1.3 Pressure

Any force acting on a surface consists of a component perpendicular to the surface and a component parallel to the surface. These two components are called normal force and shear force as shown in Figure 1.4.

Pressure is defined as a normal force per unit area on which the force acts. The SI pressure unit, N/m^2, is called a Pascal (Pa). Pressure at any point is a fluid is the same in any direction.

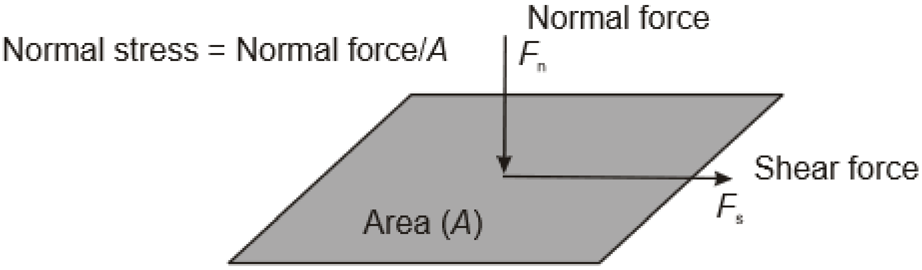


Figure 1.4 Normal and parallel components of a force on a surface.

Consider a hole in the wall of a tank or a pipe as shown in Figure 1.5.

The fluid pressure p may be defined as the ratio F/A, where F is the minimum force that would have to exerted on a frictionless plug in the hole to keep the fluid from emerging1

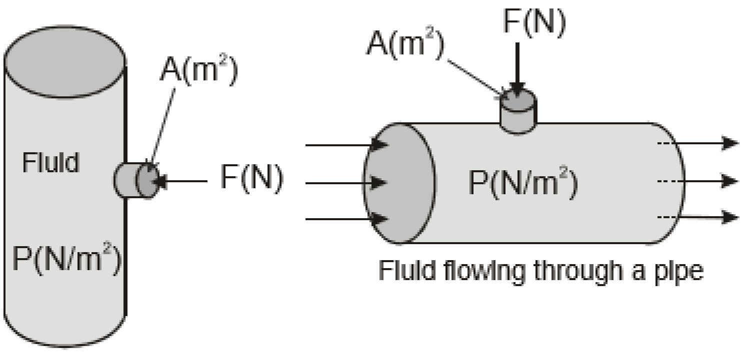


Figure 1.5 Fluid pressure in a tank and a pipe.

The pressure at a given position measured relative to absolute zero pressure or absolute vacuum is called the absolute pressure. Most pressure-measuring devices are calibrated to read zero in the atmosphere as shown in Figure 1.6. These pressure gages indicate the difference between the absolute pressure and the local atmospheric pressure. Pressures below atmospheric pressure are called vacuum pressures and are measured by vacuum gages that indicate the difference between the atmospheric pressure and the absolute pressure. Absolute, gage, and vacuum pressures are all positive quantities and are related to each other by

$$P_{gage} = P_{abs} - P_{atm} \quad \dots \quad (P_{abs} = P_{gage} + P_{atm}) \quad \dots\dots(1-1)$$

$$P_{Vac} = P_{atm} - P_{abs} \quad \dots\dots\dots\dots(1-2)$$

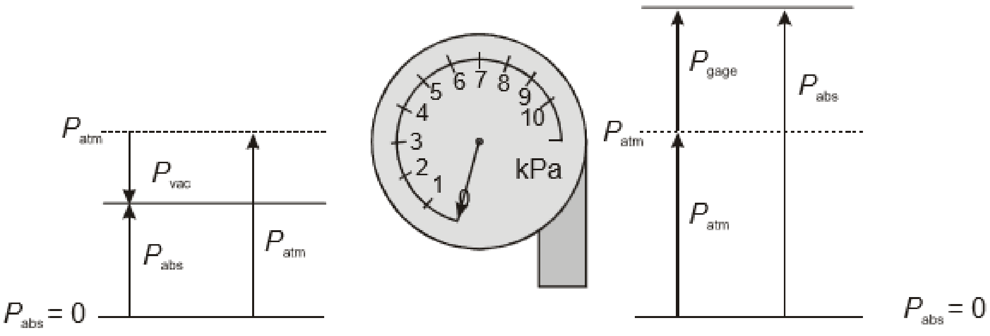


Figure 1.6 Absolute, gage, and vacuum pressures.

Two common pressure units are the bar and standard atmosphere:

1 bar = 10^5 Pa = 0.1 Mpa = 100 kPa

1 atm = 101,325 Pa = 101.325 kPa = 1.01325 bar = 14.696 psi

1.4 The specific volume v is defined as the reciprocal of the density, $\boldsymbol{v = 1/\rho}$ It is the volume per unit mass. Like density, specific volume is an intensive property and may vary from point to point. SI units for density and specific volume are kg/m^3 and m^3/kg, respectively. However, they are also often expressed, respectively, as g/cm^3 and cm^3/g. Other units used for density and specific volume in this text are lb/ft^3 and ft^3/lb, respectively. In the fluid mechanics part of the book, density also is given in slug/ft^3.

In certain applications it is convenient to express properties such as a specific volume on a molar basis rather than on a mass basis. The amount of a substance can be given on a molar basis in terms of the kilomole (kmol) or the pound mole (lbmol), as appropriate. In either case we use

$$\mathbf{n = m / M} \qquad (1.3)$$

The number of kilomoles of a substance, n, is obtained by dividing the mass, m, in kilograms by the molecular weight, M, in kg/kmol. Similarly, the number of pound moles, n, is obtained by dividing the mass, m, in pound mass by the molecular weight, M, in lb/lbmol.

In thermodynamics, we signal that a property is on a molar basis by placing a bar over its symbol. Thus, **ΰ** signifies the volume per kmol or lbmol, as appropriate. In this text the units used for ΰ are m^3/kmol and ft^3/lbmol. With Eq. 1.3, the relationship between ύ and υ is

$$\mathbf{ύ = M}\,\boldsymbol{v} \qquad (1.4)$$

Where M is the molecular weight in kg/kmol or lb/lbmol, as appropriate.

1.5 Temperature

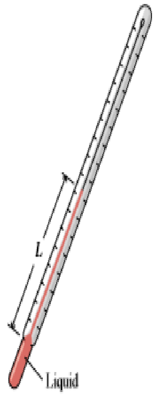
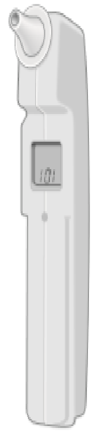


Figure 2.5 Liquid-in-glass thermometer.

When two objects are brought into contact and isolated from the surrounding, energy tends to move spontaneously from one to the other. The object that gives up energy is at a higher temperature, and the object that receives energy is at a lower temperature.

We would be able to observe that the electrical resistance *of the warmer* object decreases with time, and that of the colder block increases with time; eventually there would be no change in the electrical resistances of these objects. The two objects are then in thermal equilibrium. They are at the same Temperature. We could then define temperature as a measure of the tendency of an object to spontaneously give up energy to its surroundings.

Any object with at least one measurable property that changes as its temperature changes can be used as a thermometer. Most thermometers operate **on the principle of thermal expansion**: Materials tend to occupy more volume at a given pressure when they are at a higher temperature. A mercury thermometer is just a convenient device for measuring the volume of a fixed amount of mercury. To define actual units for temperature we arbitrary assign 0 to the freezing point and 100 to the boiling or steam point of water. We then mark these two points on our mercury thermometer, measure off a hundred equally spaced intervals in between, and declare that this thermometer now measures temperature on the **Celsius (or centigrade) scale**, by definition.



The Kelvin scale is an absolute temperature scale that measures temperature from absolute zero instead of from the freezing point of water. The relationship between these two temperature scales is given by

$$\mathbf{T(^{o}C) = T(K) - 273.15} \qquad (1.5)$$

$$T_K = T_C + 273.15$$

By definition, the Rankin scale, is related to the Kelvin scale by a factor of 1.8:

$$\mathbf{T(^{o}R) = 1.8T(K)} \qquad (1.6)$$

A degree of the same size as that on the Rankine scale is used in the Fahrenheit scale but the zero point is shifted according to the relation

T (ºF) = T(ºR) − 459.67 (1.7)

$$T_R = T_F + 459.67$$

From equations (1.5), (1.6), and (1.7) the Fahrenheit scale can be related to the Celsius scale by

T (ºF) = 1.8 T(ºC) + 32 (1.8)

Many of the equations of thermodynamics are correct only when you measure temperature on the absolute scale, Kelvin or Rankine. There will be no problem in using the Celcius and Fahrenheit scales when the difference between two temperatures is needed.

1.6. ENERGY, WORK AND HEAT

1.6.1. Energy

Energy: is a general term embracing energy in transition and stored energy. The stored energy of a substance may be in the forms of mechanical energy and internal energy (other forms of stored energy may be chemical energy and electrical energy). Part of the stored energy may take the form of either potential energy (which is the gravitational energy due to height above a chosen datum line) or kinetic energy due to velocity. The balance part of the energy is known as internal energy.

In a non-flow process usually there is no change of potential or kinetic energy and hence change of mechanical energy will not enter the calculations.

In a flow process, however, there may be changes in both potential and kinetic energy and these must be taken into account while considering the changes of stored energy.

Heat and work are the forms of energy in transition. These are the only forms in which energy can cross the boundaries of a system. Neither heat nor work can exist as stored energy.

*** Work and Heat

1.6.2 Work:

Work is said to be done when a force moves through a distance. If a part of the boundary of a system undergoes a displacement under the action of a pressure, the work done W is the product of the force (pressure × area), and the distance it moves in the direction of the force. Fig. 1.7 (a) illustrates this with the conventional piston and cylinder arrangement, the heavy line defining the boundary of the system. Fig. 1.7 (b) illustrates another way in which work might be applied to a system. A force is exerted by the paddle as it changes the momentum of the fluid, and since this force moves during rotation of the paddle work is done.

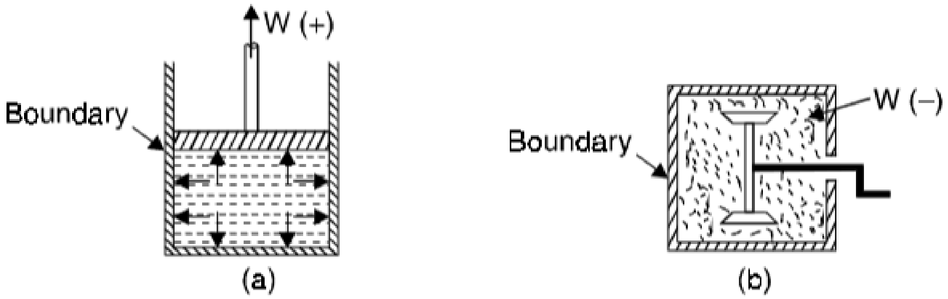


Figure 1.7

Work is a transient quantity which only appears at the boundary while a change of state is taking place within a system. Work is 'something' which appears at the boundary when a system changes its state due to the movement of a part of the boundary under the action of a force.

Sign convention:

- If the work is done by the system on the surroundings, e.g., when a fluid expands pushing a piston outwards, the work is said to be **positive.**

i.e., **Work output of the system = + W**

- If the work is done on the system by the surroundings, e.g., when a force is applied to a rotating handle, or to a piston to compress a fluid, the work is said to be negative.

i.e., **Work input to system = – W**

$$dW = F\,dl \tag{1.2}$$

$$dW = -PA\,d\frac{V^t}{A} = -P\,dV^t \tag{1.3}$$

Integration yields:

$$W = -\int_{V_1^t}^{V_2^t} P\,dV^t \tag{1.4}$$

$$W = \int_{V_1}^{V_2} P\, dV \qquad (1.9)$$

1// constant P

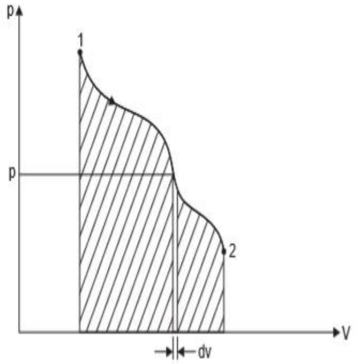
W = P (V_2 – V_1)

2// constant *V*

W= 0 d*V*

3// Relation between pressure P and volume *V*

4// drawing (area under curve) between P & *V*



1.6.3 Heat

Heat (denoted by the symbol Q), may be, defined in an analogous way to work as follows: *"Heat is '**something' which appears at the boundary when a system changes its state due to a difference in temperature between the system and its surroundings".***

Heat, like work, is a transient quantity which only appears at the boundary while a change is taking place within the system.

It is apparent that neither δW or δQ are exact differentials and therefore any integration of the elemental quantities of work or heat which appear during a change from state 1 to state 2 must be written as

$$\int_1^2 \delta W = W_2 - W_1$$

$$\int_1^2 \delta Q = Q_2 - Q_1$$

Sign convention: If the heat flows into a system from the surroundings, the quantity is said to be positive and, conversely, if heat flows from the system to the surroundings it is said to be negative.

In other words:

Heat received by the system = + Q

Heat rejected or given up by the system = – Q.

Heat

1- The Units Of Energy (J), (J/Kg) and (J/sec) or (w)

2- Constant pressure $Q = \int_{T_1}^{T_2} Cp \, dT$

3- Constant Volume $Q = \int_{T_1}^{T_2} Cv \, dT$

SI units: J = 1 N. m
English units: ft. Ibf = 1.3558 J
Other units
The thermal unit (Btu) = 1055.04 J
1 Btu = 1055 J = 252 Cal = 778 ft. Ibf.

Comparison of Work and Heat Similarities:

(i) Both are path functions and inexact differentials.
(ii) Both are boundary phenomenon i.e., both are recognized at the boundaries of the system as they cross them.
(iii) Both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.
(iv) Systems possess energy.

But not work or heat. Dissimilarities:

(i) In heat transfer temperature difference is required.
(ii) In a stable system there cannot be work transfer, however, there is no restriction for the transfer of heat.
(iii) The sole effect external to the system could be reduced to rise of a weight but in the case of a heat transfer other effects are also observed

1.7 Kinetic and Potential Energy

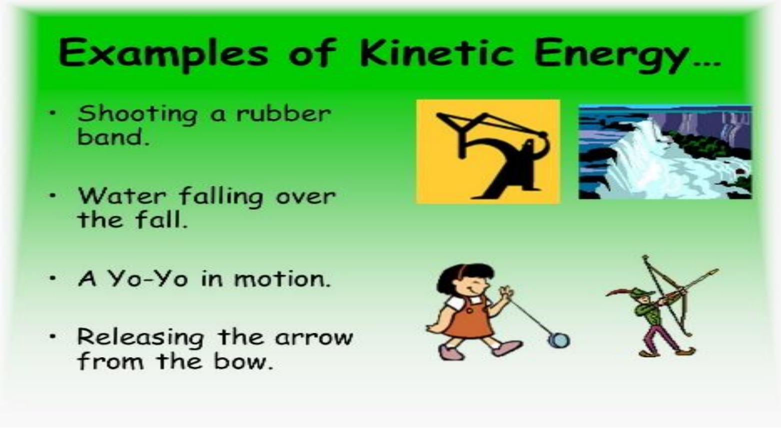
Consider a body of mass m that moves from a position where the magnitude of its velocity is V_1 and its elevation is z1 to another where its velocity is V_2 and elevation is z2, each relative to a specified coordinate frame such as the surface of the earth.

1.7.1 Kinetic Energy: **The quantity 1⁄2 mV^2 is the kinetic energy, KE,** of the body. As written as

$$\mathbf{KE = 1/2\ m\ V^2} \tag{1.10}$$

The change in **kinetic energy ΔKE of the body is**

$$\Delta KE = KE_2 - KE_1 = \tfrac{1}{2} m\left(V_2{}^2 - V_1{}^2\right) \tag{1.11}$$

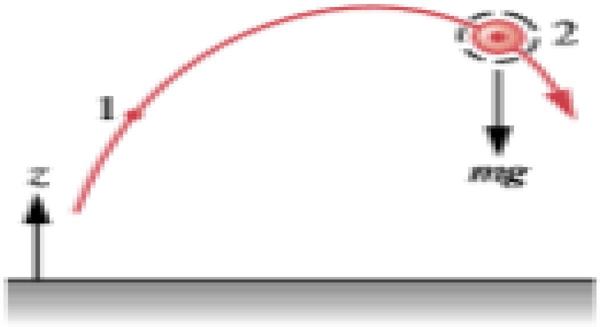


Examples of Kinetic Energy…

- Shooting a rubber band.
- Water falling over the fall.
- A Yo-Yo in motion.
- Releasing the arrow from the bow.

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.

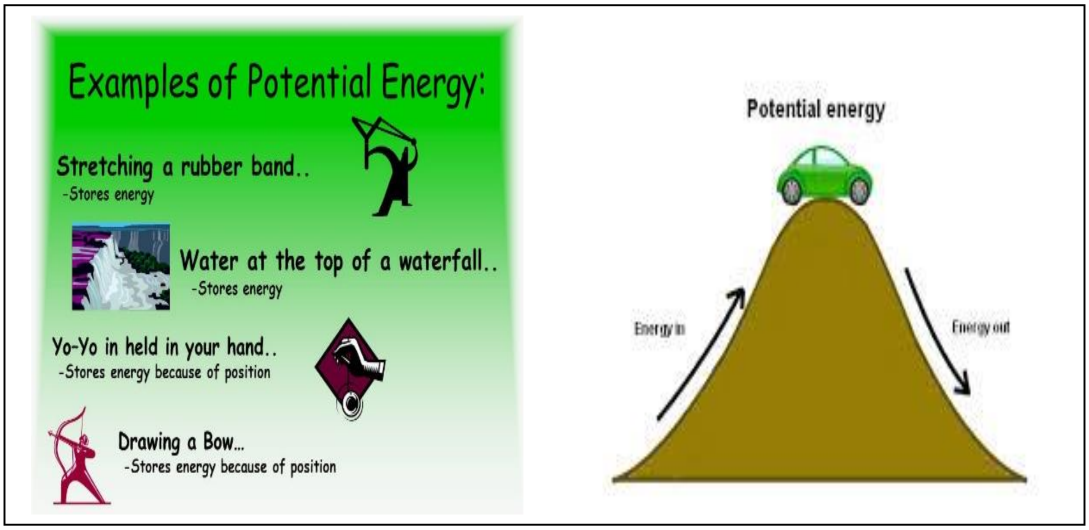


1.7.2 Potential Energy

The quantity mgz is the gravitational potential energy, PE. The change in gravitational potential energy, PE, is

$$\Delta PE = PE_2 - PE_1 = m\,g\,(Z_2 - Z_1) \tag{1.12}$$

Potential energy is associated with the force of gravity (Sec. 1.12) and is therefore an attribute of a system consisting of the body and the earth together.



Examples of Potential Energy:

Stretching a rubber band..
-Stores energy

Water at the top of a waterfall..
-Stores energy

Yo-Yo in held in your hand..
-Stores energy because of position

Drawing a Bow…
-Stores energy because of position

However, evaluating the force of gravity as mg enables the gravitational potential energy to be determined for a specified value of g knowing only the mass of the body and its elevation. With this view, potential energy is regarded as an extensive property of the body.

To assign a value to the kinetic energy or the potential energy of a system, it is necessary to assume a datum and specify a value for the quantity at the datum. Values of kinetic and potential energy are then determined relative to this arbitrary choice of datum and reference value. However, since only changes in kinetic and potential energy between two states are required, these arbitrary reference specifications cancel.

Units. In SI, the energy unit is the newton-meter, N m, called the joule, J. In this book it is convenient to use the kilojoule, kJ.

Other commonly used units for energy are the ***foot pound force,*** and the **British thermal unit, Btu.**

When a system undergoes a process where there are changes in kinetic and potential energy, special care is required to obtain a consistent set of units.

For Example… to illustrate the proper use of units in the calculation of such terms, consider a system having a mass of 1 kg whose velocity increases from 15 m/s to 30 m/s while its elevation decreases by 10 m at a location where g= 9.7 m/s^2.Then

$$\Delta KE = \tfrac{1}{2} m\left({V_2}^2 - {V_1}^2\right)$$

$$\Delta KE = \tfrac{1}{2}(1\ kg)\left[\left(30\frac{m}{s}\right)^2 - \left(15\frac{m}{s}\right)^2\right]\left|\frac{1N}{1\ kg.\ m/s^2}\right|\left|\frac{1KJ}{10^3\ N.m}\right|$$

$$\Delta KE = 0.34\ KJ$$

$$\Delta PE = m\ g\ (Z_2 - Z_1)$$

$$\Delta PE = (1\ kg)\left(9.7\ \frac{m}{S^2}\right)\ [(-10\ m)]\left|\frac{1N}{1\ kg.\ m/s^2}\right|\left|\frac{1KJ}{10^3\ N.m}\right|$$

$$\Delta PE = -0.10\ KJ$$

For a system having a mass of 1 Ib whose velocity increases from 50 ft/s to 100 ft/s while its elevation decreases by 40 ft at a location where g= 32.0 ft/s^2, we have

$$\Delta KE = \tfrac{1}{2} m\left({V_2}^2 - {V_1}^2\right)$$

$$\Delta KE = \tfrac{1}{2}(1\ Ib)\left[\left(100\frac{ft}{s}\right)^2 - \left(50\frac{ft}{s}\right)^2\right]\left|\frac{1Ibf}{32.2\ Ib.\ ft/s^2}\right|\left|\frac{1Btu}{778\ ft.Ibf}\right|$$

$$\Delta KE = 0.15\ Btu$$

$$\Delta PE = m\ g\ (Z_2 - Z_1)$$

$$\Delta PE = (1\ Ib)\left(32.0\ \frac{ft}{S^2}\right)\ [(-40\ ft)]\left|\frac{1\ Ibf}{32.2\ Ib.\ ft/s^2}\right|\left|\frac{1Btu}{778\ ft.Ibf}\right|$$

$$\Delta PE = -0.05\ Btu$$

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

Thus,

$$P = h\rho g$$

Example 1.1

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

Solution 1.1

By Newton's law, with acceleration equal to the acceleration of gravity, g,

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

Because $1\ \text{N} = 1\ \text{kg}\cdot\text{m}\cdot\text{s}^{-2}$,

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

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:

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

or

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

Example 1.2

A dead-weight gauge with a piston diameter of 1 cm is used for the accurate measurement of pressure. If a mass of 6.14 kg (including piston and pan) brings it into balance, and if $g = 9.82$ m·s^{-2}, what is the *gauge* pressure being measured? For a barometric pressure of 0.997 bar, what is the *absolute* pressure?

Solution 1.2

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

$$F = mg = 6.14 \text{ kg} \times 9.82 \text{ m·s}^{-2} = 60.295 \text{ N}$$

$$\text{Gauge pressure} = \frac{F}{A} = \frac{60.295}{(1/4)(\pi)(0.01)^2} = 7.677 \times 10^5 \text{ N·m}^{-2} = 767.7 \text{ kPa}$$

The absolute pressure is therefore:

$$P = 7.677 \times 10^5 + 0.997 \times 10^5 = 8.674 \times 10^5 \text{ N·m}^{-2}$$

or

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

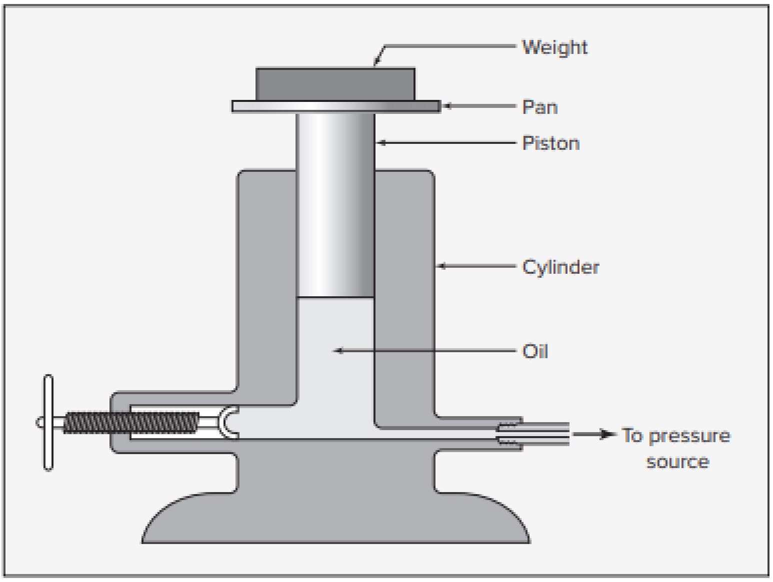
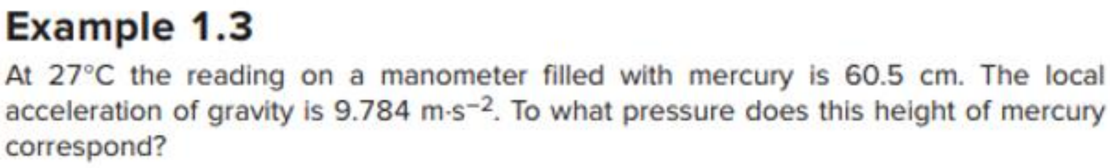


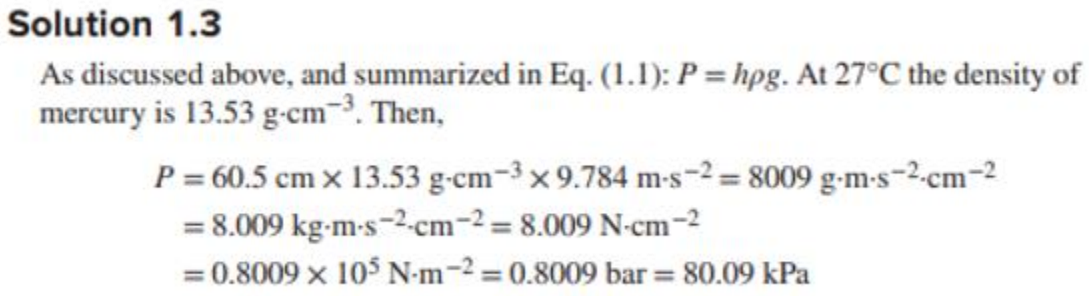
Figure 1.2: Dead-weight gauge.

Because a vertical column of fluid under the influence of gravity exerts a pressure at its base in direct proportion to its height, pressure may be 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



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 $m{\cdot}s^{-2}$. To what pressure does this height of mercury correspond?



Solution 1.3

As discussed above, and summarized in Eq. (1.1): $P = h\rho g$. At 27°C the density of mercury is 13.53 $g{\cdot}cm^{-3}$. Then,

$$\begin{aligned} P &= 60.5\ \text{cm} \times 13.53\ \text{g}{\cdot}\text{cm}^{-3} \times 9.784\ \text{m}{\cdot}\text{s}^{-2} = 8009\ \text{g}{\cdot}\text{m}{\cdot}\text{s}^{-2}{\cdot}\text{cm}^{-2} \\ &= 8.009\ \text{kg}{\cdot}\text{m}{\cdot}\text{s}^{-2}{\cdot}\text{cm}^{-2} = 8.009\ \text{N}{\cdot}\text{cm}^{-2} \\ &= 0.8009 \times 10^{5}\ \text{N}{\cdot}\text{m}^{-2} = 0.8009\ \text{bar} = 80.09\ \text{kPa} \end{aligned}$$

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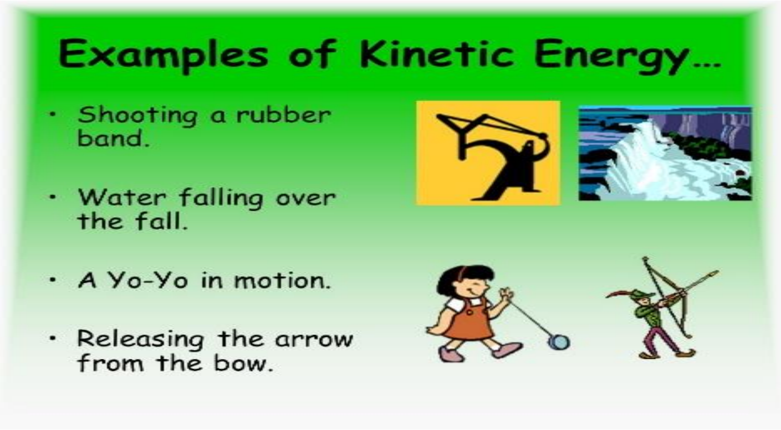

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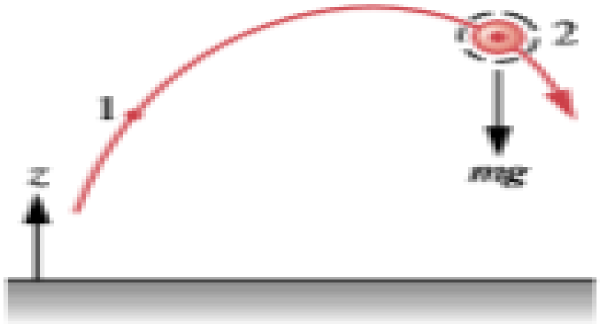

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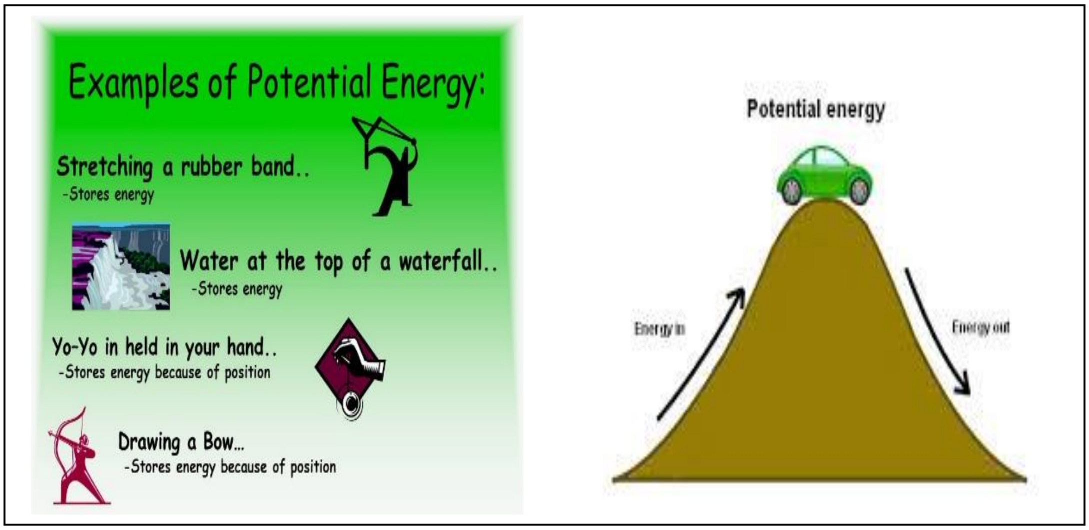

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When a system undergoes a process where there are changes in kinetic and potential energy, special care is required to obtain a consistent set of units.

For Example… to illustrate the proper use of units in the calculation of such terms, consider a system having a mass of 1 kg whose velocity increases from 15 m/s to 30 m/s while its elevation **decreases by 10 m at a location** where g= 9.7 m/s^2.Then

$$\Delta KE = \tfrac{1}{2}m\left({V_2}^2 - {V_1}^2\right)$$

$$\Delta KE = \tfrac{1}{2}(1\ kg)\ \left[\left(30\frac{m}{s}\right)^2 - \left(15\frac{m}{s}\right)^2\right]\ \left|\frac{1N}{1\ kg.\ m/s^2}\right|\left|\frac{1KJ}{10^3\ N.m}\right|$$

$$\Delta KE = 0.34\ KJ$$

$$\Delta PE = m\ g\ (Z_2 - Z_1)$$

$$\Delta PE = (1\ kg)\left(9.7\ \frac{m}{S^2}\right)\ [(-10\ m)]\ \left|\frac{1N}{1\ kg.\ m/s^2}\right|\left|\frac{1KJ}{10^3\ N.m}\right|$$

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For a system having a mass of 1 Ib whose velocity increases from 50 ft/s to 100 ft/s while its elevation **decreases by 40 ft** at a location where g= 32.0 ft/s^2, we have

$$\Delta KE = \tfrac{1}{2}m\left({V_2}^2 - {V_1}^2\right)$$

$$\Delta KE = \tfrac{1}{2}(1\ Ib)\ \left[\left(100\frac{ft}{s}\right)^2 - \left(50\frac{ft}{s}\right)^2\right]\ \left|\frac{1Ibf}{32.2\ Ib.\ ft/s^2}\right|\left|\frac{1Btu}{778\ ft.Ibf}\right|$$

$$\Delta KE = 0.15\ Btu$$

$$\Delta PE = m\ g\ (Z_2 - Z_1)$$

$$\Delta PE = (1\ Ib)\left(32.0\ \frac{ft}{S^2}\right)\ [(-40\ ft)]\ \left|\frac{1\ Ibf}{32.2\ Ib.\ ft/s^2}\right|\left|\frac{1Btu}{778\ ft.Ibf}\right|$$

$$\Delta PE = -0.05\ Btu$$

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

Thus,

$$P = h\rho g$$

Example 1.1

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

Solution 1.1

By Newton's law, with acceleration equal to the acceleration of gravity, g,

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

Because $1\ \mathrm{N} = 1\ \mathrm{kg{\cdot}m{\cdot}s^{-2}}$,

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

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:

$$F(\mathrm{moon}) = m \times g(\mathrm{moon}) = 74.55\ \mathrm{kg} \times 1.67\ \mathrm{m{\cdot}s^{-2}}$$

or

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

Example 1.2

A dead-weight gauge with a piston diameter of 1 cm is used for the accurate measurement of pressure. If a mass of 6.14 kg (including piston and pan) brings it into balance, and if $g = 9.82\ \text{m·s}^{-2}$, what is the *gauge* pressure being measured? For a barometric pressure of 0.997 bar, what is the *absolute* pressure?

Solution 1.2

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

$$F = mg = 6.14\ \text{kg} \times 9.82\ \text{m·s}^{-2} = 60.295\ \text{N}$$

$$\text{Gauge pressure} = \frac{F}{A} = \frac{60.295}{(1/4)(\pi)(0.01)^2} = 7.677 \times 10^5\ \text{N·m}^{-2} = 767.7\ \text{kPa}$$

The absolute pressure is therefore:

$$P = 7.677 \times 10^5 + 0.997 \times 10^5 = 8.674 \times 10^5\ \text{N·m}^{-2}$$

or

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

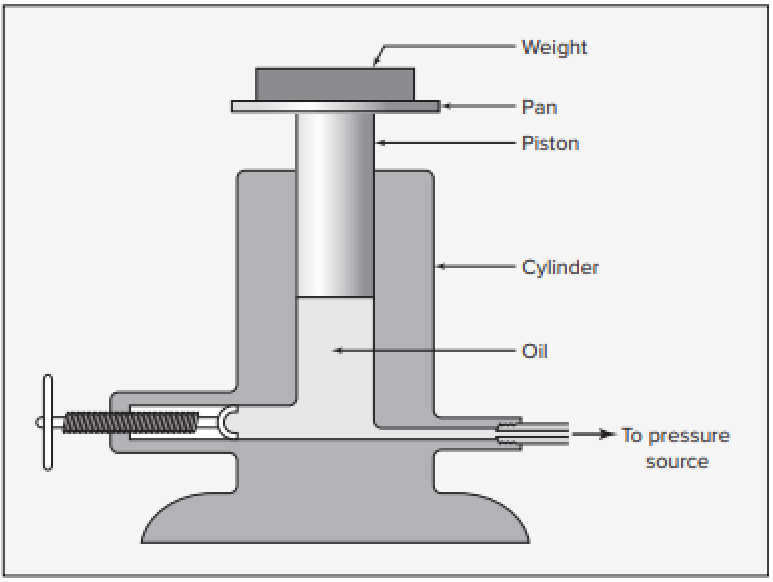
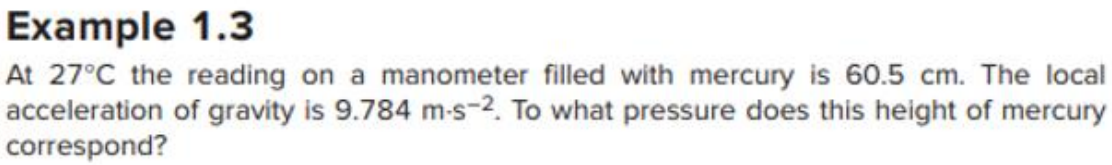


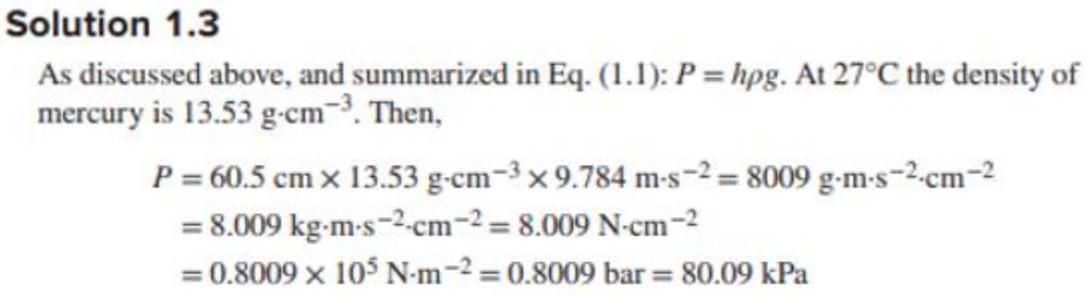
Figure 1.2: Dead-weight gauge.

Because a vertical column of fluid under the influence of gravity exerts a pressure at its base in direct proportion to its height, pressure may be 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



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 $m{\cdot}s^{-2}$. To what pressure does this height of mercury correspond?



Solution 1.3

As discussed above, and summarized in Eq. (1.1): $P = h\rho g$. At 27°C the density of mercury is 13.53 $g{\cdot}cm^{-3}$. Then,

$$\begin{aligned} P &= 60.5\ \text{cm} \times 13.53\ \text{g}{\cdot}\text{cm}^{-3} \times 9.784\ \text{m}{\cdot}\text{s}^{-2} = 8009\ \text{g}{\cdot}\text{m}{\cdot}\text{s}^{-2}{\cdot}\text{cm}^{-2} \\ &= 8.009\ \text{kg}{\cdot}\text{m}{\cdot}\text{s}^{-2}{\cdot}\text{cm}^{-2} = 8.009\ \text{N}{\cdot}\text{cm}^{-2} \\ &= 0.8009 \times 10^{5}\ \text{N}{\cdot}\text{m}^{-2} = 0.8009\ \text{bar} = 80.09\ \text{kPa} \end{aligned}$$

2.0 THERMODYNAMIC SYSTEMS

2.1 System, Boundary and Surroundings

System: A system is a finite quantity of matter or a prescribed region of space (Refer Fig. 2.1) Boundary.

The actual or hypothetical envelope enclosing the system is the boundary of the system. The boundary may be fixed or it may move, as and when a system containing a gas is compressed or expanded.

The boundary may be real or imaginary. It is not difficult to envisage a real boundary but an example of imaginary boundary would be one drawn around a system consisting of the fresh mixture about to enter the cylinder of an I.C. engine together with the remnants of the last cylinder charge after the exhaust process (Refer Fig. 2.2).

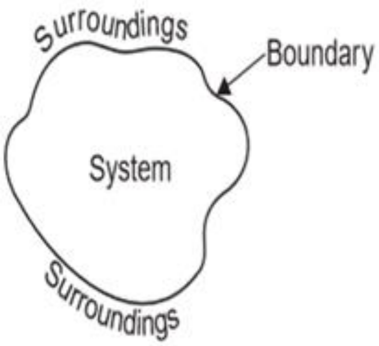


Fig. 2.1. The system.

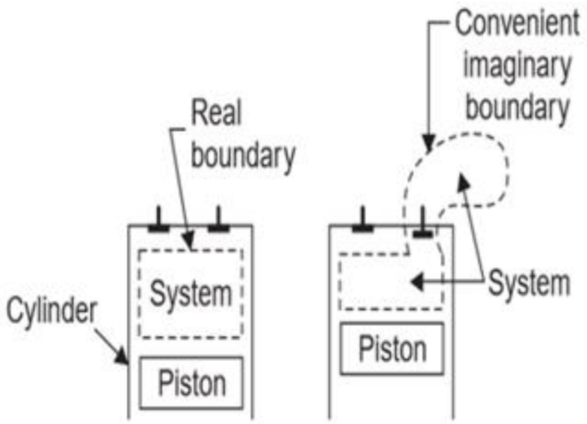


Fig. 2.2. The real and imaginary boundaries

2.2. Closed System

Refer to Fig. 2.3. If the boundary of the system is impervious to the flow of matter, it is called a *closed system*. An example of this system is mass of gas or vapour contained in an engine cylinder, the boundary of which is drawn by the cylinder walls, the cylinder head and piston crown. Here the boundary is continuous and no matter may enter or leave.

2.3. Open System Refer to Fig. 2.4. An open system is one in which matter flows into or out of the system. Most of the engineering systems are open.

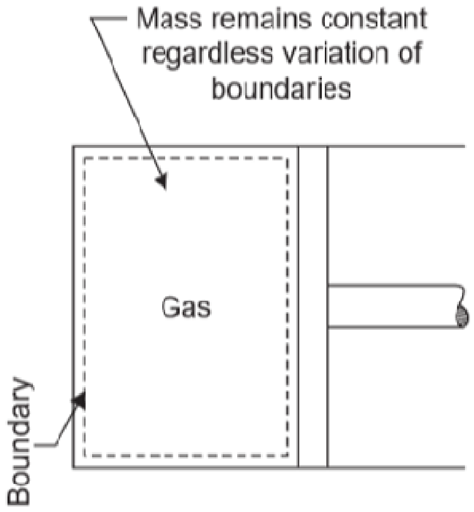


Fig. 2.3. Closed system.

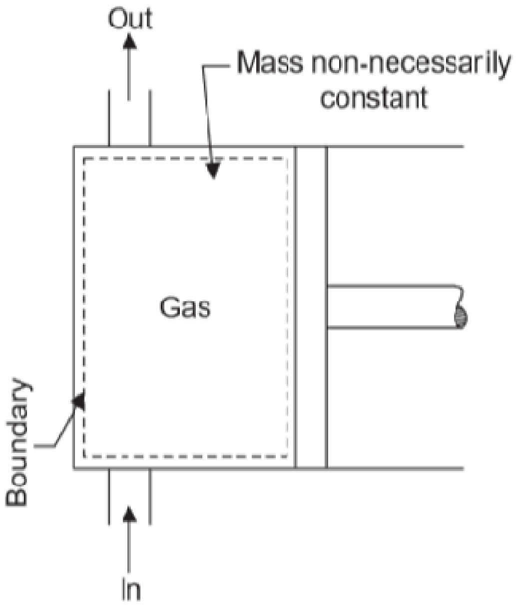


Fig. 2.4. Open system.

2.4. Isolated System An isolated system is that system which exchanges neither energy nor matter with any other system or with environment.

نظام معزول هو النظام الذي لا يتبادل الطاقة ولا المادة مع أي نظام آخر أو مع البيئة

2.5. Adiabatic System An adiabatic system is one which is thermally insulated from its surroundings. It can, however, exchange work with its surroundings. If it does not, it becomes an isolated system.

نظام ثابت الحرارة هو نظام معزول حرارياً عن البيئة المحيطة به. ومع ذلك ، يمكن أن يتبادل العمل مع محيطه. إذا لم يحدث ذلك ، يصبح نظام معزول.

2.6. Phase. A phase is a quantity of matter which is homogeneous throughout in chemical composition and physical structure.

2.7. Homogeneous System A system which consists of a single phase is termed as homogeneous system. Examples: Mixture of air and water vapour, water plus nitric acid and octane plus heptane.

2.8. Heterogeneous System A system which consists of two or more phases is called a heterogeneous system. Examples: Water plus steam, ice plus water and water plus oil.

2.9 Property

A property is a macroscopic characteristic of a system such as pressure, temperature, volume, and mass. At a given state each property has a definite value independent of how the system arrived at that **state.** The properties of air in state 1 shown in Figure 1.3 are: pressure at 1 atm, temperature at 25°C, and mass of 1 kg.

2.9.1// A property can be classified as **extensive or intensive.**

Extensive properties: The properties of a system whose value for the entire **system is equal** to the sum of their values for the individual parts of the system.

Intensive properties: The properties of the system whose value for the **entire system is not equal** to the sum of their values for the individual parts of the system.

- An extensive property depends on the mass (size of the system) for example internal energy U and enthalpy H (KJ/Kg) and all kinds of energy.
- While an intensive property is independent on the mass (size of the system) for example T (°C) and P (bar)

Consider systems (1) and (2) shown in Figure 2.5 both at 100°C and 1 atm containing 2 and 5 kg of steam, respectively.

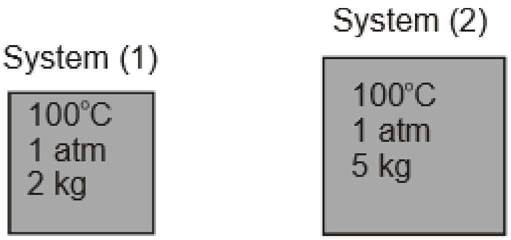


Figure 2.5 Example of intensive and extensive properties.

** **Temperature, pressure, and specific volume of both systems are intensive properties.**

** Total mass and total volume of each system are extensive property.

At 100°C and 1 atm, the **specific volume v** of each system is 1.674 m^3/kg. The mass of system (1) is $m_1 = 2$ kg and that of system (2) is $m_2 = 5$ kg.

The total volume of system (1) is $V1 = m_1 v = (2\ \text{kg})\ (1.674\ \text{m}^3/\text{kg}) = 3.348\ \text{m}^3$.

The total volume of system (2) is $V2 = m_2 v = (5\ \text{kg})\ (1.674\ \text{m}^3/\text{kg}) = 8.37\ \text{m}^3$.

An intensive property might be obtained from an extensive property by dividing the extensive property by the mass of the system.

يمكن الحصول على خاصية مكثفة من خاصية واسعة من خلال تقسيم الخاصية الواسعة على كتلة النظام.

***2.10. CYCLE**: Any process or series of processes whose end states are identical is termed **a cycle**.* The processes through which the system has passed can be shown on a state diagram, but a complete section of the path requires in addition a statement of the heat and work crossing the boundary of the system. Fig. 2.6 shows such a cycle in which a system commencing at condition ‘1’ changes in pressure and volume through a path 123 and returns to its initial condition ‘1’.

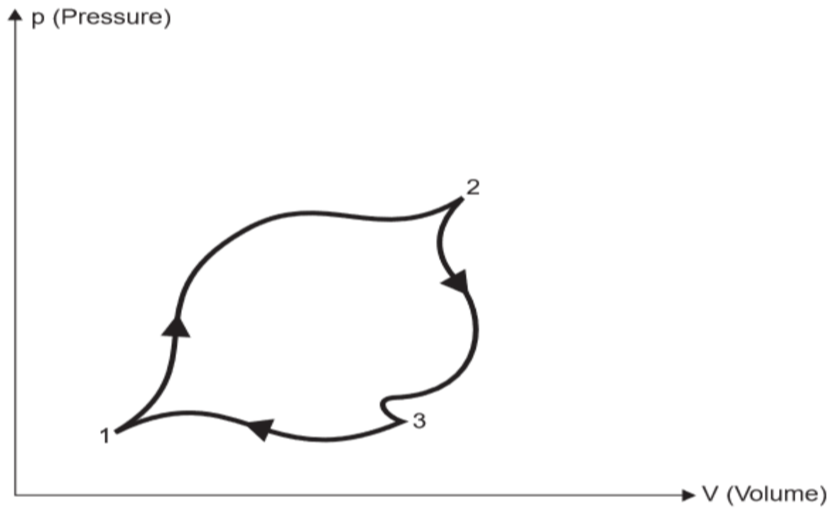


Fig. 2.6. Cycle of operations

2.11. STAT (POINT) FUNCTION

When two properties locate a point on the graph (co-ordinate axes) then those properties are called as **point function OR stat function.**

Examples. Pressure, temperature, volume, enthalpy, entropy, internal energy etc.

$$\int_1^2 dV = V_2 - V_1 \qquad \text{(an exact differential).}$$

1- Independent on the path

$\int_1^2 dV = V_2 - V_1$ (An exact differential).

$\int_1^2 dU = U_2 - U_1$

$\int_1^2 dH = H_2 - H_1$

2.12. PATH FUNCTION

There are certain quantities which cannot be located on a graph by a point but are given by the area or so, on that graph. In that case, the area on the graph, pertaining to the particular process, is a function of the path of the process. Such quantities are called ***path functions.***

Examples. **Heat, work etc**.

Heat and work are inexact differentials. Their change cannot be written as difference between their end states.

Thus $\int_1^2 \delta Q \neq Q_2 - Q_1$ and is shown as Q_{1-2}

Similarly $\int_1^2 \delta W \neq W_2 - W_1$ and is shown as W_{1-2}

Note. The operator **δ** is used to denote **inexact differentials** and operator d is used to denote exact differentials.

1. Depends on the **path**
2. $\int_1^2 \delta Q \neq Q_2 - Q_1$ and is shown as Q_{1-2}

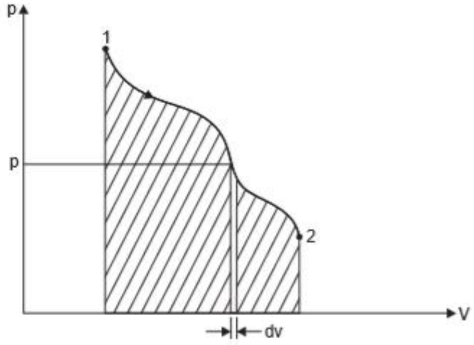
   Similarly $\int_1^2 \delta W \neq W_2 - W_1$ and is shown as W_{1-2}

THIS THE MEANING

$\int_0^Q \delta Q = Q_{1-2}$ Inexact differentials

$\int_0^W \delta W = W_{1-2}$

3- Can drawing by area under curve.



2.13. REVERSIBLE AND IRREVERSIBLE PROCESSES

2.13.1 Reversible process. A reversible process (also sometimes known as quasi-static process) is one which can be stopped at any stage and reversed so that the system and surroundings are exactly restored to their initial states.

This process has the following characteristics:

1. It must pass through the same states on the reversed path as were initially visited on the forward path.
2. This process when undone will leave no history of events in the surroundings.
3. It must pass through a continuous series of equilibrium states.

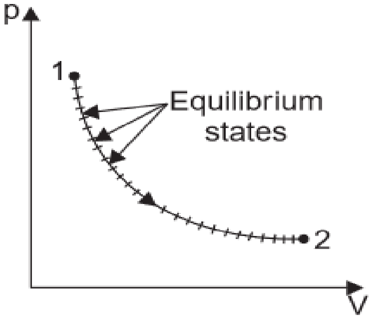


Fig. 2.7. Reversible process

No real process is truly reversible but some processes may approach reversibility, to close approximation

*** لا توجد عملية حقيقية عكسية فعلاً ولكن بعض العمليات قد تقترب من الانعكاسية ، تقترب اليها تقريبا.

Examples. Some examples of nearly reversible processes are:

- (i) Frictionless relative motion.
- (ii) Expansion and compression of spring.
- (iii) Frictionless adiabatic expansion or compression of fluid.
- (iv) Polytropic expansion or compression of fluid.
- (v) Isothermal expansion or compression.
- (vi) Electrolysis.

2.13.2 Irreversible process.

An irreversible process is one in which heat is transferred through a finite temperature. Examples.

- (i) Relative motion with friction
- (ii) Combustion
- (iii) Diffusion
- (iv) Free expansion
- (v) Throttling
- (vi) Electricity flow through a resistance
- (vii) Heat transfer
- (viii) Plastic deformation.

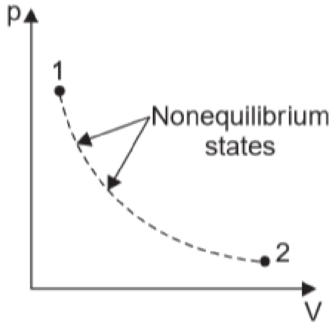


Fig. 2.8. Irreversible process.

An irreversible process is usually represented by a dotted (or discontinuous) line joining the end states to indicate that the intermediate states are indeterminate (Fig. 2.8). ******Irreversibilities are of two types:***

1. External irreversibilities.

These are associated with dissipating effects outside the working fluid. Example. Mechanical friction occurring during a process due to some external source.

اللانعكاسية الخارجية. ترتبط هذه مع تبديد الآثار خارج مائع العمل. مثال. الاحتكاك الميكانيكي الذي يحدث أثناء العملية بسبب بعض المصادر الخارجية

2. Internal irreversibilities.

These are associated with dissipating effects within the working fluid. **Example.** Unrestricted expansion of gas, viscosity and inertia of the gas

اللانعكاسية الداخلية. ترتبط هذه مع تبديد الآثار داخل مائع العمل. مثال. التمدد غير المقيد للغاز واللزوجة والجمود من الغاز.

(((((((((((((((((((((((((((((((((((((************************)))))))))))))))))))))))))))))))))

2.14. INTERNAL ENERGY

In experiments such as those conducted by Joule, energy is added to a fluid as work, but is transferred from the fluid as heat. What happens to this energy between its addition to and transfer from the fluid? A rational concept is that it is contained in the fluid in another form, called **internal energy**.

2.15. THE FIRST LAW OF THERMODYNAMICS

The recognition of heat and internal energy as forms of energy makes possible a generalization of the law of conservation of mechanical energy (Sec. 1.8) to include heat and internal energy in addition to work and external potential and kinetic energy. Indeed, the generalization can be extended to still other forms, such as surface energy, electrical energy, and magnetic energy. This generalization was at first a postulate. However, the overwhelming evidence accumulated over time has elevated it to the stature of a law of nature, known as the first law of thermodynamics. One formal statement is:

> **Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.**

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***. The region in which the process occurs is set apart as the system; everything with which the system interacts is the surroundings. The system may be of any size depending on the application, and its boundaries may be real or imaginary, rigid or flexible. Frequently a system consists of a single substance; in other cases it may be complex. In any event, the equations of thermodynamics are written with reference to some well-defined system. This focuses attention on the particular process of interest and on the equipment and material directly involved in the process. However, the first law applies to the **system and surroundings,** and not to the system alone. In its most basic form, the first law requires:

$$\Delta\ \textbf{(Energy of the system)} + \Delta\ \textbf{(Energy of surroundings)} = 0 \qquad \textbf{(2.1)}$$

Where the difference operator "Δ" signifies finite changes in the quantities enclosed in parentheses. The system may change in its internal energy, in its potential or kinetic energy, and in the potential or kinetic energy of its finite parts. Since attention is focused on the system, the nature of energy changes in the surroundings is not of interest.

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 ENERGY BALANCE FOR CLOSED SYSTEMS

If the boundary of a system does not permit the transfer of matter between the system and its surroundings, the system is said to be ***closed*****,** and its **mass is necessarily constant**.

The development of basic concepts in thermodynamics is facilitated by a careful examination of closed systems, and for this reason they are treated in detail in the following sections.

Far more important for industrial practice are processes in which matter crosses the system boundary as streams that enter and leave process equipment. ***Such systems are said to be open***.

Since no streams enter or leave a closed system, no internal energy is transported across the boundary of the system.

نظرًا لعدم دخول أو خروج أي تيار لنظام مغلق ، لا يتم نقل أي طاقة داخلية عبر حدود النظام.

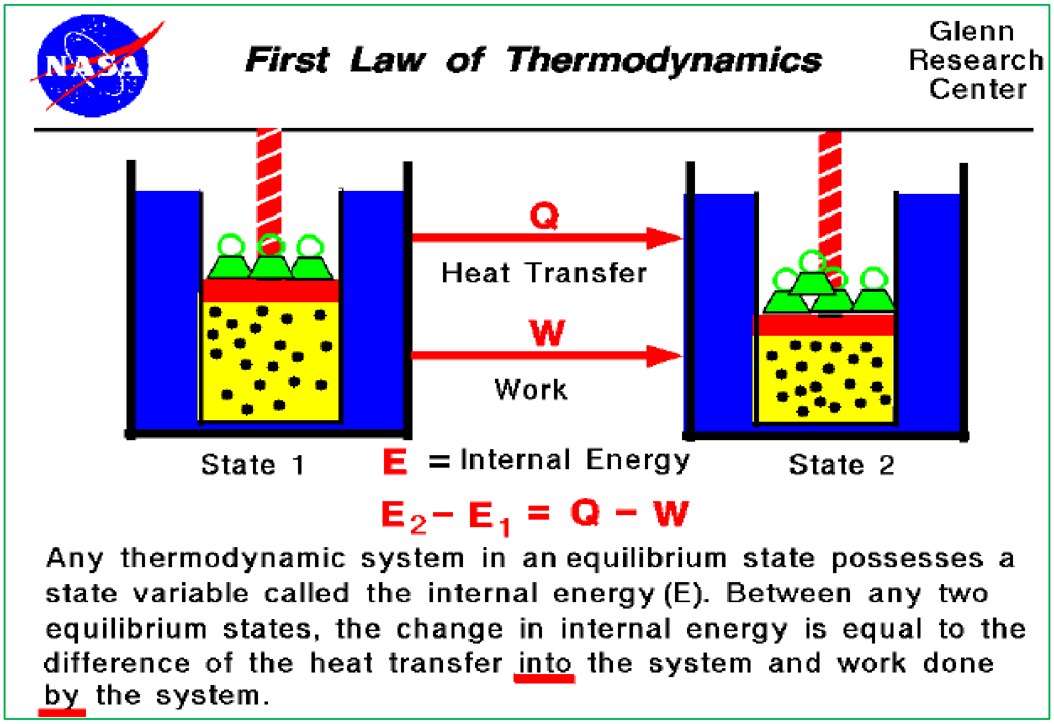
All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work.

كل الطاقة المتبادلة بين نظام مغلق ومحيطه تظهر كحرارة وشغل,

والتغير بالطاقة الكلية في المحيط يساوي صافي الطاقة المنقولة إلى أو منه كحرارة وشغل.

The second term of Eq. (2.1) may therefore be replaced by

$$\Delta\ \textbf{(Energy of surroundings)} = \mp \boldsymbol{Q} \mp \boldsymbol{W}$$



$$E_2 - E_1 = Q - W$$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

***The first law of thermodynamics.

By the end of this section, you will be able to:

- **Define the first law of thermodynamics.**
- Describe how conservation of energy relates to the first law of thermodynamics.
- Identify instances of the first law of thermodynamics working in everyday situations, including biological metabolism.
- Calculate changes in the internal energy of a system, after accounting for heat transfer and work done.

If we are interested in how heat transfer is converted into doing work, then the conservation of energy principle is important. The first law of thermodynamics applies the conservation of energy principle to systems where heat transfer and doing work are the methods of transferring energy into and out of the system. **The *first law of thermodynamics*** states that the change in internal energy of a system equals the net heat transfer *into* the system minus the net work done *by* the system. In equation form, the first law of thermodynamics is

$$\Delta U = Q - W.$$

Here ΔU is the *change in internal energy* U of the system. Q is the *net heat transferred into the system*—that is, Q is the sum of all heat transfer into and out of the system. W is the *net work done by the system*—that is, W is the sum of all work done on or by the system. We use the following sign conventions:

if Q is positive, then there is a net heat transfer into the system; if W is positive, then there is net work done by the system. So positive Q adds energy to the system and positive W takes energy from the system. Thus $\Delta U = Q - W$.

Note also that if more heat transfer into the system occurs than work done, the difference is stored as internal energy. Heat engines are a good example of this—heat transfer into them takes place so that they can do work. (See Figure 2.9) We will now examine Q, W, and ΔU further.

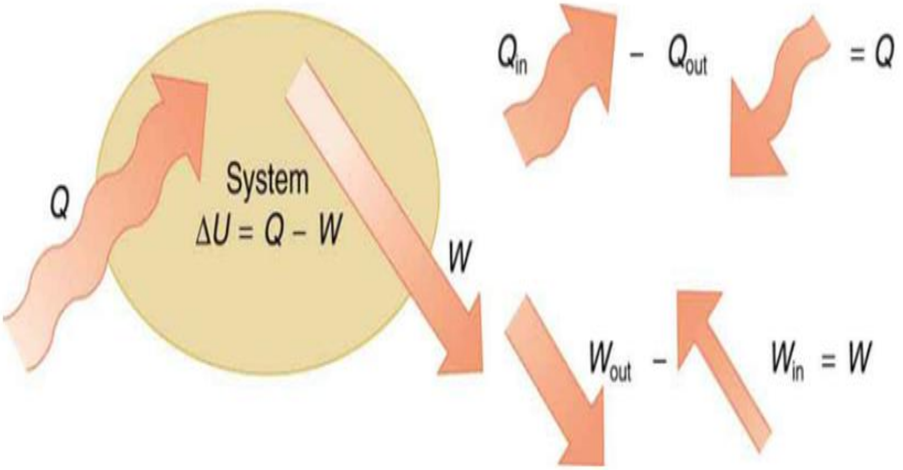


Figure 2.9. The first law of thermodynamics is the conservation-of-energy principle stated for a system where heat and work are the methods of transferring energy for a system in thermal equilibrium. Q represents the net heat transfer—it is the sum of all heat transfers into and out of the system. Q is positive for net heat transfer into the system. W is the total work done on and by the system. W is positive when more work is done by the system than on it. The change in the internal energy of the system, ΔU, is related to heat and work by the first law of thermodynamics, $\Delta U = Q - W$.

Heat *Q* and Work *W*

Heat transfer (Q) and doing work (W) are the two everyday means of bringing energy into or taking energy out of a system. The processes are quite different. Heat transfer, a less organized process, is driven by temperature differences. Work, a quite organized process, involves a macroscopic force exerted through a distance. Nevertheless, heat and work can produce identical results. For example, both can cause a temperature increase. Heat transfer into a system, such as when the Sun warms the air in a bicycle tire, can increase its temperature, and so can work done on the system, as when the bicyclist pumps air into the tire. Once the temperature increase has occurred, it is impossible to tell whether it was caused by heat transfer or by doing work. This uncertainty is an important point. Heat transfer and work are both energy in transit—neither is stored as such in a system.

However, both can change the internal energy U of a system. Internal energy is a form of energy completely different from either heat or work.

Internal Energy U

We can think about the internal energy of a system in two different but consistent ways. The first is the atomic and molecular view, which examines the system on the atomic and molecular scale. The *internal energy* U of a system is the sum of the kinetic and potential energies of its atoms and molecules. Recall that kinetic plus potential energy is called mechanical energy. Thus internal energy is the sum of atomic and molecular mechanical energy. Because it is impossible to keep track of all individual atoms and molecules, we must deal with averages and distributions. A second way to view the internal energy of a system is in terms of its macroscopic characteristics, which are very similar to atomic and molecular average values.

Macroscopically, we define the change in internal energy ΔU to be that given by the first law of thermodynamics:

$$\Delta U = Q - W.$$

Many detailed experiments have verified that $\Delta U = Q - W$, where ΔU is the change in total kinetic and potential energy of all atoms and molecules in a system. It has also been determined experimentally that the internal energy U of a system depends only on the state of the system and *not how it reached that state*. More specifically, U is found to be a function of a few macroscopic quantities (pressure, volume, and temperature, for example), independent of past history such as whether there has been heat transfer or work done. This independence means that if we know the state of a system, we can calculate changes in its internal energy U from a few macroscopic variables.

To get a better idea of how to think about the internal energy of a system, let us examine a system going from State 1 to State 2. The system has internal energy U_1 in State 1, and it has internal energy U_2 in State 2, no matter how it got to either state.

So the change in internal energy $\Delta U = U_2 - U_1$ is independent of what caused the change. In other words, ***ΔU is independent of path.*** By path, we mean the method of getting from the starting point to the ending point. Why is this independence important? Note that

$$\Delta U = Q - W$$

Both Q and W *depend on path*, but ΔU does not. This path independence means that internal energy U is easier to consider than either heat transfer or work done.

EXAMPLE 1. CALCULATING CHANGE IN INTERNAL ENERGY: THE SAME CHANGE IN *U* IS PRODUCED BY TWO DIFFERENT PROCESSES

1. Suppose there is heat transfer of 40.00 J to a system, while the system does 10.00 J of work. Later, there is heat transfer of 25.00 J out of the system while 4.00 J of work is done on the system. What is the net change in internal energy of the system?
2. What is the change in internal energy of a system when a total of 150.00 J of heat transfer occurs out of (from) the system and 159.00 J of work is done on the system? (See Figure 2.10).

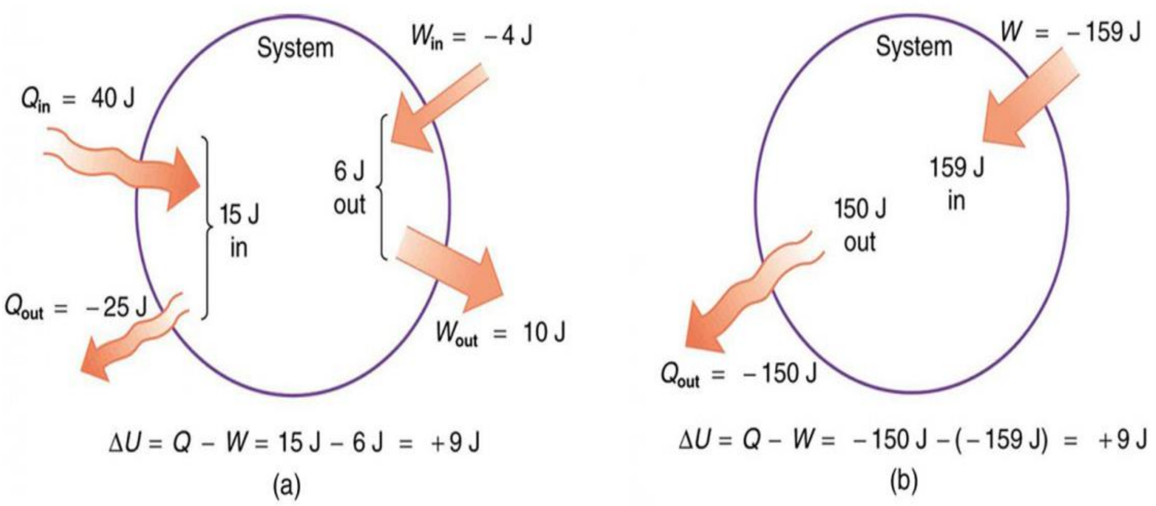


Figure 2.10. Two different processes produce the same change in a system. (a) A total of 15.00 J of heat transfer occurs into the system, while work takes out a total of 6.00 J. The change in internal energy is ΔU=Q−W=9.00 J.

(b) Heat transfer removes 150.00 J from the system while work puts 159.00 J into it, producing an increase of 9.00 J in internal energy. If the system starts out in the same state in (a) and (b), it will end up in the same final state in either case—its final state is related to internal energy, not how that energy was acquired.

Strategy

In part 1, we must first find the net heat transfer and net-work done from the given information. Then the first law of thermodynamics ($\Delta U = Q - W$) can be used to find the change in internal energy. In part (b), the net heat transfer and work done are given, so the equation can be used directly.

Solution for Part 1

The net heat transfer is the heat transfer into the system minus the heat transfer out of the system, or

$$Q = 40.00\text{ J} - 25.00\text{ J} = 15.00\text{ J}.$$

Similarly, the total work is the work done by the system minus the work done on the system, or

$$W = 10.00\text{ J} - 4.00\text{ J} = 6.00\text{ J.}$$

Thus the change in internal energy is given by the first law of thermodynamics:

$$\Delta U = Q - W = 15.00\text{ J} - 6.00\text{ J} = 9.00\text{ J.}$$

We can also find the change in internal energy for each of the two steps. First, consider 40.00 J of heat transfer in and 10.00 J of work out, or

$$\Delta U_1 = Q_1 - W_1 = 40.00\text{ J} - 10.00\text{ J} = 30.00\text{ J.}$$

Now consider 25.00 J of heat transfer out and 4.00 J of work in, or

$$\Delta U_2 = Q_2 - W_2 = -25.00\text{ J} - (-4.00\text{ J}) = -21.00\text{ J.}$$

The total change is the sum of these two steps, or

$$\Delta U = \Delta U_1 + \Delta U_2 = 30.00\text{ J} + (-21.00\text{ J}) = 9.00\text{ J.}$$

Discussion on Part 1

No matter whether you look at the overall process or break it into steps, the change in internal energy is the same.

Solution for Part 2

Here the net heat transfer and total work are given directly to be $Q = -150.00$ J and $W = -159.00$ J, so that

$$\Delta U = Q - W = -150.00\text{ J} - (-159.00\text{ J}) = 9.00\text{ J.}$$

Discussion on Part 2

A very different process in part 2 produces the same 9.00-J change in internal energy as in part 1. Note that the change in the system in both parts is related to ΔU and not to the individual Qs or Ws involved. The system ends up in the *same* state in both parts. Parts 1 and 2 present two different paths for the system to follow between the same starting and ending points, and the change in internal energy for each is the same—it is independent of path.

Example 2.1.

An artificial satellite revolves round the earth with a relative velocity of 800 m/s. If acceleration due to gravity is 9 m/s^2 and gravitational force is 3600 N, calculate its kinetic energy.

Solution. Relatively velocity of satellite, V = 800 m/s

Acceleration due to gravity, g = 9 m/s^2 Gravitational force, m.g = 3600 N

∴ Mass, m = 3600/g= 3600 /9 = 400 kg.

Kinetic energy $= 1/2\ mV^2 = 1/2 \times 400 \times (800)^2$ J $= 128 \times 10^6$ J or 128 MJ. (Ans.).

((((*********************))))

Example 2.2.

The specific heat capacity of the system during a certain process is given by

$$C_n = (0.4 + 0.004\ T)\ \text{kJ/kg°C}.$$

If the mass of the gas is 6 kg and its temperature changes from 25°C to 125°C find:

(i) Heat transferred; (ii) Mean specific heat of the gas.

Solution. Mass of the gas, m = 6 kg

Change in temperature of the gas = 25°C to 125°C

(i) Heat transferred, Q: We know that heat transferred is given by,

$$Q = \int m\, C_n\ dT \ = 6 \int_{25}^{125} (\, 0.4 + 0.004\ T) dT$$

$$= 6\ \left[0.4\ \mathrm{T} + 0.004 \left(\frac{\mathrm{T}^2}{2}\right) \right]_{25}^{125}$$

$$= 6[0.4\ (125 - 25) + 0.002\ (125^2 - 25^2)]$$

$$= 6(40 + 30) = \mathbf{420\ kJ.\ (Ans.)}$$

(ii) Mean specific heat of the gas, Cn:

$$Q = m.Cn.dT$$

i.e., $$420 = 6 \times Cn \times (125 - 25)$$

$$\therefore \quad C_n = \frac{420}{6 \times 100} = 0.7\ \frac{KJ}{Kg\ °C} \qquad (Ans.)$$

((((*************************)))))

Example 2.3.

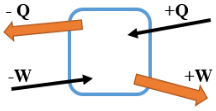
In an internal combustion engine, during the compression stroke the heat rejected to the cooling water is 50 kJ/kg and the work input is 100 kJ/kg. Calculate the change in internal energy of the working fluid stating whether it is a gain or loss.

Solution.

Heat rejected to the cooling water, $Q = -50$ kJ/kg (–ve sign since heat is rejected)

Work input, $W = -100$ kJ/kg (–ve sign since work is supplied to the system)

Using the relation, $Q - W = (u_2 - u_1)$



$$-50 - (-100) = (u_2 - u_1)$$

OR $u_2 - u_1 = -50 + 100 = 50$ kJ/kg

Hence, gain in internal energy = 50 kJ/kg. (Ans.)

((((************************))))

Example 2.4.

In an air motor cylinder the compressed air has an internal energy of 450 kJ/kg at the beginning of the expansion and an internal energy of 220 kJ/kg after expansion. If the work done by the air during the expansion is 120 kJ/kg, calculate the heat flow to and from the cylinder.

Solution.

Internal energy at beginning of the expansion, $u_1 = 450$ kJ/kg

Internal energy after expansion, $u_2 = 220$ kJ/kg

Work done by the air during expansion, $W = 120$ kJ/kg

Heat flow, Q:

Using the relation, $(u_2 - u_1) = Q - W$

$$Q = (u_2 - u_1) + W$$

$$\therefore \quad Q = (220 - 450) + 120$$

$$= -230 + 120 = -110 \text{ kJ/kg}$$

Hence, heat rejected by air = 110 kJ/kg. (Ans.)

(((************************)))))

Example 2.5.

When a stationary mass of gas was compressed without friction at constant pressure its initial state of 0.4 m^3 and 0.105 MPa was found to change to final state of 0.20 m^3 and 0.105 MPa. There was a transfer of 42.5 kJ of heat from the gas during the process. How much did the internal energy of the gas change?

Solution.

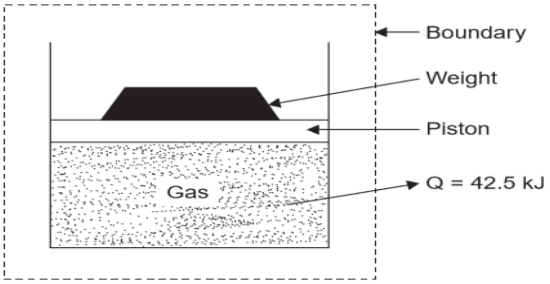


Fig.

Initial state: Pressure of gas, $p_1 = 0.105$ MPa Volume of gas, $V_1 = 0.4\ m^3$

Final state: Pressure of gas, $p_2 = 0.105$ MPa Volume of gas, $V_2 = 0.20\ m^3$

Process used: Constant pressure

Heat transferred, **$Q = -42.5$ kJ** **(–ve sign indicates that heat is rejected)**

Change in internal energy, **$\Delta U = U_2 - U_1$** :

First law for a stationary system in a process gives

$$\Delta U = Q - W$$

$$Q = \Delta U + W$$

OR $$Q_{1-2} = (U_2 - U_1) + W_{1-2} \quad \dots (i)$$

Here $$W_{1-2} = \int_{V_1}^{V_2} P dV = P(V_2 - V_1)$$

$$= 0.105(0.20 - 0.40) \text{ MJ} = -21 \text{ kJ} \qquad [1 \text{ MJ} = 10^3 \text{ kJ}]$$

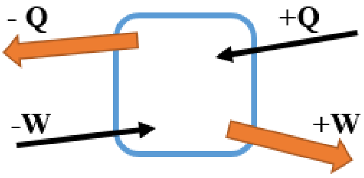
Substituting this value of W_{1-2} in equation (*i*), we get

$$-42.5 = (U_2 - U_1) - 21$$

$$\therefore \quad U_2 - U_1 = -42.5 + 21 = -21.5 \text{ kJ}$$

Hence ‘decrease’ in internal energy = 21.5 kJ. (Ans.)

((((((((((*********************)))))))



Δ = Change

Δ (Energy of the system) + Δ (Energy of surroundings) = 0 **(2.1)**

Δ (Energy of surroundings) $= \mp \boldsymbol{Q} \mp \boldsymbol{W}$ **(path function)**

Δ (Energy of system) $= \Delta\,(\boldsymbol{U} + \boldsymbol{K_E} + \boldsymbol{P_E})$ **(Stat function)**

$$\Delta\,(\boldsymbol{U} + \boldsymbol{K_E} + \boldsymbol{P_E}) = \mp \boldsymbol{Q} \mp \boldsymbol{W}$$ **(First law of thermodynamic)**

ملاحظة: 1- دائما يهمل حد potential and kinetic energy لانها قليلة جدا مقارنتا مع باقي الانواع.

2-دائما الحرارة Q عكس الشغل W بالاشارة.

$$\Delta\,\boldsymbol{U} = \boldsymbol{Q} - \boldsymbol{W}$$

$$\boldsymbol{d}\,\boldsymbol{U} = \boldsymbol{Q} - \boldsymbol{W}$$

2.7 CLOSED-SYSTEM REVERSIBLE PROCESSES; ENTHALPY

We present here the analysis of closed-system mechanically reversible processes—not that such processes are common. Indeed they are of little interest for practical application. Their value lies in the simplicity they provide for the calculation of changes in state functions for a specific change of state. For a complex industrial process that brings about a particular change of state, the calculation of changes in state functions are not made for the path of the actual process.

Rather, they are made for a simple closed-system reversible process that brings about the same change of state. This is possible because changes in state functions are independent of process. The closed-system mechanically reversible process is useful and important for this purpose, even though close approximations to such hypothetical processes are not often encountered in practice. For 1 mole of a homogeneous fluid contained in a closed system, the energy balance of Eq. (2.6) is written:

$$dU = dQ + dW$$

The work for a mechanically reversible, closed-system process is given by Eq. (1.3), here written: $dW = -PdV$. Substitution into the preceding equation yields:

$$dU = dQ - PdV \qquad (2.7)$$

This is the general energy balance for one mole or a unit mass of homogeneous fluid in a closed system undergoing a mechanically reversible process.

For a constant-volume change of state, the only possible mechanical work is that associated with stirring or mixing, which is excluded because it is inherently irreversible. Thus,

$$dU = dQ \text{ (const V)} \qquad (2.8)$$

Integration yields:

$$\Delta U = Q \text{ (const V)} \qquad (2.9)$$

- The internal energy change for a mechanically reversible, constant-volume, closed-system process equals the amount of heat transferred into the system.

For a constant-pressure change of state:

$$dU + PdV = d(U + PV) = dQ$$

The group U + PV naturally arises here and in many other applications. This suggests the definition, for convenience, of this combination as a **new thermodynamic property.** Thus, the mathematical (and only) definition of enthalpy is:

$$H \equiv U + PV \qquad (2.10) \ ***$$

Where H, U, and V are molar or unit-mass values. The preceding energy balance becomes:

$$dH = dQ \text{ (const P)} \qquad (2.11)$$

Integration yields:

$$\Delta H = Q \text{ (const P)} \qquad (2.12)$$

The enthalpy change in a mechanically reversible, constant-pressure, closed-system process equals the amount of heat transferred into the system. Comparison of Eqs. (2.11) and (2.12) with Eqs. (2.8) and (2.9) shows that the enthalpy plays a role in constant-pressure processes analogous to the internal energy in constant-volume processes.

These equations suggest the usefulness of enthalpy, but its greatest use becomes fully apparent with its appearance in energy balances for flow processes as applied to heat exchangers, chemical and biochemical reactors, distillation columns, pumps, compressors, turbines, engines, etc., for calculation of heat and work.

The tabulation of Q and W for the infinite array of conceivable processes is impossible. The intensive state functions, however, such as molar or specific volume, internal energy, and enthalpy, are intrinsic properties of matter. Once determined for a particular substance, their values can be tabulated as functions of T and P 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.

All terms of Eq. (2.10) must be expressed in the same units. The product PV has units of energy per mole or per unit mass, as does U; therefore H also has units of energy per mole or per unit mass. In the SI system the basic unit of pressure is the pascal (=1 N·m−2), and that of molar volume is cubic meters per mol (=1 m3·mol−1). For the PV product we have 1 N·m·mol−1 = 1 J·mol−1.

Because U, P, and V are all state functions, H as defined by Eq. (2.10) is also a state function. Like U and V, H is an intensive property of matter. The differential form of Eq. (2.10) is:

$$dH = dU + d(PV) \qquad (2.13)$$

This equation applies for any differential change of state. Upon integration, it becomes an equation for a finite change of state:

$$\Delta H = \Delta U + \Delta(PV) \qquad (2.14)$$

Equations (2.10), (2.13), and (2.14) apply to a unit mass or mole of a substance.

Example 2.6

Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 100°C and the constant pressure of 101.33 kPa. The specific volumes of liquid and vapor water at these conditions are 0.00104 and 1.673 $m^3 \cdot kg^{-1}$, respectively. For this change, heat in the amount of 2256.9 kJ is added to the water.

Solution 2.6

We take the 1 kg of water as the system because it alone is of interest, and we imagine it contained in a cylinder by a frictionless piston that exerts a constant pressure of 101.33 kPa. As heat is added, the water evaporates, expanding from its initial to its final volume. Equation (2.12) as written for the 1 kg system is:

$$\Delta H = Q = 2256.9 \text{ kJ}$$

By Eq. (2.14),

$$\Delta U = \Delta H - \Delta (PV) = \Delta H - P\,\Delta V$$

For the final term:

$$P\,\Delta V = 101.33 \text{ kPa} \times (1.673 - 0.001) \text{ m}^3$$

$$= 169.4 \text{ kPa}\cdot\text{m}^3 = 169.4 \text{ kN}\cdot\text{m}^{-2}\cdot\text{m}^3 = 169.4 \text{ kJ}$$

Then

$$\Delta U = 2256.9 - 169.4 = 2087.5 \text{ kJ}$$

Example 2.7

Air at 1 bar and 298.15 K is compressed to 3 bar and 298.15 K by two different closed-system mechanically reversible processes:

(a) Cooling at constant pressure followed by heating at constant volume.

(b) Heating at constant volume followed by cooling at constant pressure.

Calculate the heat and work requirements and ΔU and ΔH of the air for each path. The following heat capacities for air may be assumed independent of temperature:

CV = 20.785 and CP = 29.100 $J{\cdot}mol^{-1}{\cdot}K^{-1}$

Assume also that air remains a gas for which PV/T is a constant, regardless of the changes it undergoes. At 298.15 K and 1 bar the molar volume of air is 0.02479 $m^3{\cdot}\ mol^{-1}$.

Solution 2.7

In each case take the system as 1 mol of air contained in an imaginary piston/cylinder arrangement. Because the processes are mechanically reversible, the piston is imagined to move in the cylinder without friction. The final volume is:

$$V_2 = V_1 \frac{P_1}{P_2} = 0.02479\left(\frac{1}{3}\right) = 0.008263\ \text{m}^3$$

The two paths are shown on the V vs. P diagram of Fig. 2.3(I) and on the T vs. P diagram of Fig. 2.3(II).

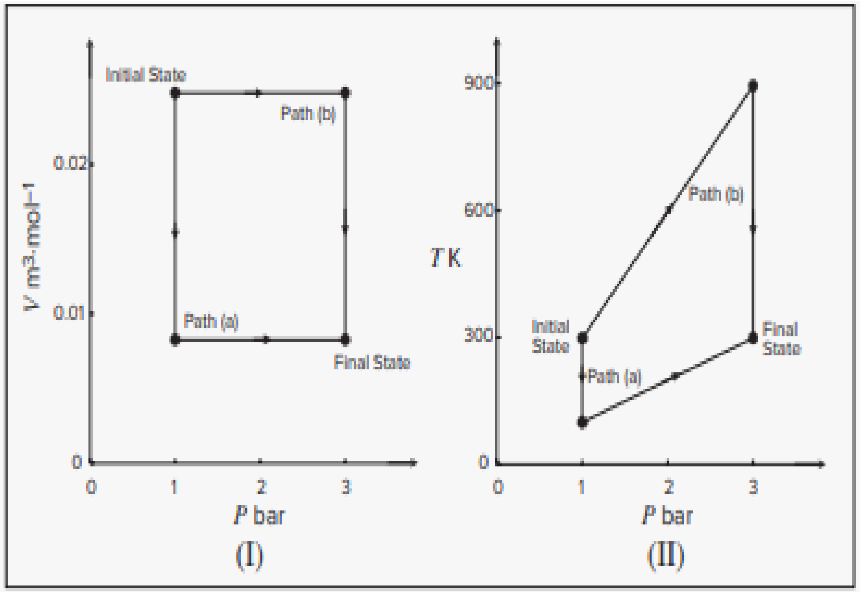


Figure 2.3: V vs. P and T vs. P diagrams for Ex. 2.7.

(a) During the first step of this path, air is cooled at the constant pressure of 1 bar until the final volume of 0.008263 m^3 is reached. The temperature of the air at the end of this cooling step is:

$$T' = T_1 \frac{V_2}{V_1} = 298.15\left(\frac{0.008263}{0.02479}\right) = 99.38 \text{ K}$$

Thus, for the first step,

$$\begin{aligned} Q &= \Delta H = C_P\,\Delta T = (29.100)(99.38 - 298.15) = -5784 \text{ J} \\ W &= -P\,\Delta V = -1 \times 10^5 \text{ Pa} \times (0.008263 - 0.02479)\ \text{m}^3 = 1653 \text{ J} \\ \Delta U &= \Delta H - \Delta(PV) = \Delta H - P\,\Delta V = -5784 + 1653 = -4131 \text{ J} \end{aligned}$$

The second step is at constant V_2 with heating to the final state. Work $W = 0$, and for this step:

$$\Delta U = Q = C_V \,\Delta T = (20.785)(298.15 - 99.38) = 4131 \text{ J}$$
$$V\,\Delta P = 0.008263 \text{ m}^3 \times (2 \times 10^5) \text{ Pa} = 1653 \text{ J}$$
$$\Delta H = \Delta U + \Delta(PV) = \Delta U + V\,\Delta P = 4131 + 1653 = 5784 \text{ J}$$

For the overall process:

$$Q = -5784 + 4131 = -1653 \text{ J}$$
$$W = 1653 + 0 = 1653 \text{ J}$$
$$\Delta U = -4131 + 4131 = 0$$
$$\Delta H = -5784 + 5784 = 0$$

Notice that the first law, $\Delta U = Q + W$, applied to the overall process is satisfied.

(*b*) Two different steps of this path produce the same final state of the air. In the first step air is heated at a constant volume equal to V_1 until the final pressure of 3 bar is reached. The air temperature at the end of this step is:

$$T' = T_1 \frac{P_2}{P_1} = 298.15\left(\frac{3}{1}\right) = 894.45 \text{ K}$$

For this first constant-volume step, $W = 0$, and

$$Q = \Delta U = C_V \,\Delta T = (20.785)(894.45 - 298.15) = 12{,}394 \text{ J}$$
$$V\,\Delta P = (0.02479)(2 \times 10^5) = 4958 \text{ J}$$
$$\Delta H = \Delta U + V\,\Delta P = 12{,}394 + 4958 = 17{,}352 \text{ J}$$

In the second step air is cooled at $P = 3$ bar to its final state:

$$Q = \Delta H = C_P \,\Delta T = (29.10)(298.15 - 894.45) = -17{,}352 \text{ J}$$
$$W = -P\,\Delta V = -(3 \times 10^5)(0.008263 - 0.02479) = 4958 \text{ J}$$
$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P\,\Delta V = -17{,}352 + 4958 = -12{,}394 \text{ J}$$

For the two steps combined,

$$Q = 12{,}394 - 17{,}352 = -4958 \text{ J}$$
$$W = 0 + 4958 = 4958 \text{ J}$$
$$\Delta U = 12{,}394 - 12{,}394 = 0$$
$$\Delta H = 17{,}352 - 17{,}352 = 0$$

This example illustrates that changes in state functions (ΔU and ΔH) are independent of path for given initial and final states. On the other hand, Q and W depend on the path. Note also that the **total changes in ΔU and ΔH are zero.** This is because the input information provided makes U and H functions of temperature only, and **T1 = T2.** While the processes of this example are not of practical interest, state-function changes (ΔU and ΔH) for actual flow processes are calculated as illustrated in this example for processes that are of practical interest. This is possible because the state-function changes are the same for a reversible process, like the ones used here, as for a real process that connects the same states.

Example 2.8

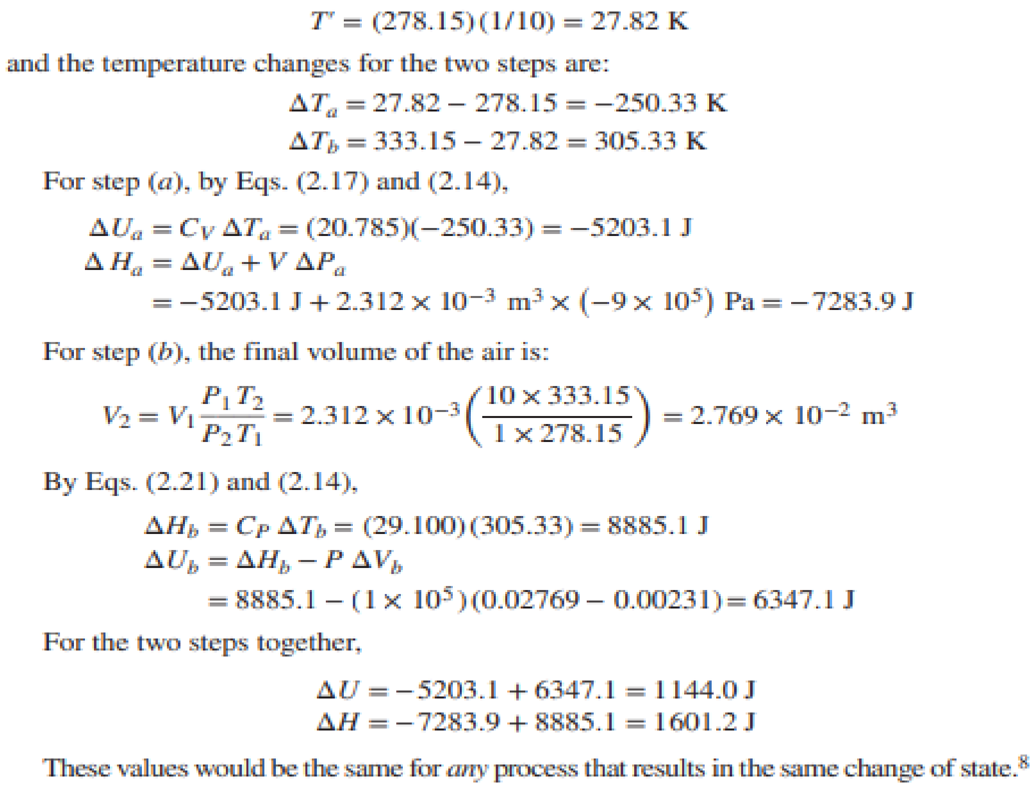
Calculate the internal energy and enthalpy changes resulting if air changes from an initial state of 5°C and 10 bar, where its molar volume is 2.312 × 10−3 m3·mol−1, to a final state of 60°C and 1 bar. Assume also that air remains a gas for which PV/T is constant and that CV = 20.785 and CP = 29.100 J·mol−1·K−1.

Solution 2.8

Because property changes are independent of process, calculations may be based on any process that accomplishes the change. Here, we choose a two-step, mechanically reversible process wherein 1 mol of air is (a) cooled at constant volume to the final pressure, and (b) heated at constant pressure to the final temperature. Of course, other paths could be chosen, and would yield the same result.

T1 = 5 + 273.15 = 278.15 K T2 = 60 + 273.15 = 333.15 K

With PV = kT, the ratio T/P is constant for step (a). The intermediate temperature between the two steps is therefore



$$T' = (278.15)(1/10) = 27.82 \text{ K}$$

and the temperature changes for the two steps are:

$$\Delta T_a = 27.82 - 278.15 = -250.33 \text{ K}$$
$$\Delta T_b = 333.15 - 27.82 = 305.33 \text{ K}$$

For step (*a*), by Eqs. (2.17) and (2.14),

$$\Delta U_a = C_V\,\Delta T_a = (20.785)(-250.33) = -5203.1 \text{ J}$$
$$\Delta H_a = \Delta U_a + V\,\Delta P_a$$
$$= -5203.1 \text{ J} + 2.312\times10^{-3} \text{ m}^3 \times \left(-9\times10^5\right) \text{ Pa} = -7283.9 \text{ J}$$

For step (*b*), the final volume of the air is:

$$V_2 = V_1\frac{P_1T_2}{P_2T_1} = 2.312\times10^{-3}\left(\frac{10\times333.15}{1\times278.15}\right) = 2.769\times10^{-2} \text{ m}^3$$

By Eqs. (2.21) and (2.14),

$$\Delta H_b = C_P\,\Delta T_b = (29.100)(305.33) = 8885.1 \text{ J}$$
$$\Delta U_b = \Delta H_b - P\,\Delta V_b$$
$$= 8885.1 - (1\times10^5)(0.02769 - 0.00231) = 6347.1 \text{ J}$$

For the two steps together,

$$\Delta U = -5203.1 + 6347.1 = 1144.0 \text{ J}$$
$$\Delta H = -7283.9 + 8885.1 = 1601.2 \text{ J}$$

These values would be the same for *any* process that results in the same change of state.[8]

2.9 MASS AND ENERGY BALANCES FOR OPEN SYSTEMS

Although the focus of the preceding sections has been on closed systems, the concepts presented find far more extensive application. **The laws of mass and energy conservation apply to all processes,** to open as well as to closed systems. Indeed, the open system includes the closed system as a special case. The remainder of this chapter is therefore devoted to the treatment of open systems and thus to the development of equations of wide practical application.

Measures of Flow

Open systems are characterized by flowing streams; there are four common measures of flow:

- Mass flow rate, $m^{\cdot}$
- Molar flow rate, $n^{\cdot}$
- Volumetric flow rate, q
- Velocity, u

The measures of flow are interrelated:

$$\dot{m} = \mathscr{M}\dot{n} \qquad \text{and} \qquad q = uA$$

$$m^{\cdot} = \mathscr{M}n^{\cdot} \text{ and } q = uA$$

Where $\mathscr{M}$ is molar mass and A is the cross-sectional area for flow. Importantly, mass and molar flow rates relate to velocity:

$$\boxed{\dot{m} = uA\rho \qquad (2.23a)} \boxed{\dot{n} = uA\rho \qquad (2.23b)}$$

The area for flow A is the cross-sectional area of a conduit, **and ρ is specific or molar density**. Although velocity is a vector quantity, its scalar magnitude u is used here as the average speed of a stream in the direction normal to A.

Flow rates $m^{\cdot}$, $n^{\cdot}$, and q represent measures of quantity per unit of time. Velocity u is quite different in nature, as it does not suggest the magnitude of flow. Nevertheless, it is an important design parameter.

Example 2.9

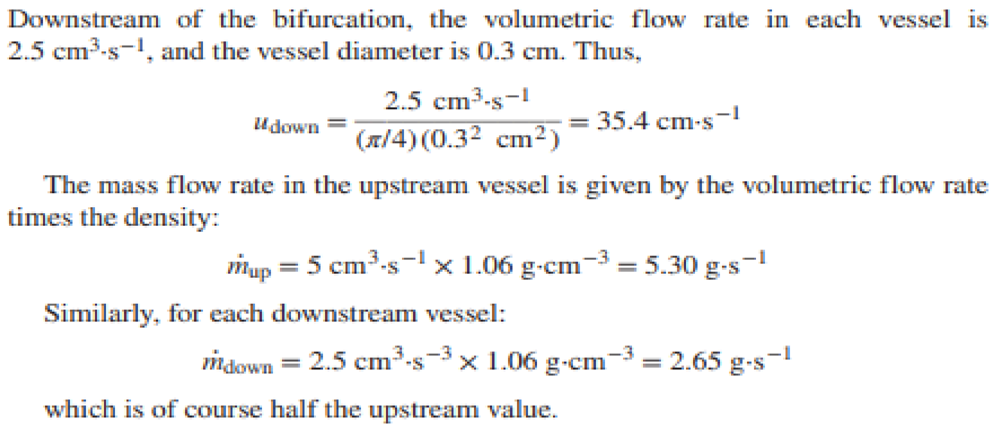
In a major human artery with an internal diameter of 5 mm, the flow of blood, averaged over the cardiac cycle, is 5 $cm^3{\cdot}s^{-1}$. The artery bifurcates (splits) into two identical blood vessels that are each 3 mm in diameter.

What are the **average velocity and the mass flow rate** upstream and downstream of the bifurcation? The density of blood is 1.06 $g{\cdot}cm^{-3}$.

Solution 2.9

The average velocity is given by the **volumetric flow rate** divided by the **area** for flow. Thus, **upstream** of the bifurcation, where the vessel diameter is 0.5 cm,

$$u_{up} = \frac{q}{A} = \frac{5\ cm^3{\cdot}s^{-1}}{(\pi/4)\,(0.5^2\ cm^2)} = 25.5\ cm{\cdot}s^{-1}$$



Downstream of the bifurcation, the volumetric flow rate in each vessel is 2.5 $cm^3{\cdot}s^{-1}$, and the vessel diameter is 0.3 cm. Thus,

$$u_{down} = \frac{2.5\ cm^3{\cdot}s^{-1}}{(\pi/4)(0.3^2\ cm^2)} = 35.4\ cm{\cdot}s^{-1}$$

The mass flow rate in the upstream vessel is given by the volumetric flow rate times the density:

$$\dot{m}_{up} = 5\ cm^3{\cdot}s^{-1} \times 1.06\ g{\cdot}cm^{-3} = 5.30\ g{\cdot}s^{-1}$$

Similarly, for each downstream vessel:

$$\dot{m}_{down} = 2.5\ cm^3{\cdot}s^{-3} \times 1.06\ g{\cdot}cm^{-3} = 2.65\ g{\cdot}s^{-1}$$

which is of course half the upstream value.

Mass Balance for Open Systems

The region of space identified for analysis of open systems is **called a control volume**; it is separated from its surroundings by a control surface. The fluid within the control volume is the thermodynamic system for which mass and energy balances are written. Because mass is conserved, the rate of change of mass within the control volume, dm_{cv}/dt, equals the net rate of flow of mass into the control volume. The convention is that flow is positive when directed into the control volume and negative when directed out. The mass balance is expressed mathematically by:

$$\boxed{\frac{dm_{cv}}{dt} + \Delta(\dot{m})_{fs} = 0} \tag{2.24}$$

For the control volume of Fig. 2.4, the second term is:

$$\Delta(\dot{m})_{fs} = \dot{m}_3 - \dot{m}_1 - \dot{m}_2$$

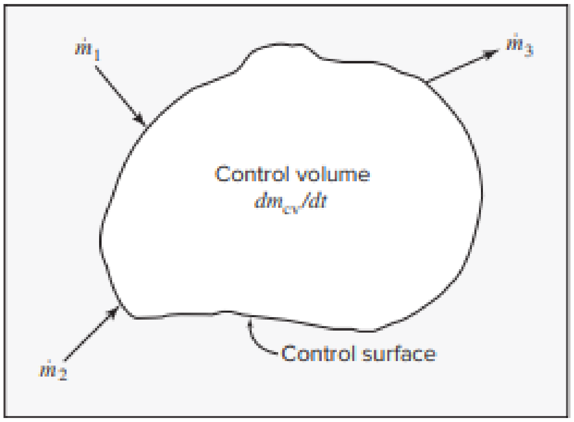


Figure 2.4: Schematic representation of a control volume. It is separated from its surroundings by an extensible control surface. Two streams with flow rates $\dot{m}_1$ and $\dot{m}_2$ are shown directed into the control volume, and one stream with flow rate $\dot{m}_3$ is directed out.

The difference operator Δ here signifies the difference between exit and entrance flows, and the subscript "fs" indicates that the term applies to all flowing streams. Note that this is a different usage of this operator compared with previous sections, where the difference was between an initial state and a final state. Both usages of the difference operator are common, and care must be taken to ensure that the correct sense is understood.

When the mass flow rate $\dot{m}$ is given by Eq. (2.23a), Eq. (2.24) becomes:

$$\frac{dm_{cv}}{dt} + \Delta(\rho u A)_{fs} = 0 \tag{2.25}$$

In this form the mass-balance equation is often called the continuity equation. Steady-state flow processes are those for which conditions within the control volume do not change with time. These are an important class of flow processes often encountered in practice. In a steady-state process, the control volume contains a constant mass of fluid, and the first or accumulation term of Eq. (2.24) is zero, reducing Eq. (2.25) to:

$$\Delta(\rho u A)_{fs} = 0$$

The term "steady state" does not necessarily imply that flow rates are constant, merely that the inflow of mass is exactly matched by the outflow of mass.

When there is a single entrance and a single exit stream, the mass flow rate m˙ is the same for both streams; then,

$$\dot{m} = \text{const} = \rho_2 u_2 A_2 = \rho_1 u_1 A_1$$

Because specific volume is the reciprocal of density,

$$\boxed{\dot{m} = \frac{u_1 A_1}{V_1} = \frac{u_2 A_2}{V_2} = \frac{uA}{V}} \qquad (2.26)$$

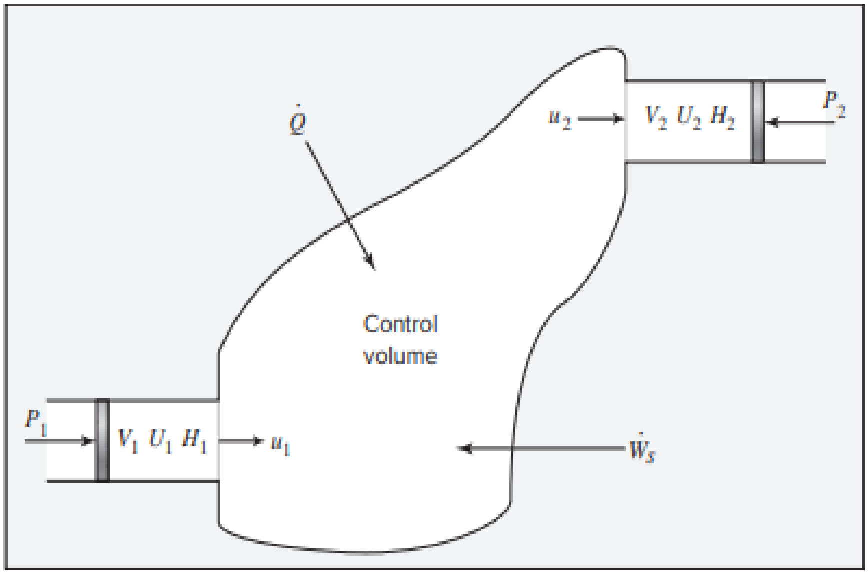
This form of the **continuity equation** finds frequent use.

The General Energy Balance

Because energy, like mass, is conserved, the rate of change of energy within the control volume equals the net rate of energy transfer into the control volume. Streams flowing into and out of the control volume have associated with them energy in its internal, potential, and kinetic forms, and all may contribute to the energy change of the system. Each unit mass of a stream carries with it a total energy U + 1 /2 u^2 + zg, where u is the average velocity of the stream, z is its elevation above a datum level, and g is the local acceleration of gravity. Thus, each stream transports energy at the rate **(U + 1 /2 u^2 + zg) m˙**. The net energy transported into the system by the flowing streams is therefore **–Δ [(U + 1/ 2 u^2 + zg) m˙] fs,** where the effect of the minus sign with "Δ" is to make the term read in – out. The rate of energy accumulation within the control volume includes this quantity in addition to the heat transfer rate Q˙ and work rate:

$$\frac{d(mU)_{cv}}{dt} = -\Delta\left[\left(U + \frac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} + \dot{Q} + \text{work rate}$$

Figure 2.5: Control volume with one entrance and one exit.



The work rate may include work of several forms. First, work is associated with moving the flowing streams through entrances and exits. The fluid at any entrance or exit has a set of average properties, P, V, U, H, etc. Imagine that a unit mass of fluid with these properties exists at an entrance or exit, as shown in Fig. 2.5. This unit mass of fluid is acted upon by additional fluid, here replaced by a piston that exerts the constant pressure P. The work done by this piston in moving the unit mass through the entrance is PV, and the work rate is (PV) m˙ . Because Δ denotes the difference between exit and entrance quantities, the net work done on the system when all entrance and exit sections are taken into account is −Δ[(PV)m˙]fs. Another form of work is the shaft work9 indicated in Fig. 2.5 by rate W˙ s. In addition, work may be associated with expansion or contraction of the entire control volume. These forms of work are all included in a rate term represented by W · . The preceding equation may now be written:

$$\frac{d(mU)_{cv}}{dt} = -\Delta\left[\left(U + \frac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} + \dot{Q} - \Delta[(PV)\dot{m}]_{fs} + \dot{W}$$

Combination of terms in accord with the definition of enthalpy, $H = U + PV$, leads to:

$$\frac{d(mU)_{cv}}{dt} = -\Delta\left[\left(H + \frac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}$$

which is usually written:

$$\boxed{\frac{d(mU)_{cv}}{dt} + \Delta\left[\left(H + \frac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}} \qquad (2.27)$$

The velocity u in the kinetic-energy terms is the bulk-mean velocity as defined by the equation $u = \dot{m}/(\rho A)$. Fluids flowing in pipes exhibit a velocity profile that rises from zero at the wall (the no-slip condition) to a maximum at the center of the pipe. The kinetic energy of a fluid in a pipe depends on its velocity profile. For the case of laminar flow, the profile is parabolic, and integration across the pipe shows that the kinetic-energy term should properly be u2. In fully developed turbulent flow, the more common case in practice, the velocity across the major portion of the pipe is not far from uniform, and the expression u2/2, as used in the energy equations, is more nearly correct. Although Eq. (2.27) is an energy balance of reasonable generality, it has limitations. In particular, it reflects the tacit assumption that the center of mass of the control volume is stationary. Thus no terms for kinetic- and potential-energy changes of the fluid in the control volume are included. For virtually all applications of interest to chemical engineers, Eq. (2.27) is adequate. For many (but not all) applications, kinetic- and potential-energy changes in the flowing streams are also negligible, and Eq. (2.27) then simplifies to:

$$\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W} \qquad (2.28)$$

Example 2.10

Show that Eq. (2.28) reduces to Eq. (2.3) for the case of a closed system.

Solution 2.10

The second term of Eq. (2.28) is omitted in the absence of flowing streams:

$$\frac{d(mU)_{cv}}{dt} = \dot{Q} + \dot{W}$$

Integration over time gives

$$\Delta(mU)_{cv} = \int_{t_1}^{t_2} \dot{Q}\,dt + \int_{t_1}^{t_2} \dot{W}\,dt$$

or

$$\Delta U^t = Q + W$$

The Q and W terms are defined by the integrals of the preceding equation. Note here that Δ indicates a change over time, not from an inlet to an outlet. One must be aware of its context to discern its meaning.

Example 2.11

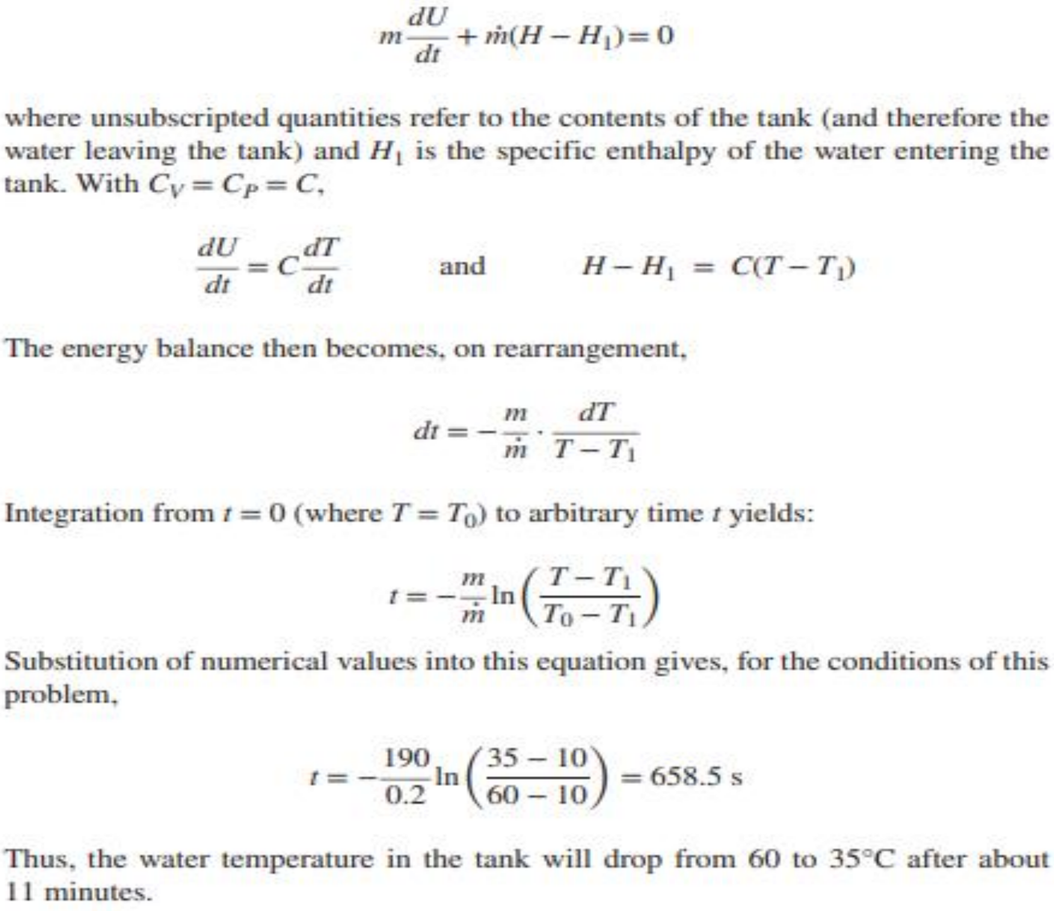
An insulated, electrically heated tank for hot water contains 190 kg of liquid water at 60°C. Imagine you are taking a shower using water from this tank when a power outage occurs. If water is withdrawn from the tank at a steady rate of m· = 0.2 kg·s−1, how long will it take for the temperature of the water in the tank to drop from 60 to 35°C? Assume that cold water enters the tank at 10°C and that heat losses from the tank are negligible. Here, an excellent assumption for liquid water is that **Cv = Cp = C, independent of T and P.**

Solution 2.11

This is an example of the application of Eq. (2.28) to a transient process for which

$$\dot{Q} = \dot{W} = 0.$$

We assume perfect mixing of the contents of the tank; this implies that the properties of the water leaving the tank are those of the water in the tank. With the mass flow rate into the tank equal to the mass flow rate out, mcv is constant; moreover, the differences between inlet and outlet kinetic and potential energies can be neglected. Equation (2.28) is therefore written:



$$m\frac{dU}{dt} + \dot{m}(H - H_1) = 0$$

where unsubscripted quantities refer to the contents of the tank (and therefore the water leaving the tank) and H_1 is the specific enthalpy of the water entering the tank. With $C_V = C_P = C$,

$$\frac{dU}{dt} = C\frac{dT}{dt} \qquad \text{and} \qquad H - H_1 = C(T - T_1)$$

The energy balance then becomes, on rearrangement,

$$dt = -\frac{m}{\dot{m}} \cdot \frac{dT}{T - T_1}$$

Integration from $t = 0$ (where $T = T_0$) to arbitrary time t yields:

$$t = -\frac{m}{\dot{m}} \ln\left(\frac{T - T_1}{T_0 - T_1}\right)$$

Substitution of numerical values into this equation gives, for the conditions of this problem,

$$t = -\frac{190}{0.2} \ln\left(\frac{35 - 10}{60 - 10}\right) = 658.5 \text{ s}$$

Thus, the water temperature in the tank will drop from 60 to 35°C after about 11 minutes.

Energy Balances for Steady-State Flow Processes

Flow processes for which the accumulation term of Eq. (2.27), d(mU)cv/dt, is zero are said to occur at steady state. As discussed with respect to the mass balance, this means that the mass Final PDF to printer 2.9. Mass and Energy Balances for Open Systems 53 smi96529_ch02_024-067.indd 53 11/18/16 10:45 PM of the system within the control volume is constant; it also means that no changes occur with time in the properties of the fluid within the control volume nor at its entrances and exits. No expansion of the control volume is possible under these circumstances. The only work of the process is shaft work, and the general energy balance, Eq. (2.27), becomes:

$$\boxed{\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{\text{fs}}=\dot{Q}+\dot{W}_s} \tag{2.29}$$

Although "steady state" does not necessarily imply "steady flow," the usual application of this equation is to steady-state, steady-flow processes, because such processes represent the industrial norm. A further specialization results when the control volume has one entrance and one exit. The same mass flow rate m˙ then applies to both streams, and Eq. (2.29) reduces to:

$$\Delta\left(H+\frac{1}{2}u^2+zg\right)\dot{m}=\dot{Q}+\dot{W}_s \tag{2.30}$$

where subscript "fs" has been omitted in this simple case and Δ denotes the change from entrance to exit. Division by $\dot{m}$ gives:

$$\Delta\left(H+\frac{1}{2}u^2+zg\right)=\frac{\dot{Q}}{\dot{m}}+\frac{\dot{W}_s}{\dot{m}}=Q+W_s$$

or

$$\boxed{\Delta H+\frac{\Delta u^2}{2}+g\Delta z=Q+W_s} \tag{2.31}$$

This equation is the mathematical expression of the first law for a steady-state, steady-flow process between one entrance and one exit. All terms represent energy per unit mass of fluid. The energy unit is usually the joule.

In many applications, kinetic- and potential-energy terms are omitted because they are negligible compared with other terms.[11] For such cases, Eq. (2.31) reduces to:

$$\Delta H=Q+W_s \tag{2.32}$$

This expression of the first law for a steady-state, steady-flow process is analogous to Eq. (2.3) for a nonflow process. However, in Eq. (2.32), enthalpy rather than internal energy is the thermodynamic property of importance, and Δ refers to a change from inlet to outlet, rather than from before to after an event.

A Flow Calorimeter for Enthalpy Measurements

The application of Eqs. (2.31) and (2.32) to the solution of practical problems requires enthalpy values. Because H is a state function, its values depend only on point conditions; once determined, they may be tabulated for subsequent use for the same sets of conditions. To this end, Eq. (2.32) may be applied to laboratory processes designed for enthalpy measurements.

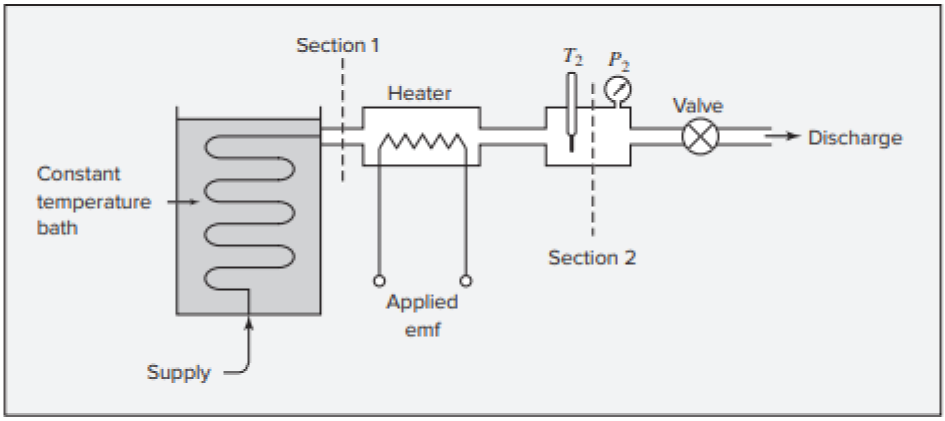


Figure 2.6: Flow calorimeter.

A simple flow calorimeter is illustrated schematically in Fig. 2.6. Its essential feature is an electric resistance heater immersed in a flowing fluid. The design provides for minimal velocity and elevation changes from section 1 to section 2, making kinetic- and potential-energy changes of the fluid negligible. **With no shaft work entering the system**, Eq. (2.32) reduces to

$$\Delta H = H_2 - H_1 = Q$$

The rate of heat transfer to the fluid is determined from the resistance of the heater and the current passing through it. In practice a number of details require careful attention, but in principle the operation of the flow calorimeter is simple. Measurements of the heat transfer rate and flow rate allow calculation of the change ΔH between sections 1 and 2.

For example, enthalpies of both liquid and vapor H2O are readily determined. The constant-temperature bath is filled with a mixture of crushed ice and water to maintain a temperature of 0°C. Liquid water is supplied to the apparatus, and the coil that carries it through the constant-temperature bath is long enough to bring it to an exit temperature of essentially 0°C. The temperature and pressure at section 2 are measured by suitable instruments. Values of the enthalpy of H2O for various conditions at section 2 are given by:

$$H_2 = H_1 + Q$$

Where Q is the heat added per unit mass of water flowing.

The pressure may vary from run to run, but in the range encountered here it has a negligible effect on the enthalpy of the entering water, and for practical purposes H1 is a constant. Absolute values of enthalpy, like absolute values of internal energy, are unknown. An arbitrary value may therefore be assigned to H1 as the basis for all other enthalpy values.

Setting H1 = 0 for liquid water at 0°C makes:

$$H_2 = H_1 + Q = 0 + Q = Q$$

Enthalpy values may be tabulated for the temperatures and pressures existing at section 2 for a large number of runs. In addition, specific-volume measurements made for these same conditions may be added to the table, along with corresponding values of the internal energy calculated by Eq. (2.10), U = H − PV. In this way, tables of thermodynamic properties are compiled over the entire useful range of conditions. The most widely used such tabulation is for H2O and is known as the steam tables. 12 The enthalpy may be taken as zero for some other state than liquid at 0°C. The choice is arbitrary. The equations of thermodynamics, such as Eqs. (2.31) and (2.32), apply to changes of state, for which the enthalpy differences are independent of the location of the zero point. However, once an arbitrary zero point is selected for the enthalpy, an arbitrary choice cannot be made for the internal energy, because internal energy is related to enthalpy by Eq. (2.10).

Example 2.12

For the flow calorimeter just discussed, the following data are taken with water as the test fluid:

Flow rate = 4.15 $g{\cdot}s^{-1}$ $t_1 = 0°C$ $t_2 = 300°C$ $P_2 = 3$ bar

Rate of heat addition from resistance heater = 12,740 W The water is completely vaporized in the process.

Calculate the enthalpy of steam at 300°C and 3 bar based on H = 0 for liquid water at 0°C.

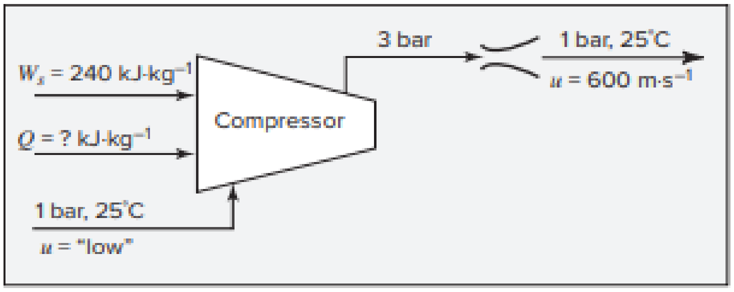
Solution 2.12

If Δz and Δu^2 are negligible and if W_s and H_1 are zero, then $H_2 = Q$, and

$$H_2 = \frac{12{,}740 \text{ J}{\cdot}\text{s}^{-1}}{4.15 \text{ g}{\cdot}\text{s}^{-1}} = 3070 \text{ J}{\cdot}\text{g}^{-1} \qquad \text{or} \qquad 3070 \text{ kJ}{\cdot}\text{kg}^{-1}$$

Example 2.13

Air at 1 bar and 25°C enters a compressor at low velocity, discharges at 3 bar, and enters a nozzle in which it expands to a final velocity of 600 m·s−1 at the initial conditions of pressure and temperature. If the work of compression is 240 kJ per kilogram of air, **how much heat must be removed during compression?**



Solution 2.13

Because the air returns to its initial conditions of T and P, the **overall process produces no change in enthalpy of the air**. Moreover, the potential-energy change of the air is presumed negligible. Neglecting also the initial kinetic energy of the air, we write Eq. (2.31) as:

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta z = 0 + \frac{u_2^2}{2} + 0 = Q + W_s$$

Then

$$Q = \frac{u_2^2}{2} - W_s$$

The kinetic-energy term is evaluated as follows:

$$\frac{1}{2}u_2^2 = \frac{1}{2}\left(600\frac{\mathrm{m}}{\mathrm{s}}\right)^2 = 180{,}000\frac{\mathrm{m}^2}{\mathrm{s}^2} = 180{,}000\frac{\mathrm{m}^2}{\mathrm{s}^2}\cdot\frac{\mathrm{kg}}{\mathrm{kg}}$$

$$= 180{,}000\ \mathrm{N{\cdot}m{\cdot}kg^{-1}} = 180\ \mathrm{kJ{\cdot}kg^{-1}}$$

Then

$$Q = 180 - 240 = -60\ \mathrm{kJ{\cdot}kg^{-1}}$$

Heat in the amount of 60 kJ must be removed per kilogram of air compressed.

Example 2.14

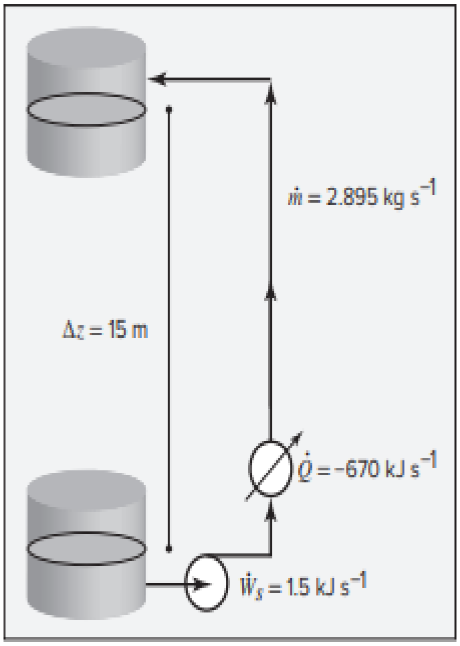
Water at 90°C is pumped from a storage tank at a rate of 3 L·s^{-1}. The motor for the pump supplies work at a rate of 1.5 kJ·s^{-1}. The water goes through a heat exchanger, giving up heat at a rate of 670 kJ·s^{-1}, and is delivered to a second storage tank at an elevation 15 m above the first tank. **What is the temperature of the water delivered to the second tank**?

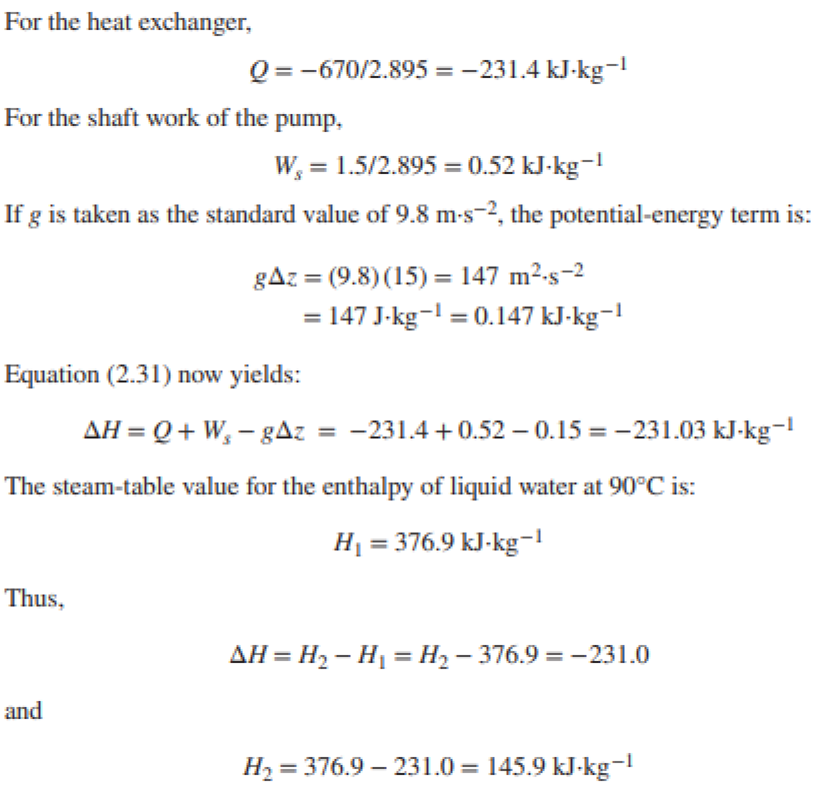
Solution 2.14

This is a steady-state, steady-flow process for which Eq. (2.31) applies. The initial and final velocities of water in the storage tanks are negligible, and the term $\Delta u^2/2$ may be omitted.

All remaining terms are expressed in units of kJ·kg^{-1}. At 90°C the density of water is 0.965 kg·L^{-1} and the mass flow rate is:

$$\dot{m} = (3)\ (0.965) = 2.895\ \text{kg}\cdot\text{s}^{-1}$$





For the heat exchanger,

$$Q = -670/2.895 = -231.4 \text{ kJ}\cdot\text{kg}^{-1}$$

For the shaft work of the pump,

$$W_s = 1.5/2.895 = 0.52 \text{ kJ}\cdot\text{kg}^{-1}$$

If g is taken as the standard value of 9.8 $\text{m}\cdot\text{s}^{-2}$, the potential-energy term is:

$$g\Delta z = (9.8)(15) = 147 \ \text{m}^2\cdot\text{s}^{-2}$$
$$= 147 \text{ J}\cdot\text{kg}^{-1} = 0.147 \text{ kJ}\cdot\text{kg}^{-1}$$

Equation (2.31) now yields:

$$\Delta H = Q + W_s - g\Delta z \ = \ -231.4 + 0.52 - 0.15 = -231.03 \text{ kJ}\cdot\text{kg}^{-1}$$

The steam-table value for the enthalpy of liquid water at 90°C is:

$$H_1 = 376.9 \text{ kJ}\cdot\text{kg}^{-1}$$

Thus,

$$\Delta H = H_2 - H_1 = H_2 - 376.9 = -231.0$$

and

$$H_2 = 376.9 - 231.0 = 145.9 \text{ kJ}\cdot\text{kg}^{-1}$$

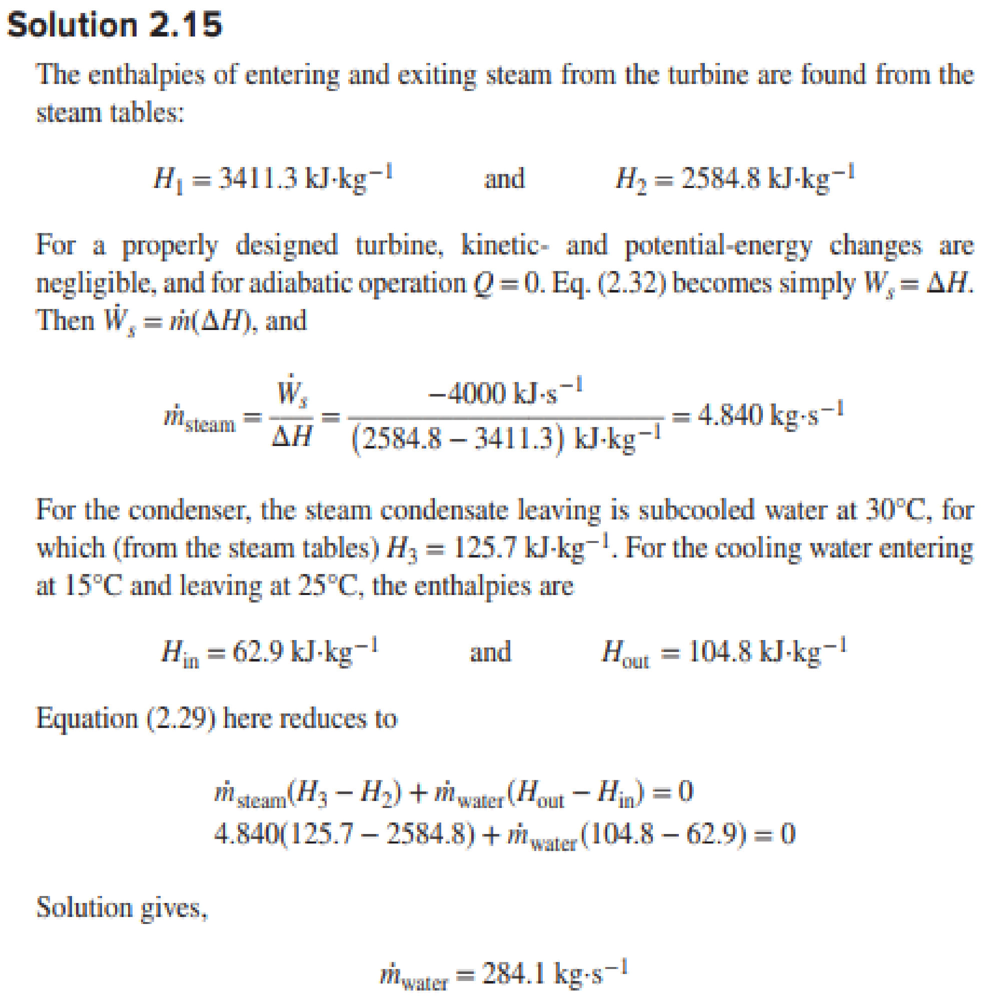
The temperature of water having this enthalpy is found from the **steam tables:**

t = 34.83°C

In this example, Ws and gΔz are small compared with Q, and for practical purposes could be neglected.

Example 2.15

A steam turbine **operates adiabatically** with a power output of 4000 kW. Steam enters the turbine at 2100 kPa and 475°C. The exhaust is saturated steam at 10 kPa that enters a condenser, where it is condensed and cooled to 30°C. **What is the mass flow rate of the steam,** and at **what rate must cooling water be supplied to the condenser**, if the water enters at 15°C and is heated to 25°C?



Solution 2.15

The enthalpies of entering and exiting steam from the turbine are found from the steam tables:

$$H_1 = 3411.3\ \text{kJ}\cdot\text{kg}^{-1} \qquad \text{and} \qquad H_2 = 2584.8\ \text{kJ}\cdot\text{kg}^{-1}$$

For a properly designed turbine, kinetic- and potential-energy changes are negligible, and for adiabatic operation $Q = 0$. Eq. (2.32) becomes simply $W_s = \Delta H$. Then $\dot{W}_s = \dot{m}(\Delta H)$, and

$$\dot{m}_{\text{steam}} = \frac{\dot{W}_s}{\Delta H} = \frac{-4000\ \text{kJ}\cdot\text{s}^{-1}}{(2584.8 - 3411.3)\ \text{kJ}\cdot\text{kg}^{-1}} = 4.840\ \text{kg}\cdot\text{s}^{-1}$$

For the condenser, the steam condensate leaving is subcooled water at 30°C, for which (from the steam tables) $H_3 = 125.7\ \text{kJ}\cdot\text{kg}^{-1}$. For the cooling water entering at 15°C and leaving at 25°C, the enthalpies are

$$H_{\text{in}} = 62.9\ \text{kJ}\cdot\text{kg}^{-1} \qquad \text{and} \qquad H_{\text{out}} = 104.8\ \text{kJ}\cdot\text{kg}^{-1}$$

Equation (2.29) here reduces to

$$\dot{m}_{\text{steam}}(H_3 - H_2) + \dot{m}_{\text{water}}(H_{\text{out}} - H_{\text{in}}) = 0$$
$$4.840(125.7 - 2584.8) + \dot{m}_{\text{water}}(104.8 - 62.9) = 0$$

Solution gives,

$$\dot{m}_{\text{water}} = 284.1\ \text{kg}\cdot\text{s}^{-1}$$

First law of thermodynamics :-

1- For closed system (non-flow system) :

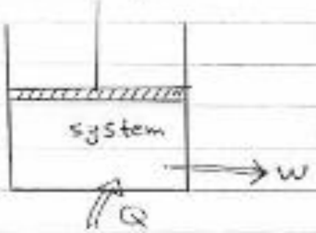
Δ(energy of the system) + Δ(energy of the surrounding) = 0

$\Delta U + \Delta KE + \Delta PE = Q - W$

if ΔKE and ΔPE are negligible

$\boxed{\Delta U = Q - W}$ First law of thermodynamics for closed system

$$\boxed{\Delta U = Q - W}$$



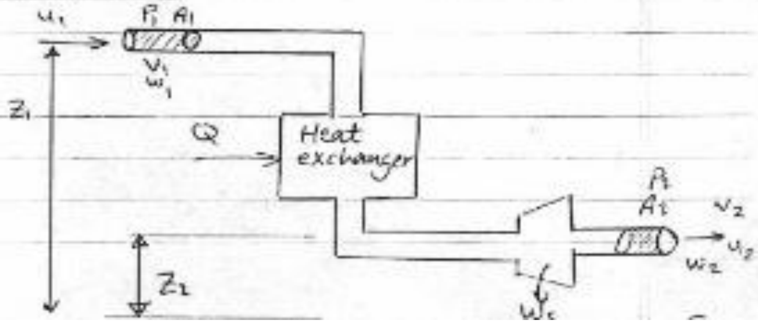
2- For open system (flow-system) :

open system can be divided into two ;

a/ steady state flow process .

b/ unsteady state flow process .

a) Steady state flow process



Basis = 1 kg unit mass

Starting with

$\Delta U + \Delta K_E + \Delta P_E = Q - W$ ------ (1)

$\Delta K_E = \frac{1}{2} V_2^2 - \frac{1}{2} V_1^2 = \frac{1}{2} \Delta V^2$

$\Delta P_E = Z_2 g - Z_1 g = g(Z_2 - Z_1) = g \Delta Z$

∴ Eqn ① becomes

$\Delta U + \frac{\Delta V^2}{2} + g \Delta Z = Q - W$ ------ (2)

$W = W_1 + W_2 + W_s$

$W_1 = P_1 A_1 \times \frac{V_1}{A_1} = P_1 V_1$

$W_2 = P_2 A_2 \times V_2 / A_2 = P_2 V_2$

$\therefore W = P_1 V_1 + P_2 V_2 + W_s$

$\therefore \Delta U + \frac{\Delta V^2}{2} + g \Delta Z = Q - (P_1 V_1 + P_2 V_2 + W_s)$

$\Delta U + \frac{\Delta V^2}{2} + g \Delta Z = Q - W_s - (P_1 V_1 + P_2 V_2)$

$\therefore \Delta U + \Delta PV + \frac{\Delta V^2}{2} + g \Delta Z = Q - W_s$

but $\Delta U + \Delta PV = \Delta H$

$\boxed{\Delta H + \frac{\Delta V^2}{2} + g \Delta Z = Q - W_s}$ ------ (3)

if ΔV & ΔZ are negligible then

$\boxed{\Delta H = Q - W_s}$ ------ (4)

First law for open steady state system.

Unsteady state process

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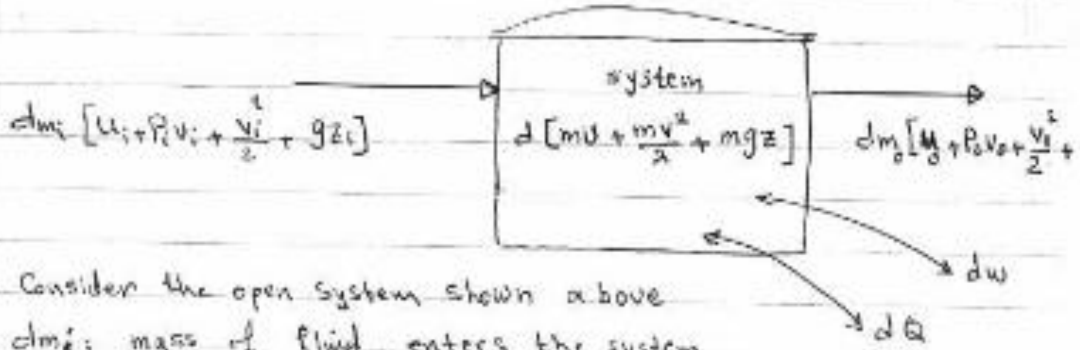


Consider the open system shown above

dm_i: mass of fluid enters the system.

dm_o = mass of fluid leaving the system.

dQ = amount of heat transfered to the system.

dW = amount of work done by the system.

$d[mu + m\frac{V^2}{2} + mgz]$ = is the total energy chang of the syste

Now if mass dm_i input to the system, the energy of the system increases by $dm_i[u_i + P_i v_i + \frac{V_i^2}{2} + gz_i]$

and if mass dm_o output from the system, the energy of the system decreases by an amount $dm_o[u_o + P_o v_o + \frac{V_o^2}{2} + gz_o]$

The total energy within the system boundary may change either because:

(i) Change in mass of the system

(ii) change in the state of the fluid within the system.

Energy balance:

In = out + Acc.

$$dQ + dm_i\left[u_i + P_iV_i + \frac{V_i^2}{2} + gZ_i\right] = dW + dm_o\left[u_o + P_oV_o + \frac{V_o^2}{2} + gZ_o\right]$$
$$+ d\left[mu + m\frac{v^2}{2} + mgZ\right]$$

Note that $H = u + PV$

$$\therefore dQ + dm_i\left[H_i + \frac{V_i^2}{2} + gZ_i\right] = dW + dm_o\left[H_o + \frac{V_o^2}{2} + gZ_o\right]$$
$$+ d\left[mu + m\frac{v^2}{2} + mgZ\right]$$

If we neglect KE & PE اذا اهملنا الطاقة الحركية والكامنة نحصل على

$$\therefore dQ + dm_i(H_i) = dW + dm_o(H_o) + d(mu)$$

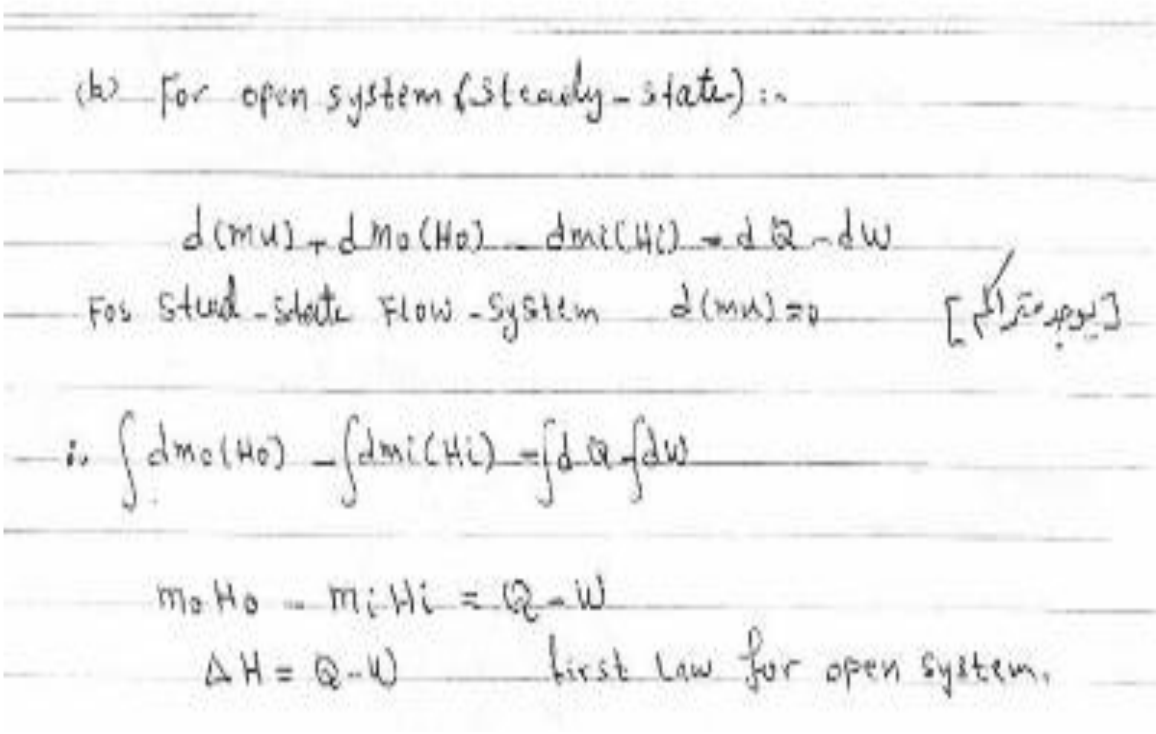
$$\text{OR}\quad \boxed{d(mu) + dm_o(H_o) - dm_i(H_i) = dQ - dW} \quad \ldots(*)$$

من هذا يمكن استخدام القانون الاول للثرموداينمك للنظام
المغلق والنظام المفتوح من المعادلة (*) كيف؟

(a) For closed system:

$dm_o = 0$ { عدم وجود تيار داخل او خارج
$dm_i = 0$ في النظام المغلق }

$$\therefore d(mu) = dQ - dW$$
$$\int d(mu) = \int dQ - \int dW$$
$$\Delta U = Q - W \qquad 1^{st}\ \text{Law for closed system.}$$



(b) For open system (Steady-state) :-

$$d(mu) + dm_o(H_o) - dm_i(H_i) = dQ - dW$$

For Steady-state Flow-System $d(mu) = 0$ [لا يوجد تراكم]

$$\therefore \int dm_o(H_o) - \int dm_i(H_i) = \int dQ - \int dW$$

$$m_o H_o - m_i H_i = Q - W$$

$\Delta H = Q - W$ first law for open system.

2.7 CLOSED-SYSTEM REVERSIBLE PROCESSES; ENTHALPY

We present here the analysis of closed-system mechanically reversible processes—not that such processes are common. Indeed they are of little interest for practical application. Their value lies in the simplicity they provide for the calculation of changes in state functions for a specific change of state. For a complex industrial process that brings about a particular change of state, the calculation of changes in state functions are not made for the path of the actual process.

Rather, they are made for a simple closed-system reversible process that brings about the same change of state. This is possible because changes in state functions are independent of process. The closed-system mechanically reversible process is useful and important for this purpose, even though close approximations to such hypothetical processes are not often encountered in practice. For 1 mole of a homogeneous fluid contained in a closed system, the energy balance of Eq. (2.6) is written:

$$dU = dQ + dW$$

The work for a mechanically reversible, closed-system process is given by Eq. (1.3), here written: $dW = -PdV$. Substitution into the preceding equation yields:

$$dU = dQ - PdV \qquad (2.7)$$

This is the general energy balance for one mole or a unit mass of homogeneous fluid in a closed system undergoing a mechanically reversible process.

For a constant-volume change of state, the only possible mechanical work is that associated with stirring or mixing, which is excluded because it is inherently irreversible. Thus,

$$dU = dQ \text{ (const V)} \qquad (2.8)$$

Integration yields:

$$\Delta U = Q \text{ (const V)} \qquad (2.9)$$

- The internal energy change for a mechanically reversible, constant-volume, closed-system process equals the amount of heat transferred into the system.

For a constant-pressure change of state:

$$dU + PdV = d(U + PV) = dQ$$

The group U + PV naturally arises here and in many other applications. This suggests the definition, for convenience, of this combination as a **new thermodynamic property.** Thus, the mathematical (and only) definition of enthalpy is:

$$H \equiv U + PV \qquad (2.10) \; ***$$

Where H, U, and V are molar or unit-mass values. The preceding energy balance becomes:

$$\mathbf{dH = dQ \text{ (const P)}} \qquad \mathbf{(2.11)}$$

Integration yields:

$$\mathbf{\Delta H = Q \text{ (const P)}} \qquad \mathbf{(2.12)}$$

The enthalpy change in a mechanically reversible, constant-pressure, closed-system process equals the amount of heat transferred into the system. Comparison of Eqs. (2.11) and (2.12) with Eqs. (2.8) and (2.9) shows that the enthalpy plays a role in constant-pressure processes analogous to the internal energy in constant-volume processes.

These equations suggest the usefulness of enthalpy, but its greatest use becomes fully apparent with its appearance in energy balances for flow processes as applied to heat exchangers, chemical and biochemical reactors, distillation columns, pumps, compressors, turbines, engines, etc., for calculation of heat and work.

The tabulation of Q and W for the infinite array of conceivable processes is impossible. The intensive state functions, however, such as molar or specific volume, internal energy, and enthalpy, are intrinsic properties of matter. Once determined for a particular substance, their values can be tabulated as functions of T and P 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.

All terms of Eq. (2.10) must be expressed in the same units. The product PV has units of energy per mole or per unit mass, as does U; therefore H also has units of energy per mole or per unit mass. In the SI system the basic unit of pressure is the pascal (=1 N·m−2), and that of molar volume is cubic meters per mol (=1 m3·mol−1). For the PV product we have 1 N·m·mol−1 = 1 J·mol−1.

Because U, P, and V are all state functions, H as defined by Eq. (2.10) is also a state function. Like U and V, H is an intensive property of matter. The differential form of Eq. (2.10) is:

$$\mathbf{dH = dU + d(PV)} \qquad \mathbf{(2.13)}$$

This equation applies for any differential change of state. Upon integration, it becomes an equation for a finite change of state:

$$\mathbf{\Delta H = \Delta U + \Delta(PV)} \qquad \mathbf{(2.14)}$$

Equations (2.10), (2.13), and (2.14) apply to a unit mass or mole of a substance.

Example 2.6

Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 100°C and the constant pressure of 101.33 kPa. The specific volumes of liquid and vapor water at these conditions are 0.00104 and 1.673 $m^3 \cdot kg^{-1}$, respectively. For this change, heat in the amount of 2256.9 kJ is added to the water.

Solution 2.6

We take the 1 kg of water as the system because it alone is of interest, and we imagine it contained in a cylinder by a frictionless piston that exerts a constant pressure of 101.33 kPa. As heat is added, the water evaporates, expanding from its initial to its final volume. Equation (2.12) as written for the 1 kg system is:

$$\Delta H = Q = 2256.9 \text{ kJ}$$

By Eq. (2.14),

$$\Delta U = \Delta H - \Delta (PV) = \Delta H - P\,\Delta V$$

For the final term:

$$P\,\Delta V = 101.33 \text{ kPa} \times (1.673 - 0.001) \text{ m}^3$$

$$= 169.4 \text{ kPa}\cdot\text{m}^3 = 169.4 \text{ kN}\cdot\text{m}^{-2}\cdot\text{m}^3 = 169.4 \text{ kJ}$$

Then

$$\Delta U = 2256.9 - 169.4 = 2087.5 \text{ kJ}$$

Chapter 1:-

Example 1.4

An elevator with a mass of 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 its base.

(b) The work done in raising the elevator.

(c) The potential energy of the elevator in its highest position.

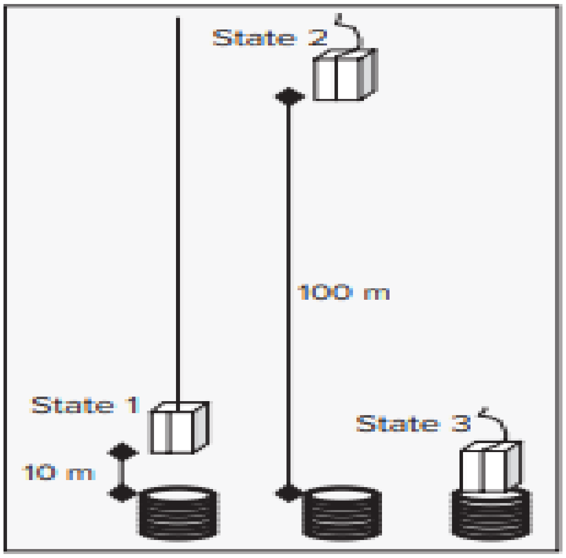
(d) The velocity and kinetic energy of the elevator just before it strikes the spring.

(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 denote the initial state; subscript 2, the state when the elevator is at its greatest elevation; and subscript 3, the state just before the elevator strikes the spring, as indicated in the figure.



(a) Potential energy is defined by Eq. (1.8):
$E_{P1} = mz_1g = 2500\ \text{kg} \times 10\ \text{m} \times 9.8\ \text{m}\cdot\text{s}^{-2}$
$= 245{,}000\ \text{kg}\cdot\text{m}^2\cdot\text{s}^{-2} = 245{,}000\ \text{J}$

(b) Work is computed by Eq. (1.7). Units are as in the preceding calculation:
$W = mg\,(z_2 - z_1) = (2500)\,(9.8)\,(100 - 10) = 2{,}205{,}000\ \text{J}$

(c) Again by Eq. (1.8),
$E_{P2} = mz_2g = (2500)\,(100)\,(9.8) = 2{,}450{,}000\ \text{J}$
Note that $W = E_{P2} - E_{P1}$

(d) The sum of the kinetic- and potential-energy changes during the process from state 2 to state 3 is zero; that is,
$\Delta E_{K2\to3} + \Delta E_{P2\to3} = 0$ or $E_{K3} - E_{K2} + E_{P3} - E_{P2} = 0$
However, E_{K2} and E_{P3} are zero; hence $E_{K3} = E_{P2} = 2{,}450{,}000$ J.
With $E_{K3} = 1/2\ mu_3{}^2$

$$u_3{}^2 = \frac{2E_{K1}}{m} = \frac{2x2{,}450{,}000\ J}{2500\ Kg} = \frac{2x2{,}450{,}000\ \ kgm^2s^{-1}}{2500\ Kg}\ 1960\ m^2s^{-2}$$

and

$$\mathbf{u_3 = 44.272\ m\cdot s^{-1}}$$

(e) 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 equals 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) With the elevator and spring as the system, the initial energy is the potential energy of the elevator, or 245,000 J. The only energy change of the system occurs when work is done in raising the elevator. This amounts to 2,205,000 J, and the energy of the system when the elevator is at maximum height is 245,000 + 2,205,000 = 2,450,000 J. Subsequent changes occur entirely within the system, without interaction with the surroundings, and 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 the conservation of mechanical energy. However, the entire process is assumed to occur without friction, and the results obtained are exact only for such an idealized process.

Example 1.5

A team from Engineers without Borders constructs a system to supply water to amountainside village located 1800 m above sea level from a spring in the valley below at 1500 m above sea level.

(a) When the pipe from the spring to the village is full of water, but no water is flowing, what is the pressure difference between the end of the pipe at the spring and the end of the pipe in the village?
(b) What is the change in gravitational potential energy of a liter of water when it is pumped from the spring to the village?
(c) What is the minimum amount of work required to pump a liter of water from the spring to the village?

Solution 1.5

(a)

Take the density of water as 1000 $\mathrm{kg \cdot m^{-3}}$ and the acceleration of gravity as 9.8 $\mathrm{m \cdot s^{-2}}$. By Eq. (1.1):

$$P = h\rho g = 300\ \mathrm{m} \times 1000\ \mathrm{kg \cdot m^{-3}} \times 9.8\ \mathrm{m \cdot s^{-2}} = 29.4 \times 105\ \mathrm{kg \cdot m^{-1} \cdot s^{-2}}$$

$$\text{Whence } P = 29.4 \text{ bar or } 2940 \text{ kPa}$$

(b) The mass of a liter of water is approximately 1 kg, and its potential-energy change is:
$\Delta E_P = \Delta\,(mzg) = mg\,\Delta z = 1\ \mathrm{kg} \times 9.8\ \mathrm{m \cdot s^{-2}} \times 300\ \mathrm{m} = 2940\ \mathrm{N \cdot m} = 2940\ \mathrm{J}$

(c)The minimum amount of work required to lift each liter of water through an elevation change of 300 m equals the potential-energy change of the water. It is a minimum value because it takes no account of fluid friction that results from finite-velocity pipe flow.

2.0 THERMODYNAMIC SYSTEMS

2.14. INTERNAL ENERGY

In experiments such as those conducted by Joule, energy is added to a fluid as work, but is transferred from the fluid as heat. What happens to this energy between its addition to and transfer from the fluid? A rational concept is that it is contained in the fluid in another form, called **internal energy**.

2.15. THE FIRST LAW OF THERMODYNAMICS

The recognition of heat and internal energy as forms of energy makes possible a generalization of the law of conservation of mechanical energy (Sec. 1.8) to include heat and internal energy in addition to work and external potential and kinetic energy. Indeed, the generalization can be extended to still other forms, such as surface energy, electrical energy, and magnetic energy. This generalization was at first a postulate. However, the overwhelming evidence accumulated over time has elevated it to the stature of a law of nature, known as the first law of thermodynamics. One formal statement is:

> **Although energy assumes many forms, the total quantity of energy is constant, and when energy disappears in one form it appears simultaneously in other forms.**

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***. The region in which the process occurs is set apart as the system; everything with which the system interacts is the surroundings. The system may be of any size depending on the application, and its boundaries may be real or imaginary, rigid or flexible. Frequently a system consists of a single substance; in other cases it may be complex. In any event, the equations of thermodynamics are written with reference to some well-defined system. This focuses attention on the particular process of interest and on the equipment and material directly involved in the process. However, the first law applies to the **system and surroundings,** and not to the system alone. In its most basic form, the first law requires:

$$\Delta\,(\textbf{Energy of the system}) + \Delta\,(\textbf{Energy of surroundings}) = 0 \qquad \textbf{(2.1)}$$

Where the difference operator "Δ" signifies finite changes in the quantities enclosed in parentheses. The system may change in its internal energy, in its potential or kinetic energy, and in the potential or kinetic energy of its finite parts. Since attention is focused on the system, the nature of energy changes in the surroundings is not of interest.

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 ENERGY BALANCE FOR CLOSED SYSTEMS

If the boundary of a system does not permit the transfer of matter between the system and its surroundings, the system is said to be ***closed***, and its **mass is necessarily constant**.

The development of basic concepts in thermodynamics is facilitated by a careful examination of closed systems, and for this reason they are treated in detail in the following sections.

Far more important for industrial practice are processes in which matter crosses the system boundary as streams that enter and leave process equipment. ***Such systems are said to be open***.

Since no streams enter or leave a closed system, no internal energy is transported across the boundary of the system.

نظرًا لعدم دخول أو خروج أي تيار لنظام مغلق ، لا يتم نقل أي طاقة داخلية عبر حدود النظام.

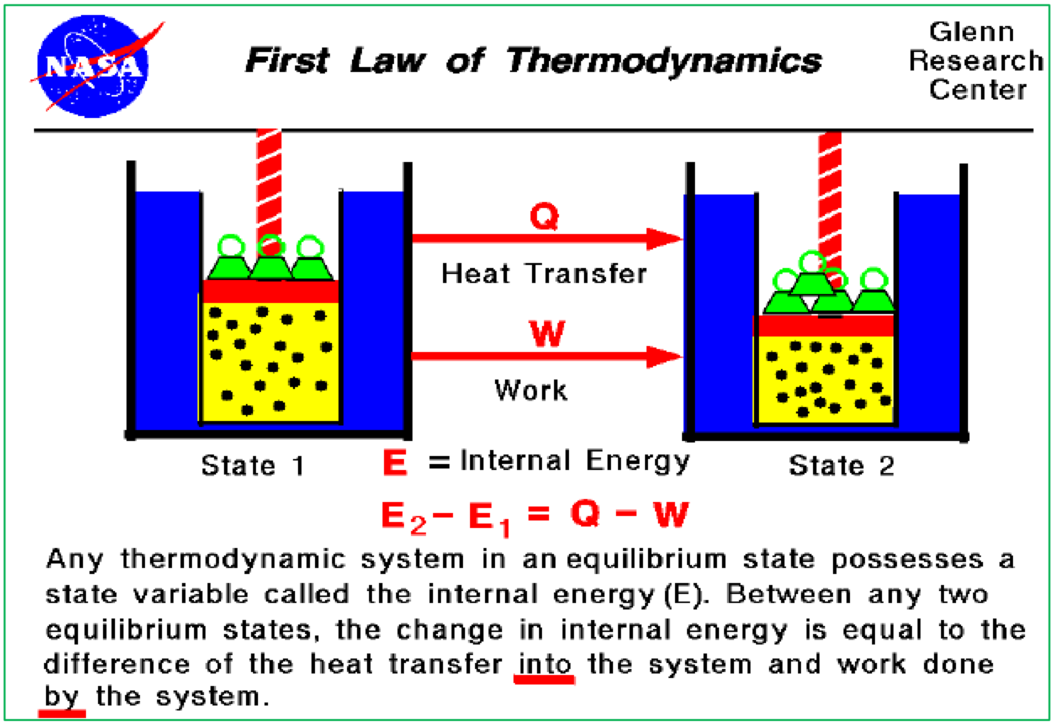
All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work.

كل الطاقة المتبادلة بين نظام مغلق ومحيطه تظهر كحرارة وشغل,

والتغير بالطاقة الكلية في المحيط يساوي صافي الطاقة المنقولة إلى أو منه كحرارة وشغل.

The second term of Eq. (2.1) may therefore be replaced by

$$\Delta\ \textbf{(Energy of surroundings)}\ = \mp Q\ \mp W$$



$$E_2 - E_1 = Q - W$$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

***The first law of thermodynamics.

By the end of this section, you will be able to:

- **Define the first law of thermodynamics.**
- Describe how conservation of energy relates to the first law of thermodynamics.
- Identify instances of the first law of thermodynamics working in everyday situations, including biological metabolism.
- Calculate changes in the internal energy of a system, after accounting for heat transfer and work done.

If we are interested in how heat transfer is converted into doing work, then the conservation of energy principle is important. The first law of thermodynamics applies the conservation of energy principle to systems where heat transfer and doing work are the methods of transferring energy into and out of the system. ***The first law of thermodynamics*** states that the change in internal energy of a system equals the net heat transfer *into* the system minus the net work done *by* the system. In equation form, the first law of thermodynamics is

$$\Delta U = Q - W.$$

Here ΔU is the *change in internal energy* U of the system. Q is the *net heat transferred into the system*—that is, Q is the sum of all heat transfer into and out of the system. W is the *net work done by the system*—that is, W is the sum of all work done on or by the system. We use the following sign conventions:

if Q is positive, then there is a net heat transfer into the system; if W is positive, then there is net work done by the system. So positive Q adds energy to the system and positive W takes energy from the system. Thus $\Delta U = Q - W$.

Note also that if more heat transfer into the system occurs than work done, the difference is stored as internal energy. Heat engines are a good example of this—heat transfer into them takes place so that they can do work. (See Figure 2.9) We will now examine Q, W, and ΔU further.

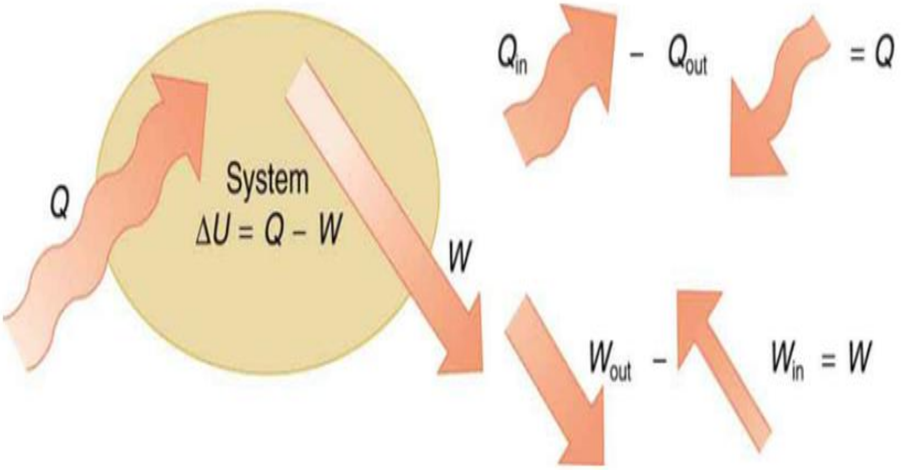


Figure 2.9. The first law of thermodynamics is the conservation-of-energy principle stated for a system where heat and work are the methods of transferring energy for a system in thermal equilibrium. Q represents the net heat transfer—it is the sum of all heat transfers into and out of the system. Q is positive for net heat transfer into the system. W is the total work done on and by the system. W is positive when more work is done by the system than on it. The change in the internal energy of the system, ΔU, is related to heat and work by the first law of thermodynamics, $\Delta U = Q - W$.

Heat *Q* and Work *W*

Heat transfer (Q) and doing work (W) are the two everyday means of bringing energy into or taking energy out of a system. The processes are quite different. Heat transfer, a less organized process, is driven by temperature differences. Work, a quite organized process, involves a macroscopic force exerted through a distance. Nevertheless, heat and work can produce identical results. For example, both can cause a temperature increase. Heat transfer into a system, such as when the Sun warms the air in a bicycle tire, can increase its temperature, and so can work done on the system, as when the bicyclist pumps air into the tire. Once the temperature increase has occurred, it is impossible to tell whether it was caused by heat transfer or by doing work. This uncertainty is an important point. Heat transfer and work are both energy in transit—neither is stored as such in a system. However, both can change the internal energy U of a system. Internal energy is a form of energy completely different from either heat or work.

Internal Energy *U*

We can think about the internal energy of a system in two different but consistent ways. The first is the atomic and molecular view, which examines the system on the atomic and molecular scale. The *internal energy U* of a system is the sum of the kinetic and potential energies of its atoms and molecules. Recall that kinetic plus potential energy is called mechanical energy. Thus internal energy is the sum of atomic and molecular mechanical energy. Because it is impossible to keep track of all individual atoms and molecules, we must deal with averages and distributions. A second way to view the internal energy of a system is in terms of its macroscopic characteristics, which are very similar to atomic and molecular average values.

Macroscopically, we define the change in internal energy ΔU to be that given by the first law of thermodynamics:

$$\boldsymbol{\Delta U = Q - W.}$$

Many detailed experiments have verified that $\Delta U = Q - W$, where ΔU is the change in total kinetic and potential energy of all atoms and molecules in a system. It has also been determined experimentally that the internal energy U of a system depends only on the state of the system and *not how it reached that state*. More specifically, U is found to be a function of a few macroscopic quantities (pressure, volume, and temperature, for example), independent of past history such as whether there has been heat transfer or work done. This independence means that if we know the state of a system, we can calculate changes in its internal energy U from a few macroscopic variables.

To get a better idea of how to think about the internal energy of a system, let us examine a system going from State 1 to State 2. The system has internal energy U_1 in State 1, and it has internal energy U_2 in State 2, no matter how it got to either state.

So the change in internal energy $\Delta U = U_2 - U_1$ is independent of what caused the change. In other words, ***ΔU is independent of path.*** By path, we mean the method of getting from the starting point to the ending point. Why is this independence important? Note that

$$\boldsymbol{\Delta U = Q - W}$$

Both Q and W *depend on path*, but ΔU does not. This path independence means that internal energy U is easier to consider than either heat transfer or work done.

EXAMPLE 1. CALCULATING CHANGE IN INTERNAL ENERGY: THE SAME CHANGE IN *U* IS PRODUCED BY TWO DIFFERENT PROCESSES

1. Suppose there is heat transfer of 40.00 J to a system, while the system does 10.00 J of work. Later, there is heat transfer of 25.00 J out of the system while 4.00 J of work is done on the system. What is the net change in internal energy of the system?
2. What is the change in internal energy of a system when a total of 150.00 J of heat transfer occurs out of (from) the system and 159.00 J of work is done on the system? (See Figure 2.10).

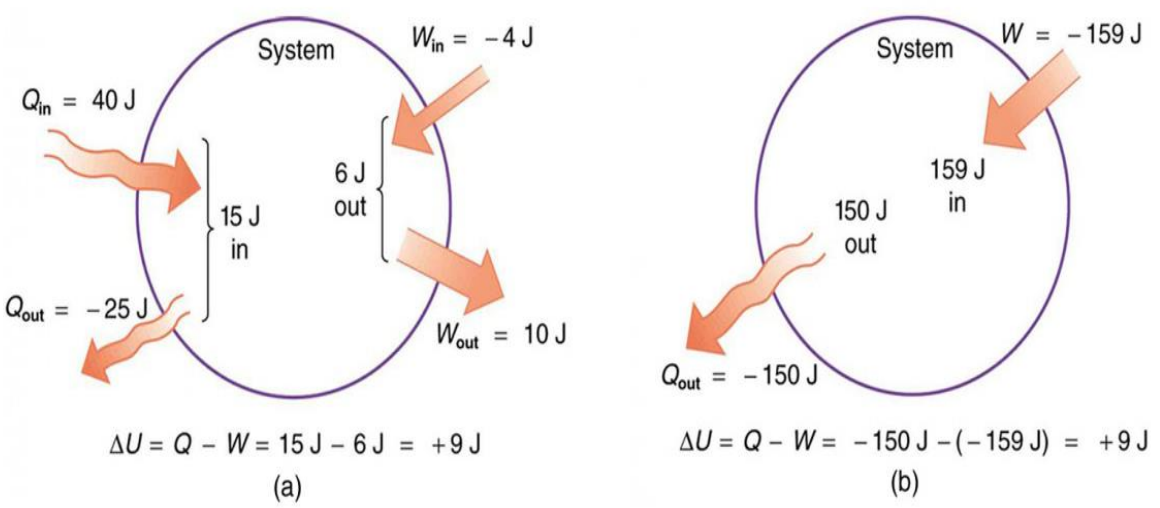


Figure 2.10. Two different processes produce the same change in a system. (a) A total of 15.00 J of heat transfer occurs into the system, while work takes out a total of 6.00 J. The change in internal energy is ΔU=Q−W=9.00 J.

(b) Heat transfer removes 150.00 J from the system while work puts 159.00 J into it, producing an increase of 9.00 J in internal energy. If the system starts out in the same state in (a) and (b), it will end up in the same final state in either case—its final state is related to internal energy, not how that energy was acquired.

Strategy

In part 1, we must first find the net heat transfer and net-work done from the given information. Then the first law of thermodynamics ($\Delta U = Q - W$) can be used to find the change in internal energy. In part (b), the net heat transfer and work done are given, so the equation can be used directly.

Solution for Part 1

The net heat transfer is the heat transfer into the system minus the heat transfer out of the system, or

$$Q = 40.00\ \text{J} - 25.00\ \text{J} = 15.00\ \text{J}.$$

Similarly, the total work is the work done by the system minus the work done on the system, or

$$W = 10.00\ \text{J} - 4.00\ \text{J} = 6.00\ \text{J}.$$

Thus the change in internal energy is given by the first law of thermodynamics:

$$\Delta U = Q - W = 15.00\ \text{J} - 6.00\ \text{J} = 9.00\ \text{J}.$$

We can also find the change in internal energy for each of the two steps. First, consider 40.00 J of heat transfer in and 10.00 J of work out, or

$$\Delta U_1 = Q_1 - W_1 = 40.00\ \text{J} - 10.00\ \text{J} = 30.00\ \text{J}.$$

Now consider 25.00 J of heat transfer out and 4.00 J of work in, or

$$\Delta U_2 = Q_2 - W_2 = -25.00\ \text{J} - (-4.00\ \text{J}) = -21.00\ \text{J}.$$

The total change is the sum of these two steps, or

$$\Delta U = \Delta U_1 + \Delta U_2 = 30.00\ \text{J} + (-21.00\ \text{J}) = 9.00\ \text{J}.$$

Discussion on Part 1

No matter whether you look at the overall process or break it into steps, the change in internal energy is the same.

Solution for Part 2

Here the net heat transfer and total work are given directly to be $Q = -150.00$ J and $W = -159.00$ J, so that

$$\Delta U = Q - W = -150.00\ \text{J} - (-159.00\ \text{J}) = 9.00\ \text{J}.$$

Discussion on Part 2

A very different process in part 2 produces the same 9.00-J change in internal energy as in part 1. Note that the change in the system in both parts is related to ΔU and not to the individual Qs or Ws involved. The system ends up in the *same* state in both parts. Parts 1 and 2 present two different paths for the system to follow between the same starting and ending points, and the change in internal energy for each is the same—it is independent of path.

Example 2.1.

An artificial satellite revolves round the earth with a relative velocity of 800 m/s. If acceleration due to gravity is 9 m/s^2 and gravitational force is 3600 N, calculate its kinetic energy.

Solution. Relatively velocity of satellite, V = 800 m/s

Acceleration due to gravity, g = 9 m/s^2 Gravitational force, m.g = 3600 N

∴ Mass, m = 3600/g= 3600 /9 = 400 kg.

Kinetic energy $= 1/2\ mV^2 = 1/2 \times 400 \times (800)^2\ \text{J} = 128 \times 10^6\ \text{J}$ or 128 MJ. (Ans.).

((((*********************))))

Example 2.2.

The specific heat capacity of the system during a certain process is given by

$$C_n = (0.4 + 0.004\ T)\ \text{kJ/kg°C}.$$

If the mass of the gas is 6 kg and its temperature changes from 25°C to 125°C find:

(i) Heat transferred; (ii) Mean specific heat of the gas.

__Solution.__ Mass of the gas, m = 6 kg

Change in temperature of the gas = 25°C to 125°C

(i) Heat transferred, Q: We know that heat transferred is given by,

$$Q = \int m\, C_n\ dT\ = 6 \int_{25}^{125} (\,0.4 + 0.004\, T)dT$$

$$= 6\ \left[\,0.4\,\mathrm{T} + 0.04\left(\frac{\mathrm{T}^2}{2}\right)\ \right]_{25}^{125}$$

$$= 6[0.4\ (125 - 25) + 0.002\ (125^2 - 25^2)]$$

= 6(40 + 30) = **420 kJ. (Ans.)**

(ii) Mean specific heat of the gas, Cn:

Q = m.Cn.dT

i.e., 420 = 6 × Cn × (125 – 25)

$$\therefore \quad C_n = \frac{420}{6 \times 100} = 0.7\ \frac{KJ}{Kg\ °C} \qquad (Ans.)$$

(((**************************)))))

Example 2.3.

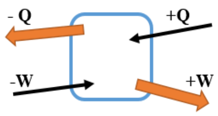
In an internal combustion engine, during the compression stroke the heat rejected to the cooling water is 50 kJ/kg and the work input is 100 kJ/kg. Calculate the change in internal energy of the working fluid stating whether it is a gain or loss.

<u>Solution.</u>

Heat rejected to the cooling water, $Q = -50$ kJ/kg (–ve sign since heat is rejected)

Work input, $W = -100$ kJ/kg (–ve sign since work is supplied to the system)

Using the relation, $Q - W = (u_2 - u_1)$



$$-50 - (-100) = (u_2 - u_1)$$

OR $u_2 - u_1 = -50 + 100 = 50$ kJ/kg

Hence, gain in internal energy = 50 kJ/kg. (Ans.)

((((*************************))))

Example 2.4.

In an air motor cylinder the compressed air has an internal energy of 450 kJ/kg at the beginning of the expansion and an internal energy of 220 kJ/kg after expansion. If the work done by the air during the expansion is 120 kJ/kg, calculate the heat flow to and from the cylinder.

<u>Solution.</u>

Internal energy at beginning of the expansion, $u_1 = 450$ kJ/kg

Internal energy after expansion, $u_2 = 220$ kJ/kg

Work done by the air during expansion, $W = 120$ kJ/kg

Heat flow, Q:

Using the relation, $(u_2 - u_1) = Q - W$

$$Q = (u_2 - u_1) + W$$

$$\therefore \quad Q = (220 - 450) + 120$$

$$= -230 + 120 = -110 \text{ kJ/kg}$$

Hence, heat rejected by air = 110 kJ/kg. (Ans.)

(((************************)))))

Example 2.5.

When a stationary mass of gas was compressed without friction at constant pressure its initial state of 0.4 m^3 and 0.105 MPa was found to change to final state of 0.20 m^3 and 0.105 MPa. There was a transfer of 42.5 kJ of heat from the gas during the process. How much did the internal energy of the gas change?

Solution.

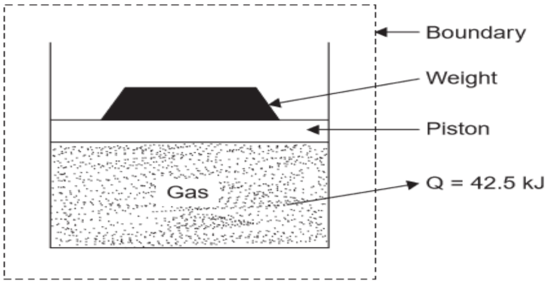


Fig.

Initial state: Pressure of gas, $p_1 = 0.105$ MPa Volume of gas, $V_1 = 0.4\ m^3$

Final state: Pressure of gas, $p_2 = 0.105$ MPa Volume of gas, $V_2 = 0.20\ m^3$

Process used: Constant pressure

Heat transferred, Q = – 42.5 kJ **(–ve sign indicates that heat is rejected)**

Change in internal energy, $\Delta U = U_2 - U_1$:

First law for a stationary system in a process gives

$$\mathbf{\Delta U = Q - W}$$

$$\mathbf{Q = \Delta U + W}$$

OR $Q_{1-2} = (U_2 - U_1) + W_{1-2}$ ... (*i*)

Here $W_{1-2} = \int_{V_1}^{V_2} PdV = P(V_2 - V_1)$

= 0.105(0.20 – 0.40) MJ = – 21 kJ [1 MJ = 103 kJ]

Substituting this value of W_{1-2} in equation (*i*), we get

$$-42.5 = (U_2 - U_1) - 21$$

∴ $U_2 - U_1 = -42.5 + 21 = -21.5$ kJ

Hence 'decrease' in internal energy = 21.5 kJ. (Ans.)

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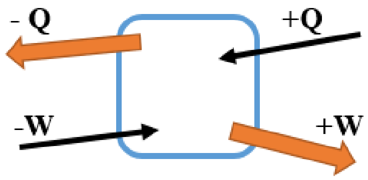


Δ = Change

Δ (Energy of the system) + Δ (Energy of surroundings) = 0 **(2.1)**

Δ (Energy of surroundings) $= \mp \boldsymbol{Q} \mp \boldsymbol{W}$ **(path function)**

Δ (Energy of system) $= \Delta\,(\boldsymbol{U} + \boldsymbol{K_E} + \boldsymbol{P_E})$ **(Stat function)**

$\Delta\,(\boldsymbol{U} + \boldsymbol{K_E} + \boldsymbol{P_E}) = \mp \boldsymbol{Q} \mp \boldsymbol{W}$ **(First law of thermodynamic)**

ملاحظة: 1- دائما يهمل حد potential and kinetic energy لانـها قليلة جدا مقارنتا مع باقي الانواع.

2-دائما الحرارة Q عكس الشغل W بالاشارة.

$$\Delta\,\boldsymbol{U} = \boldsymbol{Q} - \boldsymbol{W}$$

$$\boldsymbol{d}\,\boldsymbol{U} = \boldsymbol{Q} - \boldsymbol{W}$$

Example 2.1.

An artificial satellite revolves round the earth with a relative velocity of 800 m/s. If acceleration due to gravity is 9 m/s^2 and gravitational force is 3600 N, calculate its kinetic energy.

Solution. Relatively velocity of satellite, V = 800 m/s

Acceleration due to gravity, g = 9 m/s^2 Gravitational force, m.g = 3600 N

∴ Mass, m = 3600/g= 3600 /9 = 400 kg.

Kinetic energy = 1/ 2 mV^2 = 1/ 2 × 400 × $(800)^2$ J = 128 × 10^6 J or 128 MJ. (Ans.).

((((*********************)))))

Example 2.2.

The specific heat capacity of the system during a certain process is given by

$$C_n = (0.4 + 0.004\ T)\ \text{kJ/kg°C}.$$

If the mass of the gas is 6 kg and its temperature changes from 25°C to 125°C find:

(i) Heat transferred; (ii) Mean specific heat of the gas.

Solution. Mass of the gas, m = 6 kg

Change in temperature of the gas = 25°C to 125°C

(i) Heat transferred, Q: We know that heat transferred is given by,

$$Q = \int m\, C_n\ dT\ = 6 \int_{25}^{125} (\,0.4 + 0.004\ T)dT$$

$$= 6\ \left[\,0.4\,\mathrm{T} + 0.004\left(\frac{\mathrm{T}^2}{2}\right)\ \right]_{25}^{125}$$

$$= 6[0.4\ (125 – 25) + 0.002\ (125^2 – 25^2)]$$

$$= 6(40 + 30) = \mathbf{420\ kJ.\ (Ans.)}$$

(ii) Mean specific heat of the gas, Cn:

Q = m.Cn.dT

i.e., 420 = 6 × Cn × (125 – 25)

$$\therefore \quad C_n = \frac{420}{6\times100} = 0.7\quad \frac{KJ}{Kg\ °C} \qquad (Ans.)$$

(((************************)))))

Example 2.3.

In an internal combustion engine, during the compression stroke the heat rejected to the cooling water is 50 kJ/kg and the work input is 100 kJ/kg. Calculate the change in internal energy of the working fluid stating whether it is a gain or loss.

<u>Solution.</u>

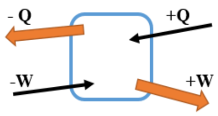
Heat rejected to the cooling water, $Q = -50$ kJ/kg (–ve sign since heat is rejected)

Work input, $W = -100$ kJ/kg (–ve sign since work is supplied to the system)

Using the relation, $Q - W = (u_2 - u_1)$

$$-50 - (-100) = (u_2 - u_1)$$

OR $u_2 - u_1 = -50 + 100 = 50$ kJ/kg



Hence, gain in internal energy = 50 kJ/kg. (Ans.)

((((*************************))))

Example 2.4.

In an air motor cylinder the compressed air has an internal energy of 450 kJ/kg at the beginning of the expansion and an internal energy of 220 kJ/kg after expansion. If the work done by the air during the expansion is 120 kJ/kg, calculate the heat flow to and from the cylinder.

<u>Solution.</u>

Internal energy at beginning of the expansion, $u_1 = 450$ kJ/kg

Internal energy after expansion, $u_2 = 220$ kJ/kg

Work done by the air during expansion, $W = 120$ kJ/kg

Heat flow, Q:

Using the relation, $(u_2 - u_1) = Q - W$

$$Q = (u_2 - u_1) + W$$

$$\therefore \quad Q = (220 - 450) + 120$$

$$= -230 + 120 = -110 \text{ kJ/kg}$$

Hence, heat rejected by air = 110 kJ/kg. (Ans.)

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Example 2.5.

When a stationary mass of gas was compressed without friction at constant pressure its initial state of 0.4 m^3 and 0.105 MPa was found to change to final state of 0.20 m^3 and 0.105 MPa. There was a transfer of 42.5 kJ of heat from the gas during the process. How much did the internal energy of the gas change?

Solution.

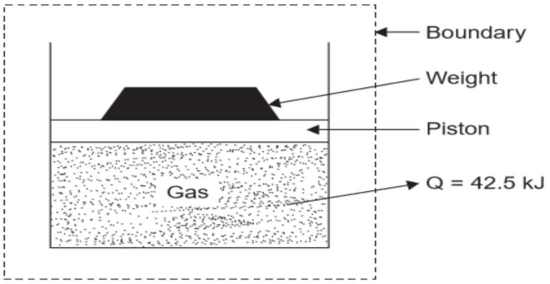

Fig.

Initial state: Pressure of gas, p_1 = 0.105 MPa Volume of gas, V_1 = 0.4 m^3

Final state: Pressure of gas, p_2 = 0.105 MPa Volume of gas, V_2 = 0.20 m^3

Process used: Constant pressure

Heat transferred, **Q = – 42.5 kJ** **(–ve sign indicates that heat is rejected)**

Change in internal energy, $\Delta U = U_2 - U_1$:

First law for a stationary system in a process gives

$$\Delta U = Q - W$$

$$Q = \Delta U + W$$

OR $$Q_{1-2} = (U_2 - U_1) + W_{1-2} \qquad \ldots (i)$$

Here $$W_{1-2} = \int_{V_1}^{V_2} PdV = P(V_2 - V_1)$$

$$= 0.105(0.20 - 0.40) \text{ MJ} = -21 \text{ kJ} \qquad [1 \text{ MJ} = 10^3 \text{ kJ}]$$

Substituting this value of W_{1-2} in equation (*i*), we get

$$-42.5 = (U_2 - U_1) - 21$$

$$\therefore \quad U_2 - U_1 = -42.5 + 21 = -21.5 \text{ kJ}$$

Hence 'decrease' in internal energy = 21.5 kJ. (Ans.)

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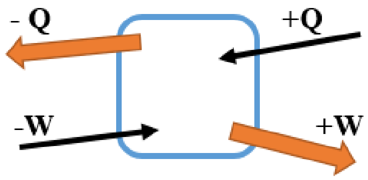

Δ = **Change**

Δ (Energy of the system) + Δ (Energy of surroundings) = 0 **(2.1)**

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$\Delta\,(\boldsymbol{U} + \boldsymbol{K_E} + \boldsymbol{P_E}) = \mp \boldsymbol{Q} \mp \boldsymbol{W}$ **(First law of thermodynamic)**

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2-دائما الحرارة Q عكس الشغل W بالاشارة.

$$\Delta\,\boldsymbol{U} = \boldsymbol{Q} - \boldsymbol{W}$$

$$\boldsymbol{d}\,\boldsymbol{U} = \boldsymbol{Q} - \boldsymbol{W}$$

2.7 CLOSED-SYSTEM REVERSIBLE PROCESSES; ENTHALPY

We present here the analysis of closed-system mechanically reversible processes—not that such processes are common. Indeed they are of little interest for practical application. Their value lies in the simplicity they provide for the calculation of changes in state functions for a specific change of state. For a complex industrial process that brings about a particular change of state, the calculation of changes in state functions are not made for the path of the actual process.

Rather, they are made for a simple closed-system reversible process that brings about the same change of state. This is possible because changes in state functions are independent of process. The closed-system mechanically reversible process is useful and important for this purpose, even though close approximations to such hypothetical processes are not often encountered in practice. For 1 mole of a homogeneous fluid contained in a closed system, the energy balance of Eq. (2.6) is written:

$$dU = dQ + dW$$

The work for a mechanically reversible, closed-system process is given by Eq. (1.3), here written: $dW = -PdV$. Substitution into the preceding equation yields:

$$dU = dQ - PdV \qquad (2.7)$$

This is the general energy balance for one mole or a unit mass of homogeneous fluid in a closed system undergoing a mechanically reversible process.

For a constant-volume change of state, the only possible mechanical work is that associated with stirring or mixing, which is excluded because it is inherently irreversible. Thus,

$$dU = dQ \text{ (const V)} \qquad (2.8)$$

Integration yields:

$$\Delta U = Q \text{ (const V)} \qquad (2.9)$$

- The internal energy change for a mechanically reversible, constant-volume, closed-system process equals the amount of heat transferred into the system.

For a constant-pressure change of state:

$$dU + PdV = d(U + PV) = dQ$$

The group U + PV naturally arises here and in many other applications. This suggests the definition, for convenience, of this combination as a **new thermodynamic property.** Thus, the mathematical (and only) definition of **enthalpy** is:

$$H \equiv U + PV \qquad (2.10)$$ ***

Where H, U, and V are molar or unit-mass values. The preceding energy balance becomes:

$$dH = dQ \text{ (const P)} \qquad (2.11)$$

Integration yields:

$$\Delta H = Q \text{ (const P)} \qquad (2.12)$$

The enthalpy change in a mechanically reversible, constant-pressure, closed-system process equals the amount of heat transferred into the system. Comparison of Eqs. (2.11) and (2.12) with Eqs. (2.8) and (2.9) shows that the enthalpy plays a role in constant-pressure processes analogous to the internal energy in constant-volume processes.

These equations suggest the usefulness of enthalpy, but its greatest use becomes fully apparent with its appearance in energy balances for flow processes as applied to heat exchangers, chemical and biochemical reactors, distillation columns, pumps, compressors, turbines, engines, etc., for calculation of heat and work.

The tabulation of Q and W for the infinite array of conceivable processes is impossible. The intensive state functions, however, such as molar or specific volume, internal energy, and enthalpy, are intrinsic properties of matter. Once determined for a particular substance, their values can be tabulated as functions of T and P 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.

All terms of Eq. (2.10) must be expressed in the same units. The product PV has units of energy per mole or per unit mass, as does U; therefore H also has units of energy per mole or per unit mass. In the SI system the basic unit of pressure is the pascal (=1 N·m−2), and that of molar volume is cubic meters per mol (=1 m3·mol−1). For the PV product we have 1 N·m·mol−1 = 1 J·mol−1.

Because U, P, and V are all state functions, H as defined by Eq. (2.10) is also a state function. Like U and V, H is an intensive property of matter. The differential form of Eq. (2.10) is:

$$dH = dU + d(PV) \qquad (2.13)$$

This equation applies for any differential change of state. Upon integration, it becomes an equation for a finite change of state:

$$\Delta H = \Delta U + \Delta(PV) \qquad (2.14)$$

Equations (2.10), (2.13), and (2.14) apply to a unit mass or mole of a substance.

Example 2.6

Calculate ΔU and ΔH for 1 kg of water when it is vaporized at the constant temperature of 100°C and the **constant pressure of 101.33 kPa**. The specific volumes of liquid and vapor water at these conditions are 0.00104 and 1.673 $m^3 \cdot kg^{-1}$, respectively. For this change, heat in the amount of 2256.9 kJ is added to the water.

Solution 2.6

We take the 1 kg of water as the system because it alone is of interest, and we imagine it contained in a cylinder by a frictionless piston that exerts a constant pressure of 101.33 kPa. As heat is added, the water evaporates, expanding from its initial to its final volume. Equation (2.12) as written for the 1 kg system is:

$$\Delta H = Q = 2256.9 \text{ kJ}$$

By Eq. (2.14),

$$\Delta U = \Delta H - \Delta (PV) = \Delta H - P\,\Delta V$$

For the final term:

$$P\,\Delta V = 101.33 \text{ kPa} \times (1.673 - 0.001)\ m^3$$

$$= 169.4 \text{ kPa}\cdot m^3 = 169.4 \text{ kN}\cdot m^{-2}\cdot m^3 = 169.4 \text{ kJ}$$

Then

$$\Delta U = 2256.9 - 169.4 = 2087.5 \text{ kJ}$$

Example 2.7

Air at 1 bar and 298.15 K is compressed to 3 bar and 298.15 K by two different closed-system mechanically reversible processes:

(a) Cooling at constant pressure followed by heating at constant volume.

(b) Heating at constant volume followed by cooling at constant pressure.

Calculate the heat and work requirements and ΔU and ΔH of the air for each path. The following heat capacities for air may be assumed independent of temperature:

CV = 20.785 and CP = 29.100 $J\cdot mol^{-1}\cdot K^{-1}$

Assume also that air remains a gas for which PV/T is a constant, regardless of the changes it undergoes. At 298.15 K and 1 bar the molar volume of air is 0.02479 $m^3\cdot mol^{-1}$.

Solution 2.7

In each case take the system as 1 mol of air contained in an imaginary piston/cylinder arrangement. Because the processes are mechanically reversible, the piston is imagined to move in the cylinder without friction. The final volume is:

$$V_2 = V_1 \frac{P_1}{P_2} = 0.02479\left(\frac{1}{3}\right) = 0.008263\ \text{m}^3$$

The two paths are shown on the V vs. P diagram of Fig. 2.3(I) and on the T vs. P diagram of Fig. 2.3(II).

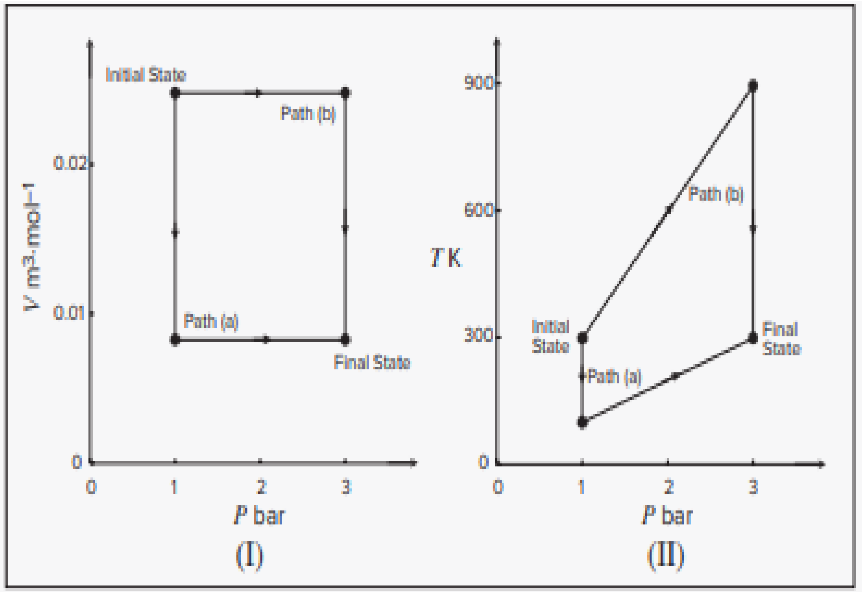


Figure 2.3: *V* vs. *P* and *T* vs. *P* diagrams for Ex. 2.7.

(a) During the first step of this path, air is cooled at the constant pressure of 1 bar until the final volume of 0.008263 m^3 is reached. The temperature of the air at the end of this cooling step is:

$$T' = T_1 \frac{V_2}{V_1} = 298.15\left(\frac{0.008263}{0.02479}\right) = 99.38\ \text{K}$$

Thus, for the first step,

$$\begin{aligned} Q &= \Delta H = C_P\,\Delta T = (29.100)(99.38 - 298.15) = -5784\ \text{J} \\ W &= -P\,\Delta V = -1 \times 10^5\ \text{Pa} \times (0.008263 - 0.02479)\ \text{m}^3 = 1653\ \text{J} \\ \Delta U &= \Delta H - \Delta(PV) = \Delta H - P\,\Delta V = -5784 + 1653 = -4131\ \text{J} \end{aligned}$$

The second step is at constant V_2 with heating to the final state. Work $W = 0$, and for this step:

$$\Delta U = Q = C_V \Delta T = (20.785)(298.15 - 99.38) = 4131 \text{ J}$$
$$V \Delta P = 0.008263 \text{ m}^3 \times (2 \times 10^5) \text{ Pa} = 1653 \text{ J}$$
$$\Delta H = \Delta U + \Delta(PV) = \Delta U + V \Delta P = 4131 + 1653 = 5784 \text{ J}$$

For the overall process:

$$Q = -5784 + 4131 = -1653 \text{ J}$$
$$W = 1653 + 0 = 1653 \text{ J}$$
$$\Delta U = -4131 + 4131 = 0$$
$$\Delta H = -5784 + 5784 = 0$$

Notice that the first law, $\Delta U = Q + W$, applied to the overall process is satisfied.

(*b*) Two different steps of this path produce the same final state of the air. In the first step air is heated at a constant volume equal to V_1 until the final pressure of 3 bar is reached. The air temperature at the end of this step is:

$$T' = T_1 \frac{P_2}{P_1} = 298.15\left(\frac{3}{1}\right) = 894.45 \text{ K}$$

For this first constant-volume step, $W = 0$, and

$$Q = \Delta U = C_V \Delta T = (20.785)(894.45 - 298.15) = 12{,}394 \text{ J}$$
$$V \Delta P = (0.02479)(2 \times 10^5) = 4958 \text{ J}$$
$$\Delta H = \Delta U + V \Delta P = 12{,}394 + 4958 = 17{,}352 \text{ J}$$

In the second step air is cooled at $P = 3$ bar to its final state:

$$Q = \Delta H = C_P \Delta T = (29.10)(298.15 - 894.45) = -17{,}352 \text{ J}$$
$$W = -P \Delta V = -(3 \times 10^5)(0.008263 - 0.02479) = 4958 \text{ J}$$
$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P \Delta V = -17{,}352 + 4958 = -12{,}394 \text{ J}$$

For the two steps combined,

$$Q = 12{,}394 - 17{,}352 = -4958 \text{ J}$$
$$W = 0 + 4958 = 4958 \text{ J}$$
$$\Delta U = 12{,}394 - 12{,}394 = 0$$
$$\Delta H = 17{,}352 - 17{,}352 = 0$$

This example illustrates that changes in state functions (ΔU and ΔH) are independent of path for given initial and final states. On the other hand, Q and W depend on the path. Note also that the **total changes in ΔU and ΔH are zero.** This is because the input information provided makes U and H functions of temperature only, and **T1 = T2.** While the processes of this example are not of practical interest, state-function changes (ΔU and ΔH) for actual flow processes are calculated as illustrated in this example for processes that are of practical interest. This is possible because the state-function changes are the same for a reversible process, like the ones used here, as for a real process that connects the same states.

Example 2.8

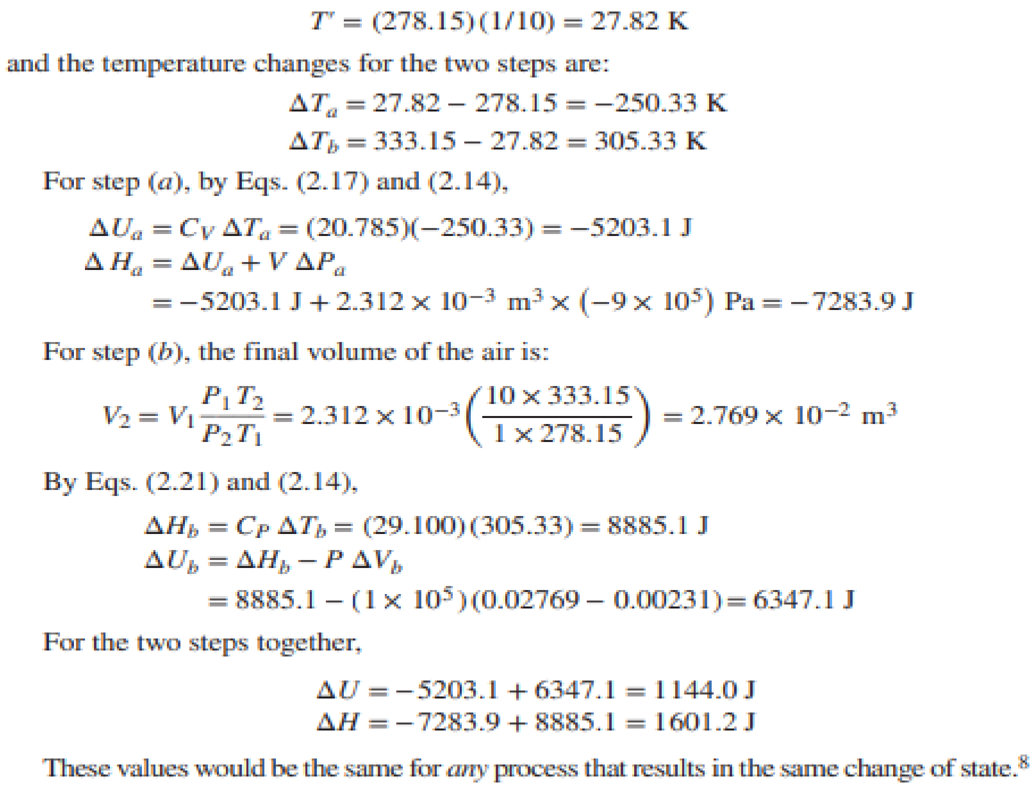
Calculate the internal energy and enthalpy changes resulting if air changes from an initial state of 5°C and 10 bar, where its molar volume is 2.312 × 10−3 m3·mol−1, to a final state of 60°C and 1 bar. Assume also that air remains a gas for which PV/T is constant and that CV = 20.785 and CP = 29.100 J·mol−1·K−1.

Solution 2.8

Because property changes are independent of process, calculations may be based on any process that accomplishes the change. Here, we choose a two-step, mechanically reversible process wherein 1 mol of air is (a) cooled at constant volume to the final pressure, and (b) heated at constant pressure to the final temperature. Of course, other paths could be chosen, and would yield the same result.

T1 = 5 + 273.15 = 278.15 K T2 = 60 + 273.15 = 333.15 K

With PV = kT, the ratio T/P is constant for step (a). The intermediate temperature between the two steps is therefore



$$T' = (278.15)(1/10) = 27.82 \text{ K}$$

and the temperature changes for the two steps are:

$$\Delta T_a = 27.82 - 278.15 = -250.33 \text{ K}$$
$$\Delta T_b = 333.15 - 27.82 = 305.33 \text{ K}$$

For step (*a*), by Eqs. (2.17) and (2.14),

$$\Delta U_a = C_V\,\Delta T_a = (20.785)(-250.33) = -5203.1 \text{ J}$$
$$\Delta H_a = \Delta U_a + V\,\Delta P_a$$
$$= -5203.1 \text{ J} + 2.312 \times 10^{-3} \text{ m}^3 \times \left(-9 \times 10^5\right) \text{ Pa} = -7283.9 \text{ J}$$

For step (*b*), the final volume of the air is:

$$V_2 = V_1 \frac{P_1 T_2}{P_2 T_1} = 2.312 \times 10^{-3} \left(\frac{10 \times 333.15}{1 \times 278.15} \right) = 2.769 \times 10^{-2} \text{ m}^3$$

By Eqs. (2.21) and (2.14),

$$\Delta H_b = C_P\,\Delta T_b = (29.100)(305.33) = 8885.1 \text{ J}$$
$$\Delta U_b = \Delta H_b - P\,\Delta V_b$$
$$= 8885.1 - (1 \times 10^5)(0.02769 - 0.00231) = 6347.1 \text{ J}$$

For the two steps together,

$$\Delta U = -5203.1 + 6347.1 = 1144.0 \text{ J}$$
$$\Delta H = -7283.9 + 8885.1 = 1601.2 \text{ J}$$

These values would be the same for *any* process that results in the same change of state.[8]

2.9 MASS AND ENERGY BALANCES FOR OPEN SYSTEMS

Although the focus of the preceding sections has been on closed systems, the concepts presented find far more extensive application. **The laws of mass and energy conservation apply to all processes,** to open as well as to closed systems. Indeed, the open system includes the closed system as a special case. The remainder of this chapter is therefore devoted to the treatment of open systems and thus to the development of equations of wide practical application.

Measures of Flow

Open systems are characterized by flowing streams; there are four common measures of flow:

- Mass flow rate, $\dot{m}$
- Molar flow rate, $\dot{n}$
- Volumetric flow rate, q
- Velocity, u

The measures of flow are interrelated:

$$\dot{m} = \mathcal{M}\dot{n} \qquad \text{and} \qquad q = uA$$

$$\dot{m} = \mathcal{M}\dot{n} \text{ and } q = uA$$

Where $\mathcal{M}$ is molar mass and A is the cross-sectional area for flow. Importantly, mass and molar flow rates relate to velocity:

$$\boxed{\dot{m} = uA\rho \qquad (2.23a)} \boxed{\dot{n} = uA\rho \qquad (2.23b)}$$

The area for flow A is the cross-sectional area of a conduit, **and ρ is specific or molar density**. Although velocity is a vector quantity, its scalar magnitude u is used here as the average speed of a stream in the direction normal to A.

Flow rates $\dot{m}$, $\dot{n}$, and q represent measures of quantity per unit of time. Velocity u is quite different in nature, as it does not suggest the magnitude of flow. Nevertheless, it is an important design parameter.

Example 2.9

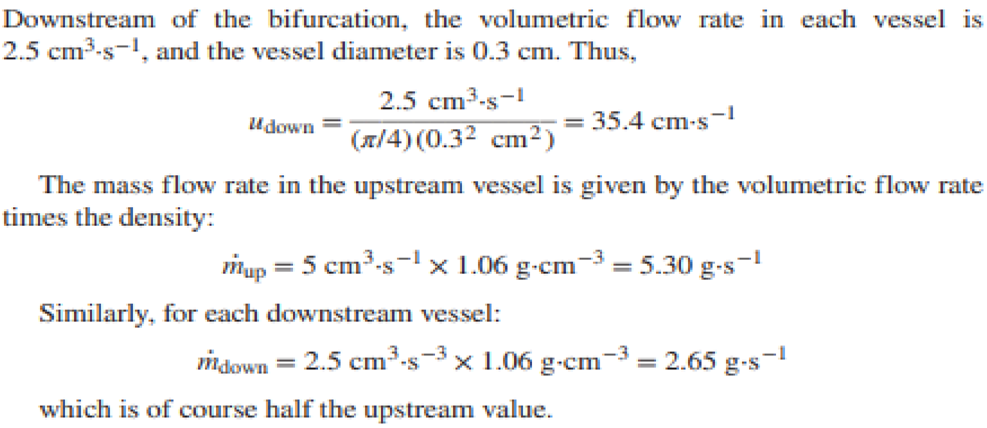
In a major human artery with an internal diameter of 5 mm, the flow of blood, averaged over the cardiac cycle, is 5 $\text{cm}^3 \cdot \text{s}^{-1}$. The artery bifurcates (splits) into two identical blood vessels that are each 3 mm in diameter.

What are the **average velocity and the mass flow rate** upstream and downstream of the bifurcation? The density of blood is 1.06 $\text{g} \cdot \text{cm}^{-3}$.

Solution 2.9

The average velocity is given by the **volumetric flow rate** divided by the **area** for flow. Thus, **upstream** of the bifurcation, where the vessel diameter is 0.5 cm,

$$u_{\text{up}} = \frac{q}{A} = \frac{5\ \text{cm}^3 \cdot \text{s}^{-1}}{(\pi/4)(0.5^2\ \text{cm}^2)} = 25.5\ \text{cm} \cdot \text{s}^{-1}$$



Downstream of the bifurcation, the volumetric flow rate in each vessel is 2.5 $\text{cm}^3 \cdot \text{s}^{-1}$, and the vessel diameter is 0.3 cm. Thus,

$$u_{\text{down}} = \frac{2.5\ \text{cm}^3 \cdot \text{s}^{-1}}{(\pi/4)(0.3^2\ \text{cm}^2)} = 35.4\ \text{cm} \cdot \text{s}^{-1}$$

The mass flow rate in the upstream vessel is given by the volumetric flow rate times the density:

$$\dot{m}_{\text{up}} = 5\ \text{cm}^3 \cdot \text{s}^{-1} \times 1.06\ \text{g} \cdot \text{cm}^{-3} = 5.30\ \text{g} \cdot \text{s}^{-1}$$

Similarly, for each downstream vessel:

$$\dot{m}_{\text{down}} = 2.5\ \text{cm}^3 \cdot \text{s}^{-3} \times 1.06\ \text{g} \cdot \text{cm}^{-3} = 2.65\ \text{g} \cdot \text{s}^{-1}$$

which is of course half the upstream value.

Mass Balance for Open Systems

The region of space identified for analysis of open systems is **called a control volume**; it is separated from its surroundings by a control surface. The fluid within the control volume is the thermodynamic system for which mass and energy balances are written. Because mass is conserved, the rate of change of mass within the control volume, dm_{cv}/dt, equals the net rate of flow of mass into the control volume. The convention is that flow is positive when directed into the control volume and negative when directed out. The mass balance is expressed mathematically by:

$$\boxed{\frac{dm_{\text{cv}}}{dt} + \Delta(\dot{m})_{\text{fs}} = 0} \tag{2.24}$$

For the control volume of Fig. 2.4, the second term is:

$$\Delta(\dot{m})_{\text{fs}} = \dot{m}_3 - \dot{m}_1 - \dot{m}_2$$

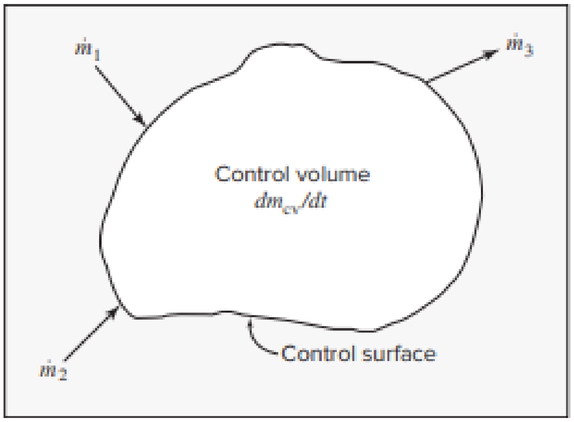


Figure 2.4: Schematic representation of a control volume. It is separated from its surroundings by an extensible control surface. Two streams with flow rates $\dot{m}_1$ and $\dot{m}_2$ are shown directed into the control volume, and one stream with flow rate $\dot{m}_3$ is directed out.

The difference operator Δ here signifies the difference between exit and entrance flows, and the subscript “fs” indicates that the term applies to all flowing streams. Note that this is a different usage of this operator compared with previous sections, where the difference was between an initial state and a final state. Both usages of the difference operator are common, and care must be taken to ensure that the correct sense is understood.

When the mass flow rate m˙ is given by Eq. (2.23a), Eq. (2.24) becomes:

$$\frac{dm_{\text{cv}}}{dt} + \Delta(\rho u A)_{\text{fs}} = 0 \tag{2.25}$$

In this form the mass-balance equation is often called the continuity equation. Steady-state flow processes are those for which conditions within the control volume do not change with time. These are an important class of flow processes often encountered in practice. In a steady-state process, the control volume contains a constant mass of fluid, and the first or accumulation term of Eq. (2.24) is zero, reducing Eq. (2.25) to:

$$\Delta(\rho u A)_{\text{fs}} = 0$$

The term “steady state” does not necessarily imply that flow rates are constant, merely that the inflow of mass is exactly matched by the outflow of mass.

When there is a single entrance and a single exit stream, the mass flow rate m˙ is the same for both streams; then,

$$\dot{m} = \text{const} = \rho_2 u_2 A_2 = \rho_1 u_1 A_1$$

Because specific volume is the reciprocal of density,

$$\boxed{\dot{m} = \frac{u_1 A_1}{V_1} = \frac{u_2 A_2}{V_2} = \frac{uA}{V}} \qquad (2.26)$$

This form of the **continuity equation** finds frequent use.

The General Energy Balance

Because energy, like mass, is conserved, the rate of change of energy within the control volume equals the net rate of energy transfer into the control volume. Streams flowing into and out of the control volume have associated with them energy in its internal, potential, and kinetic forms, and all may contribute to the energy change of the system. Each unit mass of a stream carries with it a total energy U + 1 /2 u^2 + zg, where u is the average velocity of the stream, z is its elevation above a datum level, and g is the local acceleration of gravity. Thus, each stream transports energy at the rate **(U + 1 /2 u^2 + zg) m˙**. The net energy transported into the system by the flowing streams is therefore **–Δ [(U + 1/ 2 u^2 + zg) m˙] fs,** where the effect of the minus sign with "Δ" is to make the term read in – out. The rate of energy accumulation within the control volume includes this quantity in addition to the heat transfer rate Q˙ and work rate:

$$\frac{d(mU)_{cv}}{dt} = -\Delta\left[\left(U + \frac{1}{2}u^2 + zg\right)\dot{m}\right]_{fs} + \dot{Q} + \text{work rate}$$

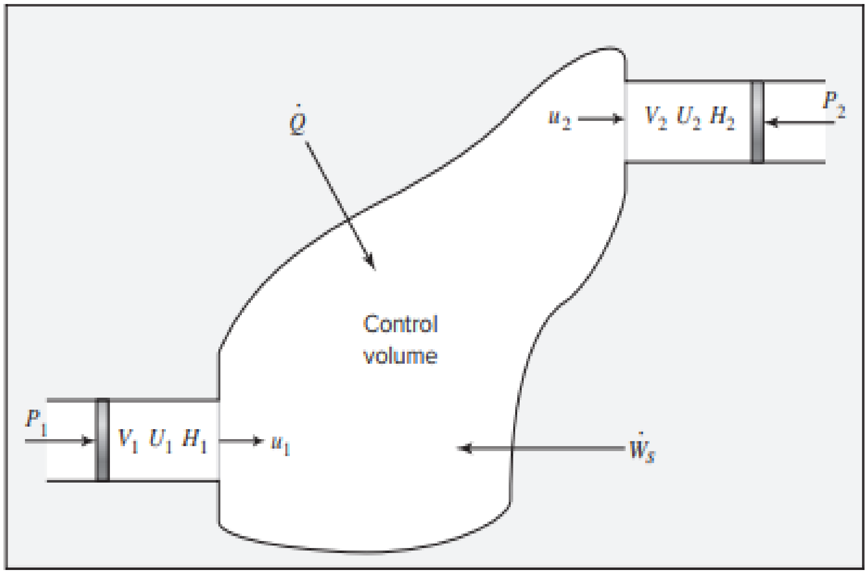


Figure 2.5: Control volume with one entrance and one exit.

The work rate may include work of several forms. First, work is associated with moving the flowing streams through entrances and exits. The fluid at any entrance or exit has a set of average properties, P, V, U, H, etc. Imagine that a unit mass of fluid with these properties exists at an entrance or exit, as shown in Fig. 2.5. This unit mass of fluid is acted upon by additional fluid, here replaced by a piston that exerts the constant pressure P. The work done by this piston in moving the unit mass through the entrance is PV, and the work rate is (PV) m˙ . Because Δ denotes the difference between exit and entrance quantities, the net work done on the system when all entrance and exit sections are taken into account is −Δ[(PV)m˙]fs. Another form of work is the shaft work9 indicated in Fig. 2.5 by rate W˙ s. In addition, work may be associated with expansion or contraction of the entire control volume. These forms of work are all included in a rate term represented by W · . The preceding equation may now be written:

$$\frac{d(mU)_{cv}}{dt} = -\Delta\left[\left(U+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{fs} + \dot{Q} - \Delta[(PV)\dot{m}]_{fs} + \dot{W}$$

Combination of terms in accord with the definition of enthalpy, $H = U + PV$, leads to:

$$\frac{d(mU)_{cv}}{dt} = -\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}$$

which is usually written:

$$\boxed{\frac{d(mU)_{cv}}{dt} + \Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}} \qquad (2.27)$$

The velocity u in the kinetic-energy terms is the bulk-mean velocity as defined by the equation $u = \dot{m}/(\rho A)$. Fluids flowing in pipes exhibit a velocity profile that rises from zero at the wall (the no-slip condition) to a maximum at the center of the pipe. The kinetic energy of a fluid in a pipe depends on its velocity profile. For the case of laminar flow, the profile is parabolic, and integration across the pipe shows that the kinetic-energy term should properly be u2. In fully developed turbulent flow, the more common case in practice, the velocity across the major portion of the pipe is not far from uniform, and the expression u2/2, as used in the energy equations, is more nearly correct. Although Eq. (2.27) is an energy balance of reasonable generality, it has limitations. In particular, it reflects the tacit assumption that the center of mass of the control volume is stationary. Thus no terms for kinetic- and potential-energy changes of the fluid in the control volume are included. For virtually all applications of interest to chemical engineers, Eq. (2.27) is adequate. For many (but not all) applications, kinetic- and potential-energy changes in the flowing streams are also negligible, and Eq. (2.27) then simplifies to:

$$\frac{d(mU)_{cv}}{dt} + \Delta(H\dot{m})_{fs} = \dot{Q} + \dot{W} \qquad (2.28)$$

Example 2.10

Show that Eq. (2.28) reduces to Eq. (2.3) for the case of a closed system.

Solution 2.10

The second term of Eq. (2.28) is omitted in the absence of flowing streams:

$$\frac{d(mU)_{cv}}{dt} = \dot{Q} + \dot{W}$$

Integration over time gives

$$\Delta(mU)_{cv} = \int_{t_1}^{t_2} \dot{Q}\, dt + \int_{t_1}^{t_2} \dot{W}\, dt$$

or

$$\Delta U^t = Q + W$$

The Q and W terms are defined by the integrals of the preceding equation. Note here that Δ indicates a change over time, not from an inlet to an outlet. One must be aware of its context to discern its meaning.

Example 2.11

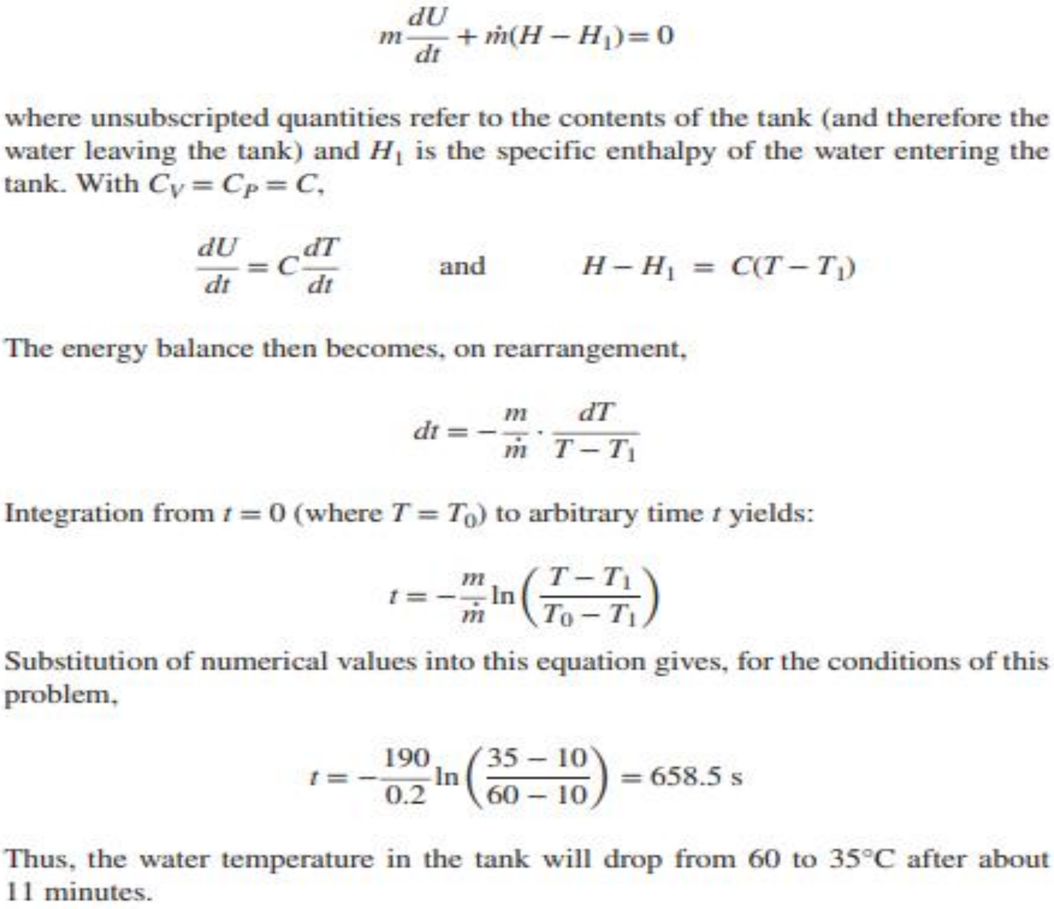
An insulated, electrically heated tank for hot water contains 190 kg of liquid water at 60°C. Imagine you are taking a shower using water from this tank when a power outage occurs. If water is withdrawn from the tank at a steady rate of m· = 0.2 kg·s−1, how long will it take for the temperature of the water in the tank to drop from 60 to 35°C? Assume that cold water enters the tank at 10°C and that heat losses from the tank are negligible. Here, an excellent assumption for liquid water is that **Cv = Cp = C, independent of T and P.**

Solution 2.11

This is an example of the application of Eq. (2.28) to a transient process for which

$$\dot{Q} = \dot{W} = 0.$$

We assume perfect mixing of the contents of the tank; this implies that the properties of the water leaving the tank are those of the water in the tank. With the mass flow rate into the tank equal to the mass flow rate out, mcv is constant; moreover, the differences between inlet and outlet kinetic and potential energies can be neglected. Equation (2.28) is therefore written:



$$m\frac{dU}{dt} + \dot{m}(H - H_1) = 0$$

where unsubscripted quantities refer to the contents of the tank (and therefore the water leaving the tank) and H_1 is the specific enthalpy of the water entering the tank. With $C_V = C_P = C$,

$$\frac{dU}{dt} = C\frac{dT}{dt} \qquad \text{and} \qquad H - H_1 = C(T - T_1)$$

The energy balance then becomes, on rearrangement,

$$dt = -\frac{m}{\dot{m}} \cdot \frac{dT}{T - T_1}$$

Integration from $t = 0$ (where $T = T_0$) to arbitrary time t yields:

$$t = -\frac{m}{\dot{m}} \ln\left(\frac{T - T_1}{T_0 - T_1}\right)$$

Substitution of numerical values into this equation gives, for the conditions of this problem,

$$t = -\frac{190}{0.2} \ln\left(\frac{35 - 10}{60 - 10}\right) = 658.5 \text{ s}$$

Thus, the water temperature in the tank will drop from 60 to 35°C after about 11 minutes.

Energy Balances for Steady-State Flow Processes

Flow processes for which the accumulation term of Eq. (2.27), d(mU)cv/dt, is zero are said to occur at steady state. As discussed with respect to the mass balance, this means that the mass Final PDF to printer 2.9. Mass and Energy Balances for Open Systems 53 smi96529_ch02_024-067.indd 53 11/18/16 10:45 PM of the system within the control volume is constant; it also means that no changes occur with time in the properties of the fluid within the control volume nor at its entrances and exits. No expansion of the control volume is possible under these circumstances. The only work of the process is shaft work, and the general energy balance, Eq. (2.27), becomes:

$$\boxed{\Delta\left[\left(H+\frac{1}{2}u^2+zg\right)\dot{m}\right]_{\text{fs}}=\dot{Q}+\dot{W}_s} \tag{2.29}$$

Although "steady state" does not necessarily imply "steady flow," the usual application of this equation is to steady-state, steady-flow processes, because such processes represent the industrial norm. A further specialization results when the control volume has one entrance and one exit. The same mass flow rate m˙ then applies to both streams, and Eq. (2.29) reduces to:

$$\Delta\left(H+\frac{1}{2}u^2+zg\right)\dot{m}=\dot{Q}+\dot{W}_s \tag{2.30}$$

where subscript "fs" has been omitted in this simple case and Δ denotes the change from entrance to exit. Division by $\dot{m}$ gives:

$$\Delta\left(H+\frac{1}{2}u^2+zg\right)=\frac{\dot{Q}}{\dot{m}}+\frac{\dot{W}_s}{\dot{m}}=Q+W_s$$

or

$$\boxed{\Delta H+\frac{\Delta u^2}{2}+g\Delta z=Q+W_s} \tag{2.31}$$

This equation is the mathematical expression of the first law for a steady-state, steady-flow process between one entrance and one exit. All terms represent energy per unit mass of fluid. The energy unit is usually the joule.

In many applications, kinetic- and potential-energy terms are omitted because they are negligible compared with other terms.[11] For such cases, Eq. (2.31) reduces to:

$$\Delta H=Q+W_s \tag{2.32}$$

This expression of the first law for a steady-state, steady-flow process is analogous to Eq. (2.3) for a nonflow process. However, in Eq. (2.32), enthalpy rather than internal energy is the thermodynamic property of importance, and Δ refers to a change from inlet to outlet, rather than from before to after an event.

A Flow Calorimeter for Enthalpy Measurements

The application of Eqs. (2.31) and (2.32) to the solution of practical problems requires enthalpy values. Because H is a state function, its values depend only on point conditions; once determined, they may be tabulated for subsequent use for the same sets of conditions. To this end, Eq. (2.32) may be applied to laboratory processes designed for enthalpy measurements.

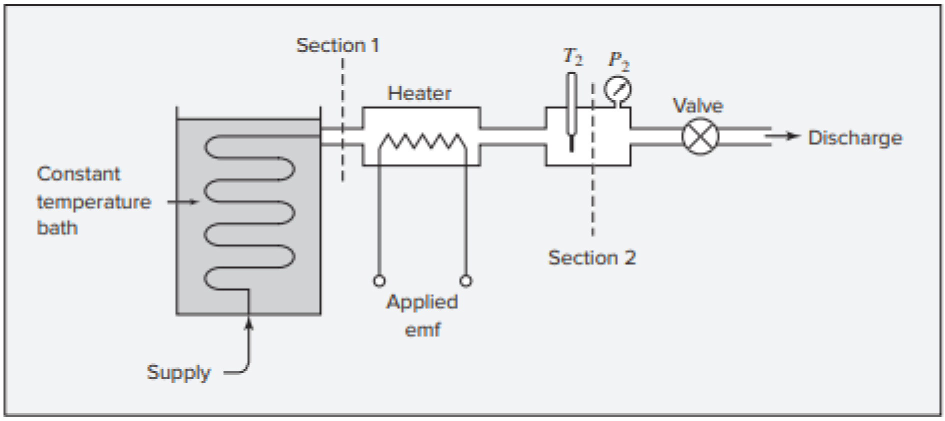


Figure 2.6: Flow calorimeter.

A simple flow calorimeter is illustrated schematically in Fig. 2.6. Its essential feature is an electric resistance heater immersed in a flowing fluid. The design provides for minimal velocity and elevation changes from section 1 to section 2, making kinetic- and potential-energy changes of the fluid negligible. **With no shaft work entering the system**, Eq. (2.32) reduces to

$$\Delta H = H_2 - H_1 = Q$$

The rate of heat transfer to the fluid is determined from the resistance of the heater and the current passing through it. In practice a number of details require careful attention, but in principle the operation of the flow calorimeter is simple. Measurements of the heat transfer rate and flow rate allow calculation of the change ΔH between sections 1 and 2.

For example, enthalpies of both liquid and vapor H2O are readily determined. The constant-temperature bath is filled with a mixture of crushed ice and water to maintain a temperature of 0°C. Liquid water is supplied to the apparatus, and the coil that carries it through the constant-temperature bath is long enough to bring it to an exit temperature of essentially 0°C. The temperature and pressure at section 2 are measured by suitable instruments. Values of the enthalpy of H2O for various conditions at section 2 are given by:

$$H_2 = H_1 + Q$$

Where Q is the heat added per unit mass of water flowing.

The pressure may vary from run to run, but in the range encountered here it has a negligible effect on the enthalpy of the entering water, and for practical purposes H1 is a constant. Absolute values of enthalpy, like absolute values of internal energy, are unknown. An arbitrary value may therefore be assigned to H1 as the basis for all other enthalpy values.

Setting H1 = 0 for liquid water at 0°C makes:

$$H_2 = H_1 + Q = 0 + Q = Q$$

Enthalpy values may be tabulated for the temperatures and pressures existing at section 2 for a large number of runs. In addition, specific-volume measurements made for these same conditions may be added to the table, along with corresponding values of the internal energy calculated by Eq. (2.10), U = H − PV. In this way, tables of thermodynamic properties are compiled over the entire useful range of conditions. The most widely used such tabulation is for H2O and is known as the steam tables. 12 The enthalpy may be taken as zero for some other state than liquid at 0°C. The choice is arbitrary. The equations of thermodynamics, such as Eqs. (2.31) and (2.32), apply to changes of state, for which the enthalpy differences are independent of the location of the zero point. However, once an arbitrary zero point is selected for the enthalpy, an arbitrary choice cannot be made for the internal energy, because internal energy is related to enthalpy by Eq. (2.10).

Example 2.12

For the flow calorimeter just discussed, the following data are taken with water as the test fluid:

Flow rate = 4.15 $g \cdot s^{-1}$ $t_1 = 0°C$ $t_2 = 300°C$ $P_2 = 3$ bar

Rate of heat addition from resistance heater = 12,740 W The water is completely vaporized in the process.

Calculate the enthalpy of steam at 300°C and 3 bar based on H = 0 for liquid water at 0°C.

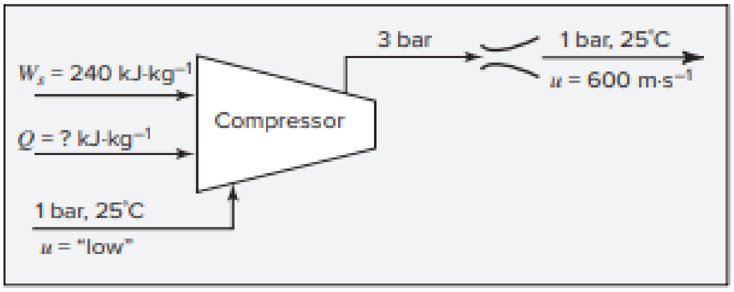
Solution 2.12

If Δz and Δu^2 are negligible and if W_s and H_1 are zero, then $H_2 = Q$, and

$$H_2 = \frac{12{,}740 \text{ J}\cdot\text{s}^{-1}}{4.15 \text{ g}\cdot\text{s}^{-1}} = 3070 \text{ J}\cdot\text{g}^{-1} \qquad \text{or} \qquad 3070 \text{ kJ}\cdot\text{kg}^{-1}$$

Example 2.13

Air at 1 bar and 25°C enters a compressor at low velocity, discharges at 3 bar, and enters a nozzle in which it expands to a final velocity of 600 m·s−1 at the initial conditions of pressure and temperature. If the work of compression is 240 kJ per kilogram of air, **how much heat must be removed during compression?**



Solution 2.13

Because the air returns to its initial conditions of T and P, the **overall process produces no change in enthalpy of the air**. Moreover, the potential-energy change of the air is presumed negligible. Neglecting also the initial kinetic energy of the air, we write Eq. (2.31) as:

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta z = 0 + \frac{u_2^2}{2} + 0 = Q + W_s$$

Then

$$Q = \frac{u_2^2}{2} - W_s$$

The kinetic-energy term is evaluated as follows:

$$\frac{1}{2}u_2^2 = \frac{1}{2}\left(600\frac{\mathrm{m}}{\mathrm{s}}\right)^2 = 180{,}000\frac{\mathrm{m}^2}{\mathrm{s}^2} = 180{,}000\frac{\mathrm{m}^2}{\mathrm{s}^2}\cdot\frac{\mathrm{kg}}{\mathrm{kg}}$$
$$= 180{,}000\ \mathrm{N \cdot m \cdot kg^{-1}} = 180\ \mathrm{kJ \cdot kg^{-1}}$$

Then

$$Q = 180 - 240 = -60\ \mathrm{kJ \cdot kg^{-1}}$$

Heat in the amount of 60 kJ must be removed per kilogram of air compressed.

Example 2.14

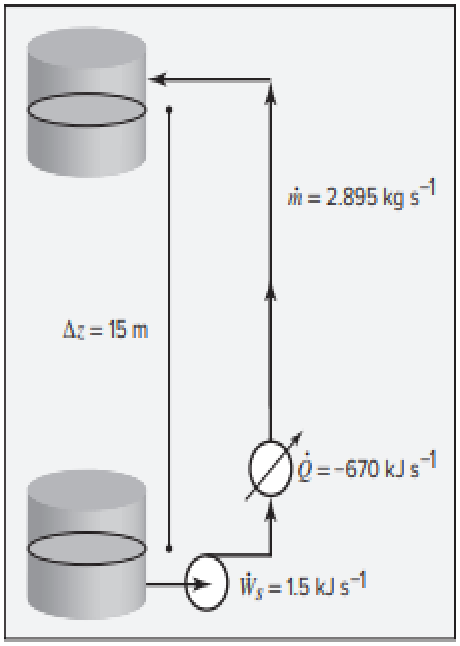
Water at 90°C is pumped from a storage tank at a rate of 3 L·s^{-1}. The motor for the pump supplies work at a rate of 1.5 kJ·s^{-1}. The water goes through a heat exchanger, giving up heat at a rate of 670 kJ·s^{-1}, and is delivered to a second storage tank at an elevation 15 m above the first tank. **What is the temperature of the water delivered to the second tank**?

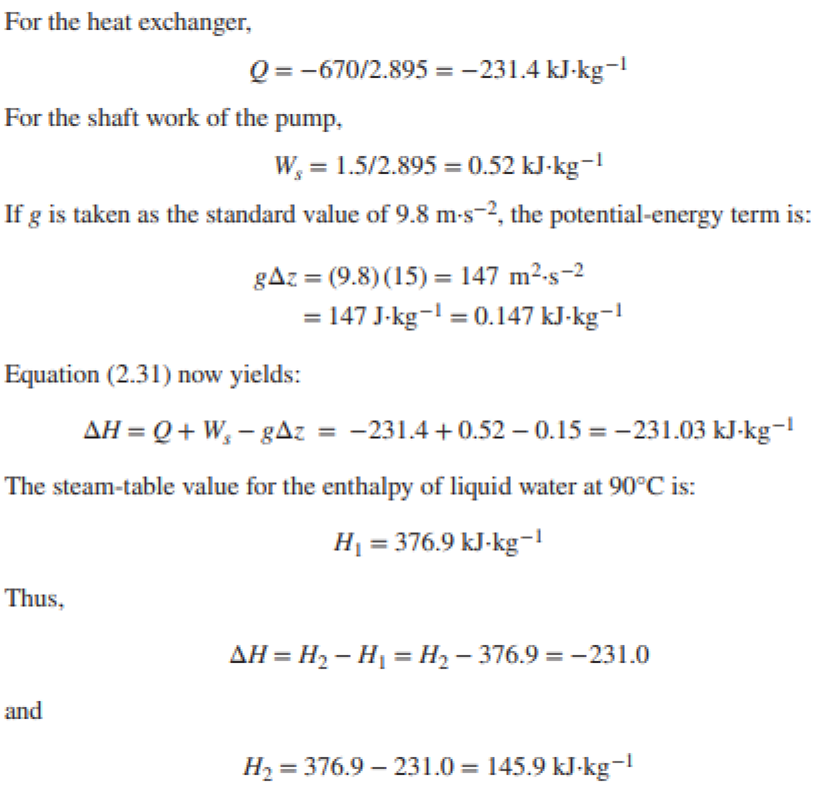
Solution 2.14

This is a steady-state, steady-flow process for which Eq. (2.31) applies. The initial and final velocities of water in the storage tanks are negligible, and the term $\Delta u^2/2$ may be omitted.

All remaining terms are expressed in units of kJ·kg^{-1}. At 90°C the density of water is 0.965 kg·L^{-1} and the mass flow rate is:

$$\dot{m} = (3)\ (0.965) = 2.895\ \text{kg}\cdot\text{s}^{-1}$$





For the heat exchanger,

$$Q = -670/2.895 = -231.4 \text{ kJ·kg}^{-1}$$

For the shaft work of the pump,

$$W_s = 1.5/2.895 = 0.52 \text{ kJ·kg}^{-1}$$

If g is taken as the standard value of 9.8 m·s^{-2}, the potential-energy term is:

$$\begin{aligned} g\Delta z &= (9.8)(15) = 147 \text{ m}^2\text{·s}^{-2} \\ &= 147 \text{ J·kg}^{-1} = 0.147 \text{ kJ·kg}^{-1} \end{aligned}$$

Equation (2.31) now yields:

$$\Delta H = Q + W_s - g\Delta z = -231.4 + 0.52 - 0.15 = -231.03 \text{ kJ·kg}^{-1}$$

The steam-table value for the enthalpy of liquid water at 90°C is:

$$H_1 = 376.9 \text{ kJ·kg}^{-1}$$

Thus,

$$\Delta H = H_2 - H_1 = H_2 - 376.9 = -231.0$$

and

$$H_2 = 376.9 - 231.0 = 145.9 \text{ kJ·kg}^{-1}$$

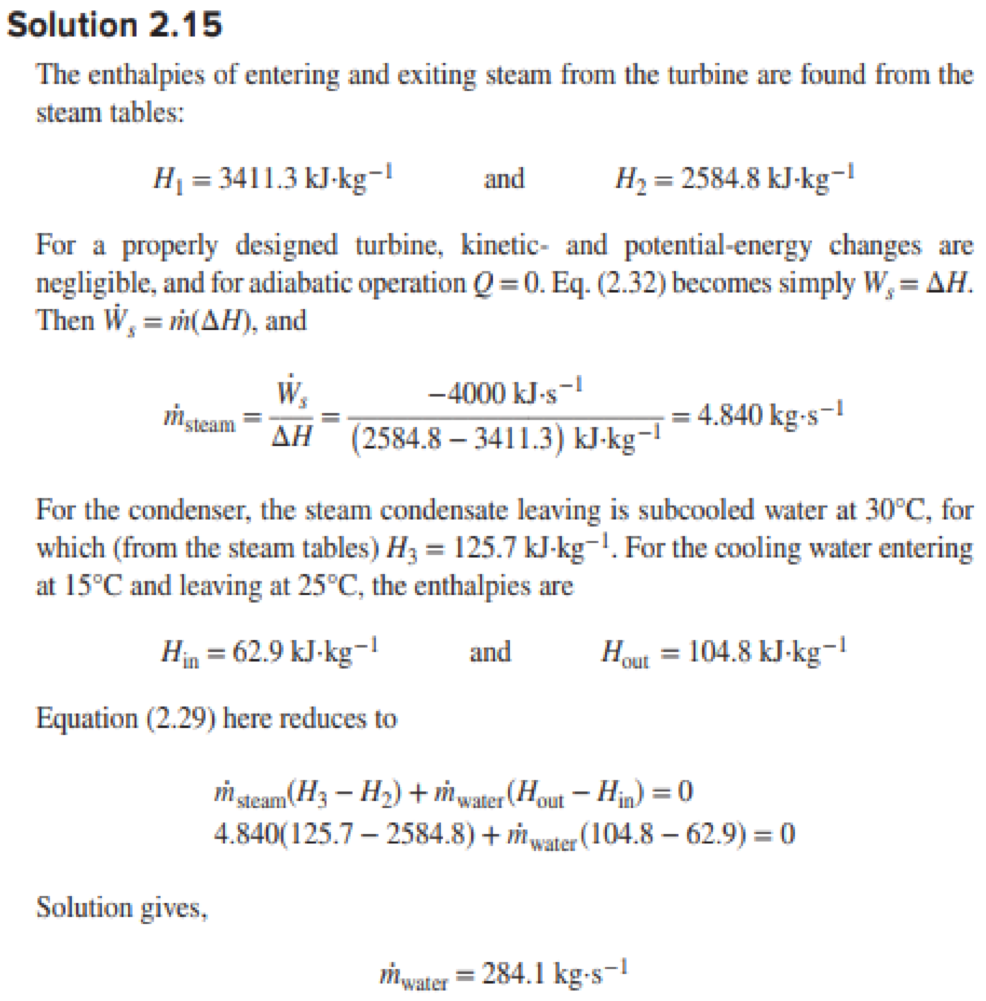
The temperature of water having this enthalpy is found from the **steam tables:**

t = 34.83°C

In this example, Ws and gΔz are small compared with Q, and for practical purposes could be neglected.

Example 2.15

A steam turbine **operates adiabatically** with a power output of 4000 kW. Steam enters the turbine at 2100 kPa and 475°C. The exhaust is saturated steam at 10 kPa that enters a condenser, where it is condensed and cooled to 30°C. **What is the mass flow rate of the steam,** and at **what rate must cooling water be supplied to the condenser**, if the water enters at 15°C and is heated to 25°C?



Solution 2.15

The enthalpies of entering and exiting steam from the turbine are found from the steam tables:

$$H_1 = 3411.3\ \text{kJ}\cdot\text{kg}^{-1} \qquad \text{and} \qquad H_2 = 2584.8\ \text{kJ}\cdot\text{kg}^{-1}$$

For a properly designed turbine, kinetic- and potential-energy changes are negligible, and for adiabatic operation $Q = 0$. Eq. (2.32) becomes simply $W_s = \Delta H$. Then $\dot{W}_s = \dot{m}(\Delta H)$, and

$$\dot{m}_{\text{steam}} = \frac{\dot{W}_s}{\Delta H} = \frac{-4000\ \text{kJ}\cdot\text{s}^{-1}}{(2584.8 - 3411.3)\ \text{kJ}\cdot\text{kg}^{-1}} = 4.840\ \text{kg}\cdot\text{s}^{-1}$$

For the condenser, the steam condensate leaving is subcooled water at 30°C, for which (from the steam tables) $H_3 = 125.7\ \text{kJ}\cdot\text{kg}^{-1}$. For the cooling water entering at 15°C and leaving at 25°C, the enthalpies are

$$H_{\text{in}} = 62.9\ \text{kJ}\cdot\text{kg}^{-1} \qquad \text{and} \qquad H_{\text{out}} = 104.8\ \text{kJ}\cdot\text{kg}^{-1}$$

Equation (2.29) here reduces to

$$\dot{m}_{\text{steam}}(H_3 - H_2) + \dot{m}_{\text{water}}(H_{\text{out}} - H_{\text{in}}) = 0$$
$$4.840(125.7 - 2584.8) + \dot{m}_{\text{water}}(104.8 - 62.9) = 0$$

Solution gives,

$$\dot{m}_{\text{water}} = 284.1\ \text{kg}\cdot\text{s}^{-1}$$

First law of thermodynamics :-

1- For closed system (non-flow system) :

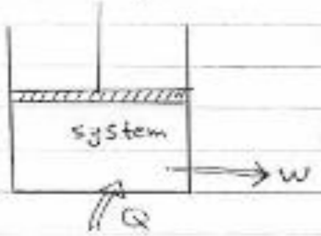
Δ (energy of the system) + Δ (energy of the surrounding) = 0

$\Delta u + \Delta KE + \Delta PE = Q - W$

if ΔKE and ΔPE are negligible

$\{\Delta U = Q - W\}$ First law of thermodynamics for closed system

$$\boxed{\Delta U = Q - W}$$



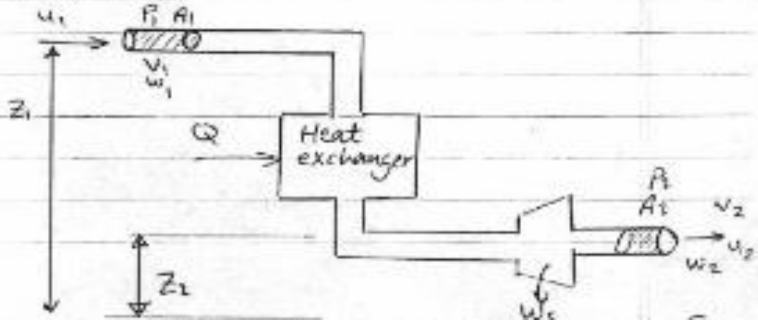
2- For open system (flow - system) :

open system can be divided into two ;

a/ steady state flow process .

b/ unsteady state flow process .

a) Steady state flow process



Basis = 1 kg unit mass

Starting with

$$\Delta U + \Delta K_E + \Delta P_E = Q - W \quad \text{......} (1)$$

$$\Delta K_E = \tfrac{1}{2} V_2^2 - \tfrac{1}{2} V_1^2 = \tfrac{1}{2} \Delta V^2$$

$$\Delta P_E = Z_2 g - Z_1 g = g(Z_2 - Z_1) = g \Delta Z$$

∴ Eqn ① becomes

$$\Delta U + \frac{\Delta V^2}{2} + g \Delta Z = Q - W \quad \text{......} (2)$$

$$W = W_1 + W_2 + W_s$$

$$W_1 = P_1 A_1 \times \frac{V_1}{A_1} = P_1 V_1$$

$$W_2 = P_2 A_2 \times V_2 / A_2 = P_2 V_2$$

$$\therefore W = P_1 V_1 + P_2 V_2 + W_s$$

$$\therefore \Delta U + \frac{\Delta V^2}{2} + g \Delta Z = Q - (P_1 V_1 + P_2 V_2 + W_s)$$

$$\Delta U + \frac{\Delta V^2}{2} + g \Delta Z = Q - W_s - (P_1 V_1 + P_2 V_2)$$

$$\therefore \Delta U + \Delta PV + \frac{\Delta V^2}{2} + g \Delta Z = Q - W_s$$

but $\Delta U + \Delta PV = \Delta H$

$$\boxed{\Delta H + \frac{\Delta V^2}{2} + g \Delta Z = Q - W_s} \quad \text{......} (3)$$

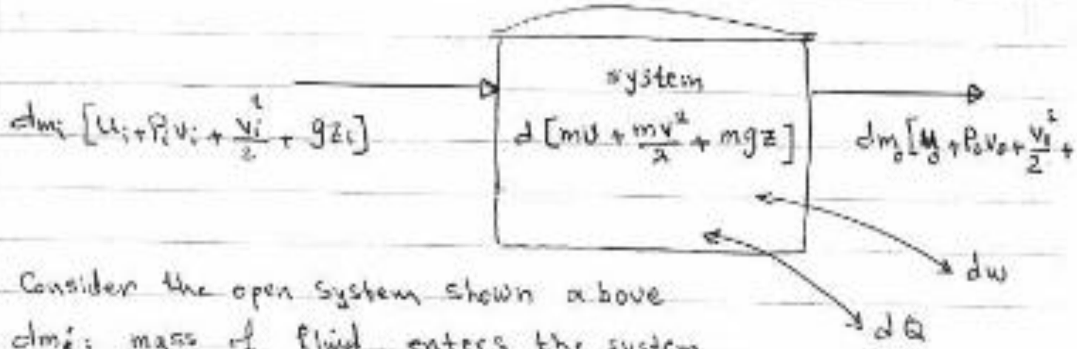
if ΔV & ΔZ are negligible then

$$\boxed{\Delta H = Q - W_s} \quad \text{......} (4)$$

First law for open steady state system.

Unsteady state process

العمليات الجريانية الغير مستقرة



Consider the open system shown above

dm_i: mass of fluid enters the system.

dm_o = mass of fluid leaving the system.

dQ = amount of heat transfered to the system.

dW = amount of work done by the system.

$d\left[mu+\frac{mV^2}{2}+mgz\right]$ = is the total energy chang of the syste

Now if mass dm_i input to the system, the energy of the system increases by $dm_i\left[u_i+P_iv_i+\frac{V_i^2}{2}+gz_i\right]$

and if mass dm_o output from the system, the energy of the system decreases by an amount $dm_o\left[u_o+P_ov_o+\frac{V_o^2}{2}+gz_o\right]$

The total energy within the system boundary may change either because:

(i) change in mass of the system

(ii) change in the state of the fluid within the system.

Energy balance:

In = out + Acc.

$$dQ + dm_i\left[u_i + P_iV_i + \frac{V_i^2}{2} + gZ_i\right] = dW + dm_o\left[u_o + P_oV_o + \frac{V_o^2}{2} + gZ_o\right]$$

$$+ d\left[mu + m\frac{V^2}{2} + mgZ\right]$$

Note that $H = u + PV$

$$\therefore dQ + dm_i\left[H_i + \frac{V_i^2}{2} + gZ_i\right] = dW + dm_o\left[H_o + \frac{V_o^2}{2} + gZ_o\right]$$

$$+ d\left[mu + m\frac{V^2}{2} + mgZ\right]$$

If we neglect KE & PE اذا اهملنا الطاقة الحركية و الكامنة نحصل على

$$\therefore dQ + dm_i(H_i) = dW + dm_o(H_o) + d(mu)$$

$$\text{or} \quad \boxed{d(mu) + dm_o(H_o) - dm_i(H_i) = dQ - dW} \quad \ldots(*)$$

من هنا يمكن استخدام القانون لحل المسائل المتعلقة بالنظام

بالنظام المفتوح من المعادلة (*) كيف ؟

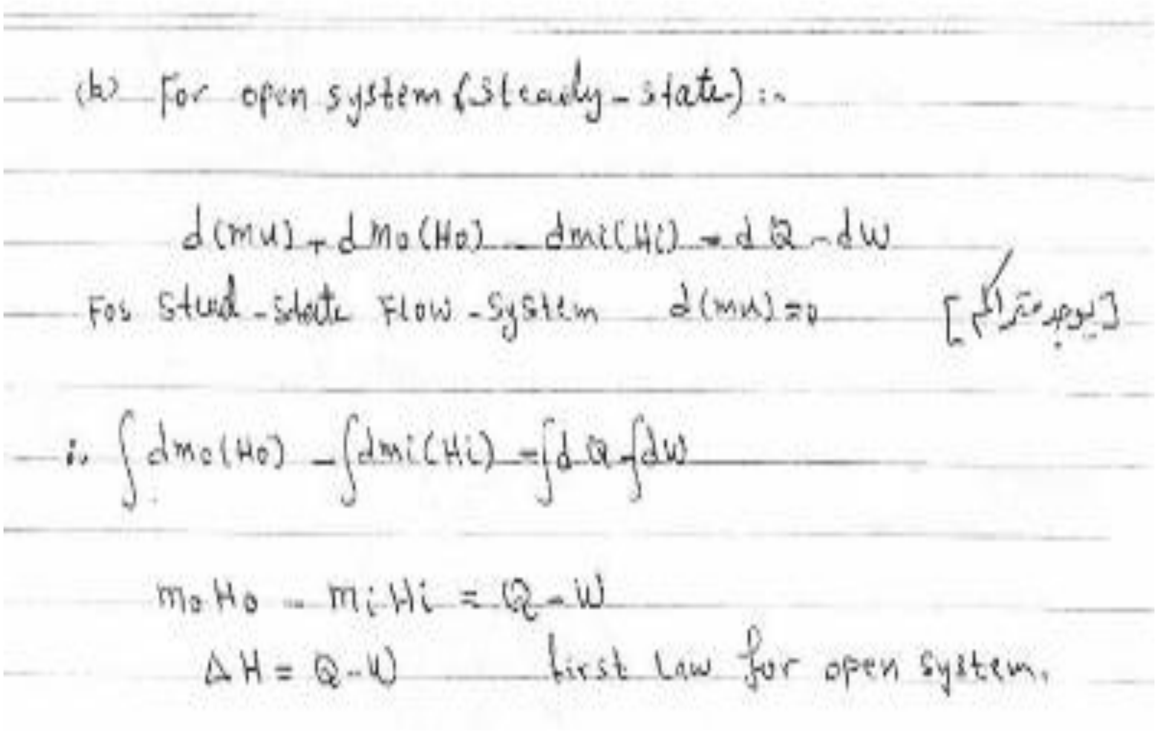
(a) For closed system:

$$\left.\begin{array}{l} dm_o = 0 \\ dm_i = 0 \end{array}\right\}$$ لا يوجد تيار داخل او خارج في النظام المغلق

$$\therefore d(mu) = dQ - dW$$

$$\int d(mu) = \int dQ - \int dW$$

$$\Delta U = Q - W$$ 1st Law for closed system.



(b) For open system (Steady-state) :-

$$d(mu) + dm_o(H_o) - dm_i(H_i) = dQ - dW$$

For Stead-state Flow-System $d(mu) = 0$ [لايوجد تراكم]

$$\therefore \int dm_o(H_o) - \int dm_i(H_i) = \int dQ - \int dW$$

$$m_o H_o - m_i H_i = Q - W$$

$$\Delta H = Q - W$$ first law for open system.

Triple point:

The point at which the three curves are meet (vaporization, fusion and sublimation).

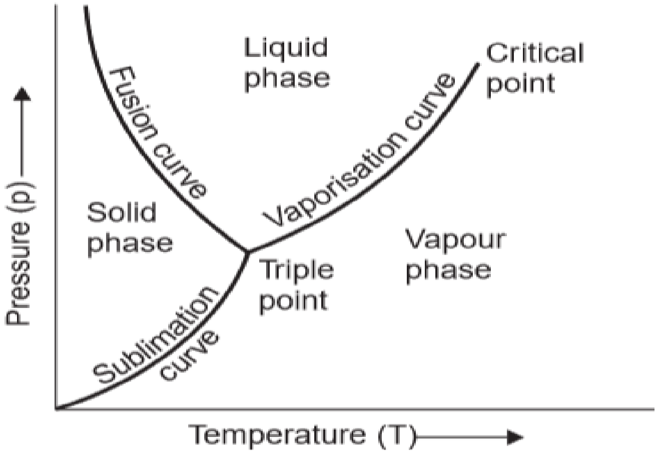


Fig. 3.1. p -T diagram for a substance such as water.

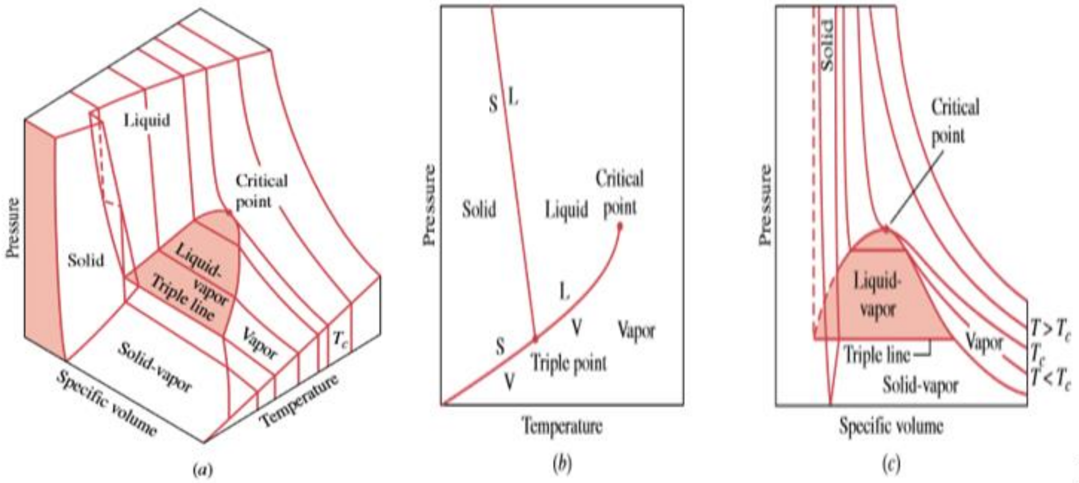


Figure 4.1 *p–v–T surface and projections for water (not to scale). (a) Three-dimensional view. (b) Phase diagram. (c) p–v diagram.*

Critical point:

The critical point. The coordinates of critical point are the critical pressure Pc and the critical temperature Tc, at the highest pressure and highest temperature at which a pure material can exist in vapor/ liquid equilibrium. At critical point liquid and vapour phases can’t be distinguish because they have the same property.

Fluid region:

Region of higher temperature and pressure than T_C, P_C and it is neither gas nor liquid.

Notes:

1. The triple point is invariant.
2. The system exist along the two phases line is univariant.
3. Single phase region is di varint.

Functional equation: Any equation which relate P, T, V

$$F(T, P, V) = 0$$

Equation of state: Equation which relate P, T, V (molar or specific) for any pure homogeneous fluid. The simplest form of equation of stat is

$$PV = RT \quad \text{(for ideal gas).}$$

Reversible process: Is defined as a process which once having taken place, can be reversed and leaves no changes in either the system or surrounding.

(هي عملية مثالية خيالية والتي تكون فيها القوة الدافعة تساوي القوة المقاومة او تقترب منها) ....

$W_{rev.} > W_{irr}$.

$W_{rev.}$ = max. Work.

$W_{irr.}$ =min. Work.

Ideal gas: is a gas of zero volume molecules and these is no interaction between molecules so that internal energy (U) is function of temperature only.

(Also Cv is function of T only).

Ideal gas characterized by.

$$PV = RT$$

Thermodynamic Process:

Closed (Non flow) system may undergoes may different kind of process, some of which will list below, it will be assumed that all process are:

1. Reversible process.
2. The work always takes the form of displacement work (not shaft work).
3. The Ke, Pe are negligible.

4.7. ENERGY OF AN ISOLATED SYSTEM

An isolated system is one in which there is no interaction of the system with the surroundings.

For an isolated system,

$$d\,Q = 0, \qquad dW = 0$$

The first law of thermodynamics gives

$$dE = 0$$

or E = constant

The energy of an isolated system is always constant.

4.8. THE PERFECT GAS (Ideal gas)

4.8.1. The Characteristic Equation of State

At temperatures that are considerably in excess of critical temperature of a fluid, and also at very low pressure, the vapour of fluid tends to obey the equation

$$\frac{PV}{T} = Constant = R$$

In practice, no gas obeys this law rigidly, but many gases tend towards it.

An imaginary ideal gas which obeys this law is called *a perfect gas*, and the equation

$\frac{PV}{T} = R$, is called *the characteristic equation of a state of a perfect gas*.

The constant R is called the gas constant. Each perfect gas has a different gas constant. Units of R are ***Nm/kg K or kJ/kg K.***

Usually, the characteristic equation is written as

$$Pv = TR \qquad \text{... (4.11)}$$

or for m kg, occupying V m^3

$$PV = m\,R\,T \qquad \text{... (4.12)}$$

*** The characteristic equation in another form, can be derived by using kilogram-mole as a unit.

The kilogram-mole is defined as a quantity of a gas equivalent to M kg of the gas, where M is the molecular weight of the gas (e.g., since the molecular weight of oxygen is 32, then 1 kg mole of oxygen is equivalent to 32 kg of oxygen).

As per definition of the kilogram-mole, for m kg of a gas, we have

$$m = n\,M \qquad \ldots\ldots\ldots\ldots\ldots..(4.13)$$

Where n = number of moles.

Note: Since the standard of mass is the kg, kilogram-mole will be written simply as mole. Substituting for m from eqn. (4.13) in eqn. (4.12) gives

$$PV = nM\,R\,T$$

or

$$MR = \frac{P\,V}{n\,T}$$

According to Avogadro's hypothesis the volume of 1 mole of any gas is the same as the volume of 1 mole of any other gas, when the gases are at the same temperature and pressure.

Therefore, $\frac{V}{n}$ is the same for all gases at the same value of p and T. That is the quantity $\frac{P\,V}{n\,T}$ is a *constant for all gases*. This constant is called *universal gas constant*, and is given the symbol, R_0.

i.e., $MR = R_0 = \frac{P\,V}{n\,T}$ or $PV = n\,R_0\,T$ ... (4.14)

Since $MR = R_0$, then

$$R = \frac{R_0}{M} \qquad \ldots (4.15)$$

***It has been found experimentally that the volume of 1 mole of any perfect gas at 1 bar and 0°C is approximately 22.71 m^3.

Therefore from eqn. (4.14),

$$R_0 = \frac{P\,V}{n\,T} = \frac{1\,\times\,10^5\,\times 22.71}{1\,\times 273.15} = 8314.3\,\frac{N\,m}{mole\;\;k.}$$

Using eqn. (4.15), the gas constant for any gas can be found when the molecular weight is known.

Example. For oxygen which has a molecular weight of 32, the gas constant

$$R = \frac{R_0}{M} = \frac{8314}{32} = 259.8\ \frac{N\ m}{Kg\ \ K}$$

4.8.2. Specific Heats:

The specific heat of a solid or liquid is usually defined as *the heat required to raise unit mass through one degree temperature rise.*

For small quantities, we have

$$dQ = m\ C\ dT$$

Where: m = mass, C = specific heat, and dT = temperature rise.

For a gas there are an infinite number of ways in which heat may be added between any two temperatures, and *hence a gas could have an infinite number of specific heats*. However, only two specific heats for gases are defined.

Specific heat at constant volume, Cv

and, Specific heat at constant pressure, Cp.

We have

$dQ = m\ Cp\ dT$ For a reversible non – flow process at *constant pressure* .... (4.16)

$dQ = m\ Cv\ dT$ For a reversible non – flow process at *constant volume* .... (4.17)

The values of *Cp* and *Cv*, for a perfect gas, are constant for any one gas at all pressures and temperatures. Hence, integrating eqns. (4.16) and (4.17), we have

Flow of heat in a reversible constant pressure process

$$= m\ Cp\ (T_2 - T_1) \qquad \text{... (4.18)}$$

Flow of heat in a reversible constant volume process

$$= m\ Cv\ (T_2 - T_1) \qquad \text{... (4.19)}$$

In case *of real gases, Cp and Cv vary with temperature*, but a suitable *average value* may be used for most practical purposes.

4.8.3. Joule's Law

Joule's law states as follows:

"The internal energy of a perfect gas is a function of the absolute temperature only."

i.e., u = f (T)

To evaluate this function let 1 kg of a perfect gas be heated at constant volume.

According to non-flow energy equation,

$$dQ = dU + dW$$

dW = 0, since volume remains constant

$$\therefore \quad d\,Q = d\,U$$

At constant volume for a perfect gas, from eqn. (4.17), for 1 kg

$$dQ = Cv\,dT$$

$$\therefore \quad dQ = dU = Cv\,dT$$

and integrating u = Cv T + K, K being constant.

According to Joule's law u = f (T), which means that internal energy varies linearly with absolute temperature. Internal energy can be made zero at any arbitrary reference temperature.

For a perfect gas it can be assumed that u = 0 when T = 0, hence constant K is zero.

i.e., Internal energy, u = Cv T for a perfect gas ... (4.20)

OR For **mass m**, of a perfect gas

Internal energy, U = m Cv T ... (4.21)

For a perfect gas, in any process between states 1 and 2, we have from Eqn. (4.21) Gain in internal energy,

$$U_2 - U_1 = m\,Cv\,(T_2 - T_1) \qquad \text{... (4.22)}$$

Eqn. (4.22) gives the gains of internal energy for a perfect gas between two states *for any process, reversible or irreversible.*

4.8.4. Relationship Between Two Specific Heats

Consider a perfect gas being heated at constant pressure from T_1 to T_2.

According to non-flow equation,

$$Q = (U_2 - U_1) + W \qquad \dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Also for a perfect gas,

$$U_2 - U_1 = m\,Cv\,(T_2 - T_1) \qquad \text{substitute in eq. 1}$$

$$Q = m\,Cv\,(T_2 - T_1) + W \qquad \dots\dots\dots\dots\dots\dots (2)$$

In a constant pressure process, the work done by the fluid,

$W = P\,(V_2 - V_1)$

$= m\,R\,(T_2 - T_1)$

$$P_1\,V_1 = m\,R\,T_1$$
$$P_2V_2 = mR\,T_2$$
$$P_1 = P_2 = P \text{ in this case}$$

On substituting

$$Q = m\,Cv\,(T_2 - T_1) + m\,R\,(T_2 - T_1) = m\,(Cv + R)\,(T_2 - T_1)$$

But for a constant pressure process,

$$Q = m\,Cp\,(T_2 - T_1)$$

By equating the two expressions, we have

$$m\,(Cv + R)\,(T_2 - T_1) = m\,Cp\,(T_2 - T_1)$$

$\therefore \quad Cv + R = Cp$

or $\quad Cp - Cv = R \quad$ ...(4.23)

Dividing both sides by Cv, we get

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$\therefore \quad C_V = \frac{R}{\gamma - 1} \quad$ ... [4.23 (a)]

(Where $\gamma = \frac{C_P}{C_V}$)

Similarly, dividing both sides by Cp, we get

$C_P = \frac{\gamma\,R}{\gamma - 1} \quad$ ... [4.23 (b)]

4.8.5. Enthalpy

- One of the fundamental quantities which occur invariably in thermodynamics is the sum of internal energy (u) and pressure volume product (PV). This sum is called Enthalpy (H).

  $i.e.,\ H = U + PV$ ………………(***)
- The enthalpy of a fluid is the property of the fluid, since it consists of the sum of a property and the product of the two properties. Since enthalpy is a property like internal energy, pressure, specific volume and temperature, it can be introduced into any problem whether the process is a flow or a non-flow process.

The total enthalpy of mass, m, of a fluid can be

H = U + PV, where H = mh.

For a perfect gas,

Referring equation (4.24),

$$\mathrm{H} = \mathrm{u} + \mathrm{pv} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .1$$

$$\mathrm{H} = \mathrm{CvT} + \mathrm{RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots ..2$$

$$\mathrm{H} = \mathrm{CvT} + \mathrm{RT} \quad \ldots\ldots\ldots\ldots ..(3) \qquad [\mathrm{PV} = \mathrm{RT}]$$

$$H = (CV + R)T \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$H = Cp\,T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5) \qquad \{Cp = Cv + R\}$$

$$i.e. \quad H = Cp\ T \quad \ldots\ldots\ldots\ldots\ldots ..(6)$$

$$and \quad H = m\ Cp\ T \quad \ldots\ldots\ldots\ldots\ldots ..(7)$$

(Note that, since it has been assumed that u = 0 at T = 0, then h = 0 at T = 0).

4.8.6. Ratio of Specific Heats

The ratio of specific heat at constant pressure to the specific heat at constant volume is given the symbol γ (gamma).

$$\mathrm{i.e.,} \qquad \gamma = \frac{Cp}{Cv} \qquad \ldots\ldots\ldots\ldots\ldots\ldots ..(8)$$

Since Cp = Cv + R, it is clear that Cp must be greater than Cv for any perfect gas. It follows, therefore, that the ratio, $\frac{Cp}{Cv} = \gamma$, is **always greater than unity**.

In general, the approximate values of γ are as follows:

For monoatomic gases such as **argon, helium** = 1.6.

For diatomic gases such **as carbon monoxide, hydrogen, nitrogen and oxygen** = 1.4.

For triatomic gases such as **carbon dioxide and sulphur dioxide** = 1.3.

For some hydro-carbons the value of γ is quite low.

[e.g., for ethane γ = 1.22, and for isobutane γ = 1.11]

4.9. Application of First Law of Thermodynamics to Non-Flow or Closed System

1. ***Reversible Constant Volume*** (or Isochoric) Process **(v = constant)**:

In a constant volume process the working substance is contained in a rigid vessel, hence the boundaries of the system are immovable and no work can be done on or by the system, other than paddle-wheel work input. It will be assumed that 'constant volume' implies zero work unless stated otherwise.

Fig. 4.5 shows the system and states before and after the heat addition at constant volume.

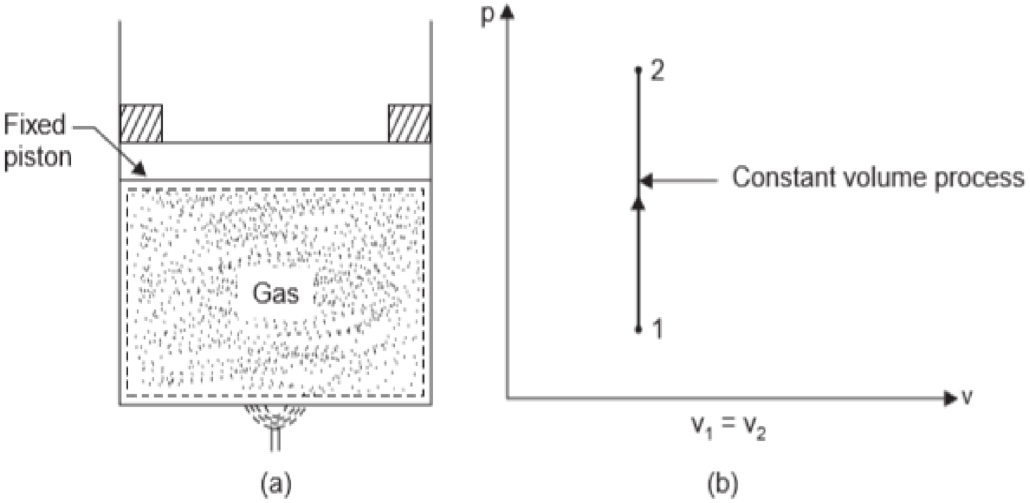


Fig. 4.5. Reversible constant volume process.

Considering mass of the working substance unity and applying first law of thermodynamics to the process

$$Q = (u_2 - u_1) + W \qquad \text{... (4.26)}$$

The work done $W = \int_1^2 PdV = 0$ as dv = 0.

$$\therefore Q = (u_2 - u_1) = C_v (T_2 - T_1) \qquad [4.27\ (a)]$$

Where Cv = Specific heat at constant volume.

For mass, m, of working substance

$$Q = U_2 - U_1 = m\, C_v (T_2 - T_1) \qquad [4.27\ (b)]$$

$$[\ \because m\,u = U]$$

2. *Reversible Constant Pressure* (or Isobaric) Process **(p = constant).**

It can be seen from Fig. 4.5 (b) that when the boundary of the system is inflexible as in a constant volume process, then the pressure rises when heat is supplied. Hence for a constant pressure process, the boundary must move against an external resistance as heat is supplied; for instance a gas [Fig. 4.6 (a)] in a cylinder behind a piston can be made to undergo a constant pressure process. *Since the piston is pushed through a certain distance* by the force exerted by the gas, then the work is done by the gas on its surroundings.

Fig. 4.6 shows the system and states before and after the heat addition at constant pressure.

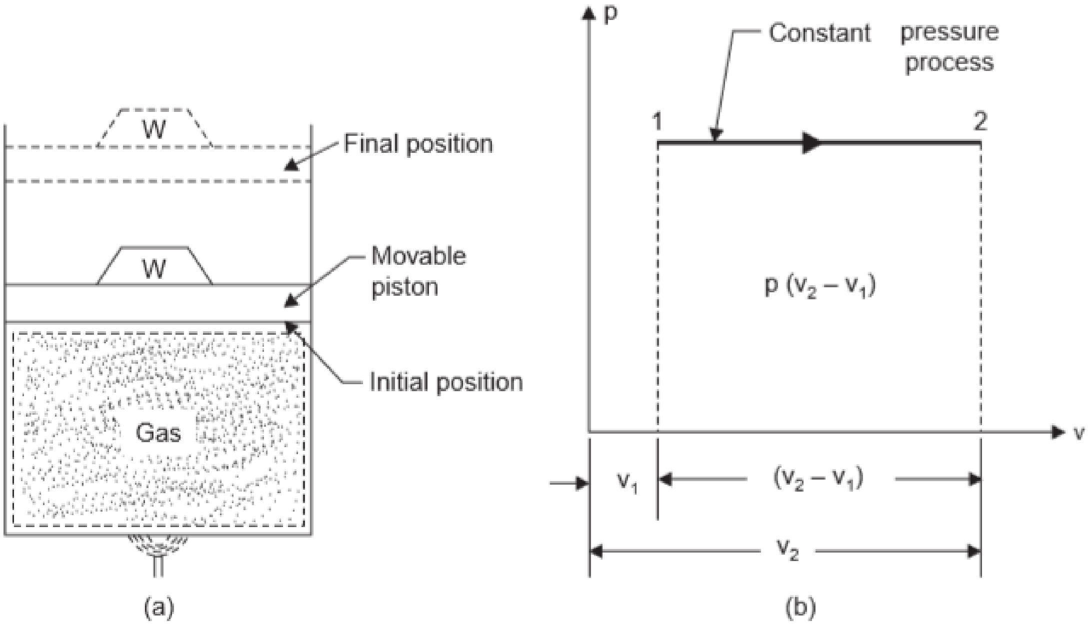


Fig. 4.6. Reversible constant pressure process

Considering unit mass of working substance and applying first law of thermodynamics to the process

$$Q = (u_2 - u_1) + W$$

The work done, $W = \int_1^2 p\,dv = p(v_2 - v_1)$

∴ $Q = (u_2 - u_1) + p(v_2 - v_1) = u_2 - u_1 + pv_2 - pv_1$

$= (u_2 + pv_2) - (u_1 + pv_1) = h_2 - h_1$ [∴ $h = u + p\,v$]

Or $Q = h_2 - h_1 = C_p(T_2 - T_1)$ ... (4.28)

Where h = Enthalpy (specific), and

Cp = Specific heat at constant pressure.

For mass, m, of working substance

$$Q = H_2 - H_1 = m\,Cp\,(T_2 - T_1) \qquad \text{... [4.28 (a)]}$$

$$[mh = H]$$

3. Reversible Temperature (or Isothermal) Process **(*PV*= constant, T = constant):**

A process at a constant temperature is called an isothermal process. When a working substance in a cylinder behind a piston expands from a high pressure to a low pressure there is a tendency for the temperature to fall. In an isothermal expansion heat must be added continuously in order to keep the temperature at the initial value. Similarly in an isothermal compression heat must be removed from the working substance continuously during the process.

Fig. 4.7 shows the system and states before and after the heat addition at constant temperature.

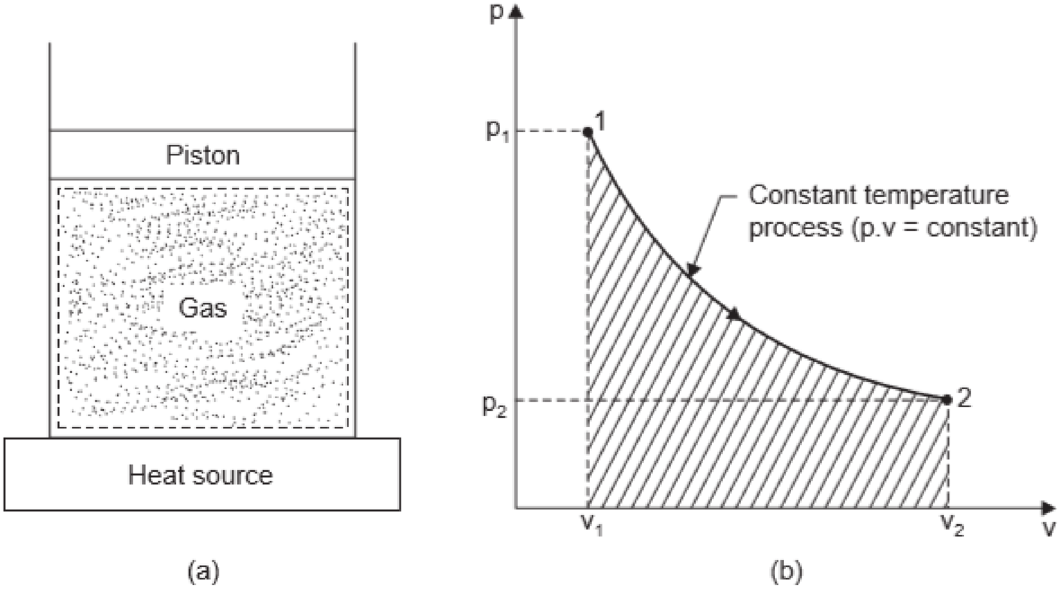


Fig. 4.7. Reversible isothermal process.

Considering unit mass of working substance and applying first law to the process

$$Q = (u_2 - u_1) + W$$

$$Q = Cv\,(T_2 - T_1) + W$$

$$Q = 0 + W \qquad [T_2 = T_1]$$

The work done, $W = \int_1^2 pdv$

In this case PV = constant or $P = \frac{C}{V}$ (where C = constant)

$$\therefore \qquad W = \int_{V_1}^{V_2} C \frac{dV}{V} = C \ln \frac{V_2}{V_1}$$

The constant C can either be written as p_1v_1 or as p_2v_2, since

$$p_1v_1 = p_2v_2 = \text{constant, } C$$

i.e., $W = P_1 V_1 \ln \frac{V_2}{V_1}$ per unit mass of working substance

or $W = P_2 V_2 \ln \frac{V_2}{V_1}$ per unit mass of working substance

$$\therefore \qquad Q = W = P_1 V_1 \ln \frac{V_2}{V_1} \qquad \text{... (4.29)}$$

For mass, m, of the working substance

$$Q = P_1 V_1 \ln \frac{V_2}{V_1} \qquad [4.29\ (a)]$$

Or $Q = P_1 V_1 \ln \frac{P_1}{P_2}$ $\left[\frac{V_2}{V_1} = \frac{P_1}{P_2} \right]$ [4.29 (b)]

4. Reversible Adiabatic Process (pv^γ = constant):

An **adiabatic process** *is one in which no heat is transferred to or from the fluid during the process*. Such a process can be reversible or irreversible. The reversible adiabatic non-flow process will be considered in this section.

Considering unit mass of working substance and applying first law to the process

$Q = (u_2 - u_1) + W$

$Q = (u_2 - u_1) + W$

Or $W = (u_1 - u_2)$ for any adiabatic process ... (4.30)

Eqn. (4.30) is true for an adiabatic process whether the process is reversible or not. In an adiabatic expansion, the work done W by the fluid is at the expense of a reduction in the internal energy of the fluid. Similarly in an adiabatic compression process all the work done on the fluid goes to increase the internal energy of the fluid.

For *an adiabatic process to take place, perfect thermal insulation for the system must be available.*

To derive the law pv^γ = constant:

To obtain a law relating p and v for a reversible adiabatic process let us consider the non-flow energy equation in differential form,

$$dQ = du + dW$$

For *a reversible process*

$$dW = p\,dv$$

$$\therefore \quad dQ = du + pdv = 0$$

(Since for an adiabatic process Q = 0)

Also for a perfect gas

$$PV = RT \; Or \quad P = \frac{R\,T}{V}$$

Hence substituting, $du + \frac{R\,T\,dV}{V} = 0$

Also $u = C_V\,T \quad or \quad du = C_V\,dT$

$$\therefore \quad C_V\,dT + \frac{R\,T\,dV}{V} = 0$$

Dividing both sides by T, we get

$$C_V \frac{dT}{T} + \frac{R\,dV}{V} = 0$$

Integrating $C_V \ln T + R \ \ln V = Constant$

Substituting $T = \frac{P\,V}{R}$

$$C_V \ln \frac{PV}{R} + R \ \ln V = Constant$$

Dividing throughout both sides by Cv

$$\ln \frac{PV}{R} + \frac{R}{C_V} \ln V = Constant$$

Again $C_V = \frac{R}{(\gamma - 1)}$ or $\frac{R}{C_V} = (\gamma - 1)$

Hence substituting

$$\ln \frac{PV}{R} + (\gamma - 1) \ \ln V = Constant$$

$$\therefore \quad \ln \frac{PV}{R} + \ln V^{\gamma - 1} = Constant$$

$$\ln \frac{PV \times V^{\gamma-1}}{R} = Constant$$

i.e. , $\ln\frac{P\,V^{\gamma}}{R} = Constant$

i.e., $\frac{P\,V^{\gamma}}{R} = e^{constant} = Constant$

Or $PV^{\gamma} = Constant$ (4.31)

Expression for work W: A reversible adiabatic process for a perfect gas is shown on a p-v diagram in Fig. 4.8 (b).

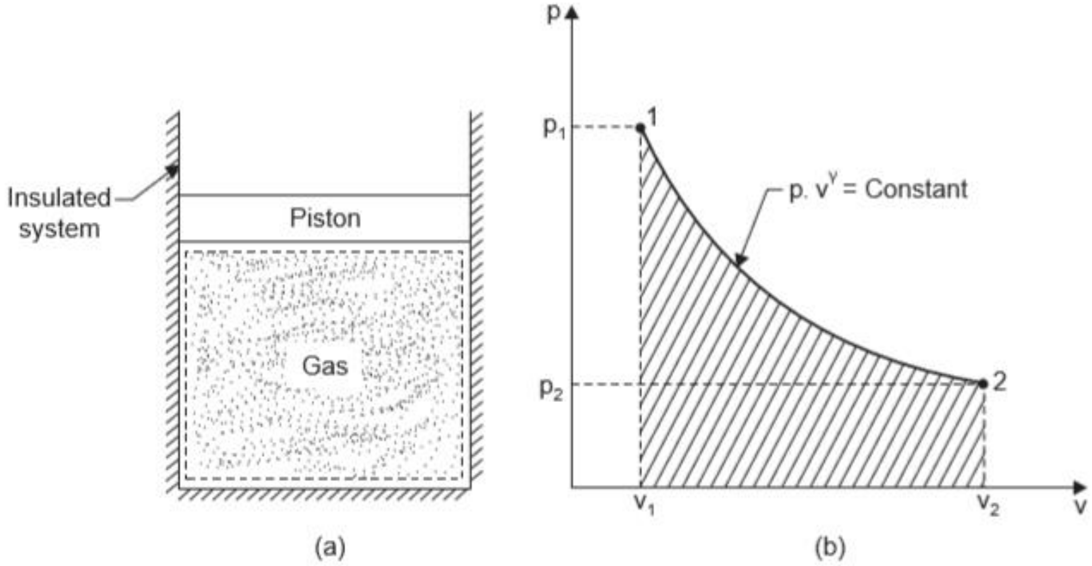


Fig. 4.8. Reversible adiabatic process.

The work done is given by the shaded area, and this area can be evaluated by integration.

i.e., $W = \int_{V_1}^{V_2} P\,dV$

Therefore, since pv^{γ} = constant, C, then

$$W = \int_{V_1}^{V_2} C\frac{dV}{V^{\gamma}} \qquad \left[\, P = \frac{C}{V^{\gamma}} \,\right]$$

i.e., $W = C\int_{V_1}^{V_2}\frac{dV}{V} = C\left|\frac{V^{-\gamma+1}}{-\gamma+1}\right|_{V_1}^{V_2}$

$$W = C\left(\frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{1-\gamma}\right) = C\left(\frac{V_1^{-\gamma+1} - V_2^{-\gamma+1}}{\gamma-1}\right)$$

The constant in this equation can be written as $p_1v_1^{\gamma}$ or as $p_2v_2^{\gamma}$. Hence,

$$W = \frac{P_1 V_1^{\gamma} V_1^{-\gamma+1} - P_2 V_2^{\gamma} V_2^{-\gamma+1}}{\gamma - 1} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

i.e., $W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$ (4.32)

or $W = \frac{R\,(T_1 - T_2)}{\gamma - 1}$ (4.33)

Relationship between T and v, and T and p:

By using equation pv = RT, the relationship between T and v, and T and p, may by derived as follows:

i.e., $P\,V = R\,T$

∴ $P = \frac{R\,T}{V}$

Putting this value in the equation $P\,V^{\gamma} = constant$

$$\frac{R\,T}{V}\,V^{\gamma} = constant$$

i.e., $T\,V^{\gamma-1} = constant$ (4.34)

Also $V = \frac{R\,T}{P}$; hence substituting in equation $P\,V^{\gamma} = constant$

$$P\left(\frac{R\,T}{P}\right)^{\gamma} = constant$$

$$\frac{T^{\gamma}}{P^{\gamma-1}} = constant$$

$$\frac{T}{P^{\frac{\gamma-1}{\gamma}}} = constant \qquad (4.35)$$

Therefore, for a reversible adiabatic process for a perfect gas between states 1 and 2, we can write:

From Eqn. (4.31),

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \quad or \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} \qquad (4.36)$$

From Eqn. (4.34),

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad or \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad (4.37)$$

From Eqn. (4.35),

$$\frac{T_1}{(P_1)^{\frac{\gamma-1}{\gamma}}} = \frac{T_2}{(P_2)^{\frac{\gamma-1}{\gamma}}} \qquad or \qquad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \qquad (4.38)$$

From eqn. (4.30), the work done in an adiabatic process per kg of gas is given by $W = (u_1 - u_2)$. The gain in internal energy of a perfect gas is given by equation:

$$u_2 - u_1 = Cv\,(T_2 - T_1) \qquad \text{(for 1 kg)}$$

$$\therefore \qquad W = Cv\,(T_1 - T_2)$$

Also, we know that

$$C_V = \frac{R}{\gamma-1}$$

Hence substituting, we get

$$W = \frac{R\,(T_1 - T_2)}{\gamma-1}$$

Using equation, $PV = RT$

$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

This is the same expression obtained before as eqn. (4.32).

5. Polytropic Reversible Process (pv^n = constant):

It is found that many processes in practice approximate to a reversible law of form

pv^n = constant, where n is a constant. Both vapours and perfect gases obey this type of law closely in many non-flow processes. Such processes are *internally reversible.*

We know that for any reversible process,

i.e., $W = \int_{V_1}^{V_2} P\, dV$

For a process in pv^n = constant, we have

Where C is a constant $\left[\, P = \frac{C}{V^n} \,\right]$

i.e., $$W = C\int_{V_1}^{V_2} \frac{dV}{V^n} = C\left|\frac{V^{-n+1}}{-n+1}\right|_{V_1}^{V_2} = C\left(\frac{V_1^{-n+1} - V_2^{-n+1}}{-n+1}\right)$$

$$W = C\left(\frac{V_1^{-n+1} - V_2^{-n+1}}{n-1}\right) = \frac{P_1 V_1^n V_1^{-n+1} - P_2 V_2^n V_2^{-n+1}}{n-1}$$

(Since the constant C, can be written as $p_1 v_1^n$ or as $p_2 v_2^n$)

i.e., Work done, $W = \frac{P_1 V_1 - P_2 V_2}{n-1}$ (4.39)

or $W = \frac{R\,(T_1 - T_2\ )}{n-1}$ (4.40)

Eqn. (4.39) is true for any working substance undergoing a reversible polytropic process. It follows also that for any polytropic process, we can write

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^n \qquad (4.41)$$

The following relations can be derived (following the same procedure as was done under reversible adiabatic process)

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1} \qquad (4.42)$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} \qquad (4.43)$$

Heat transfer during polytropic process (for perfect gas pv = RT):

Using non-flow energy equation, the heat flow/transfer during the process can be found,

i.e., $Q = (u_2 - u_1) + W$

$$= C_V(T_2 - T_1) + \frac{R(T_1 - T_2)}{n-1}$$

$$Q = \frac{R(T_1 - T_2)}{n-1} - C_v(T_1 - T_2)$$

Also $C_v = \frac{R}{\gamma - 1}$

$$Q = \frac{R}{n-1}(T_1 - T_2) - \frac{R}{\gamma - 1}\ (T_1 - T_2)$$

i.e., $Q = R(T_1 - T_2)\left(\frac{R}{n-1} - \frac{1}{\gamma - 1}\right)$

$$Q = \left(\frac{R(T_1 - T_2)(\gamma - 1 - n + 1)}{(\gamma - 1)(n-1)} = \left(\frac{R(T_1 - T_2)(\gamma - n)}{(\gamma - 1)(n-1)}\right.\right.$$

$$Q = \frac{(\gamma - n)}{(\gamma - 1)}\ \frac{R(T_1 - T_2)}{(n-1)}$$

or $Q = \left(\frac{\gamma - n}{\gamma - 1}\right)W$ $\left[W = \frac{R(T_1 - T_2)}{(n-1)}\right]$ (4.44)

In a polytropic process, the index n depends only on the heat and work quantities during the process. The various processes considered earlier are special cases of polytropic process for a perfect gas.

For example,

When $n = 0$ $pv^{\circ} = \text{constant}$ i.e., $p = \text{constant}$

When $n = \infty$ $pv^{\infty} = \text{constant}$ or $p^{1/\infty}\, v = \text{constant}$, i.e., $v = \text{constant}$

When $n = 1$ $pv = \text{constant}$, i.e., $T = \text{constant}$

[Since (pv) /T = constant for a perfect gas]

When $n = \gamma$ $pv^{\gamma} = \text{constant}$, i.e., reversible adiabatic

This is illustrated on a p-v diagram in Fig. 4.9.

i. State 1 to state A is constant pressure cooling ($n = 0$).
ii. State 1 to state B is isothermal compression ($n = 1$).
iii. State 1 to state C is reversible adiabatic compression ($n = \gamma$).
iv. State 1 to state D is constant volume heating ($n = \infty$).

Similarly,

i. State 1 to state A′ is constant pressure heating ($n = 0$).
ii. State 1 to state B′ is isothermal expansion ($n = 1$).
iii. State 1 to state C′ is reversible adiabatic expansion ($n = \gamma$).
iv. State 1 to state D′ is constant volume cooling ($n = \propto$).

It may be noted that, since γ is always greater than unity, than process 1 to C must lie between processes 1 to B and 1 to D; similarly, process 1 to C′ must lie between processes 1 to B′ and 1 to D′.

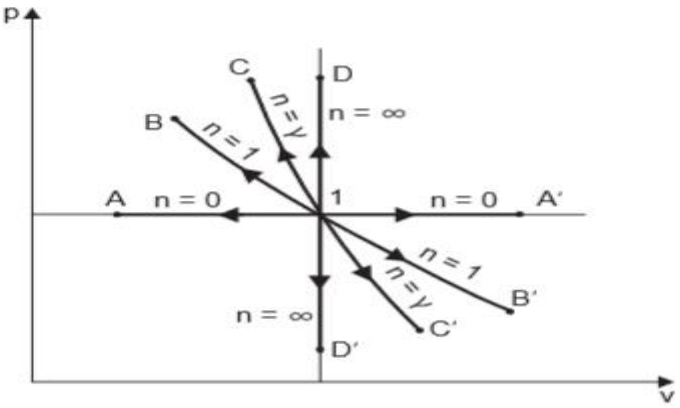


Fig. 4.9

6. Free Expansion

Consider two vessels 1 and 2 interconnected by a short pipe with a valve A, and perfectly thermally insulated [Fig. 4.10]. Initially let the vessel 1 be filled with a fluid at a certain pressure, and let 2 be completely evacuated. When the valve A is opened the fluid in 1 will expand rapidly to fill both vessels 1 and 2. The pressure finally will be lower than the initial pressure in vessel 1. This is known *as free or unresisted expansion*. The process is *highly irreversible*; since the fluid is eddying continuously during the process. Now applying first law of thermodynamics (or non-flow energy equation) between the initial and final states,

$$Q = (u_2 - u_1) + W$$

In this process, no work is done on or by the fluid, since the boundary of the system does not move. No heat flows to or from the fluid since the system is well lagged. The process is therefore, ***adiabatic but irreversible.***

i.e., $u_2 - u_1 = 0$ or $u_2 = u_1$

In a free expansion, therefore, the internal energy initially equals the initial energy finally. For a perfect gas, $u = C_v T$

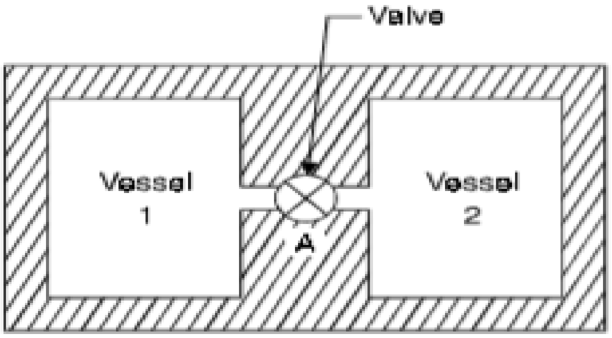


Fig. 4.10. Free expansion.

∴ For a free expansion of a perfect gas,

$$C_v T_1 = C_v T_2 \qquad \text{i.e., } T_1 = T_2$$

That is, for a perfect gas undergoing a free expansion, the initial temperature is equal to the final temperature.

Table 4.1 Summary of Processes for Perfect Gas (Unit mass)

process	Index n	Heat added	$\int p\,dv$	P, v, T, relation	Heat capacity
Constant pressure	n=0	$C_p(T_2-T_1)$	$p(v_2-v_1)$	$\frac{T_2}{T_1}=\frac{V_2}{V_1}$	Cp
Constant volume	n=α	$C_V(T_2-T_1)$	0	$\frac{T_1}{T_2}=\frac{P_1}{P_2}$	Cv
Constant temperature Isothermal	n=1	$P_1\,V_1\ln\frac{V_2}{V_1}$	$P_1\,V_1\ln\frac{V_2}{V_1}$	$P_1\,V_1=P_2V_2$	α
Reversible adiabatic	n= γ	0	$\left(\frac{P_1\,V_1-P_2V_2}{\gamma-1}\right)$	$P_1\,V_1{}^{\gamma}=P_2V_2{}^{\gamma}$ $\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $=\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$	0
Polytropic	n= n	$C_n(T_2-T_1)$ $=C_v\left(\frac{\gamma-n}{1-n}\right)$ $\times(T_2-T_1)$	$\left(\frac{P_1\,V_1-P_2V_2}{n-1}\right)$	$P_1\,V_1{}^{n}=P_2V_2{}^{n}$ $\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{n-1}$ $=\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$	C_n $=C_v\left(\frac{\gamma-n}{1-n}\right)$

Note. Equations must be used keeping dimensional consistence.

Example 4.1. *In an internal combustion engine, during the compression stroke the heat rejected to the cooling water is 50 kJ/kg and the work input is 100 kJ/kg.*

Calculate the change in internal energy of the working fluid stating whether it is a gain or loss.

Solution. Heat rejected to the cooling water, $Q = -50$ kJ/kg

(–ve sign since heat is rejected)

Work input, $W = -100$ kJ/kg

(–ve sign since work is supplied to the system)

Using the relation,

$$Q = (u_2 - u_1) + W$$

$$-50 = (u_2 - u_1) - 100$$

or

$$u_2 - u_1 = -50 + 100 = 50 \text{ kJ/kg}$$

Hence, **gain in internal energy = 50 kJ/kg. (Ans.)**

Example 4.2. *In an air motor cylinder the compressed air has an internal energy of 450 kJ/kg at the beginning of the expansion and an internal energy of 220 kJ/kg after expansion. If the work done by the air during the expansion is 120 kJ/kg, calculate the heat flow to and from the cylinder.*

Solution. Internal energy at beginning of the expansion,

$$u_1 = 450 \text{ kJ/kg}$$

Internal energy after expansion,

$$u_2 = 220 \text{ kJ/kg}$$

Work done by the air during expansion,

$$W = 120 \text{ kJ/kg}$$

Heat flow, Q :

Using the relation, $Q = (u_2 - u_1) + W$

$\therefore$ $Q = (220 - 450) + 120$

$= -230 + 120 = -110 \text{ kJ/kg}$

Hence, **heat rejected by air = 110 kJ/kg. (Ans.)**

Chapter 3: Volumetric Properties of Pure Fluids

Triple point:

The point at which the three curves are meet (vaporization, fusion and sublimation).

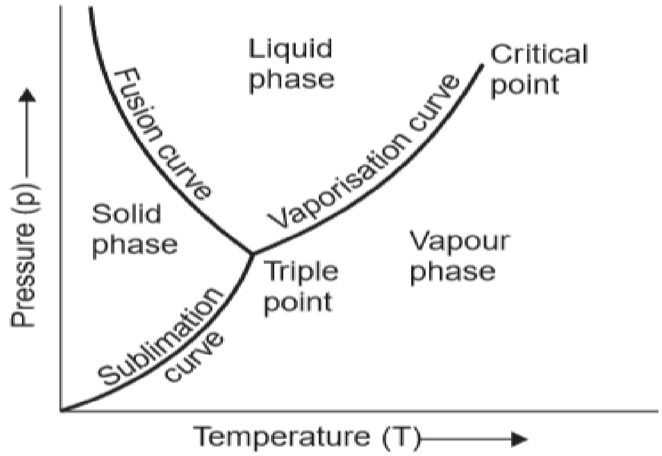


Fig. 3.1. p -T diagram for a substance such as water.

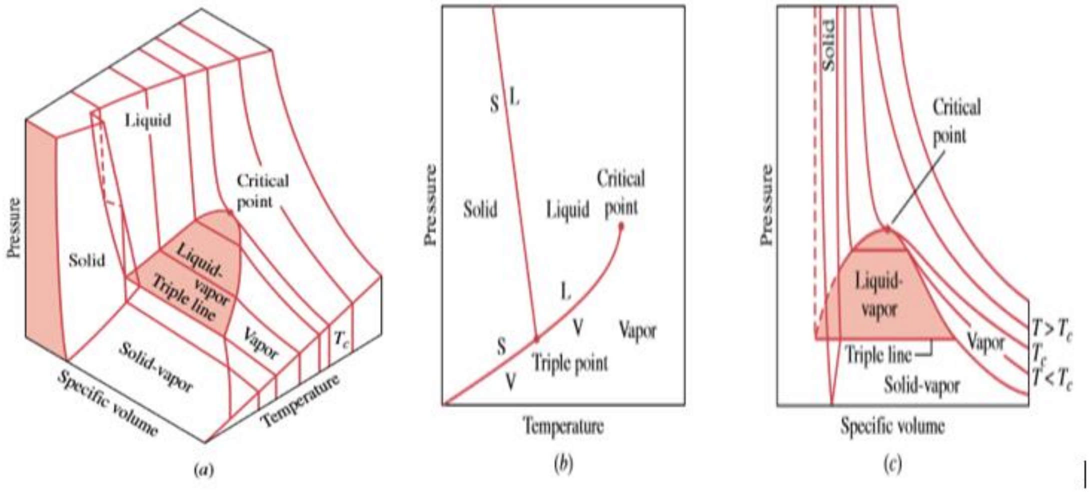


Figure 4.1 *p–v–T surface and projections for water (not to scale). (a) Three-dimensional view. (b) Phase diagram. (c) p–v diagram.*

Critical point:

The critical point. The coordinates of critical point are the critical pressure Pc and the critical temperature Tc, at the highest pressure and highest temperature at which a pure material can exist in vapor/ liquid equilibrium. At critical point liquid and vapour phases can’t be distinguish because they have the same property.

Fluid region:

Region of higher temperature and pressure than T_C, P_C and it is neither gas nor liquid.

Notes:

1. The triple point is invariant.
2. The system exist along the two phases line is univariant.
3. Single phase region is di varint.

Functional equation: Any equation which relate P, T, V

$$F(T,P,V) = 0$$

Equation of state: Equation which relate P, T, V (molar or specific) for any pure homogeneous fluid. The simplest form of equation of stat is

$$PV = RT \quad \text{(for ideal gas).}$$

Reversible process: Is defined as a process which once having taken place, can be reversed and leaves no changes in either the system or surrounding.

(هي عملية مثالية خيالية والتي تكون فيها القوة الدافعة تساوي القوة المقاومة او تقترب منها) ....

$W_{rev.} > W_{irr.}$

$W_{rev.}$ = max. Work.

$W_{irr.}$ =min. Work.

Ideal gas: is a gas of zero volume molecules and these is no interaction between molecules so that internal energy (U) is function of temperature only.

(Also Cv is function of T only).

Ideal gas characterized by.

$$PV = RT$$

Thermodynamic Process:

Closed (Non flow) system may undergoes may different kind of process, some of which will list below, it will be assumed that all process are:

1. Reversible process.
2. The work always takes the form of displacement work (not shaft work).
3. The Ke, Pe are negligible.

4.7. ENERGY OF AN ISOLATED SYSTEM

An isolated system is one in which there is no interaction of the system with the surroundings.

For an isolated system,

$dQ = 0$, $dW = 0$

The first law of thermodynamics gives

$$dE = 0$$

or $E = \text{constant}$

The energy of an isolated system is always constant.

4.8. THE PERFECT GAS

4.8.1. The Characteristic Equation of State

At temperatures that are considerably in excess of critical temperature of a fluid, and also at very low pressure, the vapour of fluid tends to obey the equation

$$\frac{PV}{T} = Constant = R$$

In practice, no gas obeys this law rigidly, but many gases tend towards it.

An imaginary ideal gas which obeys this law is called *a perfect gas*, and the equation

$\frac{PV}{T} = R$, is called *the characteristic equation of a state of a perfect gas*.

The constant R is called the gas constant. Each perfect gas has a different gas constant. Units of R are ***Nm/kg K or kJ/kg K.***

Usually, the characteristic equation is written as

$$Pv = TR \qquad \text{... (4.11)}$$

or for m kg, occupying V m^3

$$PV = m\,R\,T \qquad \text{... (4.12)}$$

*** The characteristic equation in another form, can be derived by using kilogram-mole as a unit.

The kilogram-mole is defined as a quantity of a gas equivalent to M kg of the gas, where M is the molecular weight of the gas (e.g., since the molecular weight of oxygen is 32, then 1 kg mole of oxygen is equivalent to 32 kg of oxygen).

As per definition of the kilogram-mole, for m kg of a gas, we have

$$m = n\,M \qquad \text{... (4.13)}$$

Where n = number of moles.

<u>Note:</u> Since the standard of mass is the kg, kilogram-mole will be written simply as mole. Substituting for m from eqn. (4.13) in eqn. (4.12) gives

$$PV = nM\,R\,T$$

or

$$MR = \frac{P\,V}{n\,T}$$

According to Avogadro's hypothesis the volume of 1 mole of any gas is the same as the volume of 1 mole of any other gas, when the gases are at the same temperature and pressure.

Therefore, $\frac{V}{n}$ is the same for all gases at the same value of p and T. That is the quantity $\frac{P\,V}{n\,T}$ is a *constant for all gases*. This constant is called *universal gas constant*, and is given the symbol, R_0.

i.e., $MR = R_0 = \frac{P\,V}{n\,T}$ or $PV = n\,R_0\,T$ ... (4.14)

Since $MR = R_0$, then

$$R = \frac{R_0}{M} \qquad \text{... (4.15)}$$

***It has been found experimentally that the volume of 1 mole of any perfect gas at 1 bar and 0°C is approximately 22.71 m^3.

Therefore from eqn. (4.14),

$$R_0 = \frac{P\,V}{n\,T} = \frac{1\times 10^5 \times 22.71}{1\times 273.15} = 8314.3\ \frac{N\,m}{mole\ \ k.}$$

Using eqn. (4.15), the gas constant for any gas can be found when the molecular weight is known.

Example. For oxygen which has a molecular weight of 32, the gas constant

$$R = \frac{R_0}{M} = \frac{8314}{32} = 259.8 \frac{N\,m}{Kg\ \ K}$$

4.8.2. Specific Heats:

The specific heat of a solid or liquid is usually defined as *the heat required to raise unit mass through one degree temperature rise.*

For small quantities, we have

$$dQ = m\,C\,dT$$

Where: m = mass, C = specific heat, and dT = temperature rise.

For a gas there are an infinite number of ways in which heat may be added between any two temperatures, and *hence a gas could have an infinite number of specific heats*. However, only two specific heats for gases are defined.

Specific heat at constant volume, Cv

and, Specific heat at constant pressure, Cp.

We have

$dQ = m\,Cp\,dT$ For a reversible non-flow process at *constant pressure* ... (4.16)
and, $dQ = m\,Cv\,dT$ For a reversible non-flow process at *constant volume* ... (4.17)

The values of *Cp* and *Cv*, for a perfect gas, are constant for any one gas at all pressures and temperatures. Hence, integrating eqns. (4.16) and (4.17), we have

Flow of heat in a reversible constant pressure process

$$= m\,Cp\,(T_2 - T_1) \qquad \text{... (4.18)}$$

Flow of heat in a reversible constant volume process

$$= m\,Cv\,(T_2 - T_1) \qquad \text{... (4.19)}$$

In case *of real gases, Cp and Cv vary with temperature*, but a suitable *average value* may be used for most practical purposes.

4.8.3. Joule's Law

Joule's law states as follows:

"The internal energy of a perfect gas is a function of the absolute temperature only."

i.e., $u = f\,(T)$

To evaluate this function let 1 kg of a perfect gas be heated at constant volume.

According to non-flow energy equation,

$dQ = du + dW$

$dW = 0$, since volume remains constant

$\therefore dQ = du$

At constant volume for a perfect gas, from eqn. (4.17), for 1 kg

$dQ = c_v dT$

$\therefore dQ = du = c_v dT$

and integrating $u = C_v T + K$, K being constant.

According to Joule's law $u = f(T)$, which means that internal energy varies linearly with absolute temperature. Internal energy can be made zero at any arbitrary reference temperature.

For a perfect gas it can be assumed that $u = 0$ when $T = 0$, hence constant K is zero.

i.e., Internal energy, $u = C_v T$ for a perfect gas ... (4.20)

or For mass m, of a perfect gas

Internal energy, $U = m C_v T$ ... (4.21)

For a perfect gas, in any process between states 1 and 2, we have from Eqn. (4.21) Gain in internal energy,

$$U_2 - U_1 = m C_v (T_2 - T_1) \quad \text{... (4.22)}$$

Eqn. (4.22) gives the gains of internal energy for a perfect gas between two states *for any process, reversible or irreversible.*

4.8.4. Relationship Between Two Specific Heats

Consider a perfect gas being heated at constant pressure from T_1 to T_2.

According to non-flow equation,

$Q = (U_2 - U_1) + W$ …………. (1)

Also for a perfect gas,

$$U_2 - U_1 = m C_v (T_2 - T_1) \qquad \text{substitute in eq. 1}$$

$$Q = m C_v (T_2 - T_1) + W \qquad (2)$$

In a constant pressure process, the work done by the fluid,

$W = P(V_2 - V_1)$

$= m R (T_2 - T_1)$

$$P_1 V_1 = m R T_1$$
$$P_2 V_2 = mR\, T_2$$
$$P_1 = P_2 = P \text{ in this case}$$

On substituting

$$Q = m\, Cv\,(T_2 - T_1) + m R (T_2 - T_1) = m (Cv + R)(T_2 - T_1)$$

But for a constant pressure process,

$$Q = m\, Cp\,(T_2 - T_1)$$

By equating the two expressions, we have

$$m (Cv + R)(T_2 - T_1) = m\, Cp\,(T_2 - T_1)$$

$\therefore \quad Cv + R = Cp$

or $\quad Cp - Cv = R \quad$ ...(4.23)

Dividing both sides by Cv, we get

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$\therefore \quad C_V = \frac{R}{\gamma - 1} \quad$ ... [4.23 (a)]

(Where $\gamma = \frac{C_P}{C_V}$)

Similarly, dividing both sides by Cp, we get

$C_P = \frac{\gamma R}{\gamma - 1} \quad$ ... [4.23 (b)]

4.8.5. Enthalpy

- One of the fundamental quantities which occur invariably in thermodynamics is the sum of internal energy (u) and pressure volume product (PV). This sum is called Enthalpy (h).
  i.e., $h = u + pv$ ... (4.24)
- The enthalpy of a fluid is the property of the fluid, since it consists of the sum of a property and the product of the two properties. Since enthalpy is a property like internal energy, pressure, specific volume and temperature, it can be introduced into any problem whether the process is a flow or a non-flow process.

4.9. Application of First Law of Thermodynamics to Non-Flow or Closed System

1. Reversible Constant Volume (or **Isochoric**) Process **(v = constant)**:

In a constant volume process the working substance is contained in a rigid vessel, hence the boundaries of the system are immovable and no work can be done on or by the system, other than paddle-wheel work input. It will be assumed that 'constant volume' implies zero work unless stated otherwise.

Fig. 4.5 shows the system and states before and after the heat addition at constant volume.

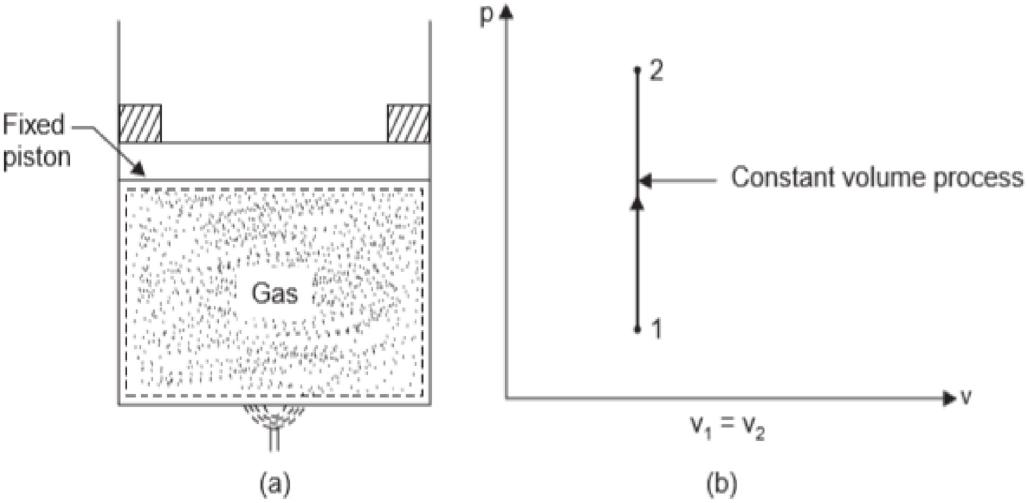


Fig. 4.5. Reversible constant volume process.

Considering mass of the working substance unity and applying first law of thermodynamics to the process

$$Q = (u_2 - u_1) + W \qquad \text{... (4.26)}$$

The work done $W = \int_1^2 PdV = 0$ as dv = 0.

$$\therefore Q = (u_2 - u_1) = C_v (T_2 - T_1) \qquad [4.27 \text{ (a)}]$$

Where Cv = Specific heat at constant volume.

For mass, m, of working substance

$$Q = U_2 - U_1 = m\, C_v (T_2 - T_1) \qquad [4.27 \text{ (b)}]$$

$$[\because m\, u = U]$$

2. Reversible Constant Pressure (**or Isobaric**) Process **(p = constant).**

It can be seen from Fig. 4.5 (b) that when the boundary of the system is inflexible as in a constant volume process, then the pressure rises when heat is supplied. Hence for a constant pressure process, the boundary must move against an external resistance as heat is supplied; for instance a gas [Fig. 4.6 (a)] in a cylinder behind a piston can be made to undergo a constant pressure process. *Since the piston is pushed through a certain distance* by the force exerted by the gas, then the work is done by the gas on its surroundings. Fig. 4.6 shows the system and states before and after the heat addition at constant pressure.

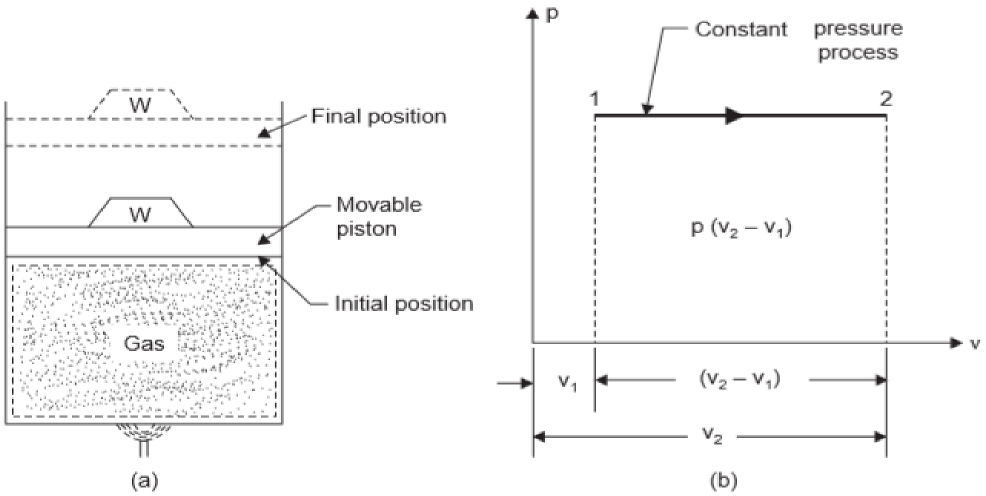


Fig. 4.6. Reversible constant pressure process

Considering unit mass of working substance and applying first law of thermodynamics to the process

$$Q = (u_2 - u_1) + W$$

The work done, $W = \int_1^2 p\,dv = p(v_2 - v_1)$

$$\therefore \quad Q = (u_2 - u_1) + p\,(v_2 - v_1) = u_2 - u_1 + pv_2 - pv_1$$

$$= (u_2 + pv_2) - (u_1 + pv_1) = h_2 - h_1 \qquad [\therefore h = u + p\,v]$$

Or $\mathbf{Q = h_2 - h_1 = Cp\,(T_2 - T_1)}$ **... (4.28)**

Where h = Enthalpy (specific), and

Cp = Specific heat at constant pressure.

For mass, m, of working substance

$\mathbf{Q = H_2 - H_1 = m\,Cp\,(T_2 - T_1)}$ **... [4.28 (a)]**

$$[mh = H]$$

3. Reversible Temperature (or Isothermal) Process (*PV*= constant, T = constant):

A process at a constant temperature is called an isothermal process. When a working substance in a cylinder behind a piston expands from a high pressure to a low pressure there is a tendency for the temperature to fall. In an isothermal expansion heat must be added continuously in order to keep the temperature at the initial value. Similarly in an isothermal compression heat must be removed from the working substance continuously during the process.

Fig. 4.7 shows the system and states before and after the heat addition at constant temperature.

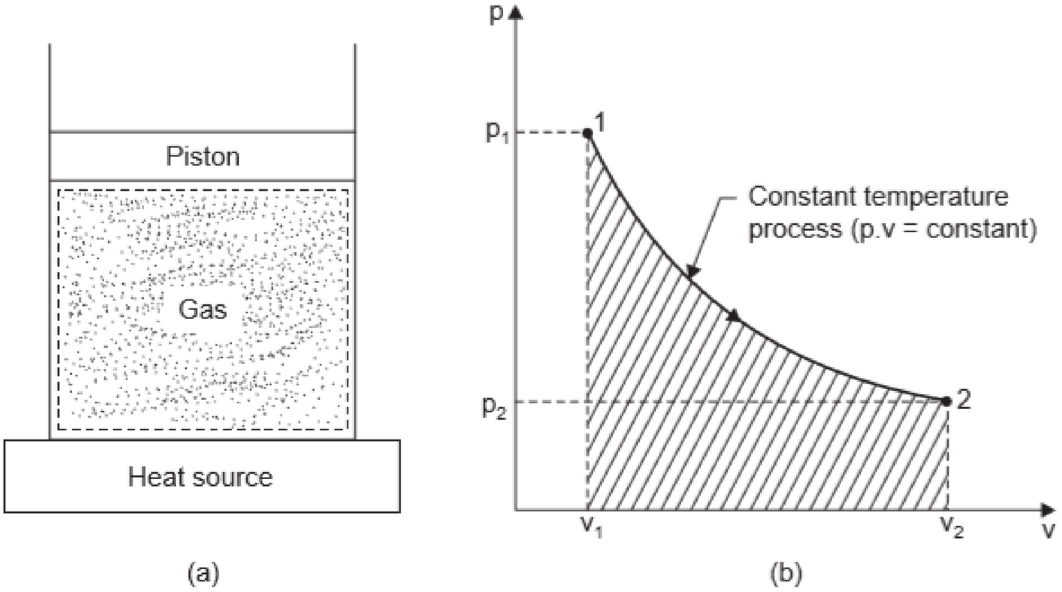


Fig. 4.7. Reversible isothermal process.

Considering unit mass of working substance and applying first law to the process

$$Q = (u_2 - u_1) + W$$

$$Q = Cv\,(T_2 - T_1) + W$$

$$Q = 0 + W \qquad [T_2 = T_1]$$

The work done, $W = \int_1^2 p\,dv$

In this case PV = constant or $P = \frac{C}{V}$ (where C = constant)

$$\therefore \quad W = \int_{V_1}^{V_2} C\,\frac{dV}{V} = C\,\ln\frac{V_2}{V_1}$$

The constant C can either be written as p_1v_1 or as p_2v_2, since

$$p_1v_1 = p_2v_2 = \text{constant, } C$$

i.e., $W = P_1 V_1 \ln\frac{V_2}{V_1}$ per unit mass of working substance

or $W = P_2 V_2 \ln\frac{V_2}{V_1}$ per unit mass of working substance

$$\therefore \quad \boldsymbol{Q = W = P_1 V_1 \ln\frac{V_2}{V_1}} \qquad \dots (4.29)$$

For mass, m, of the working substance

$$\boldsymbol{Q = P_1 V_1 \ln\frac{V_2}{V_1}} \qquad [4.29\ (a)]$$

$$or \qquad \boldsymbol{Q = P_1 V_1 \ln\frac{P_1}{P_2}} \qquad where \quad \left[\frac{V_2}{V_1} = \frac{P_1}{P_2}\right] \qquad [4.29\ (b)]$$

4. Reversible Adiabatic Process (pv^{γ} = constant):

An **adiabatic process** *is one in which no heat is transferred to or from the fluid during the process*. Such a process can be reversible or irreversible. The reversible adiabatic non-flow process will be considered in this section.

Considering unit mass of working substance and applying first law to the process

$Q = (u_2 – u_1) + W$

$Q = (u_2 – u_1) + W$

Or $W = (u_1 – u_2)$ for any adiabatic process ... (4.30)

Eqn. (4.30) is true for an adiabatic process whether the process is reversible or not. In an adiabatic expansion, the work done W by the fluid is at the expense of a reduction in the internal energy of the fluid. Similarly in an adiabatic compression process all the work done on the fluid goes to increase the internal energy of the fluid.

For *an adiabatic process to take place, perfect thermal insulation for the system must be available.*

To derive the law pv^{γ} = constant:

To obtain a law relating p and v for a reversible adiabatic process let us consider the non-flow energy equation in differential form,

$$dQ = du + dW$$

For *a reversible process*

$$dW = p\,dv$$

∴ $$dQ = du + pdv = 0$$

(Since for an adiabatic process Q = 0)

Also for a perfect gas

$$PV = RT \; Or \quad P = \frac{R\,T}{V}$$

Hence substituting, $du + \frac{R\,T\,dV}{V} = 0$

Also $u = C_V\,T \qquad or \qquad du = C_V\,dT$

∴ $$C_V\,dT + \frac{R\,T\,dV}{V} = 0$$

Dividing both sides by T, we get

$$C_V\frac{dT}{T} + \frac{R\,dV}{V} = 0$$

Integrating $C_V \ln T + R\, \ln V = Constant$

Substituting $T = \frac{P\,V}{R}$

$$C_V \ln\frac{PV}{R} + R\, \ln V = Constant$$

Dividing throughout both sides by Cv

$$\ln\frac{PV}{R} + \frac{R}{C_V}\ln V = Constant$$

Again $C_V = \frac{R}{(\gamma-1)}$ or $\frac{R}{C_V} = (\gamma - 1)$

Hence substituting

$$\ln\frac{PV}{R} + (\gamma - 1)\, \ln V = Constant$$

∴ $$\ln\frac{PV}{R} + \ln V^{\gamma-1} = Constant$$

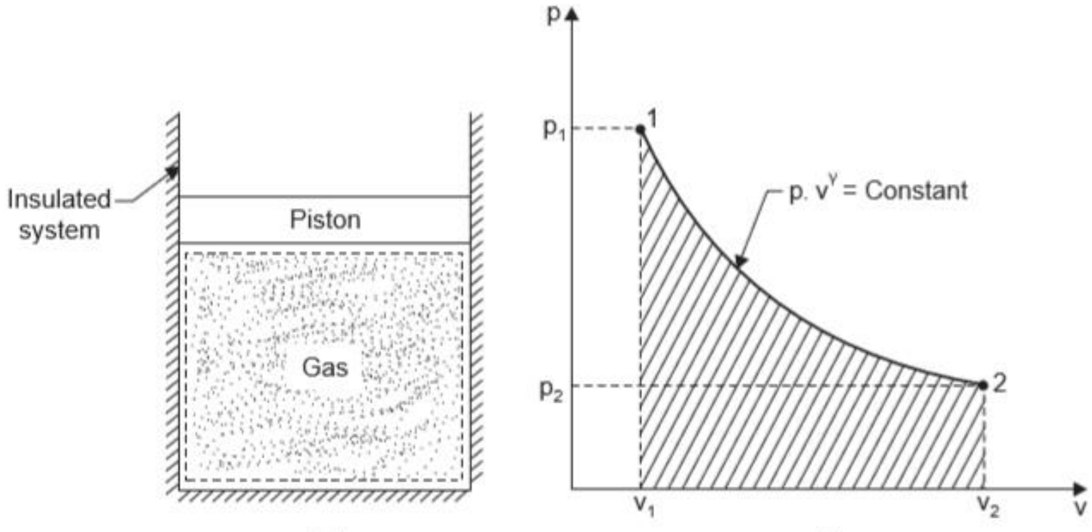
$$\ln\frac{PV \times V^{\gamma-1}}{R} = Constant$$

i.e. , $\ln\frac{P\,V^{\gamma}}{R} = Constant$

i.e., $\frac{P\,V^{\gamma}}{R} = \quad e^{constant} = Constant$

Or $PV^{\gamma} \quad = Constant$ (4.31)

Expression for work W: A reversible adiabatic process for a perfect gas is shown on a p-v diagram in Fig. 4.8 (b).



(a) (b)

Fig. 4.8. Reversible adiabatic process.

The work done is given by the shaded area, and this area can be evaluated by integration.

i.e., $W = \int_{V_1}^{V_2} P\, dV$

Therefore, since pv^γ = constant, C, then

$$W = \int_{V_1}^{V_2} C \frac{dV}{V^\gamma} \qquad [\, P = \frac{C}{V^\gamma}\,]$$

i.e., $$W = C \int_{V_1}^{V_2} \frac{dV}{V} = C \left| \frac{V^{-\gamma+1}}{-\gamma+1} \right|_{V_1}^{V_2}$$

$$W = C \left(\frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{1-\gamma} \right) = C \left(\frac{V_1^{-\gamma+1} - V_2^{-\gamma+1}}{\gamma - 1} \right)$$

The constant in this equation can be written as $p_1 v_1^\gamma$ or as $p_2 v_2{}^\gamma$. Hence,

$$W = \frac{P_1 V_1^\gamma V_1^{-\gamma+1} - P_2 V_2^\gamma V_2^{-\gamma+1}}{\gamma - 1} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

i.e., $$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1} \qquad (4.32)$$

or $$W = \frac{R\,(T_1 - T_2)}{\gamma - 1} \qquad (4.33)$$

Relationship between T and v, and T and p:

By using equation pv = RT, the relationship between T and v, and T and p, may by derived as follows:

i.e., $P\,V = R\,T$

∴ $P = \frac{R\,T}{V}$

Putting this value in the equation $P\,V^{\gamma} = constant$

$$\frac{R\,T}{V}\,V^{\gamma} = constant$$

i.e., $T\,V^{\gamma-1} = constant$ **(4.34)**

Also $V = \frac{R\,T}{P}$; hence substituting in equation $P\,V^{\gamma} = constant$

$$P\left(\frac{R\,T}{P}\right)^{\gamma} = constant$$

$$\frac{T^{\gamma}}{P^{\gamma-1}} = constant$$

$$\frac{T}{P^{\frac{\gamma-1}{\gamma}}} = constant \qquad (4.35)$$

Therefore, for a reversible adiabatic process for a perfect gas between states 1 and 2, we can write:

From Eqn. (4.31),

$$\boldsymbol{P_1V_1^{\gamma} = P_2V_2^{\gamma} \quad or \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}} \qquad \mathbf{(4.36)}$$

From Eqn. (4.34),

$$\boldsymbol{T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \quad or \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}} \qquad \mathbf{(4.37)}$$

From Eqn. (4.35),

$$\boldsymbol{\frac{T_1}{(P_1)^{\frac{\gamma-1}{\gamma}}} = \frac{T_2}{(P_2)^{\frac{\gamma-1}{\gamma}}} \quad or \quad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}} \qquad \mathbf{(4.38)}$$

From eqn. (4.30), the work done in an adiabatic process per kg of gas is given by W = $(u_1 - u_2)$. The gain in internal energy of a perfect gas is given by equation:

$u_2 - u_1 = Cv\,(T_2 - T_1)$ (for 1 kg)

∴ W = Cv (T$_1$ – T$_2$)

Also, we know that

$$C_V = \frac{R}{\gamma - 1}$$

Hence substituting, we get

$$W = \frac{R\,(T_1 - T_2)}{\gamma - 1}$$

Using equation, PV= RT

$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

This is the same expression obtained before as eqn. (4.32).

$$W_{12} = \frac{nRT_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right] = \frac{P_1 V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

5. Polytropic Reversible Process (pv^n = constant):

It is found that many processes in practice approximate to a reversible law of form **pv^n = constant**, where n is a constant. Both vapours and perfect gases obey this type of law closely in many non-flow processes. Such processes are *internally reversible.*

We know that for any reversible process,

i.e., $W = \int_{V_1}^{V_2} P\, dV$

For a process in pv^n = constant, we have

Where C is a constant $\left[\, P = \frac{C}{V^n} \,\right]$

i.e., $$W = C \int_{V_1}^{V_2} \frac{dV}{V^n} = C \left| \frac{V^{-n+1}}{-n+1} \right|_{V_1}^{V_2} = C \left(\frac{V_1^{-n+1} - V_2^{-n+1}}{-n+1} \right)$$

$$W = C \left(\frac{V_1^{-n+1} - V_2^{-n+1}}{n - 1} \right) = \frac{P_1 V_1^n V_1^{-n+1} - P_2 V_2^n V_2^{-n+1}}{n - 1}$$

(Since the constant C, can be written as $p_1 v_1^n$ or as $p_2 v_2^n$)

i.e., Work done, $W = \frac{P_1 V_1 - P_2 V_2}{n - 1}$ (4.39)

or $W = \frac{R\,(T_1 - T_2)}{n - 1}$ (4.40)

Eqn. (4.39) is true for any working substance undergoing a reversible polytropic process. It follows also that for any polytropic process, we can write

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^n \qquad (4.41)$$

The following relations can be derived (following the same procedure as was done under reversible adiabatic process)

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1} \qquad (4.42)$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} \qquad (4.43)$$

Heat transfer during polytropic process (for perfect gas pv = RT):

Using non-flow energy equation, the heat flow/transfer during the process can be found,

i.e., $$Q = (u_2 - u_1) + W$$

$$= C_V(T_2 - T_1) + \frac{R(T_1 - T_2)}{n - 1}$$

$$Q = \frac{R(T_1 - T_2)}{n - 1} - C_v(T_1 - T_2)$$

Also $$C_v = \frac{R}{\gamma - 1}$$

$$Q = \frac{R}{n - 1}(T_1 - T_2) - \frac{R}{\gamma - 1}(T_1 - T_2)$$

i.e., $$Q = R(T_1 - T_2)\left(\frac{R}{n-1} - \frac{1}{\gamma - 1}\right)$$

$$Q = (\frac{R(T_1 - T_2)(\gamma - 1 - n + 1)}{(\gamma - 1)(n - 1)} = (\frac{R(T_1 - T_2)(\gamma - n)}{(\gamma - 1)(n - 1)}$$

$$Q = \frac{(\gamma - n)}{(\gamma - 1)} \frac{R(T_1 - T_2)}{(n - 1)}$$

or $$Q = \left(\frac{\gamma - n}{\gamma - 1}\right)W \qquad \left[W = \frac{R(T_1 - T_2)}{(n-1)}\right] \qquad (4.44)$$

In a polytropic process, the index n depends only on the heat and work quantities during the process. The various processes considered earlier are special cases of polytropic process for a perfect gas.

For example,

When $n = 0$ pv° = constant i.e., p = constant

When $n = \infty$ pv^{∞} = constant or $p^{1/\infty}\ v$ = constant, i.e., v = constant

When $n = 1$ pv = constant, i.e., T = constant

[Since (pv) /T = constant for a perfect gas]

When $n = \gamma$ pv^{γ} = constant, i.e., reversible adiabatic

This is illustrated on a p-v diagram in Fig. 4.9.

i. State 1 to state A is constant pressure cooling ($n = 0$).
ii. State 1 to state B is isothermal compression ($n = 1$).
iii. State 1 to state C is reversible adiabatic compression ($n = \gamma$).
iv. State 1 to state D is constant volume heating ($n = \infty$).

Similarly,

i. State 1 to state A′ is constant pressure heating ($n = 0$).
ii. State 1 to state B′ is isothermal expansion ($n = 1$).
iii. State 1 to state C′ is reversible adiabatic expansion ($n = \gamma$).
iv. State 1 to state D′ is constant volume cooling ($n = \propto$).

It may be noted that, since γ is always greater than unity, than process 1 to C must lie between processes 1 to B and 1 to D; similarly, process 1 to C′ must lie between processes 1 to B′ and 1 to D′.

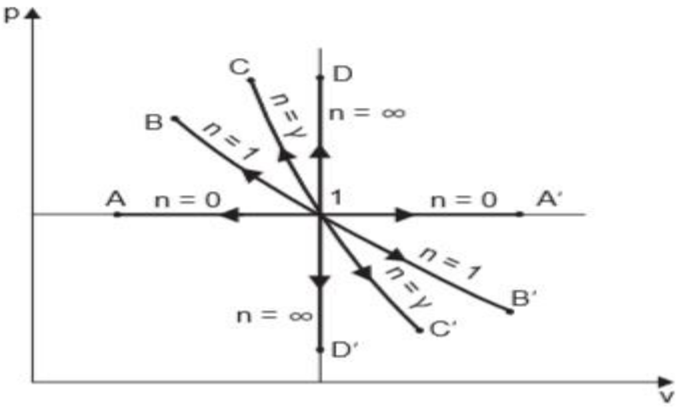


Fig. 4.9

6. Free Expansion

Consider two vessels 1 and 2 interconnected by a short pipe with a valve A, and perfectly thermally insulated [Fig. 4.10]. Initially let the vessel 1 be filled with a fluid at a certain pressure, and let 2 be completely evacuated. When the valve A is opened the fluid in 1 will expand rapidly to fill both vessels 1 and 2. The pressure finally will be **lower than the initial pressure** in vessel 1. This is known ***as free or unresisted expansion***. The process is *highly irreversible*; since the fluid is eddying continuously during the process. Now applying first law of thermodynamics (or non-flow energy equation) between the initial and final states,

$$Q = (U_2 - U_1) + W$$

In this process, no work is done on or by the fluid, since the boundary of the system does not move. **No heat flows to or from the fluid** since the system is well lagged. The process is therefore, ***adiabatic but irreversible.***

i.e., $U_2 - U_1 = 0$ or $U_2 = U_1$

In a free expansion, therefore, the internal energy initially equals the initial energy finally. For a perfect gas, $U = C_v T$

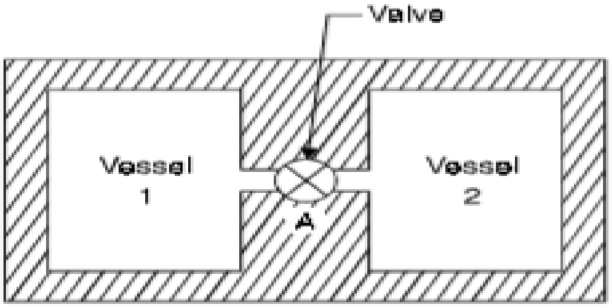


Fig. 4.10. Free expansion.

∴ For a free expansion of a **perfect gas**,

$$C_v T_1 = C_v T_2 \qquad \text{i.e., } T_1 = T_2$$

That is, for a perfect gas undergoing a free expansion, **the initial temperature is equal to the final temperature.**

Table 4.1 Summary of Processes for Perfect Gas (Unit mass)

process	**Index n**	**Heat added**	$\int p\, dv$	**P, v, T, relation**	**Heat capacity**
Constant pressure	n=0	$C_p(T_2-T_1)$	$p(v_2-v_1)$	$\frac{T_2}{T_1}=\frac{V_2}{V_1}$	Cp
Constant volume	n=α	$C_V(T_2-T_1)$	0	$\frac{T_1}{T_2}=\frac{P_1}{P_2}$	Cv
Constant temperature Isothermal	n=1	$P_1\, V_1 \ln\frac{V_2}{V_1}$	$P_1\, V_1 \ln\frac{V_2}{V_1}$	$P_1\, V_1 = P_2V_2$	α
Reversible adiabatic	n= γ	0	$\left(\frac{P_1\, V_1 - P_2V_2}{\gamma-1}\right)$	$P_1\, V_1{}^{\gamma} = P_2V_2{}^{\gamma}$ $\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$	0
Polytropic	n= n	$C_n(T_2-T_1) = C_v\left(\frac{\gamma-n}{1-n}\right) \times (T_2-T_1)$	$\left(\frac{P_1\, V_1 - P_2V_2}{n-1}\right)$	$P_1\, V_1{}^{n} = P_2V_2{}^{n}$ $\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{n-1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$	$C_n = C_v\left(\frac{\gamma-n}{1-n}\right)$

Note. Equations must be used keeping dimensional consistence.

Example 4.1.

In an internal combustion engine, during the compression stroke the heat rejected to the cooling water is 50 kJ/kg and the work input is 100 kJ/kg. Calculate the change in internal energy of the working fluid stating whether it is a gain or *loss.*

Solution.

Heat rejected to the cooling water, $Q = -50$ kJ/k **(– ve sign since heat is rejected)**

Work input, $W = -100$ kJ/kg **(– ve sign since work is supplied to the system)**

Using the relation, $Q = (U_2 - U_1) + W$

$$-50 = (U_2 - U_1) - 100$$

OR $(U_2 - U_1) = -50 + 100 = 50$ kJ/kg

Hence, gain in internal energy = 50 kJ/kg. (Ans.)

Example 4.2.

In an air motor cylinder the compressed air has an internal energy of 450 kJ/kg at the beginning of the expansion and an internal energy of 220 kJ/kg after expansion. If the work done by the air during the expansion is 120 kJ/kg, calculate the heat flow to and from the cylinder.

Solution.

Internal energy at beginning of the expansion,

$$U_1 = 450 \text{ kJ/kg}$$

Internal energy after expansion,

$$U_2 = 220 \text{ kJ/kg}$$

Work done by the air during expansion,

$$W = 120 \text{ kJ/kg}$$

Heat flow, Q:

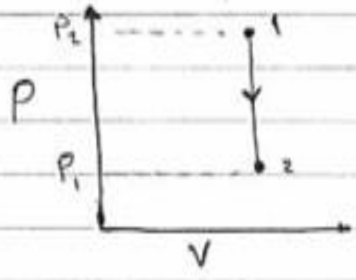
Using the relation, $Q = (U_2 - U_1) + W$

$\therefore$ $Q = (220 - 450) + 120$

$$= -230 + 120 = -110 \text{ kJ/kg}$$

Hence, heat rejected by air = 110 kJ/kg. (Ans.)

(a) Constant volume Process



$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Delta U = Q - W$$

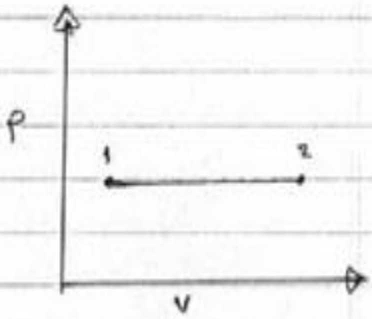
$$\Delta U_{12} = Q_{12} - W_{12}$$

$$W_{12} = 0$$

$$\Delta U = Q.$$

For perfect gas: $\Delta U = \int_1^2 C_v \, dT$

(b) Constant pressure process : (Isobaric)



$$\Delta U = Q - W$$

$$W_{12} = P \Delta V_2$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\Delta U_{12} = Q_{12} - P \Delta V_{12}$$

$$\boxed{Q_{12} = \Delta H}$$

For perfect gas,

$$\Delta H_{12} = \int_1^2 c_p \, dT$$

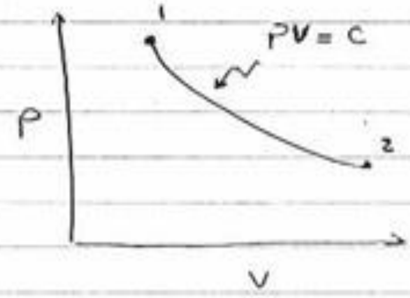
(c) Constant temp. Process (isothermal)

$\Delta u = Q - w$

$w = \int_1^2 P\,dv$

$P_1V_1 = P_2V_2$

$\Delta u_{12} = Q_{12} - \int_1^2 P\,dV$



For perfect gas.

$\Delta u_{12} = 0$ since $u = f(t)$ only

$W_{12} = Q_{12} = nRT \ln \frac{V_2}{V_1}$

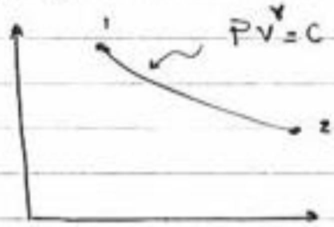
oR $\boxed{W = nRT \ln \frac{P_1}{P_2}}$

(d) Adiabatic process (isentropic) :-

$\Delta u_{12} = Q_{12} - W_{12}$

$Q_{12} = 0$

$\Delta u_{12} = -W_{12}$



For perfect gas

$\Delta u_{12} = C_v(T_2 - T_1)$

$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$

$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$

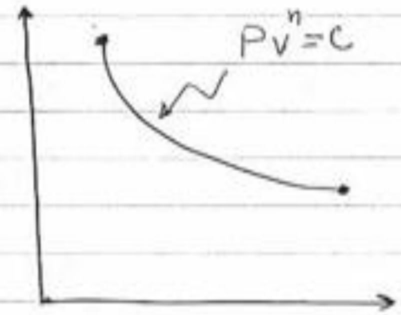
$\frac{V_2}{V_1} = \left(\frac{P_2}{P_1}\right)^{-\frac{1}{\gamma}}$

$\gamma = \frac{C_p}{C_v}$

$$W_{12} = \frac{nRT_1}{\gamma-1}\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right] = \frac{P_1V_1}{\gamma-1}\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

(E) Polytropic Process

The process which is not isothermal nor adiabatic



$$Q = \Delta U_{12} + W_{12}$$

$$W_{12} = \left(\frac{P_2V_2 - P_1V_1}{1-n}\right)$$

For perfect gas

$$W_{12} = \frac{R(T_2-T_1)}{1-n}.$$

$$\Delta u = \int c_v\,dT$$

$$Q = W_{12}\left(\frac{\gamma-n}{\gamma-1}\right)$$

Notes

1- ΔH, ΔU is independent on the process if it is reversible or irreversible since it is a state function unlike work, heat.

2- For irreversible, the work cannot be obtained from $\int p\,dv$.

3- First law of thermodynamic applies well to irreversible & reversible process.

4- Throttling process is irreversible $\Delta H = 0$

The Flow work

$$W_{nonflow} = W_{flow} - P_1V_1 + P_2V_2$$

$$W_{flow} = W_{nonflow} + P_1V_1 - P_2V_2 = W_{nonflow} - \Delta PV$$

$$dW_{flow} = dW_{nonflow} - pdv - vdp$$

$$= p\,d\cancel{v} - p\,d\cancel{v} - vdp$$

$$dW_{flow} = -vdp$$ الشغل الجرياني

Work flow for ideal gas

- **Polytropic**

$$W_{flow} = \frac{P_1V_1}{n-1}\left[1-\left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}}\right]$$

$$= \frac{RT_1}{n-1}\left[1-\left(\frac{P_1}{P_2}\right)^{\frac{1-n}{n}}\right]$$

- **adiabatic**

$$-W_{flow} = \frac{\gamma RT_1}{\gamma-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}-1\right]$$

- **isothermal**

$$W_{flow} = RT\ln\frac{V_2}{V_1}.$$

Notes

1) For diatomic gas (O_2, N_2, H_2) $C_p = \frac{7}{2}R$, $C_v = 5/2\,R$,

2) For monoatomic gas (Ar, He) $C_p = \frac{5}{2}R$, $C_v = \frac{3}{2}R$.

6. Free Expansion

Consider two vessels 1 and 2 interconnected by a short pipe with a valve A, and perfectly thermally insulated [Fig. 4.10]. Initially let the vessel 1 be filled with a fluid at a certain pressure, and let 2 be completely evacuated. When the valve A is opened the fluid in 1 will expand rapidly to fill both vessels 1 and 2. The pressure finally will be **lower than the initial pressure** in vessel 1. This is known ***as free or unresisted expansion***. The process is *highly irreversible*; since the fluid is eddying continuously during the process. Now applying first law of thermodynamics (or non-flow energy equation) between the initial and final states,

$$Q = (U_2 - U_1) + W$$

In this process, no work is done on or by the fluid, since the boundary of the system does not move. **No heat flows to or from the fluid** since the system is well lagged. The process is therefore, ***adiabatic but irreversible.***

i.e., $U_2 - U_1 = 0$ or $U_2 = U_1$

In a free expansion, therefore, the internal energy initially equals the initial energy finally. For a perfect gas, $U = Cv\,T$

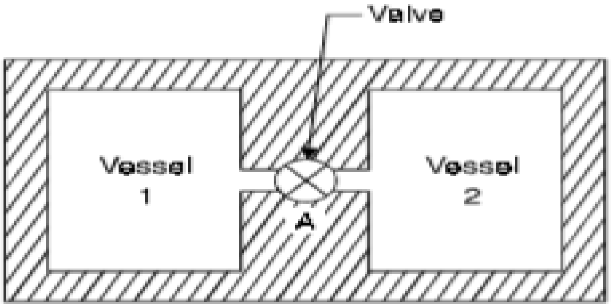


Fig. 4.10. Free expansion.

∴ For a free expansion of a **perfect gas**,

$$Cv\,T_1 = Cv\,T_2 \qquad \text{i.e., } T_1 = T_2$$

That is, for a perfect gas undergoing a free expansion, **the initial temperature is equal to the final temperature.**

Table 4.1 Summary of Processes for Perfect Gas (Unit mass)

process	**Index n**	**Heat added**	$\int p\,dv$	**P, v, T, relation**	**Heat capacity**
Constant pressure	n=0	$C_p(T_2-T_1)$	$p(v_2-v_1)$	$\frac{T_2}{T_1}=\frac{V_2}{V_1}$	Cp
Constant volume	n=α	$C_V(T_2-T_1)$	0	$\frac{T_1}{T_2}=\frac{P_1}{P_2}$	Cv
Constant temperature Isothermal	n=1	$P_1\,V_1\ln\frac{V_2}{V_1}$	$P_1\,V_1\ln\frac{V_2}{V_1}$	$P_1\,V_1=P_2V_2$	α
Reversible adiabatic	n= γ	0	$\left(\frac{P_1\,V_1-P_2V_2}{\gamma-1}\right)$	$P_1\,V_1{}^{\gamma}=P_2V_2{}^{\gamma}$ $\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$ $=\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$	0
Polytropic	n= n	$C_n(T_2-T_1)$ $=C_v\left(\frac{\gamma-n}{1-n}\right)$ $\times(T_2-T_1)$	$\left(\frac{P_1\,V_1-P_2V_2}{n-1}\right)$	$P_1\,V_1{}^{n}=P_2V_2{}^{n}$ $\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{n-1}$ $=\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}$	C_n $=C_v\left(\frac{\gamma-n}{1-n}\right)$

Note. Equations must be used keeping dimensional consistence.

Example 4.1.

In an internal combustion engine, during the compression stroke the heat rejected to the cooling water is 50 kJ/kg and the work input is 100 kJ/kg. Calculate the change in internal energy of the working fluid stating whether it is a gain or *loss.*

Solution.

Heat rejected to the cooling water, Q = – 50 kJ/k **(– ve sign since heat is rejected)**

Work input, W = – 100 kJ/kg **(– ve sign since work is supplied to the system)**

Using the relation, $Q = (U_2 - U_1) + W$

$$-50 = (U_2 - U_1) - 100$$

OR $$(U_2 - U_1) = -50 + 100 = 50 \text{ kJ/kg}$$

Hence, gain in internal energy = 50 kJ/kg. (Ans.)

Example 4.2.

In an air motor cylinder the compressed air has an internal energy of 450 kJ/kg at the beginning of the expansion and an internal energy of 220 kJ/kg after expansion. If the work done by the air during the expansion is 120 kJ/kg, calculate the heat flow to and from the cylinder.

Solution.

Internal energy at beginning of the expansion,

$$U_1 = 450 \text{ kJ/kg}$$

Internal energy after expansion,

$$U_2 = 220 \text{ kJ/kg}$$

Work done by the air during expansion,

$$W = 120 \text{ kJ/kg}$$

Heat flow, Q:

Using the relation, $Q = (U_2 - U_1) + W$

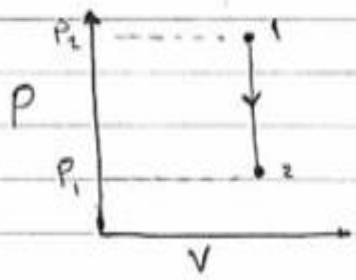
$\therefore$ $Q = (220 - 450) + 120$

$$= -230 + 120 = -110 \text{ kJ/kg}$$

Hence, heat rejected by air = 110 kJ/kg. (Ans.)

(a) Constant volume Process

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$



$\Delta U = Q - W$

$\Delta U_{12} = Q_{12} - W_{12}$

$W_{12} = 0$

$\Delta U = Q$.

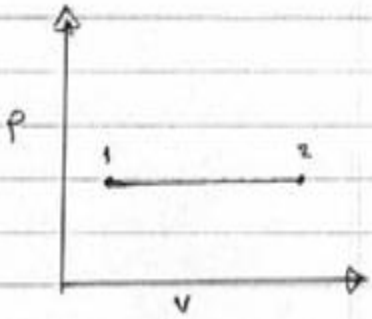
For perfect gas: $\Delta U = \int_1^2 C_v \, dT$

(b) Constant pressure process : (Isobaric)

$\Delta U = Q - W$

$W_{12} = P \Delta V_2$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



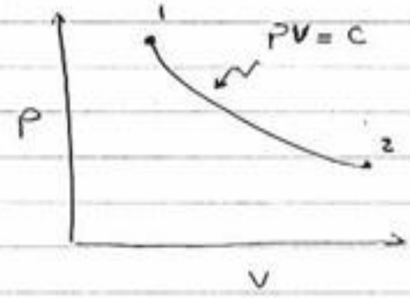
$\Delta U_{12} = Q_{12} - P \Delta V_{12}$

$$\boxed{Q_{12} = \Delta H}$$

For perfect gas,

$\Delta H_{12} = \int_1^2 c_p \, dT$

(c) Constant temp Process (isothermal)



$\Delta u = Q - W$

$W = \int_1^2 P\,dv$

$P_1V_1 = P_2V_2$

$\Delta u_{12} = Q_{12} - \int_1^2 P\,dv$

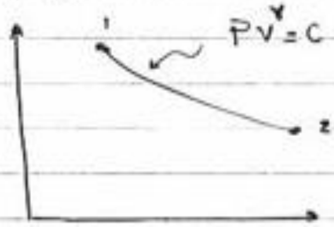
For perfect gas.

$\Delta u_{12} = 0$ since $u = f(t)$ only

$W_{12} = Q_{12} = nRT \ln \frac{V_2}{V_1}$

or $\boxed{W = nRT \ln \frac{P_1}{P_2}}$

(d) Adiabatic process (isentropic) :-



$\Delta U_{12} = Q_{12} - W_{12}$

$Q_{12} = 0$

$\Delta U_{12} = -W_{12}$

For perfect gas

$\Delta U_{12} = C_v(T_2 - T_1)$

$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$

$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$

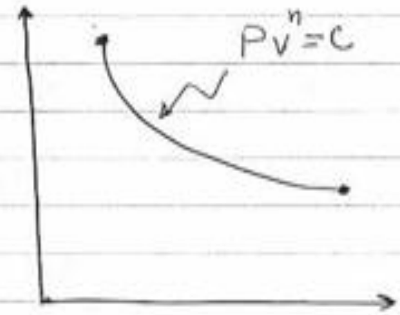
$\frac{V_2}{V_1} = \left(\frac{P_2}{P_1}\right)^{-\frac{1}{\gamma}}$

$\gamma = \frac{C_p}{C_v}$

$$W_{12} = \frac{nRT_1}{\gamma-1}\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right] = \frac{P_1V_1}{\gamma-1}\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

(E) Polytropic Process

The process which is not isothermal nor adiabatic



$$Q = \Delta U_{12} + W_{12}$$

$$W_{12} = \left(\frac{P_2V_2 - P_1V_1}{1-n}\right)$$

For perfect gas

$$W_{12} = \frac{R(T_2-T_1)}{1-n}.$$

$$\Delta u = \int c_v\, dT$$

$$Q = W_{12}\left(\frac{\gamma-n}{\gamma-1}\right)$$

Notes

1- ΔH, Δu is independent on the process if it is reversible or irreversible since it is a state function unlike work, heat.

2- For irreversible, the work cannot be obtained from $\int p\,dv$.

3- First law of thermodynamic applies well to irreversible & reversible process.

4- Throttling process is irreversible $\Delta H = 0$

The Flow work

$$W_{nonflow} = W_{flow} - P_1V_1 + P_2V_2$$

$$W_{flow} = W_{nonflow} + P_1V_1 - P_2V_2 = W_{nonflow} - \Delta PV$$

$$dW_{flow} = dW_{nonflow} - pdv - vdp$$

$$= pdv - pdv - vdp$$

$$dW_{flow} = -vdp$$ الشغل الجرياني

Work flow for ideal gas

Polytropic

$$W_{flow} = \frac{P_1V_1}{n-1}\left[1-\left(\frac{P_1}{P_2}\right)^{\frac{1-\gamma}{\gamma}}\right]$$

$$= \frac{RT_1}{n-1}\left[1-\left(\frac{P_1}{P_2}\right)^{\frac{1-n}{n}}\right]$$

adiabatic

$$-W_{flow} = \frac{\gamma RT_1}{\gamma-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}-1\right]$$

isothermal

$$W_{flow} = RT\ln\frac{V_2}{V_1}.$$

Notes

1) For diatomic gas (O_2, N_2, H_2) $C_p = \frac{7}{2}R$, $C_v = 5/2\,R$,

2) For monoatomic gas (Ar, He) $C_p = \frac{5}{2}R$, $C_v = \frac{3}{2}R$.

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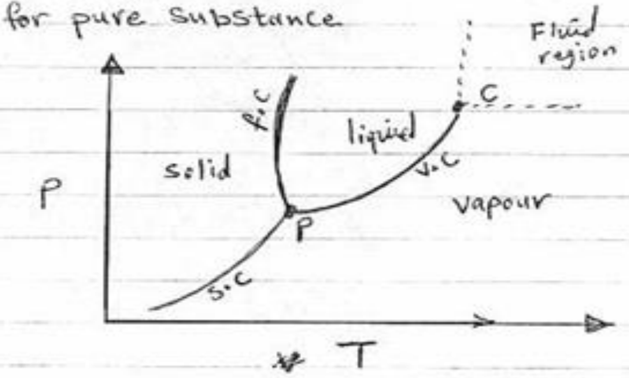
P,V,T Relationship

Chapter -3-

P.V.T Relationship

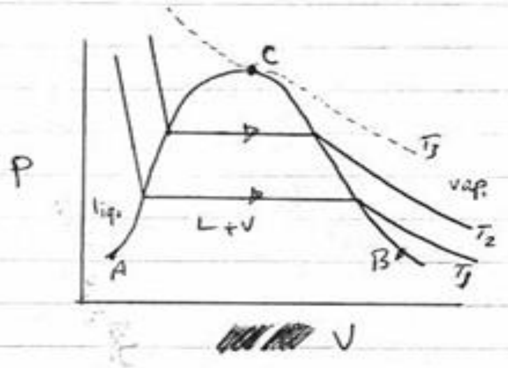
P.V.T behavior for pure substance

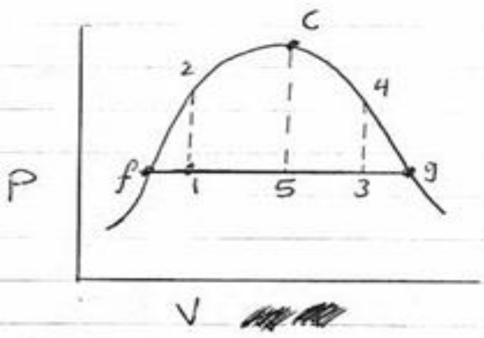


v.c : vaporization curve.

S.C : Sublimation curve.

f.c : fusion curve.





Heating at constant volume:

Rate of expansion > Rate of vaporization

In this case condensation occure when heating. Then it is possible to change a vapour to liquid without condensation.

نموذج بحجم واحد

$$\frac{\text{vapor}}{\text{Liquid}} = \frac{f-1}{1-g}$$

Heating at constant volume. نموذج رقم (2)
when heating the state is fixed until the liquid-vapour mixture reaches critical point then it disappear.
(Tube fills with neither liquid nor vapour but with fluid)

$$\frac{\text{vap.}}{\text{Liquid}} = \frac{f-5}{5-g}$$

Rate of vaporization > Rate of expansion 3 نموذج رقم

$$\frac{\text{vap}}{\text{Liquid}} = \frac{f-3}{3-g}$$

P.V.T relationships for liquid and solids

for a pvT system

$$V = f(T,P)$$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{------} (1)$$

Volume expansivity $(\beta) = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

Isothermal Compressibility $K_t = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

} تعريفين عامين

dividing eqn. (1) by V leads to

$$\frac{dV}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P dT + \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\boxed{\frac{dV}{V} = \beta\, dT - K_t\, dP} \quad \text{-------(2)}$$

1- β and K_t are function of T, P, they increases as T increases

2- β and K_t are constant when change in T and P is relatively Small

3- when a fluid is incompressible $\Rightarrow \beta, K_t \Rightarrow 0$

4- Integrating eqn. (2) leads to

$$\boxed{\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - Kt(P_2 - P_1)} \quad \text{-----(3)}$$

Ex. For acetone at 20 °C and 1 bar, $\beta = 1.487 \times 10^{-5}\ °C^{-1}$

$K_t = 62 \times 10^{-6}\ bar^{-1}$ and $V = 1.287\ cm^3/g$.

Find ; (a) The value of $\left(\frac{\partial P}{\partial T}\right)_V$

(b) The pressure generated when acetone is heated at constant volume from 20 °C and 1 bar to 30 °C

(c) The volume change when acetone is changed from 20 °C and 1 bar to 0 °C and 10 bar

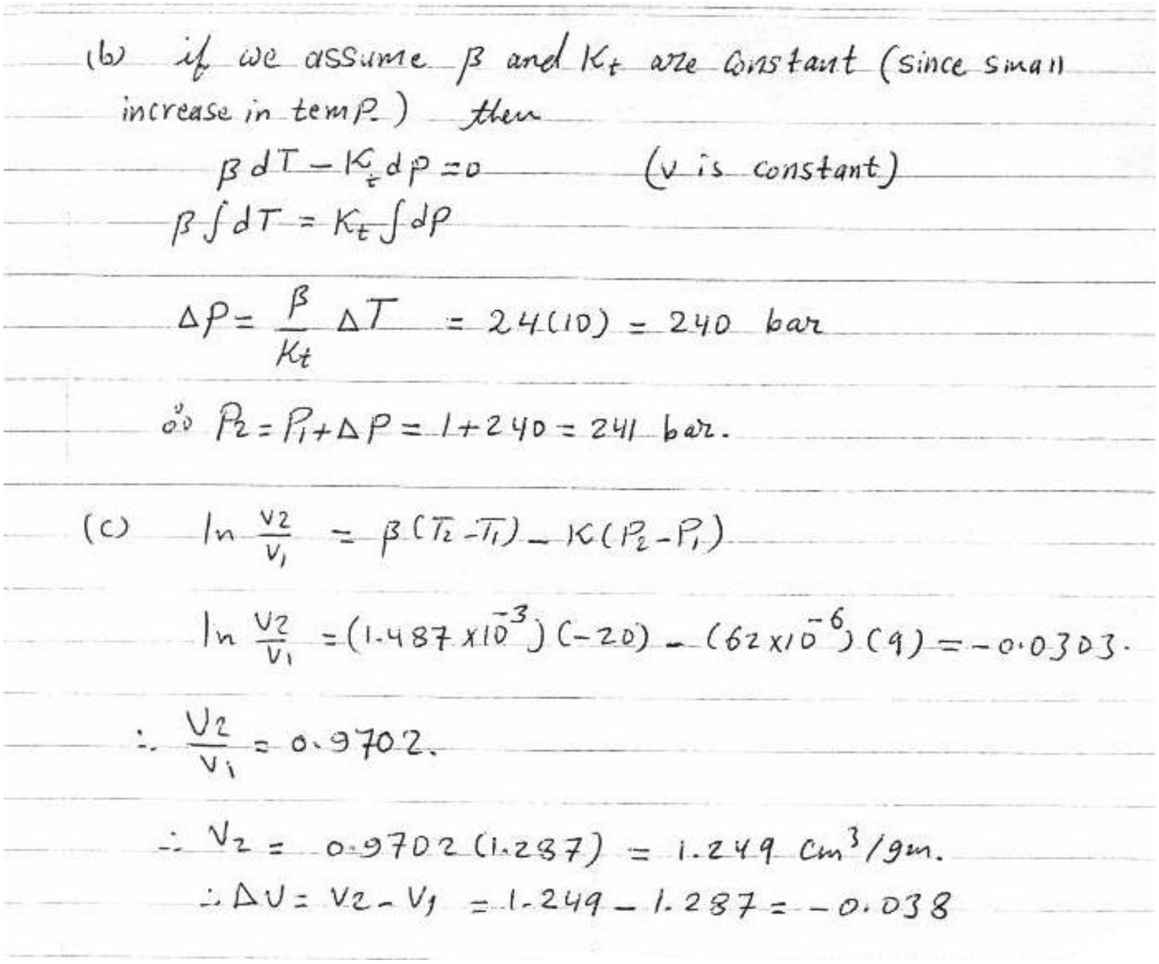
Soln.-

(a) $\frac{dV}{V} = \beta\, dT - K_t\, dP$

At constant volume $dV = 0$

$\therefore \quad \beta\, dT = K_t\, dP$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K_t} = \frac{1.487 \times 10^{-3}}{62 \times 10^{-6}} = 24\ bar\ °C^{-1}$$



(b) if we assume β and K_t are constant (since small increase in temp.) then

$$\beta \, dT - K_t \, dp = 0 \qquad (v \text{ is constant})$$

$$\beta \int dT = K_t \int dP$$

$$\Delta P = \frac{\beta}{K_t} \Delta T = 24(10) = 240 \text{ bar}$$

$$\therefore P_2 = P_1 + \Delta P = 1 + 240 = 241 \text{ bar.}$$

(c) $$\ln \frac{V_2}{V_1} = \beta (T_2 - T_1) - K(P_2 - P_1)$$

$$\ln \frac{V_2}{V_1} = (1.487 \times 10^{-3})(-20) - (62 \times 10^{-6})(9) = -0.0303.$$

$$\therefore \frac{V_2}{V_1} = 0.9702.$$

$$\therefore V_2 = 0.9702(1.287) = 1.249 \text{ cm}^3/\text{gm}.$$

$$\therefore \Delta V = V_2 - V_1 = 1.249 - 1.287 = -0.038$$

Behaviour of Real gas

Ideal gas	Real gas
1- No attraction forces between molecules.	1- There is an attraction forces between the molecules.
2- Volume of molecules is negligible.	2- The volume of molecules is not negligible.
3- Pressure = 3 atm	3- The pressure is very high $P > 3$ a
4- Equation of state is $PV = nRT$ (i.e $Z=1$)	4- Equation of state is $PV = ZnRT$ $Z \neq 1$, depends on conditions (T, P)
5- $\lim_{P \to 0} \left(\frac{PV}{RT}\right) = 1$ for all temp. 6- $\lim_{T \to \infty} \left(\frac{PV}{RT}\right) = 1$ for all press.	5- There are more than 100 equation of state express the P.V.T relations.

P.V.T relations of Real gases

1- Vanderwaal's equation :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where $a = \left(\frac{27}{64}\right)\frac{R^2 T_c^2}{P_c}$ $b = \left(\frac{1}{8}\right)\left(\frac{RT_c}{P_c}\right)$

2- Redlich – Kwong equation

$$\left[P+\frac{a}{T^{1/2}v(v+b)}\right](v-b)=RT$$

v = molar volume.

Where:

$$a=0.4278\,\frac{R^2T_c^{2.5}}{P_c}$$

$$b=0.0867\,\frac{RT_c}{P_c}$$

3- Peng – Robinson

$$P=\frac{RT}{v-b}-\frac{a\alpha}{v(v+b)+b(v-b)}$$

$$a=0.45724\left(\frac{R^2T_c^2}{P_c}\right)$$

$$b=0.0778\left(\frac{RT_r}{P_c}\right)$$

$$\alpha=\left[1+K(1-T_r^{1/2})\right]^2$$

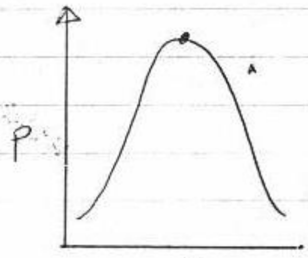
$$K=0.374+1.542\,\omega-0.26\,\omega^2$$

ω = acentric factor. العامل اللامركزي

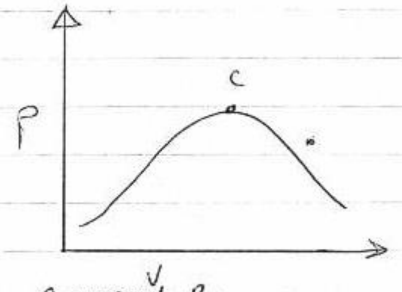
Acentric factor (ω): is a parameter uses in the relation of finding the compressibility factor (Z) of gases which are under relatively high pressure and it has a certain value for each gas.

$$\boxed{\omega = -\ln\left(P_r^{sat.}\right)_{T_r=0.7} - 1}$$

It was noted by experiment that all components has the same form of P.V diagram and the difference is in their critical point.



Component (A)



Component B.

Law of Corresponding state قانون الحالات المتناظرة

" When different substances have the same P_r & T_r, they will have the same Z "

P_r = reduced pressure , $P_r = \frac{P}{P_c}$

T_r = reduced temperature $T_r = \frac{T}{T_c}$

and $v_r = \frac{v}{v_c}$.

The correlation for Z developed by Pitzer & coworkers takes the form

$$Z = Z^0 + \omega Z^1$$

where Z^0 & Z^1 are complex functions of both T_r & P_r.

Note:

Z^0 can be found from Fig. 3-12 if $P_r < 1.0$ } Page 88, 89
Z^0 〃 〃 〃 〃 Fig. 3.13 if $P_r > 1.0$ }
Z^1 〃 〃 〃 〃 Fig 3.14 if $P_r < 1.0$ } Page, 90, 91
Z^1 〃 〃 〃 〃 Fig. 3.15 if $P_r > 1.0$ }

ω, T_c, P_c can be found from Appendix B Page 571.

Generalized Correlation for Liquids:

1- Rackett proposed a general eqn. for estimation the molar volumes of sat. Liquids

$$V^{sat}\left(\frac{cm^3}{mol}\right) = V_c Z_c^{(1-T_r)^{0.2357}}$$

(The only critical conditions are required)

2- Hyderson & coworkers developed a general method for estimations of liquids volumes, based on the principles of corresponding states:

$$\rho_r = \frac{\rho}{\rho_c} = \frac{1/V}{1/V_c} = \frac{V_c}{V}$$

3- If a volume at certain conditions is known, then we can find the new volume when the conditions differs by

$$V_1 \rho_{r_1} = V_2 \rho_{r_2}$$

$$\boxed{\frac{V_1}{V_2} = \frac{\rho_{r_2}}{\rho_{r_1}}}$$

where; V_2: required volume, V_1 = know volume

ρ_{r_1}, ρ_{r_2} are reduced densities read from Fig.

Generalized Virial-Coefficient Correlation :

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1$$

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}$$

$$Z = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r}$$

$$PV = nZRT$$

$$\frac{V}{n} = \frac{ZRT}{P}$$

Ex: (a) Estimate the density of saturated liquid ammonia at 310 °K

(b) Estimate the density of liquid ammonia at 310 °K and 100 bar.

given $T_c = 405.6$ °K, $P_c = 112.8$ bar, $V_c = 72.5 \times 10^{-6}$ cm^3/mol

$Z_c = 0.242$, $\omega = 0.25$

Soln.

$$T_r = \frac{T}{T_c} = \frac{310}{405.6} = 0.7643$$

$V_c = 72.5$, $Z_c = 0.242$

$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}} = (72.5)(0.242)^{0.2357^{0.2857}}$$

$$V^{sat} = 28.35 \text{ cm}^3/\text{mol.}$$

(b) $T_r = 0.764$, $P_r = \frac{P}{P_c} = \frac{100}{112.8} = 0.887$

From Fig. 3.17 we have $\rho_r = 2.38$

$$V = \frac{V_c}{\rho_r} = \frac{72.5}{2.38} = 30.5 \text{ cm}^3/\text{mol.}$$

oR by using eqn. $V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}}$

$V_1 = 28.35 \text{ cm}^3/\text{mol}$, $\rho_{r_1} = 2.34$, $\rho_{r_2} = 2.38$

$$V_2 = 28.35\left(\frac{2.34}{2.38}\right) = 27.87 \text{ cm}^3/\text{mol.}$$

⟷

Ex. Determine the molar volume of n- butane at 510 °K and 25 bar by;

a) The ideal gas

b) The generalized compressibility factor

c) The generalized virial - Coefficient correlation

given that $T_c = 425.2$ K $P_c = 38$ bar , $\omega = 0.193$.

Soln. (a) $PV = RT \Rightarrow V = \frac{RT}{P} = \frac{83.14(510)}{25} = 1696 \text{ cm}^3/\text{mol.}$

(b) $T_r = \frac{T}{T_c} = \frac{510}{425.2} = 1.198$, $P_r = \frac{25}{38} = 0.658$

From Figs $\Rightarrow$ $Z^0 = 0.86$, $Z^1 = 0.038$

$Z = Z^0 + \omega Z^1 = 0.865 + (0.193)(0.038) = 0.872$

$$V = \frac{ZRT}{P} = \frac{(0.872)(83.14)(510)}{25} = 1479 \ \text{cm}^3/\text{mol.}$$

(c) $B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{1.198^{1.6}} = -0.233$

$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{1.198^{4.2}} = 0.059$

$Z^1 = B^1 \frac{P_r}{T_r} = 0.059\left(\frac{0.658}{1.198}\right) = 0.0324$

$Z^0 = 1 + B^0 \frac{P_r}{T_r} = 1 - 0.233\left(\frac{0.658}{1.198}\right) = 0.872$

$Z = Z^0 + \omega Z^1 = 0.872 + 0.193(0.0324) = 0.878$

$$V = \frac{ZRT}{P} = \frac{0.878(83.14)(510)}{25} = 1489 \ \text{cm}^3/\text{mol.}$$

Example 3.10

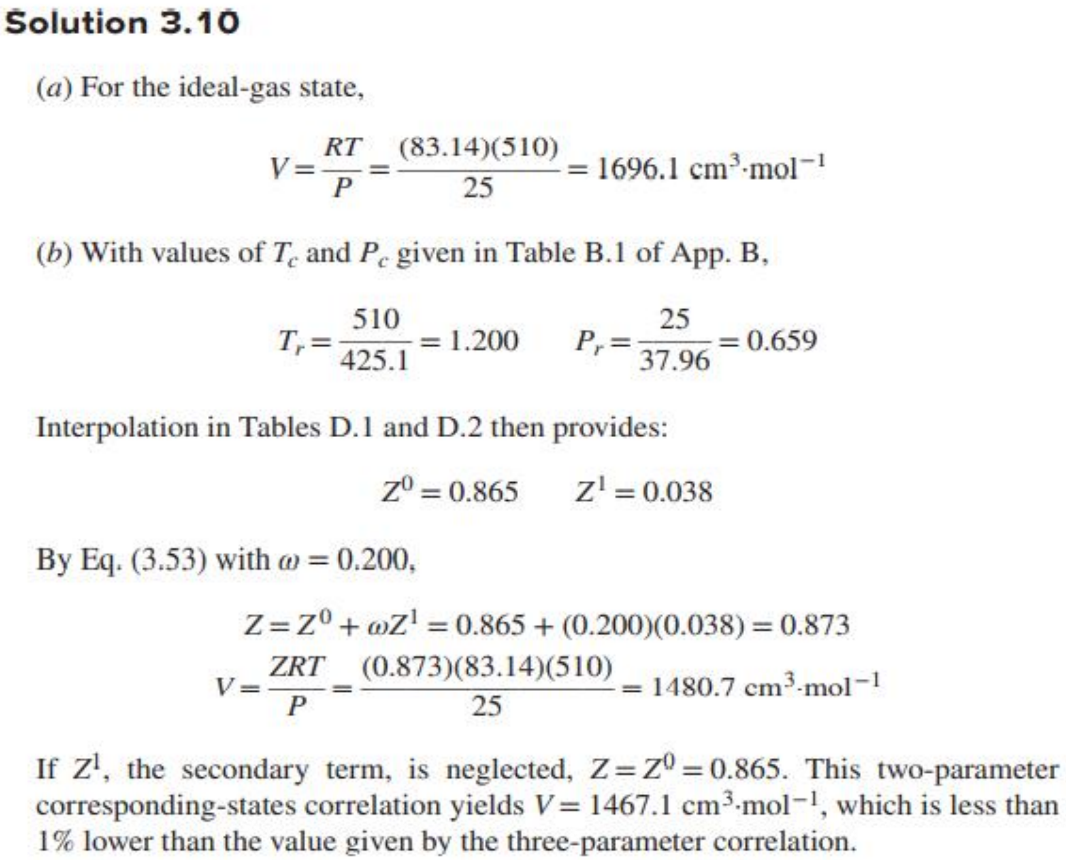
Determine the molar volume of n-butane at 510 K and 25 bar based on each of the following:

(a) The ideal-gas state.

(b) The generalized compressibility-factor correlation.

(c) Equation (3.57), with the generalized correlation for Bˆ.

(d) Equation (3.63), with the generalized correlations for Bˆ and Cˆ.



Solution 3.10

(*a*) For the ideal-gas state,

$$V = \frac{RT}{P} = \frac{(83.14)(510)}{25} = 1696.1 \text{ cm}^3\cdot\text{mol}^{-1}$$

(*b*) With values of T_c and P_c given in Table B.1 of App. B,

$$T_r = \frac{510}{425.1} = 1.200 \qquad P_r = \frac{25}{37.96} = 0.659$$

Interpolation in Tables D.1 and D.2 then provides:

$$Z^0 = 0.865 \qquad Z^1 = 0.038$$

By Eq. (3.53) with $\omega = 0.200$,

$$Z = Z^0 + \omega Z^1 = 0.865 + (0.200)(0.038) = 0.873$$

$$V = \frac{ZRT}{P} = \frac{(0.873)(83.14)(510)}{25} = 1480.7 \text{ cm}^3\cdot\text{mol}^{-1}$$

If Z^1, the secondary term, is neglected, $Z = Z^0 = 0.865$. This two-parameter corresponding-states correlation yields $V = 1467.1$ cm^3·mol^{-1}, which is less than 1% lower than the value given by the three-parameter correlation.

(*c*) Values of B^0 and B^1 are given by Eqs. (3.61) and (3.62):

$$B^0 = -0.232 \qquad B^1 = 0.059$$

Equations (3.59) and (3.57) then yield:

$$\hat{B} = B^0 + \omega B^1 = -0.232 + (0.200)(0.059) = -0.220$$

$$Z = 1 + (-0.220)\frac{0.659}{1.200} = 0.879$$

from which $V = 1489.1$ cm^3·mol^{-1}, a value less than 1% higher than that given by the compressibility-factor correlation.

(*d*) Values of C^0 and C^1 are given by Eqs. (3.66) and (3.67):

$$C^0 = 0.0339 \qquad C^1 = 0.0067$$

Equation (3.65) then yields:

$$\hat{C} = C^0 + \omega C^1 = 0.0339 + (0.200)(0.0067) = 0.0352$$

With this value of $\hat{C}$ and the value of $\hat{B}$ from part (*c*), Eq. (3.63) becomes,

$$Z = 1 + (-0.220)\left(\frac{0.659}{1.200Z}\right) + (0.0352)\left(\frac{0.659}{1.200Z}\right)^2$$

Solution for Z yields $Z = 0.876$ and $V = 1485.8$ cm^3·mol^{-1}. The value of V differs from that of part (*c*) by about 0.2%. An experimental value for V is 1480.7 cm^3·mol^{-1}. Significantly, the results of parts (*b*), (*c*), and (*d*) are in excellent agreement. Mutual agreement at these conditions is suggested by Fig. 3.13.

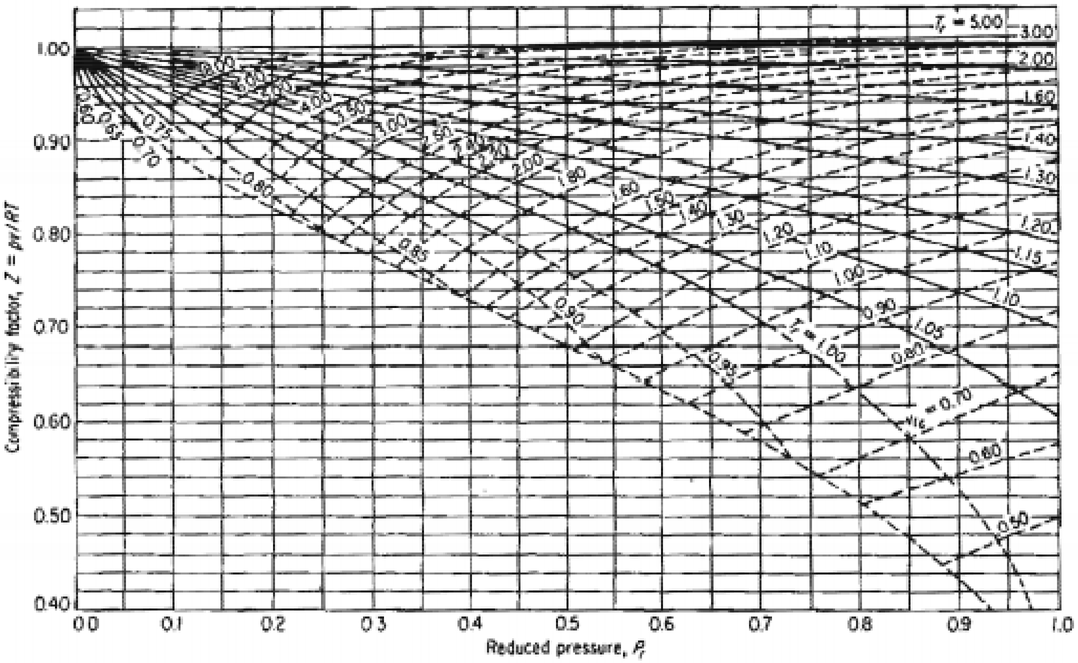


Figure 14.4a Generalized compressibility chart for lower pressures showing z as a function of p_r, T_r, and $\hat{V}_{r_i}$.

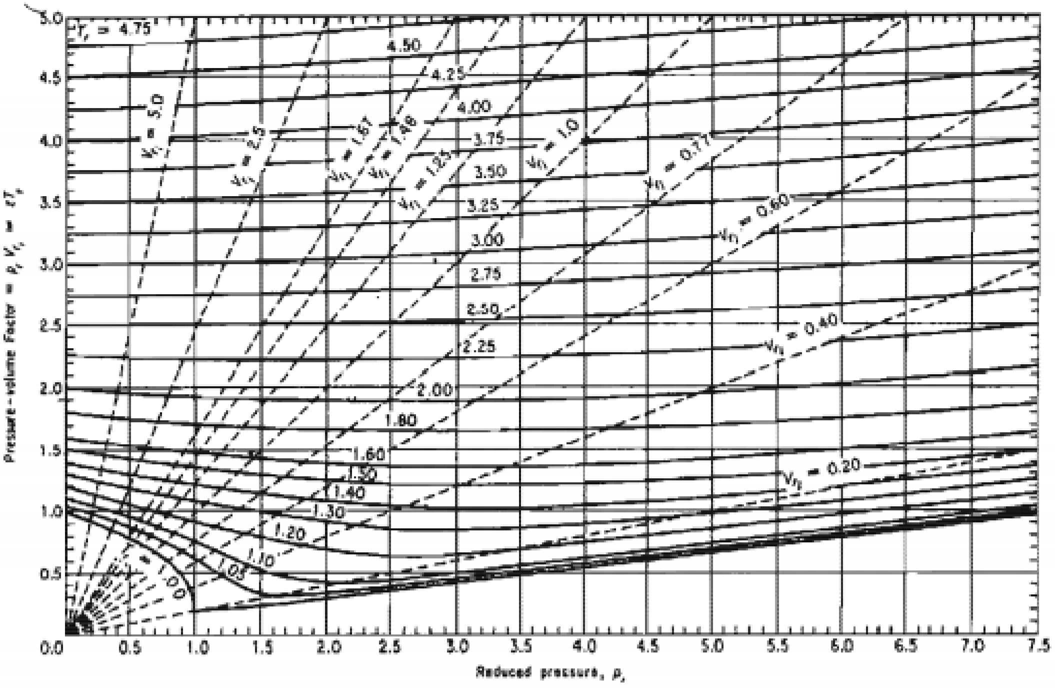


Figure 14.4b Generalized compressibility chart for higher values of p_r.

Appendix D

The Lee/Kesler Generalized-Correlation Tables

The Lee/Kesler tables are adapted and published by permission from "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States," by Byung Ik Lee and Michael G. Kesler, *AIChE J.*, **21,** 510–527 (1975). The numbers printed in italic type are liquid-phase properties.

TABLES

Tables D.1 – D.4	**Correlation for the compressibility factor**
Tables D.5 – D.8	**Correlation for the residual enthalpy**
Tables D.9 – D.12	**Correlation for the residual entropy**
Table D.13 – D.16	**Correlation for the fugacity coefficient**

Table D.1: Values of Z^0

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
0.30	*0.0029*	*0.0145*	*0.0290*	*0.0579*	*0.1158*	*0.1737*	*0.2315*	0.2892
0.35	*0.0026*	*0.0130*	*0.0261*	*0.0522*	*0.1043*	*0.1564*	*0.2084*	0.2604
0.40	*0.0024*	*0.0119*	*0.0239*	*0.0477*	*0.0953*	*0.1429*	*0.1904*	0.2379
0.45	*0.0022*	*0.0110*	*0.0221*	*0.0442*	*0.0882*	*0.1322*	*0.1762*	0.2200
0.50	*0.0021*	*0.0103*	*0.0207*	*0.0413*	*0.0825*	*0.1236*	*0.1647*	0.2056

Table D.2: Values of Z^1

$P_r =$	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
0.30	*−0.0008*	*−0.0040*	*−0.0081*	*−0.0161*	*−0.0323*	*−0.0484*	*−0.0645*	−0.0806
0.35	*−0.0009*	*−0.0046*	*−0.0093*	*−0.0185*	*−0.0370*	*−0.0554*	*−0.0738*	−0.0921
0.40	*−0.0010*	*−0.0048*	*−0.0095*	*−0.0190*	*−0.0380*	*−0.0570*	*−0.0758*	−0.0946
0.45	*−0.0009*	*−0.0047*	*−0.0094*	*−0.0187*	*−0.0374*	*−0.0560*	*−0.0745*	−0.0929
0.50	*−0.0009*	*−0.0045*	*−0.0090*	*−0.0181*	*−0.0360*	*−0.0539*	*−0.0716*	−0.0893

1.7 GENERALIZED CORRELATIONS FOR GASES

Generalized correlations find widespread use. Most popular are correlations of the kind developed by Pitzer and coworkers for the compressibility factor Z and for the second virial coefficient B. 16

Pitzer Correlations for the Compressibility Factor

The correlation for Z is: Z

$$Z = Z^0 + \omega Z^1 \tag{3.53}$$

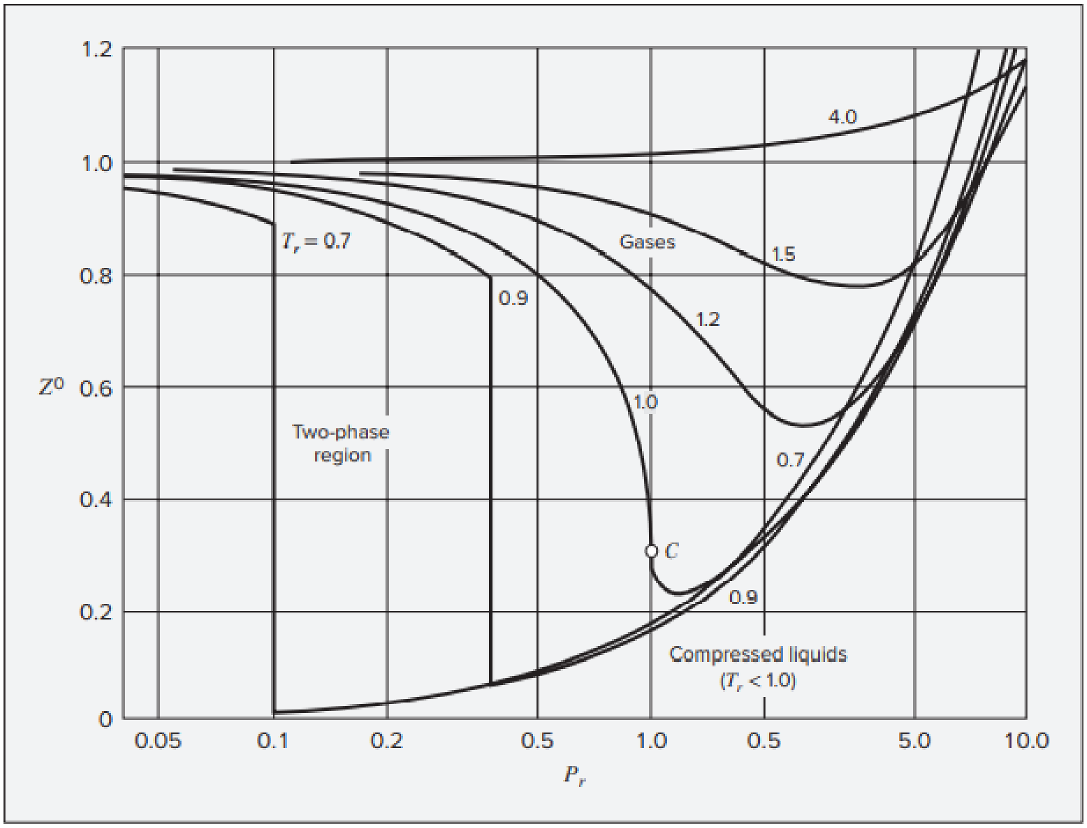


Figure 3.11: The Lee/Kesler correlation for $Z^0 = F^0(T_r, P_r)$.

1.8 GENERALIZED CORRELATIONS FOR LIQUIDS

Although the molar volumes of liquids can be calculated by means of generalized cubic equations of state, the results are often not of high accuracy. However, the Lee/Kesler correlation includes data for sub cooled liquids, and Fig. 3.11 illustrates curves for both liquids and gases. Values for both phases are provided in Tables D.1 through D.4 of App. D. Recall, however, that this correlation is most suitable for nonpolar and slightly polar fluids.

In addition, generalized equations are available for the estimation of molar volumes of saturated liquids. The simplest equation, proposed by Rackett, 22 is an example:

$$V^{sat} = V_c Z_c^{(1-T_r)^{2/7}} \qquad (3.68)$$

An alternative form of this equation is sometimes useful:

$$Z^{sat} = \frac{P_r}{T_r} Z_c^{[1+(1-T_r)^{2/7}]} \qquad (3.69)$$

The only data required are the critical constants, given in Table B.1 of App. B. Results are usually accurate to 1 or 2%. Lydersen, Greenkorn, and Hougen23 developed a two-parameter corresponding-states correlation for estimation of liquid volumes. It provides a correlation of reduced density ρr as a function of reduced temperature and pressure. By definition,

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V} \qquad (3.70)$$

Where ρc is the density at the critical point. The generalized correlation is shown by Fig. 3.15. This figure may be used directly with Eq. (3.70) for determination of liquid volumes if the value of the critical volume is known. A better procedure is to make use of a single known liquid volume (state 1) by the identity,

$$V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}} \qquad (3.71)$$

where

$V_2 =$ required volume
$V_1 =$ known volume
$\rho_{r_1}, \rho_{r_2} =$ reduced densities read from Fig. 3.15

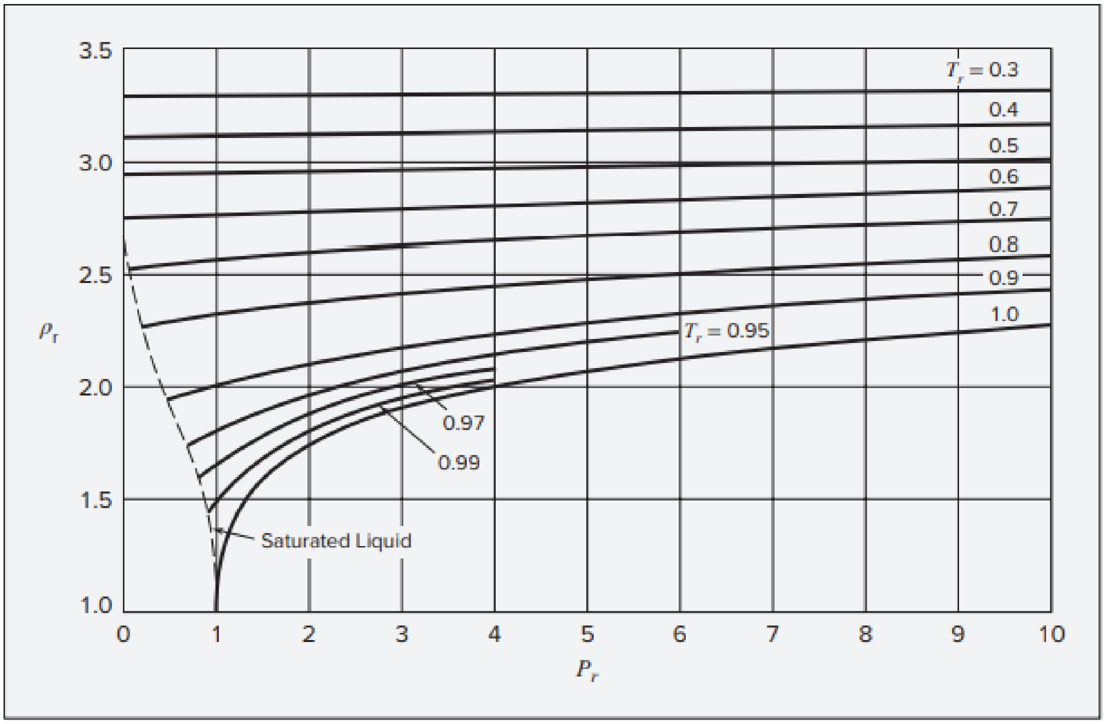
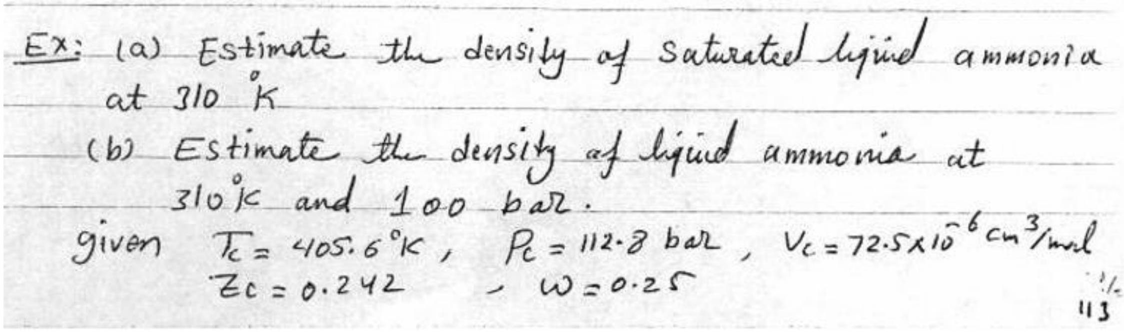


Figure 3.15: Generalized density correlation for liquids.

P,V,T Relationship



Ex: (a) Estimate the density of saturated liquid ammonia at 310 °K

(b) Estimate the density of liquid ammonia at 310 °K and 100 bar.

given $T_c = 405.6\,°K$, $P_c = 112.8$ bar, $V_c = 72.5 \times 10^{-6}\ cm^3/mol$

$Z_c = 0.242$, $\omega = 0.25$

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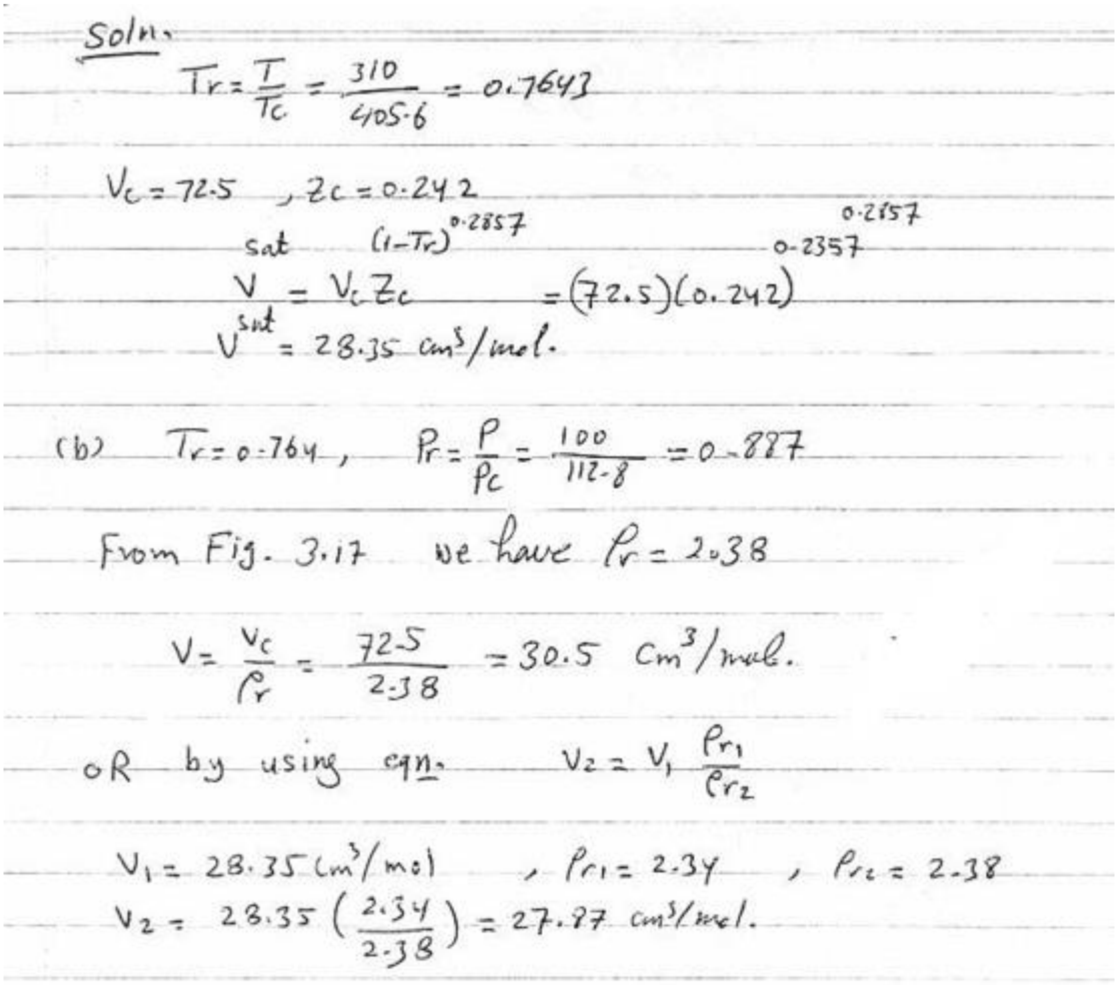


Soln.

$$T_r = \frac{T}{T_c} = \frac{310}{405.6} = 0.7643$$

$V_c = 72.5$, $Z_c = 0.242$

$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}} = (72.5)(0.242)^{0.2357^{0.2857}}$$

$$V^{sat} = 28.35\ cm^3/mol.$$

(b) $T_r = 0.764$, $P_r = \frac{P}{P_c} = \frac{100}{112.8} = 0.887$

From Fig. 3.17 we have $\rho_r = 2.38$

$$V = \frac{V_c}{\rho_r} = \frac{72.5}{2.38} = 30.5\ cm^3/mol.$$

oR by using eqn. $V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}}$

$V_1 = 28.35\ cm^3/mol$, $\rho_{r_1} = 2.34$, $\rho_{r_2} = 2.38$

$$V_2 = 28.35\left(\frac{2.34}{2.38}\right) = 27.87\ cm^3/mol.$$

Ex. Determine the molar volume of n-butane at 510 °K and 25 bar by;

a) The ideal gas

b) The generalized compressibility factor

c) The generalized virial-coefficient correlation

given that $T_c = 425.2\ K$ $P_c = 38$ bar , $\omega = 0.193$.

Soln. (a) $PV = RT \Rightarrow V = \frac{RT}{P} = \frac{83.14(510)}{25} = 1696\ cm^3/mol.$

(b) $T_r = \frac{T}{T_c} = \frac{510}{425.2} = 1.198$, $P_r = \frac{25}{38} = 0.658$

From Figs $\Rightarrow$ $Z^0 = 0.86$, $Z^1 = 0.038$

$Z = Z^0 + \omega Z^1 = 0.865 + (0.193)(0.038) = 0.872$

$$V = \frac{ZRT}{P} = \frac{(0.872)(83.14)(510)}{25} = 1479\ Cm^3/mol.$$

(c) $B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0.083 - \frac{0.422}{1.198^{1.6}} = -0.233$

$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = 0.139 - \frac{0.172}{1.198^{4.2}} = 0.059$

$Z^1 = B^1 \frac{P_r}{T_r} = 0.059\left(\frac{0.658}{1.198}\right) = 0.0324$

$Z^0 = 1 + B^0 \frac{P_r}{T_r} = 1 - 0.233\left(\frac{0.658}{1.198}\right) = 0.872$

$Z = Z^0 + \omega Z^1 = 0.872 + 0.193(0.0324) = 0.878$

$$V = \frac{ZRT}{P} = \frac{0.878(83.14)(510)}{25} = 1489\ Cm^3/mol.$$

Example 3.10

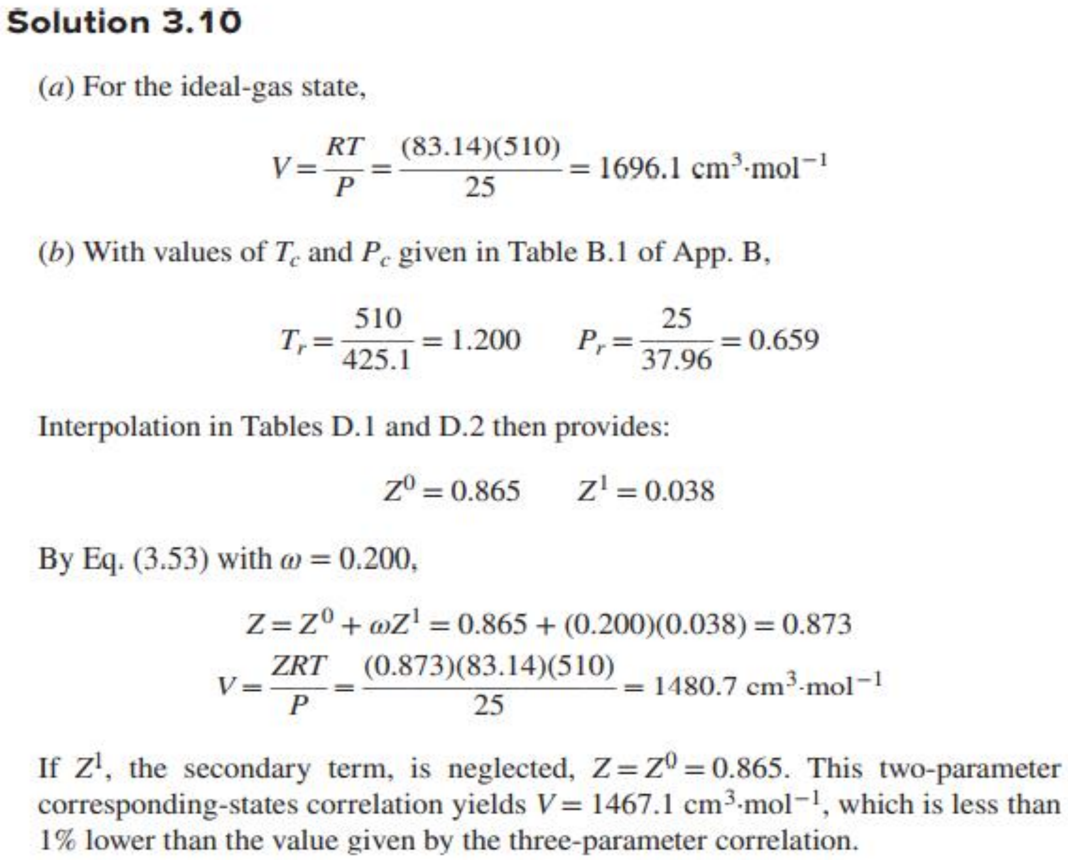
Determine the molar volume of n-butane at 510 K and 25 bar based on each of the following:

(a) The ideal-gas state.

(b) The generalized compressibility-factor correlation.

(c) Equation (3.57), with the generalized correlation for Bˆ.

(d) Equation (3.63), with the generalized correlations for Bˆ and Cˆ.



Solution 3.10

(*a*) For the ideal-gas state,

$$V = \frac{RT}{P} = \frac{(83.14)(510)}{25} = 1696.1 \text{ cm}^3\text{·mol}^{-1}$$

(*b*) With values of T_c and P_c given in Table B.1 of App. B,

$$T_r = \frac{510}{425.1} = 1.200 \qquad P_r = \frac{25}{37.96} = 0.659$$

Interpolation in Tables D.1 and D.2 then provides:

$$Z^0 = 0.865 \qquad Z^1 = 0.038$$

By Eq. (3.53) with $\omega = 0.200$,

$$Z = Z^0 + \omega Z^1 = 0.865 + (0.200)(0.038) = 0.873$$

$$V = \frac{ZRT}{P} = \frac{(0.873)(83.14)(510)}{25} = 1480.7 \text{ cm}^3\text{·mol}^{-1}$$

If Z^1, the secondary term, is neglected, $Z = Z^0 = 0.865$. This two-parameter corresponding-states correlation yields $V = 1467.1$ cm^3·mol^{-1}, which is less than 1% lower than the value given by the three-parameter correlation.

(*c*) Values of B^0 and B^1 are given by Eqs. (3.61) and (3.62):

$$B^0 = -0.232 \qquad B^1 = 0.059$$

Equations (3.59) and (3.57) then yield:

$$\hat{B} = B^0 + \omega B^1 = -0.232 + (0.200)(0.059) = -0.220$$

$$Z = 1 + (-0.220)\frac{0.659}{1.200} = 0.879$$

from which $V = 1489.1$ cm^3·mol^{-1}, a value less than 1% higher than that given by the compressibility-factor correlation.

(*d*) Values of C^0 and C^1 are given by Eqs. (3.66) and (3.67):

$$C^0 = 0.0339 \qquad C^1 = 0.0067$$

Equation (3.65) then yields:

$$\hat{C} = C^0 + \omega C^1 = 0.0339 + (0.200)(0.0067) = 0.0352$$

With this value of $\hat{C}$ and the value of $\hat{B}$ from part (*c*), Eq. (3.63) becomes,

$$Z = 1 + (-0.220)\left(\frac{0.659}{1.200Z}\right) + (0.0352)\left(\frac{0.659}{1.200Z}\right)^2$$

Solution for Z yields $Z = 0.876$ and $V = 1485.8$ cm^3·mol^{-1}. The value of V differs from that of part (*c*) by about 0.2%. An experimental value for V is 1480.7 cm^3·mol^{-1}. Significantly, the results of parts (*b*), (*c*), and (*d*) are in excellent agreement. Mutual agreement at these conditions is suggested by Fig. 3.13.

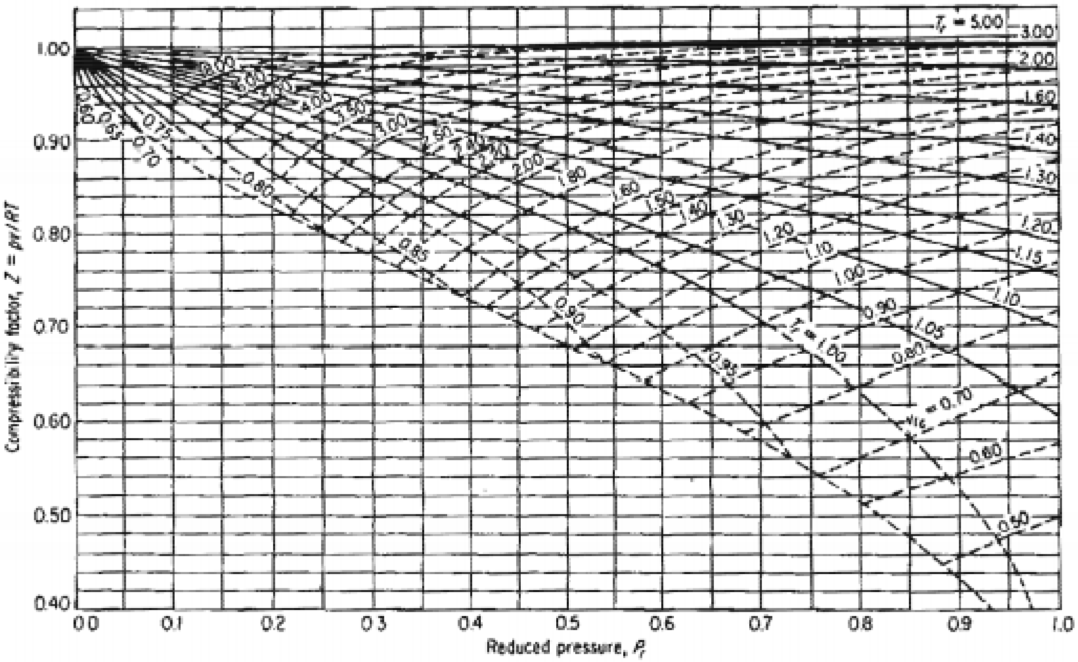


Figure 14.4a Generalized compressibility chart for lower pressures showing z as a function of p_r, T_r, and $\hat{V}_{r_i}$.

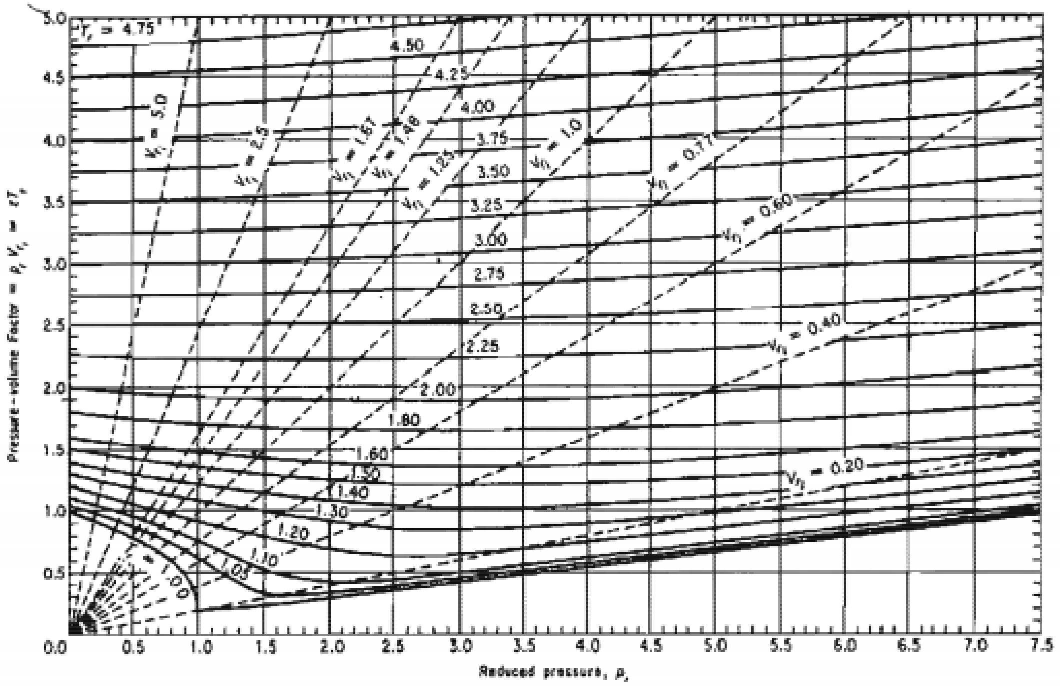
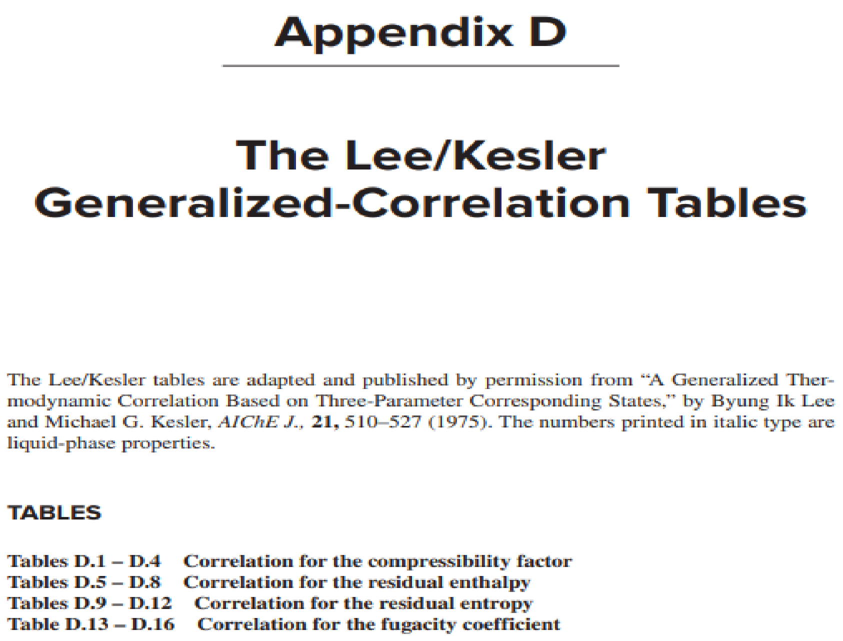


Figure 14.4b Generalized compressibility chart for higher values of p_r.



Appendix D

The Lee/Kesler Generalized-Correlation Tables

The Lee/Kesler tables are adapted and published by permission from "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States," by Byung Ik Lee and Michael G. Kesler, *AIChE J.*, **21,** 510–527 (1975). The numbers printed in italic type are liquid-phase properties.

TABLES

Tables D.1 – D.4	**Correlation for the compressibility factor**
Tables D.5 – D.8	**Correlation for the residual enthalpy**
Tables D.9 – D.12	**Correlation for the residual entropy**
Table D.13 – D.16	**Correlation for the fugacity coefficient**

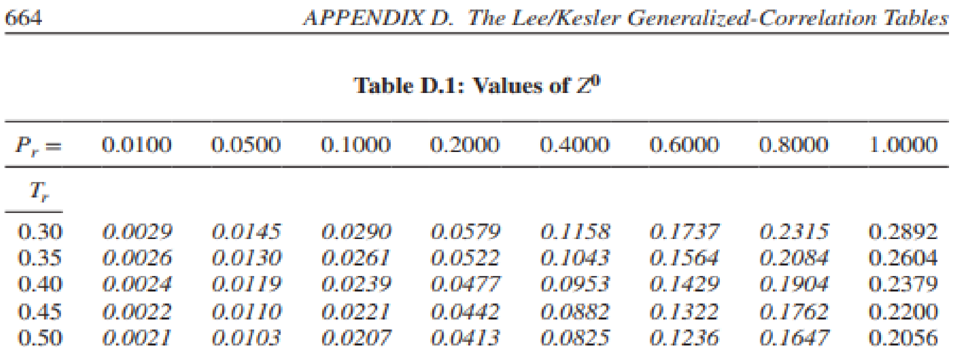


Table D.1: Values of Z^0

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T_r								
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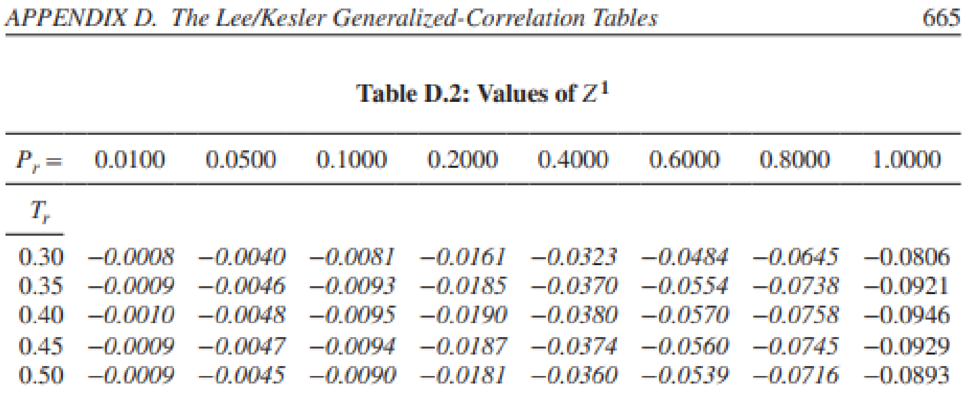

Table D.2: Values of Z^1

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Pitzer Correlations for the Compressibility Factor

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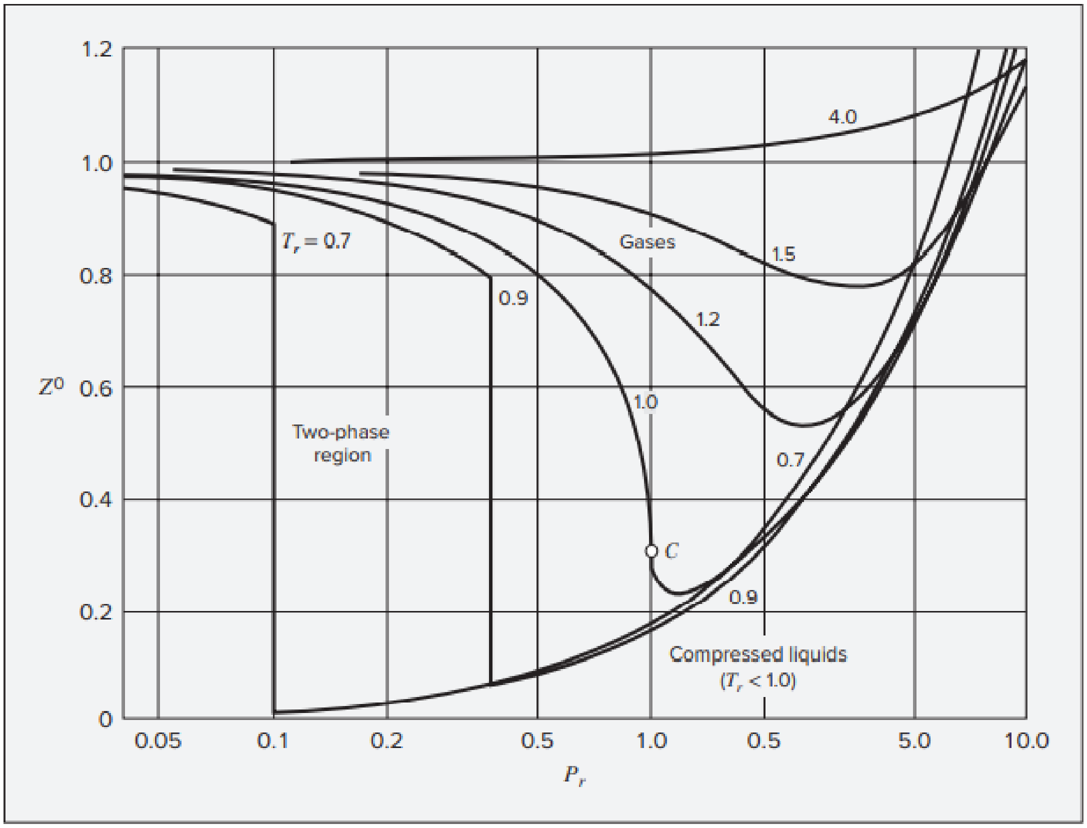

Figure 3.11: The Lee/Kesler correlation for $Z^0 = F^0(T_r, P_r)$.

1.8 GENERALIZED CORRELATIONS FOR LIQUIDS

Although the molar volumes of liquids can be calculated by means of generalized cubic equations of state, the results are often not of high accuracy. However, **the Lee/Kesler** correlation includes data for sub cooled liquids, and Fig. 3.11 illustrates curves for both liquids and gases. Values for both phases are provided in Tables D.1 through D.4 of App. D. Recall, however, that this correlation is most suitable for nonpolar and slightly polar fluids.

In addition, generalized equations are available for the estimation of molar volumes of saturated liquids. The simplest equation, proposed by Rackett, 22 is an example:p

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An alternative form of this equation is sometimes useful:

$$Z^{\text{sat}} = \frac{P_r}{T_r} Z_c^{[1+(1-T_r)^{2/7}]} \tag{3.69}$$

The only data required are the critical constants, given in Table B.1 of App. B. Results are usually accurate to 1 or 2%. Lydersen, Greenkorn, and Hougen23 developed a two-parameter corresponding-states correlation for estimation of liquid volumes. It provides a correlation of reduced density ρr as a function of reduced temperature and pressure. By definition,

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V} \tag{3.70}$$

Where ρc is the density at the critical point. The generalized correlation is shown by Fig. 3.15. This figure may be used directly with Eq. (3.70) for determination of liquid volumes if the value of the critical volume is known. A better procedure is to make use of a single known liquid volume (state 1) by the identity,

$$V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}} \tag{3.71}$$

where

V_2 = required volume

V_1 = known volume

ρ_{r_1}, ρ_{r_2} = reduced densities read from Fig. 3.15

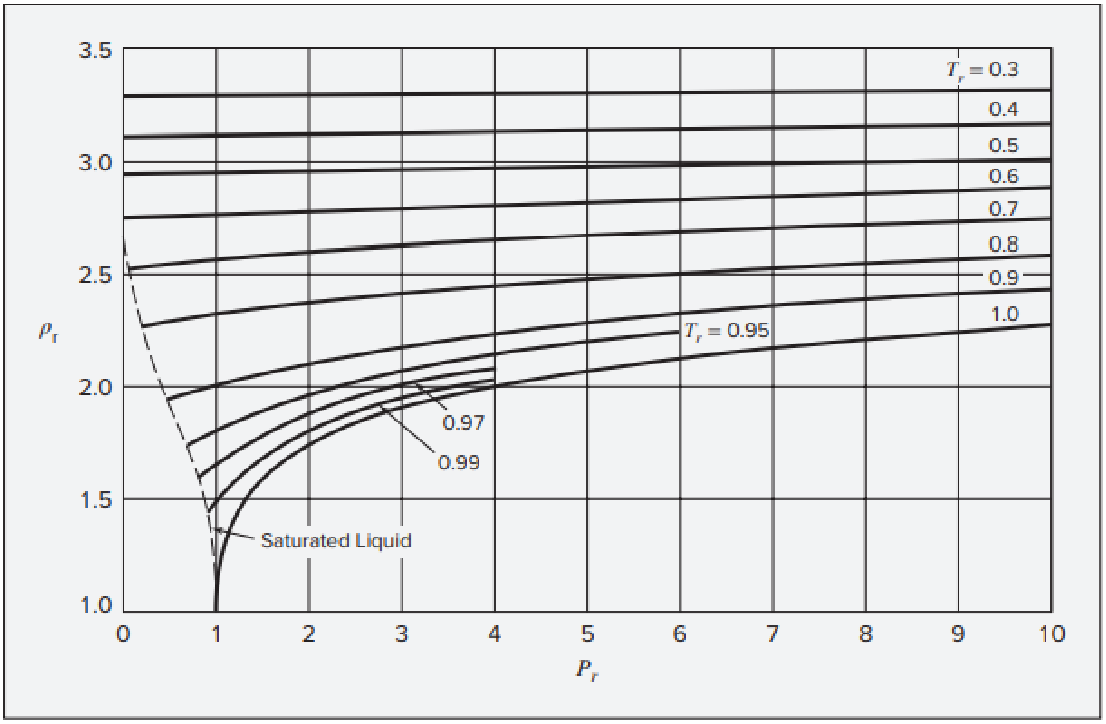


Figure 3.15: Generalized density correlation for liquids.

Chapter 4

Heat Effects

Heat effects refer to physical and chemical phenomena that are associated with heat transfer to or from a system or that result in temperature changes within a system, or both. The simplest **example** of a heat effect is the **heating or cooling** of a fluid by the purely physical direct transfer of heat to or from the fluid. The temperature changes that occur are known as because they may be detected by our sense perception of temperature. Phase changes, physical processes occurring for a pure substance at constant temperature and pressure, are accompanied by latent heats. Chemical reactions are characterized by heats of reaction, which for combustion reactions evolve heat

The following important heat effects are considered in this chapter:

- Sensible heat effects, characterized by temperature changes
- Heat capacities as a function of temperature and their use through defined functions
- Heats of phase transition, i.e., latent heats of pure substances
- Heats of reaction, combustion, and formation
- Heats of reaction as a function of temperature
- The calculation of heat effects for industrial reactions

4.1 SENSIBLE HEAT EFFECTS

Heat transfer to or from a system in which there are no phase transitions, no chemical reactions, and no changes in composition causes a sensible heat effect, i.e., the temperature of the system is caused to change. The need here is for a relation between the quantity of heat transferred and the resulting temperature change.

When the system is a homogeneous substance of constant composition, the phase rule indicates that fixing the values of two intensive properties establishes its state. The molar or specific internal energy of a substance may therefore be expressed as a function of two other state variables. The key thermodynamic variable is temperature. With molar or specific volume chosen arbitrarily, we have U = U (T, V). Then

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

With the definition of C_V provided by Eq. (2.15) this becomes:

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

The final term is zero in two circumstances:

- For any closed-system constant-volume process.
- Whenever the internal energy is independent of volume, as for the ideal-gas state and the incompressible liquid.

In either case, $dU = C_V dT$

and $$\Delta U = \int_{T_1}^{T_2} C_V dT \qquad (4.1)$$

Although real liquids are to some degree compressible, far below their critical temperature they can often be treated as incompressible fluids. The ideal-gas state is also of interest, because actual gases at low pressures approach ideality. For a **mechanically reversible constant-volume process** is simple heating (stirring work is inherently irreversible), for which Q = ΔU, and written for a unit mass or a mole becomes:

$$Q = \Delta U = \int_{T_1}^{T_2} C_V \, dT \qquad \ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

Moreover, Q = ΔH for **mechanically reversible, constant-pressure, closed-system processes** and for the transfer of heat in steady-flow processes where ΔE_P and ΔE_K are negligible and Ws = 0. In either case,

$$Q = \Delta H = \int_{T_1}^{T_2} C_P \, dT \qquad \ldots\ldots\ldots\ldots\ldots\ldots.(2)$$

This equation finds frequent application for flow processes designed for simple heating and cooling of gases, liquids, and solids.

Temperature Dependence of the Heat Capacity

Evaluation of the integral in Eq. (2) requires knowledge of the temperature dependence of the heat capacity. This is usually given by an empirical equation; the two simplest expressions of practical value are:

$$\frac{CP}{R} = \alpha + \beta\, T + \gamma\, T^2 \qquad and \qquad \frac{CP}{R} = a + b\, T + c\, T^{-2}$$

Where α, β, and γ and a, b, and c are constants characteristic of the particular substance. With the exception of the last term, these equations are of the same form. We therefore combine them to provide a single expression:

$$\frac{CP}{R} = A + B\, T + C\, T^2 + D\, T^{-2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4.4)$$

Where either C or D is usually zero, **depending on the substance** considered. Because the ratio **CP/R is dimensionless,** the units of CP are governed by the choice of R. The parameters are independent of temperature, but, at least in principle, depend on the value of the constant pressure. **However**, **for liquids and solids** the effect of pressure is usually **very small**.

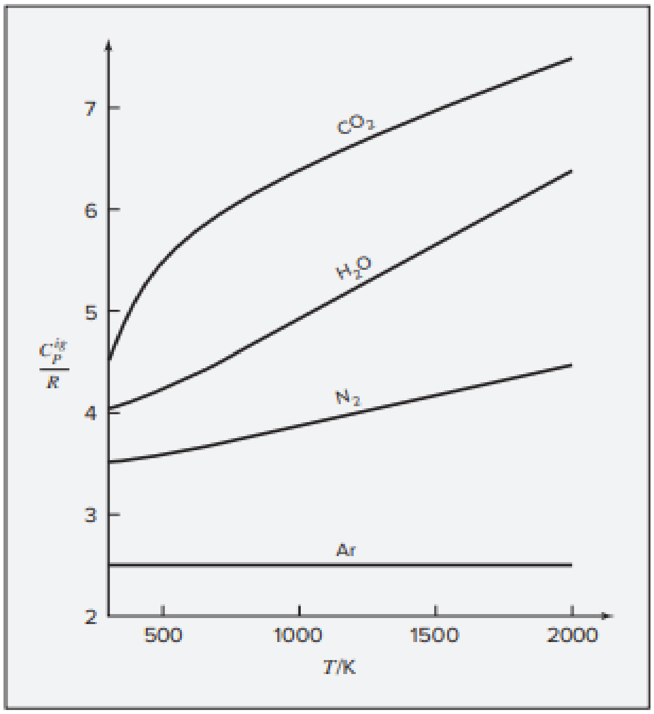
Values of the constants for selected solids and liquids are given **in Tables C.2 and C.3 of App. C**. The heat capacities of solids and liquids are usually found by direct measurement. Correlations for the heat capacities of many solids and liquids are given by Perry and Green.

Heat Capacity in the Ideal-Gas State

Accordingly, ideal-gas-state heat capacities, designated by CP^{ig} and CV^{ig}, are functions of temperature, but independent of pressure, providing for ease of correlation. Fig. 4.1 illustrates the temperature dependence of CP^{ig} for several representative substances.

The contribution becomes larger the more complex the molecule and increases monotonically with temperature, as is evident from the curves in Fig. 4.1 for H2O and CO2. The trend with molecular size and complexity is **illustrated by the values of $\frac{CP^{ig}}{R}$ at 298 K in Table C.1 of App. C.**

Figure 4.1: Ideal-gas-state heat capacities of argon, nitrogen, water, and carbon dioxide. Ideal-gas-state heat capacities increase smoothly with increasing temperature toward an upper limit, which is reached when all translational, rotational, and vibrational modes of molecular motion are fully excited.



Statistical mechanics provides a basic equation for the temperature dependence of the ideal-gas-state internal energy:

Temperature dependence is expressed analytically by equations such as Eq. (4.4), here written:

$$\frac{CP^{ig}}{R} = A + B\,T + C\,T^2 + D\,T^{-2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4.5)$$

Values of the constants are given in Table C.1 of App. C for a number of common organic and inorganic gases. More accurate but more complex equations are found in the literature. As a result of Eq. (3.12), the two ideal-gas-state heat capacities are related:

$$\frac{CV^{ig}}{R} = \frac{CP^{ig}}{R} - 1 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.(4.6)$$

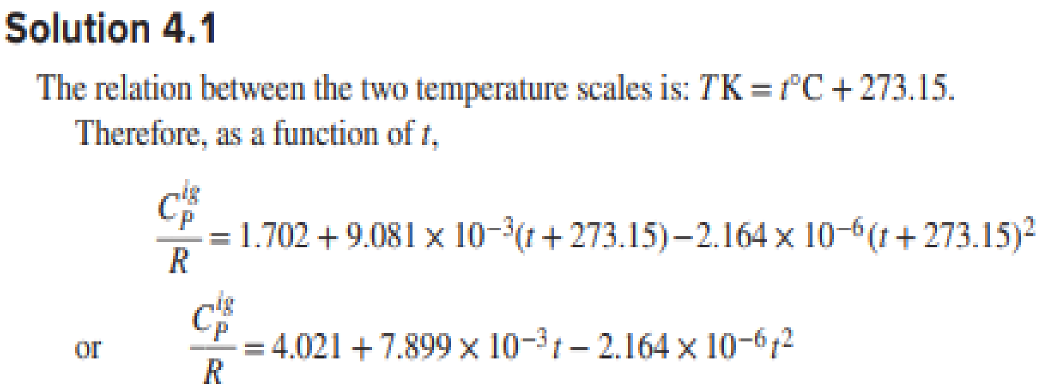
The temperature dependence of CV ig /R follows from the temperature dependence of $\frac{CP^{ig}}{R}$. Although ideal-gas-state heat capacities are exactly correct for real gases only at zero pressure, the departure of real gases from the ideal-gas state is seldom significant at pressures below several bars, and here CP^{ig} *and* CV^{ig} are usually good approximations to their true heat capacities. Reference to Fig. 3.14 indicates a vast range of conditions at Pr < 0.1 for which assumption of the ideal-gas state is usually a suitable approximation. For most substances Pc exceeds 30 bar, which means that ideal-gas state behavior is often closely approximated up to a pressure of at least 3 bar.

Example 4.1

The parameters listed in Table C.1 of Appendix C require use of Kelvin temperatures in Eq. (4.5). Equations of the same form may also be developed for use with temperatures in °C, but the parameter values are different. The molar heat capacity of methane in the ideal-gas state is given as a function of temperature in kelvins by:

$$\frac{C_P^{ig}}{R} = 1.702 + 9.081 \times 10^{-3}\,T - 2.164 \times 10^{-6}\,T^2$$

Where the parameter values are from Table C.1. Develop an equation for $\frac{CP^{ig}}{R}$ for use with temperatures in °C.



Solution 4.1

The relation between the two temperature scales is: $T\,\text{K} = t\,°\text{C} + 273.15$.

Therefore, as a function of t,

$$\frac{C_P^{ig}}{R} = 1.702 + 9.081 \times 10^{-3}(t + 273.15) - 2.164 \times 10^{-6}(t + 273.15)^2$$

or

$$\frac{C_P^{ig}}{R} = 4.021 + 7.899 \times 10^{-3}\,t - 2.164 \times 10^{-6}\,t^2$$

Gas mixtures of constant composition behave exactly as do pure gases. In the ideal-gas state, molecules in mixtures have no influence on one another, and each gas exists independent of the others. The ideal-gas-state heat capacity of a mixture is therefore the mole-fraction weighted sum of the heat capacities of the individual gases. Thus, for gases A, B, and C, the molar heat capacity of a mixture in the ideal-gas state is:

$$CP^{ig}_{mixture} = y_A\, CP^{ig}_A + y_B\, CP^{ig}_B + y_C\, CP^{ig}_C \quad \ldots\ldots\ldots\ldots\ldots..(4.7)$$

Where CP^{ig}_A, CP^{ig}_B *and* CP^{ig}_C are the molar heat capacities of pure A, B, and C in the ideal-gas state, and **yA, yB, and yC** are **mole fractions**. Because the heat-capacity polynomial, Eq. (4.5), is linear in the coefficients, the coefficients A, B, C, and D for a gas mixture are similarly given by mole-fraction weighted sums of the coefficients for the pure species.

Evaluation of the Sensible-Heat Integral

Evaluation of the integral ∫ CPdT is accomplished by substitution for CP as a function of T by Eq. (4.4), followed by formal integration. For temperature limits of T_0 and T the result is:

$$\int_{T_0}^{T} \frac{C_P}{R}\, dT = A(T - T_0) + \frac{B}{2}(T^2 - T_0^2) + \frac{C}{3}(T^3 - T_0^3) + D\left(\frac{T - T_0}{T T_0}\right) \qquad (4.8)$$

Given T0 and T, the calculation of Q or ΔH is straightforward. Less direct is the calculation of T, given T0 and Q or ΔH. Here, an iteration scheme may be useful. Factoring (T − T0) from each term on the right side of Eq. (4.8) gives:

$$\int_{T_0}^{T} \frac{C_P}{R}\, dT = \left[A + \frac{B}{2}(T + T_0) + \frac{C}{3}(T^2 + T_0^2 + T T_0) + \frac{D}{T T_0}\right](T - T_0)$$

We identify the quantity in square brackets as **⟨CP⟩H/R, where ⟨CP⟩H** is defined as **a mean heat capacity** for the temperature range from T_0 to T:

$$CP^{ig}_{mh} = \frac{\int_{T_1}^{T_2} CP\ dT}{T_2 - T_1} \qquad mh = \text{mean heat capacity}$$

And

$$\frac{CP^{ig}_{mh}}{R} = A + B\, T_{am} + \frac{C}{3}\left(4T^2_{am} + T_1T_2\right) + \frac{D}{T_1T_2}$$

$$T_{am} = \frac{T_1 + T_2}{2}$$

$$\frac{\langle C_P\rangle_H}{R} = A + \frac{B}{2}(T + T_0) + \frac{C}{3}(T^2 + T_0^2 + T T_0) + \frac{D}{T T_0} \qquad (4.9)$$

Equation (4.2) may therefore be written:

$$\boldsymbol{\Delta H = CP_{H}^{ig}(T - T_0)} \qquad \boldsymbol{\Delta H = CP_{mh}^{ig}(T_2 - T_1)} \quad \ldots\ldots\ldots.\boldsymbol{(4.10}$$

$$\Delta H = \langle C_P \rangle_H (T - T_0) \qquad (4.10)$$

The angular brackets enclosing **CP identify** it as a **mean value; subscript H** denotes a mean value specific to enthalpy calculations and distinguishes this mean heat capacity from a similar quantity introduced in the next chapter. Solution of Eq. (4.10) for T gives:

$$T = \frac{\Delta H}{CP_{H}^{ig}} + T_0 \qquad T_2 = \frac{\Delta H}{CP_{mh}^{ig}} + T_1 \quad \ldots\ldots\ldots\ldots\ldots (4.11)$$

$$T = \frac{\Delta H}{\langle C_P \rangle_H} + T_0 \qquad (4.11)$$

With a starting value for T, one can first evaluate **⟨CP⟩H by Eq. (4.9). Substitution into Eq. (4.11)** provides **a new value of T** from which to reevaluate ⟨CP⟩H. Iteration continues to convergence on a **final value of T**.

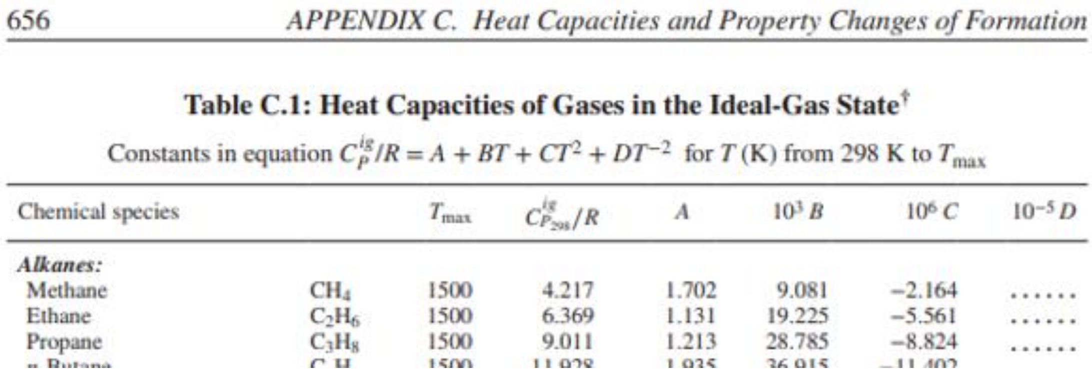
Of course, such iteration is readily automated with built-in functions in a spreadsheet or a numerical analysis software package.

Example 4.2

Calculate the heat required to raise the temperature of 1 mol of **methane** from 260 to 600°C in a steady-flow process at a pressure sufficiently low that the ideal-gas state is a suitable approximation for methane.

Solution 4.2

Equations (4.3) and **Eq. (4.8)** together provide the required result. Parameters for $\frac{\boldsymbol{CP^{ig}}}{\boldsymbol{R}}$ are from Table C.1; T_0 = 533.15 K and T = 873.15 K.



656 *APPENDIX C. Heat Capacities and Property Changes of Formation*

Table C.1: Heat Capacities of Gases in the Ideal-Gas State†

Constants in equation $C_P^{ig}/R = A + BT + CT^2 + DT^{-2}$ for T (K) from 298 K to T_{max}

Chemical species		T_{max}	$C_{P_{298}}^{ig}/R$	A	$10^3\ B$	$10^6\ C$	$10^{-5}\ D$
Alkanes:							
Methane	CH_4	1500	4.217	1.702	9.081	−2.164	......
Ethane	C_2H_6	1500	6.369	1.131	19.225	−5.561	......
Propane	C_3H_8	1500	9.011	1.213	28.785	−8.824	......

Then

$$Q = \Delta H = R\int_{533.15}^{873.15} \frac{C_P^{ig}}{R}\, dT$$

$$Q = (8.314)\left[1.702(T - T_0) + \frac{9.081 \times 10^{-3}}{2}(T^2 - T_0^2) - \frac{2.164 \times 10^{-6}}{3}(T^3 - T_0^3)\right] = 19{,}778\ \text{J}$$

$$\int_{T_0}^{T} \frac{C_P}{R}\, dT = A(T - T_0) + \frac{B}{2}(T^2 - T_0^2) + \frac{C}{3}(T^3 - T_0^3) + D\left(\frac{T - T_0}{TT_0}\right) \qquad (4.8)$$

Example 4.3

What is the final temperature when heat in the amount of 400 × 10^6 J is added to 11×10^3 mol of **ammonia** initially at 530 K in a steady-flow process at 1 bar?

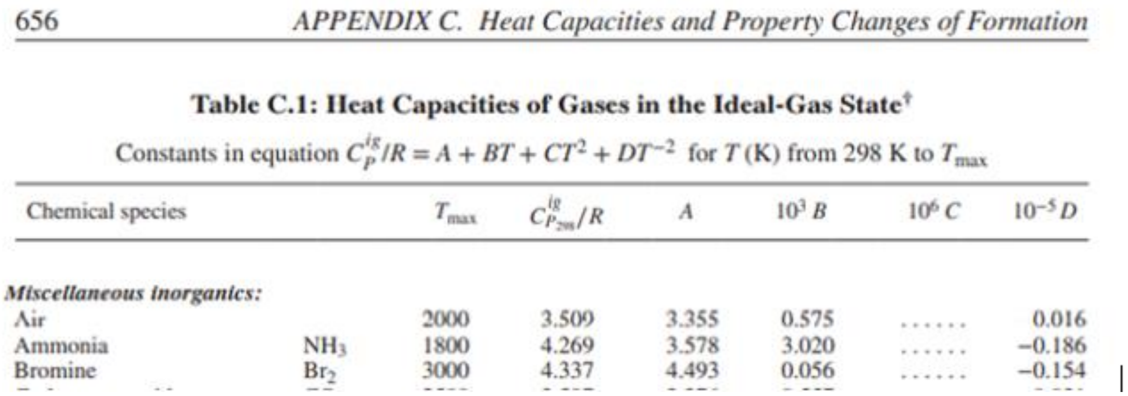
Solution 4.3

If ΔH is the enthalpy change for 1 mol, Q = n ΔH, and

$$\Delta H = \frac{Q}{n} = \frac{400 \times 10^6}{11000} = 36{,}360\ \mathrm{J}.mol.^{-1}$$

With $T_1 = 530\ K$

Then for any value of T, with parameters from Table C.1 and R = 8.314 $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$:



656 *APPENDIX C. Heat Capacities and Property Changes of Formation*

Table C.1: Heat Capacities of Gases in the Ideal-Gas State[†]

Constants in equation $C_P^{ig}/R = A + BT + CT^2 + DT^{-2}$ for T (K) from 298 K to T_{max}

Chemical species		T_{max}	$C^{ig}_{P_{298}}/R$	A	$10^3\ B$	$10^6\ C$	$10^{-5}\ D$
Miscellaneous inorganics:							
Air		2000	3.509	3.355	0.575	......	0.016
Ammonia	NH_3	1800	4.269	3.578	3.020	......	−0.186
Bromine	Br_2	3000	4.337	4.493	0.056	......	−0.154

$$\frac{\langle C_P \rangle_H}{R} = \mathrm{MCPH}(530, T; 3.578, 3.020 \times 10^{-3}, 0.0, -0.186 \times 10^5)$$

$$T = \frac{\Delta H}{CP_H^{ig}} + T_0 \qquad\qquad T_2 = \frac{\Delta H}{CP_{mh}^{ig}} + T_1 \quad \ldots\ldots\ldots\ldots\ldots (4.11)$$

$$\frac{\langle C_P \rangle_H}{R} = A + \frac{B}{2}(T + T_0) + \frac{C}{3}(T^2 + T_0^2 + TT_0) + \frac{D}{TT_0} \qquad (4.9)$$

This equation and Eq. (4.11) together may be solved for T, yielding T = 1234 K.

A trial procedure is an alternative approach to solution of this problem. At the start assume an initial value for T_2 for calculate CP_{mh}^{ig} by equation (4.9) and substitute of the value of CP_{mh}^{ig} in eq. (4.11) to provide a new value of T_2 and then revaluate CP_{mh}^{ig} and iteration continue until the value of T_2 assumed equal T_2 produced.

Microsoft Excel's Goal Seek function is an example of an automated version of this procedure.

Note:

اذا طلب T2 يعني نستخدم try & error وذلك من خلال فرض T2 حيث تفرض اكبر من T1 اذا كانت العملية تسخين.

اما اذا كانت العملية تبريد cooling تفرض T2 اصغر من T1.

No. of trial	T2 Assume	T2 Calculate	% Error
1	150	270	
2	270	210	
3	210	210	

4.2 LATENT HEATS OF PURE SUBSTANCES

When a pure substance is liquefied from the solid state or vaporized from the liquid or solid at constant pressure, no change in temperature occurs; however, these processes require the transfer of finite amounts of heat to the substance. These heat effects are called latent heats: of fusion, of vaporization, and of sublimation. Similarly, there are heats of transition accompanying the change of a substance from one allotropic solid state to another;

Thus the latent heat accompanying a phase change is a function of temperature only, and is related to other system properties by an exact thermodynamic equation:

$$\Delta H = T\Delta V \frac{dP^{sat}}{dT} \qquad \dots\dots\dots\dots\dots\dots..(4.12)$$

Where for a pure species at temperature T,

ΔH = latent heat = enthalpy change accompanying the phase change

ΔV = volume change accompanying the phase change

P^{sat} = saturation pressure, i.e., the pressure at which the phase change occurs, which is a function only of T.

At the normal boiling point, but not quite so simple, is the equation proposed by Riedel:

$$\frac{\Delta H_n}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{r_n}} \qquad (4.13)$$

Where Pc is the critical pressure in bars and Tr n is the reduced temperature at Tn. Equation (4.13) is surprisingly accurate for an empirical expression; errors rarely exceed 5 percent. Applied to water it gives:

$$\frac{\Delta H_n}{RT_n} = \frac{1.092(\ln 220.55 - 1.013)}{0.930 - 0.577} = 13.56$$

from which $\Delta H_n = (13.56)(8.314)(373.15) = 42{,}065 \text{ J}\cdot\text{mol}^{-1}$

This corresponds to 2334 $\text{J}\cdot\text{g}^{-1}$; the steam-table value of 2257 $\text{J}\cdot\text{g}^{-1}$ is lower by 3.4 percent. Estimates of the latent heat of vaporization of a pure liquid at any temperature from the known value at a single temperature are given by the method of Watson. The basis may be a known experimental value or a value estimated by Eq. (4.13):

$$\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1 - T_{r_2}}{1 - T_{r_1}}\right)^{0.38} \tag{4.14}$$

This empirical equation is simple and fairly accurate; its use is illustrated in the following example.

Example 4.4

Given that the latent heat of vaporization of water at 100°C is 2257 J·g−1, estimate the latent heat at 300°C.

Solution 4.4

Let $\Delta H_1 = \text{latent heat at } 100°\text{C} = 2257 \text{ J}\cdot\text{g}^{-1}$

$\Delta H_2 = \text{latent heat at } 300°\text{C}$

$T_{r_1} = 373.15/647.1 = 0.577$

$T_{r_2} = 573.15/647.1 = 0.886$

Then by Eq. (4.14),

$$\Delta H_2 = (2257)\left(\frac{1 - 0.886}{1 - 0.577}\right)^{0.38} = (2257)(0.270)^{0.38} = 1371 \text{ J}\cdot\text{g}^{-1}$$

The value given in the steam tables is 1406 $\text{J}\cdot\text{g}^{-1}$.

Chapter 4 Heat Effects

Summary:

1- Heat capacity for gases.

$$\frac{\boldsymbol{CP^{ig}}}{\boldsymbol{R}} = \boldsymbol{A + B\,T + C\,T^2 + D\,T^{-2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ (\mathbf{4.5})$$

Note//

$$A \to D = constat$$

Neither C= 0 or D=0

الثوابت تعطى على شكل معادلة او جدول.

في حالة الجدول تعكس الاسس B,C,D

Appendix C........table c-1 page 656

$10^3\ B = 9.081 \qquad \therefore\ B = 9.081 \times 10^{-3}$

4.3 Standard Heat of Reaction.

Heat effects of chemical processes are fully as important as those for physical processes. Chemical reactions are accompanied by the transfer of heat, by temperature changes during reaction, or by both.

4.4 Standard Heat of Formation. (ΔH_f°).

Tabulation of data for just one temperature and for just the *standard heats* of reaction for all of the vast number of possible reactions is impractical. Fortunately, the standard heat of any reaction at temperature T can be calculated if the *standard heats of formation* at the same temperature are known for the compounds taking part in the reaction.

$$\Delta H_{298}^\circ = \sum_P n_i\,\Delta H_{298}^\circ - \sum_R n_i\,\Delta H_{298}^\circ$$

They are based on a standard-state pressure of 1 bar (10^5 Pa).

(n_i) = Numbers of moles for product and reactant materials in chemical equation.

ΔH_{298}° ***value gives in the Table*** $C-4$

H_2, N_2, O_2, Cl_2 (g): Because hydrogen is an free elements $\Delta H_{298}^\circ = 0$

Attention for phase of material (stat of material) l, g and s.

$$\Delta H_T^\circ = \Delta H_{298}^\circ + R\left[\sum A\,(T-298) + \frac{\sum B}{2}(T^2-298^2) + \frac{\sum C}{3}(T^3-298^3) - \sum D\left(\frac{1}{T}-\frac{1}{298}\right)\right]$$

T= Degree of temperature question.

4.7 Heat Effects of Industrial Reactions

The preceding sections have dealt with the *standard heat of reaction.* Industrial reactions are rarely carried out under standard-state conditions. Furthermore, in actual reactions the reactants may not be present in stoichiometric proportions, the reaction may not go to completion, and the final temperature may differ from the initial temperature. Moreover, inert species may be present, and several reactions may occur simultaneously. Nevertheless, calculations of the heat effects of actual reactions are based on the principles already considered and are illustrated by the following examples, wherein the ideal-gas state is assumed for all gases.

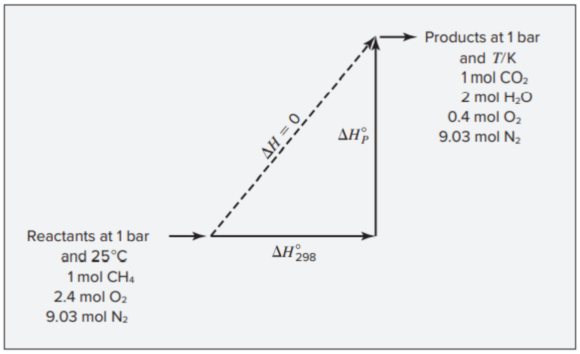
Notes//

1- **Open system** $Q = \Delta H$

2- **(Flams) Max Temp.**

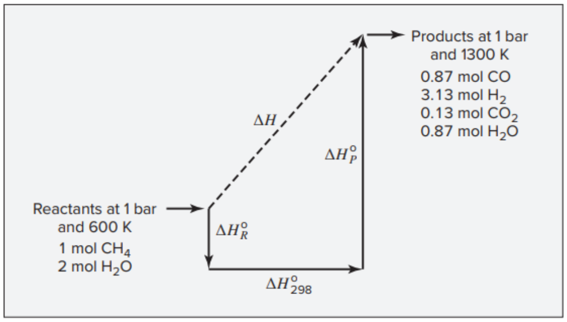
(Q = 0 Adiabatic)

i// $input \quad T = 25\ ℃$



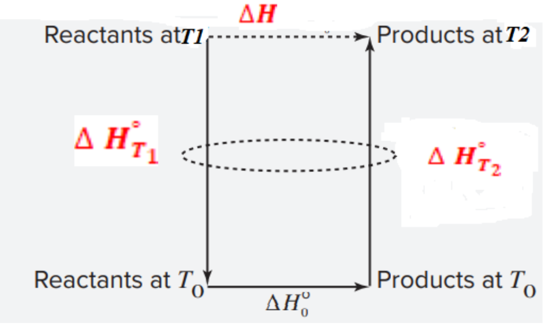
$$Q = \Delta H = \Delta H^\circ_{298} + \Delta H^\circ_{T_2}$$

(ii) // $input \quad T_1 > 25\ ℃$



$$Q = \Delta H = \Delta H^\circ_{T_1} + \Delta H^\circ_{298} + \Delta H^\circ_{T_2}$$

(iii)// $\textit{input} \quad \textit{Isothermal } T_1 = T_2$



$$Q = \Delta H = \Delta H^{\circ}_{T_1} + \Delta H^{\circ}_{298} + \Delta H^{\circ}_{T_2}$$

(iv)// $\textit{Calculate} \quad \Delta H^{\circ}_{T_1}$

$$\Delta H^{\circ}_{T_1} = R\left[\sum A\,(298 - T_1) + \frac{\sum B}{2}\,(298^2 - {T_1}^2) + \frac{\sum C}{3}(298^3 - {T_1}^3) - \sum D\left(\frac{1}{298} - \frac{1}{T_1}\right)\right]$$

$$\sum A = \sum n_i\, A_i$$

(n_i) = Numbers of moles reactant materials in chemical equation.

(v)// $\textit{Calculate} \quad \Delta H^{\circ}_{T_2}$

$$\Delta H^{\circ}_{T_2} = R\left[\sum A\,(T_2 - 298) + \frac{\sum B}{2}\,({T_2}^2 - 298^2) + \frac{\sum C}{3}({T_2}^3 - 298^3) - \sum D\left(\frac{1}{T_2} - \frac{1}{298}\right)\right]$$

$$\sum A = \sum n_i\, A_i$$

(n_i) = Numbers of moles **product materials** in chemical equation.

4// types of question:

i// give T2 and ask Q. (direct)

ii// give Q and ask T2.

5// Steps of solution

i// make calculate of material balance to find (n_i).

ii// make calculate of thermo to find (Q, or T2).

Example 4.7:

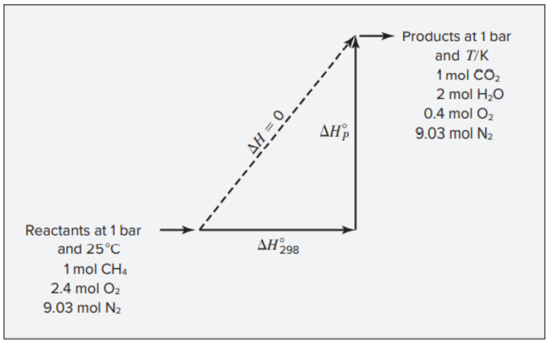
What is the maximum temperature that can be reached by the combustion of methane with 20% excess air? Both the methane and the air enter the burner at 25°C.

Solution 4.7

The reaction is $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(g)$ for which,

$$\Delta H^\circ_{298} = -393{,}509 + (2)\,(-241{,}818) - (-74{,}520) = -802{,}625\ \text{J}$$

Because the maximum attainable temperature (called the theoretical flame temperature) is sought, assume that the combustion reaction goes to completion adiabatically (Q = 0). If the kinetic- and potential-energy changes are negligible and if Ws = 0, the overall energy balance for the process reduces to **ΔH = 0.** For purposes of calculation of the final temperature, any convenient path between the initial and final states may be used. The path chosen is indicated in the diagram.



When one mole of methane burned is the basis for all calculations, the following quantities of oxygen and nitrogen are supplied by the entering air:

$$\begin{aligned}\text{Moles } O_2 \text{ required} &= 2.0\\ \text{Moles excess } O_2 &= (0.2)(2.0) = 0.4\\ \text{Moles } N_2 \text{ entering} &= (2.4)(79/21) = 9.03\end{aligned}$$

The mole numbers n_i of the gases in the product stream leaving the burner are 1 mol CO_2, 2 mol $H_2O(g)$, 0.4 mol O_2, and 9.03 mol N_2. Because the enthalpy change must be independent of path,

$$\Delta H^\circ_{298} + \Delta H^\circ_P = \Delta H = 0 \qquad (A)$$

where all enthalpies are on the basis of 1 mol CH_4 burned. The enthalpy change of the products as they are heated from 298.15 K to T is:

$$\Delta H^\circ_P = \langle C^\circ_P \rangle_H\,(T - 298.15) \qquad (B)$$

where we define $\langle C^\circ_P \rangle_H$ as the mean heat capacity for the *total* product stream:

$$\langle C^\circ_P \rangle_H \equiv \sum_i n_i \langle C^\circ_{P_i} \rangle_H$$

The simplest procedure here is to sum the mean-heat-capacity equations for the products, each multiplied by its appropriate mole number. Because $C = 0$ for each product gas (Table C.1), Eq. (4.9) yields:

$$\langle C_P^\circ \rangle_H = \sum_i n_i \langle C_{P_i}^\circ \rangle_H = R\left[\sum_i n_i A_i + \frac{\sum_i n_i B_i}{2}(T - T_0) + \frac{\sum_i n_i D_i}{T T_0}\right]$$

Data from Table C.1 are combined as follows:

$$A = \sum_i n_i A_i = (1)(5.457) + (2)(3.470) + (0.4)(3.639) + (9.03)(3.280) = 43.471$$

Similarly, $B = \sum_i n_i B_i = 9.502 \times 10^{-3}$ and $D = \sum_i n_i D_i = -0.645 \times 10^5$.

For the product stream $\langle C_P^\circ \rangle_H / R$ is therefore represented by:

MCPH(298.15, T; 43.471, 9.502×10^{-3}, 0.0, -0.645×10^5)

Equations (A) and (B) are combined and solved for T:

$$T = 298.15 - \frac{\Delta H_{298}^\circ}{\langle C_P^\circ \rangle_H}$$

Because the mean heat capacities depend on T, one first evaluates $\langle C_P^\circ \rangle_H$ for an assumed value of $T > 298.15$, then substitutes the result in the preceding equation. This yields a new value of T for which $\langle C_P^\circ \rangle_H$ is reevaluated. The procedure continues to convergence on the final value,

$$T = 2066 \text{ K} \qquad \text{or} \qquad 1793°\text{C}$$

Again, solution can be easily automated with the Goal Seek or Solver function in a spreadsheet or similar solve routines in other software packages.

Example 4.8

One method for the manufacture of "synthesis gas" (a mixture of CO and H_2) is the catalytic reforming of CH_4 with steam at high temperature and atmospheric pressure:

$$CH_{4\,(g)} + H_2O_{\,(g)} \rightarrow CO_{\,(g)} + 3H_{2\,(g)}$$

The only other reaction considered here is the water-gas-shift reaction:

$$CO_{\,(g)} + H_2O_{\,(g)} \rightarrow CO_{2\,(g)} + H_{2\,(g)}$$

Reactants are supplied in the ratio 2 mol. steam to 1 mol. CH_4, and heat is added to the reactor to bring the products to a temperature of 1300 K. The **CH_4 is completely converted**, and the product stream contains **17.4 mol. % CO**. Assuming the reactants to be preheated to 600 K, calculate the heat requirement for the reactor.

Solution 4.8

The standard heats of reaction at 25°C for the two reactions are calculated from the data of Table C.4:

$$CH_{4\,(g)} + H_2O_{\,(g)} \rightarrow CO_{\,(g)} + 3H_{2\,(g)} \qquad \Delta H^\circ_{298} = 205{,}813\ \text{J}$$

$$CO_{\,(g)} + H_2O_{\,(g)} \rightarrow CO_{2\,(g)} + H_{2\,(g)} \qquad \Delta H^\circ_{298} = -41{,}166\ \text{J}$$

These two reactions may be added to give a third reaction:

$$CH_{4\,(g)} + 2H_2O_{\,(g)} \rightarrow CO_{2\,(g)} + 4H_{2\,(g)} \qquad \Delta H^\circ_{298} = 164{,}647\ \text{J}$$

Any pair of the three reactions constitutes an independent set. The third reaction is not independent; it is obtained by combination of the other two. The reactions most convenient to work with here are the first and third:

$$CH_{4\,(g)} + H_2O_{\,(g)} \rightarrow CO_{\,(g)} + 3H_{2\,(g)} \qquad \Delta H298\ ^\circ = 205{,}813\ \text{J} \qquad \textbf{(A)}$$

$$CH_{4\,(g)} + 2H_2O_{\,(g)} \rightarrow CO_{2\,(g)} + 4H_{2\,(g)} \qquad \Delta H298\ ^\circ = 164{,}647\ \text{J} \qquad \textbf{(B)}$$

First one must determine the fraction of CH_4 converted by each of these reactions. As a basis for calculations, let **1 mol. CH_4 and 2 mol. steam** be fed to the reactor. If x mol. CH_4 reacts by Eq. (A), then 1 − x mol. reacts by Eq. (B). On this basis the products of the reaction are:

CO:	**x**
H_2:	$3x + 4(1-x) = 4 - x$
CO_2:	$1 - x$
H_2O:	$2 - x - 2(1-x) = x$
Total:	5 mol. products

The mole fraction of CO in the product stream is x/5 = 0.174; whence x = 0.870.

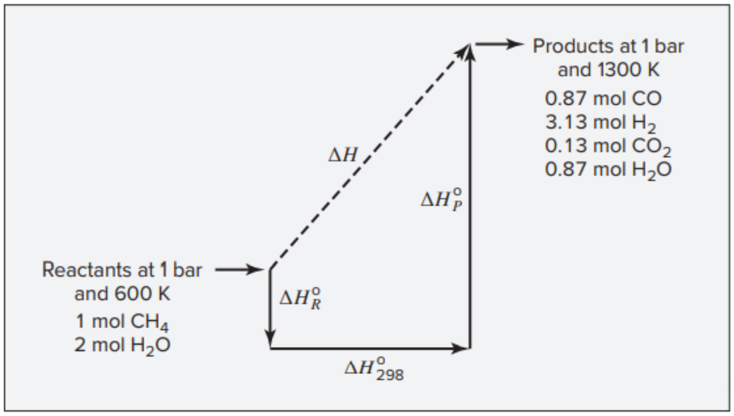
Thus, on the basis chosen, **0.870 mol. CH_4 reacts by Eq. (A) and 0.130 mol. reacts by Eq. (B).** Furthermore, the amounts of the species in the **product stream** are:

Moles CO = x = 0.87
Moles H_2 = 4 − x = 3.13
Moles CO_2 = 1 − x = 0.13
Moles H_2O = x = 0.87

We now devise a path, for purposes of calculation, to proceed from reactants at 600 K to products at 1300 K. Because data are available for the standard heats of reaction at 25°C, the most convenient path is the one which includes the reactions at 25°C (298.15 K). This is shown schematically in the accompanying diagram. The dashed line represents the actual path for which the enthalpy change is ΔH.

Because this enthalpy change is independent of path,

$$\Delta H = \Delta H^\circ_R + \Delta H^\circ_{298} + \Delta H^\circ_P$$



For the calculation of ΔH_{298} °, reactions (A) and (B) must both be taken into account. Because 0.87 mol. CH_4 reacts by (A) and 0.13 mol. reacts by (B),

$$\Delta H^\circ_{298} = (0.87)(205{,}813) + (0.13)(164{,}647) = 200{,}460 \text{ J}$$

The enthalpy change of the reactants cooled from 600 K to 298.15 K is:

$$\mathbf{\Delta H^\circ_R = \left(\sum n_i \langle C_{Pi}^\circ \rangle_H\right)(298.15 - 600)}$$

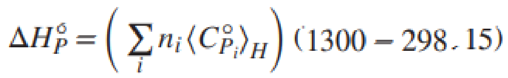
Where subscript i denotes reactants. The values of $\langle C_{P_i}^\circ \rangle_H / R$ are:

CH_4: MCPH (298.15, 600; 1.702, 9.081 × 10−3, −2.164 × 10−6, 0.0) = 5.3272

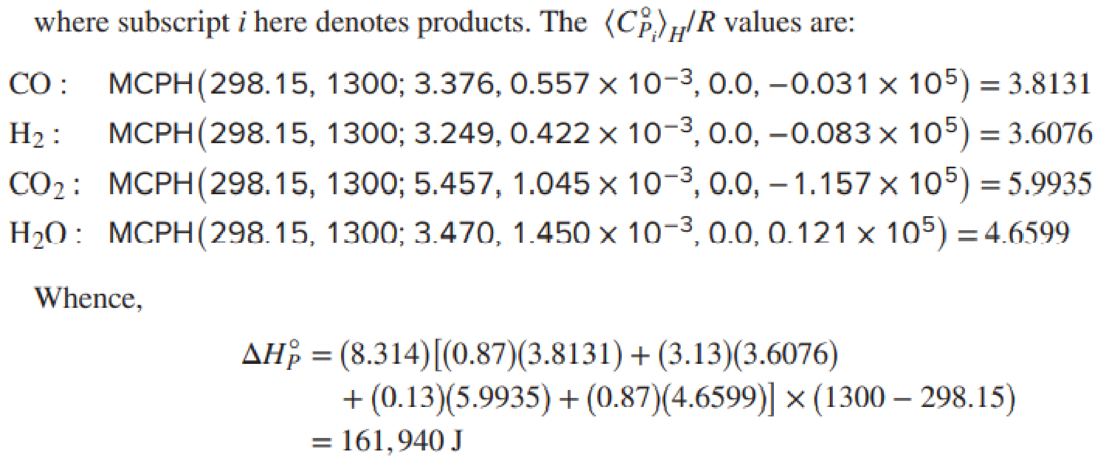
H_2O: MCPH (298.15, 600; 3.470, 1.450 × 10 −3, 0.0, 0.121 × 105) = 4.1888

And ΔH°_R = (8.314) [(1) (5.3272) + (2) (4.1888)] (298.15 − 600) = −34,390 J

The enthalpy change of the products as they are heated from 298.15 to 1300 K is calculated similarly:



$$\Delta H^\circ_P = \left(\sum_i n_i \langle C^\circ_{P_i} \rangle_H \right) (1300 - 298.15)$$



where subscript *i* here denotes products. The $\langle C^\circ_{P_i} \rangle_H / R$ values are:

CO: $\text{MCPH}(298.15, 1300; 3.376, 0.557 \times 10^{-3}, 0.0, -0.031 \times 10^5) = 3.8131$

H_2: $\text{MCPH}(298.15, 1300; 3.249, 0.422 \times 10^{-3}, 0.0, -0.083 \times 10^5) = 3.6076$

CO_2: $\text{MCPH}(298.15, 1300; 5.457, 1.045 \times 10^{-3}, 0.0, -1.157 \times 10^5) = 5.9935$

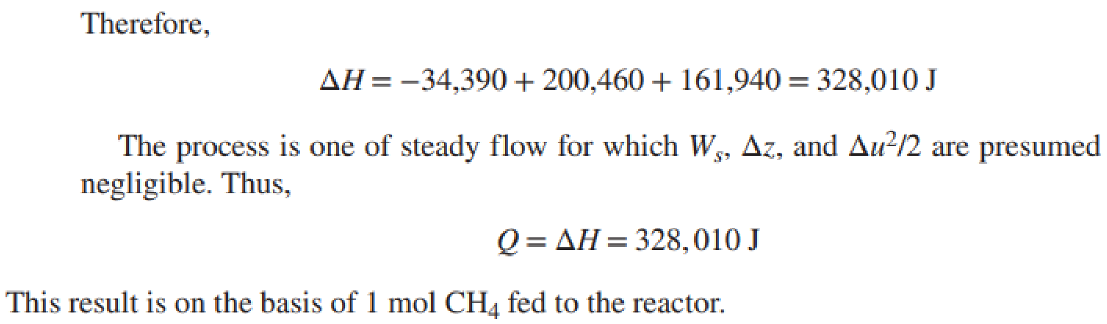
H_2O: $\text{MCPH}(298.15, 1300; 3.470, 1.450 \times 10^{-3}, 0.0, 0.121 \times 10^5) = 4.6599$

Whence,

$$\begin{aligned}\Delta H^\circ_P &= (8.314)[(0.87)(3.8131) + (3.13)(3.6076) \\ &\quad + (0.13)(5.9935) + (0.87)(4.6599)] \times (1300 - 298.15) \\ &= 161{,}940 \text{ J}\end{aligned}$$

Therefore,

$$\Delta H = -34{,}390 + 200{,}460 + 161{,}940 = 328{,}010 \text{ J}$$



Therefore,

$$\Delta H = -34{,}390 + 200{,}460 + 161{,}940 = 328{,}010 \text{ J}$$

The process is one of steady flow for which W_s, Δz, and $\Delta u^2/2$ are presumed negligible. Thus,

$$Q = \Delta H = 328{,}010 \text{ J}$$

This result is on the basis of 1 mol CH_4 fed to the reactor.

Example 4.9

Solar-grade silicon can be manufactured by thermal decomposition of silane at moderate pressure in a fluidized-bed reactor, in which the overall reaction is:

$$SiH_{4\,(g)} \rightarrow Si_{\,(s)} + 2H_{2\,(g)}$$

When pure silane is preheated to 300°C, and heat is added to the reactor to promote a reasonable reaction rate, **80% of the silane is converted to silicon** and the products leave the reactor at 750°C. How much heat must be added to the reactor for each kilogram of silicon produced?

Solution 4.9

For a continuous-flow process with no shaft work and negligible changes in kinetic and potential energy, the energy balance is simply $Q = \Delta H$, and the heat added is the enthalpy change from reactant at 300°C to products at 750°C. A convenient path for calculation of the enthalpy change is to

(1) Cool the reactant to 298.15 K,

(2) Carry out the reaction at 298.15 K, and

(3) heat the products to 750°C.

On the basis of 1 mol. SiH_4, the products consist of 0.2 mol. SiH_4, 0.8 mol. Si, and 1.6 mol. H_2. Thus, for the three steps we have:

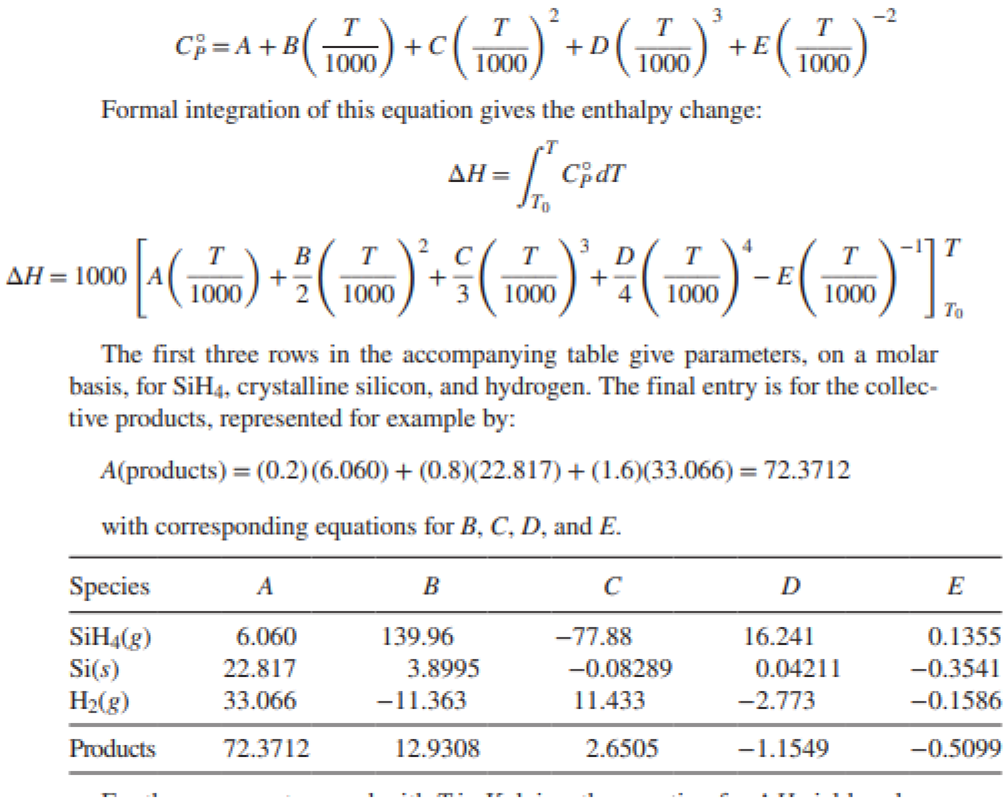
$$\Delta H_1 = \int_{573.15\mathrm{K}}^{298.15\mathrm{K}} C_P^\circ(\mathrm{SiH_4})\, dT$$

$$\Delta H_2 = 0.8 \times \Delta H_{298}^\circ$$

$$\Delta H_3 = \int_{298.15\mathrm{K}}^{1023.15\mathrm{K}} [0.2 \times C_P^\circ(\mathrm{SiH_4}) + 0.8 \times C_P^\circ(\mathrm{Si}) + 1.6 \times C_P^\circ(\mathrm{H_2})]\, dT$$

Data needed for this example are not included in App. C, but are readily obtained from the NIST Chemistry Webbook (http://webbook.nist.gov). The reaction here is the reverse of the formation reaction for silane, and its standard heat of reaction at 298.15 K is $\Delta H_{298}^\circ = -34{,}310$ J. Thus, the reaction is mildly exothermic.

Heat capacity in the NIST Chemistry Workbook is expressed by **the Shomate equation**, a polynomial of different form from that used in this text. It includes a T_3 term, and is written in terms of T/1000, with T in K:



$$C_P^\circ = A + B\left(\frac{T}{1000}\right) + C\left(\frac{T}{1000}\right)^2 + D\left(\frac{T}{1000}\right)^3 + E\left(\frac{T}{1000}\right)^{-2}$$

Formal integration of this equation gives the enthalpy change:

$$\Delta H = \int_{T_0}^{T} C_P^\circ dT$$

$$\Delta H = 1000\left[A\left(\frac{T}{1000}\right) + \frac{B}{2}\left(\frac{T}{1000}\right)^2 + \frac{C}{3}\left(\frac{T}{1000}\right)^3 + \frac{D}{4}\left(\frac{T}{1000}\right)^4 - E\left(\frac{T}{1000}\right)^{-1}\right]_{T_0}^{T}$$

The first three rows in the accompanying table give parameters, on a molar basis, for SiH_4, crystalline silicon, and hydrogen. The final entry is for the collective products, represented for example by:

$$A(\text{products}) = (0.2)(6.060) + (0.8)(22.817) + (1.6)(33.066) = 72.3712$$

with corresponding equations for *B*, *C*, *D*, and *E*.

Species	*A*	*B*	*C*	*D*	*E*
$SiH_4(g)$	6.060	139.96	−77.88	16.241	0.1355
$Si(s)$	22.817	3.8995	−0.08289	0.04211	−0.3541
$H_2(g)$	33.066	−11.363	11.433	−2.773	−0.1586
Products	72.3712	12.9308	2.6505	−1.1549	−0.5099

For these parameters, and with T in Kelvins, the equation for ΔH yields values in joules. For the three steps making up the solution to this problem, the following results are obtained:

1. Substitution of the parameters for 1 mol. of SiH_4 into the equation for ΔH leads upon evaluation to: $\Delta H_1 = -14{,}860$ J

2. Here, $\Delta H_2 = (0.8)(-34{,}310) = -27{,}450$ J

3. Substitution of the parameters for the total product stream into the equation for ΔH leads upon evaluation to: $\Delta H_3 = 58{,}060$ J For **the three steps the sum** is:

$\Delta H = -14{,}860 - 27{,}450 + 58{,}060 = 15{,}750$ J

This enthalpy change equals the heat **input per mole of SiH_4** fed to the reactor. A kilogram of silicon, with a molar mass of 28.09, is 35.60 mol. producing a kilogram of silicon therefore requires a feed of 35.60 /0.8 or 44.50 mol. of SiH_4. The heat requirement per kilogram of silicon produced is therefore

$$(15{,}750)(44.5) = 700{,}900 \text{ J.}$$

Introduction to SI Units and Conversion Factors

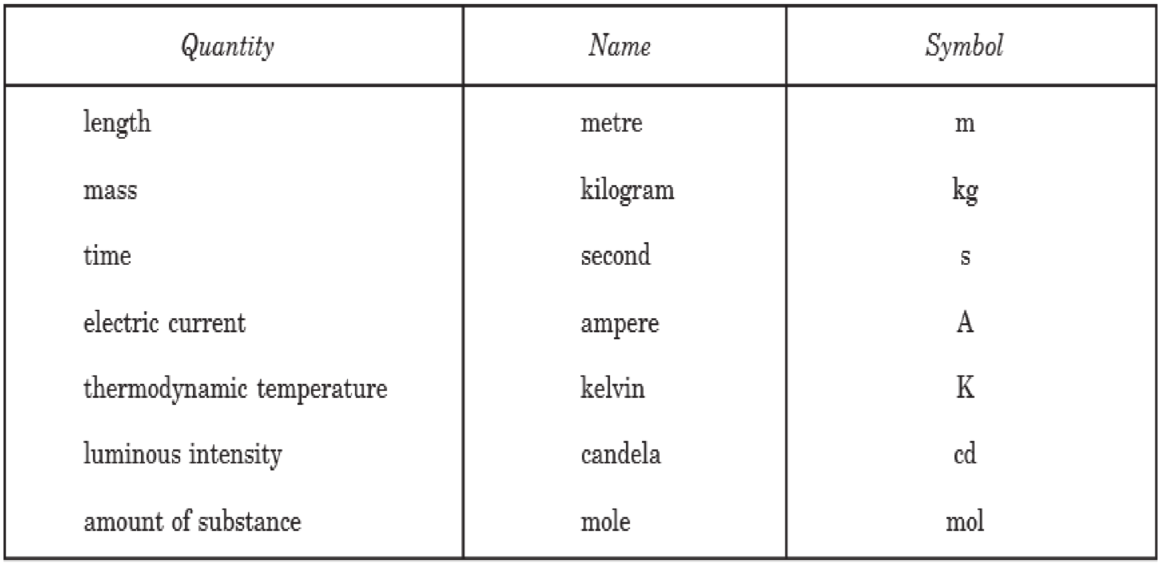
A. INTRODUCTION TO SI UNITS

SI, the international system of units are divided into three classes:-

1. Base units 2.
2. Derived units
3. 3. Supplementary units.

From the scientific point of view division of SI units into these classes is to a certain extent arbitrary, because it is not essential to the physics of the subject. Nevertheless the General Conference, considering the advantages of a single, practical, world-wide system for international relations, for teaching and for scientific work, decided to base the international system on a choice of six well-defined units given in Table 1 below :

Table 1. SI Base Units

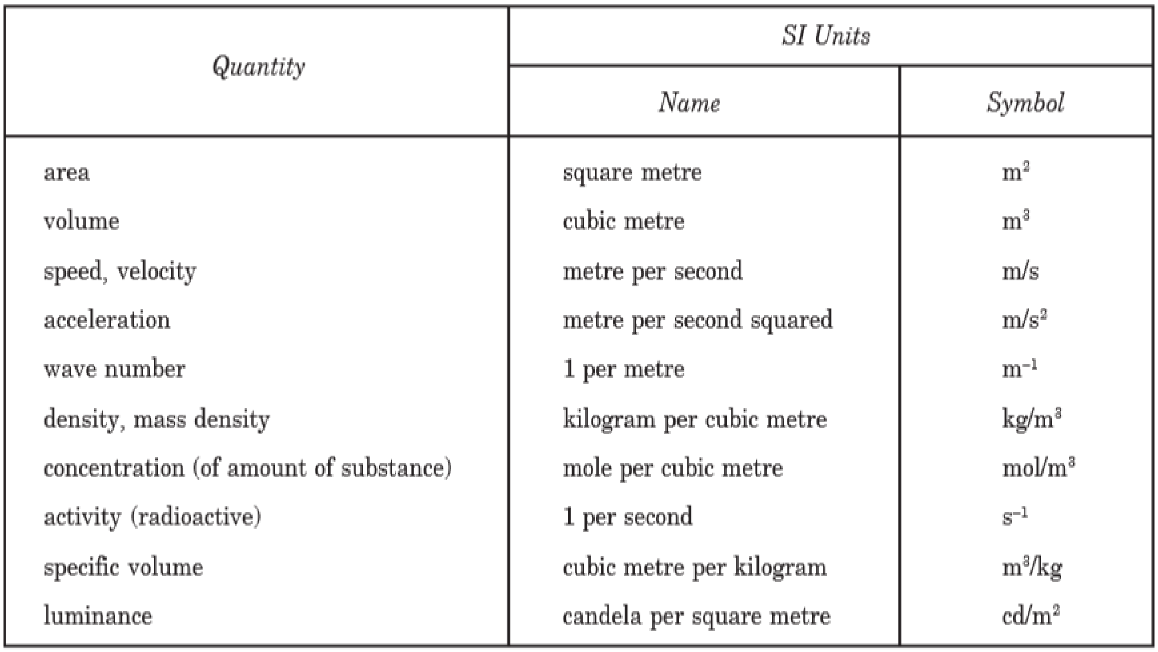


Quantity	*Name*	*Symbol*
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
luminous intensity	candela	cd
amount of substance	mole	mol

The second class of SI units contains derived units, i.e., units which can be formed by combining base units according to the algebraic relations linking the corresponding quantities. Several of these algebraic expressions in terms of base units can be replaced by special names and symbols can themselves be used to form other derived units.

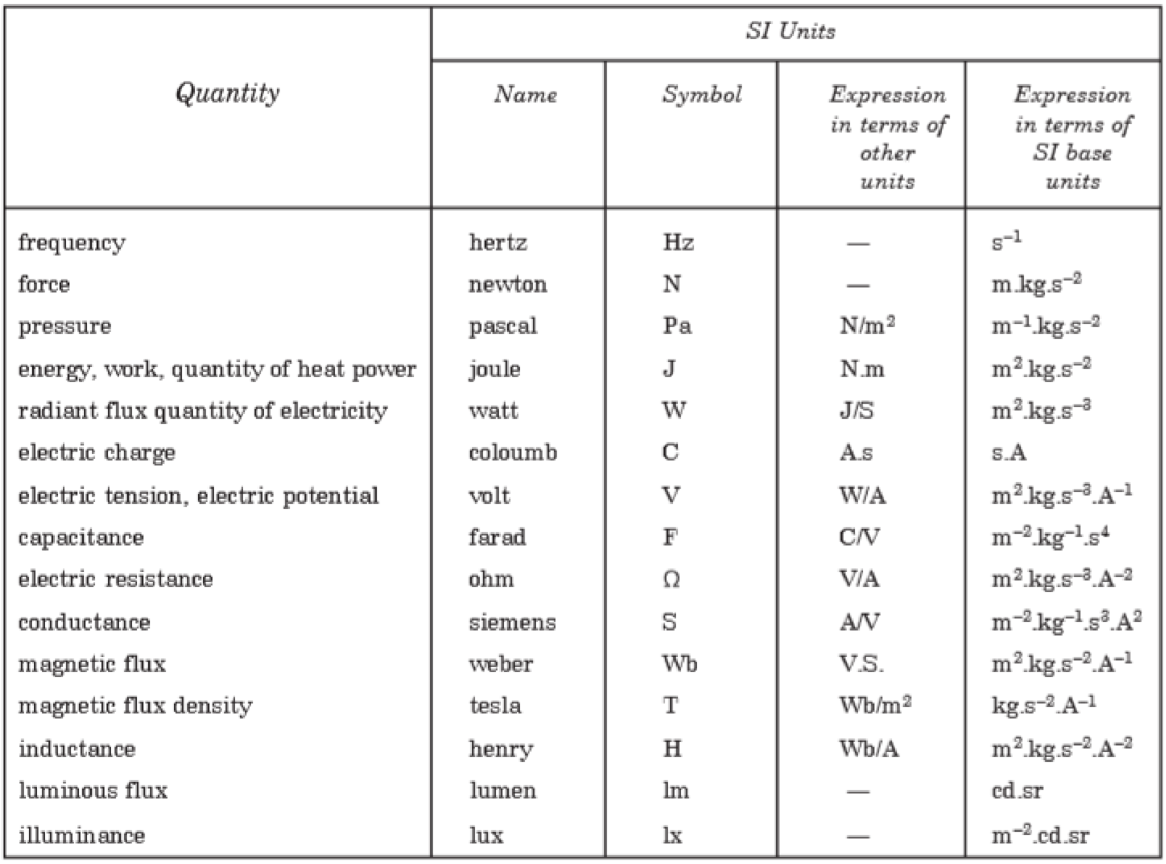
Derived units may, therefore, be classified under three headings. Some of them are given in Tables 2, 3 and 4.

Table 2. Examples of SI Derived Units Expressed in terms of Base Units



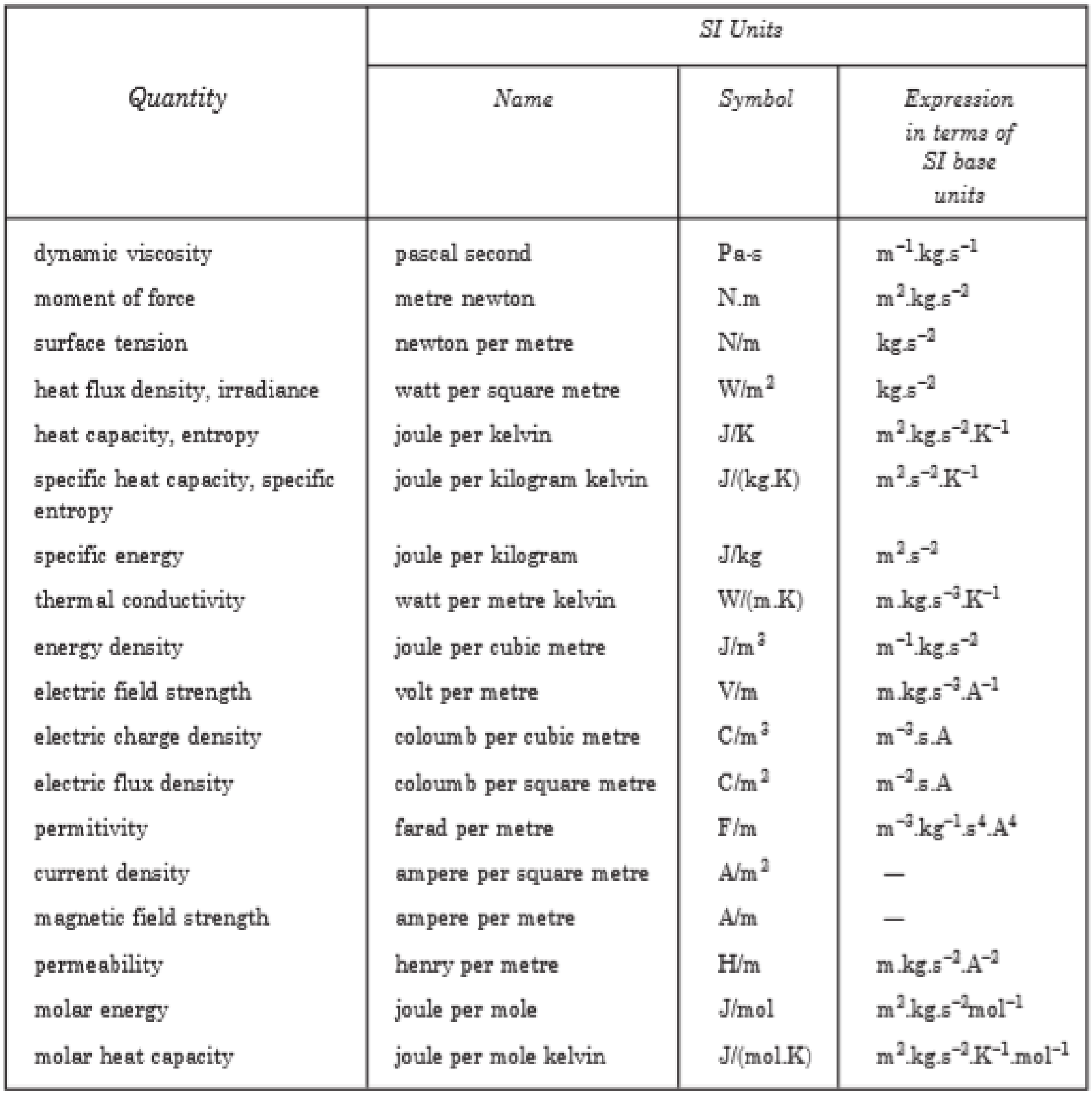
Quantity	*SI Units*	
	Name	*Symbol*
area	square metre	m^2
volume	cubic metre	m^3
speed, velocity	metre per second	m/s
acceleration	metre per second squared	m/s^2
wave number	1 per metre	m^{-1}
density, mass density	kilogram per cubic metre	kg/m^3
concentration (of amount of substance)	mole per cubic metre	mol/m^3
activity (radioactive)	1 per second	s^{-1}
specific volume	cubic metre per kilogram	m^3/kg
luminance	candela per square metre	cd/m^2

Table 3. SI Derived Units with Special Names



Quantity	*SI Units*			
	Name	*Symbol*	*Expression in terms of other units*	*Expression in terms of SI base units*
frequency	hertz	Hz	—	s^{-1}
force	newton	N	—	$m.kg.s^{-2}$
pressure	pascal	Pa	N/m^2	$m^{-1}.kg.s^{-2}$
energy, work, quantity of heat power	joule	J	N.m	$m^2.kg.s^{-2}$
radiant flux quantity of electricity	watt	W	J/S	$m^2.kg.s^{-3}$
electric charge	coloumb	C	A.s	s.A
electric tension, electric potential	volt	V	W/A	$m^2.kg.s^{-3}.A^{-1}$
capacitance	farad	F	C/V	$m^{-2}.kg^{-1}.s^4$
electric resistance	ohm	Ω	V/A	$m^2.kg.s^{-3}.A^{-2}$
conductance	siemens	S	A/V	$m^{-2}.kg^{-1}.s^3.A^2$
magnetic flux	weber	Wb	V.S.	$m^2.kg.s^{-2}.A^{-1}$
magnetic flux density	tesla	T	Wb/m^2	$kg.s^{-2}.A^{-1}$
inductance	henry	H	Wb/A	$m^2.kg.s^{-2}.A^{-2}$
luminous flux	lumen	lm	—	cd.sr
illuminance	lux	lx	—	$m^{-2}.cd.sr$

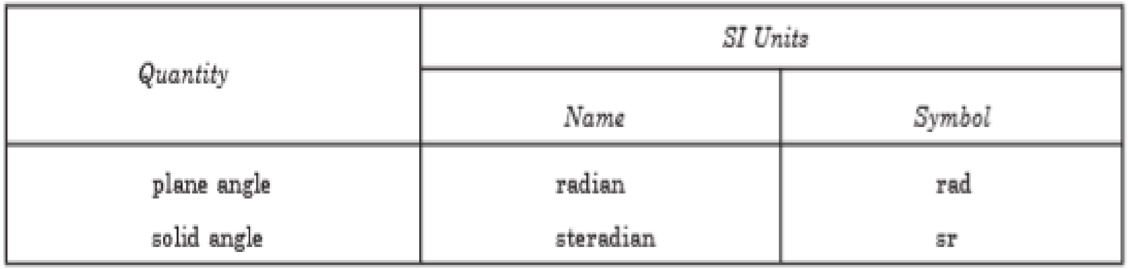
Table 4. Examples of SI Derived Units Expressed by means of Special Names



Quantity	*SI Units*		
	Name	*Symbol*	*Expression in terms of SI base units*
dynamic viscosity	pascal second	Pa-s	$m^{-1}.kg.s^{-1}$
moment of force	metre newton	N.m	$m^{2}.kg.s^{-2}$
surface tension	newton per metre	N/m	$kg.s^{-2}$
heat flux density, irradiance	watt per square metre	W/m^{2}	$kg.s^{-2}$
heat capacity, entropy	joule per kelvin	J/K	$m^{2}.kg.s^{-2}.K^{-1}$
specific heat capacity, specific entropy	joule per kilogram kelvin	J/(kg.K)	$m^{2}.s^{-2}.K^{-1}$
specific energy	joule per kilogram	J/kg	$m^{2}.s^{-2}$
thermal conductivity	watt per metre kelvin	W/(m.K)	$m.kg.s^{-3}.K^{-1}$
energy density	joule per cubic metre	J/m^{3}	$m^{-1}.kg.s^{-2}$
electric field strength	volt per metre	V/m	$m.kg.s^{-3}.A^{-1}$
electric charge density	coloumb per cubic metre	C/m^{3}	$m^{-3}.s.A$
electric flux density	coloumb per square metre	C/m^{2}	$m^{-2}.s.A$
permitivity	farad per metre	F/m	$m^{-3}.kg^{-1}.s^{4}.A^{4}$
current density	ampere per square metre	A/m^{2}	—
magnetic field strength	ampere per metre	A/m	—
permeability	henry per metre	H/m	$m.kg.s^{-2}.A^{-2}$
molar energy	joule per mole	J/mol	$m^{2}.kg.s^{-2}mol^{-1}$
molar heat capacity	joule per mole kelvin	J/(mol.K)	$m^{2}.kg.s^{-2}.K^{-1}.mol^{-1}$

The SI units assigned to third class called "Supplementary units" may be regarded either as base units or as derived units. Refer Table 5 and Table 6.

Table 5. SI Supplementary Units



Quantity	*SI Units*	
	Name	*Symbol*
plane angle	radian	rad
solid angle	steradian	sr

Table 6. Examples of SI Derived Units Formed by Using Supplementary Units

Quantity	*SI Units*	
	Name	*Symbol*
angular velocity	radian per second	rad/s
angular acceleration	radian per second squared	rad/s^2
radiant intensity	watt per steradian	W/sr
radiance	watt per square metre steradian	W-m^{-2}.sr^{-1}

Table 7. SI Prefixes

Factor	*Prefix*	*Symbol*	*Factor*	*Prefix*	*Symbol*
10^{12}	tera	T	10^{-1}	deci	d
10^{9}	giga	G	10^{-2}	centi	c
10^{6}	mega	M	10^{-3}	milli	m
10^{3}	kilo	k	10^{-6}	micro	μ
10^{2}	hecto	h	10^{-9}	nano	n
10^{1}	deca	da	10^{-12}	pico	p
			10^{-15}	fasnto	f
			10^{-18}	atto	a

B. CONVERSION FACTORS

1. Force :

$$1 \text{ newton} = \text{kg-m/sec}^2 = 0.012 \text{ kgf}$$

$$1 \text{ kgf} = 9.81 \text{ N}$$

2. Pressure :

$$1 \text{ bar} = 750.06 \text{ mm Hg} = 0.9869 \text{ atm} = 10^5 \text{ N/m}^2 = 10^5 \text{ kg/m-sec}^2$$

$$1 \text{ N/m}^2 = 1 \text{ pascal} = 10^{-5} \text{ bar} = 10^{-2} \text{ kg/m-sec}^2$$

$$1 \text{ atm} = 760 \text{ mm Hg} = 1.03 \text{ kgf/cm}^2 = 1.01325 \text{ bar}$$

$$= 1.01325 \times 10^5 \text{ N/m}^2$$

3. Work, Energy or Heat :

$$1 \text{ joule} = 1 \text{ newton metre} = 1 \text{ watt-sec}$$

$$= 2.7778 \times 10^{-7} \text{ kWh} = 0.239 \text{ cal}$$

$$= 0.239 \times 10^{-3} \text{ kcal}$$

$$1 \text{ cal} = 4.184 \text{ joule} = 1.1622 \times 10^{-6} \text{ kWh}$$

$$1 \text{ kcal} = 4.184 \times 10^3 \text{ joule} = 427 \text{ kgf-m}$$

$$= 1.1622 \times 10^{-3} \text{ kWh}$$

$$1 \text{ kWh} = 8.6042 \times 10^5 \text{ cal} = 860 \text{ kcal} = 3.6 \times 10^6 \text{ joule}$$

$$1 \text{ kgf-m} = \left(\frac{1}{427}\right) \text{ kcal} = 9.81 \text{ joules}$$

4. Power :

1 watt = 1 joule/sec = 0.860 kcal/h
1 h.p. = 75 m kgf/sec = 0.1757 kcal/sec = 735.3 watt
1 kW = 1000 watts = 860 kcal/h

5. Specific heat :

1 kcal/kg-°K = 0.4184 joules/kg-K

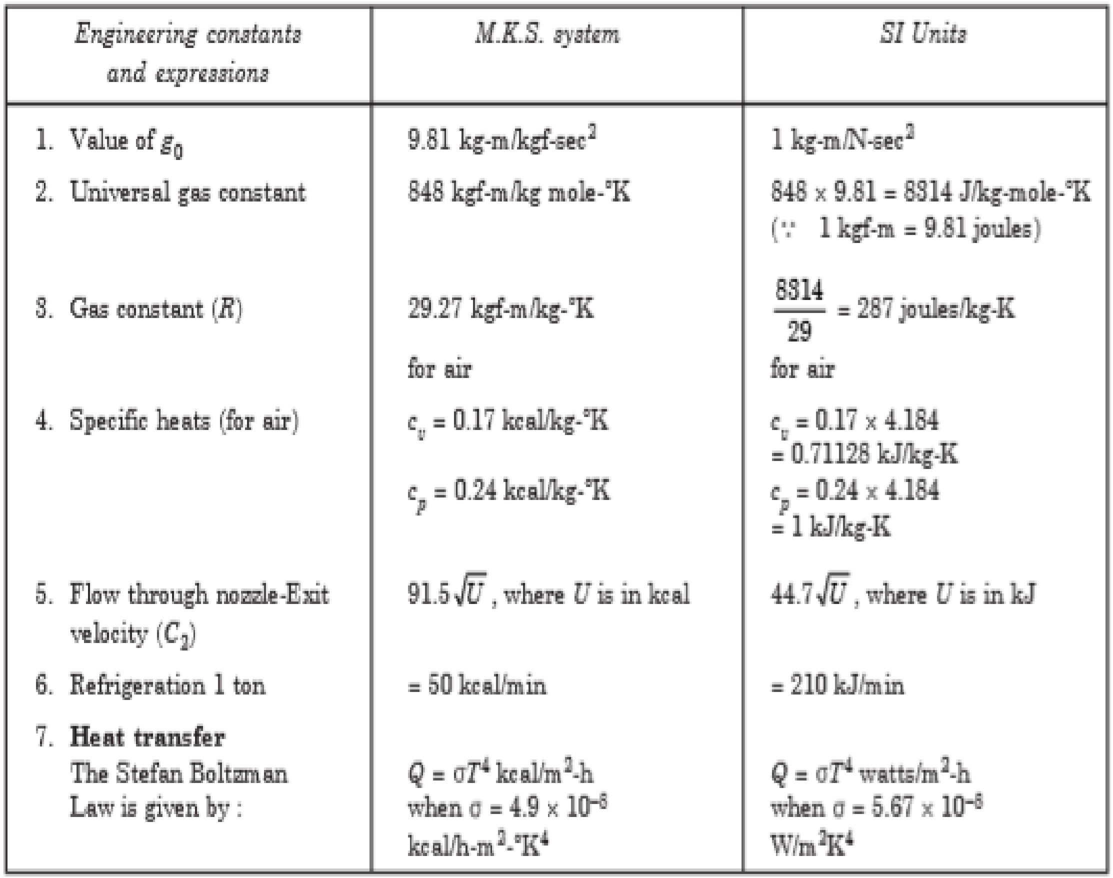
6. Thermal conductivity :

1 watt/m-K = 0.8598 kcal/h-m-°C
1 kcal/h-m-°C = 1.16123 watt/m-K = 1.16123 joules/s-m-K.

7. Heat transfer co-efficient :

1 watt/m^2-K = 0.86 kcal/m^2-h-°C
1 kcal/m^2-h-°C = 1.163 watt/m^2-K.

C. IMPORTANT ENGINEERING CONSTANTS AND EXPRESSIONS



Engineering constants and expressions	*M.K.S. system*	*SI Units*
1. Value of g_0	9.81 kg-m/kgf-sec^2	1 kg-m/N-sec^2
2. Universal gas constant	848 kgf-m/kg mole-°K	848 × 9.81 = 8314 J/kg-mole-°K (∵ 1 kgf-m = 9.81 joules)
3. Gas constant (R)	29.27 kgf-m/kg-°K for air	$\frac{8314}{29}$ = 287 joules/kg-K for air
4. Specific heats (for air)	c_v = 0.17 kcal/kg-°K c_p = 0.24 kcal/kg-°K	c_v = 0.17 × 4.184 = 0.71128 kJ/kg-K c_p = 0.24 × 4.184 = 1 kJ/kg-K
5. Flow through nozzle-Exit velocity (C_2)	$91.5\sqrt{U}$, where U is in kcal	$44.7\sqrt{U}$, where U is in kJ
6. Refrigeration 1 ton	= 50 kcal/min	= 210 kJ/min
7. **Heat transfer** The Stefan Boltzman Law is given by :	$Q = \sigma T^4$ kcal/m^2-h when $\sigma = 4.9 \times 10^{-8}$ kcal/h-m^2-°K^4	$Q = \sigma T^4$ watts/m^2-h when $\sigma = 5.67 \times 10^{-8}$ W/m^2K^4

Introduction

1.1 Basic Definitions

Thermodynamics is the science that deals with the interaction between energy and material systems.

Or

Thermodynamics is an axiomatic science which deals with **the relations among heat, work and properties of system** which are in equilibrium. It describes state and changes in state of physical systems.

- The name thermodynamics derives from the Greek **thermotis (heat)** and dynamiki **(potential, power).** Its historical roots are found in the quest to **develop heat engines**, **devices that use heat to produce mechanical work**. This quest, which was instrumental in powering the industrial revolution, gave birth to thermodynamics as a discipline that studies the relationship between heat, work, and energy.
- Chemical processes involve streams undergoing various transformations. One example is shown in Figure 1-1: raw materials are fed into a heated reactor, where they react to form products.

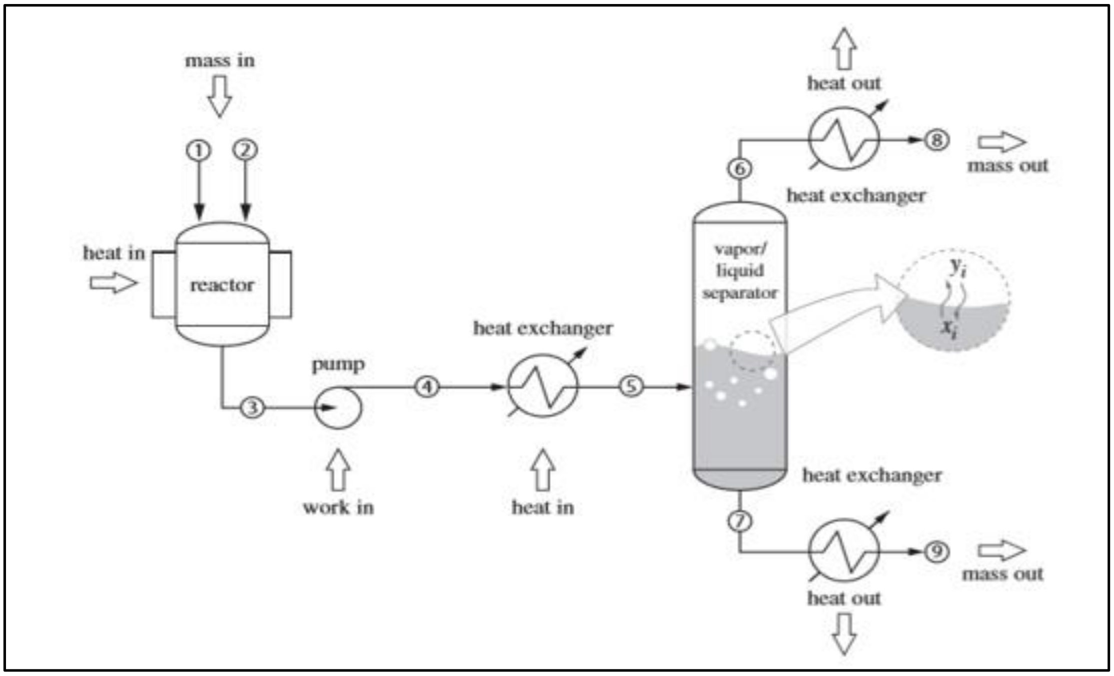


Figure 1-1: Typical chemical process

- Definition of **'heat':** Heat is energy in transit solely as a result of a temperature difference.

- Definition of **'work':** Work is energy exchange **between system and surroundings** due to any phenomenon except a temperature difference.

- Definition of 'temperature': Temperature is a measure of the mean kinetic energy of molecules. Absolute zero (0 ^{o}K) is a state of complete motionless of molecules.

- 'Rate': 'Rate' implies an element of speed, how fast an event happens, and time.

- 'System': In thermodynamics, the universe can be divided into two parts.

  - One part is the **system**,
    The ***other part*** is the rest of the universe called the **surroundings as** shown in Figure 1.2

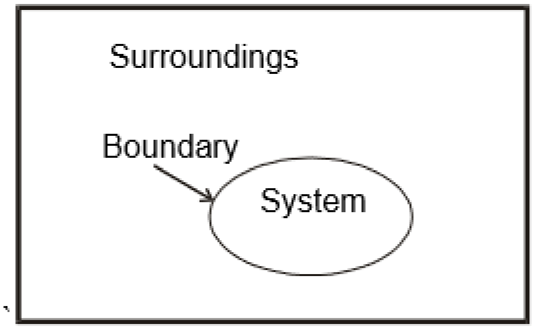


Figure 1.2 Schematic diagram of the "universe", showing a system and the surroundings.

System can be classified as

- Isolated system where **no mass or energy** is transferred across the system boundaries,
- Closed system (system) where **only energy is transfer**red across the system boundaries, or
- Open system (control volume) where **mass and energy can be transferred** across the system boundaries. A system is any designated region of a continuum of fixed

mass. The boundaries of a system may be deformable but they always enclose the same mass.

- Control volume': A 'control volume' is also any designated region of a continuum except that it may permit matter to cross its boundaries. If the boundaries of a control volume are such that matter may not enter or leave the control volume, the control volume is identical to a system. In these respects, a 'system' is a subset of a 'control volume'.

- 'Equilibrium': 'Equilibrium' means that there are no spatial differences in the variables that describe the condition of the system, also called the 'state' of a system, such as its pressure, temperature, volume, and mass (P, T, V, m), and that any changes which occur do so infinitesimally slowly.

The laws of thermodynamics are applicable only to equilibrium states which means that the state does not really change significantly with time, differences in variables between the **state of a system and its surroundings** are of infinitesimal magnitude and that within the system itself there are no spatial variations of the variables that determine its state. Using thermodynamics,

We can **predict the amount of energy needed** to change a system from an equilibrium state to another For example.

Example it will take about 75 kJ to change 1 kg of air at 25°C and 1 atm to 100°C and 1 atm. It will take much more energy, about 2257 kJ, to change 1 kg of water at 100°C and 1 atm to water vapor (steam) at the same temperature and pressure.

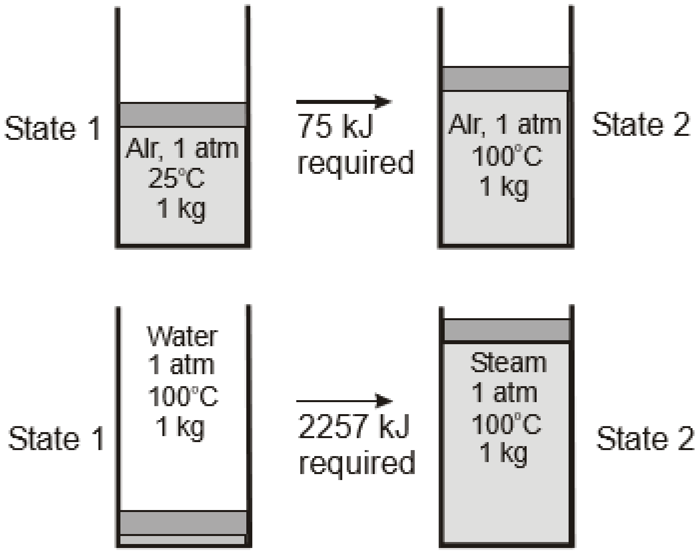


Figure 1.3 Energy required changing air or water from state 1 to state 2.

1.2 Units:

The SI units (Système International d'Unitès, translated Internal System of Units) are used in this text. It happens that seven primary quantities are needed to completely describe all natural phenomena1. The decision as to which quantities are primary is arbitrary. The units of the primary quantities and their symbols are listed in Table 1-1 and are defined arbitrarily as follows:

Meter: the length of the path traveled by light in a vacuum per 1/299,792,458 s,

Kilogram: the mass of the platinum cylinder deposited at the International Office for Weights and Measures, Sèvres, France,

Second: 9,192,631,770 times the period of radiation in energy level transitions in the fine spectral structure of 133Cs,

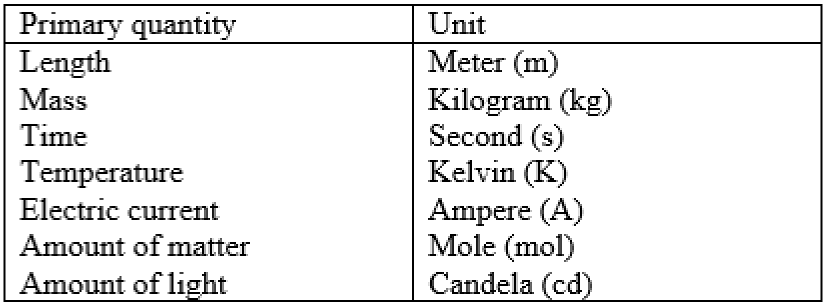
Kelvin: 1/273.16 of the triple point temperature of water with naturally occurring amounts of H and O isotopes,

Amperes: the current which, on passing through two parallel infinite conducting wires of negligible cross section, separated by 1 m and in vacuum, induces a force (per unit length) of 2×10^{-7} N/m,

Mole: the amount of a matter containing the number of particles equal to the number of atoms in 0.012 kg of the pure isotope 12 C,

Candela: the amount of perpendicular light (luminosity) of $1/60\times10^{-6}$ m^2 of the surface of an absolute black body at the melting temperature of platinum and a pressure of 101,325 Pa.

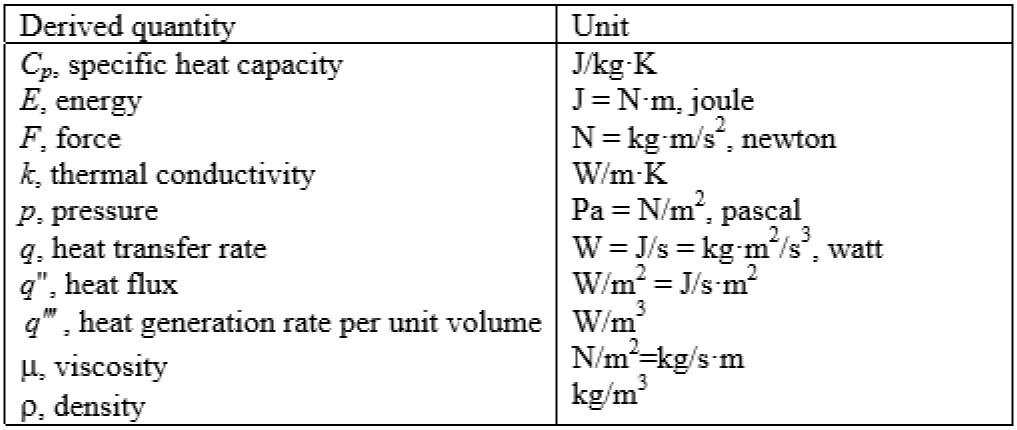
Table 1-1: The seven primary quantities and their units in SI



Primary quantity	Unit
Length	Meter (m)
Mass	Kilogram (kg)
Time	Second (s)
Temperature	Kelvin (K)
Electric current	Ampere (A)
Amount of matter	Mole (mol)
Amount of light	Candela (cd)

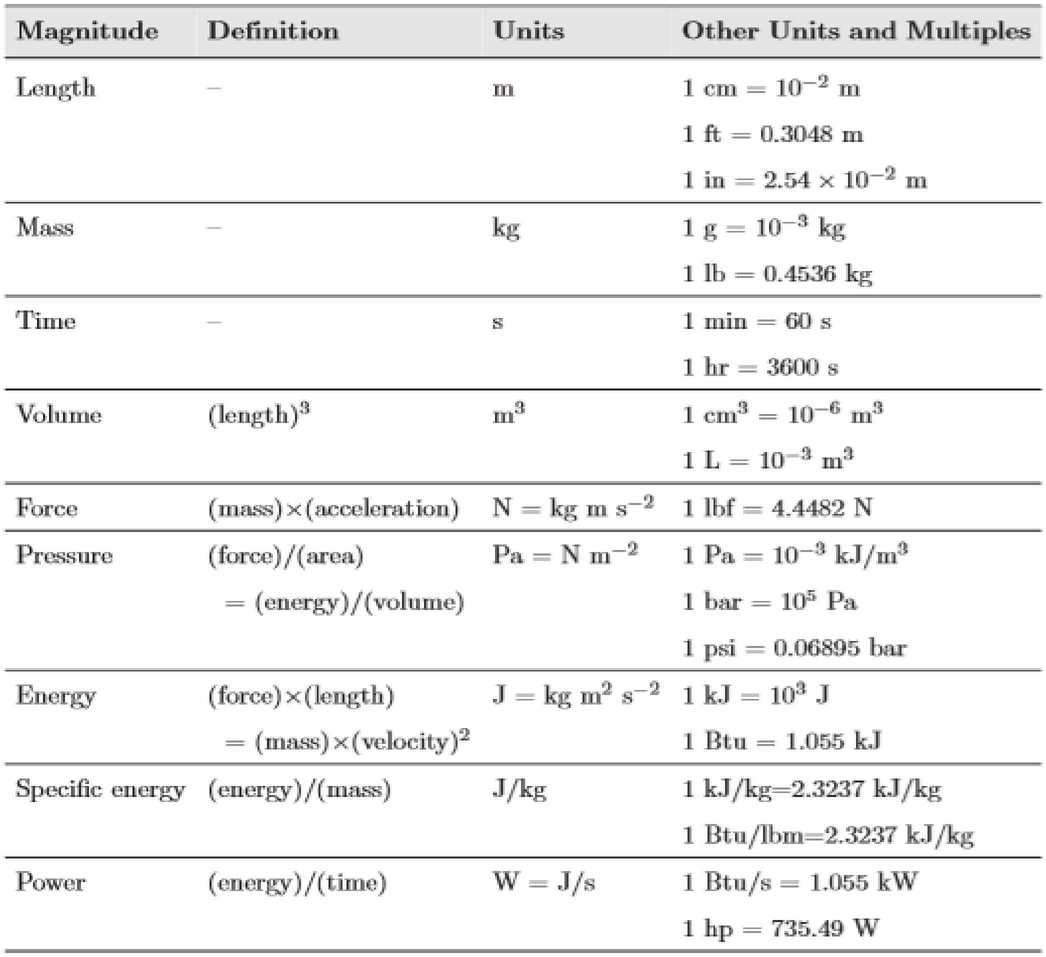
Several of the derived quantities with units are listed in Table 1.3-2. A derived unit is a quantity expressed in terms of a product and/or quotient of two or more primary units.

Table 1-2: The derived quantities and their units in SI



Derived quantity	Unit
C_p, specific heat capacity	J/kg·K
E, energy	J = N·m, joule
F, force	N = kg·m/s^2, newton
k, thermal conductivity	W/m·K
p, pressure	Pa = N/m^2, pascal
q, heat transfer rate	W = J/s = kg·m^2/s^3, watt
q'', heat flux	W/m^2 = J/s·m^2
q''', heat generation rate per unit volume	W/m^3
μ, viscosity	N/m^2=kg/s·m
ρ, density	kg/m^3

Table 1-3: Common units and conversion factors



Magnitude	Definition	Units	Other Units and Multiples
Length	–	m	1 cm = 10^{-2} m 1 ft = 0.3048 m 1 in = 2.54×10^{-2} m
Mass	–	kg	1 g = 10^{-3} kg 1 lb = 0.4536 kg
Time	–	s	1 min = 60 s 1 hr = 3600 s
Volume	(length)^3	m^3	1 cm^3 = 10^{-6} m^3 1 L = 10^{-3} m^3
Force	(mass)×(acceleration)	N = kg m s^{-2}	1 lbf = 4.4482 N
Pressure	(force)/(area) = (energy)/(volume)	Pa = N m^{-2}	1 Pa = 10^{-3} kJ/m^3 1 bar = 10^5 Pa 1 psi = 0.06895 bar
Energy	(force)×(length) = (mass)×(velocity)^2	J = kg m^2 s^{-2}	1 kJ = 10^3 J 1 Btu = 1.055 kJ
Specific energy	(energy)/(mass)	J/kg	1 kJ/kg=2.3237 kJ/kg 1 Btu/lbm=2.3237 kJ/kg
Power	(energy)/(time)	W = J/s	1 Btu/s = 1.055 kW 1 hp = 735.49 W

1.3 Pressure

Any force acting on a surface consists of a component perpendicular to the surface and a component parallel to the surface. These two components are called normal force and shear force as shown in Figure 1.4.

Pressure is defined as a normal force per unit area on which the force acts. The SI pressure unit, N/m^2, is called a Pascal (Pa). Pressure at any point is a fluid is the same in any direction.

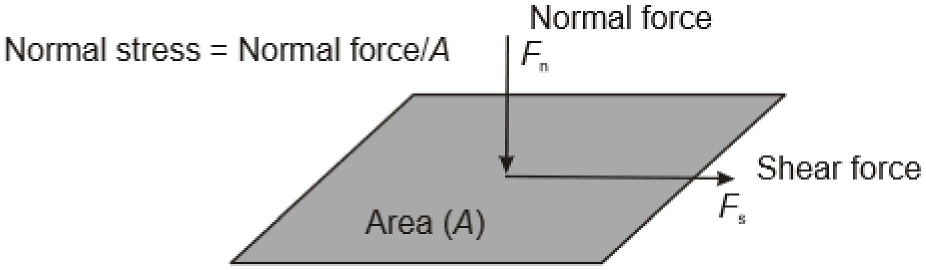


Figure 1.4 Normal and parallel components of a force on a surface.

Consider a hole in the wall of a tank or a pipe as shown in Figure 1.5. The fluid pressure p may be defined as the ratio F/A, where F is the minimum force that would have to exerted on a frictionless plug in the hole to keep the fluid from emerging1

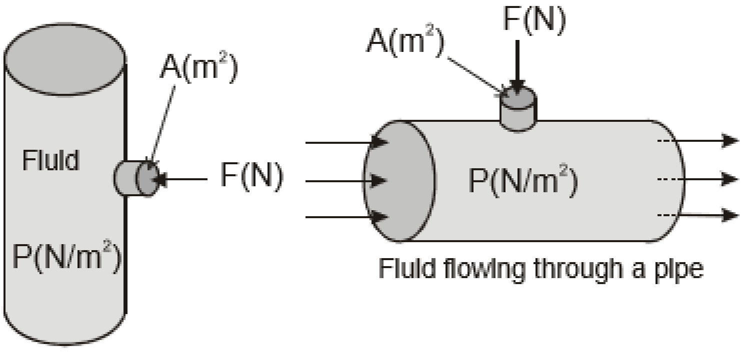


Figure 1.5 Fluid pressure in a tank and a pipe.

The pressure at a given position measured relative to absolute zero pressure or absolute vacuum is called the absolute pressure. Most pressure-measuring devices are calibrated to read zero in the atmosphere as shown in Figure 1.6. These pressure gages indicate the difference between the absolute pressure and the local atmospheric pressure. Pressures below atmospheric pressure are called vacuum pressures and are measured by vacuum gages that indicate the difference between the atmospheric pressure and the absolute pressure. Absolute, gage, and vacuum pressures are all positive quantities and are related to each other by

$$P_{gage} = P_{abs} - P_{atm} \qquad (1.1)$$

$$P_{vac} = P_{atm} - P_{abs} \qquad (1.2)$$

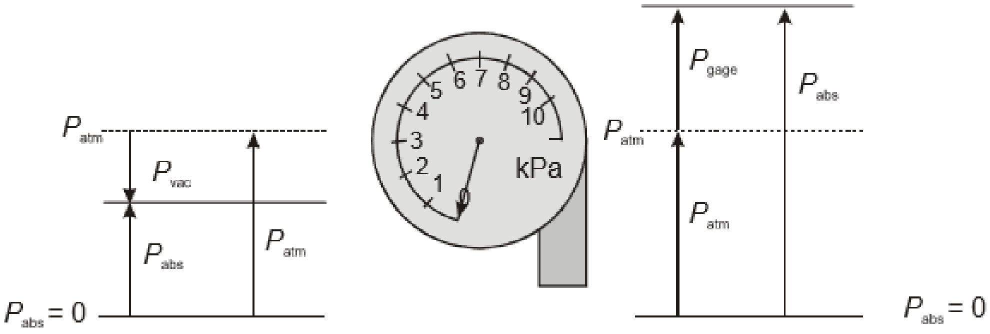


Figure 1.6 Absolute, gage, and vacuum pressures.

Two common pressure units are the bar and standard atmosphere:

1 bar = 10^5 Pa = 0.1 Mpa = 100 kPa

1 atm = 101,325 Pa = 101.325 kPa = 1.01325 bar = 14.696 psi

1.4 The specific volume v is defined as the reciprocal of the density, $\boldsymbol{v = 1/\rho}$ It is the volume per unit mass. Like density, specific volume is an intensive property and may vary from point to point. SI units for density and specific volume are kg/m^3 and m^3/kg, respectively. However, they are also often expressed, respectively, as g/cm^3 and cm^3/g. Other units used for density and specific volume in this text are lb/ft^3 and ft^3/lb, respectively. In the fluid mechanics part of the book, density also is given in $slug/ft^3$.

In certain applications it is convenient to express properties such as a specific volume on a molar basis rather than on a mass basis. The amount of a substance can be given on a molar basis in terms of the kilomole (kmol) or the pound mole (lbmol), as appropriate. In either case we use

$$\mathbf{n = m / M} \qquad (1.3)$$

The number of kilomoles of a substance, n, is obtained by dividing the mass, m, in kilograms by the molecular weight, M, in kg/kmol. Similarly, the number of pound moles, n, is obtained by dividing the mass, m, in pound mass by the molecular weight, M, in lb/lbmol.

In thermodynamics, we signal that a property is on a molar basis by placing a bar over its symbol. Thus, **ϋ** signifies the volume per kmol or lbmol, as appropriate. In this text the units used for ϋ are $m^3/kmol$ and $ft^3/lbmol$. With Eq. 1.3, the relationship between ύ and υ is

$$\mathbf{ύ = M\, \boldsymbol{v}} \qquad (1.4)$$

Where M is the molecular weight in kg/kmol or lb/lbmol, as appropriate.

1.5 Temperature

When two objects are brought into contact and isolated from the surrounding, energy tends to move spontaneously from one to the other. The object that gives up energy is at a higher temperature, and the object that receives energy is at a lower temperature.

We would be able to observe that the electrical resistance *of the warmer* object decreases with time, and that of the colder block increases with time; eventually there would be no change in the electrical resistances of these objects. The two objects are then in thermal equilibrium. They are at the same Temperature. We could then define temperature as a measure of the tendency of an object to spontaneously give up energy to its surroundings.

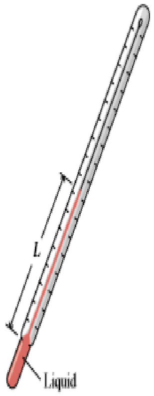
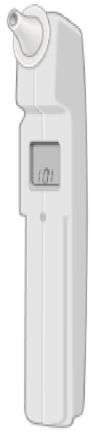


Figure 2.5 Liquid-in-glass thermometer.

Any object with at least one measurable property that changes as its temperature changes can be used as a thermometer. Most thermometers operate on the principle of thermal expansion: Materials tend to occupy more volume at a given pressure when they are at a higher temperature. A mercury thermometer is just a convenient device for measuring the volume of a fixed amount of mercury. To define actual units for temperature we arbitrary assign 0 to the freezing point and 100 to the boiling or steam point of water. We then mark these points on our mercury thermometer, measure off a hundred equally spaced intervals in between, and declare that this thermometer now measures temperature on the Celsius (or centigrade) scale, by definition.



The Kelvin scale is an absolute temperature scale that measures temperature from absolute zero instead of from the freezing point of water. The relationship between these two temperature scales is given by

$$\mathbf{T(^{o}C) = T(K) - 273.15} \qquad (1.5)$$

By definition, the Rankin scale, is related to the Kelvin scale by a factor of 1.8:

$$\mathbf{T(^{o}R) = 1.8T(K)} \qquad (1.6)$$

A degree of the same size as that on the Rankine scale is used in the Fahrenheit scale but the zero point is shifted according to the relation

$$\mathbf{T\ (^oF) = T(^oR) - 459.67} \qquad (1.7)$$

From equations (1.5), (1.6), and (1.7) the Fahrenheit scale can be related to the Celsius scale by

$$\mathbf{T\ (^oF) = 1.8\ T(^oC) + 32} \qquad (1.8)$$

Many of the equations of thermodynamics are correct only when you measure temperature on the absolute scale, Kelvin or Rankine. There will be no problem in using the Celcius and Fahrenheit scales when the difference between two temperatures is needed.

1.6. ENERGY, WORK AND HEAT

1.6.1. Energy

Energy: is a general term embracing energy in transition and stored energy. The stored energy of a substance may be in the forms of mechanical energy and internal energy (other forms of stored energy may be chemical energy and electrical energy). Part of the stored energy may take the form of either potential energy (which is the gravitational energy due to height above a chosen datum line) or kinetic energy due to velocity. The balance part of the energy is known as internal energy.

In a non-flow process usually there is no change of potential or kinetic energy and hence change of mechanical energy will not enter the calculations.

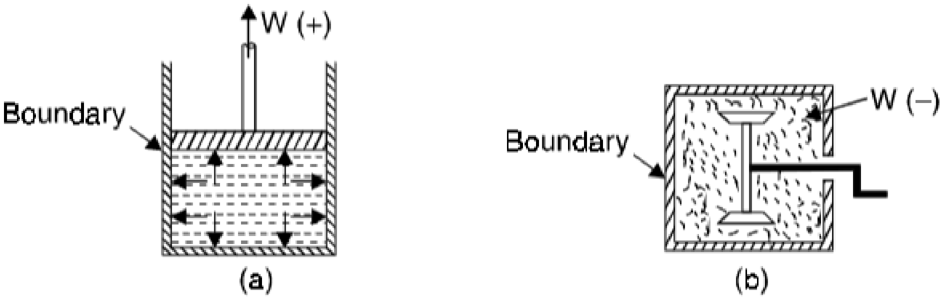
In a flow process, however, there may be changes in both potential and kinetic energy and these must be taken into account while considering the changes of stored energy.

Heat and work are the forms of energy in transition. These are the only forms in which energy can cross the boundaries of a system. Neither heat nor work can exist as stored energy.

*** Work and Heat

1.6.2 Work:

Work is said to be done when a force moves through a distance. If a part of the boundary of a system undergoes a displacement under the action of a pressure, the work done W is the product of the force (pressure × area), and the distance it moves in the direction of the force. Fig. 1.7 (a) illustrates this with the conventional piston and cylinder arrangement, the heavy line defining the boundary of the system. Fig. 1.7 (b) illustrates another way in which work might be applied to a system. A force is exerted by the paddle as it changes the momentum of the fluid, and since this force moves during rotation of the paddle work is done.



(a) (b)

Figure 1.7

Work is a transient quantity which only appears at the boundary while a change of state is taking place within a system. Work is 'something' which appears at the boundary when a system changes its state due to the movement of a part of the boundary under the action of a force.

Sign convention:

- If the work is done by the system on the surroundings, e.g., when a fluid expands pushing a piston outwards, the work is said to be positive.

i.e., **Work output of the system = + W**

- If the work is done on the system by the surroundings, e.g., when a force is applied to a rotating handle, or to a piston to compress a fluid, the work is said to be negative.

  i.e., **Work input to system = – W**

$$W = \int_{V_1}^{V_2} P\, dV \qquad (1.9)$$

1// constant P

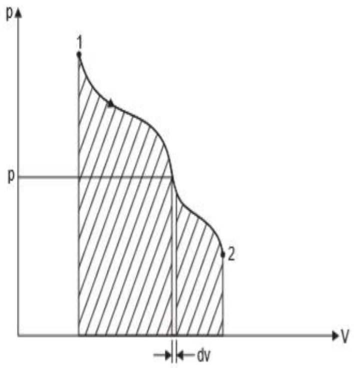
W = P ($V_2 - V_1$)

2// constant *V*

W= 0   d*V*

3// Relation between pressure P and volume *V*

4// drawing   (area under curve) between P & *V*



1.6.3 Heat

Heat (denoted by the symbol Q), may be, defined in an analogous way to work as follows: *"Heat is* ***'something' which appears at the boundary when a system changes its state due to a difference in temperature between the system and its surroundings".***

Heat, like work, is a transient quantity which only appears at the boundary while a change is taking place within the system.

It is apparent that neither δW or δQ are exact differentials and therefore any integration of the elemental quantities of work or heat which appear during a change from state 1 to state 2 must be written as

$$\int_1^2 \delta W = W_2 - W_1$$

$$\int_1^2 \delta Q = Q_2 - Q_1$$

Sign convention: If the heat flows into a system from the surroundings, the quantity is said to be positive and, conversely, if heat flows from the system to the surroundings it is said to be negative.

In other words:

Heat received by the system = + Q

Heat rejected or given up by the system = – Q.

Heat

1- The Units Of Energy (J), (J/Kg) and (J/sec) or (w)
2- Constant pressure $Q = \int_{T_1}^{T_2} Cp\, dT$
3- Constant Volume $Q = \int_{T_1}^{T_2} Cv\, dT$

SI units: J = 1 N. m
English units: ft. Ibf = 1.3558 J
Other units
The thermal unit (Btu) = 1055.04 J
1 Btu = 1055 J = 252 Cal = 778 ft. Ibf.

Comparison of Work and Heat Similarities:

(i) Both are path functions and inexact differentials.
(ii) Both are boundary phenomenon i.e., both are recognized at the boundaries of the system as they cross them.
(iii) Both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.
(iv) Systems possess energy.

But not work or heat. Dissimilarities:

(i) In heat transfer temperature difference is required.
(ii) In a stable system there cannot be work transfer, however, there is no restriction for the transfer of heat.
(iii) The sole effect external to the system could be reduced to rise of a weight but in the case of a heat transfer other effects are also observed

1.7 Kinetic and Potential Energy

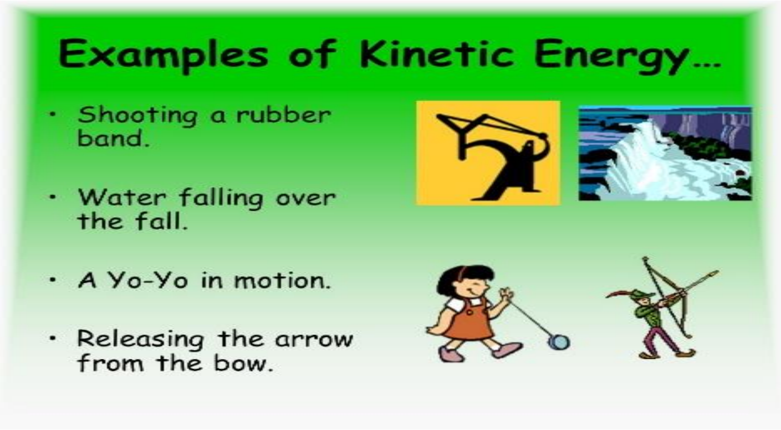
Consider a body of mass m that moves from a position where the magnitude of its velocity is V_1 and its elevation is z1 to another where its velocity is V_2 and elevation is z2, each relative to a specified coordinate frame such as the surface of the earth.

1.7.1 Kinetic Energy: **The quantity $1/2\ mV^2$ is the kinetic energy, KE,** of the body. As written as

$$\mathbf{KE = 1/2\ m\ V^2} \qquad (1.10)$$

The change in **kinetic energy ΔKE of the body is**

$$\Delta KE = KE_2 - KE_1 = \tfrac{1}{2}m\left(V_2{}^2 - V_1{}^2\right) \qquad (1.11)$$

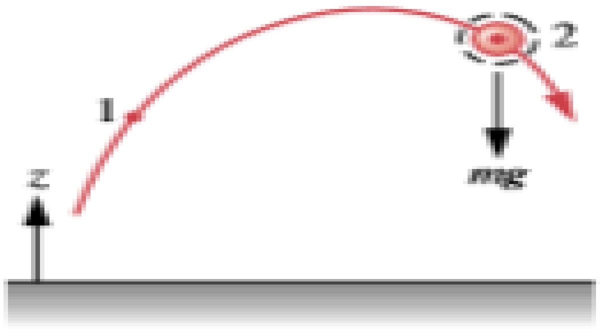


Examples of Kinetic Energy…

- Shooting a rubber band.
- Water falling over the fall.
- A Yo-Yo in motion.
- Releasing the arrow from the bow.

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.

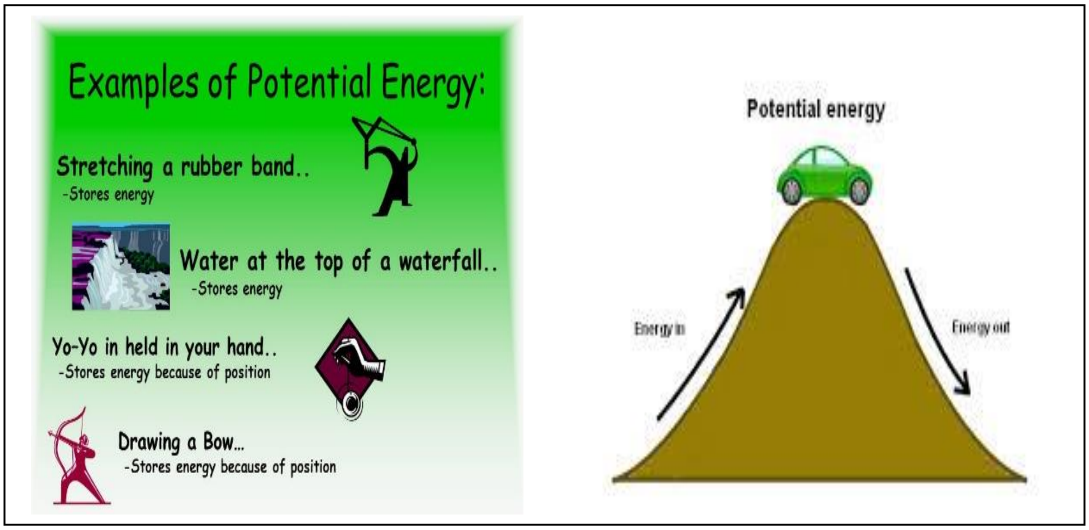


1.7.2 Potential Energy

The quantity mgz is the gravitational potential energy, PE. The change in gravitational potential energy, PE, is

$$\Delta PE = PE_2 - PE_1 = m\,g\,(Z_2 - Z_1) \qquad (1.12)$$

Potential energy is associated with the force of gravity (Sec. 1.12) and is therefore an attribute of a system consisting of the body and the earth together.



Examples of Potential Energy:

Stretching a rubber band..
-Stores energy

Water at the top of a waterfall..
-Stores energy

Yo-Yo in held in your hand..
-Stores energy because of position

Drawing a Bow...
-Stores energy because of position

However, evaluating the force of gravity as mg enables the gravitational potential energy to be determined for a specified value of g knowing only the mass of the body and its elevation. With this view, potential energy is regarded as an extensive property of the body.

To assign a value to the kinetic energy or the potential energy of a system, it is necessary to assume a datum and specify a value for the quantity at the datum. Values of kinetic and potential energy are then determined relative to this arbitrary choice of datum and reference value. However, since only changes in kinetic and potential energy between two states are required, these arbitrary reference specifications cancel.

Units. In SI, the energy unit is the newton-meter, N m, called the joule, J. In this book it is convenient to use the kilojoule, kJ.

Other commonly used units for energy are the ***foot pound force,*** and the **British thermal unit, Btu.**

When a system undergoes a process where there are changes in kinetic and potential energy, special care is required to obtain a consistent set of units.

For Example… to illustrate the proper use of units in the calculation of such terms, consider a system having a mass of 1 kg whose velocity increases from 15 m/s to 30 m/s while its elevation decreases by 10 m at a location where g= 9.7 m/s^2.Then

$$\Delta KE = \tfrac{1}{2}m\left({V_2}^2 - {V_1}^2\right)$$

$$\Delta KE = \tfrac{1}{2}(1\ kg)\left[\left(30\frac{m}{s}\right)^2 - \left(15\frac{m}{s}\right)^2\right]\left|\frac{1N}{1\ kg.\ m/s^2}\right|\left|\frac{1KJ}{10^3\ N.m}\right|$$

$$\Delta KE = 0.34\ KJ$$

$$\Delta PE = m\ g\ (Z_2 - Z_1)$$

$$\Delta PE = (1\ kg)\left(9.7\ \frac{m}{S^2}\right)\ [(-\ 10\ m)]\ \left|\frac{1N}{1\ kg.\ m/s^2}\right|\left|\frac{1KJ}{10^3\ N.m}\right|$$

$$\Delta PE = -0.10\ KJ$$

For a system having a mass of 1 Ib whose velocity increases from 50 ft/s to 100 ft/s while its elevation decreases by 40 ft at a location where g= 32.0 ft/s^2, we have

$$\Delta KE = \tfrac{1}{2}m\left({V_2}^2 - {V_1}^2\right)$$

$$\Delta KE = \tfrac{1}{2}(1\ Ib)\left[\left(100\frac{ft}{s}\right)^2 - \left(50\frac{ft}{s}\right)^2\right]\left|\frac{1Ibf}{32.2\ Ib.\ ft/s^2}\right|\left|\frac{1Btu}{778\ ft.Ibf}\right|$$

$$\Delta KE = 0.15\ Btu$$

$$\Delta PE = m\ g\ (Z_2 - Z_1)$$

$$\Delta PE = (1\ Ib)\left(32.0\ \frac{ft}{S^2}\right)\ [(-\ 40\ ft)]\ \left|\frac{1\ Ibf}{32.2\ Ib.\ ft/s^2}\right|\left|\frac{1Btu}{778\ ft.Ibf}\right|$$

$$\Delta PE = -0.05\ Btu$$

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