Department of Chemical Engineering

College of Engineering

KNUST

CHE 253

CHEMICAL ENGINEERING THERMODYNAMICS I

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Objectives

- Understand the general scope of thermodynamics.
- Explain the basic concepts of thermodynamics such as system, state, state postulate, equilibrium, process, and cycle.
- Review concepts of temperature, temperature scales, pressure, and absolute and gauge pressure.
- Discuss these terms in brief; work, heat and energy with respect to its thermodynamic applications.

## 1.0 INTRODUCTION

1.1 Definition and Scope

What is thermodynamics?

Thermodynamics can simply be defined as the science of *energy.* It is the branch of science that embodies the principles of energy transformation in macroscopic systems. The general restrictions which experience has shown to apply to all such transformations are known as the *laws of thermodynamics.* These laws are primitive; they cannot be derived from anything more basic and comprises of a network of equations which find application in all branches of science and engineering. Presently it is broadly interpreted to include all aspects of energy and energy transformations, including power generation, refrigeration, and relationships among the properties of matter. The chemical engineer copes with a particularly wide variety of problems. Among them are calculation of heat and work requirements for physical and chemical processes, and the determination of equilibrium conditions for chemical reactions and for the transfer of chemical species between phases. The application of thermodynamics to any real problem starts with the identification of a particular body of matter as the focus of attention. This body of matter is called the *system,* and its thermodynamic state is defined by a few measurable macroscopic properties. These depend on the fundamental *dimensions* of science such as length, time, mass, temperature, and amount of substance.

1.2 Basic Concepts

Systems and Control volume

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 surroundings is called the *boundary.* The boundary serves either to isolate the system from its surroundings or to provide for interaction in specific ways between system and surroundings.

SURROUNDINGS

SYSTEM

BOUNDARY
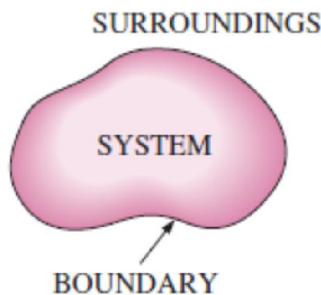
Systems may be considered to be *closed* or *open,* depending on whether a fixed mass or a fixed volume in space is chosen for study.

1.2.1 Closed System

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. But energy, in the form of heat or work, can cross the boundary; and the volume of a closed system does not have to be fixed. See figure 1.2

CLOSED
SYSTEM

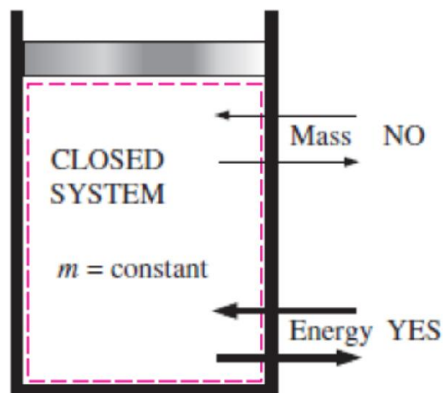Mass   NO

m = constant

Energy YES

Fig. 1.2 A closed system

1.2.2 Open System

An open system, or a control volume, as it is often called, is a properly selected region in space. 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.
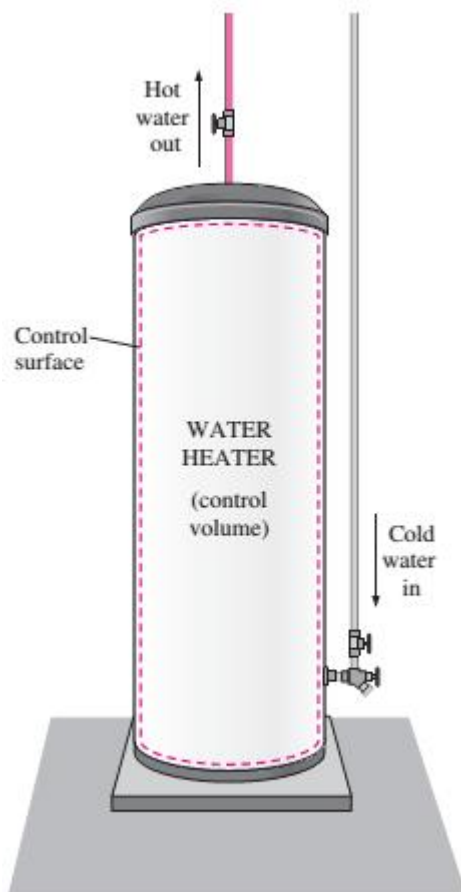

Figure 1.3 An open system (a control volume) with one inlet and one exit.

1.2.3 Isolated system

An isolated system can exchange neither matter nor energy with its surroundings.

1.3 Dimensions and Units

Primary units have been set by international agreement, and are codified as the International System of Units (abbreviated SI, for Système International).

The *second,* symbol s, the SI unit of time, is the duration of 9 192 631 770 cycles of radiation associated with a specified transition of the cesium atom.

The *meter,* symbol m, is the fundamental unit of length, defined as the distance light travels in a vacuum during 11299 792 458 of a second.

The *kilogram,* symbol kg, is the mass of a platinum/iridium cylinder kept at the International Bureau of Weights and Measures at Sèvres, France.

The unit of temperature is the *kelvin,* symbol K, equal to 11273.16 of the thermodynamic temperature of the triple point of water.

Table 1.1 Prefixes for SI Units

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-24}	yocto	y	$10'$	deca	da
	zepto	z	10^2	hecto	n
10^{-18}	atto	a	10^3	kilo	k
10^{-15}	femto	f	10^6	mega	M
10^{-12}	pico	p	10^9	giga	G
	nano	n	10^{12}	tera	T
	micro	μ	10^{15}	peta	P
10^{-3}	milli	m	10^{18}	exa	E
	centi	c	10^{21}	zetta	Z
10^{-1}	deci	d	10^{24}	yotta	Y

Other systems of units, such as the English engineering system, use units that are related to SI units by fixed conversion factors eg. Foot (ft) is defined as 0.3048 m.

(Ask students to read on the conversion factors from EES to SI units)

Any physical quantity can be characterized by **dimensions.** The magnitudes assigned to the dimensions are called **units.** Some basic dimensions such as mass m, length L, time t, and temperature T are selected as **primary** or **fundamental dimensions,** while others such as velocity V, energy E, and volume V are expressed in terms of the primary dimensions and are called **secondary dimensions,** or **derived dimensions.**

1.4 Properties of a System

Any characteristic of a system is called a **property.** Examples of some familiar properties are 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.

1.4.1 Intensive Properties

Intensive properties are those that are independent of the mass of a system, such as temperature, pressure, and density.

1.4.2 Extensive Properties

Extensive properties are those whose values depend on the size or extent of the system. Total mass, total volume, and total momentum are some examples of extensive properties.

1.4.3 Specific Properties

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

1.5 Measures of amount or size

Three measures of amount or size are in common use:
- Mass, m
- Number of moles, n
- Total volume, V^t

These measures for a specific system are in direct proportion to one another. Mass, *a primitive* without definition, may be divided by the molar mass M, commonly called the molecular weight, to yield number of moles:

$$n = \frac{m}{M} \qquad\qquad (1.1)$$

Total volume, representing the size of a system, is a defined quantity given as the product of three lengths. It may be divided by the mass or number of moles of the system to yield *specific* or *molar volume:*

- Specific volume:
$$V = \frac{V^t}{m} \qquad (1.2)$$

- Molar volume:
$$V = \frac{V^t}{n} \qquad (1.3)$$

Specific or molar density is defined as the reciprocal of specific or molar volume: $p = V^{-1}$

These quantities *(V* and p) are independent of the size of a system, and are examples of *intensive* thermodynamic variables. They are functions of the temperature, pressure, and composition of a system, additional quantities that are independent of system size.

In performing evaluations of systems and cycles with steam, a convenient variable is the quality of steam, x. It is defined as the ratio of the mass of steam to total mass of steam and water in a

mixture, i.e., $x = \dfrac{m_v}{m_t}$ (1.4)

where $m_t = m_v + m_l$.

It is frequently used to compute thermodynamic properties of two-phase mixtures of steam and water:

$$\phi_{mix} = \phi_v x + \phi_l (1 - x) \qquad (1.5)$$

In this equation, ϕ can be specific volume, internal energy, enthalpy, or entropy.

1.6 Force

The SI unit of force is the *newton,* symbol N, derived from Newton's second law, which expresses force *F* as the product of mass *m* and acceleration *a:*

$$F = ma \qquad (1.6)$$

Thus force is measured in the composite unit kg.m.s^{-2} also referred to as the newton (N).

In the metric engineering system of units, force is treated as an additional independent dimension along with length, time, and mass. The kilogram *force* (kgf) is defined as that force which accelerates 1 kilogram *mass* 9.806 65 meters per second per second.

$$F = \frac{1}{g_c} ma \qquad (1.7)$$

$$1kgf = \frac{1}{g_c} \times 1kg \times 9.80665 kgm.s^{-2}$$

$g_c = 9.80665 kgm.kgf^{-1}s^{-2}$

1.7 Temperature

Temperature is commonly measured with liquid-in-glass thermometers, wherein the liquid expands when heated.

Kelvin temperatures are given the symbol T; Celsius temperatures, given the symbol t, are defined in relation to Kelvin temperatures:

$$t^oC = TK - 273.15 \qquad (1.8)$$

The unit of Celsius temperature is the degree Celsius, °C, equal in size to the kelvin. However, temperatures on the Celsius scale are 273.15 degrees lower than on the Kelvin scale. Thus the lower limit of temperature, called absolute zero on the Kelvin scale, occurs at -273.15°C.

The Rankine scale is an absolute scale directly related to the Kelvin scale by:

$$T(R) = 1.8TK \qquad (1.9)$$

The Fahrenheit scale is related to the Rankine scale by an equation analogous to the relation between the Celsius and Kelvin scales:

$$t(^oF) = T(R) - 459.67 \qquad (1.10)$$

Thus the lower limit of temperature on the Fahrenheit scale is -459.67(°F). The relation between the Fahrenheit and Celsius scales is:

$$t(^oF) = 1.8t^oC + 32 \qquad (1.11)$$

The ice point is therefore 32(°F) and the normal boiling point of water is 212(°F).

The Celsius degree and the kelvin represent the same temperature *interval,* as do the Fahrenheit degree and the rankine.

1.8 Pressure

In the ideal gas law, absolute pressure, P, is required. Absolute pressure is defined as the normal component of force exerted by the fluid per unit area acting on a surface in the system, and it has SI units of Newtons per square meter (N/m^2) or Pascals (Pa). Most instruments measure pressure relative to local atmospheric pressure, i.e., they give readings in gauge pressure. Consequently, the

local atmospheric pressure or barometric pressure must be added to the gauge pressure to convert it to absolute pressure for use.

$$\text{absolute pressure} = \text{gauge pressure} + \text{barometric pressure}$$

$$\text{gauge pressure} = \frac{F}{A} = \frac{mg}{A} = \frac{Ah\rho g}{A} = h\rho g$$

The pressure to which a fluid height corresponds is determined by the density of the fluid (which depends on its identity and temperature) and the local acceleration of gravity. Thus the (torr) is the pressure equivalent of 1 millimeter of mercury at 273.15 K (0°C) in a standard gravitational field, and is equal to 133.322 Pa. Another unit of pressure is the standard atmosphere (atm), the approximate average pressure exerted by the earth's atmosphere at sea level, defined as 101 325 Pa, 101.325 kPa, or 0.101 325 MPa. The bar, an SI unit defined as 10^5 Pa, is equal to 0.986 923 atm.

1.9 Work

Work, W, is done when a force acts through a distance, and the amount of work is the product of the distance and the force acting through this distance. In thermodynamics an important type of work occurs when a change in the volume of a fluid causes the movement of a piston. A force, F, exerted on a piston by the fluid is equal to the product of the fluid pressure, P, and the cross-sectional area, A, of the piston. The distance through which the force acts is the displacement of the piston, and this is equal to the volume change of the fluid divided by the cross-sectional area of the piston, d (V/A). The pressure and the volume of the fluid vary according to an equation of state, so the work must be written in a differential form as:

$$dW = Fdx = PAd(V/A) \qquad (1.12)$$

For a piston with a constant cross-sectional area A, Eq. (1.12) becomes:

$$dW = PdV \qquad (1.13)$$

This equation can be integrated over the volume change from point 1 to point 2 to obtain the work for the process, i.e.,

$$W = \int_{V_1}^{V_2} PdV \qquad (1.14)$$

The pressure must be known as a function of this change in volume to evaluate the integral and determine the work. The SI units of work are the Newton-meter or joule, and in English units foot-pounds of force are frequently used.

Work can be related to kinetic and potential energy using concepts from particle mechanics. For example, the work done on a body to accelerate it from velocity u_1 to velocity u_2 is the change in kinetic energy. To show this relation, the definition of work $dW = Fdl$ is used, where F is the force on the body of mass, m.

$$W = m\left(\frac{u_2^2}{2} - \frac{u_1^2}{2}\right) \tag{1.15}$$

Thus, the work required to accelerate mass from u_1 to u_2 is the change in kinetic energy of this body.

The work required to raise a mass from an initial elevation z_1 to a final higher elevation z_2 is the change in potential energy of the body. Using the definition of work for this case, $dW = Fdl = madl = mgdl$, and integrating dl from z_1 to z_2 gives:

$$W = m\left(z_2 - z_1\right) \tag{1.16}$$

Thus, work is equal to the change in potential energy for this case.

Changes in kinetic energy and potential energy will appear in the first law of thermodynamics along with the work done by the system. The ideas presented above are to show that work is a quantitative and unambiguous physical entity. Also, work is energy in transit. When work is done it does not appear simultaneously as work elsewhere. It is converted into a form of energy. As described above, work done on a mass increases it's kinetic and potential energy.

Work is done by a system, and the system can be many useful devices, from an elevator to an automobile engine. When work is performed, it is either done by the system on the surroundings or vice versa. Also, energy is transferred to the system from the surroundings or in the reverse direction. Work is done only when there is a change in energy, as described by the first law of thermodynamics.

There is a sign convention associated with work being performed. If work is being performed on, or transferred to, the system by the surroundings, it is considered negative, i.e., work consumed by compressors, pumps, and mixers is negative. If work is being performed by or transferred from the

system to the surroundings, it is considered positive, i.e., work produced by turbines and engines is positive. Using this sign convention, the first law of thermodynamics is written as:

$$\Delta E = Q - W \qquad (1.17)$$

where ΔE is the change in total energy of the system, Q is heat transferred to the system, and W is work done by the system on the surroundings.

There are several forms of work as implied above. One is shaft work, which means work done on or by a fluid flowing through a piece of equipment like a pump, compressor, or turbine which causes the shaft to rotate or reciprocate. This shaft is connected to another machine which uses the motion for another purpose, e.g., a generator to produce electricity. Another form of work is called PV work, and this was described earlier in terms of the action of a fluid volume change on a piston. Also, work is required when a wire is stretched in the elastic region, when a magnetic field is charged on a ferromagnet, and when an electrical conductor passes through a magnetic field.

The concept of a **reversible process** for a closed system is used to represent the upper limit for the performance of an actual process. It is convenient to use the work of compression or expansion from a frictionless piston to describe a reversible process for a closed system. In a reversible process there is only infinitesimal displacement from equilibrium, and work and heat effects are sufficient to restore the system to its original state, i.e., there is no lost work to friction or turbulence. The first law of thermodynamics is written in terms of differential changes to describe the infinitesimal displacement from equilibrium for a closed system:

$$dU = dQ - dW \qquad (1.18)$$

For a closed system, the change in total energy, dE, is equal to the change in internal energy, dU.

1.9.1 Adiabatic Process

In an adiabatic process, no heat is transferred between the system and the surroundings, and compressors, pumps, and turbines operate essentially adiabatically. The upper limit of performance of these systems is described by an adiabatic, reversible process.

To evaluate the work, W, for an adiabatic, reversible, closed system, the first law of thermodynamics, Eq. (1.18), has $dQ = 0$. Also, $dW = PdV$ from Eq. (1.13), and Eq. (1.18) becomes:

$$dU = -PdV \tag{1.19}$$

Next, to obtain equations that relate the pressure, volume, and temperature changes of an ideal gas in an adiabatic, reversible, closed system, the equation for internal energy is used: $dU = C_v dT$. This can be combined with the ideal gas law, $PV = nRT$ to give the following relations for changes in temperature, pressure, and volume between points 1 and 2:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} \tag{1.20}$$

Another form of this equation is:

$$P_1 V_1^k = P_2 V_2^k = PV^k = \text{constant} \tag{1.21}$$

where $k = C_p/C_v$ the ratio of heat capacities at constant pressure and volume which has approximate values of 1.67 for monatomic gases, 1.4 for diatomic gases, and 1.3 for simple polyatomic gases.

The above results can be used to evaluate the work for an adiabatic, reversible, closed system. Two equivalent, frequently used equations are given below. One is in terms of initial and final pressures and volumes, and the other is in terms of the initial temperature and pressure and final pressure to compute the work for this case:

$$W = (P_1 V_1 - P_2 V_2)/(k-1) \tag{1.22}$$

$$W = \frac{RT_1}{(k-1)}\left[1 - \left(\frac{P_2}{P_1}\right)^{(k-1)/k}\right] \tag{1.23}$$

In an isothermal process, heat is transferred between the system and its surroundings, and boilers and condensers essentially operate isothermally (at constant temperature). The upper limit of performance of these systems is described by an isothermal, reversible process.

To evaluate the work for an isothermal, reversible, closed system, the first law of thermodynamics, has dU = 0 because dT = 0. Thus, the heat transferred to the system Q is equal to the work done by the system W. Using Eq. (1.13) to evaluate the work for an ideal gas gives:

$$W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} RT \frac{dV}{V} = RT \ln\left(\frac{V_2}{V_1}\right)$$ (1.24)

Using $P_1/P_2 = V_2/V_1$ from the ideal gas law gives another frequently used form of Eqn. (1.24) to compute work for this case:

$$W = RT \ln\left(\frac{P_1}{P_2}\right)$$ (1.25)

For work associated with a steady state flow system, the first law of thermodynamics has the following form:

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta z = Q - W_s$$ (1.26)

where Ws is the shaft work. This equation is used to compute the shaft work for reversible and irreversible processes.

For a reversible process, Eq. (1.26) is written in terms of differential changes. Using the fundamental relation $dH = TdS + VdP$ with $dQ = TdS + VdP$ for a reversible change, Eq. (1.26) can be written as:

$$-W_s = \int_{P_1}^{P_2} VdP + \frac{\Delta u^2}{2} + g\Delta z$$ (1.27)

For an incompressible fluid (constant density ρ or specific volume V), the integral can be replaced by $\Delta P/\rho$, and the shaft work is given by:

$$-W_s = \frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z$$ (1.28)

For an irreversible process, an additional lost work term can be added to Eq. (1.28). This lost work term for pipe flow is $2f(L/D)u^2$, where f, is the Fanning friction factor and u is the average fluid velocity in the pipe of length L and diameter D. The equation for pipeline calculations is:

$$-W_s = \frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta z + 2f\left(\frac{L}{D}\right)u^2 \qquad (1.29)$$

This equation is used to compute the shaft work to pump the fluid from point 1 to point 2 where the pressure, velocities, and elevations are known at these points.

In turbines and expanders, shaft work is obtained from a high velocity gas stream impinging on blades attached to a rotating shaft. The first law of thermodynamics for this system, simplifies to the following equation because they are operated adiabatically and kinetic and potential energy, changes are small compared to the enthalpy change:

$$W_s = -\Delta H = H_1 - H_2 \qquad (1.30)$$

Here the shaft work is equal to the change in enthalpy of the entering and exiting streams. If the expansion is isentropic and the entrance conditions are known, then the maximum shaft work can be computed as a function of exit conditions. Turbines and expanders have efficiencies which are in the range of 70 to 80 percent of the isentropic approximation.

Work computed by Eq. (1.30) is also applicable to compressors, and the isentropic approximation gives the minimum shaft work to compress a fluid from an initial state to a final state. Compressor efficiencies also range from 70 to 80 percent of the isentropic approximation.

For work done by pumps moving liquids, a convenient design equation is given below. This is a simplification of Eq. (1.27), neglecting kinetic and potential energy changes:

$$W_s = V\left(P_1 - P_2\right) \qquad (1.31)$$

where V is the liquid specific volume. Pump efficiencies are in the range of 70 to 80 percent.

1.9.2 Lost work

Lost work is energy that is unavailable for work due to irreversibilities in a process. It is defined as the difference between the ideal and actual work of the process. The amount of lost work is given by the following equation, which is obtained from the definition of lost work and the first and second laws of thermodynamics:

$$W_{lost} = T_o \Delta S_{total} \qquad (1.32)$$

where W_{lost} is the lost work per unit mass of fluid flowing in the system, T_o is the temperature of the heat reservoir, and ΔS_{total} is the total change in entropy for the actual process.

1.10 Energy

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.

1.10.1 Kinetic Energy

The curved line in Fig. 1.4 represents the path of a body of mass m (closed system) moving relative to the x-y coordinate frame shown. Let us consider the body as it moves from $s = s_1$, where the magnitude of its velocity is V_1, to $s = s_2$, where its velocity is V_2. If we assume that the only interaction between the body and its surroundings involves the force F, then by Newtons 2nd Law, the magnitude of the component F_s is related to the change in the magnitude of V by
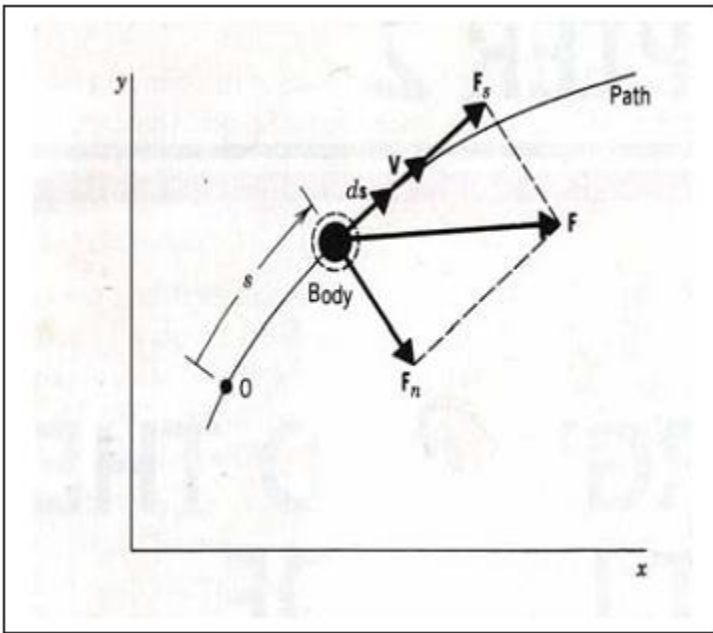

Fig.1.4 Forces acting on a moving system

$$F_s = m\frac{dV}{dt} = m\frac{dV}{ds}\frac{ds}{dt},$$

(1.33)

where, V = ds/dt. Rearranging Eq. 1.33 and integrating from s1and s2 gives

$$\int_{V_1}^{V_2} mV \, dV = \int_{s_1}^{s_2} F_s \, ds$$

(1.34)

The integral on the left of Eq. 1.33 is evaluated as follows:

$$\int_{V_1}^{V_2} mV \, dV = \frac{1}{2} mV^2 \Big]_{V_1}^{V_2} = \frac{1}{2} m \left(V_2^2 - V_1^2 \right)$$

(1.35)

The quantity $1/2mV^2$ is the kinetic energy, KE, of the body. Kinetic energy is a scalar quantity. The change in kinetic energy, of the body is

$$\Delta KE = KE_2 - KE_1 = \frac{1}{2} m (V_2^2 - V_1^2)$$

The integral on the right side of Eq. 1.34 is the work of the force F_s as the body moves from s_1 to s_2 along the path. Work is also a scalar quantity. Combining Eqs. 1.34 and 1.35 we have

$$\frac{1}{2} m (V_2^2 - V_1^2) = \int_{s_1}^{s_2} F_s \cdot ds$$

(1.36)

Equation 1.36 states that the work of the resultant force on the body equals the change in its kinetic energy. When the resultant force accelerates the body, the work done on the body can be considered a transfer of energy to the body, where it is stored as the kinetic energy.

Kinetic energy can be assigned a value knowing only the mass of the body and the magnitude of its instantaneous velocity relative to a specified coordinate frame, without regard for how this velocity was attained. Hence, kinetic energy is a property of the body. Since kinetic energy is associated with the body as a whole, it is an extensive property of the body. The units of kinetic energy are the same as that of work. The SI unit of work is the Newtonmetre, N m, called the joule, J.

1.10.2 Potential Energy
Consider a body of mass m that moves vertically from an elevation z_1 to an elevation z_2 relative to the surface of the earth, as shown in Fig. 1.4. Two forces are shown acting on the system: a downward force due to gravity with magnitude mg and a vertical force with magnitude R representing the resultant of all other forces acting on the system.

In accordance with Eq. 1.36, the total work equals the change in kinetic energy. That is,

$$\frac{1}{2}m(V_2{}^2 - V_1{}^2) = \int_{z_1}^{z_2} R\,dz \quad - \quad \int_{z_1}^{z_2} m\,g\,dz$$

(1.37)

Assuming acceleration due to gravity to be constant we obtain

$$\frac{1}{2}m(V_2{}^2 - V_1{}^2) + m\,g(z_2 - z_1) = \int_{z_1}^{z_2} R\,dz$$

(1.38)

The quantity mgz is called the gravitational potential energy. Like kinetic energy, potential energy is an extensive property.

Equation 1.38 states that when a resultant force causes the elevation of a body to be increased, the body to be accelerated, or both, the work done by the force can be considered a transfer of energy to the body, where it is stored as gravitational potential energy and/or kinetic energy. If we consider a body on which the only force acting is that due to gravity, the right side of equation (1.38) vanishes and it reduces to

$$\frac{1}{2}m(V_2{}^2 - V_1{}^2) + m\,g(z_2 - z_1) = 0$$

(1.39)

or

$$\frac{1}{2}mV_2{}^2 + mgz_2 = \frac{1}{2}mV_1{}^2 + mgz_1$$

(1.40)

Equation 1.40 also illustrates that energy can be transformed from one form to another: For the object falling under the influence of gravity only, the potential energy would decrease as the kinetic energy increases by an equal amount.

1.11 Energy Conservation

In any examination of physical processes, an attempt is made to find or to define quantities which remain constant regardless of the changes which occur. One such quantity, early recognized in the development of mechanics, is mass. The great utility of the law of conservation of mass suggests that further conservation principles could be of comparable value. Thus the development of the concept of energy logically led to the principle of its conservation in mechanical processes. If a body is given energy when it is elevated, then the body conserves or retains this energy until it performs the work of which it is capable. An elevated body, allowed to fall freely, gains in kinetic

energy what it loses in potential energy so that its capacity for doing work remains unchanged. For a freely falling body this means that:

$$\Delta E_k + \Delta E_p = 0 \qquad\qquad (1.41)$$

Or

$$\frac{mu_2^2}{2} - \frac{mu_1^2}{2} + mz_2 g - mz_1 g = 0 \qquad (1.42)$$

Other forms of mechanical energy besides kinetic and gravitational potential energy are possible. The most obvious is potential energy of configuration. When a spring is compressed, work is done by an external force. Since the spring can later perform this work against a resisting force, the spring possesses capacity for doing work. This is potential energy of configuration. Energy of the same form exists in a stretched rubber band or in a bar of metal deformed in the elastic region.

1.11 Heat

Heat is energy in transit from one body to another, and it flows from a higher to a lower temperature. The rate of heat transfer is proportional to the local temperature gradient, and the proportionality constant is the thermal conductivity. Like work, it only exists in transit between a system and its surroundings, and a body does not store heat but stores internal, kinetic, and potential energy. Joule's experiment demonstrated that work was quantitatively converted to heat, and this heat increased the internal energy of water in the experimental apparatus. This experiment provided a basis for the first law of thermodynamics.

The first law of thermodynamics for a closed system (nonflow process) is given by:

$$\Delta U = Q - W \qquad\qquad (1.43)$$

There are three cases that can be considered for heat being added to a closed system. They are a constant volume process, a constant pressure process, and a constant temperature process.

For a nonflow constant volume process, heat added to the system is given by the change in internal energy of the system. No work is performed (W = 0), and Eq. (1.43) becomes:

$$Q = \Delta U = \int_{T_1}^{T_2} C_v dT = C_{v,avg}\left(T_2 - T_1\right) \qquad\qquad (1.44)$$

where the change in internal energy ΔU is given in terms of C_v, the heat capacity at constant volume.

For a nonflow constant pressure (isobaric) process, heat added to the system is given by the change in enthalpy of the system from the first law of thermodynamics, i.e., in Eq. (1.43) $W = P\Delta V$, and $\Delta H = \Delta U + P\Delta V$ to have $\Delta H = Q$

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT = C_{p,avg}\left(T_2 - T_1\right) \qquad (1.45)$$

where the change in enthalpy, ΔH is given in terms of C_P, the heat capacity at constant pressure. This equation is used to analyze calorimetry data to measure heats of reaction.

For a nonflow constant temperature (isothermal) process, heat added to the system Q is equal to the work done by the system W from the first law of thermodynamics, i.e., $\Delta U = 0$ in Eq. (1.43). For an ideal gas, the amount of heat transferred was given by;

$$Q = RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{P_1}{P_2}\right) \qquad (1.46)$$

Sensible heat is heat causing the temperature change in a system given by either Eq. (1.44) or (1.45), and does not include heat from phase changes, chemical reactions, or concentration changes.

Latent heat is the heat transferred at constant temperature to a substance undergoing a phase transition, such as being vaporized or liquefied.

WORKED EXAMPLES

1. Calculate the absolute pressure for a system, given a gauge pressure of 1.5 MPa and a barometric pressure (atmospheric pressure) of 104 kPa.

Solution

$$P_{abs} = P_{atm} + P_{gauge}$$
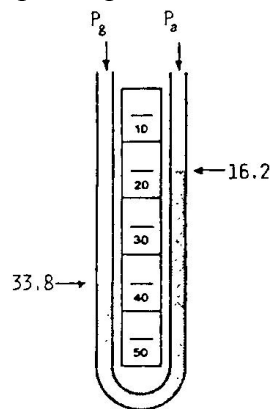$$P_{gauge} = 1.5 \text{ MPa}$$
$$= 1.5 \times 1000 \text{ kPa}$$
$$= 1500 \text{ kPa}$$
$$P_{abs} = 1500 + 104$$
$$= 1604 \text{ kPa}$$

2. An open end mercurial manometer shown below in the figure is connected to a gas tank. The mercury meniscus in the left leg of the manometer is opposite 33.8 cm on the meter stick; in the right leg it is opposite 16.2 cm. Atmospheric pressure is 747 mm Hg. Find the pressure of the gas.

Solution

Always equate pressures at the lower liquid surface, that is, $P_g = P_a + P_{Hg}$. The gas pressure is greater than atmospheric pressure as shown in the figure.
$$P_{Hg} = 33.8 - 16.2 = 17.6 \text{ cm} = 176 \text{ mm Hg}$$
$$P_a = 747 \text{ mm Hg}$$
$$P_g = 747 + 176$$
$$= 923 \text{ mm Hg.}$$

3. A 0.2 m³ container holds oxygen at 70°C and 25 bars. Calculate the amount of oxygen in the container if the atmospheric pressure is 1 bar.

Solution

$$\text{For ideal gas, } PV = \frac{mRT}{M}$$

$$\therefore \ m = \frac{PVM}{RT}$$

where

$$P = 25 + 1 = 26 \text{ bars}$$
$$= 26 \times 10^5 \text{ N/m}^2$$

$$V = 0.2 \text{ m}^3, \ R = 8314.3 \text{ J/kg.mol-}^o\text{K}, \ T = 273 + 70 = 343^o\text{K}, \ M = 32 \text{ kg/kg.mol}$$

$$m = \frac{26 \times 10^5 \text{ N/m}^2 \times 0.2 \text{ m}^3 \times 32 \text{ kg/kg.mol}}{8314.3 \text{ J/kg.mol-}^o\text{K} \times 343 \ ^o\text{K}}$$

$$= 5.8354 \text{ kg}$$

4. A container having a volume of 2.5 ft³ initially contains oxygen gas at a pressure of 125 psia and a temperature of 75°F. Oxygen then leaks from the container until the pressure drops to 100 psia, while the temperature remains the same. Assuming ideal gas behavior, determine how many pounds of oxygen leaked out of the container.

Solution
For ideal gas

$$m_1 = \frac{P_1 V_1 M}{R T_1}$$

$$m_2 = \frac{P_2 V_2 M}{R T_2}$$

$$\text{For oxygen, } R = 1545.3 \text{ ft-lb/lbm.mol-}^o\text{R and } M = 32 \text{ lbm/lbm.mol}$$

$$P_1 = 125 \text{ psia}$$

$$T_1 = 75 + 460 = 535 \ ^o\text{R}$$

$$V_1 = 2.5 \text{ ft}^3$$

$$m_1 = \frac{125 \text{ lb/in}^2 \times 12^2 \text{ in}^2 / \text{ft}^2 \times 2.5 \text{ ft}^3 \times 32 \text{ lbm/lbm.mol}}{1545.3 \text{ ft-lb/lbm.mol-}^o\text{R} \times 535^o\text{R}}$$

$$= 1.74 \text{ lbm}$$

$$P_2 = 100 \text{ psia}$$

$$T_2 = T_1 = 535 \text{ }^{\circ}\text{R}$$

$$V_2 = V_1 = 2.5 \text{ ft}^3$$

$$m_2 = \frac{100 \text{ lb/in}^2 \times 12^2 \text{ in}^2 / \text{ft}^2 \times 2.5 \text{ ft}^3 \times 32 \text{ lbm/lbm.mol}}{1545.3 \text{ ft-lb/lbm.mol-}^{\circ}\text{R} \times 535^{\circ}\text{R}}$$

$$= 1.393 \text{ lbm}$$

$$\therefore \ m_1 - m_2 = 1.74 - 1.393$$

$$= 0.347 \text{ lbm}$$

SAMPLE QUESTIONS

1. A cylinder contains 3 kg if water and water vapour mixture in equilibrium at a pressure of 500 kN/m². The volume of the cylinder is 1 m³. Calculate:
   a. The temperature of the mixture,

   [ANS: T_{sat} at $P = 500 \, kN/m^2$ is $434.95 \, °K$]

   b. The volume and mass of water

$$\text{the volume of the liquid} = m_f v_f$$

   [ANS:
   $$\text{the mass of liquid} = 3(1\text{-}x)$$
   $$= 0.333 \, kg \, '$$
   $$= 0.333 \times 0.0011$$
   $$= 0.000366 \, m^3$$
   $$= 0.366 \, liter$$
   ]

   and

   c. The volume and mass of vapor.
   [ANS:
   the mass of vapor $= mx = 0.889 \times 3$
   $$= 2.667 \, kg$$
   the volume of vapor $= m_g v_g$]
   $$= 2.667(0.3737 + 0.0011)$$
   $$= 0.9995 \, m^3$$

2. A cylinder which contains 3 pounds of saturated liquid water at a constant pressure of 30 psia is heated until the quality of the mixture is 70%. Calculate:
   a. The initial temperature
   b. The final pressure and temperature
   c. The volume change of the mixture

(Answer: a. 250.34°F, b. 30 psia and 250.34°F (because fluid is not completely vapourised) read from steam tables, 28.8 ft³)

3. 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 ms⁻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 $C_p = 4.18 \, kJ \, kg^{-1} \, °C^{-1}$.

(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

TRY

TUTORIAL SET 1

1. Determine the weight, in newtons, of an object whose mass is 10 kg at a location where the acceleration due to gravity is 9.81 m/s^2

2. An object occupies a volume of 25 ft^3 and weighs 20 lbf at a location where the acceleration of gravity is 31.0 ft/s^2. Determine its weight, in lbf, and its average density, in lbf/ft^3, on the moon, where g = 5.57 ft/s^2.

3. A spring stretches 0.2 cm per Newton of applied force. An object is suspended from the spring and a deflection of 3 cm is observed. If g = 9.81 m/s^2, what is the mass of the object, in kg?

4. Determine the absolute pressure exerted on an object submerged 1000 m below the surface of the sea, in bars. The density of seawater is 1020 kg/m^3 and the acceleration of gravity is 9.7 m/s^2. The local atmospheric pressure is 0.98 bar.

5. The following table lists temperatures and specific volumes of water at two pressures.

P = 0.1 MPa		P = 0.12 MPa	
T/(°C)	V/m^{3}kg	T/(°C)	V/m^{3}kg
200	2.172	200	1.808
240	2.359	240	1.965
280	2.546	280	2.120

Data encountered in solving problems often do not exactly on the grid values provided by property tables and linear interpolation between adjacent table entries becomes necessary. Using the data provided, estimate

(a) The specific volume at $T = 200$ °C, $p = 0.113$Mpa.
(b) The temperature at p = 0.12 MPa, $v = 1.85$ m^3/kg in °C
(c) The temperature at p = 0.11 MPa, $v = 2.20$ m^3/kg, in K