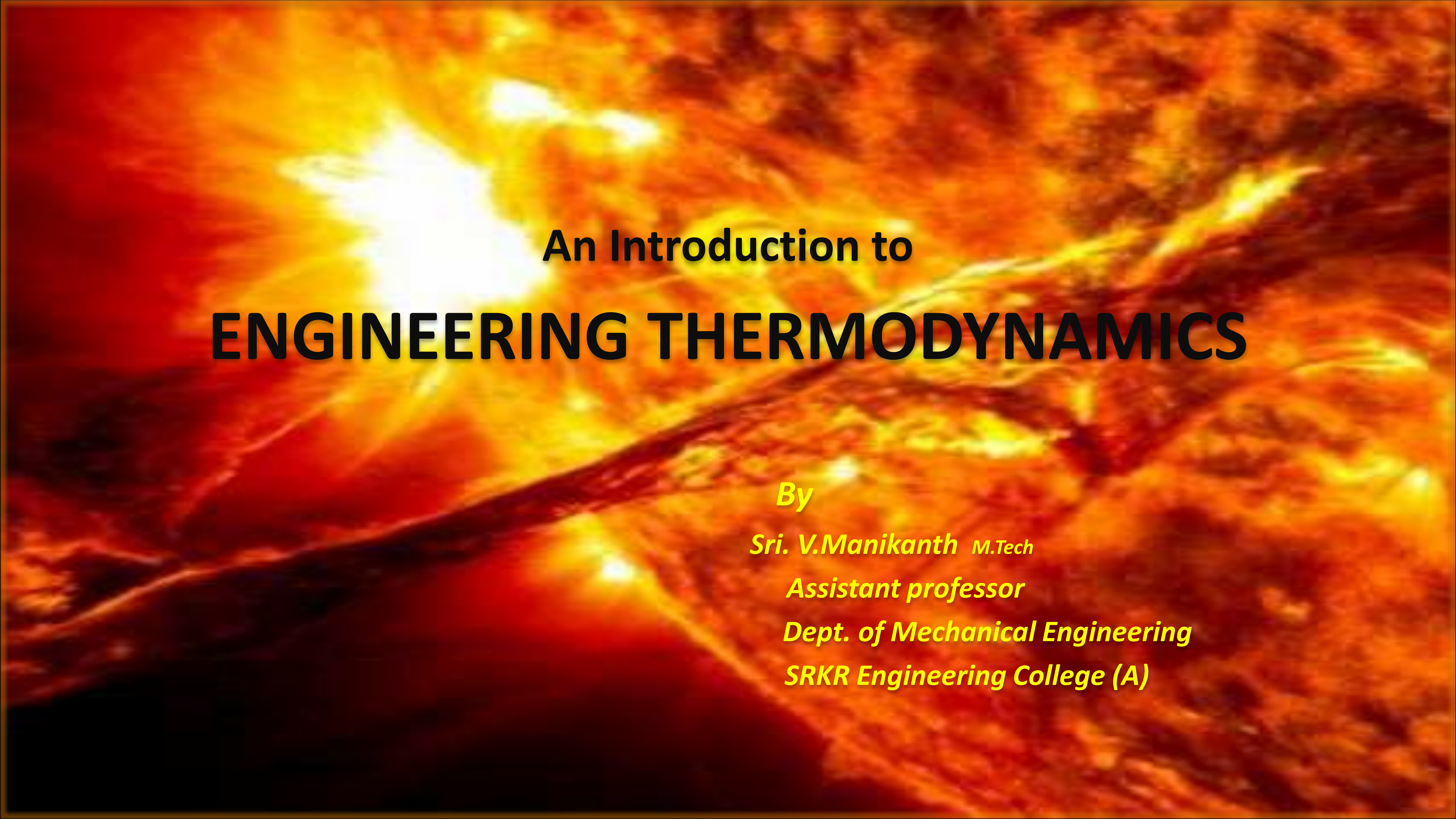

An Introduction to

ENGINEERING THERMODYNAMICS

By

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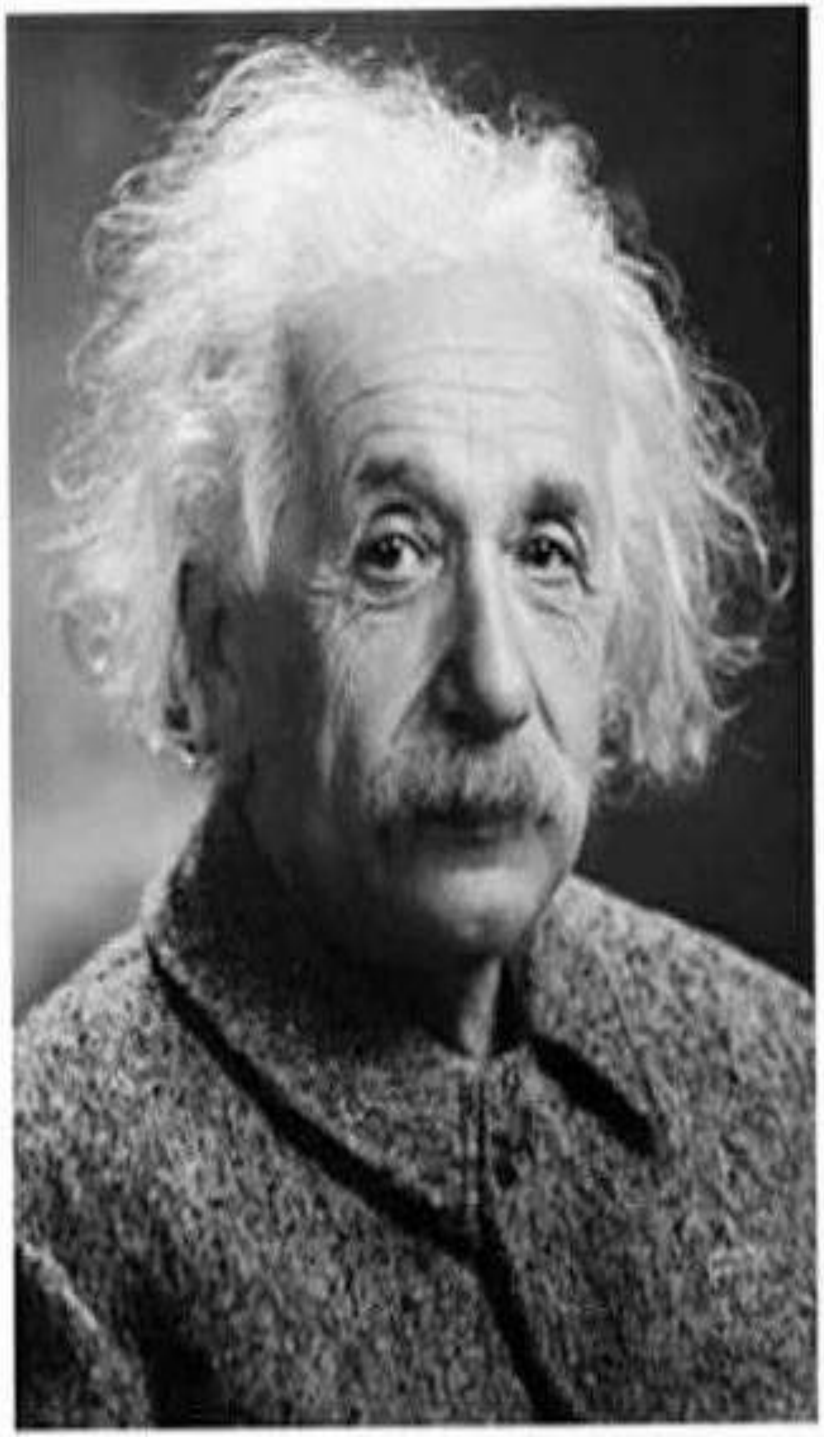
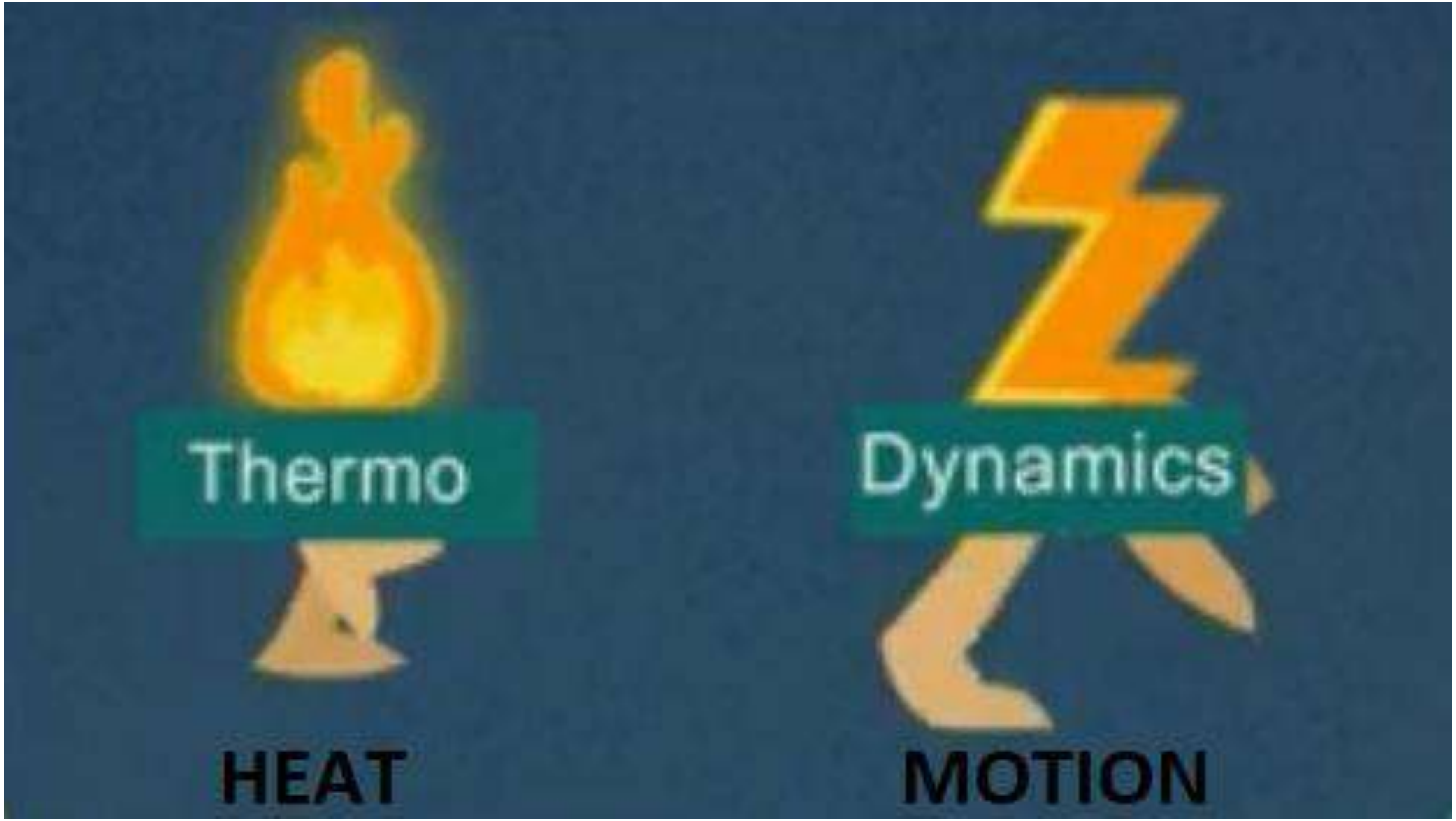


Classical Thermodynamics is the only physical theory of universal content, which I am convinced, that within the framework of applicability of its basic concepts will never be overthrown.

-Albert Einstein, quoted in M.J. Klein, Thermodynamics in Einstein's Universe

What is Thermodynamics ?

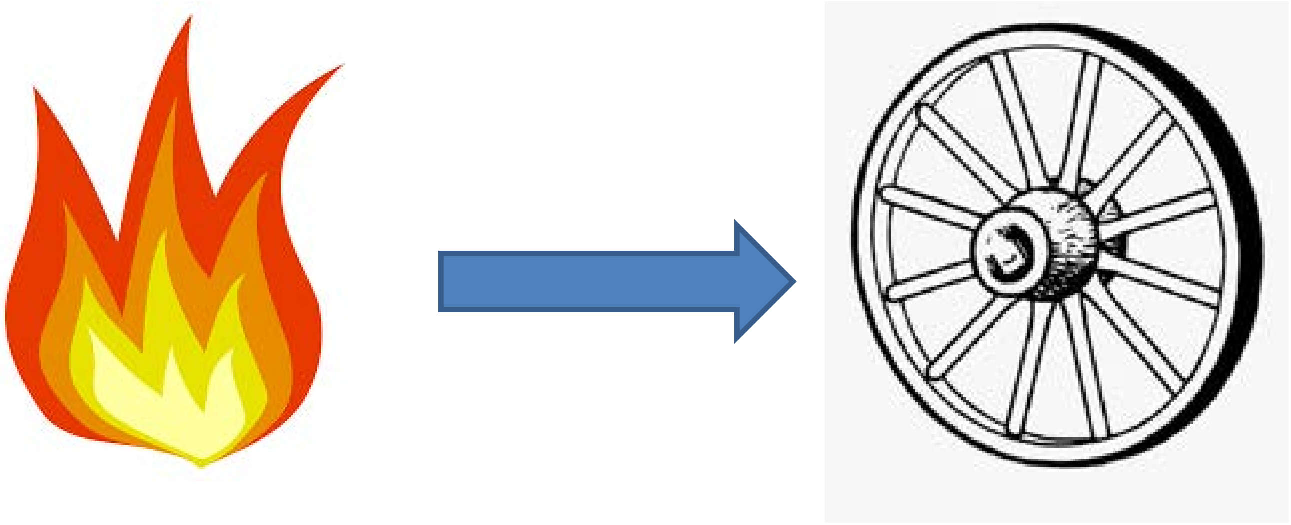
It is a combination of two Greek words



Thermodynamics

"It is the science of energy transfer and its effects on properties of system."

The main aim of thermodynamics is to convert disorganized form of energy (Heat) into organized form of energy (Work)



(*a*) Refrigerator (*b*) Boats (*c*) Aircraft and spacecraft

(*d*) Power plants (*e*) Human body (*f*) Cars

(*g*) Wind turbines (*h*) Food processing (*i*) A piping network in an industrial facility.

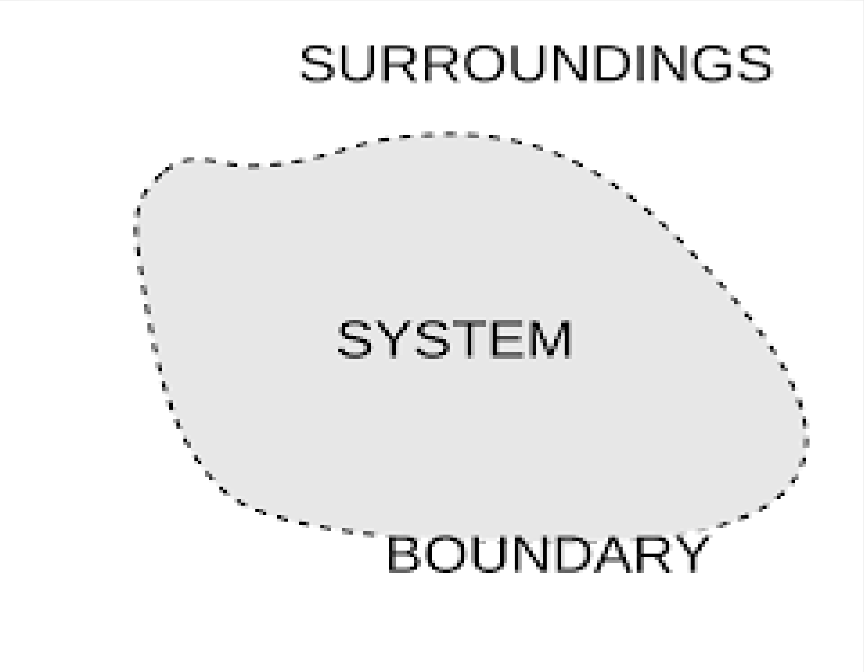
FIGURE Some application areas of thermodynamics.

System, Surroundings and Boundary

A ***Thermodynamic System****,* or simply ***System*** is defined as a quantity of matter or a region in space chosen for study.

Surroundings is the mass or region outside the system.

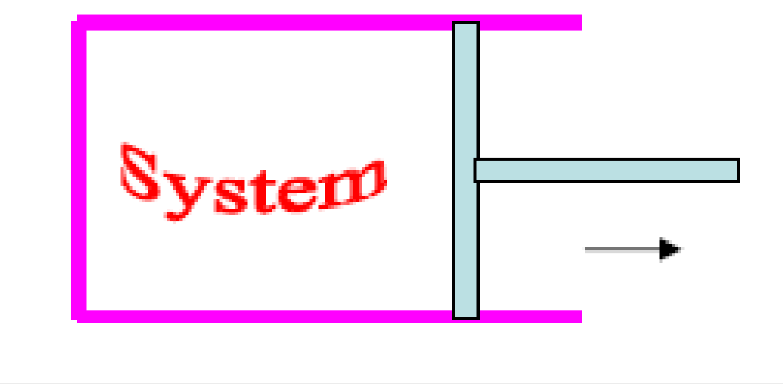
Boundary is the real or imaginary surface that separates the system from its surroundings.



Choice of the System and Boundaries Are at Our Convenience :

The boundaries may be at rest or in motion.

If we choose a system that has a certain defined quantity of mass (such as gas contained in a piston cylinder device) the boundaries must move in such way that they always enclose that particular quantity of mass if it changes shape or moves from one place to another.



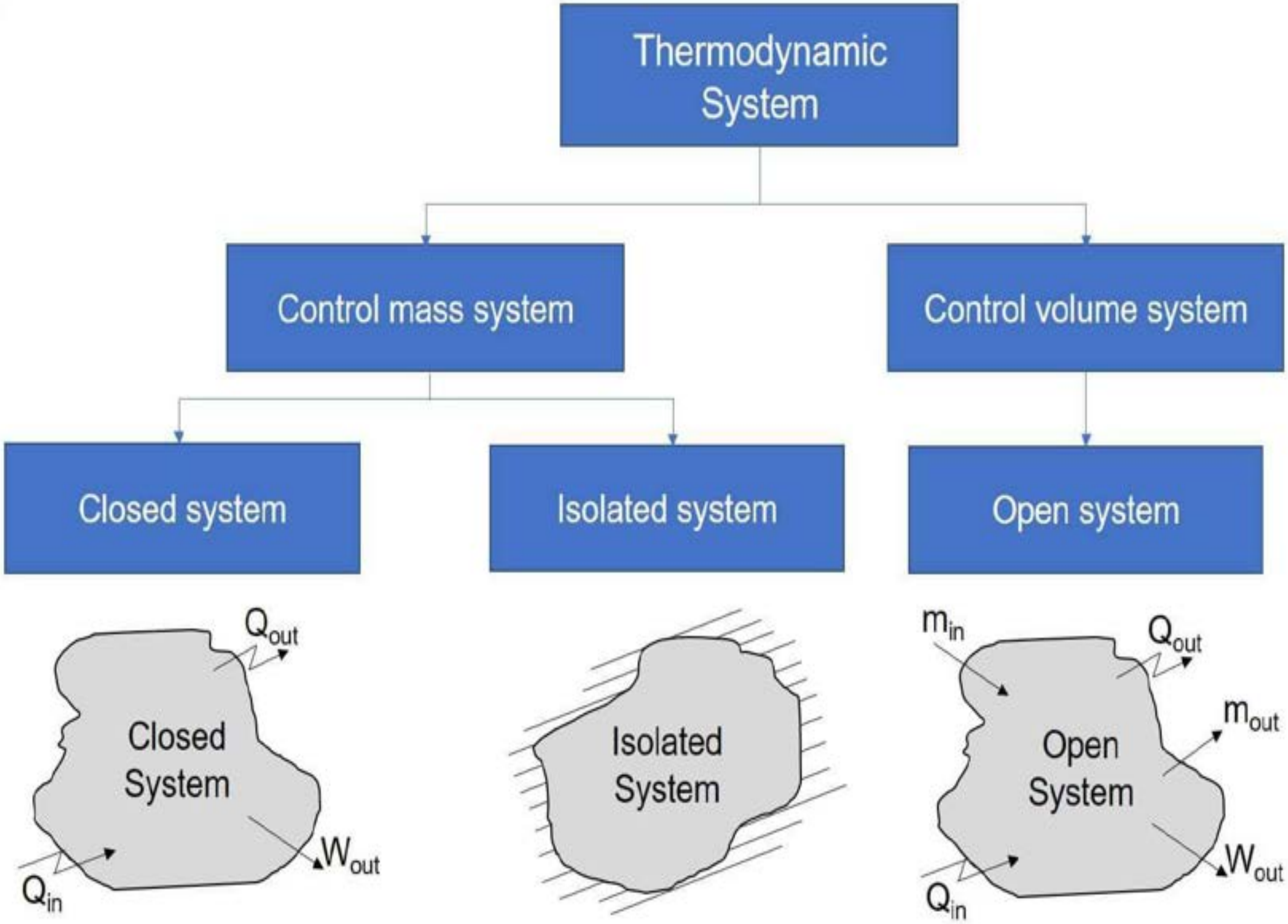
Thermodynamic systems:

Thermodynamic systems can be either closed, or open or isolated.

Closed systems: A closed system is defined when a particular quantity of matter is under study. A closed system always contains the same matter. There can be no mass transfers across the boundary. There may be energy transfer across the boundary.

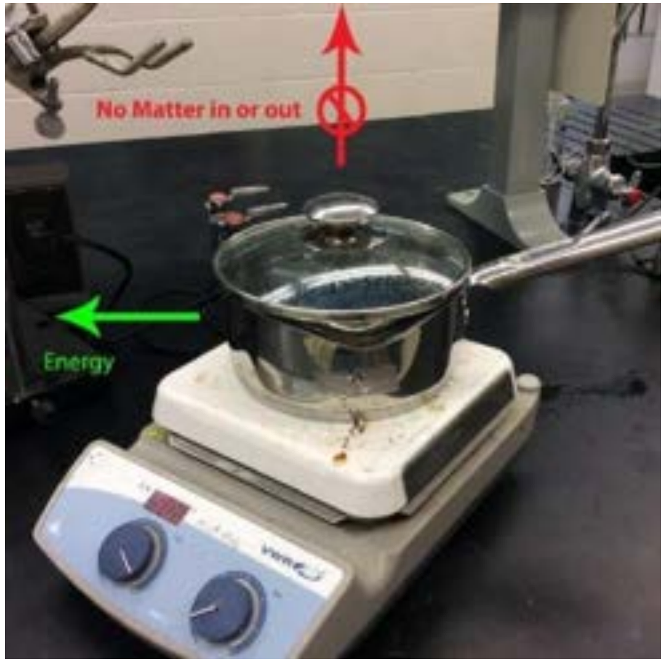
Open systems: A closed system is defined when a fixed volume is under study. There can be mass transfers as well as energy transfers across the boundary.

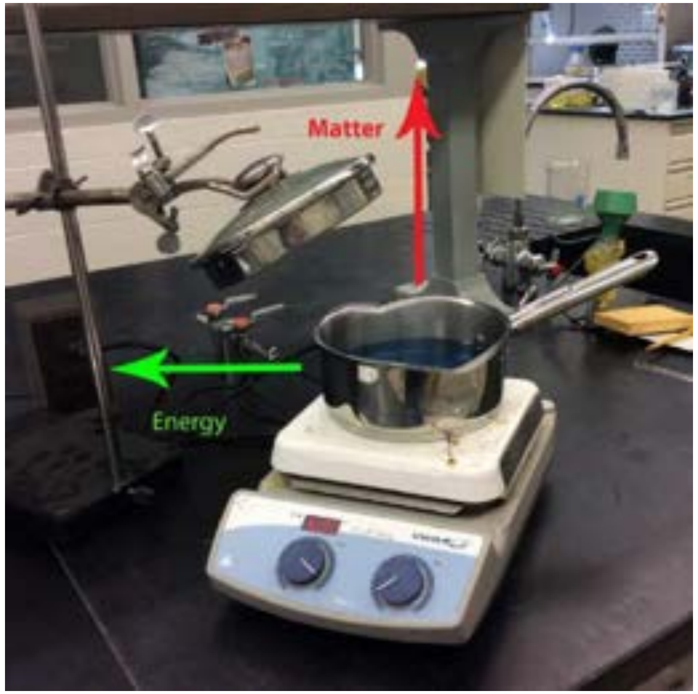
Isolated systems: An isolated system is special type of closed system that does not even transfer energy across the boundary. There will be no interactions with the surroundings.



Thermodynamic System

- Control mass system
  - Closed system
  - Isolated system
- Control volume system
  - Open system


No Matter in or out
Energy


Matter
Energy


304
STAINLESS STEEL
DOUBLE
WALLED
VACUUM
INSULATED
LEAK
PROOF
INSIDE & OUTSIDE
SS
304
STAINLESS
STEEL
MILTON
MILTON

Identify the types of thermodynamic system



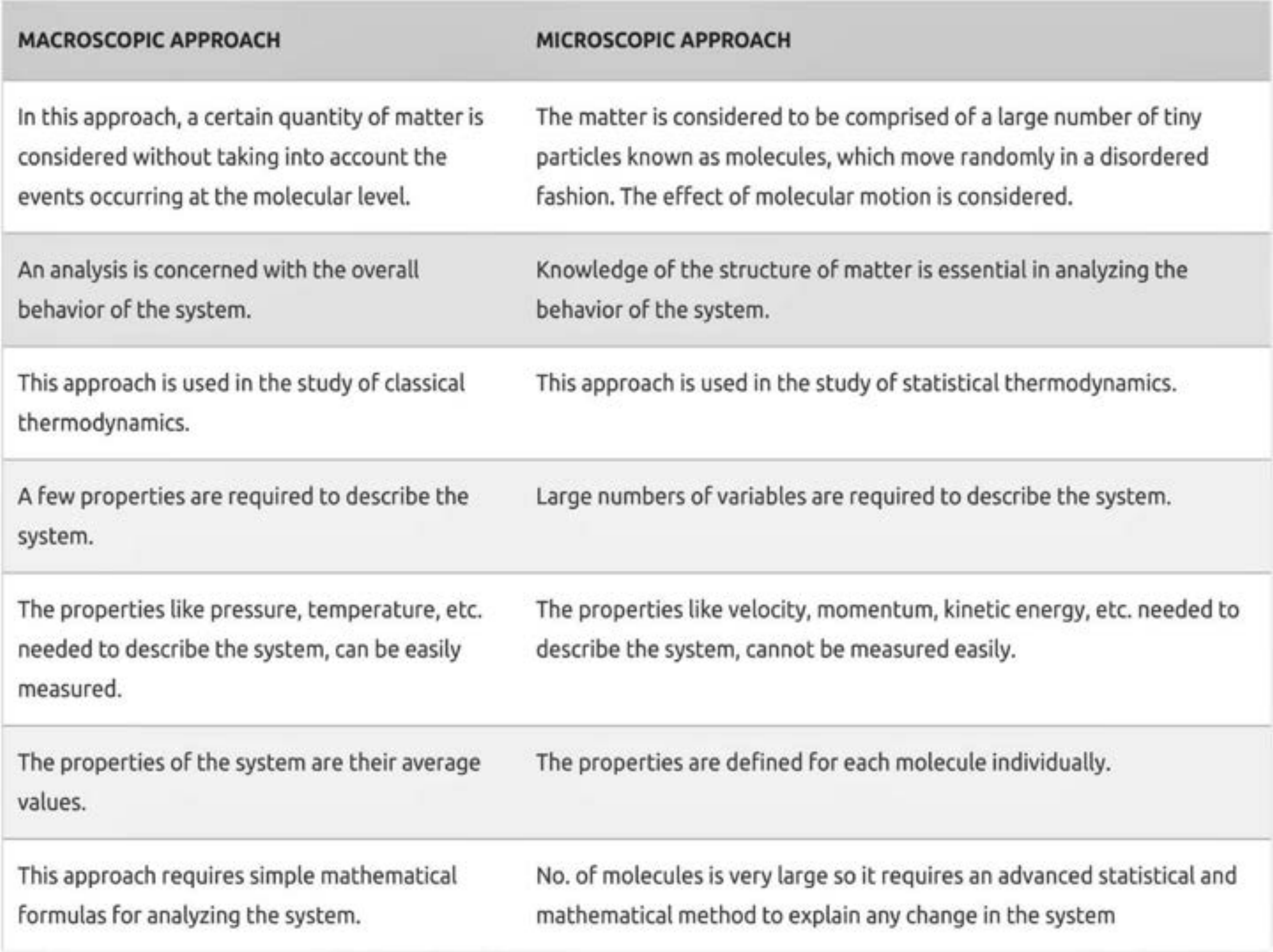



Macroscopic and Microscopic Approaches

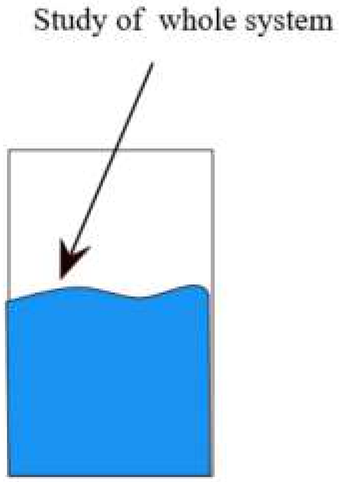
Behavior of matter can be studied by these two approaches.

- In macroscopic approach (Macro mean big or total) or classical thermodynamics, certain quantity of matter is considered, without a concern on the events occurring at the molecular level. These effects can be perceived by human senses or measured by instruments.
- The analysis of a thermodynamics system by macroscopic approach requires simple mathematical formulae
- In order to describe the system, the average of the properties of molecules are defined

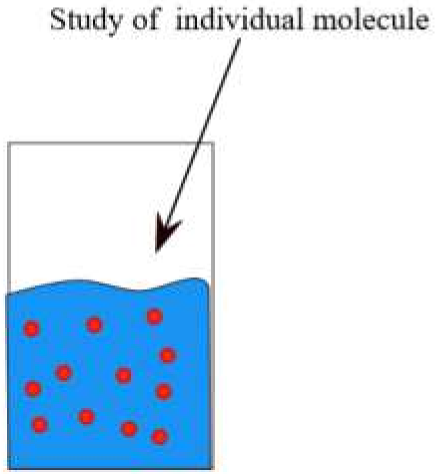
Eg: pressure (consider a gas container whose pressure is average value of pressure exerted by all molecules), temperature



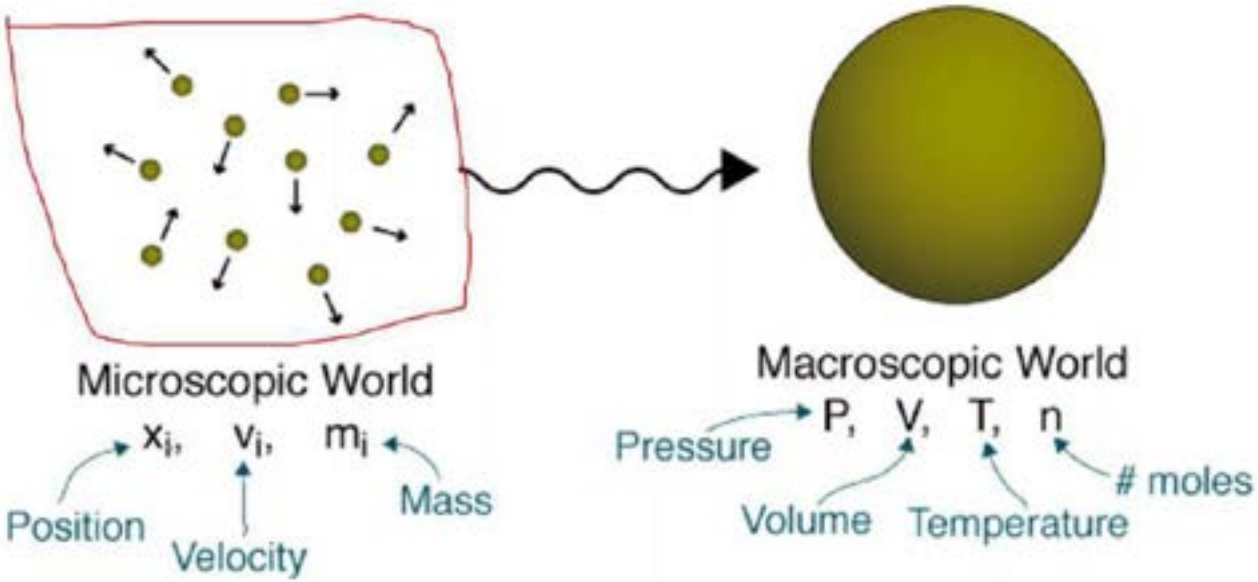
MACROSCOPIC APPROACH	MICROSCOPIC APPROACH
In this approach, a certain quantity of matter is considered without taking into account the events occurring at the molecular level.	The matter is considered to be comprised of a large number of tiny particles known as molecules, which move randomly in a disordered fashion. The effect of molecular motion is considered.
An analysis is concerned with the overall behavior of the system.	Knowledge of the structure of matter is essential in analyzing the behavior of the system.
This approach is used in the study of classical thermodynamics.	This approach is used in the study of statistical thermodynamics.
A few properties are required to describe the system.	Large numbers of variables are required to describe the system.
The properties like pressure, temperature, etc. needed to describe the system, can be easily measured.	The properties like velocity, momentum, kinetic energy, etc. needed to describe the system, cannot be measured easily.
The properties of the system are their average values.	The properties are defined for each molecule individually.
This approach requires simple mathematical formulas for analyzing the system.	No. of molecules is very large so it requires an advanced statistical and mathematical method to explain any change in the system



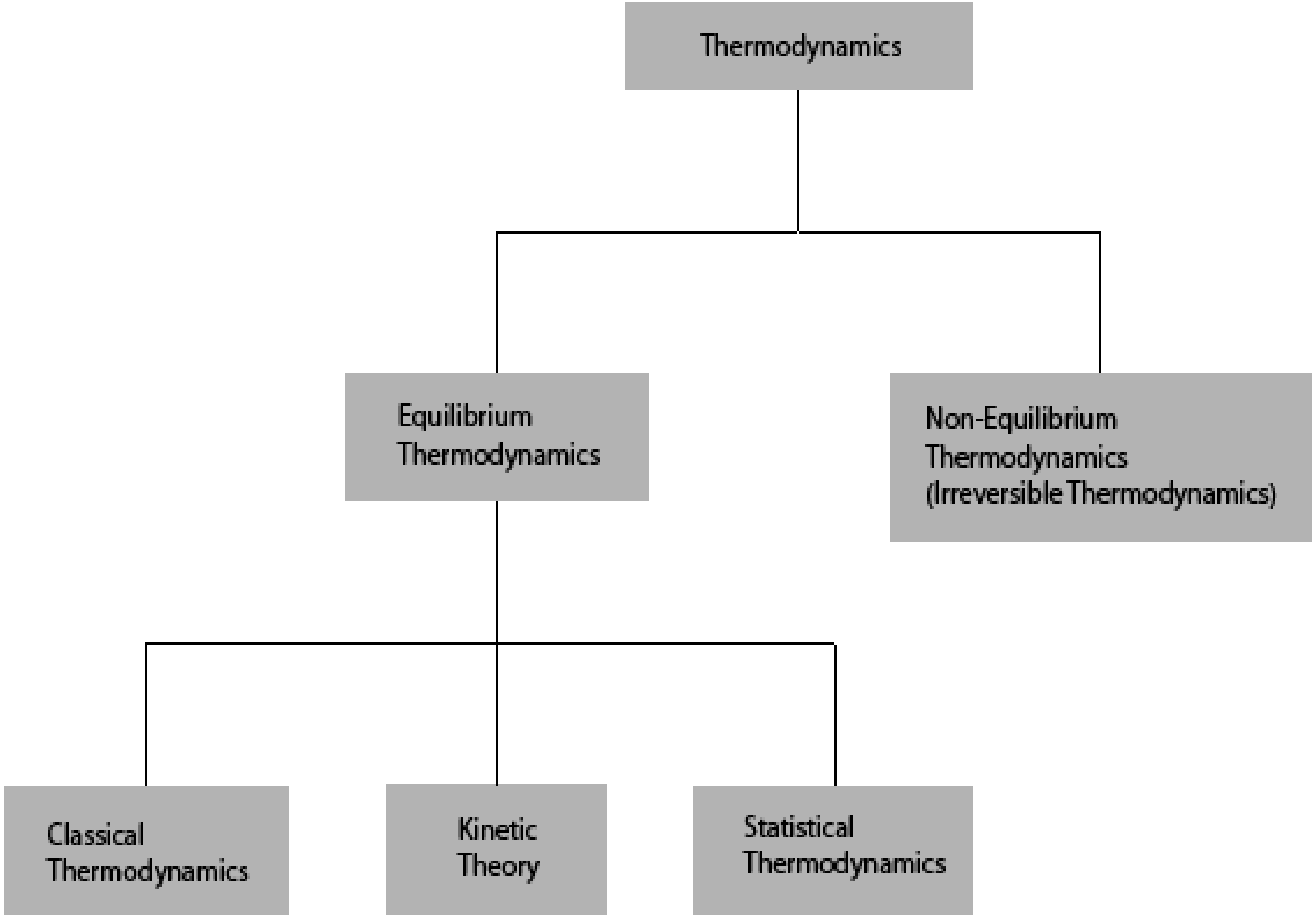
(A) Classical Thermodynamics



(B) Statistical Thermodynamics



Classification of thermodynamics



Thermodynamics

Equilibrium Thermodynamics

Non-Equilibrium Thermodynamics (Irreversible Thermodynamics)

Classical Thermodynamics

Kinetic Theory

Statistical Thermodynamics

Continuum

Matter is made up of atoms that are widely spaced in the gas phase. Yet it is very convenient to disregard the atomic nature of a substance and view it as a continuous, homogeneous matter with no holes, that is, a **continuum**. The continuum idealization allows us to treat properties as point functions and to assume the properties vary continually in space with no jump discontinuities. This idealization is valid as long as the size of the system we deal with is large relative to the space between the molecules. This is the case in practically all problems, except some specialized ones. The continuum idealization is implicit in many statements we make, such as "the density of water in a glass is the same at any point."

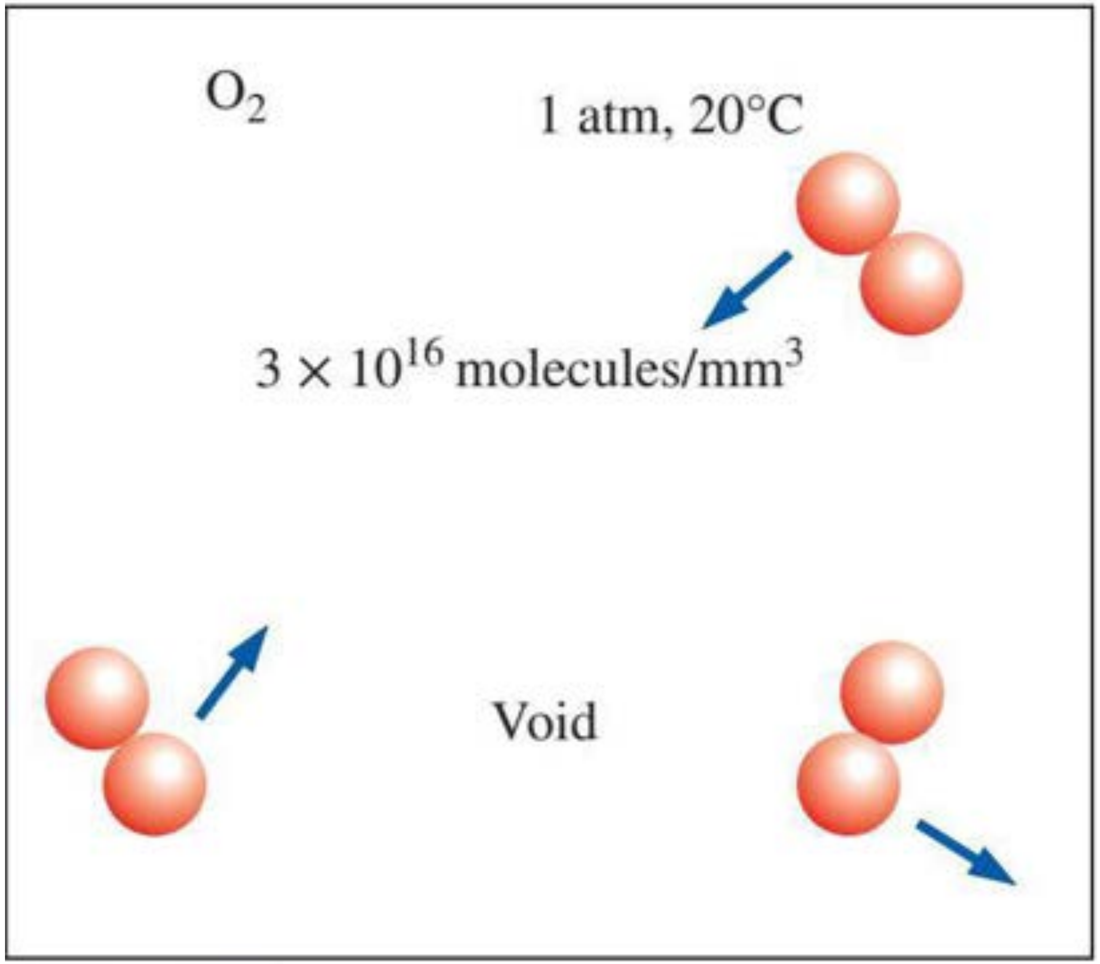


FIGURE
Despite the relatively large gaps between molecules, a gas can usually be treated as a continuum because of the very large number of molecules even in an extremely small volume.

To have a sense of the distance involved at the molecular level, consider a container filled with oxygen at atmospheric conditions. The diameter of the oxygen molecule is about 3×10^{-10} m and its mass is 5.3×10^{-26} kg. Also, the *mean free path* of oxygen at 1 atm pressure and 20°C is 6.3×10^{-8} m. That is, an oxygen molecule travels, on average, a distance of 6.3×10^{-8} m (about 200 times its diameter) before it collides with another molecule.

Also, there are about 3×10^{16} molecules of oxygen in the tiny volume of 1 mm^3 at 1 atm pressure and 20°C (Fig. 1–24). The continuum model is applicable as long as the characteristic length of the system (such as its diameter) is much larger than the mean free path of the molecules. At very high vacuums or very high elevations, the mean free path may become large (for example, it is about 0.1 m for atmospheric air at an elevation of 100 km). For such cases the **rarefied gas flow theory** should be used, and the impact of individual molecules should be considered. In this text we will limit our consideration to substances that can be modeled as a continuum.

▪ PURE SUBSTANCE

A substance that has a fixed chemical composition throughout is called a **pure substance**. Water, nitrogen, helium, and carbon dioxide, for example, are all pure substances.

A pure substance does not have to be of a single chemical element or compound, however. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous. Air, for example, is a mixture of several gases, but it is often considered to be a pure substance because it has a uniform chemical composition However, a mixture of oil and water is not a pure substance. Since oil is not soluble in water, it will collect on top of the water, forming two chemically dissimilar regions.

A mixture of two or more phases of a pure substance is still a pure substance as long as the chemical composition of all phases is the same (Fig.). A mixture of ice and liquid water, for example, is a pure substance because both phases have the same chemical composition. A mixture of liquid air and gaseous air, however, is not a pure substance since the composition of liquid air is different from the composition of gaseous air, and thus the mixture is no longer chemically homogeneous. This is due to different components in air condensing at different temperatures at a specified pressure.

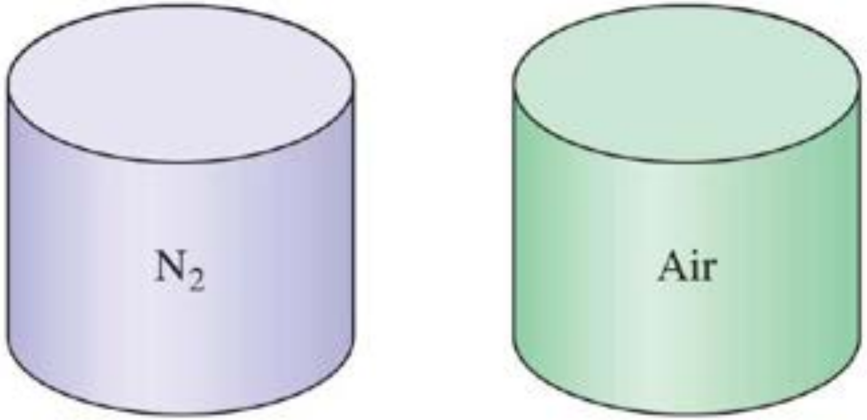
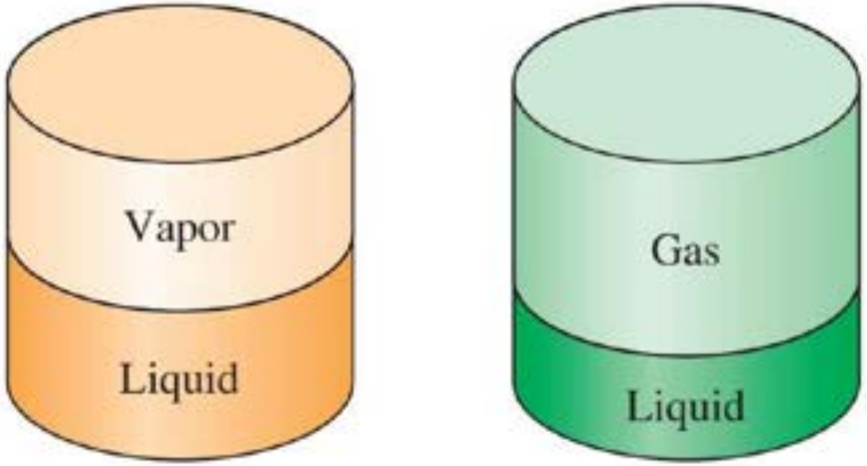


FIGURE 1
Nitrogen and gaseous air are pure substances.



(*a*) H_2O (*b*) Air

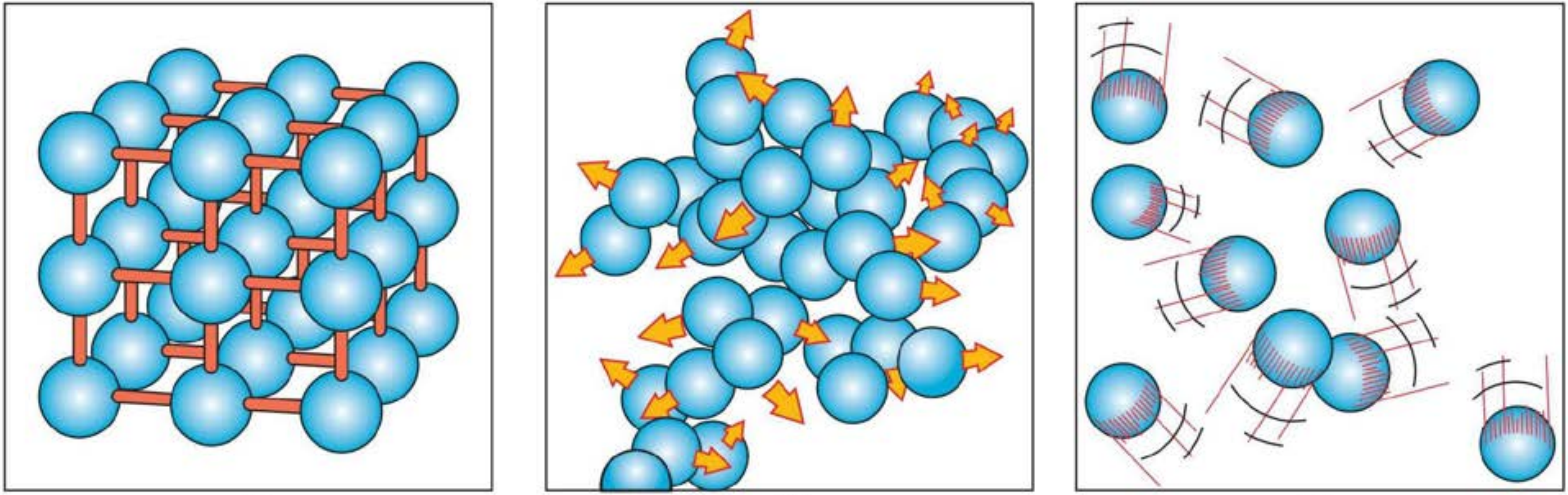
FIGURE 2
A mixture of liquid and gaseous water is a pure substance, but a mixture of liquid and gaseous air is not.

PHASES OF A PURE SUBSTANCE

A phase is identified as having a distinct molecular arrangement that is homogeneous throughout and separated from the others by easily identifiable boundary surfaces. The two phases of H_2O in iced water represent a good example of this.

When studying phases or phase changes in thermodynamics, one does not need to be concerned with the molecular structure and behavior of different phases. However, it is very helpful to have some understanding of the molecular phenomena involved in each phase.

Intermolecular bonds are strongest in solids and weakest in gases. This is why molecules in solids are closely packed together, whereas in gases they are separated by relatively large distances.


(*a*) (*b*) (*c*)

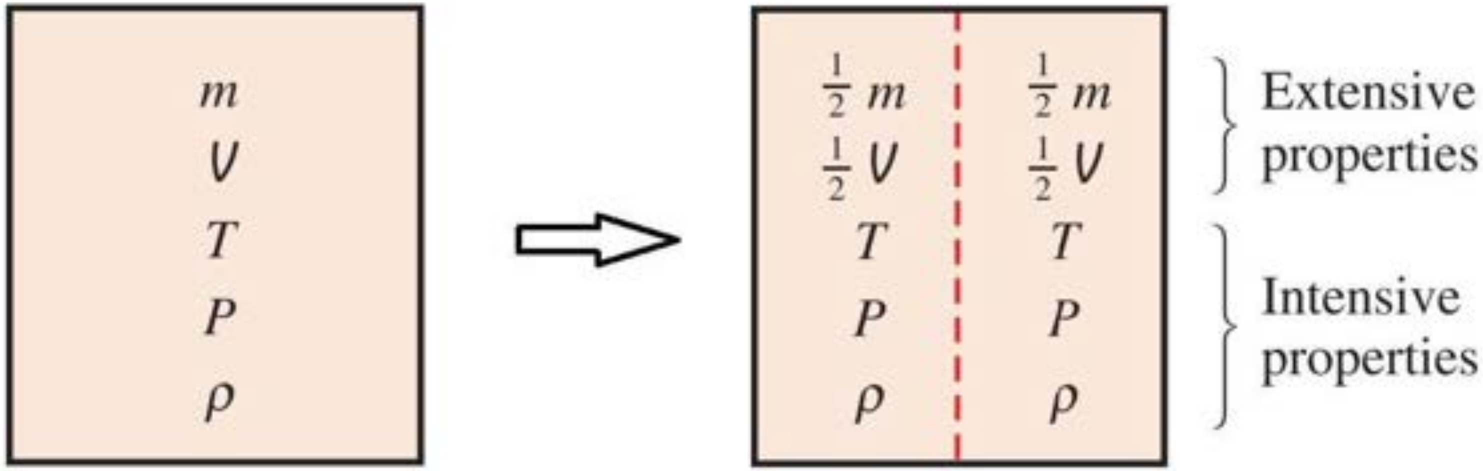
FIGURE

The arrangement of atoms in different phases: (*a*) molecules are at relatively fixed positions in a solid, (*b*) groups of molecules move about each other in the liquid phase, and (*c*) molecules move about at random in the gas phase.

PROPERTIES OF A SYSTEM

Any characteristic of a system is called a **property**. Some familiar properties are pressure P, temperature T, volume V, and mass m. The list can be extended to include less familiar ones such as viscosity, thermal conductivity, modulus of elasticity, thermal expansion coefficient, electric resistivity, and even velocity and elevation.

Properties are considered to be either *intensive* or *extensive*. **Intensive properties** are those that are independent of the mass of a system, such as temperature, pressure, and density. **Extensive properties** are those whose values depend on the size—or extent—of the system. Total mass, total volume, and



Thermodynamic Property

Intensive property

(Independent of mass of the system)

1. Pressure
2. Temperature
3. Density
4. Concentration
5. Melting point
6. Boiling point
7. Surface tension
8. Viscosity, etc.

Extensive property

(depends on the mass of the system)

1. Mass
2. Volume
3. Internal energy
4. Heat capacity
5. Enthalpy
6. Entropy
7. Helmholtz energy
8. Gibbs energy, etc.

Intensive Properties


Boiling Point


Color


Temperature

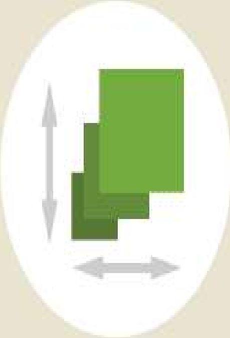

Luster


Hardness

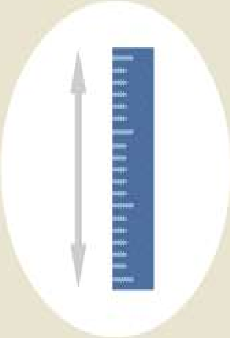
Extensive Properties


Volume


Mass


Size

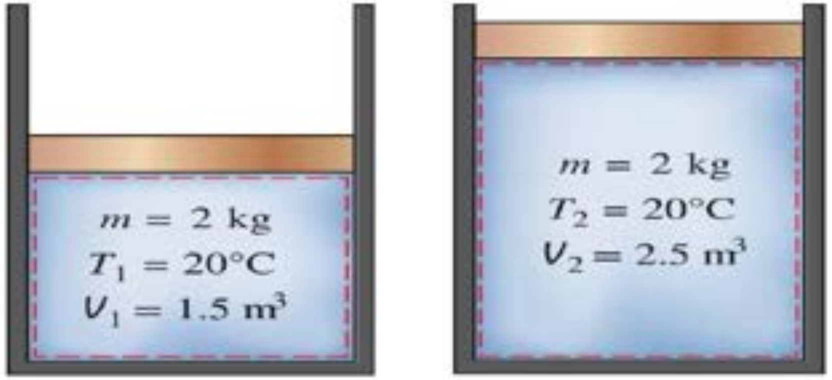

Weight


Length

STATE AND EQUILIBRIUM

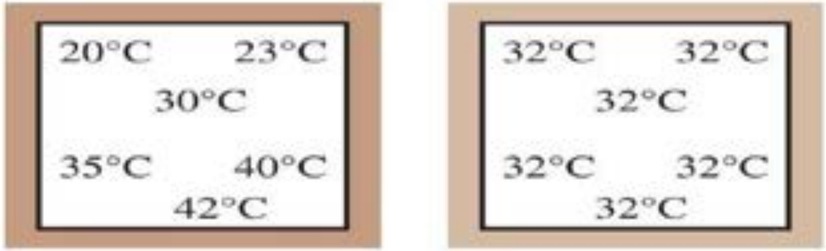
Consider a system not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describes the condition, or the **state**, of the system. At a given state, all the properties of a system have fixed values. If the value of even one property changes, the state will change to a different one. In Fig. a system is shown at two different states.

Thermodynamics deals with *equilibrium* states. The word **equilibrium** implies a state of balance. In an equilibrium state there are no unbalanced potentials (or driving forces) within the system. A system in equilibrium experiences no changes when it is isolated from its surroundings.



(*a*) State 1 (*b*) State 2

FIGURE
A system at two different states.



(*a*) Before (*b*) After

FIGURE
A closed system reaching thermal equilibrium.

There are many types of equilibrium, and a system is not in thermodynamic equilibrium unless the conditions of all the relevant types of equilibrium are satisfied. For example, a system is in **thermal equilibrium** if the temperature is the same throughout the entire system, as shown in Fig. . That is, the system involves no temperature differential, which is the driving force for heat flow. **Mechanical equilibrium** is related to pressure, and a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time. However, the pressure may vary within the system with elevation as a result of gravitational effects.

For example, the higher pressure at a bottom layer is balanced by the extra weight it must carry, and, therefore, there is no imbalance of forces. The variation of pressure as a result of gravity in most thermodynamic systems is relatively small and usually disregarded. If a system involves two phases, it is in **phase equilibrium** when the mass of each phase reaches an equilibrium level and stays there. Finally, a system is in **chemical equilibrium** if its chemical composition does not change with time, that is, no chemical reactions occur. A system will not be in equilibrium unless all the relevant equilibrium criteria are satisfied.

PROCESSES AND CYCLES

Any change that a system undergoes from one equilibrium state to another is called a **process**, and the series of states through which a system passes during a process is called the **path** of the process To describe a process completely, one should specify the initial and final states of the process, as well as the path it follows, and the interactions with the surroundings.

When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a **quasi-static**, or **quasi-equilibrium**, **process**. A quasi-equilibrium process can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.

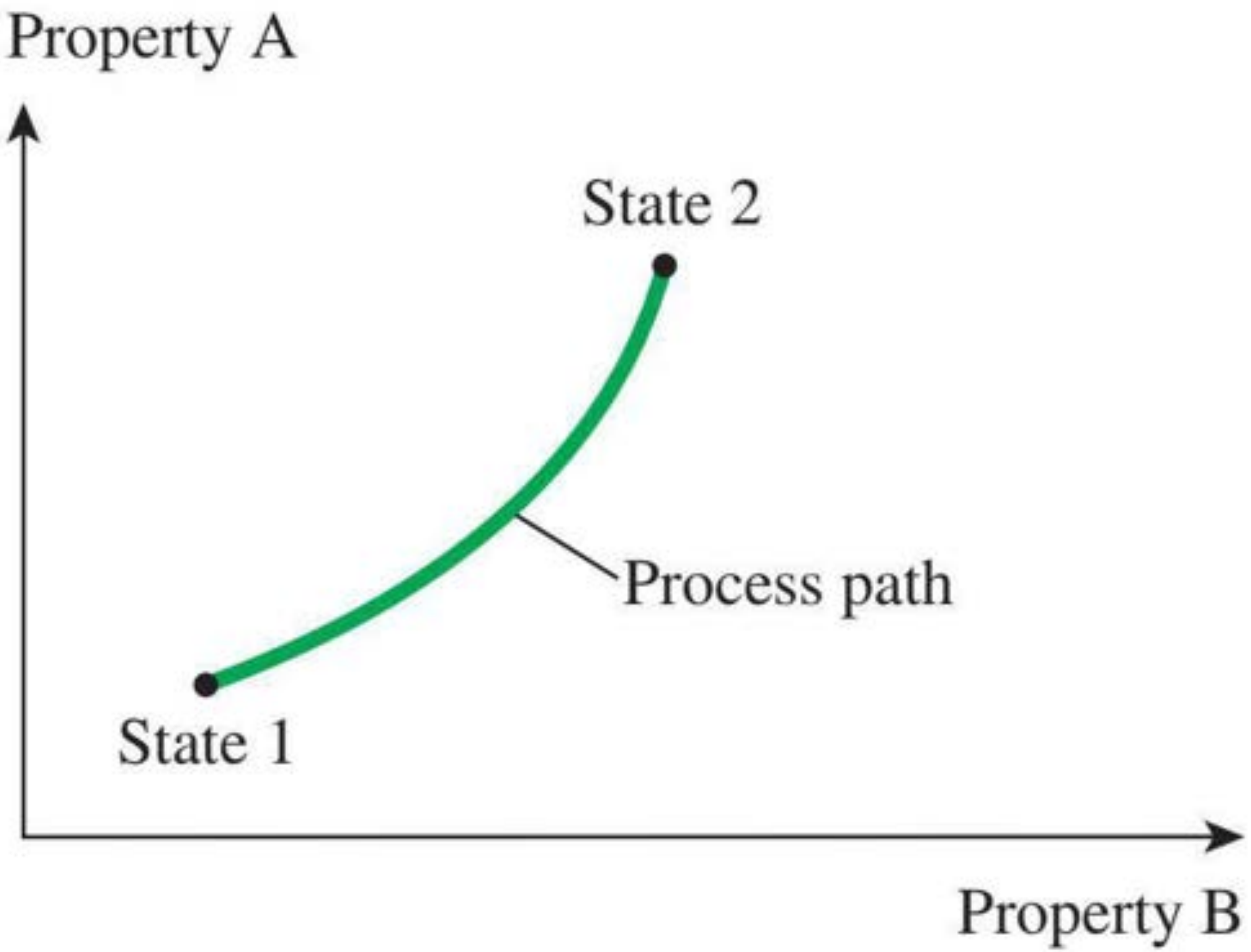
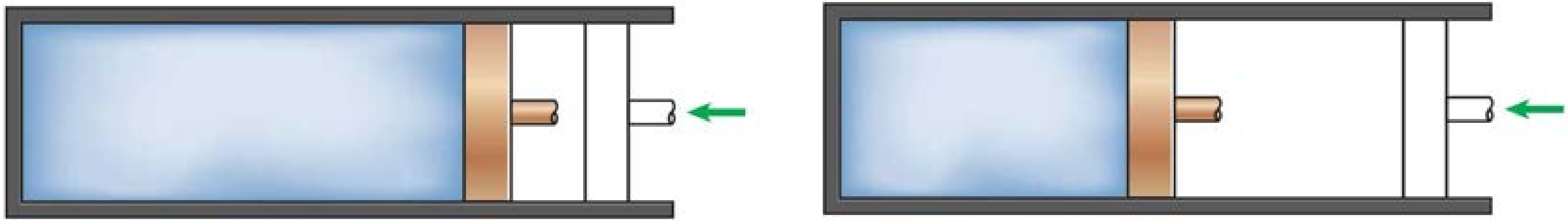


FIGURE
A process between states 1 and 2 and the process path.



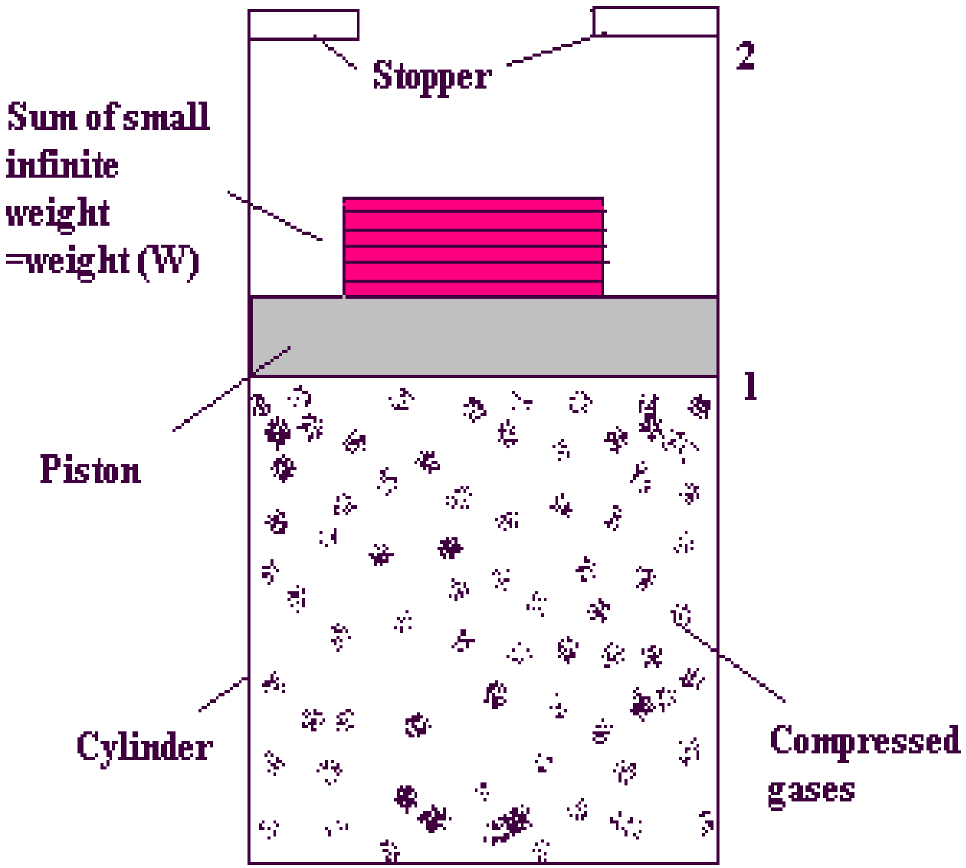
(*a*) Slow compression
(quasi-equilibrium)

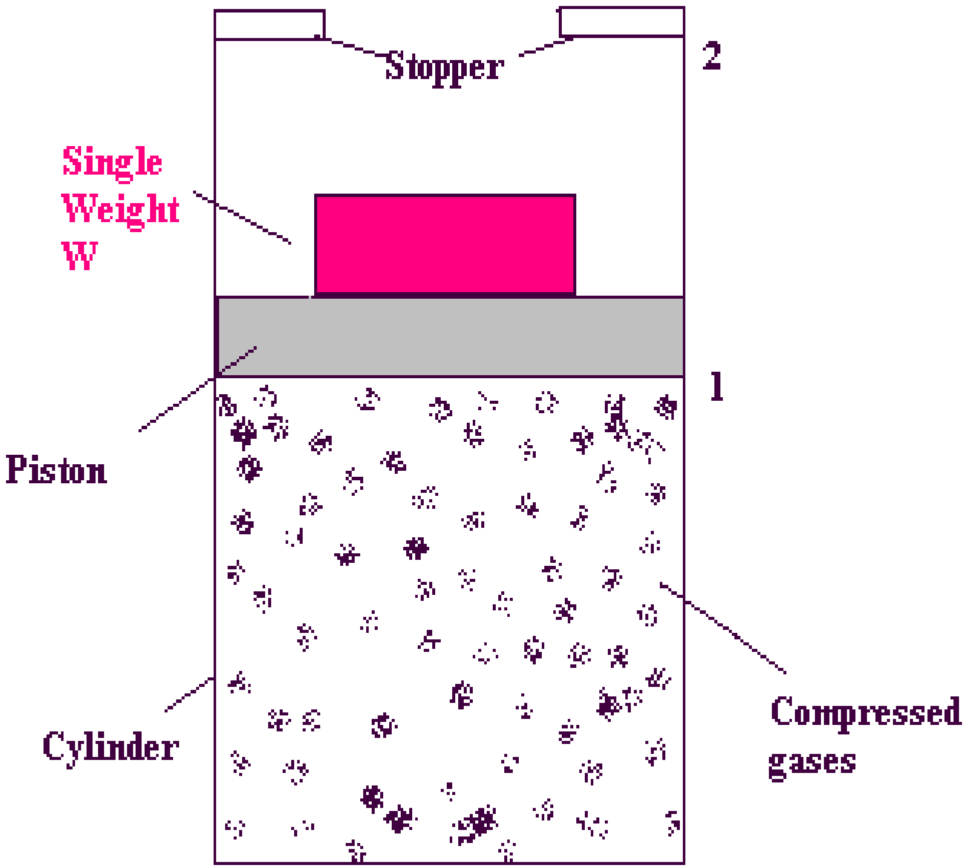
(*b*) Very fast compression
(nonquasi-equilibrium)

This is illustrated in Fig.   . When a gas in a piston-cylinder device is compressed suddenly, the molecules near the face of the piston will not have enough time to escape, and they will have to pile up in a small region in front of the piston, thus creating a high-pressure region there. Because of this pressure difference, the system can no longer be said to be in equilibrium, and this makes the entire process nonquasi-equilibrium. However, if the piston is moved slowly, the molecules will have sufficient time to redistribute, and there will not be a molecule pileup in front of the piston. As a result, the pressure inside the cylinder will always be nearly uniform and will rise at the same rate at all locations. Since equilibrium is maintained at all times, this is a quasi-equilibrium process.

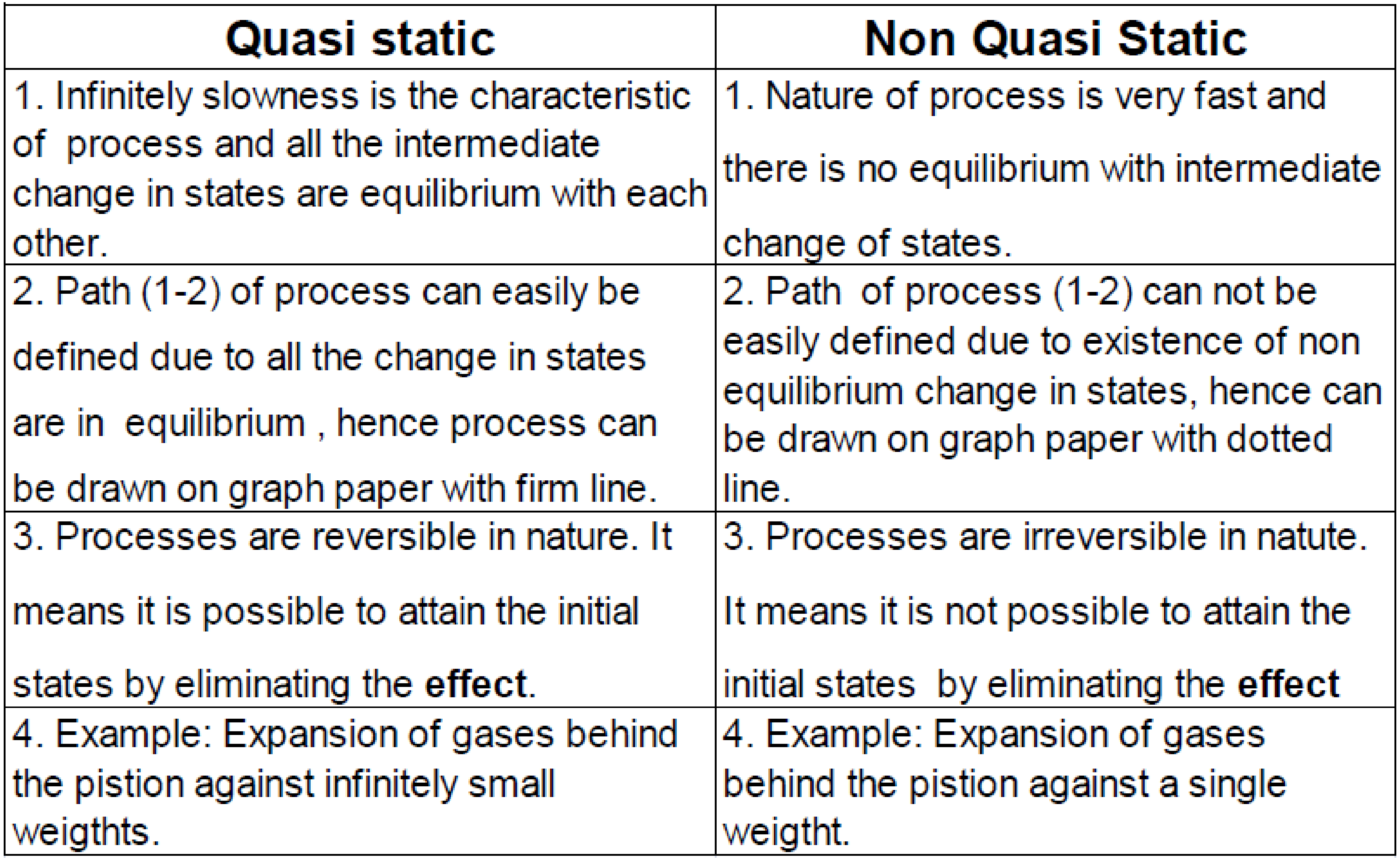
Quasi Static Vs Non Quasi Static (contd..)

$W = W1 + W2 + W3 + \ldots\ldots\ Wn$

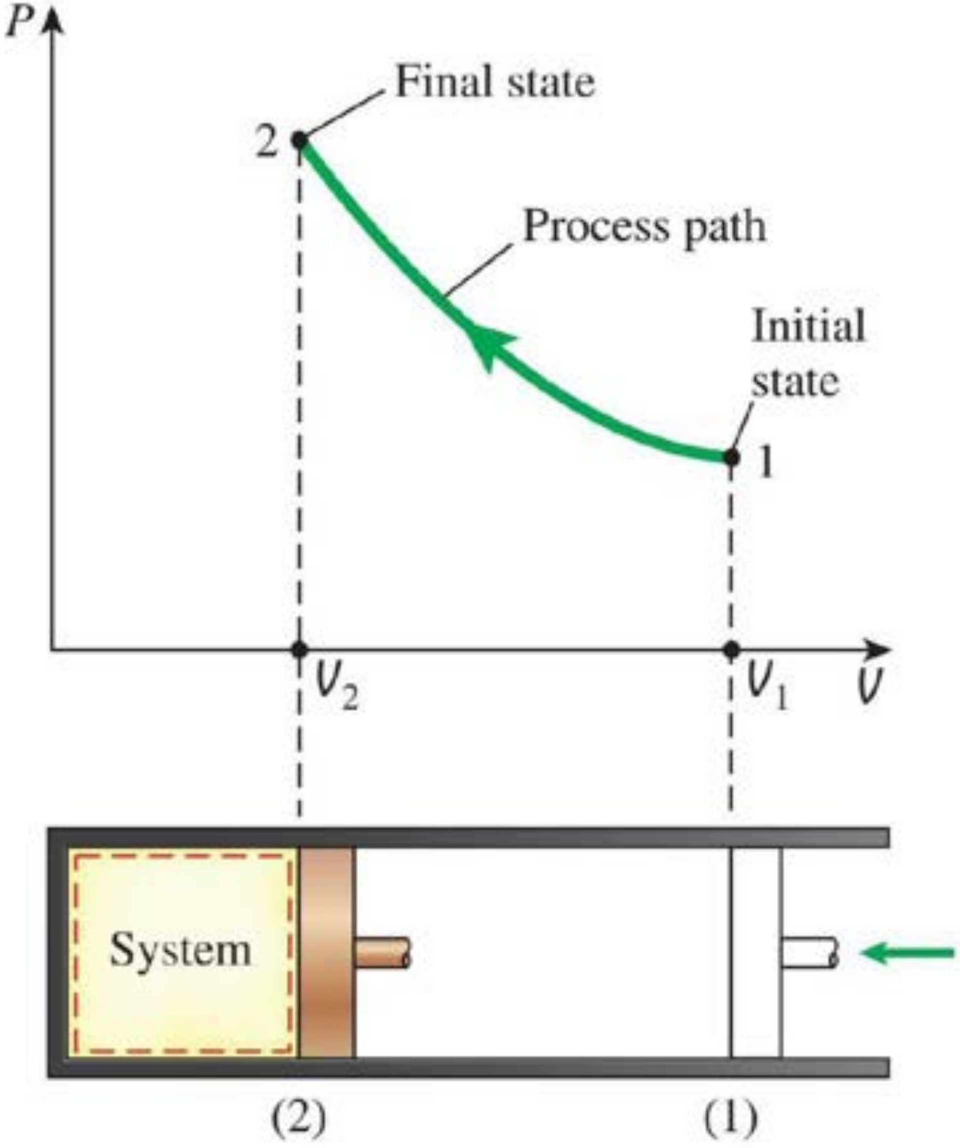




Quasi Static Vs Non Quasi Static (Quasi-Almost slow, or infinitely slow)

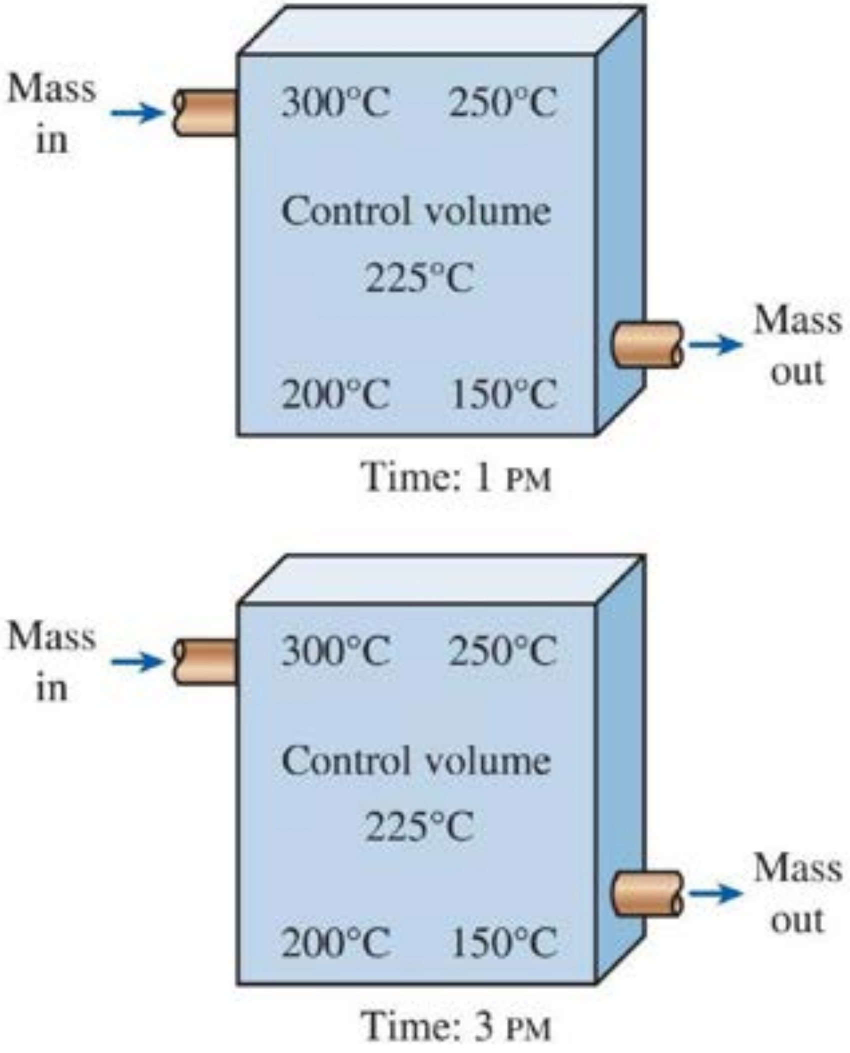


Quasi static	Non Quasi Static
1. Infinitely slowness is the characteristic of process and all the intermediate change in states are equilibrium with each other.	1. Nature of process is very fast and there is no equilibrium with intermediate change of states.
2. Path (1-2) of process can easily be defined due to all the change in states are in equilibrium , hence process can be drawn on graph paper with firm line.	2. Path of process (1-2) can not be easily defined due to existence of non equilibrium change in states, hence can be drawn on graph paper with dotted line.
3. Processes are reversible in nature. It means it is possible to attain the initial states by eliminating the **effect**.	3. Processes are irreversible in natute. It means it is not possible to attain the initial states by eliminating the **effect**
4. Example: Expansion of gases behind the pistion against infinitely small weigthts.	4. Example: Expansion of gases behind the pistion against a single weigtht.



FIGURE

The P-V diagram of a compression process.

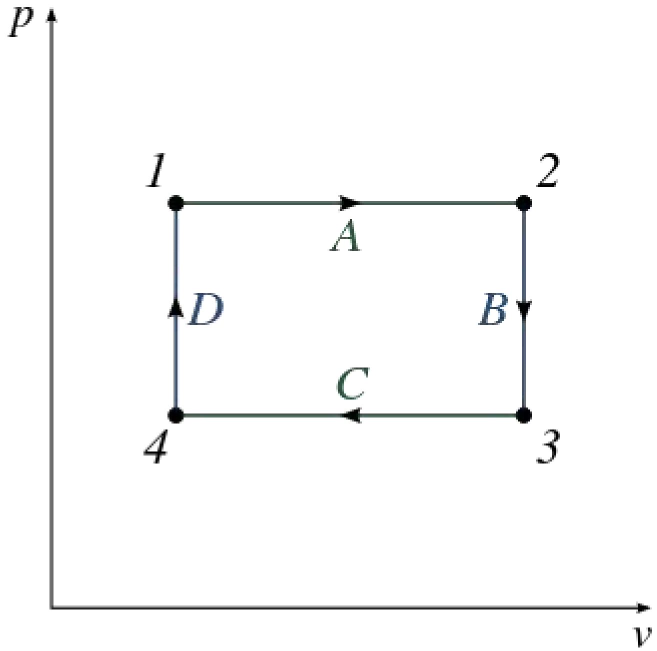


FIGURE

During a steady-flow process, fluid properties within the control volume may change with position but not with time.

Thermodynamic cycle

A thermodynamic cycle consists of a linked sequence of thermodynamic processes that involve transfer of heat and work into and out of the system, while varying pressure, temperature, and other state variables within the system, and that eventually returns the system to its initial state.

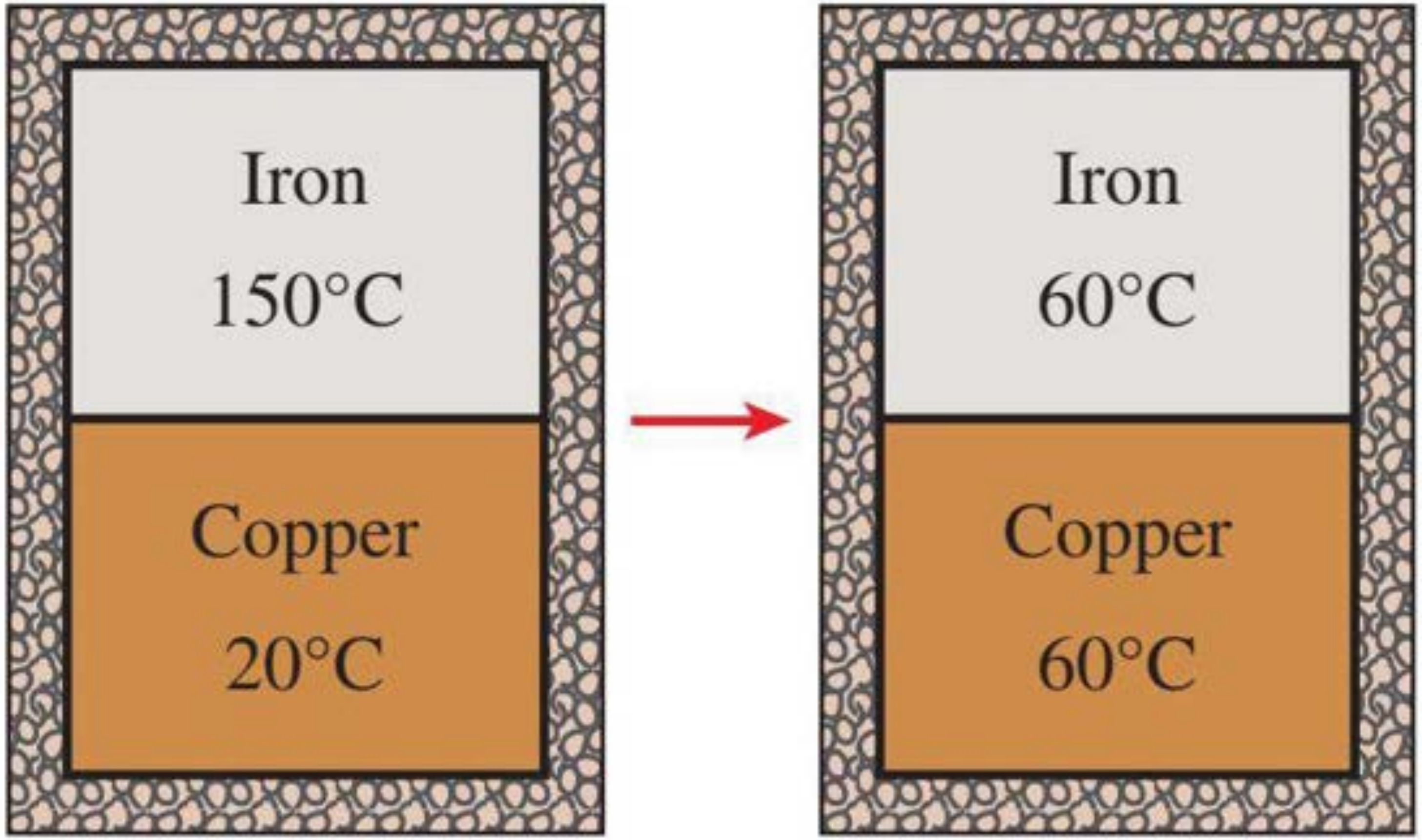


ZEROTH LAW AND TEMPERATURE

It is a common experience that a cup of hot coffee left on the table eventually cools off and a cold drink eventually warms up. That is, when a body is brought into contact with another body that is at a different temperature, heat is transferred from the body at higher temperature to the one at lower temperature until both bodies attain the same temperature. At that point, the heat transfer stops, and the two bodies are said to have reached **thermal equilibrium**. The equality of temperature is the only requirement for thermal equilibrium.

The **zeroth law of thermodynamics** states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. It may seem silly that such an obvious fact is called one of the basic laws of thermodynamics. However, it cannot be concluded from the other laws of thermodynamics, and it serves as a basis for the validity of temperature measurement. By replacing the third body with a thermometer, the zeroth law can be restated as *two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact.*

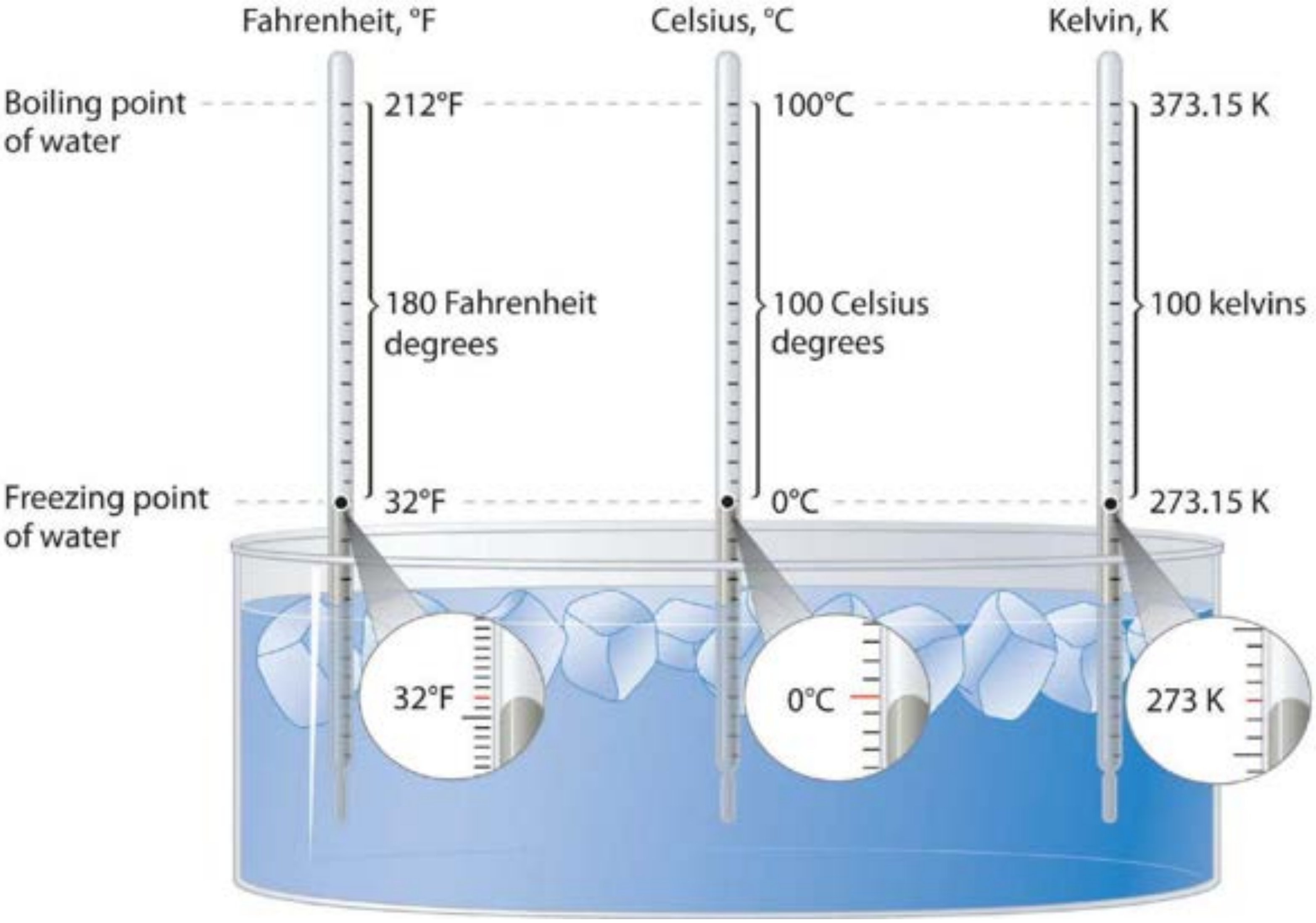
The zeroth law was first formulated and labeled by R. H. Fowler in 1931. As the name suggests, its value as a fundamental physical principle was recognized more than half a century after the formulation of the first and the second laws of thermodynamics. It was named the zeroth law since it should have preceded the first and the second laws of thermodynamics.



FIGURE

Two bodies reaching thermal equilibrium after being brought into contact in an isolated enclosure.

Temperature Scales



All temperature scales are based on some easily reproducible states, such as freezing and boiling point of water, also known as the ice point and steam point.

A mixture of ice and water which is in equilibrium with air saturated with vapour at 1 atm pressure is said to be the ***ice point***.

A mixture of liquid water and water vapour with no air in equilibrium at 1 atm pressure is said to be at the ***steam point***.

The thermodynamic temperature scale in the SI system is the ***Kelvin scale***, named after Lord Kelvin (1824–1907). The temperature unit on this scale is the Kelvin, which is designated by K.

The thermodynamic temperature scale in the English system is the ***Rankine scale***, named after William Rankine (1820–1872). The temperature unit on this scale is the Rankine, which is designated by R.

Method in Use Before 1954

Until 1954, the temperature scales were based on two fixed points, the steam point (the temperature of equilibrium between pure water and pure steam at 1 atm pressure) and the ice point (the temperature at which pure ice coexisted in equilibrium with air-saturated water at 1 atm pressure).

The temperature scales used in the SI and in the English system are the ***Celsius scale*** and the ***Fahrenheit scale***, respectively. On the Celsius scale, the ice and steam points were originally assigned the values of 0°C and 100°C, respectively. The corresponding values on the Fahrenheit scale are 32 and 212°F.

The relations for the temperature in terms of values of the thermometric property in the Celsius and Fahrenheit scale are given as

$$t, {}^\circ\mathrm{C} = 100\,\frac{X - X_i}{X_s - X_i}$$

$$t, {}^\circ\mathrm{F} = 32 + 180\,\frac{X - X_i}{X_s - X_i}$$

where X_i and X_s are the values of the thermometric property at the ice point ad the steam point respectively and X is the value of the thermometric property at the temperature to be measured.

Method in Use After 1954

Kelvin suggested that only a single fixed point was necessary to establish a temperature scale. He pointed out that the ***triple point of water*** (the states in which the solid, liquid and the vapour phases of water coexist in equilibrium) could be used as the single fixed point. At the tenth CGPM in 1954, the value of the triple point of water was set at 0.01°C or 273.16 K in the Kelvin scale.

$$t = 273.16\,\frac{X}{X_{TP}}$$

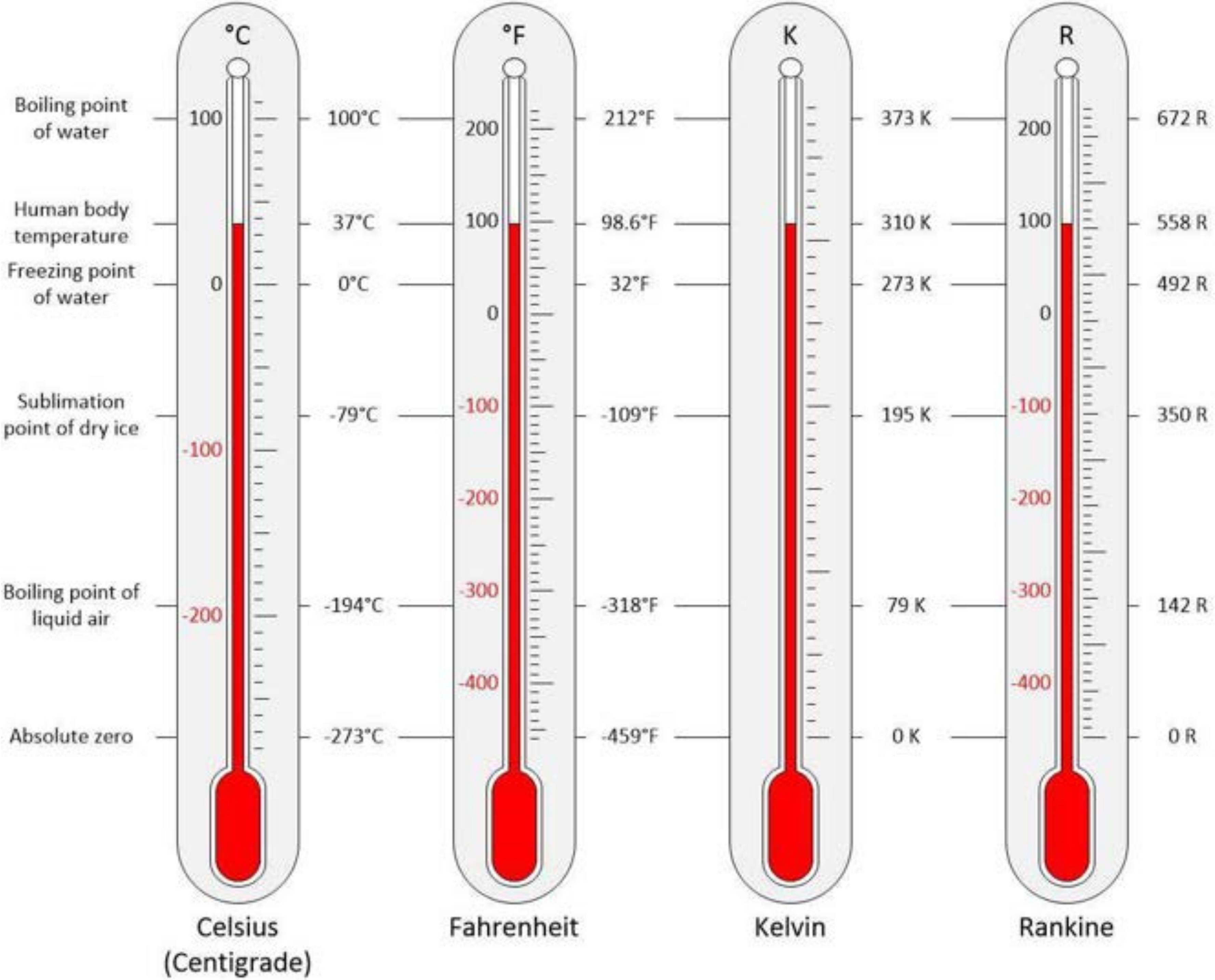

°C
°F
K
R
Boiling point of water
100
100°C
200
212°F
373 K
200
672 R
Human body temperature
100
37°C
98.6°F
310 K
100
558 R
Freezing point of water
0
0°C
32°F
273 K
492 R
0
0
Sublimation point of dry ice
-79°C
-100
-109°F
195 K
-100
350 R
-100
-200
-200
-300
-300
Boiling point of liquid air
-200
-194°C
-318°F
79 K
142 R
-400
-400
Absolute zero
-273°C
-459°F
0 K
0 R
Celsius (Centigrade)
Fahrenheit
Kelvin
Rankine

Table *Thermometers and thermometric properties*

	Thermometer	*Thermometric Property*
1.	Mercury-in-glass gas	Length
2.	Electric resistance	Resistance
3.	Thermocouple	Electromotive force of two dissimilar solids
4.	Constant pressure gas	Volume
5.	Constant volume gas	Pressure
6.	Radiation	Black body radiation

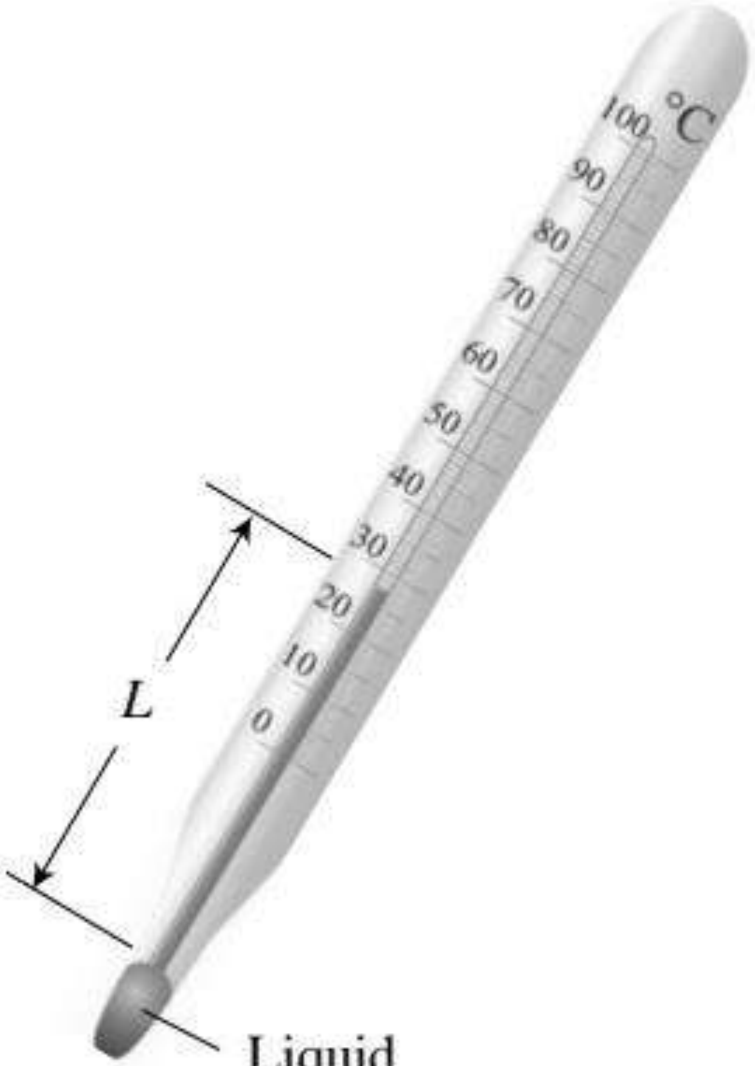


Figure *Liquid-in-glass thermometer*

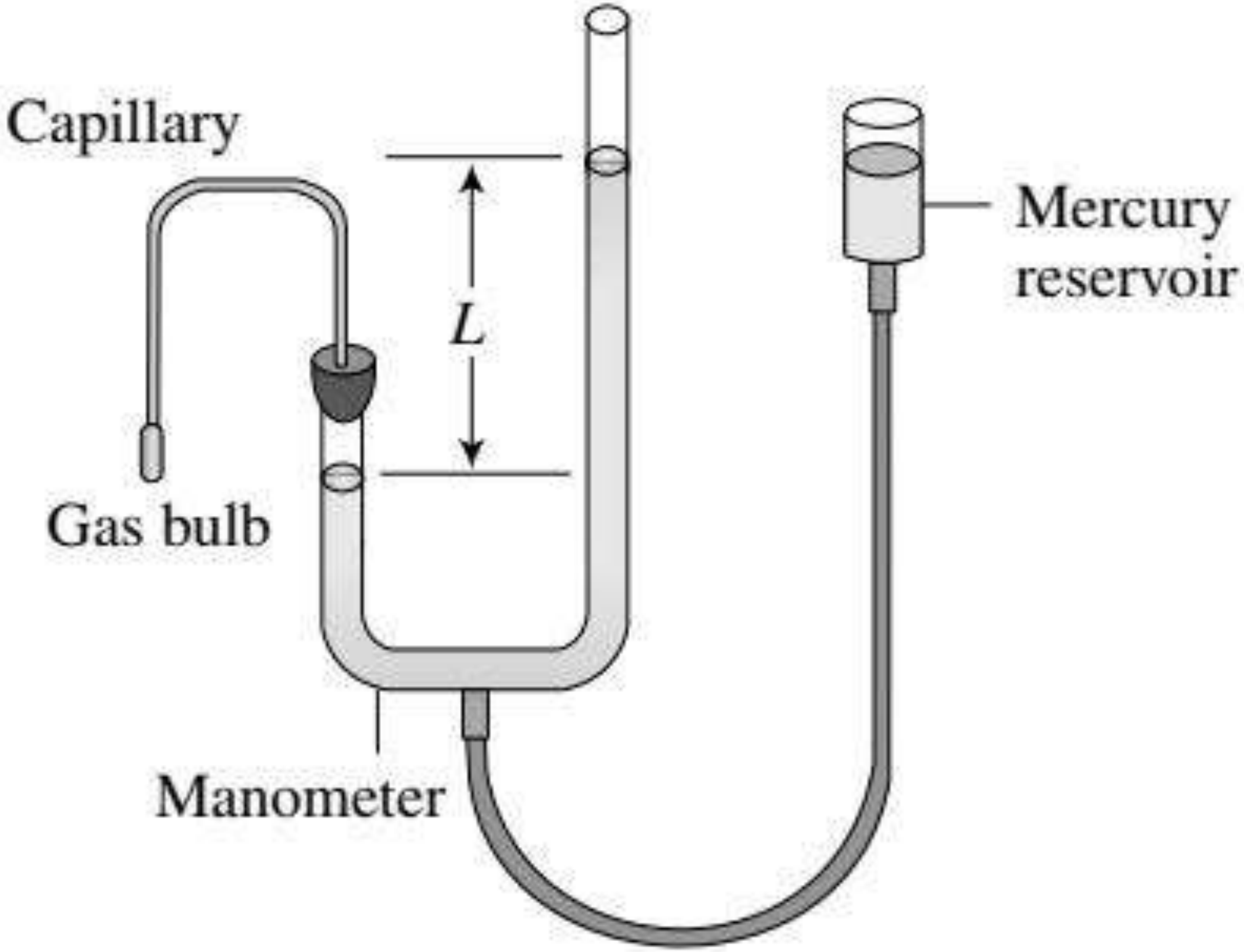


Figure *Constant-volume gas thermometer*

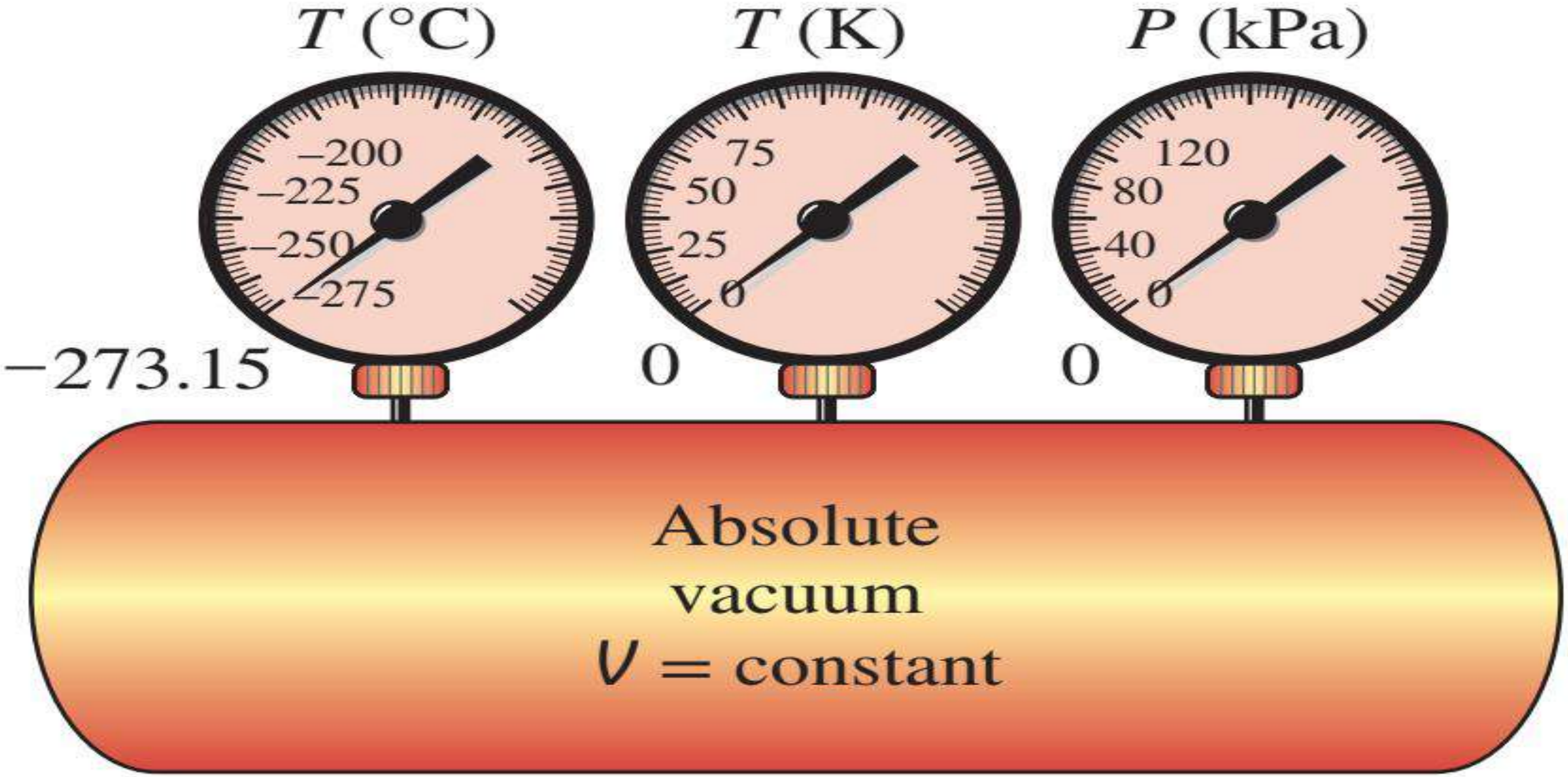


FIGURE 1–36

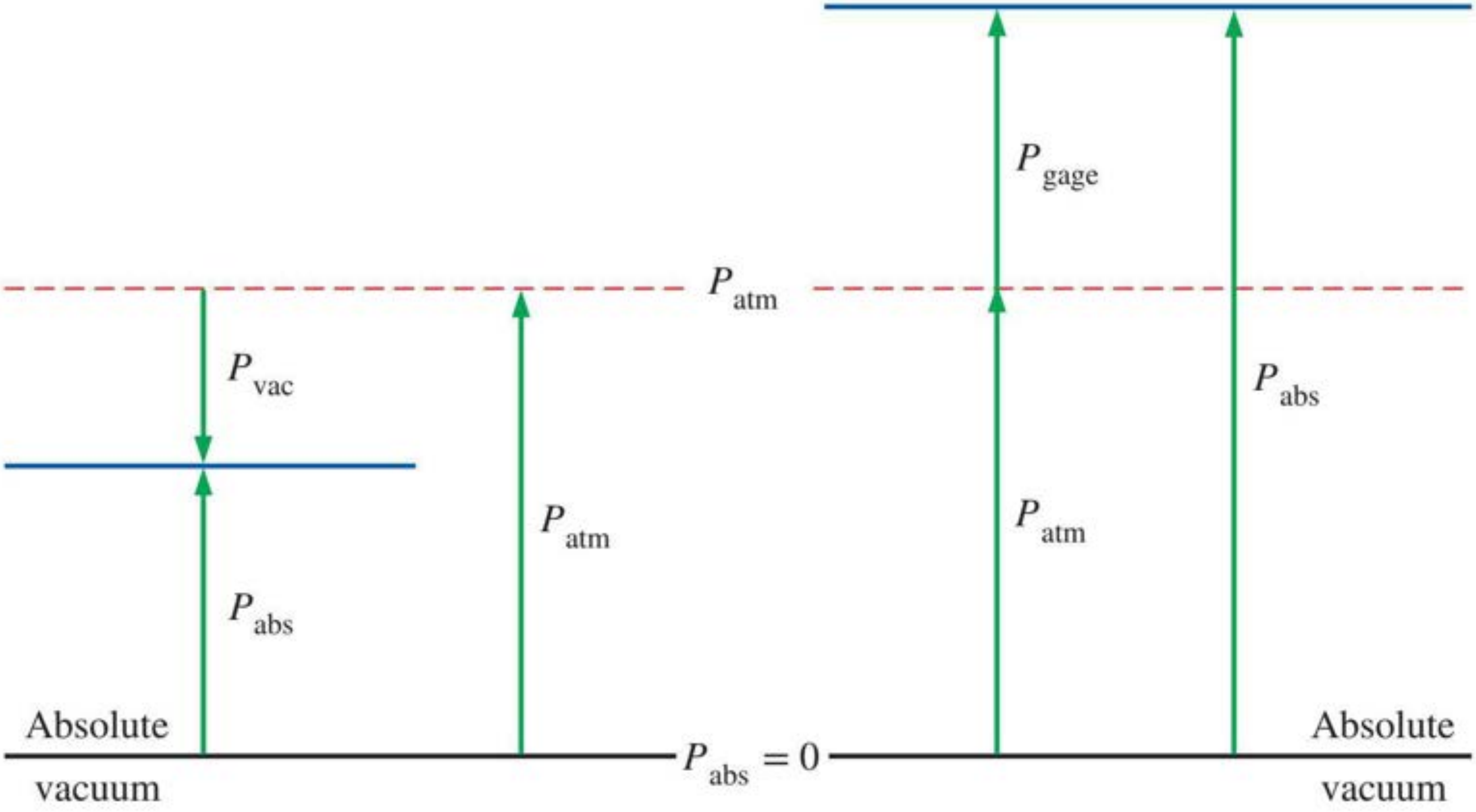
A constant-volume gas thermometer would read −273.15°C at absolute zero pressure.

▪ PRESSURE

Pressure is defined as *a normal force exerted by a fluid per unit area.* Normally, we speak of pressure when we deal with a gas or a liquid. The counterpart of pressure in solids is *normal stress.* Note, however, that pressure is a scalar quantity while stress is a tensor. Since pressure is defined as force per unit area, it has the unit of newtons per square meter (N/m^2), which is called a **pascal** (Pa). That is,

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

$$
\begin{aligned}
1\ \text{bar} &= 10^5\ \text{Pa} = 0.1\ \text{MPa} = 100\ \text{kPa} \\
1\ \text{atm} &= 101{,}325\ \text{Pa} = 101.325\ \text{kPa} = 1.01325\ \text{bars} \\
1\ \text{kgf/cm}^2 &= 9.807\ \text{N/cm}^2 = 9.807 \times 10^4\ \text{N/m}^2 = 9.807 \times 10^4\ \text{Pa} \\
&= 0.9807\ \text{bar} \\
&= 0.9679\ \text{atm}
\end{aligned}
$$



FIGURE

Absolute, gage, and vacuum pressures.

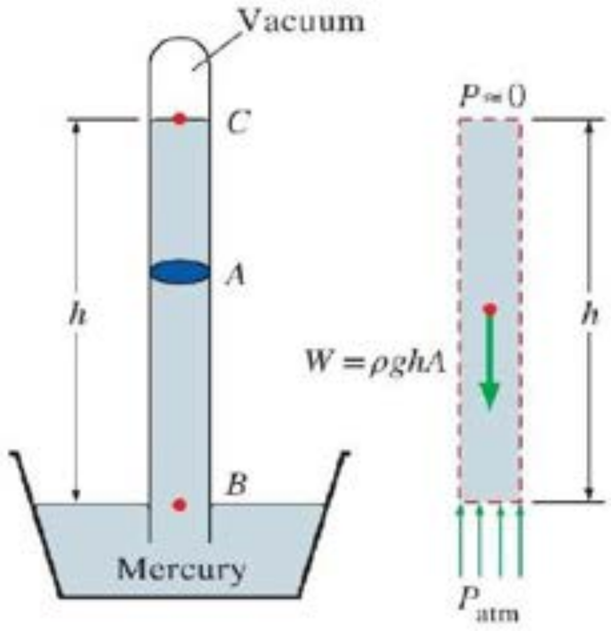
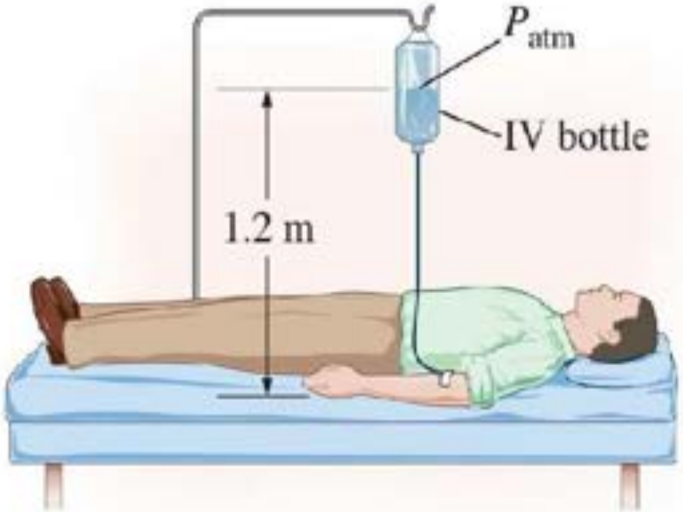
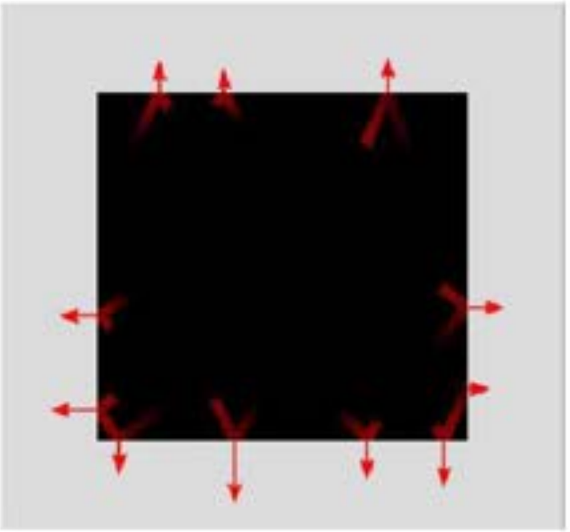


FIGURE
The basic barometer.

FIGURE
At high altitudes, a car engine generates less power and a person gets less oxygen because of the lower density of air.





ENERGY TRANSFER BY HEAT

ENERGY

Energy can exist in various forms such as mechanical, chemical, thermal, kinetic, potential, electrical, magnetic etc. and the sum of all forms of energy is called the total energy of the system. Thermodynamics deals with the change of total energy, not with the absolute value of the total energy. Thermodynamics is the science of study of energy in the form of heat and work. In fact energy can cross the system boundary of a closed system in two distinct forms: *heat* and *work*. Therefore, it is important to distinguish between these two forms of energy.

ENERGY TRANSFER BY HEAT

Heat is defined as the form of energy transferred across the boundaries of a system because of temperature difference between a system and its surroundings, and in the direction from higher temperature to lower temperature

Heat is energy in transit. It is recognized only as it crosses the system boundary. Consider a hot metal body as a system. The outer surface of the body represents the system boundary. It contains energy but this energy is called heat only as it passes through the outer surface of the body (the system boundary) to reach the surroundings. Once in the surroundings, the transferred heat becomes part of the internal energy of the surroundings. Thus, in thermodynamics, heat simply means the heat transfer.

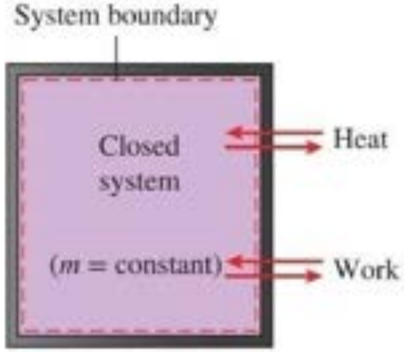


FIGURE
Energy can cross the boundaries of a closed system in the form of heat and work.

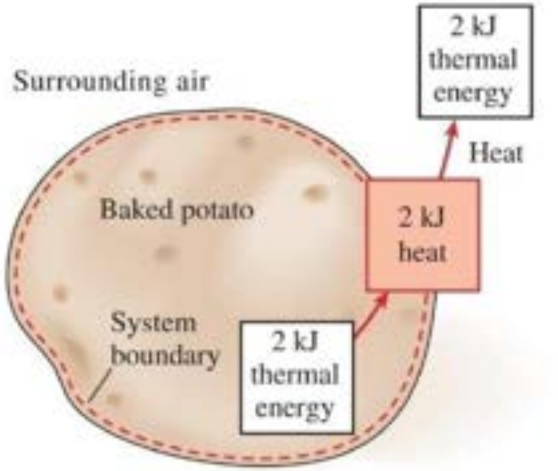


FIGURE
Energy is recognized as heat transfer only as it crosses the system boundary.

FIGURE
Temperature difference is the driving force for heat transfer. The larger the temperature difference, the higher is the rate of heat transfer.

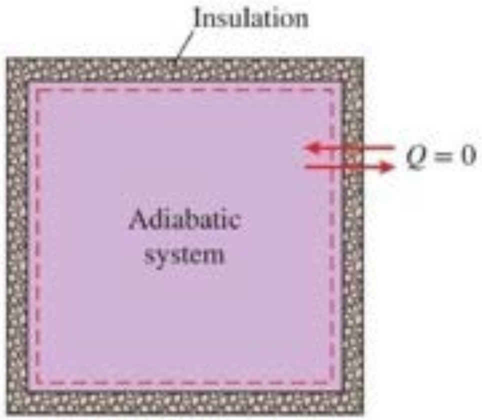
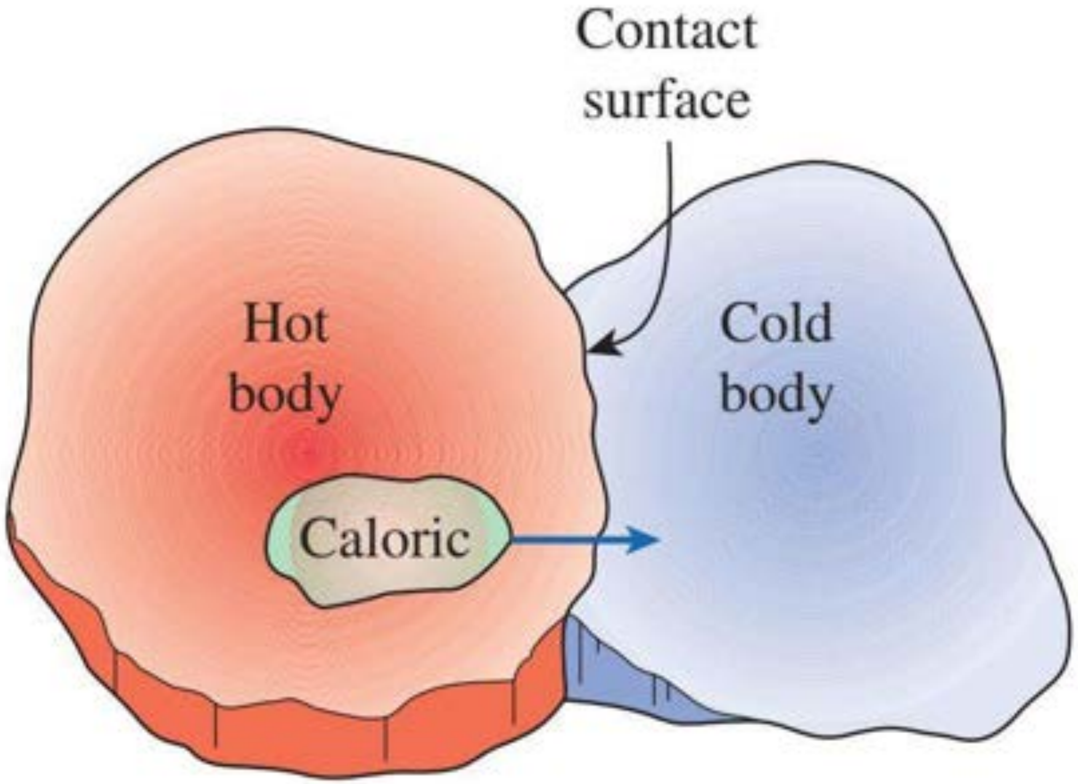
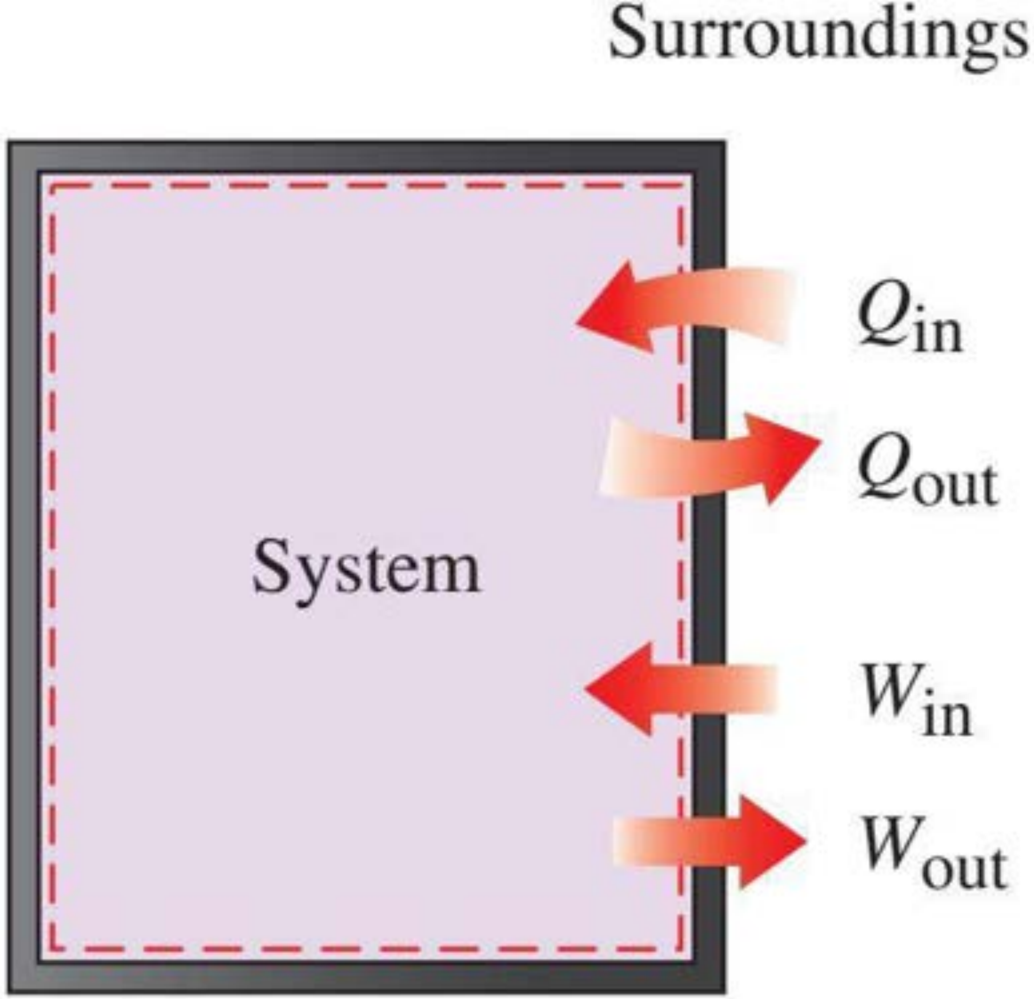


FIGURE 2–17
During an adiabatic process, a system exchanges no heat with its surroundings.



FIGURE

In the early 19th century, heat was thought to be an invisible fluid called the *caloric* that flowed from warmer bodies to cooler ones.



FIGURE

Specifying the directions of heat and work.

As a form of energy, heat has energy units, kJ (or Btu) being the most common one. The amount of heat transferred during the process between two states (states 1 and 2) is denoted by Q_{12}, or just Q. Heat transfer *per unit mass* of a system is denoted q and is determined from

$$q = \frac{Q}{m} \qquad \text{(kJ/kg)}$$

Sometimes it is desirable to know the *rate of heat transfer* (the amount of heat transferred per unit time) instead of the total heat transferred over some time interval (Fig. 2–18). The heat transfer rate is denoted $\dot{Q}$, where the overdot stands for the time derivative, or "per unit time." The heat transfer rate $\dot{Q}$ has the unit kJ/s, which is equivalent to kW. When $\dot{Q}$ varies with time, the amount of heat transfer during a process is determined by integrating $\dot{Q}$ over the time interval of the process:

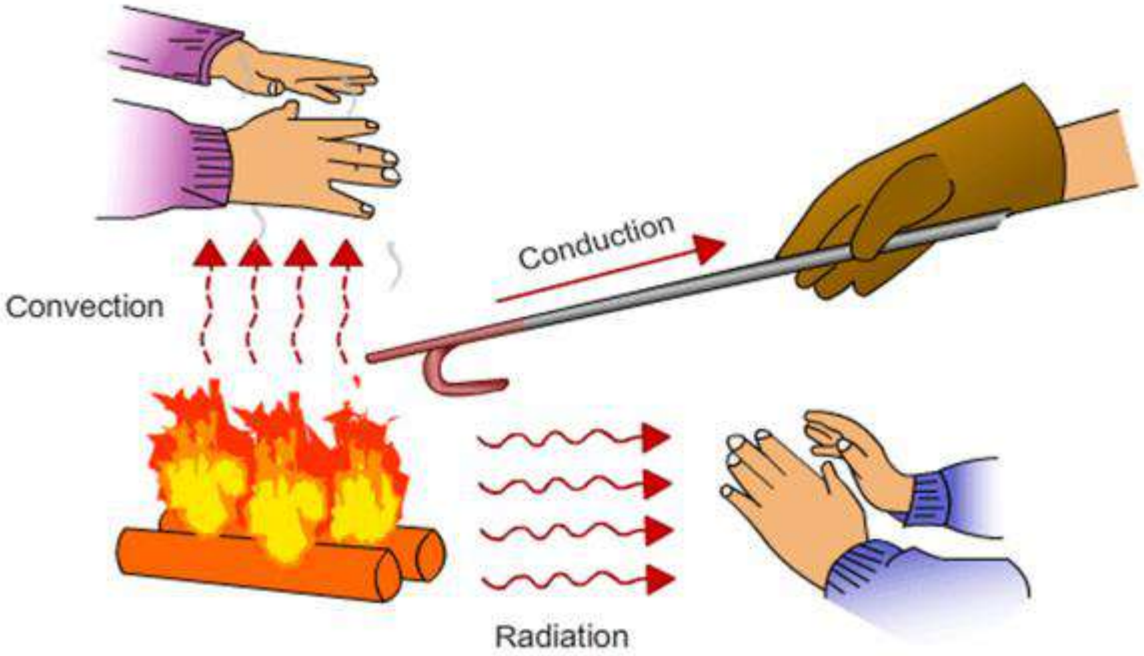
$$Q = \int_{t_1}^{t_2} \dot{Q}\, dt \qquad \text{(kJ)}$$

When $\dot{Q}$ remains constant during a process, this relation reduces to

$$Q = \dot{Q}\,\Delta t \qquad \text{(kJ)}$$

where $\Delta t = t_2 - t_1$ is the time interval during which the process takes place.

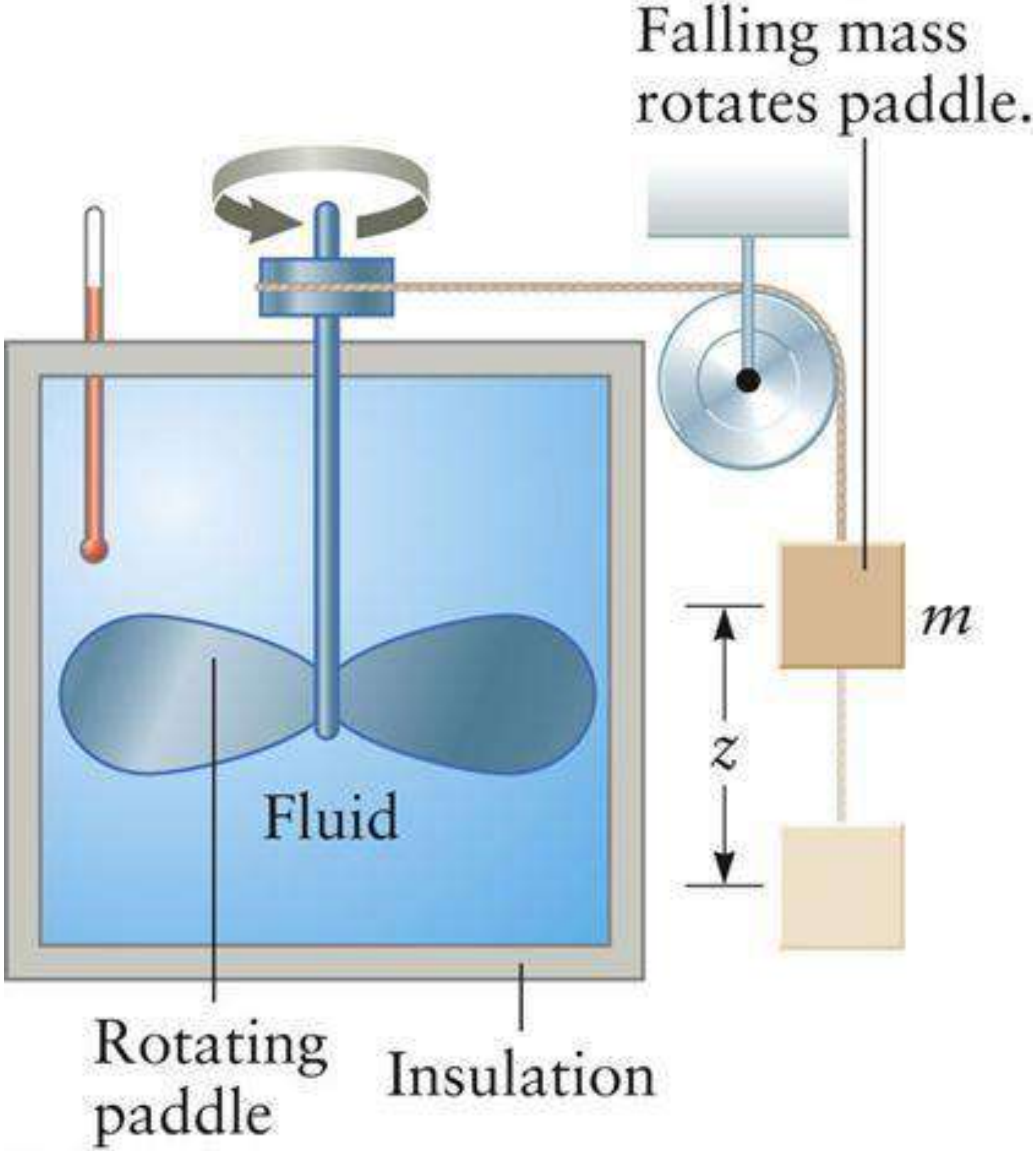
Heat is transferred by three mechanisms: conduction, convection, and radiation. **Conduction** is the transfer of energy from the more energetic particles of a substance to the adjacent less energetic ones as a result of interaction between particles. **Convection** is the transfer of energy between a solid surface and the adjacent fluid that is in motion, and it involves the combined effects of conduction and fluid motion. **Radiation** is the transfer of energy due to the emission of electromagnetic waves (or photons). An overview of the three mechanisms of heat transfer is given at the end of this chapter as a Topic of Special Interest.



ENERGY TRANSFER BY WORK

Work, like heat, is an energy interaction between a system and its surroundings. As mentioned earlier, energy can cross the boundary of a closed system in the form of heat or work. Therefore, *if the energy crossing the boundary of a closed system is not heat, it must be work.* Heat is easy to recognize: Its driving force is a temperature difference between the system and its surroundings. Then we can simply say that an energy interaction that is not caused by a temperature difference between a system and its surroundings is work. More specifically, *work is the energy transfer associated with a force acting through a distance*. A rising piston, a rotating shaft, and an electric wire crossing the system boundaries are all associated with work interactions.

Work is also a form of energy transferred like heat and, therefore, has energy units such as kJ. The work done during a process between states 1 and 2 is denoted by W_{12}, or simply W.


Falling mass rotates paddle.
m
z
Fluid
Rotating paddle
Insulation

The basic unit of work in the SI system is the Newton-metre (N-m) called the Joule (J). We shall use the more conventional kilojoule (kJ) which is 10^3 N-m.

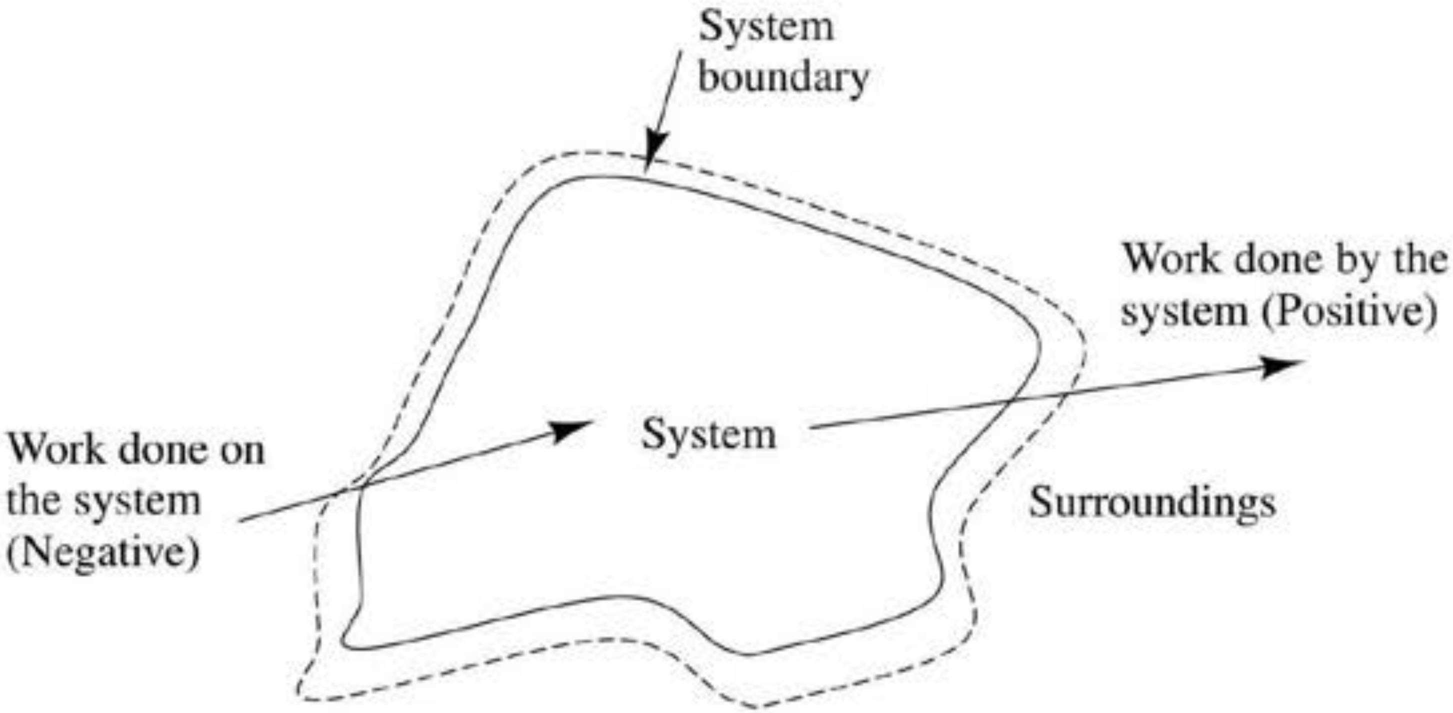
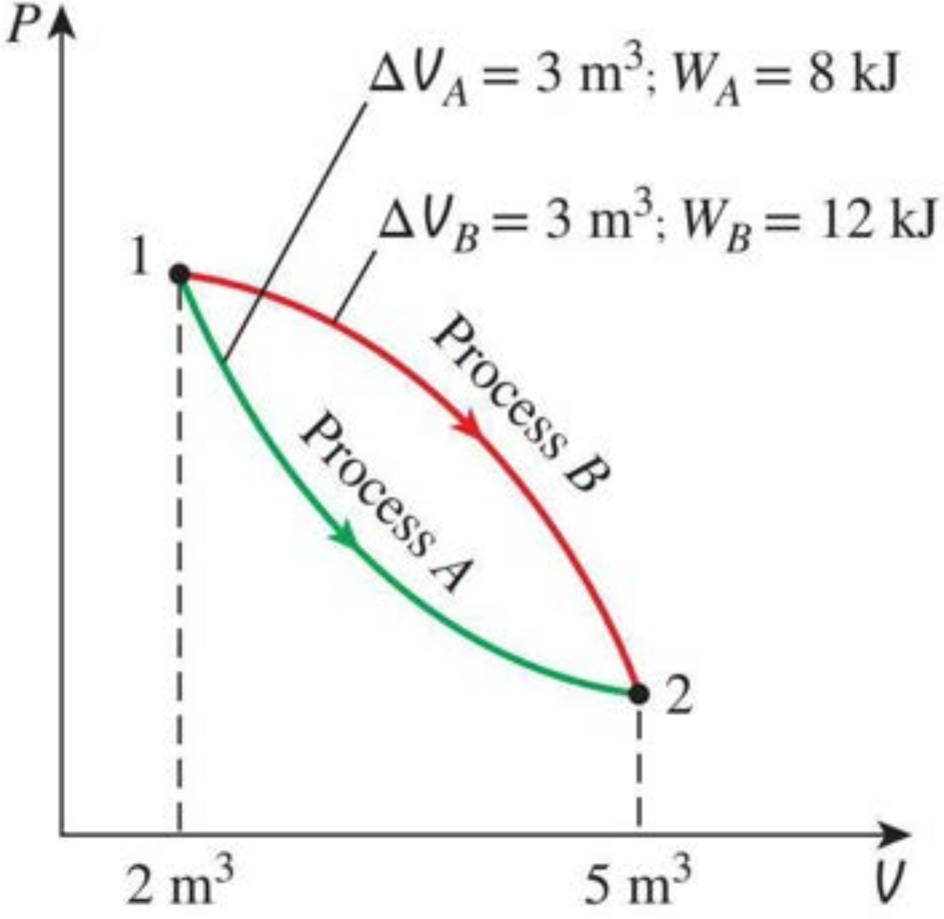


Figure *Sign convention for work transfer*

The universally accepted sign convention for work transfer is as follows

- Work done by a system is positive.
- Work done on a system is negative.



FIGURE

Properties are point functions; but heat and work are path functions (their magnitudes depend on the path followed).

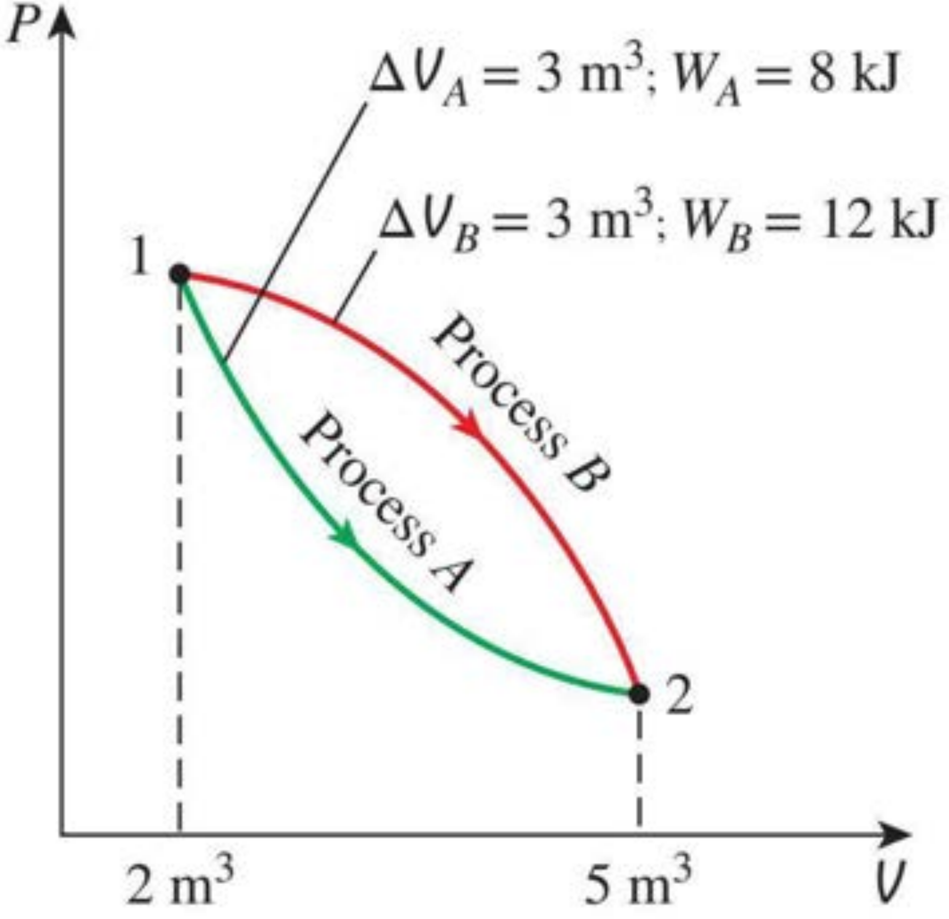
Path functions have **inexact differentials** designated by the symbol δ. Therefore, a differential amount of heat or work is represented by δQ or δW, respectively, instead of dQ or dW. Properties, however, are **point functions** (i.e., they depend on the state only, and not on how a system reaches that state), and they have **exact differentials** designated by the symbol d. A small change in volume, for example, is represented by dV, and the total volume change during a process between states 1 and 2 is

$$\int_1^2 dV = V_2 - V_1 = \Delta V$$

That is, the volume change during process 1–2 is always the volume at state 2 minus the volume at state 1, regardless of the path followed . The total work done during process 1–2, however, is

$$\int_1^2 \delta W = W_{12} \qquad (not\ \Delta W)$$

That is, the total work is obtained by following the process path and adding the differential amounts of work (δW) done along the way. The integral of δW *is not* $W_2 - W_1$ (i.e., the work at state 2 minus work at state 1), which is meaningless since work is not a property and systems do not possess work at a state.



FIGURE

Properties are point functions; but heat and work are path functions (their magnitudes depend on the path followed).

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.

REVERSIBLE WORK

Let us consider an ideal frictionless fluid contained in a cylinder above a piston as shown in Fig. *Assume that the pressure and temperature of the fluid are uniform and that there is no friction between the piston and the cylinder walls.*

Let A = Cross-sectional area of the piston,

p = Pressure of the fluid at any instant,

$(p - dp)\,A$ = Restraining *force exerted* by the surroundings on the piston, and

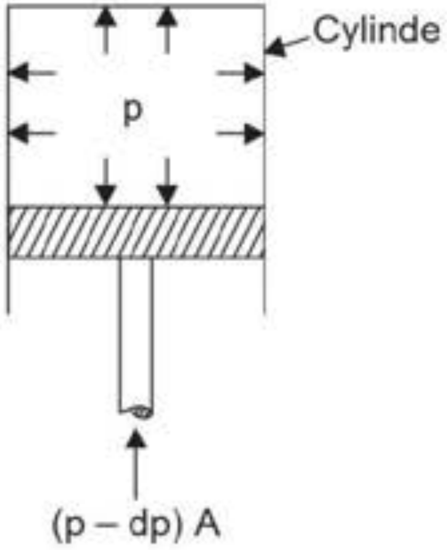
dl = The distance moved by the piston under the action of the *force exerted.*

Then work done by the fluid on the piston is given by force times the distance moved,

i.e., Work done by the fluid

$$= (pA) \times dl = pdV$$

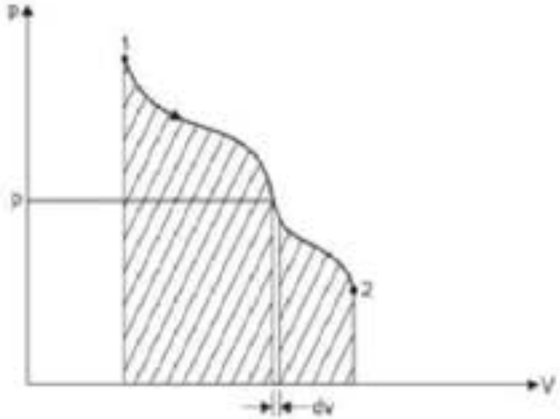
(where dV = a small increase in volume)



Or considering unit mass

Work done = pdv (where v = specific volume)

This is only *true* when (a) the *process is frictionless and (b) the difference in pressure between the fluid and its surroundings during the process is infinitely small*. Hence when a reversible process takes place between state 1 and state 2, we have



$$\text{Work done by the unit mass of fluid} = \int_1^2 pdv$$

When a fluid undergoes a reversible process a series of state points can be joined up to form a line on a diagram of properties. The work done by the fluid during any reversible process is therefore given by the area under the line of process plotted on a p-v diagram (Fig. 2.32).

i.e., Work done = Shaded area on Fig. 2.33

$$= \int_1^2 pdv\,.$$

When p can be expressed in terms of v then the integral, $\int_1^2 pdv$, can be evaluated.

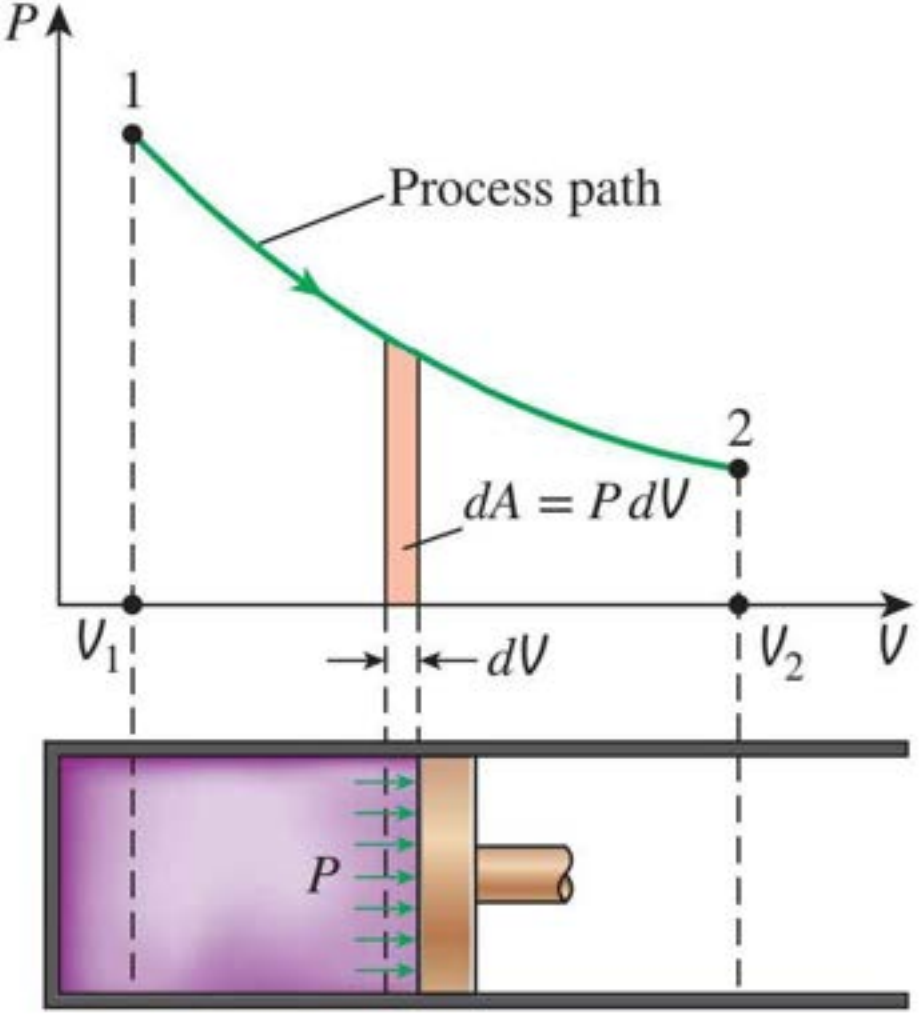
Limitations of the Use of $\int P\mathrm{d}V$

For $\int P\mathrm{d}V$ *to* represent work, the following conditions must be satisfied:

(i) The system is a closed one and the process taking place is a non-flow process.

(ii) The process is quasi-static. Such a process is often referred to as a reversible process since a quasi-static expansion process according to a particular P–V relationship between two states can be reversed as a quasi-static compression process according to the same P–V relationship between the same states.

(iii) The boundary of the system should move in order that work may be transferred.



FIGURE

The area under the process curve on a P-V diagram represents the boundary work.

REVERSIBLE AND IRREVERSIBLE PROCESSES

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.

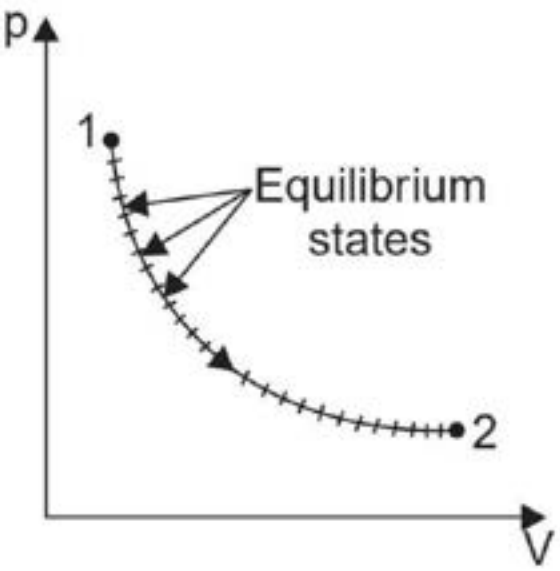


Fig. Reversible process.

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

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.

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.

An irreversible process is usually represented by a dotted (or discontinuous) line joining the end states to indicate that the intermediate states are indeterminate .

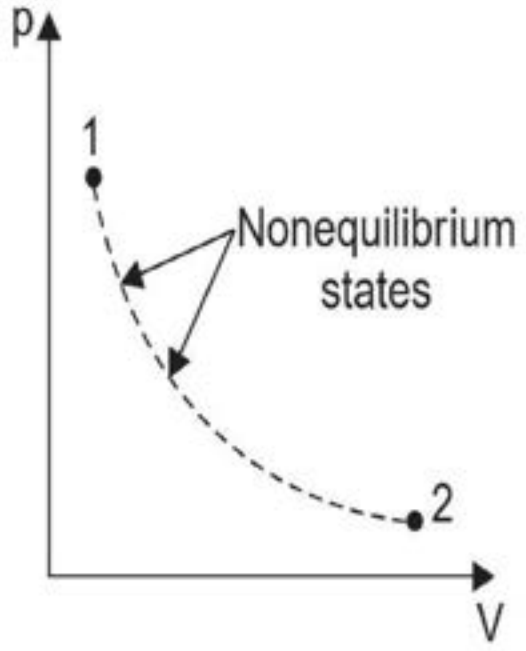


Fig. Irreversible process.

Irreversibilities are of *two types* :

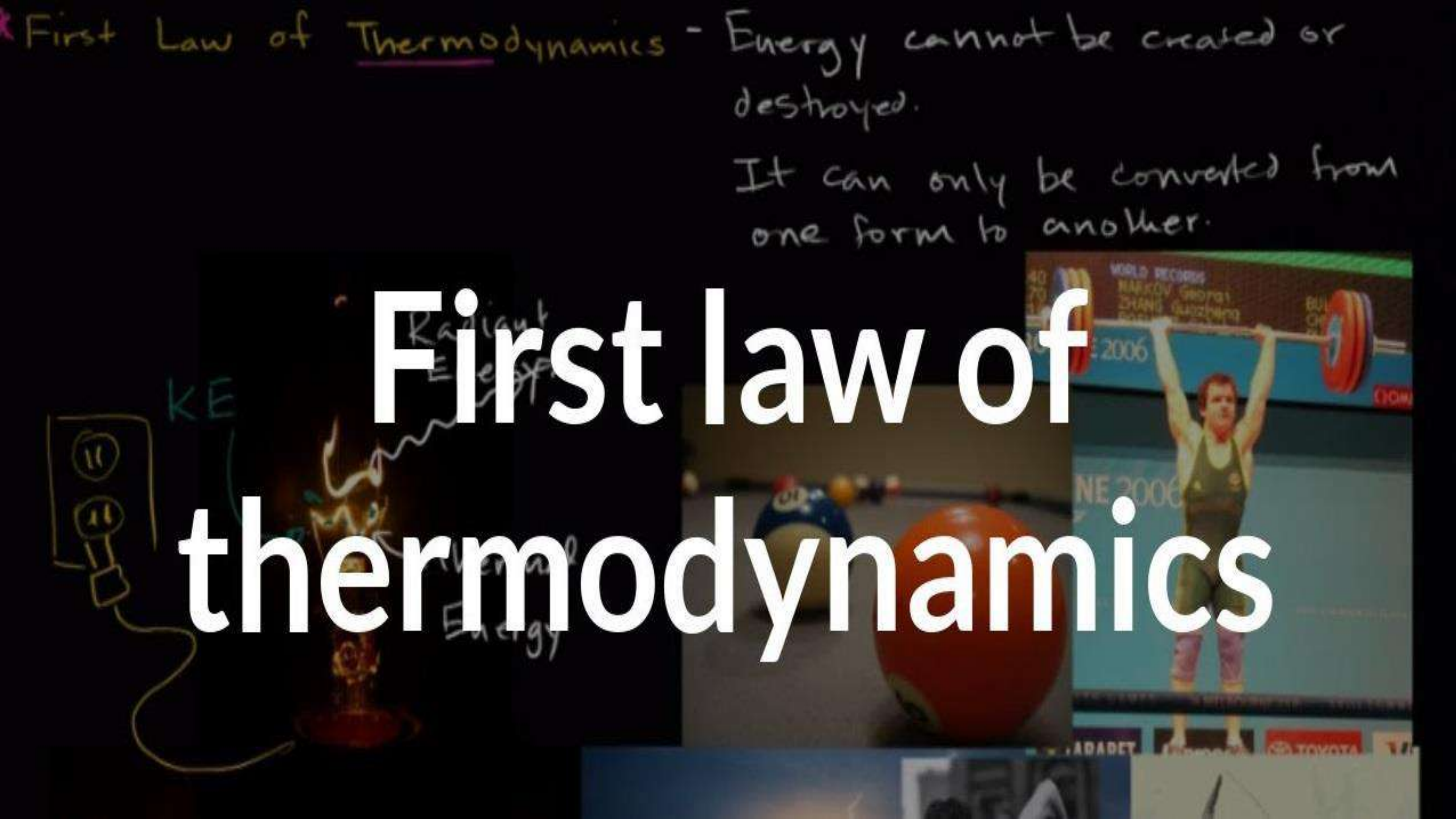
1. **External irreversibilities.** These are associated with *dissipating effects outside the working fluid.*

Example. *Mechanical friction occurring during a process due to some external source.*

2. **Internal irreversibilities.** These are associated with *dissipating effects within the working fluid.*

Example. *Unrestricted expansion of gas, viscosity and inertia of the gas.*

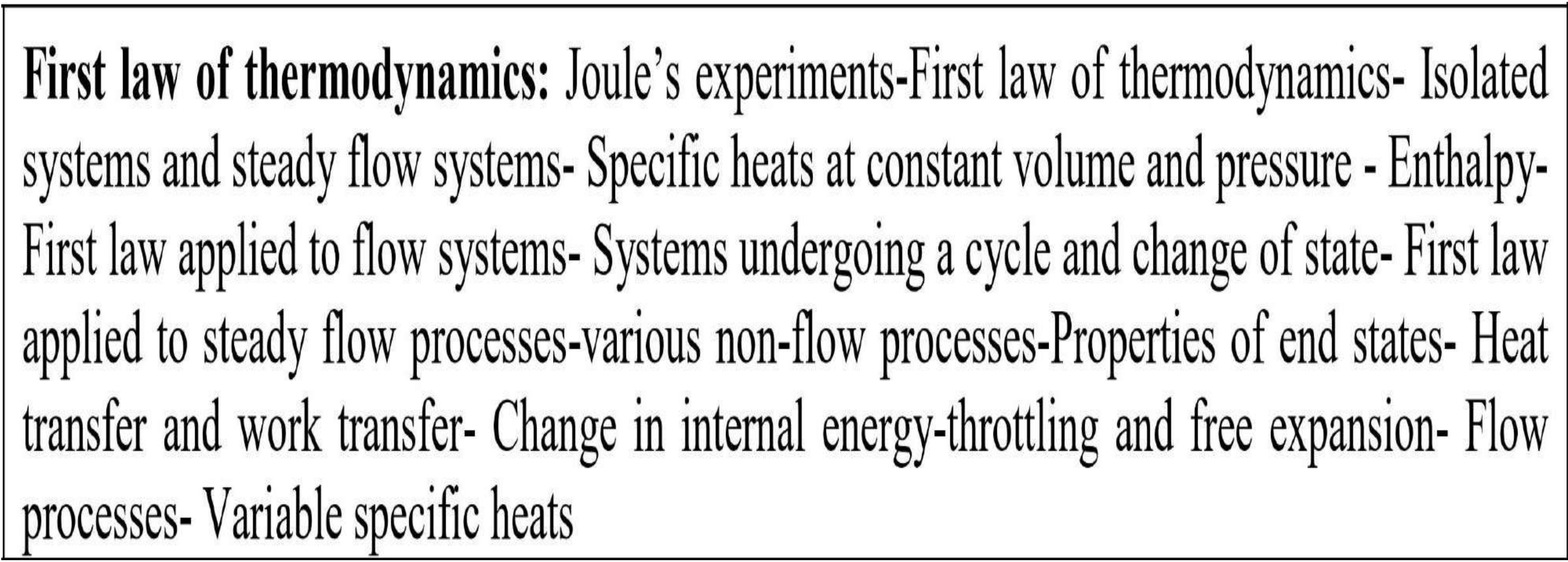
First law of thermodynamics



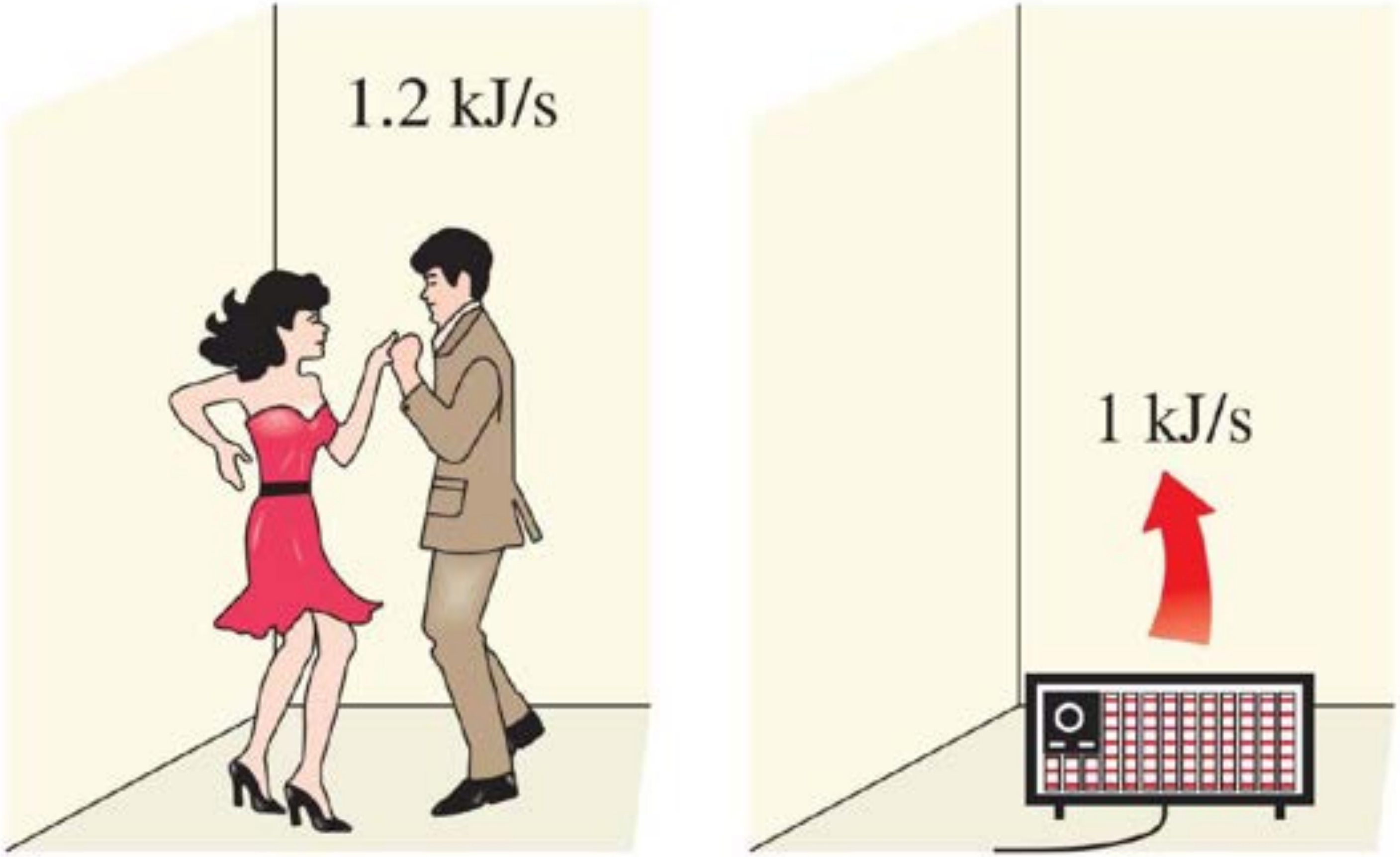
First Law of Thermodynamics - Energy cannot be created or destroyed.

It can only be converted from one form to another.

Topics: UNIT-II

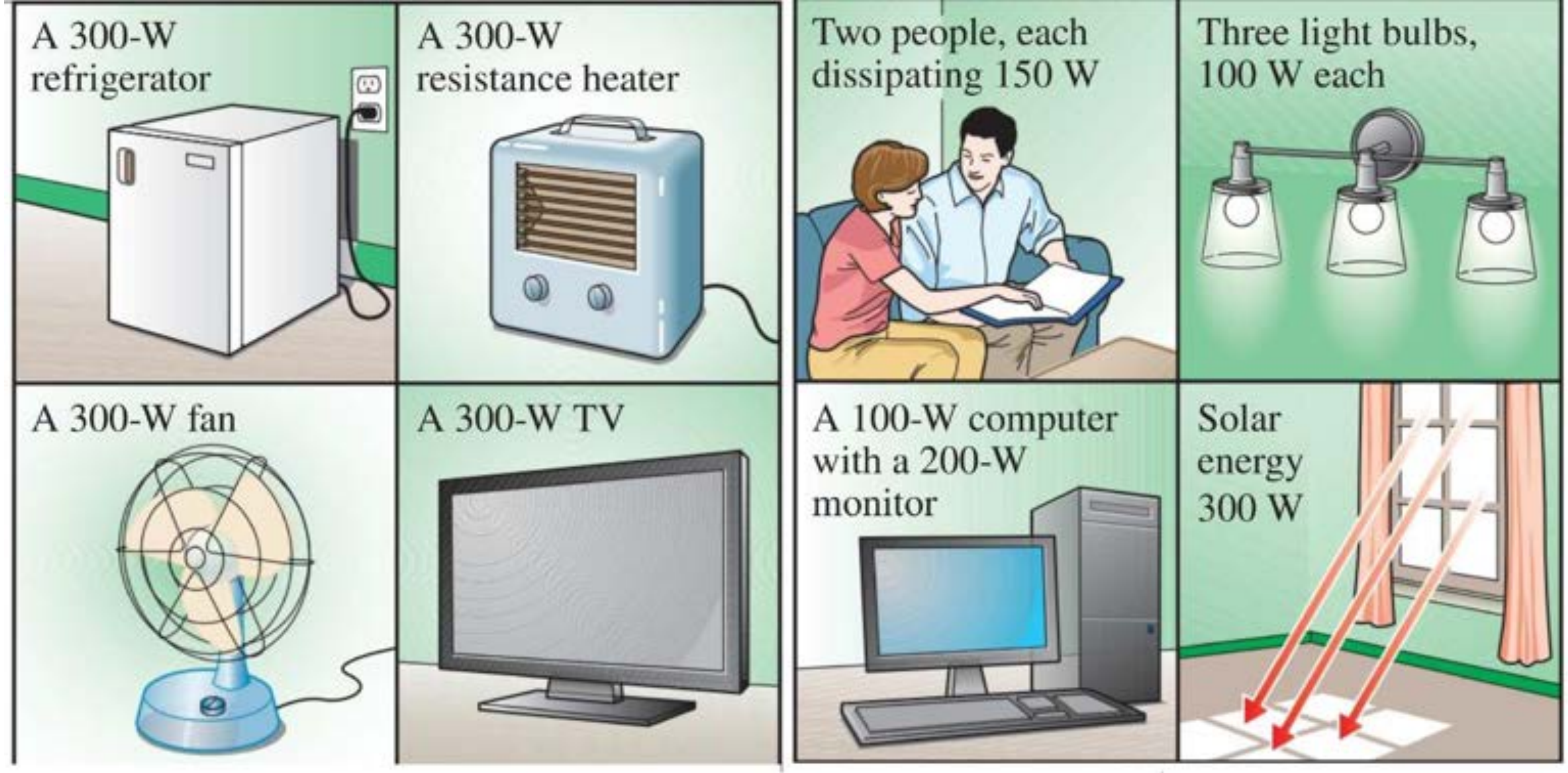


First law of thermodynamics: Joule's experiments-First law of thermodynamics- Isolated systems and steady flow systems- Specific heats at constant volume and pressure - Enthalpy-First law applied to flow systems- Systems undergoing a cycle and change of state- First law applied to steady flow processes-various non-flow processes-Properties of end states- Heat transfer and work transfer- Change in internal energy-throttling and free expansion- Flow processes- Variable specific heats



FIGURE

Two fast-dancing people supply more energy to a room than a 1-kW electric resistance heater.



FIGURE

Some arrangements that supply a room with the same amount of energy as a 300-W electric resistance heater.

— The First Law of Thermodynamics may also be stated as follows :

"Heat and work are mutually convertible but since energy can neither be created nor destroyed, the total energy associated with an energy conversion remains constant".

Or

— **"No machine can produce energy without corresponding expenditure of energy, *i.e.*, it is impossible to construct a perpetual motion machine of first kind".**

Fig. shows the experiment for checking first law of thermodynamics.

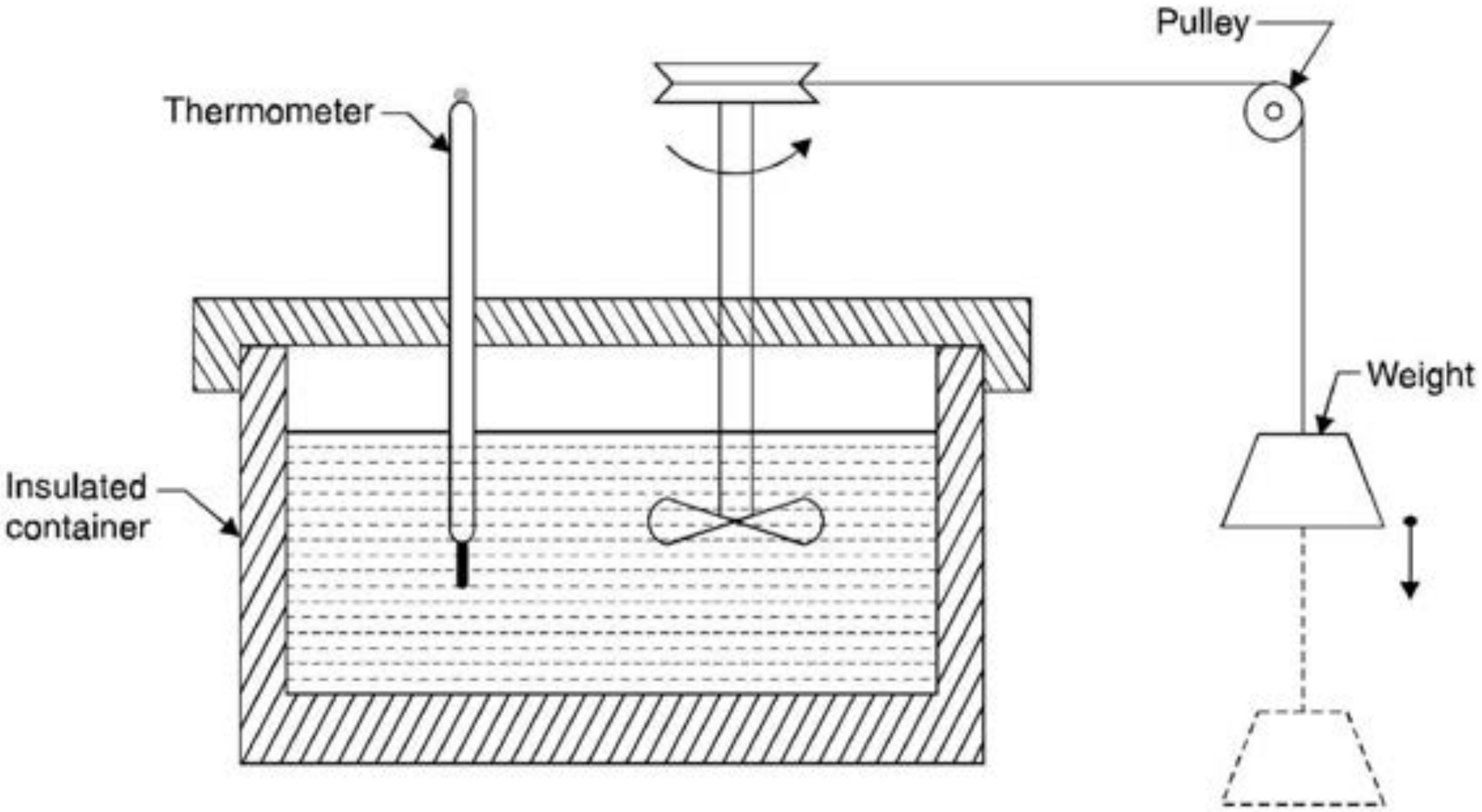


Fig. Heat and work.

LOADING...

100 %

The experiments show : (*i*) A definite quantity of work is always required to accomplish the same temperature rise obtained with a unit amount of heat. (*ii*) Regardless of whether the temperature of liquid is raised by work transfer or heat transfer, the liquid can be returned by heat transfer in opposite direction to the identical state from which it started. The above results lead to the inference that *work and heat* are different forms of something more general, which is called *energy*.

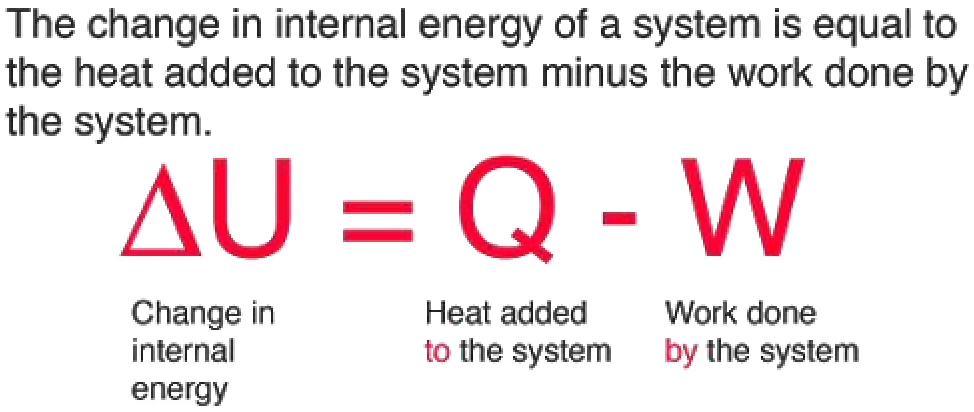
— It can be stated as an invariable experience that whenever a physical system passes through a complete cycle the algebraic sum of the work transfers during the cycle $\oint dW$ bears a definite ratio to the algebraic sum of the heat transfers during the cycle, $\oint dQ$. This may be expressed by the equation,

$$\oint dW = J \oint dQ$$

where J is the proportionality constant and is known as *Mechanical Equivalent of heat*. In S.I. units its value is unity, *i.e.*, 1 Nm/J.

The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic processes, distinguishing two kinds of transfer of energy, as heat and as thermodynamic work, and relating them to a function of a body's state, called Internal energy.

The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but can be neither created nor destroyed.



The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

$$\Delta U = Q - W$$

Change in internal energy

Heat added to the system

Work done by the system

Some Physical Insight to Internal Energy

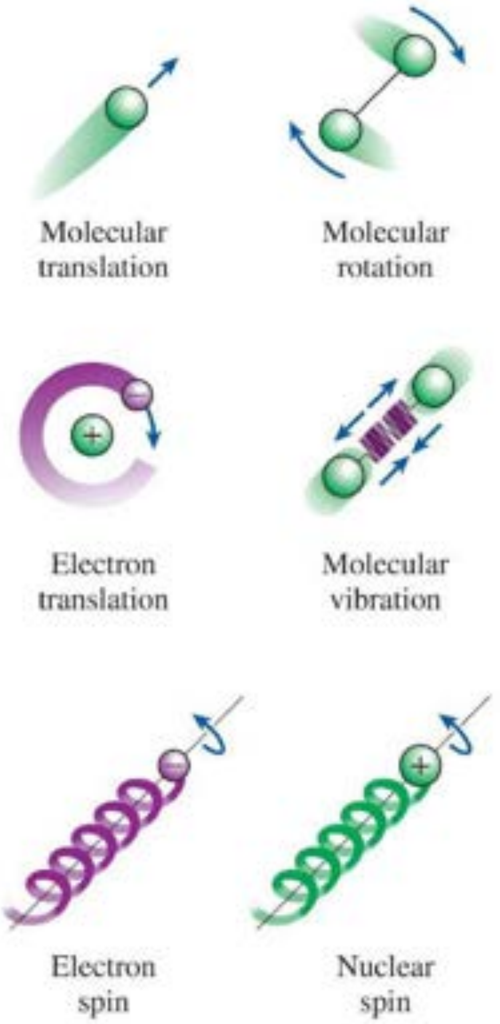


FIGURE
The various forms of microscopic energies that make up *sensible* energy.

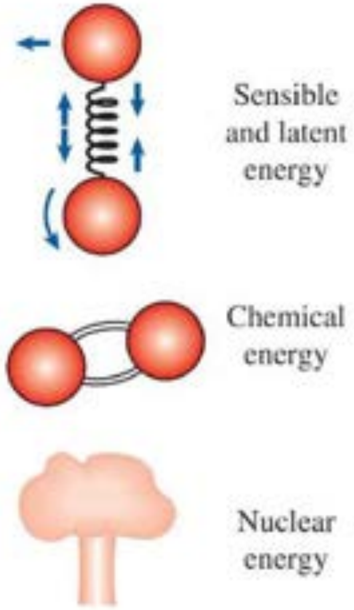


FIGURE
The internal energy of a system is the sum of all forms of the microscopic energies.

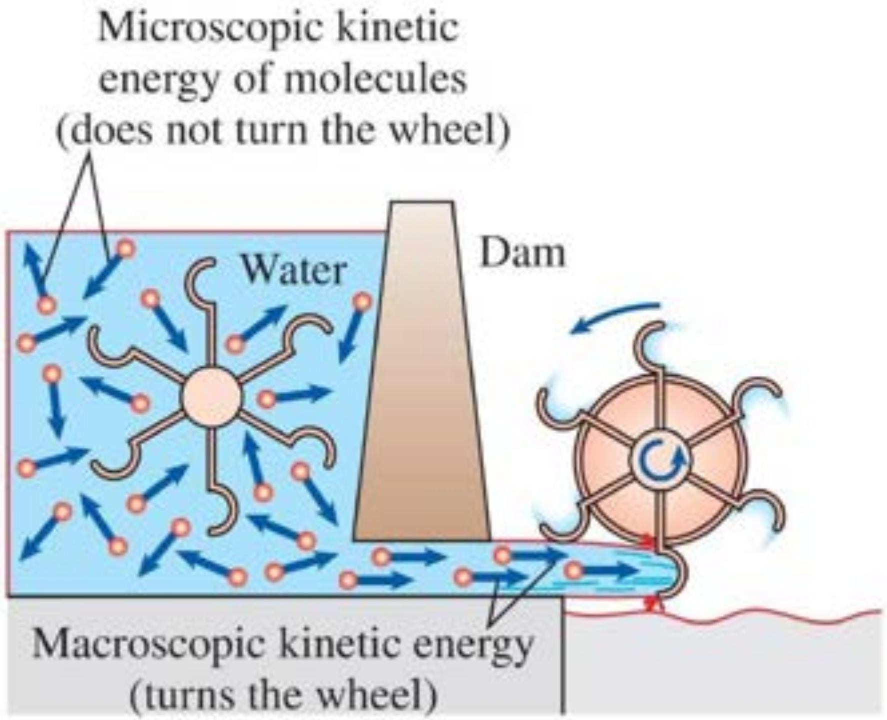


FIGURE
The *macroscopic* kinetic energy is an organized form of energy and is much more useful than the disorganized *microscopic* kinetic energies of the molecules.

For a closed system or a fixed mass, the first law may be expressed as follows:

Net energy transferred to (or from) the system as heat and work=Net increase (or decrease) in the total energy of the system

$$\begin{aligned} Q - W &= \Delta E \\ &= \Delta U + \Delta KE + \Delta PE + \ldots \end{aligned} \tag{3.1}$$

Neglecting the effects of magnetic and electric fields and surface tension, the above equation reduces to

$$Q - W = \Delta U + \Delta KE + \Delta PE \tag{3.2}$$

For a stationary closed system (the extrinsic effects on a closed system, such as the effects of motion and gravity, are neglected)

$$Q - W = \Delta U \tag{3.3}$$

Eq. (3.3) can be written in differential form as

$$\delta Q - \delta W = \mathrm{d}U \tag{3.4}$$

And per unit mass basis, Eqs (3.3) and (3.4) become

$$q - w = u \tag{3.5}$$

$$\delta q - \delta w = \mathrm{d}u \tag{3.6}$$

Internal energy is defined as the sum of all the microscopic forms of energy of a system. It is the energy associated with the molecular structure, and the molecular activity of the constituent particles of the system. It may be viewed as the sum of the kinetic and potential energies of the molecules.

First Law of Thermodynamics for a Closed System Undergoing a Cycle

If a system executes a cycle transferring heat and work through its boundary, the net work transfer is equivalent to the net heat transfer.

Mathematically,

$$\oint \delta W = \oint \delta Q$$

First Law of Thermodynamics for a Non-flow, Non-cyclic Process

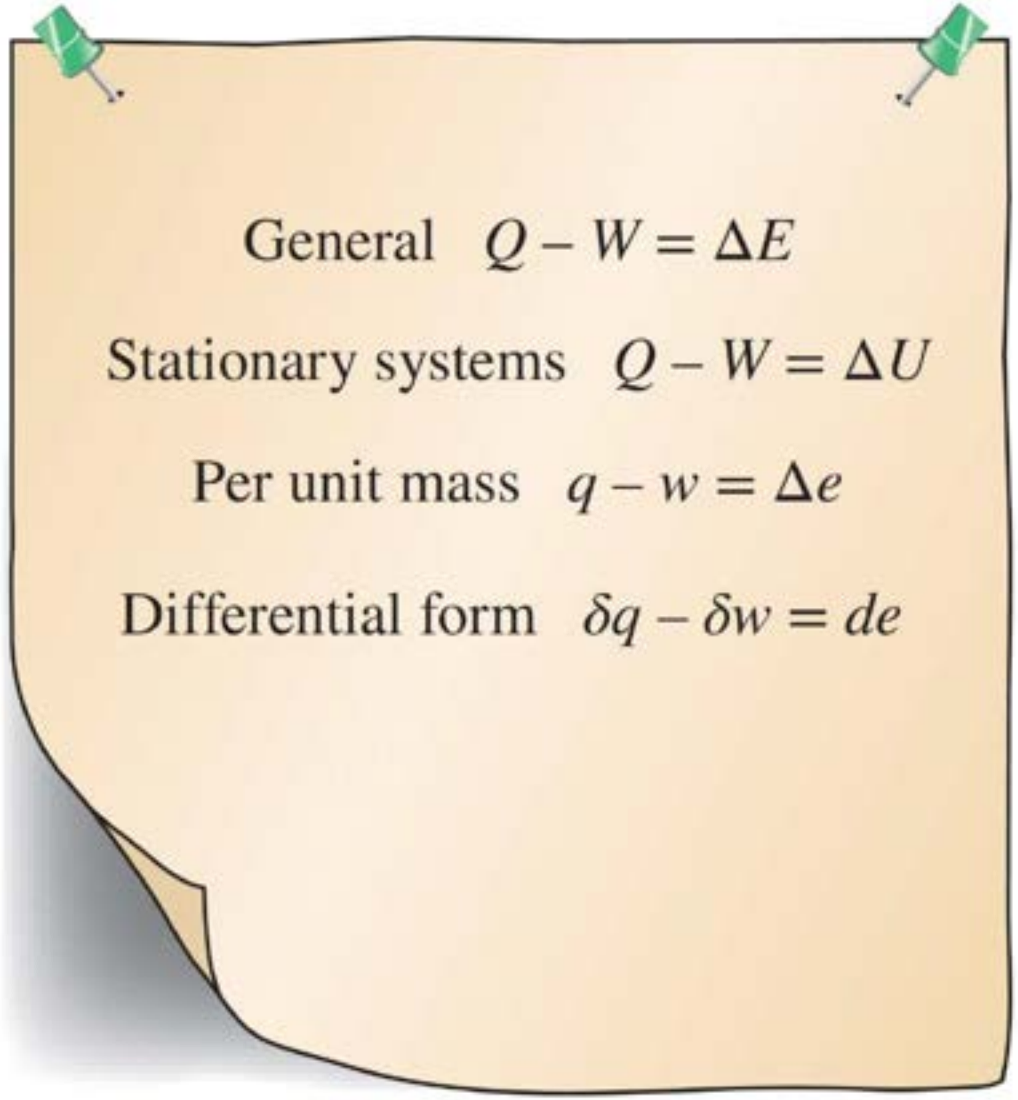
The net algebraic sum of heat and work during a process is equal to the change in internal energy during the same process.

Mathematically,

$$\delta Q - \delta W = \mathrm{d}U$$

Since for a quasi-equilibrium process, $\delta W = P dV$, Eq. becomes

$$\delta Q - P\mathrm{d}V = \mathrm{d}U$$



General $Q - W = \Delta E$

Stationary systems $Q - W = \Delta U$

Per unit mass $q - w = \Delta e$

Differential form $\delta q - \delta w = de$

FIGURE
Various forms of the first-law relation for closed systems.

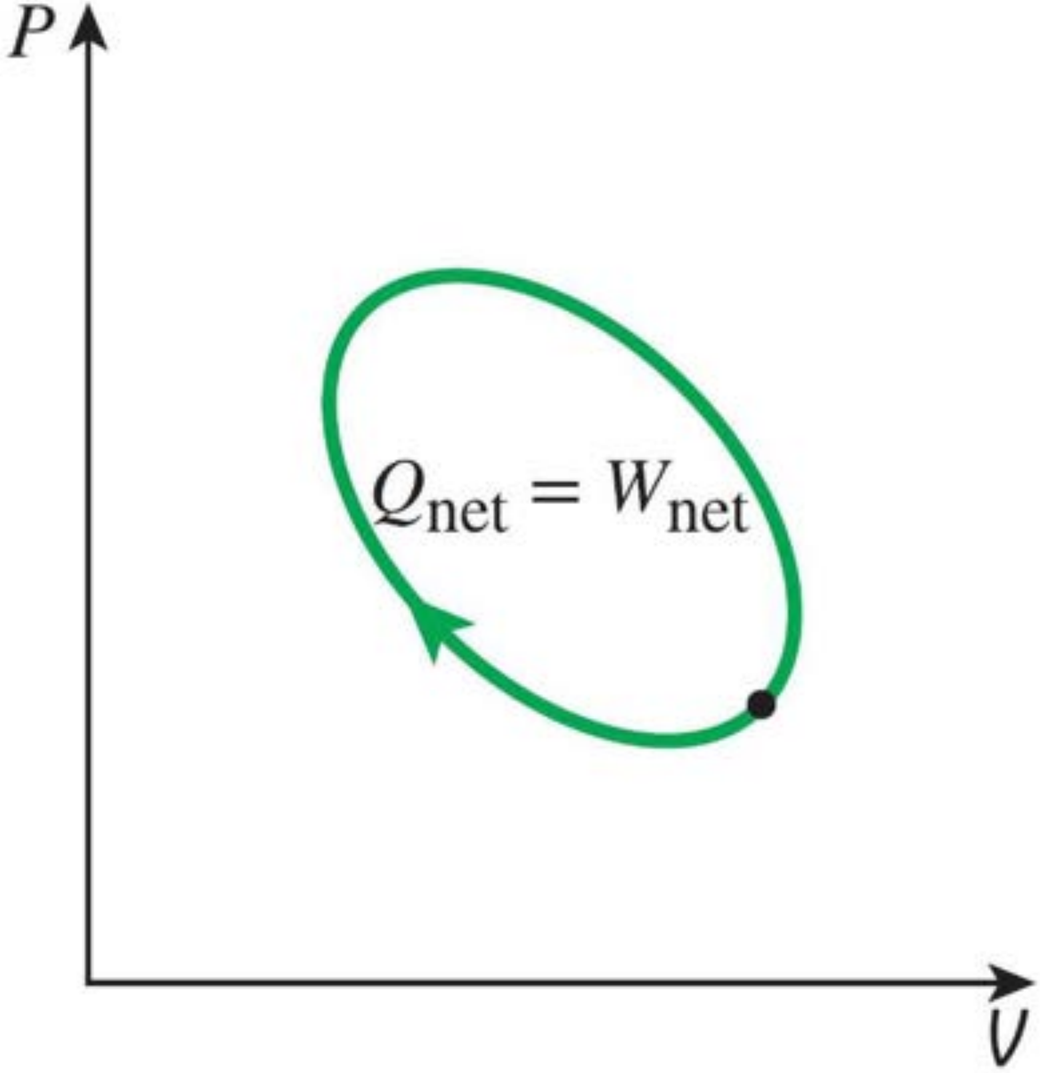


FIGURE
For a cycle $\Delta E = 0$, thus $Q = W$.

Example A system undergoes a cycle composed of four processes, 1–2, 2–3, 3–4 and 4–1. The rate of energy transfers are tabulated below:

Process	*Q(kW)*	*W(kW)*	*ΔU(kW)*
1–2	400	150	*A*
2–3	200	*B*	300
3–4	–200	*C*	*D*
4–1	0	75	*E*

(i) Calculate the value of *A*, *B*, *C*, *D* and *E*.

(ii) Determine the rate of work in kW.

Solution For process 1–2,

$$Q_{1-2} = \Delta U + W_{1-2}$$
$$400 = A + 150$$
$$A = 250 \text{ kW}$$

For process 2–3,

$$Q_{2-3} = \Delta U + W_{2-3}$$
$$200 = 300 + B$$
$$B = -100 \text{ kW}$$

For process 4–1,

$$Q_{4-1} = \Delta U + W_{4-1}$$
$$0 = E + 75$$
$$E = -75 \text{ kW}$$

Now,

$$\oint U = 0$$
$$A + 300 + D + E = 0$$
$$250 + 300 + D - 75 = 0$$
$$D = -475 \text{ kW}$$

For process 3–4,

$$Q_{3-4} = \Delta U + W_{3-4}$$
$$-200 = D + C$$
$$-200 = -475 + C$$
$$C = 275 \text{ kW}$$

Since

$$\oint \delta Q = \oint \delta W$$

Net cyclic work done $= 400 + 200 - 200 + 0 = 400$ kW

Negative sign indicates that heat is lost from the system.

Example A system undergoes a process 1-2 in which it absorbs 200 kJ energy as heat while it does 100 kJ work. Then it follows path 2-3 in which it rejects 50 kJ energy as heat when 80 kJ work is done on it. If it is required to restore the system to state 1 through an adiabatic path, calculate the work and heat transfer along the adiabatic path. Also calculate net heat transfer.

Solution From the given data, we have

$$Q_{1-2} = 200 \text{ kJ}, \; W_{1-2} = 100 \text{ kJ},$$

$$Q_{2-3} = -50 \text{ kJ}, \; W_{2-3} = -80 \text{ kJ}$$

$$Q_{3-1} = 0$$

The processes 1-2, 2-3 and 3-1 together constitute a cycle. Thus from Eq. (3.7), we have

$$\sum Q = \sum W$$

or,

$$Q_{1-2} + Q_{2-3} + Q_{3-1} = W_{1-2} + W_{2-3} + W_{3-1}$$

or,

$$200 - 50 + 0 = 100 - 80 + W_{3-1}$$

or,

$$W_{3-1} = 130 \text{ kJ} \; W_{31} = 130 \text{ kJ}$$

Net heat transfer is $Q_{1-2} + Q_{2-3} + Q_{3-1} = 200 - 50 + 0 = 150$ kJ

COROLLARIES OF THE FIRST LAW OF THERMODYNAMICS

Corollary-1 ***There exists a property of a closed system such that a change in its value is equal to the difference between heat supplied and work done during the change of state.***

Proof

Let the system be taken from state 1 to state 2 by the two different processes 1-a-2 and 1-b-2 as shown in Fig.

Let us consider,

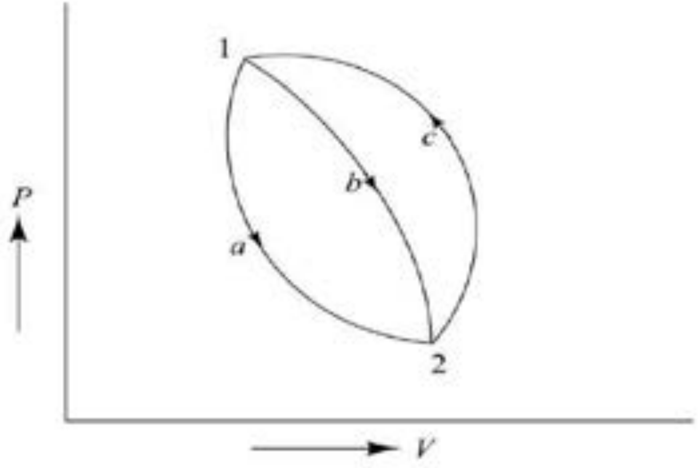
$$(\delta Q - \delta W)_a \neq (\delta Q - \delta W)_b \tag{3.9}$$

where δQ the net heat is supplied to the system and δW is the net work done by the system during a process. Let the system be taken from state 2 to 1 through path 2-c-1.Now the processes 1-a-2 and 2-c-1 together constitute a cycle. From the first law of thermodynamics for a cyclic process, we can write

$$\oint \delta Q = \oint \delta W$$

$$\delta Q_a + \delta Q_c = \delta W_a + \delta W_c$$

$$(\delta Q - \delta W)_a = -(\delta Q - \delta W)_c \tag{3.10}$$



Figure

Similarly, the processes 1-a-2 and 2-c-1 together constitute a cycle for which the first law of thermodynamics becomes

$$\oint \delta Q = \oint \delta W$$

$$\delta Q_b + \delta Q_c = \delta W_b + \delta W_c$$

$$(\delta Q - \delta W)_b = -(\delta Q - \delta W)_c \tag{3.11}$$

If inequality (3.9) is true, then Eqs (3.10) and (3.11) contradict each other which implies that these quantities must be equal. Therefore $(\delta Q - \delta W)$ is independent of the path the system follows during a change of state. If the property denoted by U, the corollary can be expressed mathematically as $\delta Q - \delta W = dU$.

The property *U* is called the internal energy of the system. The adjective “internal” has been adopted to distinguish this form of energy from the mechanical forms of energy.

Corollary-2   The internal energy of a closed system remains unchanged if the system is isolated from the surroundings.

Proof

A system which exchanges neither mass nor energy with the surroundings is called an isolated system. It is thus a closed system having no energy interaction ($\delta Q = 0$, $\delta W = 0$) with the surroundings.

Then the first law of thermodynamics in differential form becomes

$$dU = 0$$

or,

$$U = \text{Constant}$$

Figure 3.3 shows an isolated system. All that happens during a process is a spontaneous redistribution of energy between parts of the system which continues until a state of equilibrium is reached. There is no change in the total energy within the system during the process.

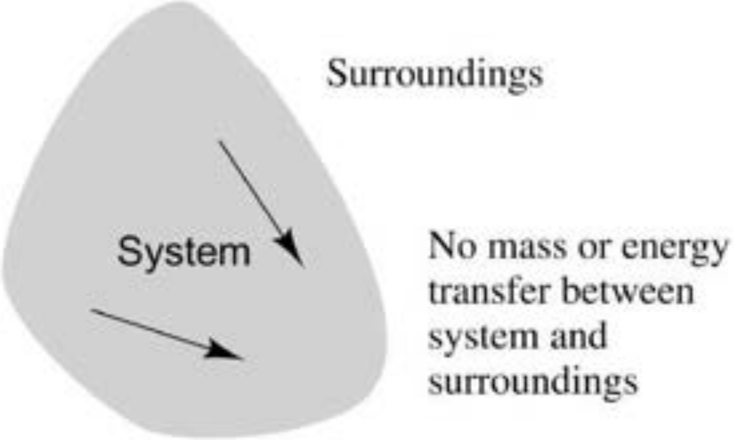


Figure *An isolated system*

Corollary-3 A perpetual motion machine of first kind is impossible.

Proof A hypothetical device which would produce work continuously without absorbing any energy from its surroundings is called a perpetual motion machine of the first kind. A perpetual motion machine of the first kind must operate on a cycle to produce work continuously. If it does not operate on a cycle, its state would change continuously and it could not go on indefinitely. For such a device there cannot be any energy transfer in the form of heat from the surroundings, hence $\oint \delta Q = 0$. Therefore, $\oint \delta W = 0$, that means the work delivered by it is zero. Therefore, it is impossible to construct a perpetual motion machine of the first kind. *A perpetual motion machine of the first kind is a machine which violates the first law of thermodynamics.*

It is always possible to devise a machine to deliver a limited (certain) quantity of work without requiring a source of energy in the surroundings. For example, a compressed gas in a piston-cylinder arrangement will expand and do work at the expense of the internal energy of the gas. Such a device can not produce work continuously.

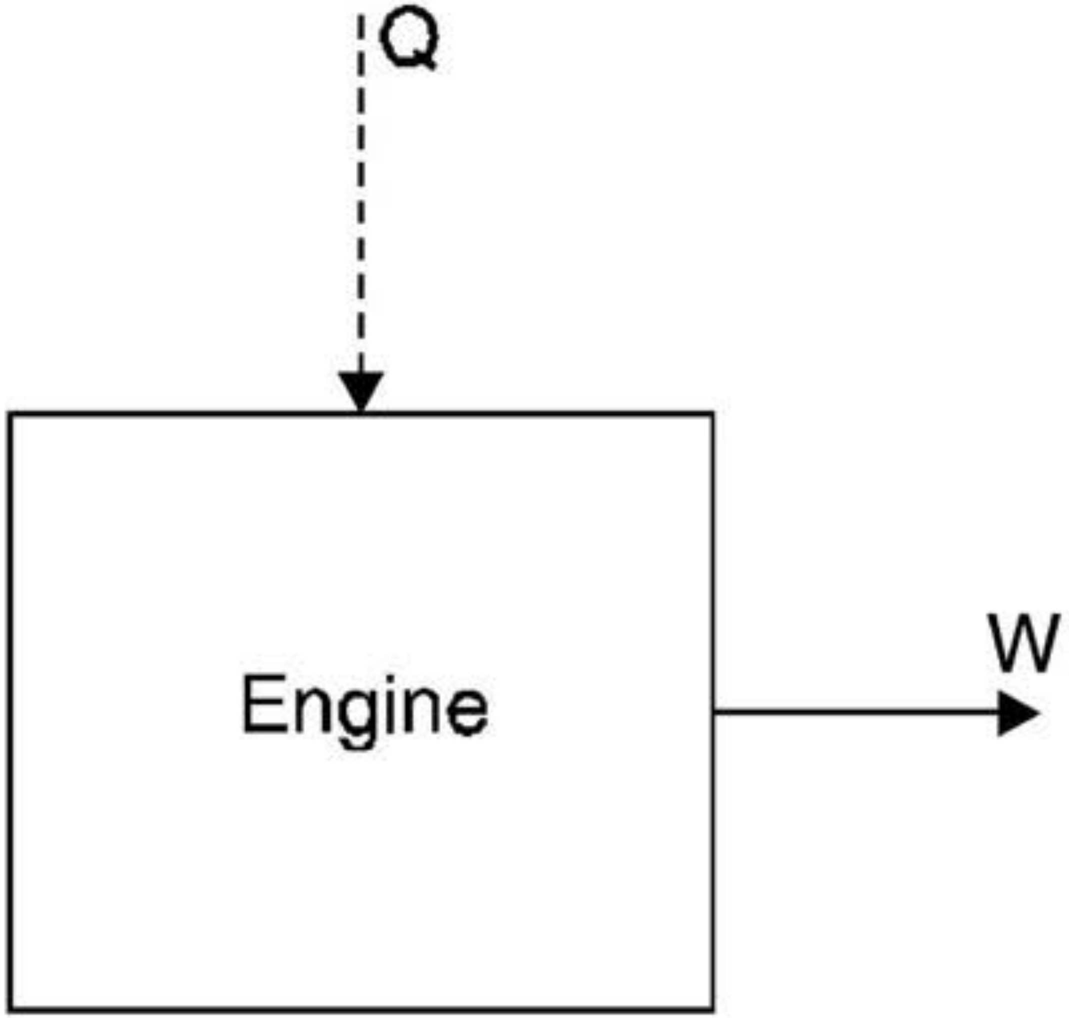


Fig. A PPM 1.

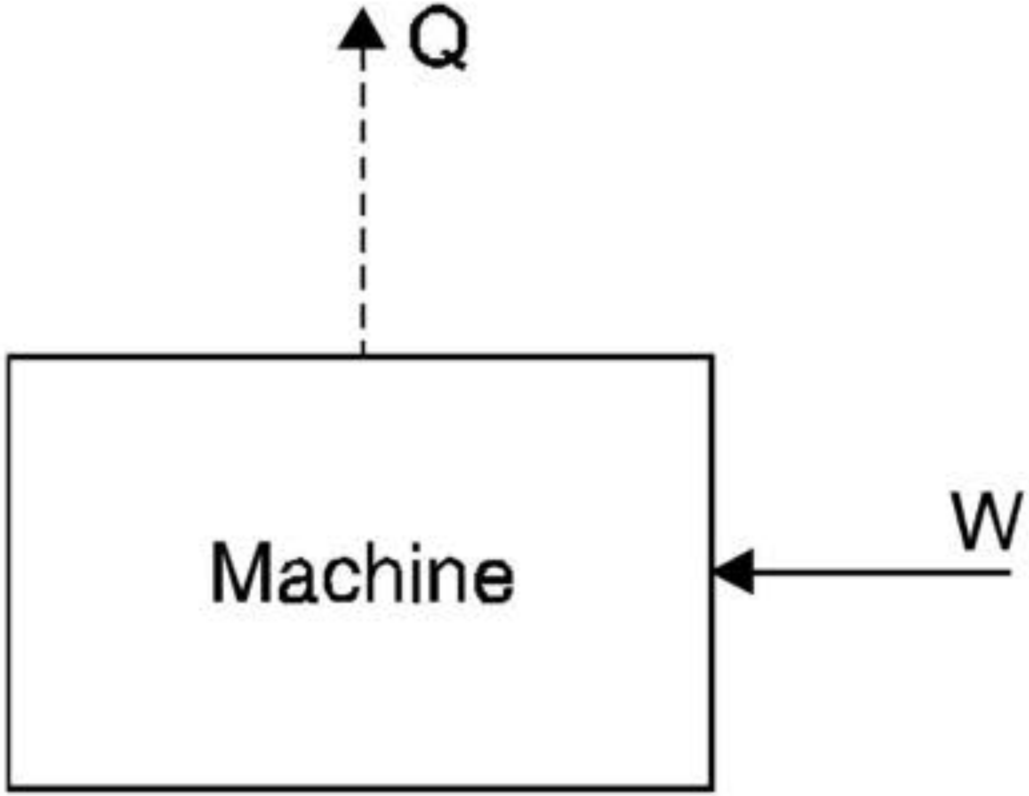


Fig. The converse of PMM 1.

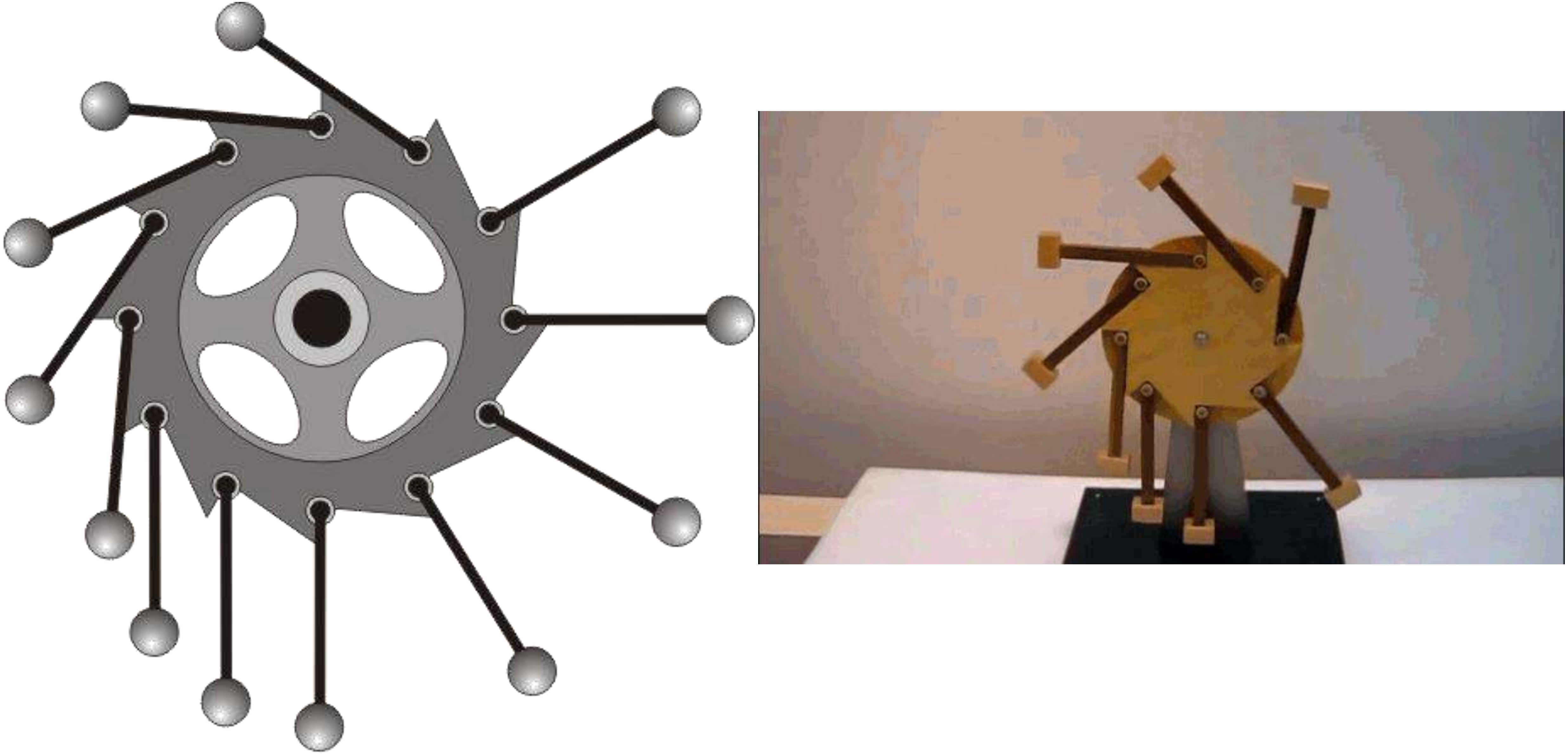


Fig: Some claimed perpetual models come across the internet

HEAT TRANSFER: NOT A PROPERTY OF A SYSTEM

Let the system be taken from state 1 to state 2 by the two different processes 1-a-2 and 1-b-2. Let the system be taken from state 2 to 1 through path 2-c-1.Now the processes 1-a-2 and 2-c-1 together constitute a cycle.

Applying the first law of thermodynamics for the cyclic process

$$\oint \delta Q = \oint \delta W$$

$$\int_{1-a-2} \delta Q + \int_{2-c-1} \delta Q = \int_{1-a-2} \delta W + \int_{2-c-1} \delta W \tag{3.12}$$

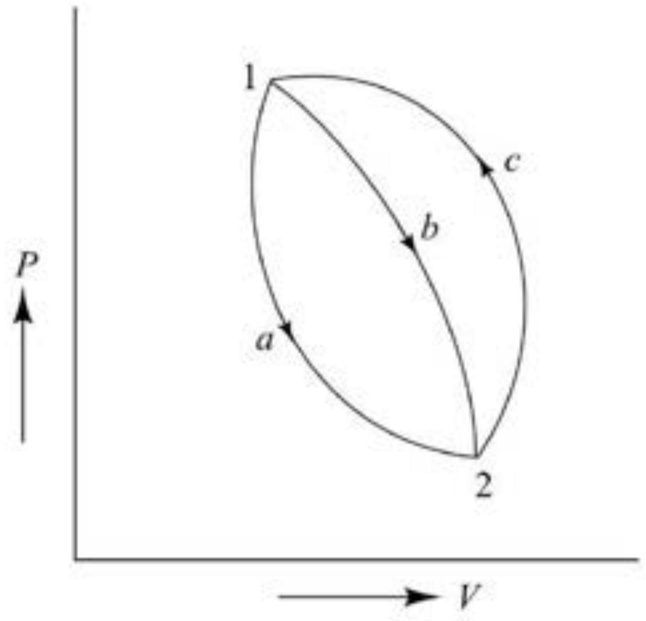


Figure 3.4

Similarly, the processes 1-b-2 and 2-c-1 together constitute a cycle for which

$$\int_{1-b-2} \delta Q + \int_{2-c-1} \delta Q = \int_{1-b-2} \delta W + \int_{2-c-1} \delta W \tag{3.13}$$

Subtracting Eq. (3.13) from Eq. (3.12), we get

$$\int_{1-a-2} \delta Q - \int_{1-b-2} \delta Q = \int_{1-a-2} \delta W - \int_{1-b-2} \delta W \tag{3.14}$$

Since work transfer is a path function,

$$\int_{1-a-2} \delta W - \int_{1-b-2} \delta W \neq 0 \tag{3.15}$$

Therefore,

$$\int_{1-a-2} \delta Q - \int_{1-b-2} \delta Q \neq 0 \tag{3.16}$$

That is the heat transfer in a process depends not only the initial and final states, but also the path followed by system during a change of state, i.e., *heat transfer is a path function and not a property of a system*.

THE PERFECT GAS

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

$$\frac{pv}{T} = \text{constant} = R$$

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

$$pv = RT \quad \text{...(4.11)}$$

or for m kg, occupying V m^3

$$pV = mRT \quad \text{...(4.12)}$$

— 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

$$m = nM \quad \text{...(4.13)}$$

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

$$pV = nMRT$$

or

$$MR = \frac{pV}{nT}$$

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 $\frac{pV}{nT}$ is a *constant* for all gases. This constant is called *universal gas constant*, and is given the symbol, R_0.

i.e.,
$$MR = R_0 = \frac{pV}{nT}$$

or
$$pV = nR_0T \qquad ...(4.14)$$

Since $MR = R_0$, then

$$R = \frac{R_0}{M} \qquad ...(4.15)$$

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),

$$R_0 = \frac{pV}{nT} = \frac{1 \times 10^5 \times 22.71}{1 \times 273.15}$$

$$= 8314.3 \text{ Nm/mole K}$$

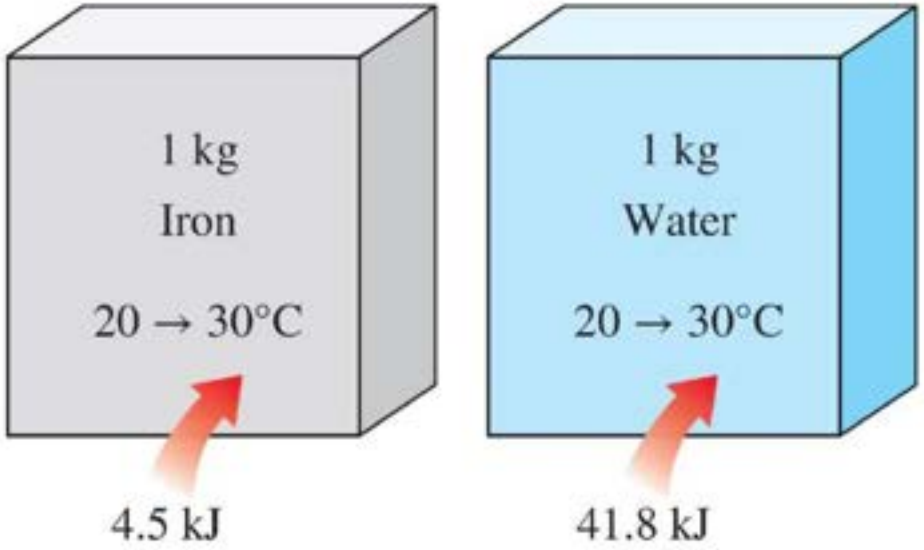
Using eqn. (4.15), the gas constant for any gas can be found when the molecular weight is known.

Example. For oxygen which has a molecular weight of 32, the gas constant

$$R = \frac{R_0}{M} = \frac{8314}{32} = 259.8 \text{ Nm/kg K.}$$

Specific Heat or Heat Capacity

We know from experience that it takes different amounts of energy to raise the temperature of identical masses of different substances by one degree. For example, we need about 4.5 kJ of energy to raise the temperature of 1 kg of iron from 20 to 30°C, whereas it takes about nine times this much energy (41.8 kJ to be exact) to raise the temperature of 1 kg of liquid water by the same amount (Fig.). Therefore, it is useful to have a property that will enable us to compare the energy storage capabilities of various substances. This property is the specific heat.



FIGURE

It takes different amounts of energy to raise the temperature of different substances by the same amount.

The **specific heat** is defined as *the energy required to raise the temperature of a unit mass of a substance by one degree* (Fig). In general, this energy depends on how the process is executed. In thermodynamics, we are interested in two kinds of specific heats: **specific heat at constant volume** c_υ and **specific heat at constant pressure** c_p.

Physically, the specific heat at constant volume c_υ can be viewed as *the energy required to raise the temperature of the unit mass of a substance by one degree as the volume is maintained constant*. The energy required to do the same as the pressure is maintained constant is the specific heat at constant pressure c_p. This is illustrated in Fig. The specific heat at constant pressure c_p is always greater than c_υ because at constant pressure the system is allowed to expand, and the energy for this expansion work must also be supplied to the system.

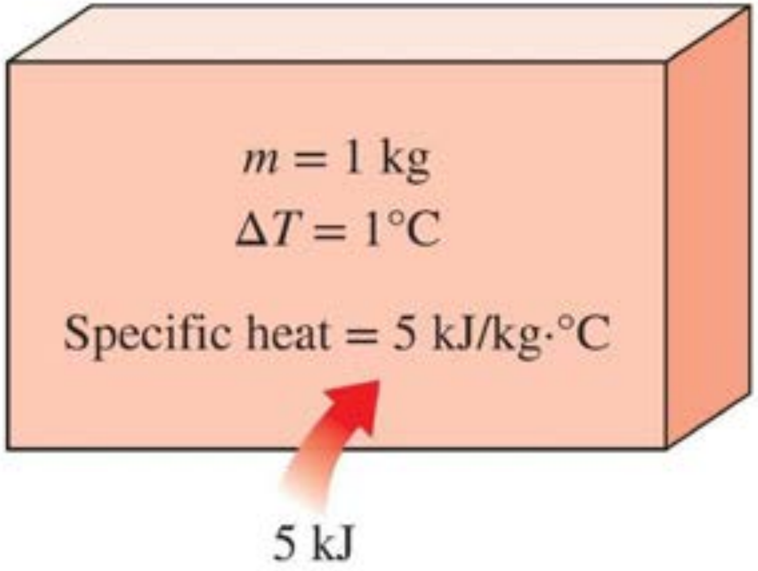


FIGURE
Specific heat is the energy required to raise the temperature of a unit mass of a substance by one degree in a specified way.

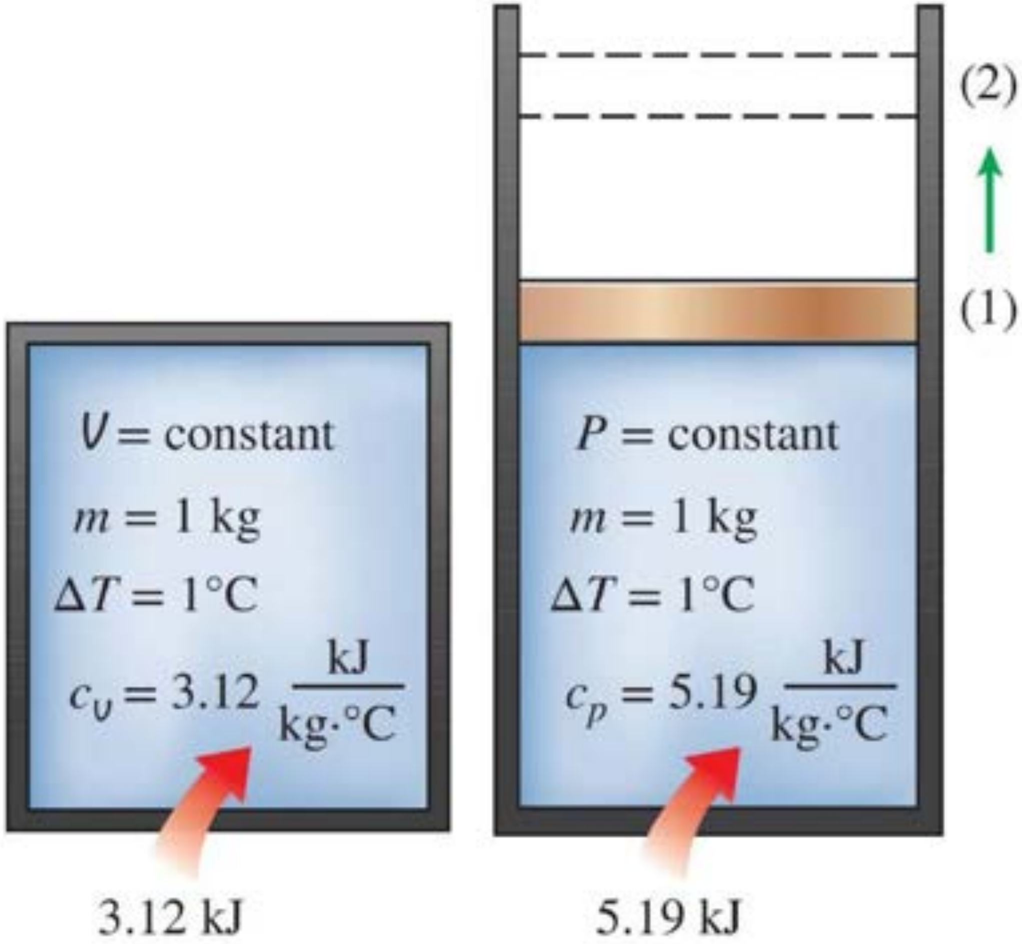
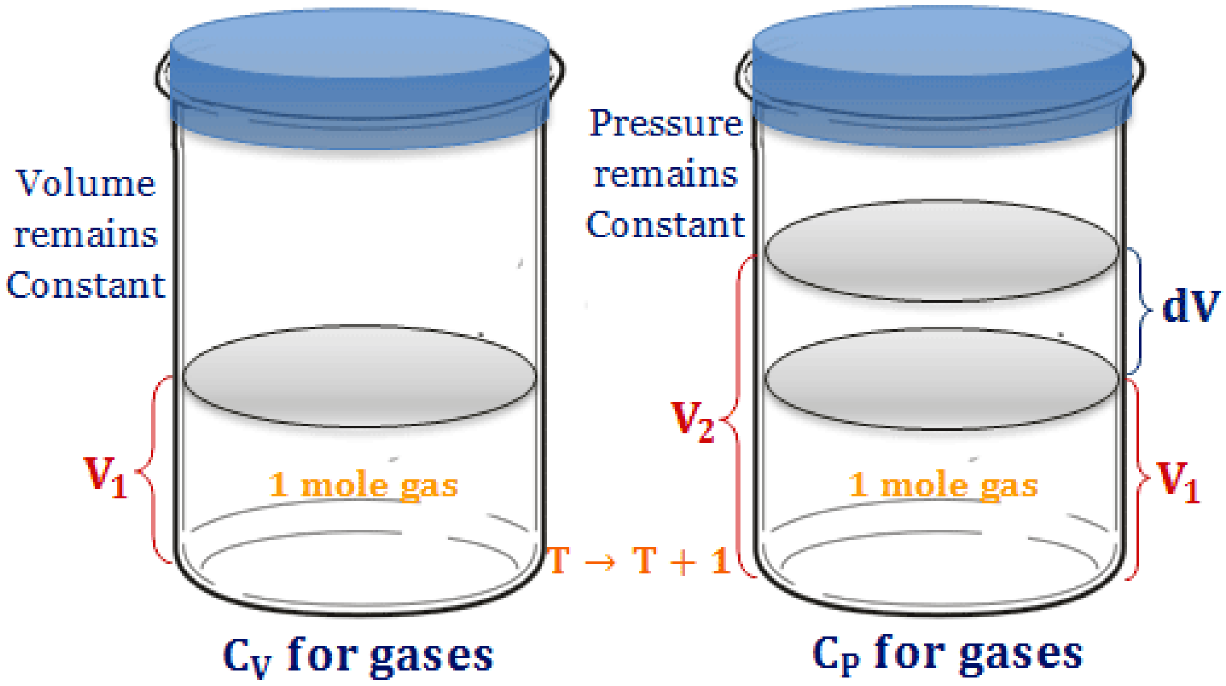


FIGURE
Constant-volume and constant-pressure specific heats c_v and c_p (values given are for helium gas).



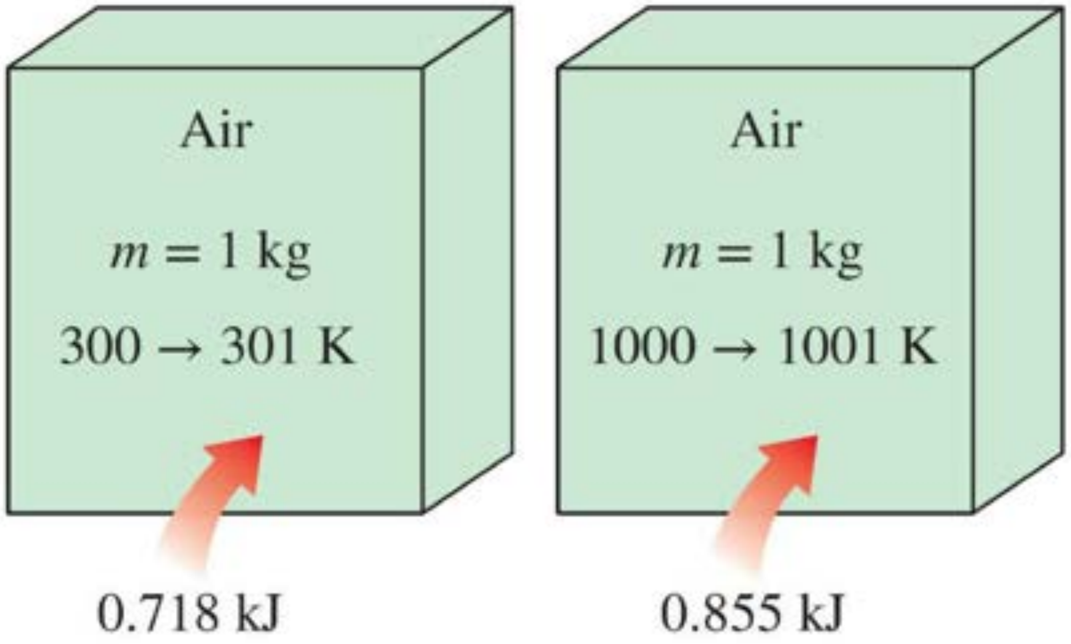
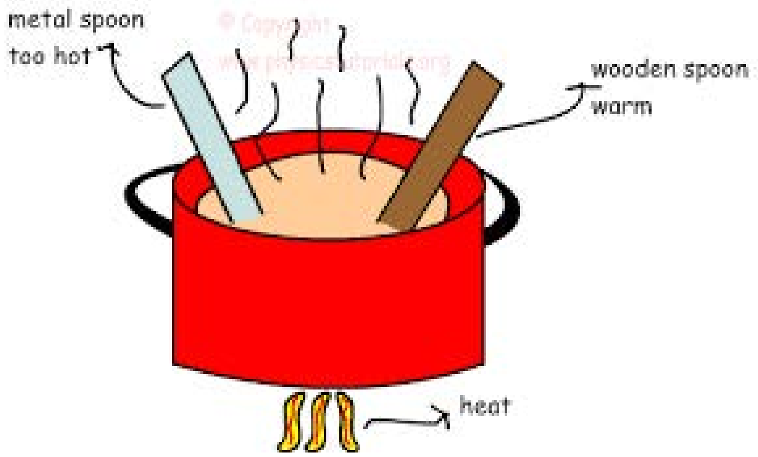


FIGURE
The specific heat of a substance changes with temperature.



For small quantities, we have

$$dQ = mcdT$$

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, c_v

and, *Specific heat at constant pressure,* c_p.

We have

$dQ = m\ c_p\ dT$ For a reversible non-flow process at *constant pressure*

and, $dQ = m\ c_v\ dT$ For a reversible non-flow process at *constant volume*

The values of c_p and c_v, 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

$$= mc_p\,(T_2 - T_1)$$

Flow of heat in a reversible constant volume process

$$= mc_v\,(T_2 - T_1)$$

In case of *real gases,* c_p and c_v *vary with temperature,* but a suitable *average value* may be used for most practical purposes.

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,

$$dQ = du + dW$$

$$dW = 0, \text{ since volume remains constant}$$

$$\therefore \quad dQ = du$$

At constant volume for a perfect gas, from eqn. (4.17), for 1 kg

$$dQ = c_v dT$$

$$\therefore \quad dQ = du = c_v dT$$

and integrating $$u = c_v\, T + K, \ K \text{ being constant.}$$

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, $U = mc_v\, T$ ...(4.21)

For a perfect gas, in any process between states 1 and 2, we have from Eqn. (4.21)

Gain in internal energy,

$$U_2 - U_1 = mc_v\, (T_2 - T_1) \qquad \text{...(4.22)}$$

Eqn. (4.22) gives the gains of internal energy for a perfect gas between two states *for any process, reversible* or *irreversible.*

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,

$$Q = (U_2 - U_1) + W$$

Also for a perfect gas,

$$U_2 - U_1 = mc_v\,(T_2 - T_1)$$

$$Q = mc_v\,(T_2 - T_1) + W$$

In a constant pressure process, the work done by the fluid,

$$W = p(V_2 - V_1)$$

$$= mR(T_2 - T_1) \qquad \left[\begin{array}{l} \because\ p_1V_1 = mRT_1 \\ \quad p_2V_2 = mRT_2 \\ \qquad p_1 = p_2 = p \text{ in this case} \end{array}\right]$$

On substituting

$$Q = mc_v\,(T_2 - T_1) + mR\,(T_2 - T_1) = m(c_v + R)\,(T_2 - T_1)$$

But for a constant pressure process,

$$Q = mc_p\,(T_2 - T_1)$$

By equating the two expressions, we have

$$m(c_v + R)(T_2 - T_1) = mc_p(T_2 - T_1)$$

$\therefore$

$$c_v + R = c_p$$

or

$$c_p - c_v = R \qquad \text{...(4.23)}$$

Dividing both sides by c_v, we get

$$\frac{c_p}{c_v} - 1 = \frac{R}{c_v}$$

$\therefore$

$$c_v = \frac{R}{\gamma - 1} \qquad \text{...[4.23 }(a)\text{]}$$

(where $\gamma = c_p/c_v$)

Similarly, dividing both sides by c_p, we get

$$c_p = \frac{\gamma R}{\gamma - 1} \qquad \text{...[4.23 }(b)\text{]}$$

$$\left[\begin{array}{l}\text{In M.K.S. units}: c_p - c_v = \dfrac{R}{J}; c_v = \dfrac{R}{J(\gamma - 1)}, c_p = \dfrac{\gamma R}{(\gamma - 1)J} \\ \text{In SI units the value of } J \text{ is unity.}\end{array}\right]$$

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).

i.e.,
$$\gamma = \frac{c_p}{c_v}$$

Since $c_p = c_v + R$, it is clear that c_p must be *greater* than c_v for any perfect gas. It follows, therefore, that the ratio, $\frac{c_p}{c_v} = \gamma$ is *always greater than unity.*

In general, the approximate values of γ are as follows :

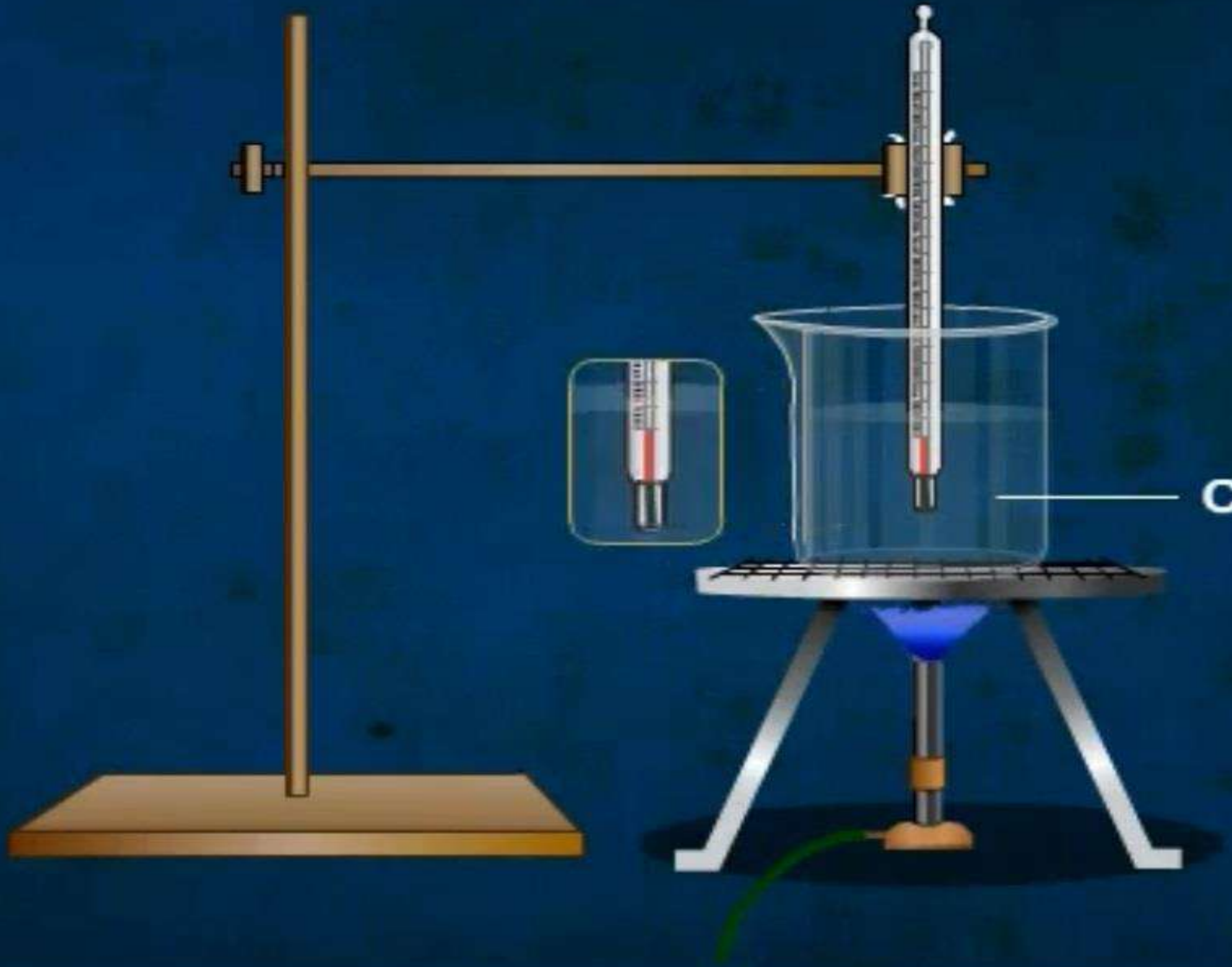
For *monoatomic* gases such as *argon, helium* = 1.6.

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.

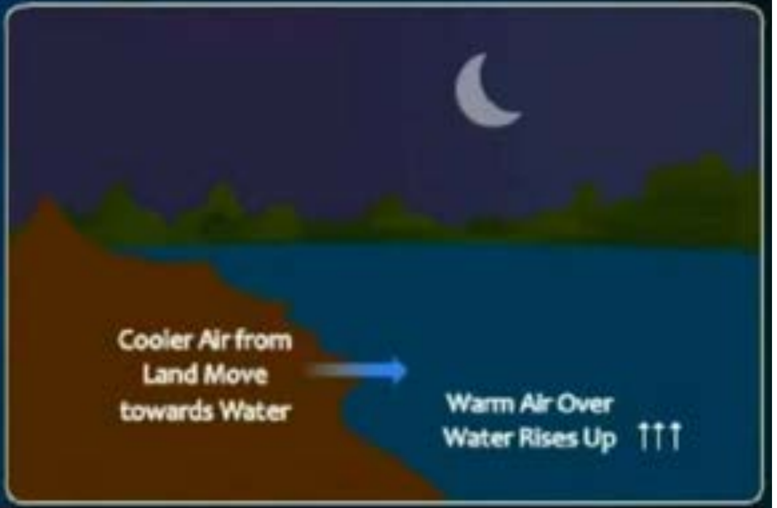
[*e.g.*, for ethane $\gamma = 1.22$, and for isobutane $\gamma = 1.11$]



Specific Heat Capacity of Water is 4200 J/Kg^{0}C

The specific heat capacity of water is 4200 J/Kg^{0}C. Thus, 4200 J of heat is required to raise the temperature of 1 kg of water by 1^{0}C.

The specific heat capacity of water is about five times more than that of sand.



Hence, a moderate climate is maintained near the sea-shore.

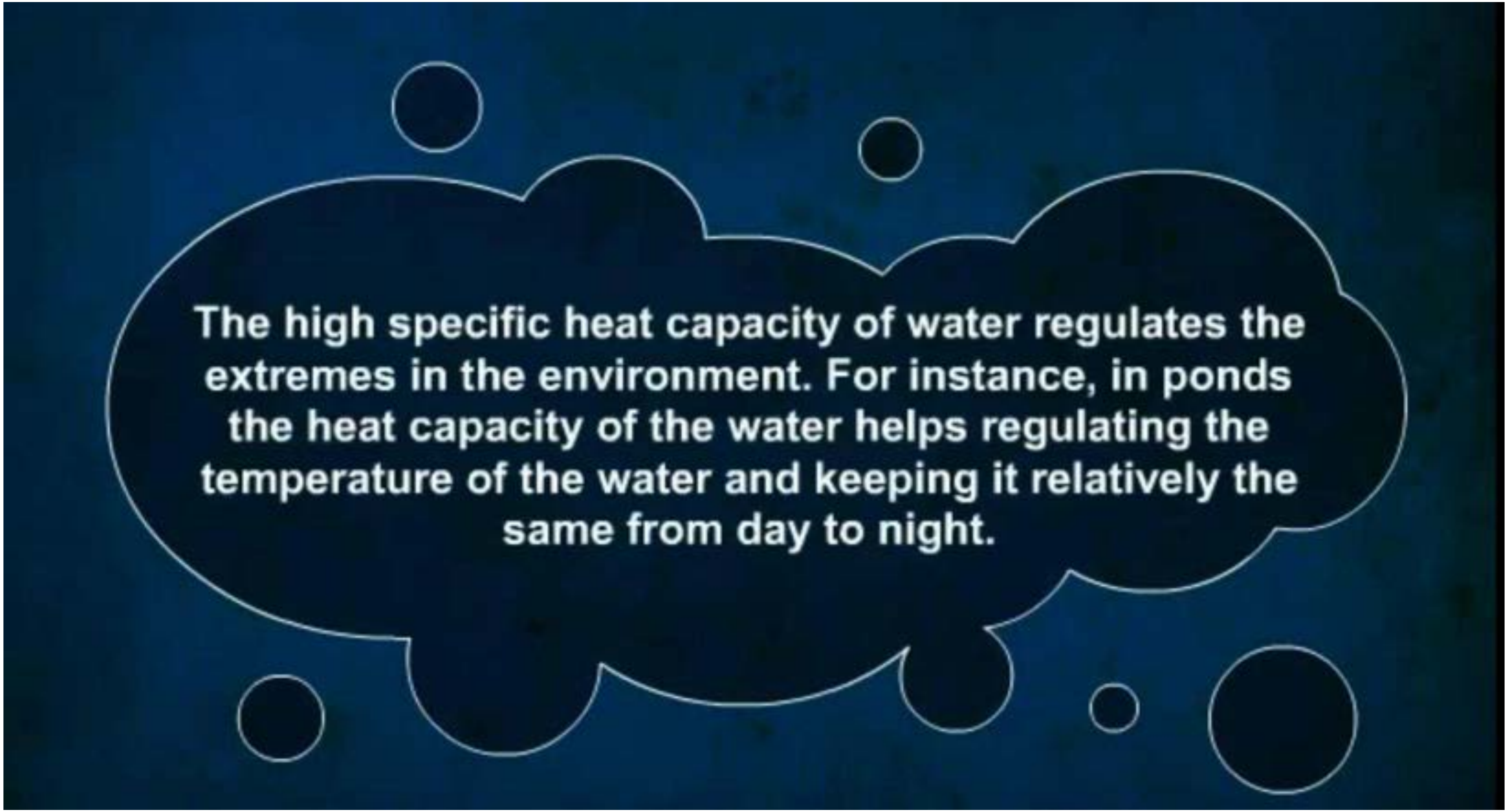
Copper

Aluminium

Iron

Metals like copper, aluminium, iron, etc. are good conductors of heat and they have low specific heat capacity.

Therefore, cooking utensils are made up of these metals so that they can quickly attain a high temperature for a known quantity of heat supplied.



The high specific heat capacity of water regulates the extremes in the environment. For instance, in ponds the heat capacity of the water helps regulating the temperature of the water and keeping it relatively the same from day to night.

In cold countries, wine and juice bottles are kept under water to avoid freezing because water does not cool quickly owing to its high specific heat capacity.

Fields filled with water during winters

Farmers protect their crops from frost by filling the fields with water during winters.

Temperature of Surrounding Plants does not decrease.

Thus, it does not allow the temperature of the surrounding area
of the plants to decrease.

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., $$h = u + pv \qquad \text{...(4.24)}$$

- 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.

The total enthalpy of mass, m, of a fluid can be

$$H = U + pV, \text{ where } H = mh.$$

For a **perfect gas,**

Referring equation (4.24),

$$h = u + pv$$

$$= c_v T + RT \qquad [\because \quad pv = RT]$$

$$= (c_v + R)T$$

$$= c_p T \qquad [\because \quad c_p = c_v + R]$$

$$h = c_p T$$

$$H = mc_p T.$$

(Note that, since it has been assumed that $u = 0$ at $T = 0$, then $h = 0$ at $T = 0$).

Relation between C_p and C_V for an Ideal Gas

$$dh = du + d(Pv) \tag{3.32}$$

From the specific heat relations for an ideal gas we have

$$dh = C_p dT \text{ and } du = C_v dT$$

From the characteristic equation of state for an ideal gas, one can write

$$Pv = RT$$

or,

$$d(Pv) = RdT$$

Thus, from Eq. (3.32), one can write

$$C_p dT = C_v dT + RdT \tag{3.33}$$

Dividing by *dT*, Eq. (3.33) becomes

$$C_p = C_v + R \tag{3.34}$$

It is evident from Eq. (3.34) that although C_p and C_v for ideal gases are function of temperatures only, the difference between them is always a constant (since R is constant).

The specific heat ratio, γ is defined as

$$\gamma = \frac{C_p}{C_v} \tag{3.35}$$

From Eqs (3.34) and (3.35), we have

$$C_p = \frac{\gamma R}{\gamma - 1} \tag{3.36}$$

$$C_v = \frac{R}{\gamma - 1} \tag{3.37}$$

For air we will use $C_p = 1.005 \text{ kJ/kg-K}$ and $C_v = 0.718 \text{ kJ/kg-K}$ unless otherwise stated.

At low pressures all real gases approach ideal-gas behaviour, and therefore, their specific heats depend on temperature only. The specific heats of gases with complex molecules (molecules with two or more atoms) are higher and increase with temperature. The variation of specific heats with temperature is smooth and may be approximated as linear over small temperature intervals. The ideal-gas specific heats of monatomic gases such as argon, neon, and helium remain constant over the entire range of temperature.

Application of first law of thermodynamics to Non-flow or Closed systems:

1. ***Reversible Constant Volume (or Isochoric) Process***
2. ***Reversible Constant Pressure (or Isobaric) Process***
3. ***Reversible Constant Temperature (or Isothermal) Process***
4. ***Reversible Adiabatic Process***
5. ***Polytropic Reversible Process***
6. ***Free Expansion***

1. Reversible Constant Volume (or Isochoric) Process (v = constant) :

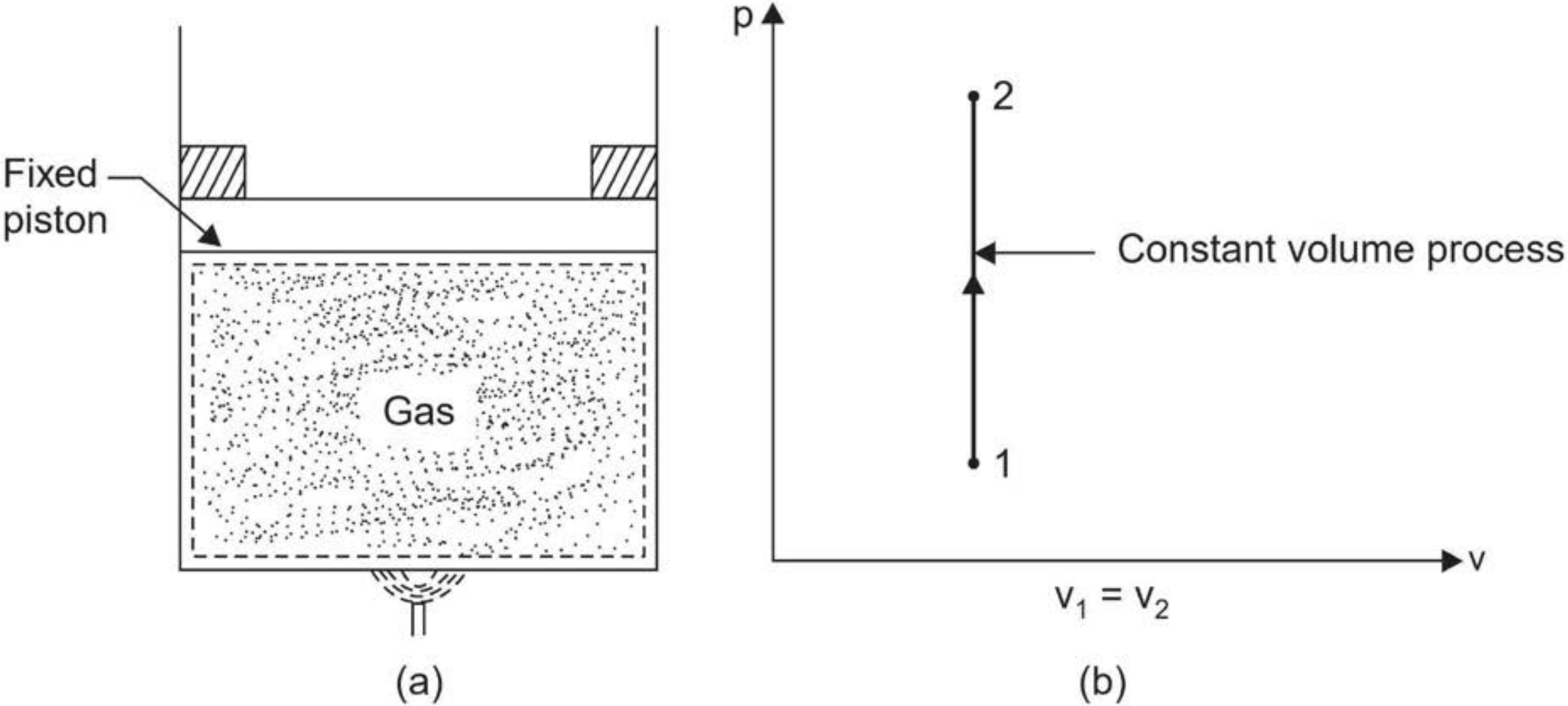
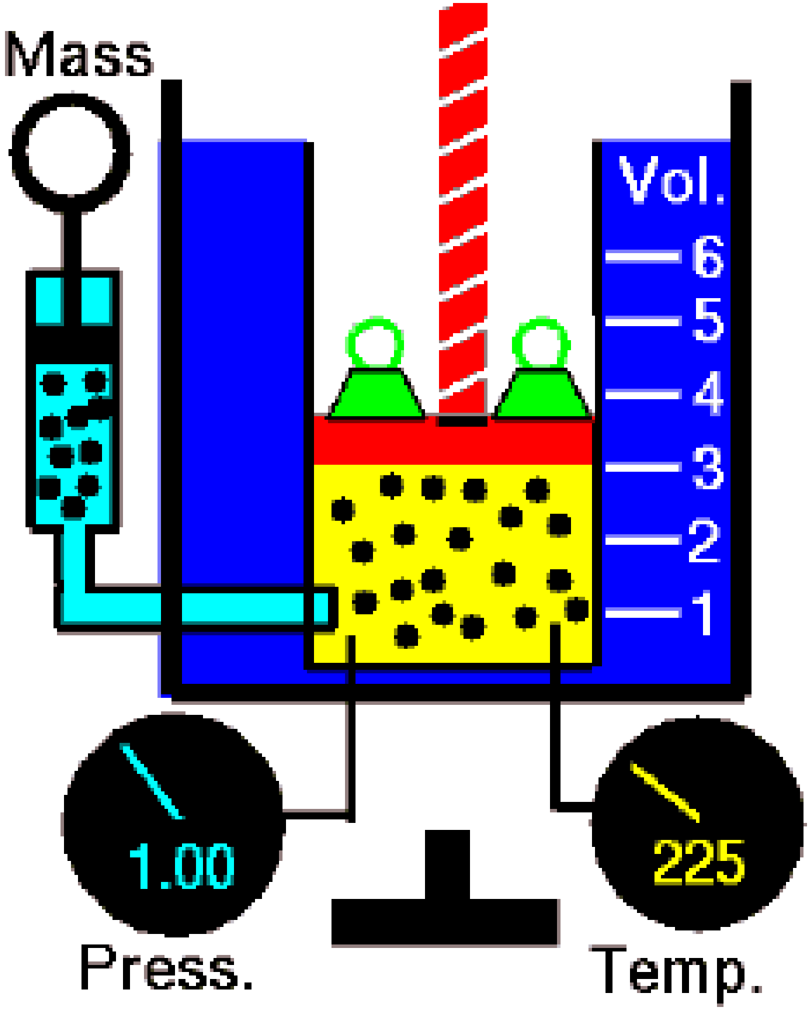


Fig. Reversible constant volume process.



Guy-Lussac's Law: For a fixed mass of gas at constant volume, the pressure is directly proportional to the Kelvin temperature.

$$P = T \times \text{Constant}$$

Considering mass of the working substance *unity* and applying first law of thermodynamics to the process

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

The work done $\quad W = \int_1^2 p\,dv = 0$ as $dv = 0$.

$$\therefore \quad Q = (u_2 - u_1) = c_v(T_2 - T_1)$$

where c_v = Specific heat at constant volume.

For mass, m, of working substance

$$Q = U_2 - U_1 = mc_v(T_2 - T_1) \qquad [\because \quad mu = U]$$

2. Reversible Constant Pressure (or Isobaric) Process (p = constant).

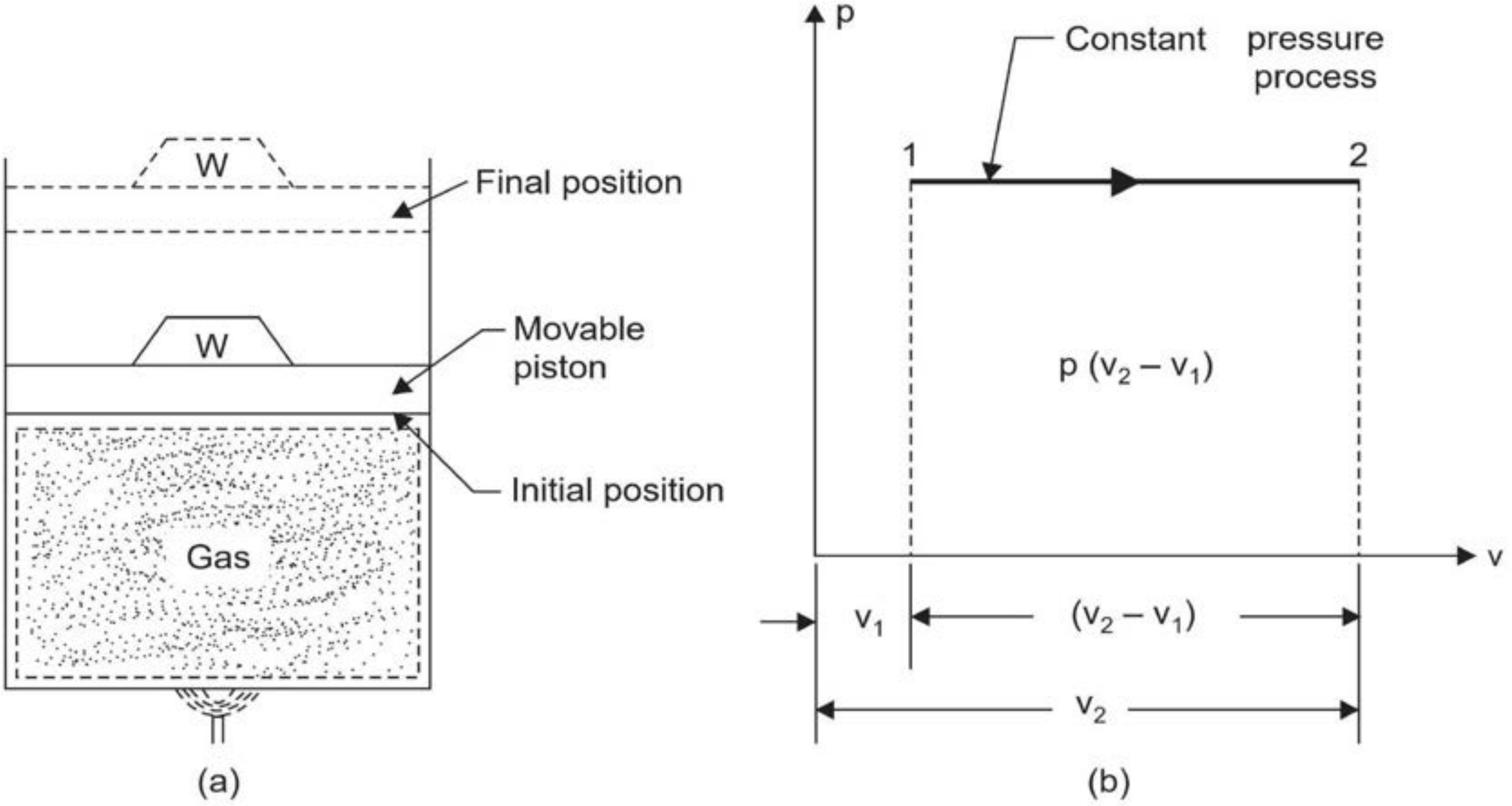
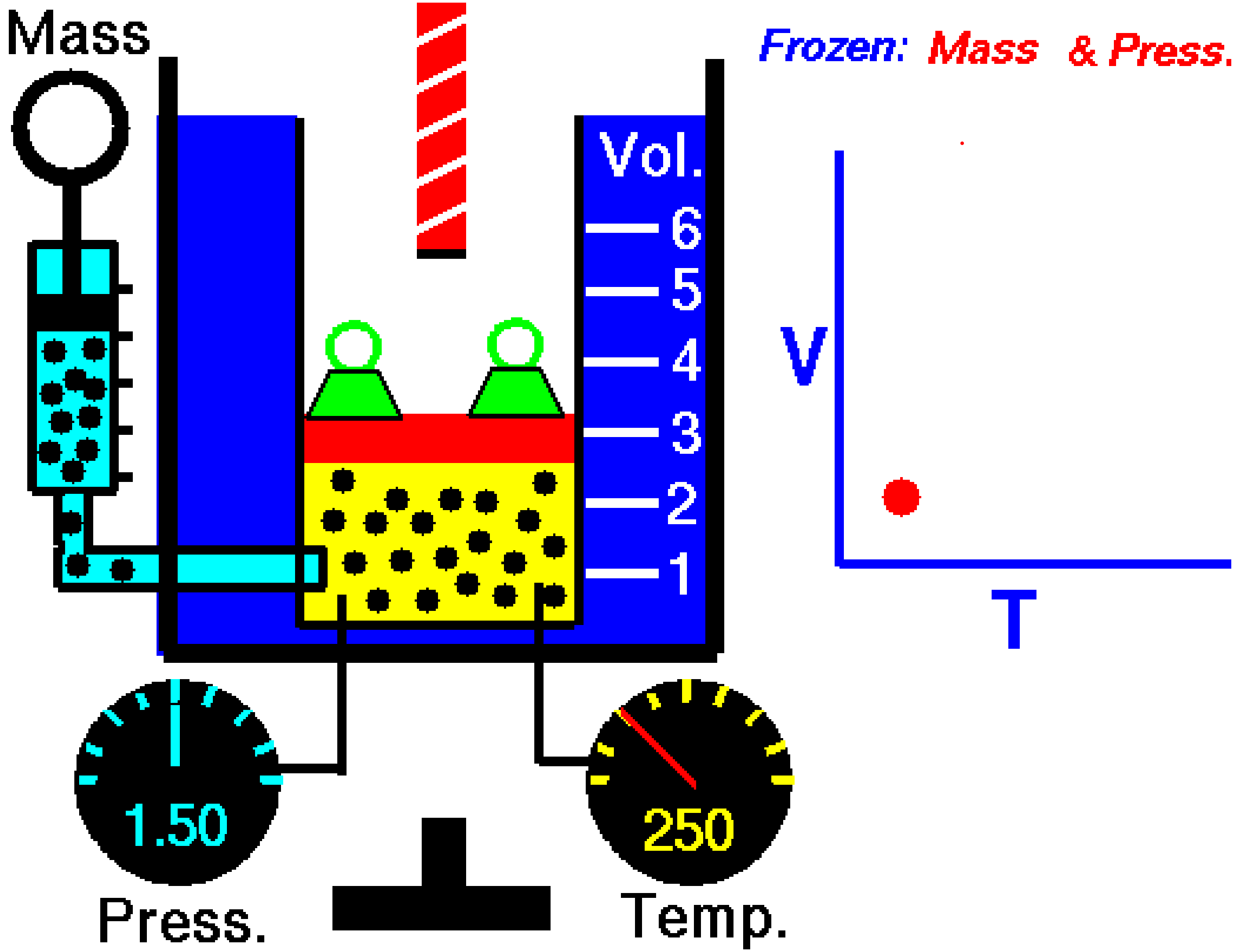


Fig. Reversible constant pressure process.



Charles law: For a fixed mass of gas at constant pressure, the volume is directly proportional to the Kelvin temperature

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Considering unit mass of working substance and applying first law of thermodynamics to the process

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

The work done, $W = \int_1^2 p\,dv = p(v_2 - v_1)$

$\therefore$ $Q = (u_2 - u_1) + p(v_2 - v_1) = u_2 - u_1 + pv_2 - pv_1$

$$= (u_2 + pv_2) - (u_1 + pv_1) = h_2 - h_1 \quad [\because \quad h = u + pv]$$

or $Q = h_2 - h_1 = c_p\,(T_2 - T_1)$

where h = Enthalpy (specific), and

c_p = Specific heat at constant pressure.

For mass, m, of working substance

$$Q = H_2 - H_1 = mc_p\,(T_2 - T_1) \qquad [\because \quad mh = H]$$

3. Reversible Temperature (or Isothermal) Process (pv = constant, T = constant) :

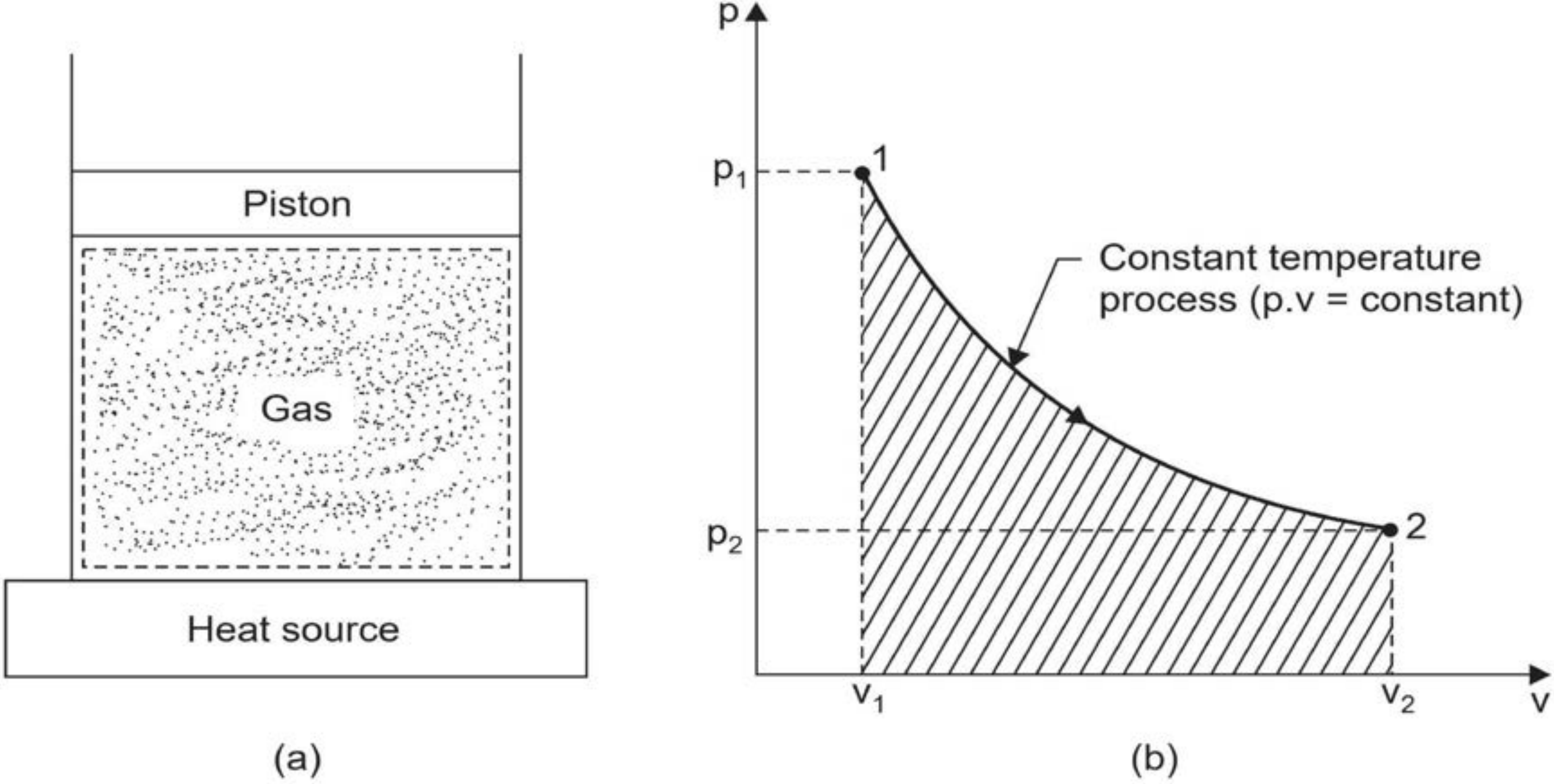
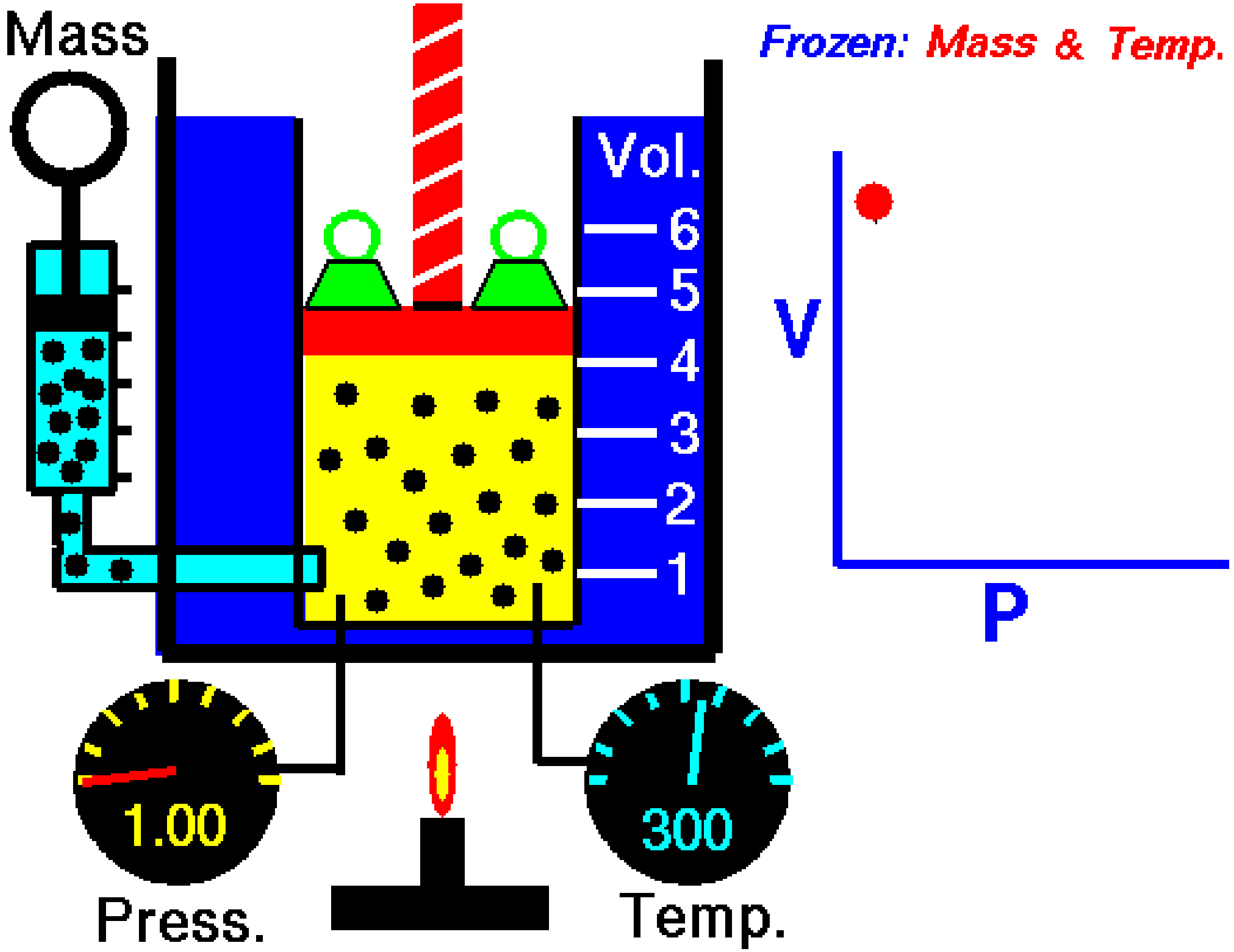


Fig. Reversible isothermal process.



Boyle-Mariotte Law:

For a fixed mass of gas at constant temperature, the volume is inversely proportional to the pressure.

pV = constant

Considering unit mass of working substance and applying first law to the process

$$\begin{aligned} Q &= (u_2 - u_1) + W \\ &= c_v (T_2 - T_1) + W \\ &= 0 + W \end{aligned} \qquad [\because \quad T_2 = T_1]$$

The work done, $W = \int_1^2 p dv$

In this case pv = constant or $p = \dfrac{C}{v}$ (where C = constant)

$$\therefore \qquad W = \int_{v_1}^{v_2} C \frac{dv}{v} = C[\log_e v]_{v_1}^{v_2} = C \log_e \frac{v_2}{v_1}$$

The constant C can either be written as p_1v_1 or as p_2v_2, since

$$p_1 v_1 = p_2 v_2 = \text{constant, } C$$

$$W = p_1 v_1 \log_e \frac{v_2}{v_1} \text{ per unit mass of working substance}$$

$$W = p_2 v_2 \log_e \frac{v_2}{v_1} \text{ per unit mass of working substance}$$

$$\therefore \qquad Q = W = p_1 v_1 \log_e \frac{v_2}{v_1}$$

For mass, m, of the working substance

$$Q = p_1 V_1 \log_e \frac{V_2}{V_1}$$

$$Q = p_1 V_1 \log_e \frac{p_1}{p_2} \qquad \left[\because \frac{V_2}{V_1} = \frac{p_1}{p_2}\right]$$

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

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

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

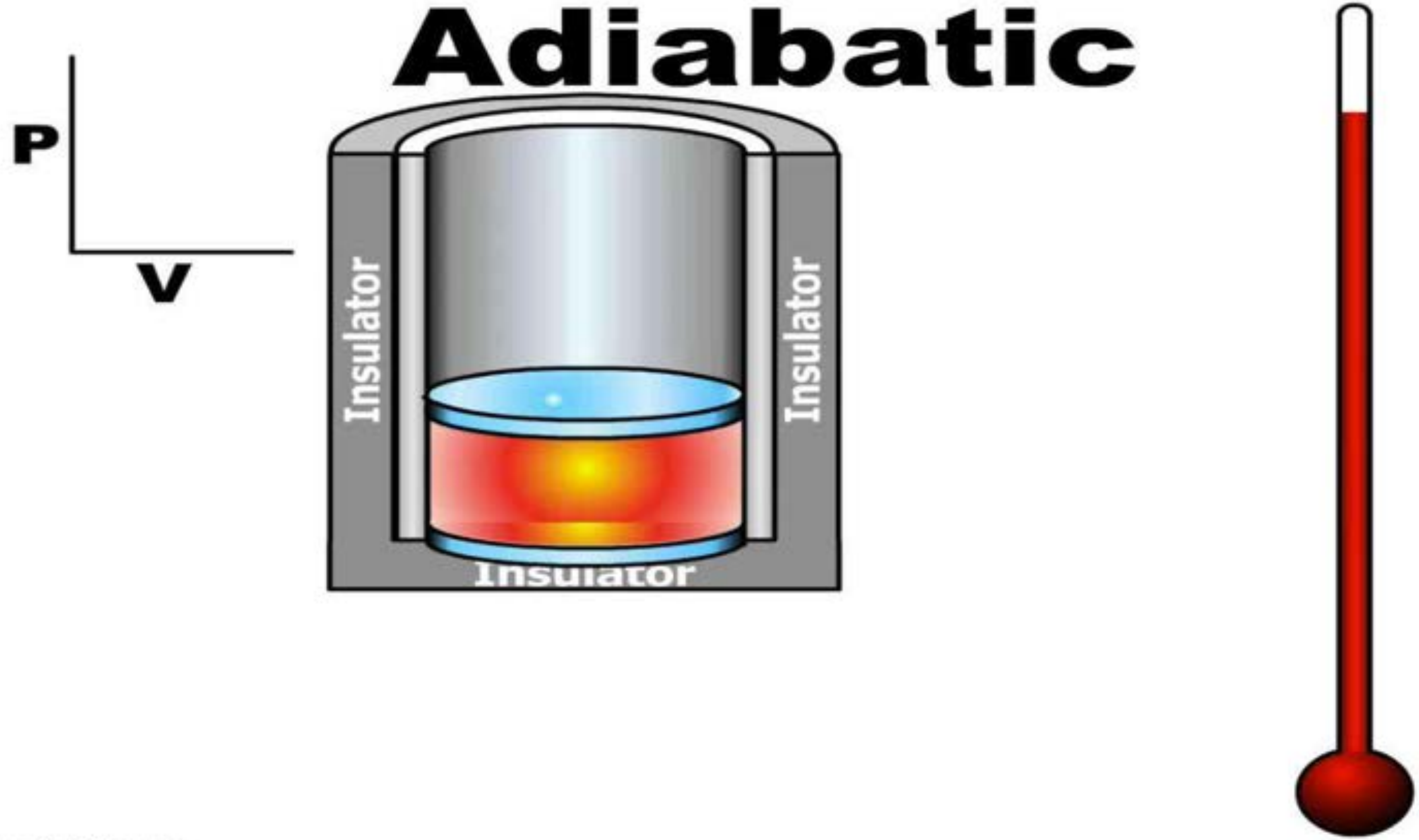
or

$$W = (u_1 - u_2) \text{ for any adiabatic process} \qquad ...(4.30)$$

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.

Adiabatic



by T. Wayne

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*

$$dW = pdv$$

$$\therefore \qquad dQ = du + pdv = 0$$

(Since for an adiabatic process $Q = 0$)

Also for a perfect gas

$$pv = RT \text{ or } p = \frac{RT}{v}$$

Hence substituting,

$$du + \frac{RTdv}{v} = 0$$

Also $\qquad u = c_v T \text{ or } du = c_v dT$

$$\therefore \qquad c_v dT + \frac{RTdv}{v} = 0$$

Dividing both sides by T, we get

$$c_v \frac{dT}{T} + \frac{Rdv}{v} = 0$$

Integrating

$$c_v \log_e T + R \log_e v = \text{constant}$$

Substituting $T = \dfrac{pv}{R}$

$$c_v \log_e \frac{pv}{R} + R \log_e v = \text{constant}$$

Dividing throughout both sides by c_v

$$\log_e \frac{pv}{R} + \frac{R}{c_v} . \log_e v = \text{constant}$$

Again $$c_v = \frac{R}{(\gamma - 1)} \quad \text{or} \quad \frac{R}{c_v} = \gamma - 1$$

Hence substituting

$$\log_e \frac{pv}{R} + (\gamma - 1) \log_e v = \text{constant}$$

$\therefore$ $$\log_e \frac{pv}{R} + \log_e v^{\gamma - 1} = \text{constant}$$

$$\log_e \frac{pv \times v^{\gamma - 1}}{R} = \text{constant}$$

i.e., $$\log_e \frac{pv^\gamma}{R} = \text{constant}$$

i.e., $$\frac{pv^\gamma}{R} = e^{\text{constant}} = \text{constant}$$

or $$pv^\gamma = \text{constant} \qquad \text{...(4.31)}$$

Expression for work W :

A reversible adiabatic process for a perfect gas is shown on a *p-v* diagram in Fig. 4.8 (*b*).

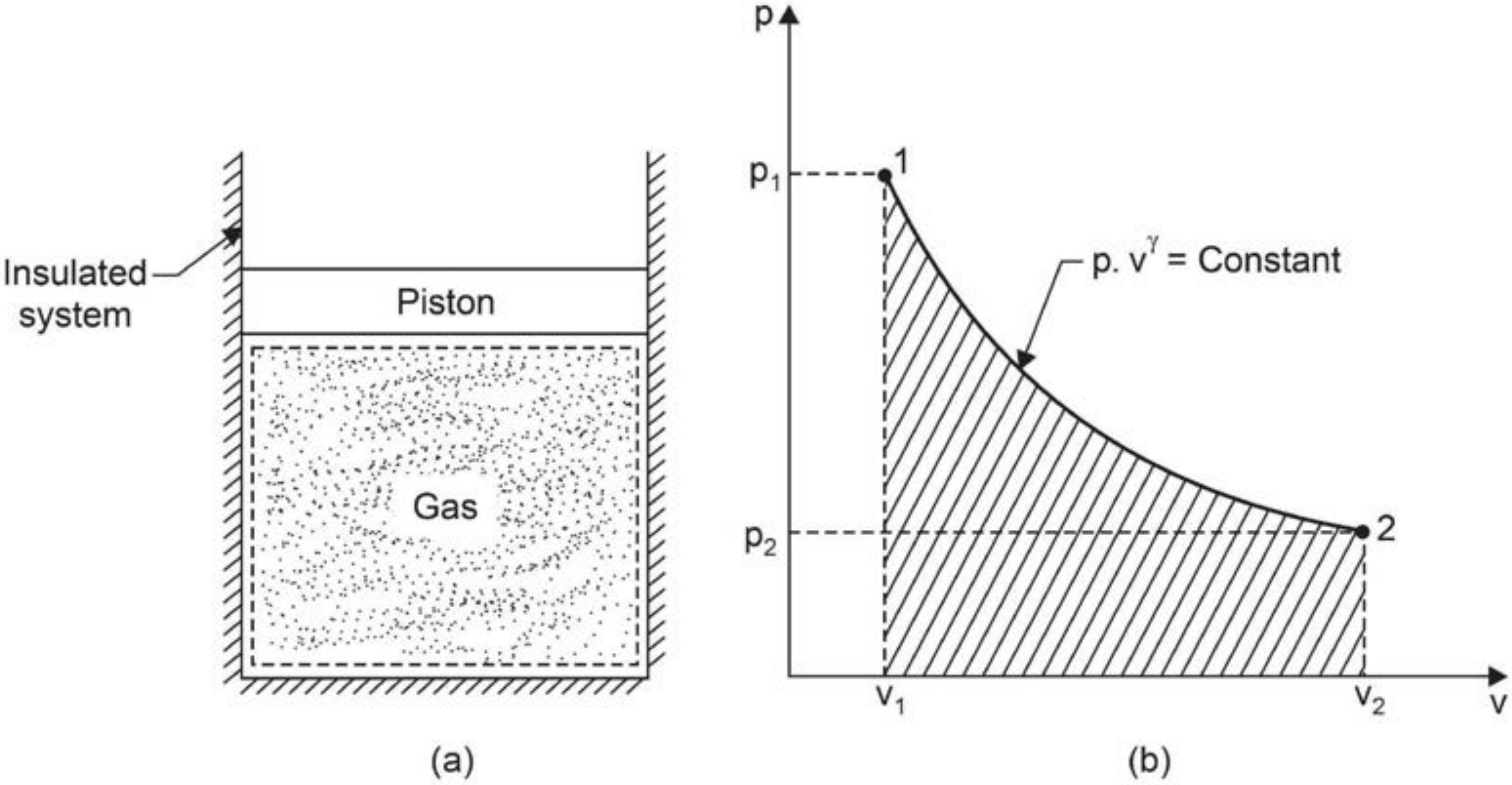


Fig. 4.8. Reversible adiabatic process.

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

$$W = \int_{v_1}^{v_2} C\,\frac{dv}{v^{\gamma}} \qquad \left[\because\ p = \frac{C}{v^{\gamma}}\right]$$

i.e.,
$$W = C\int_{v_1}^{v_2} \frac{dv}{v^{\gamma}} = C\left|\frac{v^{-\gamma+1}}{-\gamma+1}\right|_{v_1}^{v_2}$$

$$= C\left(\frac{{v_2}^{-\gamma+1} - {v_1}^{-\gamma+1}}{1-\gamma}\right) = C\left(\frac{{v_1}^{-\gamma+1} - {v_2}^{-\gamma+1}}{\gamma-1}\right)$$

The constant in this equation can be written as $p_1 {v_1}^{\gamma}$ or as $p_2{v_2}^{\gamma}$. Hence,

$$W = \frac{p_1\,{v_1}^{\gamma}{v_1}^{-\gamma+1} - p_2\,{v_2}^{\gamma}{v_2}^{-\gamma+1}}{\gamma-1} = \frac{p_1v_1 - p_2v_2}{\gamma-1}$$

i.e.,
$$W = \frac{p_1v_1 - p_2v_2}{\gamma-1} \qquad \text{...(4.32)}$$

or
$$W = \frac{R(T_1 - T_2)}{\gamma-1} \qquad \text{...(4.33)}$$

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.,
$$pv = RT$$

$$\therefore \quad p = \frac{RT}{v}$$

Putting this value in the equation pv^γ = constant

$$\frac{RT}{v} . v^\gamma = \text{constant}$$

i.e.,
$$Tv^{\gamma-1} = \text{constant} \qquad \text{...(4.34)}$$

Also $v = \dfrac{RT}{p}$; hence substituting in equation pv^γ = constant

$$p\left(\frac{RT}{p}\right)^\gamma = \text{constant}$$

$$\therefore \quad \frac{T^\gamma}{p^{\gamma-1}} = \text{constant}$$

or
$$\frac{T}{(p)^{\frac{\gamma-1}{\gamma}}} = \text{constant} \qquad \text{...(4.35)}$$

Therefore, for a reversible adiabatic process for a perfect gas between states 1 and 2, we can write :

From Eqn. (4.31),

$$p_1 v_1^{\gamma} = p_2 v_2^{\gamma} \quad \text{or} \quad \frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^{\gamma} \qquad ...(4.36)$$

From Eqn. (4.34),

$$T_1 v_1^{\gamma - 1} = T_2 v_2^{\gamma - 1} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma - 1} \qquad ...(4.37)$$

From Eqn. (4.35),

$$\frac{T_1}{(p_1)^{\frac{\gamma - 1}{\gamma}}} = \frac{T_2}{(p_2)^{\frac{\gamma - 1}{\gamma}}} \quad \text{or} \quad \frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma - 1}{\gamma}} \qquad ...(4.38)$$

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 :

$$u_2 - u_1 = c_v (T_2 - T_1) \qquad \text{(for 1 kg)}$$

$$\therefore \qquad W = c_v (T_1 - T_2)$$

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,

$$W = \int p\,dv$$

For a process in pv^n = constant, we have

$$p = \frac{C}{v^n}\text{ , where } C \text{ is a constant}$$

$\therefore$

$$W = C\int_{v_1}^{v_2} \frac{dv}{v^n} = C\left|\frac{v^{-n+1}}{-n+1}\right| = C\left(\frac{{v_2}^{-n+1} - {v_1}^{-n+1}}{-n+1}\right)$$

i.e.,

$$W = C\left(\frac{{v_1}^{-n+1} - {v_2}^{-n+1}}{n-1}\right) = \frac{p_1{v_1}^n{v_1}^{-n+1} - p_2{v_2}^n{v_2}^{-n+1}}{n-1}$$

(since the constant C, can be written as $p_1{v_1}^n$ or as $p_2{v_2}^n$)

i.e., Work done, $$W = \frac{p_1 v_1 - p_2 v_2}{n-1} \qquad \text{...(4.39)}$$

or $$W = \frac{R(T_1 - T_2)}{n-1} \qquad \text{...(4.40)}$$

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

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^n \qquad \text{...(4.41)}$$

The following relations can be derived (following the same procedure as was done under reversible adiabatic process)

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n-1} \qquad \text{...(4.42)}$$

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} \qquad \text{...(4.43)}$$

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

$$= c_v(T_2 - T_1) + \frac{R(T_1 - T_2)}{n-1}$$

i.e.,
$$Q = \frac{R(T_1 - T_2)}{n-1} - c_v\,(T_1 - T_2)$$

Also
$$c_v = \frac{R}{(\gamma - 1)}$$

On substituting,

$$Q = \frac{R}{n-1}(T_1 - T_2) - \frac{R}{(\gamma-1)}\,(T_1 - T_2)$$

i.e.,
$$Q = R(T_1 - T_2)\left(\frac{1}{n-1} - \frac{1}{\gamma-1}\right)$$

$$= \frac{R\,(T_1 - T_2)(\gamma - 1 - n + 1)}{(\gamma-1)(n-1)} = \frac{R(T_1 - T_2)(\gamma - n)}{(\gamma-1)(n-1)}$$

∴
$$Q = \frac{(\gamma - n)}{(\gamma - 1)}\frac{R(T_1 - T_2)}{(n-1)}$$

or
$$Q = \left(\frac{\gamma - n}{\gamma - 1}\right)W \qquad \left[\because\ W = \frac{R(T_1 - T_2)}{(n-1)}\right] \qquad \text{...(4.44)}$$

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.*, $p = \text{constant}$

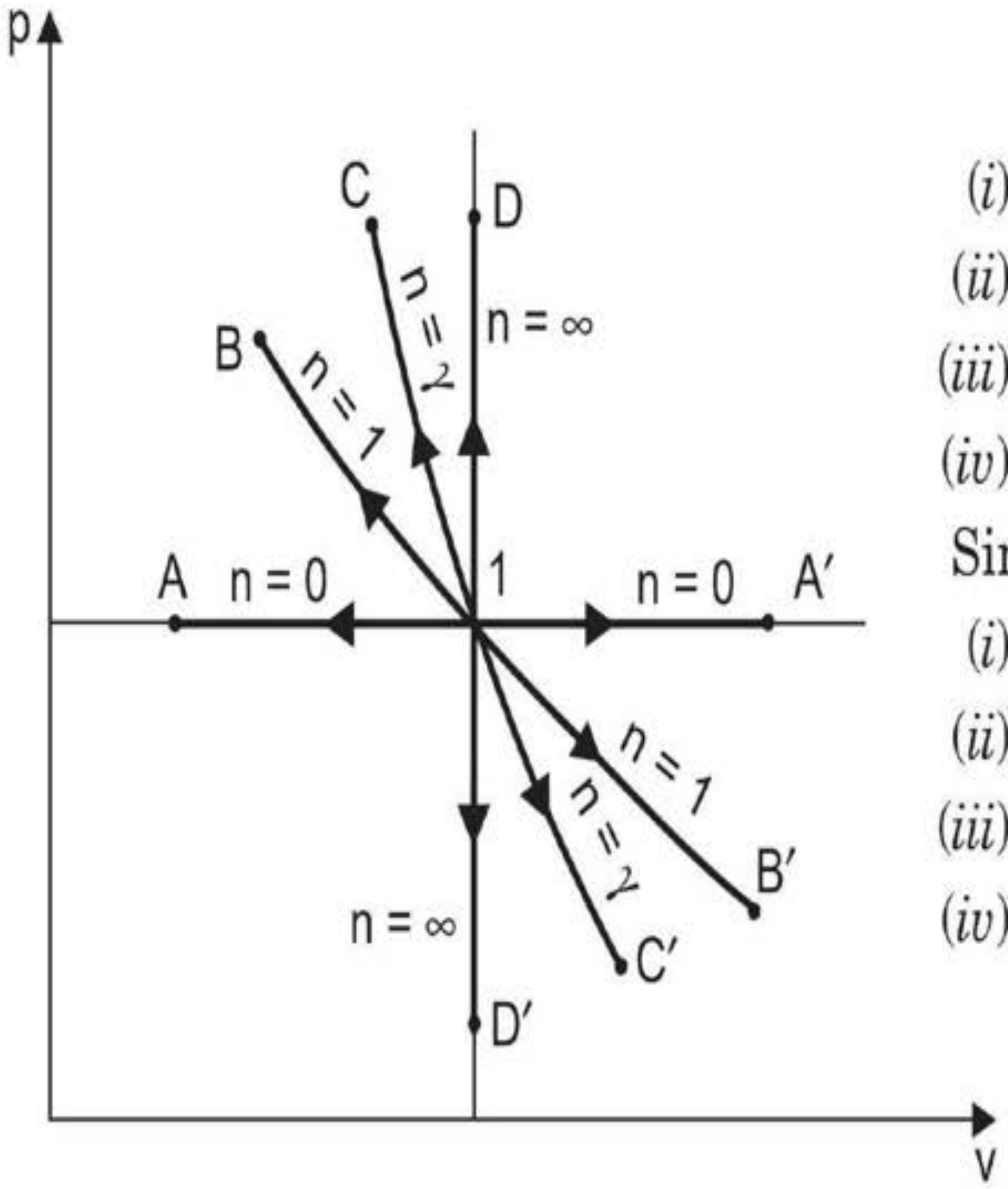
When $n = \infty$ $pv^{\infty} = \text{constant}$

or $p^{1/\infty}\, v = \text{constant}$, *i.e.*, $v = \text{constant}$

When $n = 1$ $pv = \text{constant}$, *i.e.*, $T = \text{constant}$

[since $(pv)/T = \text{constant}$ for a perfect gas]

When $n = \gamma$ $pv^{\gamma} = \text{constant}$, *i.e.*, reversible adiabatic



(*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* ($n = \propto$).

Starting from the initial state the lower right quadrant shows the expansion processes and the upper left quadrant shows the compression processes.

The important observations from the process diagram are summarized below:

(i) As the value of polytropic index increases, the area included by the curve in the *P*-*V* diagram decreases, hence the work done by the process decreases.

(ii) As the value of polytropic index increases, the process curve comes closer to *y*-axis.

The larger the value of *n*, the more nearly does the polytropic curve approach the vertical line representing the constant volume process. This can be demonstrated by differentiating $PV^n = \text{constant}$ to give

$$V^n dP + PnV^{n-1} dV = 0$$

or,

$$\frac{dP}{dV} = n\frac{P}{V}$$

Thus the slope of the curve increases in the negative direction with increase of *n*.

6.Free Expansion Process:

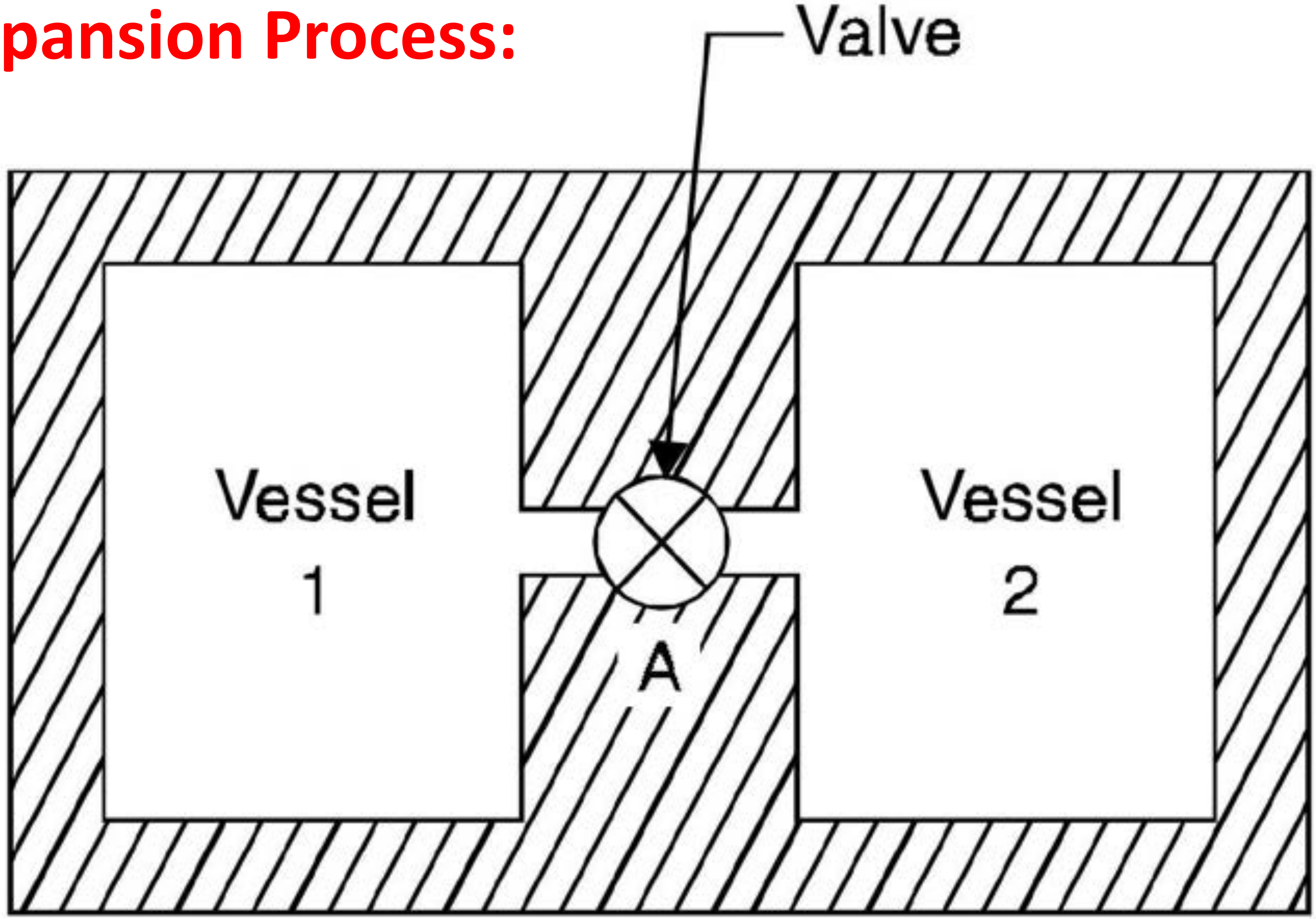


Fig. Free expansion.

Consider two vessels 1 and 2 interconnected by a short pipe with a valve *A*, and perfectly thermally insulated . 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., $$u_2 - u_1 = 0 \quad \text{or} \quad u_2 = u_1$$

In a free expansion, therefore, the internal energy initially equals the initial energy finally.

For a perfect gas,

$$u = c_v T$$

∴ For a free expansion of a perfect gas,

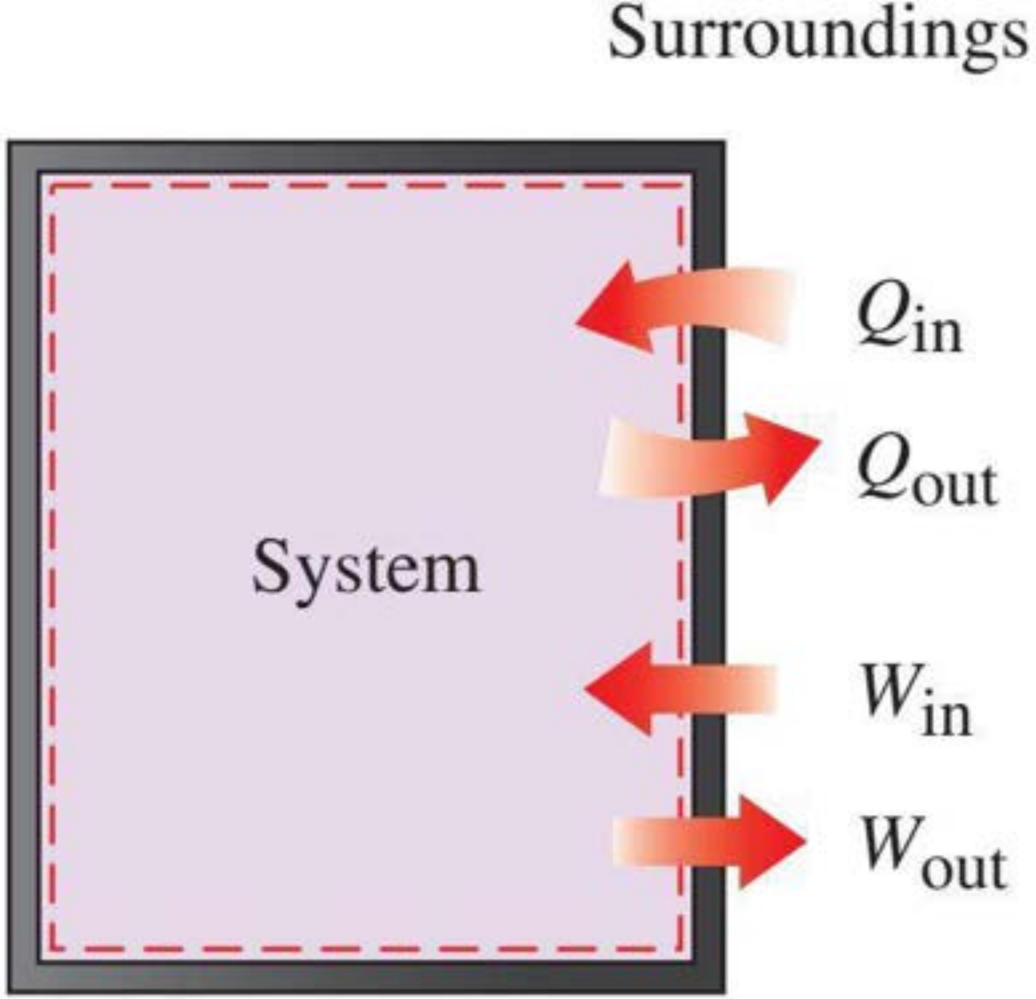
$$c_v T_1 = c_v T_2 \quad i.e., \quad T_1 = T_2$$

That is, for a perfect gas undergoing a free expansion, the initial temperature is equal to the final temperature.

Table Summary of Processes for Perfect Gas (Unit mass)

Process	*Index* *n*	*Heat added*	$\int_1^2 p\,dv$	*p, v, T relations*	*Specific heat, c*
Constant pressure	$n = 0$	$c_p(T_2 - T_1)$	$p(v_2 - v_1)$	$\frac{T_2}{T_1} = \frac{v_2}{v_1}$	c_p
Constant volume	$n = \infty$	$c_v(T_2 - T_1)$	0	$\frac{T_1}{T_2} = \frac{p_1}{p_2}$	c_v
Constant temperature	$n = 1$	$p_1 v_1 \log_e \frac{v_2}{v_1}$	$p_1 v_1 \log_e \frac{v_2}{v_1}$	$p_1 v_1 = p_2 v_2$	∞
Reversible adiabatic	$n = \gamma$	0	$\frac{p_1 v_1 - p_2 v_2}{\gamma - 1}$	$p_1 {v_1}^{\gamma} = p_2 {v_2}^{\gamma}$ $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma - 1}$ $= \left(\frac{p_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}}$	0
Polytropic	$n = n$	$c_n(T_2 - T_1)$ $= c_v\left(\frac{\gamma - n}{1 - n}\right) \times (T_2 - T_1)$ $= \frac{\gamma - n}{\gamma - 1} \times$ work done (non–flow)	$\frac{p_1 v_1 - p_2 v_2}{n - 1}$	$p_1 {v_1}^{n} = p_2 {v_2}^{n}$ $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{n - 1}$ $= \left(\frac{p_2}{p_1}\right)^{\frac{n - 1}{n}}$	$c_n = c_v\left(\frac{\gamma - n}{1 - n}\right)$

Note. Equations must be used keeping dimensional consistence.



FIGURE

Specifying the directions of heat and work.

Example 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

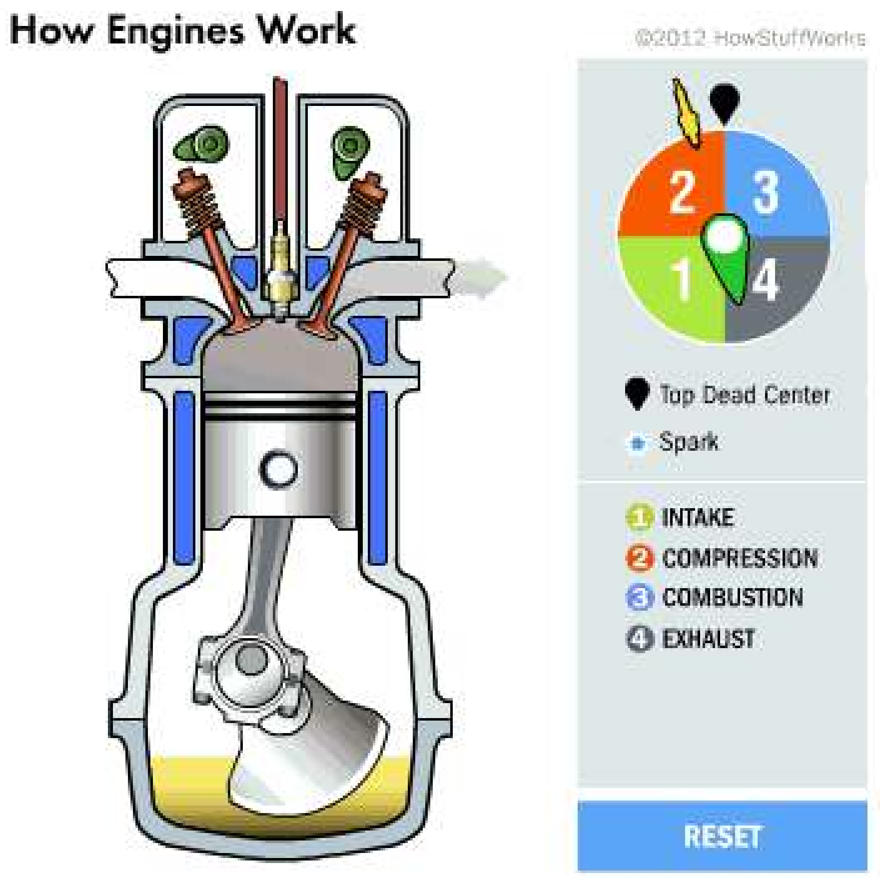
(–ve sign since work is supplied to the system)

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

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

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

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



Example 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.)**

Example 5. *A container is divided into compartments by a partition. The container is completely insulated so that there is no heat transfer. One portion contains gas at temperature T_1 and pressure p_1 while the other portion also has the same gas but at temperature T_2 and pressure p_2.*

How will the First Law of Thermodynamics conclude the result if partition is removed ?

Solution. Refer Fig.

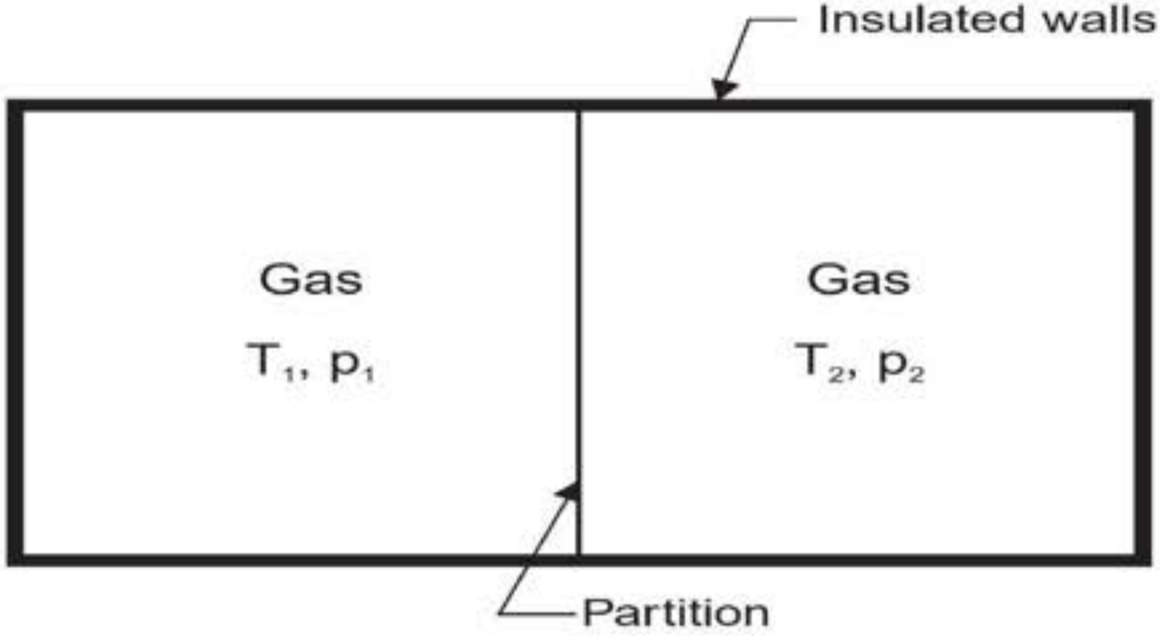
According to First Law of Thermodynamics,

$$\delta Q = \delta U + \delta W$$

When partition removed, $\delta Q = 0$

$$\delta W = 0$$

$\therefore$ $\delta U = 0.$

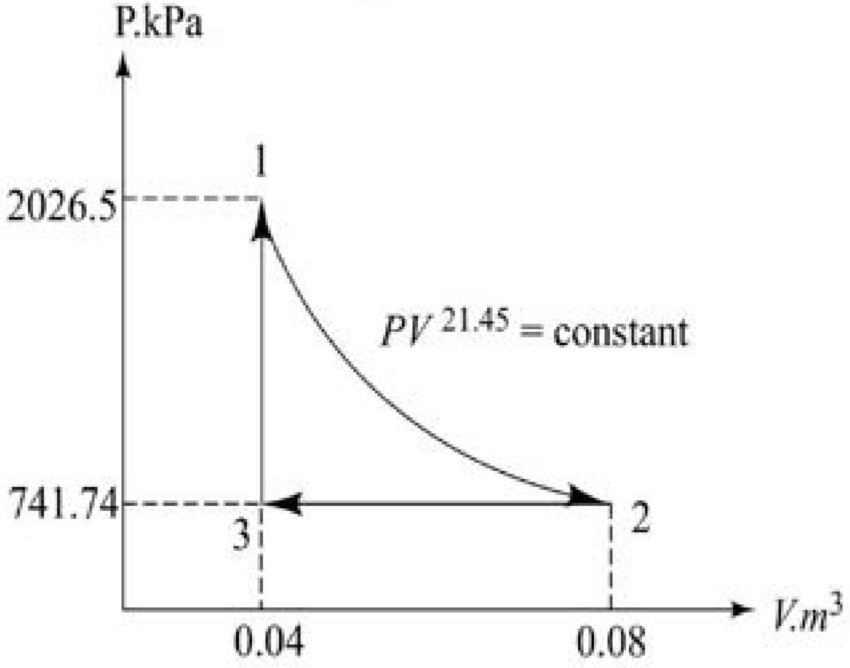


Conclusion. *There is conservation of internal energy.*

Example

A piston–cylinder device contains 1 kg of fluid at 20 atmospheric pressure. The initial volume is 0.04 m^3. The fluid is allowed to expand reversibly following a process $PV^{1.45} = C$ so that the volume becomes double. The fluid is then cooled reversibly at constant pressure until the piston comes back to the original position. Keeping the position of the piston unaltered, heat is added reversibly to restore the initial pressure. Calculate the cyclic work done. Plot the process in P–V coordinates, given that 1 atmospheric pressure = 101.325 kN/m^2.

The processes are shown in Fig.



From the given data, $P_1 = 20$ atm $= 20 \times 101.325 = 2026.5$ kN/m^2

$$V_1 = 0.04 \text{ m}^3;\ V_2 = 2\,V_1 = 0.08 \text{ m}^3,$$

$$P_1V_1^n = P_2V_2^n$$

$$\therefore \qquad P_2 = \left(\frac{V_1}{V_2}\right)^n \times P_1 = \left(\frac{1}{2}\right)^{1.45} \times 2026.5 \text{ kPa} = 741.74 \text{ kPa}.$$

The work done during the polytropic expansion 1-2 is

$$\therefore \qquad W_{1-2} = \frac{P_1V_1 - P_2V_2}{n-1} = \frac{2026.5 \times 0.04 - 741.74 \times 0.08}{1.45 - 1} \text{ kJ}$$

$$= 48.27 \text{ kJ}$$

The work done during the constant pressure process 2-3 is

$$W_{2-3} = P_2(V_3 - V_2) = P_2(V_1 - V_2) = 741.74\ (0.04 - 0.08) \text{ kJ}$$

$$= -\ 29.67 \text{ kJ}$$

Since the volume does not change during the process 3-1, the work done $W_{3\text{-}1}$ is zero.

The cyclic work done is $\sum W = W_{1-2} + \mathrm{W}_{2-3} + W_{3-1} = 48.27 - 29.67 + 0 = 18.6 \text{ kJ}$

Example

A piston–cylinder device with air at an initial temperature of 30°C undergoes an expansion process for which pressure and volume are related as given below:

P(kPa)	100	37.9	14.4
V(m^3)	0.1	0.2	0.4

Calculate the work done by the system.

Solution

Let the expansion process be represented by a polytropic process

$$P_1 V_1{}^n = P_2 V_2{}^n$$

where n is the polytropic index of expansion.

$$n = \frac{\ln \frac{P_1}{P_2}}{\ln \frac{V_2}{V_1}}$$

$$n = \frac{\ln \frac{100}{37.9}}{\ln \frac{0.2}{0.1}} = 1.4$$

$$n = \frac{\ln \frac{37.9}{14.4}}{\ln \frac{0.4}{0.2}} = 1.4$$

The process obeys the relation $PV^{1.4} = \text{constant}$.

The work done is found from Eq. (2.7) to be

$$W_{1-3} = \frac{P_1V_1 - P_3V_3}{n-1}$$

$$= \frac{100 \times 0.1 - 14.4 \times 0.4}{1.4 - 1} = 10.6 \text{ kJ}$$

Example

A mass of gas is compressed in a quasi-static process from 80 kPa, 0.1 m^3 to 0.4 MPa, 0.03 m^3. Assuming that the pressure and volume are related by PV^n = constant, find the workd done by the gas system.

Solution

Initial pressure	$P_1 = 80\ \text{kPa} = 80 \times 10^3\ \text{Pa}$
Initial volume	$V_1 = 0.1\ \text{m}^3$
Final pressure	$P_2 = 0.4\ \text{MPa} = 0.4 \times 10^6\ \text{Pa}$
Final volume	$V_2 = 0.03\ \text{m}^3$

The polytropic index of compression is

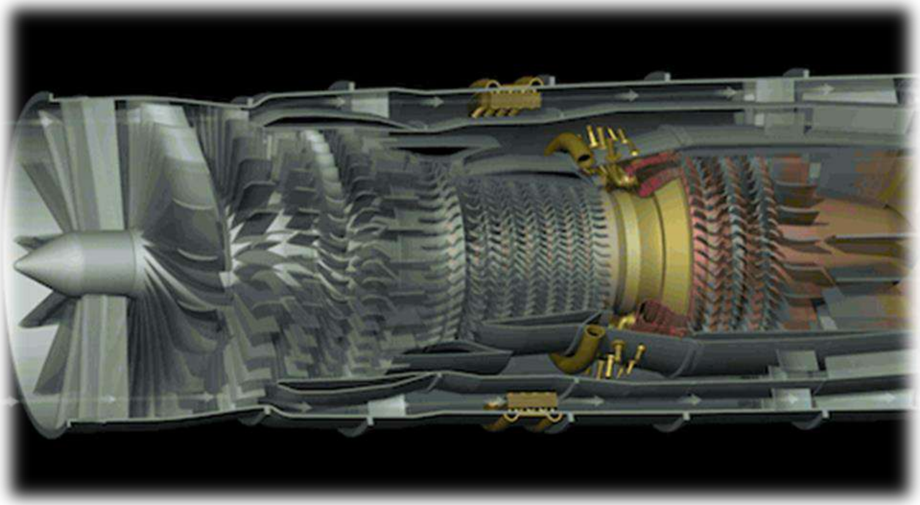
$$n=\frac{\ln\dfrac{P_1}{P_2}}{\ln\dfrac{V_2}{V_1}}=\frac{\ln\dfrac{80}{0.4\times10^3}}{\ln\dfrac{0.03}{0.1}}=1.337$$

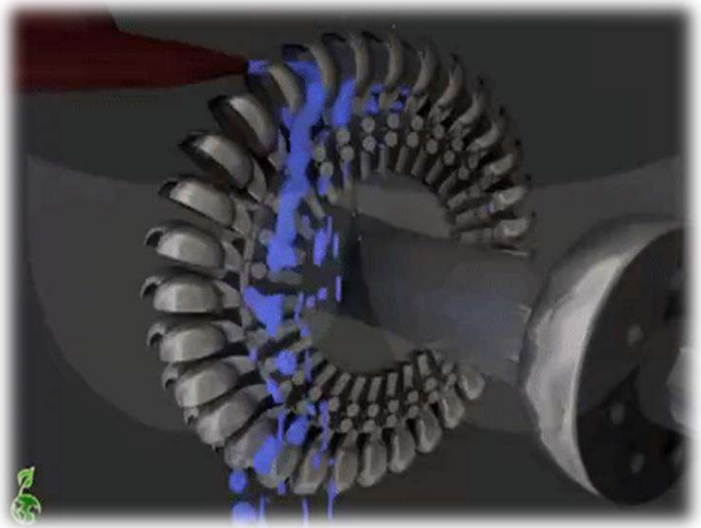
$$W_{1-2}=\frac{P_1V_1-P_2V_2}{n-1}$$

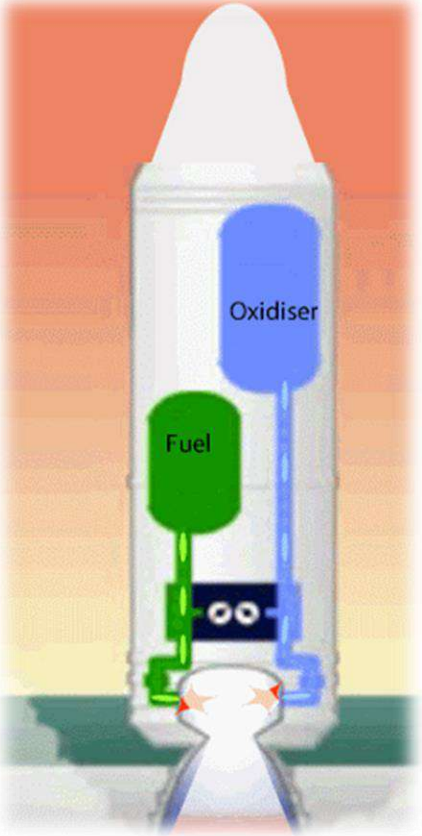
$$=\frac{80\times10^3\times0.1-0.4\times10^6\times0.03}{1.337-1}$$

$$=-11869.44\ \text{J}=-11.869\ \text{kJ}$$

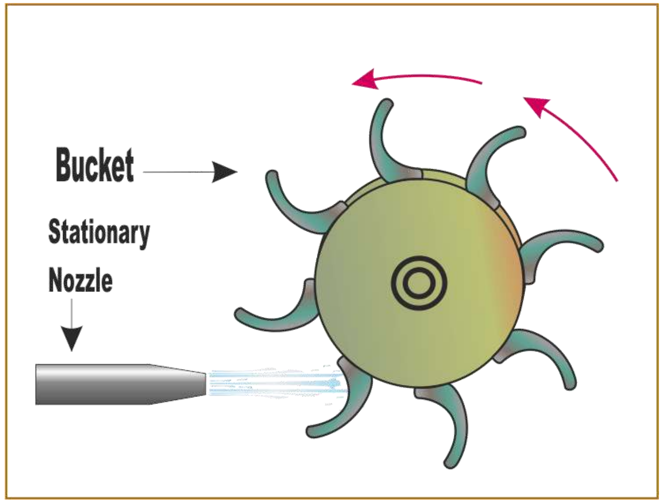
Negative sign indicates that work is done on the gas.







First Law Applied to Flow Processes



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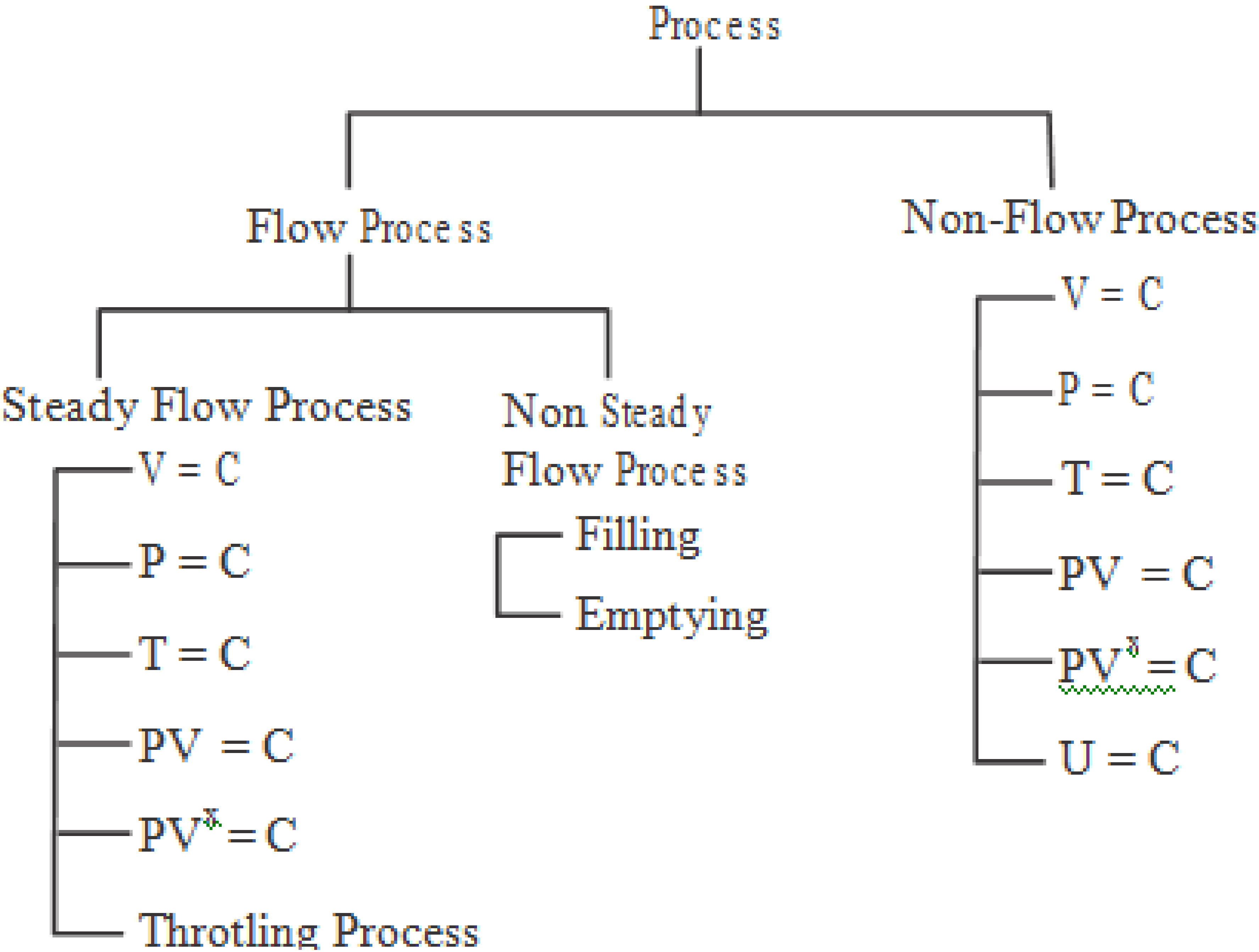

Process
Flow Process
Non-Flow Process
Steady Flow Process
$V = C$
$P = C$
$T = C$
$PV = C$
$PV^{\gamma} = C$
Throtling Process
Non Steady Flow Process
Filling
Emptying
$V = C$
$P = C$
$T = C$
$PV = C$
$PV^{\gamma} = C$
$U = C$

CONTROL VOLUME

In flow processes we normally are concerned with the flow of fluids through devices such as an air compressor, a turbine, a nozzle, a pump, a blower, a fan, a car radiator, a water heater etc. In these cases it is difficult to focus attention on a fixed identifiable quantity of mass. It is much more convenient, for analysis, to focus attention on a volume in space through which the fluid flows.

A control volume is a properly selected region in space. The boundary, which remains fixed in space, enveloping this control volume is called the control surface.

STEADY FLOW PROCESSES AND DEVICES

A steady flow is defined for a control volume as that type of flow in which the thermodynamic properties at a given position within or at the boundaries of the control volume are invariant with time. The properties include temperature, pressure, density, internal energy as well as velocity and acceleration of the flow stream. However, in a steady flow process the state of the fluid can change as it passes through the control volume.

Many engineering devices such as turbines, pumps, compressors, boilers, condensers, etc., operate over long periods of time under the same working conditions and they are classified as steady-flow devices.

APPLICATION OF FIRST LAW TO STEADY FLOW PROCESS

Steady Flow Energy Equation (S.F.E.E.)

In many practical problems, the rate at which the fluid flows through a machine or piece of apparatus is constant. This type of flow is called *steady flow*.

Assumptions :

The following *assumptions* are made in the system analysis :

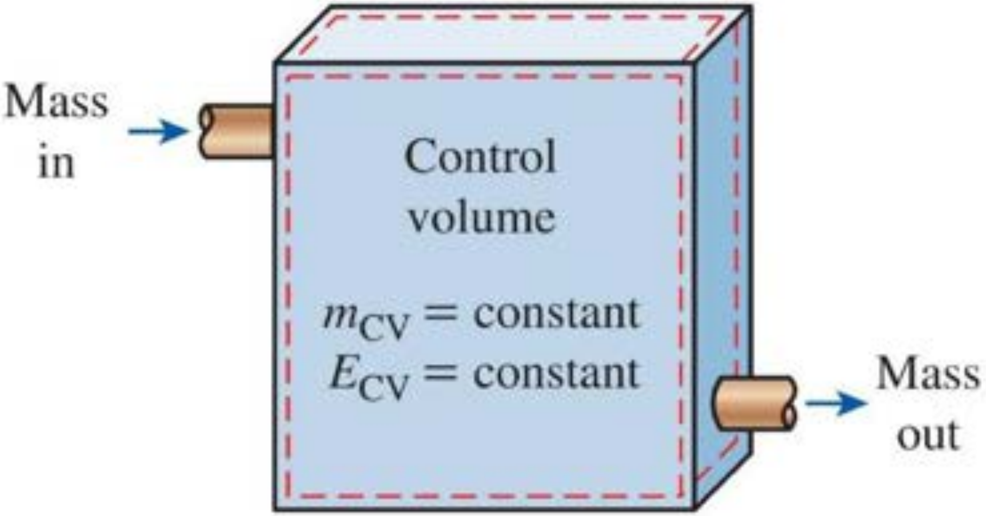
(*i*) The mass flow through the system remains constant.

(*ii*) Fluid is uniform in composition.

(*iii*) The only interaction between the system and surroundings are work and heat.

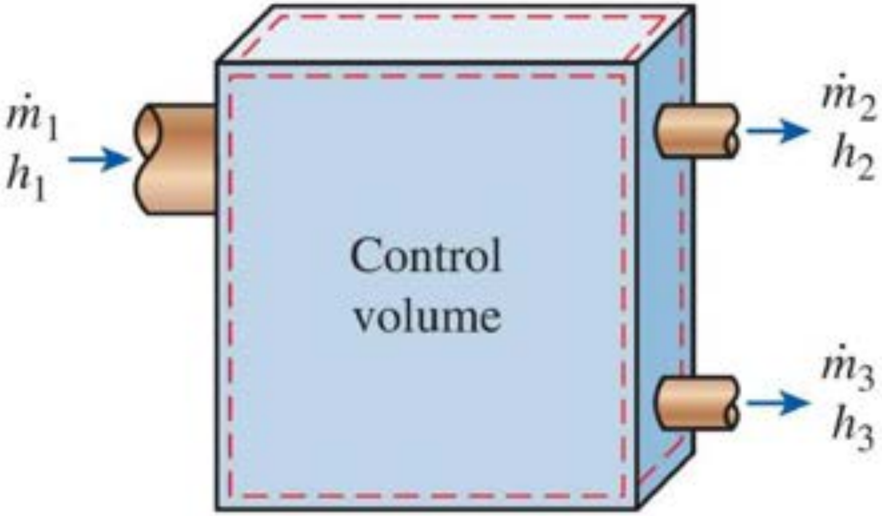
(*iv*) The state of fluid at any point remains constant with time.

(*v*) In the analysis only potential, kinetic and flow energies are considered.



FIGURE

Under steady-flow conditions, the mass and energy contents of a control volume remain constant.



FIGURE

Under steady-flow conditions, the fluid properties at an inlet or exit remain constant (do not change with time).

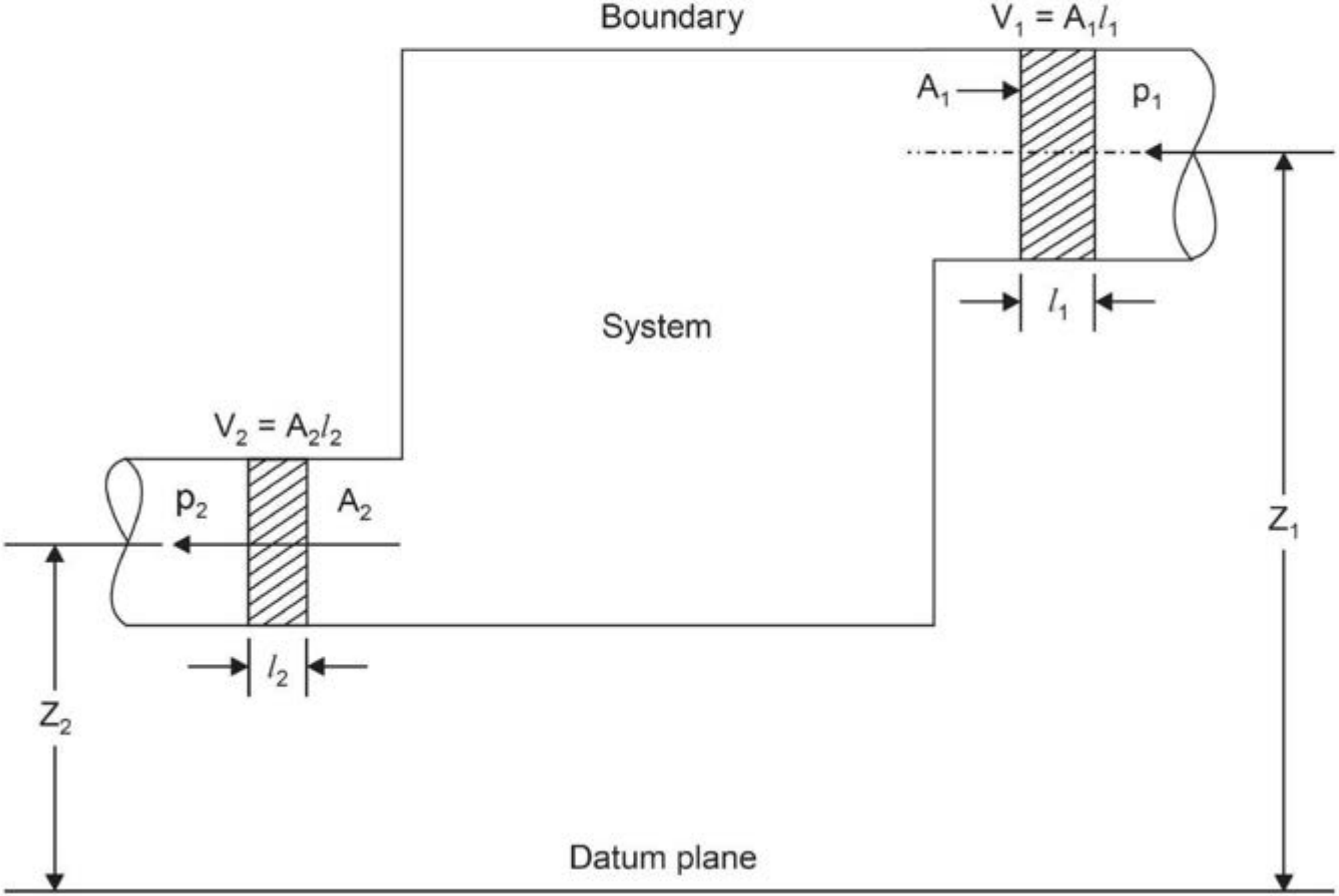

Boundary
$V_1 = A_1 l_1$
A_1
p_1
System
l_1
Z_1
$V_2 = A_2 l_2$
p_2
A_2
l_2
Z_2
Datum plane

Fig.

The steady flow equation can be expressed as follows :

$$u_1 + \frac{C_1^2}{2} + Z_1g + p_1v_1 + Q = u_2 + \frac{C_2^2}{2} + Z_2g + p_2v_2 + W \qquad \text{...(4.45)}$$

$$(u_1 + p_1v_1) + \frac{C_1^2}{2} + Z_1g + Q = (u_2 + p_2v_2) + \frac{C_2^2}{2} + Z_2g + W$$

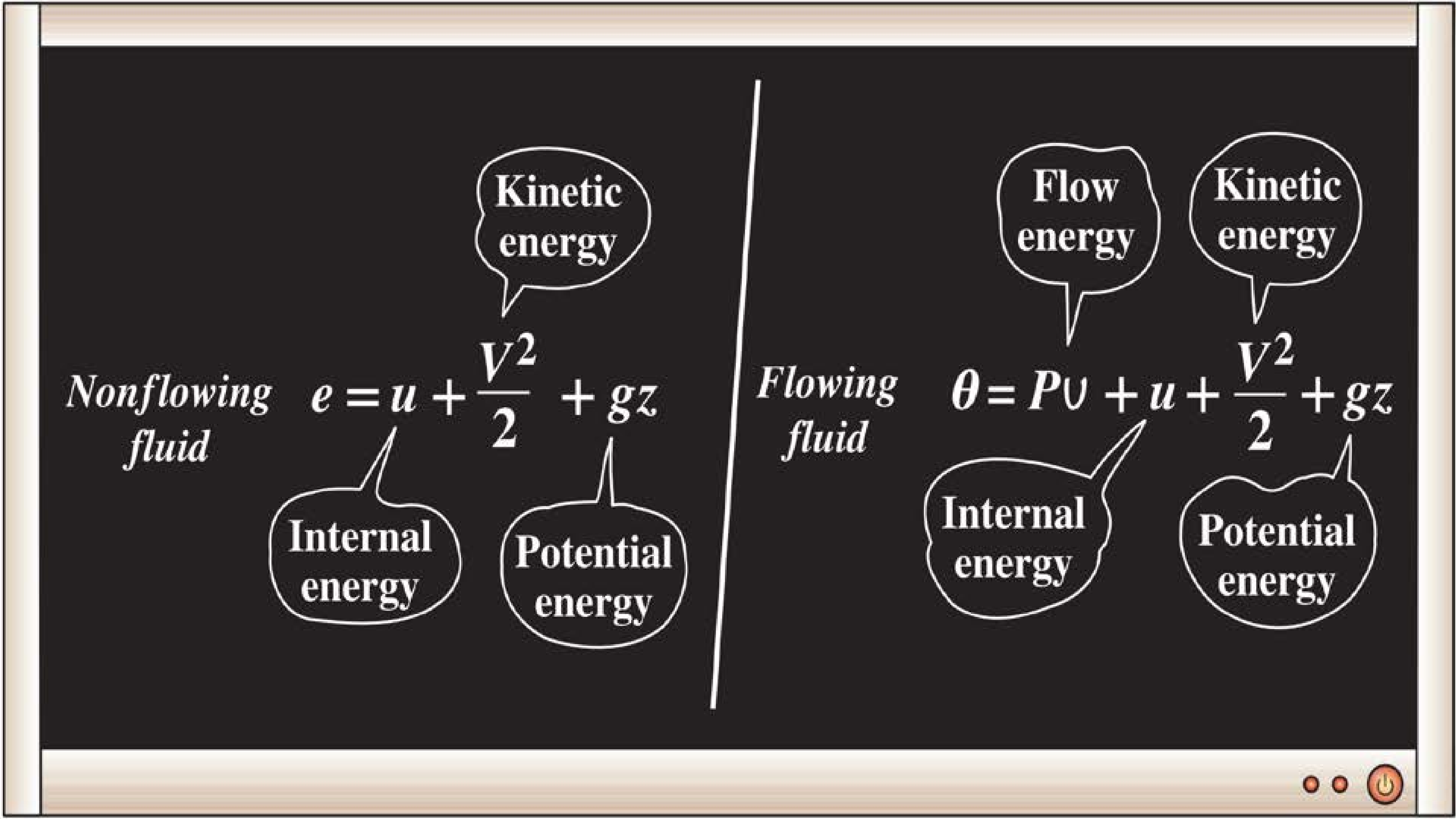
$$h_1 + \frac{C_1^2}{2} + Z_1g + Q = h_2 + \frac{C_2^2}{2} + Z_2g + W \qquad [\because \quad h = u + pv]$$

If Z_1 and Z_2 are neglected, we get

$$h_1 + \frac{C_1^2}{2} + Q = h_2 + \frac{C_2^2}{2} + W \qquad \text{...[4.45 } (a)\text{]}$$

where, Q = Heat supplied (or entering the boundary) per kg of fluid,
W = Work done by (or work coming out of the boundary) 1 kg of fluid,
C = Velocity of fluid ,
Z = Height above datum,
p = Pressure of the fluid,
u = Internal energy per kg of fluid, and
pv = Energy required for 1 kg of fluid.

This equation is applicable to any medium in any steady flow. It is applicable not only to rotary machines such as centrifugal fans, pumps and compressors but also to reciprocating machines such as steam engines.



$$e = u + \frac{V^2}{2} + gz$$

$$\theta = P\upsilon + u + \frac{V^2}{2} + gz$$

In a steady flow the rate of mass flow of fluid at any section is the same as at any other section. Consider any section of cross-sectional area A, where the fluid velocity is C, the rate of volume flow past the section is CA. Also, since mass flow is volume flow divided by specific volume,

$$\therefore \qquad \text{Mass flow rate, } \dot{m} = \frac{CA}{v} \qquad \text{...(4.46)}$$

(where v = *Specific volume* at the section)

This equation is known as the **continuity of mass equation**.

With reference to Fig. 4.30.

$$\therefore \qquad \dot{m} = \frac{C_1A_1}{v_1} = \frac{C_2A_2}{v_2} \qquad \text{...[4.46 }(a)]$$

ENERGY RELATIONS FOR FLOW PROCESS

The energy equation (m kg of fluid) for a steady flow system is given as follows :

$$m\left(u_1 + \frac{C_1^{\,2}}{2} + Z_1 g + p_1 v_1\right) + Q = m\left(u_2 + \frac{C_2^{\,2}}{2} + Z_2 g + p_2 v_2\right) + W$$

i.e.,
$$Q = m\left[(u_2 - u_1) + (Z_2 g - Z_1 g) + \left(\frac{C_2^{\,2}}{2} - \frac{C_1^{\,2}}{2}\right) + (p_2 v_2 - p_1 v_1)\right] + W$$

i.e.,
$$Q = m\left[(u_2 - u_1) + g(Z_2 - Z_1) + \left(\frac{C_2^{\,2} - C_1^{\,2}}{2}\right) + (p_2 v_2 - p_1 v_1)\right] + W$$

$$= \Delta U + \Delta PE + \Delta KE + \Delta\,(pv) + W$$

where
$$\Delta U = m\,(u_2 - u_1)$$
$$\Delta PE = mg\,(Z_2 - Z_1)$$
$$\Delta KE = m\left(\frac{C_2^{\,2} - C_1^{\,2}}{2}\right)$$
$$\Delta pv = m(p_2 v_2 - p_1 v_1)$$

$\therefore$
$$Q - \Delta U = [\Delta PE + \Delta KE + \Delta(pV) + W] \quad ...(4.47)$$

For non-flow process,

$$Q = \Delta U + W = \Delta U + \int_1^2 p dV$$

i.e.,
$$Q - \Delta U = \int_1^2 p.dV \quad ...(4.48)$$

The internal energy is a function of temperature only and it is a point function. Therefore, for the same two temperatures, change in internal energy is the same whatever may be the process, non-flow, or steady flow, reversible or irreversible.

For the same value of Q transferred to non-flow and steady flow process and for the same temperature range, we can equate the values of eqns. (4.47) and (4.48) for $(Q - \Delta U)$.

$$\therefore \qquad \int_1^2 p.dV = \Delta\, PE + \Delta\, KE + \Delta\,(pV) + W \qquad \text{...(4.49)}$$

where, W = Work transfer in flow process

and $\int_1^2 p.dV$ = Total change in mechanical energy of reversible steady flow process.

Property Relations for Energy Equations

We know that

$$h = u + pv$$

Differentiating above equation

$$dh = du + pdv + vdp$$

But $dQ = du + p.dv$ (as per first law applied to closed system)

or $du = dQ - p.dv$

Substituting this value of *du* in the above equation, we get

$$dh = dQ - p.dv + pdv + vdp$$

$$= dQ + vdp$$

$$\therefore \quad vdp = dh - dQ$$

$$\therefore \quad -\int_1^2 vdp = Q - \Delta h \qquad \text{...(4.50)}$$

where $-\int_1^2 vdp$ represents on a *p-v* diagram the area behind 1-2 as shown in Fig. 4.31 (*b*).

The eqn. (4.47) for a unit mass flow can be written as

$$dQ = d(PE) + d(KE) + du + d(pv) + dW$$

Substituting the value of $dQ = du + p.dv$ in the above equation, we get

$$du + pdv = d(PE) + d(KE) + du + pdv + vdp + dW$$

$$\therefore \qquad - vdp = d(PE) + d(KE) + dW$$

$$\therefore \qquad - \int_1^2 vdp = \Delta PE + \Delta KE + W \qquad \text{...[4.50 (a)]}$$

If $\Delta PE = 0$ (as in most of thermodynamic systems)

$$- \int_1^2 vdp = \Delta KE + W \qquad \text{...[4.50 (b)]}$$

If $W = 0$, the area behind the curve represents ΔKE and if $\Delta KE = 0$, area behind the curve represents W which is shaft work.

$- \int_1^2 vdp$ is a *positive quantity and represents work done by the system.*

If $\Delta PE = 0$ and $W = 0$, then

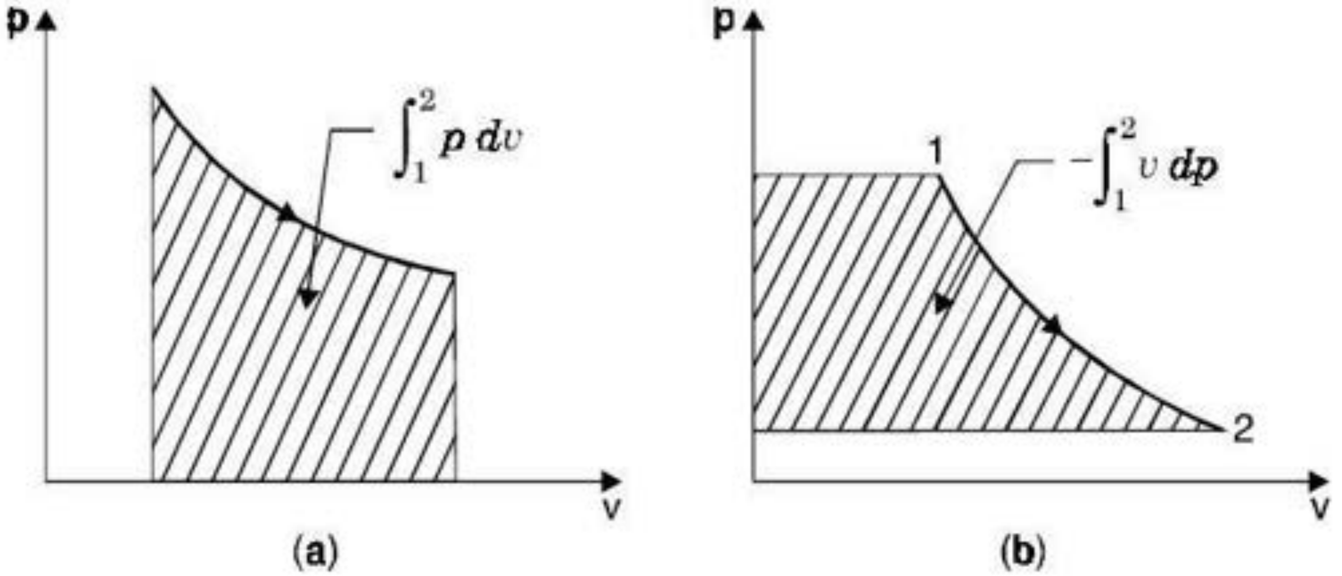
$- \int_1^2 vdp = \Delta KE$, this is applicable in case of a *nozzle.*

i.e.,
$$\int_1^2 v\,dp = \frac{C^2}{2} \text{ in the case of a nozzle.}$$

If $\Delta\,PE = 0$ and $\Delta\,KE = 0$, as in case of a *compressor*, $-\int_1^2 v\,dp = W$

or
$$W = \int_1^2 v\,dp \text{ in the case of a } \textit{compressor}.$$

The integral $\int_1^2 p\,dv$ and $\int_1^2 v\,dp$ are shown in Fig. 4.31 (*a*) and (*b*).



(*a*) Work done in non-flow process. (*b*) Work done in flow process.

Fig. 4.31. Representation of work on *p-v* diagram.

The work done during *non-flow process* is given by

$$\int_1^2 pdv = Q - \Delta u \qquad \text{...[4.50 (c)]}$$

For isothermal process, we have

$$\Delta u = 0 \text{ and } \Delta h = 0.$$

Substituting these values in (equations) 4.50 and [4.50 (c)]

$$-\int_1^2 vdp = Q \text{ and } \int_1^2 pdv = Q$$

$$\therefore \qquad \int_1^2 pdv = -\int_1^2 vdp$$

The above equation indicates that the *area under both curves is same for an isothermal process.*

Note. In all the above equations 'v' represents volume per unit mass as mass flow is considered unity.

Now let us find out expressions for work done for different flow processes as follows :

(*i*) **Steady flow constant pressure process :**

$$W = -\int_1^2 v\,.\,dp = 0 \qquad [\because \quad dp = 0]$$

(*ii*) **Steady flow constant volume process :**

$$W = -\int_1^2 V dp = -V(p_2 - p_1) = V(p_1 - p_2)$$

$$W = V(p_1 - p_2)$$

(*iii*) **Steady flow constant temperature process :**

The constant temperature process is represented by

$$pV = p_1V_1 = p_2V_2 = C \text{ (constant)}$$

$$\therefore \qquad W = -\int_1^2 V dp$$

$$= -\int_1^2 \frac{C}{p}\,dp$$

$$= -C\int_1^2 \frac{dp}{p} = -C\left|\log_e p\right|_1^2$$

$$= -C \log_e \frac{p_2}{p_1} = C \log_e \frac{p_1}{p_2}$$

i.e.,
$$W = p_1V_1 \log_e \left(\frac{p_1}{p_2}\right) \qquad \ldots(4.53)$$

Now substituting the values of W in the equation (4.49), considering unit mass flow :

(*a*) The energy equation for *constant pressure flow process*

$$dQ = \Delta PE + \Delta KE + \Delta h$$
$$= \Delta h \text{ (if } \Delta PE = 0 \text{ and } \Delta KE = 0).$$

(*b*) The energy equation for constant volume flow process

$$dQ = -\int_1^2 vdp + \Delta PE + \Delta KE + \Delta u + pdv + vdp$$
$$= \Delta PE + \Delta KE + \Delta u \qquad \left[\because\ pdv = 0 \text{ and } v\,.\,dp = \int_1^2 vdp\right]$$

$\therefore$
$$dQ = \Delta u \text{ (if } \Delta PE = 0 \text{ and } \Delta KE = 0)$$

ENGINEERING APPLICATIONS OF STEADY FLOW ENERGY EQUATION (S.F.E.E.)

1. Water Turbine

Refer to Fig. 4.32. In a water turbine, water is supplied from a height. The potential energy of water is converted into kinetic energy when it enters into the turbine and part of it is converted into useful work which is used to generate electricity.

Considering centre of turbine shaft as *datum*, the energy equation can be written as follows :

$$\left(u_1 + p_1v_1 + Z_1g + \frac{C_1^{\,2}}{2}\right) + Q = \left(u_2 + p_2v_2 + Z_2g + \frac{C_2^{\,2}}{2}\right) + W$$

In this case,

$$Q = 0$$

$$\Delta u = u_2 - u_1 = 0$$

$$\therefore \quad v_1 = v_2 = v$$

$$Z_2 = 0$$

$$\therefore \quad \left(p_1v + Z_1g + \frac{C_1^{\,2}}{2}\right) = \left(p_2v + Z_2g + \frac{C_2^{\,2}}{2}\right) + W \qquad \ldots(4.54)$$

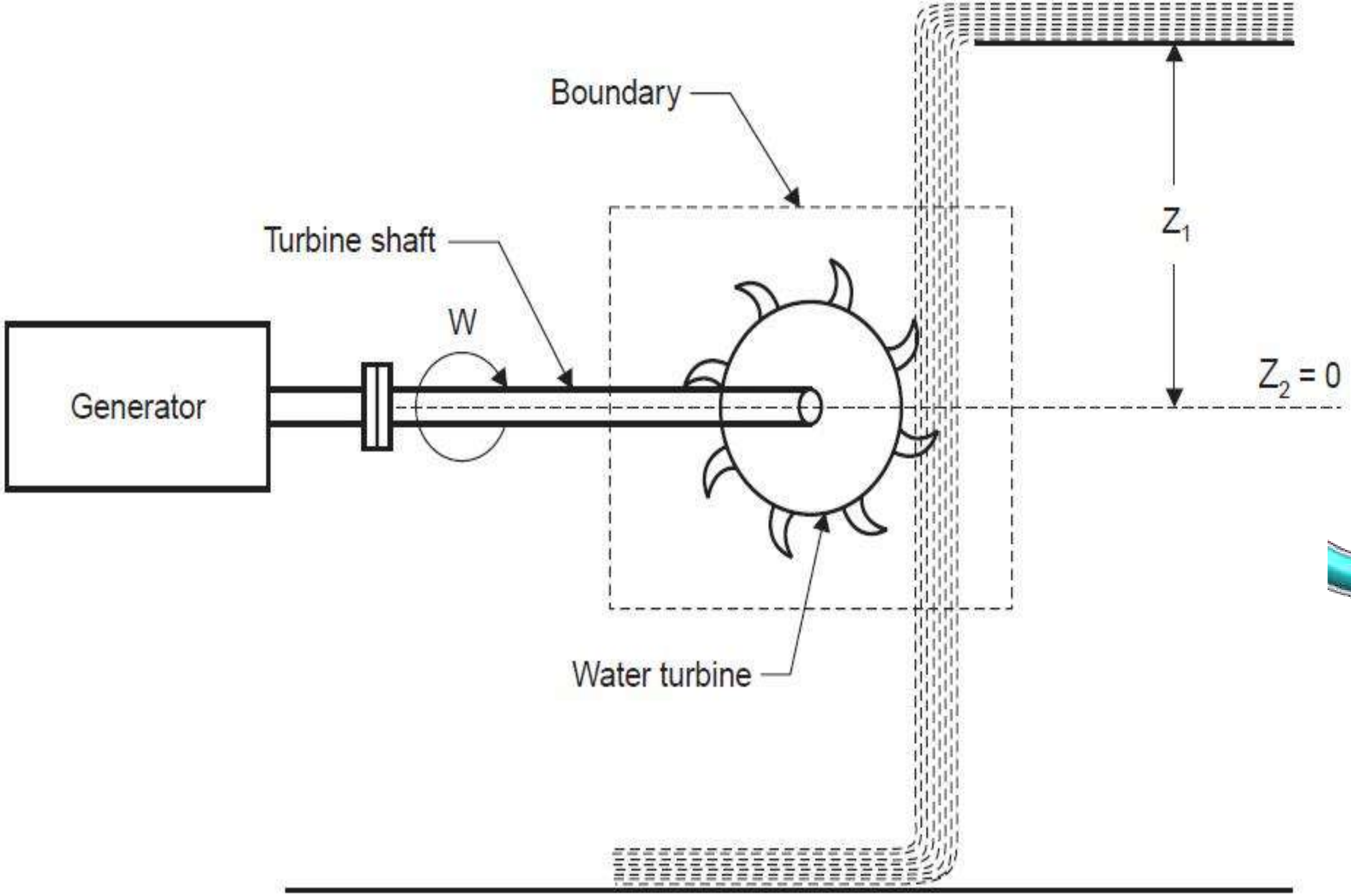


Fig. Water turbine.

W is *positive* because work is done by the system (or work comes out of the boundary).

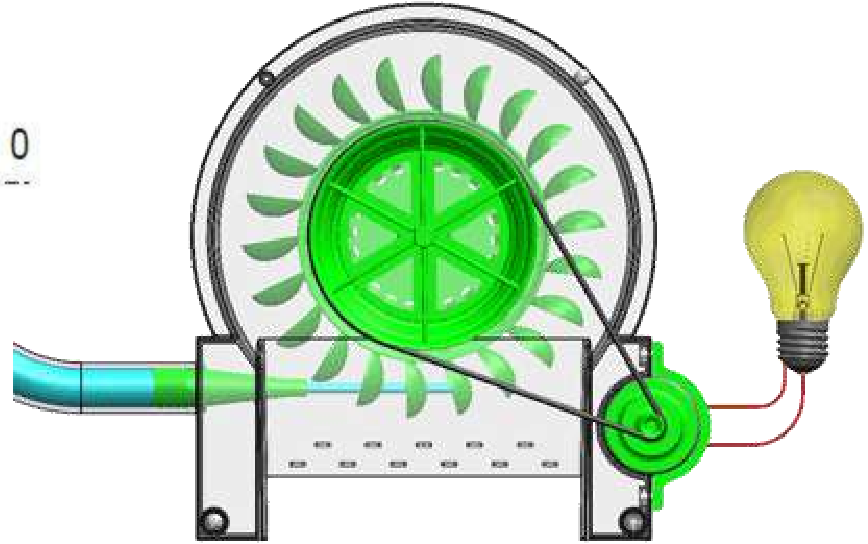


Fig: Pelton turbine

2. Steam or Gas Turbine

In a steam or gas turbine steam or gas is passed through the turbine and part of its energy is converted into work in the turbine. This output of the turbine runs a generator to produce electricity as shown in Fig. The steam or gas leaves the turbine at lower pressure or temperature.

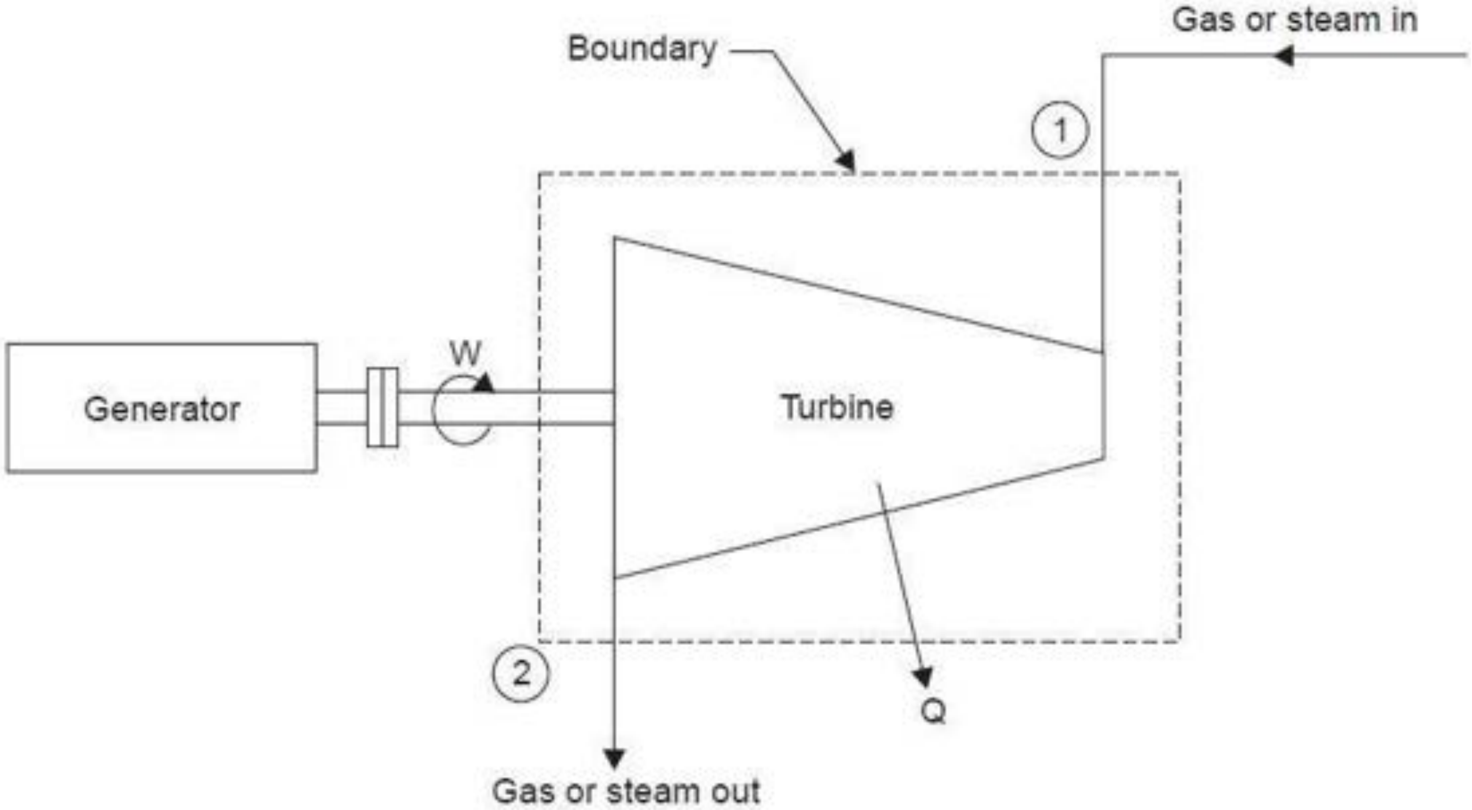


Fig. Steam or gas turbine.

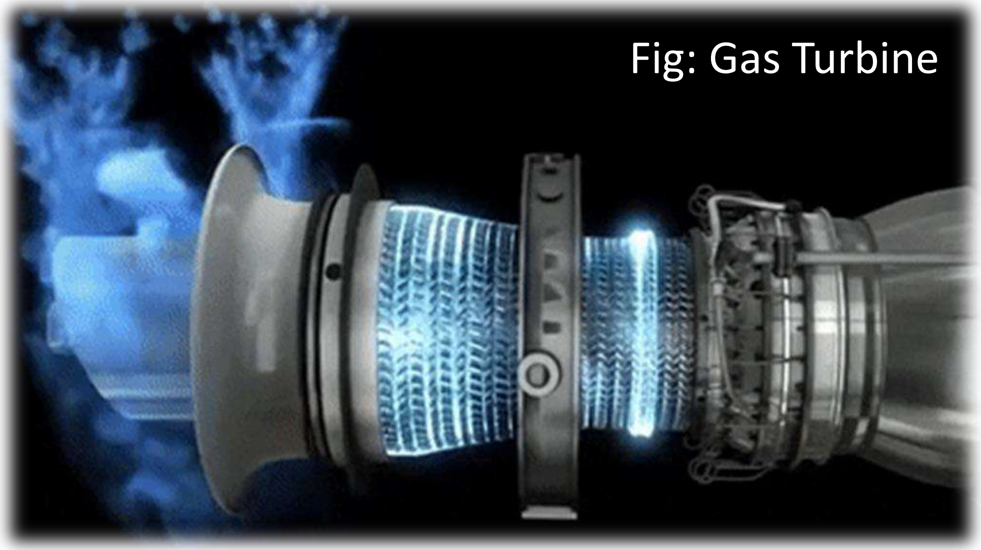


Fig: Gas Turbine

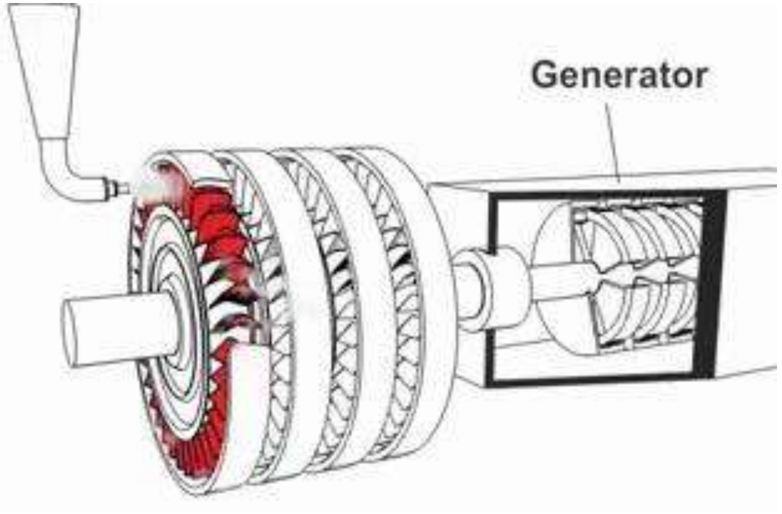


Fig: Steam Turbine

Applying energy equation to the system.

Here, $Z_1 = Z_2$ (*i.e.*, $\Delta Z = 0$)

$$h_1 + \frac{C_1^2}{2} - Q = h_2 + \frac{C_2^2}{2} + W \qquad \text{...(4.55)}$$

The sign of Q is *negative* because heat is *rejected* (or comes out of the boundary).

The sign of W is *positive* because work is done by the system (or work comes out of the boundary).

3. Centrifugal Water Pump

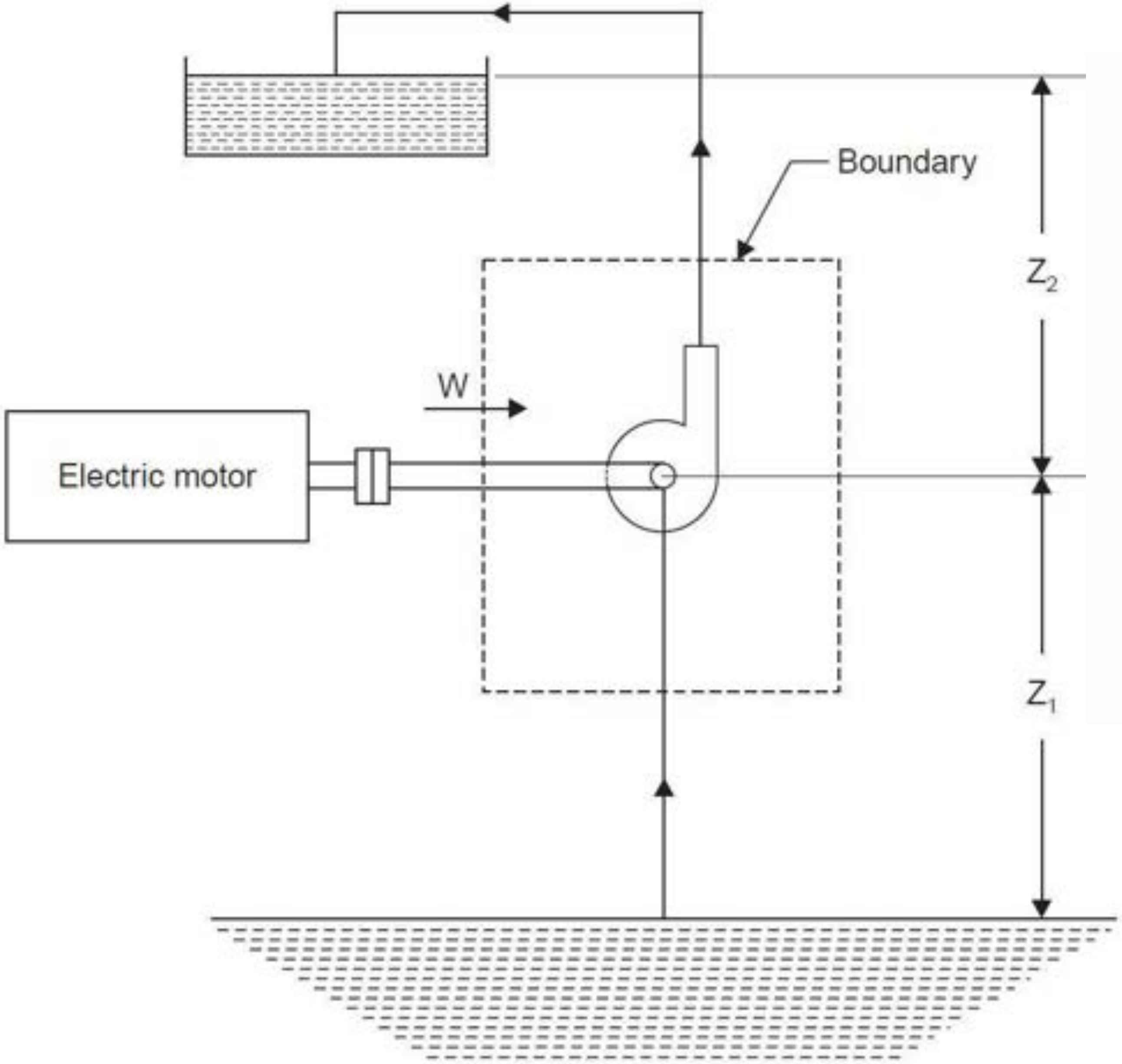


Fig. Centrifugal water pump.

A centrifugal water pump draws water from a lower level and pumps to higher level as shown in Fig. 4.34. Work is required to run the pump and this may be supplied from an external source such as an electric motor or a diesel engine.

Here $Q = 0$ and $\Delta u = 0$ as there is no change in temperature of water ; $v_1 = v_2 = v$.

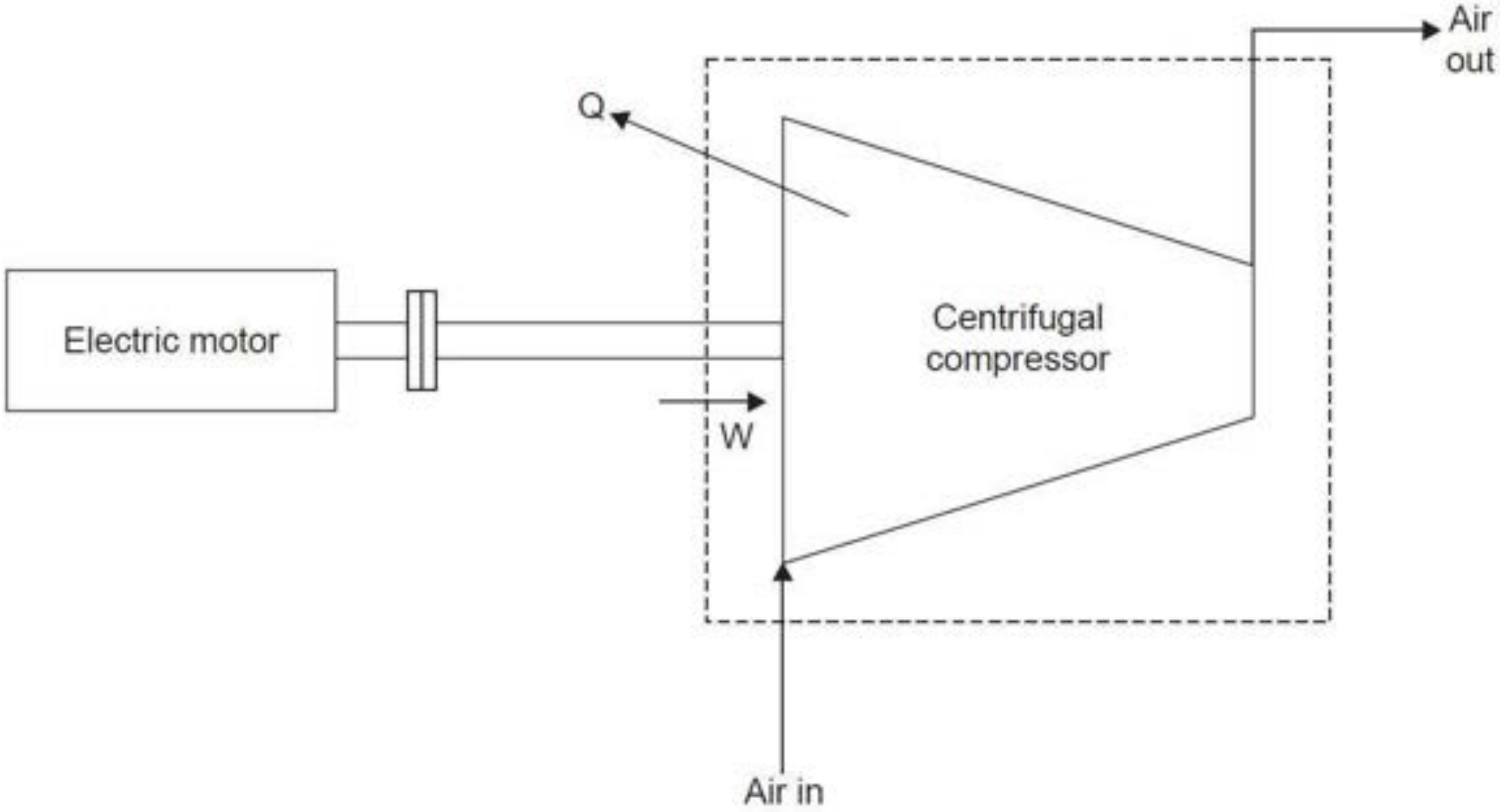
Applying the energy equation to the system

or
$$p_1v_1 + Z_1g + \frac{C_1^2}{2} = p_2v_2 + Z_2g + \frac{C_2^2}{2} - W \quad ...(4.56)$$

The sign of W is *negative* because *work is done on the system* (or *work enters the boundary*).

4. Centrifugal Compressor

A centrifugal compressor compresses air and supplies the same at moderate pressure and in large quantity.



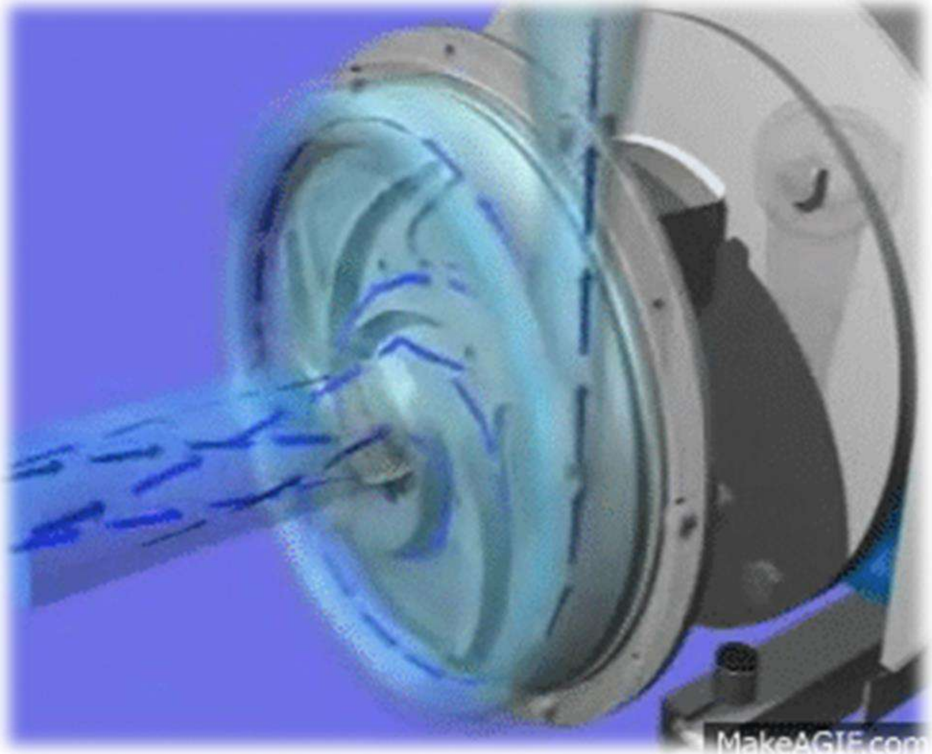


Fig. Centrifugal compressor.

Applying energy equation to the system (Fig. 4.35)

$$\Delta Z = 0 \text{ (generally taken)}$$

$$\left(h_1 + \frac{C_1^2}{2}\right) - Q = \left(h_2 + \frac{C_1^2}{2}\right) - W$$

The Q is taken as *negative* as heat is *lost* from the system and W is taken as *negative* as work is *supplied* to the system.

or $$\left(h_1 + \frac{C_1^2}{2}\right) - Q = \left(h_2 + \frac{C_2^2}{2}\right) - W \qquad ...(4.57)$$

5. Reciprocating Compressor

The reciprocating compressor draws in air from atmosphere and supplies at a considerable higher pressure in small quantities (compared with centrifugal compressor). The reciprocating compressor can be considered as steady flow system *provided the control volume includes the receiver which reduces the fluctuations of flow considerably.*

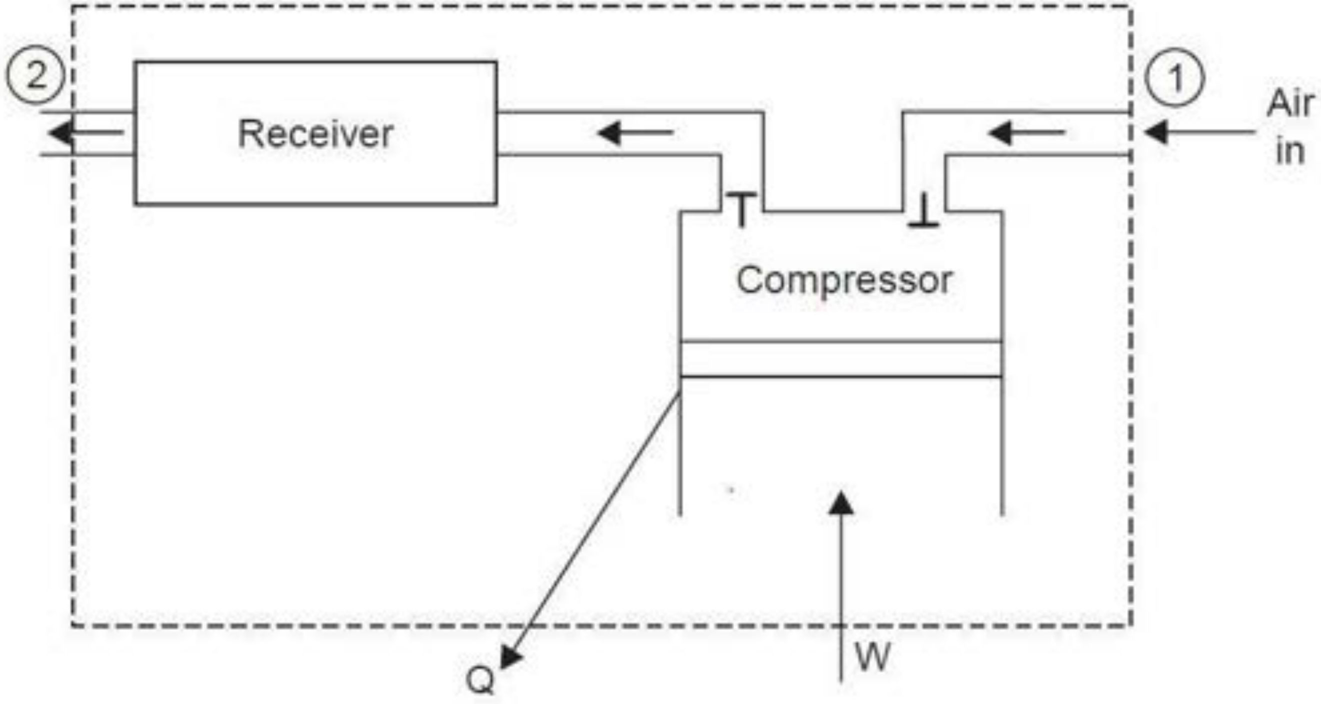
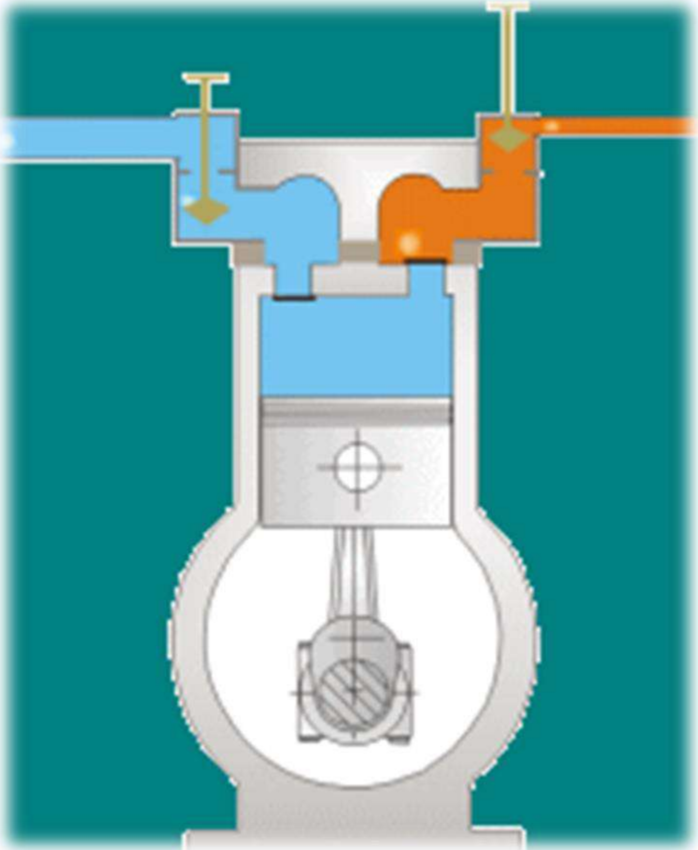


Fig. Reciprocating compressor.



Applying energy equation to the system, we have :

$\Delta PE = 0$ and $\Delta KE = 0$ since these changes are negligible compared with other energies.

$$\therefore \quad h_1 - Q = h_2 - W \quad \text{...(4.58)}$$

6. Boiler

A boiler transfers heat to the incoming water and generates the steam. The system is shown in Fig.

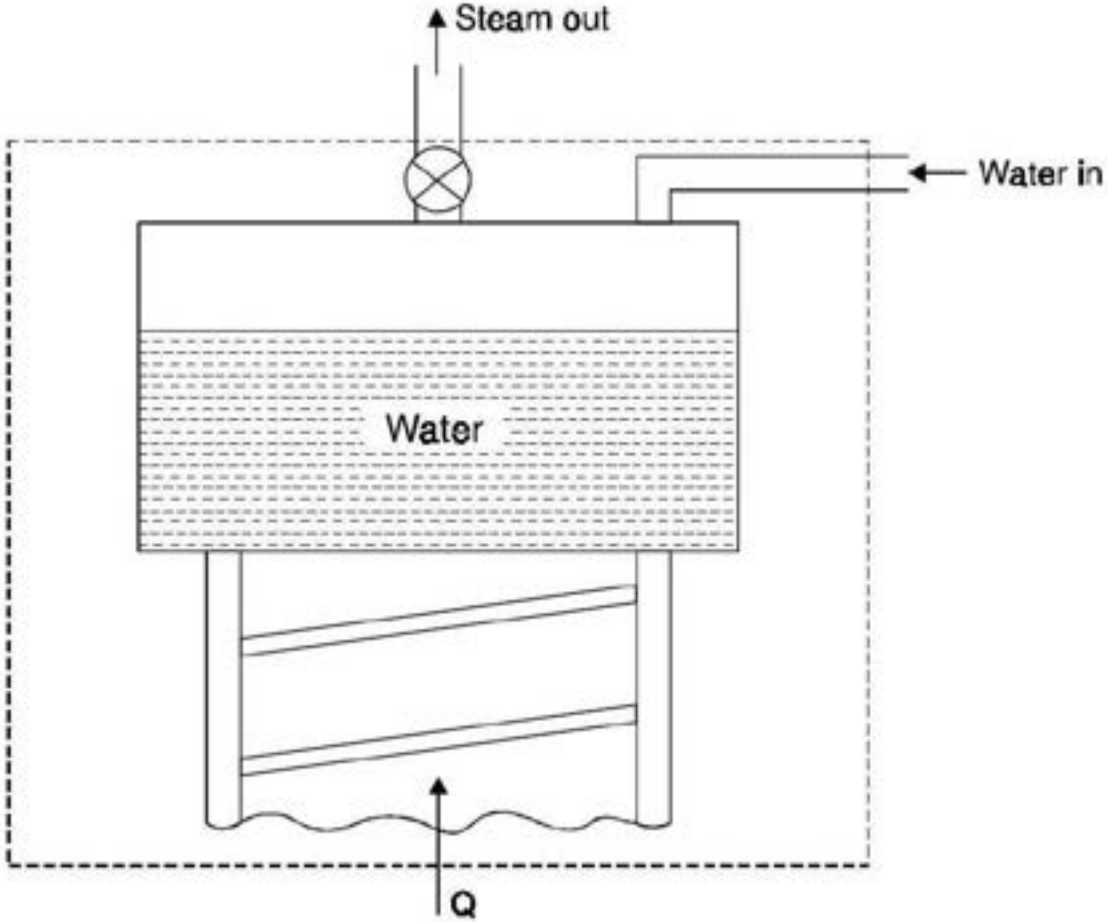
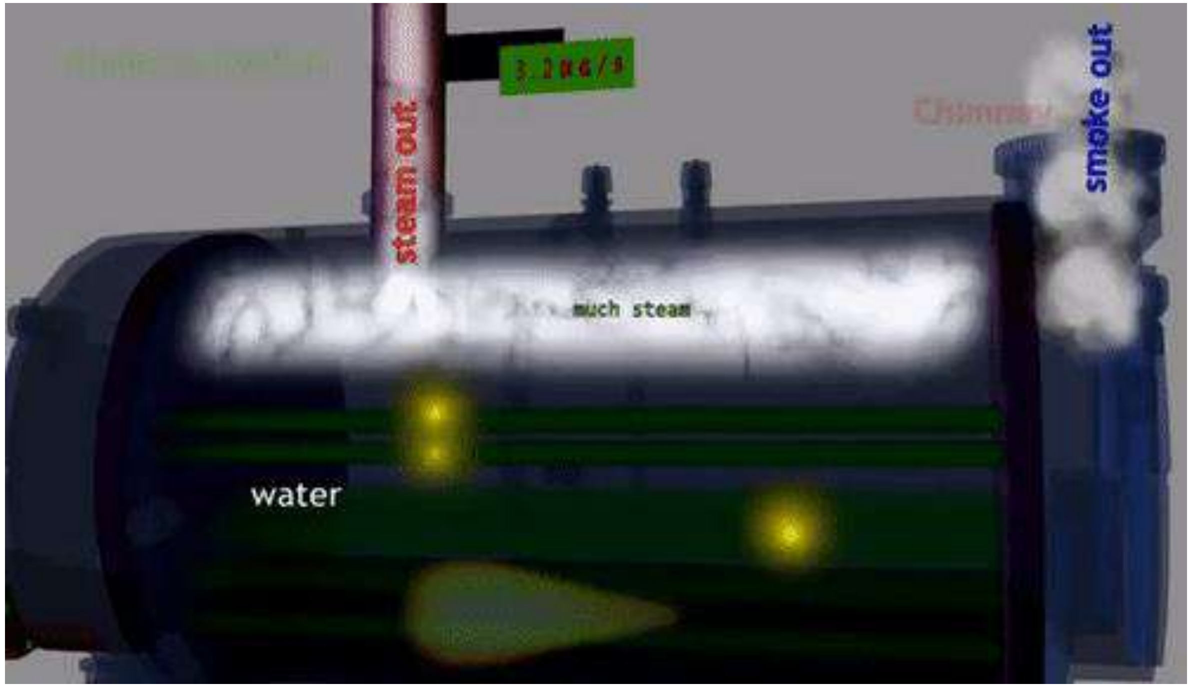


Fig. Boiler.



For this system, $\Delta Z = 0$ and $\Delta\left(\frac{C_2^2}{2}\right) = 0$

$W = 0$ since neither any work is developed nor absorbed.

Applying energy equation to the system

$$h_1 + Q = h_2 \qquad \text{...(4.59)}$$

7. Condenser

The condenser is used to condense the steam in case of steam power plant and condense the refrigerant vapour in the refrigeration system using water or air as cooling medium. Fig. 4.38 shows the system.

For this system :

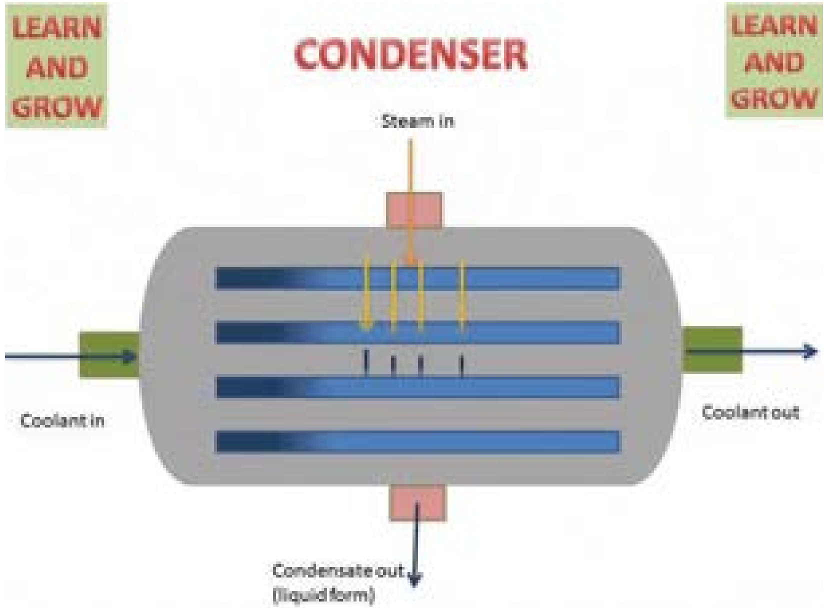
$\Delta PE = 0$, $\Delta KE = 0$ (as their values are very small compared with enthalpies)

$W = 0$ (since neither any work is developed nor absorbed)

Using energy equation to steam flow

$$h_1 - Q = h_2 \qquad \text{...[4.60 } (a)\text{]}$$

where Q = Heat lost by 1 kg of steam passing through the condenser.



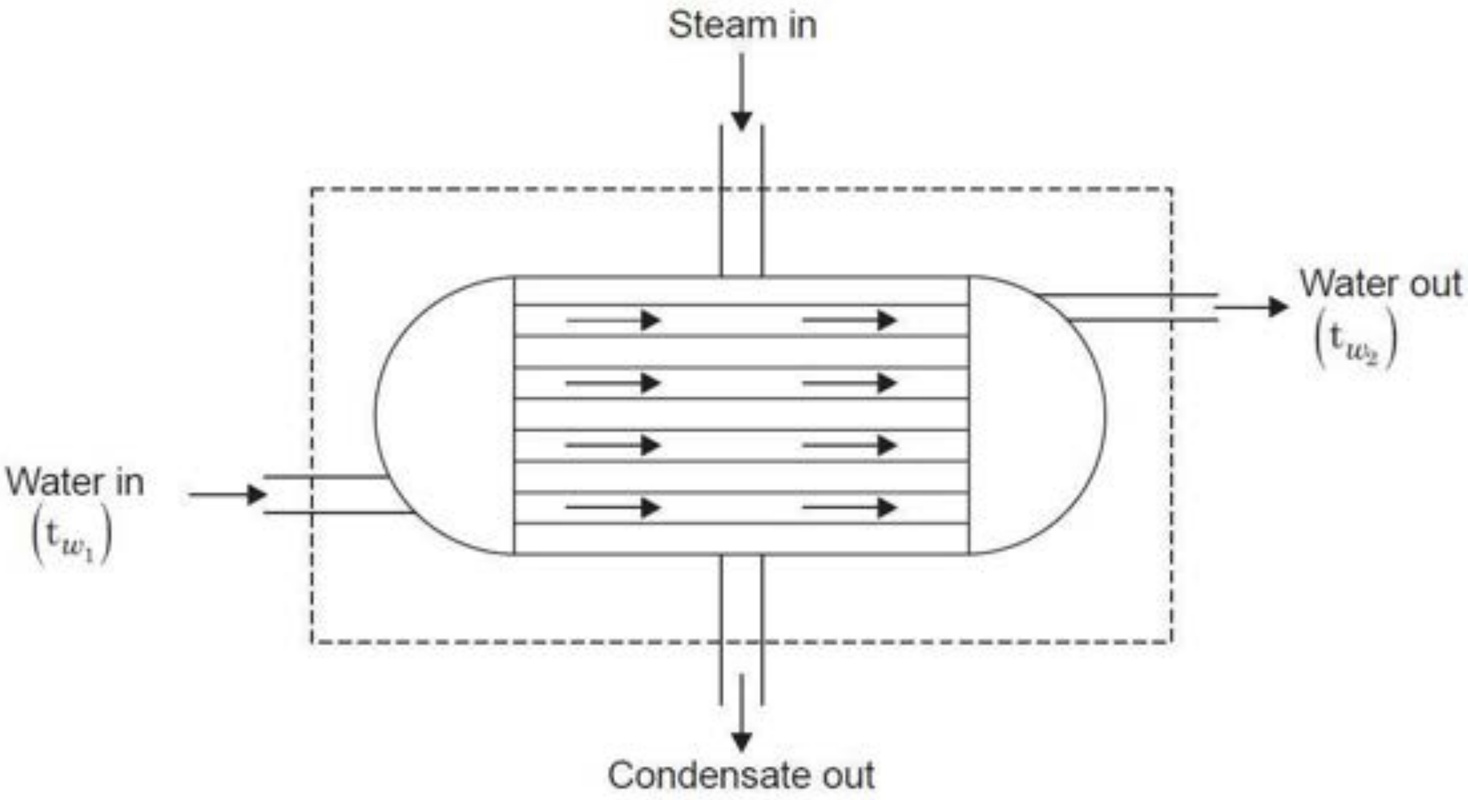


Fig. 4.38. Condenser.

Assuming there are no other heat interactions except the heat transfer between steam and water, then

$$Q = \text{Heat gained by water passing through the condenser}$$

$$= m_w (h_{w2} - h_{w1}) = m_w c_w (t_{w2} - t_{w1})$$

Substituting this value of Q in eqn. [4.60 (*a*)], we get

$$h_1 - h_2 = m_w (h_{w2} - h_{w1}) = m_w c_w (t_{w2} - t_{w1}) \qquad \text{...[4.60 (b)]}$$

where, m_w = Mass of cooling water passing through the condenser, and

c_w = Specific heat of water.

8. Evaporator

An evaporator is an equipment used in refrigeration plant to carry heat from the refrigerator to maintain the low temperature. Here the refrigerant liquid is passed through the evaporator and it comes out as vapour absorbing its latent heat from the surroundings of the evaporator. Fig. 4.39 shows the system. For this system

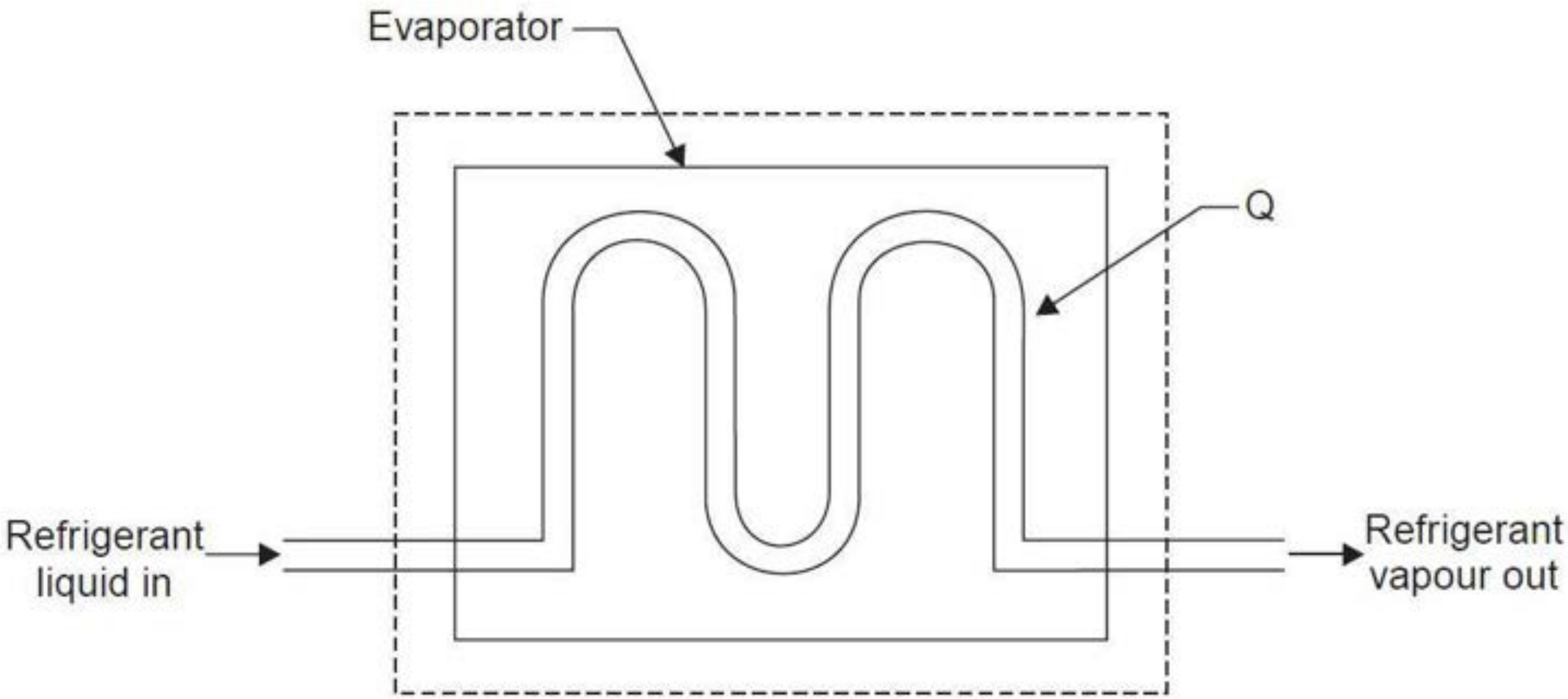


Fig. Evaporator.

$$\Delta PE = 0,\ \Delta KE = 0$$

$$W = 0 \qquad [\because \text{ No work is absorbed or supplied}]$$

Applying the energy equation to the system

$$h_1 + Q = h_2 \qquad ...(4.61)$$

Q is taken as + ve because heat *flows from the surroundings to the system* as the temperature in the system is lower than the surroundings.

9. Steam Nozzle

In case of a nozzle as the enthalpy of the fluid decreases and pressure drops simultaneously the flow of fluid is *accelerated*. This is generally used to convert the part of the energy of steam into *kinetic energy of steam* supplied to the turbine.

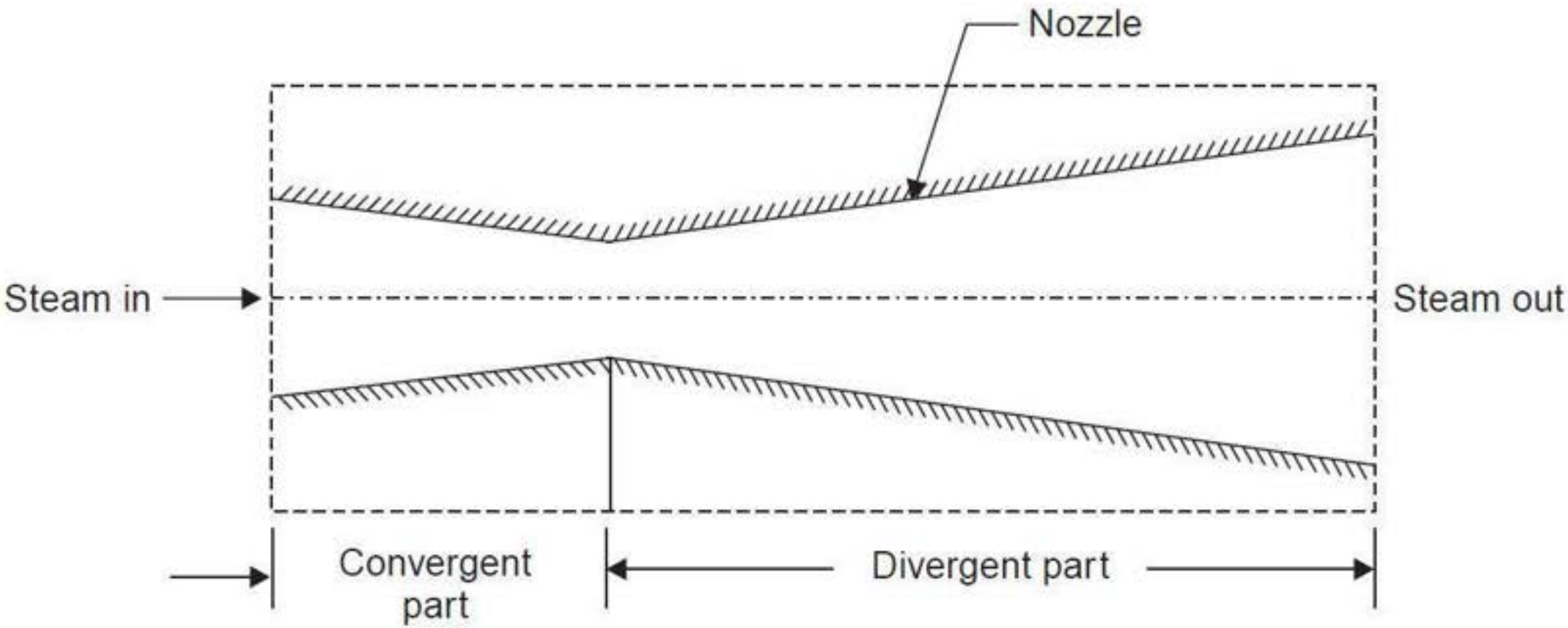


Fig. Steam nozzle.

Fig. shows a commonly used convergent-divergent nozzle.

For this system,

$$\Delta PE = 0$$

$$W = 0$$

$$Q = 0$$

Applying the energy equation to the system,

$$h_1 + \frac{C_1^2}{2} = h_2 + \frac{C_2^2}{2}$$

or $$\frac{C_2^2}{2} - \frac{C_1^2}{2} = h_1 - h_2 \quad \text{or} \quad C_2^2 - C_1^2 = 2(h_1 - h_2)$$

or $$C_2^2 = C_1^2 + 2(h_1 - h_2)$$

$\therefore$ $$C_2 = \sqrt{C_1^2 + 2(h_1 - h_2)} \qquad \ldots(4.62)$$

where velocity C is in m/s and enthalpy h in joules.

If $C_1 << C_2$, then

$$C_2 = \sqrt{2(h_1 - h_2)} \qquad \ldots[4.63\ (a)]$$

$\therefore$ $$C_2 = \sqrt{2\Delta h}\,. \qquad \ldots[4.63\ (b)]$$

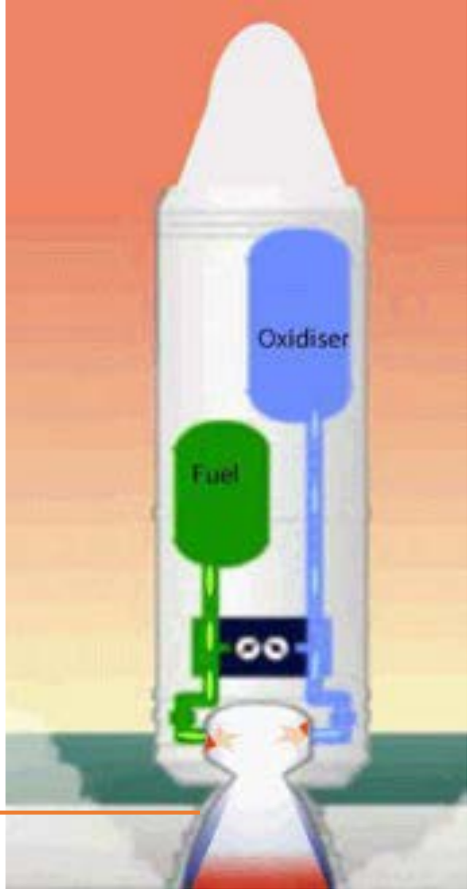


Fig: Convergent-Divergent Nozzle in Rockets

Throttling Devices:

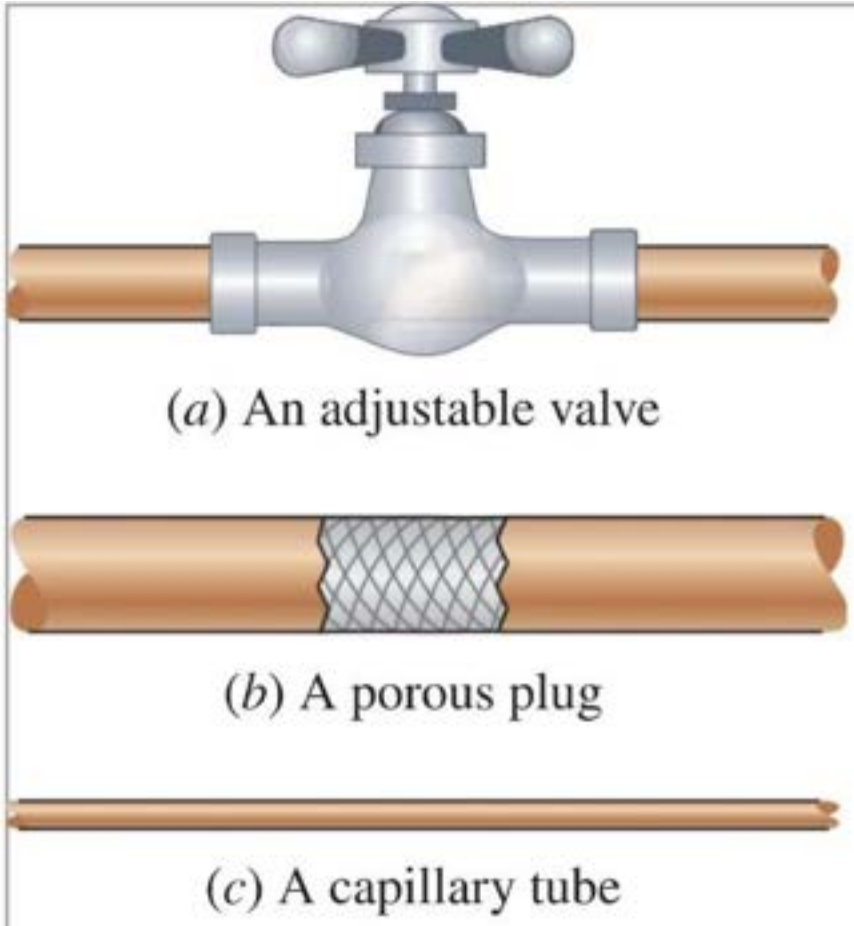
The main purpose of the throttling process is a significant pressure drop without any work interactions or changes in kinetic or potential energy. Flow through a restriction such as a valve or a porous plug fulfills the necessary condition. By decreasing the cross sectional area for flow, a greater flow resistance is introduced. For a given mass flow rate, the greater flow resistance requires a greater pressure drop across the valve.

Although the velocity may be quite high in the region of the restriction, measurements upstream and downstream from the actual valve area will indicate that the change in velocity, and hence the change in kinetic energy, across the restriction is very small. Since no rotating shaft is present, no work interaction is involved.

In most applications, either the throttling devices are properly insulated or the heat transfer is insignificant.

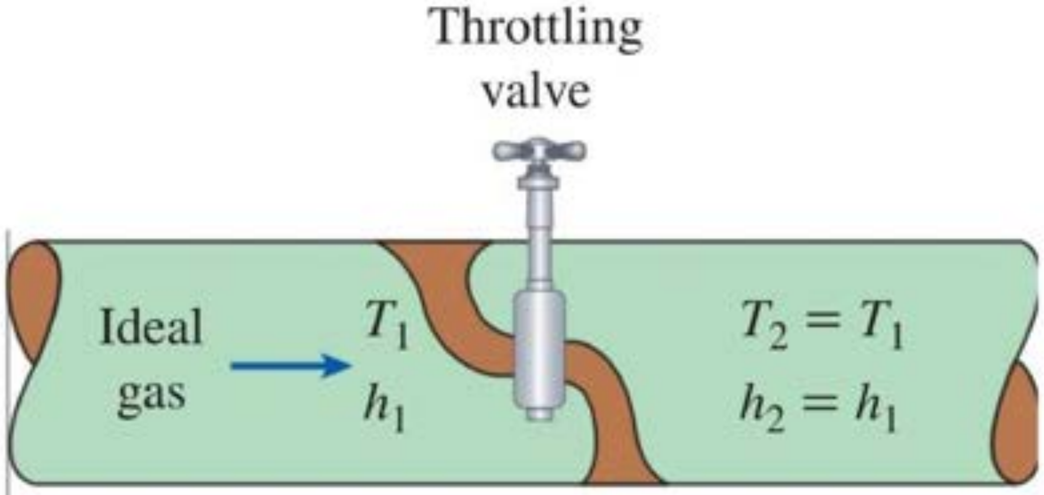
$$h_1 = h_2$$

Thus for a throttling process, the enthalpy change is zero.



FIGURE

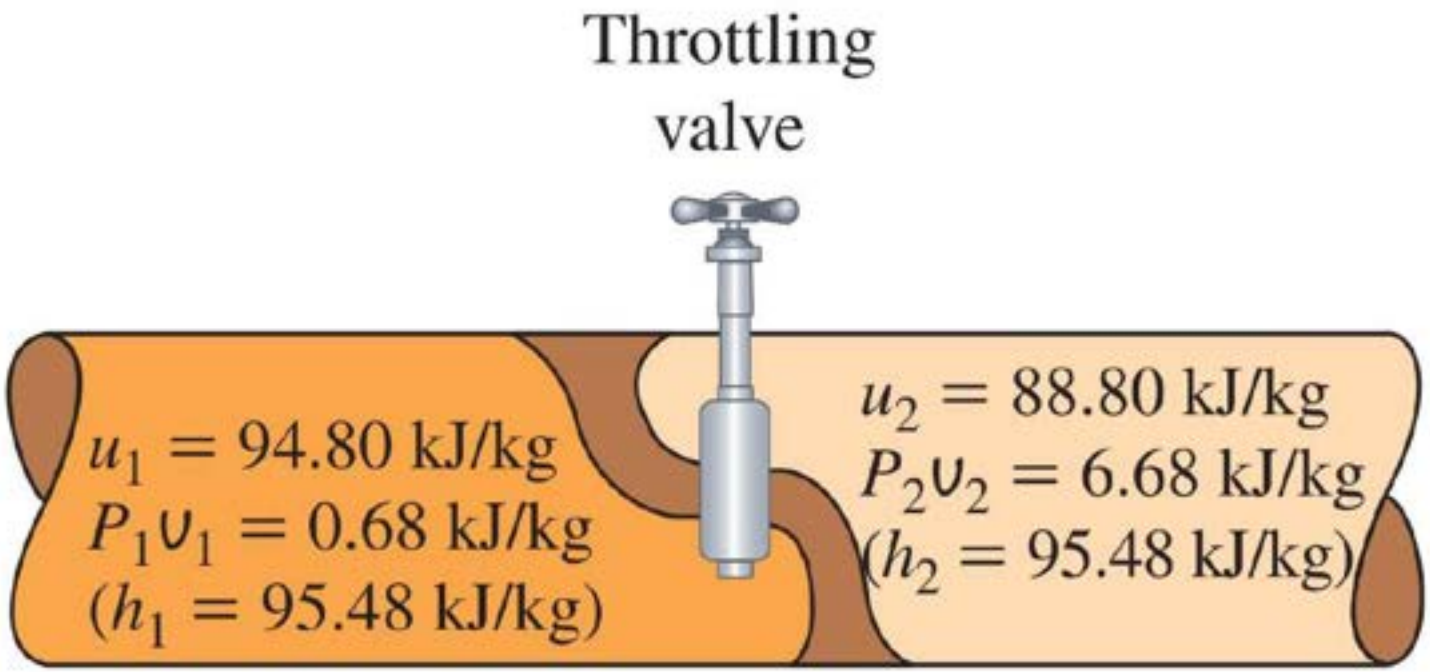
Throttling valves are devices that cause large pressure drops in the fluid.



FIGURE

The temperature of an ideal gas does not change during a throttling (h = constant) process since $h = h(T)$.

Case study:



FIGURE

During a throttling process, the enthalpy (flow energy + internal energy) of a fluid remains constant. But internal and flow energies may be converted to each other.

The throttling process is commonly used for the following purposes :

(i) For determining the condition of steam (dryness fraction).

(ii) For controlling the speed of the turbine.

(iii) Used in refrigeration plant for reducing the pressure of the refrigerant before entry into the evaporator.

Fig: Expansion/throttle vale in refrigerator

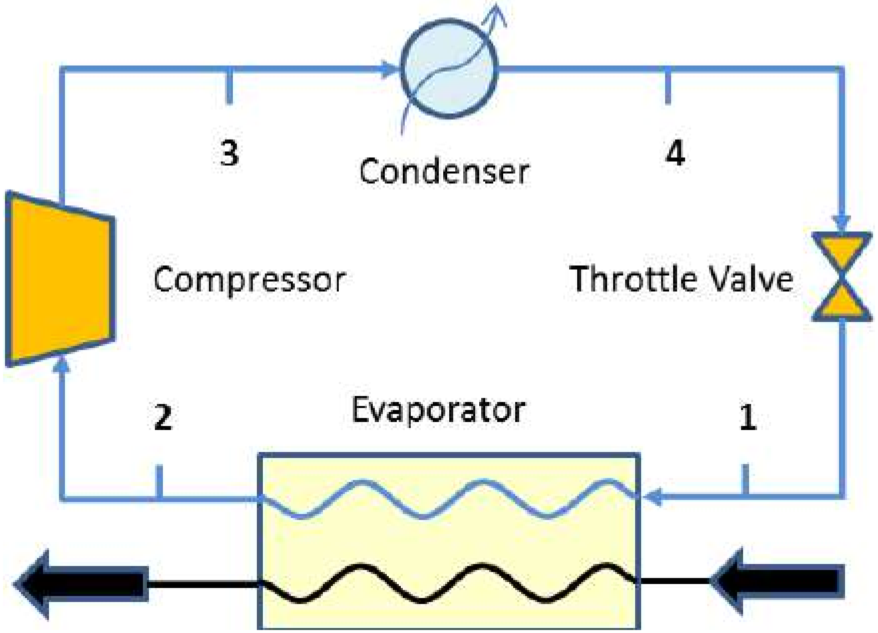
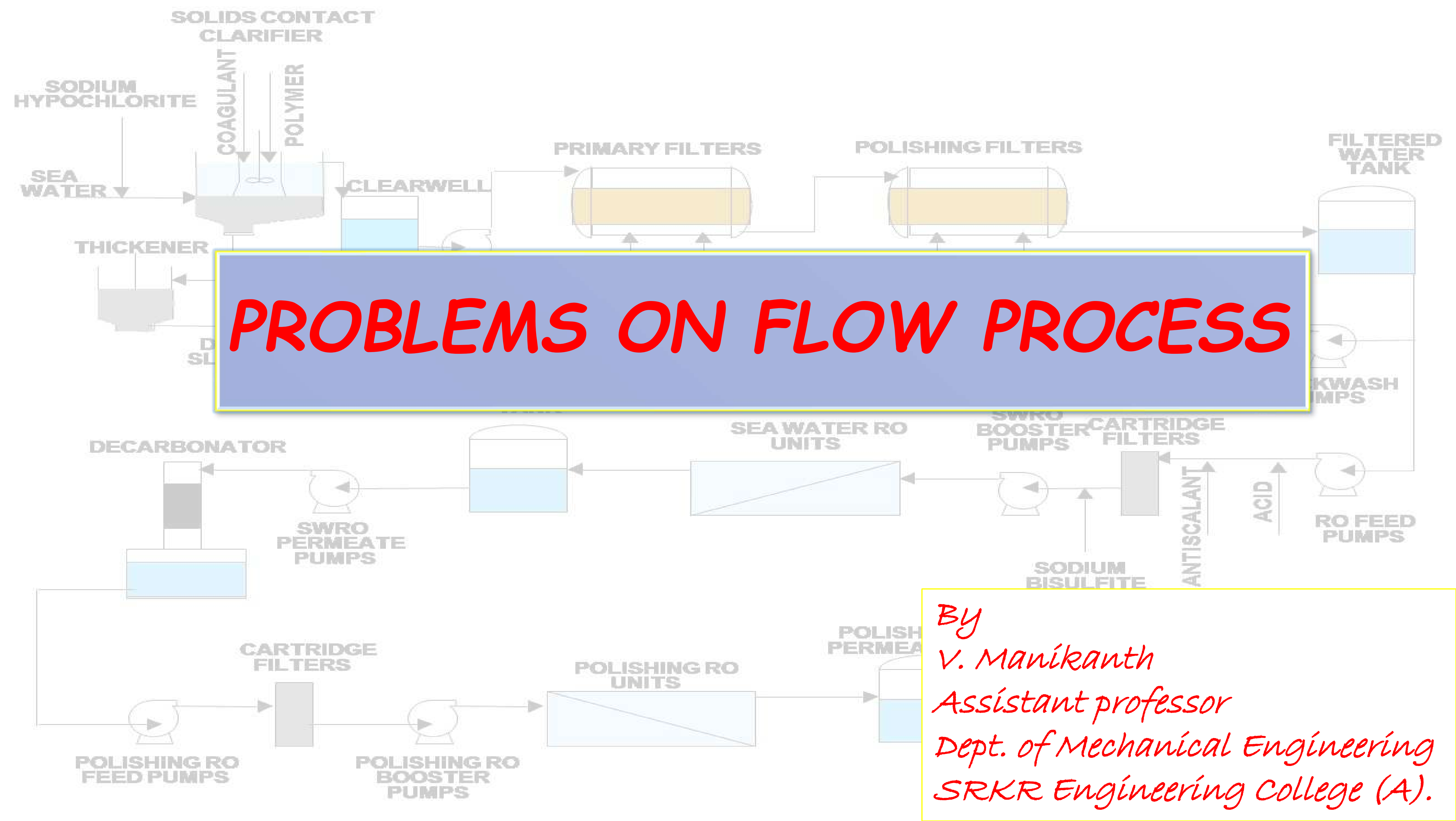


Fig: A simple Refrigeration cycle



PROBLEMS ON FLOW PROCESS

By
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How to solve a flow problem

1. Read the problem carefully and confirm it whether it is non-flow or flow system

2. Understand all the given parameters and convert into SI units.

3. Find out which type of application process it comes under.

4. Apply the basic SFEE equation.

5. Find out the missing parameters.

6 Solve the required parameters.

Formulae to be keep in mind

The steady flow equation can be expressed as follows :

$$\left(u_1 + p_1 v_1 + Z_1 g + \frac{{C_1}^2}{2}\right) + Q = \left(u_2 + p_2 v_2 + Z_2 g + \frac{{C_2}^2}{2}\right) + W$$

Mass flow rate, $\dot{m} = \frac{CA}{v}$

$$\dot{m} = \frac{C_1 A_1}{v_1} = \frac{C_2 A_2}{v_2}$$

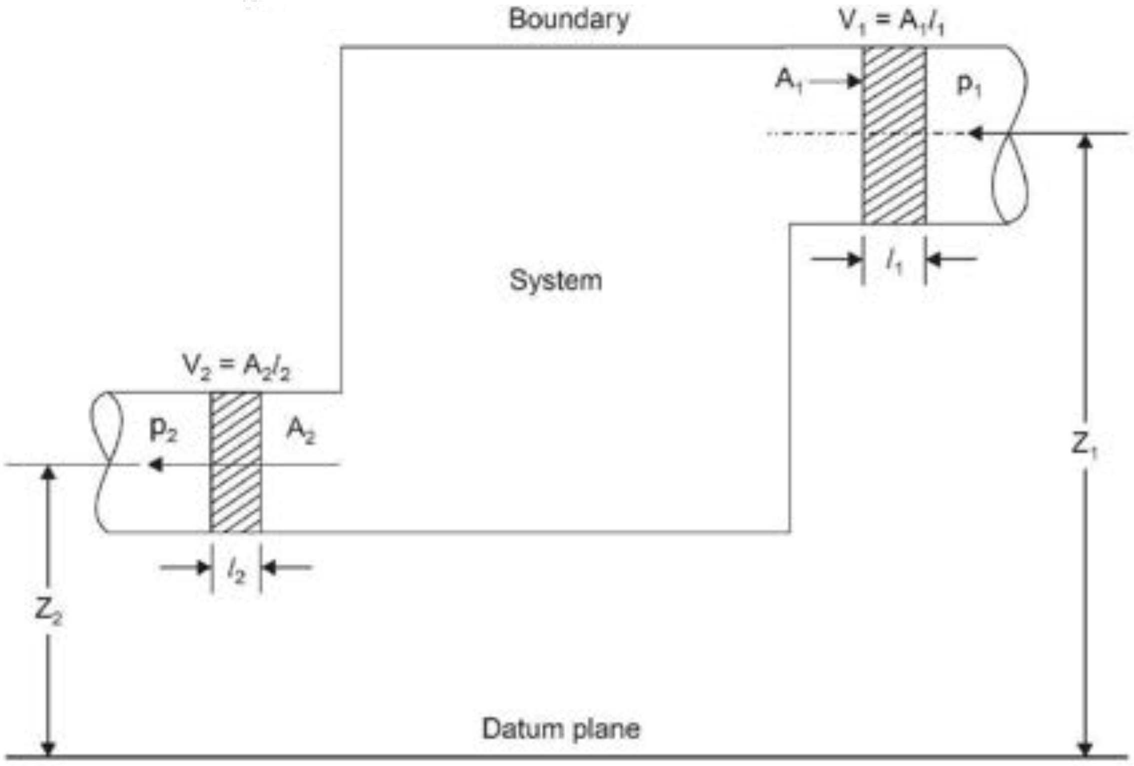


Fig.

Example.3 *In a gas turbine unit, the gases flow through the turbine is 15 kg/s and the power developed by the turbine is 12000 kW. The enthalpies of gases at the inlet and outlet are 1260 kJ/kg and 400 kJ/kg respectively, and the velocity of gases at the inlet and outlet are 50 m/s and 110 m/s respectively. Calculate :*

(*i*) *The rate at which heat is rejected to the turbine, and*

(*ii*) *The area of the inlet pipe given that the specific volume of the gases at the inlet is 0.45* m^3/kg.

Solution. Rate of flow of gases, $\dot{m} = 15$ kg/s

Volume of gases at the inlet, $v = 0.45\ \text{m}^3/\text{kg}$

Power developed by the turbine, $P = 12000$ kW

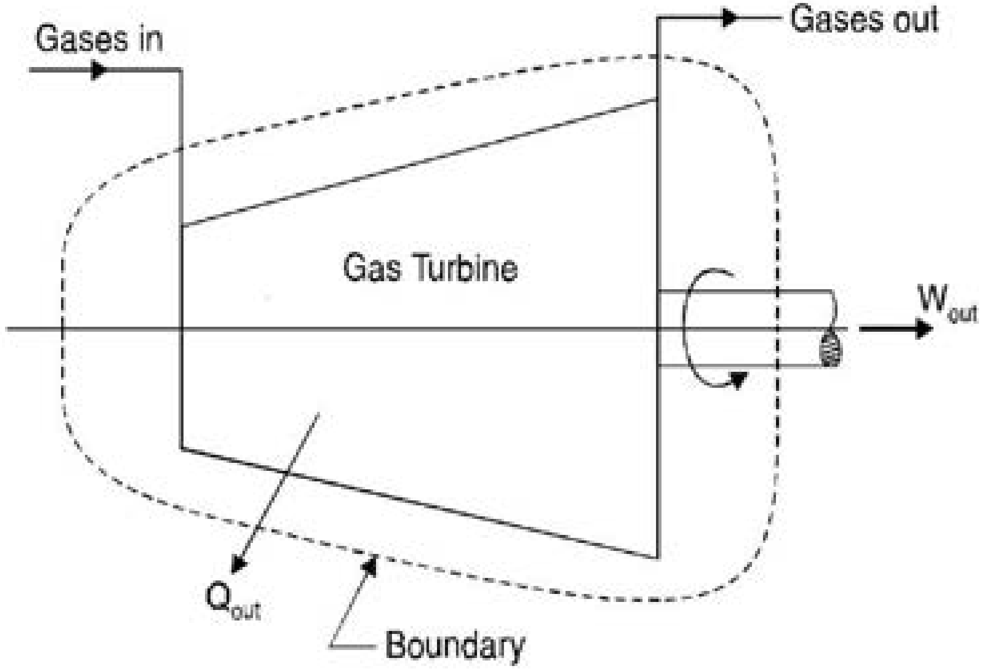
$\therefore$ Work done, $W = \dfrac{12000}{15} = 800$ kJ/kg

Enthalpy of gases at the inlet, $h_1 = 1260$ kJ/kg

Enthalpy of gases at the oulet, $h_2 = 400$ kJ/kg

Velocity of gases at the inlet, $C_1 = 50$ m/s

Velocity of gases at the outlet, $C_2 = 110$ m/s.



The steady flow equation can be expressed as follows :

$$\left(u_1 + p_1v_1 + Z_1g + \frac{C_1^{\,2}}{2}\right) + Q = \left(u_2 + p_2v_2 + Z_2g + \frac{C_2^{\,2}}{2}\right) + W$$

(*i*) **Heat rejected, Q :**

Using the flow equation,

$$h_1 + \frac{C_1^{\,2}}{2} + Q = h_2 + \frac{C_2^{\,2}}{2} + W \qquad \text{...}(i) \ [\because \ Z_1 = Z_2]$$

$$\text{Kinetic energy at inlet} = \frac{C_1^{\,2}}{2} = \frac{50^2}{2} \ \text{m}^2/\text{s}^2 = \frac{50^2 \text{ kg m}^3}{2 \text{ s}^2 \text{kg}} = 1250 \text{ Nm/kg} = 1.25 \text{ kJ/kg}$$

$$\text{Kinetic energy at outlet} = \frac{C_1^{\,2}}{2} = \frac{110^2}{2 \times 1000} = 6.05 \text{ kJ/kg}$$

Substituting these values in eqn. (*i*), we get

$$1260 + 1.25 + Q = 400 + 6.05 + 800$$

$$Q = -\ 55.2 \text{ kJ/kg}$$

$$= +\ 55.2 \text{ kJ/kg} = 55.2 \times 15 \text{ kJ/s} = \mathbf{828\ kW.} \quad \textbf{(Ans.)}$$

(*ii*) **Inlet area, A :**

Using the relation,

$$\dot{m} = \frac{CA}{v}$$

$$\therefore \qquad A = \frac{v\dot{m}}{C} = \frac{0.45 \times 15}{50} = \mathbf{0.135\ m^2.} \quad \textbf{(Ans.)}$$

Example 4. *In a steam plant, 1 kg of water per second is supplied to the boiler. The enthalpy and velocity of water entering the boiler are 800 kJ/kg and 5 m/s. The water receives 2200 kJ/kg of heat in the boiler at constant pressure. The steam after passing through the turbine comes out with a velocity of 50 m/s, and its enthalpy is 2520 kJ/kg. The inlet is 4 m above the turbine exit. Assuming the heat losses from the boiler and the turbine to the surroundings are 20 kJ/s, calculate the power developed by the turbine. Consider the boiler and turbine as single system.*

Solution. Enthalpy of water entering the boiler, $h_1 = 800$ kJ/kg

Velocity of water entering the boiler, $C_1 = 5$ m/s

Enthalpy of steam at the outlet of the turbine, $h_2 = 2520$ kJ/kg

Velocity of steam at the outlet of the turbine, $C_2 = 50$ m/s

Elevation difference, $(Z_1 - Z_2) = 4$ m

Net heat added to the water in the boiler, $Q = 2200 - 20 = 2180$ kJ/kg

Power developed by the turbine :

Using the flow equation,

$$h_1 + \frac{C_1^2}{2} + Z_1 g + Q = h_2 + \frac{C_2^2}{2} + Z_2 g + W$$

$$\therefore \qquad W = (h_1 - h_2) + \left(\frac{{C_1}^2}{2} - \frac{{C_2}^2}{2}\right) + (Z_1 - Z_2)\, g + Q$$

$$= (800 - 2520) + \frac{1}{1000}\left[\frac{5^2}{2} - \frac{50^2}{2}\right] + \frac{4 \times 9.81}{1000} + 2180$$

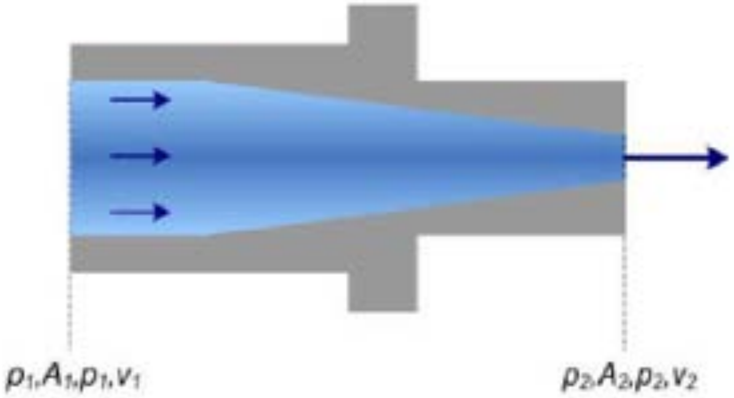
$$= -\,1720 + \frac{1}{1000}(12.5 - 1250) + \frac{39.24}{1000} + 2180$$

$$= -\,1720 - 1.2375 + 0.03924 + 2180$$

$$= 458.8 \text{ kJ/kg} = 458.8 \text{ kJ/s} = 458.8 \text{ kW}$$

Hence, **power developed by the turbine = 458.8 kW. (Ans.)**

Example 1 The steam flows through a nozzle with negligible heat transfer. At the inlet the enthalpy of steam is 3159.3 kJ/kg and the velocity is 30 m/s. At the exit, the enthalpy is 2855.4 kJ/kg. The mass flow rate of steam is 7 kg/s. At the exit the specific volume of steam is 0.2275 m^3/kg. Determine the velocity at exit from the nozzle and the exit area of the nozzle.



Solution

Mass flow rate $\dot{m} = 7$ kg/s

Enthalpy at inlet $h_1 = 3159.3$ kJ/kg $= 3159.3 \times 10^3$ J/kg

Velocity at inlet $V_1 = 30$ m/s

Enthalpy at exit $h_2 = 2855.4$ kJ/kg $= 2855.4 \times 10^3$ J/kg

Specific volume at exit $v_2 = 0.2275\ m^3/kg$

The steady flow energy equation for the nozzle is given by Eq.

$$h_1 + \frac{V_1^2}{2} = h_2 + \frac{V_2^2}{2}$$

or $$3159.3 \times 10^3 + \frac{30^2}{2} = 2855.4 \times 10^3 + \frac{V_2^2}{2}$$

or $$V_2 = 780.19 \text{ m/s}$$

Mass flow rate can be expressed as

$$\dot{m} = \frac{A_2 V_2}{v_2}$$

or $$7 = \frac{A_2 \times 780.19}{0.2275}$$

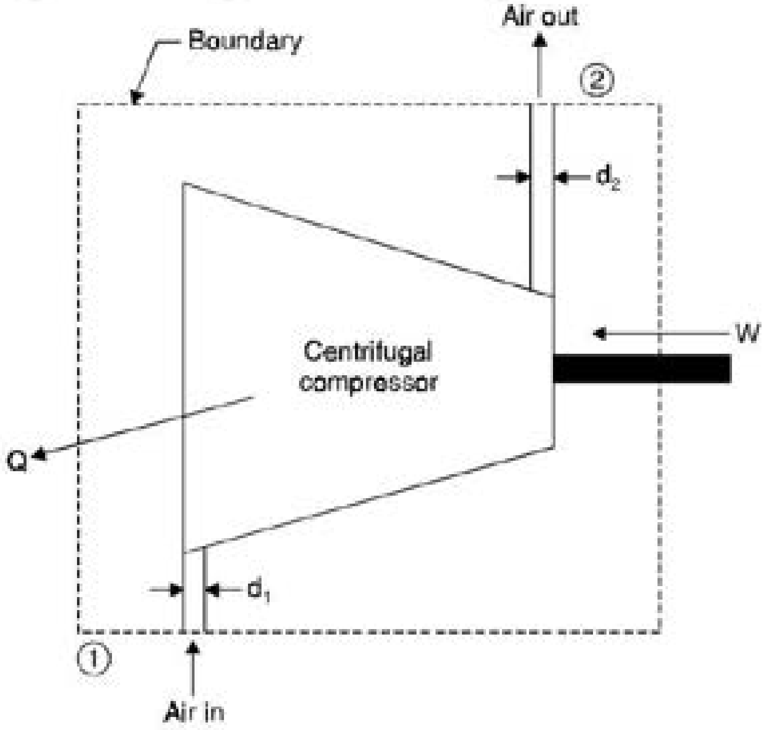
or $$A_2 = 0.002 \text{ m}^2$$

Example 5. *12 kg of air per minute is delivered by a centrifugal air compressor. The inlet and outlet conditions of air are* $C_1 = 12$ *m/s,* $p_1 = 1$ *bar,* $v_1 = 0.5$ *m³/kg and* $C_2 = 90$ *m/s,* $p_2 = 8$ *bar,* $v_2 = 0.14$ *m³/kg. The increase in enthalpy of air passing through the compressor is 150 kJ/kg and heat loss to the surroundings is 700 kJ/min.*

Find : (i) Motor power required to drive the compressor ;

(ii) Ratio of inlet to outlet pipe diameter.

Assume that inlet and discharge lines are at the same level.



Solution. Quantity of air delivered by the compressor, $m = \frac{12}{60} = 0.2$ kg/s.

Conditions of air at the inlet 1 :

Velocity, $C_1 = 12$ m/s

Pressure, $p_1 = 1 \text{ bar} = 1 \times 10^5 \text{ N/m}^2$

Specific volume, $v_1 = 0.5 \text{ m}^3\text{/kg}$

Conditions of air at the outlet 2 :

Velocity, $C_2 = 90$ m/s

Pressure, $p_2 = 8 \text{ bar} = 8 \times 10^5 \text{ N/m}^2$

Specific volume, $v_2 = 0.14 \text{ m}^3\text{/kg}$

Increase in enthalpy of air passing through the compressor,

$$(h_2 - h_1) = 150 \text{ kJ/kg}$$

Heat lost to the surroundings,

$$Q = -\ 700 \text{ kJ/min} = -\ 11.67 \text{ kJ/s.}$$

(*i*) **Motor power required to drive the compressor :**

Applying energy equation to the system,

$$m\left(h_1 + \frac{C_1^2}{2} + Z_1 g\right) + Q = m\left(h_2 + \frac{C_2^2}{2} + Z_2 g\right) + W$$

Now $\qquad Z_1 = Z_2 \qquad$ (given)

$$\therefore \qquad m\left(h_1 + \frac{C_1^2}{2}\right) + Q = m\left(h_2 + \frac{C_2^2}{2}\right) + W$$

$$W = m\left[(h_1 - h_2) + \frac{C_1^2 - C_2^2}{2}\right] + Q$$

$$= 0.2\left[-\ 150 + \frac{12^2 - 90^2}{2 \times 1000}\right] + (-\ 11.67)$$

$$= -\ 42.46 \text{ kJ/s} = -\ 42.46 \text{ kW}$$

∴ **Motor power required (or work done on the air) = 42.46 kW. (Ans.)**

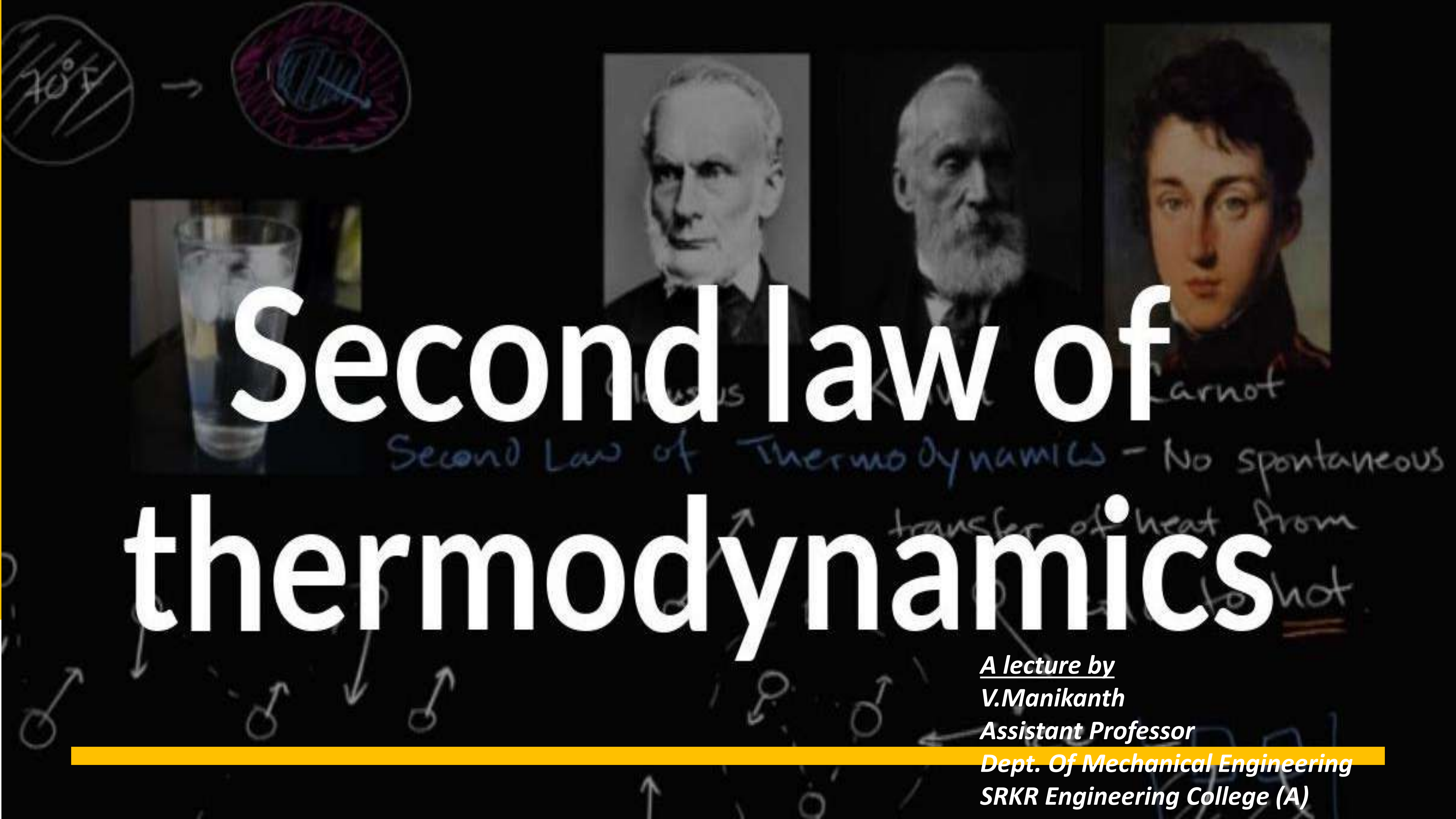
(*ii*) **Ratio of inlet to outlet pipe diameter, $\mathbf{\dfrac{d_1}{d_2}}$:**

The mass of air passing through the compressor is given by

$$m = \frac{A_1 C_1}{v_1} = \frac{A_2 C_2}{v_2}$$

$$\therefore \qquad \frac{A_1}{A_2} = \frac{C_2}{C_1} \times \frac{v_1}{v_2} = \frac{90}{12} \times \frac{0.5}{0.14} = 26.78$$

$$\therefore \qquad \left(\frac{d_1}{d_2}\right)^2 = 26.78 \quad \text{or} \quad \frac{d_1}{d_2} = 5.175$$



Second law of thermodynamics

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UNIT-III: Second Law of Thermodynamics

Limitations of the First Law, Thermal Reservoir, Heat Engine, Heat pump, Parameters of performance, Second Law of Thermodynamics, Kelvin Planck and Clausius Statements and their Equivalence / Corollaries, PMM of Second kind, Carnot's principle, Carnot cycle and its specialties, Clausius theorem Clausius Inequality, Entropy, Principle of Entropy Increase, Third Law of Thermodynamics

LIMITATIONS OF FIRST LAW OF THERMODYNAMICS:

The first law of thermodynamics establishes *equivalence between the quantity of heat used and the mechanical work but does not specify the conditions under which conversion of heat into work is possible, neither the direction in which heat transfer can take place*. This gap has been bridged by the second law of thermodynamics.

It has been observed that energy can flow from a system in the form of heat or work. The first law of thermodynamics sets no limit to the amount of the total energy of a system which can be caused to flow out as work. A limit is imposed, however, as a result of the principle enunciated in the second law of thermodynamics which states that heat will flow naturally from one energy reservoir to another at a lower temperature, but not in opposite direction without assistance. This is very important because a heat engine operates between two energy reservoirs at different temperatures.

All spontaneous processes in nature proceed in one direction only. Reversal of these processes is not possible without the assistance of any external agency. For example, a hot cup of tea left in a cool surrounding eventually cools down. The reverse process, i.e., hot cup of tea getting even hotter in a cool surrounding can never take place, even though doing so would not violate the first law of thermodynamics. There exists a directional law which determines the direction in which a spontaneous process will take place. This law is called the second law of thermodynamics.

FIGURE
Processes occur in a certain direction, and not in the reverse direction.

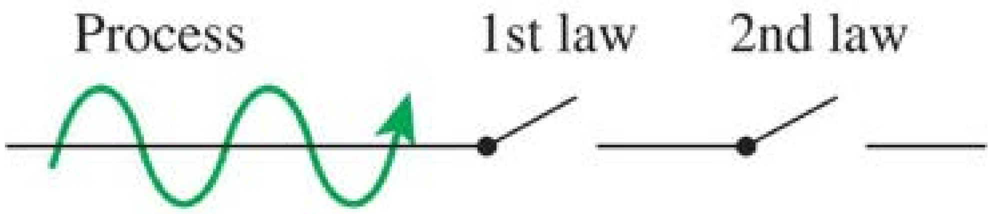


FIGURE
A process must satisfy both the first and second laws of thermodynamics to proceed.

FIGURE
A cup of hot coffee does not get hotter in a cooler room.

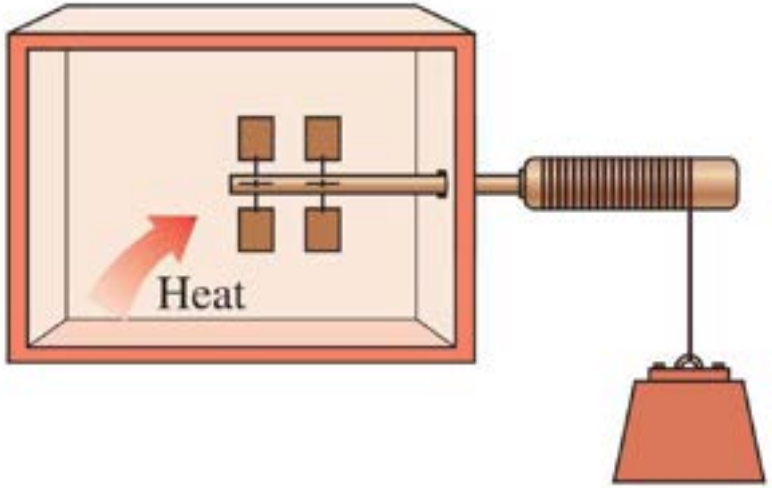


FIGURE
Transferring heat to a paddle wheel will not cause it to rotate.

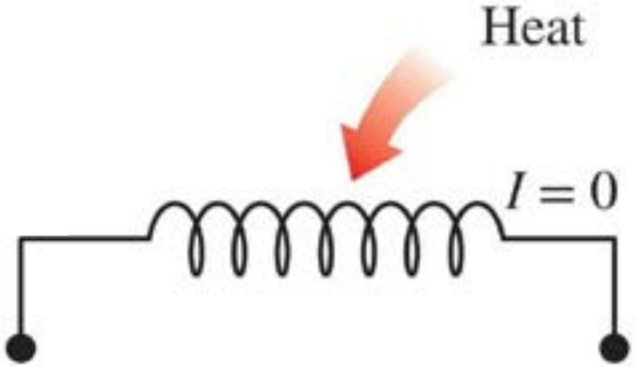


FIGURE
Transferring heat to a wire will not generate electricity.

The use of the second law of thermodynamics is not limited to identifying the direction of processes. The second law also asserts that energy has quality as well as quantity. The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality. Preserving the quality of energy is a major concern to engineers, and the second law provides the necessary means to determine the quality as well as the degree of degradation of energy during a process. As discussed later in this chapter, more of high-temperature energy can be converted to work, and thus it has a higher quality than the same amount of energy at a lower temperature.

The second law of thermodynamics is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators, as well as predicting the degree of completion of chemical reactions. The second law is also closely associated with the concept of perfection. In fact, the second law *defines* perfection for thermodynamic processes. It can be used to quantify the level of perfection of a process and to point in the direction to eliminate imperfections effectively.

THERMAL ENERGY RESERVOIRS

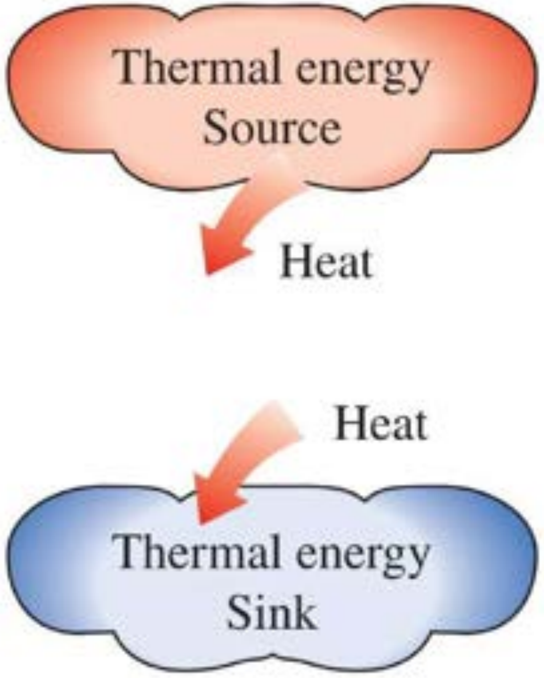
In the development of the second law of thermodynamics, it is very convenient to have a hypothetical body with a relatively large thermal energy capacity (mass × specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature. Such a body is called a thermal energy reservoir, or just a reservoir.

The atmosphere, for example, does not warm up as a result of heat losses from residential buildings in winter. Likewise, megajoules of waste energy dumped into large rivers by power plants do not cause any significant change in water temperature. A body does not actually have to be very large to be considered a reservoir. *Any physical body whose thermal energy capacity is large relative to the amount of energy it supplies or absorbs can be modeled as one.*

FIGURE
Bodies with relatively large thermal masses can be modeled as thermal energy reservoirs.

A reservoir that supplies energy in the form of heat is called a **source**, and one that absorbs energy in the form of heat is called a **Sink**. Thermal energy reservoirs are often referred to as heat reservoirs since they supply or absorb energy in the form of heat.

Heat transfer from industrial sources to the environment is of major concern to environmentalists as well as to engineers. Irresponsible management of waste energy can significantly increase the temperature of portions of the environment, causing what is called ***thermal pollution***. If it is not carefully controlled, thermal pollution can seriously disrupt marine life in lakes and rivers.



FIGURE

A source supplies energy in the form of heat, and a sink absorbs it.

HEAT ENGINES

work can easily be converted to other forms of energy, but converting other forms of energy to work is not that easy. The mechanical work done by the shaft shown in Fig., for example, is first converted to the internal energy of the water. This energy may then leave the water as heat. We know from experience that any attempt to reverse this process will fail. That is, transferring heat to the water does not cause the shaft to rotate. From this and other observations, we conclude that work can be converted to heat directly and completely, but converting heat to work requires the use of some special devices. These devices are called ***heat engines.***

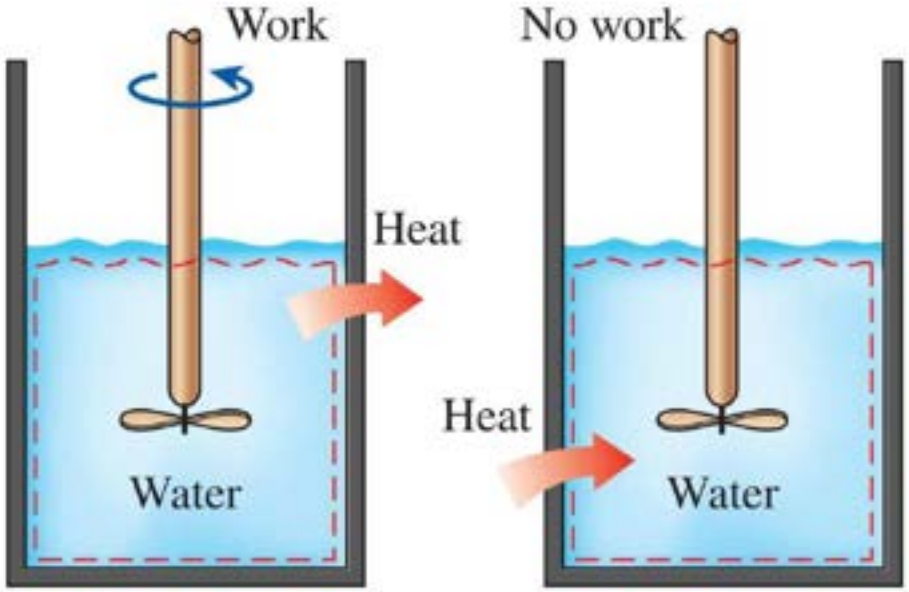


FIGURE
Work can always be converted to heat directly and completely, but the reverse is not true.

Heat engines differ considerably from one another, but all can be characterized by the following :

1. They receive heat from a high-temperature source (solar energy, oil furnace, nuclear reactor, etc.).
2. They convert part of this heat to work (usually in the form of a rotating shaft).
3. They reject the remaining waste heat to a low-temperature sink (the atmosphere, rivers, etc.).
4. They operate on a cycle.

Heat engines and other cyclic devices usually involve a fluid to and from which heat is transferred while undergoing a cycle. This fluid is called the ***working fluid*** or ***Working medium.***

The term *heat engine* is often used in a broader sense to include work producing devices that do not operate in a thermodynamic cycle. Engines that involve internal combustion such as gas turbines and car engines fall into this category.

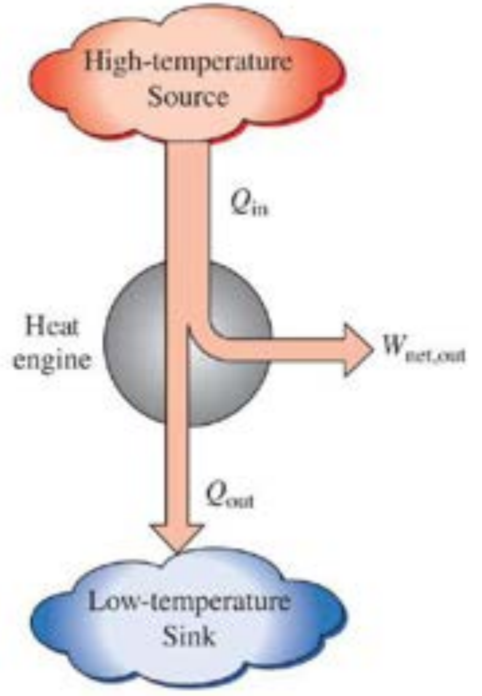
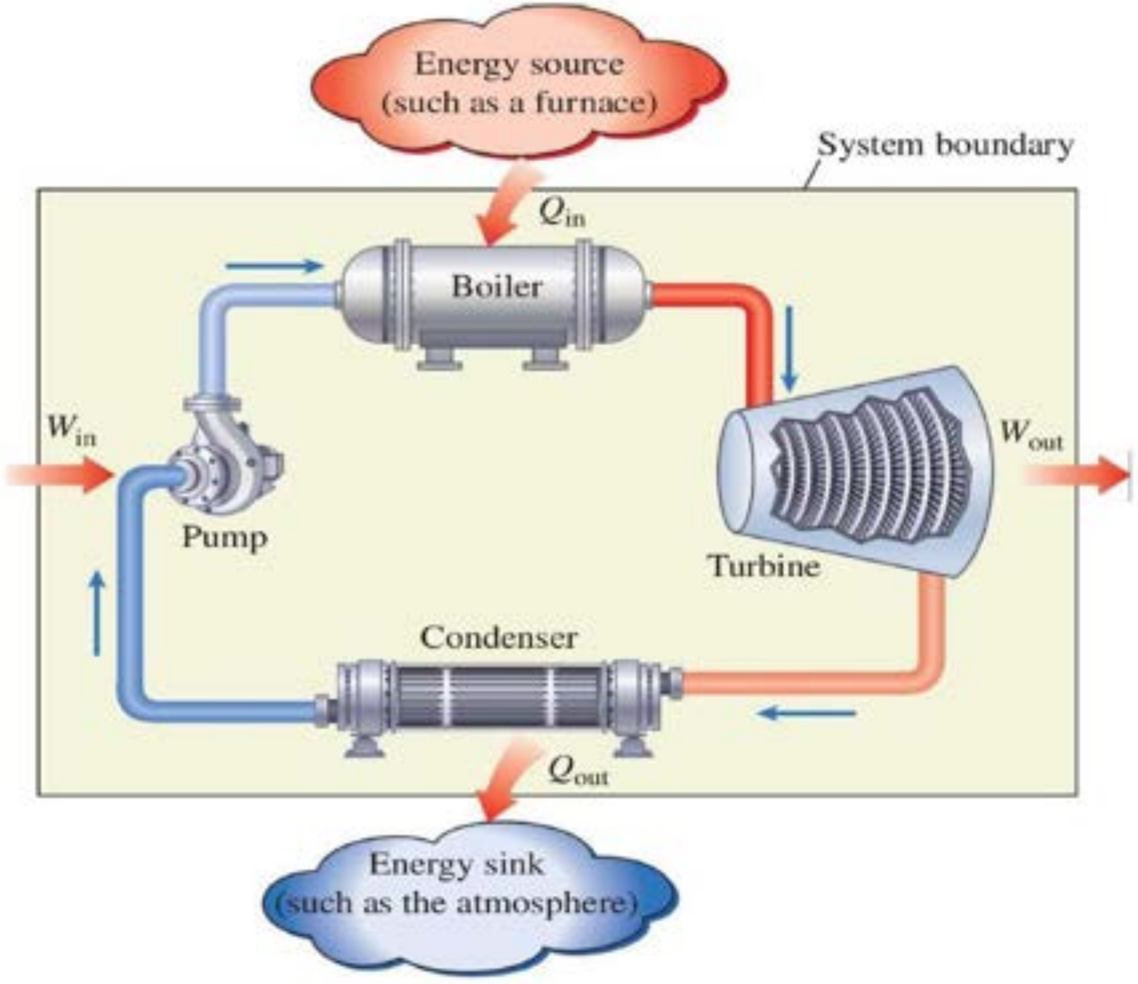
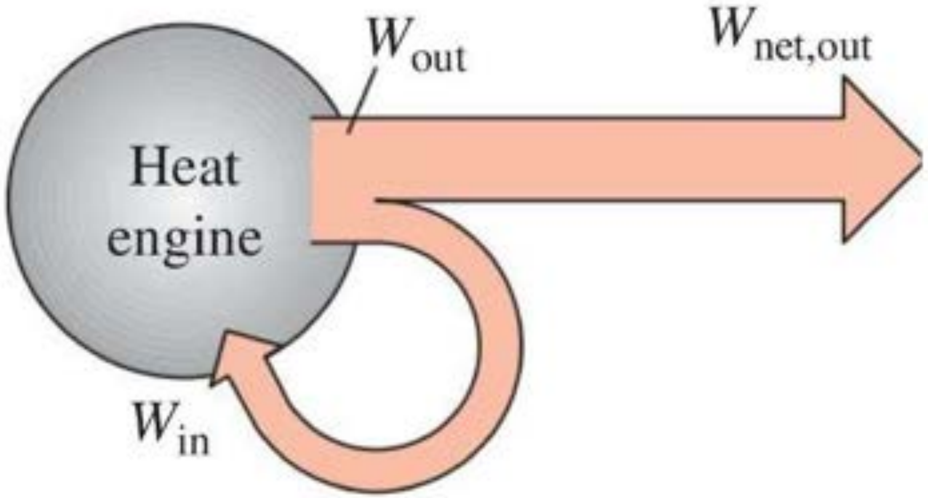


FIGURE
Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

The work-producing device that best fits into the definition of a heat engine is the *steam power plant*, which is an externa-combustion engine. That is, combustion takes place outside the engine, and the thermal energy released during this process is transferred to the steam as heat. The schematic of a basic steam power plant is shown in Fig.



$$W_{net,out} = W_{out} - W_{in} \qquad (kJ)$$



FIGURE

A portion of the work output of a heat engine is consumed internally to maintain continuous operation.

The various quantities shown on this figure are as follows:

Q_{in} = amount of heat supplied to steam in boiler from a high-temperature source (furnace)
Q_{out} = amount of heat rejected from steam in condenser to a low-temperature sink (the atmosphere, a river, etc.)
W_{out} = amount of work delivered by steam as it expands in turbine
W_{in} = amount of work required to compress water to boiler pressure

Notice that the directions of the heat and work interactions are indicated by the subscripts in and out. Therefore, all four of the described quantities are always positive.

Engines that involve internal combustion such as gas turbines and car engines fall into this category. These devices operate in a mechanical cycle but not in a thermodynamic cycle since the working fluid (the combustion gases) does not undergo a complete cycle. Instead of being cooled to the initial temperature, the exhaust gases are purged and replaced by fresh air-and-fuel mixture at the end of the cycle.

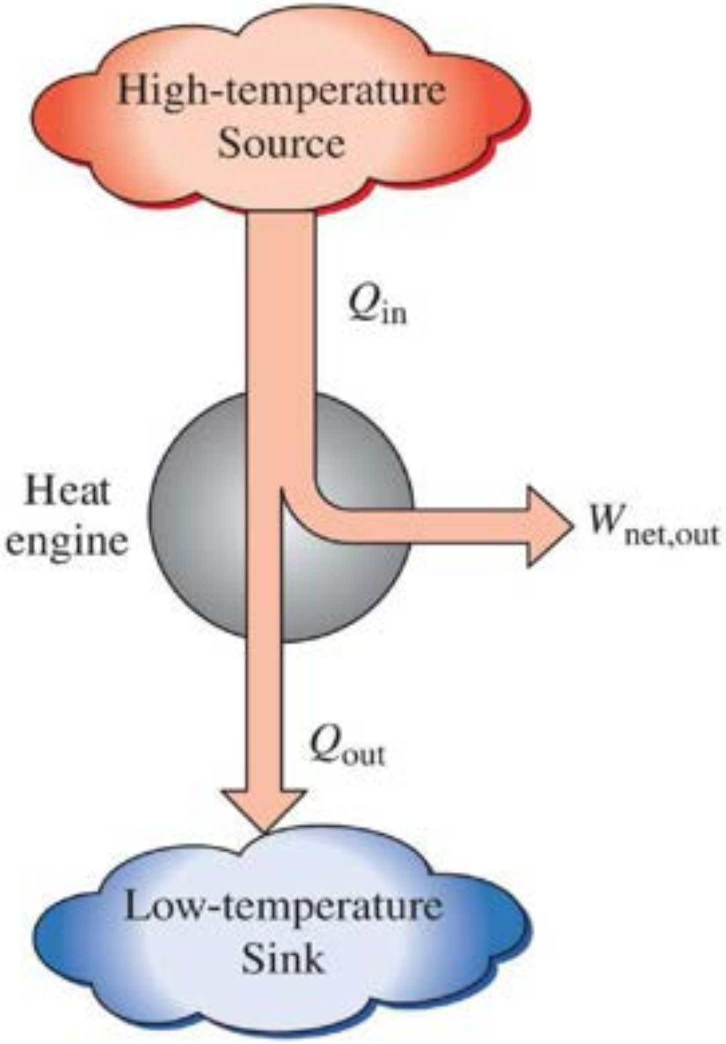


FIGURE
Part of the heat received by a heat engine is converted to work, while the rest is rejected to a sink.

Thermal Efficiency of Heat Engine

An index of performance of a heat engine is expressed by the thermal efficiency η_{ther}. which is defined as the ratio of the net work done to the energy absorbed as heat.

Thermal efficiency, $$\eta_{ther} = \frac{\text{Work done}}{\text{Heat supplied}}$$

Let Q_1 = magnitude of heat transfer between the heat engine and the source

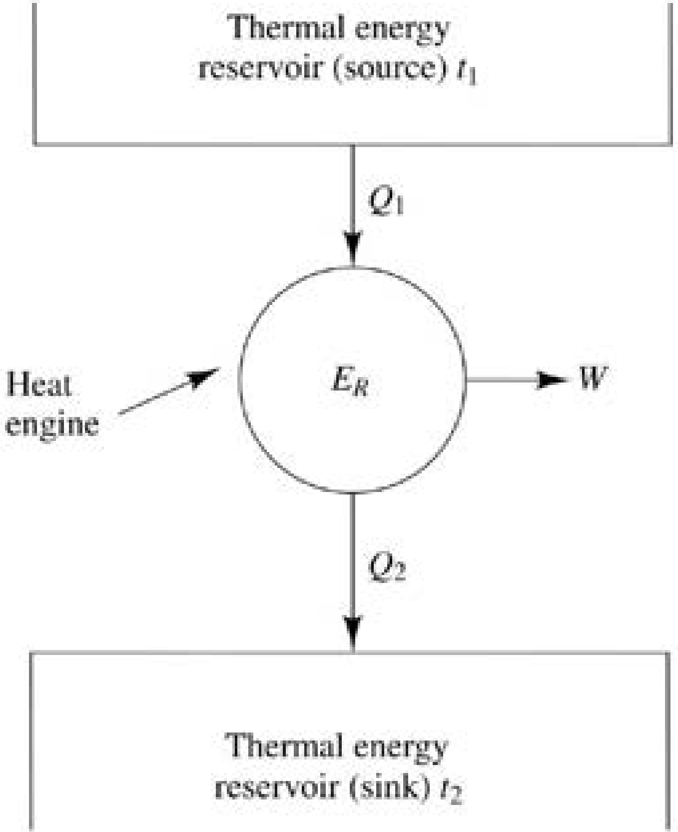
Q_2 = magnitude of heat transfer between the heat engine and the sink

W = Work done by the heat engine

$$\eta_{ther} = \frac{W}{Q_1}$$

Again, applying the first law of thermodynamics, $W = Q_1 - Q_2$

$$\eta_{ther} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$



Schematic diagram of a heat engine

The thermal efficiency of a heat engine is a measure of how successfully it converts the heat received to work. It is always less than unity. Engineers are constantly trying to improve the efficiencies of heat engines.

EXAMPLE **Net Power Production of a Heat Engine**

Heat is transferred to a heat engine from a furnace at a rate of 80 MW. If the rate of waste heat rejection to a nearby river is 50 MW, determine the net power output and the thermal efficiency for this heat engine.

SOLUTION The rates of heat transfer to and from a heat engine are given. The net power output and the thermal efficiency are to be determined.

Assumptions Heat losses through the pipes and other components are negligible.

Analysis A schematic of the heat engine is given in Fig. 6–16. The furnace serves as the high-temperature reservoir for this heat engine and the river as the low-temperature reservoir. The given quantities can be expressed as

$$\dot{Q}_H = 80 \text{ MW} \quad \text{and} \quad \dot{Q}_L = 50 \text{ MW}$$

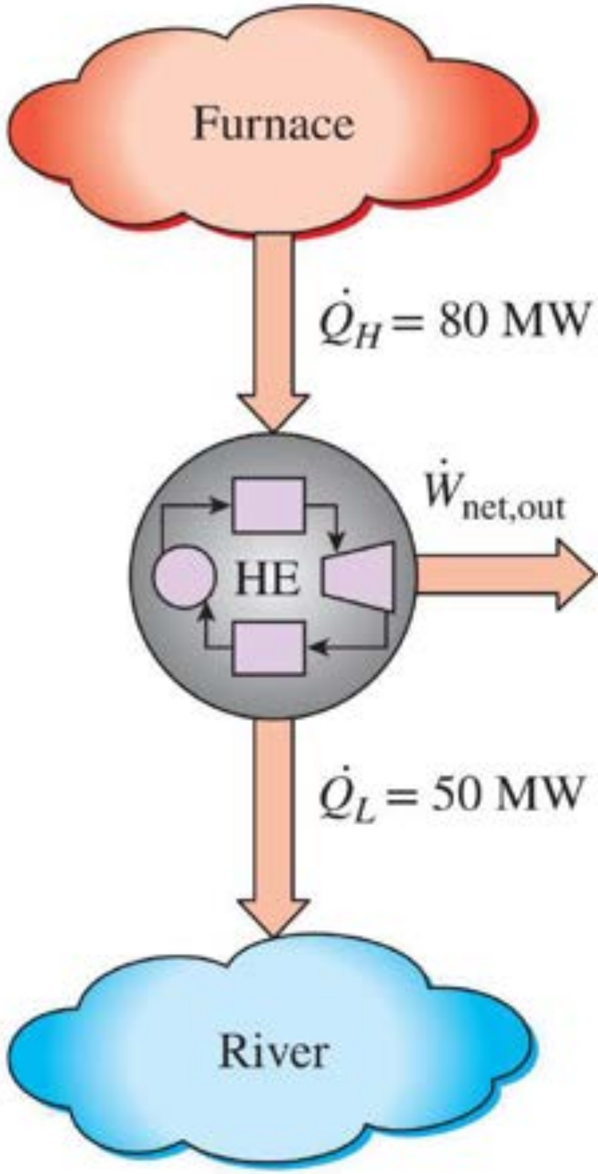
The net power output of this heat engine is

$$\dot{W}_{\text{net,out}} = \dot{Q}_H - \dot{Q}_L = (80 - 50) \text{ MW} = \mathbf{30\ MW}$$

Then the thermal efficiency is easily determined to be

$$\eta_{\text{th}} = \frac{\dot{W}_{\text{net,out}}}{\dot{Q}_H} = \frac{30 \text{ MW}}{80 \text{ MW}} = \mathbf{0.375} \text{ (or 37.5 percent)}$$

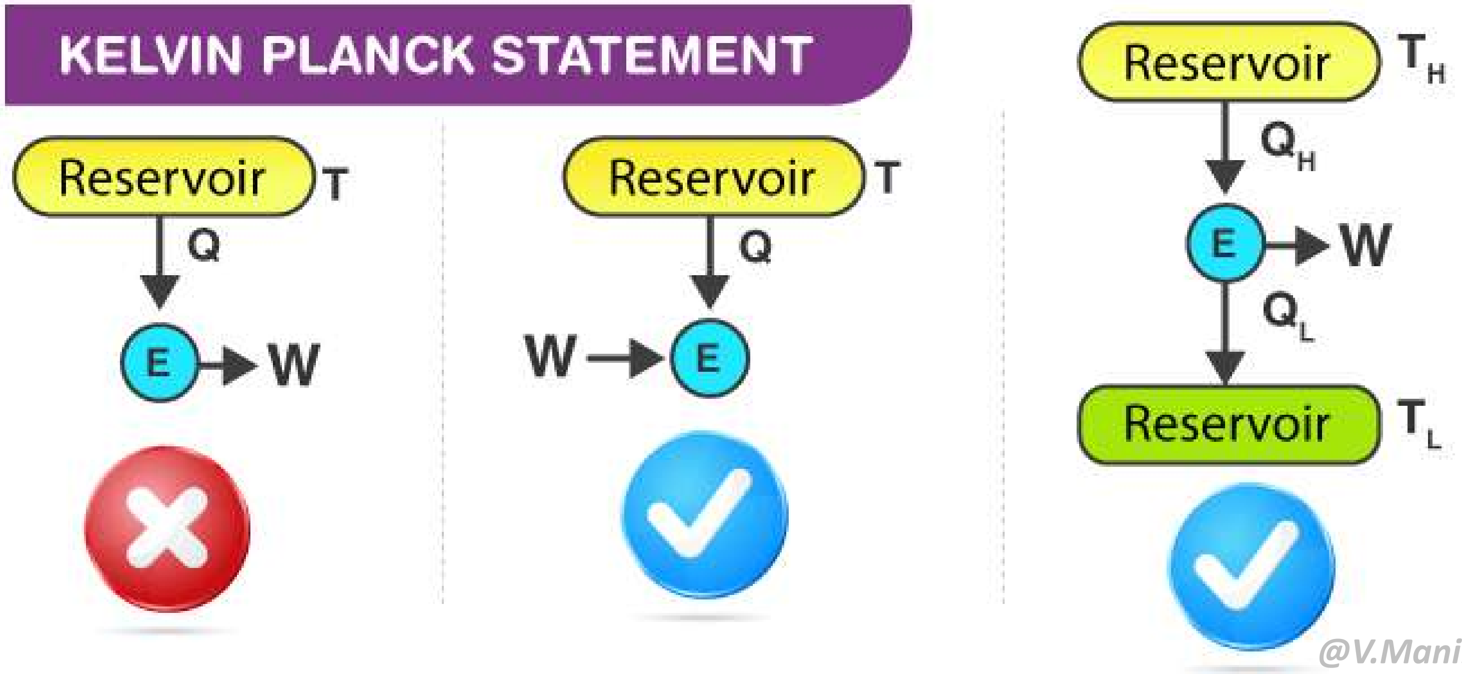
Discussion Note that the heat engine converts 37.5 percent of the heat it receives to work.



The Second Law of Thermodynamics: Kelvin–Planck Statement

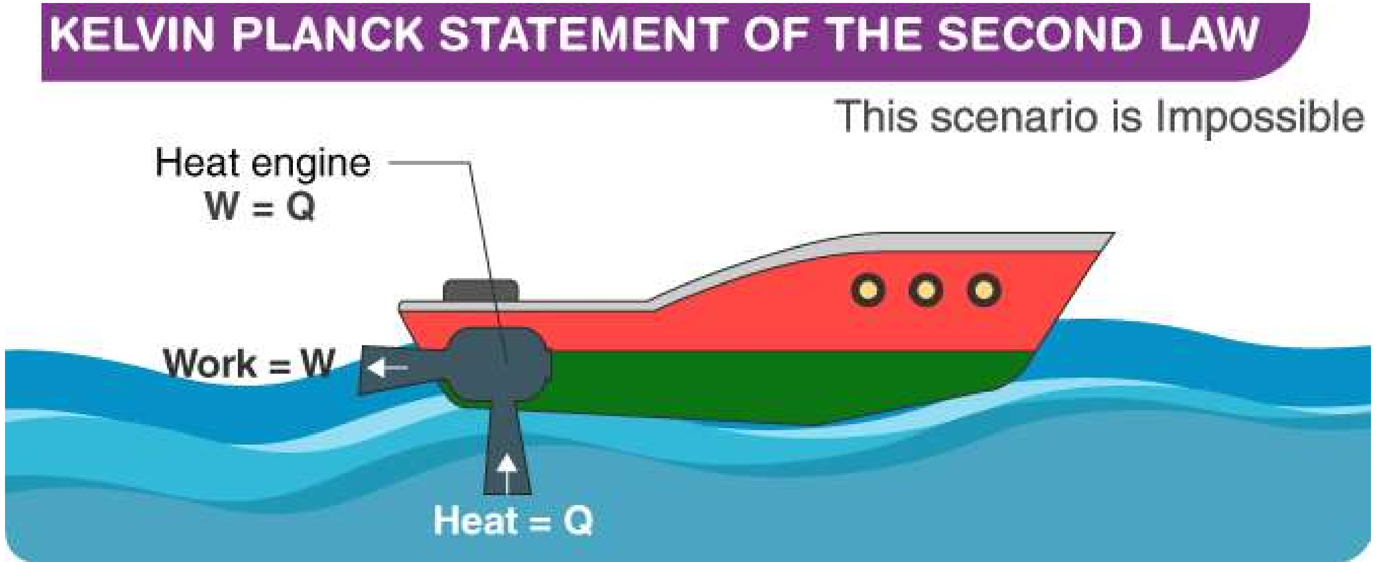
A heat engine even under ideal conditions must reject some heat to a low temperature reservoir in order to complete the cycle. That is, no heat engine can convert all the heat it receives to useful work. This limitation on the thermal efficiency of heat engines forms the basis for the Kelvin–Planck statement of the second law of thermodynamics, which is expressed as follows:

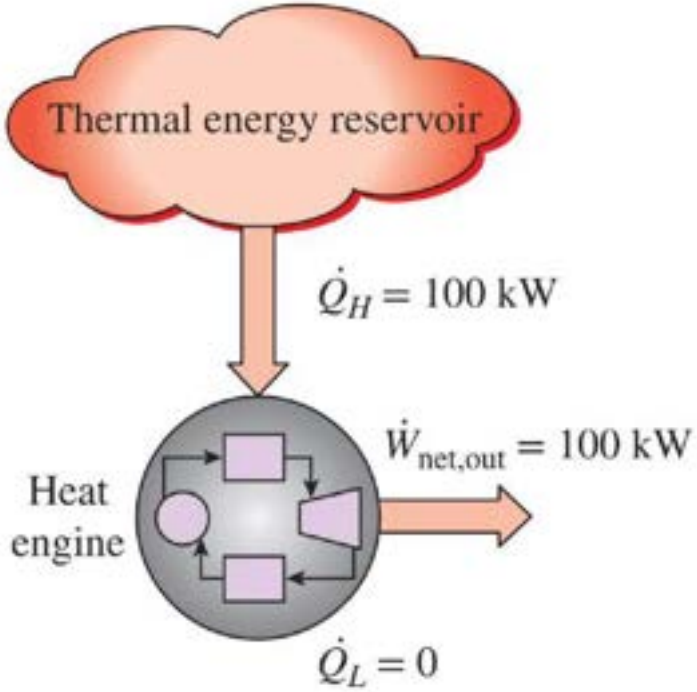
"It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work."



That is, a heat engine must exchange heat with a low-temperature sink as well as a high-temperature source to keep operating. The Kelvin–Planck statement can also be expressed as *no heat engine can have a thermal efficiency of 100 percent (Fig.), or as for a power plant to operate, the working fluid must exchange heat with the environment as well as the furnace.*

Note that the impossibility of having a 100 percent efficient heat engine is not due to friction or other dissipative effects. It is a limitation that applies to both the idealized and the actual heat engines.





FIGURE

A heat engine that violates the Kelvin–Planck statement of the second law.

REFRIGERATORS AND HEAT PUMPS

We know that heat is transferred spontaneously from a high temperature medium to a low temperature medium. The reverse process, however, cannot occur by itself. The transfer of heat from a low temperature medium to a high temperature medium requires special devices called *Refrigerators* and *heat pumps*.

Refrigerators and heat pumps are simply heat engines operated in the reverse direction.

The objective of a *refrigerator* is to maintain the refrigerated space at a low temperature by removing heat from it. A refrigerator operates between the ambient temperature and a low temperature

The objective of a *heat pump* is to reject heat to a high temperature body. A heat pump operates between the ambient temperature and a high temperature

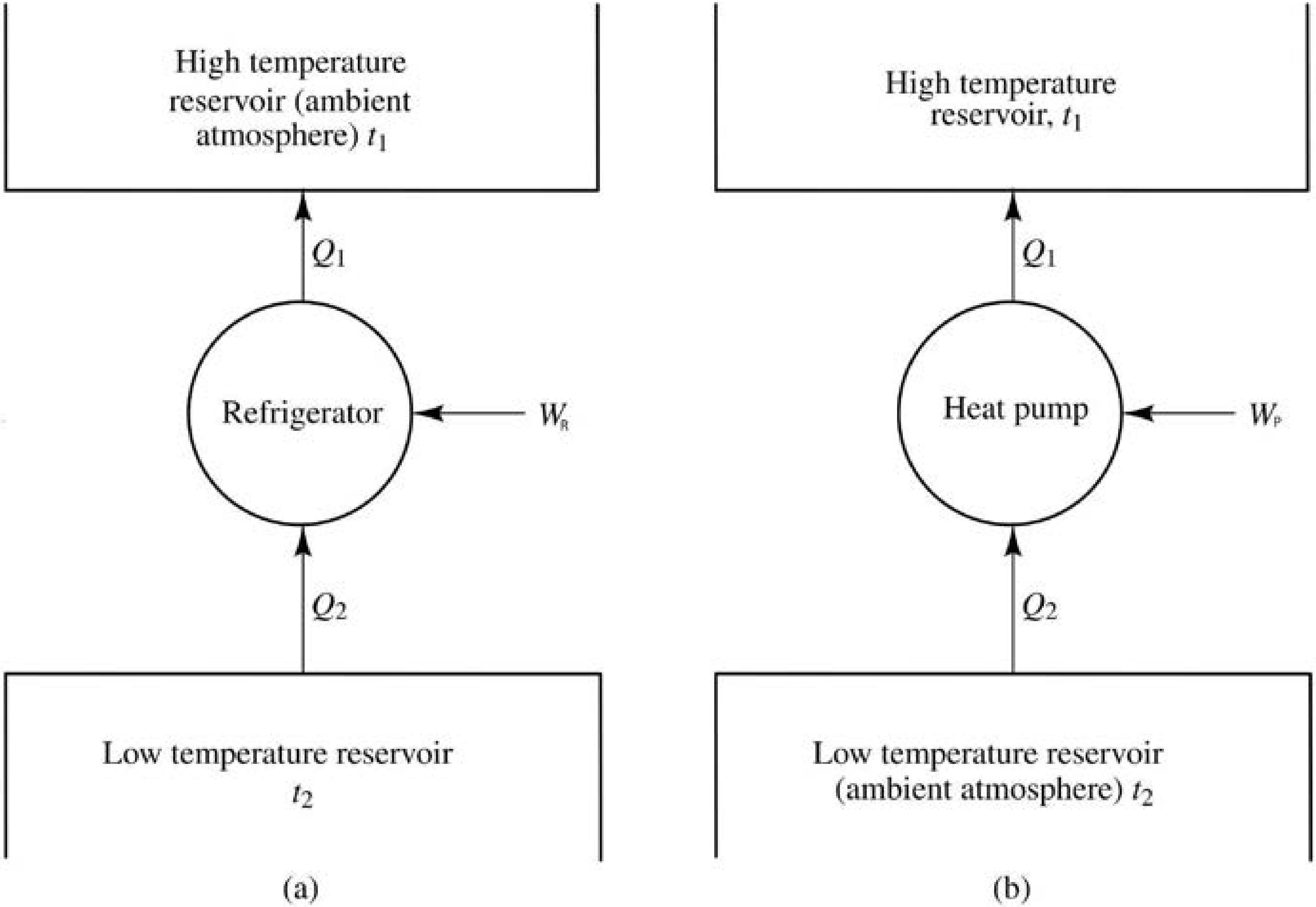


Figure *Schematic diagram of (a) a refrigerator and (b) a heat pump*

REFRIGERATORS

We all know from experience that heat is transferred in the direction of decreasing temperature, that is, from high-temperature mediums to low temperature ones. This heat transfer process occurs in nature without requiring any devices. The reverse process, however, cannot occur by itself. The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called *refrigerators*. Refrigerators, like heat engines, are cyclic devices. The working fluid used in the refrigeration cycle is called a *refrigerant*.

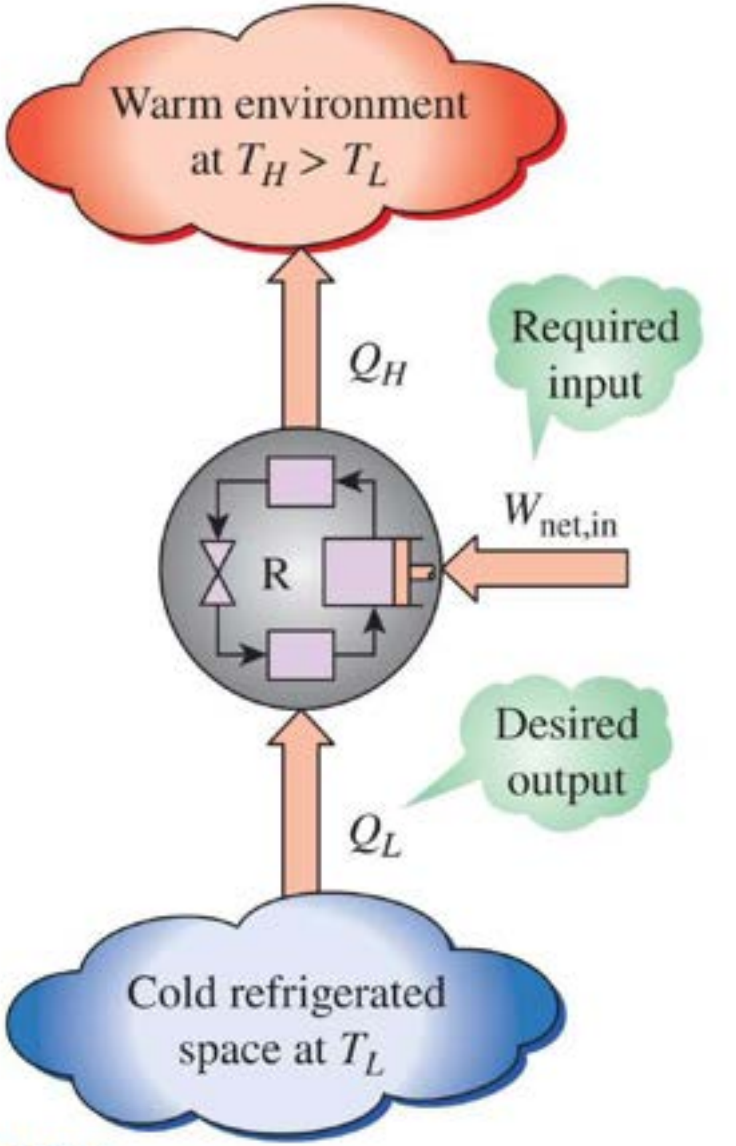
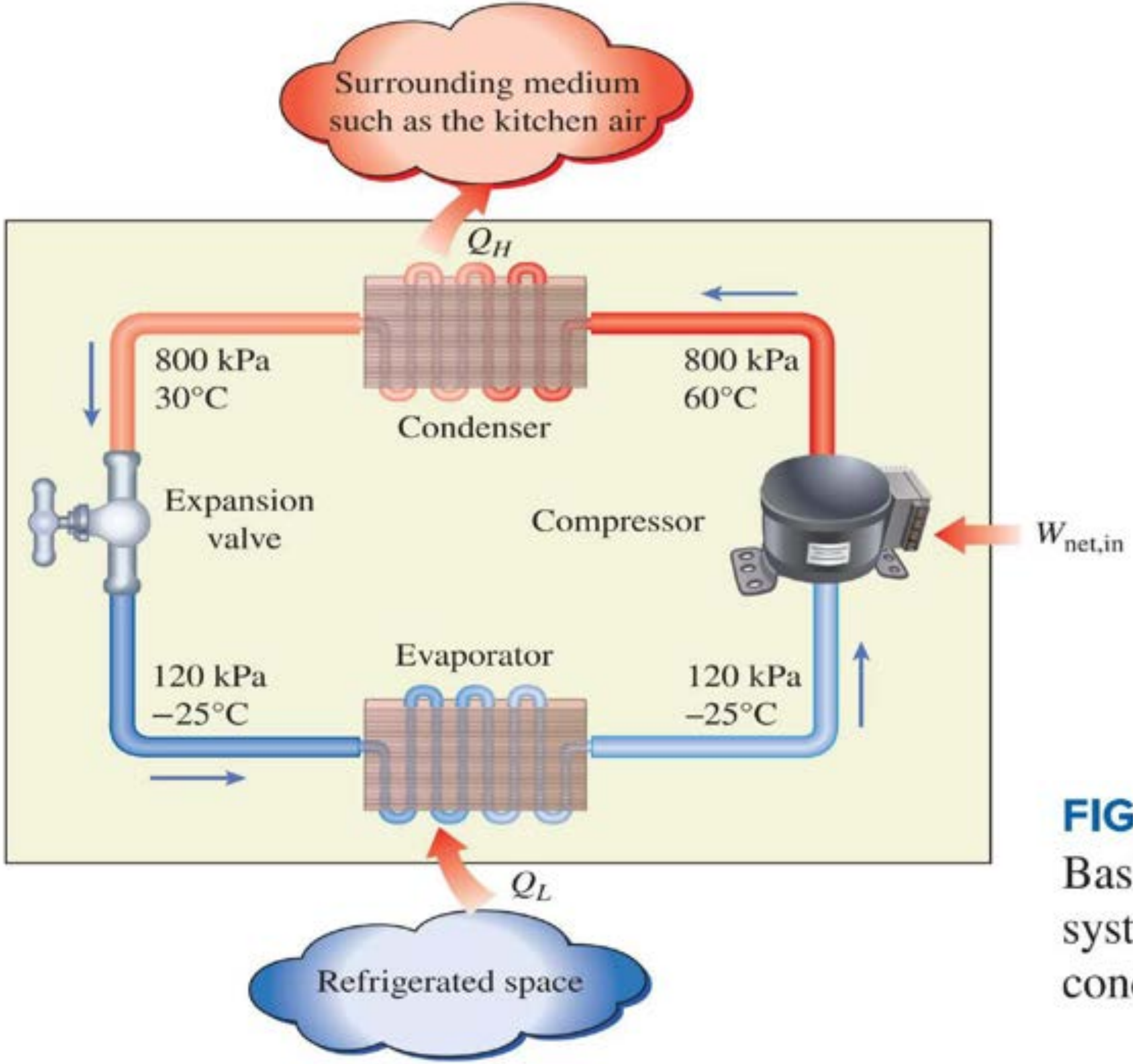


FIGURE
The objective of a refrigerator is to remove Q_L from the cooled space.



FIGURE

Basic components of a refrigeration system and typical operating conditions.

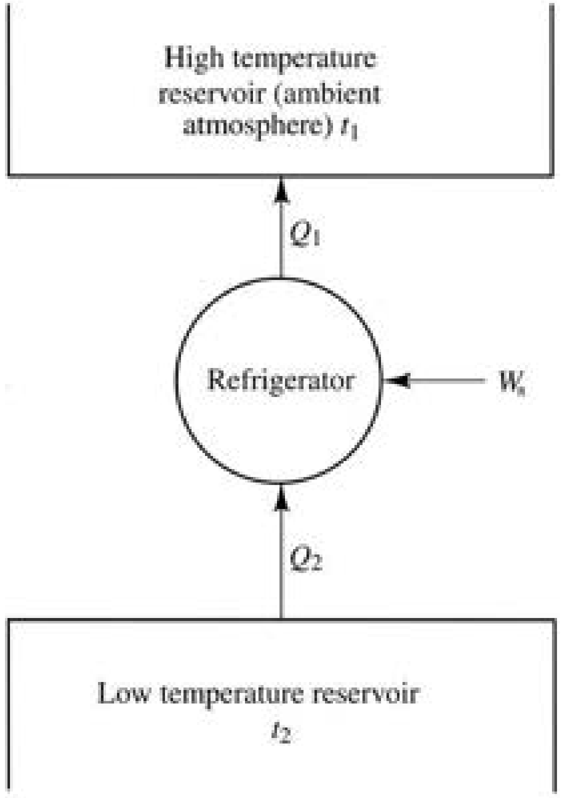
Coefficient of Performance (COP) of a Refrigerator:

For a refrigerator, the performance parameter is not called efficiency, because that term is usually reserved for the ratio of output to input. The ratio of output to input would be misleading applied to a refrigeration system because the output is usually wasted. The concept of performance parameter of the refrigeration cycle is tantamount to efficiency of the heat engine. The efficiency of a refrigerator is expressed in terms of the coefficient of performance (COP), denoted by $\mathbf{COP_R}$. The objective of a refrigerator is to remove heat ($\mathbf{Q_2}$) from the refrigerated space. To accomplish this

$$\mathrm{COP_R} = \frac{\text{Desired output}}{\text{Required input}}$$

$$[\mathrm{COP}]_R = \frac{\text{Useful refrigeration}}{\text{Net work}}$$

$$\mathrm{COP}_R = \frac{Q_2}{Q_1 - Q_2}$$



Notice that the value of **COP_R** can be greater than unity. That is, the amount of heat removed from the refrigerated space can be greater than the amount of work input. This is in contrast to the thermal efficiency, which can never be greater than 1. In fact, one reason for expressing the efficiency of a refrigerator with another term—the *coefficient of performance*—is the desire to avoid the oddity of having efficiencies greater than unity.

EXAMPLE Analysis of a Household Refrigerator

A household refrigerator with a COP of 1.2 removes heat from the refrigerated space at a rate of 60 kJ/min (Fig. 6-23). Determine (*a*) the electric power consumed by the refrigerator and (*b*) the rate of heat transfer to the kitchen air.

SOLUTION The COP and the refrigeration rate of a refrigerator are given. The power consumption and the rate of heat rejection are to be determined.

Assumptions The refrigerator operates steadily.

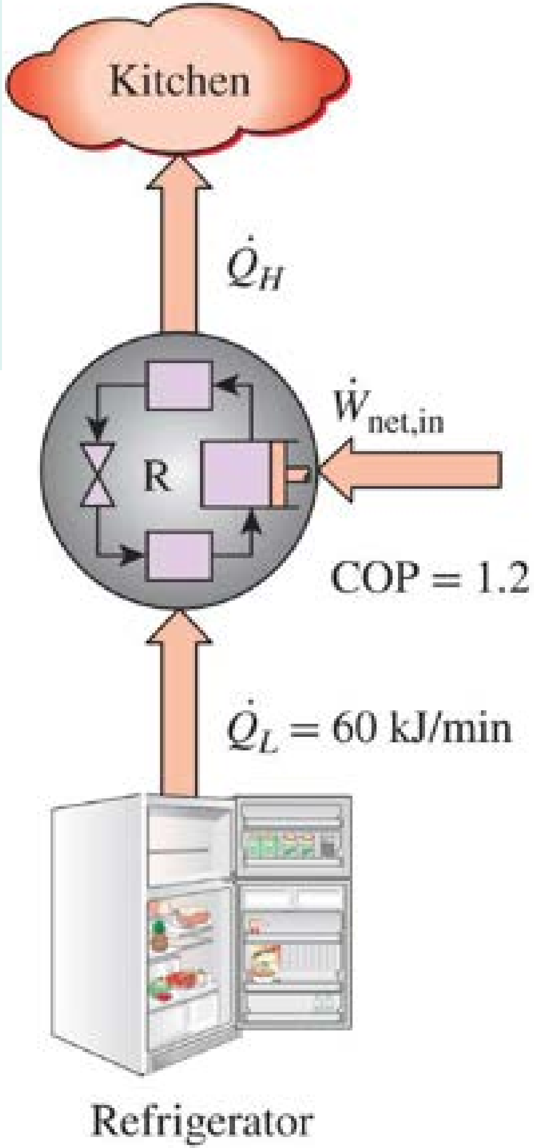
Analysis (*a*) Using the definition of the coefficient of performance, the power input to the refrigerator is determined to be

$$\dot{W}_{\text{net,in}} = \frac{\dot{Q}_L}{\text{COP}_\text{R}} = \frac{60\ \text{kJ/min}}{1.2} = 50\ \text{kJ/min} = \mathbf{0.833\ kW}$$

(*b*) The heat transfer rate to the kitchen air is determined from the energy balance,

$$\dot{Q}_H = \dot{Q}_L + \dot{W}_{\text{net,in}} = 60 + 50 = \mathbf{110\ kJ/min}$$

Discussion Notice that both the energy removed from the refrigerated space as heat and the energy supplied to the refrigerator as electrical work eventually show up in the room air and become part of the internal energy of the air. This demonstrates that energy can change from one form to another and can move from one place to another, but it is never destroyed during a process.



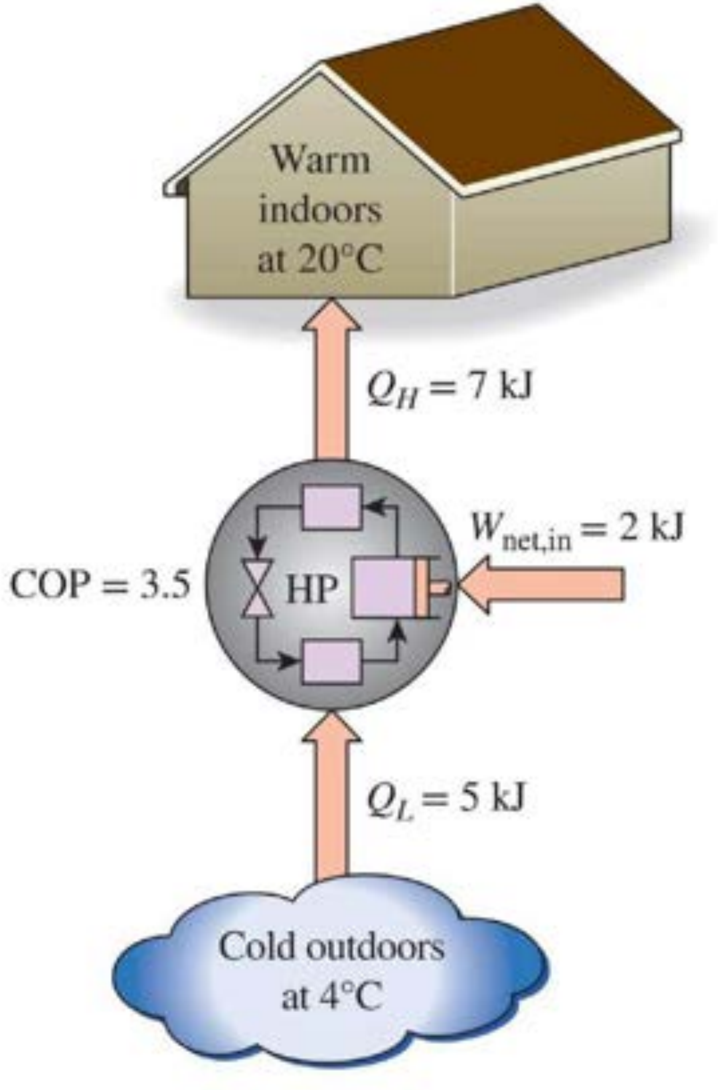
FIGURE

Schematic for Example

Heat Pumps

Another device that transfers heat from a low-temperature medium to a high temperature one is the ***heat pump***, shown schematically in Fig. Refrigerators and heat pumps operate on the same cycle but differ in their objectives.

The objective of a heat pump, however, is to maintain a heated space at a high temperature. This is accomplished by absorbing heat from a low-temperature source, such as well water or cold outside air in winter, and supplying this heat to the high-temperature medium such as a house



FIGURE

The work supplied to a heat pump is used to extract energy from the cold outdoors and carry it into the warm indoors.

An ordinary refrigerator that is placed in the window of a house with its door open to the cold outside air in winter will function as a heat pump since it will try to cool the outside by absorbing heat from it and rejecting this heat into the house through the coils behind it.

Air conditioners are basically refrigerators whose refrigerated space is a room or a building instead of the food compartment. A window air conditioning unit cools a room by absorbing heat from the room air and discharging it to the outside. The same air-conditioning unit can be used as a heat pump in winter by installing it backwards. In this mode, the unit absorbs heat from the cold outside and delivers it to the room. Air-conditioning systems that are equipped with proper controls and a reversing valve operate as air conditioners in summer and as heat pumps in winter.

FIGURE
When installed backward, an air conditioner functions as a heat pump.

Coefficient of Performance (COP) of a Heat Pump:

The objective of a heat pump is to pump in heat to a chamber for the purpose of heating and this is also possible only when some work is expended.

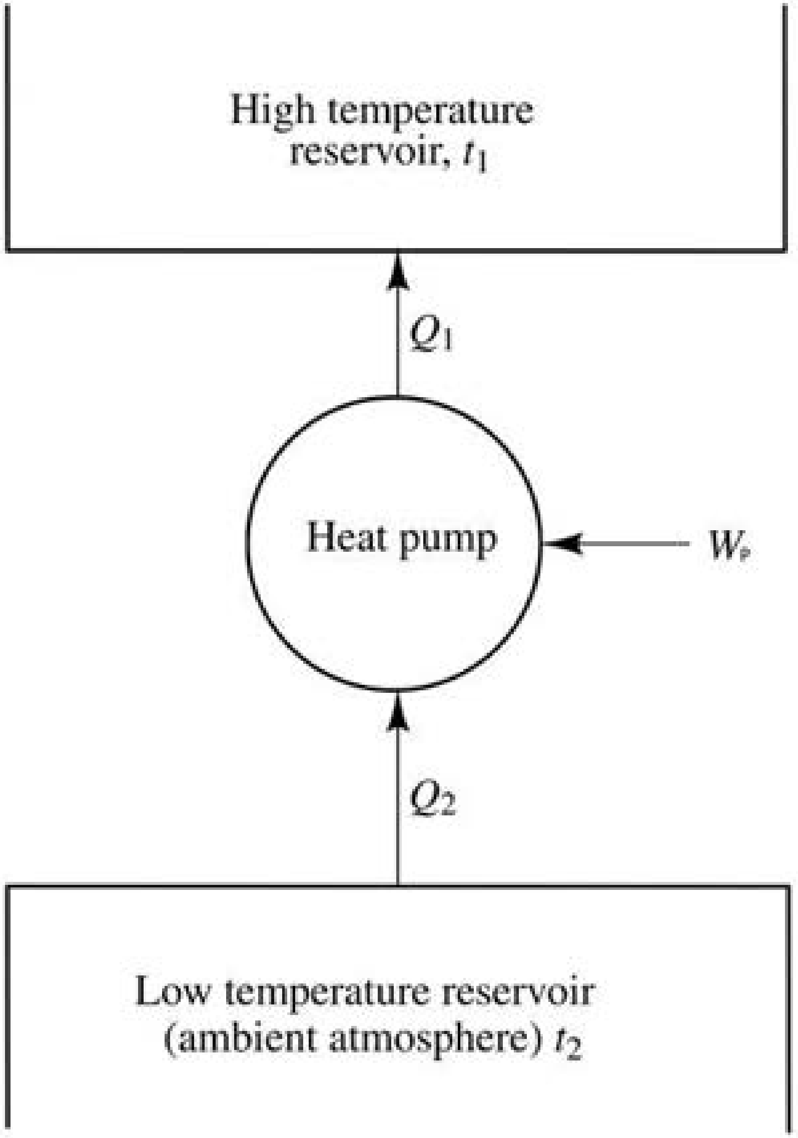
Hence,
$$[\mathrm{COP}]_{HP} = \frac{\text{Heat delivered to the chamber}}{\text{Net work}}$$

$$\mathrm{COP}_{HP} = \frac{Q_1}{Q_1 - Q_2}$$

From the expression of COP of refrigerator and heat pump, it is evident that the two are related by the following expressions.

$$\boxed{\mathrm{COP}_{HP} = \mathrm{COP}_R + 1}$$

- **The COP of a heat pump is greater than the COP of a refrigerator by unity.**
- **The coefficient of performance of a heat pump is always greater than unity since COPR is a positive quantity.**



Applications of Heat pumps:

- Heating, ventilation, and air conditioning (HVAC) of schools, hospitals, commercial buildings, restaurants, hotels, health clubs etc.,
- Water heating of houses, swimming pools, commercial buildings etc.,
- District heating
- Industrial heating and industrial washing machines
- Automobiles cabin space heating
- To maintain Indoor environmental quality (IEQ) in industries and large commercial spaces.

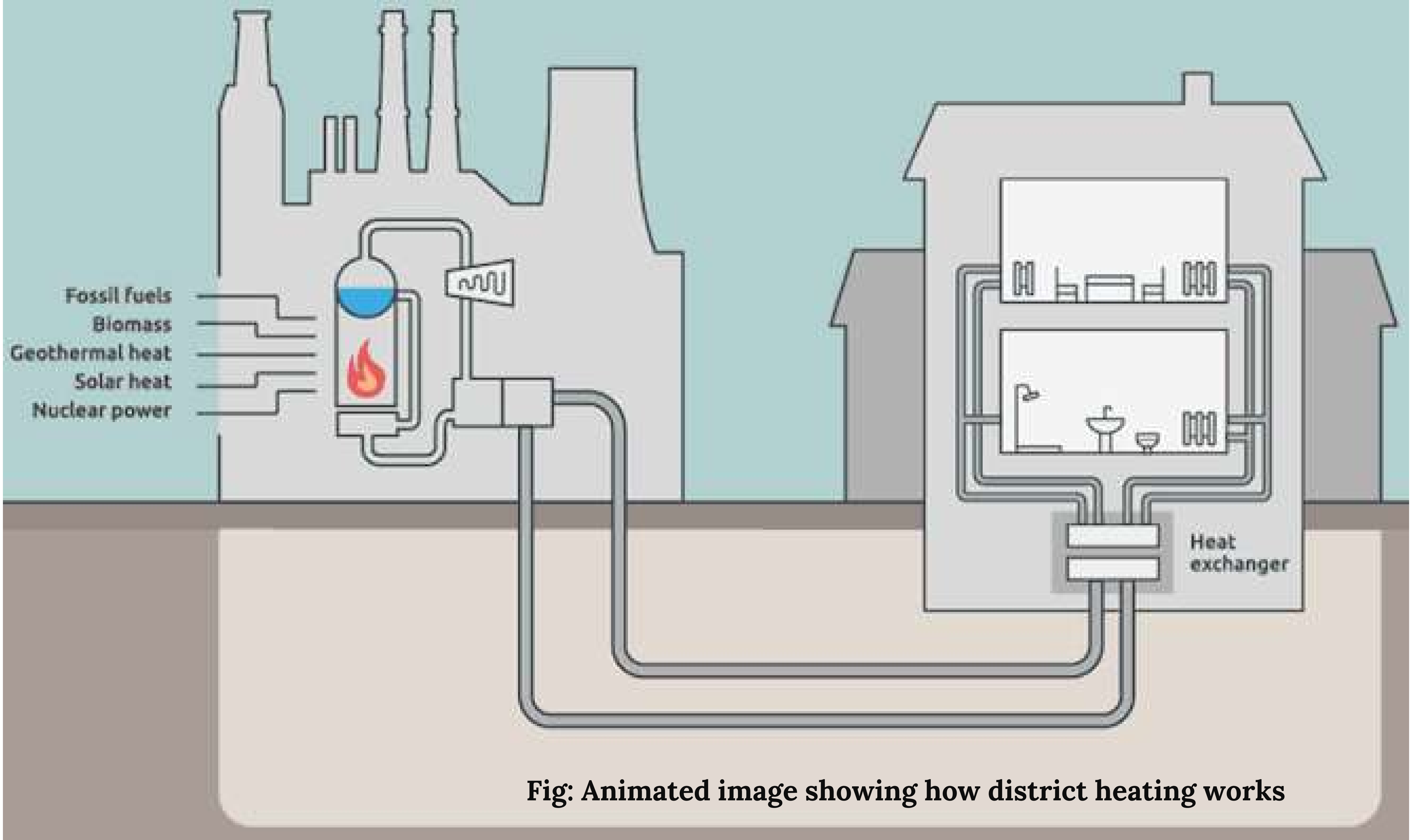
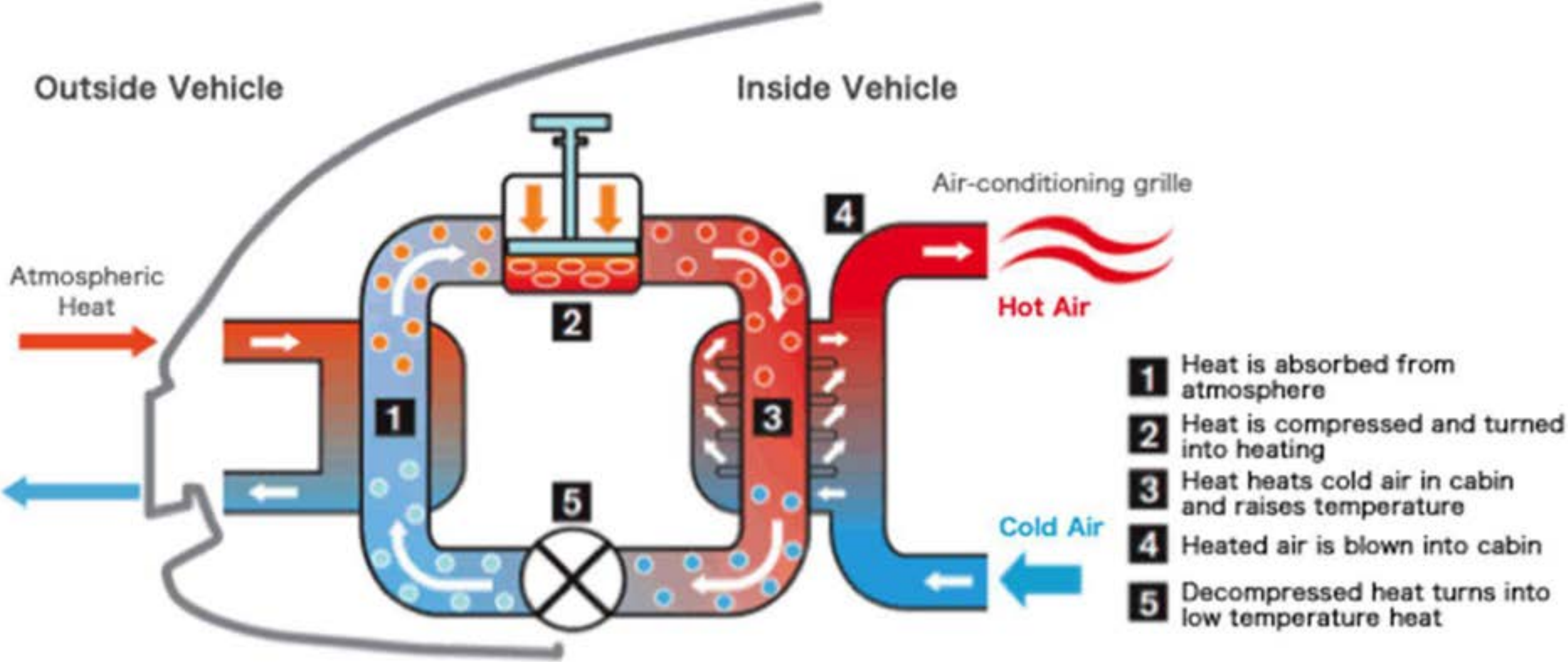


Fig: Animated image showing how district heating works

Model Y is the first Tesla with a heat pump



1 Heat is absorbed from atmosphere
2 Heat is compressed and turned into heating
3 Heat heats cold air in cabin and raises temperature
4 Heated air is blown into cabin
5 Decompressed heat turns into low temperature heat

Diagram of a Nissan Leaf heat pump. | Image source: Nissan

Heat Pump vs Electric Resistance Heater

For the purpose of heating, the use of a heat pump is more economical than an electric resistance heater.

$$\text{COP}_{HP} = \text{COP}_R + 1 \tag{5.5}$$

Since, COP_R is a positive quantity, from Eq. (5.5) it is clear that COP_{HP} is always greater than unity.

If W is the energy consumption of an electric resistance heater, the heat released by the heater to the space will be W only.

Now, if the same amount of energy is utilized to run a heat pump, the heat pumped to the space will be

$$Q_1 = \text{COP}_{HP} \,.\, W \tag{5.6}$$

From Eq. (5.6), Q_1 will always be greater than W.

Let the COP_{HP} be 3.

The power consumption by an electric resistance heater

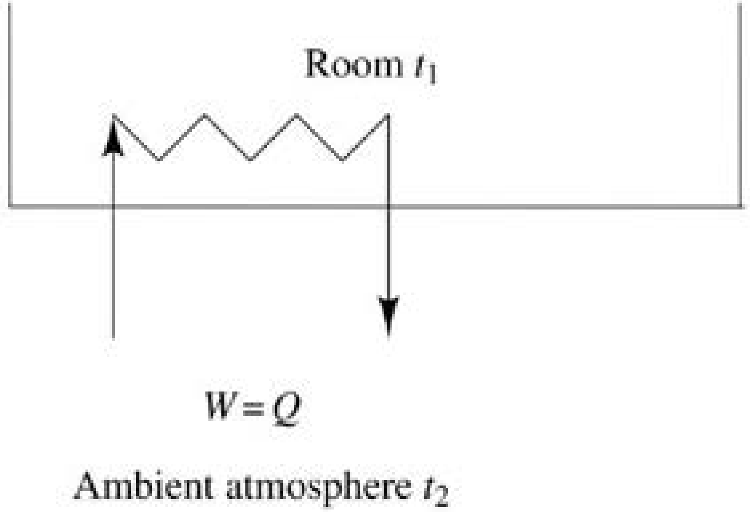
$$\dot{W} = \dot{Q}_1$$

The power consumption by a heat pump is

$$\dot{W} = \frac{\dot{Q}_1}{\text{COP}_{HP}} = \frac{\dot{Q}_1}{3}$$

Thus, the power consumption of the heat pump is lower than that of the electric resistance heater.

Therefore, heat pump is more effective than electric resistance heater.



(a) an electric resistance heater

The Second Law of Thermodynamics: Clausius Statement

There are two classic statements of the second law—the Kelvin–Planck statement, which is related to heat engines and discussed in the preceding section, and the Clausius statement, which is related to refrigerators or heat pumps.

The Clausius statement is expressed as follows:

“It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.”

It is common knowledge that heat does not, of its own volition, transfer from a cold medium to a warmer one. The Clausius statement does not imply that a cyclic device that transfers heat from a cold medium to a warmer one is impossible to construct. In fact, this is precisely what a common household refrigerator does. It simply states that a refrigerator cannot operate unless its compressor is driven by an external power source, such as an electric motor.

Both the Kelvin–Planck and the Clausius statements of the second law are negative statements, and a negative statement cannot be proved. Like any other physical law, the second law of thermodynamics is based on experimental observations. To date, no experiment has been conducted that contradicts the second law, and this should be taken as sufficient proof of its validity.

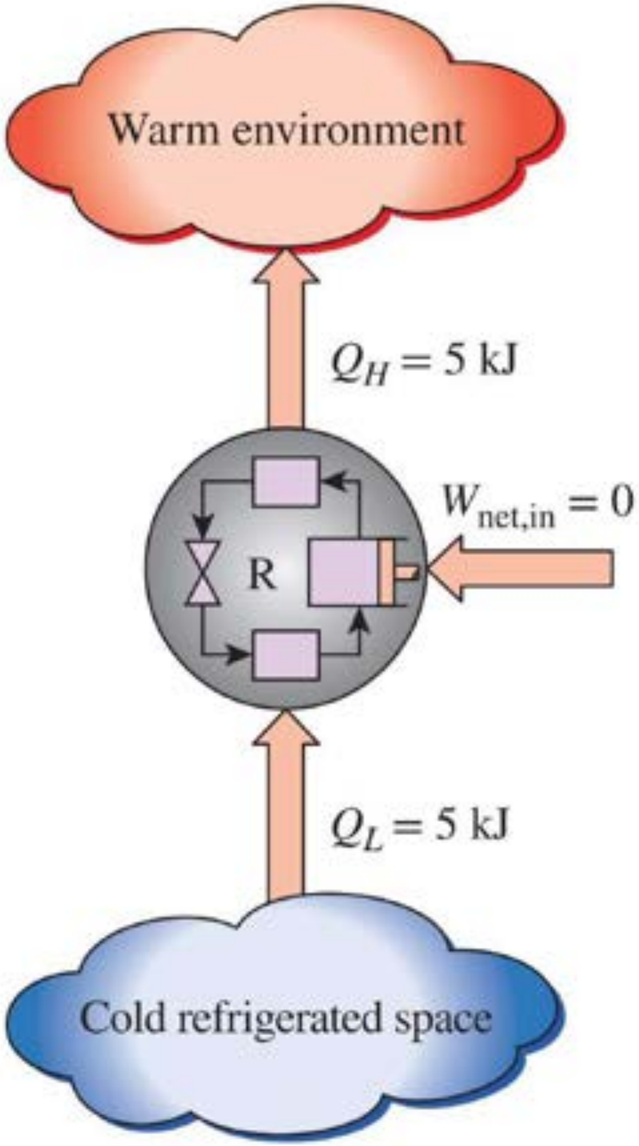


FIGURE
A refrigerator that violates the Clausius statement of the second law.

EQUIVALENCE OF KELVIN–PLANCK AND CLAUSIUS STATEMENTS

At first, it appears as if the Kelvin–Planck and Clausius statements are different together. However, it can be shown that the Kelvin-Planck and Clausius statements are in fact, equivalent. The equivalence of the Kelvin–Planck and Clausius statements is demonstrated by showing that the violation of each statement implies the violation of the other.

To prove that violation of the Kelvin–Planck statement leads to a violation of the Clausius statement, let us suppose that the Kelvin–Planck statement is wrong. That is, it is possible to construct a heat engine, which, operating on a cycle, absorbs heat (Q1) from a source at temperature t1 and produces an equivalent amount of work (W = Q1). Suppose that a heat pump also operates between the same two reservoirs and uses up all the work produced by the heat engine. The engine and pump together constitute a heat pump that transfers heat from the low-temperature reservoir to the high-temperature reservoir without producing any changes elsewhere. Therefore, the engine and the pump together constitute a heat pump that violates the Clausius statement.

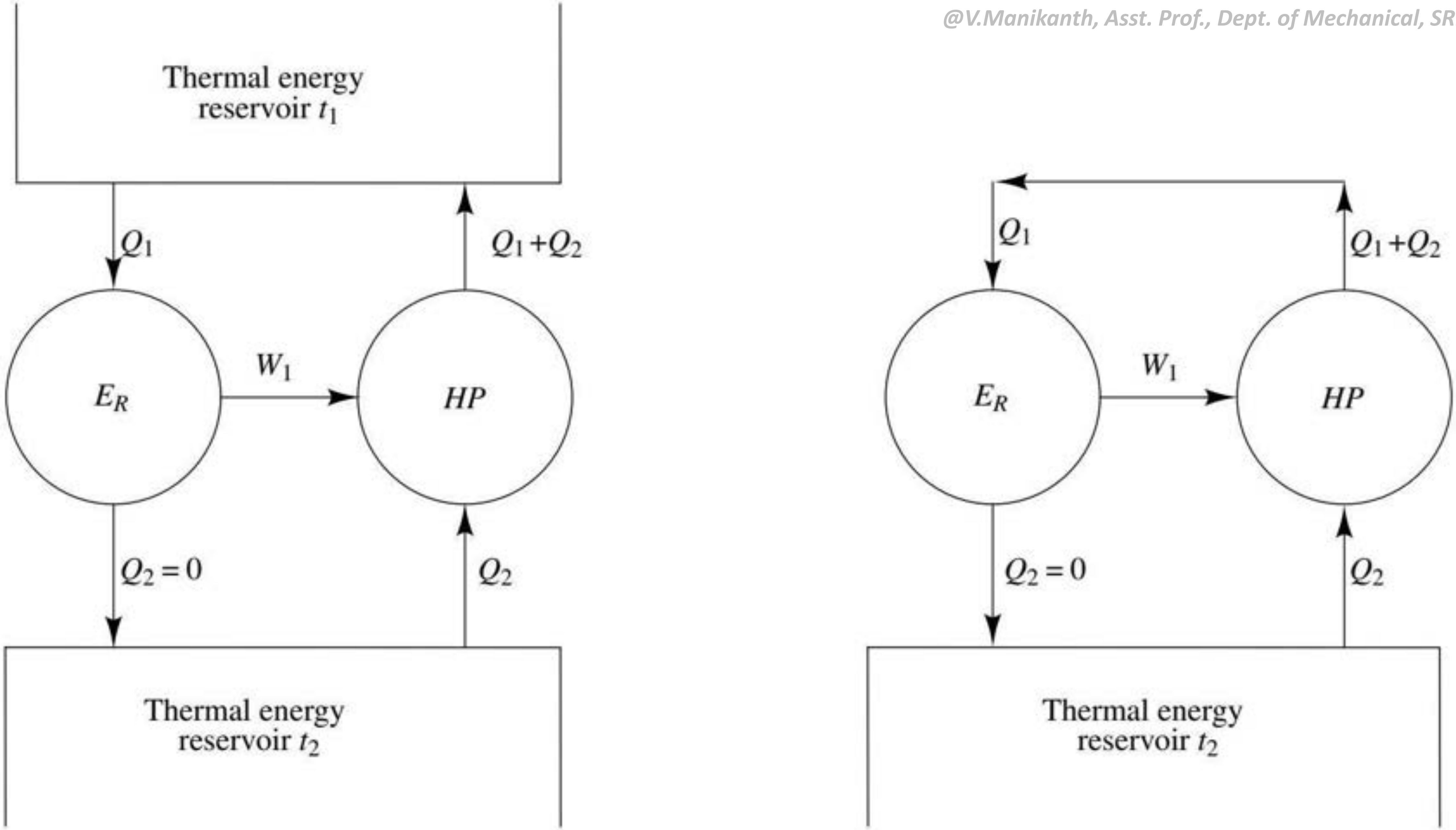
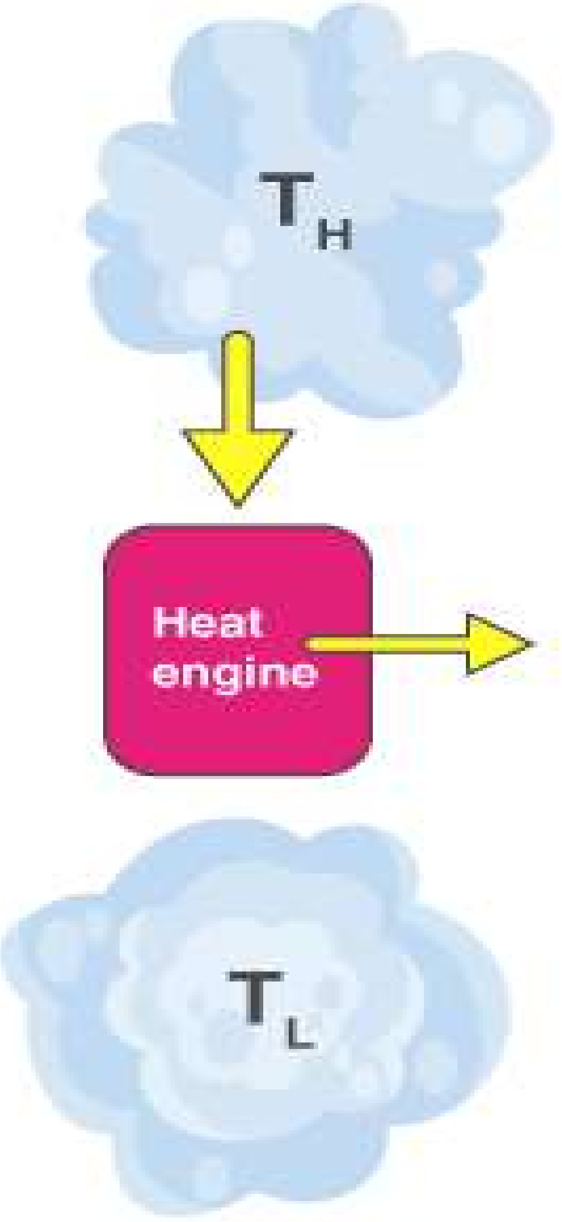
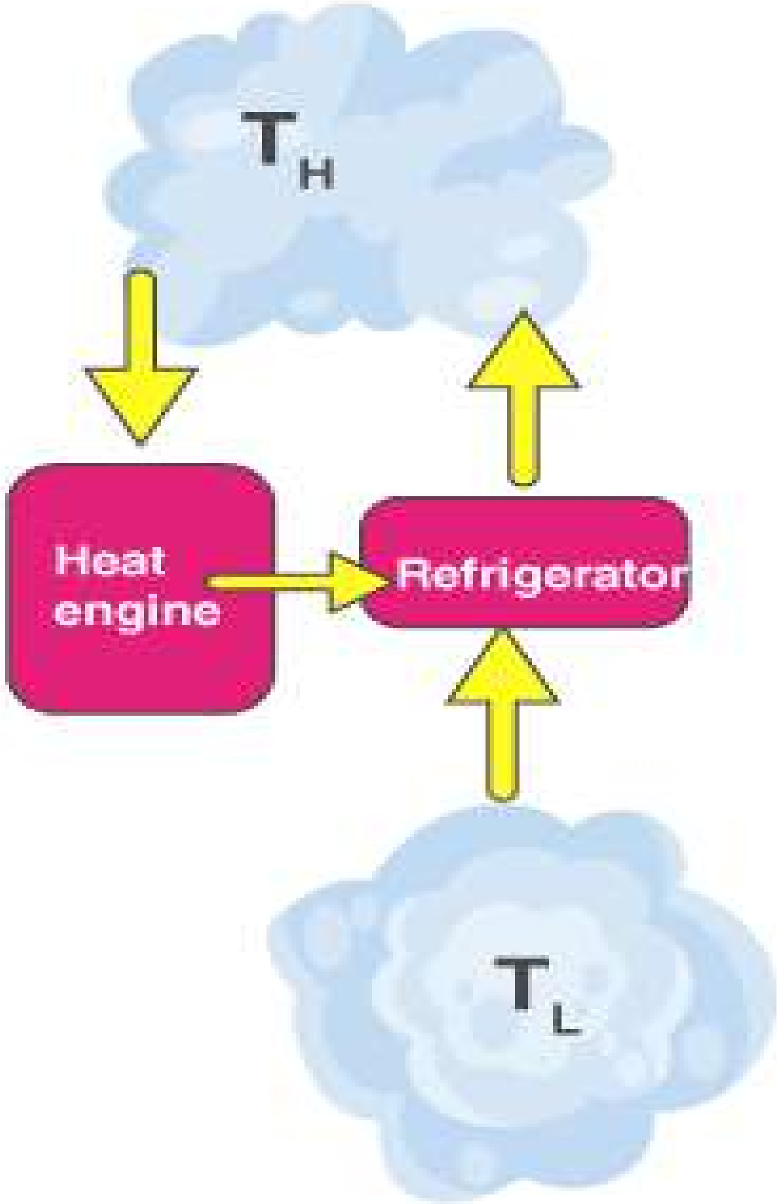


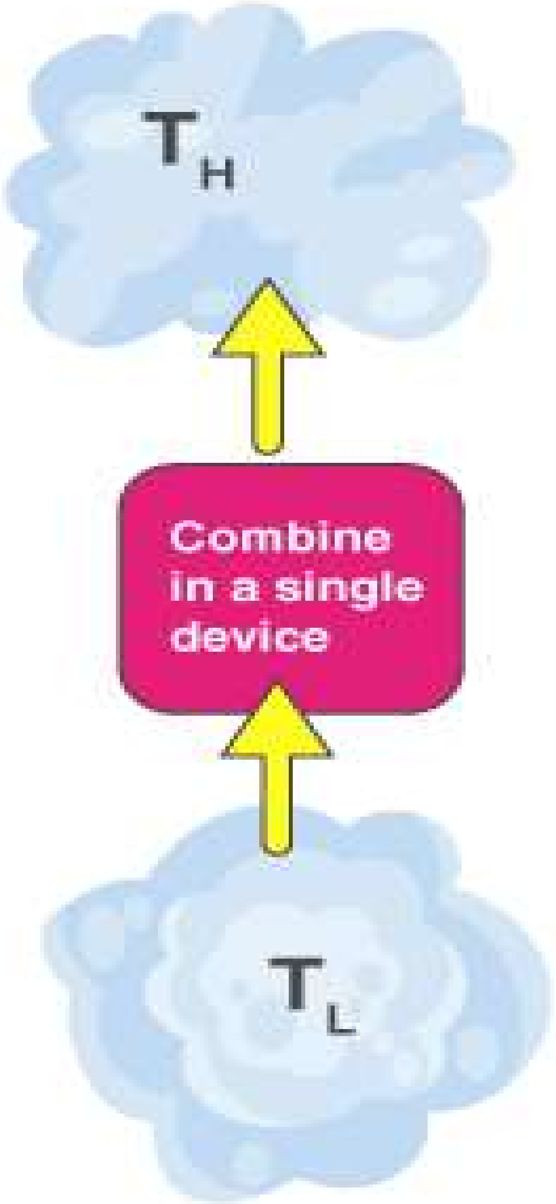
Figure. *Violation of the Kelvin–Planck statement leads to a violation of the Clausius statement*



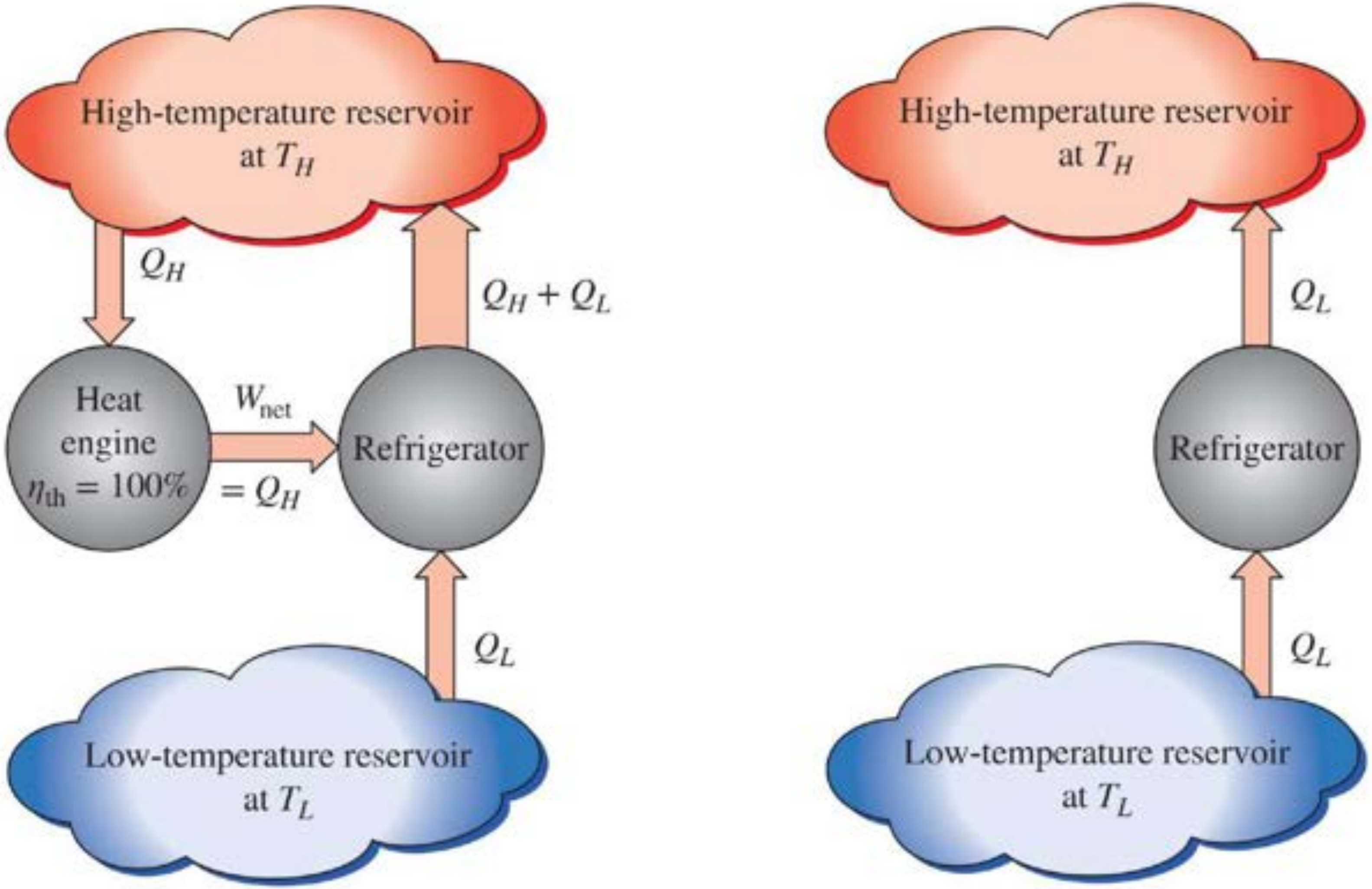
Assume that Kelvin-planck statement is violated



Attach heat engine to refrigerator



Violation of Clausias statement



(*a*) A refrigerator that is powered by a 100 percent efficient heat engine

(*b*) The equivalent refrigerator

FIGURE

Proof that the violation of the Kelvin–Planck statement leads to the violation of the Clausius statement.

To prove that the violation of the Clausius statement leads to a violation of the Kelvin–Planck statement, let us suppose that the Clausius statement is wrong. Consider a heat pump that requires no work to transfer heat from a low-temperature to a high-temperature reservoir and that, therefore, violates the Clausius statement.

Let us assume a heat engine operates between the same two reservoirs in such a way that the engine draws an amount of heat which is delivered by the heat pump. The engine and pump together constitute a heat engine that produces no effect other than the absorption of energy as heat from a single reservoir and produces an equivalent amount of work. Therefore, the engine and the pump together constitute a heat engine that violates the Kelvin–Planck statement.

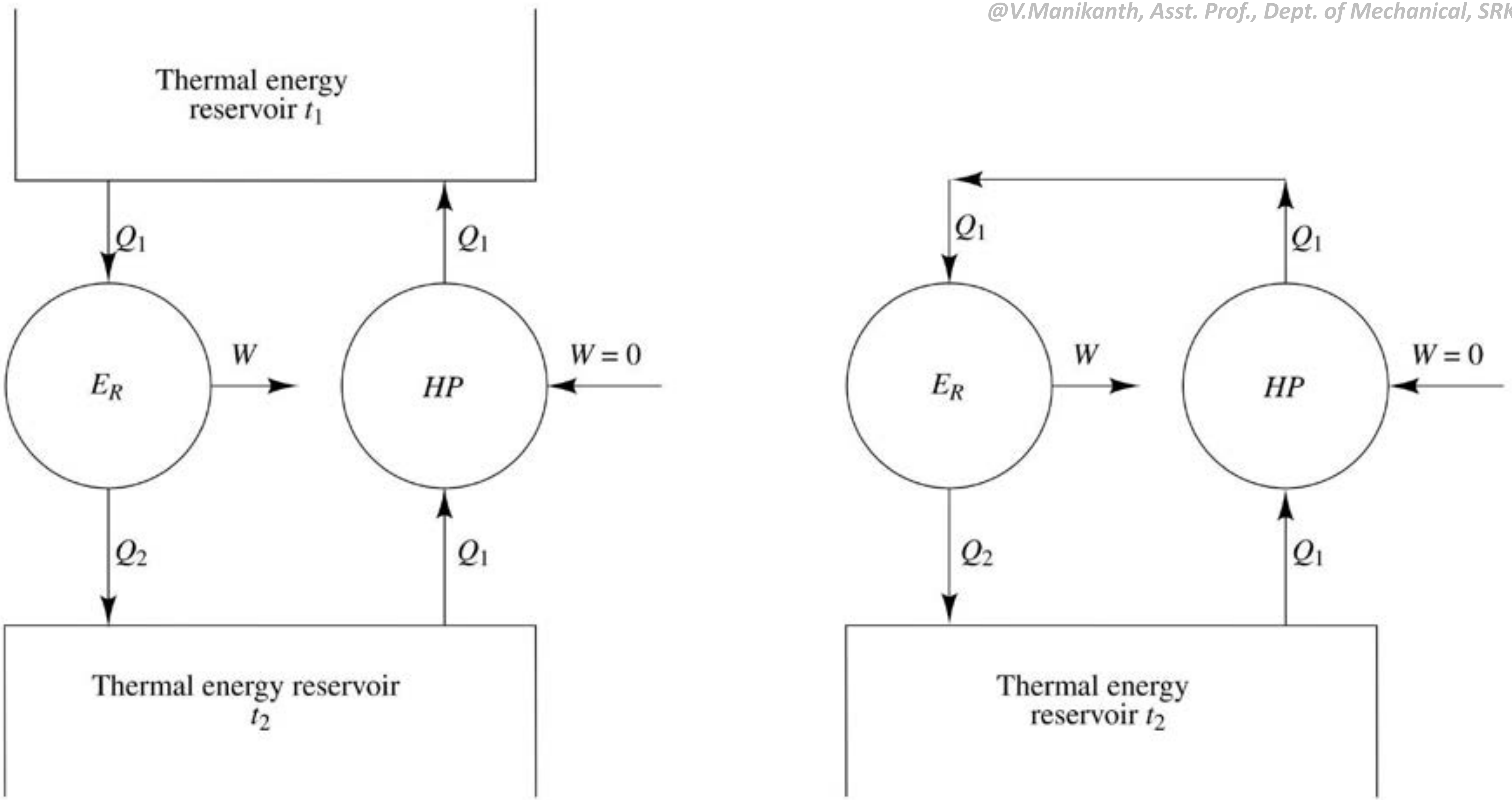
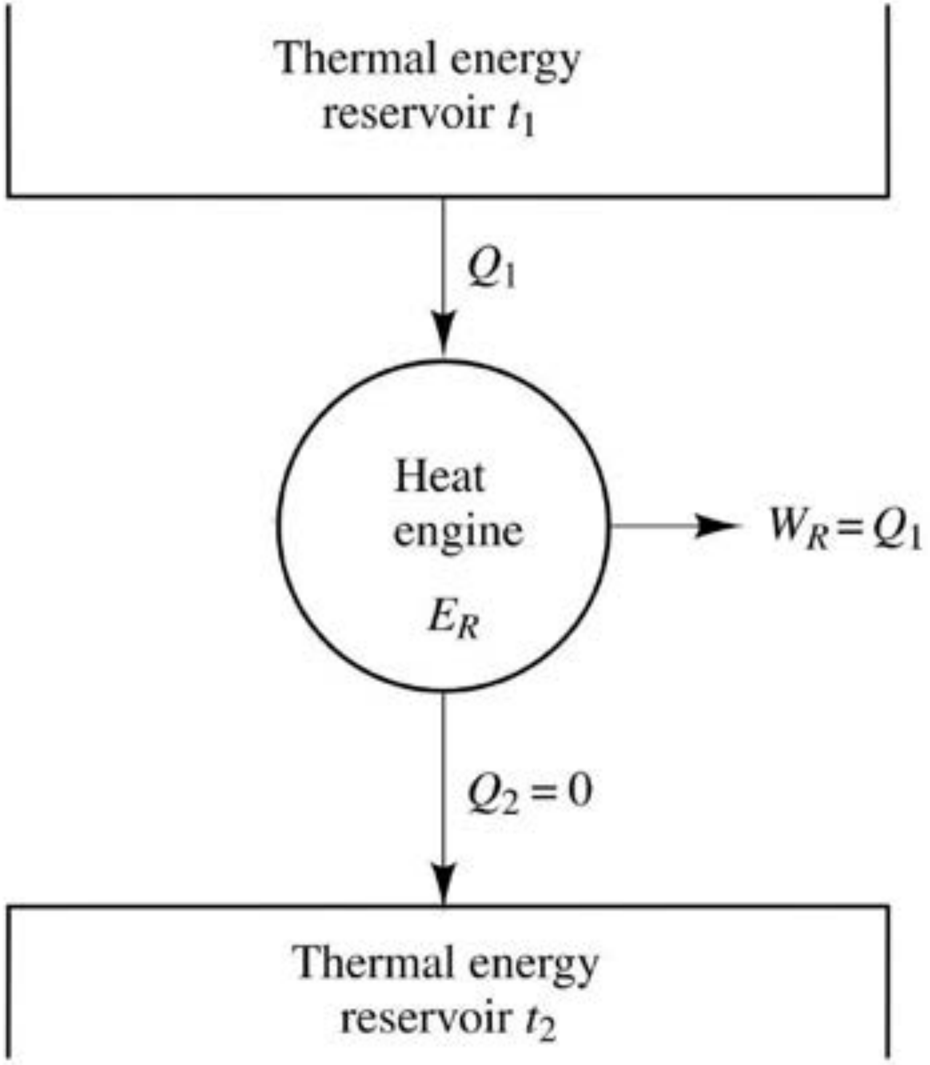


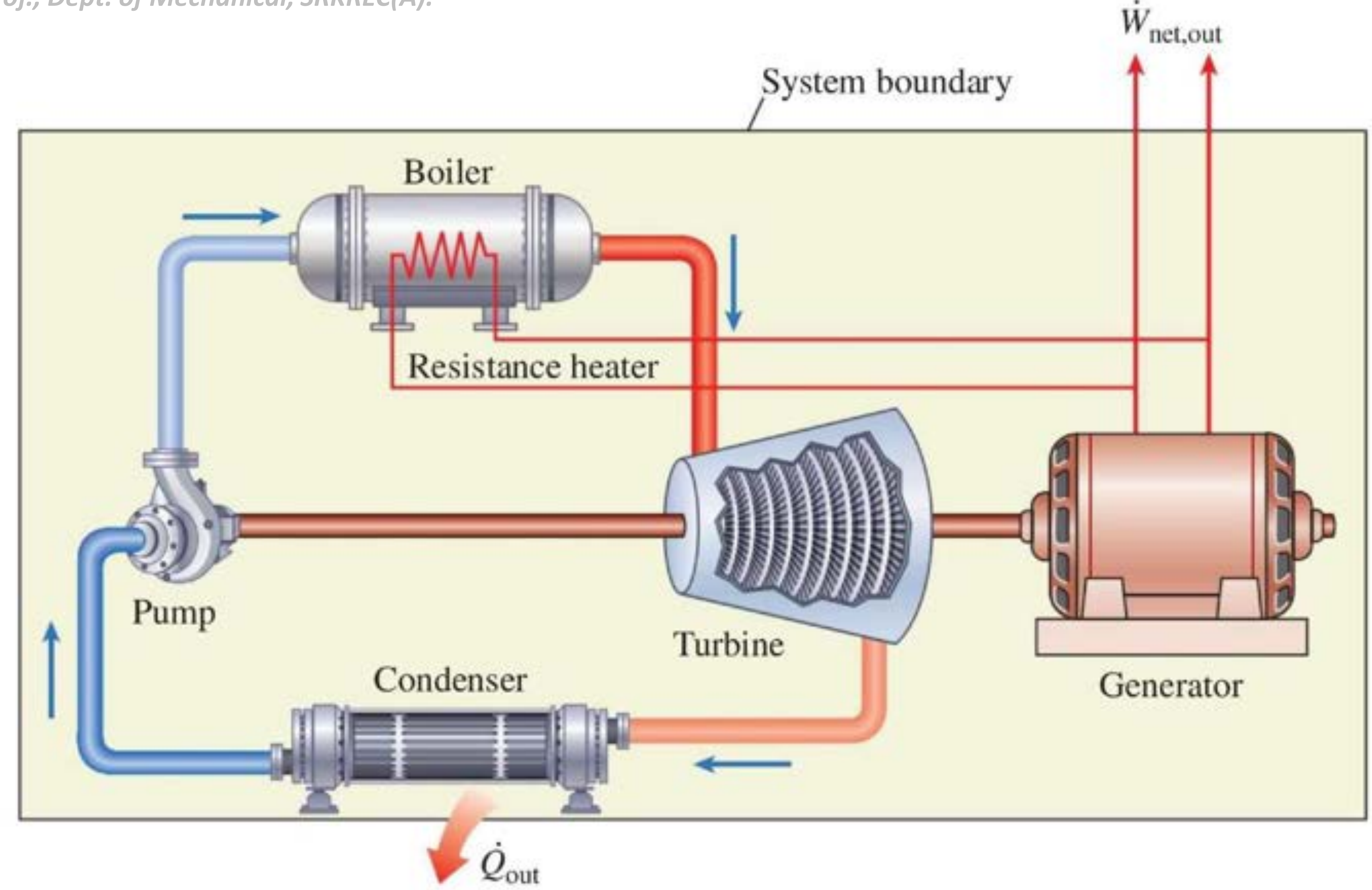
Figure. *Violation of the Clausius statement leads to a violation of the Kelvin–Planck statement*

PERPETUAL-MOTION MACHINES OF SECOND KIND (PMM-II):

Wilhelm Ostwald introduced the concept of a perpetual motion machine of the second kind. *A perpetual motion machine of the second kind is a device which would perform work solely by absorbing energy as heat from a single reservoir.* Such a device does not violate the first law of thermodynamics because it would perform work at the expense of the internal energy of a body. It is to be noted that the efficiency of the perpetual motion machine of the second kind is 100%. A perpetual motion machine of the second kind is a machine which violates the second law of thermodynamics.



Heat engine exchanging heat with one TER: Impossible



FIGURE

A perpetual-motion machine that violates the first law of thermodynamics (PMM1).

CASE STUDY:

Now let us study a novel idea by an inventor. Convinced that energy cannot be created, the inventor suggests the following modification that will greatly improve the thermal efficiency of that power plant without violating the first law. Aware that more than one-half of the heat transferred to the steam in the furnace is discarded in the condenser to the environment, the inventor suggests getting rid of this wasteful component and sending the steam to the pump as soon as it leaves the turbine, as shown in Fig. This way, all the heat transferred to the steam in the boiler will be converted to work, and thus the power plant will have a theoretical efficiency of 100 percent. The inventor realizes that some heat losses and friction between the moving components are unavoidable and that these effects will hurt the efficiency somewhat, but still expects the efficiency to be no less than 80 percent (as opposed to 40 percent in most actual power plants) for a carefully designed system.

A student of thermodynamics, however, will immediately label this device as a PMM2, since it works on a cycle and does a net amount of work while exchanging heat with a single reservoir (the furnace) only. It satisfies the first law but violates the second law, and therefore it will not work. Well, the possibility of doubling the efficiency would certainly be very tempting to plant managers and, if not properly trained, they would probably give this idea a chance, since intuitively they see nothing wrong with it.

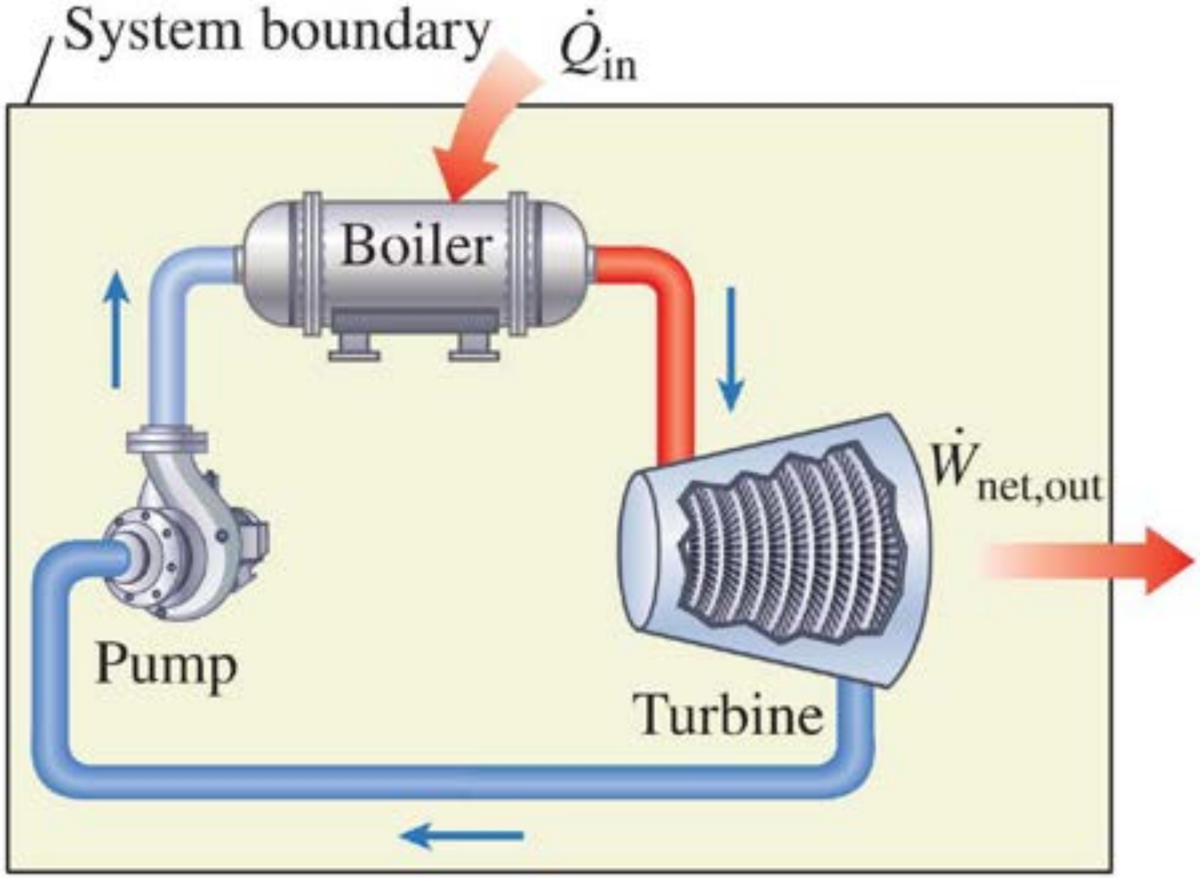


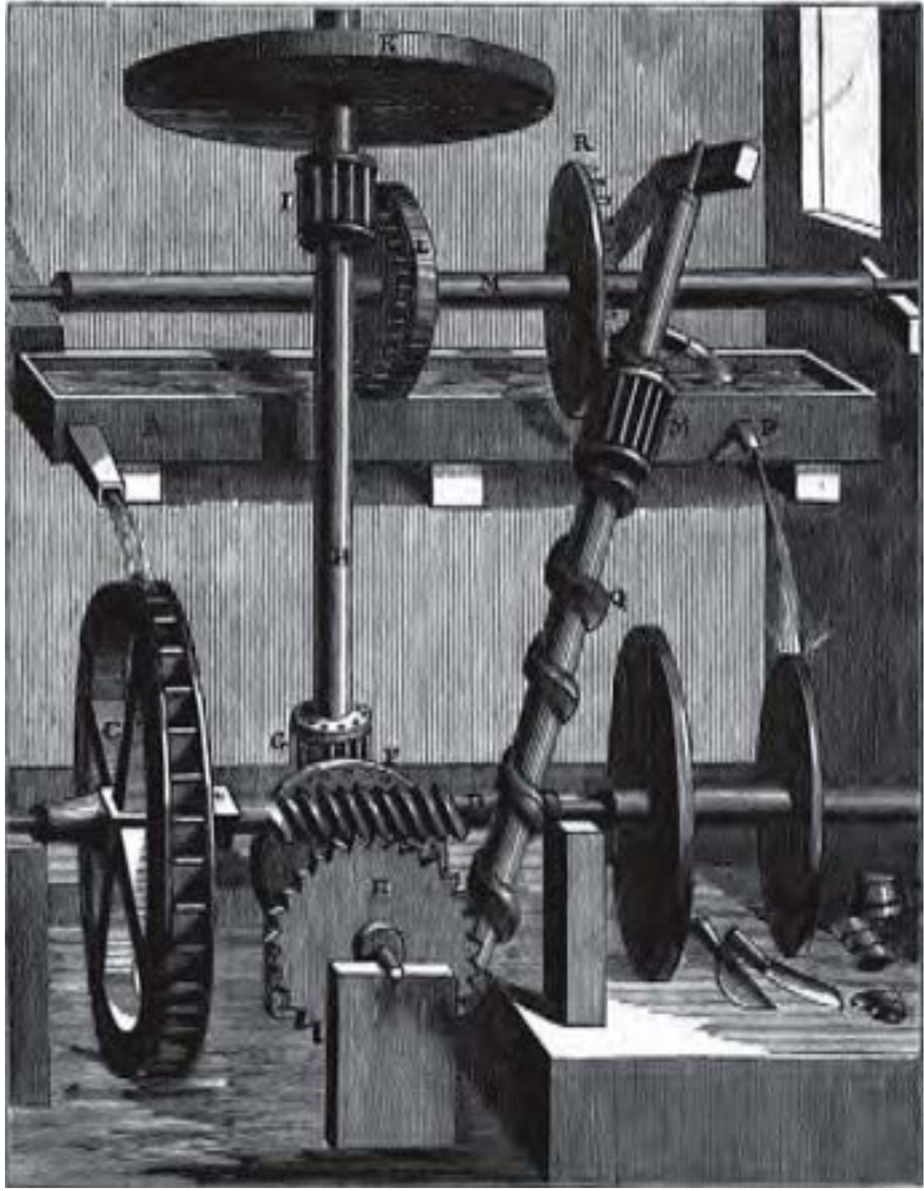
FIGURE
A perpetual-motion machine that violates the second law of thermodynamics (PMM2).

Some perpetual-motion machine inventors were very successful in fundraising. For example, a Philadelphia carpenter named J. W. Kelly collected millions of dollars between 1874 and 1898 from investors in his *hydropneumatic-pulsating-vacu-engine*, which supposedly could push a railroad train 3000 miles on 1 L of water. Of course, it never did. After his death in 1898, the investigators discovered that the demonstration machine was powered by a hidden motor.

In another case, a group of investors was set to invest $2.5 million in a mysterious energy augmenter, which multiplied whatever power it took in, but their lawyer wanted an expert opinion first. Confronted by the scientists, the “inventor” fled the scene without even trying to run his demo machine.

Perpetual motion wheels from a drawing by Leonardo da Vinci

For example, in 1982 the U.S. Patent Office dismissed as just another perpetual-motion machine a huge device that involves several hundred kilograms of rotating magnets and kilometers of copper wire that is supposed to be generating more electricity than it is consuming from a battery pack. However, the inventor challenged the decision, and in 1985 the National Bureau of Standards finally tested the machine just to certify that it is battery-operated.



Robert Fludd's 1618 "water screw" perpetual motion machine from a 1660 wood engraving. It is widely credited as the first attempt to describe such a device in order to produce useful work, that of driving millstones.

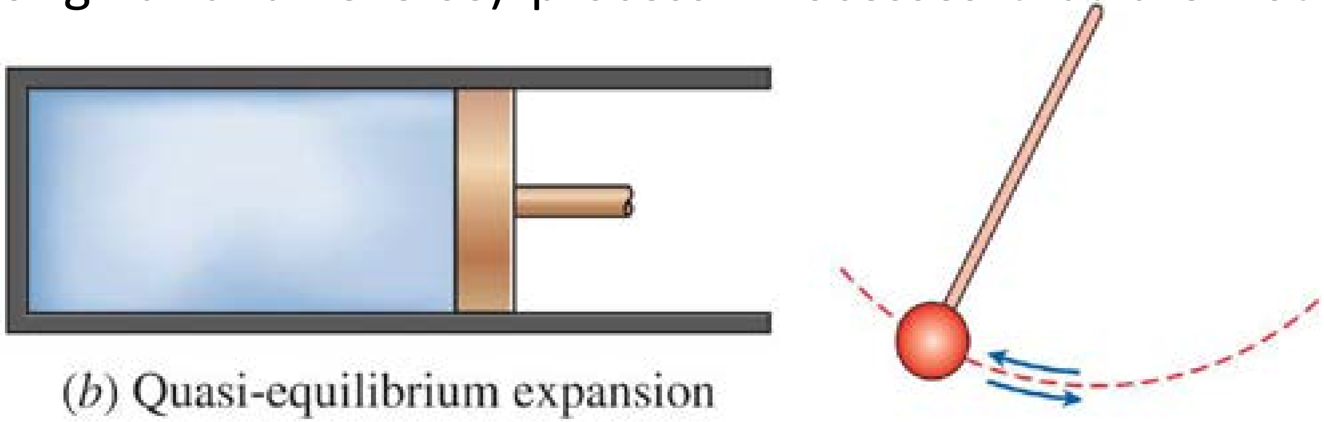
Tired of applications for perpetual-motion machines, the U.S. Patent Office decreed in 1918 that it would no longer consider any perpetual-motion machine applications. However, several such patent applications were still filed, and some made it through the patent office undetected. Some applicants whose patent applications were denied sought legal action.

October 1920 issue of Popular Science magazine, on perpetual motion. Although scientists have established them to be impossible under the laws of physics, perpetual motion continues to capture the imagination of inventors.

REVERSIBLE AND IRREVERSIBLE PROCESSES

The second law of thermodynamics states that no heat engine can have an efficiency of 100 percent. Then one may ask, what is the highest efficiency that a heat engine can possibly have? Before we can answer this question, we need to define an idealized process first, which is called the ***reversible process.***

'*A reversible process is defined as a process that can be reversed without leaving any trace on the surroundings',* That is, both the system and the surroundings are returned to their initial states at the end of the reverse process. This is possible only if the net heat and net work exchange between the system and the surroundings is zero for the combined (original and reverse) process. Processes that are not reversible are called irreversible processes.



(*b*) Quasi-equilibrium expansion and compression of a gas

(*a*) Frictionless pendulum

FIGURE

Two familiar reversible processes

Reversible processes actually do not occur in nature. They are merely idealizations of actual processes. Reversible processes can be approximated by actual devices, but they can never be achieved. That is, all the processes occurring in nature are irreversible.

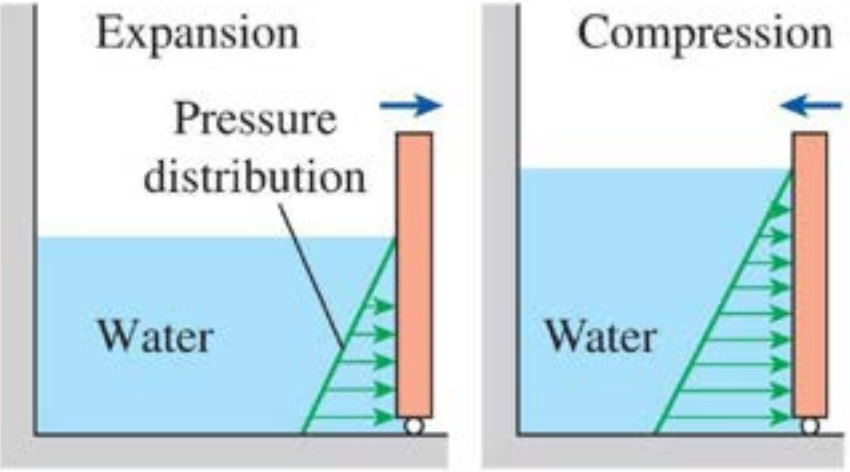
You may be wondering, then, why we are bothering with such fictitious processes.

There are two reasons.

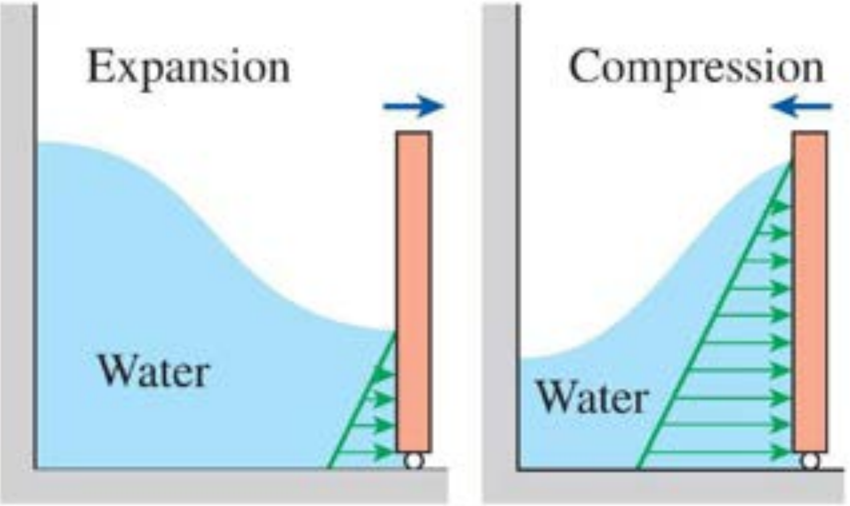
1. **They are easy to analyze, since a system passes through a series of equilibrium states during a reversible process.**
2. **They serve as idealized models to which actual processes can be compared.**

Engineers are interested in reversible processes because work-producing devices such as car engines and gas or steam turbines deliver the most work, and work-consuming devices such as compressors, fans, and pumps consume the least work when reversible processes are used instead of irreversible ones.

The concept of reversible processes leads to the definition of ***the second-law efficiency*** for actual processes, which is the degree of approximation to the corresponding reversible processes. This enables us to compare the performance of different devices that are designed to do the same task on the basis of their efficiencies. The better the design, the lower the irreversibilities and the higher the second-law efficiency.

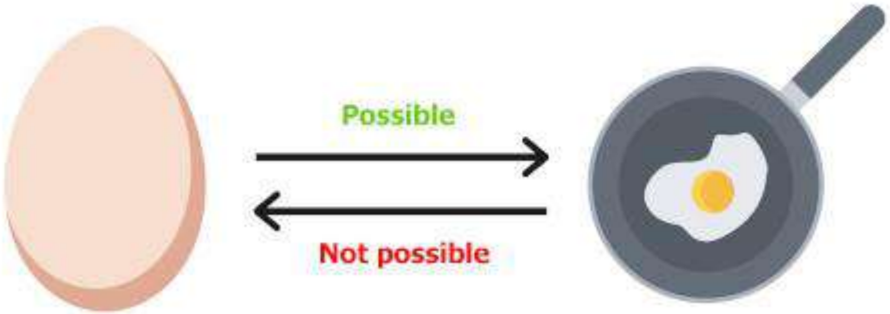


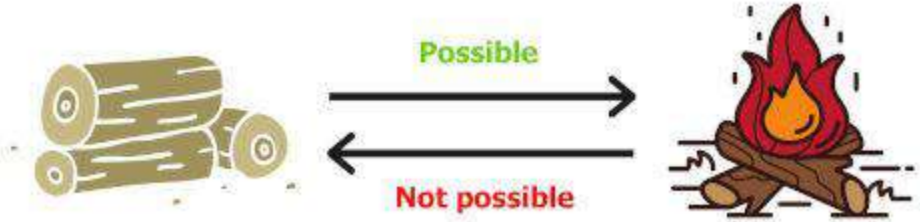
(*a*) Slow (reversible) process



(*b*) Fast (irreversible) process

FIGURE
Reversible processes deliver the most and consume the least work.





Irreversibilities

The factors that cause a process to be irreversible are called ***irreversibilities***. They include *friction, unrestrained expansion, mixing of two fluids, heat transfer across a finite temperature difference, electric resistance, inelastic deformation of solids, and chemical reactions*. The presence of any of these effects renders a process irreversible. A reversible process involves none of these.

(*a*) Fast compression

(*b*) Fast expansion

(*c*) Unrestrained expansion

FIGURE Irreversible compression and expansion processes.

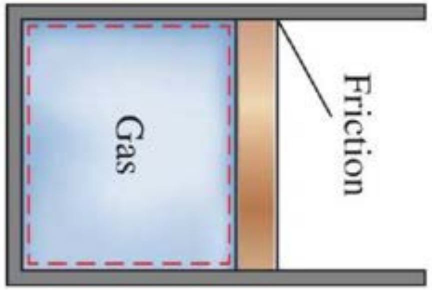
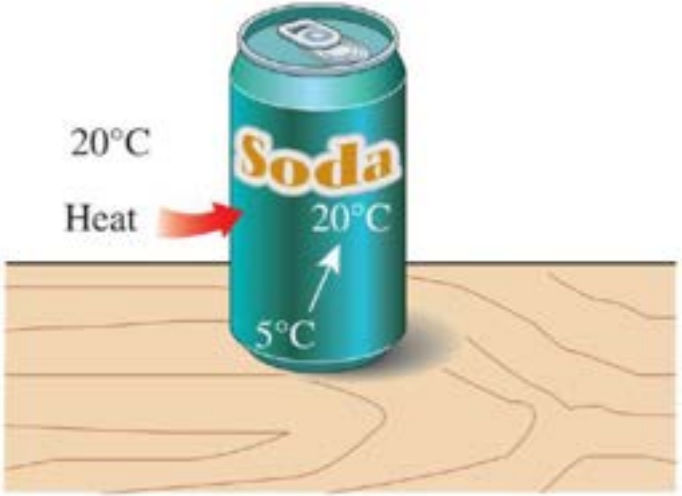
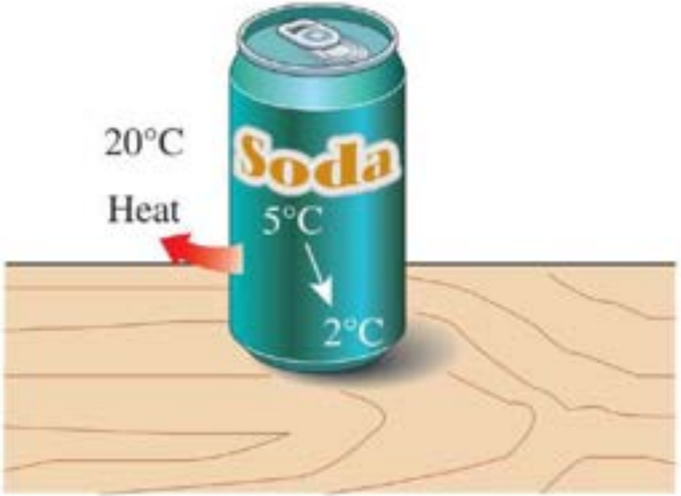


FIGURE
Friction renders a process irreversible.



(*a*) An irreversible heat transfer process



(*b*) An impossible heat transfer process

FIGURE (*a*) Heat transfer through a temperature difference is irreversible and (*b*) the reverse process is impossible.

Internally and Externally Reversible Processes

A typical process involves interactions between a system and its surroundings, and a reversible process involves no irreversibilities associated with either of them.

A process is called ***internally reversible*** if no irreversibilities occur within the boundaries of the system during the process. During an internally reversible process, a system proceeds through a series of equilibrium states, and when the process is reversed, the system passes through exactly the same states.

A process is called ***externally reversible*** if no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the outer surface of the system is at the temperature of the reservoir.

A process is called totally ***reversible***, or simply reversible, if it involves no irreversibilities within the system or its surroundings. A totally reversible process involves no heat transfer through a finite temperature difference, no non quasi-equilibrium changes, and no friction or other dissipative effects.

A reversible process involves no internal and external irreversibilities.

As an example, consider the transfer of heat to two identical systems that are undergoing a constant-pressure (thus constant-temperature) phase-change process, as shown in Fig. Both processes are internally reversible, since both take place isothermally and both pass through exactly the same equilibrium states. The first process shown is externally reversible also, since heat transfer for this process takes place through an infinitesimal temperature difference dT. The second process, however, is externally irreversible, since it involves heat transfer through a finite temperature difference ΔT.

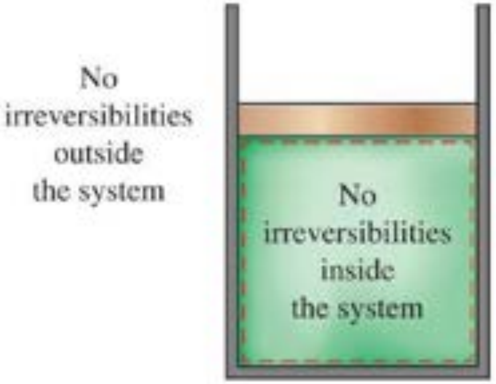
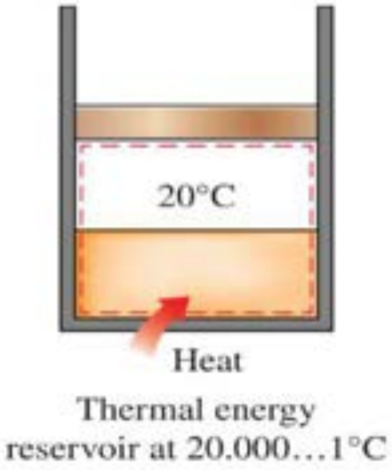
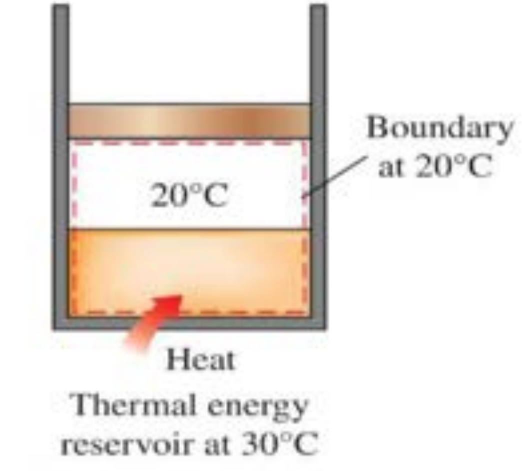


FIGURE
A reversible process involves no internal and external irreversibilities.



(*a*) Totally reversible



(*b*) Internally reversible

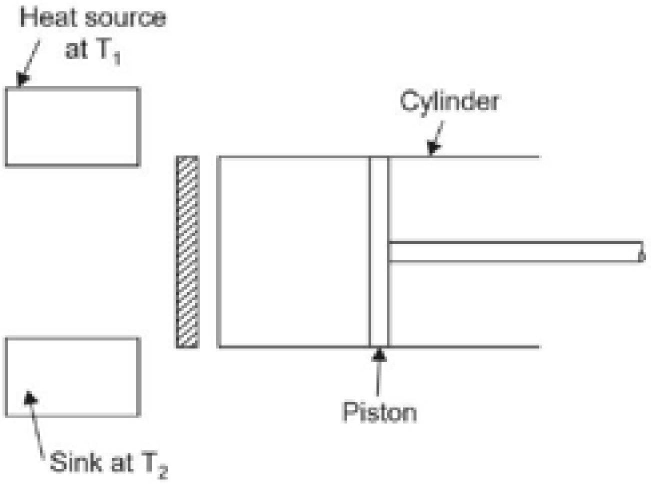
FIGURE
Totally and internally reversible heat transfer processes.

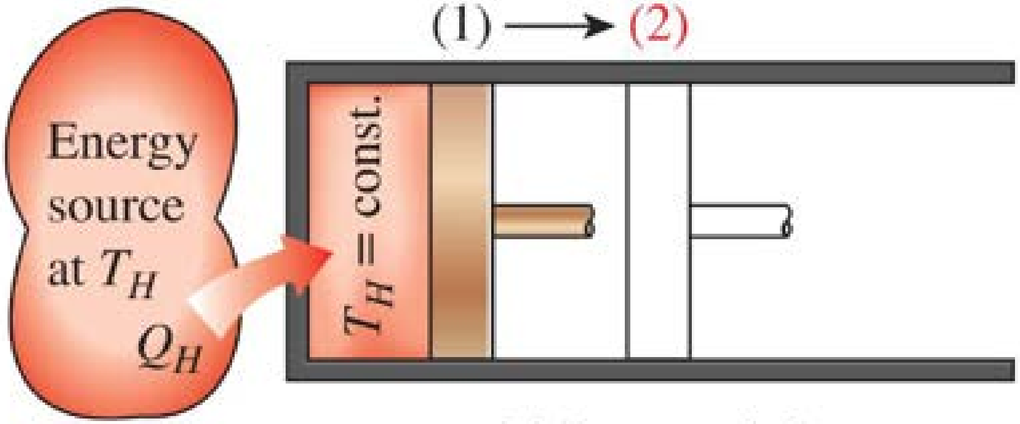
CARNOT CYCLE

Nicolas Léonard Sadi Carnot (1 June 1796 – 24 August 1832) was a French mechanical engineer in the French Army, military scientist and physicist, often described as the "*father of thermodynamics*." he published only one book, *'The Reflections on the Motive Power of Fire'* (Paris, 1824), in which he expressed, at the age of 27 years, the first successful theory of the maximum efficiency of heat engines.

The theoretical heat engine that operates on the Carnot cycle is called the **Carnot heat engine**. The Carnot cycle is composed of four reversible processes—two isothermal and two adiabatic—and it can be executed either in a closed or a steady-flow system.

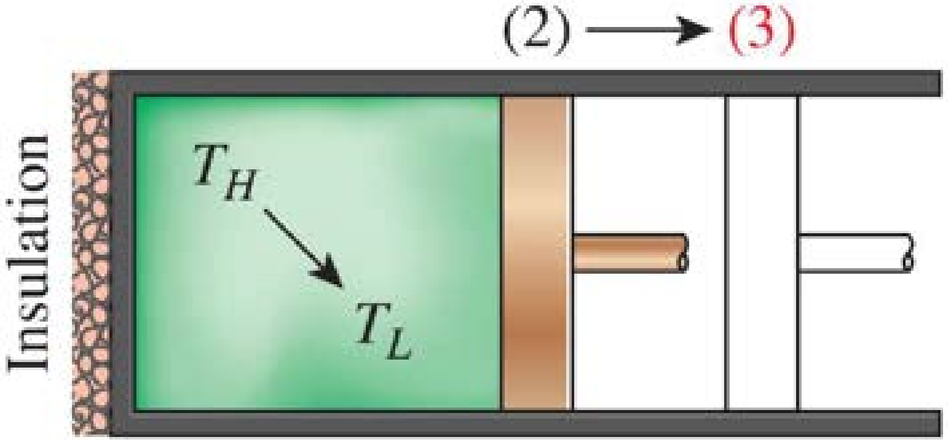
Nicolas Léonard Sadi Carnot





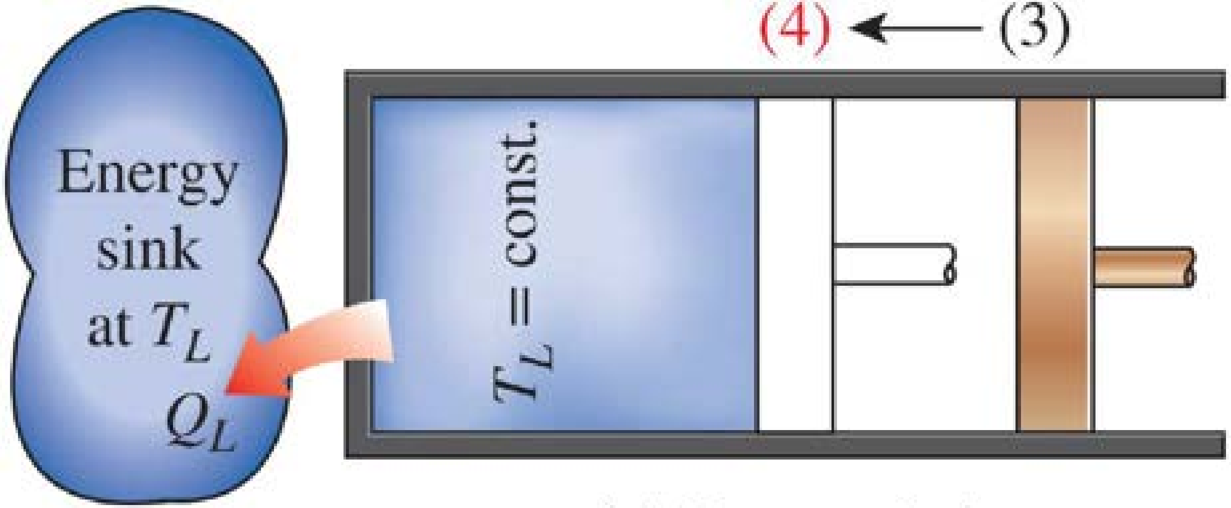
(*a*) Process 1-2

Reversible Isothermal Expansion



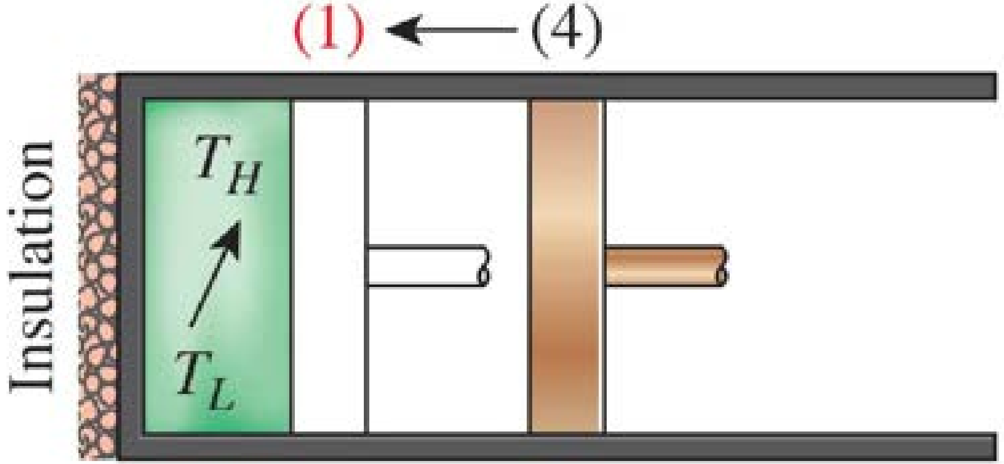
(*b*) Process 2-3

Reversible Adiabatic Expansion



(*c*) Process 3-4

Reversible Isothermal Compression



(*d*) Process 4-1

Reversible Adiabatic Compression

FIGURE: Execution of the Carnot cycle in a closed system.

1. **Reversible Isothermal Expansion** (process 1-2, T_H = constant).

2. **Reversible Adiabatic Expansion** (process 2-3, temperature drops from T_H to T_L)

3. **Reversible Isothermal Compression** (process 3-4, T_L = constant)

4. **Reversible Adiabatic Compression** (process 4-1, temperature rises from T_L to T_H)

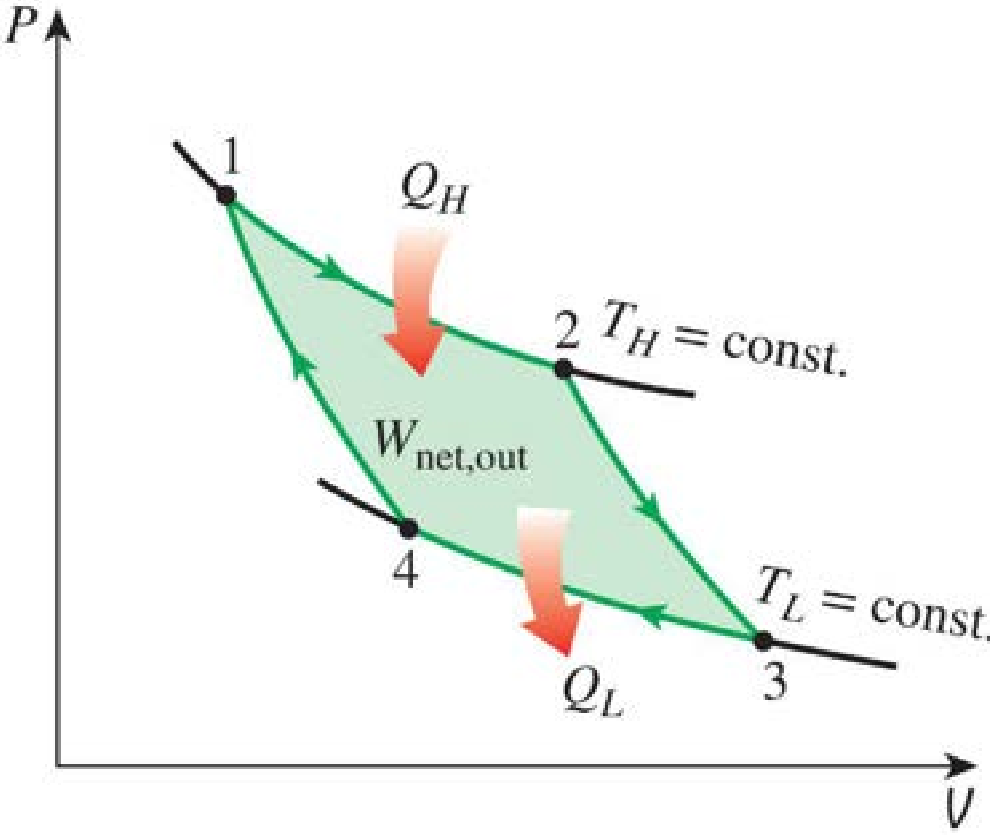


FIGURE
P-V diagram of the Carnot cycle.

The P-V diagram of this cycle is shown in Fig. Remembering that on a P-V diagram the area under the process curve represents the boundary work for quasi-equilibrium (internally reversible) processes, we see that the area under curve 1-2-3 is the work done by the gas during the expansion part of the cycle, and the area under curve 3-4-1 is the work done on the gas during the compression part of the cycle.

The area enclosed by the path of the cycle (area 1-2-3-4-1) is the difference between these two and represents the net work done during the cycle.

The assumptions made for describing the working of the Carnot engine are as follows :

(i) The piston moving in a cylinder does not develop any friction during motion.

(ii) The walls of piston and cylinder are considered as perfect insulators of heat.

(iii) The cylinder head is so arranged that it can be a perfect heat conductor or perfect heat insulator.

(iv) The transfer of heat does not affect the temperature of source or sink.

(v) Working medium is a perfect gas and has constant specific heat.

(vi) Compression and expansion are reversible.

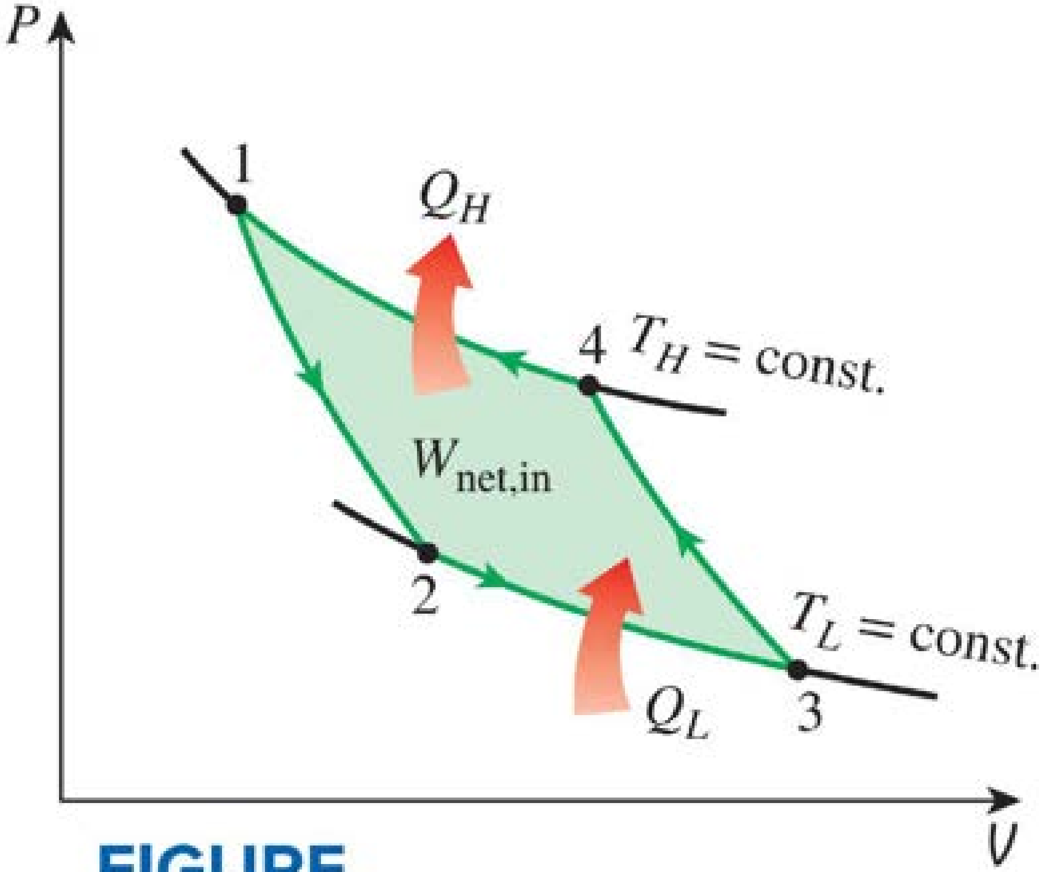
The Carnot cycle cannot be performed in practice because of the following reasons :

1. It is impossible to perform a frictionless process.
2. It is impossible to transfer the heat without temperature potential.
3. Isothermal process can be achieved only if the piston moves very slowly to allow heat transfer so that the temperature remains constant. Adiabatic process can be achieved only if the piston moves as fast as possible so that the heat transfer is negligible due to very short time available.

4.The isothermal and adiabatic processes take place during the same stroke therefore the piston has to move very slowly for part of the stroke, and it must move very fast during remaining stroke. This variation of motion of the piston during the same stroke is not possible

The Reversed Carnot Cycle

The Carnot heat-engine cycle just described is a totally reversible cycle. Therefore, all the processes that comprise it can be reversed, in which case it becomes the Carnot refrigeration cycle. This time, the cycle remains the same, except that the directions of any heat and work interactions are reversed: The P-V diagram of the reversed Carnot cycle is the same as the one given for the Carnot cycle, except that the directions of the processes are reversed, as shown in Fig.



FIGURE

P-V diagram of the reversed Carnot cycle.

$$\therefore \qquad W = Q_1 - Q_2$$

$$\text{Also, thermal efficiency, } \eta_{th} = \frac{\text{Work done}}{\text{Heat supplied by the source}} = \frac{Q_1 - Q_2}{Q_1}$$

$$= 1 - \frac{Q_2}{Q_1} \left(= 1 - \frac{T_2}{T_1} \right)$$

Here, the heat supplied by the source =*Q*1 and the heat rejected to the sink =*Q*2.

$$\begin{bmatrix} \because \qquad Q_1 = m\, c_p\, T_1 \\ Q_2 = m\, c_p\, T_2 \\ \text{where, } m = \text{mass of fluid.} \end{bmatrix}$$

Carnot Refrigerator and Carnot Heat Pump

A refrigerator of a heat pump that operates on the reversed Carnot cycle is called a Carnot refrigerator or a Carnot heat pump. The coefficient of performance of any refrigerator or heat pump is given by

$$\mathrm{COP}_R = \frac{Q_2}{Q_1 - Q_2}$$

$$\mathrm{COP}_R = \frac{Q_1}{Q_1 - Q_2}$$

where Q_1 is the heat rejected to the high-temperature medium (T_1) and Q_2 is the heat absorbed from the low-temperature medium (T_2).

From the thermodynamic temperature scale

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Then the coefficient of performance becomes

$$\mathrm{COP}_R = \frac{T_2}{T_1 - T_2}$$

$$\mathrm{COP}_{HP} = \frac{T_1}{T_1 - T_2}$$

THE CARNOT PRINCIPLES

The second law of thermodynamics puts limits on the operation of cyclic devices as expressed by the Kelvin–Planck and Clausius statements. A heat engine cannot operate by exchanging heat with a single reservoir, and a refrigerator cannot operate without a net energy input from an external source.

We can draw valuable conclusions from these statements. Two conclusions pertain to the thermal efficiency of reversible and irreversible (i.e., actual) heat engines, and they are known as the Carnot principles, expressed as follows:

1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible one operating between the same two reservoirs.
2. The efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

These two statements can be proved by demonstrating that the violation of either statement results in the violation of the second law of thermodynamics

COROLLARIES OF CARNOT THEOREM

"It is impossible to construct a heat engine operating between only two reservoirs, which will have a higher efficiency than a reversible heat engine operating between the same two reservoirs.".

By assumption, the efficiency of the reversible engine E_R is less than the efficiency of the irreversible engine E_I.

$$\eta_I > \eta_R$$

Let the rate of working of the engines be such that $Q_{1R} =$

Thermal efficiency of reversible engine $\eta_R = \dfrac{W_R}{Q_{1R}}$

Thermal efficiency of irreversible engine $\eta_I = \dfrac{W_I}{Q_{1I}}$

Since, $\eta_I > \eta_R$

$$W_I > W_R$$

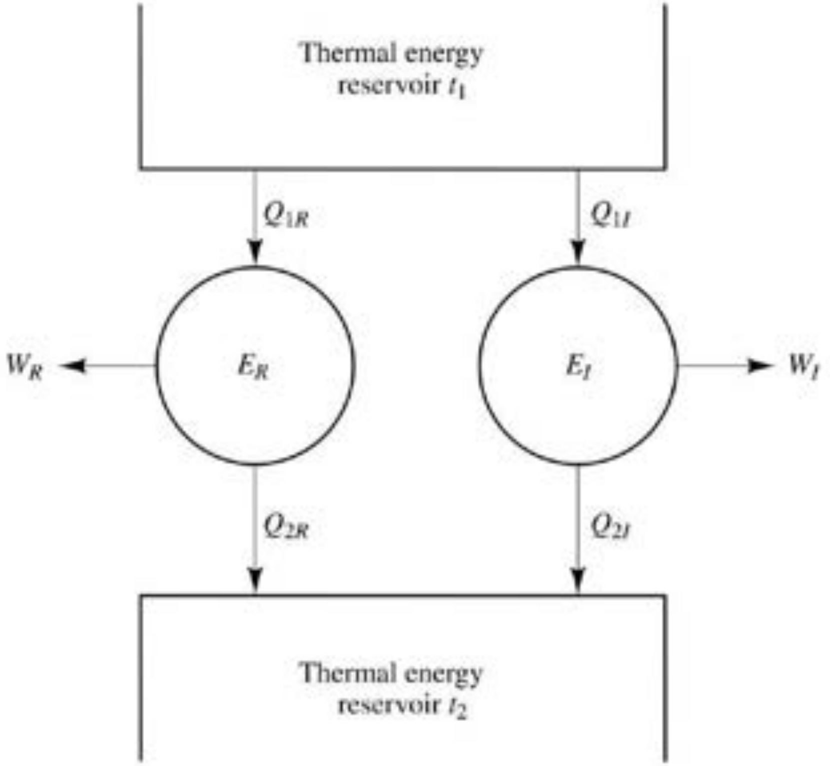


Figure. *Two heat engines operating between the same two reservoirs*

Therefore, for the same amount of energy input, the reversible engine E_R does less work than the irreversible engine E_I. Since the heat engine E_R is a reversible, it can be executed in a reversed order i.e., the magnitudes of energy transfer will remain the same, but the direction will be the reversed. Since W_I is greater than W_R, some part of W_I (equal to W_R) may be fed to execute the reversed heat engine E_R.

Now, ER and EI together constitute a heat engine as shown in Fig., which, operating in a cycle, delivers net work $W_I – W_R$. The combined device absorbs energy as heat ($Q_{2R} – Q_{2I}$) from the thermal energy reservoir at t2 and does equivalent amount of work without rejecting energy to thermal energy reservoir at t_1. Thus, it becomes a perpetual motion machine of the second kind which violates the Kelvin–Planck statement of the second law of thermodynamics. Hence, the assumption that the efficiency of the irreversible engine is greater than the efficiency of the reversible engine is wrong.

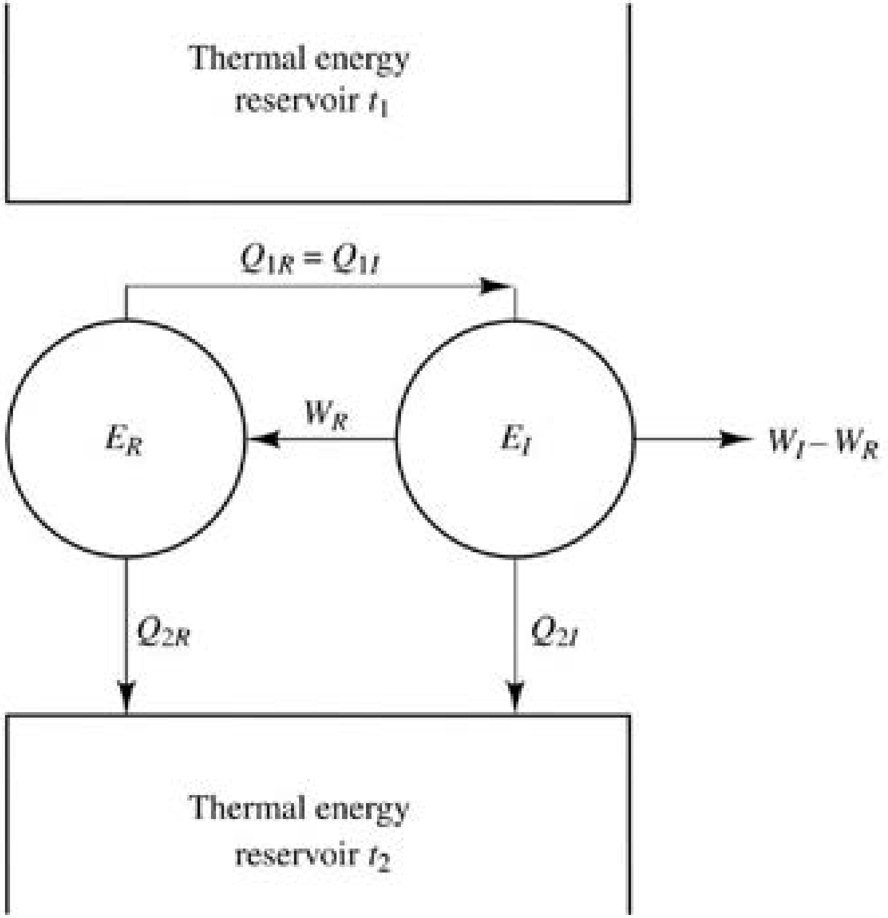


Figure. *Combined system violates the Kelvin–Planck statement of the second law*

Therefore, $\eta_R \geq \eta_I$

"All reversible heat engines operating between the same two reservoirs have the same efficiency".

Consider two reversible heat engines E_{R1} and E_{R2} are operating between the same two thermal energy reservoirs as shown in Fig. 5.13.

Let us assume that the efficiency of the reversible heat engine E_{R1} is greater than the efficiency of the reversible heat engine E_{R2}.

$$\eta_{R1} > \eta_{R2}$$

Let the rate of working of the engines be such that $Q_{11} = Q_{12}$

Thermal efficiency of reversible engine E_{R1}, $\quad \eta_{R1} = \dfrac{W_R}{Q_{11}}$

Thermal efficiency of reversible engine E_{R2}, $\quad \eta_{R2} = \dfrac{W_2}{Q_{12}}$

Since, $$\eta_{R1} > \eta_{R2}$$

$$W_1 > W_2$$

Since the heat engine E_{R2} is a reversible one, it can be executed in a reverse order, i.e., the magnitudes of energy transfer will remain the same, but the direction will be reversed. Since W_1 is greater than W_2, some part of W_1 (equal to W_2) may be fed to execute the reversed heat engine E_{R2}.

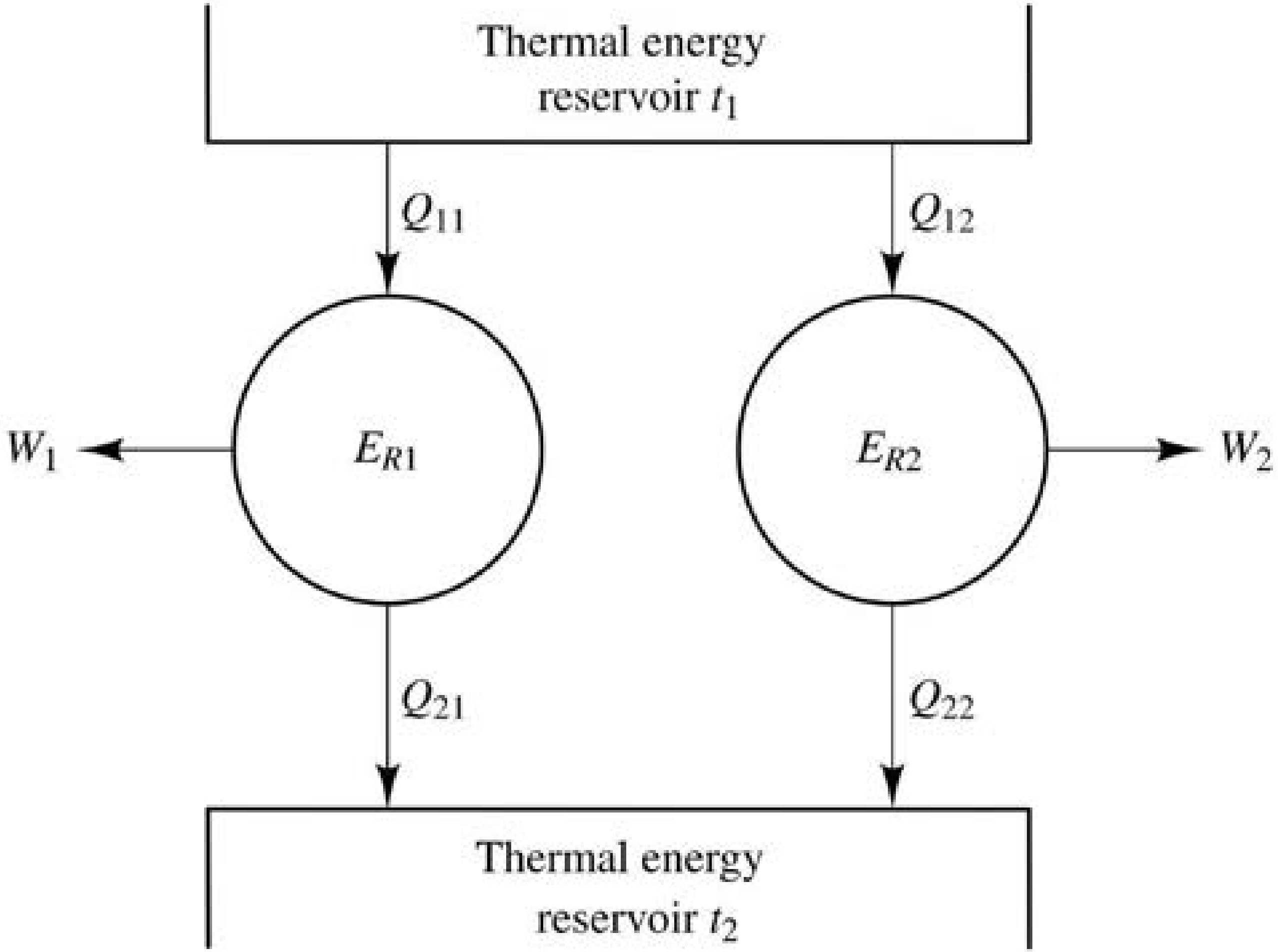
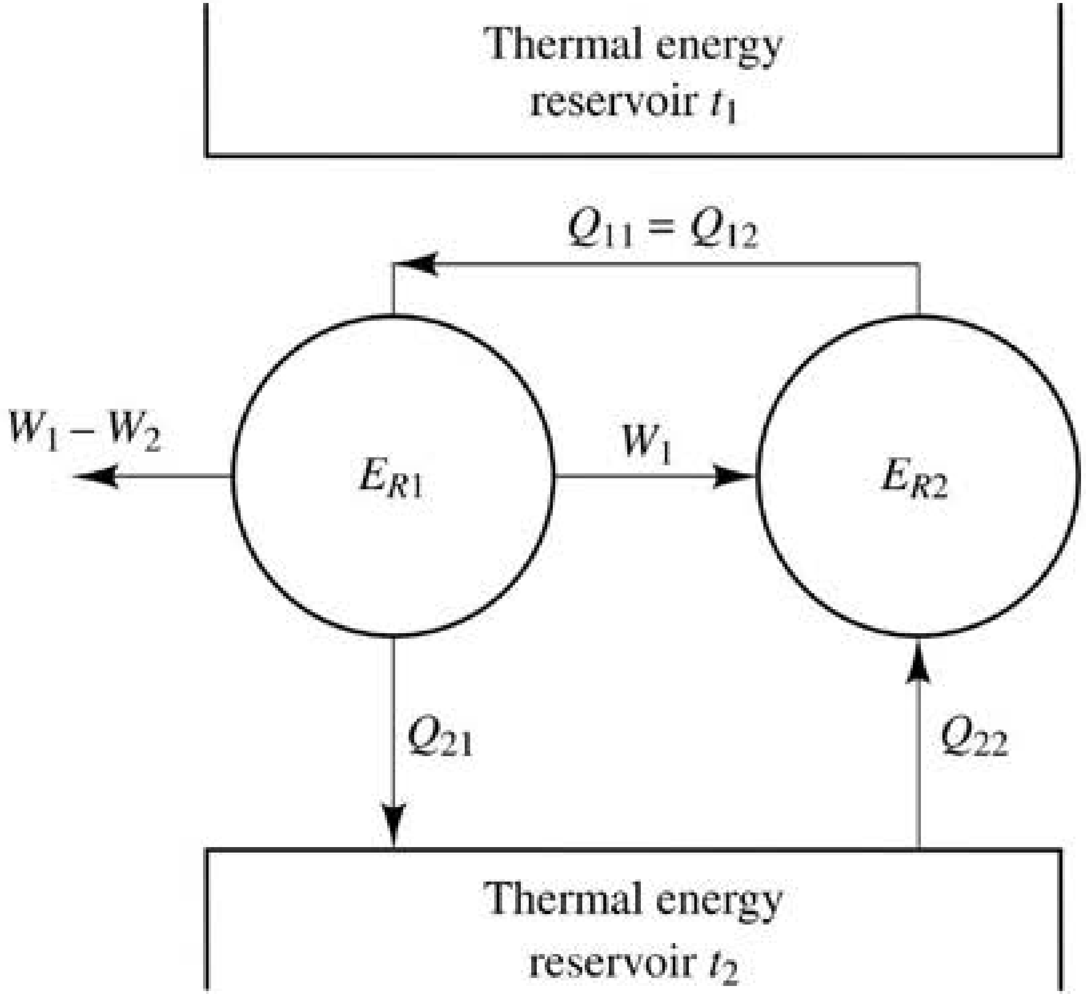


Figure 5.13

Therefore, $$\eta_{R2} \geq \eta_{R1}$$



Combined heat engines E_{R1} and E_{R2} violates the Kelvin–plank statement of the second law

Now, let us assume that the efficiency of the reversible heat engine E_{R2} is greater than the efficiency of the reversible heat engine E_{R1}.

The reversible heat engine E_{R1} can be executed in a reversed, utilizing part of work done by E_{R2}. By following a similar argument we can arrive at the result that

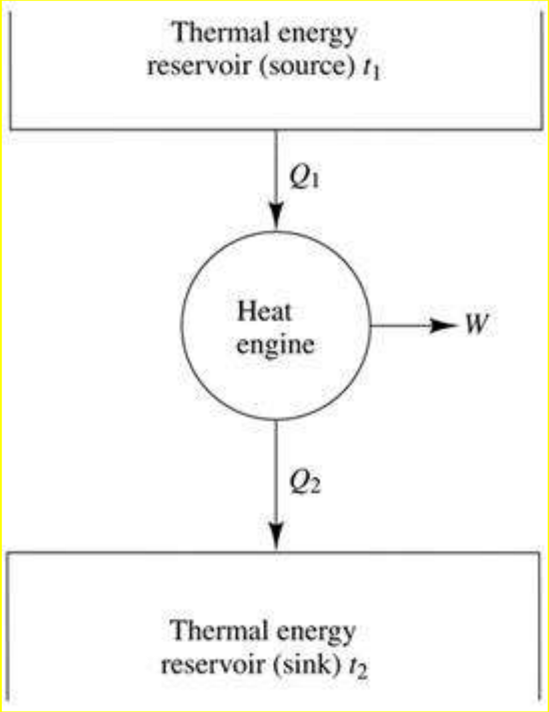
$$\eta_{R1} \geq \eta_{R2} \tag{5.8}$$

From Eqs (5.7) and (5.8), it can be concluded that

$$\eta_{R1} = \eta_{R2} \tag{5.9}$$

This is also known as Carnot Theorem 2. This theorem states *that the efficiency of a reversible heat engine is independent of the nature of the working substance and depends only on the temperature of the reservoirs between which it operates.*

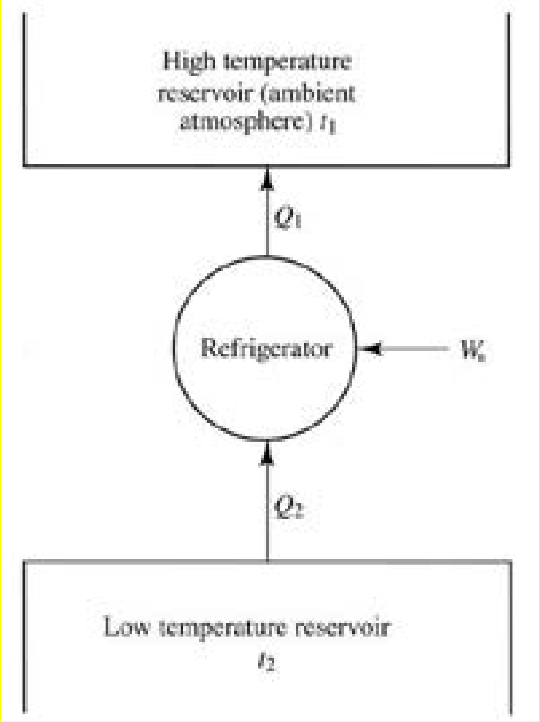
Important observations



$$\eta_{\text{ther}} = \frac{\text{Work done}}{\text{Heat supplied}} = \frac{W}{Q_1}$$

$$\eta_{\text{ther}} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$\eta_{\text{th}} \begin{cases} < \eta_{\text{th,rev}} & \text{irreversible heat engine} \\ = \eta_{\text{th,rev}} & \text{reversible heat engine} \\ > \eta_{\text{th,rev}} & \text{impossible heat engine} \end{cases}$$

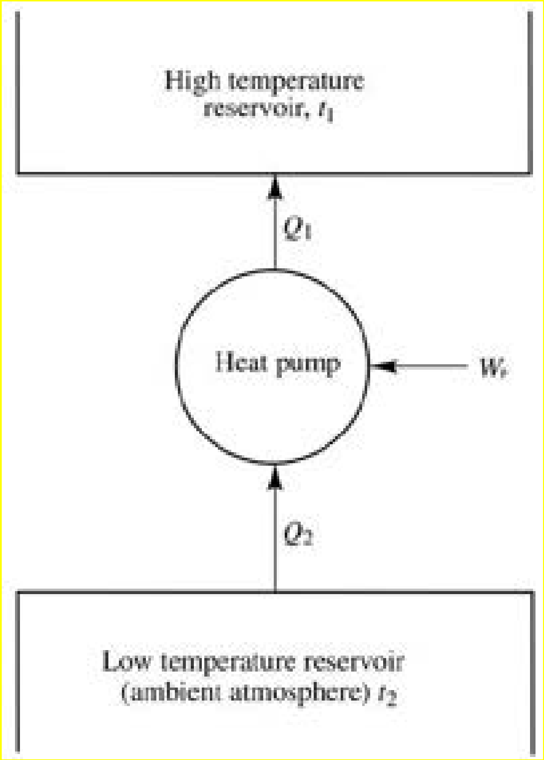


$$[\text{COP}]_R = \frac{\text{Useful refrigeration}}{\text{Net work}}$$

$$\text{COP}_R = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

$$\boxed{\text{COP}_{HP} = \text{COP}_R + 1}$$

$$\boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}$$



$$[\text{COP}]_{HP} = \frac{\text{Heat delivered to the chamber}}{\text{Net work}}$$

$$\text{COP}_{HP} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}$$

$$\text{COP}_{\text{R}} \begin{cases} < \text{COP}_{\text{R,rev}} & \text{irreversible refrigerator} \\ = \text{COP}_{\text{R,rev}} & \text{reversible refrigerator} \\ > \text{COP}_{\text{R,rev}} & \text{impossible refrigerator} \end{cases}$$

Example.2 If the thermal efficiency of a Carnot engine is $\frac{1}{6}$, calculate the coefficient of performance of (i) a Carnot heat pump, and (ii) a Carnot refrigerator.

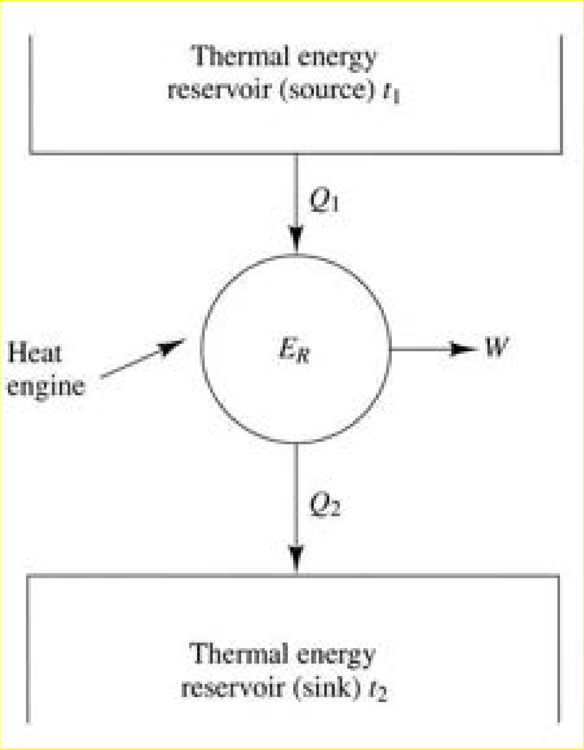
Solution The efficiency of a Carnot engine is given by $\eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1}$

where, T_1 is the source temperature and T_2 is the sink temperature.

Therefore, $$\eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1} = \frac{1}{6}$$

or, $$\frac{T_1 - T_2}{T_1} = \frac{1}{6}$$

or, $$\frac{T_1}{T_1 - T_2} = 6$$



The coefficient of performance of Carnot heat pump is

$$\text{COP}_{HP} = \frac{T_1}{T_1 - T_2} = 6$$

we have $\text{COP}_{HP} = \text{COP}_R + 1$

Therefore, the coefficient of performance of Carnot refrigerator is $\text{COP}_R = 5$.

Example .5 A heat engine operates between a source at 550°C and a sink at 25°C. If heat is supplied to the heat engine at a steady rate of 1200 kJ/min. Determine the maximum power output of this heat engine.

Solution A heat engine delivers maximum power only when it is a Carnot heat engine.

Thermal efficiency of Carnot heat engine is

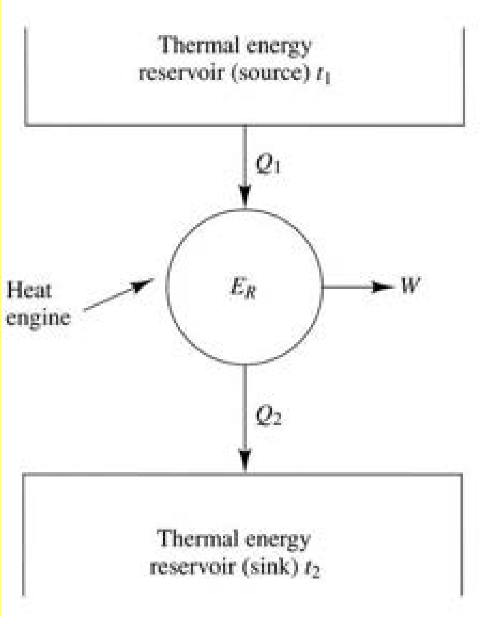
$$\eta_{\text{th, Carnot}} = 1 - \frac{T_2}{T_1} = 1 - \frac{25+273}{550+273} = 1 - \frac{298}{823} = 0.6379$$

Rate of heat transferred to the engine is given as $\dot{Q}_1 = 1200 \text{ kJ/min} = 1200 \text{ kJ/60s}$ $= 20 \text{ kJ/s} = 20 \text{ kW}$

Now, from the condition of maximum power delivery, we get

$$\eta_{\text{th, Carnot}} = \frac{\dot{W}_{\max}}{Q_1}$$

or, $$\dot{W}_{\max} = \dot{\eta}_{\max} \times \dot{Q}_1 = 0.6379 \times 20 = 12.76 \text{ kW}$$



Example.8 An inventor comes to an industrialist and claims to have developed a heat engine that receives 700 kJ of heat from a source at 500 K and produces 300 kJ of net work while rejecting the waste heat to a sink at 290 K. What would you advise to the industrialist, he should invest or not.

Solution The maximum possible efficiency of a heat engine is the same as the efficiency of a Carnot heat engine operating between the same source and sink and is given by

$$\eta_{\text{th, max}} = \eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1}$$

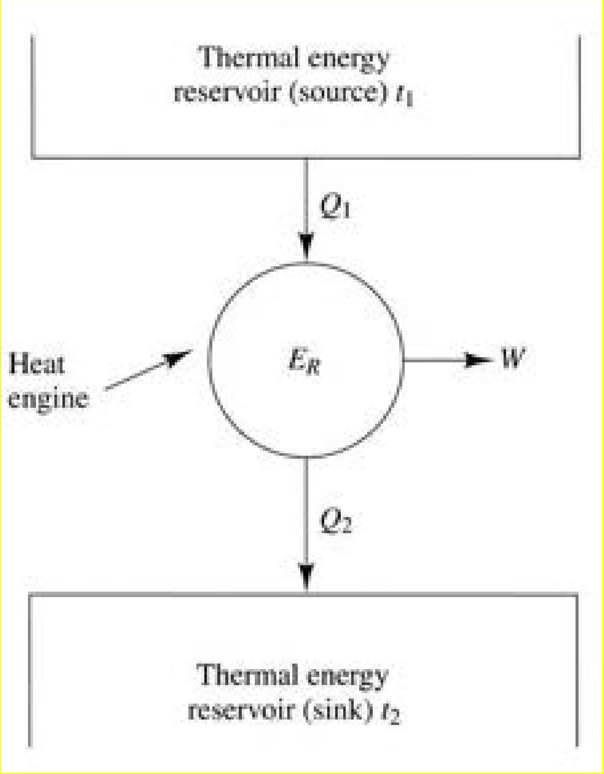
where, T_1 is the source temperature and T_2 is the sink temperature.

The efficiency of a Carnot heat engine is

$$\eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1} = 1 - \frac{290}{500} = 0.42$$

The efficiency of the heat engine is

$$\eta_{\text{ther}} = \frac{W}{Q_1} = \frac{300}{700} = 0.4285$$



Since the efficiency of the heat engine is higher than the efficiency of Carnot heat engine operating between the same source and sink, his claim is not reasonable.

Example.10 Two Carnot heat engines work in series between the source and sink temperatures of 600 K and 300 K respectively. If both engines develop equal power, determine the intermediate temperature.

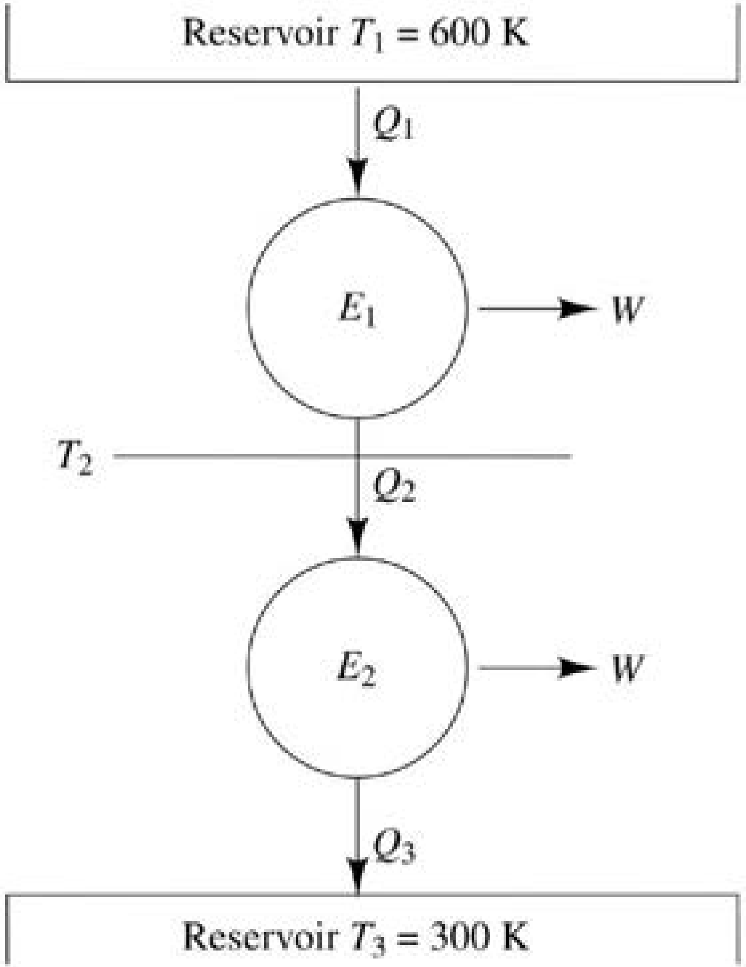
Solution Let the intermediate temperature be T_2.

For the heat engine 1,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$$

$$\frac{W}{Q_2} = \frac{T_1 - T_2}{T_2} \qquad (5.18)$$

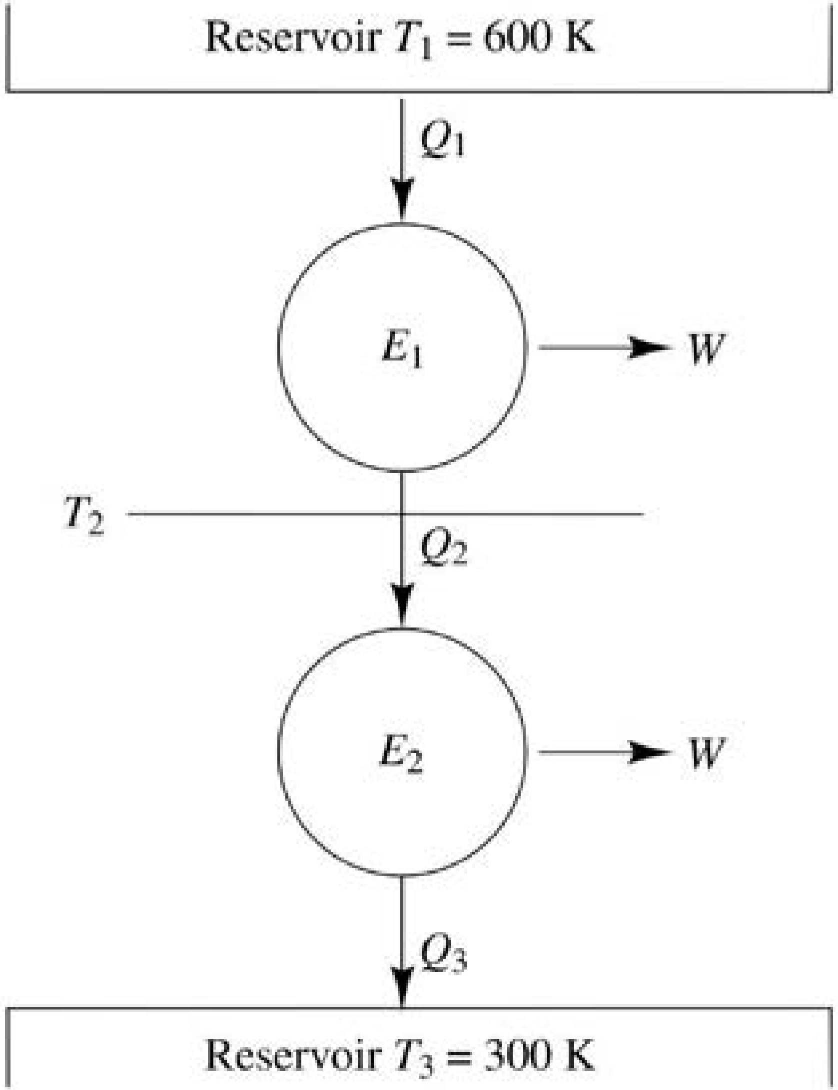


For the heat engine 2,

$$\frac{Q_3}{Q_2} = \frac{T_3}{T_2}$$

$$\frac{Q_2 - Q_3}{Q_2} = \frac{T_2 - T_3}{T_2}$$

$$\frac{W}{Q_2} = \frac{T_2 - T_3}{T_2} \qquad (5.19)$$



Equating Eqs (5.18) and (5.19), we get

$$T_1 - T_2 = T_2 - T_3$$

$$T_2 = \frac{T_1 + T_3}{2} = \frac{600 + 300}{2} = 450 \text{ K}$$

The intermediate temperature is 450 K.

Example.14 Electric solar cells can produce power with 12 % efficiency. Assume a heat engine with a low temperature heat rejection at 27ºC driving an electric generator with 85 % efficiency. What should the effective high temperature in the heat engine be to have the same overall efficiency as the solar cells?

Solution Given data:

Efficiency of solar cell,

$$\eta_{SC} = 0.12$$

Efficiency of electric generator,

$$\eta_{EG} = 0.85$$

Temperature of sink of heat engine,

$$T_2 = 27^{\circ}\text{C} = 300\text{K}$$

Efficiency of heat engine,

$$\eta_{HE} = \frac{W}{Q_1} = 1 - \frac{T_2}{T_1}$$

Now, overall efficiency of heat engine and electrical generator,

$$\eta_{\text{overall}} = \eta_{HE} \times \eta_{EG}$$

Again,

$$\eta_{\text{overall}} = \eta_{SC} = 0.12$$

$$0.12 = \eta_{HE} \times \eta_{EG}$$

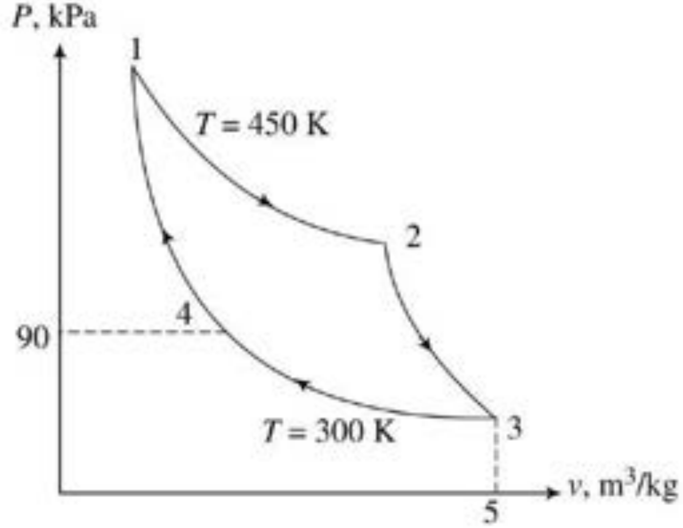
$$\eta_{HE} = \frac{\eta_{\text{overall}}}{\eta_{EG}} = \frac{0.12}{0.85} = 0.141$$

$$1 - \frac{T_2}{T_1} = 0.141$$

$$\frac{T_2}{T_1} = 0.859$$

$$T_1 = \frac{T_2}{0.859} = \frac{300}{0.859} = 349.24 \text{ K}$$

Example.18 A Carnot engine operates on air with the cycle shown in Fig. Determine the thermal efficiency and the power output for each cycle of operation,



Solution The thermal efficiency of the Carnot engine is given by

$$\eta_{\text{Carnot}} = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{450} = 0.3333 \text{ or } 33.33\%$$

Specific volume at 4 is

$$v_4 = \frac{RT_2}{P_4} = \frac{0.287 \times 300}{90} = 0.957 \text{ m}^3/\text{kg}$$

Specific volume at 1 is

$$v_1 = v_4 \left(\frac{T_4}{T_1}\right)^{\frac{1}{\gamma - 1}} = 0.957 \left(\frac{300}{450}\right)^{\frac{1}{1.4-1}} = 0.347 \text{ m}^3/\text{kg}$$

Specific volume at 2 is

$$v_2 = v_3 \left(\frac{T_3}{T_2}\right)^{\frac{1}{\gamma - 1}} = 5 \left(\frac{300}{450}\right)^{\frac{1}{1.4-1}} = 1.814 \text{ m}^3/\text{kg}$$

The heat transfer during the process 1-2 is

$$q_{1-2} = w_{1-2} = \int_{V_1}^{V_2} P dv = RT_1 \ln \frac{v_2}{v_1}$$

$$= 0.287 \times 450 \ln \frac{1.814}{0.347} = 213.61 \text{ kJ/kg}$$

The work done for each cycle is

$$w_{cycle} = \eta_{\text{Carnot}} q_{1-2} = 0.3333 \times 213.61 = 71.2 \text{ kJ/kg}$$

Example

A reversible heat engine operates between two reservoirs at temperatures of 600°C and 40°C. The engine drives a reversible refrigerator which operates between reservoirs at temperatures of 40°C and –20°C. The heat transfer to the heat engine is 2000 kJ and the net work output of the combined engine refrigerator plant is 360 kJ.

(*a*) *Evaluate the heat transfer to the refrigerant and the net heat transfer to the reservoir at 40°C.*

(*b*) *Reconsider (a) given that the efficiency of the heat engine and the COP of the refrigerator are each 40% of their maximum possible values.*

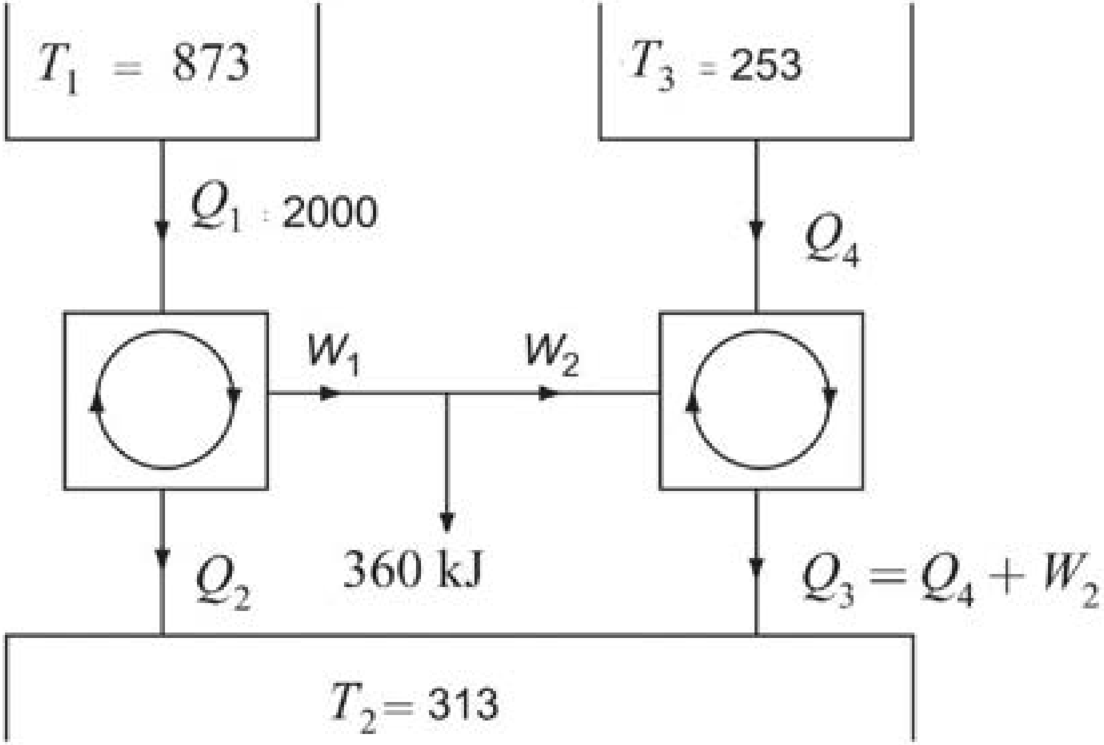
Solution (a) Maximum efficiency of the heat engine cycle (Fig.) is given by

$$\eta_{\max} = 1 - \frac{T_2}{T_1} = 1 - \frac{313}{873}$$

$$= 1 - 0.358 = 0.642$$

Again $$\frac{W_1}{Q_1} = 0.642$$

$$\therefore \quad W_1 = 0.642 \times 2000 = 1284 \text{ kJ}$$



Maximum COP of the refrigerator cycle

$$(\text{COP})_{\max} = \frac{T_3}{T_2 - T_3} = \frac{253}{313 - 253} = 4.22$$

Also $\quad \text{COP} = \dfrac{Q_4}{W_2} = 4.22$

Since $\qquad W_1 - W_2 = W = 360 \text{ kJ}$

$\therefore \quad W_2 = W_1 - W = 1284 - 360 = 924 \text{ kJ}$

$\therefore \quad Q_4 = 4.22 \times 924 = 3899 \text{ kJ}$

$\therefore \quad Q_3 = Q_4 + W_2 = 924 + 3899 = 4823 \text{ kJ}$

$\quad Q_2 = Q_1 - W_1 = 2000 - 1284 = 716 \text{ kJ}$

Heat rejection to the 40°C reservoir

$$= Q_2 + Q_3 = 716 + 4823 = 5539 \text{ kJ} \quad \textit{Ans.} \text{ (a)}$$

(b) Efficiency of the actual heat engine cycle

$$\eta = 0.4\, \eta_{\max} = 0.4 \times 0.642$$

$$\therefore \quad W_1 = 0.4 \times 0.642 \times 2000 = 513.6 \text{ kJ}$$

$$\therefore \quad W_2 = 513.6 - 360 = 153.6 \text{ kJ}$$

COP of the actual refrigerator cycle

$$\text{COP} = \frac{Q_4}{W_2} = 0.4 \times 4.22 = 1.69$$

Therefore $Q_4 = 153.6 \times 1.69 = 259.6 \text{ kJ}$

$$Q_3 = 259.6 + 153.6 = 413.2 \text{ kJ} \qquad \textit{Ans. } \text{(b)}$$

$$Q_2 = Q_1 - W_1 = 2000 - 513.6 = 1486.4 \text{ kJ}$$

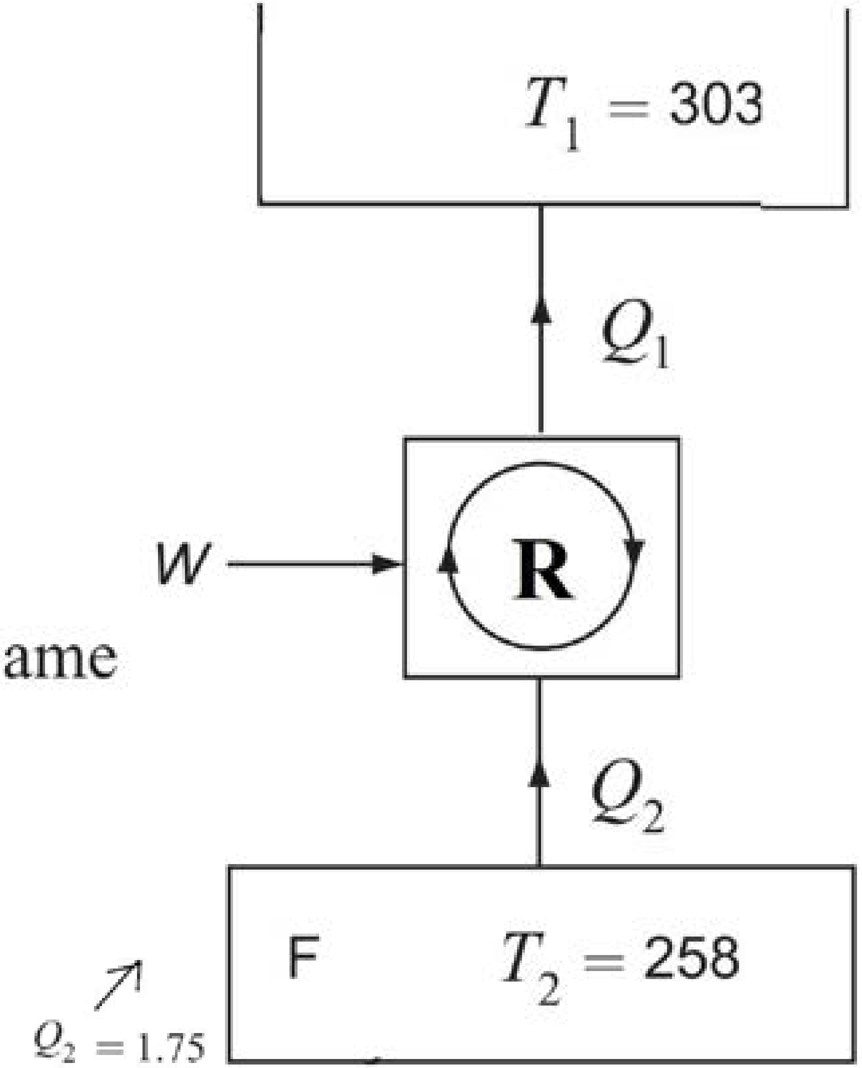
Heat rejected to the 40°C reservoir

$$= Q_2 + Q_3 = 413.2 + 1486.4 = 1899.6 \text{ kJ} \qquad \textit{Ans. } \text{(b)}$$

Example

A domestic food freezer maintains a temperature of −15 C. The ambient air temperature is 30 C. If heat leaks into the freezer at the continuous rate of 1.75 kJ s what is the least power necessary to pump this heat out continuously

Solution



Freezer temperature,

$$T_2 = -15 + 273 = 258 \text{ K}$$

Ambient air temperature,

$$T_1 = 30 + 273 = 303 \text{ K}$$

The refrigerator cycle removes heat from the freezer at the same rate at which heat leaks into it

For minimum power requirement

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}$$

$$\therefore \qquad Q_1 = \frac{1.75}{2.8} \times 303 = 2.06 \text{ kJ/s}$$

$$\therefore \qquad W = Q_1 - Q_2$$

$$= 2.06 - 1.75 = 0.31 \text{ kJ/s} = 0.31 \text{ kW}$$

AIR STANDARD CYCLES

A **cycle** is defined as a repeated series of operations occurring in a certain order. It may be repeated by repeating the processes in the same order. The cycle may be of imaginary perfect engine or actual engine. The former is called **ideal cycle** and the latter **actual cycle.** In ideal cycle all accidental heat losses are prevented and the working substance is assumed to behave like a perfect working substance.

To compare the effects of different cycles, it is of paramount importance that the effect of the calorific value of the fuel is altogether eliminated and this can be achieved by considering air (which is assumed to behave as a perfect gas) as the working substance in the engine cylinder. The efficiency of engine using air as the working medium is known as an **"Air standard efficiency".** This efficiency is often called **ideal efficiency**.

The actual gas power cycles are rather complex. To reduce the analysis to a manageable level, we utilize the following approximations, commonly known as the **air-standard assumptions.** These assumptions provide considerable simplification in the analysis without significantly deviating from the actual cycles. These simplified model enables us to study qualitatively the influence of major parameters on the performance of the actual engines.

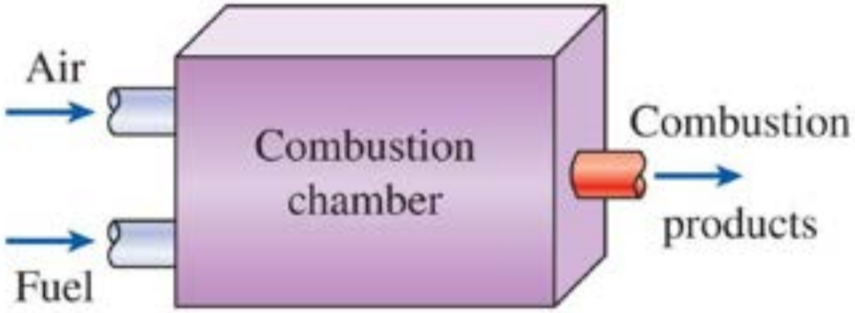
Air standard assumptions:

1. The working fluid is air, which continuously circulates in a closed loop and always behaves as an ideal gas.

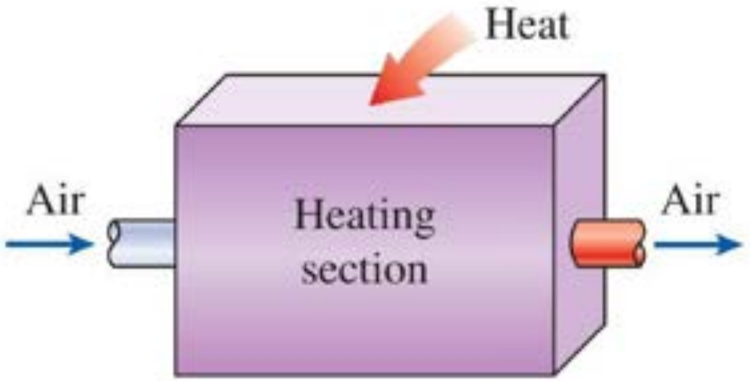
2. All the processes that make up the cycle are internally reversible.

3. The combustion process is replaced by a heat-addition process from an external source.

4. The exhaust process is replaced by a heat-rejection process that restores the working fluid to its initial state.



(*a*) Actual



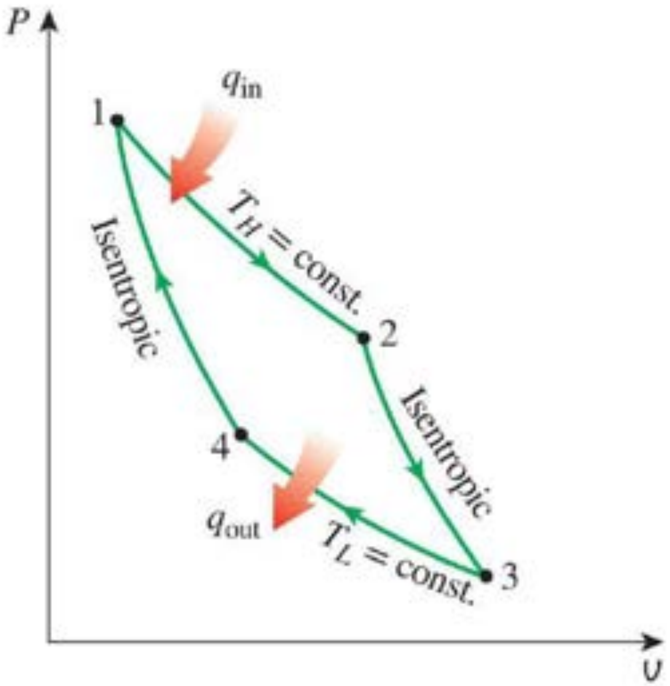
(*b*) Ideal

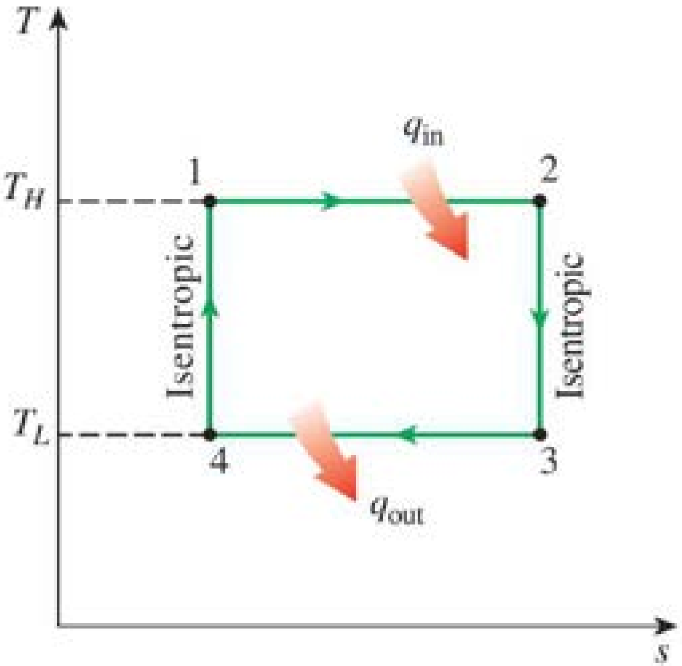
FIGURE
The combustion process is replaced by a heat-addition process in ideal cycles.

5. The air has constant specific heats whose values are determined at room temperature (25°C, or 77°F).

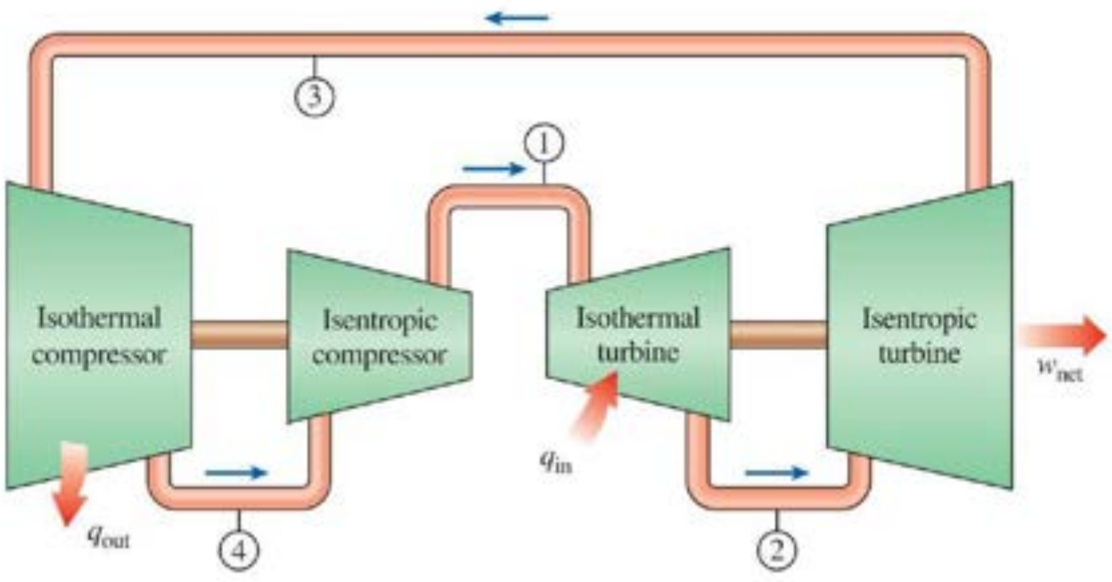
When this assumption is used, the air-standard assumptions are called the *cold-air-standard assumptions*.

CARNOT CYCLE





$$\eta_{\text{th,Carnot}} = 1 - \frac{T_L}{T_H}$$



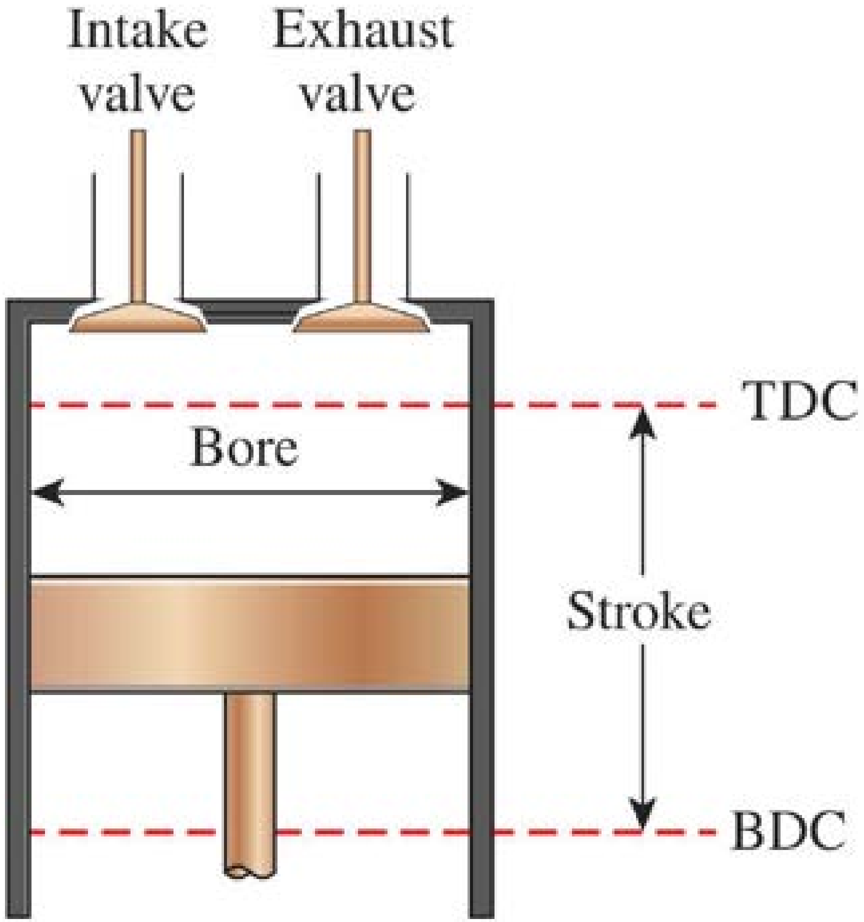
1. Reversible Isothermal Expansion (process 1-2, T_H = constant).

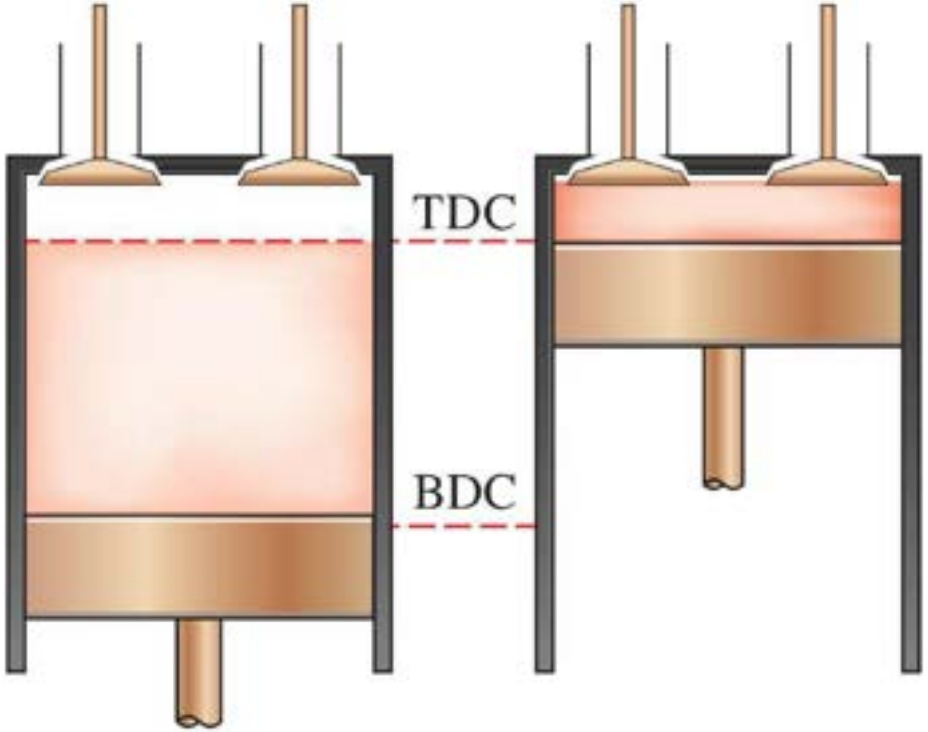
2.Reversible Adiabatic Expansion (process 2-3, temperature drops from T_H to T_L)

3.Reversible Isothermal Compression (process 3-4, T_L = constant)

4.Reversible Adiabatic Compression (process 4-1, temperature rises from T_L to T_H)

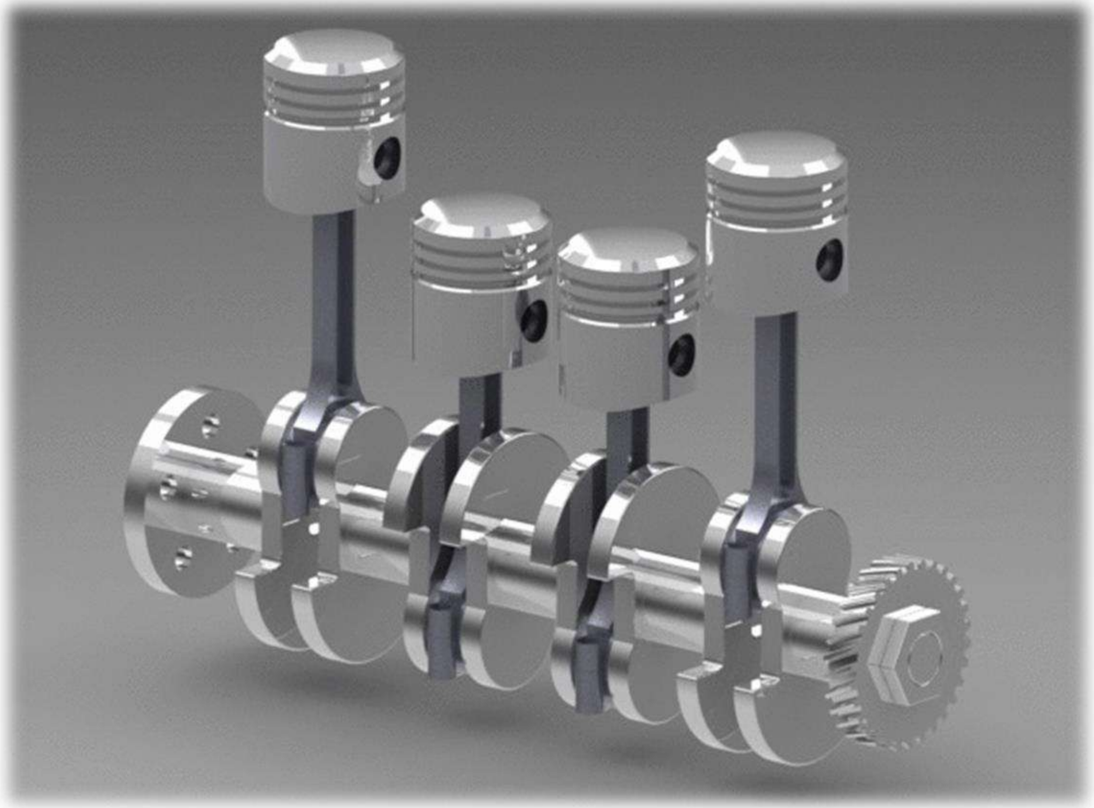
AN OVERVIEW OF RECIPROCATING ENGINES

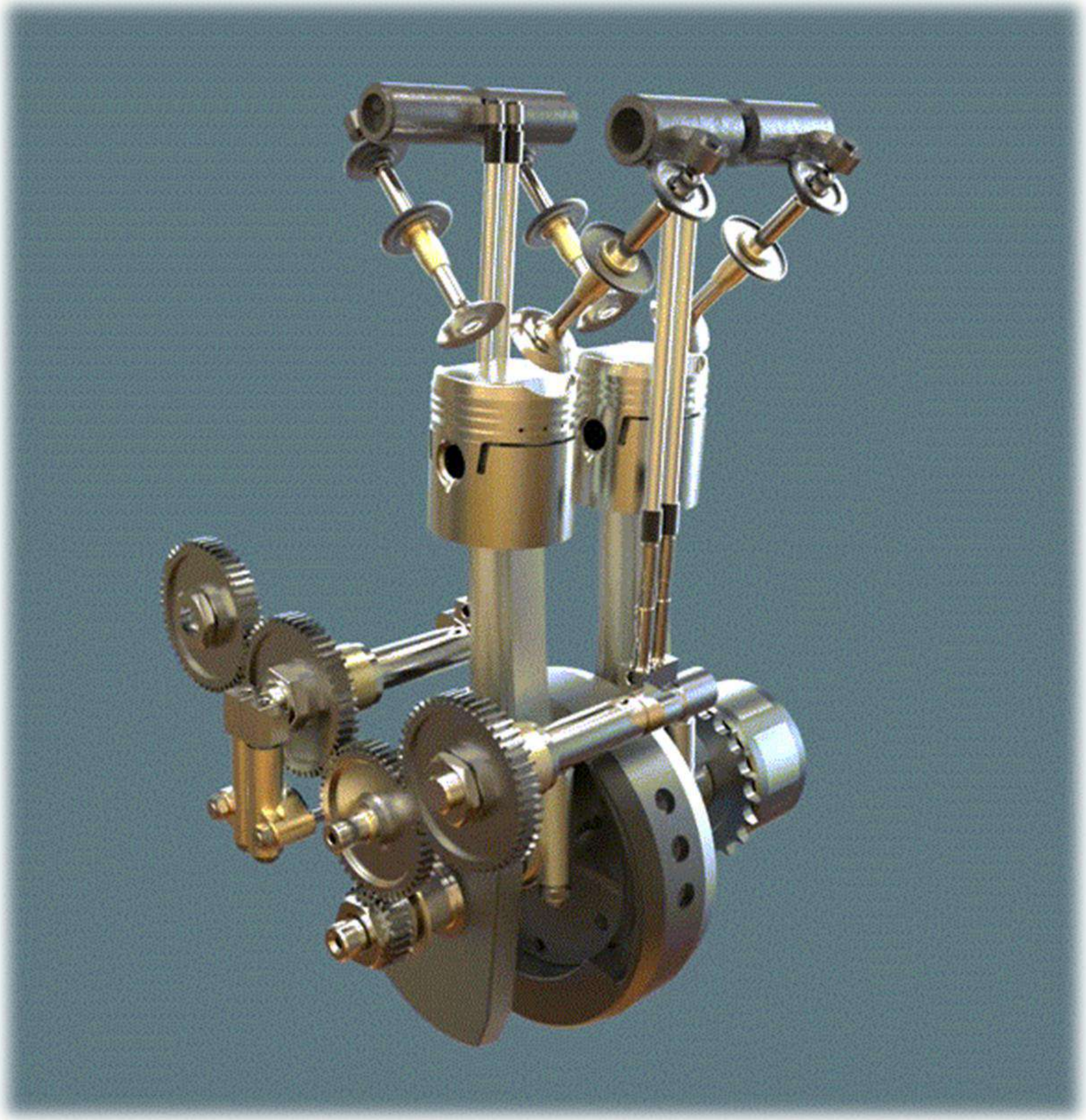




(*a*) Displacement volume

(*b*) Clearance volume



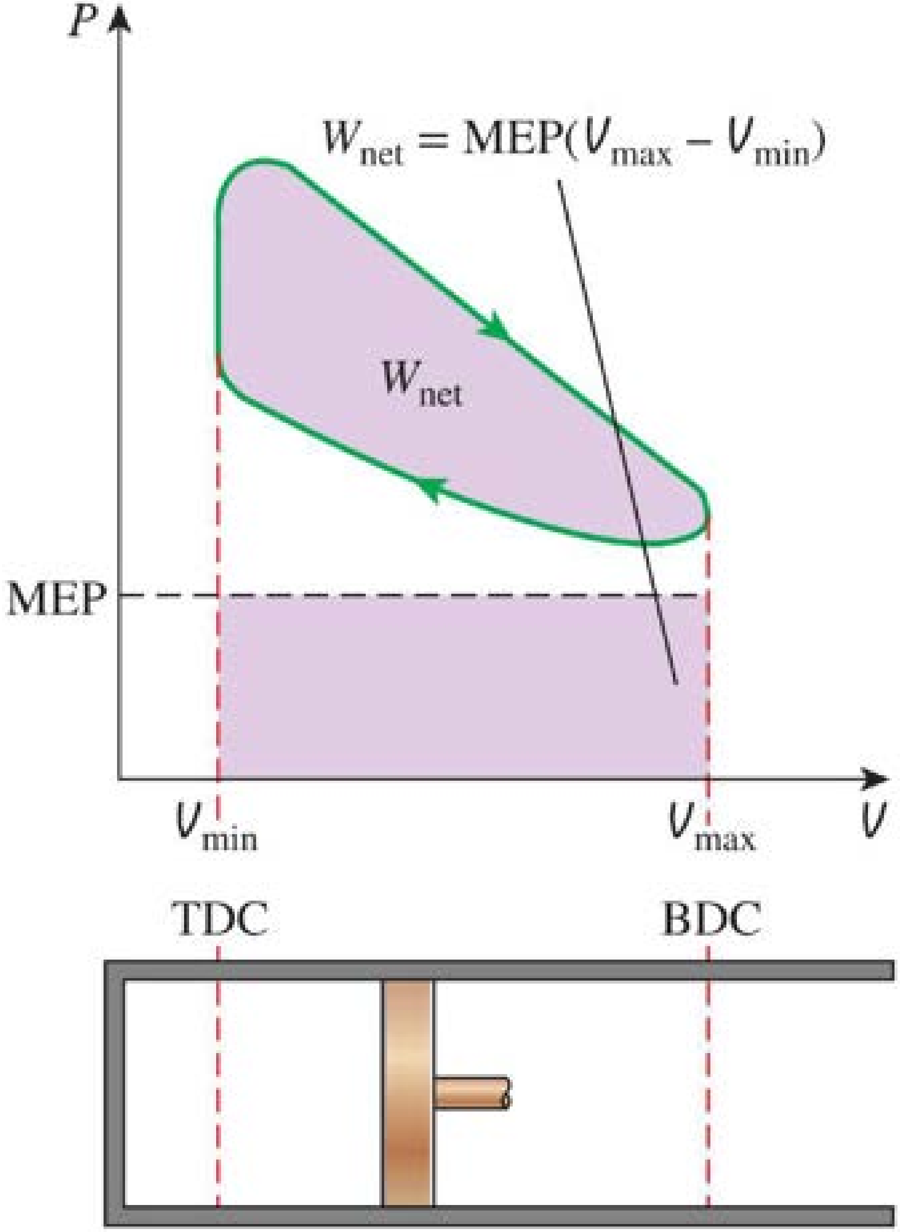


Mean effective pressure (MEP):

It is a fictitious pressure that, if it acted on the piston during the entire power stroke, would produce the same amount of net work as that produced during the actual cycle. The mean effective pressure can be used as a parameter to compare the performances of reciprocating engines of equal size. The engine with a larger value of MEP delivers more net work per cycle and thus performs better.

$$W_{\text{net}} = \text{MEP} \times \text{Piston area} \times \text{Stroke} = \text{MEP} \times \text{Displacement volume}$$

$$\text{MEP} = \frac{W_{\text{net}}}{V_{\max} - V_{\min}} = \frac{w_{\text{net}}}{v_{\max} - v_{\min}} \qquad \text{(kPa)}$$

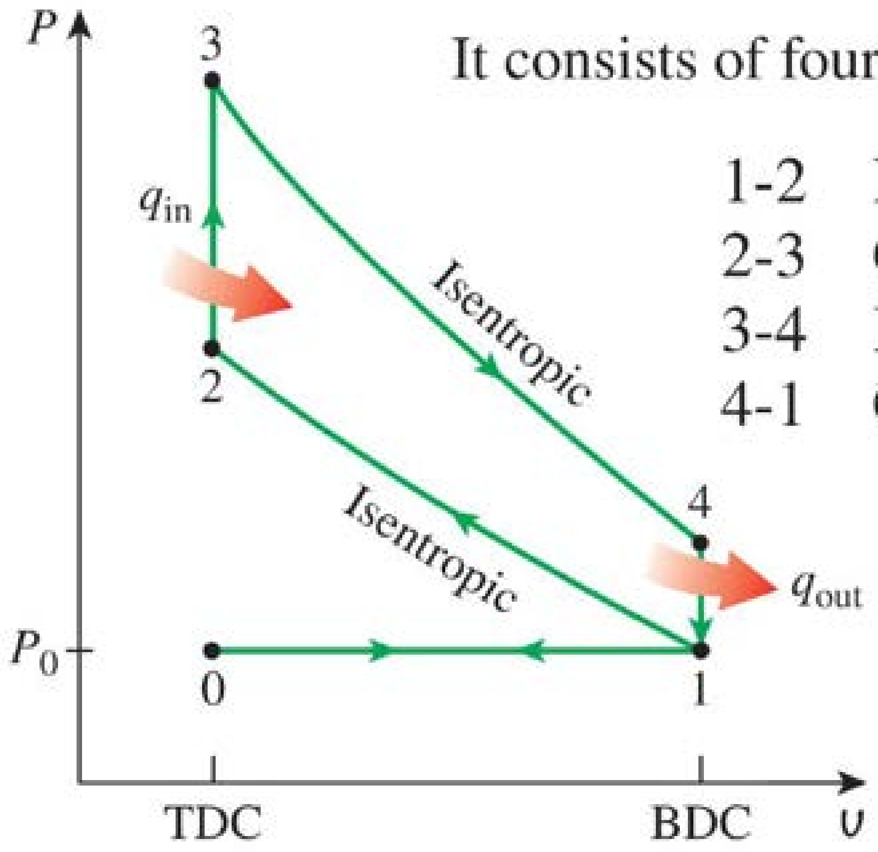


OTTO CYCLE or Constant Volume cycle

The Otto cycle is the ideal cycle for spark-ignition reciprocating engines. It is named after a German sentient **Nikolaus A. Otto**, who built a successful four-stroke engine in 1876.

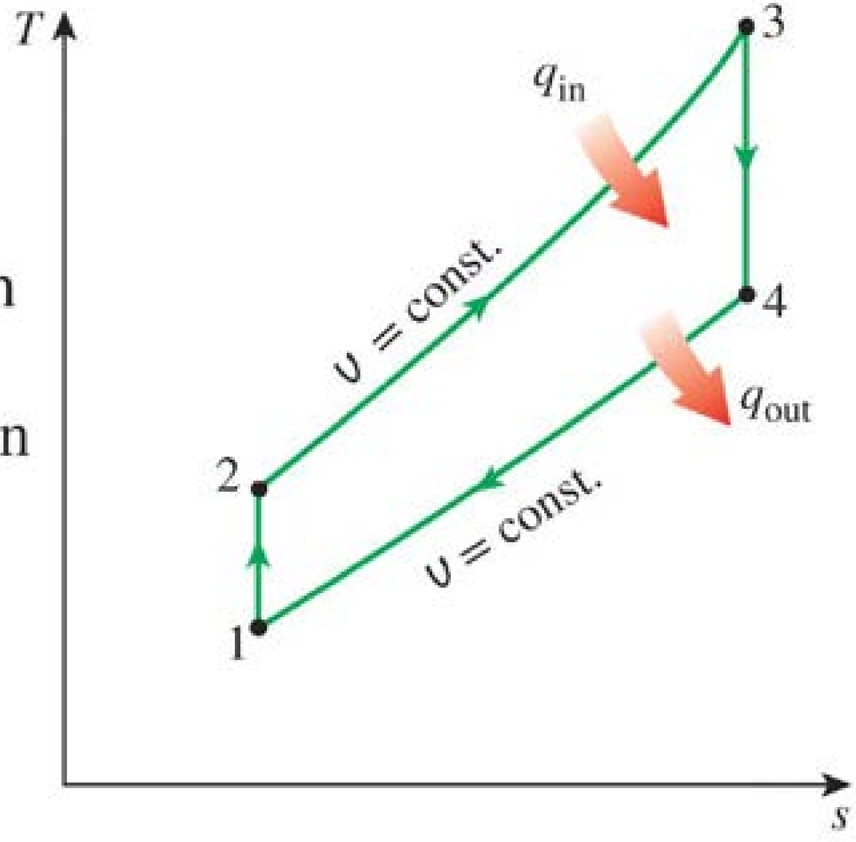
It consists of four internally reversible processes:

1-2 Isentropic compression
2-3 Constant-volume heat addition
3-4 Isentropic expansion
4-1 Constant-volume heat rejection



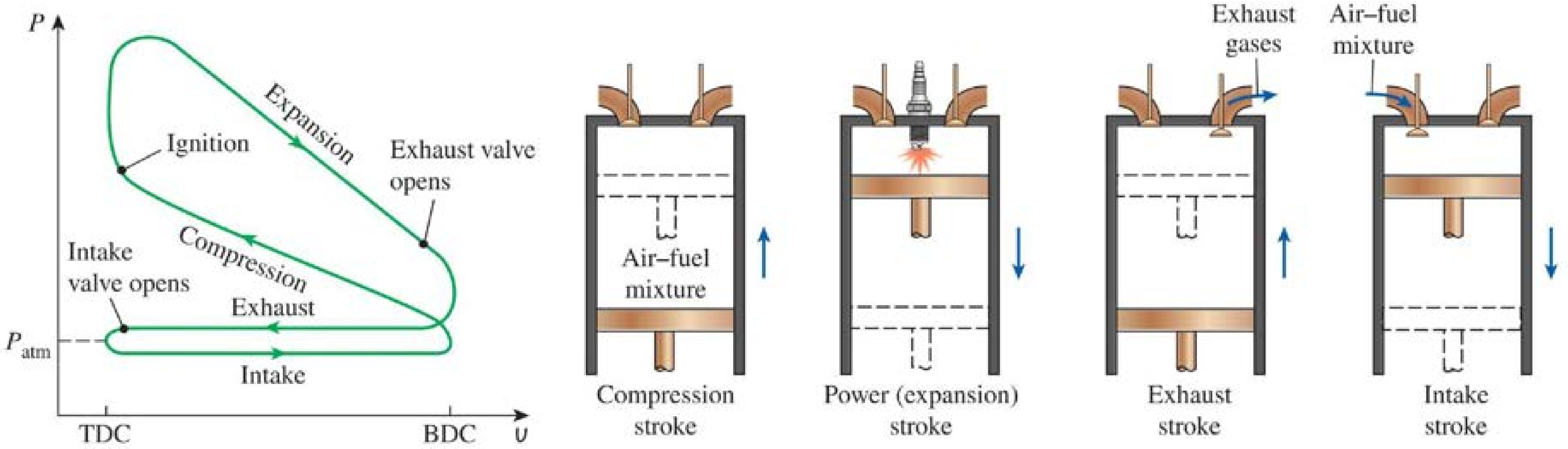
FIGURE

P-υ diagram of the ideal Otto cycle

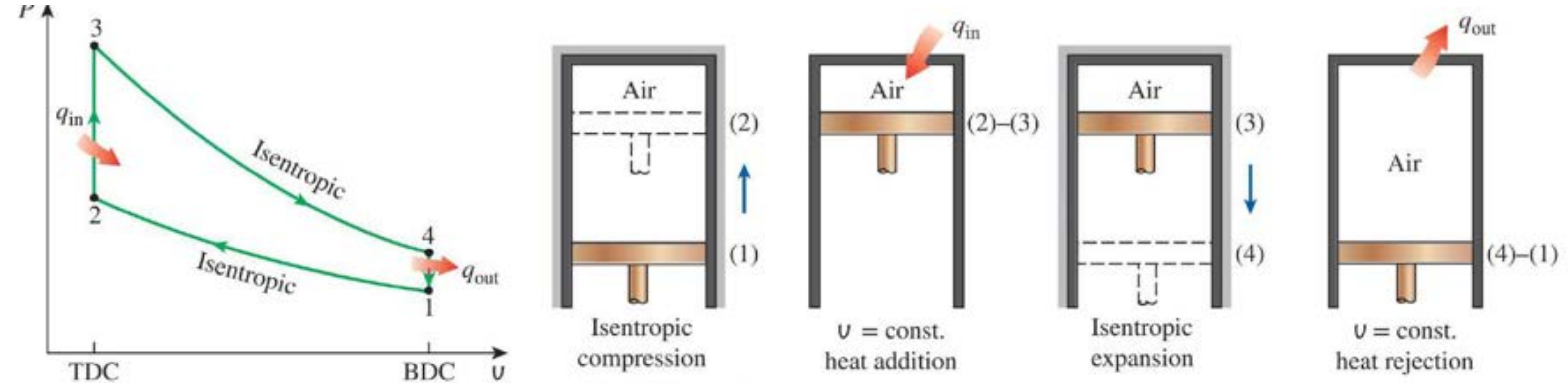


FIGURE

T-s diagram of the ideal Otto cycle.



(*a*) Actual four-stroke spark-ignition engine



(*b*) Ideal Otto cycle

Consider **1 kg of air** (working substance) :

Heat supplied at constant volume $= c_v(T_3 - T_2)$.

Heat rejected at constant volume $= c_v (T_4 - T_1)$.

But, work done = Heat supplied – Heat rejected

$$= c_v (T_3 - T_2) - c_v (T_4 - T_1)$$

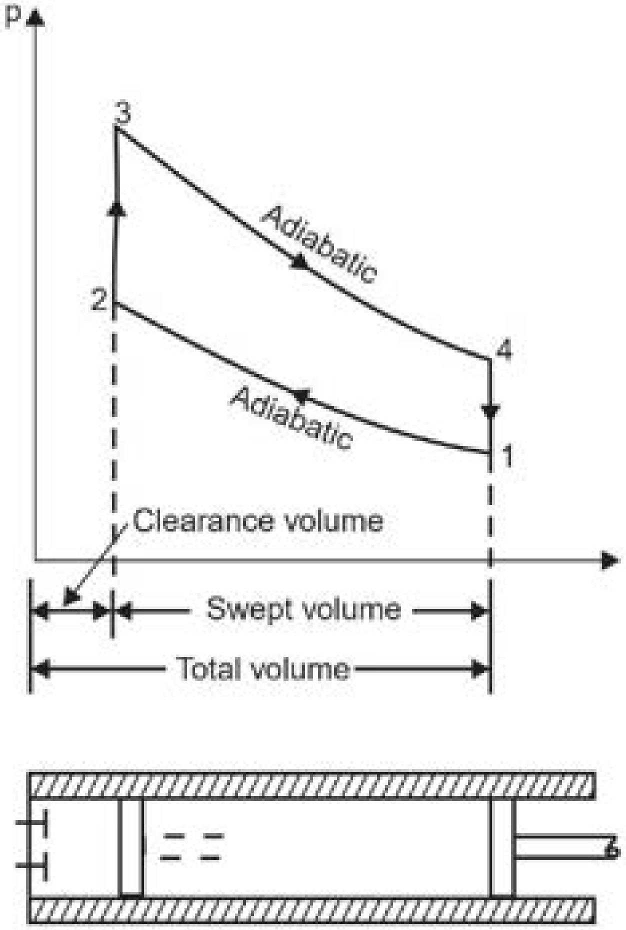
$$\therefore \qquad \text{Efficiency} = \frac{\text{Work done}}{\text{Heat supplied}} = \frac{c_v (T_3 - T_2) - c_v (T_4 - T_1)}{c_v (T_3 - T_2)}$$

$$= 1 - \frac{T_4 - T_1}{T_3 - T_2} \qquad \ldots(i)$$

Let compression ratio, $r_c\ (= r) = \dfrac{v_1}{v_2}$

and expansion ratio, $r_e\ (= r) = \dfrac{v_4}{v_3}$

(These *two ratios are same* in this cycle)



As $$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma - 1}$$

Then, $$T_2 = T_1 \, . \, (r)^{\gamma - 1}$$

Similarly, $$\frac{T_3}{T_4} = \left(\frac{v_4}{v_3}\right)^{\gamma - 1}$$

or $$T_3 = T_4 \, . \, (r)^{\gamma - 1}$$

Inserting the values of T_2 and T_3 in equation (i), we get

$$\eta_{otto} = 1 - \frac{T_4 - T_1}{T_4 \, . (r)^{\gamma - 1} - T_1 \, . (r)^{\gamma - 1}} = 1 - \frac{T_4 - T_1}{r^{\gamma - 1}(T_4 - T_1)}$$

$$\boxed{= 1 - \frac{1}{(r)^{\gamma - 1}}}$$

This expression is known as the ***air standard efficiency of the Otto cycle.***

DIESEL CYCLE or Constant Pressure cycle:

The Diesel cycle is the ideal cycle for CI reciprocating engines. The CI engine, first proposed by ***Rudolph Diesel*** in the 1890s, is very similar to the SI engine discussed in the last section, differing mainly in the method of initiating combustion. In CI engines, the air is compressed to a temperature that is above the autoignition temperature of the fuel, and combustion starts on contact as the fuel is injected into this hot air.

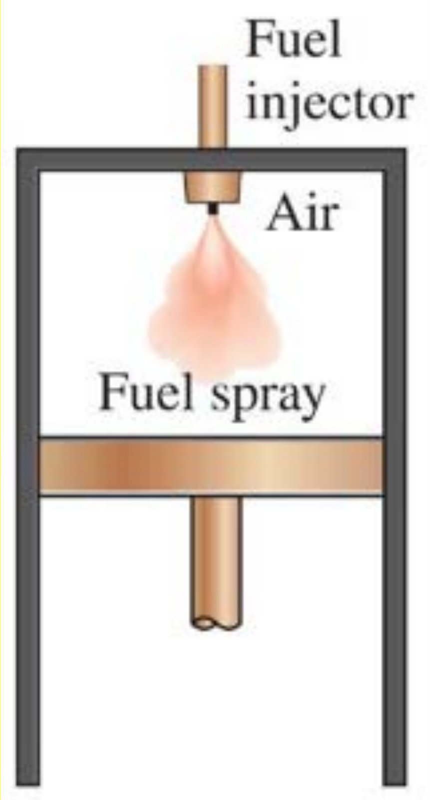
Salient features of diesel engines:

*Limitation on compression ratio in S.I engine can be overcome by compressing air alone, so that the diesel engines can operate at much higher compression ratios typically between 12 to 24.

*Fuel is injected when combustion is desired.

* Auto ignition and engine knock can be avoided.

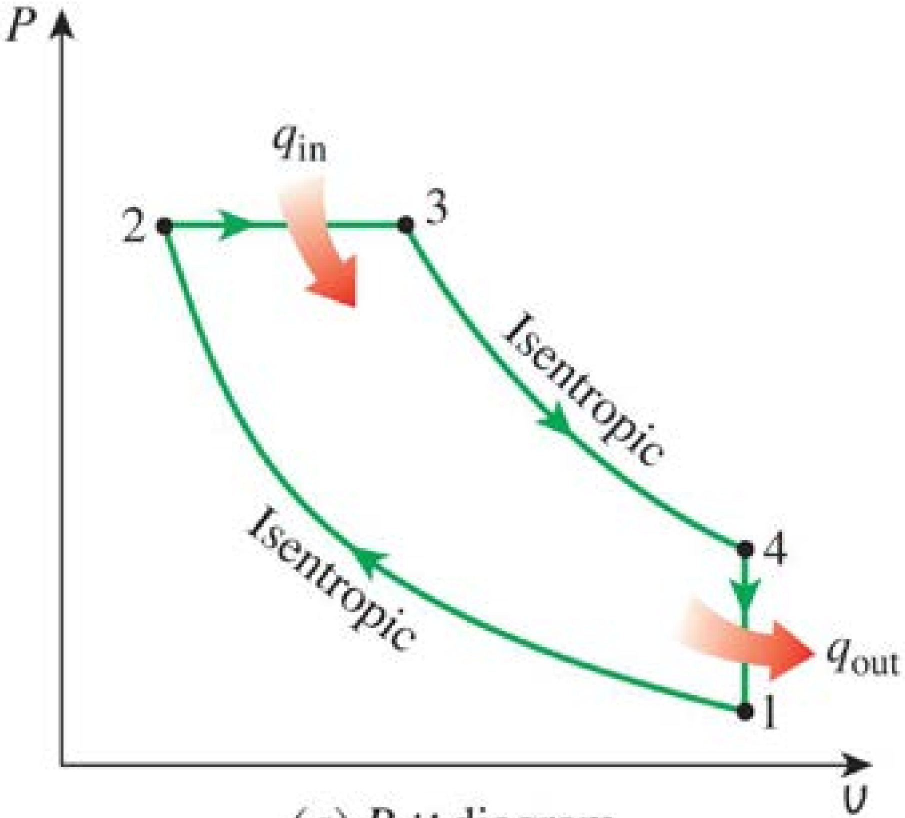
* Temperature after compression of air is more than sufficient to start the ignition process spontaneously whenever the fuel is sprayed into the combustion chamber.



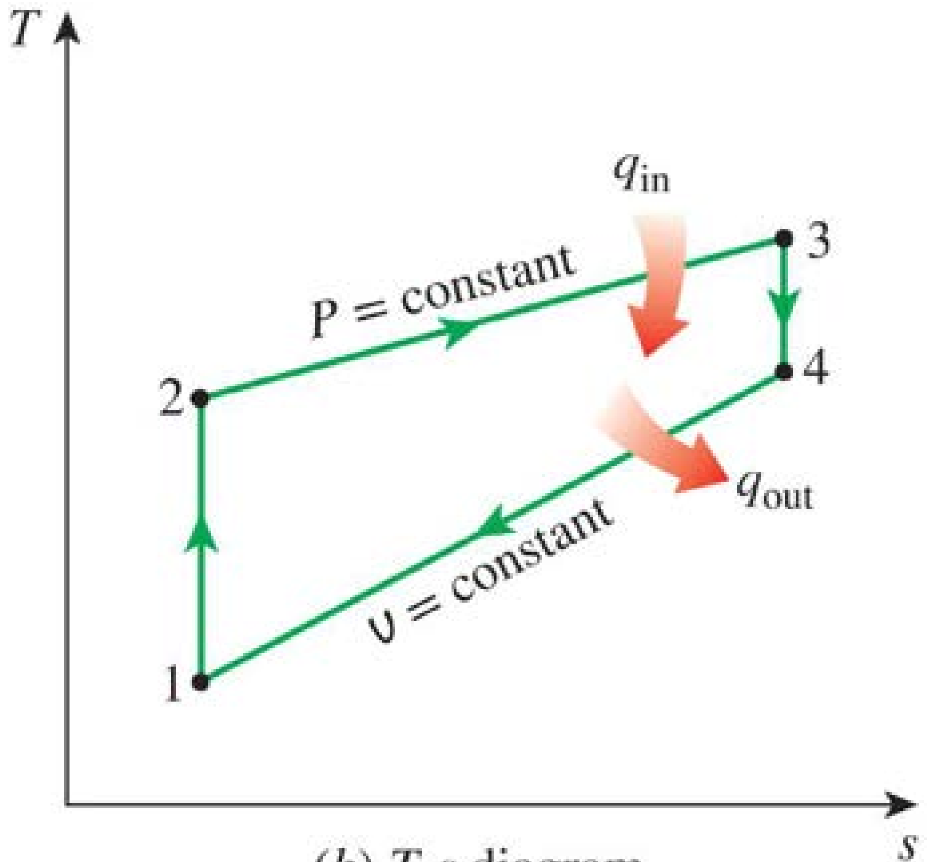
Diesel engine

It consists of four internally reversible processes:

1-2 is isentropic compression,
2-3 is constant-pressure heat addition,
3-4 is isentropic expansion, and
4-1 is constant-volume heat rejection.



(a) P-υ diagram



(b) T-s diagram

Consider 1 kg of air.

Heat supplied at constant pressure $= c_p(T_3 - T_2)$

Heat rejected at constant volume $= c_v(T_4 - T_1)$

Work done = Heat supplied – heat rejected

$$= c_p(T_3 - T_2) - c_v(T_4 - T_1)$$

$$\therefore \qquad \eta_{\text{diesel}} = \frac{\text{Work done}}{\text{Heat supplied}}$$

$$= \frac{c_p(T_3 - T_2) - c_v(T_4 - T_1)}{c_p(T_3 - T_2)}$$

$$= 1 - \frac{(T_4 - T_1)}{\gamma(T_3 - T_2)} \qquad \ldots(i) \left[\because \frac{c_p}{c_v} = \gamma\right]$$

Let compression ratio, $r = \dfrac{v_1}{v_2}$, and cut-off ratio, $\rho = \dfrac{v_3}{v_2}$ *i.e.*, $\dfrac{\text{Volume at cut-off}}{\text{Clearance volume}}$

Now, during *adiabatic compression 1-2,*

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{\gamma - 1} = (r)^{\gamma - 1} \quad \text{or} \quad T_2 = T_1 \,.\, (r)^{\gamma - 1}$$

During *constant pressure process 2-3,*

$$\frac{T_3}{T_2} = \frac{v_3}{v_2} = \rho \quad \text{or} \quad T_3 = \rho \,.\, T_2 = \rho \,.\, T_1 \,.\, (r)^{\gamma - 1}$$

During *adiabatic expansion 3-4*

$$\frac{T_3}{T_4} = \left(\frac{v_4}{v_3}\right)^{\gamma - 1}$$

$$= \left(\frac{r}{\rho}\right)^{\gamma - 1} \qquad \left(\because \quad \frac{v_4}{v_3} = \frac{v_1}{v_3} = \frac{v_1}{v_2} \times \frac{v_2}{v_3} = \frac{r}{\rho}\right)$$

$$\therefore \quad T_4 = \frac{T_3}{\left(\frac{r}{\rho}\right)^{\gamma - 1}} = \frac{\rho \,.\, T_1 (r)^{\gamma - 1}}{\left(\frac{r}{\rho}\right)^{\gamma - 1}} = T_1 \,.\, \rho^{\gamma}$$

By inserting values of T_2, T_3 and T_4 in eqn. (i), we get

$$\eta_{\text{diesel}} = 1 - \frac{(T_1 \,.\, \rho^{\gamma} - T_1)}{\gamma\,(\rho \,.\, T_1 \,.\, (r)^{\gamma-1} - T_1 \,.\, (r)^{\gamma-1})} = 1 - \frac{(\rho^{\gamma} - 1)}{\gamma (r)^{\gamma-1} (\rho - 1)}$$

$$\boxed{\eta_{\text{diesel}} = 1 - \frac{1}{\gamma (r)^{\gamma-1}} \left[\frac{\rho^{\gamma} - 1}{\rho - 1} \right]}$$

It may be observed that eqn. for efficiency of diesel cycle is different from that of the Otto cycle only in bracketed factor. This factor is always greater than unity, because ρ > 1. Hence for a given compression ratio, the Otto cycle is more efficient.

General Relations, Availability and Unavailability

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General Relations, Availability and Unavailability

- Helmholtz function and Gibbs function, Maxwell’s equations- Tds relations, relation between specific heats, Available energy, unavailable energy, Available and unavailable forms of energy for a flow and non-flow process-irrevesibility

GENERAL ASPECTS

- Eight properties of a system, namely pressure (p), volume (v), temperature (T), internal energy (u), enthalpy (h), entropy (s), Helmholtz function (f) and Gibbs function (g) have been introduced in the previous chapters. h, f and g are sometimes referred to as **thermodynamic potentials. Both f and g are useful when considering chemical reactions,** and the former is of fundamental importance in statistical thermodynamics. The Gibbs function is also useful when considering processes involving a change of phase.

GENERAL ASPECTS

- Of the above eight properties only the first three, i.e., p, v and T are directly measurable. We shall find it convenient to introduce other combination of properties which are relatively easily measurable and which, together with measurements of p, v and T, enable the values of the remaining properties to be determined. These combinations of properties might be called ‘**thermodynamic gradients’ ; they are all defined as the rate of change of one property with another** while a third is kept constant.

INTERNAL ENERGY (U)

- The first law applied to a closed system undergoing a reversible process states that $dQ = du + pdv$

According to second law $dQ = T\,ds$

Combining these equations, we get $Tds = du + pdv$

or $du = Tds – pdv$ (i)

Since du, the exact differentials, we can express them as $u = f(s, v)$

$$du = \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv, \qquad .....(ii)$$

Comparing equation(i) & (ii)

ENTHALPY

- Enthalpy is a thermodynamic property and it is defined as $h = u + pv$
- The properties h may also be put in terms of T, s, p and v as follows :

$$dh = du + pdv + vdp \qquad \text{(i.e } du = Tds - pdv\text{)}$$

$$dh = Tds + vdp \quad .....(i)$$

Since dh the exact differentials, we can express them as $h = f(s, p)$

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp, \quad .(ii)$$

Comparing equation(i) & (ii)

Gibbs and Helmholtz Functions

- For a simple compressible system of fixed chemical composition thermodynamic properties can be given from combination of first law and second law of thermodynamics as,

$$u = f(s, v)\ ; \qquad du = T \cdot ds - pdv$$

$$h = f(s, p)\ ; \qquad dh = T \cdot ds + vdp$$

Gibbs function (g) and Helmholtz function (f) are properties defined as below.

Gibbs function $\qquad G = H - T \cdot S$

$g = h - T \cdot s$, on unit mass basis i.e. specific Gibb's function

Gibbs and Helmholtz Functions

Helmholtz function, F = U – T · S

f = u – T · s , on unit mass basis i.e. specific Helmholtz function

- In differential form Gibbs function can be given as below for an infinitesimal reversible process

$$g = h - T \cdot s; \quad dg = dh - T \cdot ds - s \cdot dT$$

dg = vdp − sdT for a reversible isothermal process

$$dg = \left(\frac{\partial g}{\partial p}\right)_T dp + \left(\frac{\partial g}{\partial T}\right)_p dT. \qquad \int_1^2 dg = \int_1^2 v dp$$

also dG =Vdp − SdT for reversible isothermal process

$$\int_1^2 dG = \int_1^2 V dp$$

Gibbs and Helmholtz Functions

- For a “reversible isobaric and isothermal process”, $dp = 0$, $dT = 0$ $dG = 0$

  i.e. G = constant

- Gibbs function’ is also termed as ‘Gibbs free energy’. For a reversible isobaric and isothermal process Gibbs free energy remains constant or Gibbs function of the process remains constant. Such reversible thermodynamic processes may occur in the processes involving change of phase, such as sublimation, fusion, vaporization etc., in which Gibbs free energy remains constant

Gibbs and Helmholtz Functions

- ‘Helmholtz function’ is also called ‘Helmholtz free energy’. For any infinitesimal reversible process Helmholtz function can be given in differential form as, $df = du - T \cdot ds - sdT$

$$\text{or,} \quad df = -pdv - sdT$$

$$\text{or,} \quad dF = -pdV - SdT$$

$$df = \left(\frac{\partial f}{\partial v}\right)_T dv + \left(\frac{\partial f}{\partial T}\right)_v dT,$$

For a reversible isothermal process

$$df = -pdv$$

$$\int_1^2 df = -\int_1^2 p \cdot dv$$

$$\int_1^2 dF = -\int_1^2 pdV$$

Gibbs and Helmholtz Functions

- For a reversible isothermal and isochoric process, $dT = 0$, $dV = 0$

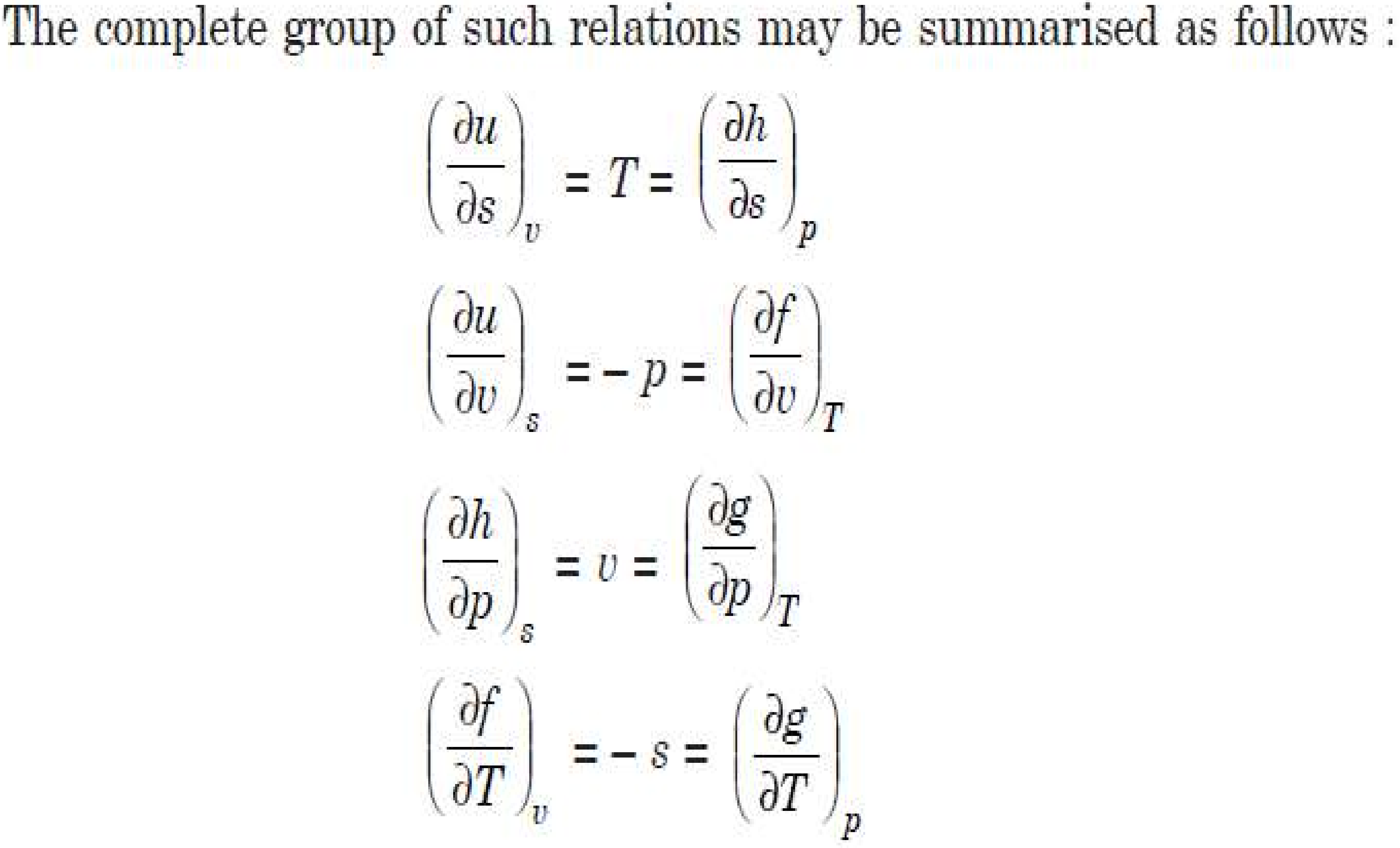
$$df = 0$$

$$\text{or, } dF = 0$$

$$F = \text{Constant}$$

- Above concludes that the Helmholtz free energy remains constant during a reversible isothermal and isochoric process. Such processes may occur during chemical reactions occurring isothermally and isochorically.

Comparison of two equations du , dg , dh and df



The complete group of such relations may be summarised as follows :

$$\left(\frac{\partial u}{\partial s}\right)_v = T = \left(\frac{\partial h}{\partial s}\right)_p$$

$$\left(\frac{\partial u}{\partial v}\right)_s = -p = \left(\frac{\partial f}{\partial v}\right)_T$$

$$\left(\frac{\partial h}{\partial p}\right)_s = v = \left(\frac{\partial g}{\partial p}\right)_T$$

$$\left(\frac{\partial f}{\partial T}\right)_v = -s = \left(\frac{\partial g}{\partial T}\right)_p$$

Some Mathematical Theorems

Theorem 1: If a relation exists among the variables x, y, and z, then Z may be expressed as a function of x and y,

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$dz = M \cdot dx + N \cdot dy$$

$$, M = \left(\frac{\partial z}{\partial x}\right)_y , N = \left(\frac{\partial z}{\partial y}\right)_x$$

i.e. M is partial derivative of z with respect to x when variable y is held constant and N is partial derivative of z with respect to y when variable x is held constant

Some Mathematical Theorems

Differentiating M partially with respect to y, and N with respect to x

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x \cdot \partial y}$$

$$\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y \cdot \partial x}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

This is the condition of exact (or perfect) differential

Some Mathematical Theorems

- **Theorem 2:** If a quantity f is a function of x, y, and z, and a relation exists among x, y and z, Then f is a function of any two of x, y, and z. Similarly any one of x, y, and z may be regarded to be a function of f and any one of x, y, and z.
- Then we have a relation between the variables as given below

$$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial x}\right)_f = 1$$

Some Mathematical Theorems

Theorem 3: Among the variables x, y, and z, any one variable may be considered as a function of the other two. Thus

$$x = x(y, z)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

Then we have a relation between these variables as given below

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

Among the thermodynamic variables p, V, and T, the following relation hold good

$$\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V = -1$$

Maxwell's Equations

- A pure substance existing in a single phase has only two independent variables. Of the eight quantities p, V, T, S, U, H, F (Helmholtz function), and G (Gibbs function) any one may be expressed as a function of any two others
- The first law applied to a closed system undergoing a reversible process states that $dQ = du + pdv$

According to second law $dQ = T\,ds$

- Combining these equations, we get $Tds = du + pdv$

  or $du = Tds - pdv$
- The properties h, f and g may also be put in terms of T, s, p and v as follows : $dh = du + pdv + vdp = Tds + vdp$

Maxwell's Equations

Helmholtz free energy function,

$$df = du - Tds - sdT$$

$$= -pdv - sdT$$

Gibb’s free energy function,

$$dg = dh - Tds - sdT = vdp - sdT$$

Each of these equations is a result of the two laws of thermodynamics

Maxwell's Equations

For a pure substance undergoing an infinitesimal reversible process

(a) $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$

(b) $\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p = T\mathrm{d}S + V\mathrm{d}p$

(c) $\mathrm{d}F = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T = -p\mathrm{d}V - S\mathrm{d}T$

(d) $\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T = V\mathrm{d}p - S\mathrm{d}T$

- Since U, H, F and G are thermodynamic properties and exact differentials of the type

$$\mathrm{d}z = M\,\mathrm{d}x + N\,\mathrm{d}y, \text{ then}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Maxwell's Equations

Applying this to the four equations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial p}\right)_T$$

These four equations are known as Maxwell's equations.

Maxwell's Equations : significance

- It should be noted that P, V and T can be measured by experimental methods where as S can not be determined experimentally by using maxwells relations, change in entropy can be determined by the quantities that can be measured i.e P, V and T

First TdS Equations

- Let entropy S be imagined as a function of T and V. Then

If $S=f(T, V)$

$$dS=\left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$TdS=T\left(\frac{\partial S}{\partial T}\right)_V dT+T\left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dq = c_v\,(dT)_v = T(ds)_v$$

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

Since $T\left(\frac{\partial S}{\partial T}\right)_V = C_v$, heat capacity at constant volume, and

$$\left(\frac{\partial S}{\partial T}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$, Maxwell's third equation,

$$TdS = C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

Second TdS Equation

- Let entropy S be imagined as a function of T and P. Then   If   S=f(T,P)

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial p}\right)_T dp$$

$$T\left(\frac{\partial S}{\partial T}\right)_p = C_p, \text{ and } \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

This is known as the second TdS equation

Energy Equation

- For a system undergoing an infinitesimal reversible process between two equilibrium states, the change of internal energy is

$$dU = T\,dS - p\,dV$$

- Substituting the first *T dS equation*

$$dU = C_v\,dT + T\left(\frac{\partial p}{\partial T}\right)_v dV - p\,dV$$

$$= C_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dV$$

$$U = U(T, V)$$

Energy Equation

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

- This is known as the energy equation.

Difference in Heat Capacities

Equating the first and second TdS equations

$$TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_p dp = C_v\, dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

$$(C_p - C_v)\, dT = T\left(\frac{\partial p}{\partial T}\right)_V dV + T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$dT = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_p - C_v} dV + \frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p - C_v} dp$$

$$dT = \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial T}{\partial p}\right)_V dp$$

Difference in Heat Capacities

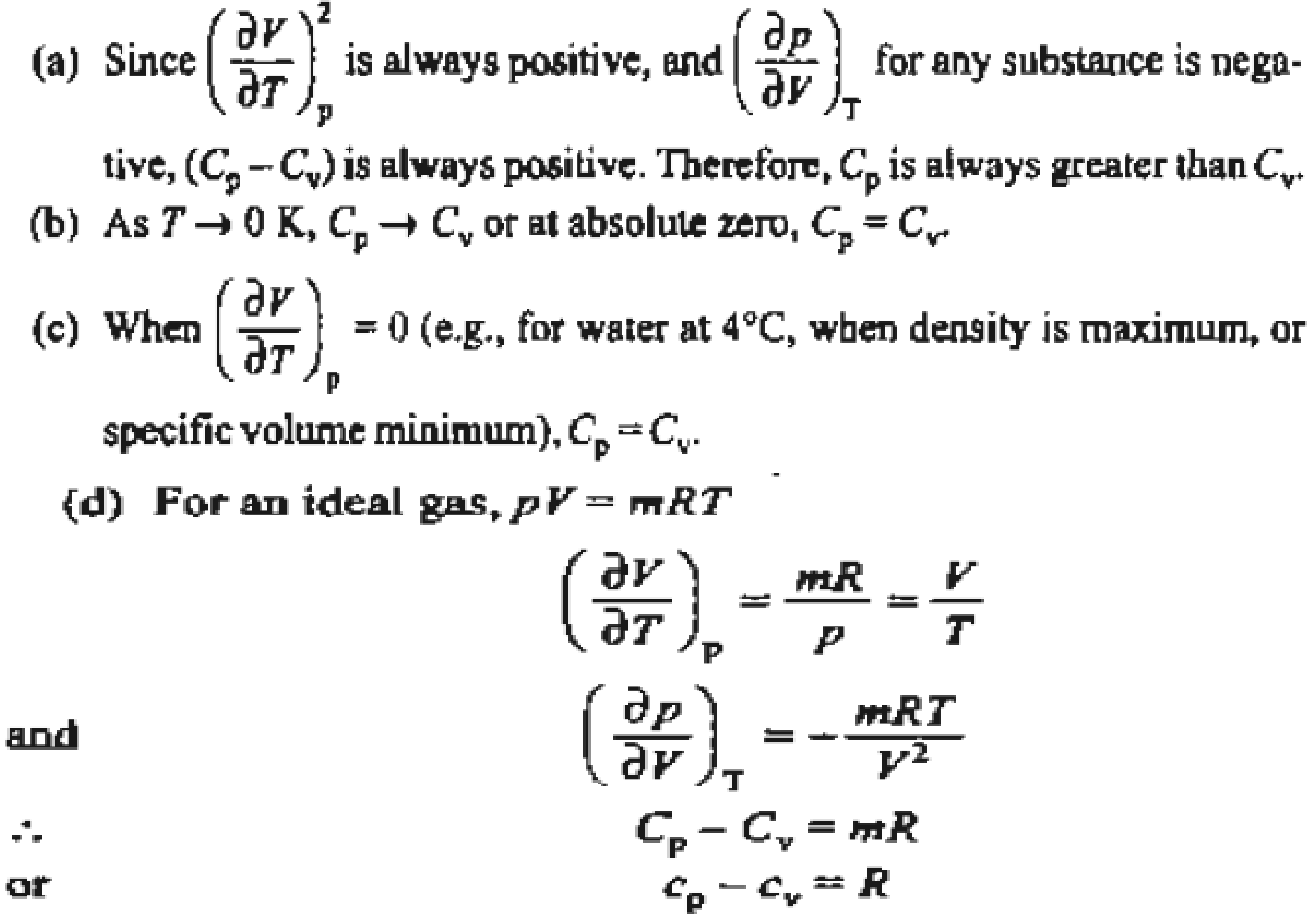
$$\frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_p - C_v} = \left(\frac{\partial T}{\partial V}\right)_p \text{ and } \frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p - C_v} = \left(\frac{\partial T}{\partial p}\right)_V$$

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

$$\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T = -1$$

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T$$

Difference in Heat Capacities



(a) Since $\left(\frac{\partial V}{\partial T}\right)_p^2$ is always positive, and $\left(\frac{\partial p}{\partial V}\right)_T$ for any substance is negative, $(C_p - C_v)$ is always positive. Therefore, C_p is always greater than C_v.

(b) As $T \to 0$ K, $C_p \to C_v$ or at absolute zero, $C_p = C_v$.

(c) When $\left(\frac{\partial V}{\partial T}\right)_p = 0$ (e.g., for water at 4°C, when density is maximum, or specific volume minimum), $C_p = C_v$.

(d) For an ideal gas, $pV = mRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{mR}{p} = \frac{V}{T}$$

and

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{mRT}{V^2}$$

$\therefore$

$$C_p - C_v = mR$$

or

$$c_p - c_v = R$$

Difference in Heat Capacities

Equation (11.10) may also be expressed in terms of volume expansivity β, defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

and isothermal compressibility (kT), defined as

$$k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T$$

$$C_p - C_v = \frac{TV\left[\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T}$$

$$C_p - C_v = \frac{TV\beta^2}{k_T}$$

Ratio of Heat Capacities

At constant S. the two TdS equations become

$$C_p \mathrm{d}T_s = T\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p_s$$

$$C_v \mathrm{d}T_s = -T\left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V,$$

$$\frac{C_p}{C_v} = -\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial T}{\partial p}\right)_V\left(\frac{\partial p}{\partial V}\right)_S = \frac{\left(\frac{\partial p}{\partial V}\right)_S}{\left(\frac{\partial p}{\partial V}\right)_T} = \gamma$$

AVAILABLE AND UNAVAILABLE ENERGY

- There are many forms in which an energy can exist. But even under ideal conditions all these forms cannot be converted completely into work. This indicates that energy has two parts :

— Available part.

— Unavailable part

- ‘**Available energy’** is the maximum portion of energy which could be converted into useful work by ideal processes
- The sources of energy can be divided into two groups, viz. high grade energy and low grade energy. The conversion of high grade energy to shaft work is exempted from the limitations of the second law, while conversion of low grade energy is subject to them.

AVAILABLE AND UNAVAILABLE ENERGY

- The examples of two kinds of energy are:

High grade energy

(a) Mechanical work

(b) Electrical energy

(c) Water power

(d) Wind power

(e) Kinetic energy of a jet

(f) Tidal power

Low grade energy

(a) Heat or thermal energy

(b) Heat derived from nuclear fission or fusion

(c) Heat derived from combustion of fossil fuels

AVAILABLE AND UNAVAILABLE ENERGY

The bulk of the high grade energy in the form of mechanical work or electrical energy is obtained from sources of low grade energy, such as fuels, through the medium of the cyclic heat engine.

The complete conversion of low grade energy, heat, into high grade energy, shaft-work, is impossible by virtue of the second law of thermodynamics.

That part of the low grade energy which is available for conversion is referred to as available energy,

while the part which, according to the second law, must be rejected, is known as unavailable energy

AVAILABLE ENERGY REFERRED TO A CYCLE

- The **available energy (A.E.) or** the available part of the energy supplied is the maximum work output obtainable from a certain heat input in a cyclic heat engine (Fig. 6.1). The minimum energy that has to be rejected to the sink by the second law is called the **unavailable energy(U.E.), or** the unavailable part of the energy supplied.

$$Q1 = A.E. + U.E.$$

$$\text{or } W_{max} = A.E. = Q1 – U.E.$$

For the given values of the source temperature T_1 and sink temperature T_2, the reversible efficiency,

$$\eta_{rev.} = 1 - \frac{T_2}{T_1}$$

For a given T_1, $\eta_{rev.}$ will increase with the decrease of T_2. *The lowest practicable temperature of heat rejection is the temperature of the surroundings,* T_0.

$$\therefore \qquad \eta_{max} = 1 - \frac{T_0}{T_1}$$

and
$$W_{max} = \left(1 - \frac{T_0}{T_1}\right) Q_1$$

Consider a finite process *l-m*, in which heat is supplied reversibly to a heat engine (Fig. 6.2). Taking an elementary cycle, if dQ_1 is the heat received by the engine reversibly at T_1,

Then
$$dW_{max} = \frac{T_1 - T_0}{T_1} dQ_1$$

$$= dQ_1 - \frac{T_0}{T_1} dQ_1 = \text{A.E.}$$

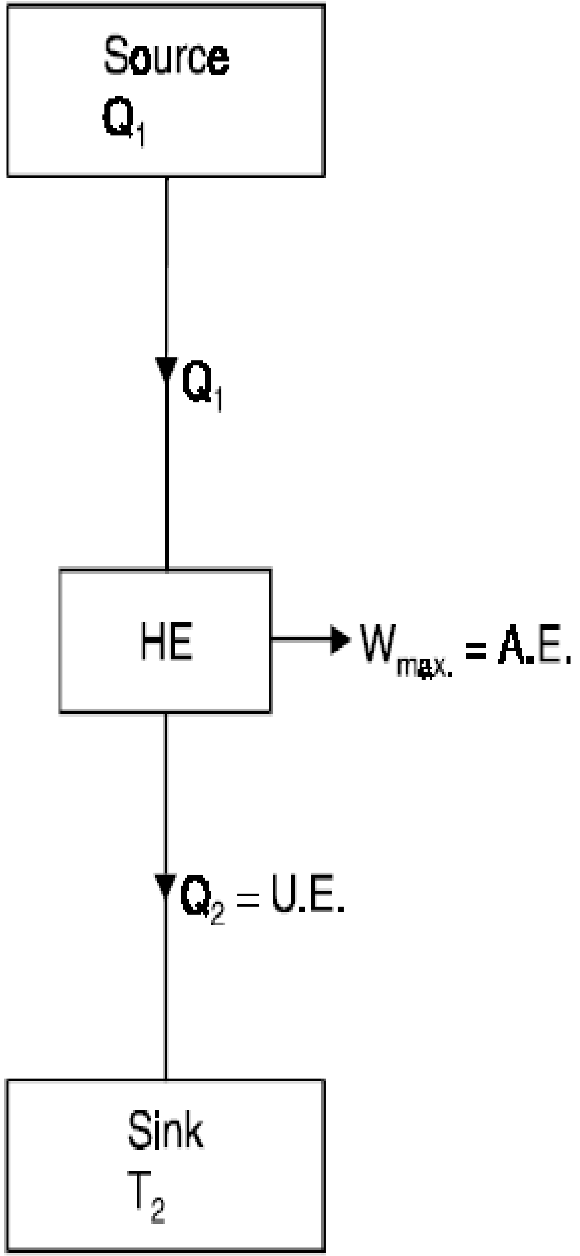


Fig. 6.1. Available and unavailable energy in a cycle.

AVAILABLE ENERGY REFERRED TO A CYCLE

Fig. 6.1. Av
ene

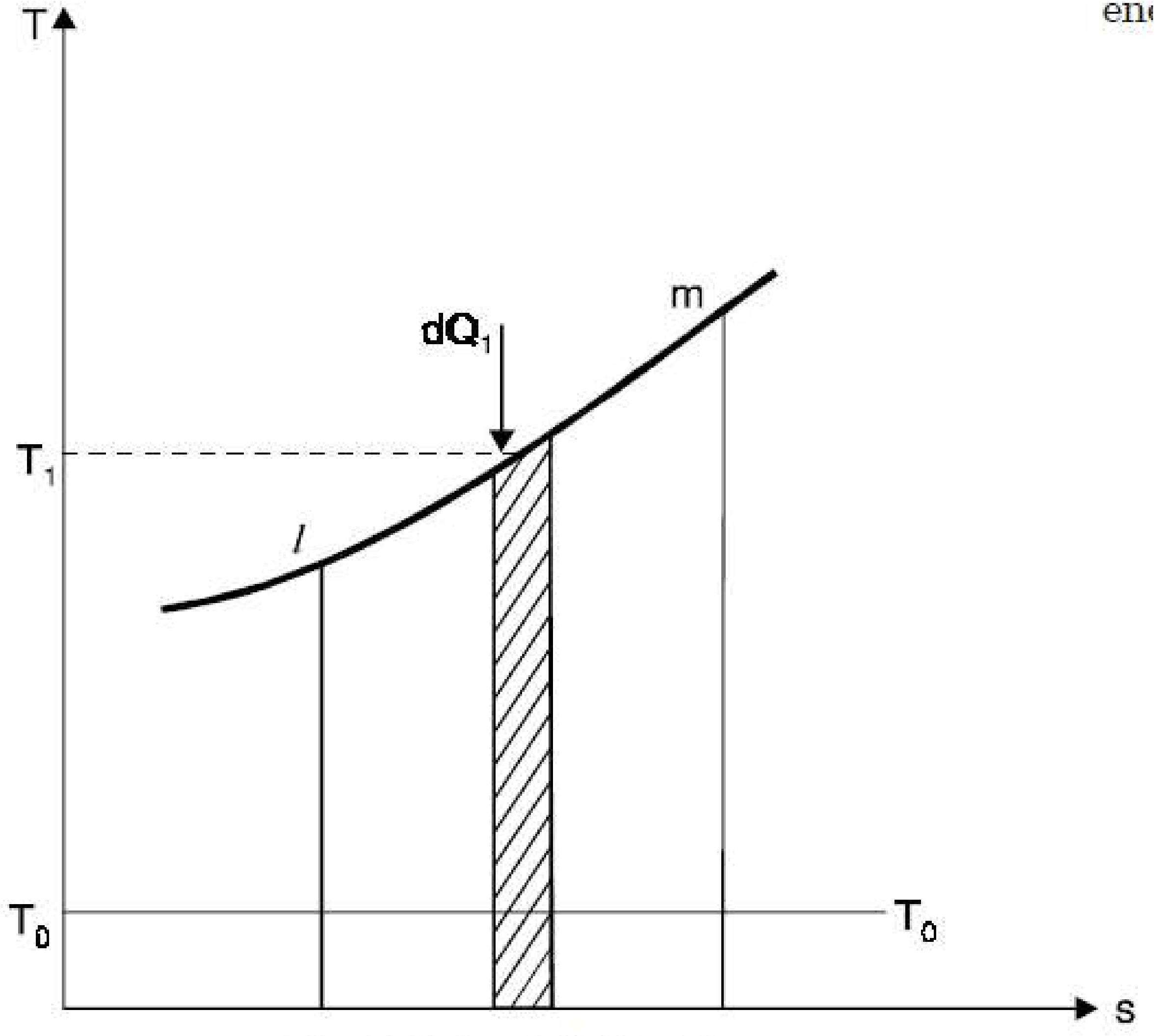


Fig. 6.2. Availability of energy.

AVAILABLE ENERGY REFERRED TO A CYCLE

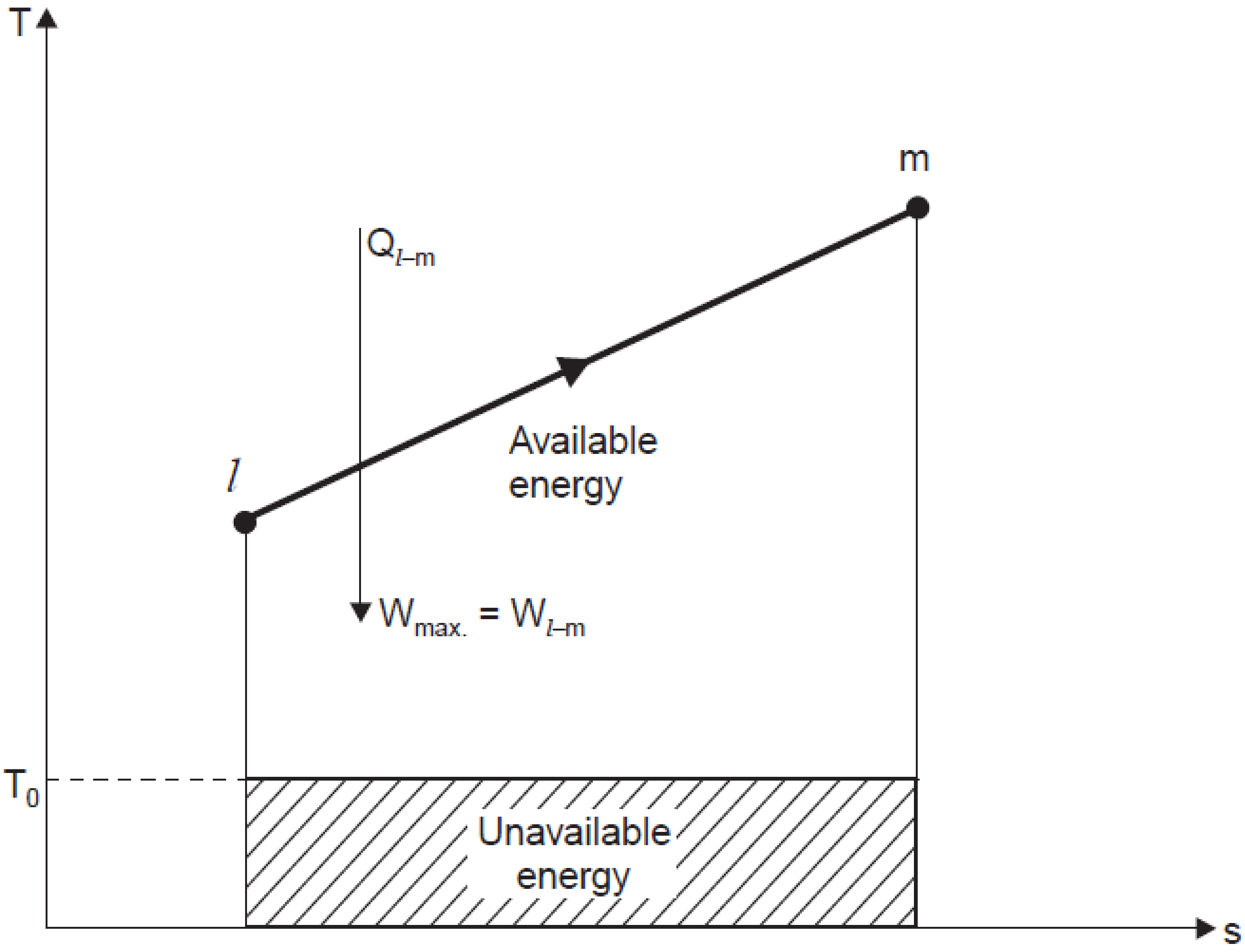
For the heat engine receiving heat for the whole process *l*-*m*, and rejecting heat at T_0

$$\int_l^m dW_{max} = \int_l^m dQ_1 - \int_l^m \frac{T_0}{T_1} dQ_1$$

$$\therefore \quad W_{max} = \text{A.E.} = Q_{l-m} - T_0 (s_l - s_m) \qquad \text{...(6.1)}$$

unavailable energy, $\quad \text{U.E.} = Q_{l-m} - W_{max}$

$$\text{U.E.} = T_0 (s_l - s_m)$$



- Thus unavailable energy is the product of the lowest temperature of heat rejection, and the change of entropy of the system during the process of supplying heat (Fig. 6.3).

Useful Work

- All of the work W of the system with a flexible boundary would not be available for delivery, since a certain portion of it would be spent in pushing out the atmosphere (Fig. 8.12). The useful work is defined as the actual work delivered by a system less the work performed on the atmosphere. If V1 and V2 are the initial and final volume of the system and P0 is the atmospheric pressure, then the work done on the atmosphere is P0 (V2 - V1) . Therefore, the useful work Wu becomes

$$W_u = W_{act} - p_0 \left(V_2 - V_1\right)$$

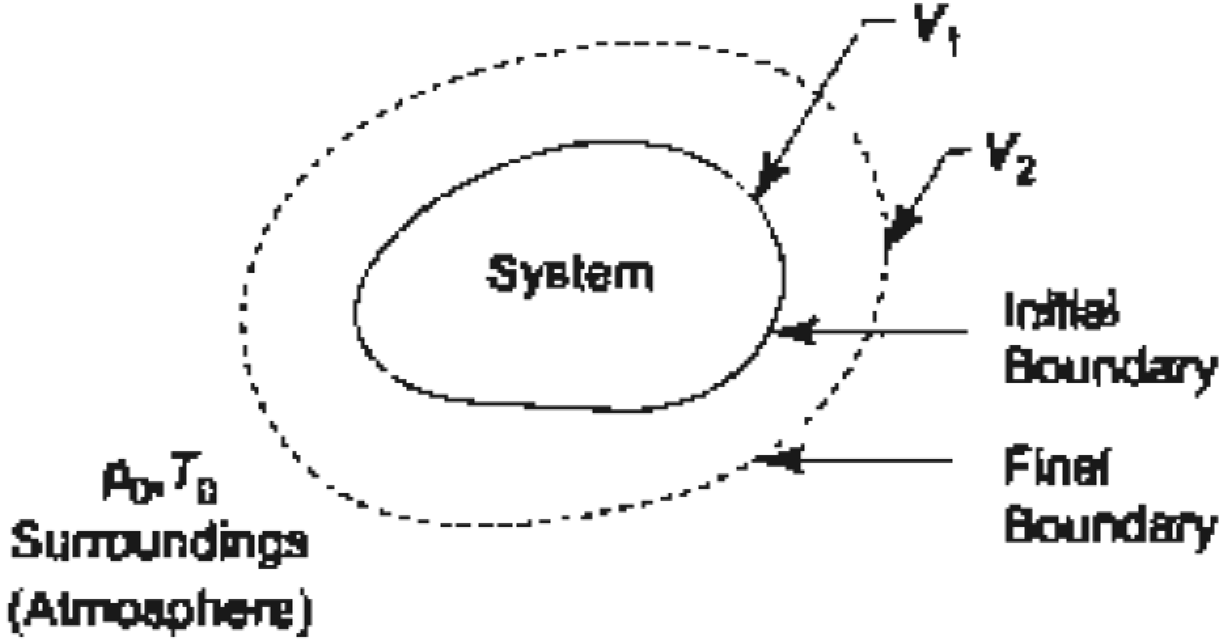


Fig. 8.12 *Work done by a closed system in pushing out the atmosphere*

Similarly, the maximum useful work will be

$$(W_u)_{\max} = W_{\max} - p_0 (V_2 - V_1)$$

In differential form

$$(dW_u)_{\max} = dW_{\max} - p_0 \, dV$$

Useful Work

In a steady now system, the volume of the system does not change. Hence, the maximum useful work would remain the same, i.e., no work is done on the atmosphere, or

$$(\text{đ}W_u)_{\max} = dW_{\max}$$

Useful Work

- But in the case of an unsteady-flow open system or a closed system, the volume of the system changes. Hence, when a system exchanges heat only with the atmosphere, the maximum useful work becomes

$$(\text{đ}W_u)_{max} = \text{đ}W_{max} - p_0\,\mathrm{d}V$$

Substituting dW max from Eq. (8.24),

$$(\text{đ}W_u)_{max} = \mathrm{d}m_1\left(h_1 - T_0 s_1 + \frac{\mathbf{V}_1^2}{2} + gz_1\right) - \mathrm{d}m_2\left(h_2 - T_0 s_2 + \frac{\mathbf{V}_2^2}{2} + gz_2\right)$$

$$-\mathrm{d}\left[U + p_0V - T_0S + \frac{m\mathbf{V}^2}{2} + mgz\right]_\sigma \tag{8.38}$$

This is the maximum useful work for an unsteady open system

Useful Work

- For the closed system, Eq. (8.38) reduces to

$$
\begin{aligned}
(\mathrm{d}W_u)_{\max} &= -\mathrm{d}\left[U + p_0V - T_0S + \frac{mV^2}{2} + mgz\right]_\sigma \\
&= -\mathrm{d}\,[E + p_0\,V - T_0S]_\sigma \qquad (8.39) \\
(W_u)_{\max} &= E_1 - E_2 + p_0\,(V_1 - V_2) - T_0\,(S_1 - S_2) \qquad (8.40)
\end{aligned}
$$

- If K.E, and P.E. changes are neglected, Eq. (8.40) becomes

$$(W_u)_{\max} = U_1 - U_2 + p_0\,(V_1 - V_2) - T_0\,(S_1 - S_2)$$

Useful Work

- This can also be written in the following form

$$(W_u)_{max} = (U_1 + p_0 V_1 - T_0 S_1) - (U_2 + p_0 V_2 - T_0 S_2)$$

$$= \phi_1 - \phi_2$$

- where ϕ is called the availability function for a closed system given by

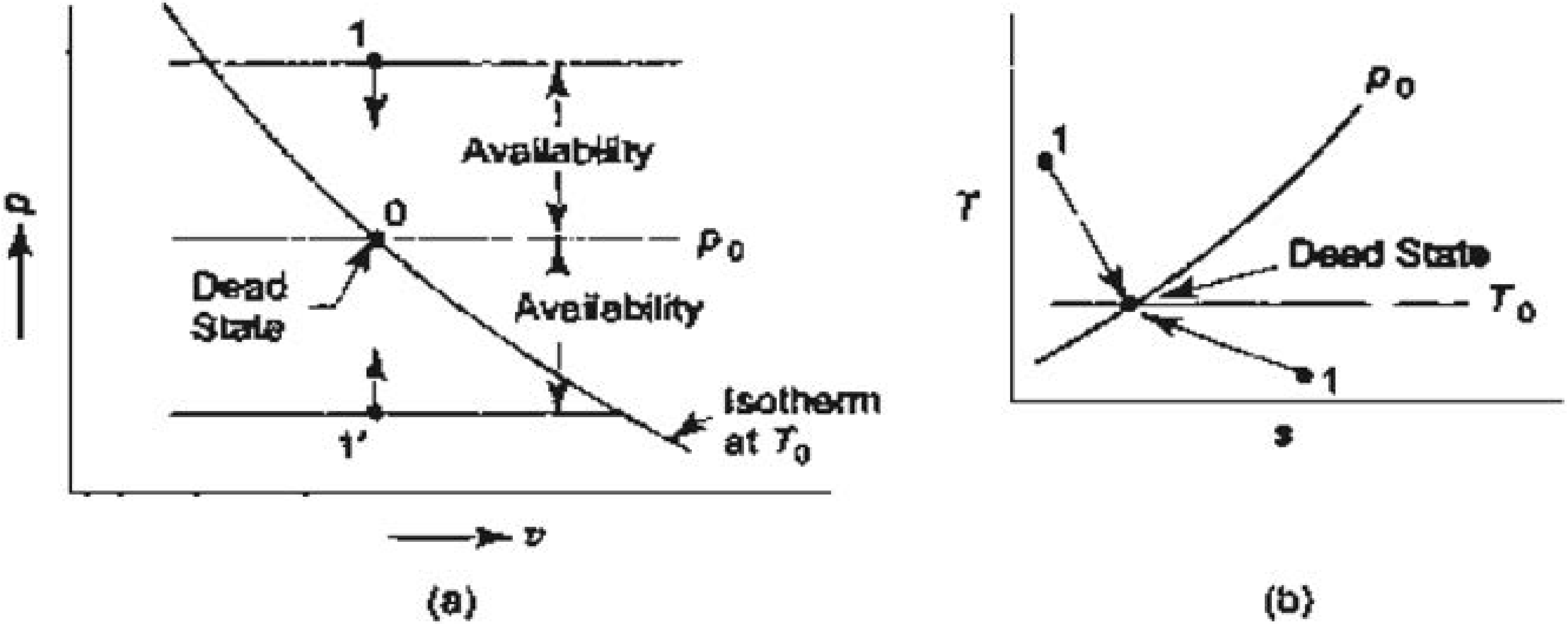
$$\phi = U + p_0 V - T_0 S$$

- The useful work per unit mass becomes

$$(W_u)_{max} = (u_1 + p_0 v_1 - T_0 s_1) - (u_2 + p_0 v_2 - T_0 s_2)$$

Dead State

The system must have zero velocity and minimum potential energy. This state of the system is known as the dead state, which is designated by affixing subscript 'O' to the properties. Any change in the state of the system from the dead state is a measure of the available work that can be extracted from it



(a)

(b)

Fig. 8.13 *Available work of a system decreases as its state approaches P_0, T_0*

Availability

- The availability (A) of a given system is defined as the maximum useful work (total work minus pdV work) that is obtainable in a process in which the system comes to equilibrium with its surroundings.

Availability in a Non Flow Process

Let us consider a closed system and denote its initial state by parameters without any subscript and the final dead state with subscript 'O'. The availability of the system A, i.e., the maximum useful work obtainable as the system reaches the dead state, is given by Eq. (8.40).

$$
\begin{aligned}
A = (W_u)_{\max} &= E - E_0 + p_0(V - V_0) - T_0(S - S_0) \\
&= \left(U + \frac{m\mathbf{V}^2}{2} + mgz\right) - (U_0 + mgz_0) + p_0(V - V_0) - T_0(S - S_0)
\end{aligned}
$$

Availability in a Non Flow Process

- If K. E. and P.E. changes are neglected and for unit mass, the availabilitv becomes

$$
\begin{aligned}
a &= u - u_0 + p_0(v - v_0) - T_0(s - s_0) \\
&= (u + p_0 v - T_0 s) - (u_0 - p_0 v_0 - T_0 s_0) \\
&= \phi - \phi_0
\end{aligned}
$$

where ϕ is the availability function of the closed system.

Availability in a Non Flow Process

- If the system undergoes a change of state from 1 to 2, the decrease in availability will be

$$
\begin{aligned}
a &= (\phi_1 - \phi_0) - (\phi_2 - \phi_0) \\
&= \phi_1 - \phi_2 \\
&= (u_1 - u_2) + p_0\,(v_1 - v_2) - T_0(s_1 - s_2)
\end{aligned}
$$

This is the maximum useful work obtainable under the given surroundings.

Availability in a Steady Flow Process

- The reversible {maximum) work associated with a steady flow process for a single flow is given by Eq. (8.26)

$$W_{rev} = \left(H_1 - T_0 S_1 + \frac{mV_1^2}{2} + mgz_1\right) - \left(H_2 - T_0 S_2 + \frac{mV_2^2}{2} + mgz_2\right)$$

- With a given state for the mass entering the control volume, the maximum useful work obtainable (i.e., the availability) would be when this mass leaves the control volume in equilibrium with the surroundings (i.e., at the dead state). Since there is no change in volume, no work will be done on the atmosphere. Let us designate the initial state of the mass entering the C.V. with parameters having no subscript and the final dead state of the mass leaving the C.V. with parameters having subscript 0. The maximum work or availability, A, would be

Availability in a Steady Flow Process

$$A = \left(H - T_0 S + \frac{mV^2}{2} + mgz \right) - (H_0 - T_0 S_0 + mgz_0) = \psi - \psi_0$$

where ψ is called the availability function for a steady flow system and VO= 0. This is the availability of a system at any state as it enters a C. V. in a steady now process. The availability per unit mass would be

$$a = \left(h - T_0 s + \frac{V^2}{2} + gz \right) - (h_0 - T_0 s_0 + gz) = \psi - \psi_0$$

If subscripts I and 2 denote the states of a system entering and leaving a C.V., the decrease in availability or maximum work obtainable for the given system surronndings combination would be

Availability in a Steady Flow Process

$$
\begin{aligned}
W_{\max} &= a_1 - a_2 = \psi_1 - \psi_2 \\
&= \left[\left(h_1 - T_0 s_1 + \frac{V_1^2}{2} + g z_1\right) - (h_0 - T_0 s_0 + g z_0)\right] \\
&\quad - \left[\left(h_2 - T_0 s_0 + \frac{V_2^2}{2} + g z_2\right) - (h_0 - T_0 s_0 + g z_0)\right] \\
&= (h_1 - h_2) - T_0 (s_1 - s_2) + \frac{V_1^2 - V_2^2}{2} + g(z_1 - z_2)
\end{aligned}
$$

If K.E. and P.E. changes are neglected,

$$
\begin{aligned}
W_{\max} &= (h_1 - T_0 s_1) - (h_2 - T_0 s_2) \\
&= b_1 - b_2
\end{aligned}
$$

where b is the specific Keenan function.

If more than one flow into and out of the C.V. is involved.

$$W_{\max} = \sum_{i} m_i \psi_i - \sum_{i} m_e \psi_e$$

IRREVERSIBILITY

- The actual work which a system does is always less than the idealized reversible work, and the difference between the two is called the irreversibility of the process.
- Thus, Irreversibility, I = W max – W ...(6.8)
- This is also sometimes referred to as ‘**degradation’ or ‘dissipation’.**

For a non-flow process between the equilibrium states, when the system exchanges heat only with environment, irreversibility (per unit mass)

IRREVERSIBILITY

$i = [(u_1 - u_2) - T_0(s_1 - s_2)] - [(u_1 - u_2) + Q]$

$= T_0\,(s_2 - s_1) - Q$

$= T_0\,(\Delta s)_{system} + T_0\,(\Delta s)_{surr.}$

i.e., $i = T_0\,[(\Delta s)_{system} + (\Delta s)_{surr.}]$ ...(6.9)

$\therefore\ i \geq 0$

HELMHOLTZ AND GIBBS FUNCTIONS

- The work done in a non-flow reversible system (per unit mass) is given by :

$$W = Q - (u_0 - u_1)$$

$$= T.dS - (u_0 - u_1)$$

$$= T\,(S_0 - S_1) - (u_0 - u_1)$$

$$\text{i.e., } W = (u_1 - TS_1) - (u_0 - TS_0)$$

- The term $(u - TS)$ is known as Helmholtz function. This gives maximum possible output when the heat Q is transferred at constant temperature and is the case with a very large source

HELMHOLTZ AND GIBBS FUNCTIONS

- If work against atmosphere is equal to P0 (v0 – v1), then the maximum work available,

W_{max} = W – work against atmosphere

$= W - P_0 (v_0 - v_1)$

$= (u1 - TS_1) - (u_0 - TS_0) - P_0 (V_0 - V_1)$

$= (u1 + P_0 v1 - TS_1) - (u_0 + P_0 V_0 - TS_0)$

$= (h1 - TS_1) - (h_0 - TS_0)$

i.e., W max = g1 – g0 ...(6.5)

Where g = h – T.s is known as **Gibb's function or free energy function**

- A system at 500 K receives 7200 kJ/min from a source at 1000 K. The temperature of atmosphere is 300 K. Assuming that the temperatures of system and source remain constant during heat transfer find out :

(i) The entropy produced during heat transfer ;

(ii) The decrease in available energy after heat transfer

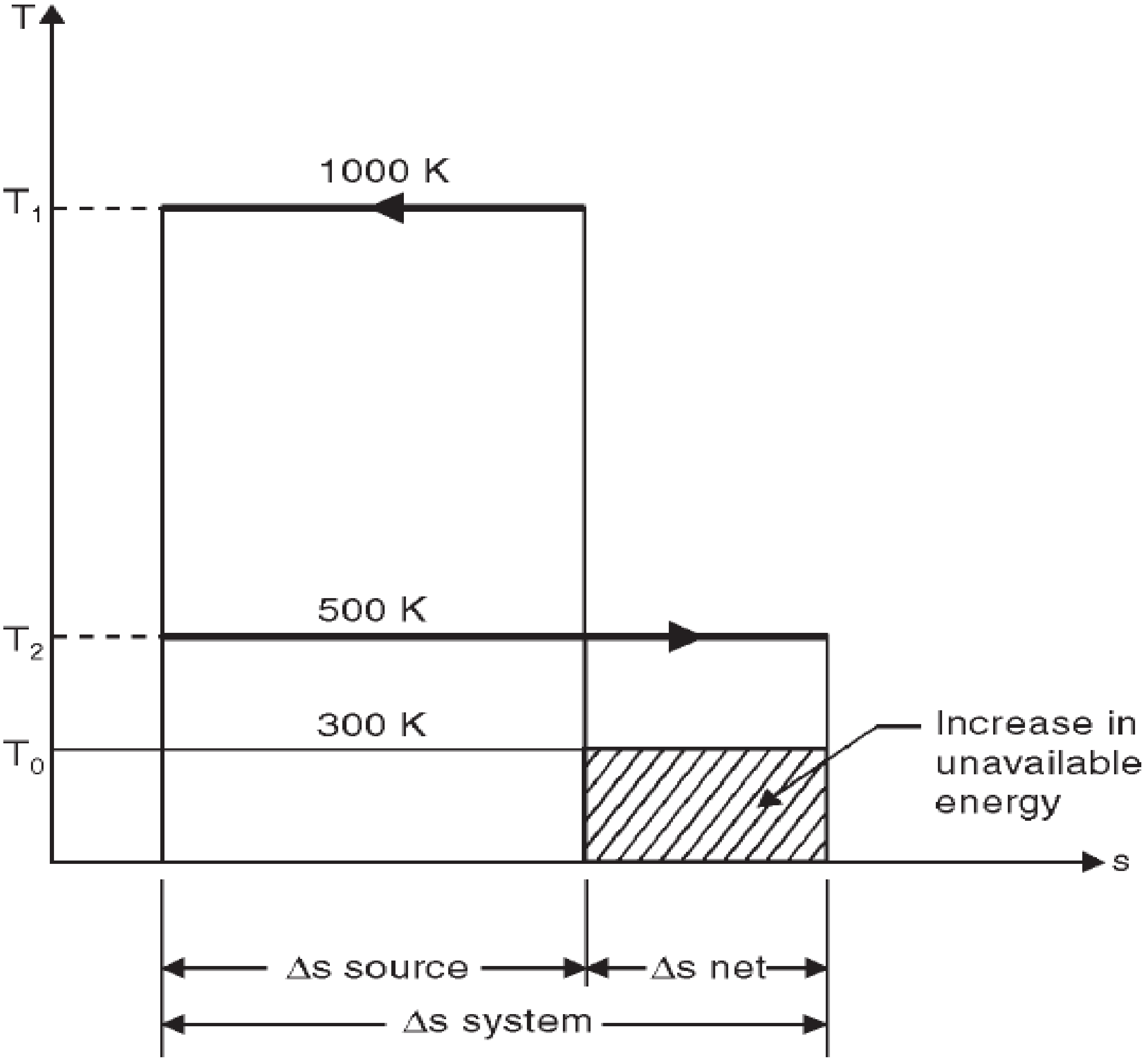
Solution:

Temperature of source, T1 = 1000 K

Temperature of system, T2 = 500 K

Temperature of atmosphere, T0 = 300 K

Heat received by the system, Q = 7200 kJ/min


T
T$_1$
T$_2$
T$_0$
1000 K
500 K
300 K
Increase in unavailable energy
s
Δs source
Δs net
Δs system

(*i*) **Net change of entropy :**

Change in entropy of the *source* during heat transfer

$$= \frac{-Q}{T_1} = \frac{-7200}{1000} = -7.2 \text{ kJ/min-K}$$

Change in entropy of the *system* during heat transfer

$$= \frac{Q}{T_2} = \frac{7200}{500} = 14.4 \text{ kJ/min-K}$$

The net change of entropy, $\Delta S = -7.2 + 14.4 =$ **7.2 kJ/min-K. (Ans.)**

(ii) **Decrease in available energy :**

Available energy with source = (1000 – 300) × 7.2 = 5040kj

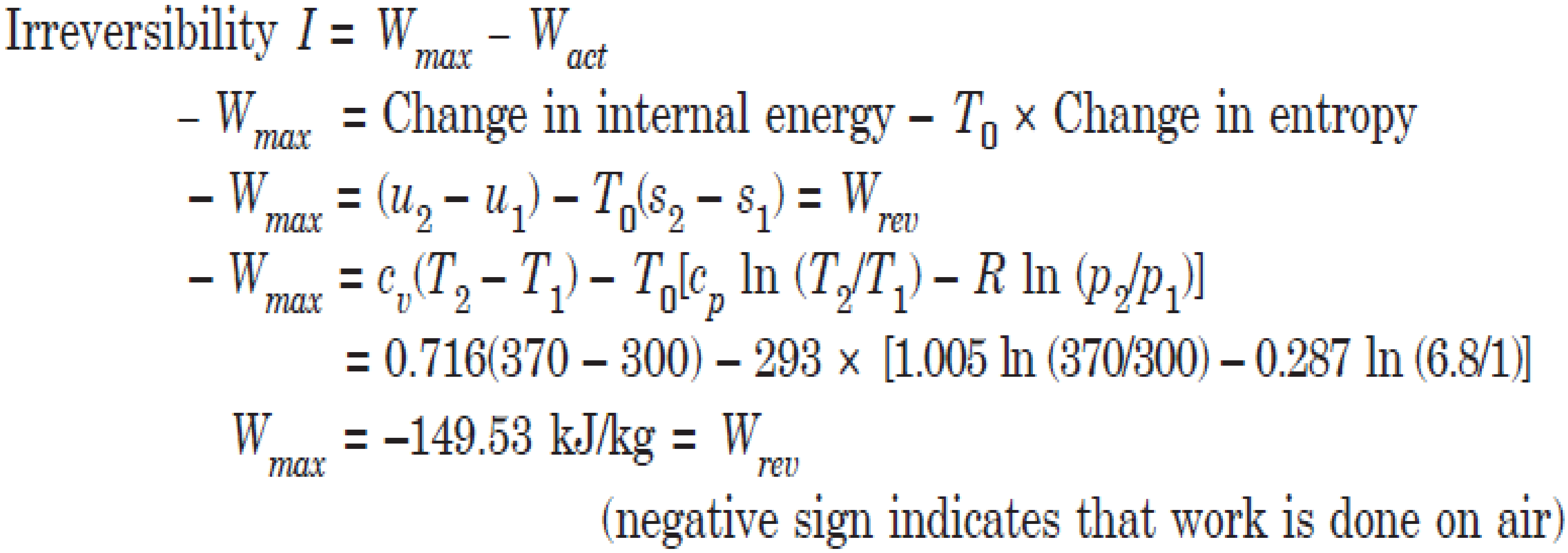
Available energy with the system =(500 – 300) × 14.4 = 2880 kJ

∴ **Decrease in available energy = 5040 – 2880 = 2160 kJ.**

$$\left[\begin{array}{l}\text{Also, increase in available energy} \\ \qquad = T_0(S_2 - S_1) = T_0\,\Delta S \\ \qquad = 300 \times 7.2 = 2160 \text{ kJ}\end{array}\right]$$

- One kg of air is compressed polytropically from 1 bar pressure and temperature of 300 K to a pressure of 6.8 bar and temperature of 370 K. Determine the irreversibility if the sink temperature is 293 K. Assume R = 0.287 kJ/kg K, cp = 1.004 kJ/kg K and cv = 0.716 kJ/kg K.

SOLUTION:



Irreversibility $I = W_{max} - W_{act}$

$$-W_{max} = \text{Change in internal energy} - T_0 \times \text{Change in entropy}$$

$$-W_{max} = (u_2 - u_1) - T_0(s_2 - s_1) = W_{rev}$$

$$-W_{max} = c_v(T_2 - T_1) - T_0[c_p \ln (T_2/T_1) - R \ln (p_2/p_1)]$$

$$= 0.716(370 - 300) - 293 \times [1.005 \ln (370/300) - 0.287 \ln (6.8/1)]$$

$$W_{max} = -149.53 \text{ kJ/kg} = W_{rev}$$

(negative sign indicates that work is done on air)

The index of compression '*n*' is given by

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{[(n-1)/n]}$$

$$\frac{n-1}{n} = \frac{\ln(T_2/T_1)}{\ln(p_2/p_1)} = \frac{\ln(370/300)}{\ln(6.8/1)}$$

$$n = 1.123$$

$$W_{actual} = \frac{mR(T_1 - T_2)}{n-1} = \frac{1 \times 0.287(300-370)}{1.123-1} = -163.33 \text{ kJ/kg}$$

$$I = W_{rev} - W_{act} = -149.53 - (-163.33) = \mathbf{13.8\ kJ/kg.} \quad \textbf{(Ans.)}$$

- 15 kg of water is heated in an insulated tank by a churning process from300 K to 340 K. If the surrounding temperature is 300 K, find the loss in availability for the process.

Solution.

Mass of water, $m = 15$ *kg*

Temperature, $T1 = 340$ *K*

Surrounding temperature, $T0 = 300$ *K*

Specific heat of water, $cp = 4.187$ *kJ/kg K*

Loss in availability :

Work added during churning

$$= \text{Increase in enthalpy of the water}$$

$$= 15 \times 4.187 \times (340 - 300) = 2512.2 \text{ kJ}$$

Now the energy in the water = 2512.2 kJ

The availability out of this energy is given by

$$m[(u_1 - u_0) - T_0\,\Delta s]$$

e

$$\Delta s = c_p \log_e \left(\frac{T_1}{T_0}\right)$$

$$\therefore \quad \Delta s = 4.187 \log_e \left(\frac{340}{300}\right) = 0.524 \text{ kJ/kg K}$$

∴ Available energy

$$= m\,[c_v\,(T_1 - T_0) - T_0\,\Delta s]$$

$$= 15\,[4.187\,(340 - 300) - 300 \times 0.524] = 158.7 \text{ kJ}$$

∴ **Loss in availability**

$$= 2508 - 158.7 = \mathbf{2349.3\ kJ.} \quad \textbf{(Ans.)}$$

This shows that conversion of work into heat is highly irreversible process (since out of2512.2 kJ of work energy supplied to increase the temperature, only 158.7 kJ will be available again for conversion into work).