CH2303 Chemical Engineering Thermodynamics I

Unit – I

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Basic Concepts

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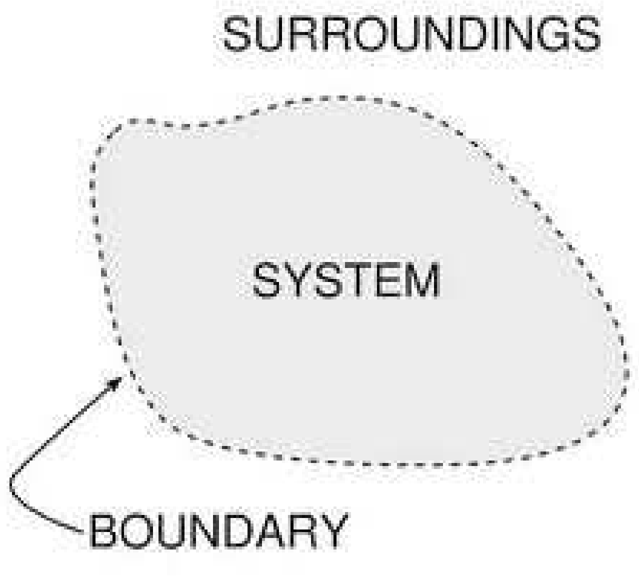
Contents

- The terminologies of thermodynamics, the variables and quantities of thermodynamics:
  - Categorization of systems and processes.
  - point and path properties
  - Energy classifications
  - energy in transition, heat and work
  - reversible and irreversible processes
  - phase rule

Categorization of Systems and Processes

- System and Surroundings
  - Open, closed, isolated systems
- Intensive and extensive properties
- Point and path properties
- Thermodynamic processes
  - Constant pressure, constant volume, constant temperature, adiabatic, polytropic

System and Surrounding



System: Quantity of matter or a region of space which is under consideration in the analysis of a problem.

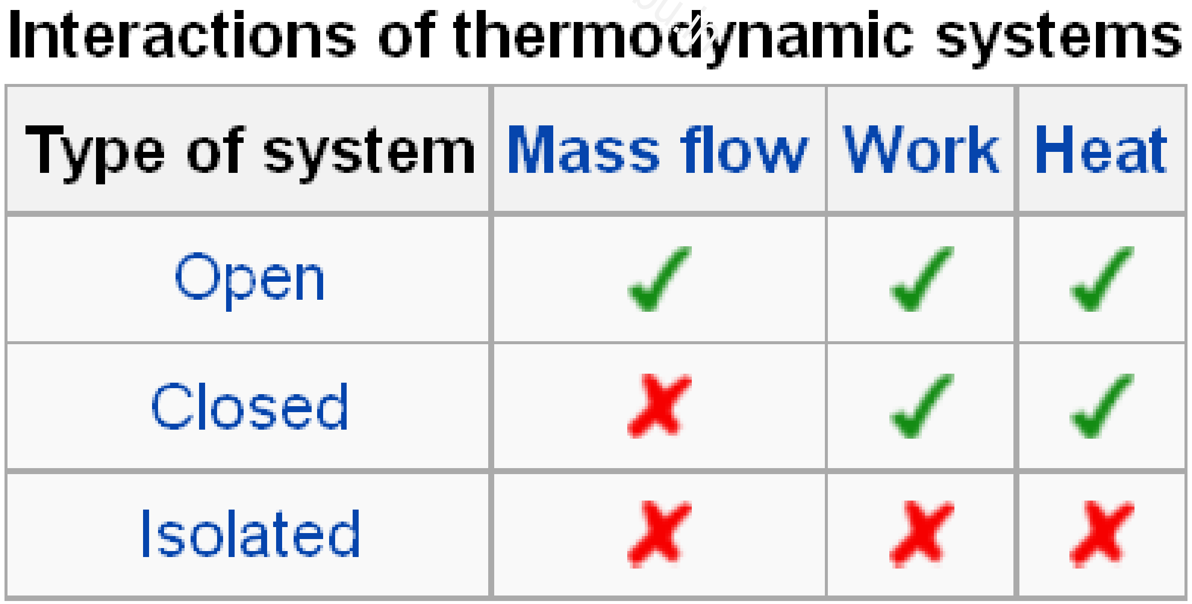
Surroundings: Anything outside the thermodynamic system is called the surroundings. The system is separated from the surroundings by the boundary. The boundary may be either fixed or moving.

Types of Thermodynamic Systems

- **Open system**: There may be both matter and energy transfer across the boundary of the system.

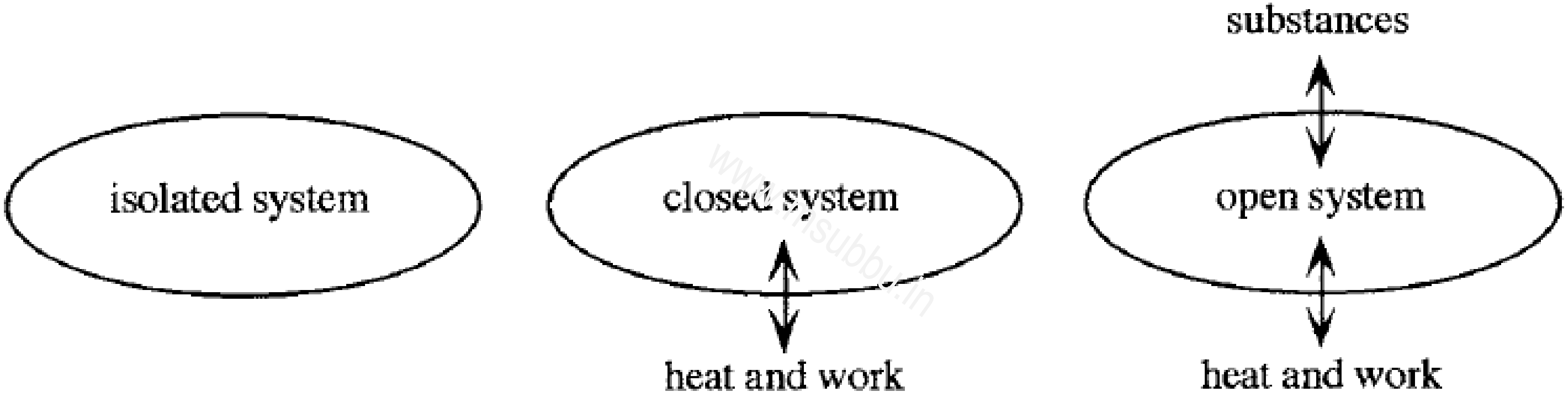
- **Closed system**: There is no mass transfer across the system boundary. Energy transfer may be there.

- **Isolated system**: There is neither matter nor energy transfer across the boundary of the system.

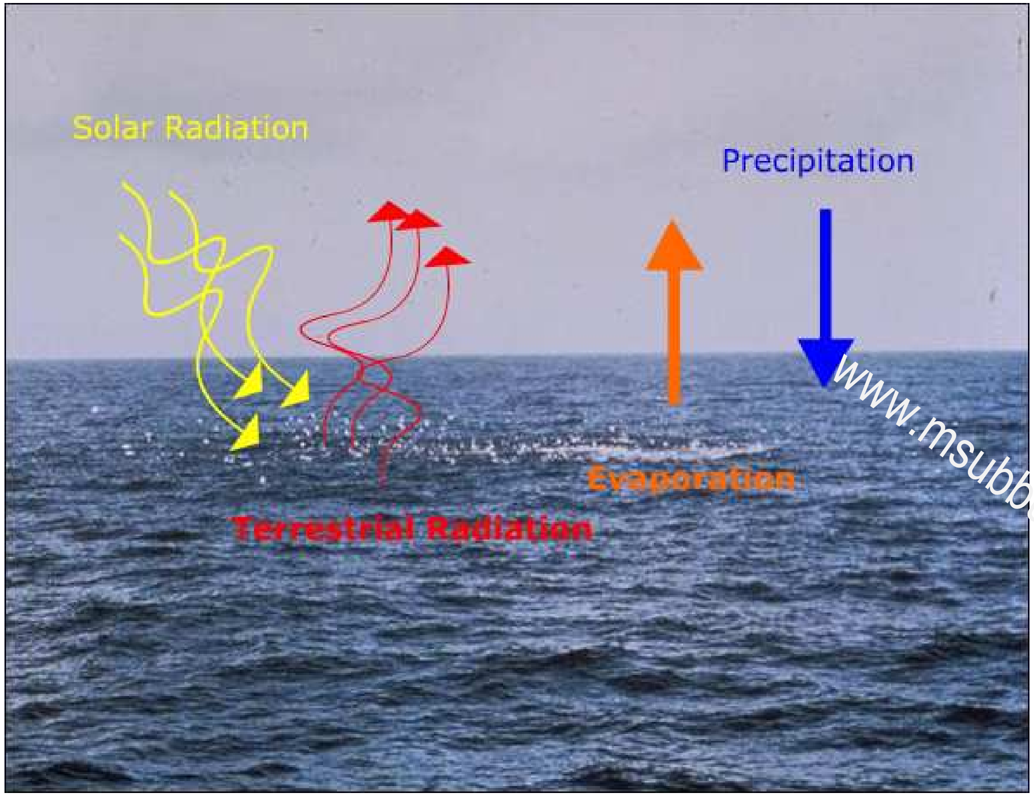


Interactions of thermodynamic systems

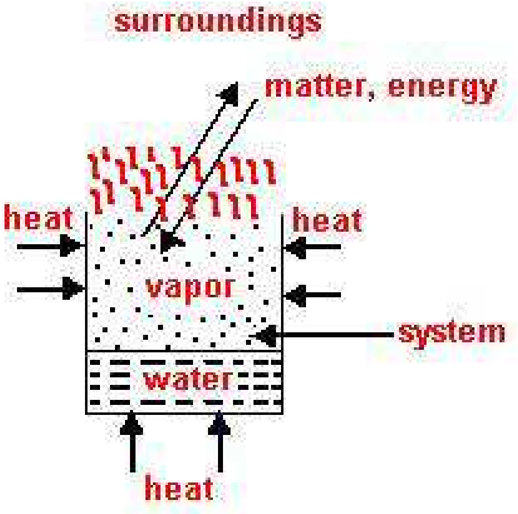
Type of system	Mass flow	Work	Heat
Open	✓	✓	✓
Closed	✗	✓	✓
Isolated	✗	✗	✗


substances
isolated system
closed system
open system
heat and work
heat and work

Open System - Example



An **open system** is one that allows energy and mass exchange across the system boundary. Most natural systems are open systems. Ocean is an open system.



An open system

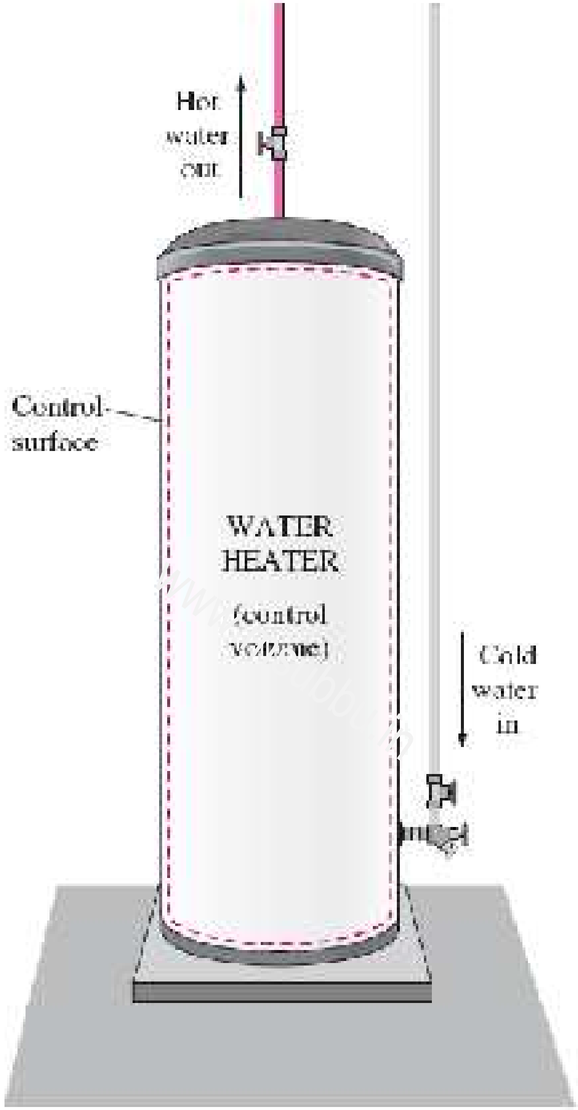
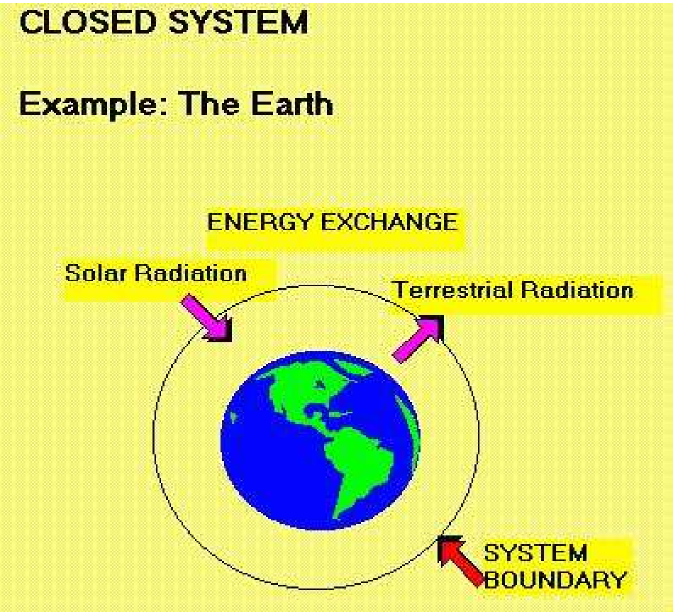
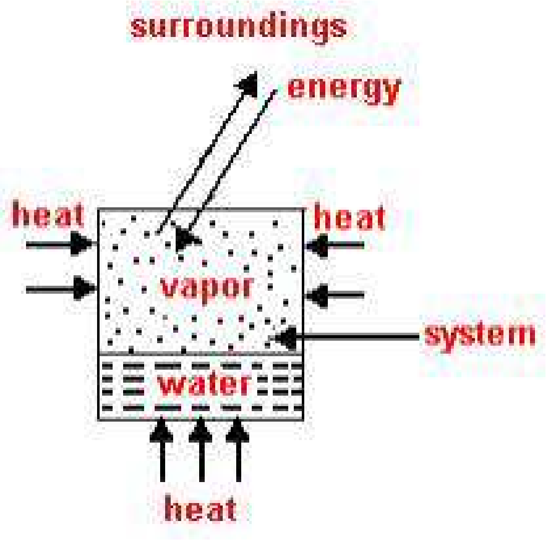


FIGURE 1–19

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

Closed System - Example

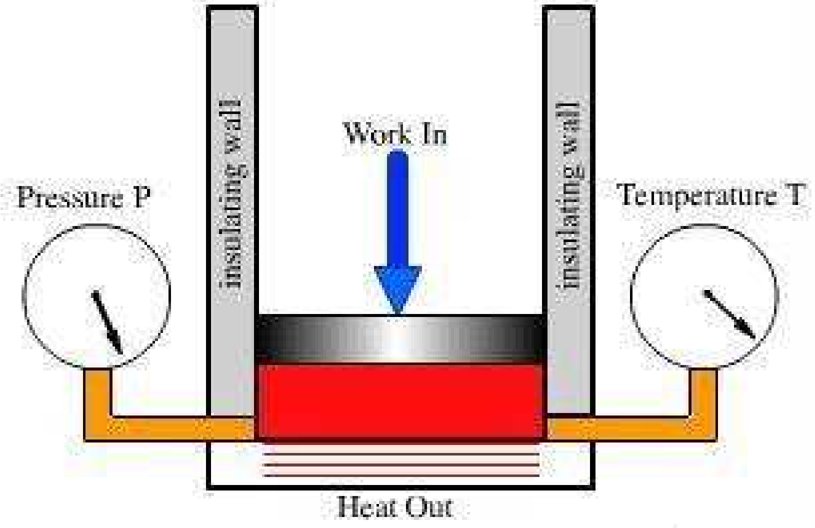


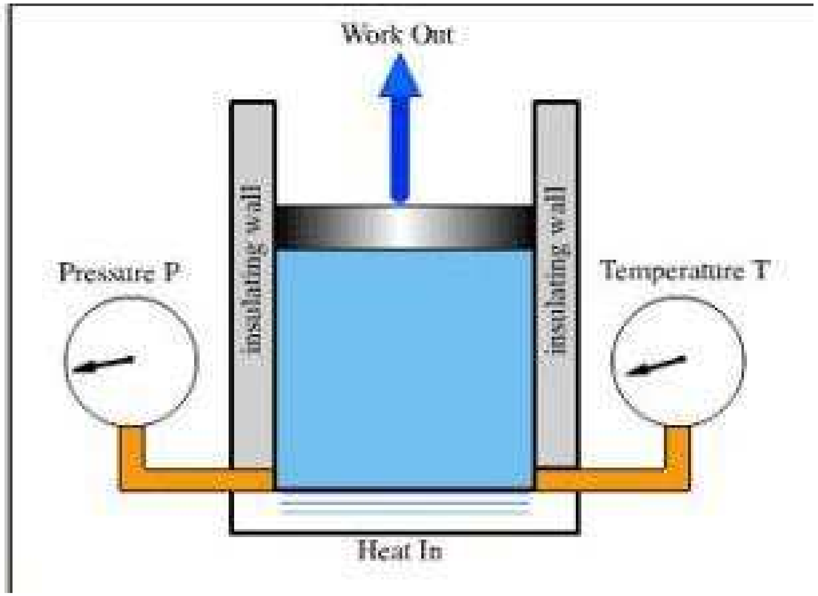


The Earth system *as a whole* is a closed system. The boundary of the Earth system is the outer edge of the atmosphere.

Virtually no mass is exchanged between the Earth system and the rest of the universe (except for an occasional meteorite).

However, energy in the form of solar radiation passes from the Sun, through the atmosphere to the surface. The Earth in turn emits radiation back out to space across the system boundary.





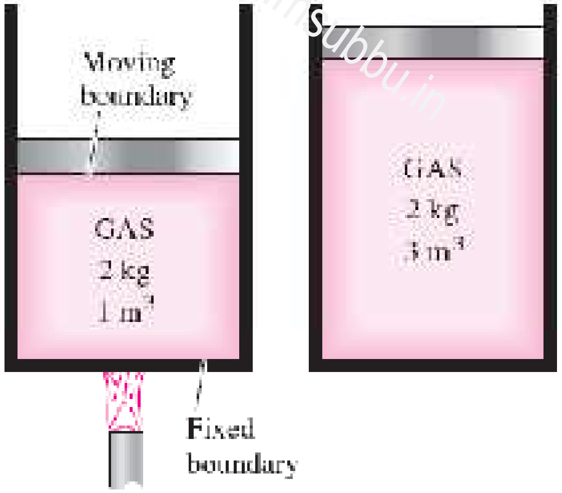


FIGURE 1–17

A closed system with a moving boundary.

Pressure Cooker as a Closed System

Cooking in a pot - Open system;

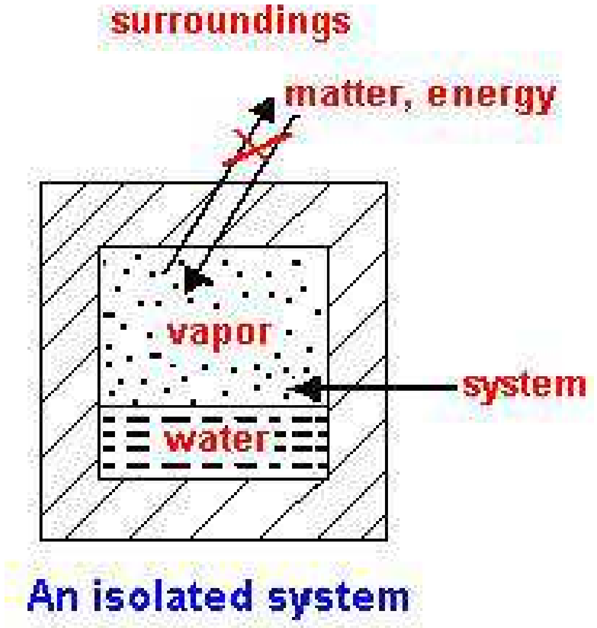
As mass in the form of water vapor is crossing the boundary of system (i.e. pot)

Cooking with pressure-cooker - Closed system (while it's not whistling)

Courtesy: the example as given by Mr. S. Mohan Kumar, 2009-2013 batch)

Isolated System

Universe



An isolated system

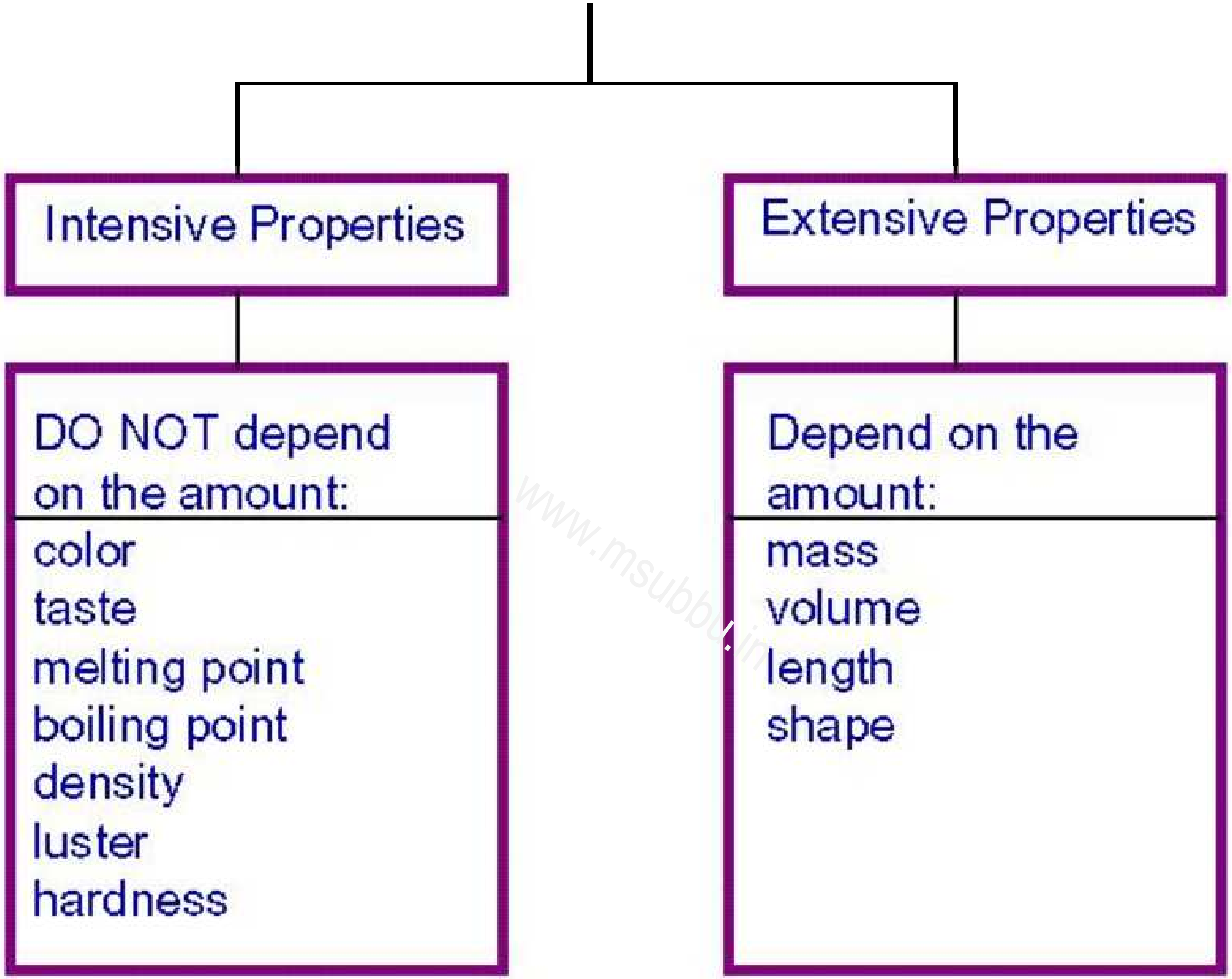
Macroscopic system and its properties

If a system contains a large number of chemical species such as atoms, ions, and molecules, it is called macroscopic system.

- **Extensive properties**: These properties depend upon the quantity of matter contained in the system. Examples are; mass, volume, heat capacity, internal energy, enthalpy, entropy, Gibb's free energy.

- **Intensive properties:** These properties does not depend upon the amount of the substance present in the system, for example, temperature, refractive index, density, surface tension, specific heat, freezing point, and boiling point.

Properties



Intensive Properties

DO NOT depend on the amount:

- color
- taste
- melting point
- boiling point
- density
- luster
- hardness

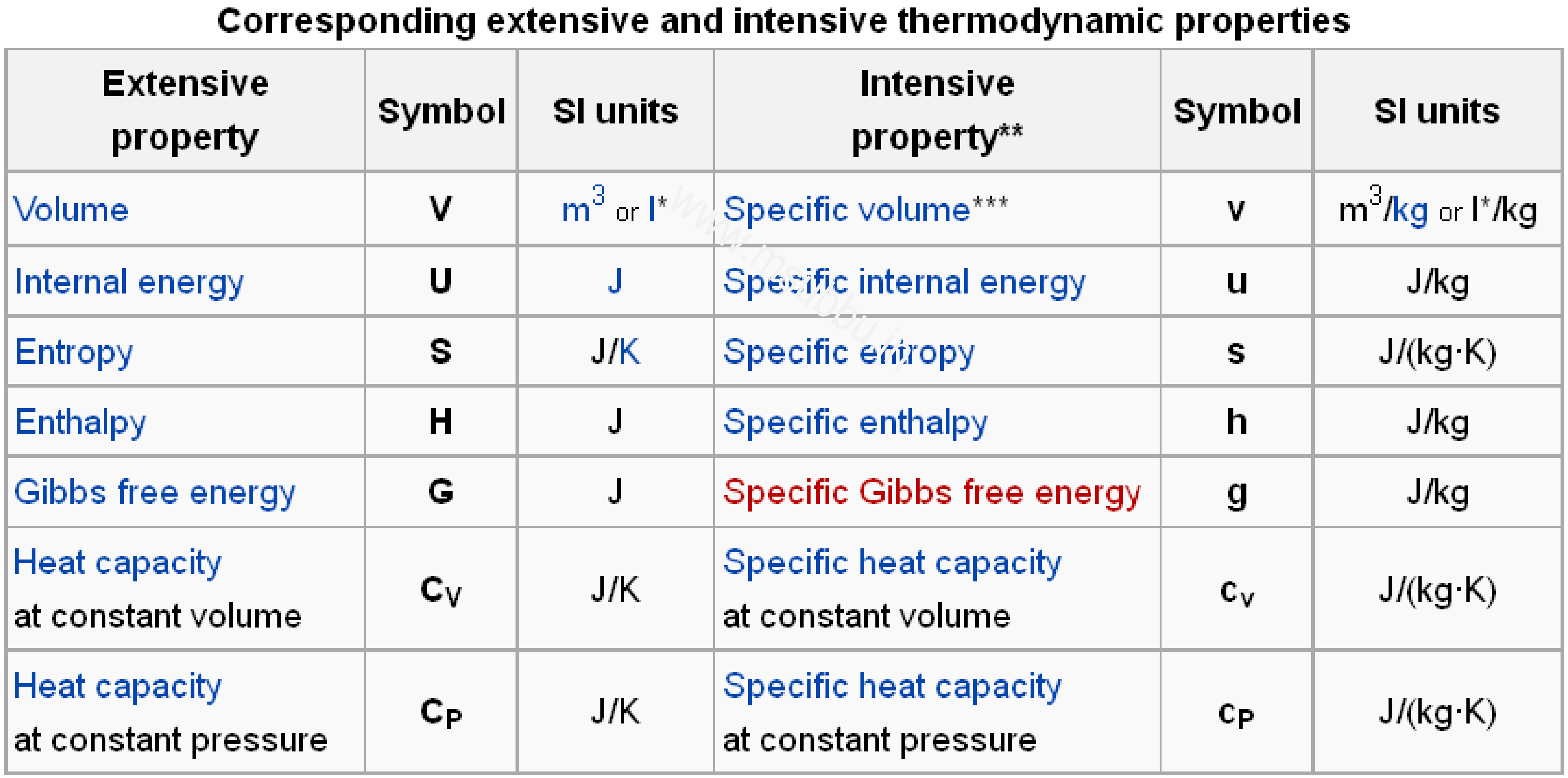
Extensive Properties

Depend on the amount:

- mass
- volume
- length
- shape

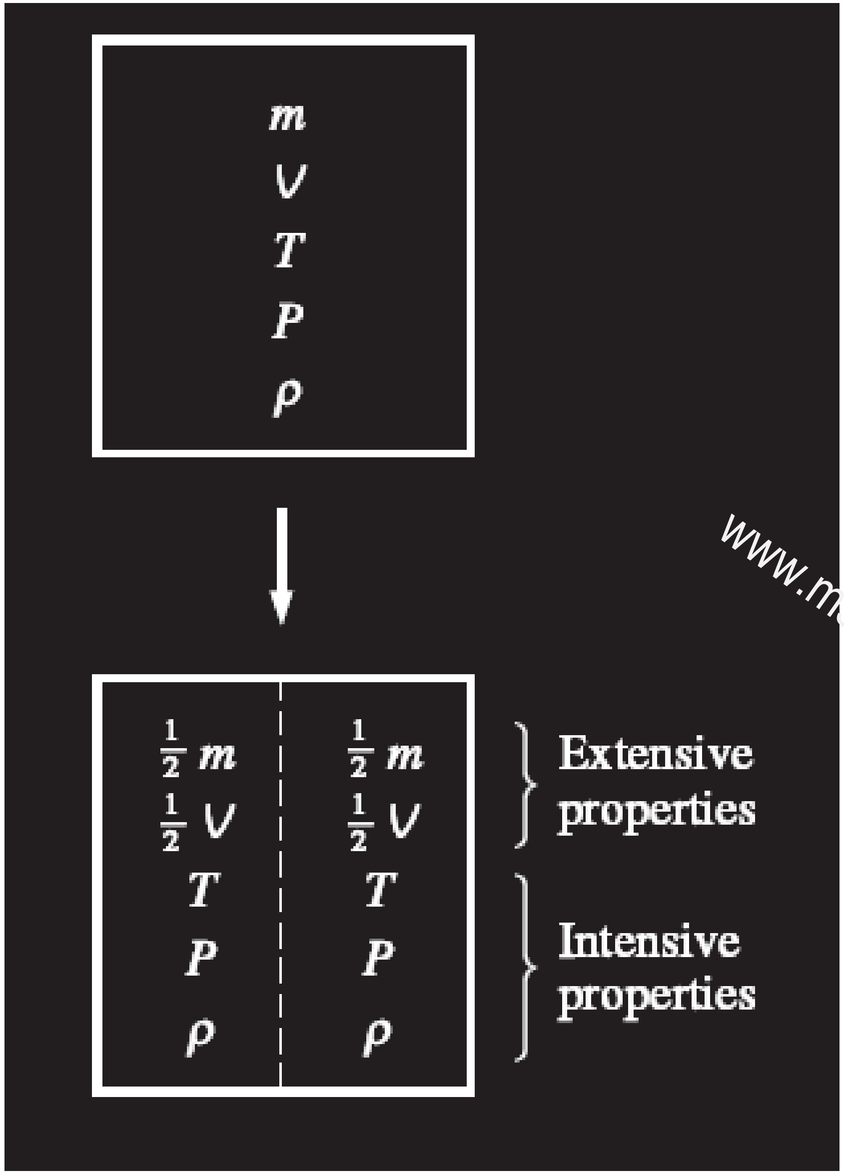
Note: most of the above are not thermodynamic properties

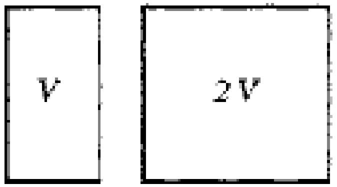
Dividing one type of extensive property by a different type of extensive property will in general give an intensive value. For example, mass (extensive) divided by volume (extensive) gives density (intensive).



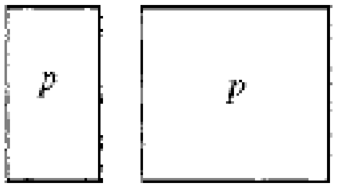
Corresponding extensive and intensive thermodynamic properties

Extensive property	Symbol	SI units	Intensive property**	Symbol	SI units
Volume	V	m^3 or l*	Specific volume***	v	m^3/kg or l*/kg
Internal energy	U	J	Specific internal energy	u	J/kg
Entropy	S	J/K	Specific entropy	s	J/(kg·K)
Enthalpy	H	J	Specific enthalpy	h	J/kg
Gibbs free energy	G	J	Specific Gibbs free energy	g	J/kg
Heat capacity at constant volume	C_V	J/K	Specific heat capacity at constant volume	c_V	J/(kg·K)
Heat capacity at constant pressure	C_P	J/K	Specific heat capacity at constant pressure	c_P	J/(kg·K)





Extensive variable V



Intensive variable p

Equilibrium

- The word **equilibrium** implies a state of balance. In an equilibrium state there are no unbalanced potentials (or driving forces) within the system. A system in equilibrium experiences no changes when it is isolated from its surroundings. Thermodynamics deals with equilibrium states.
- There are many types of equilibrium, and a system is not in thermodynamic equilibrium unless the conditions of all the relevant types of equilibrium are satisfied.
  - a system is in **thermal equilibrium** if the temperature is the same throughout the entire system
  - **Mechanical equilibrium** is related to pressure, and a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time.
  - If a system involves two phases, it is in **phase equilibrium** when the mass of each phase reaches an equilibrium level and stays there.
  - a system is in **chemical equilibrium** if its chemical composition does not change with time, that is, no chemical reactions occur.

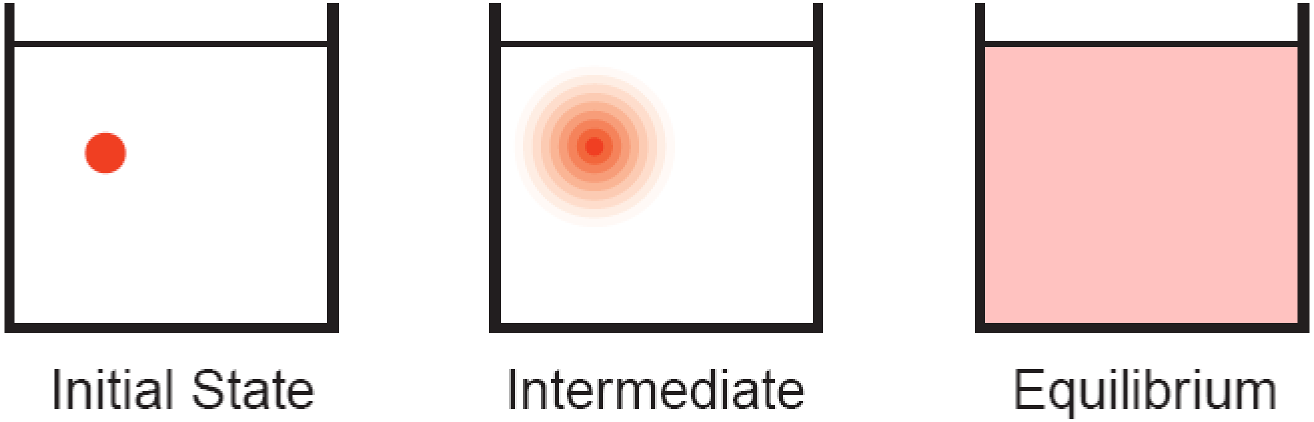


Figure 3.1: Diffusion of a drop of dye in water.

Thermodynamics deals primarily with the properties of matter in the simple-to-describe equilibrium states. To describe matter in non-equilibrium states, we would have to supplement thermodynamics with results from the theories of fluid mechanics, diffusion, heat conduction, electromagnetics, or other areas of physics beyond the scope of thermodynamics. The nature of these states and how they evolve with time is the subject of courses in these other fields.

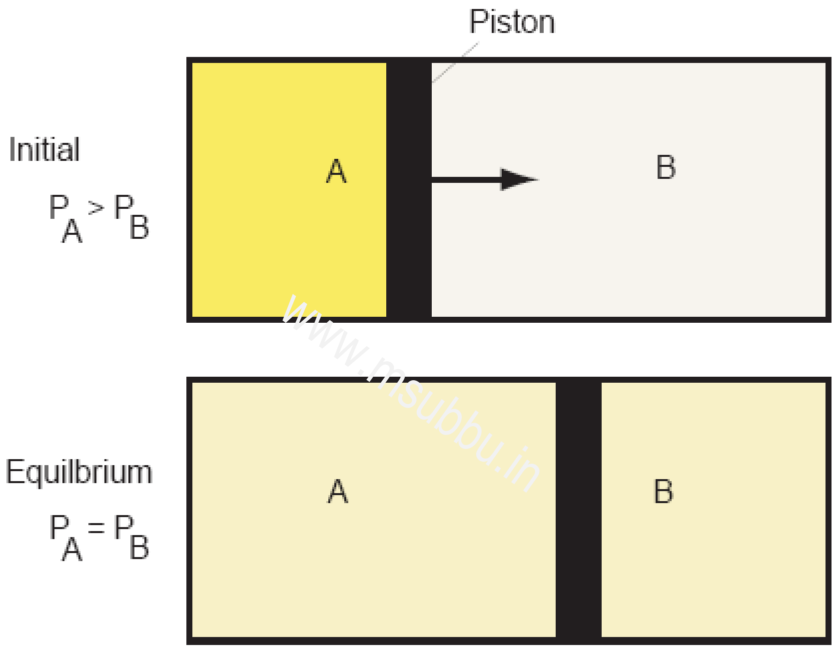


Figure 3.2: Mechanical equilibrium: the piston moves until $P_A = P_B$.

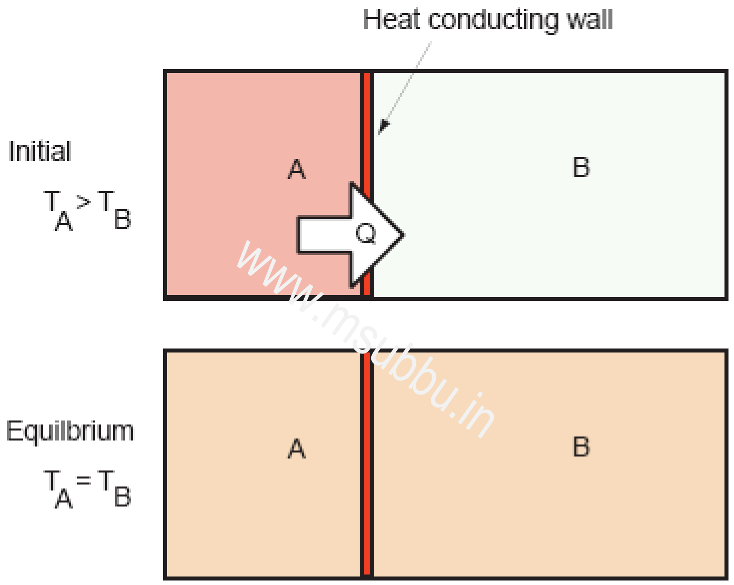


Figure 3.3: Thermal equilibrium: heat flows until $T_A = T_B$.

3.2.6 Thermodynamic Equilibrium

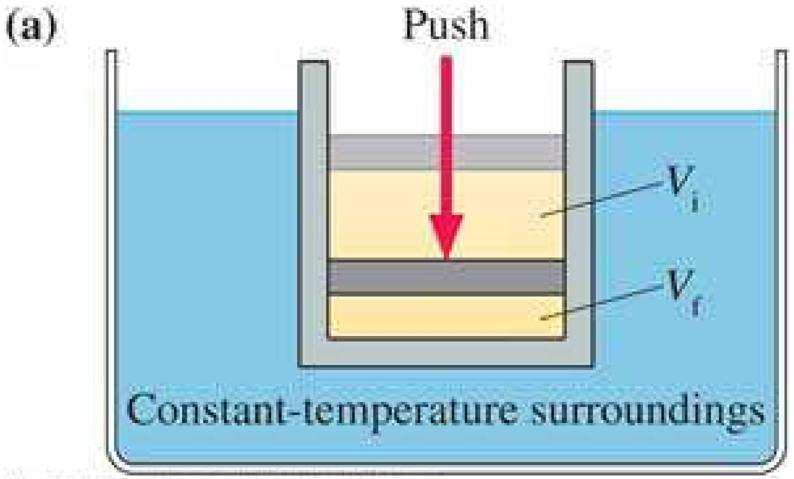
When all parts of a system are equilibrated in all ways (mechanical, thermal, diffusive, phase, chemical), we say the system is in *thermodynamic equilibrium*. The temperature, pressure, and chemical potential will be the same in all parts of a system in thermodynamic equilibrium, and the concentrations of every chemical species will be constant in time.

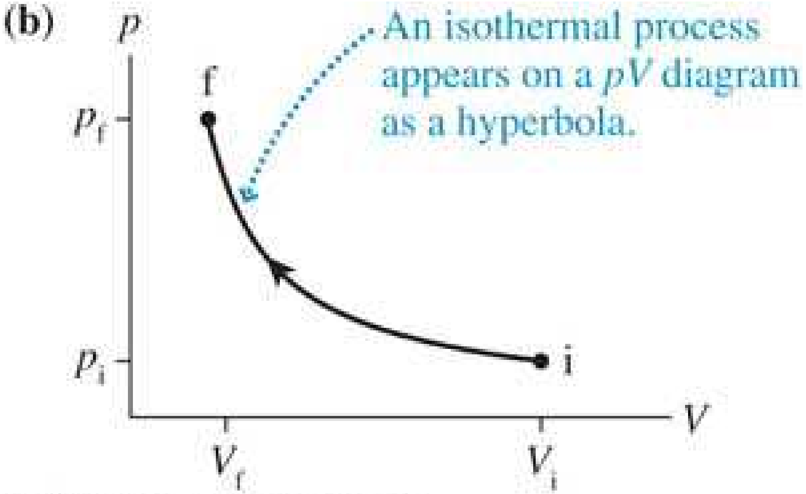
Types of thermodynamic processes

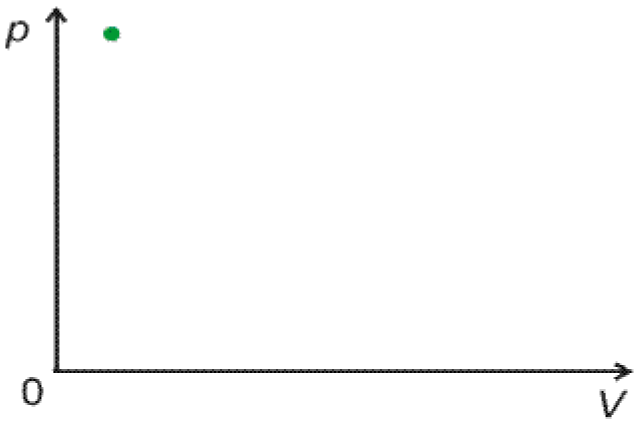
We say that a thermodynamic process has occurred when the system changes from one state (initial) to another state (final).

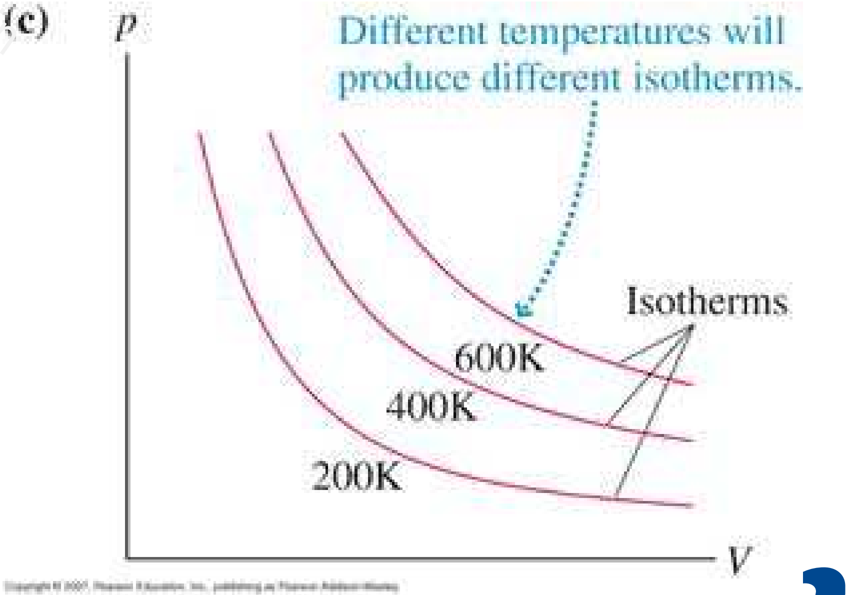
- **Isothermal process**: When the temperature of a system remains constant during a process, we call it isothermal. Heat may flow in or out of the system during an isothermal process.
- **Adiabatic process**: No heat can flow from the system to the surroundings or vice versa.
- **Isochoric process**: It is a process during which the volume of the system is kept constant.
- **Isobaric process**: It is a process during which the pressure of the system is kept constant.

Isothermal Process

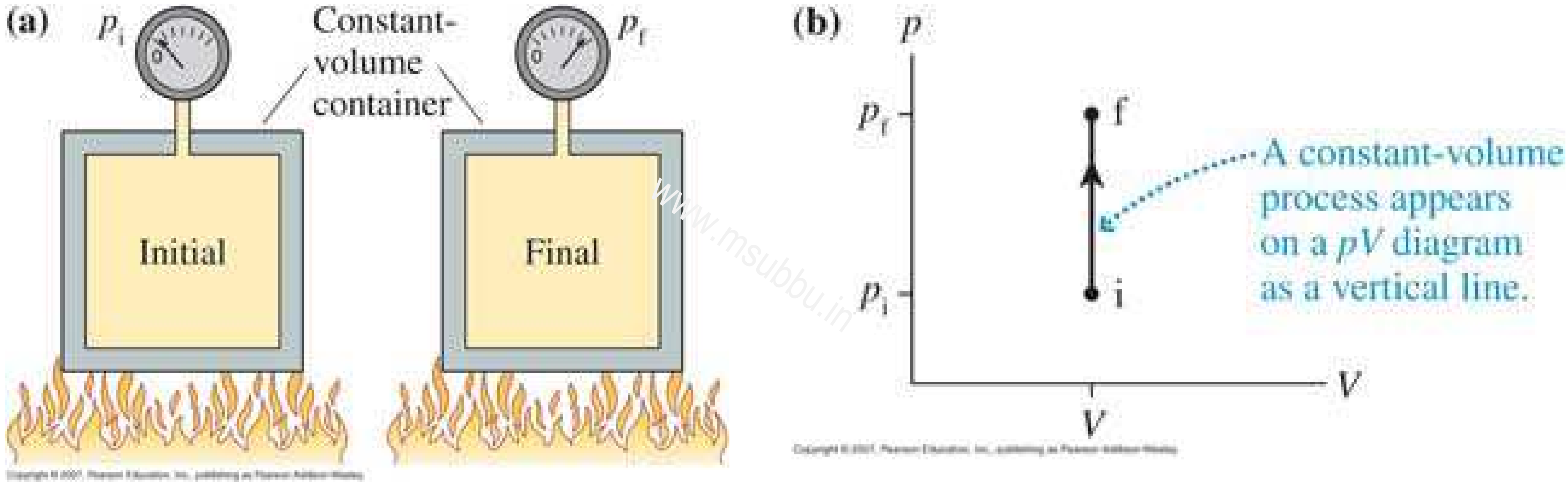




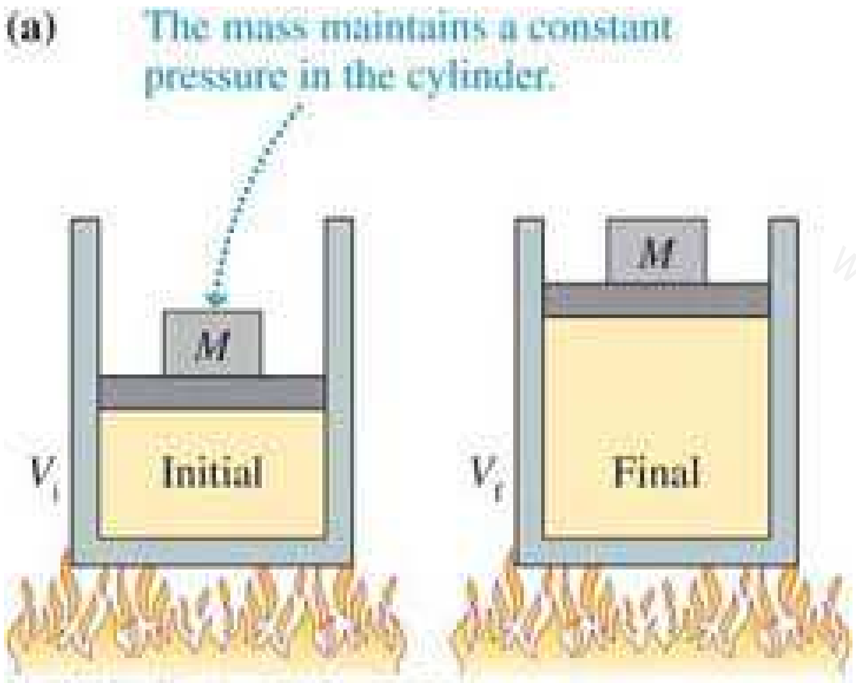


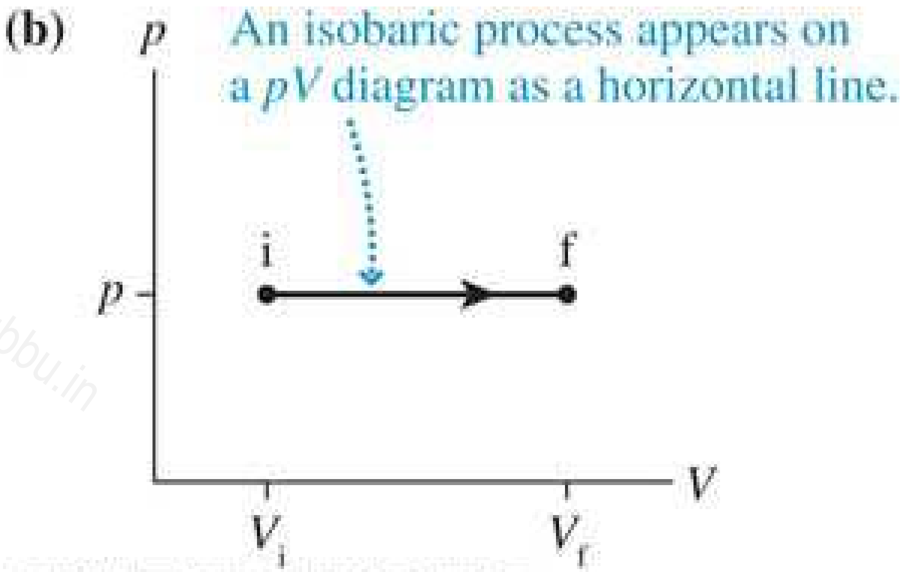


Constant Volume Process

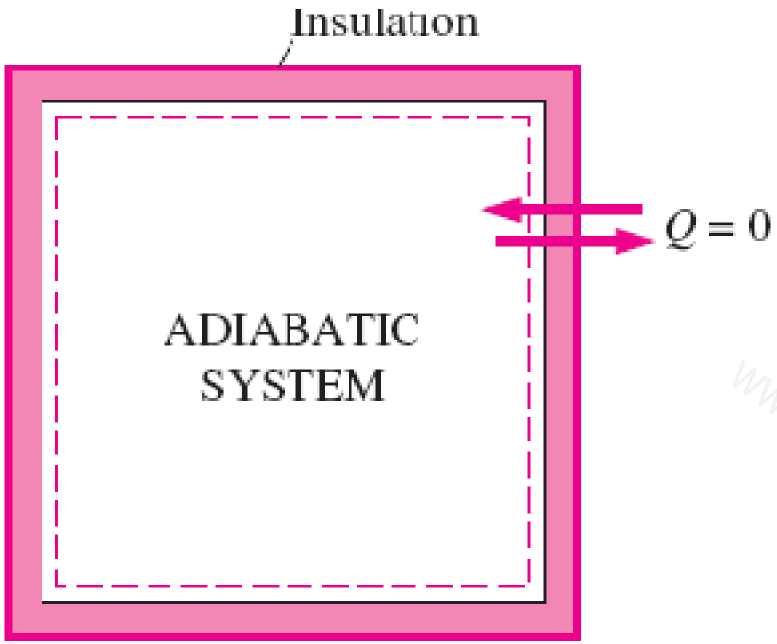


Constant Pressure Process

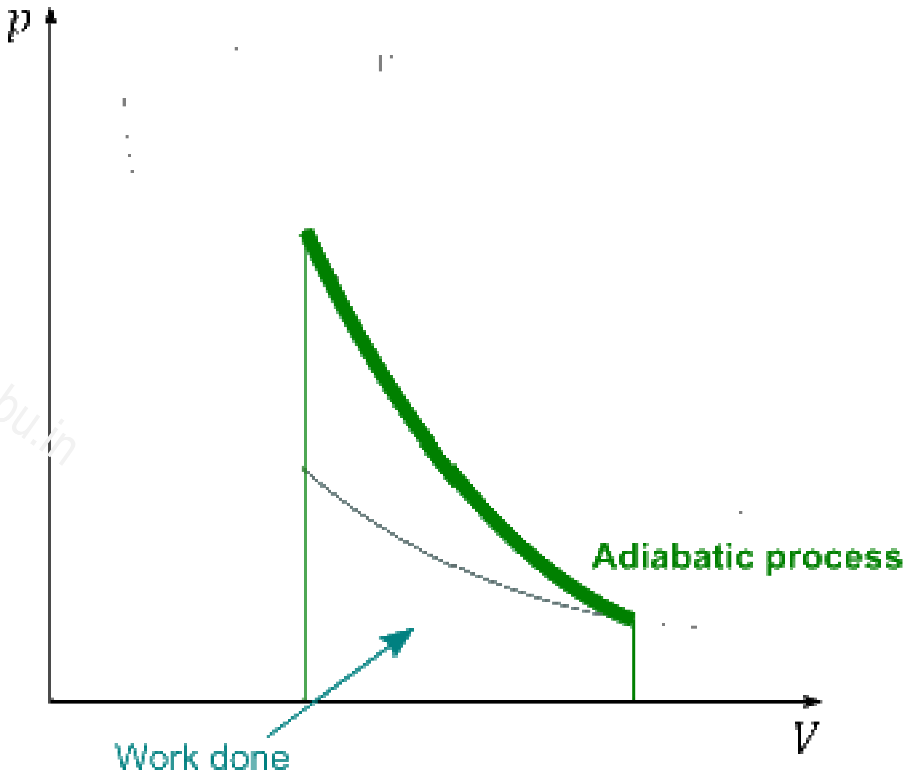




Adiabatic Process

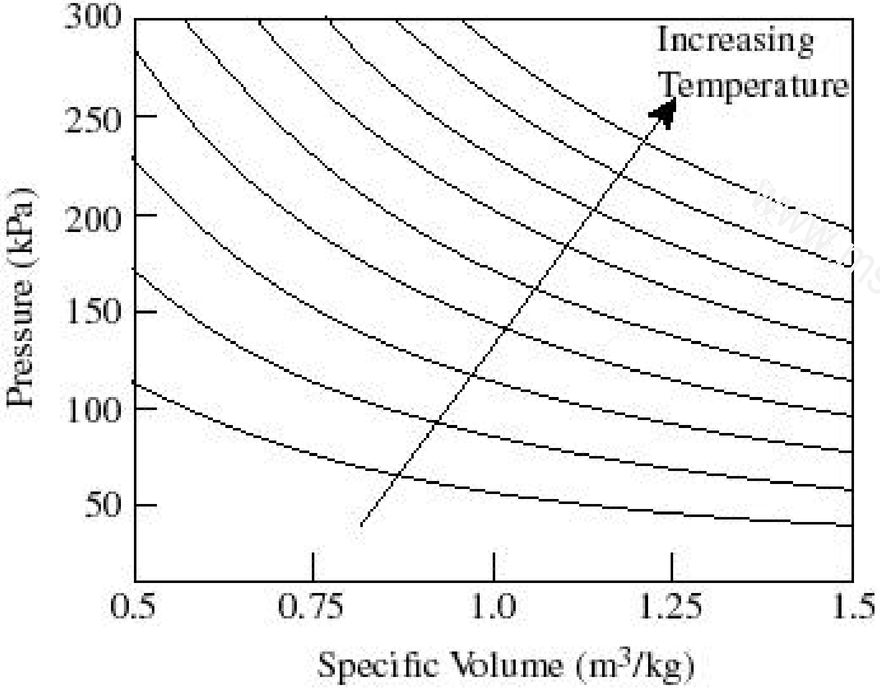


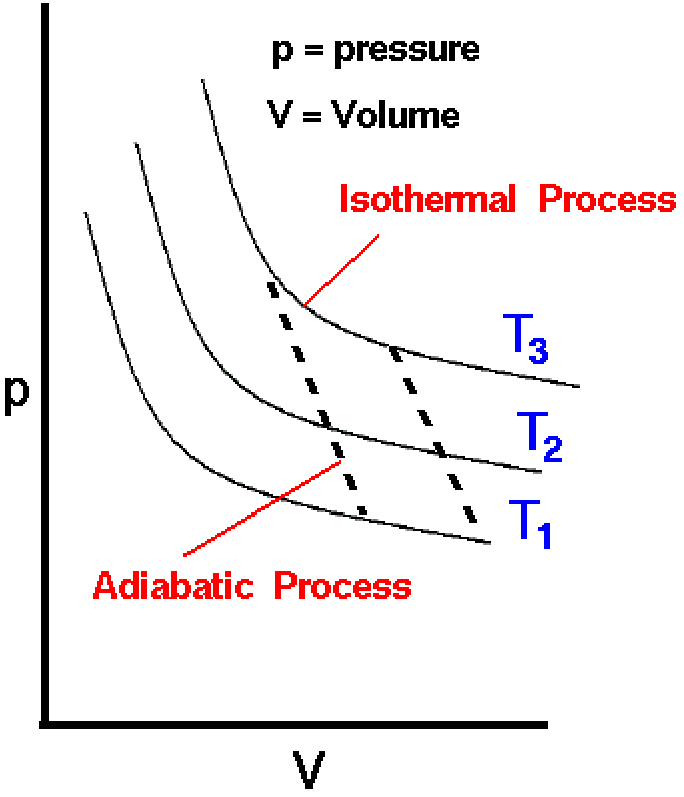
During an adiabatic process, a system exchanges no heat with its surroundings.

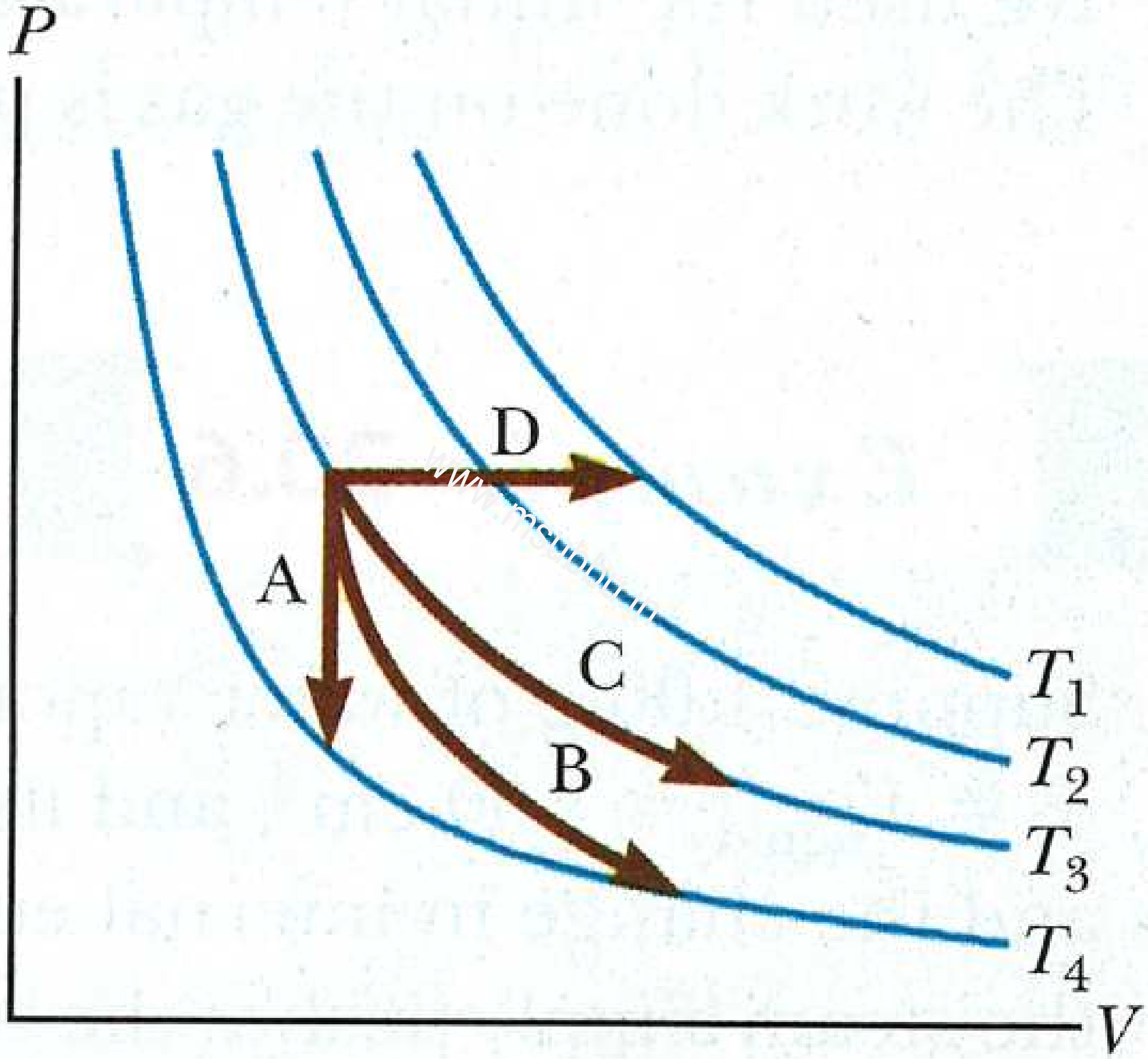


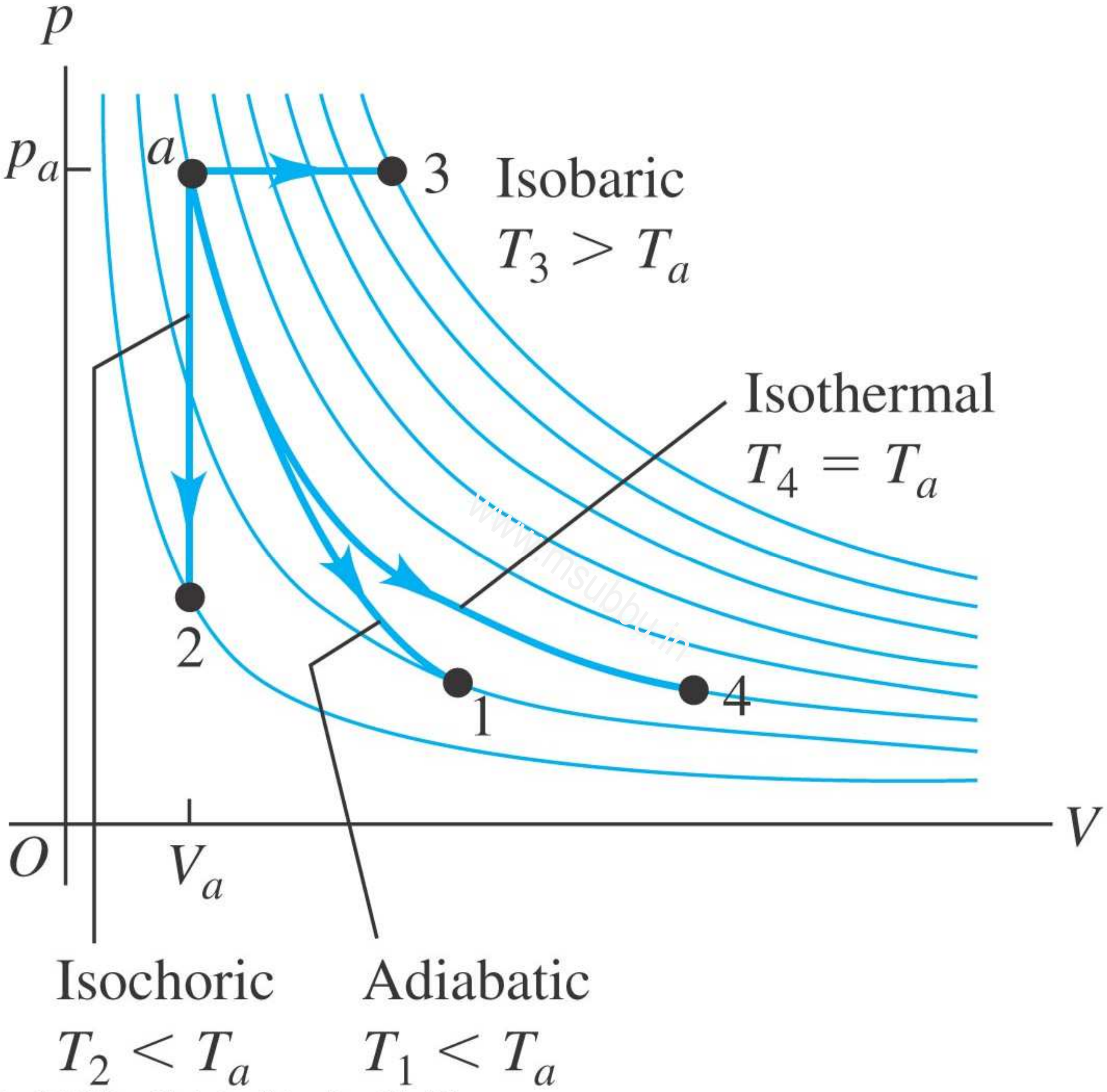
No transfer of heat;
But there is transfer of work

Comparison of Isothermal and Adiabatic Processes






P
D
A
C
B
T_1
T_2
T_3
T_4
V


p
p_a
a
3
Isobaric
$T_3 > T_a$
Isothermal
$T_4 = T_a$
2
1
4
O
V_a
V
Isochoric
$T_2 < T_a$
Adiabatic
$T_1 < T_a$

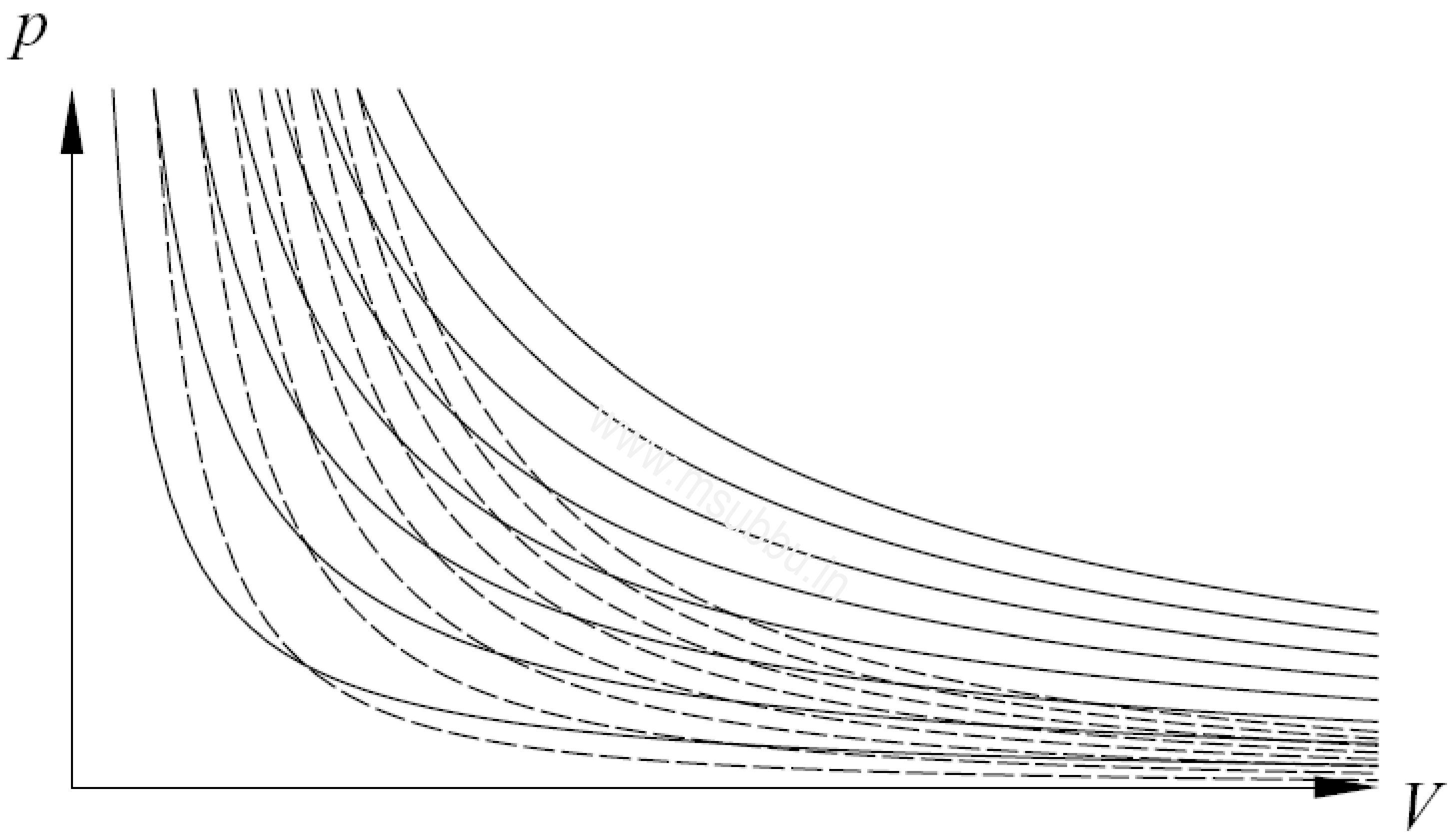
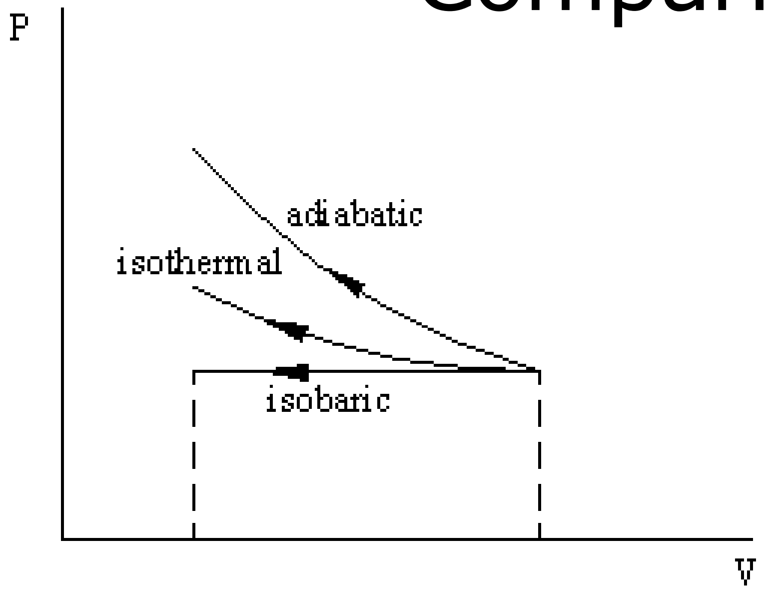
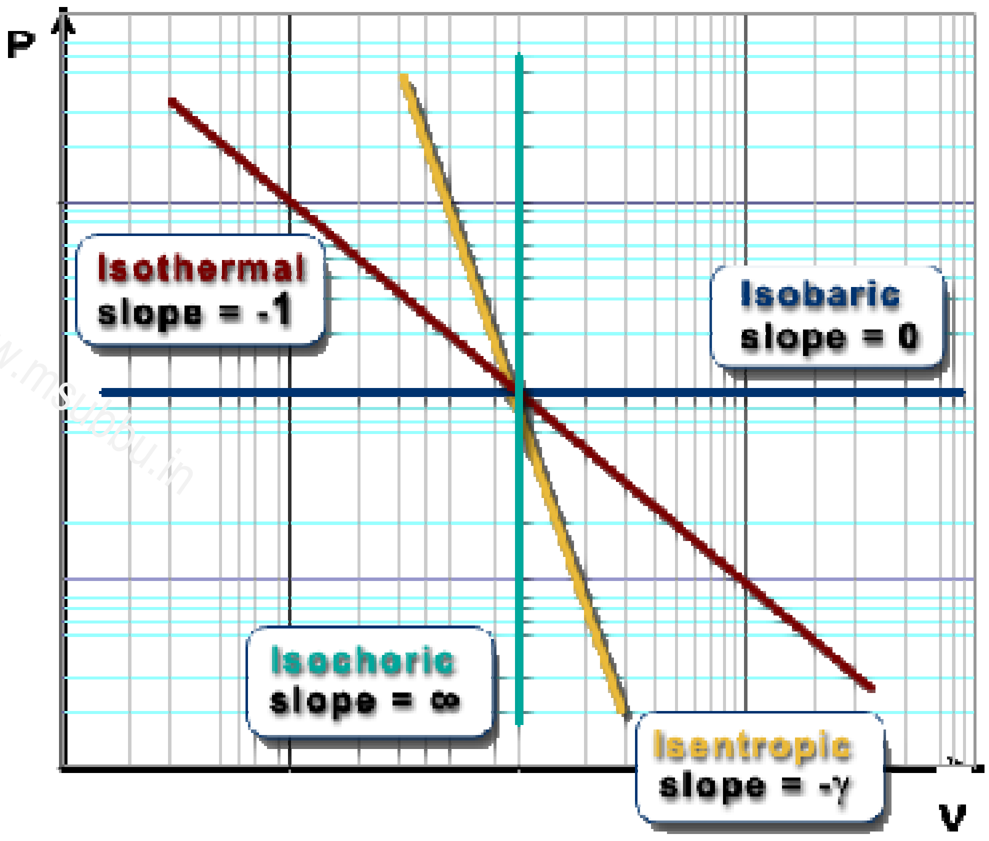
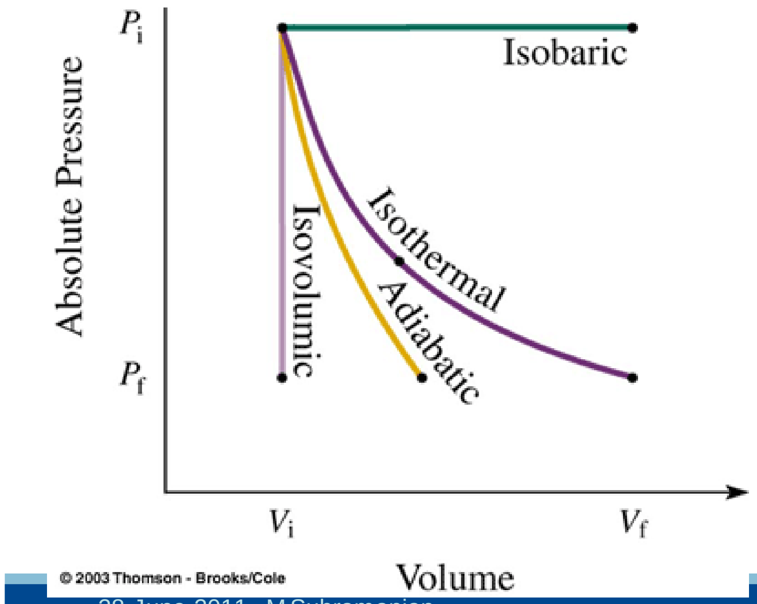


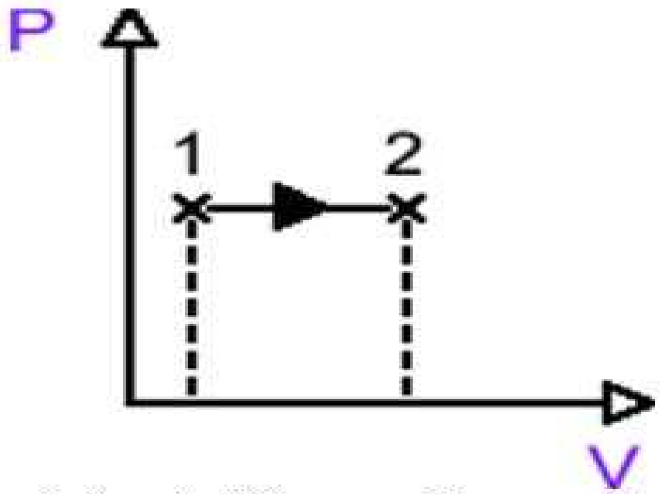
Fig. 12.1 Isotherms (solid lines) and adiabats (dashed lines).

Comparison of Processes

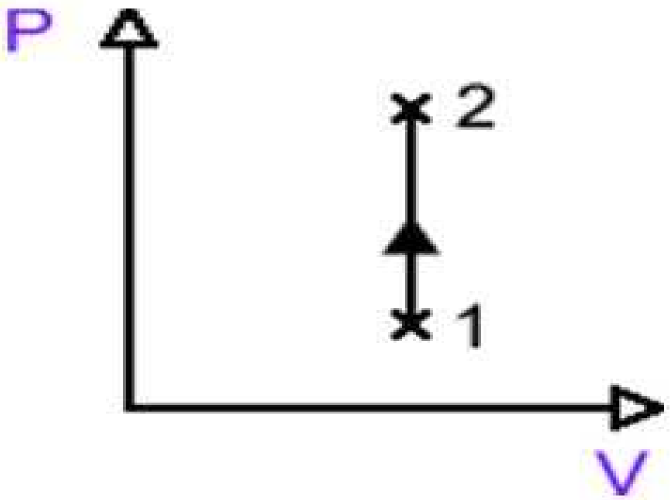




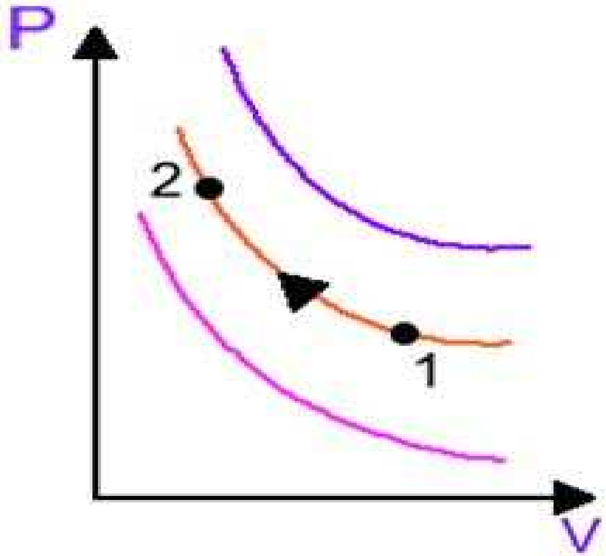




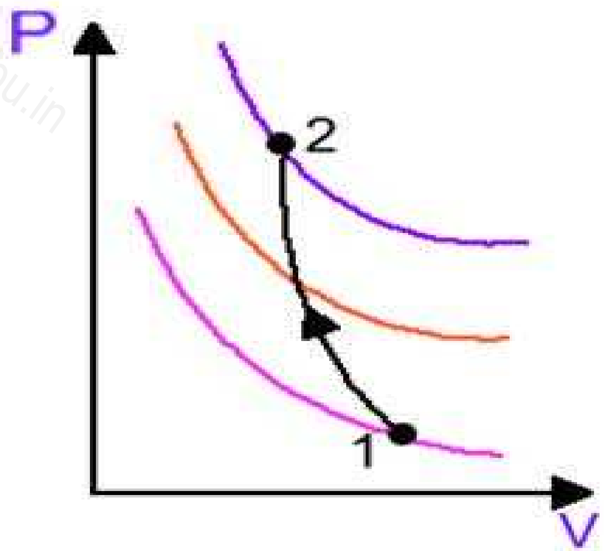
Isobaric (Constant Pressure)



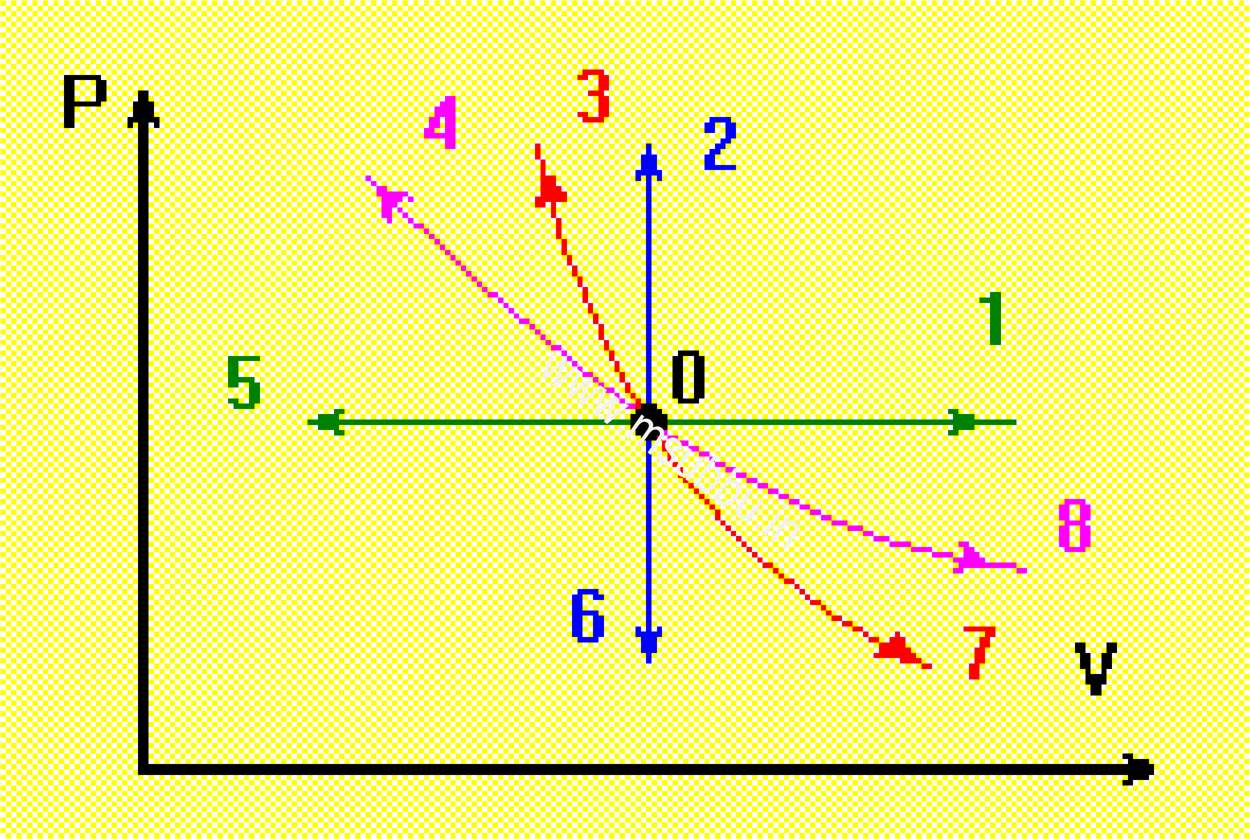
Isochoric (constant volume)



Isothermal (constant temperature)



Adiabatic


P
4
3
2
1
0
5
8
6
7
V

0 to 1= constant pressure heating,
0 to 2= constant volume heating,
0 to 3= reversible adiabatic compression,
0 to 4= isothermal compression,
0 to 5= constant pressure cooling,
0 to 6= constant volume cooling,
0 to 7= reversible adiabatic expansion,
0 to 8= isothermal expansion.

Work

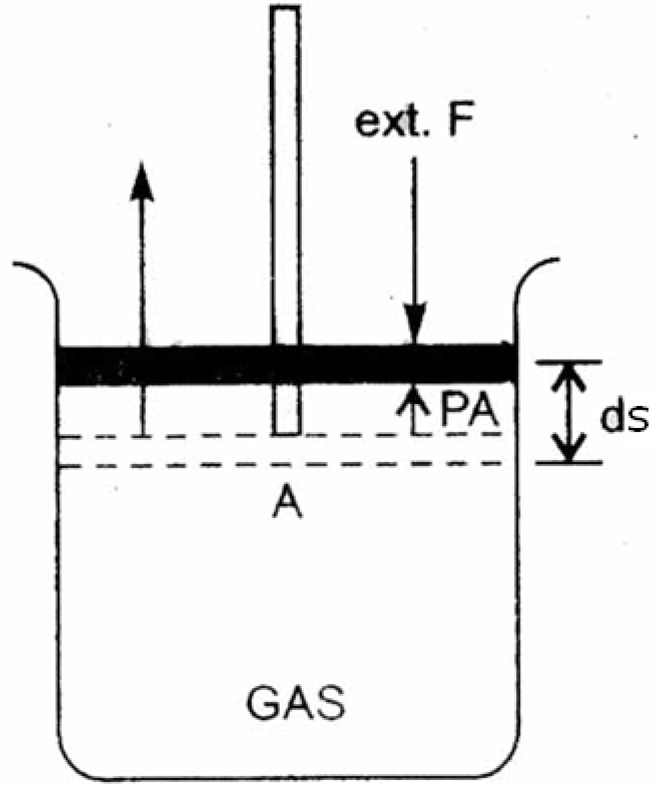
- Work is energy related to a force acting over a distance.
- There are many different forms of work, but in chemical engineering we are interested in only one of them - Pressure volume work (or PV work) which is related to compression or expansion of materials.
- Pressure volume work is important when a system is changing volume. This is because in order to change its volume it will have to push against the force of the pressure that is exerted on the system.

Work

- Work is done whenever a force acts through a distance.
- If the force is constant, then $W = Fs$
- If the force is a variable, the equation for work is expressed in terms of differentials

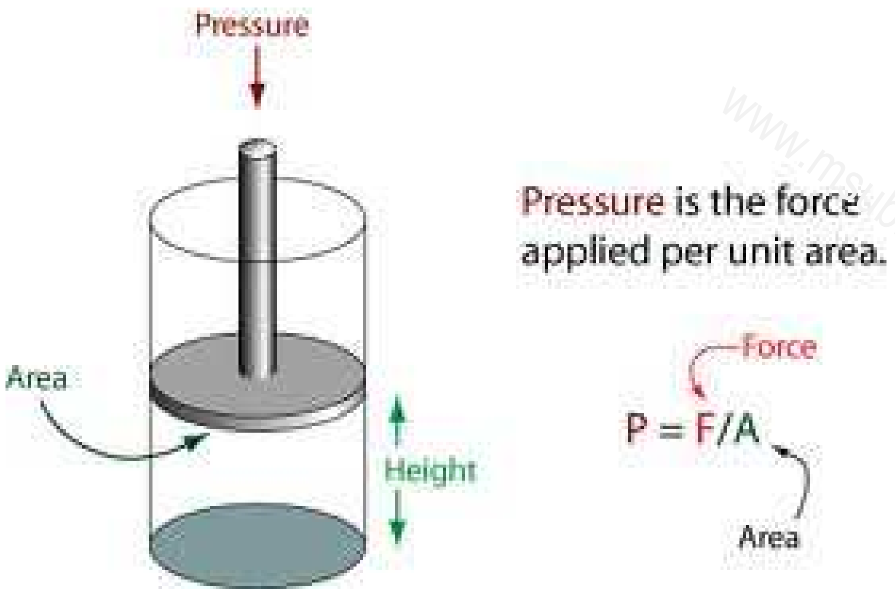
$$dW = F ds$$

- The above equation must be integrated if the work for a finite process is required



Work of Compression or Expansion of a Gas

- In thermodynamics the most important type of work is that which accompanies a change in volume of a gas



Pressure is the force applied per unit area.

$$dW = (PA)d\left(\frac{V}{A}\right)$$

$$W = \int PdV$$

$$F = PA \qquad s = V/A$$

Sign Convention for Work

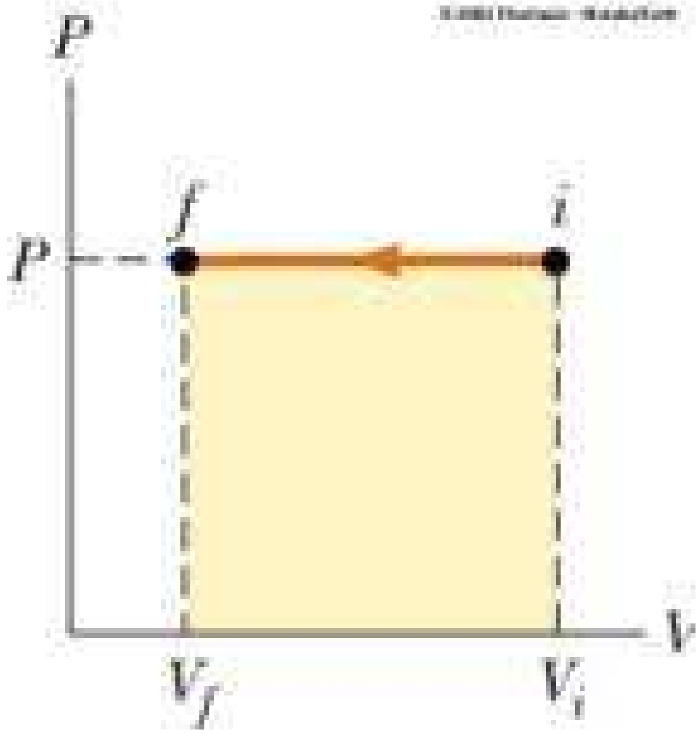
- Work done the system is taken as positive; Work done by the system is taken as negative.
- With the above sign convention, the formula for work is taken as:

$$dW = -PdV$$

and

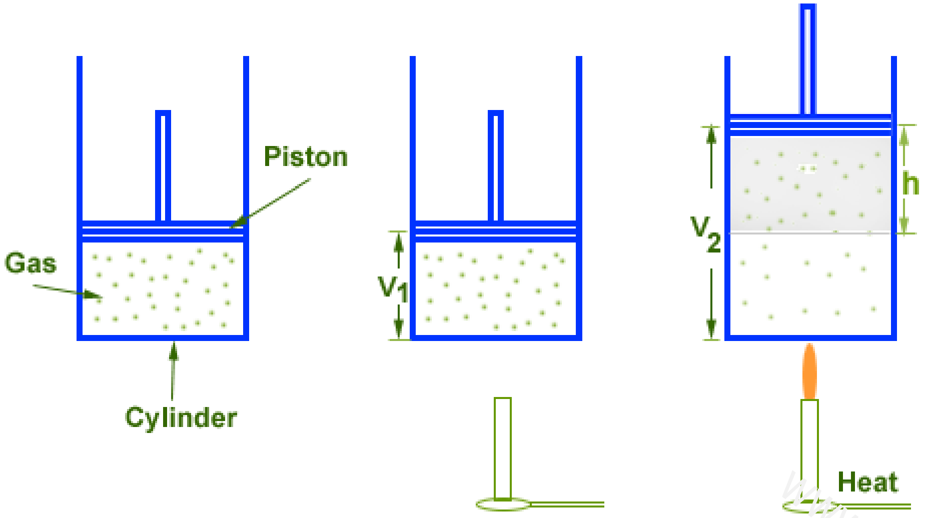
$$W = -\int PdV$$

PV Work

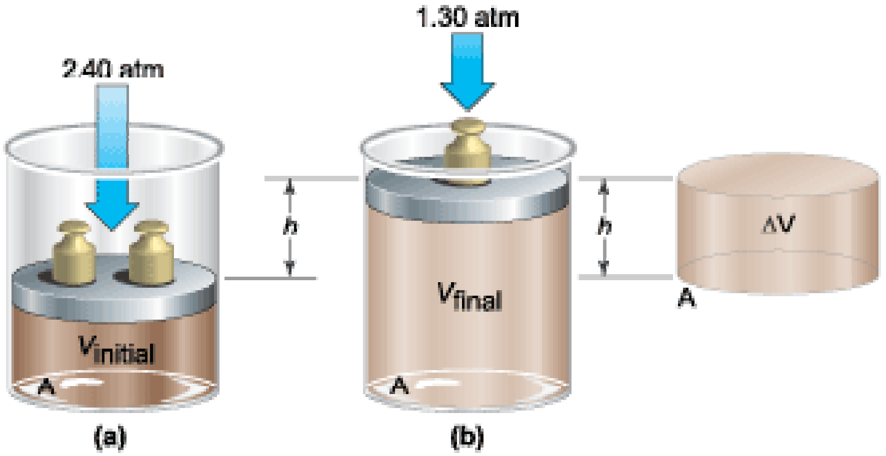


The amount of work involved is equal to the area under the curve. In compression, ΔV is negative and the work done on the gas, $W=-P\Delta V$ will be positive.

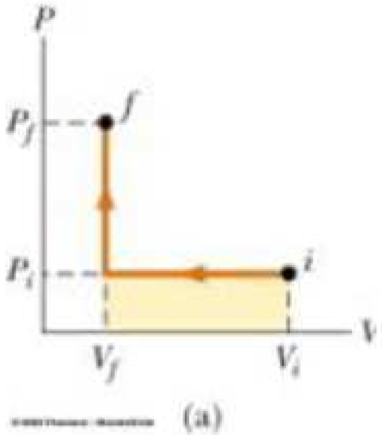
In expansion, ΔV is positive, and the work done ON the gas $W=-P\Delta V$ is negative, i.e. work is actually done BY the gas.



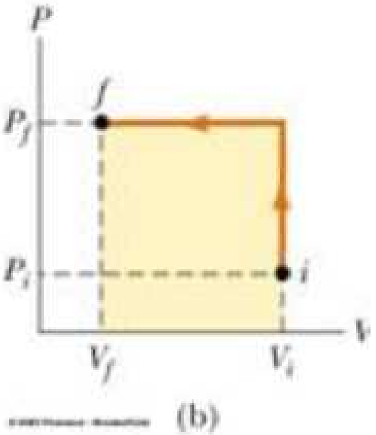
P is constant



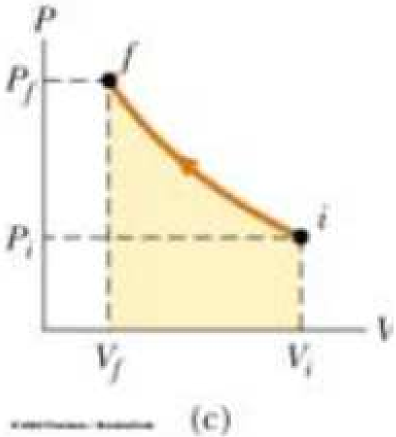
P varies



Decrease V at constant P
Then increase P

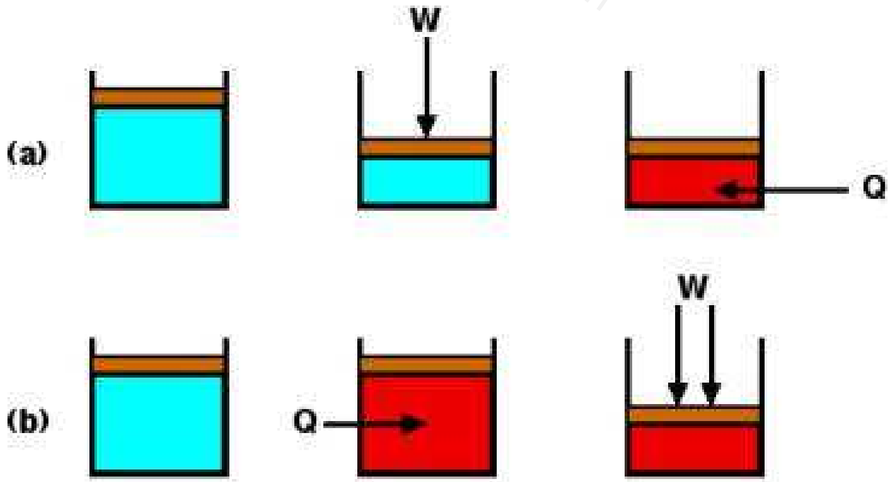


Increase P at constant V
Then decrease V



P and V both change
simultaneously

W depends on the way the system goes from one state to another

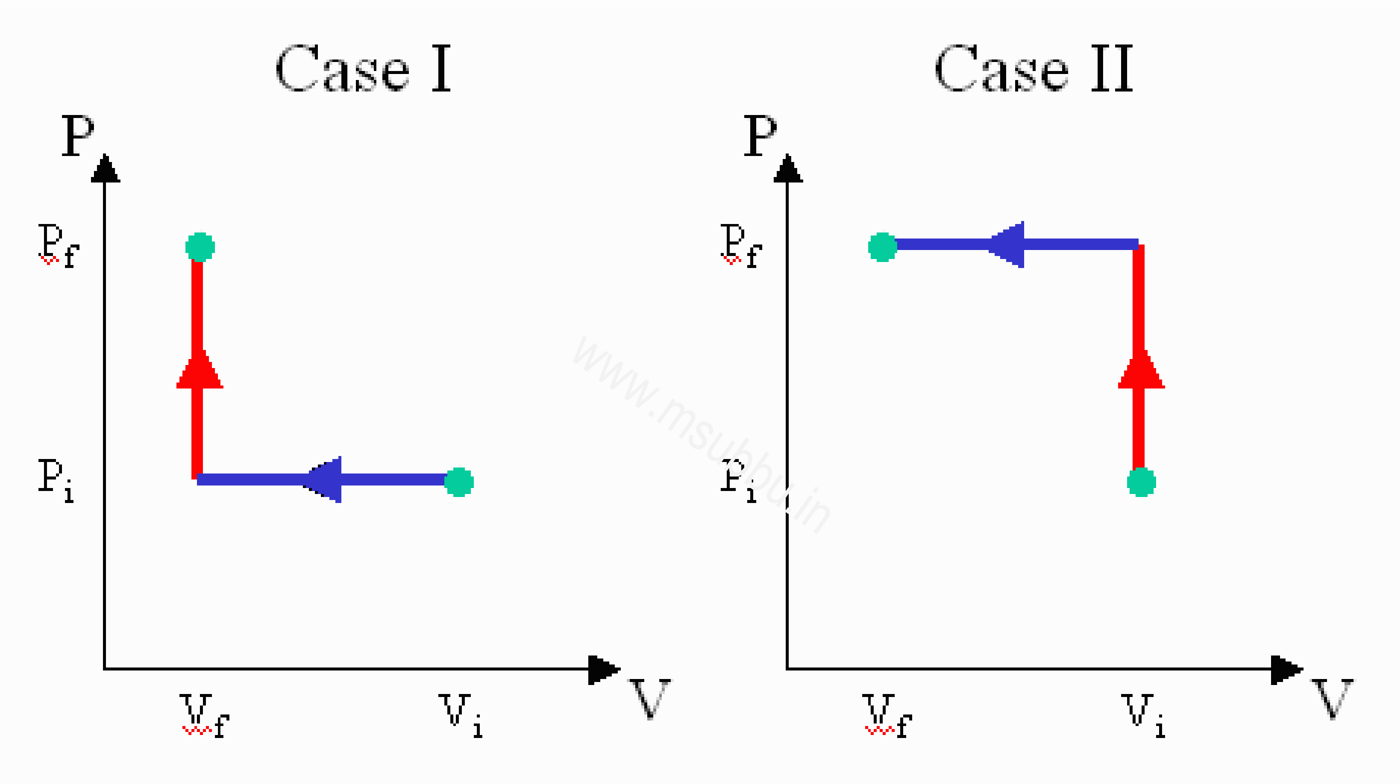


Sketch a PV diagram of the following processes:

(I) A gas is compressed at constant pressure P_i from volume V_i to volume V_f. It is then kept at constant volume while the pressure is increased to P_f.

(II) A gas is increased in pressure from P_i to P_f while its volume is held constant at V_i. It is then compressed at constant pressure to a final volume V_f.

In which process is more work done on the gas? Why?


Case I
P
P_f
P_i
V_f
V_i
V
Case II
P
P_f
P_i
V_f
V_i
V

Heat

- **Heat** is ‘energy in transit’.
- Though you can add heat to an object, you cannot say that ‘an object contains a certain quantity of heat.’
- Heat flow from a high to a low temperature body occurs spontaneously.
- Latent heat is associated with phase changes without temperature change, while sensible heat is associated with temperature change.

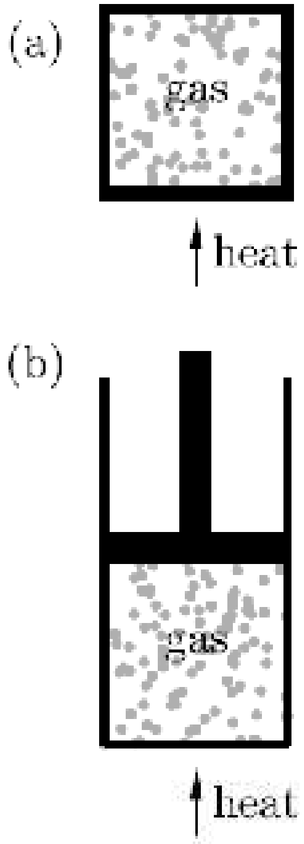
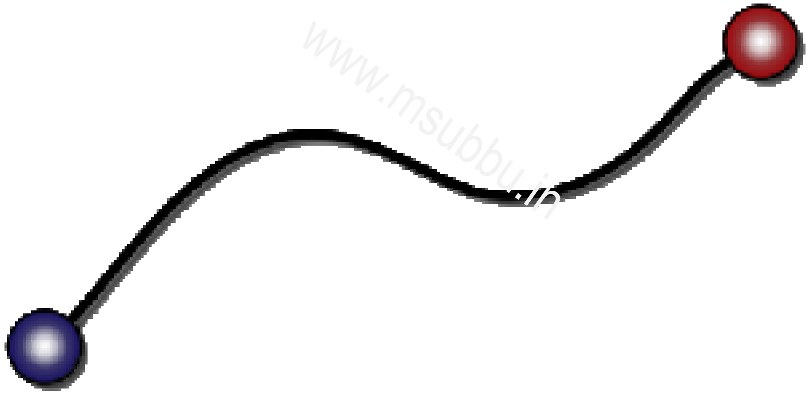


Fig. 2.1 Two methods of heating a gas: (a) constant volume, (b) constant pressure.

Point and path properties



State (or Point) Functions

- **State functions**, also called **thermodynamic variables**, **state quantities**, or a **functions of state** describe the momentary condition of a thermodynamic system. Regardless of the path by which a system goes from one state to another — i.e., the sequence of intermediate states — the total *change* in any state variable will be the same. This means that the incremental changes in such variables are *exact differentials*.

- Examples include entropy, pressure, temperature, volume, etc.

- Various thermodynamic diagrams have been developed to model the transitions between thermodynamic states.

Heat and Work are path functions

- To see this, consider your cold hands on a chilly winter day. You can increase the temperature of your hands in two different ways:
  (i) by adding heat, for example by putting your hands close to something hot, like a roaring fire; (ii) by rubbing your hands together.
- In one case you have added heat from the outside, in the other case you have not added any heat but have done some work. In both cases, you end up with the same final situation: hands which have increased in temperature. There is no physical difference between hands which have been warmed by heat and hands which have been warmed by work.

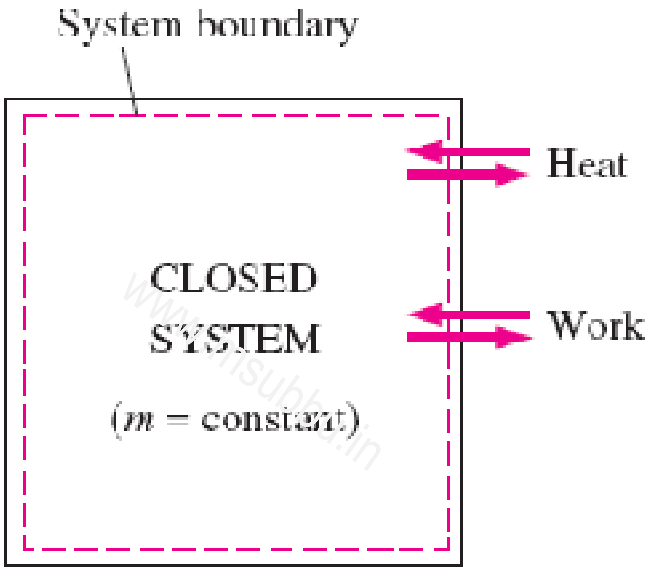
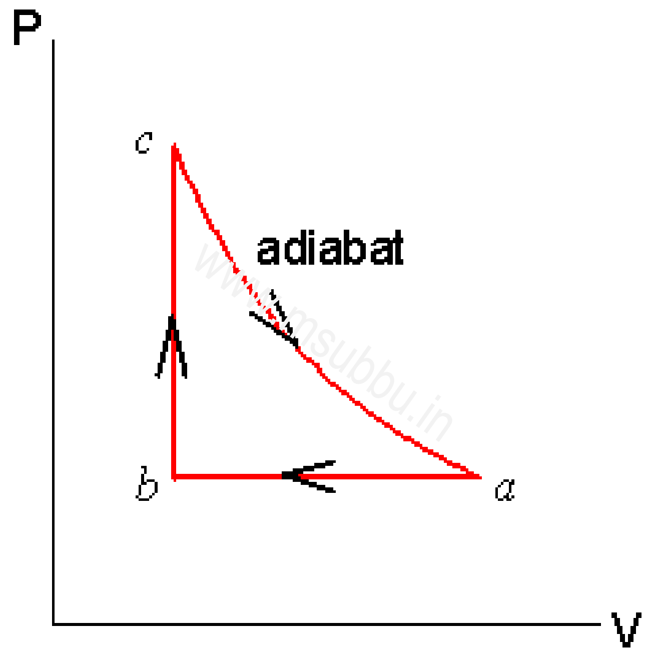
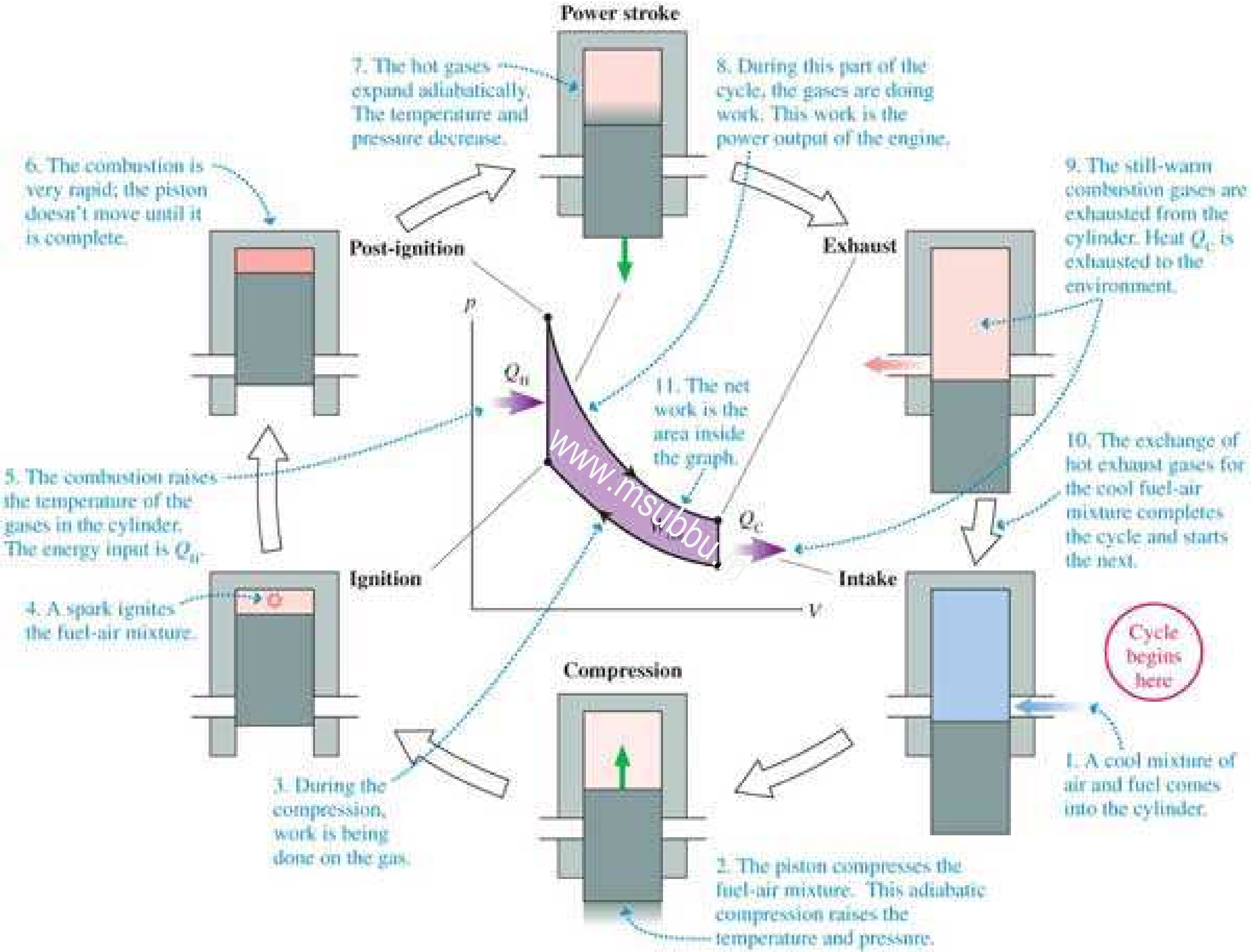


FIGURE 2–11

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

Thermodynamic Cycle





1. A cool mixture of air and fuel comes into the cylinder.

2. The piston compresses the fuel-air mixture. This adiabatic compression raises the temperature and pressure.

3. During the compression, work is being done on the gas.

4. A spark ignites the fuel-air mixture.

5. The combustion raises the temperature of the gases in the cylinder. The energy input is Q_H.

6. The combustion is very rapid; the piston doesn't move until it is complete.

7. The hot gases expand adiabatically. The temperature and pressure decrease.

8. During this part of the cycle, the gases are doing work. This work is the power output of the engine.

9. The still-warm combustion gases are exhausted from the cylinder. Heat Q_C is exhausted to the environment.

10. The exchange of hot exhaust gases for the cool fuel-air mixture completes the cycle and starts the next.

11. The net work is the area inside the graph.

Ideal Otto Cycle

p–V diagram

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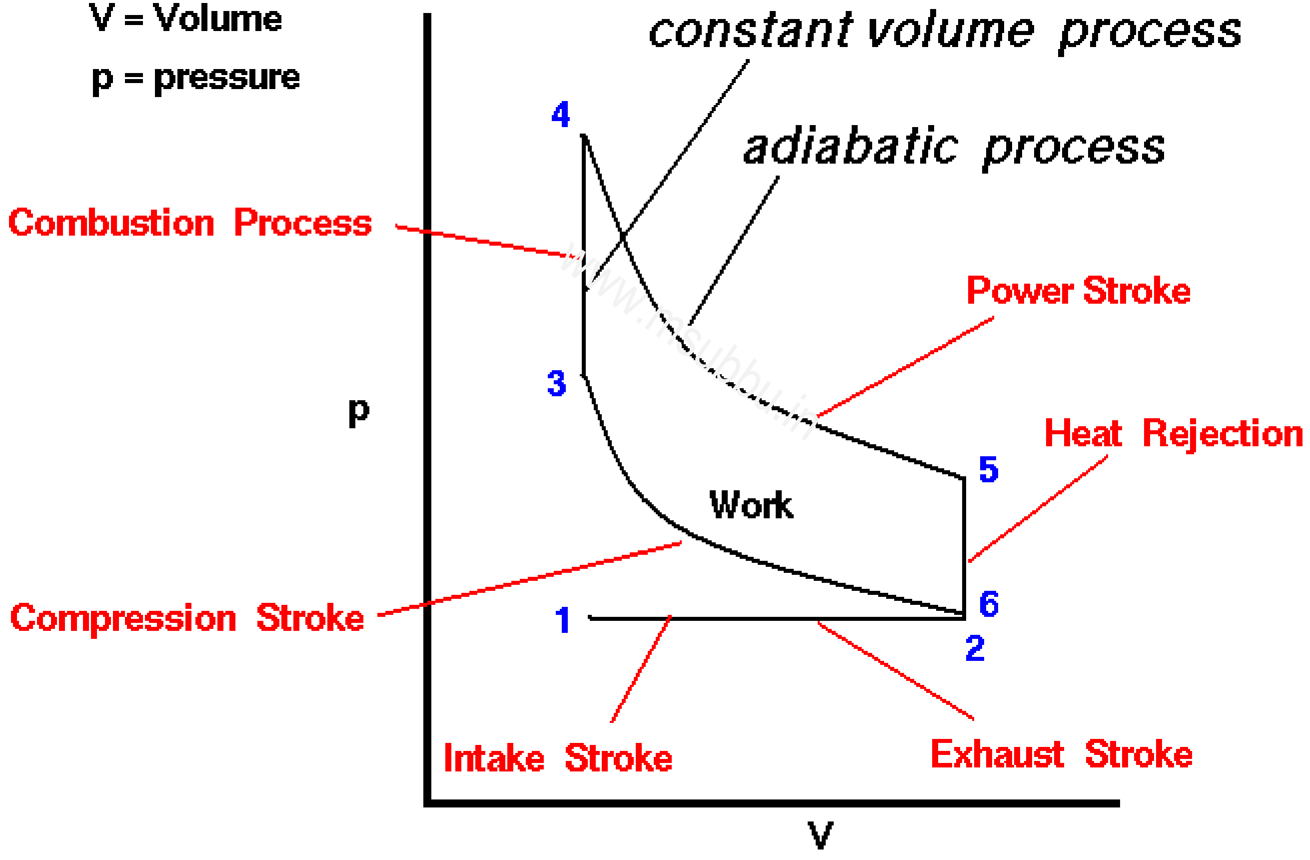
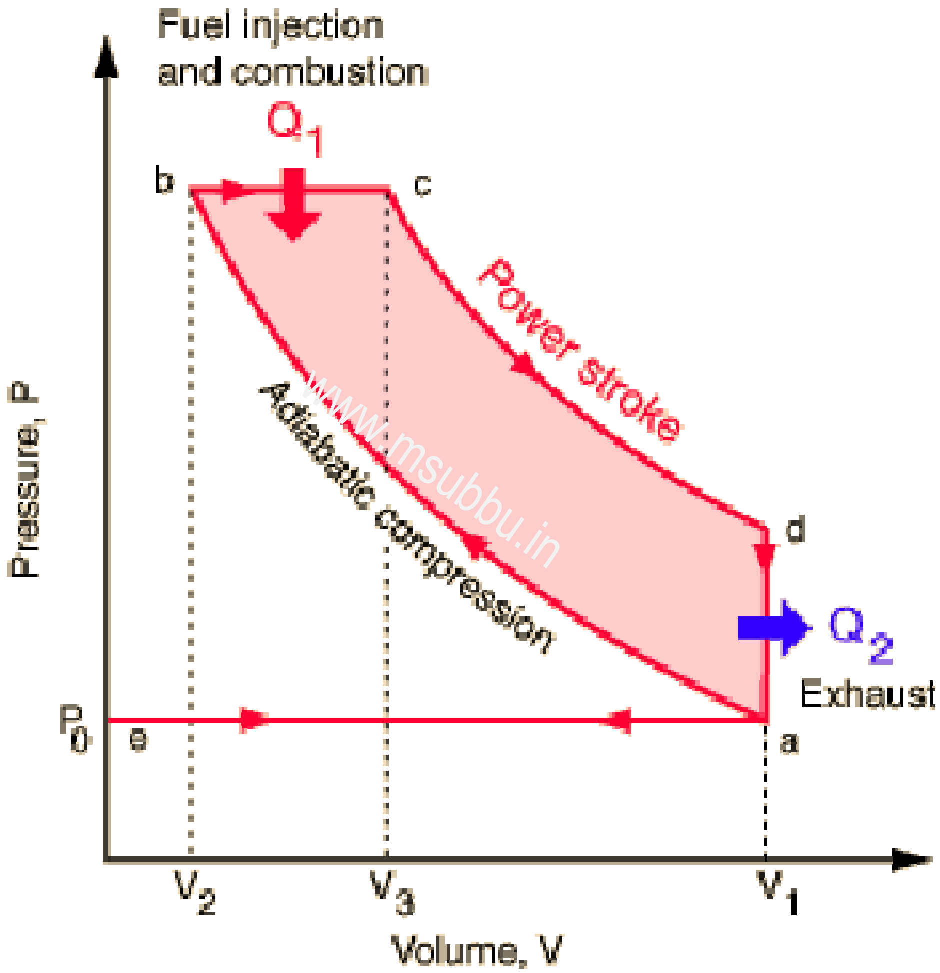
Research
Center

V = Volume

p = pressure



Diesel Cycle

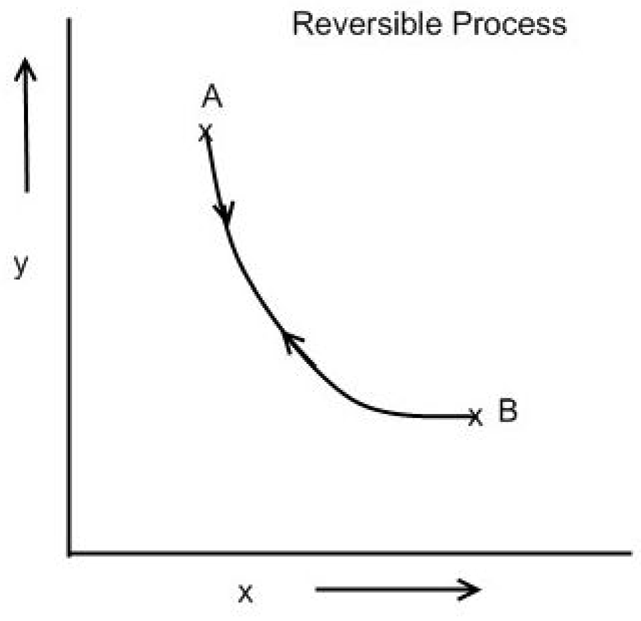


Reversible and Irreversible Processes

- Processes occur when there exists a driving force for a change of state between parts of the system or between the system and surroundings

- If the driving force is finite, the process is irreversible, and if it is infinitesimal in magnitude, the process is reversible.

- All spontaneous processes occurring in nature are irreversible.



Irreversible Process

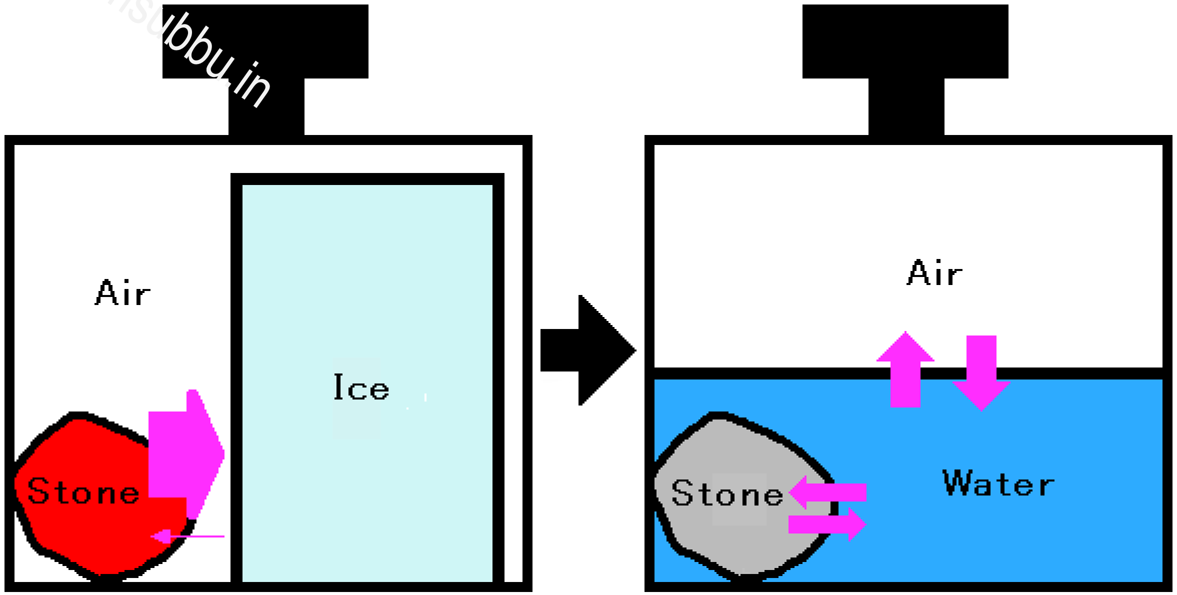


Figure 2

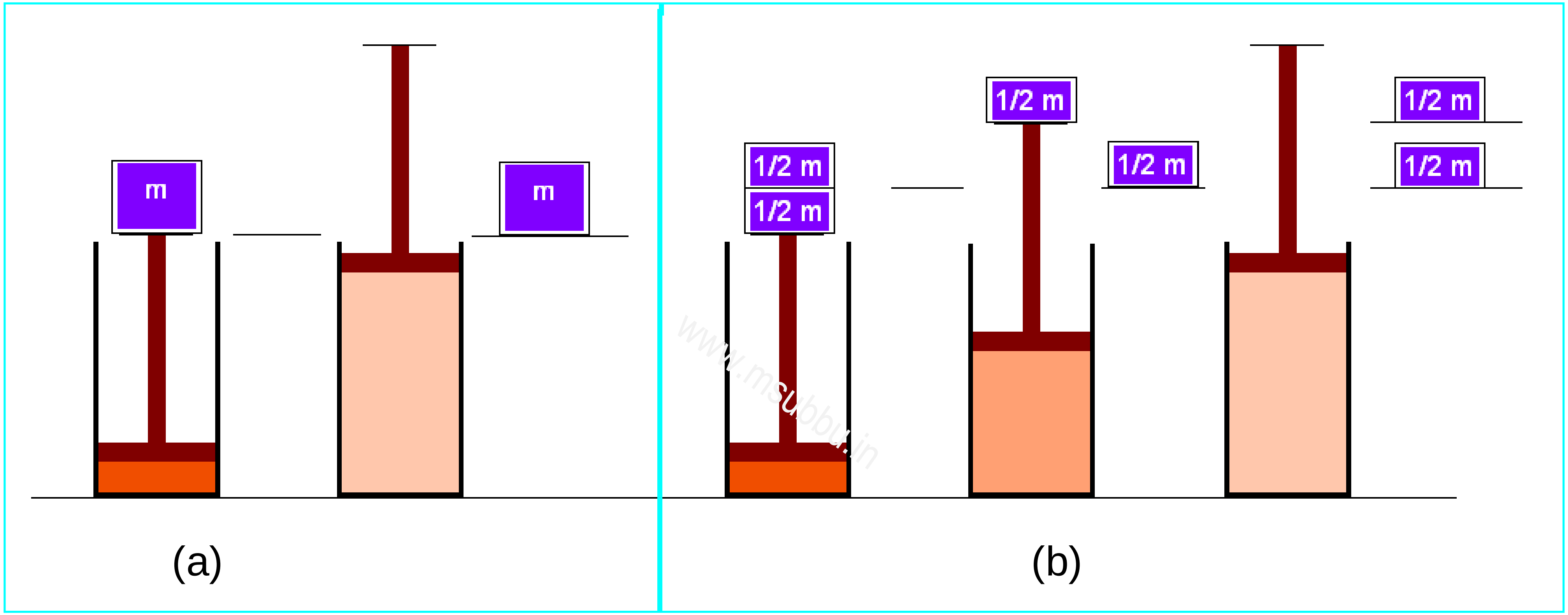
Reversible Process

- A **reversible process** is a process that can be reversed by means of infinitesimal changes in some property of the system without loss or dissipation of energy, and can be reversed without causing change in the surroundings.

- Due to these infinitesimal changes, the system is in thermodynamic equilibrium throughout the entire process.

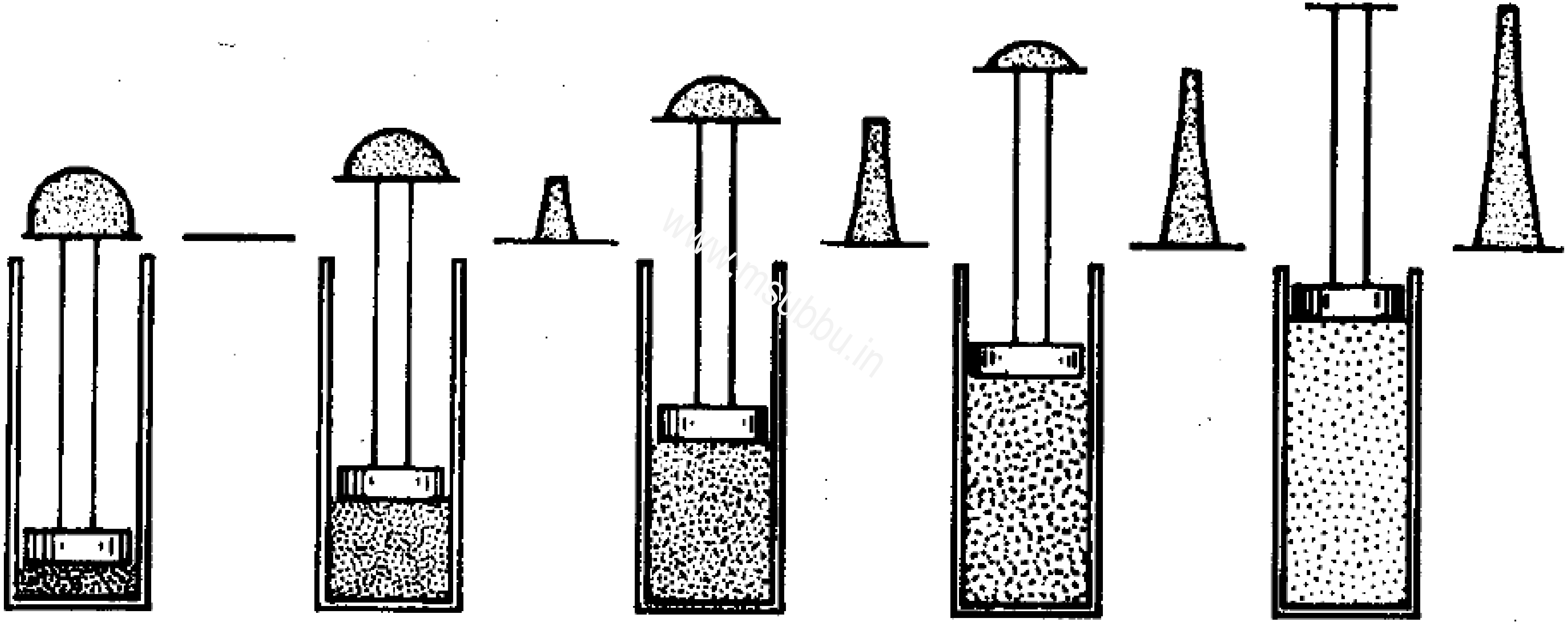
- For the system to undergo reversible change, it should occur infinitely slowly due to an infinitesimal gradient. During a reversible process all the changes in a state that occurs in a system are in thermodynamic equilibrium with each other

Making a irreversible process to approach a reversible process



In the process as shown in Fig. (a), no useful work has been done.

In an improved process as shown in Fig. (b), the weight m is divided into two parts. In this process, part of the weight (1/2 m) has been raised roughly half the distance of the pistons' travel, and useful work has been accomplished.



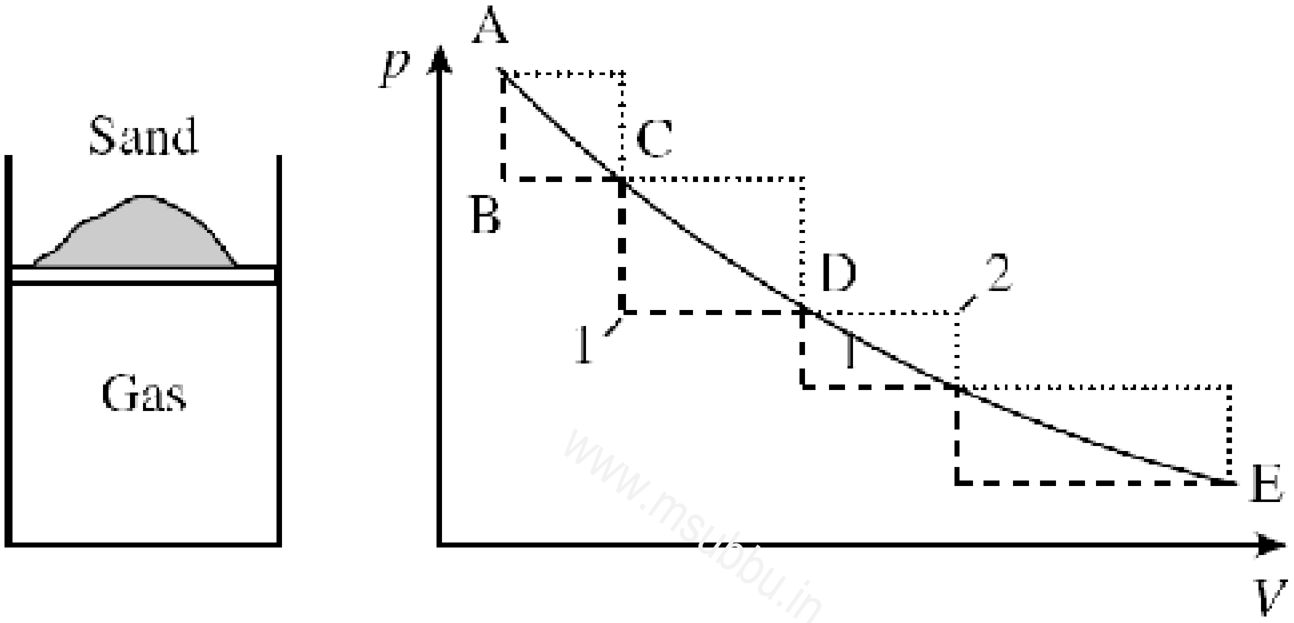
F	s	W	F	s	W	F	s	W	F	s	W	F	s	W
100	0	0	50	0		25	0		10	0		5	0	
0	10	**0**	50	5	250	25	2.5	62.5	10	1	10	5	0.5	2.5
			0	10	**0**	25	5	125	10	2	20	5	1	5
					250	25	7.5	187.5	10	3	30	5	1.5	7.5
						0	10	**375**	10	4	40	5	2	10
									10	5	50	5	2.5	12.5
									10	6	60	5	3	15
									10	7	70	5	3.5	17.5
									10	8	80	5	4	20
									10	9	90	5	4.5	22.5
									0	10	**450**	5	5	25
												5	5.5	27.5
												5	6	30
												5	6.5	32.5
												5	7	35
												5	7.5	37.5
												5	8	40
												5	8.5	42.5
												5	9	45
												5	9.5	47.5
												0	10	**475**

Let us assume that a resisting force 100 N will make a piston maximum displacement of 10 m. The work in the form of lifting the weight that could be obtained, is given below:

Resisting force removal at a time	Total Work (Nm)
1 unit of 100 N	0
2 units of 50 N each	250
4 units of 25 N each	375
10 units of 10 N each	450
20 units of 5 N each	475
50 units of 2 N each	490
100 units of 1 N each	495
1000 units of 0.1 N each	499.5
Infinite units of infinitesimal N each	500

W = Potential energy of raising the units = $m\,g\,s = F\,s$

Reversible Process - example



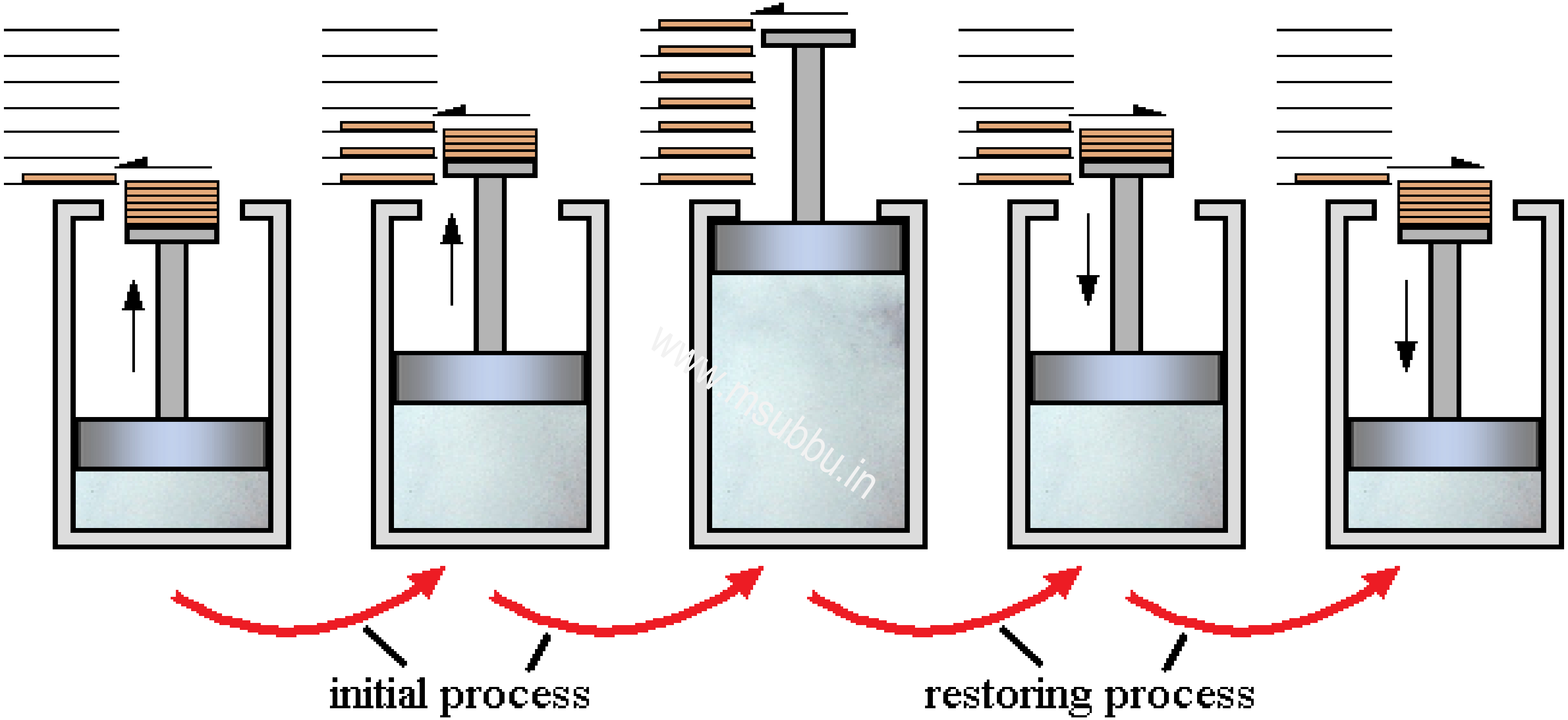
1 – removing sand by shovel; 2 – adding sand by shovel

In the limit that we remove one sand particle at a time, path 1 and path 2 will be indistinguishable. In this case, the excess work is (almost exactly) zero and the process corresponding to path AE is reversible.

Maximum amount of work a system can perform in going from one state to another is achieved when the system moves along a reversible path.

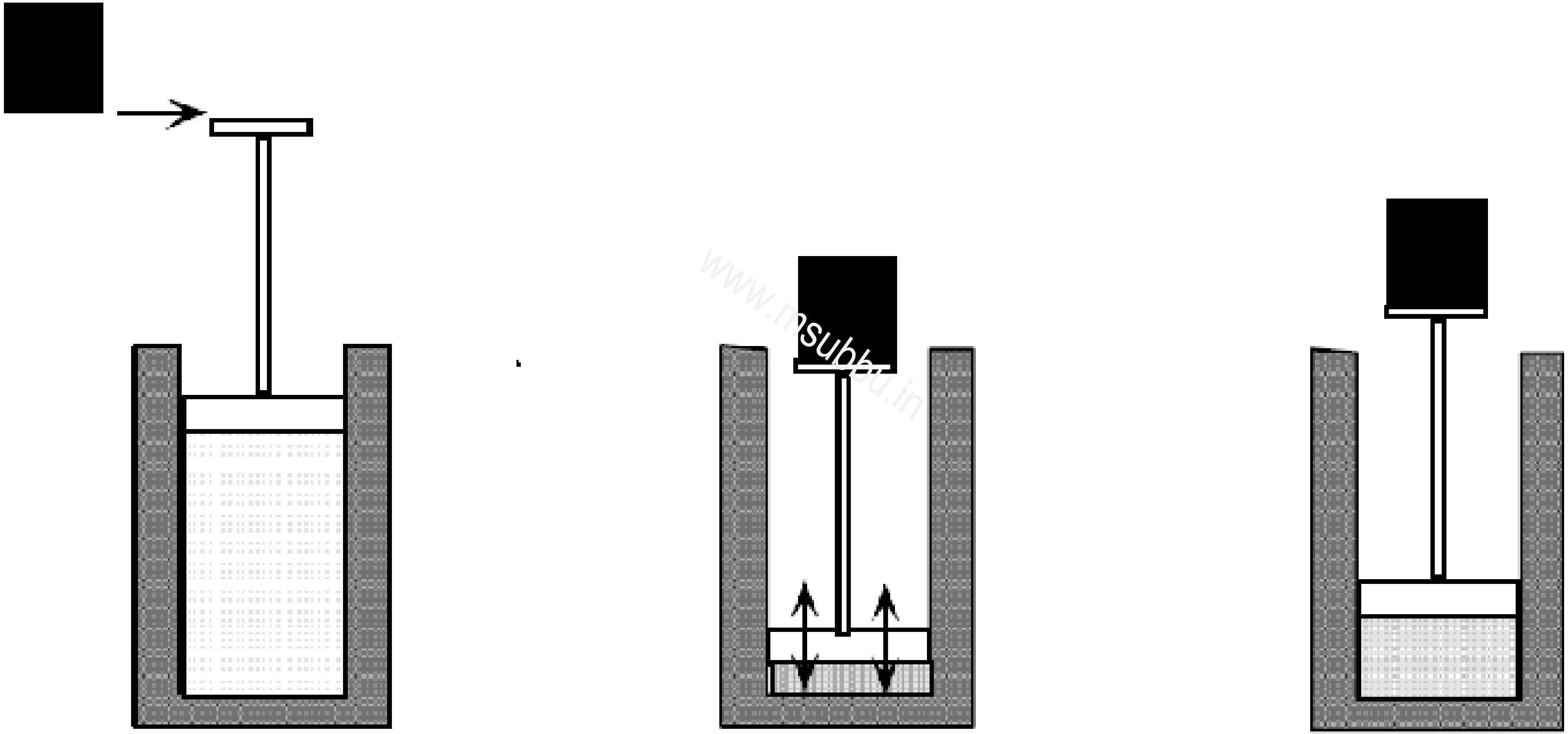
Work in Reversible and Irreversible Processes

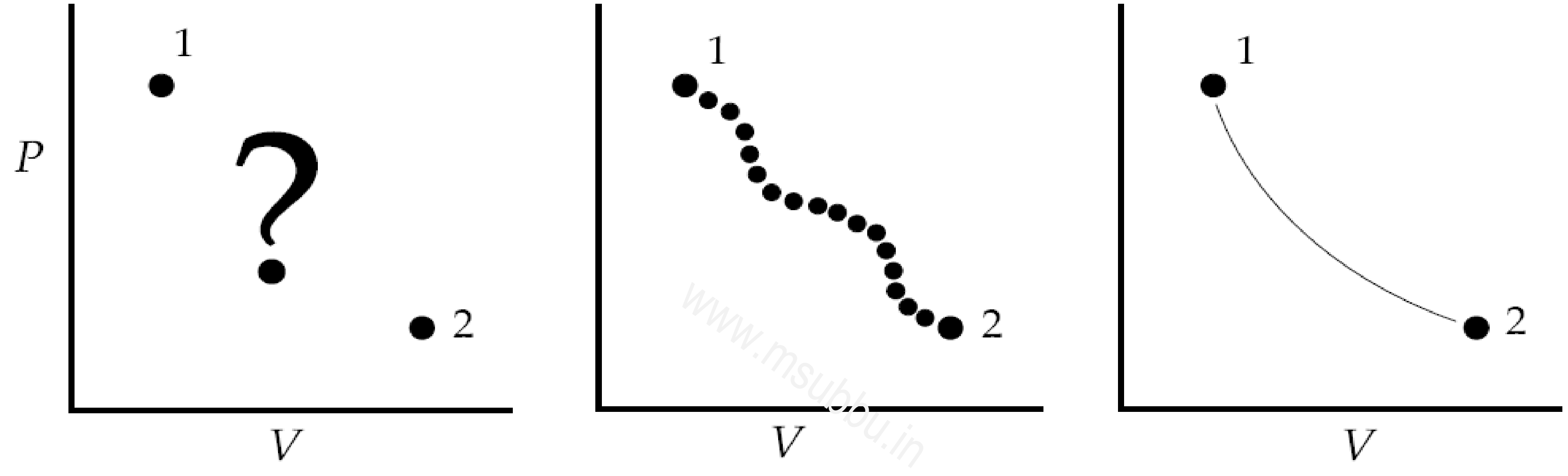
- A reversible change is more efficient than any irreversible process between the same two states.
- During a compression the irreversible work done to the system is larger than W_{rev} because part of W_{irr} is wasted in overcoming dissipative forces that oppose the compression.
- Likewise, during an expansion the irreversible work done by the system is less than W_{rev} because part of W_{irr} must overcome dissipative forces that oppose the expansion.



In theory there is no heat loss or work performed. This may be hard to visualize because how can the weights move without work being performed, but as the weights approach 0 in weight, the work approaches 0.

Irreversible Process





(a) finite irreversible process (b) quasi-static process (c) reversible change

Figure 1.4 Comparison of changes of state as represented on a state (PV) diagram for a pure, one-phase substance. During an (a) irreversible process, intermediate states are unknown and unknowable; during a (b) quasi-static process, the system moves in small discrete steps between identifiable equilibrium states; during a (c) reversible change, every intermediate state is a well-defined equilibrium state.

Expansion Process

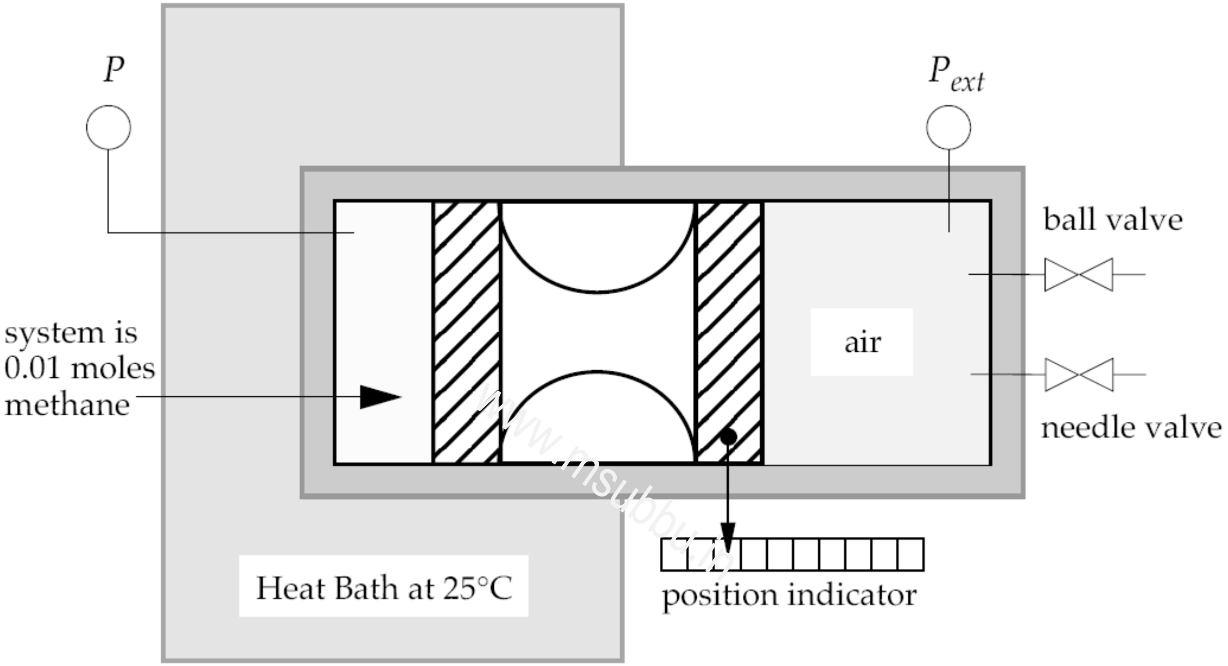
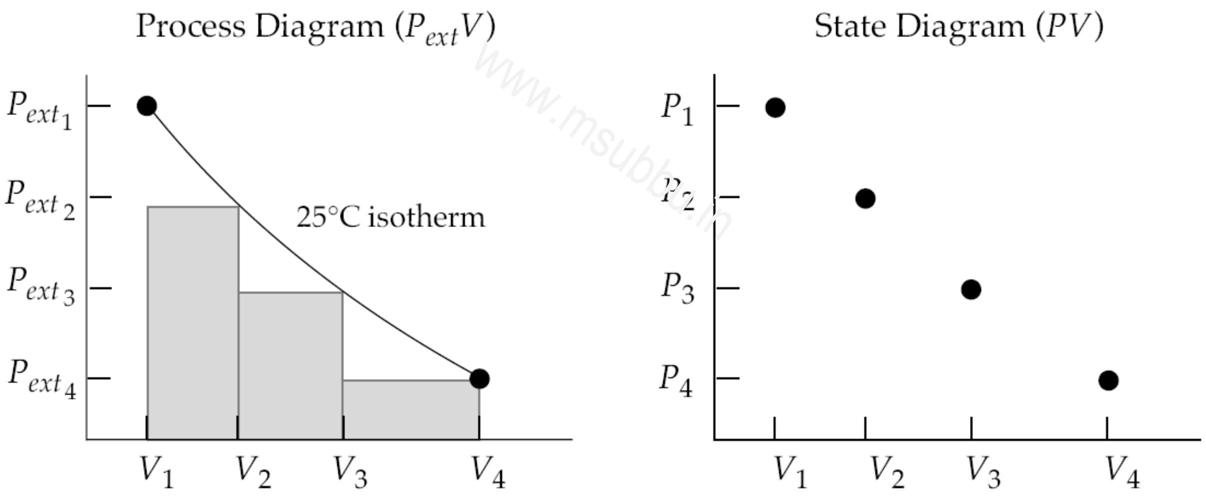


Figure 2.4 Schematic diagram of the double-headed piston-cylinder apparatus. To move the piston, any pressure imbalance between the methane and air chambers must overcome friction at the surfaces of contact between the piston heads and cylinder walls.

Ref: O'Connel, J.P., and J.M.Haile, Thermodynamics – Fundamentals for Applications, Cambridge University Press, 2005.

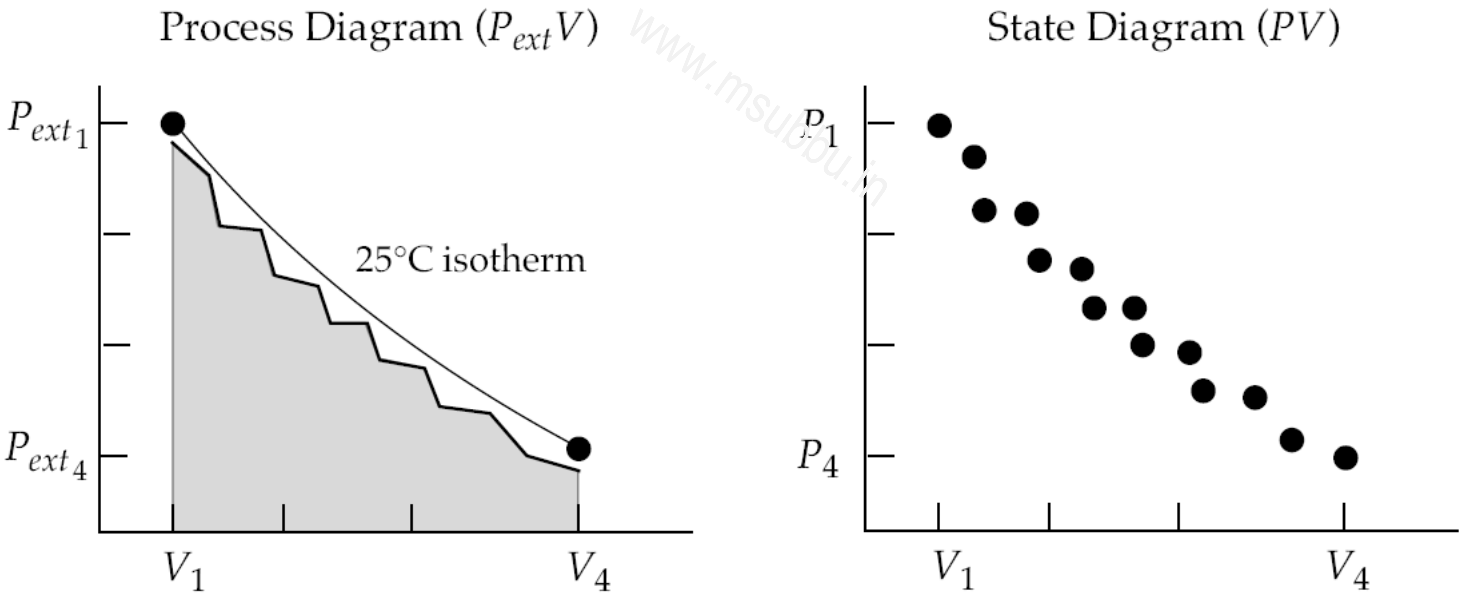
Irreversible Expansion

Air is removed by cycling the ball valve open and shut three times



Quasistatic Irreversible Expansion

From the initial conditions, we now expand the methane by just barely opening the needle valve, slowly venting air. The process path is a continuous curve on the process diagram, but the curve is not smooth; even though the air is vented continuously, the piston does not move continuously because of friction between the piston and cylinder walls.



Reversible Process

To convert Process into the reversible change we must remove any friction.

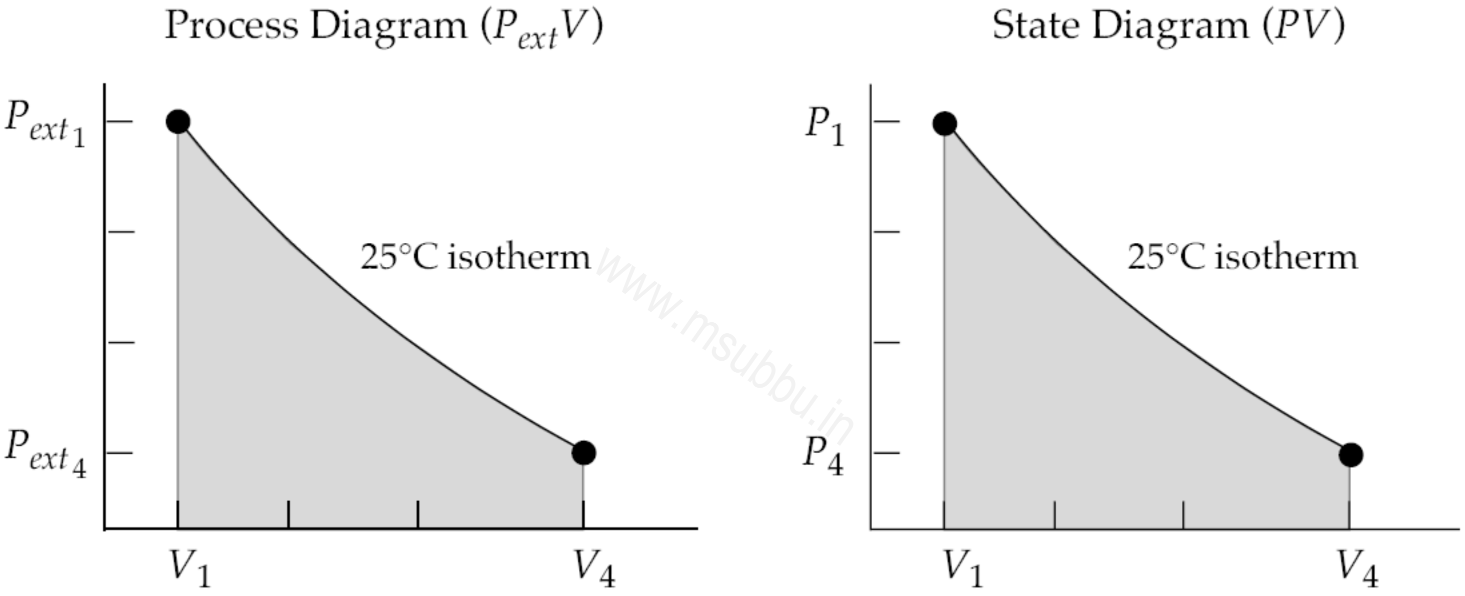


Figure 2.7 In the limiting case of a reversible change (Process 3), the process path would appear the same on both a process diagram (*left*) and a state diagram (*right*).

$$W = -\int_{V_1}^{V_4} P_{ext}\, dV = -\int_{V_1}^{V_4} P\, dV$$

Reversible Process

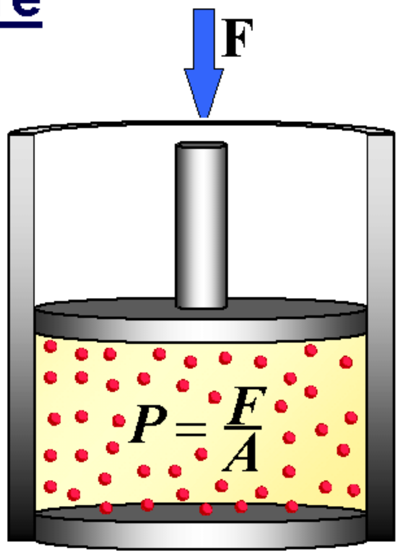
- For a reversible process the net force driving is only differential in size.
- The process can be reversed, leaving no change in the system or surroundings.
- Work is transferred reversibly when the pressure difference between the system and surrounding are low.
  - During reversible expansion, maximum work is produced by the system
  - During reversible compression, minimum work is spent by the surroundings.

- Heat is transferred reversibly when it flows from an object at temperature T to another object at temperature T – dT

- All processes in real World are irreversible. Then why do we spend much time on discussing reversible processes?
  - In the first place, reversible process represent a limiting behavior, i.e., the best we can hope for.
  - Secondly, the reversible process is one for which we can readily do the calculations. However, we do not always need the assumption of reversibility.

- If the work done **by the system in returning to its original state is equal to the work we** originally did **on the system, that process is called *reversible. If there is friction between the piston*** and the cylinder walls, the process is not reversible

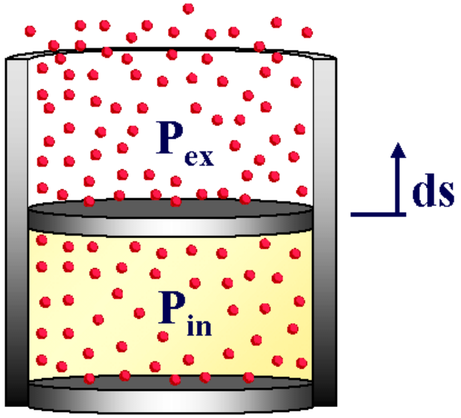
Pressure



(c) C. Rose-Petruck, Brown University, 7-Jan-99, Chem 201 #1

$$dW = -Fds$$

Expansion against external pressure



(c) C. Rose-Petruck, Brown University, 7-Jan-99, Chem 201 #1

$$dW = -P_{ex} A ds = -P_{ex} dV$$

Quasistatic Process

We assume that the outside pressure is always nearly equal to the inside pressure, a situation called *quasistatic*. In such a case, the motion of the movable wall separating the system from the surroundings is infinitely slow. Compression can easily be reversed by expansion; i.e. the process is *reversible*. If the pressure difference is larger the motion of this wall will not be slow any more and complicated effects, such as shock waves or turbulence, can occur. Such processes are certainly *irreversible*. Therefore, quasistatic processes are reversible.

Then:

$$W = -\int_{path} P_{ex}\,dV = -\int_{path} P_{in}\,dV$$

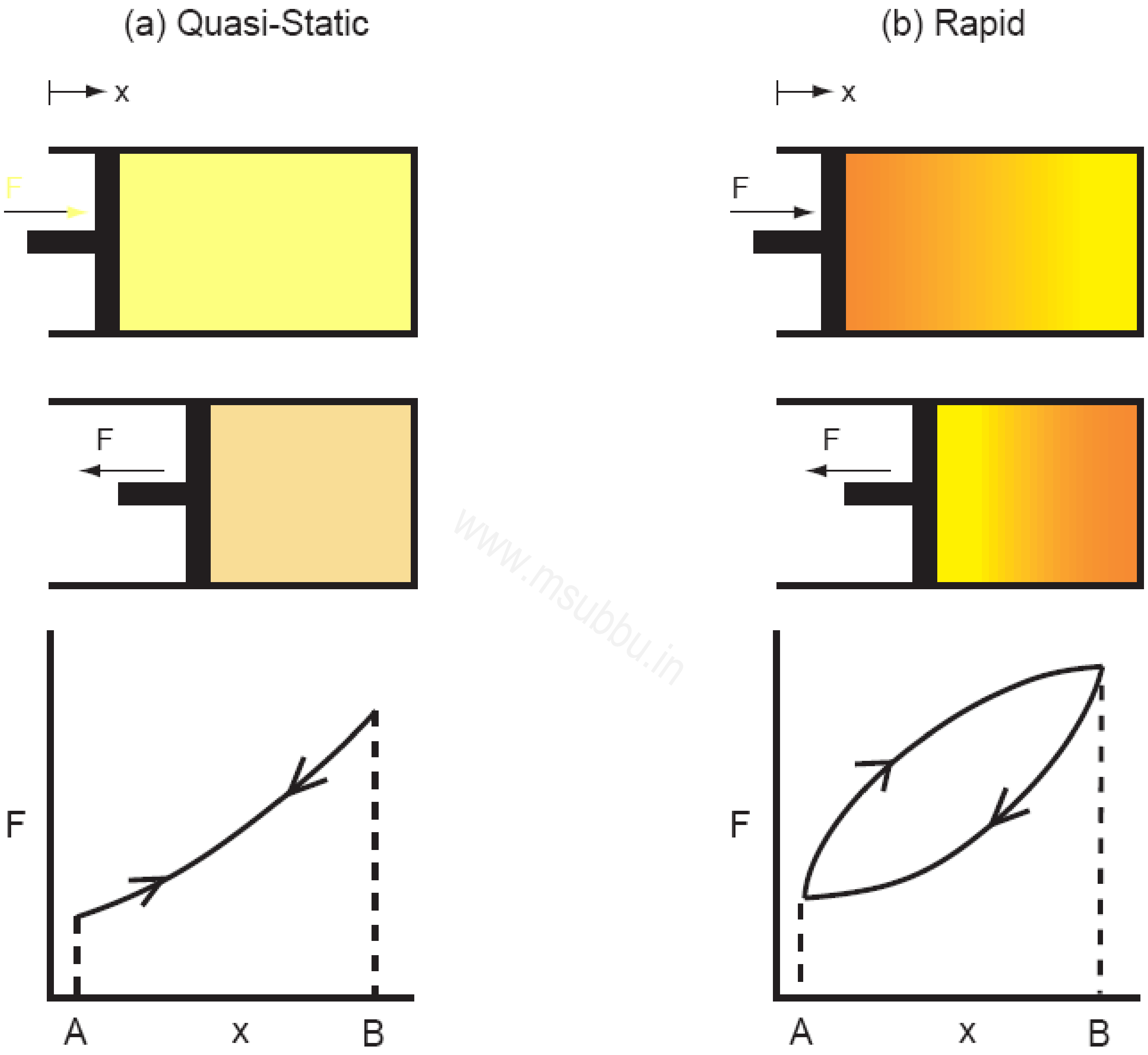
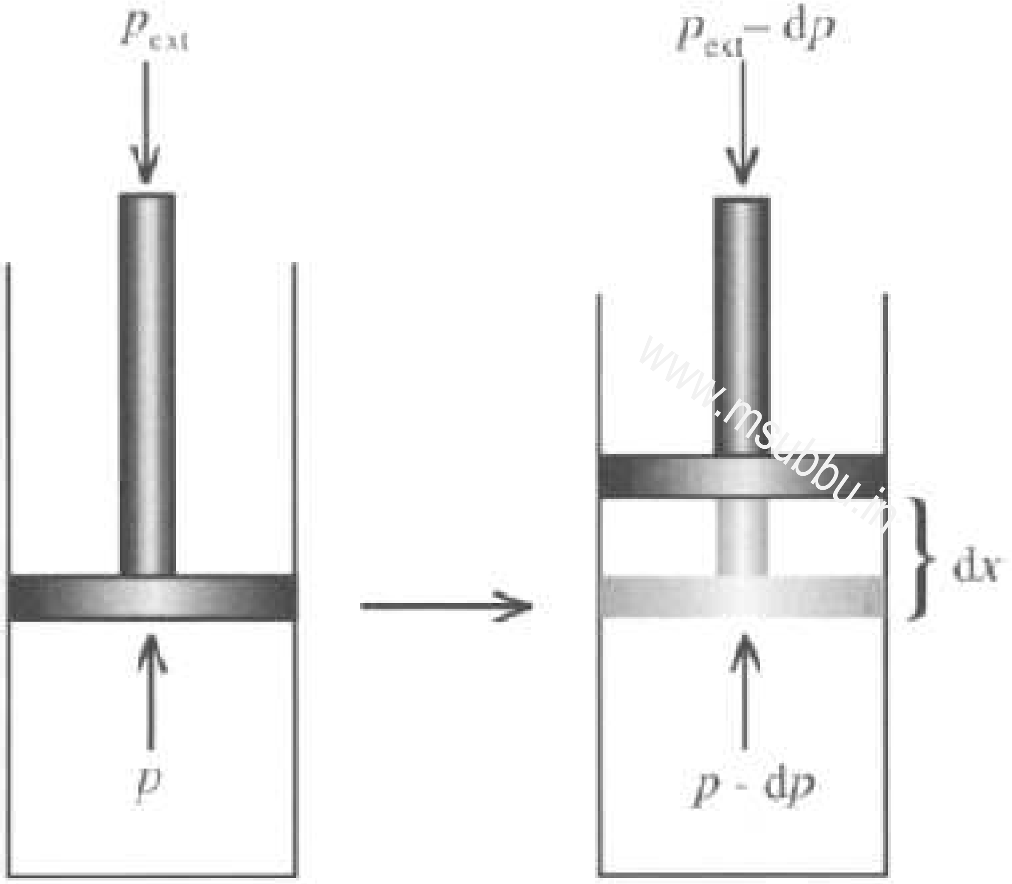


Figure 2.9: (a) Quasi-static and (b) rapid compression and expansion of a gas.



$$w = -\int_{V_1}^{V_2} p_{ext}\, dV.$$

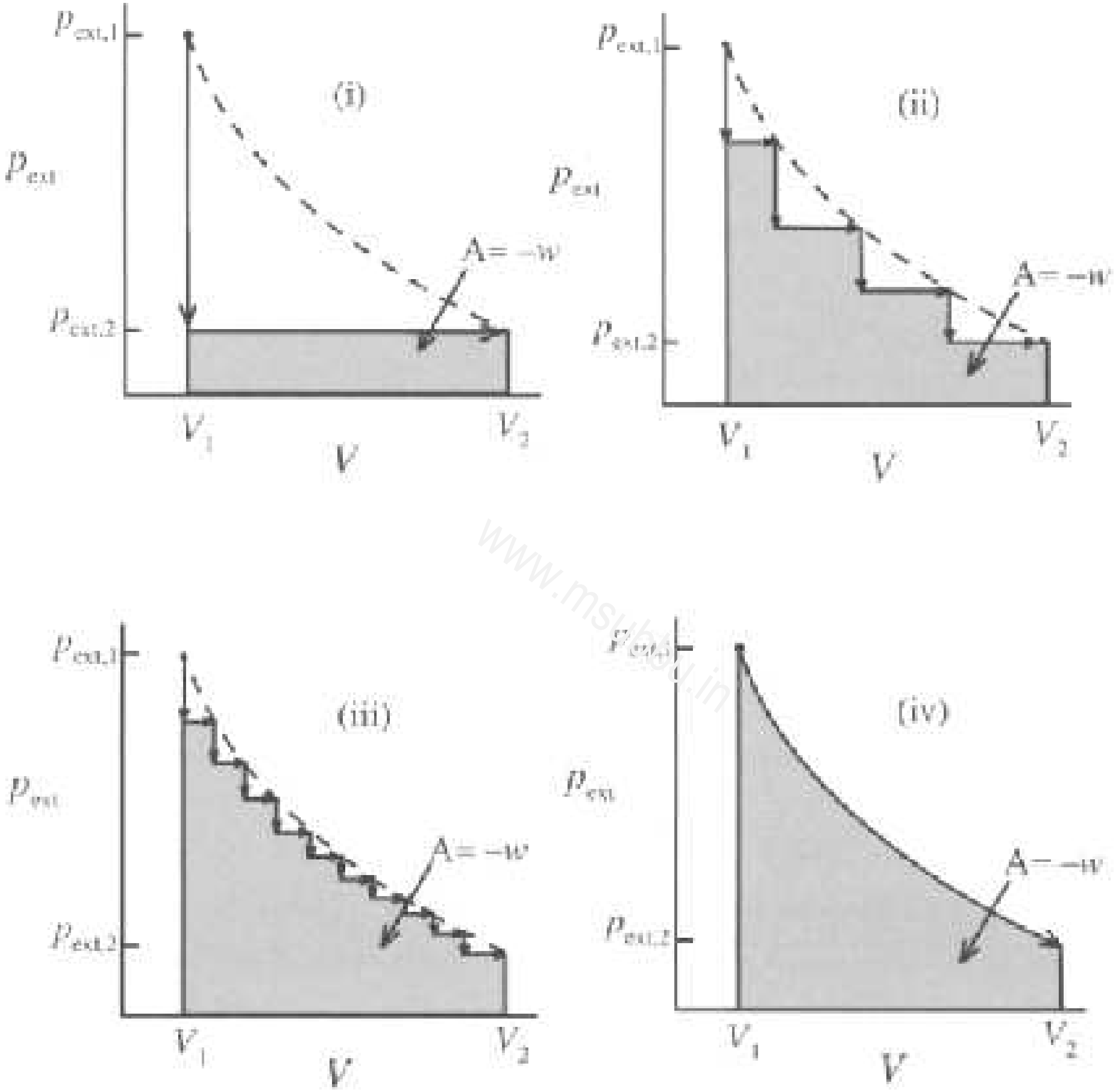
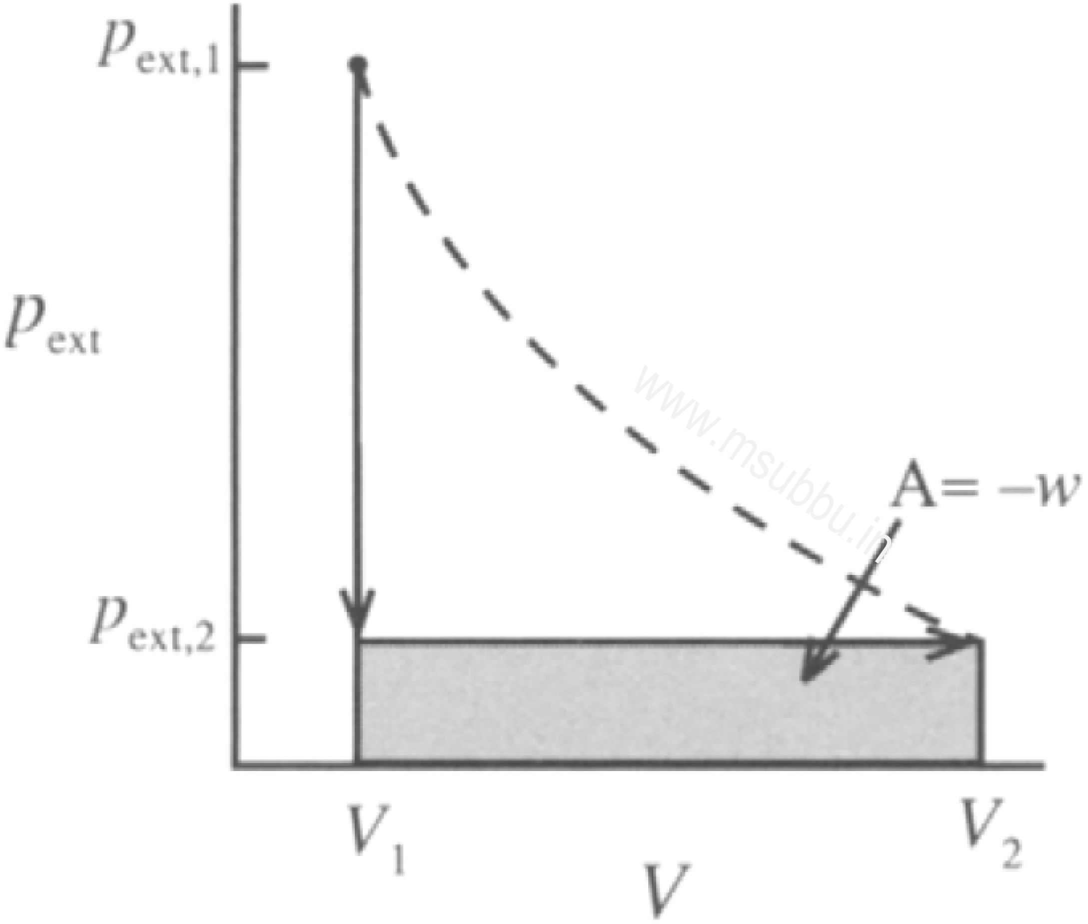
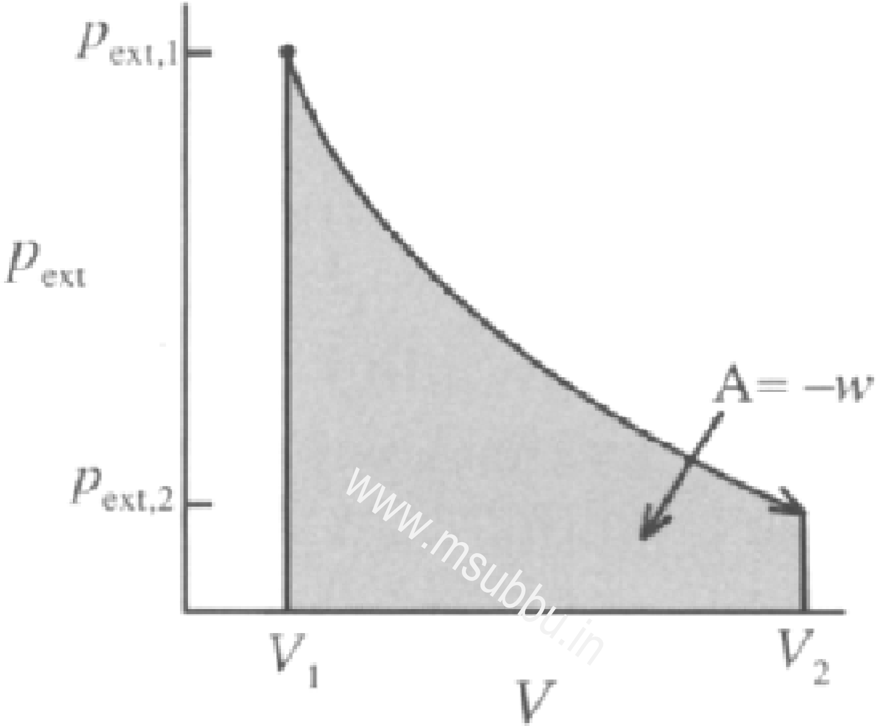


Figure 2.5 Comparison of the work accomplished following four different paths during an isothermal expansion.



$$w = -\int_{V_1}^{V_2} p_{ext,2}\,dV$$

$$= -p_{ext,2}\Delta V.$$



Since in the reversible process, P and P_{ext} never differ by more than an infinitesimal amount, P can replace P_{ext} in equations to calculate W.

$$w = -\int_{V_1}^{V_2} p \, dV \text{ (reversible process)}$$

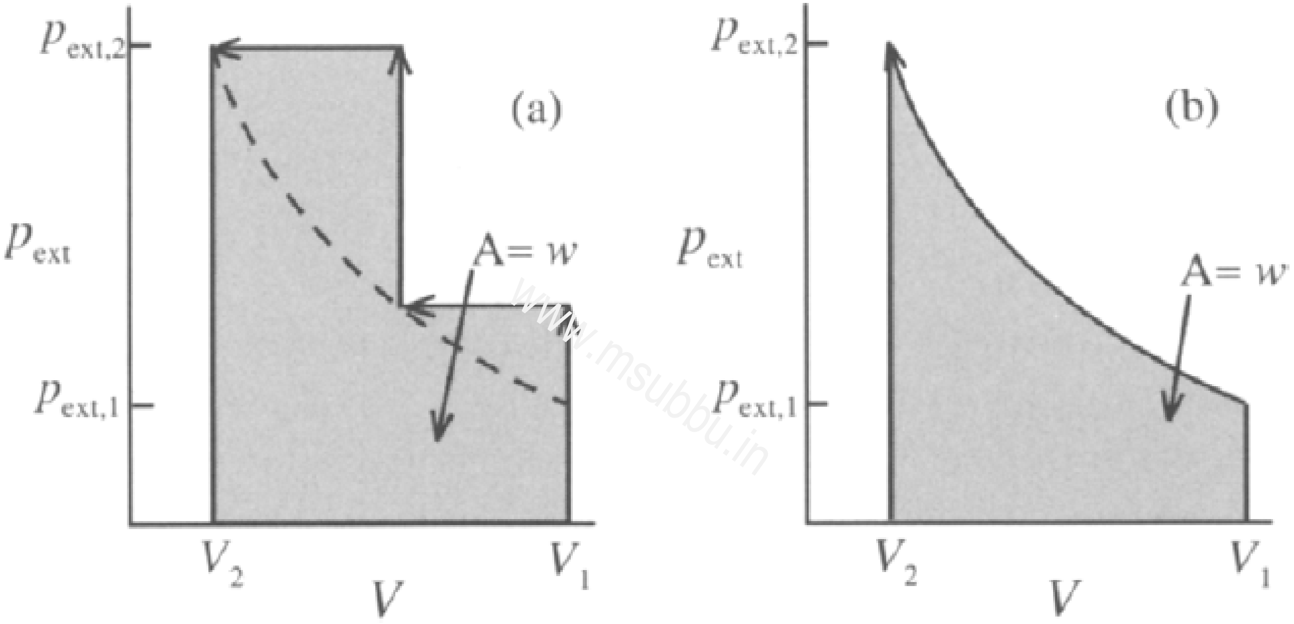
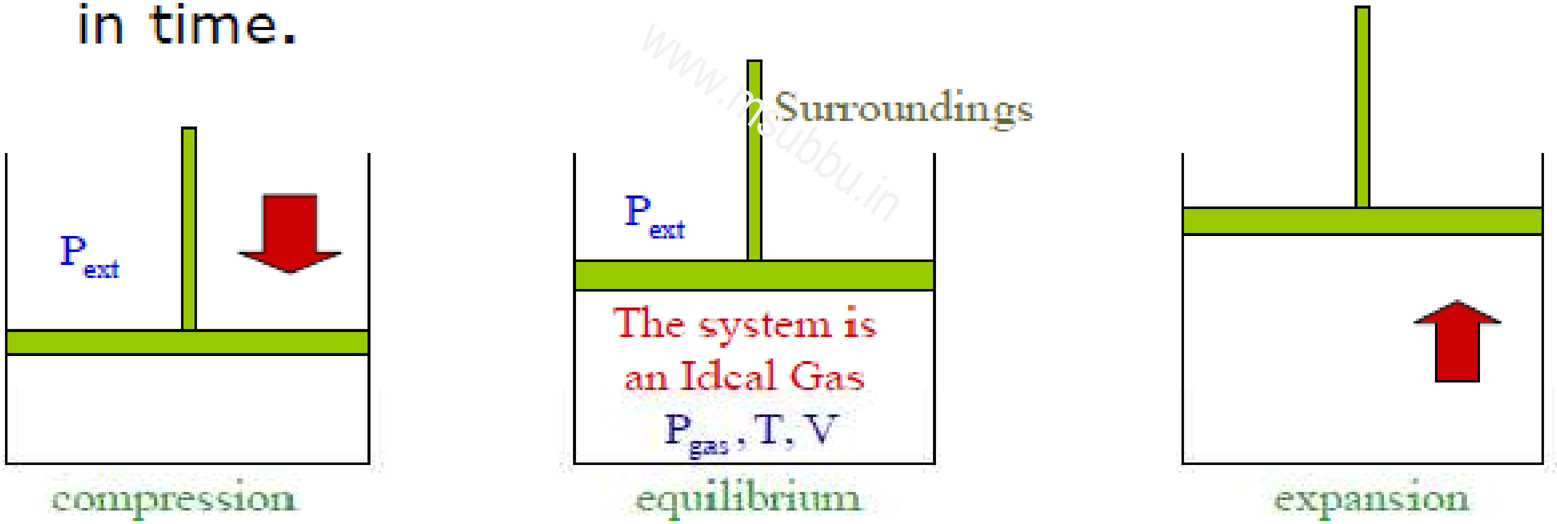


Figure 2.7 Comparison of isothermal work of compression. Graph (b) represents the reversible process for which the work required for the compression is a minimum.

Reversible Processes

- **Reversible Process:** Here, a thermodynamic transformation is able to retrace its history in time, when external condition retraces its history in time.



For a reversible process, $\left(P_{ext} - P_{gas}\right) \equiv \Delta P \rightarrow 0$

Energy

- It is a quantity that can be stored with the system and can be exchanged between the system and surroundings.
- The exchange of energy occurs either as heat or as work.
- Types of energy: Potential energy, kinetic energy, internal energy, etc.
- Kinetic and potential energy are not thermodynamic properties of the system, as they do not change with temperature or pressure of the body. Internal energy is a thermodynamic property of the system

Internal Energy

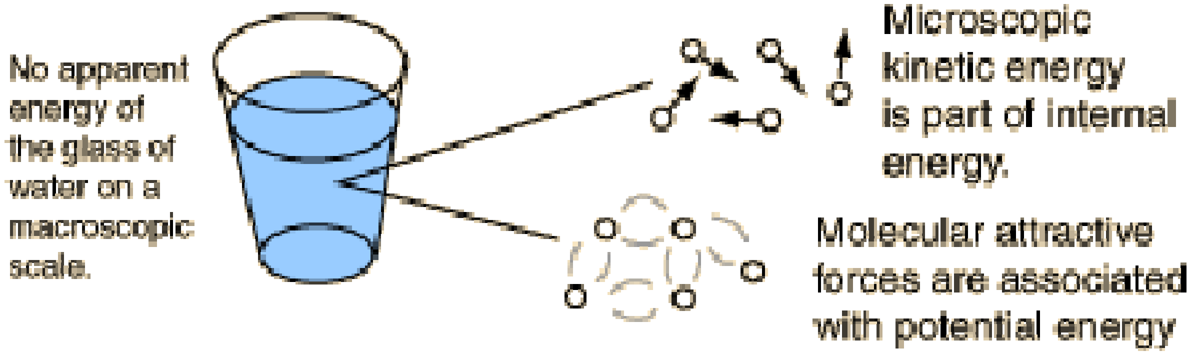
- The energy stored in the system by virtue of the configuration and motion of molecules constituting the system is called *internal energy* (U). The energy due to mass motion of the system as a whole (the kinetic energy), and that due to its external position in gravitational, electrical, or magnetic field (the potential energy) are not included in the internal energy.

- The molecules constituting the system possess kinetic energy of translation, rotation, and vibration. They also possess potential energy due to the forces of attraction between them. These molecular potential and kinetic energies contribute to the internal energy of the system.

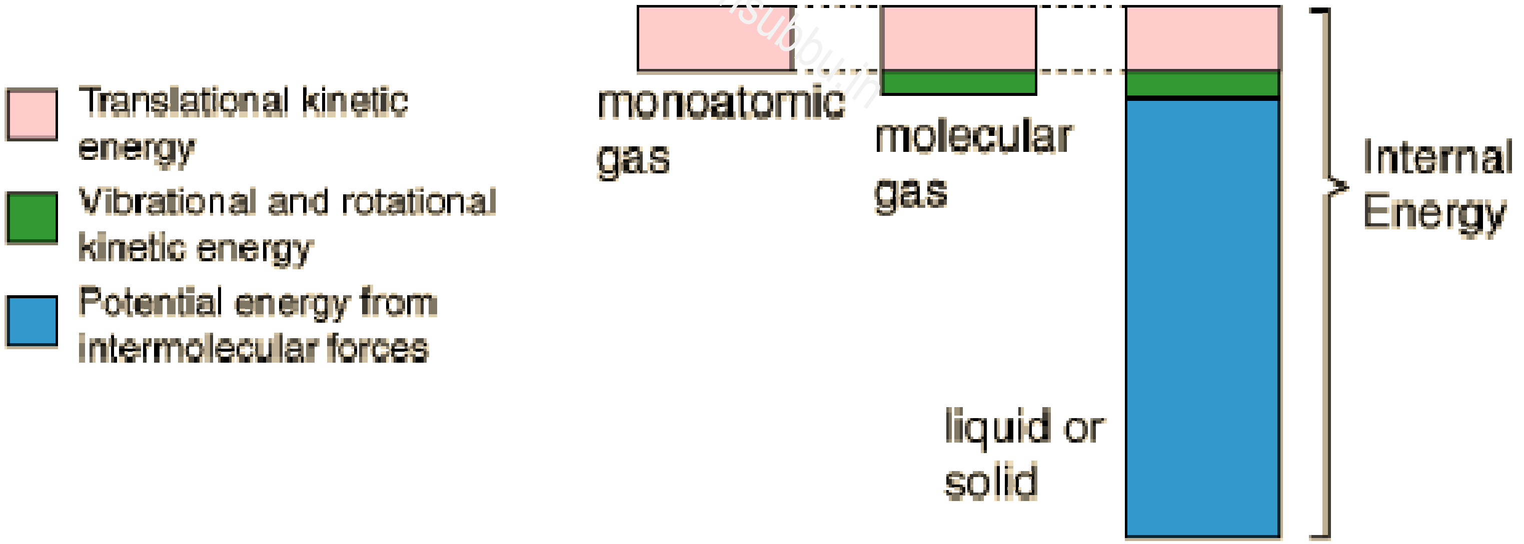
- A system under a given set of conditions has a definite internal energy.

- It is impossible to measure the total internal energy of the substance and therefore absolute values of internal energy are not known. This is not a serious limitation because it is the changes in internal energy and not the absolute values that are usually needed in thermodynamic analysis

Does a glass of water sitting on a table have any energy?



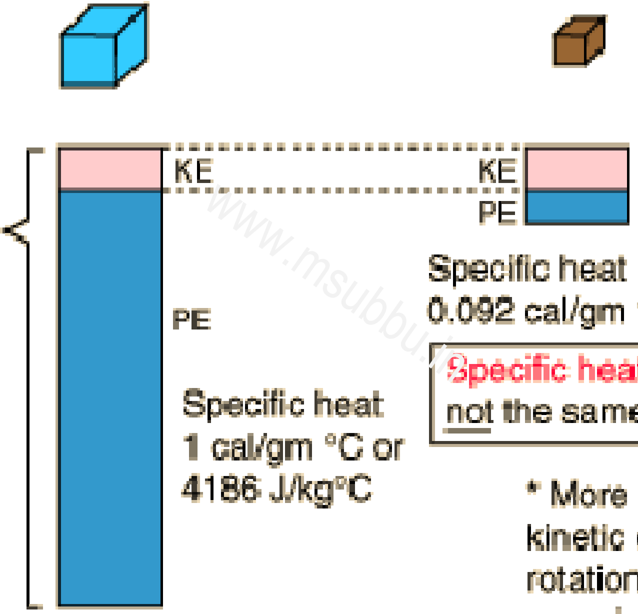
Systems with the same temperature



What is the same and what is different?

1 gram of water at 0°C

1 gram of copper at 0°C



The same temperature implies that the average molecular kinetic energy is the same*

The internal energy is not the same.

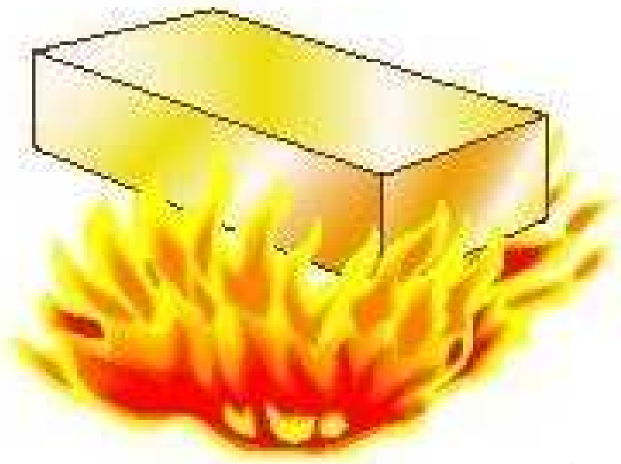
Specific heat 0.092 cal/gm °C or 386 J/kg°C

Specific heats are not the same.

Specific heat 1 cal/gm °C or 4186 J/kg°C

Why is the specific heat of water more than 10 times that of copper?!

* More precisely, the translational kinetic energies are the same. The rotational and vibrational kinetic energies are neglected in this simplified illustration.

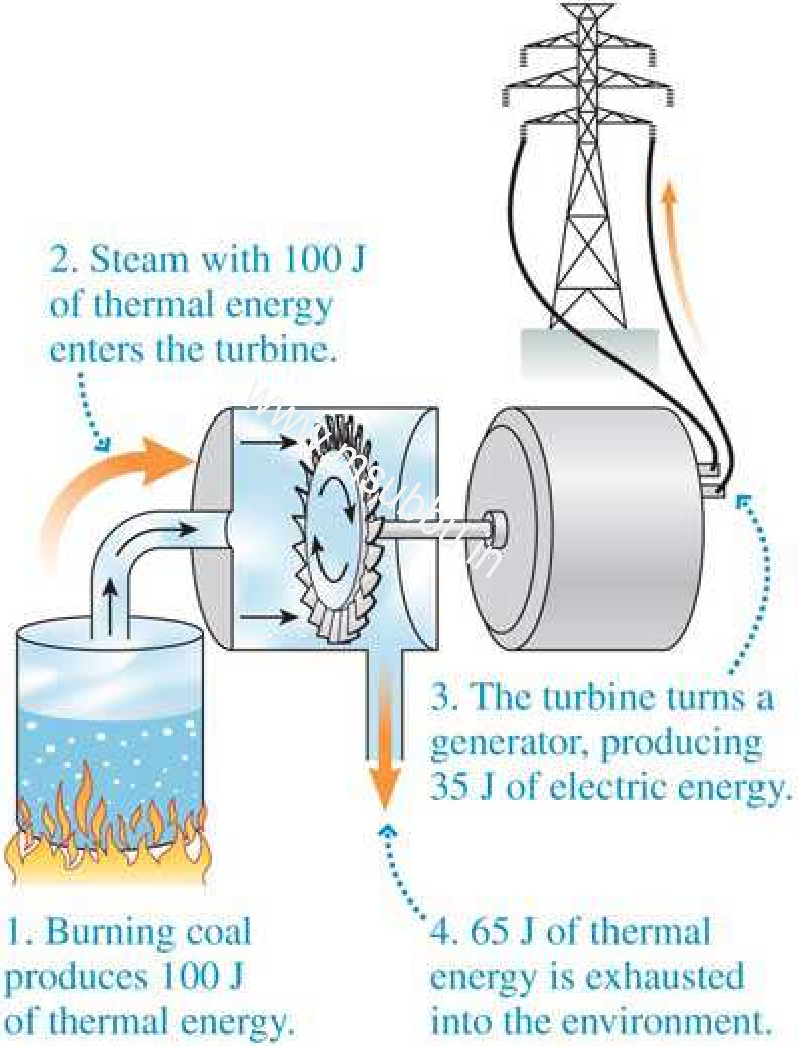


(i) A metal block heated in a flame gains energy from the flame and its temperature increases. The energy transferred to the metal block is stored as internal energy.

(ii) An ice cube melting under the Sun gains energy from the surroundings (it remains at 0 °C). The energy transferred to the ice cube is also stored as internal energy.

Internal energy of a body is the energy stored in the body. It is the sum of kinetic energy and potential energy of all particles in the body. It increases with the temperature of the body and increases when the body changes state from solid to liquid and from liquid to gas.

Energy classifications

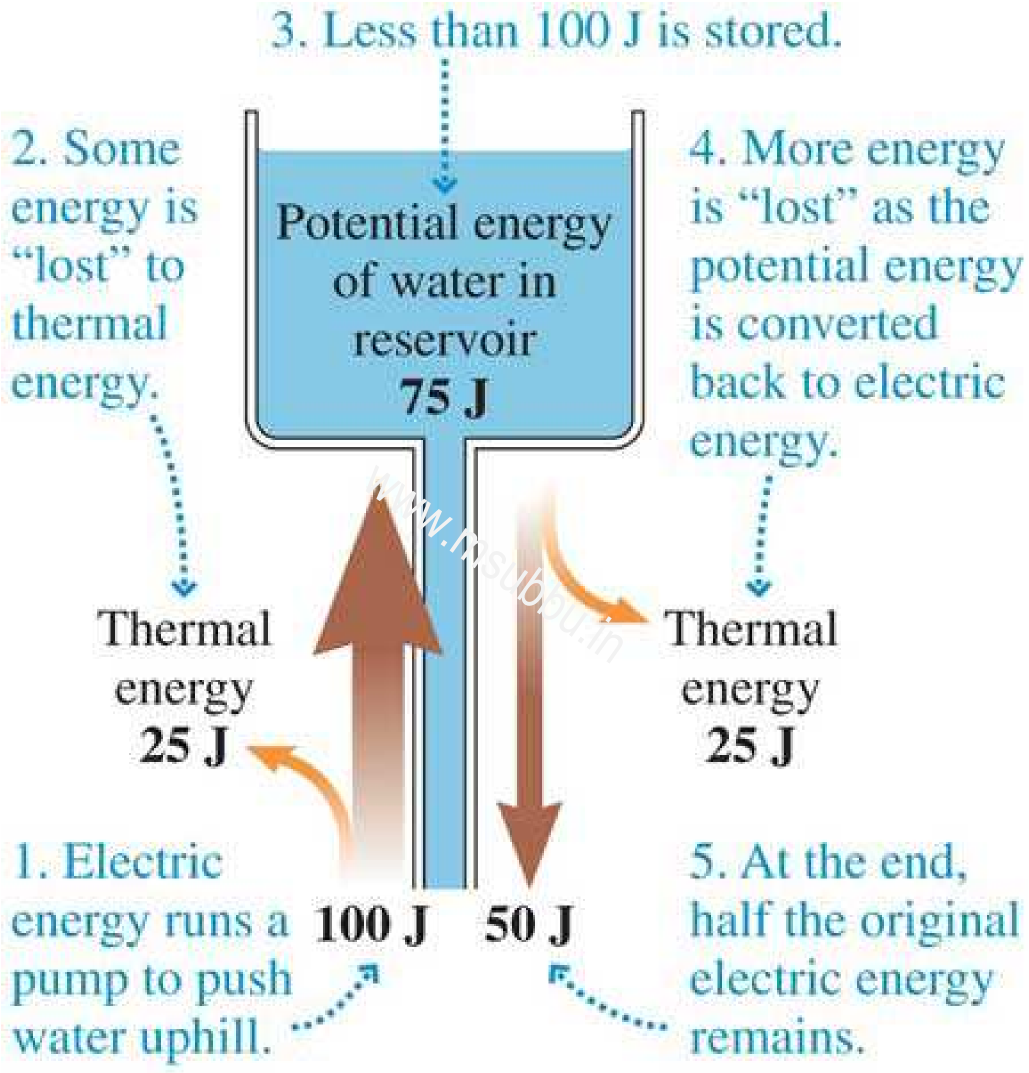


2. Steam with 100 J of thermal energy enters the turbine.

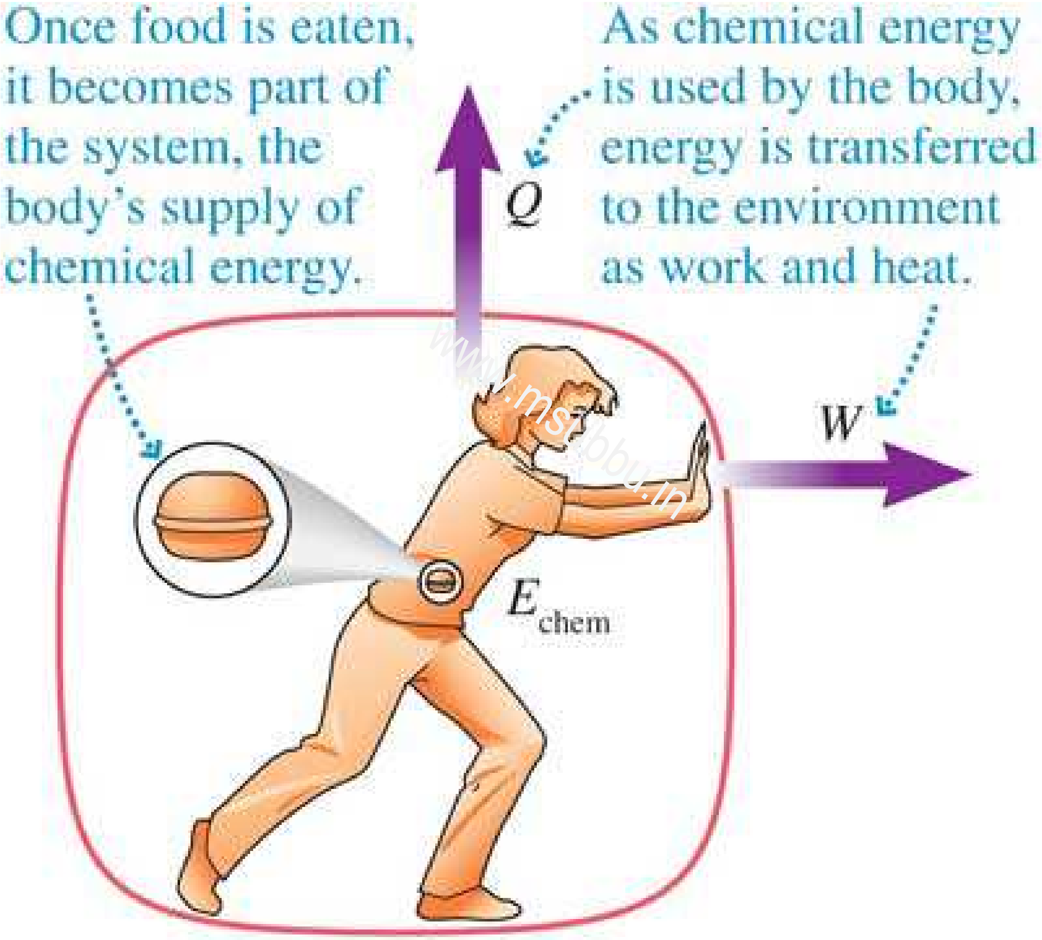
3. The turbine turns a generator, producing 35 J of electric energy.

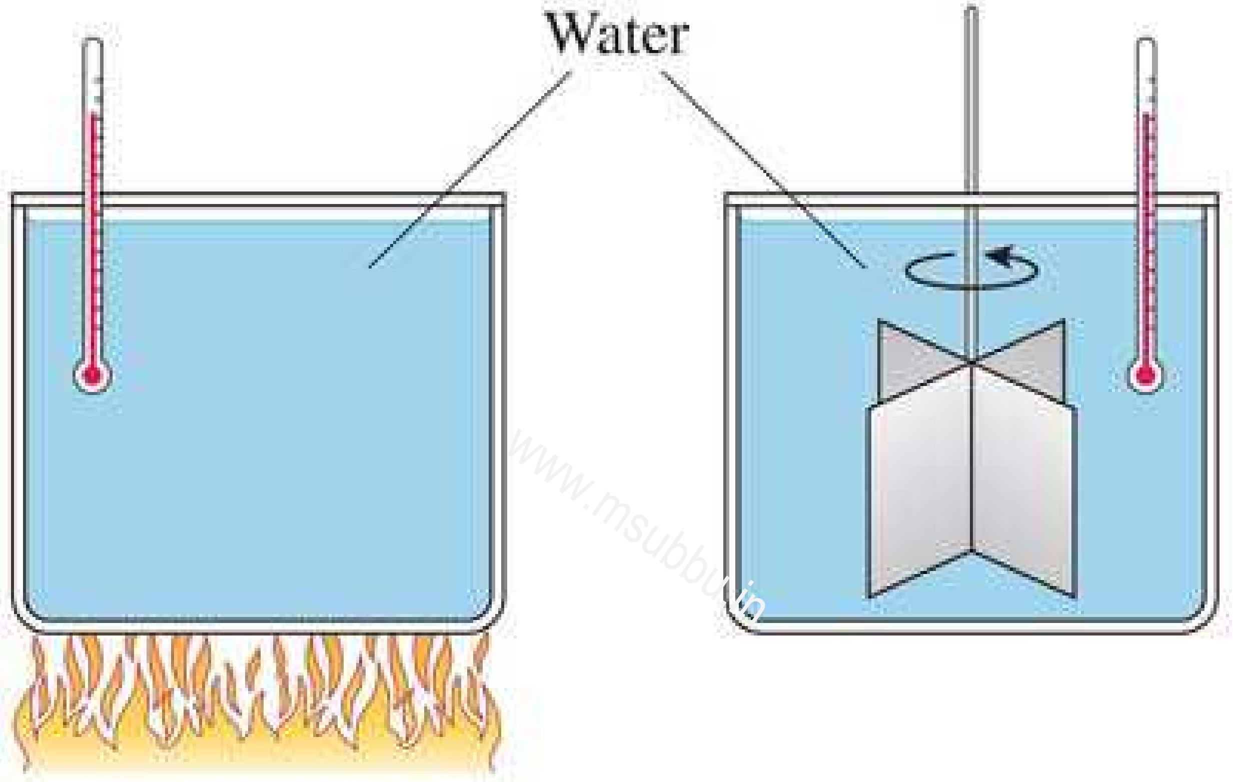
1. Burning coal produces 100 J of thermal energy.

4. 65 J of thermal energy is exhausted into the environment.


3. Less than 100 J is stored.
2. Some energy is "lost" to thermal energy.
Potential energy of water in reservoir
75 J
4. More energy is "lost" as the potential energy is converted back to electric energy.
Thermal energy
25 J
Thermal energy
25 J
1. Electric energy runs a pump to push water uphill.
100 J
50 J
5. At the end, half the original electric energy remains.

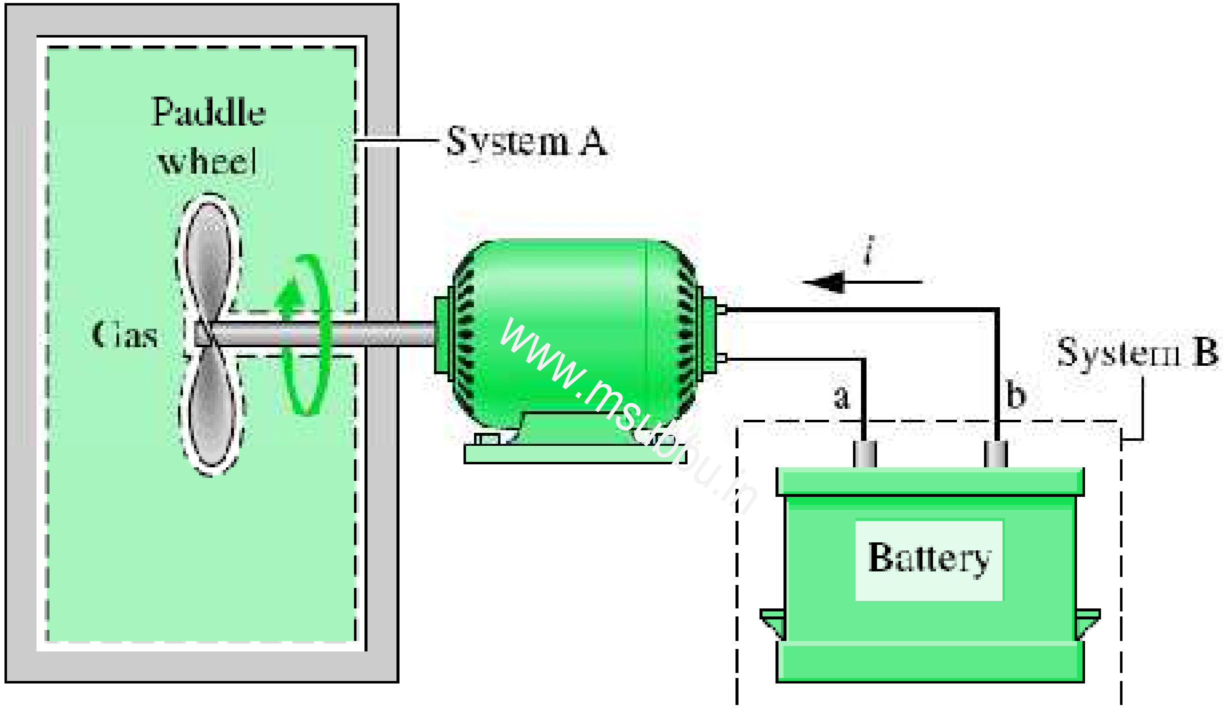
Energy in transition - heat and work





The flame heats the water.

The spinning paddle does work on the water.


Paddle wheel
System A
Gas
i
System B
a
b
Battery

Phase Rule

- Gibbs phase rule (developed in 1875) allows us to determine the number of degrees of freedom (F), which are the number of independent variables that must be fixed to specify the intensive state of the system

$$F = C - P + 2$$

where *P* is the number of phases in thermodynamic equilibrium with each other, and *C* is the number of components

- The above relationship is valid for non-reactive systems in equilibrium

For a single component, two phase mixture the number of independent variables are (GATE-1992-7.d)

(a) two (b) one (c) zero (d) three

The system liquid water in equilibrium with a mixture of water vapor and nitrogen has the following degrees of freedom

(a) 4 (b) 3 (c) 0 (d) 2

A gas mixture of three components is brought in contact with a dispersion of an organic phase in water. The degrees of freedom of the system are (GATE-1999-1.08)

(a) 4 (b) 3 (c) 5 (d) 6

At the triple point of a pure substance, the number of degrees of freedom is: (GATE-1993-5.i)

(a) 0 (b) 1 (c) 2 (d) 3

The number of degrees of freedom for a mixture of ice and water (liquid) are (GATE-1996-1.02)

(a) 2 (b) 3 (c) 1 (d) 0

34. A gas mixture of three components is brought in contact with a dispersion of an organic phase in water. The degrees of freedom of the system are (GATE-1999-1.08)

(a) 4 (b) 3 (c) 5 (d) 6

Answer: **(a)** $C = 3 + 1 + 1 = 5$; $P = 3$; $F = C - P + 2 = 5 - 3 + 2 = 4$

35. The system liquid water in equilibrium with a mixture of water vapor and nitrogen has the following degrees of freedom

(a) 4 (b) 3 (c) 0 (d) 2

Answer: **(d)** $F = C - P + 2 = 2 - 2 + 2 = 2$.

36. For a single component, two phase mixture the number of independent variables are (GATE-1992-7.d)

(a) two (b) one (c) zero (d) three

Answer: **(b)** $F = C - P + 2 = 1 - 2 + 2 = 1$.

38. At the triple point of a pure substance, the number of degrees of freedom is: (GATE-1993-5.i)

(a) 0 (b) 1 (c) 2 (d) 3

Answer: **(a)**

39. The number of degrees of freedom for a mixture of ice and water (liquid) are (GATE-1996-1.02)

(a) 2 (b) 3 (c) 1 (d) 0

Answer: **(c)** $F = C - P + 2 = 1 - 2 + 2 = 1.$