INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS

Third Class

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1. Introduction

1.1 What is the thermodynamics? Thermodynamic: The science that deals with heat and work and those properties of matter that relate to heat and work, or (Energy differences and transfers between systems).

1.2 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:

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: $V = V^t/m$ or $V^t = mV$

Molar volume: $V = V^t/n$ or $V^t = nV$

Specific or molar density is defined as the reciprocal of specific or molar volume: $\rho = V^{-1}$ These quantities (V and ρ) 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.

1.3 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):

$$F = ma$$

The newton is defined as the force which when applied to a mass of 1 kg produces an acceleration of 1 m s^{-2}; thus the newton is a derived unit representing 1 kg m s-^{2}

The mass unit in SI is kg , in English unit is Ibm

Ibm=0.454 kg

$$F = \frac{ma}{gc}$$

$1/gc$: is the proportionality constant,

In SI unit F=ma/gc : $1N = \frac{1kg \times 1m/_{s^2}}{gc}$ then

$gc = \frac{kg.m}{N.s^2}$ $g_c = 9.806\,65\ \text{kg m. kgf}^{-1}\text{s}^{-2}$

In English unit gc= 32.174 Ibm.ft/Ibf.sec

Ibf= 4.448

Example 1.1

An astronaut weighs 730 N in Houston, Texas, where the local acceleration of gravity is $g = 9.792$ m s^{-2}. What are the astronaut's mass and weight on the moon, where $g = 1.67$ m s^{-2}?

Solution 1.1

With $a = g$, Newton's law is: $F = mg$. Whence,

$$m = \frac{F}{g} = \frac{730\ \text{N}}{9.792\ \text{m s}^{-2}} = 74.55\ \text{N m}^{-1}\ \text{s}^2$$

Because the newton N has the units kg m s^{-2},

$$m = 74.55\ \text{kg}$$

This *mass* of the astronaut is independent of location, but *weight* depends on the local acceleration of gravity. Thus on the moon the astronaut's weight is:

$$F(\text{moon}) = mg(\text{moon}) = 74.55\ \text{kg} \times 1.67\ \text{m s}^{-2}$$

or $$F(\text{moon}) = 124.5\ \text{kg m s}^{-2} = 124.5\ \text{N}$$

Use of the English engineering system of units requires conversion of the astronaut's weight to (lb_f) and the values of g to (ft)(s)$^{-2}$. With 1 N equivalent to 0.224809(lb_f) and 1 m to 3.28084(ft):

$$\text{Weight of astronaut in Houston} = 164.1(\text{lb}_f)$$

$$g(\text{Houston}) = 32.13 \qquad \text{and} \qquad g(\text{moon}) = 5.48(\text{ft})(\text{s})^{-2}$$

Newton's law then gives:

$$m = \frac{Fg_c}{g} = \frac{164.1(\text{lb}_f) \times 32.1740(\text{lb}_m)(\text{ft})(\text{lb}_f)^{-1}(\text{s})^{-2}}{32.13(\text{ft})(\text{s})^{-2}}$$

or $$m = 164.3(\text{lb}_m)$$

Thus the astronaut's mass in (lb_m) and weight in (lb_f) in Houston are *numerically* almost the same, but on the moon this is not the case:

$$F(\text{moon}) = \frac{mg(\text{moon})}{g_c} = \frac{(164.3)(5.48)}{32.1740} = 28.0(\text{lb}_f)$$

1.4 TEMPERATURE

Temperature is commonly measured with liquid-in-glass thermometers, wherein the liquid expands when heated. Thus a uniform tube partially filled with mercury, alcohol, or some other fluid, can indicate degree of "hotness" simply by the length of the fluid column. However, numerical values are assigned to the various degrees of hotness by arbitrary definition.

1. Celsius scale: (ºC) formally called centigrate
2. Absolute temperature
   a. Kelven scale
   b. Rankin scale

t° 9.67

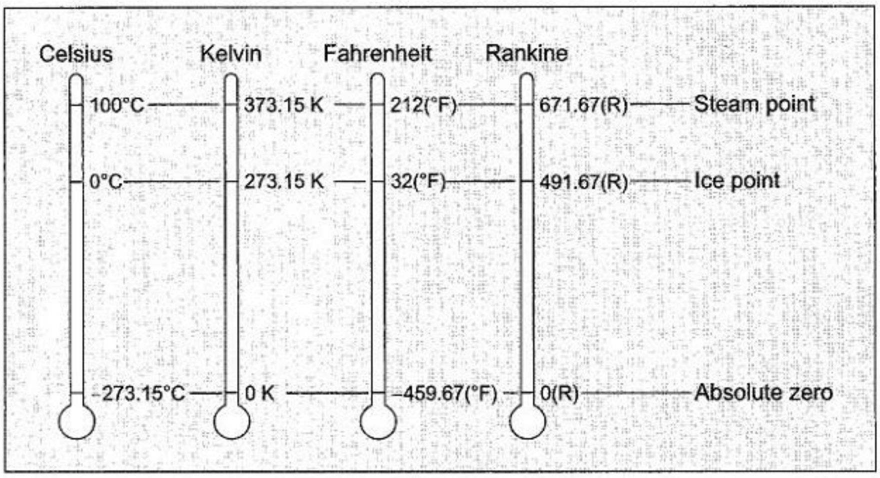


Figure 1.1 Relations among temperature scales

1.5 PRESSURE

The pressure P exerted by a fluid on a surface is defined as the normal force exerted by the fluid per unit area of the surface. If force is measured in N and area in m2, the unit is the newton per square meter or N/m^2, called the pascal, symbol Pa, the basic SI unit of pressure. In the metric engineering system a common unit is the kilogram force per square centimeter (kgf cmP2)

The primary standard for pressure measurement is the dead-weight gauge in which a known force is balanced by a fluid pressure acting on a known area; whence P = F/A. A

simple design is shown in Fig. 1.2. (in slides). The piston is carefully fitted to the cylinder making the clearance small. Weights are placed on the pan until the pressure of the oil, which tends to make the piston rise, is just balanced by the force of gravity on the piston and all that it supports. With this force given by Newton's law, the pressure of the oil is:

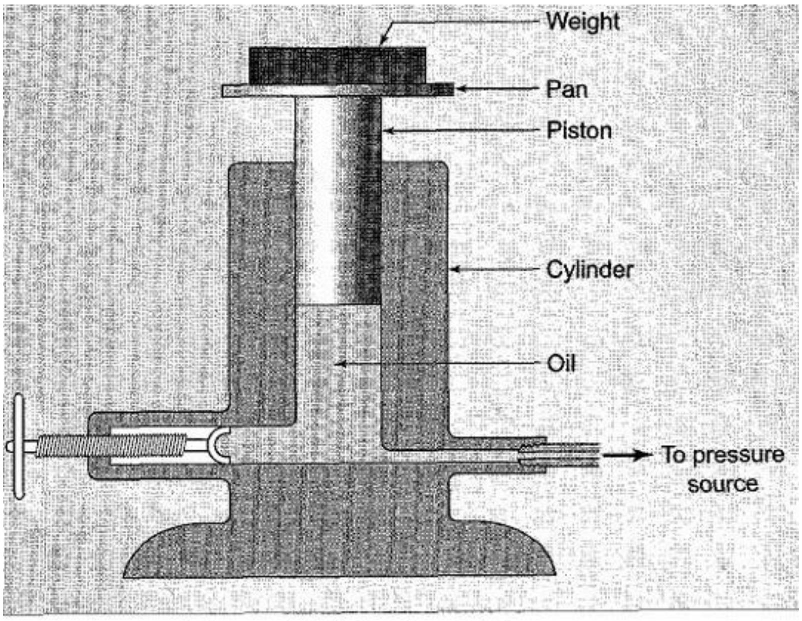


Figure 1.2 Dead-weight gauge

$$\boldsymbol{P = \frac{F}{A} = \frac{mg}{A}}$$

where m is the mass of the piston, pan, and weights; g is the local acceleration of gravity; and A is the cross-sectional area of the piston. Gauges in common use, such as Bourdon gauges, are calibrated by comparison with dead-weight gauges.

Since a vertical column of a given fluid under the influence of gravity exerts a pressure at its base in direct proportion to its height, pressure is also expressed as the equivalent height of a fluid column. This is the basis for the use of manometers for pressure measurement. Conversion of height to force per unit area follows from Newton's law applied to the force of gravity acting on the mass of fluid in the column. The mass is given by:

$$\mathbf{m = Ahp}$$

where A is the cross-sectional area of the column, h is its height, and p is the fluid density. Therefore,

$$P = \frac{F}{A} = \frac{mg}{A} = \frac{Ah\rho g}{A} = h\rho g$$

Example 1.2

A dead-weight gauge with a 1-cm-diameter piston is used to measure pressures very accurately. In a particular instance a mass of 6.14 kg (including piston and pan) brings it into balance. If the local acceleration of gravity is 9.82 m s^{-2}, what is the *gauge* pressure being measured? If the barometric pressure is 748(torr), what is the *absolute* pressure?

Solution 1.2

The force exerted by gravity on the piston, pan, and weights is:

$$F = mg = (6.14)(9.82) = 60.295 \text{ N}$$

$$\text{Gauge pressure} = \frac{F}{A} = \frac{60.295}{(1/4)(\pi)(1)^2} = 76.77 \text{ N cm}^{-2}$$

The absolute pressure is therefore:

$$P = 76.77 + (748)(0.013332) = 86.74 \text{ N cm}^{-2}$$

or

$$P = 867.4 \text{ kPa}$$

Example 1.3

At 27°C the reading on a manometer filled with mercury is 60.5 cm. The local acceleration of gravity is 9.784 m s^{-2}. To what pressure does this height of mercury correspond?

Solution 1.3

Recall the equation in the preceding text, $P = h\rho g$. At 27°C the density of mercury is 13.53 g cm^{-3}. Then,

$$P = 60.5 \text{ cm} \times 13.53 \text{ g cm}^{-3} \times 9.784 \text{ m s}^{-2} = 8{,}009 \text{ g m s}^{-2} \text{ cm}^{-2}$$

or

$$P = 8.009 \text{ kg m s}^{-2} \text{ cm}^{-2} = 8.009 \text{ N cm}^{-2} = 80.09 \text{ kPa} = 0.8009 \text{ bar}$$

1.6 WORK

Work W is performed whenever a force acts through a distance. By definition, the quantity of work is given by the equation:

$$dW = Fdl \tag{1.1}$$

Joul= N.m in SI

Ft.Ibf=Ibf.ft

where F is the component of force acting along the line of the displacement dl. When integrated, this equation yields the work of a finite process. 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.

The work which occurs with a change in volume of a fluid is often encountered in thermodynamics. A common example is the compression or expansion of a fluid in a cylinder resulting from the movement of a piston. The force exerted by the piston on the fluid is equal to the product of the piston area and the pressure of the fluid. The displacement of the piston is equal to the total volume change of the fluid divided by the area of the piston. Equation (1.1) therefore becomes:

$$dW = -PA\,d\frac{V^t}{A}$$

or, since A is constant,

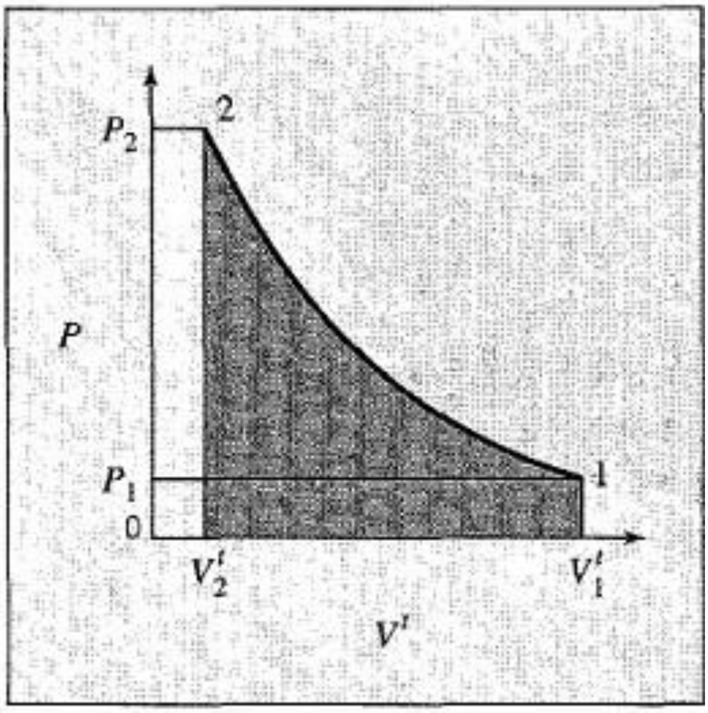
$$dW = -PdV^t \tag{1.2}$$

Integrating,

$$W = -\int_{V_1^t}^{V_2^t} P\,dV^t \tag{1.3}$$

The minus signs in these equations are made necessary by the sign convention adopted for work. When the piston moves into the cylinder so as to compress the fluid, the applied force and its displacement are in the same direction; the work is therefore positive. The minus sign is required because the volume change is negative. For an expansion process, the applied force and its displacement are in opposite directions. The volume change in this case is positive, and the minus sign is required to make the work negative.

Equation (1.3) expresses the work done by a finite compression or expansion process. Figure 1.3 shows a path for compression of a gas from point 1 with initial volume V_1^t at pressure P_1 to point 2 with volume V_2^t at pressure P_2. This path relates the pressure at any point of the process to the volume. The work required is given by Eq. (1.3) and is proportional to the area under the curve of Fig. 1.3.



1.7 ENERGY

Indeed, it follows directly from Newton's second law of motion once work is defined as the product of force and displacement.

1.7.1 Kinetic Energy (Ek)

When a body of mass m, acted upon by a force F, is displaced a distance dl during a differential interval of time dt, the work done is given by Eq. (1.1. (dW = Fdl). In combination with Newton's second law this equation becomes:

$$dW = ma\,dl$$

By definition the acceleration is a – du/dt, where u is the velocity of the body. Thus,

$$dW = m\frac{du}{dt}dl = m\frac{dl}{dt}\,du$$

Since the definition of velocity is u = dl/dt, the expression for work becomes:

$$dW = mu\,du$$

This equation may now be integrated for a finite change in velocity from u_l to u_2:

$$W = m\int_{u_1}^{u_2} u\,du = m\left(\frac{u_2^2}{2} - \frac{u_1^2}{2}\right)$$

Or

$$W = \frac{mu_2^2}{2} - \frac{mu_1^2}{2} = \Delta\left(\frac{mu^2}{2}\right) \tag{1.4}$$

Each of the quantities $mu^2/2$ in Eq. (1.4) is a kinetic energy, a term introduced to

$$E_K \equiv \frac{1}{2}\mathrm{mu}^2 \tag{1.5}$$

Equation (1.4) shows that the work done on a body in accelerating it from an initial velocity u_l to a final velocity u_2 is equal to the change in kinetic energy of the body. Conversely, if a moving body is decelerated by the action of a resisting force, the work done by the body is equal to its change in kinetic energy.

In SI system the units is $kg.m^2/s^2$= kg. m/s^2 .m = N.m= joule

In English system

$$E_K = \frac{\mathrm{mu}^2}{2g_c} = \frac{\mathrm{kg\ m^2\ s^{-2}}}{\mathrm{kg\ m\ kgf^{-1}\ s^{-2}}} = \mathrm{m\ kgf}$$

That mean equal to =ft.Ibf

1.7.2 Potential Energy (Ep)

If a body of mass m is raised from an initial elevation z_l to a final elevation z_2, an upward force at least equal to the weight of the body must be exerted on it, and this force must move through the distance $z_2 - z_1$.

$$F = ma = mg$$

where g is the local acceleration of gravity. The minimum work required to raise the body is the product of this force and the change in elevation:

$$W = F(z_2 - z_1) = mg(z_2 - z_1)$$

or

$$W = mz_2g - mz_1g = \Delta(mzg) \tag{1.6}$$

We see from Eq. (1.6) that the work done on the body in raising it is equal to the change in the quantity ***mzg***. Conversely, if the body is lowered against a resisting force equal to its weight, the work done by the body is equal to the change in the quantity ***mzg***. Equation (1.6) is similar in form to Eq. (1.4), and both show that the work done is equal to the change in a quantity which describes the condition of the body in relation to its surroundings.

The work done on a body in elevating it is said to produce a change in its potential energy:

$$E_P \equiv mzg \tag{1.7}$$

The units is same with the kinetic energy

In SI system the units is kg.m^2/s^2= kg. m/s^2 .m = N.m= joule

In English system

$$E_K = \frac{mu^2}{2g_c} = \frac{\text{kg m}^2\ \text{s}^{-2}}{\text{kg m kgf}^{-1}\ \text{s}^{-2}} = \text{m kgf}$$

That mean equal to =ft.Ibf

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:

$$\Delta E_K + \Delta E_P = 0$$

Or

$$\frac{mu_2^2}{2} - \frac{mu_1^2}{2} + mz_2g - mz_1g = 0$$

Example 1.4

An elevator with a mass 2500 kg rests at a level 10 m above the base of an elevator shaft. It is raised to 100 m above the base of the shaft, where the cable holding it breaks. The elevator falls freely to the base of the shaft and strikes a strong spring. The spring is designed to bring the elevator to rest and, by means of a catch arrangement, to hold the elevator at the position of maximum spring compression. Assuming the entire process to be frictionless & and taking g = 9.8 m/s^2. Calculate:

(a) The potential energy of the elevator in its initial position relative to the base of the shaft.

(b) The work done in raising the elevator

(c) The potential energy of the elevator in its highest position relative to the base of the shaft.

(d) The velocity and kinetic energy of the elevator just before it strikes the spring.

(e) The potential energy of the compressed spring.

(f) The energy of the system consisting of the elevator and spring (1) at the start of the process, (2) when the elevator reaches its maximum height. (3) Just before the elevator strikes the spring, (4) after the elevator has come to rest

Solution 1.4

Let subscript 1 designate the initial conditions; subscript 2, conditions when the elevator is at its highest position; and subscript 3, conditions just before the elevator strikes the spring.

(*a*) By Eq. (1.7), $E_{P_1} = mz_1g = (2{,}500)(10)(9.8) = 245{,}000\ \text{J}$

(*b*) By Eq. (1.1), $W = \int_{z_1}^{z_2} F\,dl = \int_{z_1}^{z_2} mg\,dl = mg(z_2 - z_1)$

whence $W = (2{,}500)(9.8)(100 - 10) = 2{,}205{,}000\ \text{J}$

(*c*) By Eq. (1.7), $E_{P_2} = mz_2g = (2{,}500)(100)(9.8) = 2{,}450{,}000\ \text{J}$

Note that $W = E_{P_2} - E_{P_1}$.

(*d*) From the principle of conservation of mechanical energy, one may write that the sum of the kinetic- and potential-energy changes during the process from conditions 2 to 3 is zero; that is,

$$\Delta E_{K_{2\to3}} + \Delta E_{P_{2\to3}} = 0 \qquad \text{or} \qquad E_{K_3} - E_{K_2} + E_{P_3} - E_{P_2} = 0$$

However, E_{K_2} and E_{P_3} are zero. Therefore,

$$E_{K_3} = E_{P_2} = 2{,}450{,}000\ \text{J}$$

With $E_{K_3} = \frac{1}{2}mu_3^2$, $\quad u_3^2 = \frac{2E_{K_3}}{m} = \frac{(2)(2{,}450{,}000)}{2{,}500}$

Whence, $\quad u_3 = 44.27\ \text{m s}^{-1}$

(*e*) Because the changes in the potential energy of the spring and the kinetic energy of the elevator must sum to zero,

$$\Delta E_P(\text{spring}) + \Delta E_K(\text{elevator}) = 0$$

The initial potential energy of the spring and the final kinetic energy of the elevator are zero; therefore, the final potential energy of the spring must equal the kinetic energy of the elevator just before it strikes the spring. Thus the final potential energy of the spring is 2,450,000 J.

(f) If the elevator and the spring together are taken as the system. The initial energy of the system is the potential energy of the elevator, or 245,000J. The total energy of the system can change only if work is transferred between it and the surroundings. As the elevator is raised, work is done on the system by the surroundings in the amount of 2,205,000 J, Thus the energy of the system when the elevator reaches its maximum height is 245.000 + 2,205,000 = 2,450,000 J.

Subsequent changes occur entirely within the system, with no work transfer between the system and surroundings. Hence the total energy of the system remains constant at 2,450,000 J. It merely changes from potential energy of position (elevation) of the elevator to kinetic energy of the elevator to potential energy of configuration of the spring.

This example illustrates application of the law of conservation of mechanical energy. However, the entire process is assumed to occur without friction: the results obtained are exact only for such an idealized process.

1.8 HEAT

We know from experience that a hot object brought in contact with a cold object becomes cooler, whereas the cold object becomes warmer. A reasonable view is that something is transferred from the hot object to the cold one, and we call that something heat Q. Thus we say that heat always flows from a higher temperature to a lower one. This leads to the concept of temperature as the driving force for the transfer of energy as heat. More precisely, the rate of heat transfer from one body to another is proportional to the temperature difference between the two bodies; when there is no temperature difference, there is no net transfer of heat. In the thermodynamic sense, heat is never regarded as being stored within a body. Like work, it exists only as energy in transit from one body to another, or between a system and its surroundings. When energy in the form of heat is added to a body, it is stored not as heat but as kinetic and potential energy of the atoms and molecules making up the body.