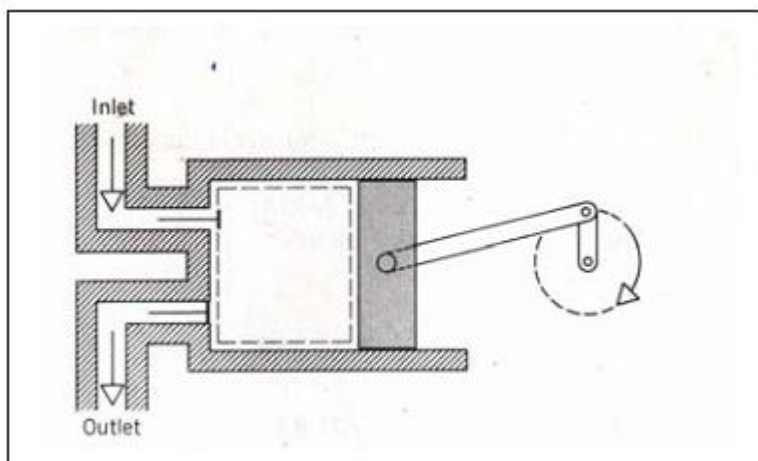


Fig. 2.10 Reciprocating compressor



### 2.10.3.3 Throttling devices

A throttling device is a restriction in a fluid flow channel, which is designed to effect a significant pressure drop with no work transfer and no change in potential and kinetic energies. In this regard, the ordinary valve in pipeline may be considered as a throttling device. The throttling process takes place over a short distance so that heat transfer is also considered negligible. The SFEE then reduces to

$$h_2 = h_1 \quad (2.55)$$

That is a throttling process is an isentropic process. Throttling valves are used extensively to reduce the pressure refrigerant flowing through the valve. In the vapour-compression refrigerator a valve is used to reduce the pressure of the refrigerant from the pressure at the exit of the condenser to the power pressure existing in the evaporator. Schematic representations of throttling devices are illustrated in Figure 2.11.

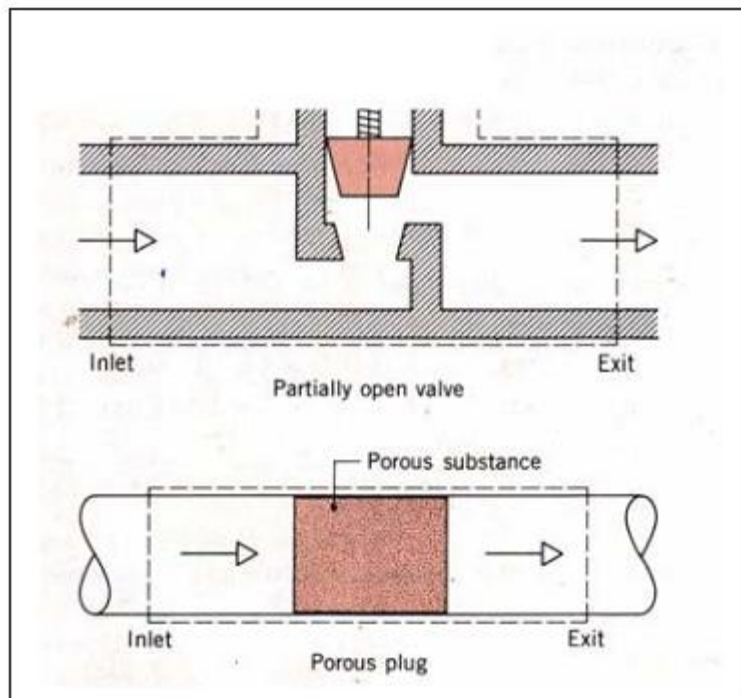


Fig. 2.11 Throttling devices

## SOLVED EXAMPLES

(1) A nonconducting container filled with 25 kg of water at 293.15 K (20°C) is fitted with a stirrer, which is made to turn by gravity acting on a weight of mass 35 kg. The weight falls slowly through a distance of 5 m in driving the stirrer. Assuming that all work done on the weight is transferred to the water and that the local acceleration of gravity is  $9.8 \text{ m s}^{-2}$ , determine:

- (a) The amount of work done on the water.
- (b) The internal-energy change of the water.
- (c) The final temperature of the water, for which  $C_p = 4.18 \text{ kJ kg}^{-1}\text{°C}^{-1}$ .
- (d) The amount of heat that must be removed from the water to return it to its initial temperature.
- (e) The total energy change of the universe because of (1) the process of lowering the weight, (2) the process of cooling the water back to its initial temperature, and (3) both processes together.

## SOLUTION

(a)

**Mass of the weight,  $M_{wt} = 35\text{kg}$ , Acceleration due to gravity,  $g = 9.8 \text{ ms}^{-2}$ ,  $\Delta z = 5\text{m}$**

$$\text{Work} = M_{wt}.g.\Delta z = 1.715\text{kJ}$$

(b)

$$\Delta U_{total} = \text{Work} = 1.715\text{kJ}$$

(c)

$$dU + d(PV) = C_p.dT$$

**Since P is constant, this can be written as:**

$$M_{H_2O}.C_p.dT = M_{H_2O}.dU + M_{H_2O}.P.dV$$

**Take  $C_p$  and  $V$  constant and integrate:**

$$M_{H_2O}.C_p.dT = U_{total}$$

$$t_1 = 20^\circ\text{C}$$

$$C_p = 4.18 \text{ kJ/kg}^\circ\text{C}$$

$$M_{H_2O} = 30\text{kg}$$

$$t_2 = t_1 + \frac{\Delta U_{total}}{M_{H_2O} \cdot C_p}$$

$$t_2 = 20.014^\circ\text{C}$$

**(d) For the restoration process, the change in internal energy is equal but of opposite sign to that of the initial process. Thus**

$$Q = -\Delta U_{\text{total}} \qquad Q = -1.715 \text{ kJ}$$

**(e) In all cases the total internal energy change of the universe is zero.**

(2) Heat in the amount of 7.5 kJ is added to a closed system while its internal energy decreases by 12 kJ. How much energy is transferred as work? For a process causing the same change of state but for which the work is zero, how much heat is transferred?

**SOLUTION**

$$Q = 7.5 \text{ kJ} \qquad \Delta U = -12 \text{ kJ} \qquad W = \Delta U - Q = -19.5 \text{ kJ}$$

$$\Delta U = Q, W = 0 = -12 \text{ kJ}$$

## TUTORIAL SET 2

1. A 5 kg of steam is contained within a piston-cylinder assembly. The steam undergoes an expansion from state 1, where the specific internal energy is  $u_1 = 2709 \text{ kJ/kg}$  to state 2, where  $u_2 = 2659.6 \text{ kJ/kg}$ . During this process, there is heat transfer of energy to the steam with a magnitude of 80 kJ. Also, a paddle wheel transfers energy to the steam by work in the amount of 18.5 kJ. There is no significant change in the kinetic or potential energy of the steam. Determine the amount of energy transfer by work from the steam to the piston during the process, in kJ. [- 350 kJ]
2. A gas is compressed from  $V_1 = 0.09 \text{ m}^3$  to  $V_2 = 0.03 \text{ m}^3$ . The relation between pressure and volume during the process is  $p = -14V + 2.44$ , where the units of  $p$  and  $V$  are bar and  $\text{m}^3$ , respectively. For the gas, find the work, in kJ. [+ 9.6 kJ]