Module -1

Fundamental Concepts & Definitions
&
Work and Heat

MODULE 1

Fundamental Concepts & Definitions

Thermodynamics definition and scope, Microscopic and Macroscopic approaches. Some practical applications of engineering thermodynamic Systems, Characteristics of system boundary and control surface, examples.

Thermodynamic properties; definition and units, intensive and extensive properties.

Thermodynamic state, state point, state diagram, path and process, quasi-static process, cyclic and non-cyclic processes.

Thermodynamic equilibrium; definition, mechanical equilibrium; diathermic wall, thermal equilibrium, chemical equilibrium, Zeroth law of thermodynamics, Temperature; concepts, scales, fixed points and measurements.

Work and Heat

Mechanics, definition of work and its limitations.

Thermodynamic definition of work; examples, sign convention. Displacement work; as a part of a system boundary, as a whole of a system boundary, expressions for displacement work in various processes through p-v diagrams.

Shaft work; Electrical work. Other types of work.

Heat; definition, units and sign convention.

10 Hours

1st Hour

Brain storming session on subject topics

Thermodynamics definition and scope, Microscopic and Macroscopic approaches. Some practical applications of engineering thermodynamic Systems

2nd Hour

Characteristics of system boundary and control surface, examples. Thermodynamic properties; definition and units, intensive and extensive properties.

3rd Hour

Thermodynamic state, state point, state diagram, path and process, quasi-static process, cyclic and non-cyclic processes. Thermodynamic equilibrium; definition, mechanical equilibrium; diathermic wall, thermal equilibrium, chemical equilibrium

4th Hour

Zeroth law of thermodynamics,

Temperature; concepts, scales, fixed points and measurements

5th Hour

Problems on temperature measurement based on comparison of thermometers.

6th Hour

Work and Heat

Mechanics, definition of work and its limitations.

Thermodynamic definition of work; examples, sign convention.

7th Hour

Displacement work; as a part of a system boundary, as a whole of a system boundary, expressions for displacement work in various processes through p-v Diagrams.

8th Hour

Shaft work; Electrical work. Other types of work.

Heat; definition, units and sign convention.

9th & 10th Hour

Problems on work and heat involving different types of process.

- Thermodynamics is a branch of science that deals with energy in all its forms and the laws governing the transformation of energy from one form to another. The form of energy are mechanical, thermal or heat, chemical, electrical etc.
- Thermodynamics deals with the behavior of gases and vapours i.e., the working substances when subjected to variation of temperature and pressure and the relationship between heat energy and mechanical energy commonly referred to as work.
- Energy transformation takes place when a substance undergoes a change from one condition to another in a process. The processes are heating or cooling and expansion or compression in the cylinder or passages with or without production or supply of mechanical work.

Work producing and work absorbing devices:

Work producing devices	**Work absorbing devices**
a) Steam power plants	a) Cold storages
b) Nuclear power plants	b) Central air conditioning and heating plants
c) Petrol and diesel engines	c) Domestic refrigerators
d) Gas turbine for aircraft propulsion and power generation	d) Room air conditioners
e) Jet propulsion engines for aircrafts	e) Ice plants
f) Rocket engines	f) Food freezing and freeze-drying plants
g) Fuel cells, Solar cells, thermoelectric generators etc.	g) Air liquefaction plants and separation plants
	h) Thermoelectric refrigerators

Macroscopic and Microscopic aspects:

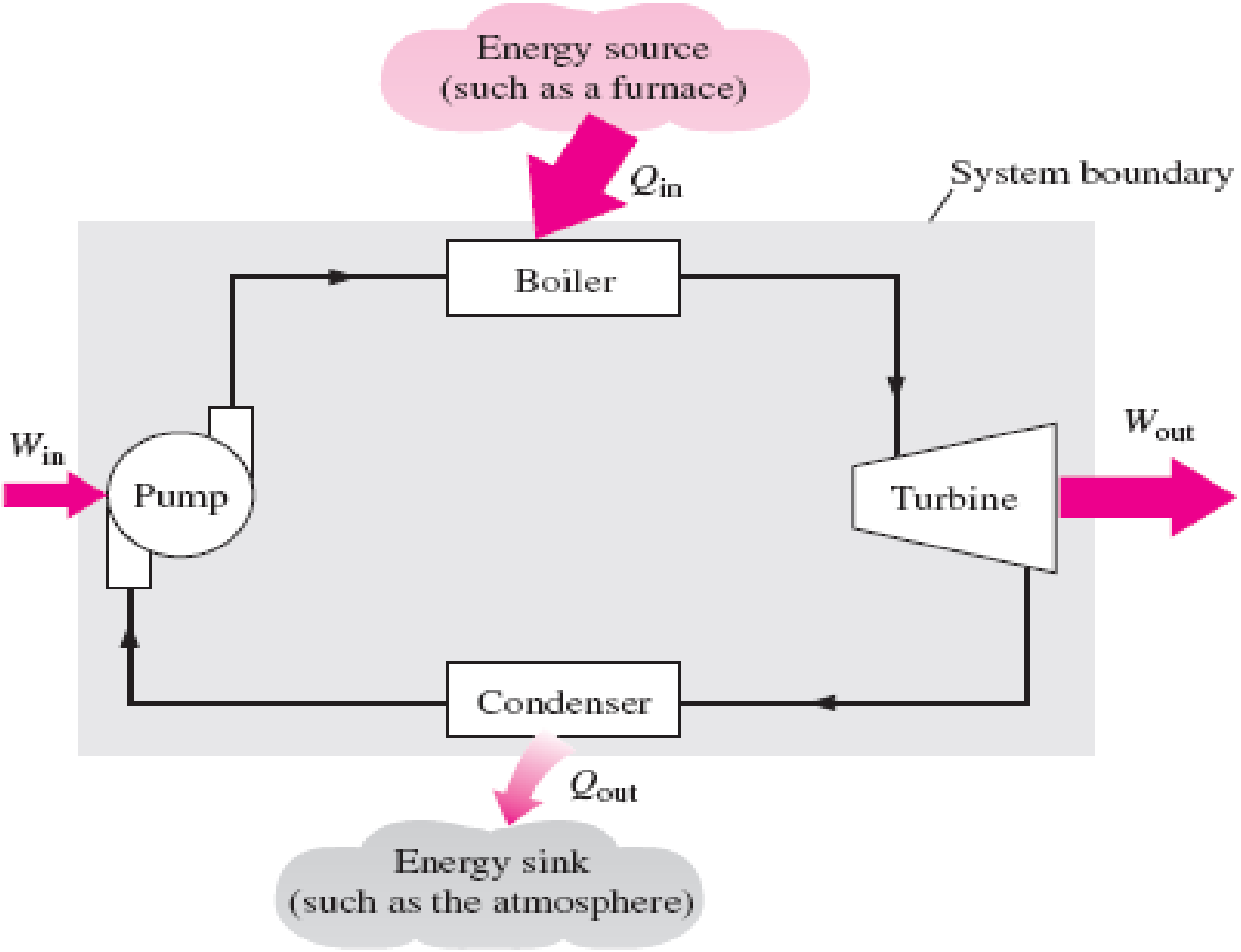
The description of a system or matter using a few of its measurable bulk properties constitutes a point of view called Macroscopic.

The measurable properties are pressure, volume, temperature etc. The state or condition of the system is completely described by means of above large scale characteristics or properties of the system. Such properties are called macroscopic properties and these describe the system from macroscopic point of view.

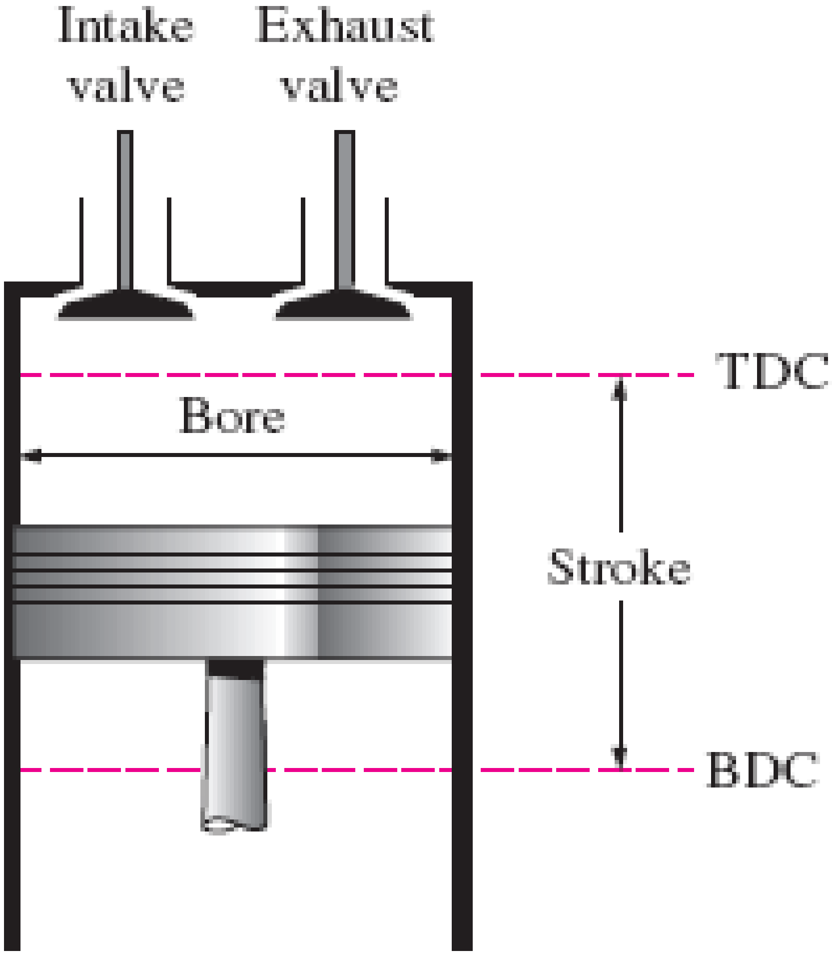
The study of the behavior of the gas described by summing up the behavior of each molecule is microscopic or statistical thermodynamics.

Some practical applications:

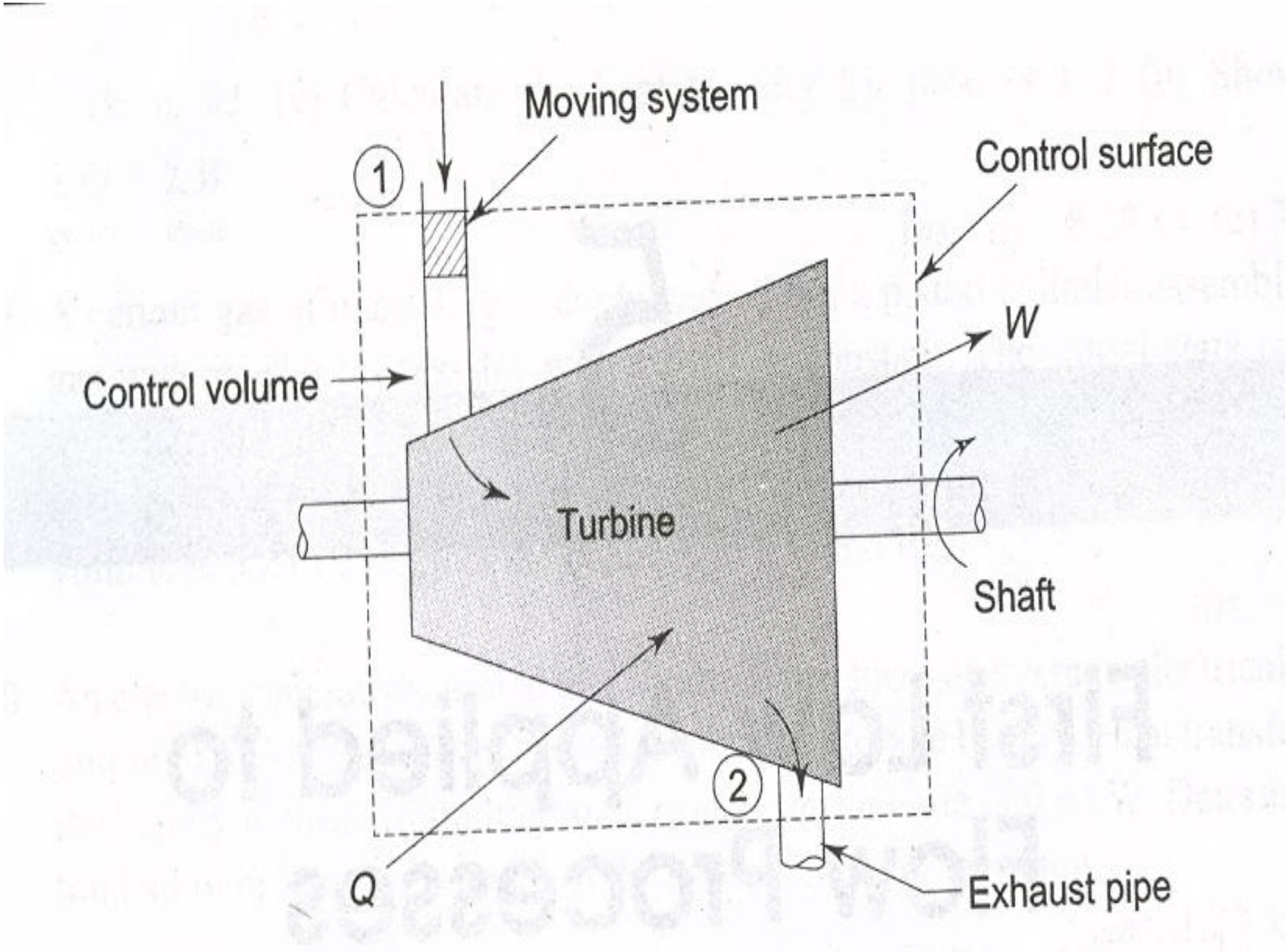
1. Steam power plant:-



2. I.C Engines:-

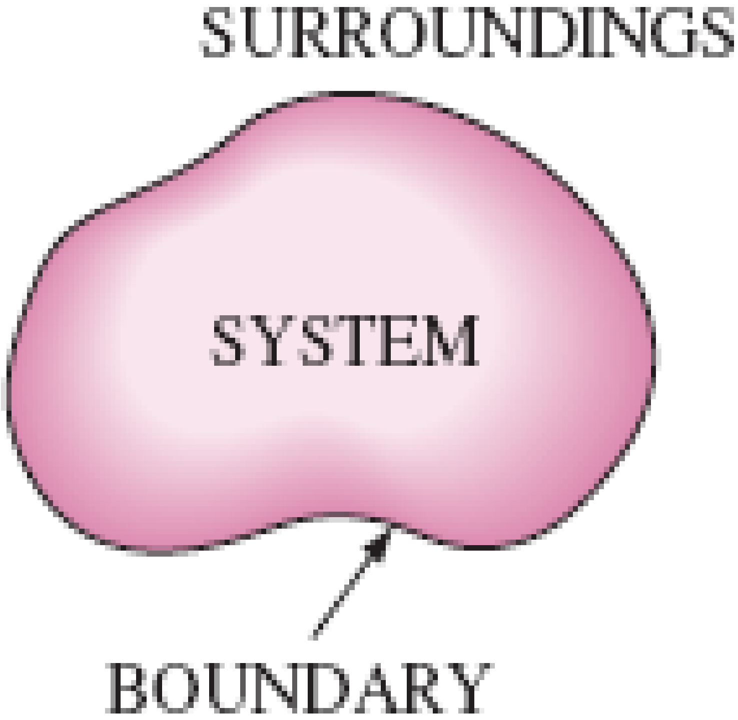


3. Gas turbines:-



Thermodynamic system:

In the analysis of energy interaction, it becomes convenient to define and restrict study to a region. Such a specified region where transfer of energy and/or mass is to be studied is known as system.



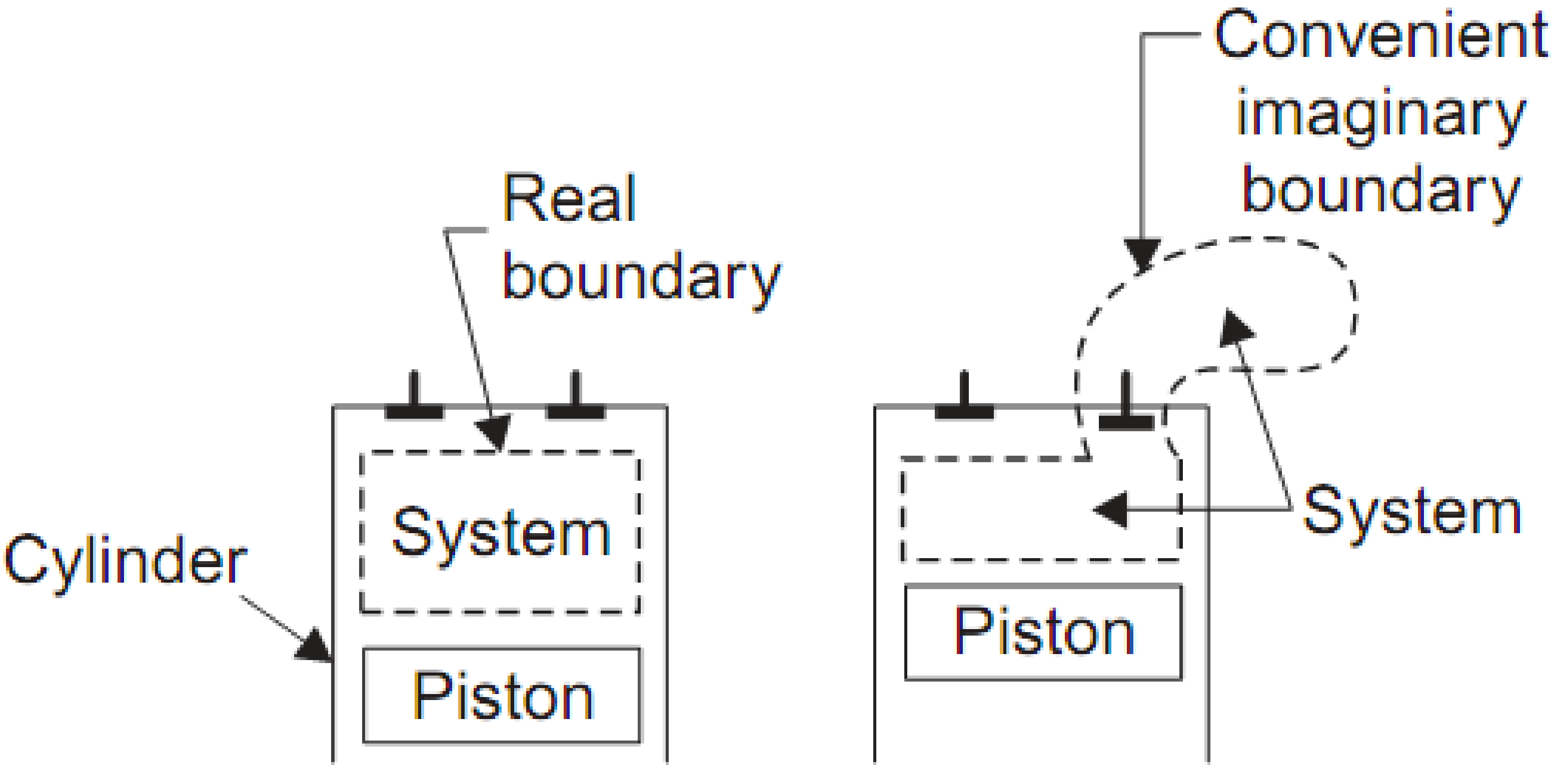


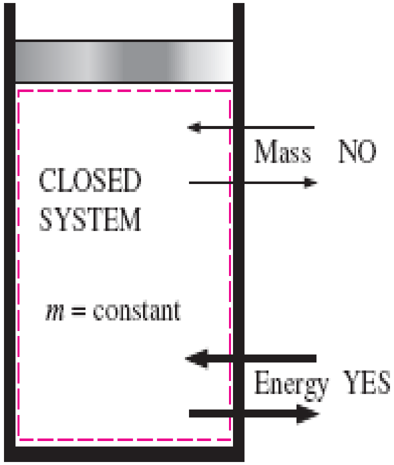
Fig. 2.3. The real and imaginary boundaries.

Classification of thermodynamic systems

a) Isolated system: These systems cannot have either *energy* or *mass* transfer with the surroundings. This system is of purely theoretical interest to study and analyse thermodynamic principle and laws.

b) Control mass or closed system:

Across the boundary of a closed system the transfer of *energy* (Work and/or heat) takes place but transfer of *mass* does not takes place. E.g.: Piston and cylinder.



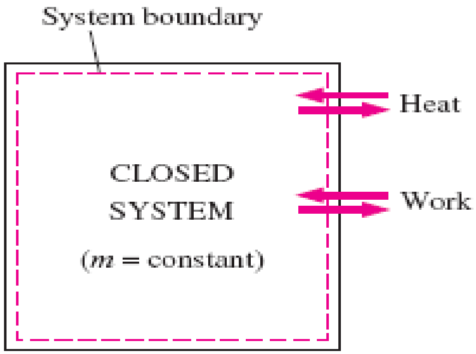


FIGURE 2–11
Energy can cross the boundaries of a closed system in the form of heat and work.

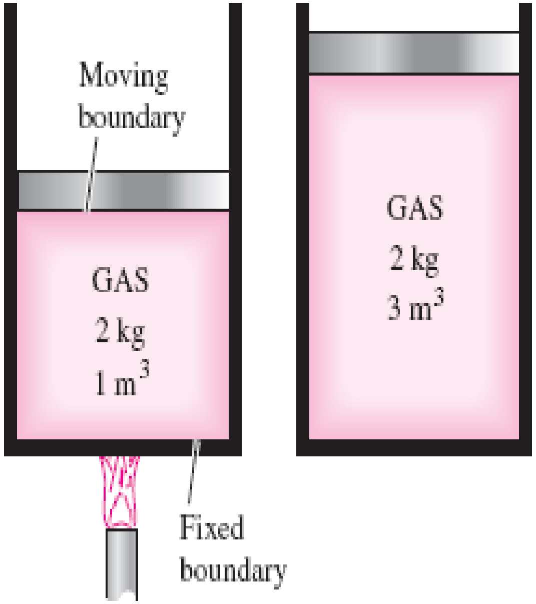
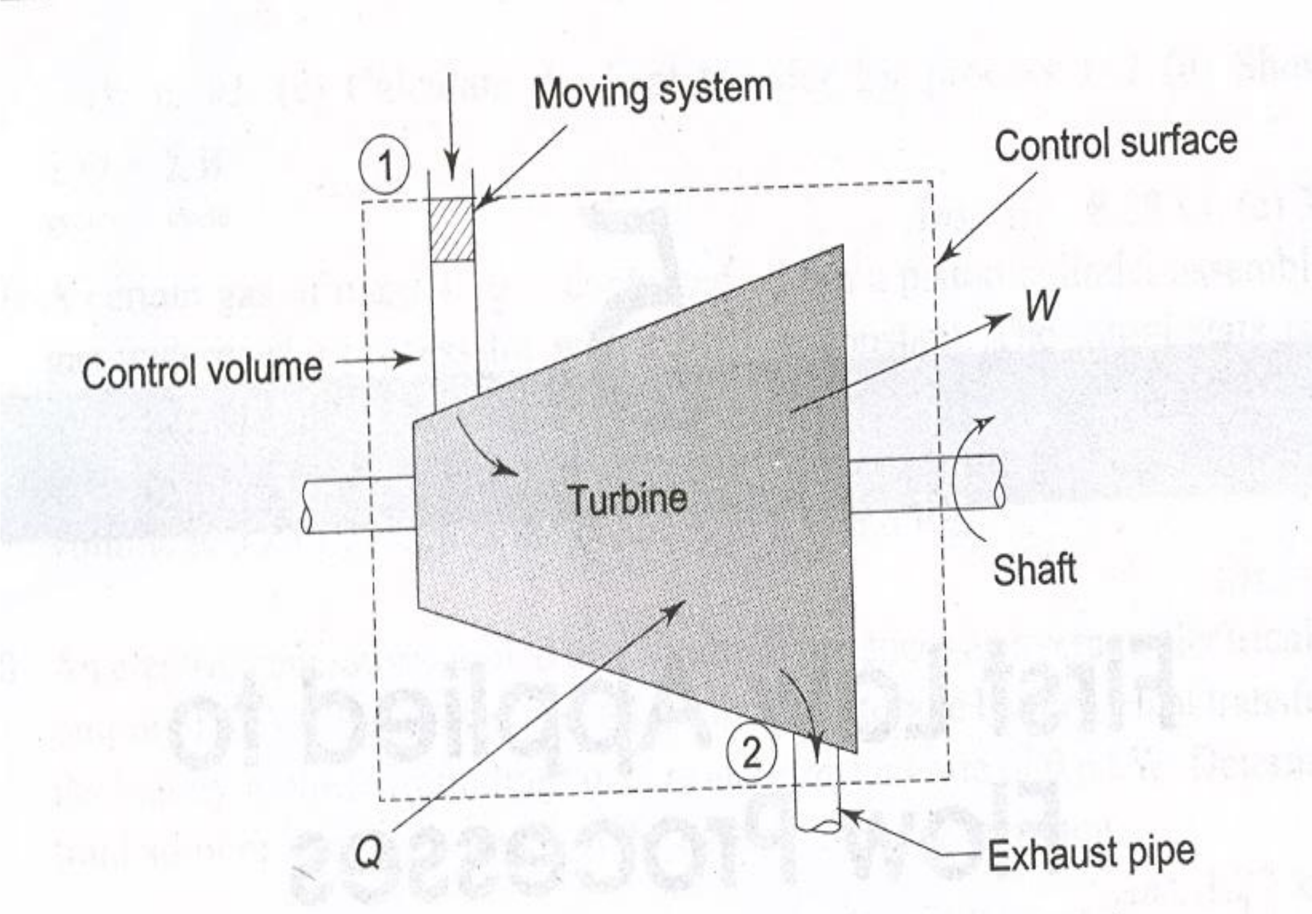


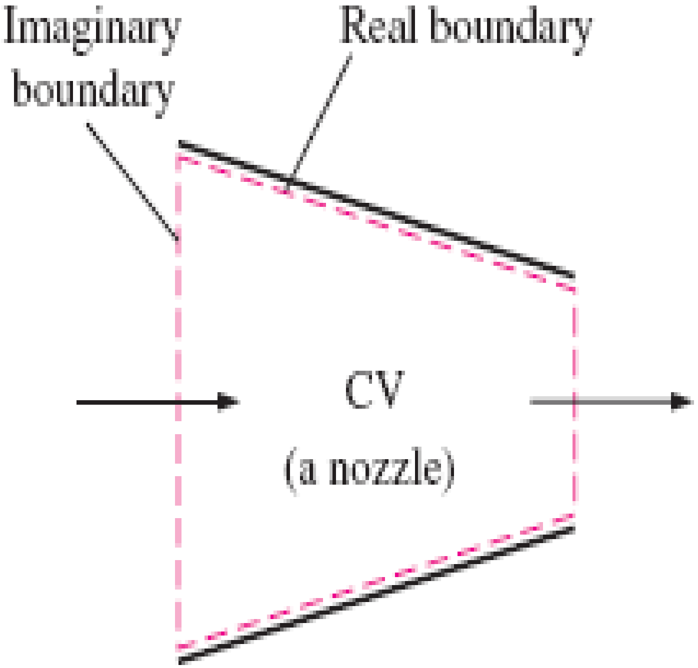
Fig. Closed System

Fig. A Closed System with moving boundary

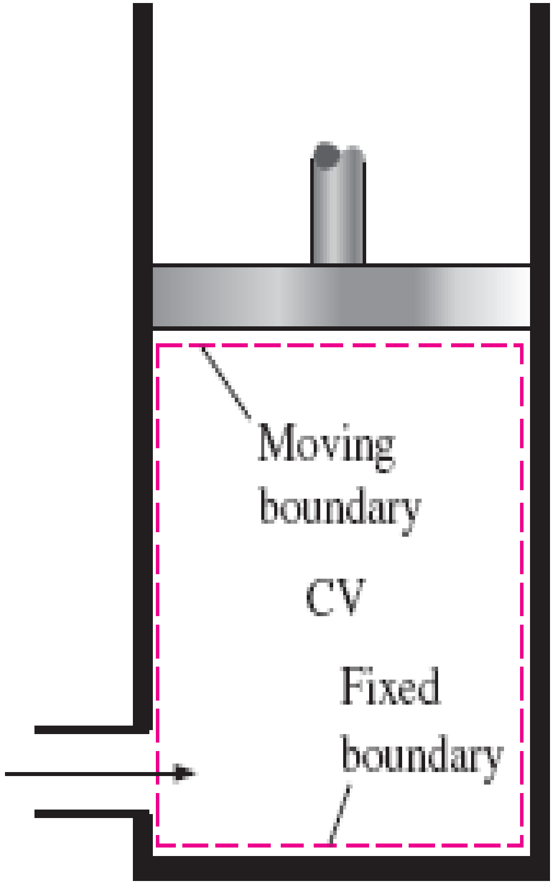
c) Control volume or open system:

In this system *mass* and *energy* both may be transferred between the system and the surroundings. E.g.: Gas turbine, Steam turbine, Compressor, Boiler etc.





(*a*) A control volume with real and imaginary boundaries



(*b*) A control volume with fixed and moving boundaries

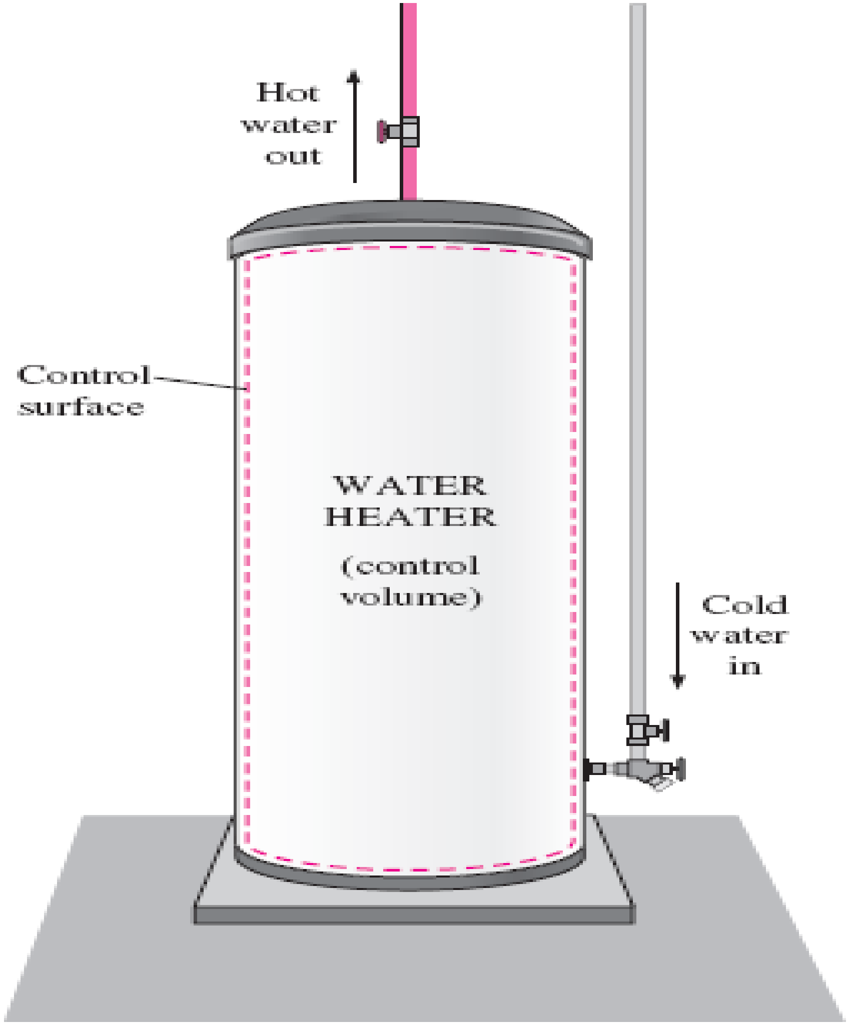


Fig. A Open System with one inlet and one exit

Thermodynamic properties:

The variables which determine state or exact condition of a substance or system is called as its properties. The various properties of thermodynamic system are *pressure, temperature, specific volume, internal energy, enthalpy, entropy*, etc.

Definitions and units:

a) Pressure:

Pressure may be defined as normal force per unit area. In S.I system the unit of pressure is *pascal (Pa)*.

$1Pa = 1N/m^2$; $1kPa = 1000Pa$; $1MPa = 10^6Pa = 1000kPa$

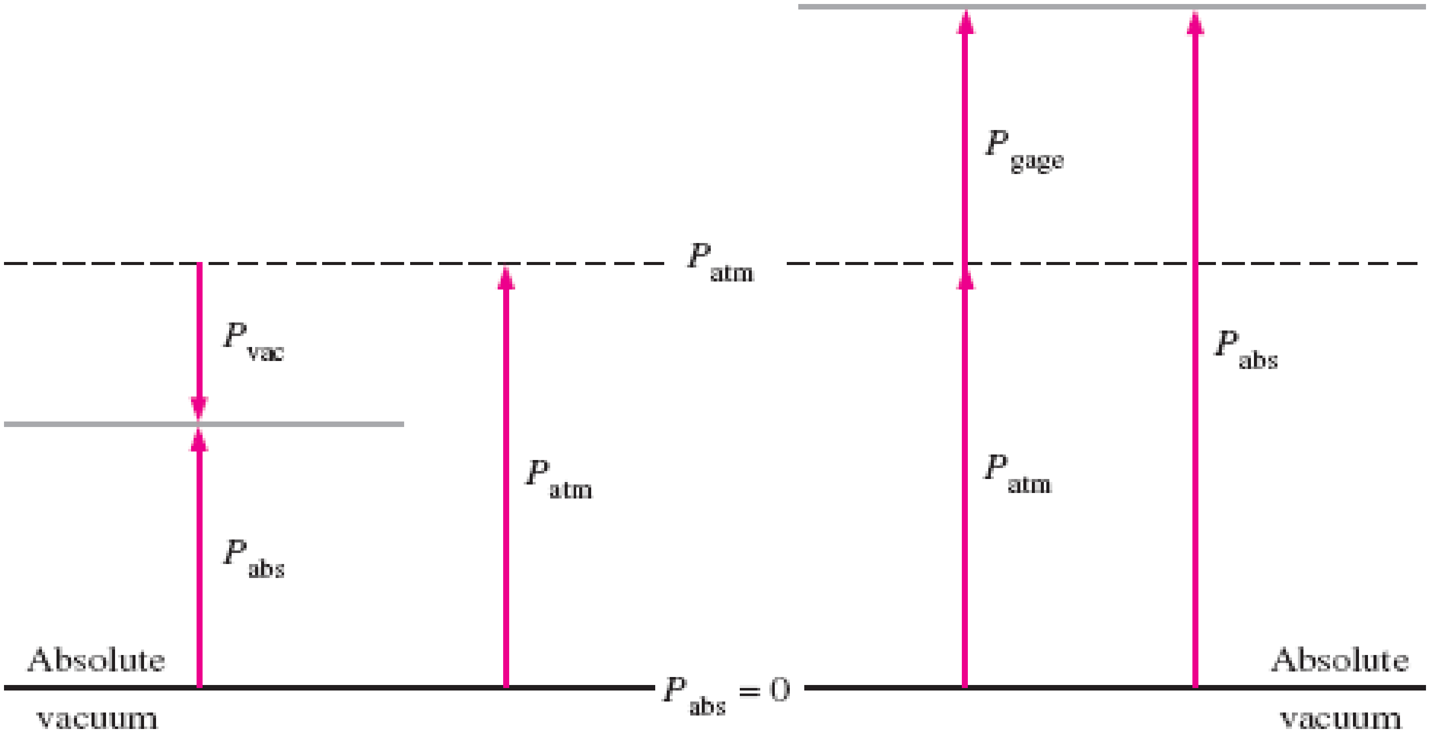
1 standard atmospheric pressure $= 1.01325bar = 101.325kPa = 101325Pa = 760mm$ *of Hg*

$1mm$ *of Hg* $= 0.1333kPa = 13.6mm$ *of* H_20

$1bar = 10^5Pa = 100kPa$;
$1N/mm^2 = 10^6N/m^2 = 10^6Pa = 1000kPa$

The pressure exerted by atmosphere on earth surface is known as atmospheric pressure, measured by barometer. At the sea level and at 0^0C, 760mm of Hg is known as *standard atmospheric pressure*.

Gauges, Gauge pressure, Vacuum pressure, Absolute pressure



The actual pressure of the working substance is called the *absolute pressure*.

For gauge pressure or positive pressure,

$$P_{absolute} = P_{atm} + P_{gauge}$$

For vacuum or negative pressure

$$P_{absolute} = P_{atm} - P_{gauge}$$

OR

$$P_{\text{gage}} = P_{\text{abs}} - P_{\text{atm}}$$

$$P_{\text{vac}} = P_{\text{atm}} - P_{\text{abs}}$$

b) Volume:

The space occupied by the substance is called volume. It is measured in m^3.

$$1\,litre = 1000cc = 10^{-3}m^3$$

c) Specific volume:

Specific volume of a substance is its volume per unit mass. Its unit is m^3/kg.

Density of a substance is its mass per unit volume. Unit - kg/m^3.

Density: $\rho = \dfrac{m}{V}$ $(\mathrm{kg/m^3})$

Specific volume $v = \dfrac{V}{m} = \dfrac{1}{\rho}$

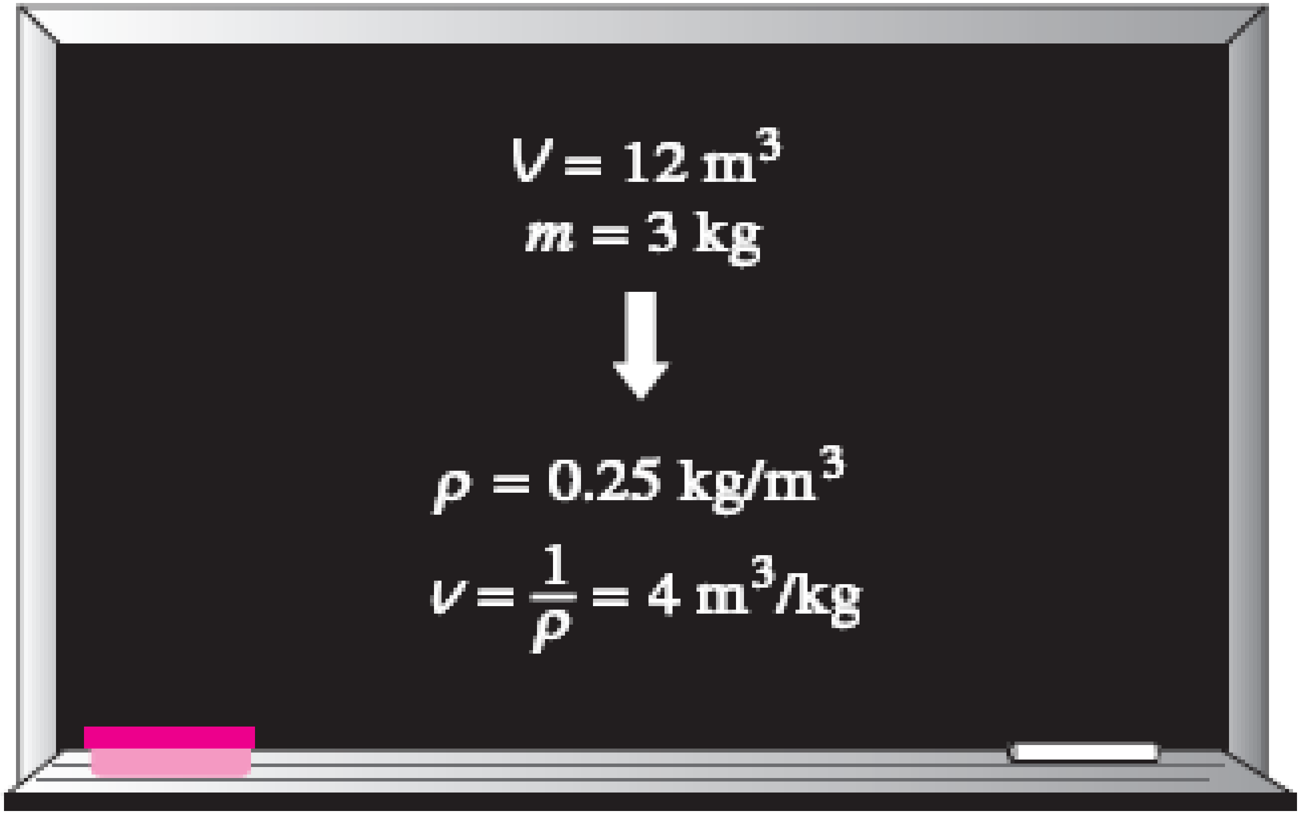


FIGURE 1–22

Density is mass per unit volume; specific volume is volume per unit mass.

d) Temperature: It is a thermodynamic property which determines the degree of hotness or the level of heat intensity of a body.

A body is said to be at a high temperature or hot if it shows a high level of heat intensity in it. Similarly a body is said to be at low temperature or cold, if it shows a low level of heat intensity in it.

Usually temperature is measured by *thermometer*. Very high temperature is measured by *pyrometer*. Small and precise changes in temperature can be measured by *resistance thermometers or thermocouple*.

e) Energy: Energy may be defined as the capacity a body possesses for doing work. All forms of energy are mainly classified as i) Stored energy ii) Transient energy or energy in transition or transient energy.

Stored energy is the energy possessed by a system within its boundaries. E.g., *K.E, P.E, and I.E*.

Transit energy is the energy possessed by a system which is capable of crossing its boundaries. E.g. *Heat and Work.*

f) Heat: Heat is defined as the energy transferred without transfer of mass across the boundary of a system due temperature difference between the system and the surroundings. The energy in transition is called heat. Heat energy cannot be stored in a system.

Unit for heat and any other form of energy is *joule (J).*

Heat flow into a system is *positive* and heat flow out of a system is *negative*.

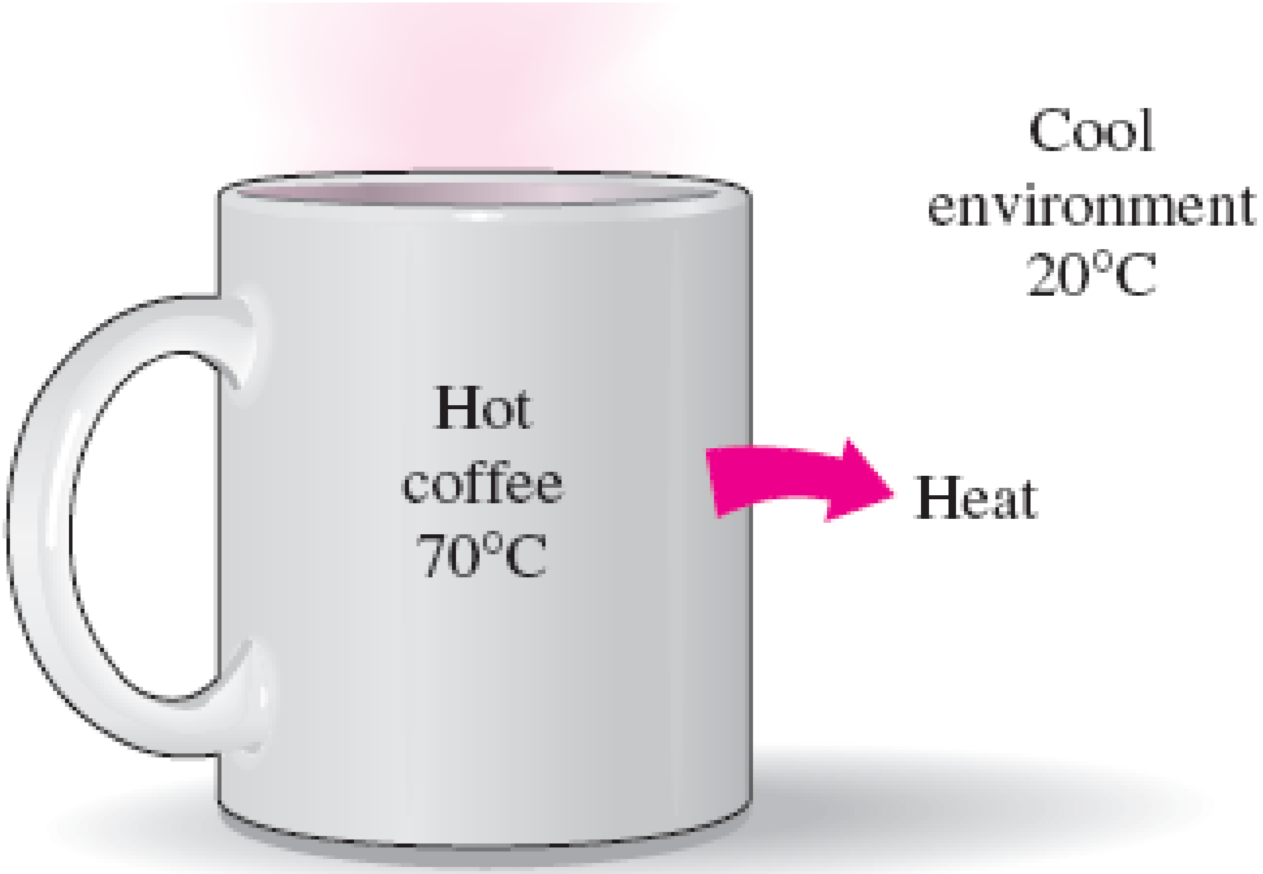


FIGURE 1–3

Heat flows in the direction of decreasing temperature.

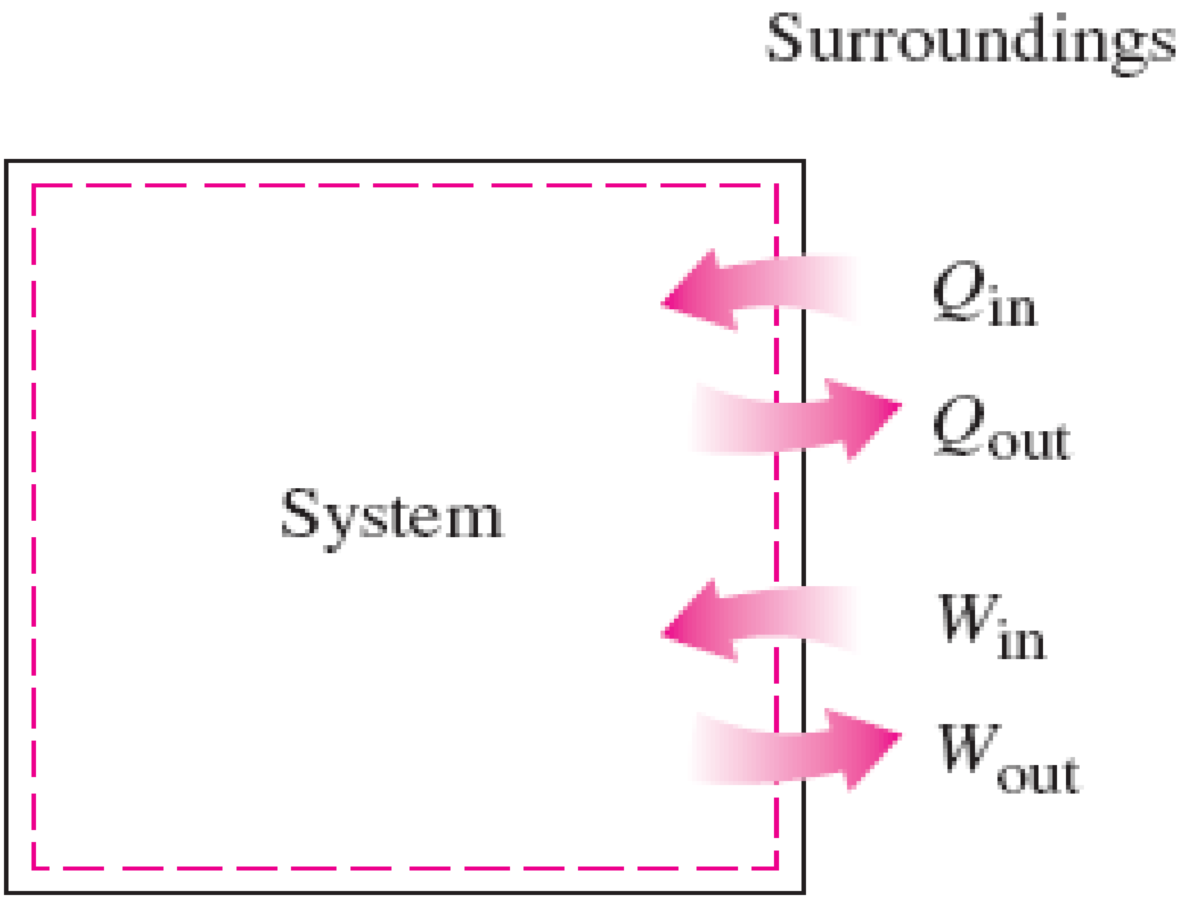


FIGURE 2–18

Specifying the directions of heat and work.

g) Work: Work is defined as the energy transferred without transfer of mass across the boundary of a system because of intensive property difference other than temperature that exists between the system and the surroundings. Work also cannot be stored in a system.

Unit of work done is *N-m or joule*.

Work done by the system is *positive* and work done upon the system is *negative.*

h) Internal energy: It is the energy possessed by a body or system due to its molecular arrangement and motion of the molecules.

It is the sum of internal K.E and internal P.E of the molecules. It is a function of temperature and can be increased or decreased by adding or subtracting heat to or from the substance.

Absolute value of the I.E cannot be measured but change in I.E can be measured when a substance undergoes a change of state from 1 to 2. It can be expressed in general way as;

$$du = u_2 - u_1$$

i) Enthalpy:

Enthalpy is nothing but total heat and heat content. Enthalpy or total heat = Internal energy + Product of absolute pressure and volume.

$$h = u + pv$$

Absolute value of enthalpy cannot be measured, only change in enthalpy can be measured.

$$dh = h_2 - h_1 = (u_2 - u_1) + (pv_2 - pv_1)$$

j) Entropy

It is represented by the symbol ‘s’. Small increase of entropy ‘ds’ of a substance is defined as the ratio of small addition of heat dQ to the absolute temperature T of the working substance at which the heat is supplied.

$$ds = dQ/T \qquad \text{or} \qquad dQ = T.ds$$

Unit of entropy is *J/kg/K.*

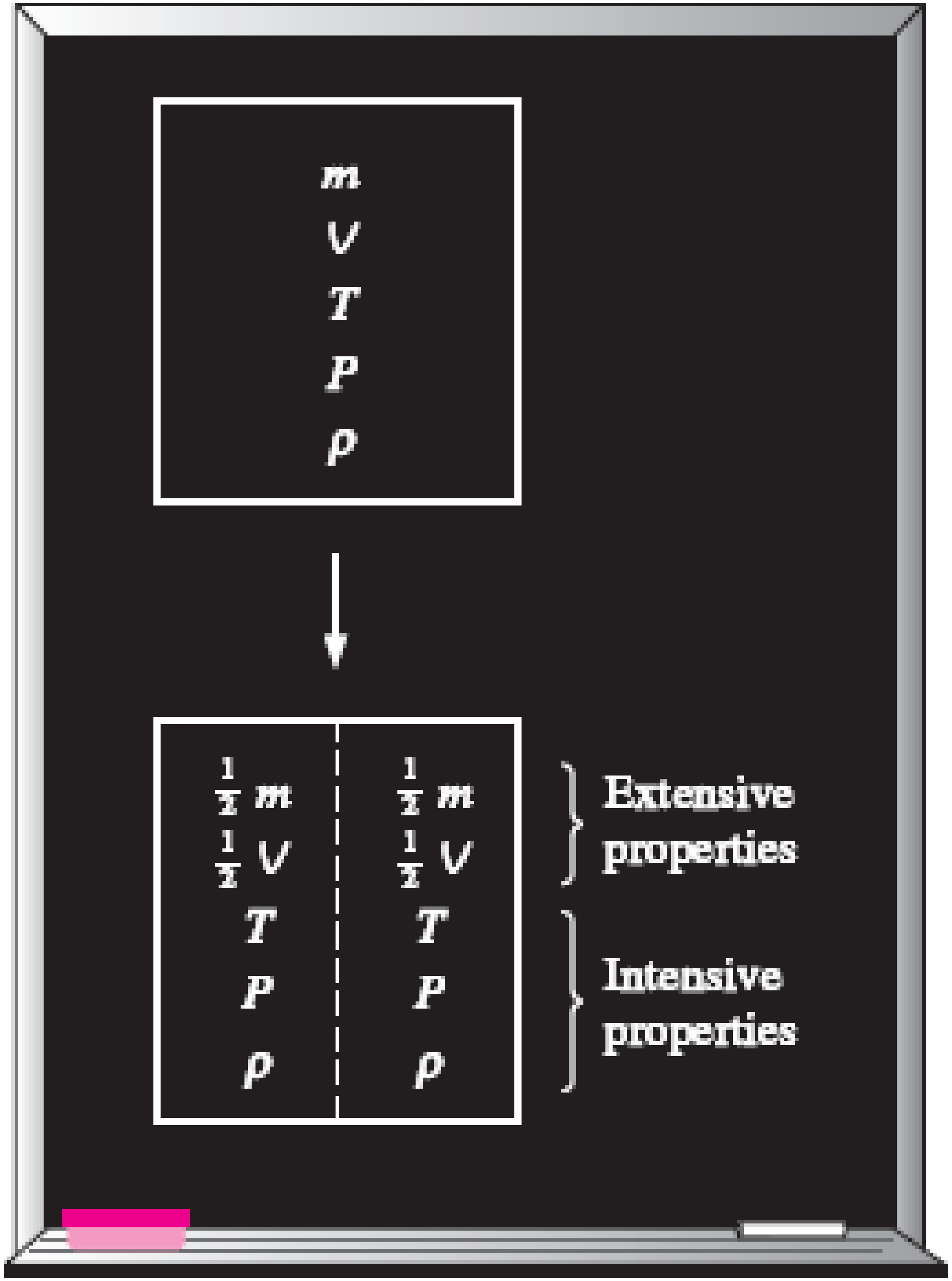
Classification of properties:

1. **Extensive property:** The properties of the system, whose value for the entire system is equal to the sum of their values for the individual parts of the system, are called extensive properties. These properties depend on the mass of the system.

E.g. *K.E, P.E, I.E, Total volume, Total mass, Enthalpy,* etc.

2. **Intensive properties:** It is the property of the system whose value for the entire system is not equal to the sum of their values for the individual parts of the system. This property does not depend on the mass.

E.g., *temperature, Pressure, Density, Specific volume,* heat and work etc.


m
V
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½ m
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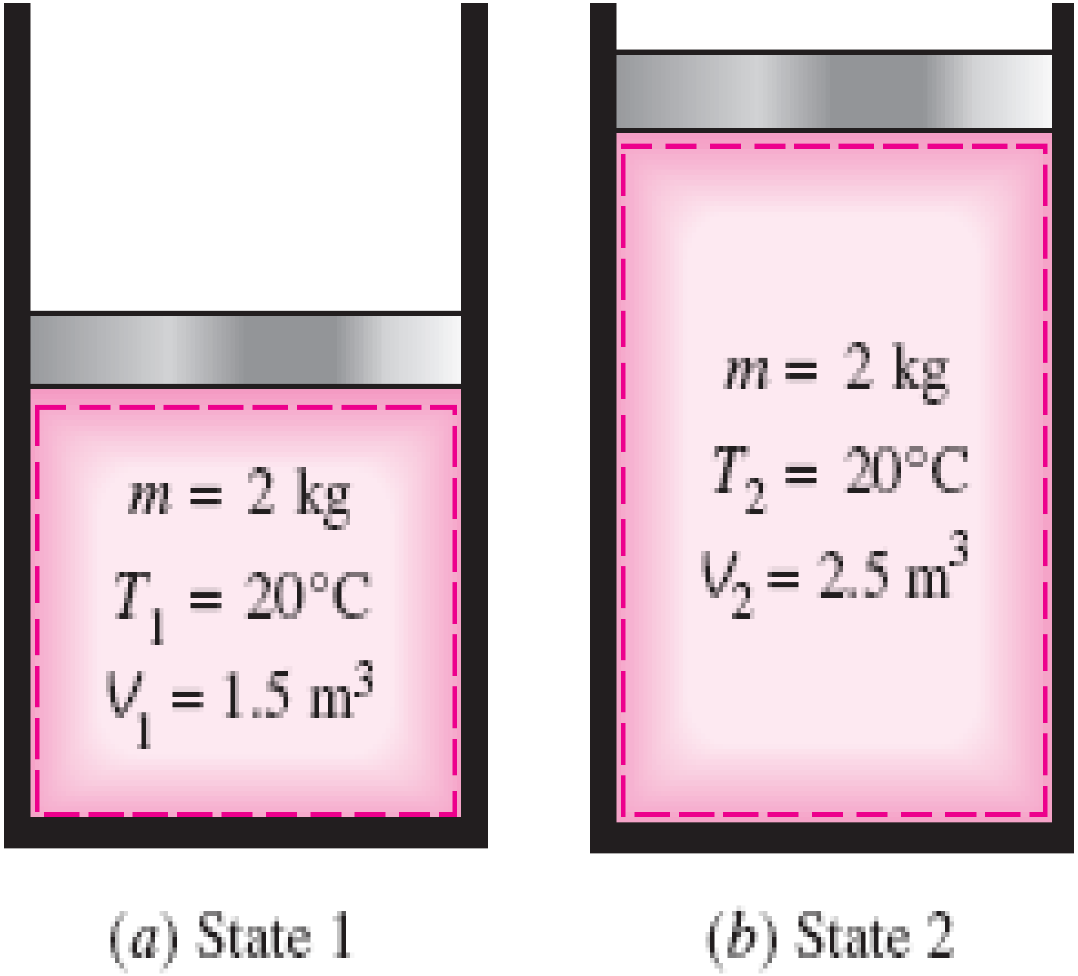
Extensive properties
Intensive properties

Thermodynamic state of a system/substance: Exact condition of a system/substance is called state.



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

Thermodynamic process: When one or more of the thermodynamic properties of a system change, we say that there is a change of state of the system. This change of state of a system is referred to as thermodynamic process.

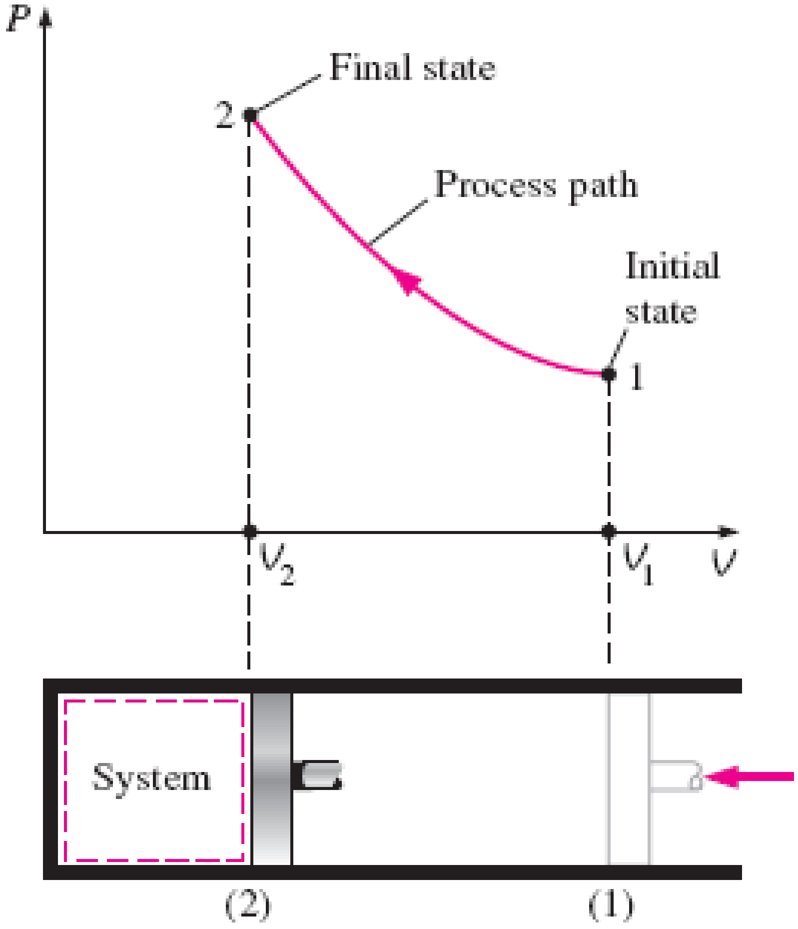
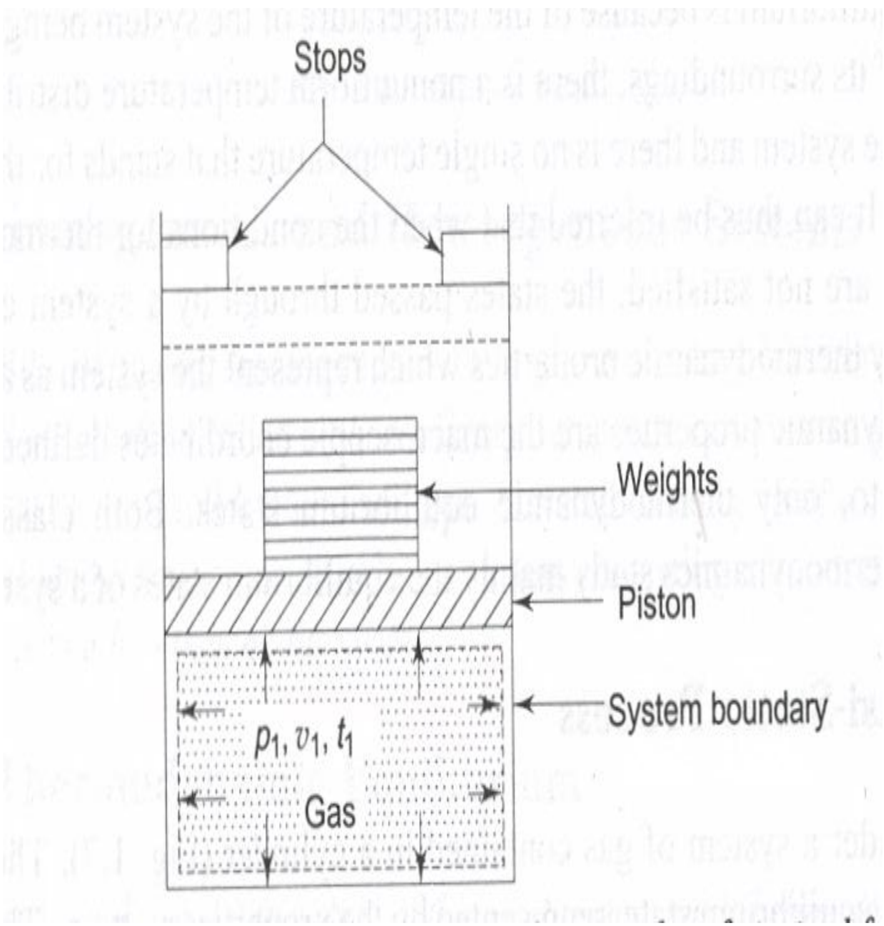
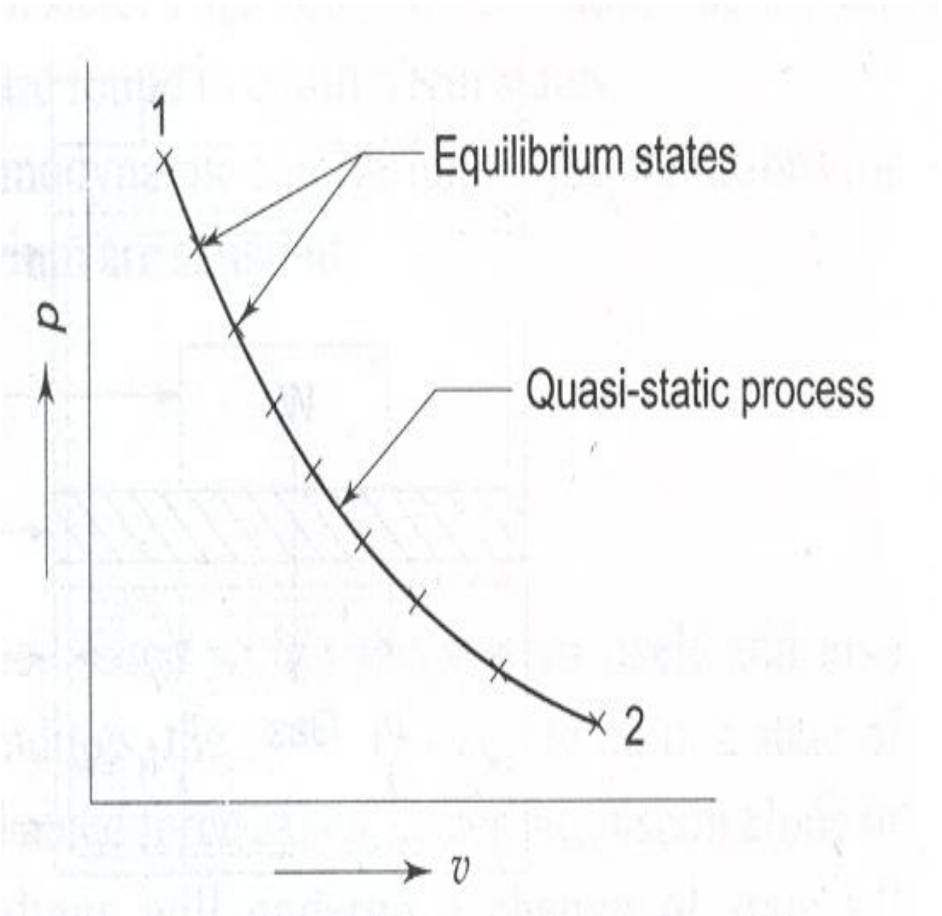


Fig. A Process between state 1 and state 2 and process path

<u>Quasi-static process:</u> A quasi-static process is one in which the deviation from equilibrium is infinitesimally small. All the states through which a system passes during a process can be considered as a succession of equilibrium states.





Thus quasi-equilibrium process takes place very slowly. If one property remains constant during a process, the prefix “iso” is used to describe such a process.

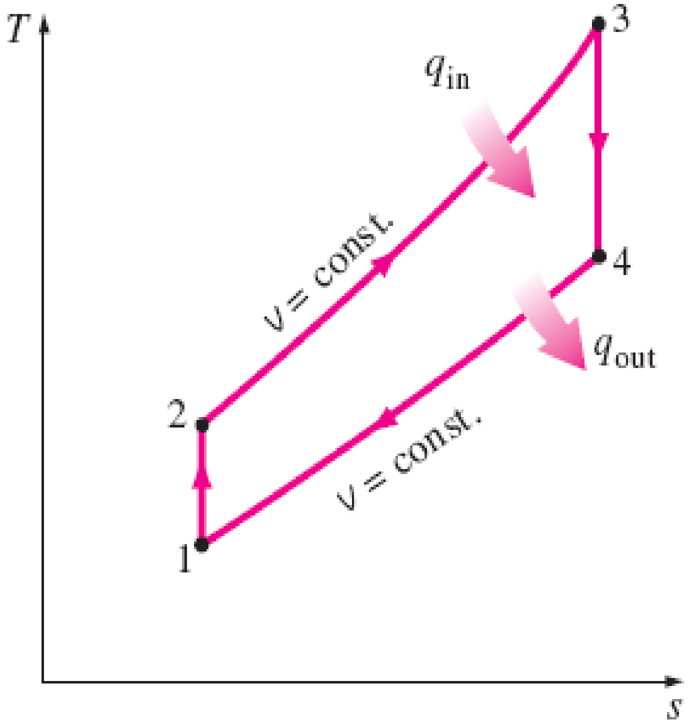
E.g. Isothermal process – Constant temperature process
Isobaric process – Constant pressure process
Isochoric process – Constant volume process.

Reversible and irreversible process:

A process is called a reversible process if it can be completely reversed and the system and the surroundings come back to its original states.

A process which cannot be exactly reversed and the system cannot be brought back to the initial state without leaving a net change in the surroundings is called irreversible process.

Thermodynamic cycle: When a number of processes in sequence bring the system back to its initial state, then the system is said to have undergone a thermodynamic cycle.



$$\oint dp = 0$$

$$\oint dV = 0$$

In Fig 1-2-3-4-1 is cycle consisting of four processes. The change in value of any property is zero for a cyclic process.

Thermodynamic equilibrium: A system is in thermodynamic equilibrium if it is not capable of a finite spontaneous change to another state.

i) **Thermal equilibrium:** When a system is in contact with its surroundings across a diathermal wall and if there is no spontaneous change in any of the properties of the system, the system is said to exist in thermal equilibrium with its surroundings.

ii) **Mechanical equilibrium:** A system is said to be in mechanical equilibrium, when there is no unbalanced force acting on any part of the system or the system as a whole.

iii) **Chemical equilibrium:** A system is said to be in chemical equilibrium, when there is no chemical reaction within the system and also there is no movement of any chemical constituent from one part of the system to the other.

Diathermal wall and Adiabatic wall:

The envelope or boundary or surface enclosing a system may be a conductor or insulator.

If this contacting wall or surface is a conductor which allows heat energy to pass through it, then it is called diathermal wall.

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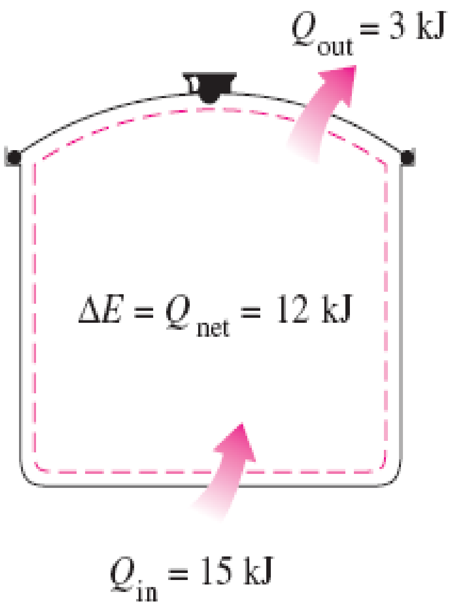


Fig. Diathermal wall

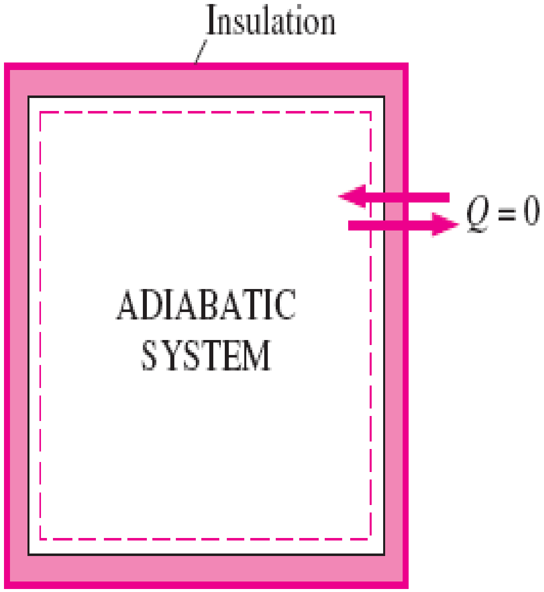
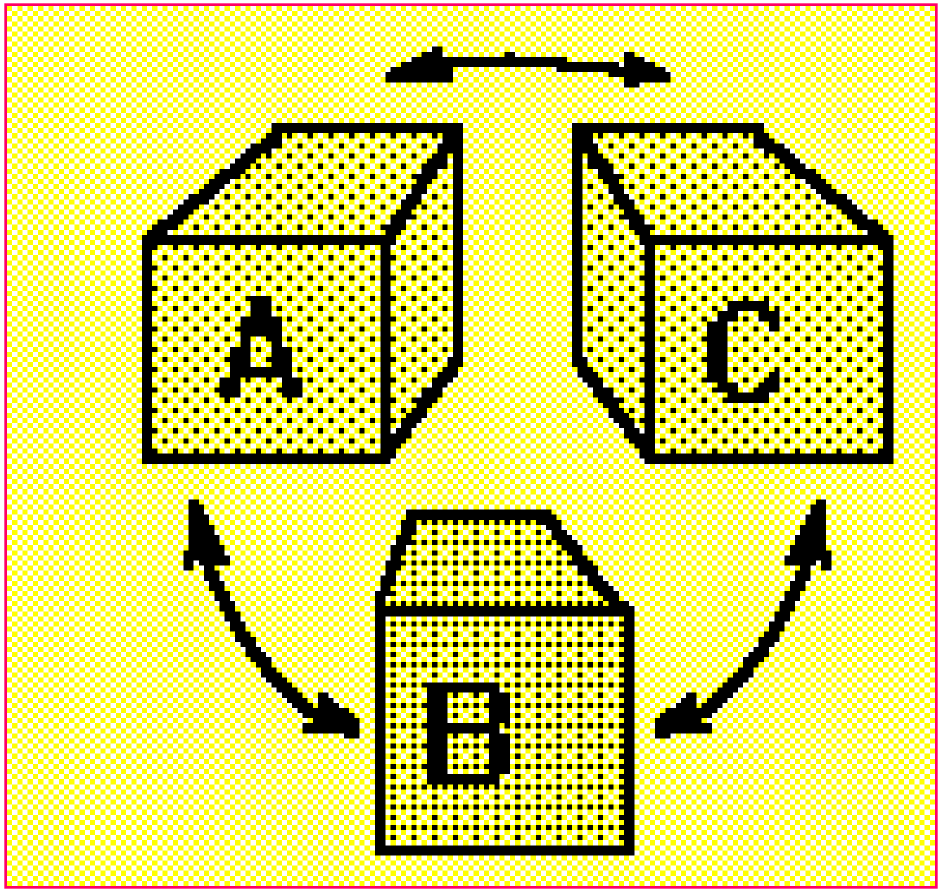


Fig. Adiabatic wall

Zeroth law of thermodynamics:

Statement: When two systems have thermal equilibrium with a third system, they in turn have thermal equilibrium with each other.



Thermometer and thermometric property: The Zeroth law provides the basis for the measurement of temperature. The third body 3 in Zeroth law is called the thermometer.

THERMOMETER	THERMOMETRIC PROPERTY
1. Alcohol or mercury in glass	Length
2. Electrical resistance	Resistance
3. Thermocouple	Electromotive force
4. Constant volume gas	Pressure
5. Constant pressure gas	Volume
6. Radiation (Pyrometer)	Intensity of radiation

Temperature scales: We know that temperature is a function of resistance R, emf E, pressure P, volume V and radiation intensity I in case of electric resistance thermometer, thermocouple, constant volume thermometer, constant pressure thermometer and radiation thermometer respectively. In establishing a temperature scale we need a relationship between the temperature and the thermometric property.

Direct proportionality : $t = Ax$

Linear relation : $t = ax + b$

Quadratic relation : $t = \alpha x^2 + \beta x + \Upsilon$

Polynomial : $A' + B'x + C'x^2 + D'x^3 + \ldots\ldots..$

The temperature of -273^{0}**C** in Celsius scale and -460^{0}**F** in case of Fahrenheit scale is called absolute zero temperature. The temperature measured from this zero is called *absolute temperature*.

The absolute temperature in Celsius scale is called degree *Kelvin (K),*

$$T(\mathrm{K}) = T(^{\circ}\mathrm{C}) + 273.15$$

Similarly the absolute temperature in Fahrenheit scale is called degree *Rankine (R),*

$$T(\mathrm{R}) = T(^{\circ}\mathrm{F}) + 459.67$$

WORK AND HEAT

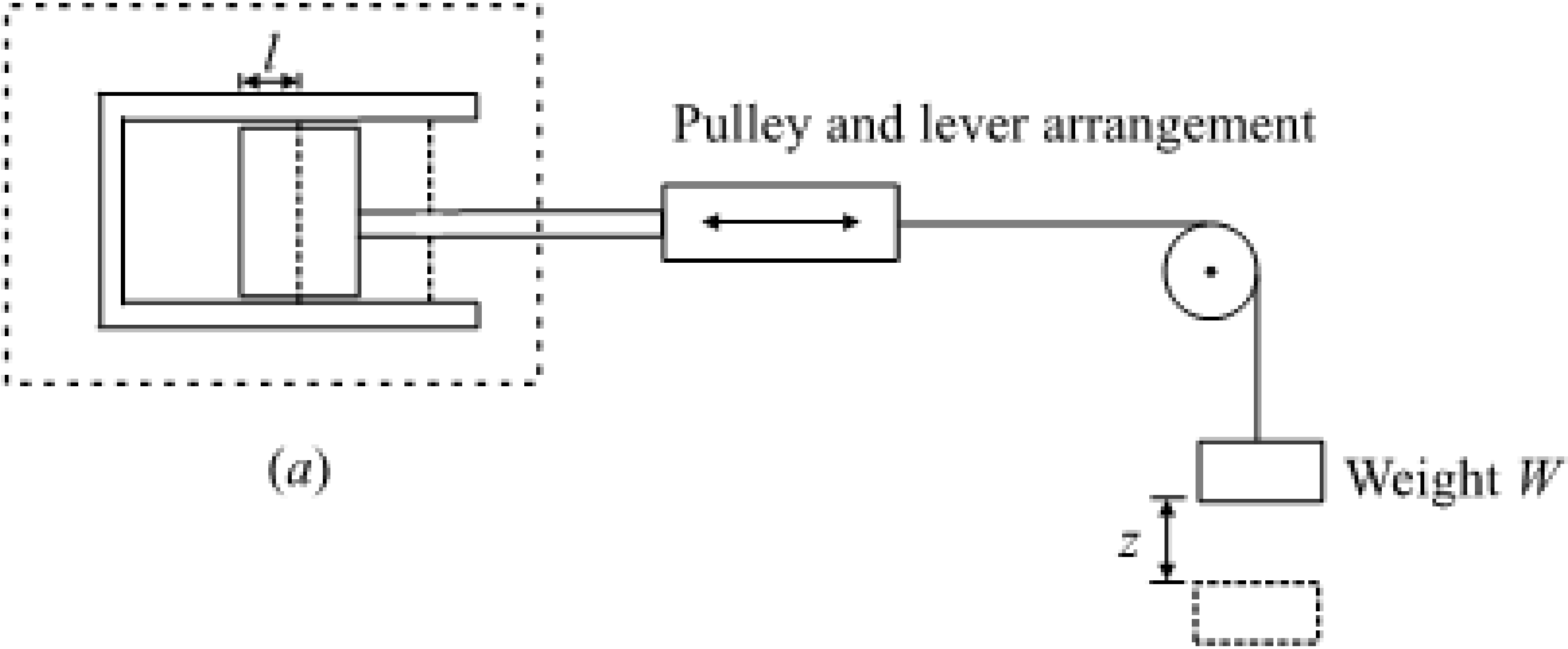
Definition of work in Mechanics: *The work is done by a force as it acts upon a body moving in the direction of the force.*

The action of a force through a distance is called mechanical work. The product of the force and the distance moved parallel to the force is the magnitude of the mechanical work.

Thermodynamic work:

In thermodynamics, work transfer is considered as occurring between system and surroundings. *Work is said to be done by a system if the sole effect on things external to the system can be reduced to the raising of a weight.*

- “Work shall be done by the system if the total effect outside the system is equivalent to the raising of weight and this work shall be positive work ”.
- The weight may not actually be raised, but the net effect external to the system would be reduced to the raising of a weight.



Piston and cylinder arrangement

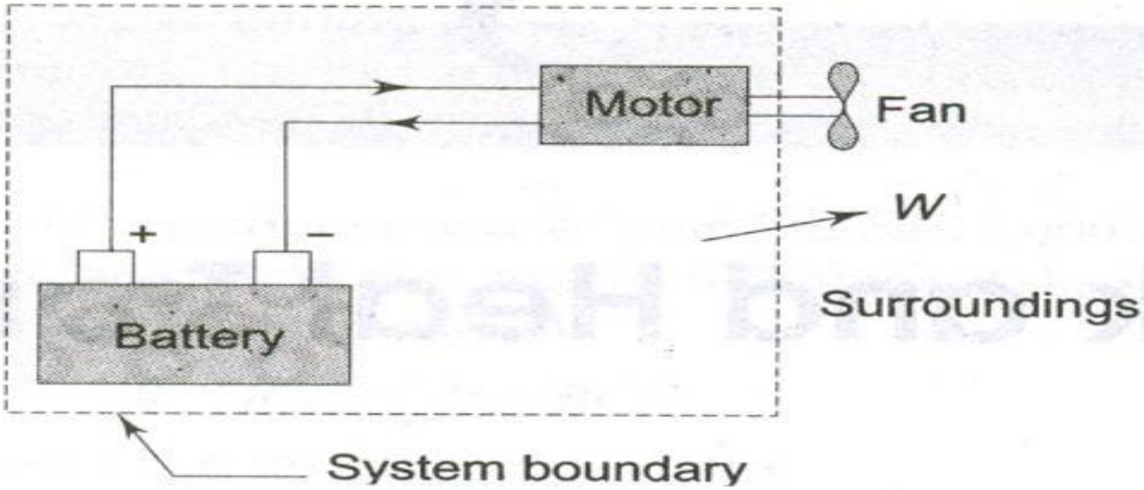
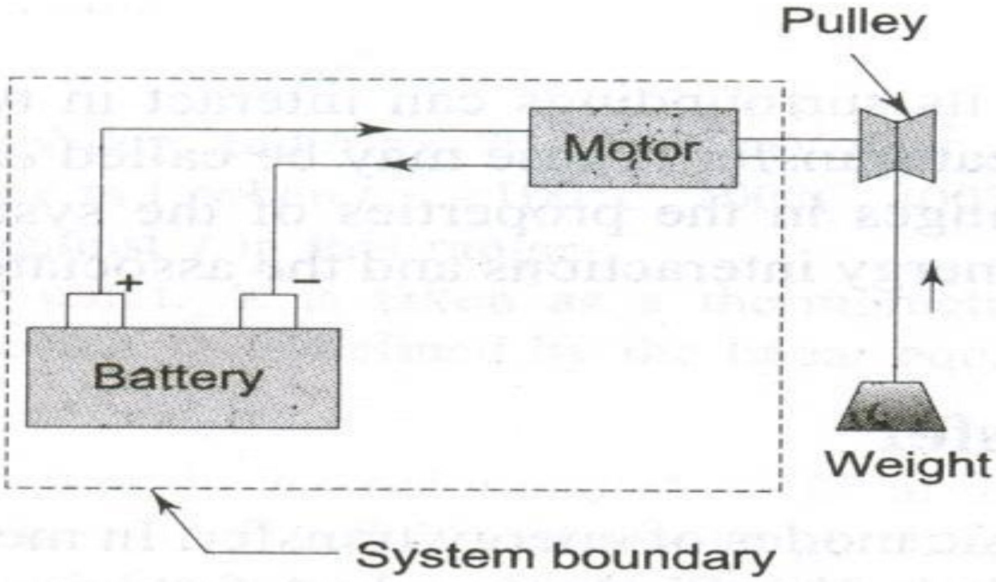
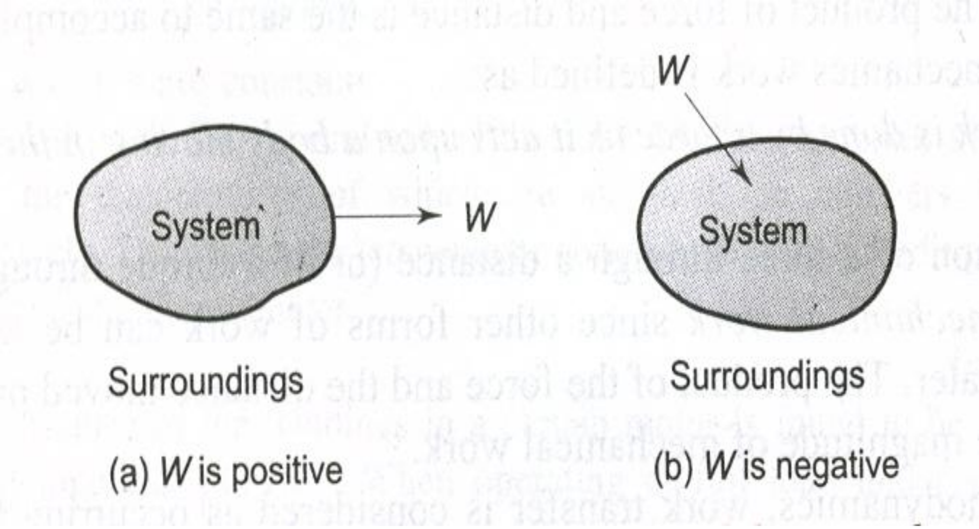


Fig. *Battery-motor system driving a fan*



In thermodynamics by convention, the work done by a system is considered as *positive* and the work done on a system is considered *negative*.



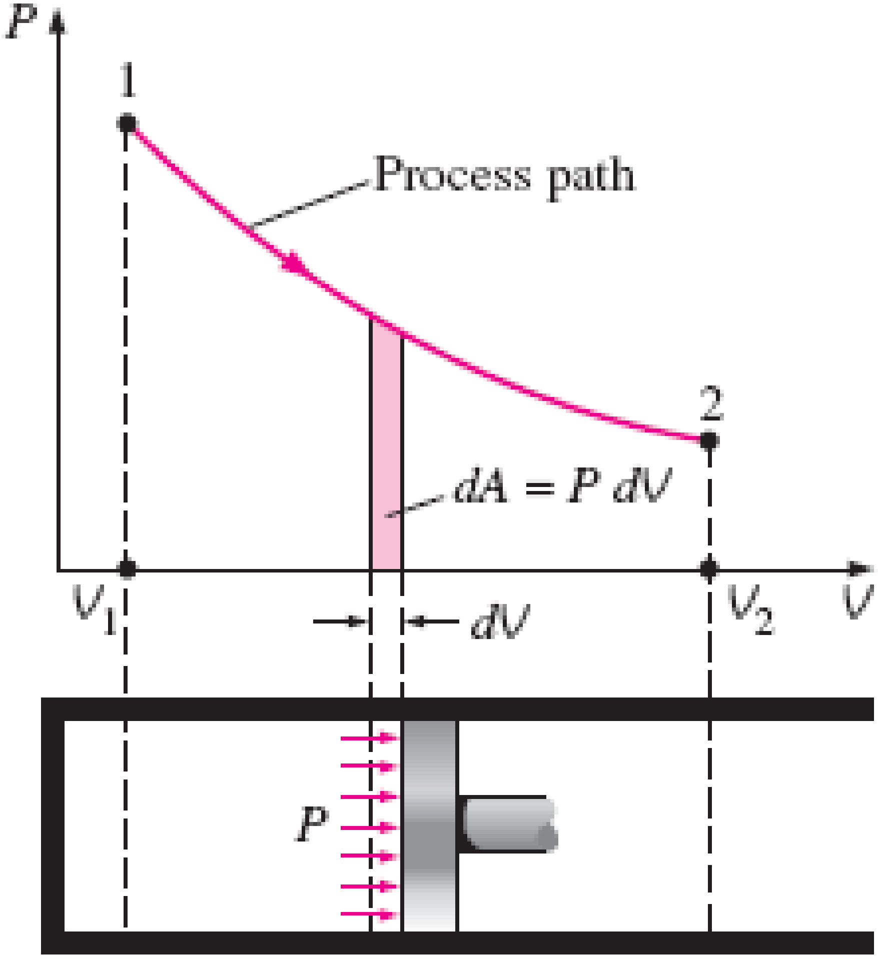
(a) *W* is positive

(b) *W* is negative

When a system does positive work, its surroundings do an equal amount of negative work and vice versa. Thus in any process

Work done in a frictionless quasi-equilibrium process (displacement work or p-dV work):

Consider a gas in thermodynamic equilibrium in a frictionless piston and cylinder arrangement as shown in Fig.



- When the piston moves an infinitesimal distance dl, and if *A* be the area of the piston, the force *F* acting on the piston **F = pA** and infinitesimal work done by the gas on the piston

$$dW = F.dl = (pA)dl = pdV$$

Where ***dV* = *Adl***, represents displacement or change in volume of the system.

When the piston moves out from position 1 to position 2 with the volume changing from V_1 to V_2, the amount of work *W* by the system will be

$$W_{1-2} = \int_1^2 dW = \int_1^2 p\,dV$$

The magnitude of the work done is given by the area under the path 1-2, as shown in Fig above.

Point function v/s path function:

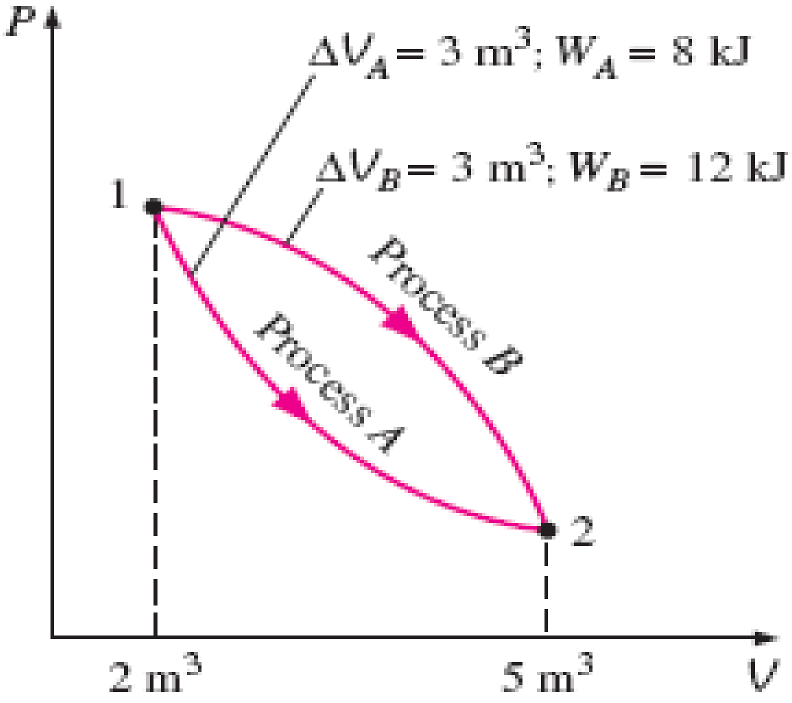
Any quantity whose change is independent of the path is a point function and hence is a property.

The quantity, the value of which depends on the path followed during a change of state is a path

$$\int_1^2 dp = p_2 - p_1$$

$$\int_1^2 dv = V_2 - V_1$$

$$\int_1^2 dW = W_{1-2} \qquad \int_1^2 dQ = Q_{1-2}$$



Displacement work in various processes:

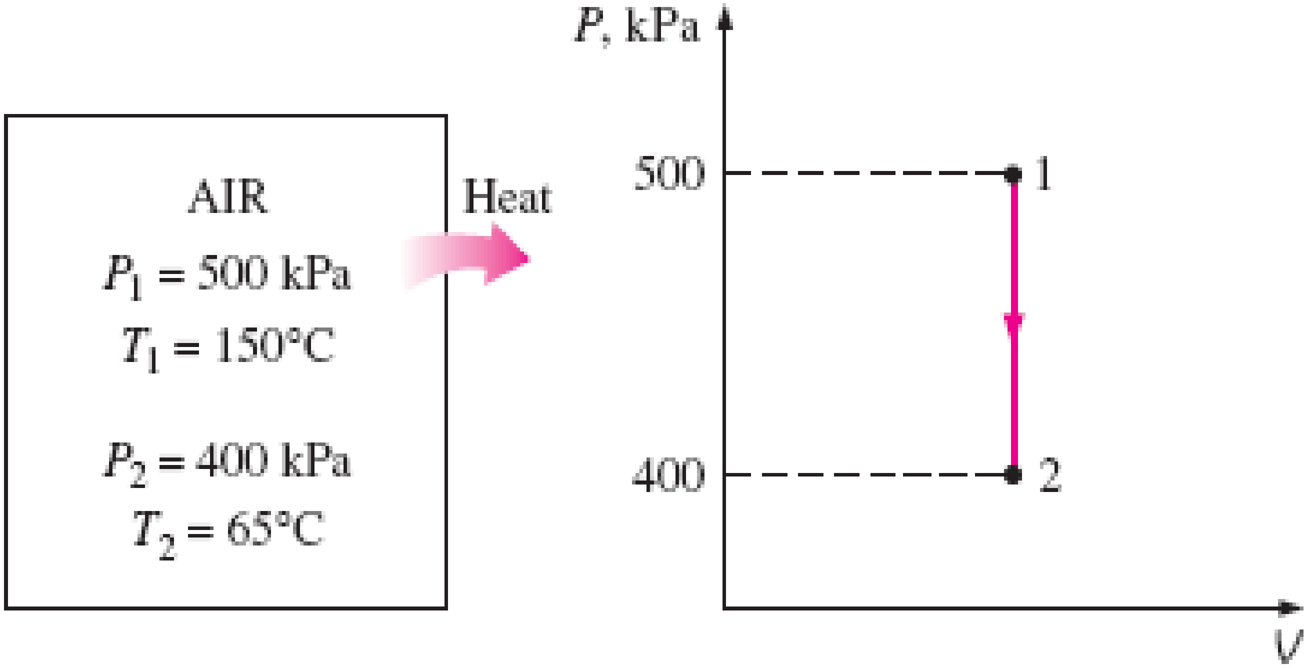
a) Constant pressure process:

$$W_{1-2} = \int_1^2 p\, dV = p \int_1^2 dV = p(V_2 - V_1)$$

b) Constant volume process: (Isochoric process)

Here $dV = 0$, hence

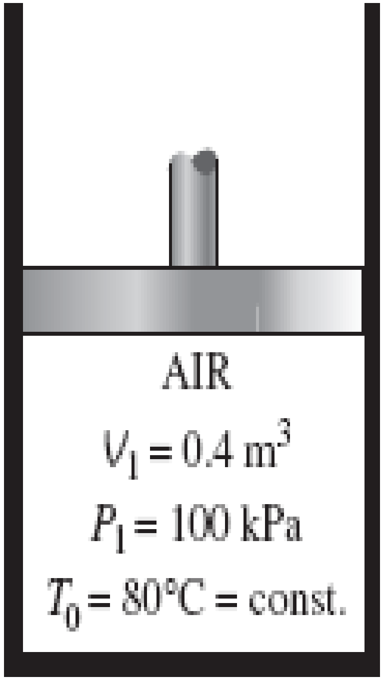
$$W_{1-2} = 0$$

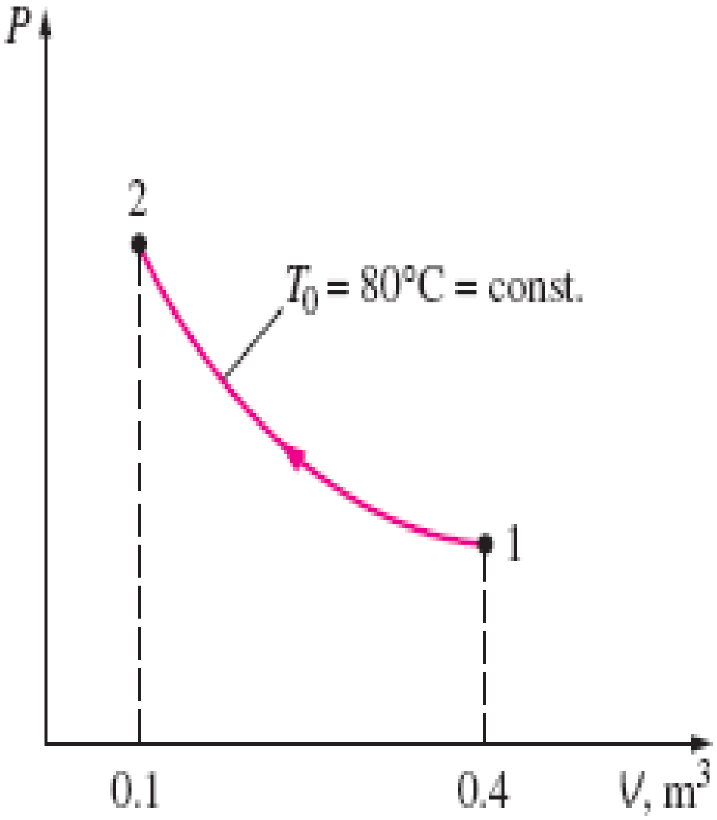


c) Hyperbolic process:

For a hyperbolic process, $pV = p_1V_1 = p_2V_2$

$$i.e., p = \frac{p_1V_1}{V}$$





$$W_{1-2} = \int_1^2 p\,dV = \int_1^2 \frac{p_1 V_1}{V}\,dV$$

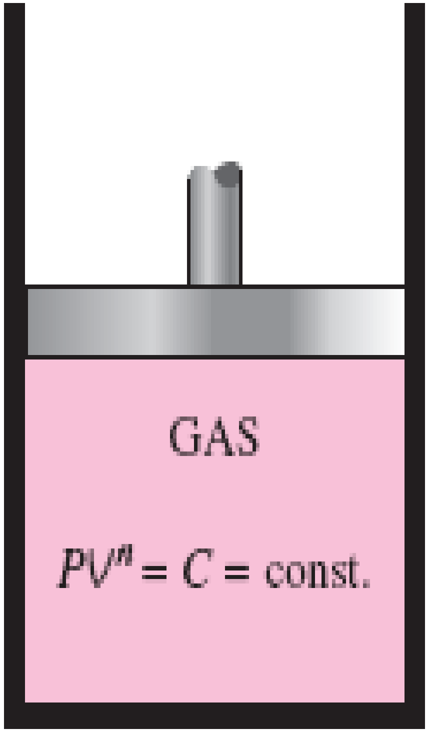
$$W_{1-2} = p_1 V_1 \ln\frac{V_2}{V_1} \quad OR \qquad W_{1-2} = p_2 V_2 \ln\frac{V_2}{V_1}$$

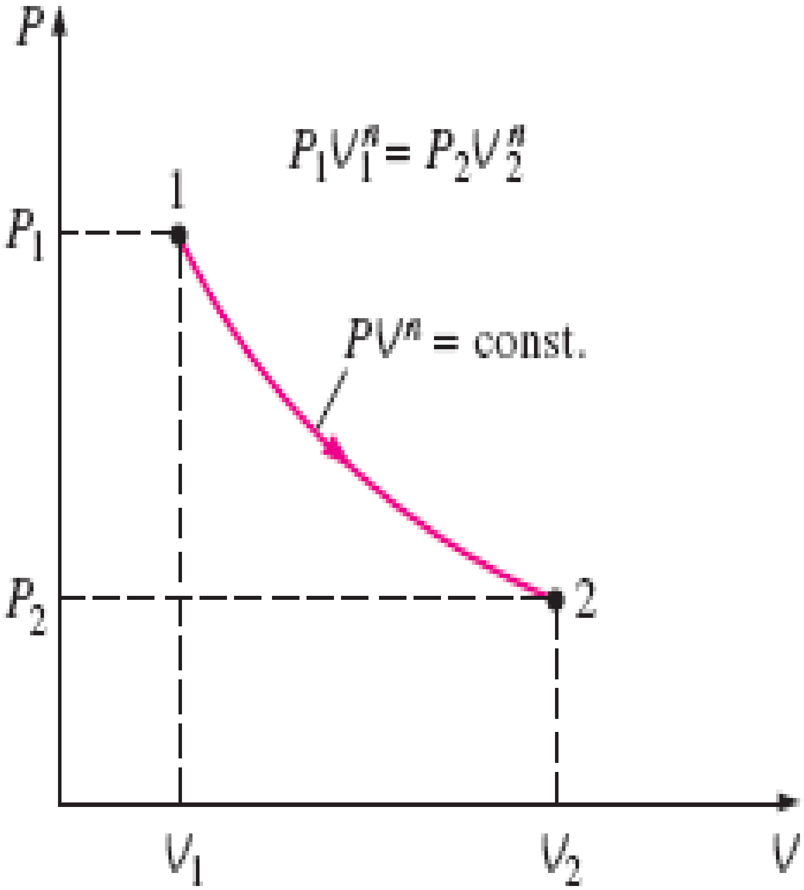
$$W_{1-2} = p_1 V_1 \ln\frac{p_1}{p_2} \quad OR \qquad W_{1-2} = p_2 V_2 \ln\frac{p_1}{p_2}$$

The *hyperbolic process* becomes an *isothermal process* for an ideal gas for which at constant temperature

pV = RT = C

d) Polytropic process:





For polytropic process $pV^n = p_1V_1^n = p_2V_2^n = C$

The index *'n'* is referred to as the polytropic index OR the polytropic exponent. It can be found out if p_1V_1 and p_2V_2 values are known by following relation

$$n = \frac{\ln p_1/p_2}{\ln V_2/V_1}$$

$$W_{1-2} = \int_1^2 p\, dV = \int_1^2 \frac{p_1 {V_1}^n}{V^n}\, dV$$

$$= (p_1 \, V_1^{\mathrm{n}}) \left[\frac{V^{-\mathrm{n}+1}}{-n+1} \right]_{V_1}^{V_2}$$

$$= \frac{p_1 V_1^{\mathrm{n}}}{1-n} (V_2^{1-\mathrm{n}} - V_1^{1-\mathrm{n}})$$

$$= \frac{p_2 V_2^{\mathrm{n}} \times V_2^{1-\mathrm{n}} - p_1 V_1^{\mathrm{n}} \times V_1^{1-\mathrm{n}}}{1-n}$$

$$= \frac{p_1V_1 - p_2V_2}{n-1} \qquad \text{.....} \quad (1)$$

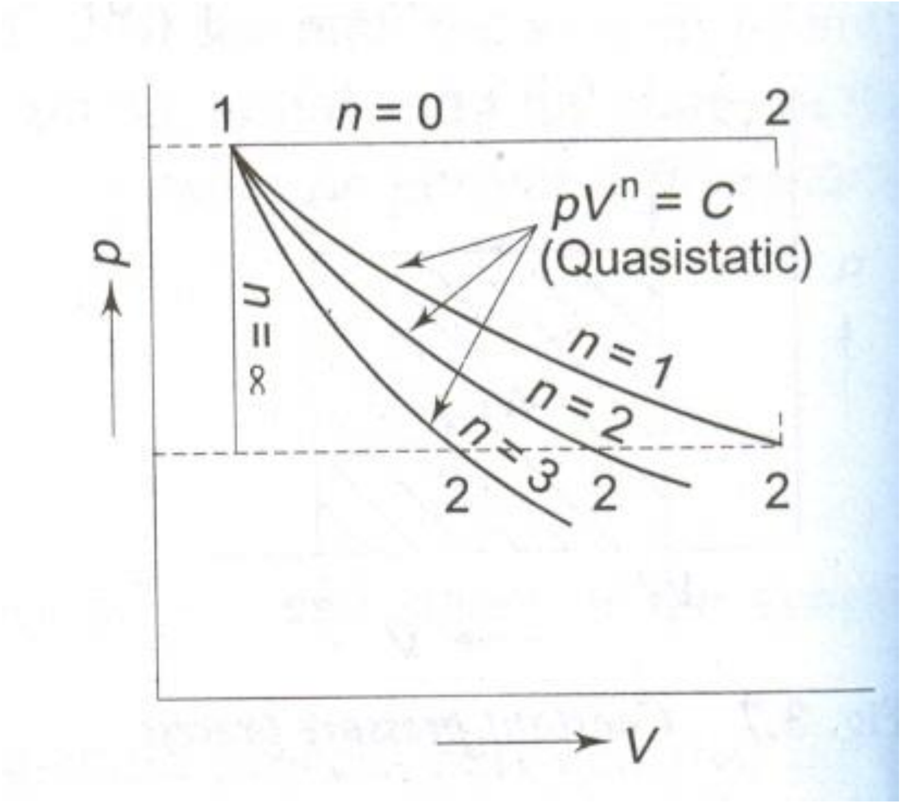
Note: 1) Polytropic process is regarded as general process because

If $n = 0$, it corresponds to constant pressure process

If $n = \infty$, it corresponds to constant volume process

If $n = 1$, it corresponds to hyperbolic process

All these processes can be represented on a single p-V diagram as shown in Fig below:



2) If the system comprises of an ideal gas, then we have

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

And we get equations,

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{(n-1)/n}$$

and

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{n-1}$$

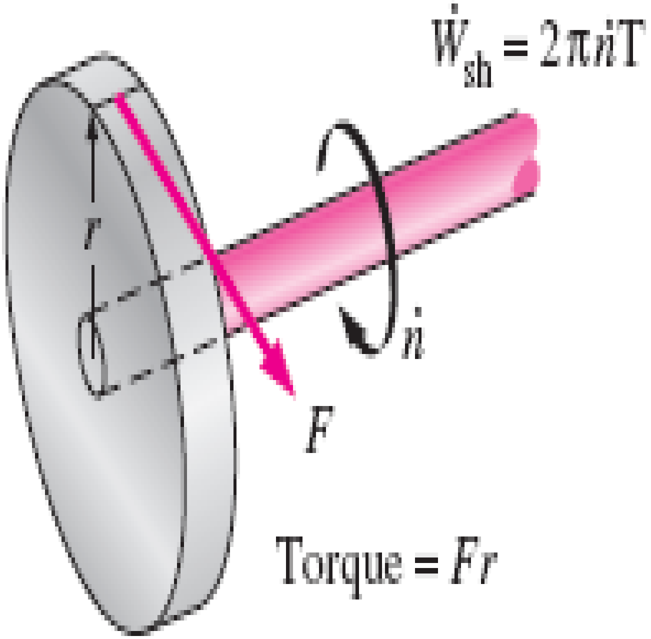
3) For an ideal gas, $p_2V_2 = mRT_2$ and $p_1V_1 = mRT_1$ and we have for polytropic work for an ideal gas

$$W_{1-2} = \frac{mR(T_2 - T_1)}{1 - n}$$

$$W_{1-2} = \frac{p_1 V_1}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{n-1/n}\right]$$

Other types of work transfer:

a) **Shaft work:** When a shaft, taken as the system (Fig below), is rotated by a motor, there is work transfer into the system. This is because the shaft can rotate a pulley which can raise a weight. If *T* is the torque applied to the shaft and is the angular displacement of the shaft, the shaft work is



$$W = \int_1^2 T\, d\theta$$

And the shaft power is given by

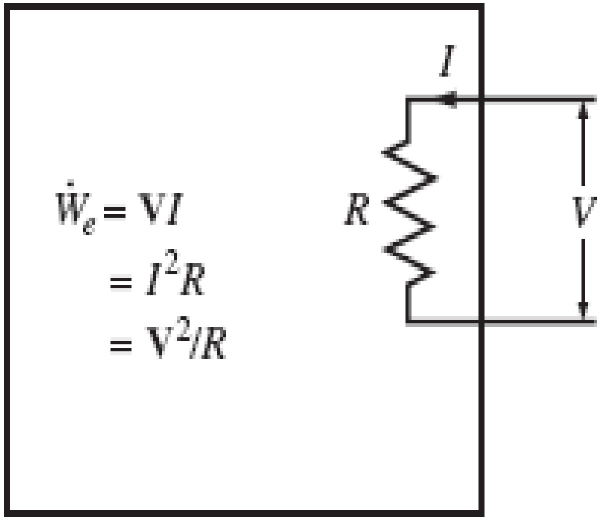
$$\int_1^2 T\left(\frac{d\theta}{d\tau}\right) = T\omega$$

Where, ω is the angular velocity.

b) Electrical work: When a current flows through a resistor (Fig below), taken as a system, there is work transfer into the system. This is because the current can drive a motor, the motor can drive a pulley and the pulley can raise a weight. The current flow *I*, in amperes, is given by

$$I = \frac{dC}{dt}$$

Where *C* is the charge in coulombs and *τ* is time in seconds. Thus *dC* is the charge crossing a boundary during time *dτ*. If *E* is the voltage potential, the work is



$$\boldsymbol{dW = E.dC = \mathrm{EI}.\,\mathrm{a}\tau}$$

$$\boldsymbol{W = \int_1^2 EI.d\tau}$$

c) Paddle-wheel work or stirring work: As the weight is lowered, and the paddle wheel turns (Fig below), there is work transfer into the fluid system which gets stirred. Since the volume of system remains constant. If *m* is the mass of the weight lowered through a distance dz and T is the torque transmitted by the shaft in rotating through an angle dθ, the differential work transfer to the fluid is given by

$$dW = mgdz = T\,d\theta$$

And

$$W = \int_1^2 T\,d\theta$$

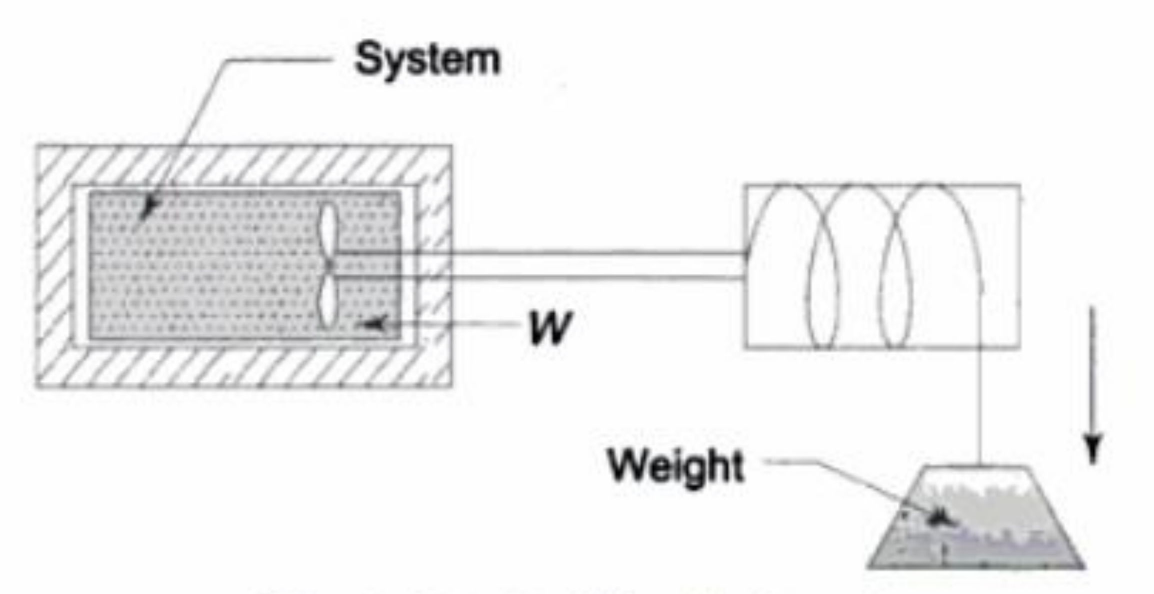


Fig. 3.15 *Paddle-wheel work*

Flow work :

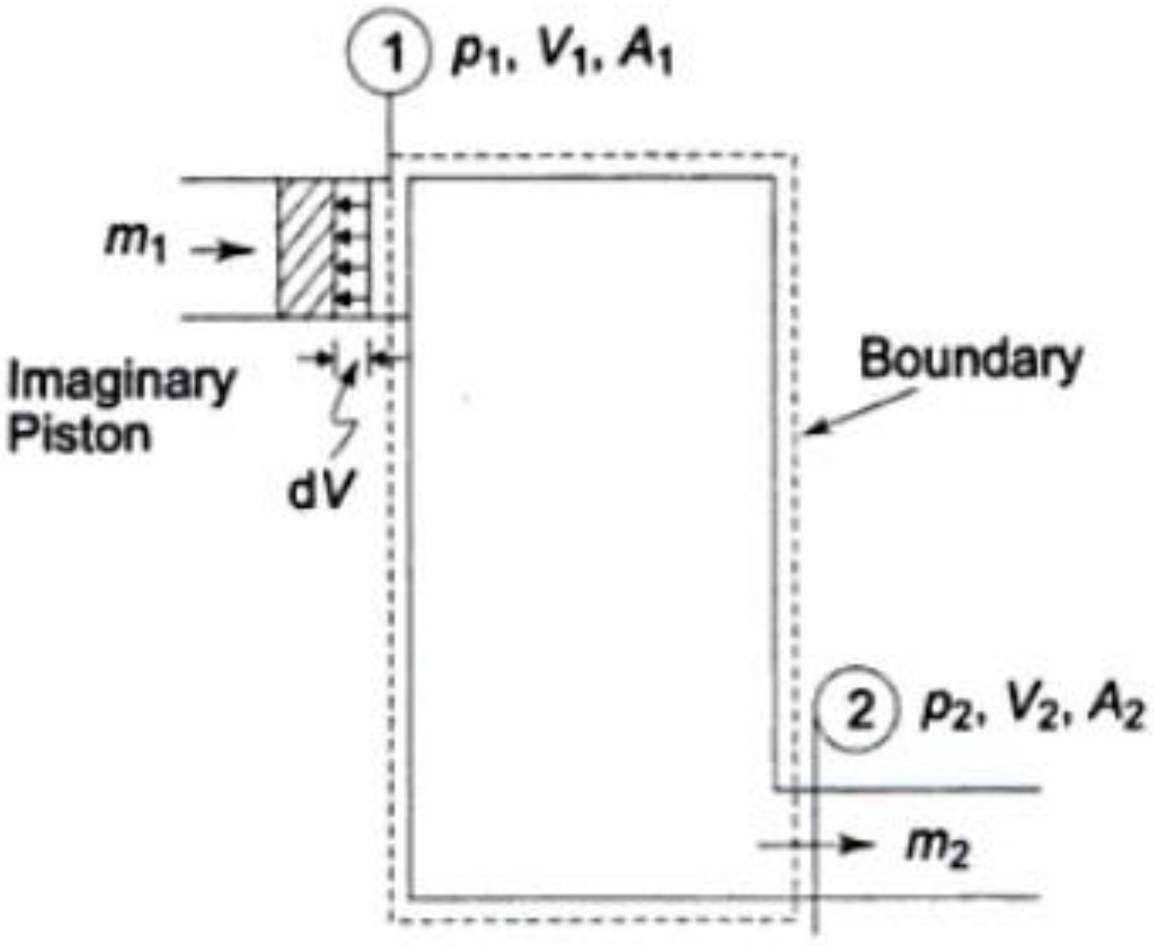
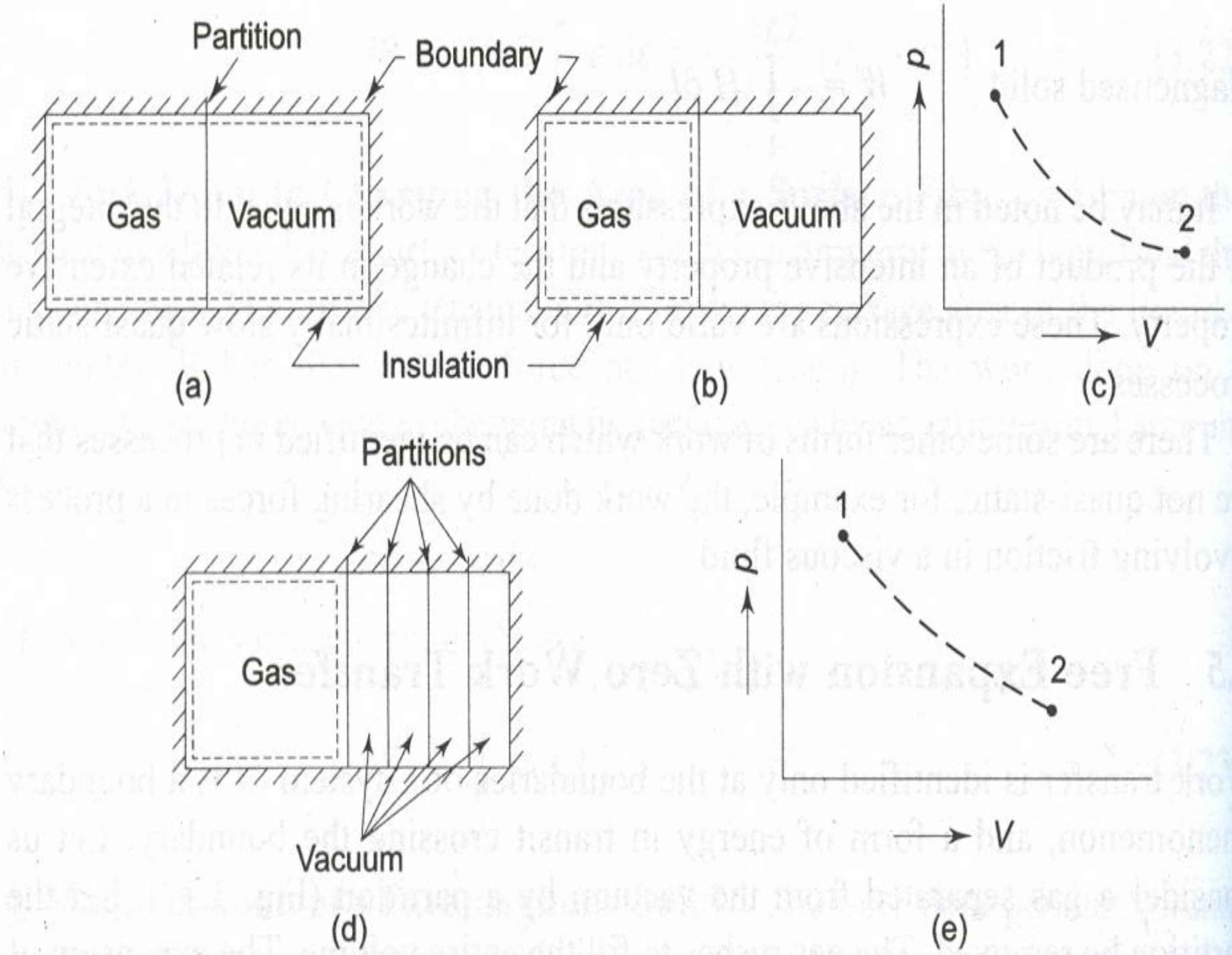


Fig. 3.16 *Flow work*

Free expansion with zero work transfer:



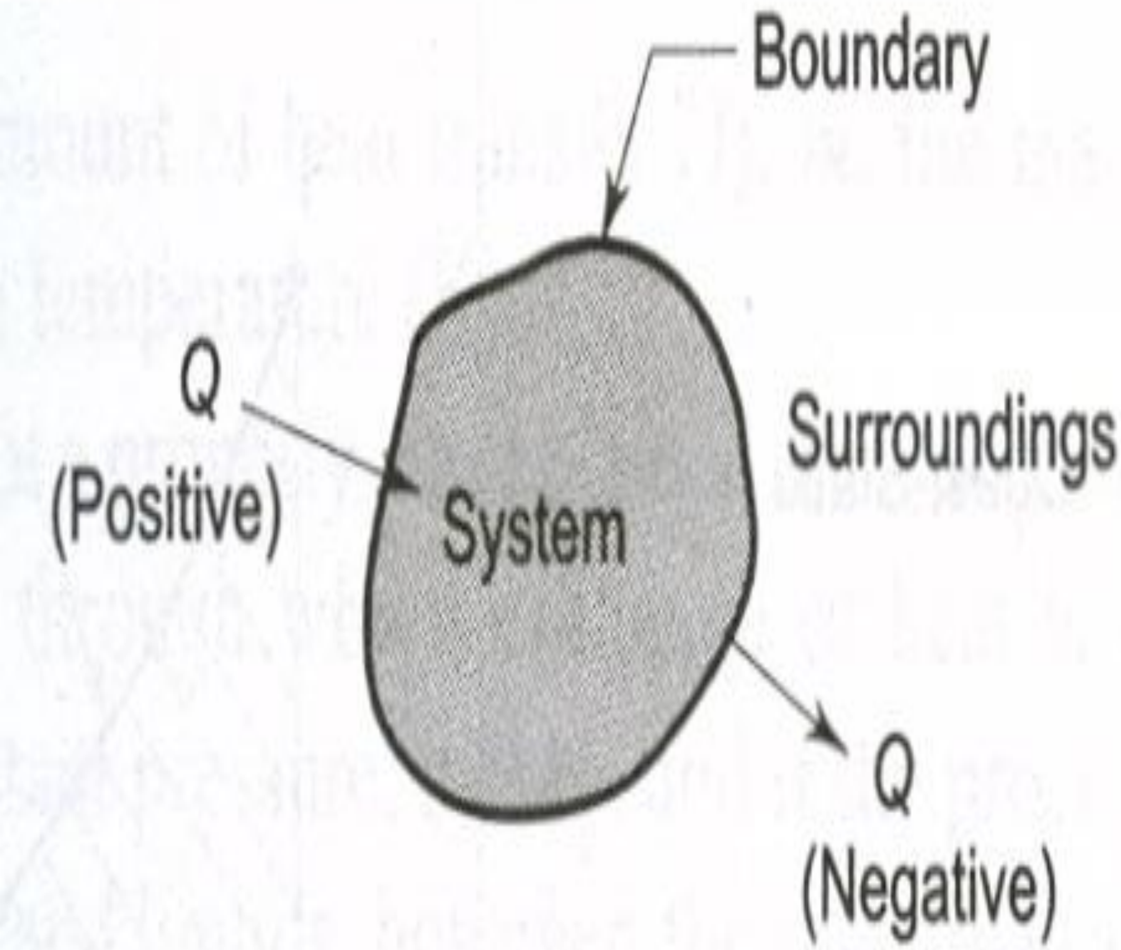
Consider a gas separated from the vacuum by a partition. Let the partition be removed. The gas rushes to fill the entire volume. The expansion of a gas against vacuum is called free expansion. If we neglect the work associated with the removal of partition, and consider the gas and vacuum together as our system, there is no work transfer involved here, since no work crosses the boundary of the system, and hence, W = 0.

If only gas is taken as the system, when the partition is removed there is a change in the volume of the gas, and one is tempted to calculate the work from the expression. However, this is not quasi-static process, although the initial and final end states are in equilibrium. This type of process is

Net work done by a system: Often different forms of a work transfer occur simultaneously during a process executed by a system. When all these work interactions have been evaluated, the total or net work done by the system would be equal to the algebraic sum of these as given below

$$W_{total} = W_{displacement} + W_{electrical} + W_{stirring} + ...$$

Heat transfer:



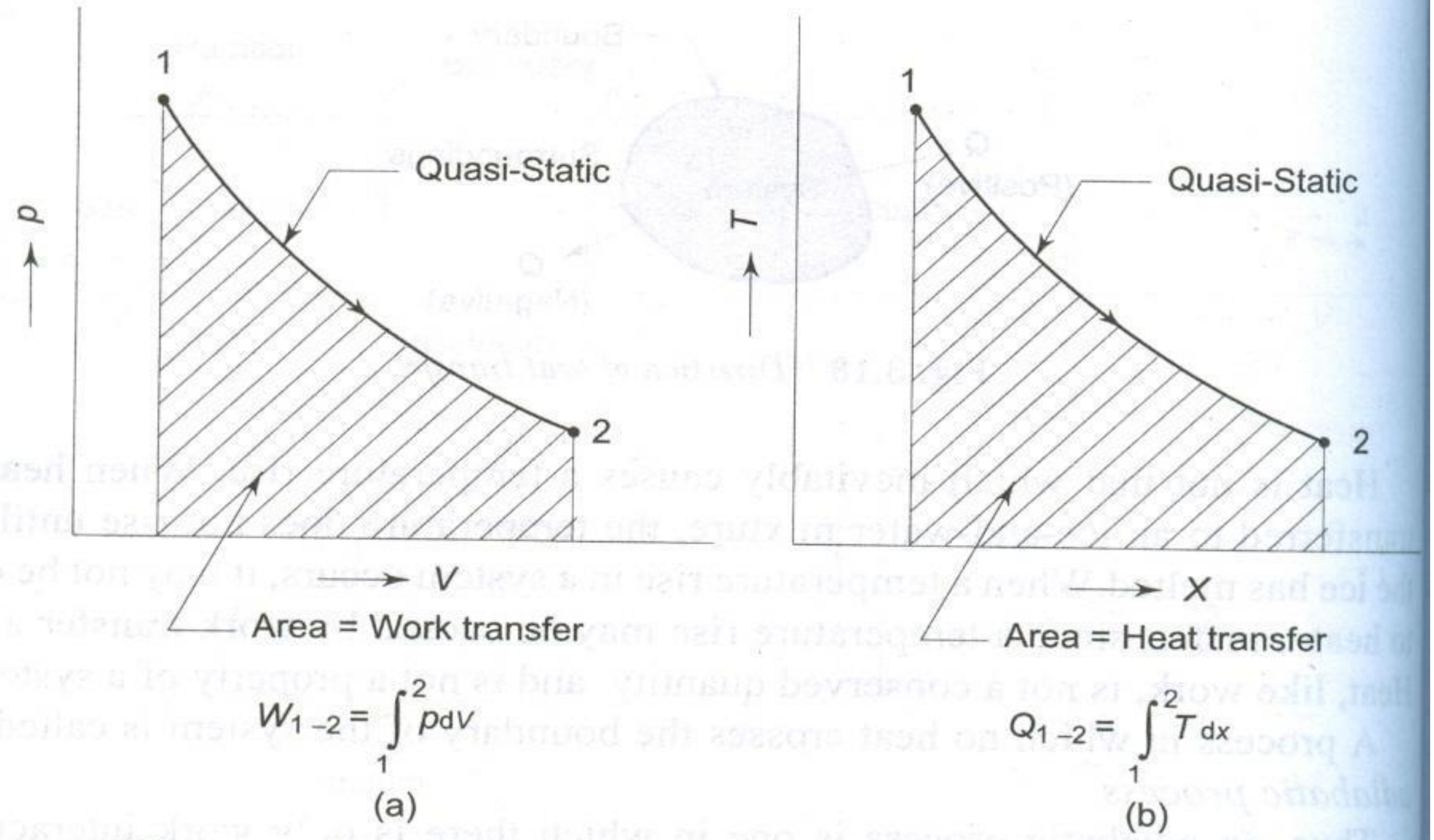
- *Heat* is defined as the form of energy that is transferred across a boundary by virtue of a temperature difference.
- The transfer of heat between two bodies in direct contact is called *conduction*.
- Heat may be transferred between two bodies separated by empty space or gases by the mechanism of *radiation* through electromagnetic waves.
- A third method of heat transfer is *convection* which refers to the transfer of heat between a wall and a fluid system in motion.
- *The direction of heat transfer is taken from the high temperature system to the low temperature system.* Heat flow into the system is taken to be *positive*, and heat flow out of a system is taken as *negative* (Fig above).

- **Heat is a form of energy in transit. It occurs only at the boundary of the system.**

- **Energy transfer by virtue of temperature difference only is called heat transfer.**
- **All other forms of energy interactions may be termed as work transfer.**
- **Heat like work, is not a property of the system.**

- **A process in which no heat crosses the boundary of the system is called an *adiabatic process*. Here only work interaction takes place between the system and the surroundings.**

Heat transfer- A path function:



$$W_{1-2} = \int_1^2 p\,dV$$

(a)

$$Q_{1-2} = \int_1^2 T\,dx$$

(b)

Fig. *Representation of work transfer and heat transfer in quasi-static processes on p-v and T-x coordinates*

Specific heat:

The *specific heat* of a substance is defined as the amount of heat required to raise the temperature of unit mass of the substance through one degree.

For gases, if the process is at constant pressure, it is c_p, and if the process is at constant volume, it is c_v.

For solids and liquids, however, the specific heat does not depend on the process.

Latent heat: Fusion, vaporization and sublimation.

- The *latent heat* is the amount of heat transfer required to cause a phase change in unit mass of a substance at a constant pressure and temperature.
- The *latent heat of fusion* (l_{fu}) is the amount of heat transferred to melt unit mass of solid into liquid or freeze unit mass of liquid into solid.
- The *latent heat of vaporization* (l_{vap}) is the quantity of heat required to vaporize unit mass of liquid into vapor, or condense unit mass of vapor into liquid.
- The *latent heat of sublimation* (l_{sub}) is the amount of heat transferred to convert unit mass of solid into vapor or vice versa.

MODULE 2

FIRST LAW OF THERMODYNAMICS

&

SECOND LAW OF THERMODYNAMICS

First Law of Thermodynamics

Joules experiments, equivalence of heat and work.

Statement of the First law of thermodynamics,

extension of the First law to non - cyclic processes, energy,

energy as a property, modes of energy, pure substance; definition, two property rule, Specific heat at constant volume, enthalpy, specific heat at constant pressure. Extension of the First law to control volume; steady state-steady flow energy equation, important applications, analysis of unsteady processes such as film and evacuation of vessels with and without heat transfer.

Second Law of Thermodynamics

Devices converting heat to work; (a) in a thermodynamic cycle, (b) in a mechanical cycle. Thermal reservoir. Direct heat engine; schematic representation and efficiency. Devices converting work to heat in a thermodynamic cycle; reversed heat engine, schematic representation, coefficients of performance. Kelvin - Planck statement of the Second law of Thermodynamics; PMM I and PMM II, Clausius statement of Second law of Thermodynamics, Equivalence of the two statements; Reversible and irreversible processes; factors that make a process irreversible, reversible heat engines, Carnot cycle, Carnot principles.

10 Hours

1st Hour

Brain storming session on subject topics

Joules experiments, equivalence of heat and work.

Statement of the First law of thermodynamics,

extension of the First law to non - cyclic processes

2nd Hour

Energy, energy as a property, modes of energy, pure substance; definition, two property rule, Specific heat at constant volume, enthalpy, specific heat at constant pressure

3rd Hour

Extension of the First law to control volume; steady state-steady flow energy equation

4th Hour

important applications, analysis of unsteady processes such as film and evacuation of vessels with and without heat transfer.

5th Hour

Problems on SFEE

6th Hour

Second Law of Thermodynamics

Devices converting heat to work; (a) in a thermodynamic cycle, (b) in a mechanical cycle. Thermal reservoir. Direct heat engine; schematic representation and efficiency.

7th Hour

Devices converting work to heat in a thermodynamic cycle; reversed heat engine, schematic representation, coefficients of performance

8th Hour

Kelvin - Planck statement of the Second law of Thermodynamics; PMM I and PMM II, Clausius statement of Second law of Thermodynamics, Equivalence of the two statements

9th Hour

Reversible and irreversible processes; factors that make a process irreversible, reversible heat engines, Carnot cycle, Carnot principles

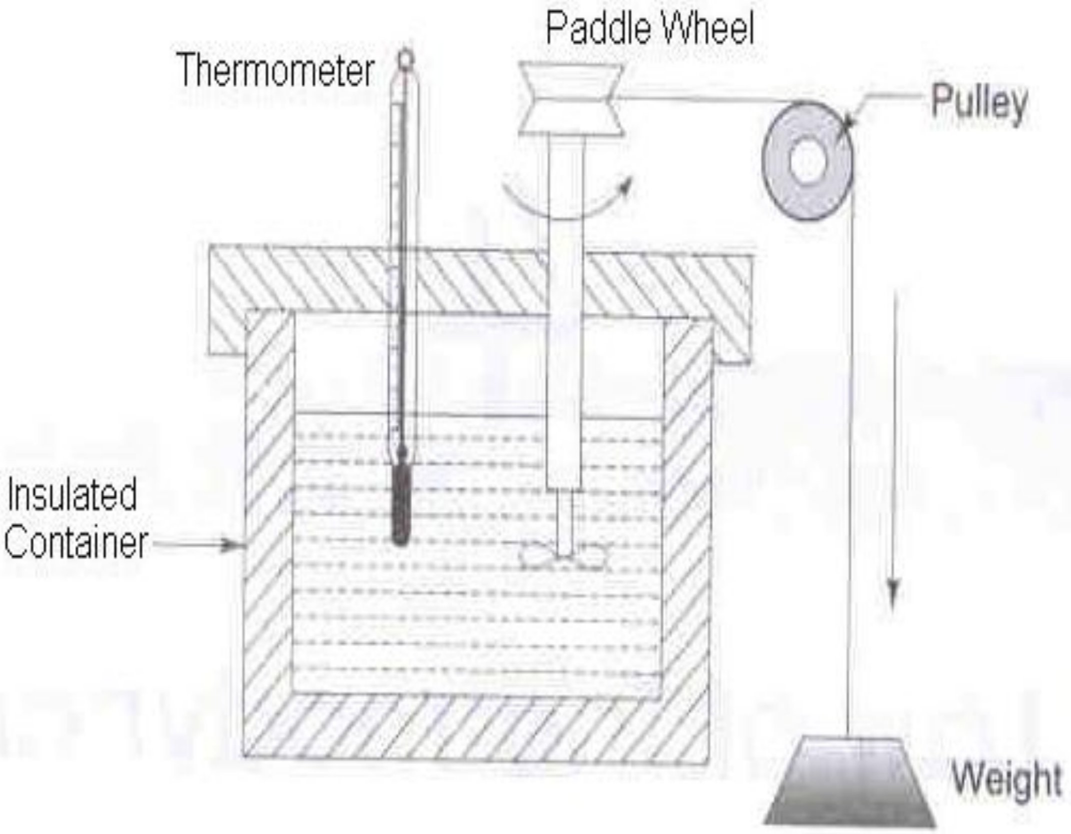
10th Hour

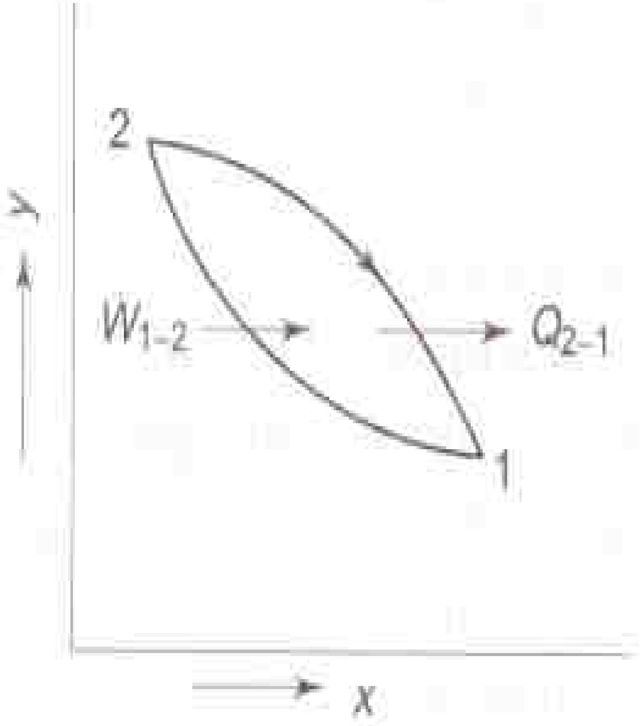
Problems on 2nd law of thermodynamics

First law of thermodynamics gives

1. Energy Conservation principle.
2. Definition of two important thermodynamic properties.
    i) Enthalpy
    ii) Internal energy
3. Specific heat at constant pressure and constant volume.
4. Expression for enthalpy and internal energy in terms of specific heat and temperature.

Joule's Experiment:





First law of thermodynamics for a closed system undergoing a cycle :

Statement: “During a cycle, a system undergoes, the cyclic integral of heat transfer is equal to the cyclic integral of work done”.

Mathematically first law may be written as

$$\oint dQ = \oint dW$$

The first law is applicable to a closed system and to a thermodynamic cycle and not to a process.

If different units are used for heat and work, then a proportionality factor called *mechanical equivalent of heat* denoted by symbol J is required, so that first law may be written as

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

In MKS units J = 427kgf-m/kcal

In SI units both heat and works are expressed in same units, therefore it is not necessary to use any proportionality factor.

First law for a closed system undergoing a change of state:

For a closed system during a cyclic process the sum of work transferred is equal to the sum of heat transferred.

i.e., $$\oint dQ = \oint dW$$

For a closed system during non-cyclic process the work transferred and heat transferred may not be equal and this difference is accounted for by a change in *Internal Energy ΔE (OR simply energy)* of the system.

i.e., $Q = \Delta E + W$

Here Q, W and ΔE are all expressed in same units (in joules).

Energy – A property of the system:

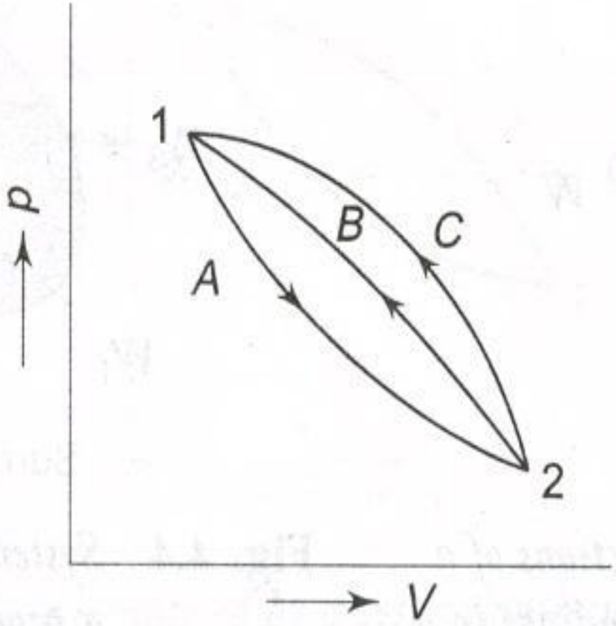


Fig. *Energy–a property of a system*

For path A $$Q_A = \Delta E_A + W_A \tag{2}$$

And for path B $$Q_B = \Delta E_B + W_B \tag{3}$$

The process A and B together constitute a cycle, for which

$$(\Sigma W)_{cycle} = (\Sigma Q)_{cycle}$$

Or $$W_A + W_B = Q_A + Q_B$$

Or $$Q_A - W_A = W_B - Q_B \tag{4}$$

From equations (2), (3), and (4), it yields

$$\Delta E_A = -\Delta E_B \tag{5}$$

Similarly, had the system returned from state 2 to state 1 by following the path *C* instead of path *B*

$$\Delta E_A = -\Delta E_C \tag{6}$$

From equation (5) and (6)

$$\Delta E_B = \Delta E_C$$

Engineering implications

The first law introduces a new property of the system called the energy of the system.

We have “energy in transition between the system and the surroundings” which is not a property and “energy of the system” which is a property.

Energy is a point function.

INTERNAL ENERGY

Modes of energy:

Basically there are two modes in which energy can be stored in a system:

(a) Macroscopic energy mode (b) Microscopic energy mode

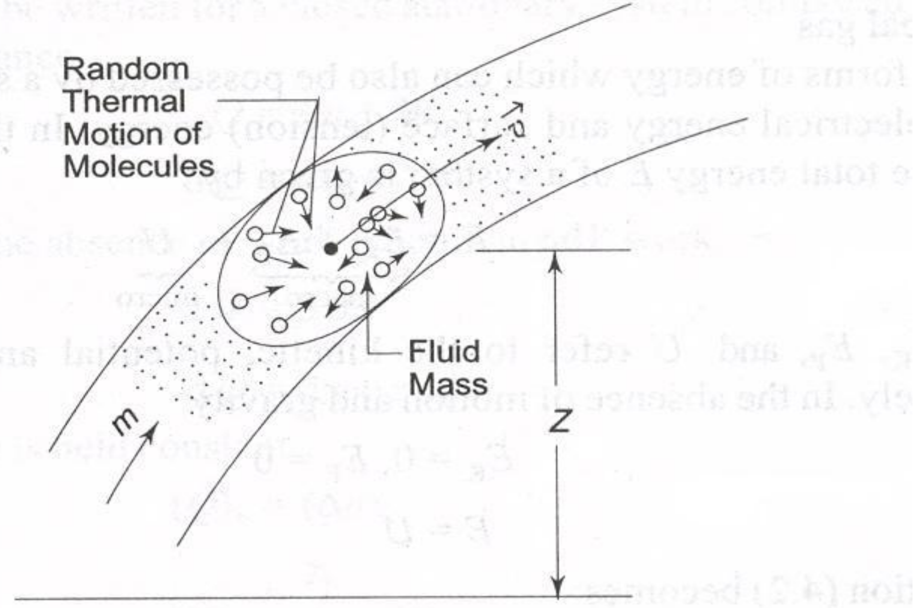


Fig. *Macroscopic and microscopic energy*

The macroscopic energy mode includes the macroscopic kinetic energy and potential energy of a system. Let us consider a fluid element of mass m having the centre of mass velocity V. The macroscopic kinetic energy E_K of the fluid element by virtue of its motion is given by

$$E_K = \frac{mV^2}{2}$$

If the elevation of the fluid element from an arbitrary point is z, then the macroscopic potential energy E_p by virtue of its position is given by

$$E_P = mgz$$

The microscopic energy mode refers to the energy stored in the molecular and atomic structure of the system, which is called *molecular internal energy or simply internal energy*, customarily denoted by symbol U.

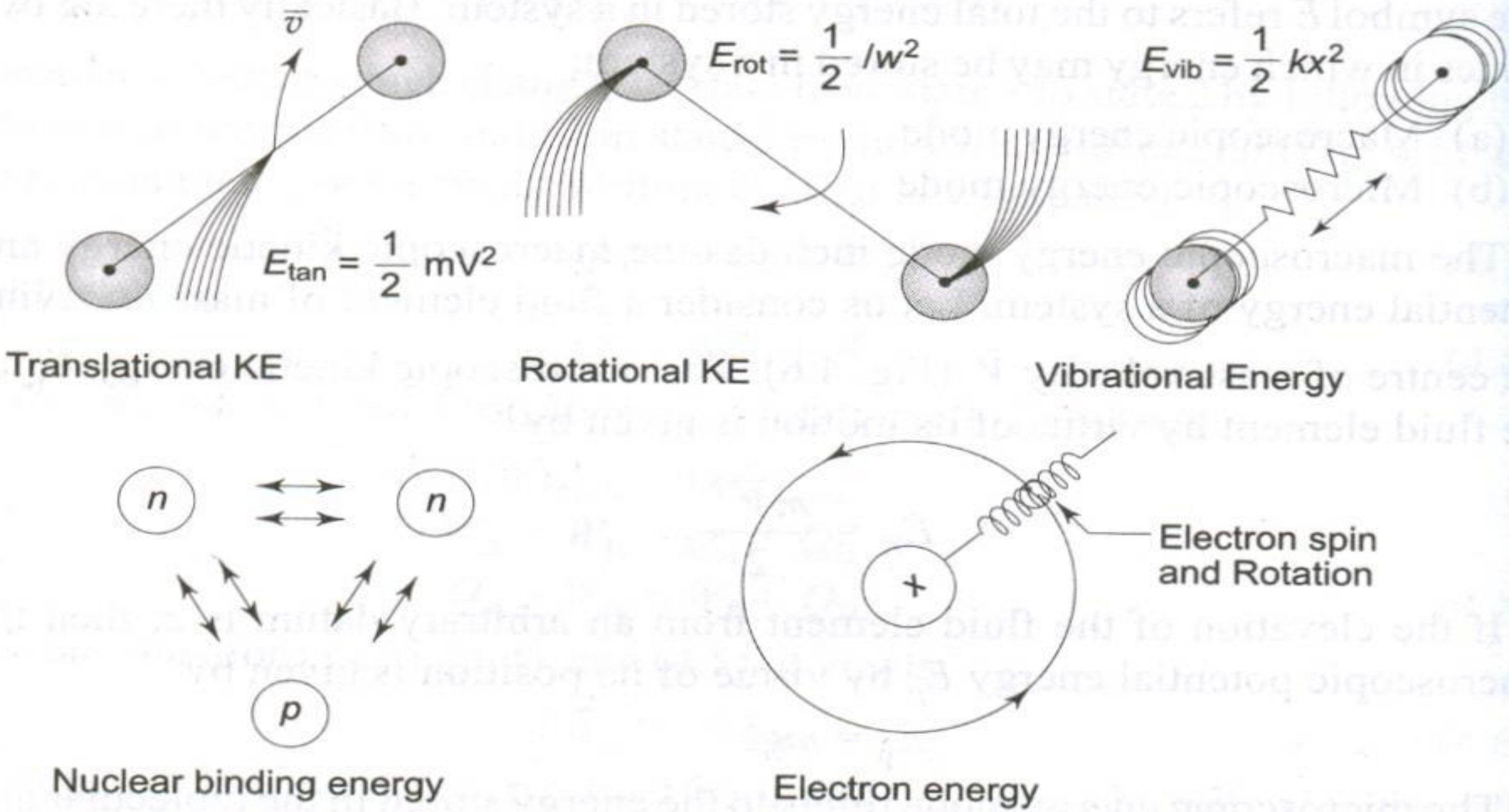


Fig. *Various components of internal energy stored in a molecule*

Matter is composed of molecules. Molecules are random in thermal motion (for gas) with an average velocity v, constantly colliding with one another and with the walls. Due to a collision, the molecules may be subjected to rotation as well as vibration. They can have translational kinetic energy, rotational kinetic energy, vibrational energy, electronic energy, chemical energy and nuclear energy. If ε represents the energy of one molecule, then

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{chem} + \varepsilon_{electronic} + \varepsilon_{nuclear}$$

If N is the total of molecules in the system, then the total internal energy

$$U = N\varepsilon$$

In an ideal gas there are no intermolecular forces of attraction and repulsion, and the internal energy depends only on temperature. Thus

$$U = f(T) \text{ only}$$

For an ideal gas

Other forms of energy which can also be possessed by a system are magnetic energy, electrical energy and surface (tension) energy. In the absence of these forms, the total energy E of a system is given by

$$E = \underline{E_K + E_P} + U$$

Where, E_K, E_P *and* U refer to the kinetic, potential and internal energy respectively.

In the absence of motion and gravity

$$E_K = 0,\ E_P = 0$$

$$E = U$$

Therefore we can write

$$Q = \Delta U + W$$

U is an extensive property of the system. The specific internal energy u is equal to U/m and its unit is J/kg.

Writing in the differential form, we get

$$dQ = dE + dW$$

$$dQ = dU + dW$$

where $dW = dW_{pdV} + dW_{shaft} + dW_{electrical} + \ldots\ldots,$ considering different forms of work transfer which may be present.

When only *pdV* work is present, the equations become

$$dQ = dE + pdV$$

$$dQ = dU + pdV$$

or, in integral form

$$Q = \Delta E + \int pdV$$

$$Q = \Delta U + \int pdV$$

- Enthalpy (*H*)*: of a substance at any point is quantification of energy content in it, which could be given* by summation of internal energy and flow energy. Enthalpy is very useful thermodynamic property for the analysis of engineering systems.

  Mathematically, it is given as,

$$H = U + PV$$

On unit mass basis, the specific enthalpy(or enthaply) could be given as, $h = u + pv$

- From the definition of enthalpy;

$$h = u + pv \qquad \text{..........1}$$

$$\text{or } dh = du + p \cdot dv + v \cdot dp.$$

- For a constant pressure process, $dp = 0.$

$$dh = du + p.dv \qquad \text{...........2}$$

$$Now \quad p.dv = d(pv)$$

$$\text{Then } dq = du + d(pv)$$

$$= d(u + pv)$$

$$dq = dh \qquad \text{...........3}$$

Specific heat :

- *Specific heats of the substance refer to the amount of heat interaction required for causing unit change* in temperature of the unit mass of substance. This unit change in temperature may be realized under constant volume and constant pressure conditions separately.
- Therefore, the above heat value obtained with heat interaction occurring under constant volume conditions is called specific heat at constant volume, denoted as *cv.*
- *Whereas the above heat value* obtained with heat interaction occurring under constant pressure conditions is called specific heat at constant pressure, denoted as *cp.*

Specific Heat at constant volume: C_V

The specific heat at constant volume c_V is defined as the rate of change of specific internal energy with respect to temperature when the volume is held constant, i.e.

$$C_V = \left(\frac{\partial u}{\partial T} \right)_v$$

For a constant volume process ΔW=0

$$(\Delta u)_v = \int_{T_1}^{T_2} Cv.dT$$

From 1st law dQ=du

$$(Q)_v = \int_{T_1}^{T_2} Cv.dT$$

The first law may be written for a closed stationary system composed of a unit mass of a pure substance

$$Q = \Delta u + W$$

or $\quad dQ = du + dW$

For a process in the absence of work other than *pdV* work

$$dW = pdV$$

therefore $\quad dQ = du + pdV$

When the volume is held constant

$$(Q)_v = (\Delta u)_v$$

Therefore $\quad (Q)_v = \int_{T_1}^{T_2} C_v . dT$

Heat transferred at constant volume increases the internal energy of the system.

Since *u*, *T*, and *v* are properties, c_V is a property of the system. The product $mc_V = C_V$ is called the *heat capacity at constant volume* (J/K).

Specific Heat at Constant pressure: C_p

The specific heat at constant pressure c_p is defined as the rate of change of enthalpy with respect to temperature when the pressure is held constant.

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p$$

For a constant pressure process

$$(\Delta h)_p = \int_{T_1}^{T_1} Cp.dT$$

The first law for a closed stationary system of unit mass

$$dQ = du + pdv$$

again $h = u + pv$

:. $dh = du + pdV + vdp$ (u+pv=h)

$$= dQ + vdp$$

:. $dQ = dh - vdp$

:. $(dQ)_p = dh$

Or $(Q)_p = (\Delta h)_p$

Therefore we can write,

$$(Q)_p = \int_{T_1}^{T_2} Cp.dT$$

c_p is a property of the system, just like c_v. The *heat capacity at constant pressure* C_p is equal to mc_p (J/K).

Steady flow process:

‘Steady flow’ means that rates of flow of mass and energy through the control surface are constant.

In most engineering devices, there is a constant rate of flow of mass and energy through the control surface, and the control volume in course of time attains a steady state.

At the steady state of a system, any thermodynamic property will have a fixed value at a particular location, and will not alter with time.

Thermodynamic properties may vary along space coordinates, but do not vary with time. ‘Steady state’ means the state is steady or invariant with time.

Mass Balance and Energy Balance in a Simple Steady Flow Process:

Fig. shows a steady flow system in which one stream of fluid enters and one stream leaves the control volume. There is no accumulation of mass and energy within the control volume, and the properties at any location within the control volume are steady with time.

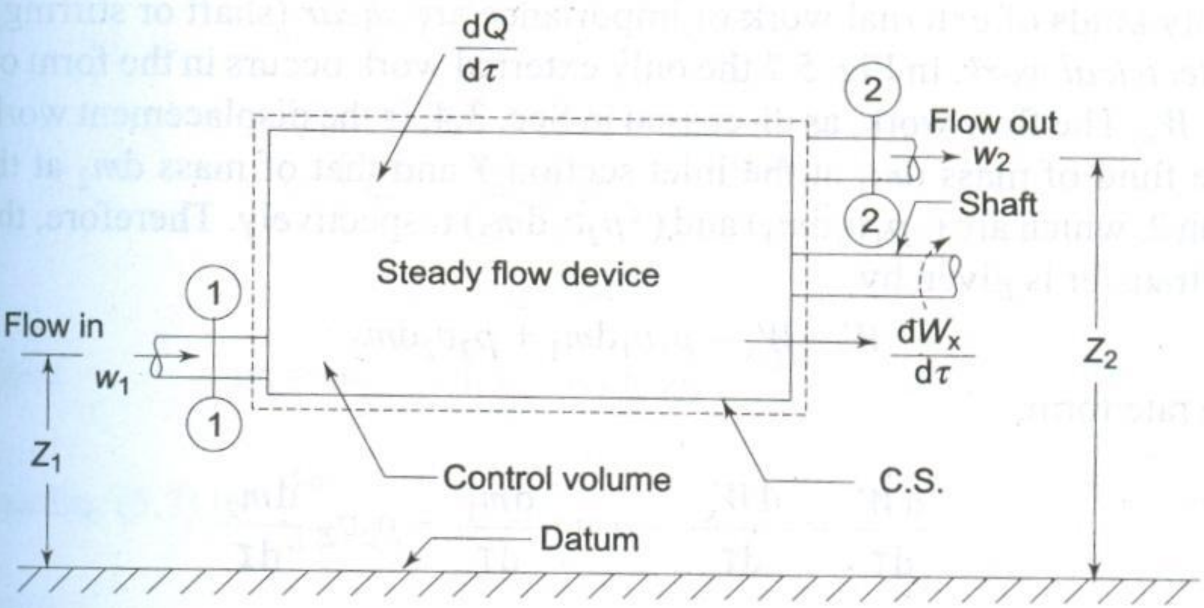


Fig. *Steady flow Process*

A_1, A_2 – cross section of stream, m^2

m_1, m_2 – mass flow rate, kg/s

p_1, p_2 – absolute pressure, $N/m^{2,}$

v_1, v_2 – specific volume, m^3/kg

u_1, u_2 – specific internal energy, J/kg

V_1, V_2 – velocity, m/s

Z_1, Z_2 – elevation above an arbitrary datum, m

$\frac{dQ}{d\tau}$ - net rate of heat transfer through the control surface, J/s

$\frac{dW}{d\tau}$ - net rate of work transfer through the control surface, J/s

Mass Balance

By the conservation of mass, if there is no accumulation of mass within the control volume, the mass flow rate entering must be equal the mass flow rate leaving, or

$$m_1 = m_2$$

or

$$\frac{A_1 V_1}{v_1} = \frac{A_2 V_2}{v_2}$$

This is known as *equation of continuity*.

Energy Balance

In a flow process, the work transfer may be of two types: the *external work* and the *flow work*. The external work refers to all the work transfer across the control surface. In the Fig above the only external work occurs in the form of shaft work, W_X. The flow work is the displacement work done by the fluid of mass dm_1 at the inlet section 1 and that of dm_2 at the exit section2, which are $(-p_1v_1dm_1)$ and $(p_2v_2dm_2)$ respectively. Therefore, the total work transfer is given by

$$W = W_X - p_1v_1dm_1 + p_2v_2dm_2 \qquad (1)$$

In the rate form,

$$\frac{dW}{d\tau} = \frac{dW_x}{d\tau} - p_1v_1\frac{dm_1}{d\tau} + p_2v_2\frac{dm_2}{d\tau}$$

Or

$$\frac{dW}{d\tau} = \frac{dW_x}{d\tau} - w_1p_1v_1 + w_2p_2v_2 \qquad (2)$$

Since there is no accumulation of the energy, by the conservation of energy, the total rate of flow of all energy streams entering the control volume must be equal the total flow rate of all energy streams leaving the control volume. This may be expressed in the following equation.

$$w_1 e_1 + \frac{dQ}{d\tau} = w_2 e_2 + \frac{dW}{d\tau}$$

Substituting for $\frac{dW}{d\tau}$ in equation (2)

$$w_1 e_1 + \frac{dQ}{d\tau} = w_2 e_2 + \frac{dW_x}{d\tau} - w_1 p_1 v_1 + w_2 p_2 v_2$$

$$w_1 e_1 + w_1 p_1 v_1 + \frac{dQ}{d\tau} = w_2 e_2 + w_2 p_2 v_2 + \frac{dW_x}{d\tau} \qquad (3)$$

where e_1 and e_2 refer to the energy carried into or out of the control volume with unit mass of fluid.

The specific energy e is given by

$$e = e_k + e_p + u$$

$$= \frac{V^2}{2} + Zg + u \qquad (4)$$

Substituting the expression for e in equation (3)

$$w_1\left(\frac{V_1^2}{2} + Z_1 g + u_1\right) + w_1 p_1 v_1 + \frac{dQ}{d\tau} = w_2\left(\frac{V_2^2}{2} + Z_2 g + u_2\right) + w_2 p_2 v_2 + \frac{dW_x}{d\tau}$$

or

$$w_1\left(h_1 + \frac{V_1^2}{2} + Z_1 g\right) + \frac{dQ}{d\tau} = w_2\left(h_2 + \frac{V_2^2}{2} + Z_2 g\right) + \frac{dW_x}{d\tau} \qquad (5)$$

where $h = u + pv$

And, since $m_1 = m_2$, let $m = m_1 = m_2 = \frac{dm}{d\tau}$

Dividing equation (5) by $\frac{dm}{d\tau}$

$$h_1 + \frac{V_1^2}{2} + Z_1 g + \frac{dQ}{dm} = h_2 + \frac{V_2^2}{2} + Z_2 g + \frac{dW_x}{dm} \qquad (6)$$

Equations (5) and (6) are known as *steady flow energy equations* (S.F.E.E), for a single stream of fluid entering and single stream of fluid leaving the control volume.

Application of S.F.E.E:

a) Nozzle and Diffuser:-

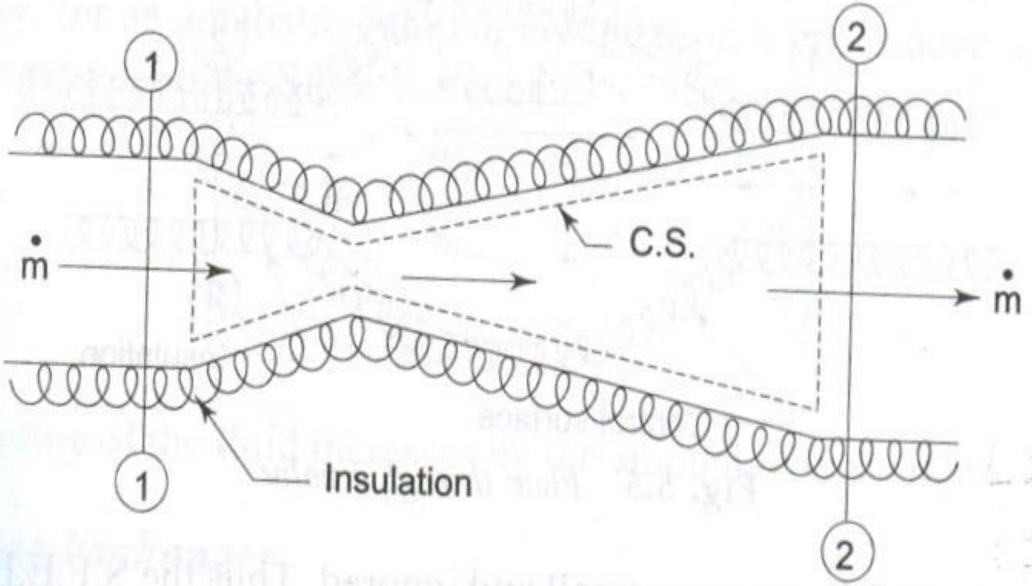


Fig. *Steady flow process involving one fluid stream at the inlet and at exit of the control volume*

A nozzle is a device which increases the velocity or K.E. of a fluid at the expense of the pressure drop, whereas a diffuser increases the pressure of a fluid at the expense of its K.E. Fig shows a nozzle which is insulated. The S.F.E.E of the control surface gives

$$h_1 + \frac{V_1^2}{2} + Z_1 g + \frac{dQ}{dm} = h_2 + \frac{V_2^2}{2} + Z_2 g + \frac{dW_x}{dm}$$

Here $\frac{dQ}{dm} = 0$, $\frac{dW_x}{dm} = 0$, and the change in potential energy is zero. The equation reduces to

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

When the inlet velocity or the 'velocity of approach' V_1 is small compared to the exit velocity V_2, equation (1) becomes

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

or $$V_2 = \sqrt{2(h_1 - h_2)} \text{ m/s}$$

b) Turbine and Compressor:

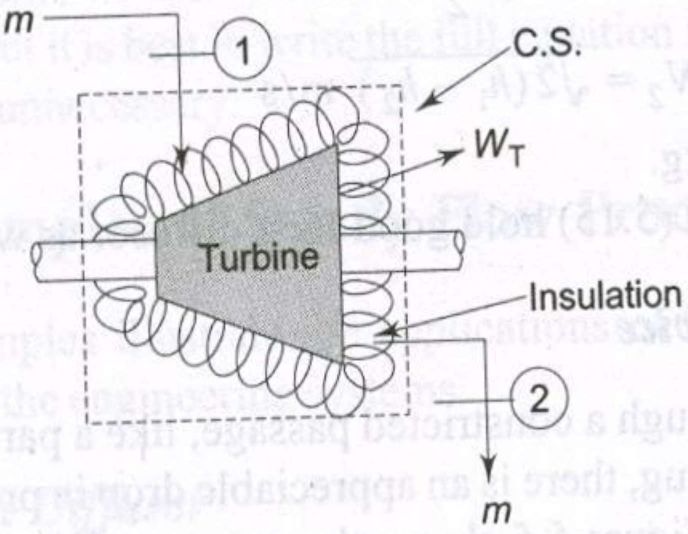


Fig. *Flow through a turbine*

$$h_1 = h_2 + \frac{dW_x}{dm}$$

or

$$\frac{W_x}{m} = (h_1 - h_2)$$

It is seen that work is done by the fluid at the expense of its enthalpy.

c) Heat Exchanger:

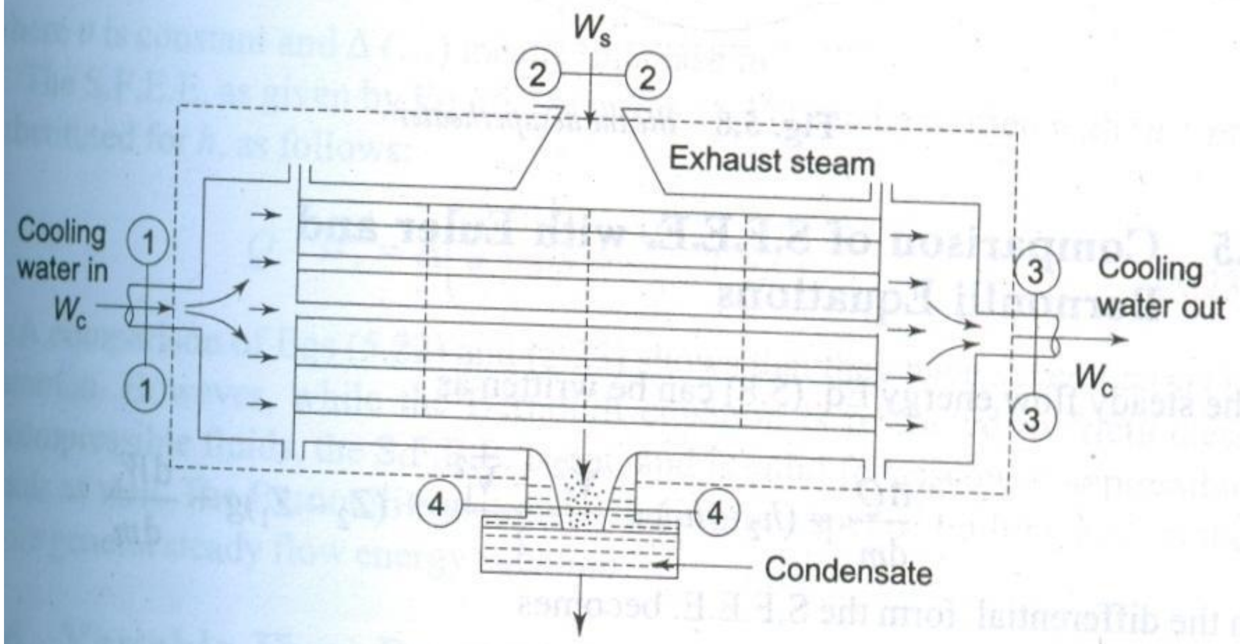


Fig. *Steam condenser*

The S.F.E.E. for the system is

$$m_c h_1 + m_s h_2 = m_c h_3 + m_s h_4$$

$$m_s \,(h_2 - h_4) = m_c \,(h_3 - h_1)$$

Steam desuperheator:

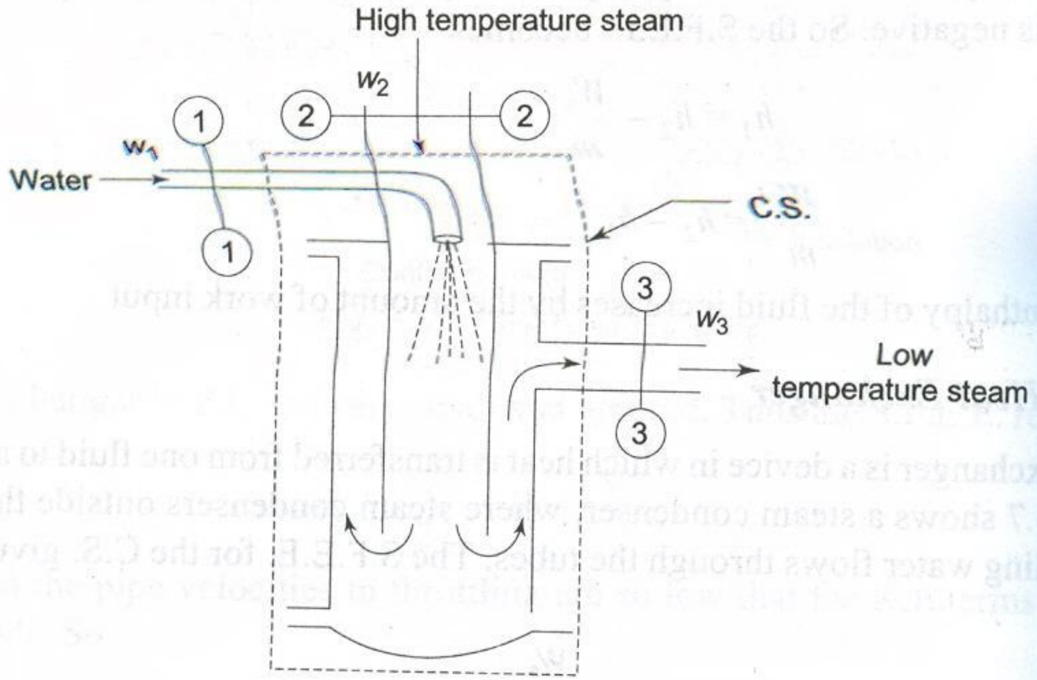


Fig. *Steam desuperheater*

$$m_1h_1 + m_2h_2 = m_3h_3$$

and the mass balance gives

$$m_1 + m_2 = m_3$$

Unsteady state analysis:

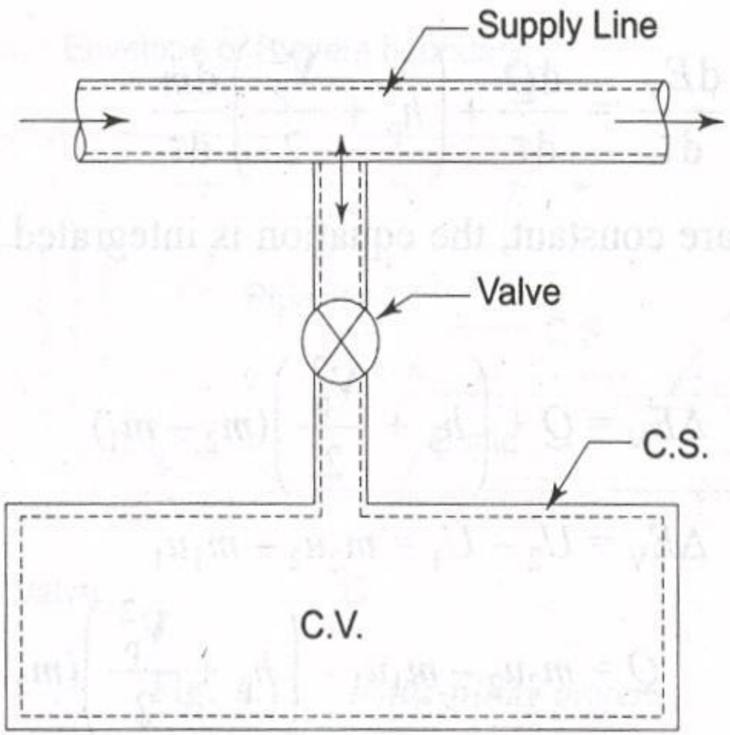


Fig. *Charging and discharging a tank*

Consider discharging:

$dW_X = 0$ and $dm_{in} = 0$, applying first law to the control volume,

$$dU_V = dQ + \left(h + \frac{V^2}{2} + gz\right)_{out} dm_{out} \qquad (1)$$

Assuming K.E. and P.E. of the fluid to be small and dQ = 0

$$d(mu) = h\,dm$$

$$m\,du + u\,dm = u\,dm + pv\,dm$$

$$\frac{dm}{m} = \frac{du}{pv} \qquad (2)$$

Again $V = vm = \text{constant}$

$$v\,dm + m\,dv = 0$$

or

$$\frac{dm}{m} = -\frac{dv}{v} \qquad (3)$$

From Eqs. (2) and (3)

$$\frac{du}{pv} = -\frac{dv}{v}$$

$$d(u + pv) = 0$$

or $$dQ = 0$$

which shows that the process is adiabatic and quasi-static.

For charging the tank:

$$\int (h\,dm)_{\text{in}} = \Delta U_V = m_2u_2 - m_1u_1$$

$$m_ph_p = m_2u_2 - m_1u_1 \qquad (4)$$

where the subscript *p* refers to the constant state of the fluid in the pipeline. If the tank is initially empty, $m_1 = 0$.

$$m_p h_p = m_2 u_2$$

Since

$$m_p = m_2$$

$$h_p = u_2$$

Enthalpy is converted into internal energy.

If the fluid is an ideal gas, the temperature of the gas in the tank after it is charged is given by

$$c_p T_p = c_v T_2$$

or

$$T_2 = \Upsilon T_p$$

Classification of Energy of the System:

The energy E is an extensive property and the specific energy, e = E/m (J/kg) is an intensive property. Energy E represents the total energy of the system.

i.e., E = kinetic energy (KE) + Potential Energy (PE) + remaining forms of energy.

Since K.E. and P.E. are macroscopic quantities and can be measured very easily, so they are considered separately in thermodynamics. The remaining energies (associated with the motion and position of the molecules, energy associated with the structure of the atom, chemical energy etc), which cannot be measured directly and is the summation of all microscopic energies is called internal energy of the system.

Internal energy:

It is the energy associated with internal structure of matter. This energy cannot be determined in its absolute values. But it is possible to determine the change in internal energy of the system undergoing a process by first law of thermodynamics.

$$\therefore \text{ Total energy } E = KE + PE + IE$$

Since the terms comprising E are point functions, we can write

$$dE = d(KE) + d\,(PE) + dU$$

The first law of thermodynamics for a change of state of a system may therefore be written as

$$\delta Q = dU + d\,(KE) + d\,(PE) + \delta W$$

In words this equation states that as a system undergoes a change of state, energy may cross the boundary as either heat or work, and each may be positive or negative. The net change in the energy of the system will be exactly equal to the net energy that crosses the boundary of the system.

$$\delta Q = dU + \frac{d(mV^2)}{2} + d\,(mgZ) + \delta W$$

In the integral form this equation can be written as,

$$Q_{1\text{-}2} = U_2 - U_1 + \frac{m\left(V_2^2 - V_1^2\right)}{2} + mg\,(Z_2 - Z_1) + W_{1\text{-}2}$$

K.E. and P.E. changes can be neglected.

$$\therefore \delta Q = dU + \delta W$$

Or

$$Q_{1\text{-}2} = U_2 - U_1 + W_{1\text{-}2}$$

Law of conservation of energy (2nd corollary of first law of thermodynamics):

From first law of thermodynamics

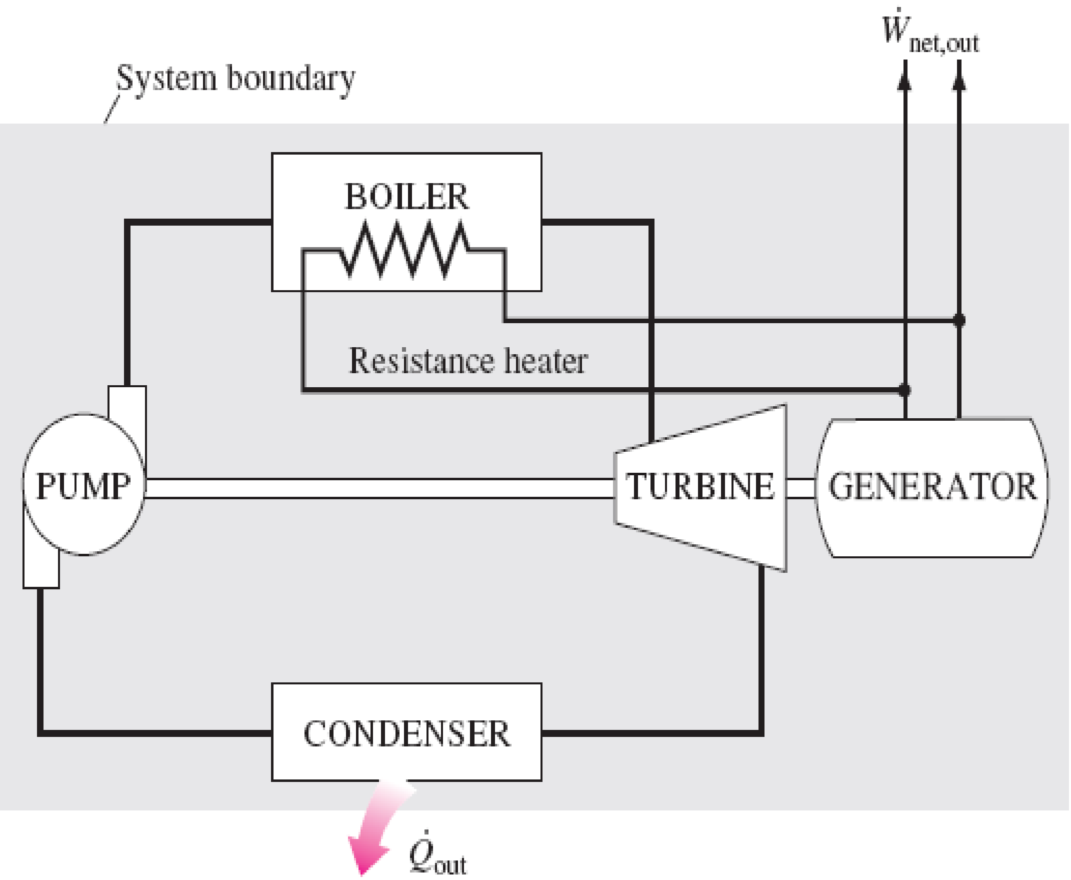
$$Q_{1\text{-}2} = E_2 - E_1 + W_{1\text{-}2}$$

This equation is in fact, a statement of the conservation of energy. The net change of the energy of the system is always equal to the net transfer of energy across the system boundary as heat and work. For an isolated system, $Q = 0$, $W = 0$ $\therefore E_2 - E_1 = 0$

$\therefore$ For an isolated system, the energy of the system remains constant.

Therefore, 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".

Perpetual Machine of first kind (3^{rd} Corollary):

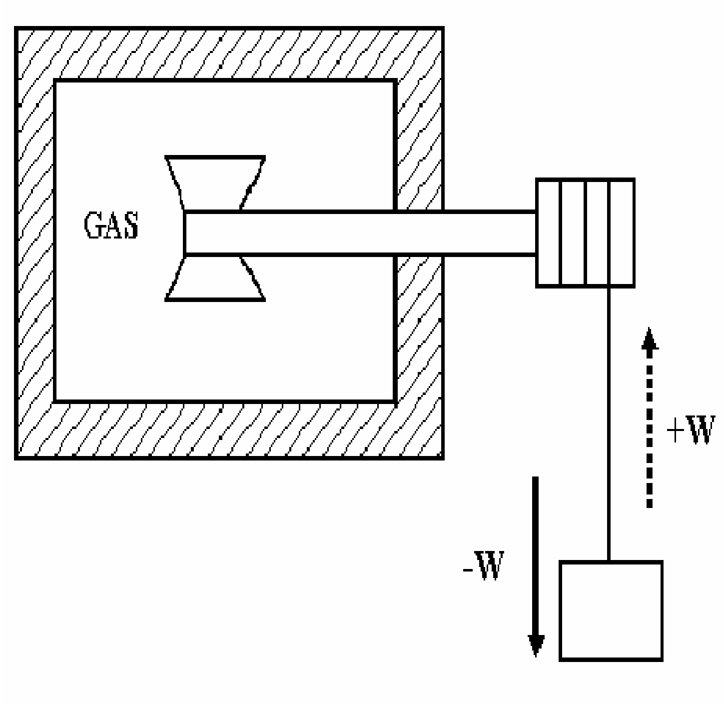


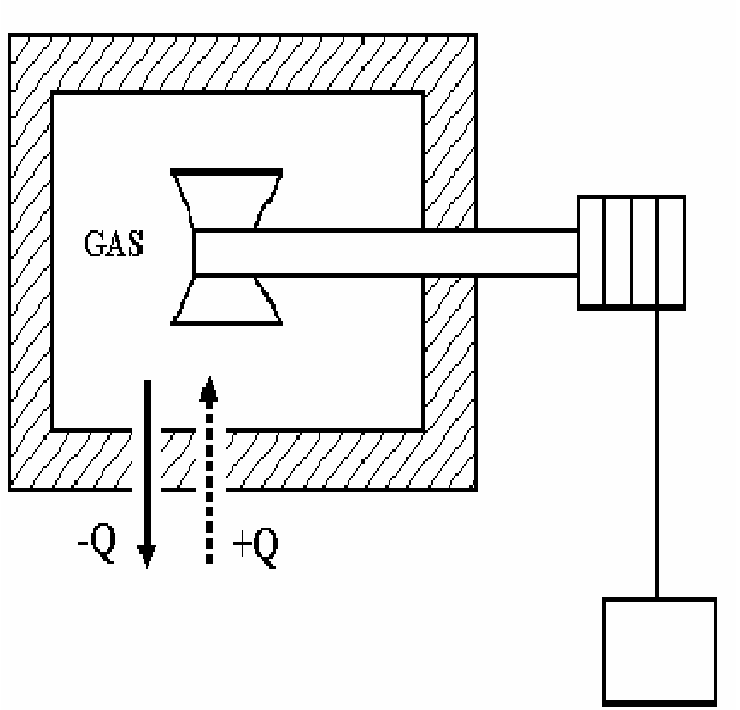
SECOND LAW OF THERMODYNAMICS

Introduction:

- It is common experience that a cup of hot coffee left in a cooler room eventually cools off.
- This process satisfies the first law of thermodynamics, since the amount of the energy lost by the coffee is equal to the amount of energy gained by the surrounding air.
- Now let us consider the reverse process the cold coffee getting hotter in a cooler room as a result of heat transfer from the room air.
- We all know that this process never takes place.
- Yet doing so would not violate the first law as long as the amount of energy lost by the air is equal to the amount of energy gained by the coffee.

Example 1:

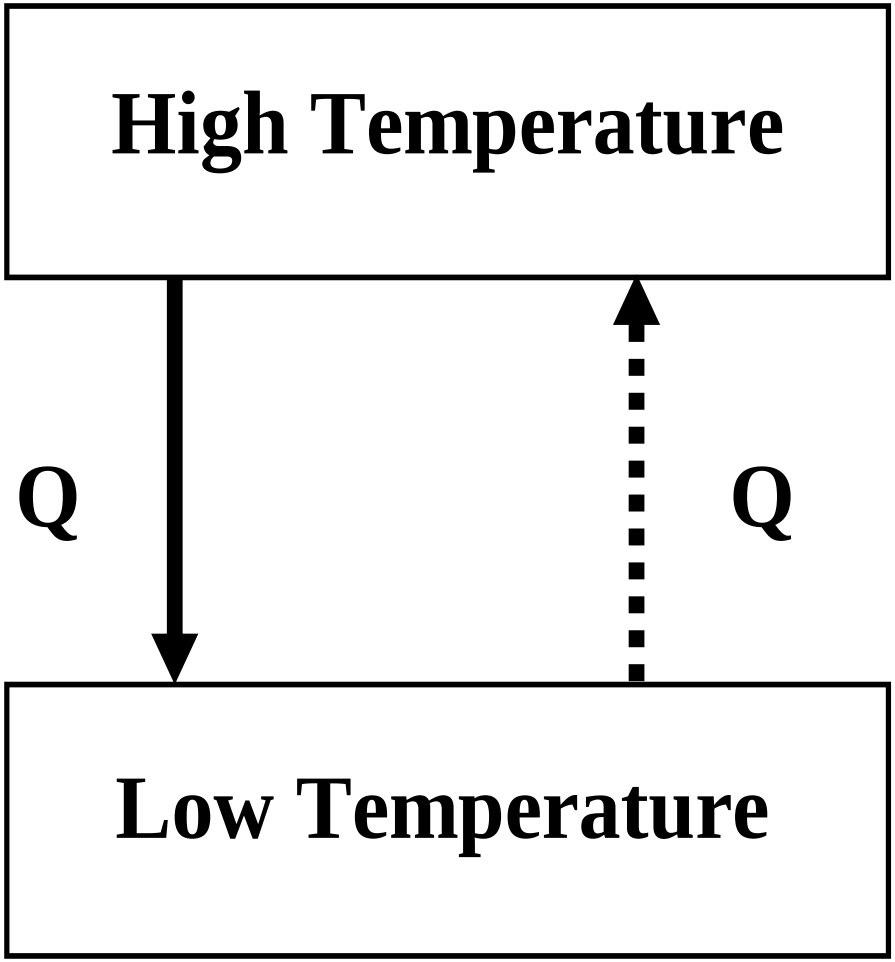




- In the example considered the system undergoes a cycle in which work is first done on the system by the paddle wheel as the weight is lowered.
- Then let the cycle be completed by transferring heat to the surrounding.

- From experience it has been learnt that we cannot reverse this cycle. i.e., if we transfer heat to the gas, as shown by the dotted line, the temperature of the gas will increase, but the paddle wheel will not turn and lift the weight.
- This system can operate in a cycle in which the heat and work transfers are both negative, but it cannot operate in a cycle when both are positive, even though this would not violate the first law.

Example 2:



High Temperature

Q

Q

Low Temperature

- Let two systems, one at a high temperature and the other at a low temperature undergoes a process in which a quantity of heat is transferred from the high – temperature system to the low temperature system.
- From experience we know that this process can take place.
- But the reverse process in which heat is transferred from the low temperature system to the high temperature system does not occur and that it is impossible to complete the cycle by heat transfer only.
- These two examples lead us to the consideration of the heat engine and heat pump (i.e., refrigerator).

Important points:

- Processes proceed in a certain direction and not in the reverse direction.
- The first law places no restriction on the direction of a process, but satisfying the first law does not ensure that the process will actually occur.
- This inadequacy is overcome by second law of thermodynamics.
- This violation is easily detected with the help of a property called entropy, which is discussed in the next chapter.
- A process will not occur unless it satisfies both the first and the second laws of thermodynamics.

- The use of second law of thermodynamics is not limited to identifying the direction of processes; however, 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 transformation of energy from one form to another, with no regard to its quality.
- The second law provides the necessary means the quality as well as the degree of degradation of energy during a process.
- Thus 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.

Thermal energy reservoirs:

A hypothetical body with a relatively large thermal energy capacity (mass X specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature is called a thermal energy reservoir or just a reservoir. The medium in the environment which are used as reservoir are:

a) Atmospheric air b) ocean, lake, rivers c) ground

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

Heat Engines:

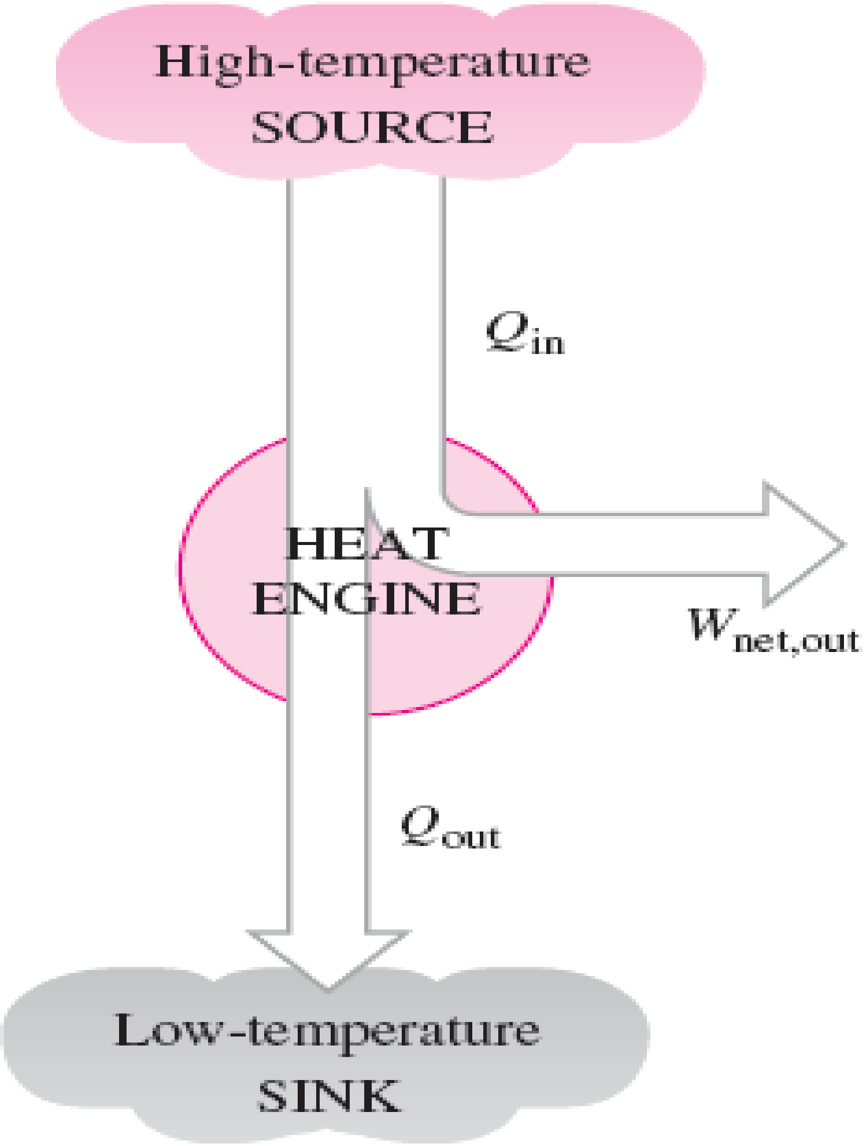
We know that, work can easily be converted into other forms of energy, but converting other forms of energy to work is not that easy. The mechanical work done by the shaft is converted into the internal energy of water in a paddle work. This increases the heat of water. But the reverse process i.e., transferring heat to the water will not cause the shaft to rotate. Thus it is clear that work can be converted into heat directly and completely, but converting heat to work requires the use of some special devices. These devices are called heat engines. The heat engines have the following characteristics:

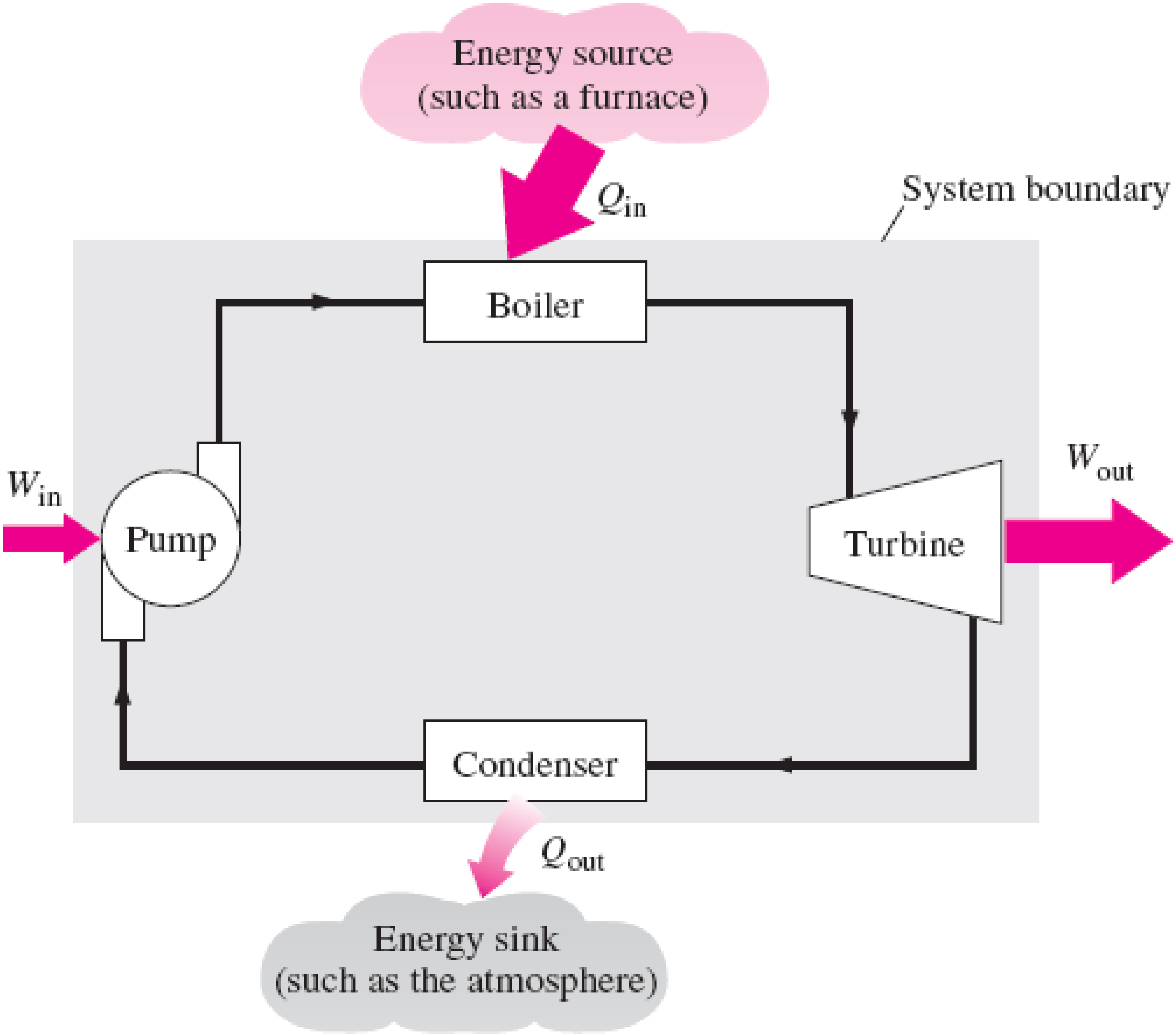
a) They receive heat from a high temp source.

b) They convert part of this heat into work.

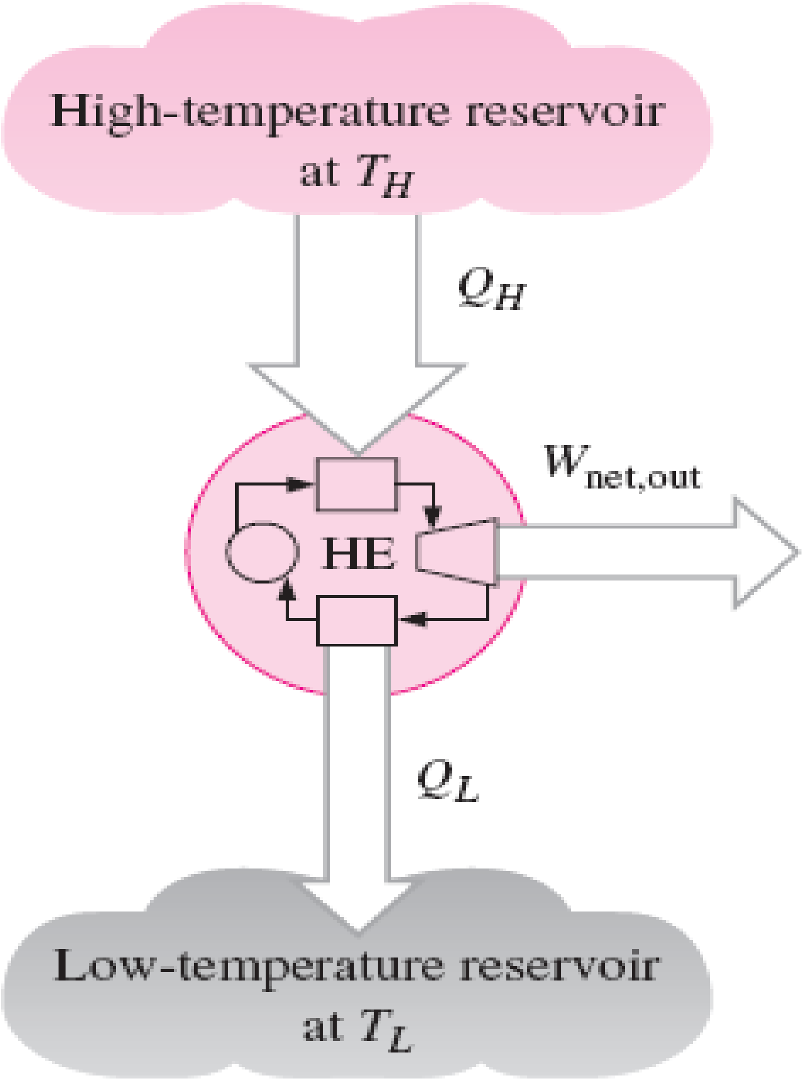
c) They reject the remaining waste heat into low temperature sink.

d) They operate on a cycle.


High-temperature
SOURCE
Q_{in}
HEAT
ENGINE
$W_{net,out}$
Q_{out}
Low-temperature
SINK


Energy source
(such as a furnace)
Q_{in}
System boundary
Boiler
W_{in}
Pump
Turbine
W_{out}
Condenser
Q_{out}
Energy sink
(such as the atmosphere)

Thermal efficiency:



In general efficiency or performance = $\frac{Desired\ output}{required\ input}$

For heat engines,

Thermal efficiency = $\frac{Net\ work\ output}{Total\ heat\ input}$

$$\eta_{ith} = \frac{W_{net,out}}{Q_{in}}$$

It can also be expressed as, $\eta_{ith} = 1 - \frac{Q_{out}}{Q_{in}}$

If Q_H = magnitude of heat transfer between the cyclic device and the source at temperature T_H.

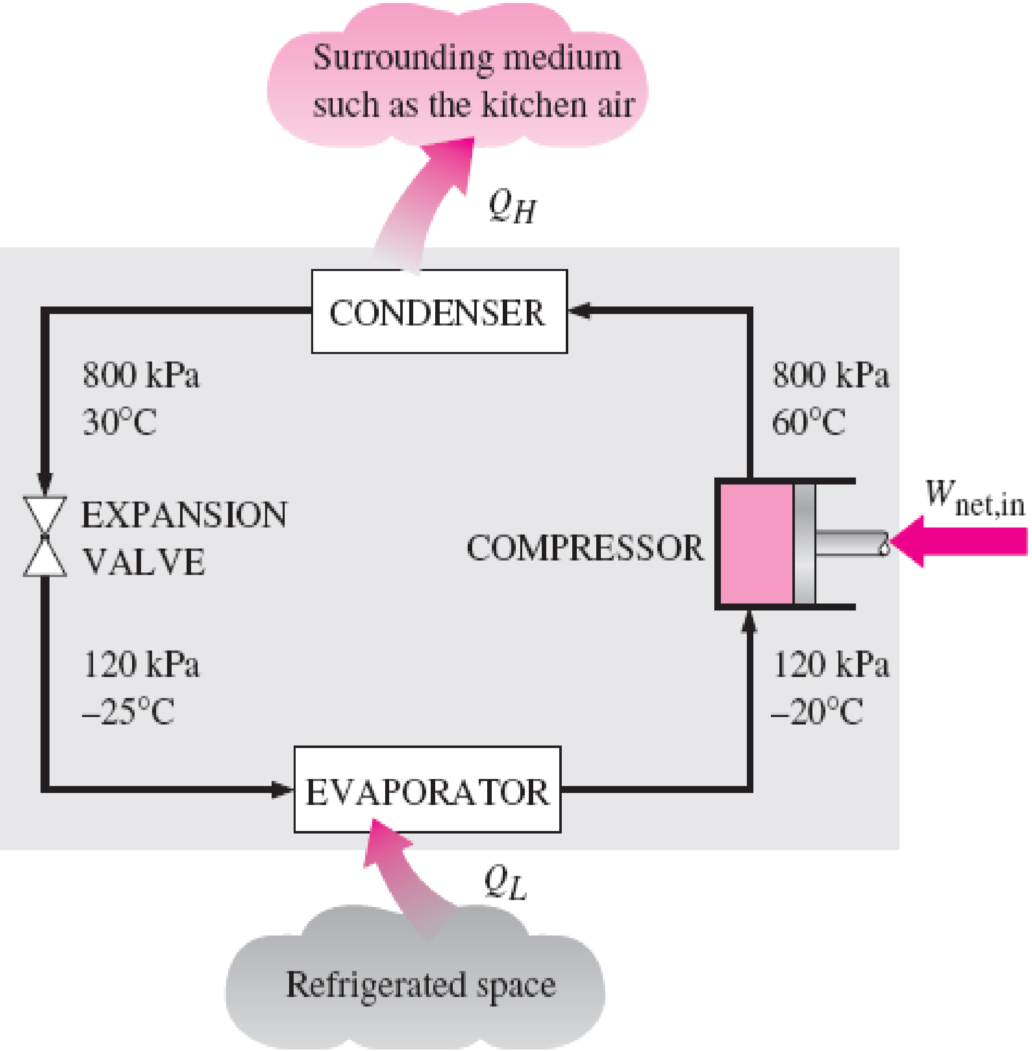
Q_L = magnitude of heat transfer between the cyclic device and the sink at temperature T_L.

Then net work output, $W_{net,out} = Q_H - Q_L$

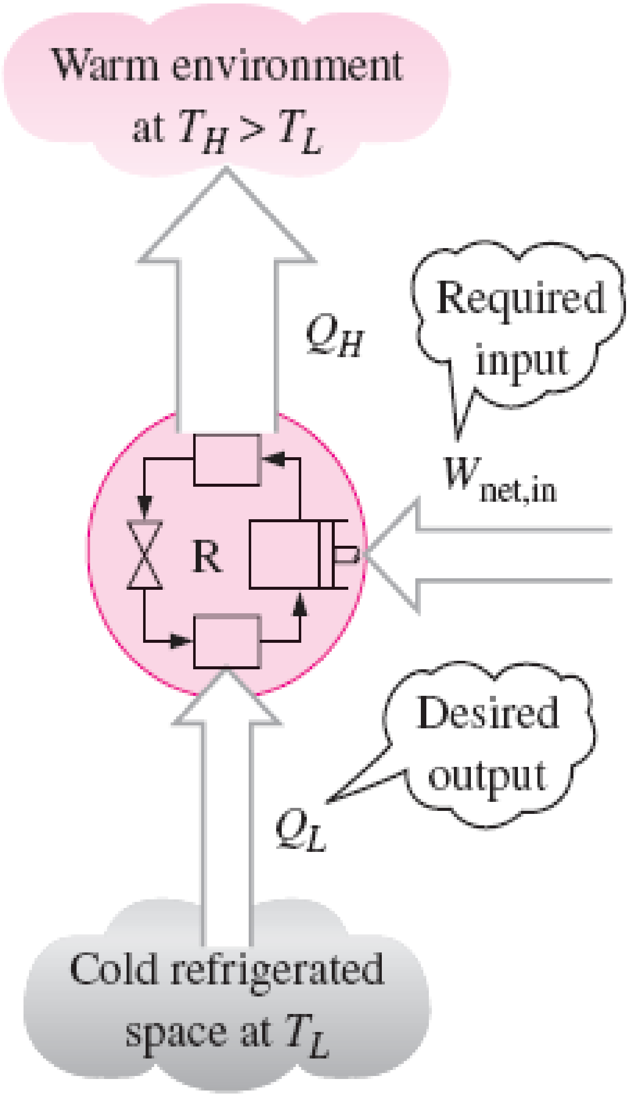
And

$$\eta_{ith} = \frac{W_{net,out}}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

Refrigerators and Heat pumps:



Coefficient of performance:



The objective of a refrigerator is to remove heat (Q_L) from the refrigerated space. To accomplish this objective it requires a work input of $W_{net.in.}$ Then COP of the refrigerator can be expressed as,

$$\text{COP}_R = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_L}{W_{\text{net,in}}}$$

This relation can also be expressed in rate form by replacing Q_L by $\dot{Q}_L$ and $W_{net,in}$ by $\dot{W}_{net,in}$.

The conservation of energy principle for a cyclic device requires that,

$$W_{\text{net,in}} = Q_H - Q_L$$

Therefore,

$$\text{COP}_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

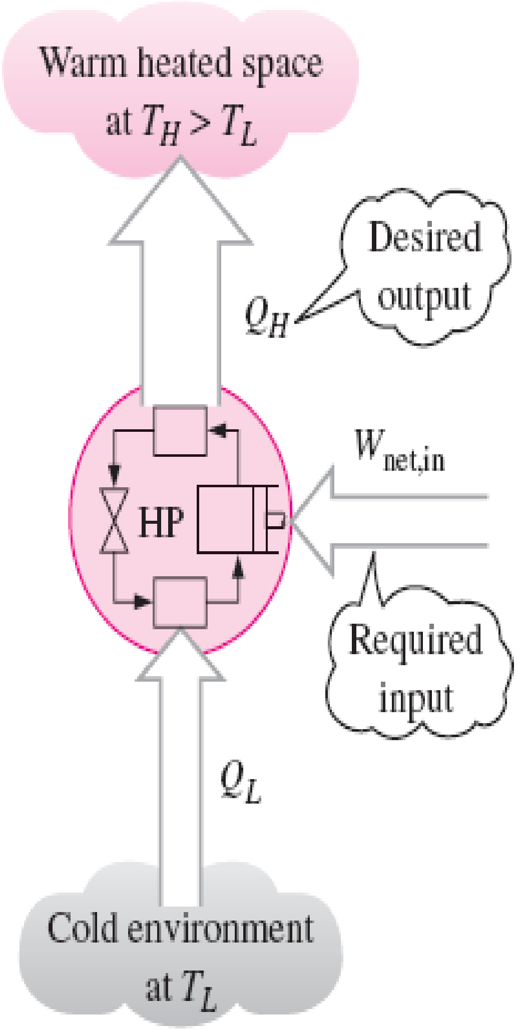
The value of COP is always greater than unity.

Heat Pumps:

$$\mathrm{COP_{HP}} = \frac{\text{Desired output}}{\text{Required input}} = \frac{Q_H}{W_{\mathrm{net,in}}}$$

$$\mathrm{COP_{HP}} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$

$$\mathrm{COP_{HP}} = \mathrm{COP_R} + 1$$



Second law of thermodynamics:

Kelvin-Planck Statement:

“It is impossible for any device that operates in a cycle to receive heat from a single reservoir and produce a net amount of work”

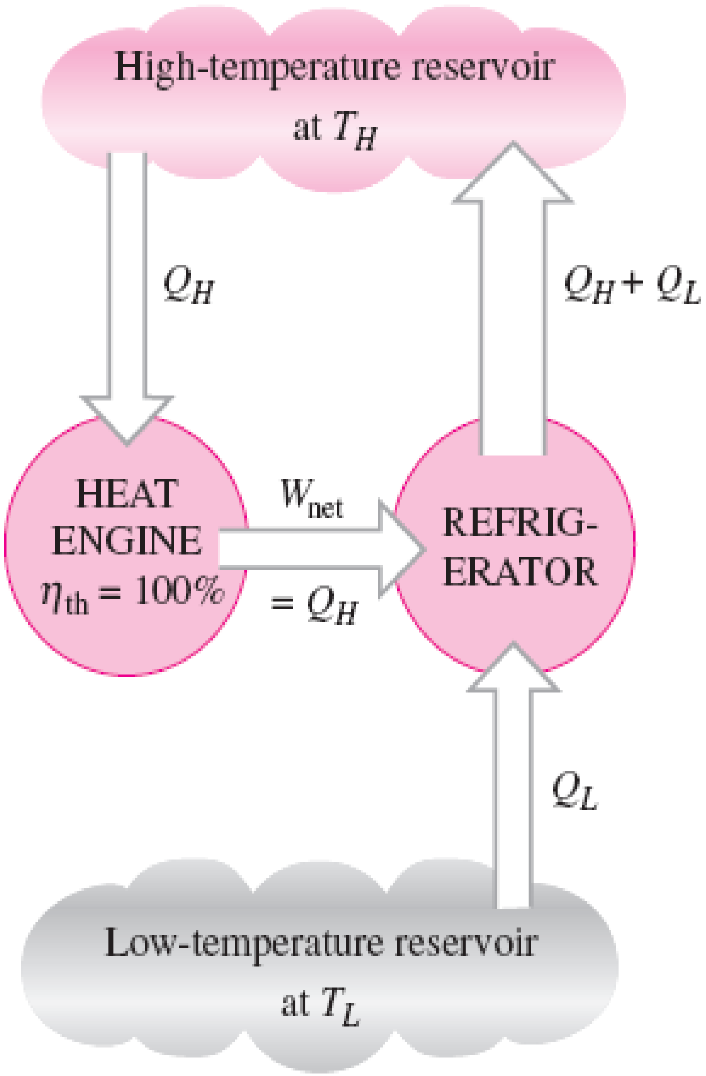
The Kelvin-Planck statement can also be expressed as;

“No heat engine can have a thermal efficiency of 100% OR as *for a power plant to operate; the working fluid must exchange heat with the environment as well as the furnace.”*

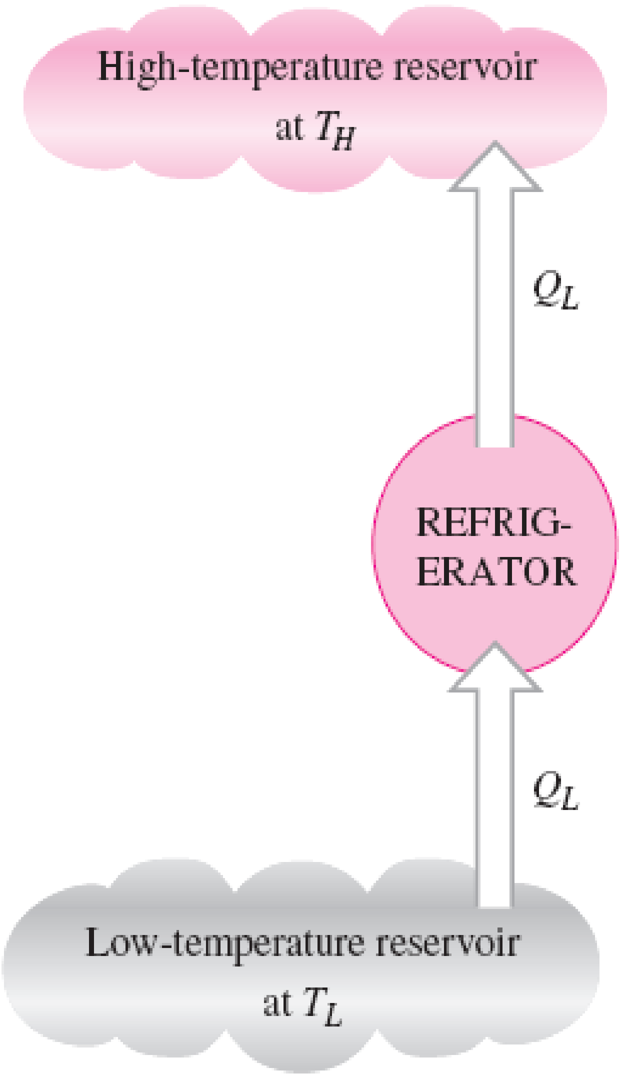
Clausius Statement:

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

Equivalence of the TWO statements:



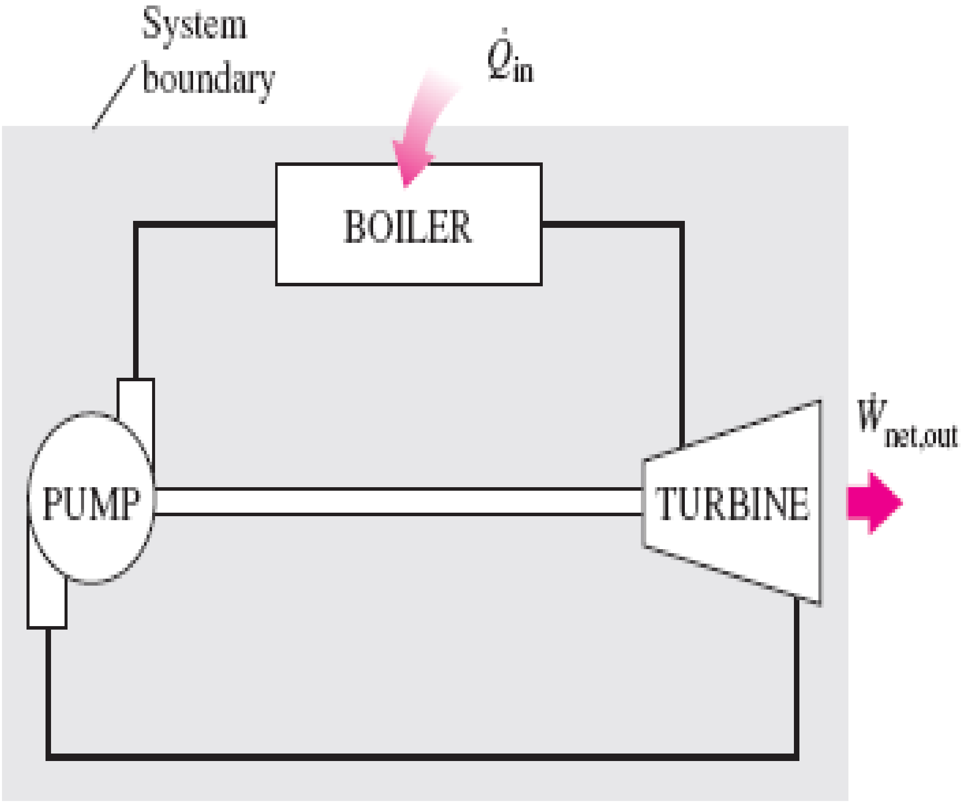
(*a*) A refrigerator that is powered by a 100 percent efficient heat engine



(*b*) The equivalent refrigerator

Perpetual motion machine of second kind (PMM2):

A device that violates the second law of thermodynamics is called a perpetual motion machine of the second kind (PMM2).



Reversible and irreversible processes:

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 (both original and reverse) process.

Processes that are not reversible are called irreversible processes.

It should be pointed out that a system can be restored to its initial state following a process, regardless of whether the process is reversible or irreversible. But for reversible processes, this restoration is made without leaving any net change on the surroundings, whereas for irreversible processes, the surroundings usually do some work on the system and therefore will not return to their original state.

Factors that make process irreversible:

The factors that cause a process to be irreversible are called irreversibilities. They are:

i) Friction

ii) Unrestrained expansion

iii) Mixing of two fluids

iv) Heat transfer across a finite temperature difference

v) Electric resistance

vi) Inelastic deformation of solids

vii) Chemical reactions

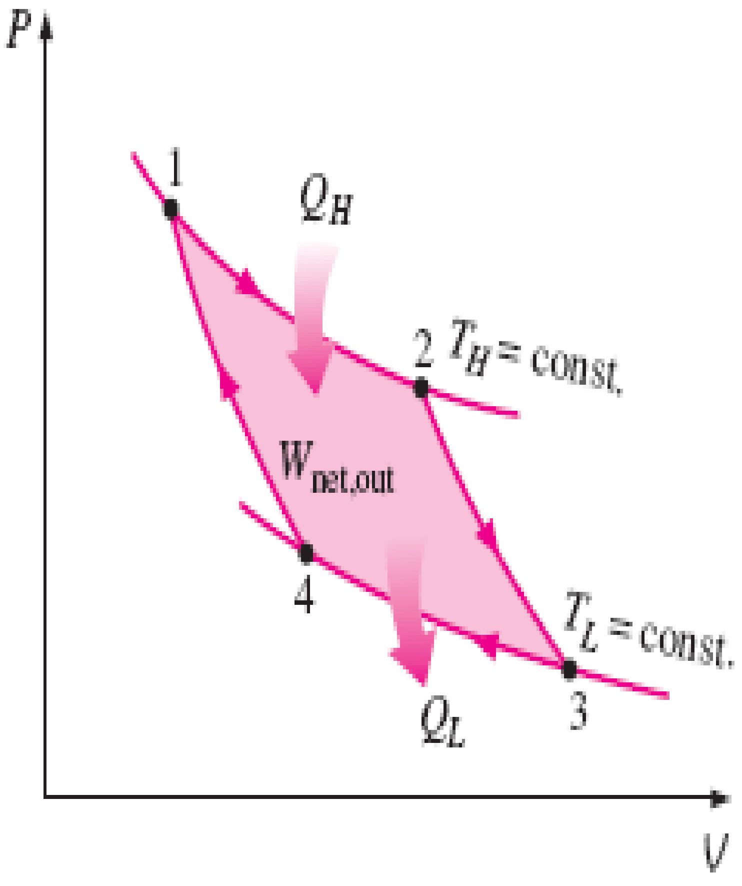
Carnot cycle:

Process 1-2, reversible isothermal expansion

Process 2-3, reversible adiabatic expansion

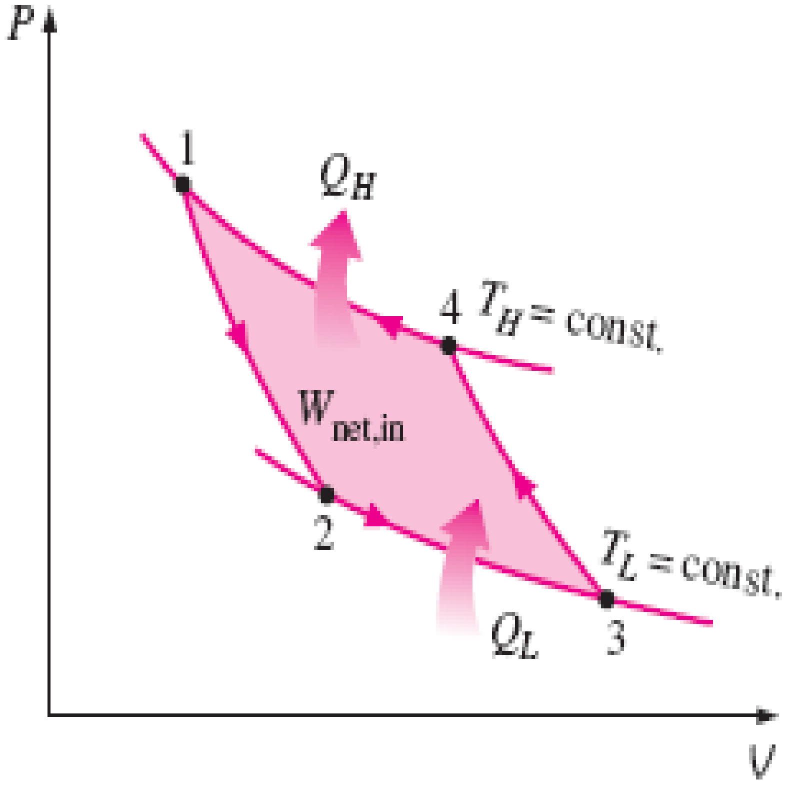
Process 3-4, reversible isothermal compression

Process 4-1, reversible adiabatic compression

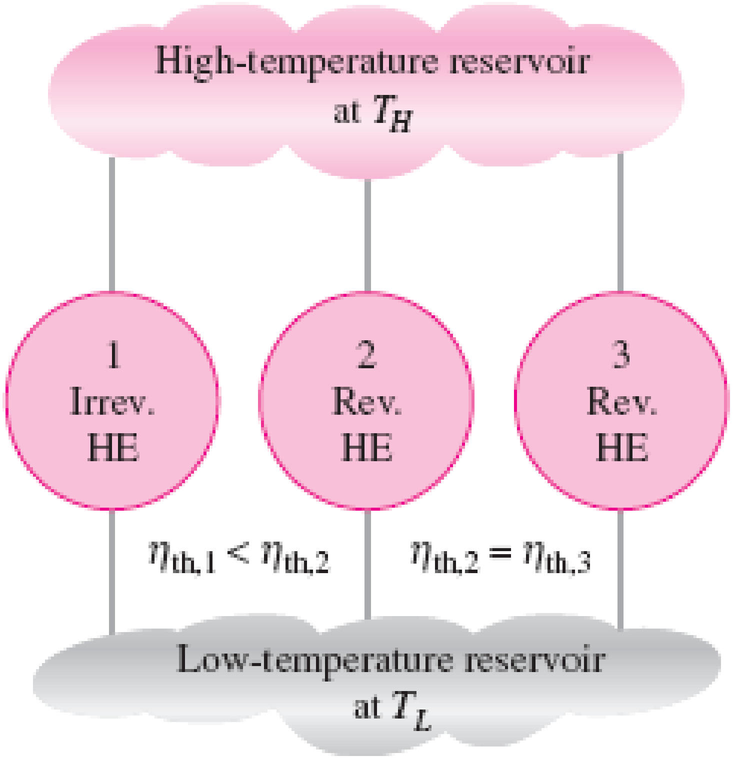


Reversed Carnot cycle:

The Carnot cycle is a reversible cycle. If the processes of Carnot cycle are carried out in the reverse direction as shown in Fig. it will become a refrigeration or heat pump cycle. It is then referred to as reversed Carnot cycle.



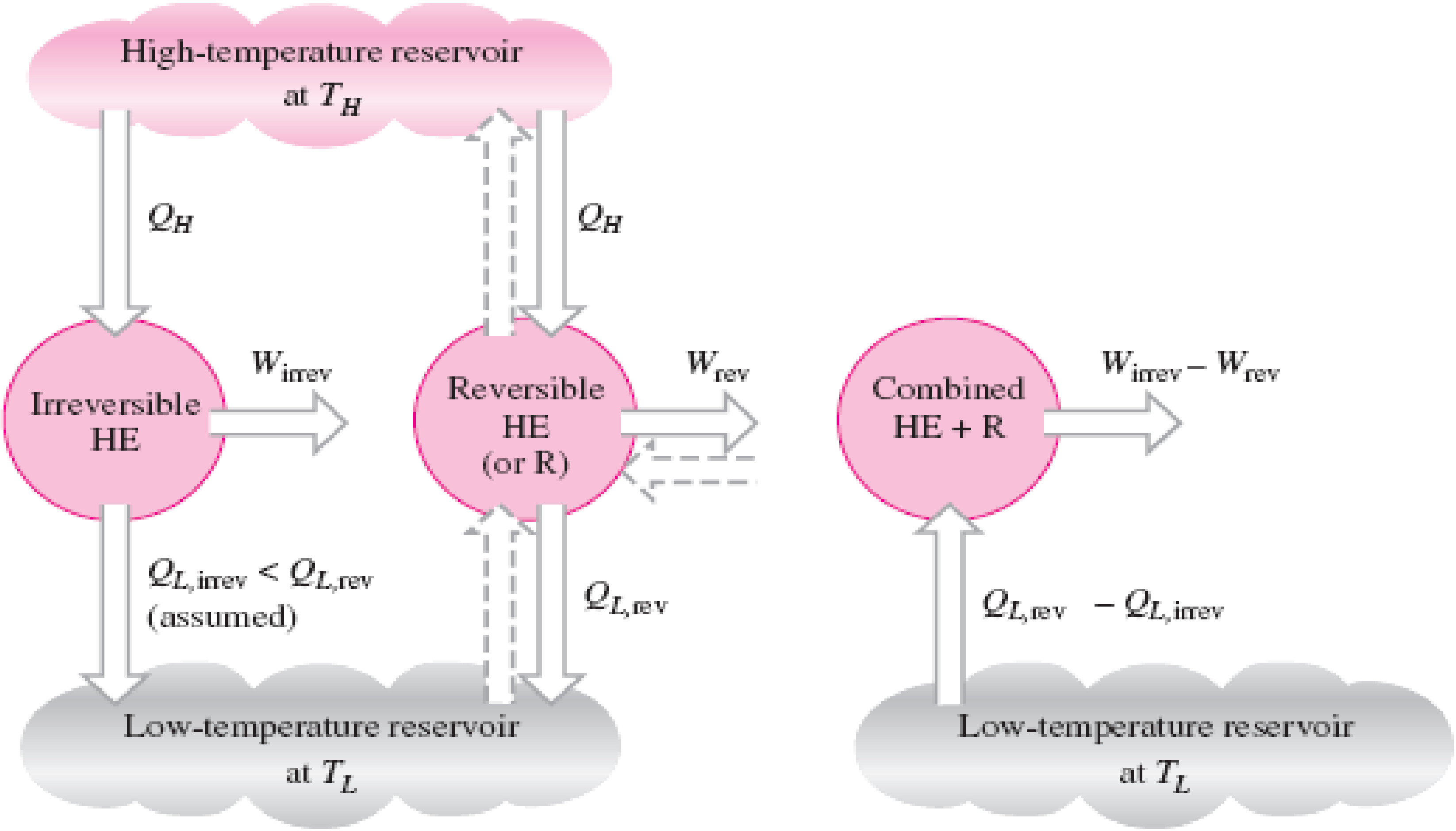
The Carnot principle:



1. The efficiency of an irreversible heat engine is always less than the efficiency of a reversible heat engine operating between same two thermal reservoirs.

2. The efficiencies of all reversible heat engines operating between the same two reservoirs are same.

Proof of 1st statement:



(*a*) A reversible and an irreversible heat engine operating between the same two reservoirs (the reversible heat engine is then reversed to run as a refrigerator)

(*b*) The equivalent combined system

Thermodynamic temperature scale:

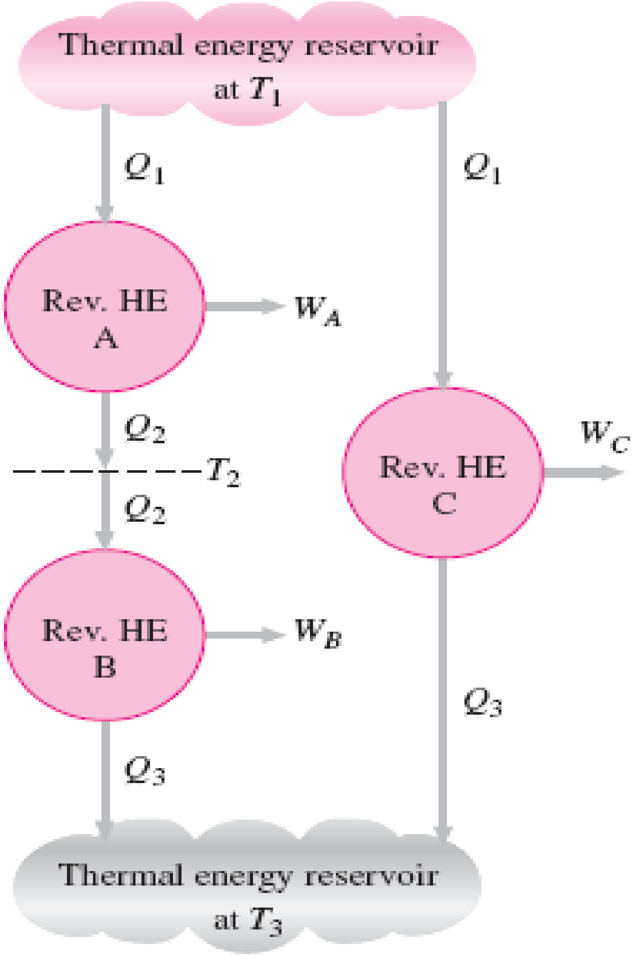
A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a thermodynamic temperature scale. Such a temperature scale offers great convenience in thermodynamic calculations.

As per second Carnot principle all reversible heat engines have the same thermal efficiency when operating between the same two reservoirs. That is the efficiency is independent of the working fluid employed, its properties, the way cycle is executed. Since energy reservoirs are characterized by their temperatures, the thermal efficiency of a reversible heat engines is a function of the reservoir temperature only. That is,

$$\eta_{th,rev} = g(T_H, T_L)$$

$$\frac{Q_H}{Q_L} = f(T_H, T_L) \qquad (1)$$

Since, $\eta_{th} = 1 - \frac{Q_L}{Q_H}$. In these relations T_H and T_L are the temperatures of the high- and low-temperature reservoirs, respectively.



Applying Eq. (1) to all three engines separately, we get

$$\frac{Q_1}{Q_2} = f(T_1, T_2), \quad \frac{Q_2}{Q_3} = f(T_2, T_3), \quad \text{and} \quad \frac{Q_1}{Q_3} = f(T_1, T_3)$$

Now consider the identity

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2}\frac{Q_2}{Q_3}$$

This corresponds to,

$$f(T_1, T_3) = f(T_1, T_2) \cdot f(T_2, T_3)$$

The left hand side of this equation is a function of T_1 and T_3, and therefore the right hand side must also be function of T_1 and T_3 only, and not T_2. This condition will be satisfied only if the function has the following form:

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \quad \text{and} \quad f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

So that will cancel from the product of and, yielding

$$\frac{Q_1}{Q_3} = f(T_1, T_3) = \frac{\varnothing(T_1)}{\varnothing(T_3)} \qquad (2)$$

This relation is much more specific than Eq. (1) for the functional form of Q_1/Q_3 in terms of T_1 and T_3.

For a reversible heat engine operating between two reservoirs at temperature TH and TL, Eq. (2) can be written as

$$\frac{Q_H}{Q_L} = \frac{\varnothing(T_H)}{\varnothing(T_L)} \qquad (3)$$

This is the only requirement that the second law places on the ratio of heat transfers to and from the reversible heat engines. Several functions satisfy this equation, and the choice is completely arbitrary.

Lord Kelvin first proposed taking to define a thermodynamic temperature scale as

$$\left(\frac{Q_H}{Q_L}\right)_{rev} = \frac{T_H}{T_L} \qquad (4)$$

This temperature scale is called the Kelvin scale, and the temperatures on this scale are called absolute temperatures. On the Kelvin scale, the temperature ratios depend on the ratios of heat transfer between a reversible heat engine and the reservoirs and are independent of the physical properties of any substance. On this scale temperatures vary between zero and infinity.

Efficiency of the reversible heat engine:

The efficiency of a reversible heat engine in which heat is received solely at T_H is found to be,

$$\eta_{rev} = \eta_{max} = 1 - \left(\frac{Q_L}{Q_H}\right)_{rev} = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H}$$

It is observed that as T_H decreases and T_L increases the efficiency of the reversible cycle increases.

Since η is always less than unity, T_L is always greater than zero and positive.

The COP of a refrigerator is given by,

$$(COP)_{ref} = \frac{Q_L}{Q_{H-Q_L}} = \frac{1}{\frac{Q_H}{Q_L} - 1}$$

For a reversible refrigerator

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \qquad \text{OR} \qquad \left[(COP)_{ref}\right]_{rev} = \frac{T_L}{T_H - T_L}$$

Similarly for a reversible heat pump,

$$\left[(COP)_{HP}\right]_{rev} = \frac{T_H}{T_H - T_L}$$

Note: 1. The thermal efficiencies of actual and reversible heat engines operating between the same temperature limits can be compared as follows:

$$\eta_{\text{th}}\begin{cases} < \eta_{\text{th,rev}} & \text{irreversible heat engine}\\ = \eta_{\text{th,rev}} & \text{reversible heat engine}\\ > \eta_{\text{th,rev}} & \text{impossible heat engine}\end{cases}$$

2. The coefficients of performance of actual and reversible refrigerators operating between the same temperature limits can be compared as follows:

$$\text{COP}_{\text{R}}\begin{cases} < \text{COP}_{\text{R,rev}} & \text{irreversible refrigerator}\\ = \text{COP}_{\text{R,rev}} & \text{reversible refrigerator}\\ > \text{COP}_{\text{R,rev}} & \text{impossible refrigerator}\end{cases}$$

BASIC THERMODYNAMICS

MODULE 3

REVERSIBILITY

&

ENTROPY

Reversibility:

Definitions of a reversible process, reversible heat engine, importance and superiority of a reversible heat engine and irreversible processes; factors that make a process irreversible, reversible heat engines. Unresisted expansion, remarks on Carnot’s engine, internal and external reversibility, Definition of the thermodynamic temperature scale. Problems

Entropy

Clasius inequality; Statement, proof, application to a reversible cycle. Entropy; definition, a property, change of entropy, principle of increase in entropy, entropy as a quantitative test for irreversibility, calculation of entropy using Tds relations, entropy as a coordinate, numerical problems. Available and unavailable energy. Reversible work and irreversibility, (no numerical problems)

Introduction:

- First law of thermodynamics- concept of the internal energy U
- Second law of thermodynamics- concept of the entropy S
- Like internal energy, entropy is also a thermodynamic property and is defined only in terms of mathematical operations.
- Entropy content of an isolated system is not conserved

General Discussion:

For a system undergoing a quasi-static process, work done at the boundary is given by,

$$\delta W = P\,dV -------------(1)$$

This relation gives the work done at the boundary of a system during a reversible process, since a reversible process is a quasi-static process

Now Consider a reversible cycle in which only work involved is done at the boundary of the system , we have

$$\oint \delta Q = \oint \delta W = \oint P\,dV ------(2)$$

Form the equation (2) ,

- Work is given by the cyclic integral of product of two properties viz. P is an intensive property & dV is change in an extensive property.
- For a reversible cycle when work (which is a path function) is defined by the product of two properties one is intensive and the other is change in an extensive property, why can't Heat (which is also a path function) is defined by the cyclic integral of product of two properties one intensive and the other change in an extensive property.
- Yes, the intensive property most closely associated with heat is temperature and the other extensive property for this answer is ENTROPY

Then what exactly is entropy?

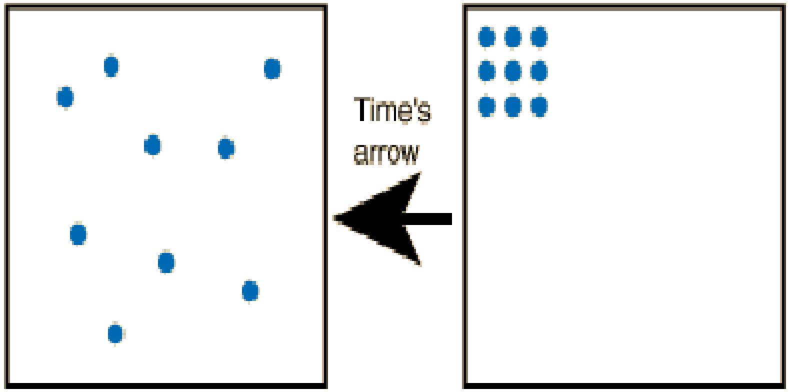
Entropy is:

- An extensive property
- A measure of the disorder of a system, the greater the disorder, the greater the entropy.
- The state of disorder in a thermodynamic system: the more energy the higher the entropy
- A measure of the dispersal or degradation of energy.
- A measure of the disorder or randomness in a closed system. For example, the entropy of an unburned piece of wood and its surroundings is lower than the entropy of the ashes, burnt remains, and warmed surroundings due to burning that piece of wood

- **Defined as a measure of unusable energy within a closed isolated system (the universe for example). As usable energy decreases and unusable energy increases, "entropy" increases.**
- **Entropy is also a gauge of randomness or chaos within a closed system. As usable energy is irretrievably lost, disorganization, randomness and chaos increase.**

Understanding entropy:

Example 1



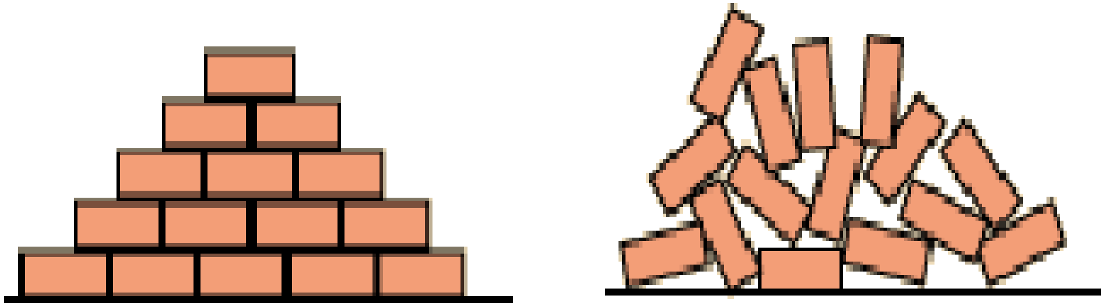
One of the ideas involved in the concept of entropy is that nature tends from order to disorder in isolated systems

This tells us that the right hand box of molecules happened before the left

If the particles represents gas molecules at normal temperatures inside a closed container, which of the illustration came first ?

Example 2

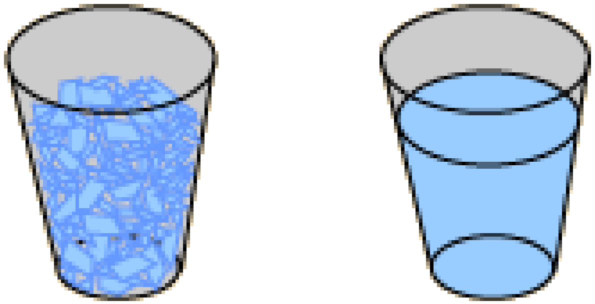
If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce ?



Disorder is more probable than order

Example 3

Which is more disordered? The glass of ice chips or the glass of water?



The jumble of ice chips may look more disordered in comparison to the glass of water which looks uniform and homogeneous

For a glass of water the number of molecules is astronomical

Ice chips place limits on the number of ways the molecules can be arranged but not the water

The water molecules in the glass can be arranged in many more ways They have greater "multiplicity" and therefore greater entropy

Solids have lesser entropy than liquids. Statistically, in solids the atoms or molecules are in their fixed places, whereas in liquids and even more in gases you never know exactly where to find them. The fixed sequence of atoms in solids reflects a higher ordered state.

- Consider a body which is heated and another one is cooled. What happens to the entropy of the two bodies? Entropy increases on heating. Does disorder increase, too?

Yes, it does. We know that heat is stored in a piece of matter as the random motion of particles. The hotter a body, the more its atoms and molecules jiggle around. It is not difficult to identify disorder by faster jiggling motion.

Clausius Theorem:

Proof: The thermal efficiency of reversible Carnot cycle is

$$\eta_{Carnot} = 1 - \frac{\mathrm{Q_L}}{\mathrm{Q_H}} = 1 - \frac{T_L}{T_H} \; or \; \frac{\mathrm{Q_H}}{\mathrm{T_H}} = \frac{\mathrm{Q_L}}{\mathrm{T_L}} \quad ----------(1)$$

Considering the usual sign convention, +ve for the heat absorbed and –ve for the heat rejected, we may write,

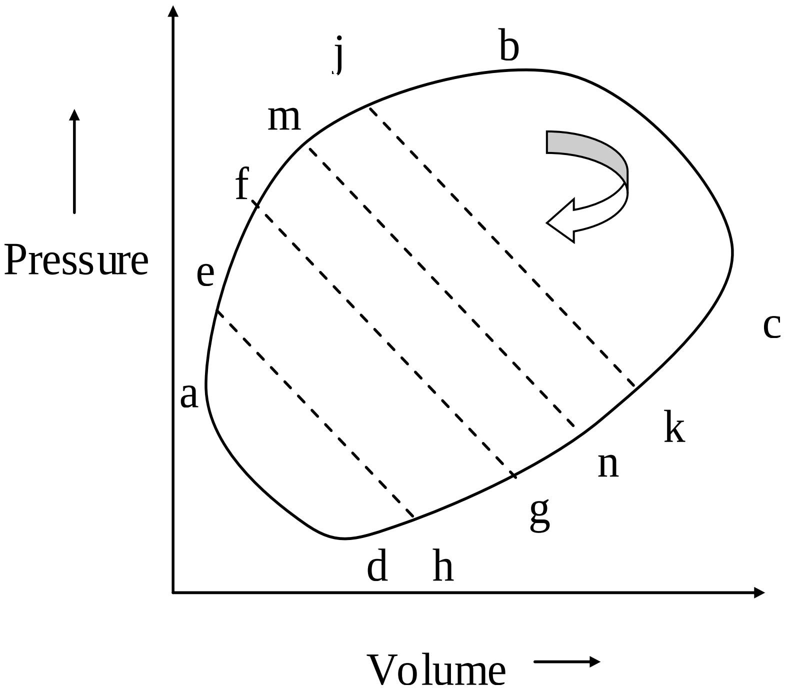
$$\frac{Q_H}{T_H} = -\frac{Q_L}{T_L} \; or \; \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 -----------(2)$$

Equation (2) shows that the sum of the quantities, $\frac{Q_H}{T_H}$ *and* $\frac{Q_L}{T_L}$ associated with absorption and rejection of heat by the fluid of a reversible heat engine is zero for the entire cycle

Since the working fluid returns to its initial state at the end of the cycle, it undergoes no net change in properties, suggesting that the quantities $\frac{Q_H}{T_H}$ *and* $\frac{Q_L}{T_L}$ represents property changes of the working fluid because their sum is zero for the cycle

This is the characteristic of a property or state function.

- Q_H and Q_L are path functions. However if they are divided by the temperatures at which the transfer takes place, the result is independent on the path. This conclusion is for Carnot cycle.
- The above conclusion is also valid for any reversible cycle.



Consider any arbitrary reversible cycle a-b-c-d-a as shown. In this absorption and rejection of heat do not occur at two constant temperatures but take place at continuously changing temperatures.

The cycle can be now broken into an infinite number elementary Carnot cycle

Draw a series of infinitely close adiabatic lines, eh, fg, mn, etc. efgh, fmng etc represents elementary Carnot cycle in which sections ef, gh etc can be considered as isothermal lines.

For any differential Carnot cycle, efgh, we may write

$$\frac{Q_{H1}}{T_{H1}} = \frac{Q_{L1}}{T_{L1}}$$

Using proper sign convention

$$\frac{Q_{H1}}{T_{H1}} + \frac{Q_{L1}}{T_{L1}} = 0 ------------(1)$$

Similarly,

$$\frac{Q_{H2}}{T_{H2}} + \frac{Q_{L2}}{T_{L2}} = 0------------(2)$$

for the cycle fmng

From these relations we see that the algebraic sum of the ratios of the amounts of heat transferred to the absolute temperature for the Carnot cycles taken together is equal to zero, thus,

$$\left(\frac{Q_{H1}}{T_{H1}} + \frac{Q_{L1}}{T_{L1}}\right) + \left(\frac{Q_{H2}}{T_{H2}} + \frac{Q_{L2}}{T_{L2}}\right) + ---------- = 0$$

i.e.,

$$\sum\left(\frac{Q_H}{T_H}+\frac{Q_L}{T_L}\right)=0-----------(3)$$

As the number of Carnot cycles is very large, the sum of the terms $\frac{Q}{T}$ over the complete cycle becomes equal to the cyclic integral of $\frac{\delta Q}{T}$

We may , therefore write

$$\oint_R \frac{\delta Q}{T}=0---------(4)$$

Where R represents reversible cycle

Therefore the cyclic integral of $\frac{\delta Q}{T}$ for a reversible cycle is zero.

This result is known as CLAUSIUS THEOREM

$\frac{\delta Q}{T}$ is known as ENTROPY

MODULE 4

THERMODYNAMIC RELATIONS

Thermodynamic relations

Helmholtz and Gibbs functions, .Maxwell relation, Clausius Clayperon's equation .Ideal gas; equation of state, internal energy and enthalpy as functions of temperature only, universal and particular gas constants, specific heats, perfect and semi-perfect gases. Evaluation of heat, work, change in internal energy ,enthalpy and entropy in various quasi-static processes.

10 Hours

1st Hour

Brain storming session on subject topics

Helmholtz and Gibbs functions, .Maxwell relation

2nd Hour

Clausius- Clayperon's equation .Ideal gas

3rd Hour

equation of state, internal energy and enthalpy as functions of temperature only

4th Hour

universal and particular gas constants, specific heats

5th Hour

perfect and semi-perfect gases

6th Hour

Evaluation of heat, work , change in internal energy

7th Hour

enthalpy and entropy in various quasi-static processes.

8th ,9th & 10th Hour

Problems

Introduction

Definition: A substance is said to be an ideal gas if it satisfies the following equations

i.e., $Pv = RT$ and $u = f(T)$

Where P is the pressure exerted by the substance, v is the specific volume of the substance, T is the temperature in degree Kelvin, u is the specific internal energy and R is the gas constant.

Experience has shown that almost all real gases satisfy the above equations over wide ranges of pressures and temperatures. However there are certain situations where the real gases cannot be treated as ideal gases.

Mole of a Gas:

A mole of a gas is that quantity of gas whose mass is numerically equal to its molecular weight.

For example, 1 kg mol of hydrogen is equal to 2 kg, has molecular weight of hydrogen is 2. Therefore if n is the total number of moles, m is mass and M is the molecular weight then, $nM=m$

Avogadro's Hypothesis:

Avogadro's law states that equal volumes of all gases measured at the same temperature and pressure contain the same number of moles.

Consider two gases A and B. The law states that if $V_A = V_B$, $T_A = T_B$ and $P_A = P_B$ then $n_A = n_B$

For gas A, the equation of state can be written as

$P_A V_A = m_A R_A T_A = n_A M_A R_A T_A$

$$Or \quad n_A = \frac{P_A V_A}{(M_A R_A T_A)}$$

Similarly for gas B we have

$$n_B = \frac{P_B V_B}{(M_B R_B T_B)}$$

According to Avogadro's law, $V_A = V_B$, $T_A = T_B$ and $P_A = P_B$ then $n_A = n_B$. Therefore it follows that

$$M_A R_A = M_B R_B = \overline{R}$$

Where is called the universal gas constant and R is called the characteristic gas constant. The value is 8.3143 kJ/kg-mol-K.

The ideal gas equation can also be written in terms of as pV = nMRT = n T where = R/M

The Maxwell Relations:

The equations that relate the partial derivatives of properties P, v, T, and s of a simple compressible system to each other are called Maxwell relations. They are obtained from the four Gibbs equations by exploiting the exactness of the differentials of thermodynamic properties.

Two of the Gibbs relations are,

$$du = T\,ds - P\,dv \quad \text{---- (1)}$$

$$dh = T\,ds + v\,dP \quad \text{---- (2)}$$

The other two Gibbs relations are based on two new combination properties – the Helmholtz function ‘a’ and the Gibbs function ‘g’, defined as

$$a = u - Ts \quad \text{---- (3)}$$

$$g = h - Ts \quad \text{---- (4)}$$

Differentiating, we get

$$da = du - T\,ds - s\,dT$$

$$dg = gh - T\,ds - s\,dT$$

Simplifying the above relations by using eqs. (1) and (2), we obtain the other two Gibbs relations for simple compressible systems:

$$da = -s\,dT - Pdv \quad ---- (5)$$

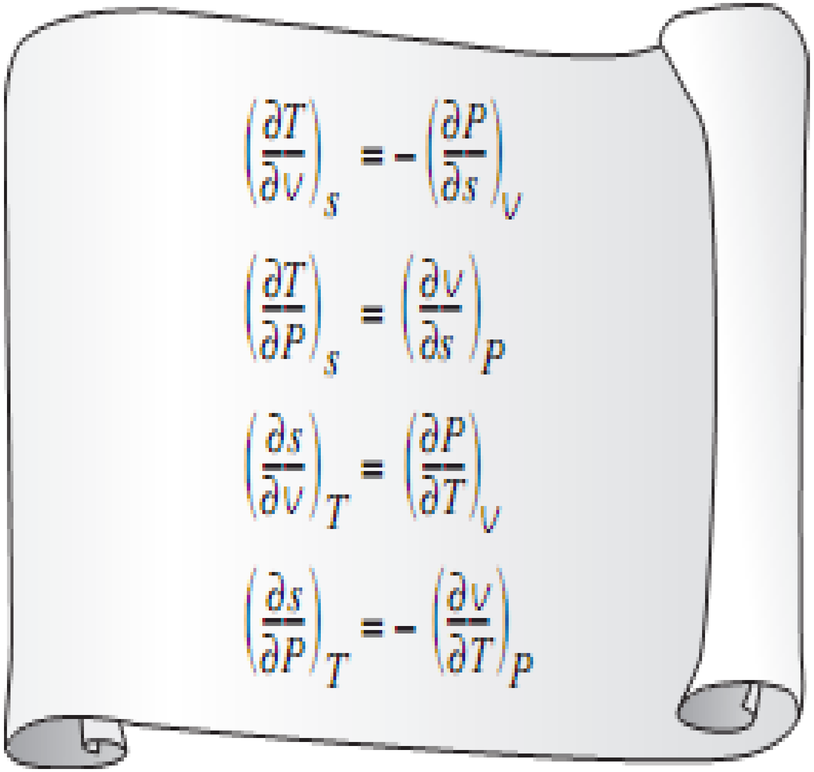
$$dg = -s\,dT + v\,dP \quad ---- (6)$$

A careful examination of the four Gibbs relations reveals that they are of the form

$$dz = M\,dx + N\,dy \quad ---- (7)$$

with

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$



$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

These are called the Maxwell relations. They are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties P, v, and T. Note that the Maxwell relations given above are limited to simple compressible systems.

The Clayperon's Equation:

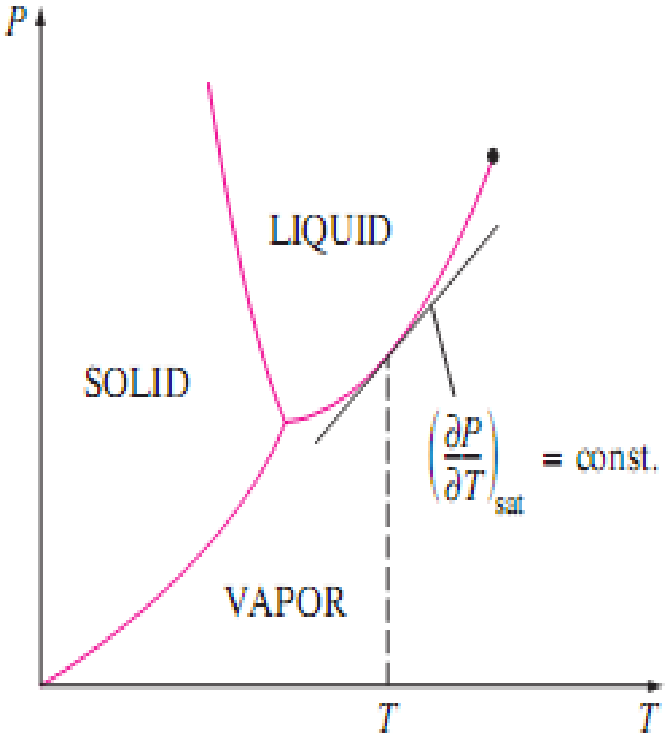
The Maxwell relations have far-reaching implications in thermodynamics and are frequently used to derive useful thermodynamic relations. The Clapeyron equation is one such relation, and it enables us to determine the enthalpy of vaporization (h_{fg}) from a knowledge of P, v, and T data alone.

Consider the third Maxwell relation,

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \qquad \text{----- (1)}$$

During a phase-change process, the pressure is the saturation pressure, which depends on the temperature only and is independent of the specific volume.

That is $P_{sat} = f(T_{sat})$. Therefore, the partial derivative $(\partial P/\partial T)_v$ can be expressed as a total derivative $(dP/dT)_{sat}$, which is the slope of the saturation curve on a P-T diagram at a specified saturation state (Fig. below).



This slope is independent of the specific volume, and thus it can be treated as a constant during the integration of equation (1) between two saturation states at the same temperature. For a isothermal liquid-vapor phase-change process, for example, the integration yields

$$s_g - s_f = \left(\frac{dP}{dT}\right)_{\text{sat}} (v_g - v_f) \qquad \text{------- (2)}$$

Or

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{s_{fg}}{v_{fg}} \qquad \text{------- (3)}$$

During this process the pressure also remains constant. There

$$dh = T\,ds + v\,\overset{\nearrow 0}{dP} \rightarrow \int_f^g dh = \int_f^g T\,ds \rightarrow h_{fg} = T s_{fg} \qquad \text{------ (4)}$$

Substituting this result into Eq. (3), we obtain

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{Tv_{fg}} \qquad \text{-------}\ (5)$$

This is called the **Clapeyron equation** after the French engineer and physicist E. Clapeyron. This is an important thermodynamic relation since it enables us to determine the enthalpy of vaporization h_{fg} at a given temperature by simply measuring the slope of the saturation curve on a *P-T* diagram and the specific volume of a saturated liquid and saturated vapor at the given temperature.

The Clapeyron equation is applicable to any phase-change process that occurs at a constant temperature and pressure. It can be expressed in a general form as

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{12}}{Tv_{12}}$$

Where subscript 1 and 2 indicate the two phases.

Specific Heat of Ideal Gases:

From the definition of specific heat at constant volume and the specific heat at constant pressure, we have

$$c_v = \frac{du}{dT} = f(T)$$

$$c_P = \frac{dh}{dT} = f(T)$$

as u and h are functions of temperature.

From the above equations, du = C_V dT   and dh = C_P dT

For a mass of m kg of gas the equations become

dU = m c_V dT and dH = m c_P dT

On integrating we get

$$U_2 - U_1 = m\int_{T_1}^{T_2} c_v dT$$

$$and\ H_2 - H_1 = m\int_{T_1}^{T_2} c_P dT$$

Relation between specific heats for an ideal gas:

For an ideal gas h = u + RT

Therefore $$\frac{dh}{dT} = \left(\frac{du}{dT}\right) + R$$

Or $C_P = C_V + R$

i.e., $C_P - C_V = R$

Dividing the above equation by C_V, we get

$$\gamma - 1 = \frac{R}{c_V} \qquad Or\ c_V = \frac{R}{\gamma - 1}$$

Similarly, dividing the above equation by C_P, we get

$$c_P = \frac{\gamma R}{\gamma - 1}$$

Changes in internal energy, enthalpy and entropy for an ideal gas:

i) Change in internal energy

Let an ideal gas of fixed mass m undergoes a finite change of state from temperature T_1 to temperature T_2. Then the change in internal energy is given by

$$U_2 - U_1 = m(u_2 - u_1) = m\int_1^2 du$$

$$= m\int_{T_1}^{T_2} (C_V \, dT)$$

To integrate the above equation we should know the functional relationship between C_V and dT. A perfect gas equation is one for which C_v is a constant.

Therefore, $U_2 - U_1 = m\, C_v (T_2 - T_1)$

ii) Change in Enthalpy

$$We\ have\ H_2 - H_1 = m(h_2 - h_1) = m\int_1^2 dh$$

$$= m\int_{T_1}^{T_2} (C_P dT)$$

For a perfect gas C_P is constant. Therefore the above equation can be integrated and we get

$$H_2 - H_1 = m\ C_P\ (T_2 - T_1)$$

Work done by a perfect gas during a reversible adiabatic process in a closed system:

From the first law of TD,

$$\delta q = du + \delta w$$

For an adiabatic process, $\delta q=0$

Hence the work done by a unit mass of a perfect gas on a piston during an adiabatic expansion process is equal to the decrease in internal energy, i.e., $\delta w = -du$

Whereas, for an adiabatic compression process, the internal energy of the gas will increase with a consequent increase in temperature.

For a perfect gas, $du = C_v dT$

$$\therefore \delta w = -C_v dT$$

$$But, C_v = \frac{R}{\gamma - 1} \quad \therefore \delta w = -\frac{R}{\gamma - 1} dT$$

Hence the work done during an adiabatic non-flow process between states 1 and 2 is given by

$$W_{1-2} = \frac{R}{\gamma - 1}\left(T_1 - T_2\right)$$

$$= \frac{P_1 v_1 - P_2 v_2}{\gamma - 1}$$

$$= \frac{P_1 v_1}{\gamma - 1}\left[1 - \frac{P_2 v_2}{P_1 v_1}\right]$$

$$= \frac{P_1 v_1}{\gamma - 1}\ [1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}}]$$

Work done by a perfect gas during a reversible adiabatic Steady Flow process:

Neglecting the effect of changes in velocity and elevation, SFEE for a unit mass of fluid is given by $q_{1-2} - w_{1-2} = \Delta h$

Since the process is adiabatic, q=0. Hence work done per unit mass of a perfect gas during an adiabatic steady flow expansion process is equal to the decrease in enthalpy,

i.e., $w_{1-2} = h_1 - h_2$

For a perfect gas, $dh = c_p dT$

Therefore, $w_{1-2} = C_p(T_1 - T_2)$

$$But, C_p = \frac{\gamma R}{\gamma - 1},$$

the work done during an adiabatic steady flow process between states 1 and 2 is given by,

$$w_{1-2} = \frac{\gamma R}{\gamma - 1}\left(T_1 - T_2\right)$$

$$= \frac{\gamma}{\gamma - 1}\left(P_1 v_1 - P_2 v_2\right)$$

$$= \frac{\gamma\ P_1 v_1}{\gamma - 1}\left[1 - \frac{P_2 v_2}{P_1 v_1}\right]$$

$$= \frac{\gamma\ P_1 v_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}}\right]$$

It may be noted that the work done for a steady flow system is γ times that for a closed system.

The polytropic process of a perfect gas:

A Polytropic process is one for which the pressure volume relation is given by pV^n = constant, where the exponent n for the given process is a constant and may have any numerical value ranging from plus infinity to minus infinity.

From the above equation, it is evident that the properties at the end states of the reversible or irreversible polytropic process of a perfect gas may be written in the form

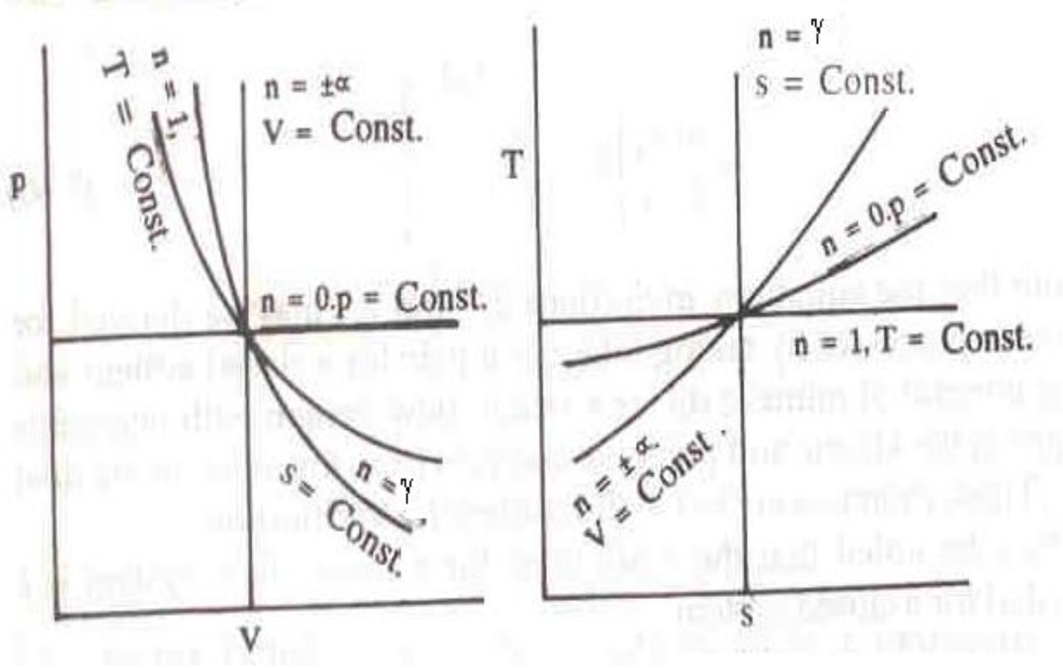
$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2}\right)^n$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} = \left(\frac{v_2}{v_1}\right)^{n-1}$$

There are four values of the exponent n that indicate processes of particular interest. When

- n = 0, constant pressure or isobaric process
- n = ± ∞, constant volume or isochoric process
- n = 1, constant temperature or isothermal process and
- n = γ, constant entropy or isentropic process

These processes are shown in the fig. on p-v and T-s diagrams.



Work done and heat transfer by a perfect gas during a polytropic process:

For the closed system, the work done during a polytropic expansion process is given by,

$$w_{1-2} = \int_1^2 pdv = \frac{R}{n-1}(T_1 - T_2)$$

$$= \frac{P_1 v_1 - P_2 v_2}{n-1}$$

$$= \frac{P_1 v_1}{n-1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}\right]$$

The work done for a steady flow system during a polytropic expansion process is given by,

$$w_{1-2} = -\int_1^2 vdp = \frac{nR}{n-1}\left(T_1 - T_2\right)$$

$$= \frac{n}{n-1}\left(P_1 v_1 - P_2 v_2\right)$$

$$= \frac{n\ P_1 v_1}{n-1}\left[1-\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}}\right]$$

It may be noted that the work done for a steady flow system is n times that for a closed system.

i) The heat transfer for a closed system:

From the first law of thermodynamics for a unit mass of substance

$$\delta q = \delta w + du$$

Since $du = C_v dT$ and for a reversible process $\delta w = pdv$

$$\delta q = C_v dT + pdv$$

Therefore heat transfer per unit mass during a polytropic process in a closed system from the initial state to final state is given by

$$q_{1-2} = C_v\left(T_2 - T_1\right) + \int_1^2 pdv$$

$$But\ w_{1-2} = \int_1^2 pdv = \frac{R}{n-1}\left(T_1 - T_2\right)$$

$$\therefore q_{1-2} = C_v\left(T_2 - T_1\right) + \frac{R}{n-1}\left(T_1 - T_2\right)$$

$$= \left(T_1 - T_2\right)\left(\frac{R}{n-1} - C_v\right)$$

$$= \left(T_1 - T_2\right)\left(\frac{C_p - nC_v}{n-1}\right)$$

$$= \frac{\left(T_1 - T_2\right)}{n-1}\left(\gamma - 1\right)C_v$$

$$= \left(\frac{\gamma - n}{\gamma - 1}\right)\frac{R\left(T_1 - T_2\right)}{n-1}$$

$$Or \quad q_{1-2} = \left(\frac{\gamma - n}{\gamma - 1}\right)w_{1-2}$$

ii) The heat transfer in a steady flow process:

From the first law for steady flow system for a unit mass of fluid

$$\delta q = \delta w + dh$$

But $dh = C_p dT$ and for a reversible steady flow process

$$\delta w = -Vdp$$

Therefore $\delta q = C_p dT - Vdp$

$$q_{1-2} = C_p\left(T_2 - T_1\right) - \int_1^2 vdp$$

$$But\ w_{1-2} = -\int_1^2 vdp = \frac{nR}{n-1}\left(T_1 - T_2\right)$$

Therefore heat transfer,

$$q_{1-2} = C_p\left(T_2 - T_1\right) + \frac{nR}{n-1}\left(T_1 - T_2\right)$$

$$= \left(T_1 - T_2\right)\left(\frac{nR}{n-1} - C_p\right)$$

$$= \left(T_1 - T_2\right)\frac{C_p - nC_v}{n-1}$$

$$= \left(\frac{\gamma - n}{n-1}\right)C_v\left(T_1 - T_2\right)$$

$$= \left(\frac{\gamma - n}{n-1}\right)R\frac{\left(T_1 - T_2\right)}{n-1}$$

$$= \left(\frac{\gamma - n}{n-1}\right)\frac{w_{1-2}}{n}$$

iii) Change in Entropy:

Let P_1, v_1, T_1, S_1 apply to the initial conditions of certain amount of gas. P_2, v_2, T_2, S_2, apply to the final conditions after adding some heat.

From first law of TD, $\delta q = \delta w + du$

$$\delta q = P.dv + du$$

Also by definition, $du = C_v\, dT$

Therefore $\delta q = Pdv + C_v dT$

Divide by T,

$$\frac{\delta q}{T} = P\frac{dv}{T} + C_v\frac{dT}{T}$$

$$But\ \frac{\delta q}{T} = dS$$

$$\therefore dS = \frac{P}{T}dv + C_v\frac{dT}{T}$$

From perfect gas equation for unit mass of gas, Pv = RT, therefore P/T = R/v

$$\therefore dS = \frac{R}{v} dv + C_v \frac{dT}{T}$$

Therefore integrating,

$$\int_1^2 dS = \int_1^2 R \frac{dv}{v} + \int_1^2 C_v \frac{dT}{T}$$

i.e., the change in entropy is given by

$$S_2 - S_1 = R \ln \frac{v_2}{v_1} + C_v \ln \frac{T_2}{T_1} \quad \text{----- (1)}$$

Equation (1) can also be express in terms of pressure and volume.

We have $$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

$$\therefore \frac{T_2}{T_1} = \frac{P_2 v_2}{P_1 v_1}$$

Substituting this in equation (1) we get,

$$i.e., \quad S_1 - S_1 = \left(C_v + R\right) \ln \frac{v_2}{v_1} + C_v \ln \frac{P_2}{P_1}$$

But $C_P - C_v = R$, i.e., $C_v + R = C_P$

$$\therefore S_1 - S_1 = C_P \ln \frac{v_2}{v_1} + C_v \ln \frac{P_2}{P_1} \quad \text{----- (2)}$$

Equation (1) can also be represented in terms of temperature and volume.

We have $$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

$$\therefore \frac{v_2}{v_1} = \frac{P_2 T_2}{P_1 T_1}$$

Substituting this in equation (1) we get

$$S_2 - S_1 = R.\ln \frac{P_1}{P_2}\frac{T_2}{T_1} + C_v \ln \frac{T_2}{T_1}$$

$$Or\ S_2 - S_1 = C_P \ln \frac{T_2}{T_1} - R.\ln \frac{P_2}{P_1} \quad \text{---- (3)}$$

Evaluation of change in entropy in various quasi static processes:

i) Constant Volume Process

We have δQ = δW + dU

δW = 0 for a constant volume process.

Therefore heat added, $\delta Q = dU = m\,C_v dT$

Divide by T

$$\frac{\delta Q}{T} = mC_v \frac{dT}{T}$$

Integrating,

$$\int_1^2 \frac{\delta Q}{T} = \int_1^2 mC_v \frac{dT}{T}$$

$$\therefore S_2 - S_1 = mC_v.\ln\frac{T_2}{T_1}$$

ii) Constant Pressure Process:

$\delta Q = \delta W + dU$

$= Pdv + dU$

$= mRdT + mC_v dT$

$= m\,(R + C_v)dT$

$= m(C_P - C_v + C_v)dT$

$= mC_P dT$

Divide by T, $$\frac{\delta Q}{T} = mC_P \frac{dT}{T}$$

Integrating, $$\int_1^2 \frac{\delta Q}{T} = \int_1^2 mC_P \frac{dT}{T}$$

$$\therefore S_2 - S_1 = mC_P . \ln \frac{T_2}{T_1}$$

iii) Isothermal Process

We have δQ = δW + dU

But dU = 0

$$\therefore \delta Q = P_1 v_1 \ln \frac{v_2}{v_1}$$

Divide by T,

$$\frac{\delta Q}{T} = \frac{mRT_1}{T_1} \ln \frac{v_2}{v_1}$$

Integrating we get,

$$S_2 - S_1 = mR \ln \frac{v_2}{v_1}$$

Reversible Adiabatic Process δQ = 0

Therefore $S_2 - S_1 = 0$

Hence the process is called isentropic process

iv) Polytropic Process

We know that for a perfect gas $\delta Q = \frac{\gamma - n}{\gamma - 1} P.dv$

Divide by T,

$$\frac{\delta Q}{T} = \frac{\gamma - n}{\gamma - 1} \frac{P.dv}{T}$$

$$\therefore \int_1^2 \frac{\delta Q}{T} = \frac{\gamma - n}{\gamma - 1} \int_1^2 P \frac{dv}{T}$$

We know Pv = RT, i.e., P = RT/v

$$S_2 - S_1 = \frac{\gamma - n}{\gamma - 1} \int_1^2 \frac{RT}{v} \frac{dv}{T}$$

$$= \frac{\gamma - n}{\gamma - 1} R \int_1^2 \frac{dv}{v}$$

$$\therefore S_2 - S_1 = \frac{\gamma - n}{\gamma - 1} R.\ln \frac{v_2}{v_1}$$

Show that the entropy change for an ideal gas undergoing a polytropic process according to the equation PV^n = c is given by

$$S_2 - S_1 = \frac{n-\gamma}{(\gamma-1)(n-1)} R.\ln\frac{T_2}{T_1}$$

We have the change in entropy for unit mass of a substance between states (1) and (2) is given by

$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T}$$

For a perfect gas, we know that $\delta Q = \frac{\gamma - n}{\gamma - 1} P.dv$

Divide by T and integrating,

$$\int_1^2 \frac{\delta Q}{T} = S_2 - S_1 = \int_1^2 \frac{\gamma - n}{\gamma - 1}\frac{P.dv}{T}$$

$$= \frac{\gamma - n}{\gamma - 1} \frac{1}{T} \int_1^2 p.dv$$

$$= \frac{\gamma - n}{\gamma - 1} \frac{1}{T} \frac{R(T_1 - T_2)}{n-1} \left(\because \int_1^2 P.dv = W_{1-2} = \frac{P_1 v_1 - P_2 v_2}{n-1} = \frac{R(T_1 - T_2)}{n-1} \right)$$

$$= \frac{n - \gamma}{\gamma - 1} \frac{R}{T} \left[\frac{T_2 - T_1}{n-1} \right]$$

$$= \frac{n - \gamma}{(n-1)(\gamma - 1)} \frac{R}{T} \int_1^2 dT$$

$$= \frac{n - \gamma}{(n-1)(\gamma - 1)} R \int_1^2 \frac{dT}{T}$$

$$\therefore S_2 - S_1 = \frac{n - \gamma}{(n-1)(\gamma - 1)} R \ln \frac{T_2}{T_1}$$

$$S_2 - S_1 = C_v \frac{(n - \gamma)}{(n-1)} ln \frac{T_2}{T_1}$$

MODULE 5

IDEAL GASES

&

REAL GASES

Ideal gases: Ideal gas mixtures, Daltons law of partial pressures, Amagat’s law of additive volumes, evaluation of properties of perfect and ideal gases, Air- Water mixtures and related properties, Psychrometric properties, Construction and use of Psychrometric chart.

Real gases – Introduction , Air water mixture and related properties, Van-der Waal's Equation of state, Van-der Waal's constants in terms of critical properties, Redlich and Kwong equation of state Beattie-Bridgeman equation , Law of corresponding states, compressibility factor; compressibility chart.Difference between Ideal and real gases.

10 Hours

1st Hour

Brain storming session on subject topics

Ideal gas mixture; Dalton's laws of partial pressures,

2nd Hour

Amagat's law of additive volumes, evaluation of properties

3rd Hour

Analysis of various processes

4th Hour

Real Gases: Introduction, Van-der Waal's Equation of state

5th Hour

Van-der Waal's constants in terms of critical properties, Law of corresponding states

6th Hour

compressibility factor; compressibility chart

7th Hour

Redllich Kwong equation ,Beattie-bridgeman equation

8th ,9th & 10th Hour

Problems

Introduction:

- An ideal gas is a gas having no forces of intermolecular attraction.
- The gases which follow the gas laws at all range of pressures and temperatures are considered as ‘ideal gases’.
- An ideal gas obeys the perfect gas equation Pv = RT and has constant specific heat capacities.
- A real gas is a gas having forces of inter molecular attraction.
- At very low pressure relative to the critical pressure or at very high temperatures relative to the critical temperature, real gases behave nearly the same way as a perfect gas.

- But at high pressure or at low temperatures the deviation of real gases from the perfect gas relation is appreciable.
- These conditions must be observed carefully, otherwise errors are likely to result from inappropriate application of the perfect gas laws.
- Due to these facts, numerous equations of state for real gas have been developed, the derivation of which is analytical, based on the kinetic theory of gases, or empirical, derived from an experimental data.

Thermodynamics of Non-reactive Mixtures:

Assumptions:

- Each individual constituent of the mixture behaves like a perfect gas.
- The mixture behaves like a perfect gas.
- Individual constituents do not react chemically when the mixture is undergoing a process.

Mixture characteristics:

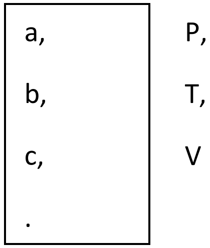


Figure: Homogeneous gas mixture

Consider a mixture of gases a, b, c, …. existing in equilibrium at a pressure P, temperature T and having a volume V as shown in figure.

The total mass of the mixture is equal to the sum of the masses of the individual gases,

i.e., $m_m = m_a + m_{b-} + m_c + \ldots\ldots..$ where subscript m = mixture, a, b, c = individual gases.

Mass fraction: The mass fraction of any component is defined as the ratio of the mass of that component to the total mass of the mixture. It is denoted by m_f.

$$Thus, \quad m_{fa} = \frac{m_a}{m}, \quad m_{fb} = \frac{m_b}{m}, \quad m_{fc} = \frac{m_c}{m}$$

$$\therefore m_{fa} + m_{fb} + m_{fc} + ... = \sum_i m_{f_i} = 1$$

Where the subscript i stands for the i^{th} component. It shows that the sum of the mass fraction of all components in a mixture is unity.

Mole fraction:

If the analysis of a gas mixture is made on the basis of the number of moles of each component present, it is termed a molar analysis. The total number of moles for the mixture is equal to the sum of the number of moles of the individual gases

i.e., $n_m = n_a + n_b + n_c + \ldots\ldots$ where subscript m = mixture, a, b, c = individual gases.

(A mole of a substance has a mass numerically equal to the molecular weight of the substance, i.e., 1 kg mol of O_2 has a mass of 32 kg, 1 kg mol of N_2 has a mass of 28 kg, etc.,) The mole fraction of any component is defined as the ratio of the number of moles of that component to the total number of moles. It is denoted by y

$$i.e., \quad y_a = \frac{n_a}{n_m}, y_b = \frac{n_b}{n_m}, y_c = \frac{n_c}{n_m}$$

$$and \quad \therefore \quad y_a + y_b + y_c + ... = \sum_i y_i = 1$$

i.e., the sum of the mole fraction of all components in a mixture is unity.

The mass of a substance m is equal to the product of the number of moles n and the molecular weight (molar mass) M, or $m = nM$

$\therefore$ For each of the components we can write,

$$n_m M_m = n_a M_a + n_b M_b + n_c M_c + \ldots\ldots$$

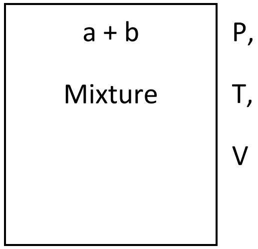
Where M_m is the average molar mass or molecular weight of the mixture.

Or $M_m = y_a M_a + y_b M_b + y_c M_c$

Thus, the average molecular weight of a gas mixture is the sum of the products of all the components of the mole fraction and corresponding molecular weight of each component.

Note: Universal gas constant $\bar{R} = MR$ where M = molecular weight, R: specific gas constant, and =8.3143 kJ/kg-mole K

Partial Pressure:


a + b

Mixture

P,

T,

V

a & b = gases of the mixture

V = Total volume of the mixture

T = Temperature of the mixture

P = Pressure of the mixture

Partial pressure of a constituent in a mixture is the pressure exerted when it alone occupies the mixture volume at mixture temperature. If P_a is partial pressure of gas ‘a’, then

$$P_aV = m_aR_aT$$

Where m_a = mass of gas ‘a’, R_a = gas constant for gas ‘a’, similarly $P_bV = m_bR_bT$

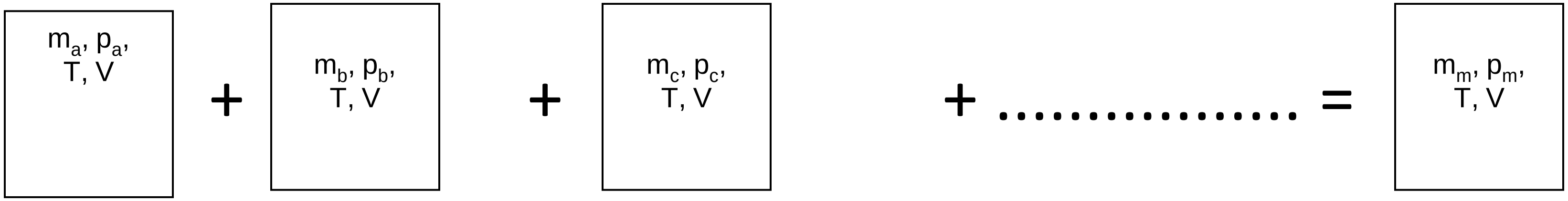
Partial Volume:

Partial volume of a gas in a mixture is the volume occupied by the gas component at mixture pressure and temperature. Let V_a = partial volume of gas ‘a’ and V_b = partial volume of gas ‘b’

i.e., $PV_a = m_aR_aT$ & $PV_b = m_bR_bT$

The Gibbs-Dalton Law:

Consider a mixture of gases, each component at the temperature of the mixture occupying the entire volume occupied by the mixture, and exerting only a fraction of the total pressure as shown in figure.



$m_a, p_a,$ T, V + $m_b, p_b,$ T, V + $m_c, p_c,$ T, V + ... = $m_m, p_m,$ T, V

Applying the equation of state for this mixture we may write,

$$P_m V = m_m R_m T = n_m M_m R_m T = n_m \overline{R} T$$

$$Similarly \quad p_a V = n_a \overline{R} T$$

$$p_b V = n_b \overline{R} T \qquad p_c V = n_c \overline{R} T$$

We know that $n_m = n_a + n_b + n_c + \ldots\ldots$

$$Hence \quad \frac{p_m V}{\overline{R}T} = \frac{p_a V}{\overline{R}T} + \frac{p_b V}{\overline{R}T} + \frac{p_c V}{\overline{R}T} + \ldots\ldots.$$

Or $\quad p_m = p_a + p_b + p_c + \ldots\ldots \Big|_{V,T} = \Sigma p_i$

The above equation is known as the Gibbs Dalton Law of partial pressure, which states that the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the individual components, if each component is considered to exist alone at the temperature and volume of the mixture.

Gas constant for the mixture:

We have $P_aV = m_aR_aT$

$P_bV = m_bR_bT$

Or $(P_a + P_b) V = (m_aR_a + m_bR_b) T$

Also, since the mixture behaves like a perfect gas,

We have $PV = mRT$ --- (1)

By Dalton’s law of partial pressure,

i.e., $P = P_a + P_b$

$\therefore PV = (m_aR_a + m_bR_b) T$ --- (2)

From equation (1) and (2), $mR = m_aR_a + m_bR_b$

$$\therefore R = \frac{m_aR_a + m_bR_b}{m}$$

Also for gas mixture, $P_aV = m_aR_aT$

$$= n_aM_aR_aT$$

$$\therefore P_aV = n_a\overline{R}T \quad \left(\because MR = \overline{R}\right)$$

Similarly $PV = n\overline{R}T$

$$\therefore \frac{P_a}{P} = \frac{n_a}{n} = y_a$$

Similarly it can be shown that mole fraction = volume fraction

$$Hence, \quad y_a = \frac{P_a}{P} = \frac{n_a}{n} = \frac{V_a}{V}$$

Molecular weight of the mixture:

We have, $P_aV = m_aR_aT$

$P_aV = n_aM_aR_aT$ Similarly $P_bV = n_{b-}M_bR_bT$

$\therefore (P_a + P_b)\, V = (n{-}_aM_aR_a + n_bM_bR_b)\, T$

Also $PV = nMRT$

By Dalton's law of partial pressure, $P = P_a + P_b$

$\therefore nMRT = (n_aM_aR_a + n_bM_bR_b)\, T$

$MR = y_aM_aR_a + y_bM_bR_b$

$$\therefore M = \frac{y_a M_a R_a + y_b M_b R_b}{R}$$

Also, $mR = m_a R_a + m_b R_b$

$$R = m_{fa} R_a + m_{fb} R_b$$

$$But \quad R = \frac{\overline{R}}{M}; R_a = \frac{\overline{R}}{M_a}, R_b = \frac{\overline{R}}{M_b}$$

$$\therefore \frac{\overline{R}}{M} = m_{f_a} . \frac{\overline{R}}{M_a} + m_{f_b} . \frac{\overline{R}}{M_b}$$

$$i.e., \quad \frac{1}{M} = \frac{m_{fa}}{M_a} + \frac{m_{fb}}{M_b} = \frac{m_{fa}.M_b + m_{fb}.M_a}{M_a M_b}$$

$$\therefore M = \frac{M_a M_b}{m_{fa}.M_b + m_{fb}.M_a}$$

The Amagat-Leduc Law:

Expresses the law of additive volume which, states that the volume of a mixture of gases is equal to the sum of the volumes of the individual components at the pressure and temperature of the mixture.

i.e., $V_m = V_a + V_b + V_c \ldots \big|_{P,\,T} = \sum_i V_i$

For Dalton law, $P_m = P_a + P_b + P_c + \ldots \big|_{V,\,T} = \sum_i P_i$

Gibb's Law:

It states that the internal energy, the enthalpy and the entropy of a mixture of gas is equal to sum of the internal energies, the enthalpies and entropies respectively of the individual gases evaluated at mixture temperature and pressure.

$$\therefore U = U_a + U_b$$

$$mU = m_aU_a + m_bU_b$$

$$U = m_{fa}U_a + m_{fb}U_b$$

$$\therefore \frac{dU}{dT} = m_{fa}\frac{dU_a}{dT} + m_{fb}\frac{dU_b}{dT} \quad C_V = m_{fa}(C_V)_a + m_{fb}(C_V)_b$$

Similarly $C_P = m_{fa} (C_p)_a + m_{fb} (C_p)_b$

If $\overline{C_V} =$ Specific heat at constant volume on mole basis

$\overline{C_P} =$ Specific heat at constant pressure on mole basis

$$\overline{C_V} = y_a\left(\overline{C_V}\right)_a + y_b\left(\overline{C_V}\right)_b \quad \&$$

$$\overline{C_P} = y_a\left(\overline{C_P}\right)_a + y_b\left(\overline{C_P}\right)_b$$

Isentropic process of gaseous mixture: When a mixture of say two gases, a & b, is compressed or expanded isentropically, the entropy of the mixture remains constant i.e., there is no change in the entropy of the entire system. i.e., $\Delta S_m = \Delta S_a + \Delta S_b = 0$

Entropy of a Gas Mixture:

Entropy of a gas mixture $S_m = S_a + S_b + S_c + \ldots\ldots.$

The specific entropy on the mass basis

$$S_m = m_{fa}\, s_a + m_{fb}\, s_b + m_{fc}\, s_c + \ldots.. = \sum_i m_{fi} s_i$$

On differentiating we get

$$(dS)_m = m_{fa}\,(ds)_a + m_{fb}\,(ds)_b + m_{fc}\,(ds)_c + \ldots\ldots$$

Expressing the entropy of a perfect gas as a function of temperature and pressure, the change in entropy is given by

$$dS = c_p \frac{dT}{T} - R\frac{dp}{p}$$

On substituting this expression in the above equation, the change in entropy of a gas mixture in the differential form becomes

$$(dS)_m = m_{fa}\left[(c_p)_a \frac{dT}{T} - R_a \frac{dp_a}{p_a}\right] + m_{fb}\left[(c_p)_b \frac{dT}{T} - R_b \frac{dp_b}{p_b}\right] + m_{fc}\left[(c_p)_c \frac{dT}{T} - R_c \frac{dp_c}{p_c}\right] + \ldots\ldots$$

Assuming the specific heats as constant and integrating the above equation between states (1) and (2), the change in entropy of the perfect gas mixture on the mass basis can be written as

$$(s_2 - s_1)_m = m_{fa}\left[(c_p)_a \ln\frac{T_2}{T_1} - R_a \ln\frac{p_{a,2}}{p_{a,1}}\right] + m_{fb}\left[(c_p)_b \ln\frac{T_2}{T_1} - R_b \ln\frac{p_{b,2}}{p_{b,1}}\right]$$

$$+ m_{fc}\left[(c_p)_c \ln\frac{T_2}{T_1} - R_c \ln\frac{p_{c,2}}{p_{c,1}}\right] + \ldots..$$

Similarly the change in entropy in the gas mixture on molal basis

$$\left(\bar{s}_2 - \bar{s}_1\right)_m = y_a\left[\left(\bar{c}_p\right)_a \ln\frac{T_2}{T_1} - \bar{R}_a \ln\frac{p_{a,2}}{p_{a,1}}\right] + y_b\left[\left(\bar{c}_p\right)_b \ln\frac{T_2}{T_1} - \bar{R}_b \ln\frac{p_{b,2}}{p_{b,1}}\right]$$

$$+ y_c\left[\left(\bar{c}_p\right)_c \ln\frac{T_2}{T_1} - \bar{R}_c \ln\frac{p_{c,2}}{p_{c,1}}\right] + \ldots.$$

where $p_{a,1}$, $p_{b,1}$ $p_{c,1}$ etc are partial pressures at state one and $p_{a,2}$, $p_{b,2}$ $p_{c,2}$ etc are partial pressures at state 2 of the constituent gases, a, b, c, etc respectively.

Isentropic process of gaseous mixture:

When the mixture of gases is compressed or expanded from state (1) to state (2) isentropically, we have

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{\gamma_m - 1}{\gamma_m}}$$

Where γ_m is the specific heat ratio of the gaseous mixture, which is given by

$$\gamma_m = \frac{\left(c_p\right)_m}{\left(c_v\right)_m} = \frac{m_{fa}\left(c_p\right)_a + m_{fb}\left(c_p\right)_b}{m_{fa}\left(c_v\right)_a + m_{fb}\left(c_v\right)_b}$$

$$= \frac{m_a\left(c_p\right)_a + m_b\left(c_p\right)_b}{m_a\left(c_v\right)_a + m_b\left(c_v\right)_b}$$

On molal basis

$$\bar{\gamma}_m = \frac{\left(\bar{c}_p\right)_m}{\left(\bar{c}_v\right)_m} = \frac{y_a\left(\bar{c}_p\right)_a + y_b\left(\bar{c}_p\right)_b}{y_a\left(\bar{c}_v\right)_a + y_b\left(\bar{c}_v\right)_b}$$

$$= \frac{n_a\left(\bar{c}_p\right)_a + n_b\left(c_p\right)_b}{n_a\left(\bar{c}_v\right)_a + n_b\left(\bar{c}_v\right)_b}$$

Volumetric and Gravimetric Analysis:

When the analysis of a gaseous mixture is based on the measurement of volume, it is called a volumetric analysis, whereas when it is based on the measurement of mass, it is called the gravimetric analysis.

Real gas

- Real gas behaviour can be shown by a perfect gas at the changed thermodynamic states such as high pressure.
- Deviation of real gas from ideal gas necessitates the suitable equation of state which can be used for interrelating the thermodynamic properties P,V,T.
- A number of mathematical equations of state suggested by **Vander- Waals**, Berthelot, Dieterici, Redlich – Kwong, Beattie-Bridgeman are available for analysing the real gas behaviour.

Vander Waals' Equation of State:

In deriving the equation of state for perfect gases it is assumed that the volume occupied by the molecules of the gas in comparison to the total volume occupied by the gas and the force of attraction between the adjacent molecules is very small and hence the molecules of gas are neglected.

At low pressures, where the mean free path is large compared to the size of the molecules, these assumptions are quite reasonable. But at high pressure, where the molecules come close to each other, these are far from correct.

Vander Waals' equation introduces terms to take into account of these two modifying factors into the equation of state for a perfect gas.

The Vander Waals' equation of state is given by,

$$\left[P+\frac{a}{v^2}\right](v-b)=RT \qquad \text{--- (1)}$$

$$or \quad P=\frac{RT}{v-b}-\frac{a}{v^2}$$

P = Pressure, v = Volume/unit mass, R = gas constant

where a and b are constants for any one gas, which can be determined experimentally, the constants account for the intermolecular attractions and finite size of the molecules which were assumed to be non-existent in an ideal gas. The term accounts for the intermolecular forces i.e., force of cohesion and the term b was introduced to account for the volume occupied by the molecules i.e., co-volume.

If the volume of one mole is considered, then the above equation can be written as,

$$\left[P+\frac{a}{\bar{v}^{2}}\right]\left(\bar{v}-b\right)=\bar{R}T$$

Units P (N/m^2),

$$\bar{v}\left(m^{3}/kg-mole\right)$$

$$\bar{R}\quad 8314\,Nm/kg-mol^{0}K \quad Or \quad \bar{R}=0.083143\,bar\;m^{3}/kg-mol^{0}K$$

$$a\quad (Nm^{4}/\left(kg-mol\right)^{2}$$

$$b\quad m^{3}/kg-mol$$

Determination of Vander Waals constants in terms of critical properties:

The determination of two constants a and b in the Vander Waals equation is based on the fact that the critical isotherm on a p-v diagram has a horizontal inflexion point at the critical point. Therefore the first and second derivative of P with respect v at the critical point must be zero.

$$i.e., \quad \left(\frac{\partial p}{\partial v}\right)_{T=T_c} = 0 \, and \left(\frac{\partial^2 p}{\partial v^2}\right)_{T=T_c} = 0$$

From equation (1) we have, $$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\therefore \left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3}$$

$$and\left(\frac{\partial^2 p}{\partial v^2}\right)_T = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4}$$

At critical points the above equation reduces to

$$\frac{-RT}{(v-b)^2} + \frac{2a}{v^3} = 0$$ --- (2a)

$$and\ \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$$ --- (2b)

Also from equation (1) we have, $P_c = \frac{RT_c}{v-b} - \frac{a}{v^2}$ --- (2c)

Dividing equation (2a) by equation (2b) and simplifying we get $b = \frac{v_c}{3}$

Substituting for b and solving for 'a' from equation (2b) we get

$a = 9RT_c v_c$

Substituting these expressions for a and b in equation (2c) and solving for v_c, we get

$$v_c = \frac{3RT_c}{8p_c}$$

$$\therefore b = \frac{RT_c}{8p_c}$$

$$and \quad a = \left(\frac{27}{64}\right)\frac{R^2T_c^{\,2}}{p_c}$$

If the volume of one mole is considered then the above equation can be written as

$$\left(P + \frac{a}{\bar{v}^2}\right)\left(\bar{v} - b\right) = \bar{R}T$$

Units: P (N/m^2), $\bar{v}\left(m^3 / kg - mol\right)$

R = 8314 Nm/kg mol^{0}K $\overline{R} = 0.083143\, bar \frac{m^3}{kg - mole\ K}$

a = Nm^4 / (kg–mol)^2 Or bar (m^3/kg-mole)^2 b = m^3/kg-mol

Note: Usually constants a and b for different gases are given.

Compressibility Factor and Compressibility Chart:

The specific volume of a gas becomes very large when the pressure is low or temperature is high. Thus it is not possible to conveniently represent the behaviour of real gases at low pressure and high temperature.

For a perfect gas, the equation of state is Pv = RT. But, for a real gas, a correction factor has to be introduced in the perfect gas to take into account the deviation of the real gas from the perfect gas equation. This factor is known as the compressibility factor, Z and is defined as,

$$Z = \frac{Pv}{RT}$$

Z = 1 for a perfect gas. For real gases the value of Z is finite and it may be less or more than unity depending on the temperature and pressure of the gas.

Reduced Properties:

- The real gases follow closely the ideal gas equation only at low pressures and high temperatures. The pressures and temperatures depend on the critical pressure and critical temperature of the real gases.
- For example – 100^0C is a low temperature for most of the gases, but not for air or nitrogen. Air or nitrogen can be treated as ideal gas at this temperature and atmospheric pressure with an error which is <1%.
- This is because nitrogen is well over its critical temperature of -147^0C and away from the saturation region. At this temperature and pressure most of the substances would exist in solid phase. Hence, the pressure and temperature of a substance is high or low relative to its critical pressure or temperature.

Gases behave differently at a given pressure and temperature, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures. The ratios of pressure, temperature and specific volume of a real gas to the corresponding critical values are called the reduced properties.

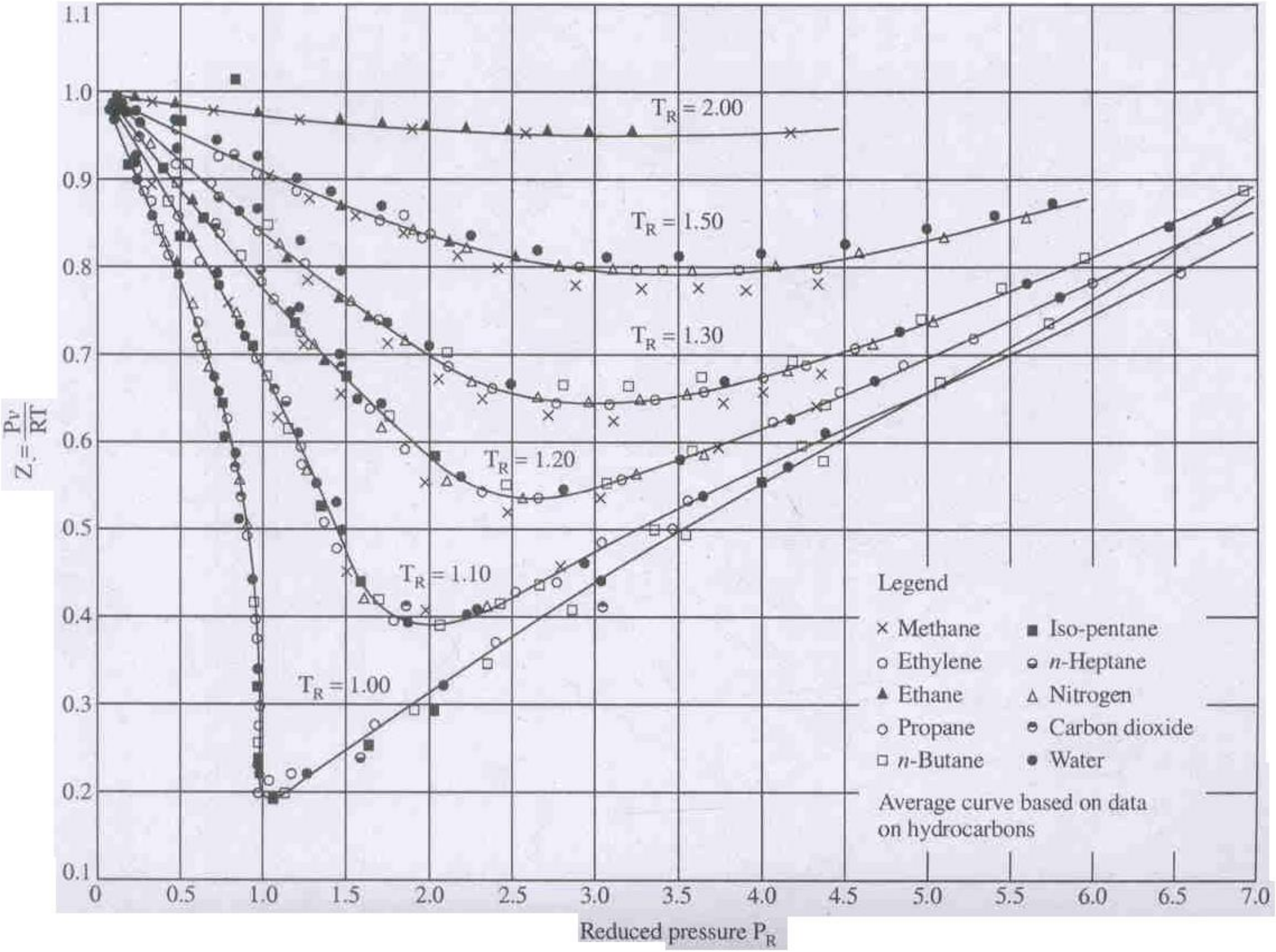
$$i.e., \quad P_R = \frac{P}{P_c}, \quad T_R = \frac{T}{T_c} \,\&\, v_R = \frac{v}{v_c}$$

Law of Corresponding states:

- This law is used in the approximate determination of the properties of real gases when their properties at the critical state are known.
- According to this law, there is a functional relationship for all substances, which may be expressed mathematically as $v_R = f(P_R, T_R)$.
- From this law it is clear that if any two gases have equal values of reduced pressure and reduced temperature, they will have the same value of reduced volume.
- This law is most accurate in the vicinity of the critical point.

Generalized Compressibility Chart:

- The compressibility factor of any gas is a function of only two properties, usually temperature and pressure so that $Z_1 = f\ (T_R, P_R)$ except near the critical point. This is the basis for the generalized compressibility chart.
- The generalized compressibility chart is plotted with Z versus P_R for various values of T_R. This is constructed by plotting the known data of one or more gases and can be used for any gas.


$Z = \frac{Pv}{RT}$
Reduced pressure P_R
$T_R = 2.00$
$T_R = 1.50$
$T_R = 1.30$
$T_R = 1.20$
$T_R = 1.10$
$T_R = 1.00$
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Legend
× Methane
○ Ethylene
▲ Ethane
○ Propane
□ n-Butane
■ Iso-pentane
◒ n-Heptane
△ Nitrogen
◓ Carbon dioxide
● Water
Average curve based on data on hydrocarbons

It may be seen from the chart that the value of the compressibility factor at the critical state is about 0.25. Note that the value of Z obtained from Vander Waals equation of state at the critical point, $Z_c = \frac{P_c v_c}{RT_c} = \frac{3}{8}$ which is higher than the actual value.

The following observations can be made from the generalized compressibility chart:

At very low pressures (P_R <<1), the gases behave as an ideal gas regardless of temperature.

At high temperature ($T_R > 2$), ideal gas behaviour can be assumed with good accuracy regardless of pressure except when (P_R >> 1).

The deviation of a gas from ideal gas behaviour is greatest in the vicinity of the critical point.

The compressibility factor can also be obtained from v-T or v-P data. Since the critical volume may not be consistent with the generalized chart, the pseudo critical specific volume v_c^1 is used in the definition of reduced volume. It is defined by .

$$v_c^1 = RT_c / P_c$$

The pseudo reduced volume v_c^1 is defined as

$$v_R^1 = \frac{v}{v_c^1} = \frac{vP_c}{RT_c}$$