Engineering Thermodynamics

Basic Concepts of Thermodynamics

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DEFINITION OF THERMODYNAMICS

Thermodynamics may be *defined* as follows :

- *Thermodynamics is an axiomatic science which deals with the relations among heat, work and properties of system which are in equilibrium. It describes state and changes in state of physical systems*.

Or

- Thermodynamics is *the science of the regularities governing processes of energy conversion*.

Or

- Thermodynamics is *the science that deals with the interaction between energy and material systems*.

DEFINITION OF THERMODYNAMICS

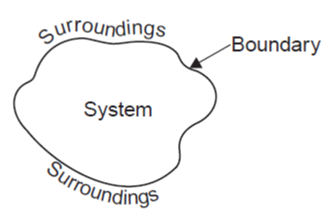
- Thermodynamics, basically entails *four laws* or axioms known as Zeroth, First, Second and Third law of thermodynamics.
- The ***First law*** throws light on *concept of internal energy*.
- The ***Zeroth law*** deals with *thermal equilibrium* and establishes a *concept of temperature*.
- The ***Second law*** indicates the limit of *converting heat into work* and introduces the *principle of increase of entropy*.
- The ***Third law*** defines the *absolute zero of entropy*.
- These laws are based on experimental observations and have no *mathematical proof*. Like all physical laws, these laws are based on *logical reasoning*.

THERMODYNAMIC SYSTEMS

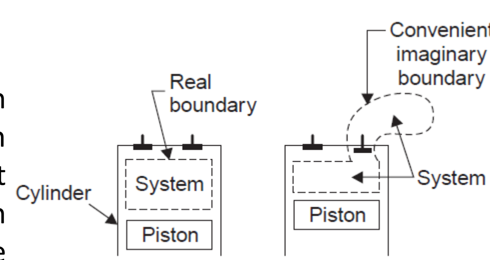
System, Boundary and Surroundings

- **System.** A system is *a finite quantity of matter or a prescribed region of space*
- **Boundary.** The *actual or hypothetical envelope enclosing the system* is the boundary of the system. The boundary may be fixed or it may move, as and when a system containing a gas is compressed or expanded.
- The boundary may be *real* or *imaginary.*

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



The system

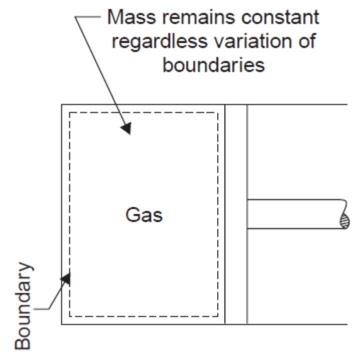


The real and imaginary boundaries.

THERMODYNAMIC SYSTEMS

Closed System

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

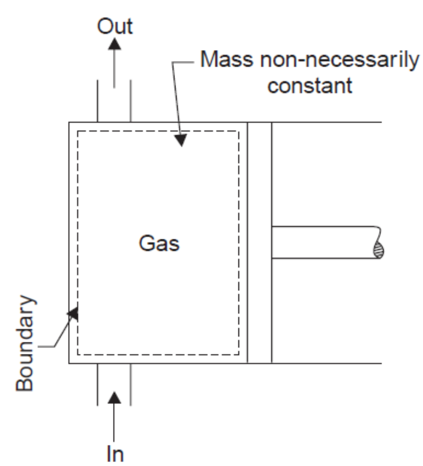


closed system

THERMODYNAMIC SYSTEMS

Open System

- An open system is one in which *matter flows into or out of the system*.
- Most of the engineering systems are open.



Open system

THERMODYNAMIC SYSTEMS

- **Isolated System** An isolated system is that system *which exchanges neither energy nor matter with any other system or with environment*.
- **Adiabatic System** An adiabatic system is one *which is thermally insulated from its surroundings* (system exchanges **no** heat with its surroundings). It can, however, *exchange work with its surroundings*. If it does not, it becomes an isolated system.
- **Phase.** A phase is a quantity of matter which is homogeneous throughout in chemical composition and physical structure.
- **Homogeneous System** A system which consists of a single phase is termed as *homogeneous system.* Examples : Mixture of air and water vapour, water plus nitric acid and octane plus heptane.
- **Heterogeneous System** A system which consists of two or more phases is called a *heterogeneous system.* Examples : Water plus steam, ice plus water and water plus oil.

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MACROSCOPIC AND MICROSCOPIC POINTS OF VIEW

- Thermodynamic studies are undertaken by the following two different approaches.

1. Macroscopic approach—(*Macro* mean *big* or *total*)
2. Microscopic approach —(*Micro* means *small*)

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MACROSCOPIC AND MICROSCOPIC POINTS OF VIEW

S. No.	*Macroscopic approach*	*Microscopic approach*
1.	In this approach a certain quantity of matter is considered *without* taking into account the events occurring at molecular level. In other words this approach to thermodynamics is concerned with *gross or overall behaviour*. This is known as *classical thermodynamics*.	The approach considers that the system is made up of a very large number of discrete particles known as *molecules*. These molecules have different velocities and energies. The values of these energies are constantly changing with time. This approach to thermodynamics which is concerned directly with the *structure of the matter* is known as *statistical thermodynamics*.
2.	The analysis of macroscopic system requires simple mathematical formulae.	The behaviour of the system is found by using statistical methods as the number of molecules is very large. So advanced statistical and mathematical methods are needed to explain the changes in the system.

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MACROSCOPIC AND MICROSCOPIC POINTS OF VIEW

S. No.	*Macroscopic approach*	*Microscopic approach*
3.	The values of the properties of the system are their average values. For example, consider a sample of a gas in a closed container. The *pressure* of the gas is the average value of the pressure exerted by millions of individual molecules. Similarly the *temperature* of this gas is the average value of translational kinetic energies of millions of individual molecules. These properties like *pressure* and *temperature* can be measured very easily. *The changes in properties can be felt by our senses.*	The properties like *velocity, momentum*, impulse, kinetic energy, force of impact etc. which describe the molecule *cannot be easily measured by instruments. Our senses cannot feel them.*
4.	In order to describe a system only a few properties are needed.	Large number of variables are needed to describe a system. So the approach is complicated.

Note. Although the macroscopic approach seems to be different from microscopic one, there exists a relation between them. Hence when both the methods are applied to a particular system, they give the same result

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PURE SUBSTANCE

- A **pure substance** is one that has a homogeneous and invariable chemical composition even though there is a change of phase.
- In other words, it is a system which is

(*a*) homogeneous in composition,

(*b*) homogeneous in chemical aggregation.

- **Examples**: Liquid, water, mixture of liquid water and steam, mixture of ice and water.
- The mixture of liquid air and gaseous air is not a pure substance.

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THERMODYNAMIC EQUILIBRIUM

- A system is in *thermodynamic equilibrium* if:
  1. the temperature and pressure at all points are same;
  2. there should be no velocity gradient;
  3. the chemical equilibrium is also necessary.
- Systems under temperature and pressure equilibrium but not under chemical equilibrium are sometimes said to be in metastable equilibrium conditions.
- *It is only under thermodynamic equilibrium conditions that the properties of a system can be fixed.*

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THERMODYNAMIC EQUILIBRIUM

- Thus for attaining a state of *thermodynamic equilibrium* the following *three* types of equilibrium states must be achieved:

1. **Thermal equilibrium.** The temperature of the system does not change with time and has same value at all points of the system.

2. **Mechanical equilibrium.** There are no unbalanced forces within the system or between the surroundings. The pressure in the system is same at all points and does not change with respect to time.

3. **Chemical equilibrium.** No chemical reaction takes place in the system and the chemical composition which is same throughout the system does not vary with time.

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PROPERTIES OF SYSTEMS

- A property of a system is a characteristic of the system which depends upon its state, but not upon how the state is reached. There are two sorts of property :

1. **Intensive properties.** These properties *do not depend on the mass of the system*.

Examples: Temperature and pressure.

2. **Extensive properties.** These properties *depend on the mass of the system*.

Example: Volume.

- Extensive properties are often divided by mass associated with them to obtain the intensive properties. For example, if the volume of a system of mass m is V, then the specific volume of matter within the system is $V/m = v$ which is an intensive property.

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STATE

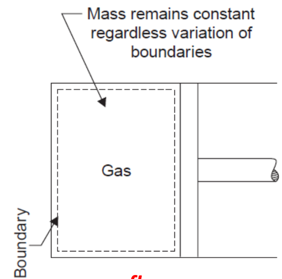
- ***State*** *is the condition of the system at an instant of time as described or measured by its properties. Or each unique condition of a system is called a* ***state***.
- It follows from the definition of state that each property has a single value at each state.
- Stated differently, all properties are ***state*** or ***point functions****.* Therefore, all properties are identical for identical states.

STATE

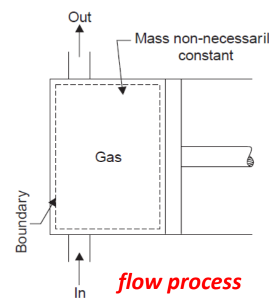
- On the basis of the previous discussion, we can determine if a given variable is *property* or not by applying the following *tests* :
- ➢ *A variable is a property, if and only if, it has a single value at each equilibrium state*.
- ➢ A variable is a property, if and only if, the change in its value between any two prescribed equilibrium states is single-valued.
- Therefore, *any variable whose change is fixed by the end states is a property*.

PROCESS

- A process occurs when the system undergoes a change in a state or an energy transfer at a steady state.
- A process may be *non-flow* in which a fixed mass within the defined boundary is undergoing a change of state.
    - *Example* : A substance which is being heated in a closed cylinder undergoes a ***non-flow process.***
- *Closed systems undergo non-flow processes*.
- A process may be a ***flow process*** *in which mass is entering and leaving through the boundary of an open system*.
- In a steady flow process mass is crossing the boundary from surroundings at entry, and an equal mass is crossing the boundary at the exit so that the total mass of the system remains constant.



non-flow process

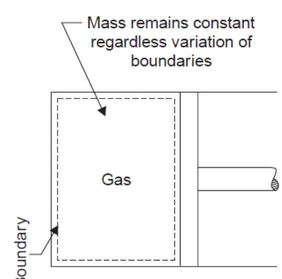


flow process

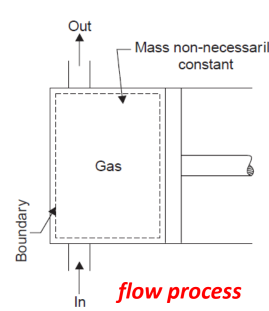
steady flow process

PROCESS

- In an open system it is necessary to take account of the work delivered from the surroundings to the system at entry to cause the mass to enter, and also of the work delivered from the system at surroundings to cause the mass to leave, as well as any heat or work crossing the boundary of the system.
- **Quasi-static process.** Quasi means '*almost*'. A quasi-static process is also called a *reversible process. This process is a succession of equilibrium states and infinite slowness is its characteristic feature.*



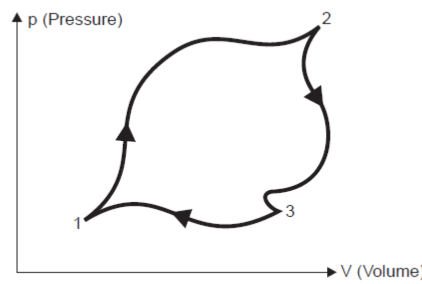
non-flow process



flow process

CYCLE

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



Cycle of operations.

POINT FUNCTION

- *When two properties locate a point on the graph (co-ordinate axes) then those properties are called as* **point function.**
- *Examples*: Pressure, temperature, volume etc.

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

PATH FUNCTION

- There are certain quantities which cannot be located on a graph by a *point* but are given by the *area* or so, on that graph.
- In that case, the area on the graph, pertaining to the particular process, *is a function of the path of the process.* Such quantities are called **path functions.**
- *Examples*. Heat, work etc.
- Heat and work are *inexact differentials*. Their change cannot be written as difference between their end states.

$$\text{Thus } \int_1^2 \delta Q \neq Q_2 - Q_1 \text{ and is shown as } {}_1Q_2 \text{ or } Q_{1-2}$$

$$\text{Similarly } \int_1^2 \delta W \neq W_2 - W_1, \text{ and is shown as } {}_1W_2 \text{ or } W_{1-2}$$

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

TEMPERATURE

- *The temperature is a thermal state of a body which distinguishes a hot body from a cold body*.
- The temperature of a body is *proportional to the stored molecular energy i.e.,* the average molecular kinetic energy of the molecules in a system.
- A particular molecule does not have a temperature, it has energy. The gas as a system has temperature.
- Instruments for measuring *ordinary temperatures* are known as ***thermometers*** and those for measuring *high temperatures* are known as ***pyrometers*.**

TEMPERATURE

- It has been found that a gas will not occupy any volume at a certain temperature.
- This temperature is known as *absolute zero temperature*.
- The temperatures measured with absolute zero as basis are called *absolute temperatures*.
- Absolute temperature is stated in degrees centigrade.
- The point of absolute temperature is found to occur at 273.15°C below the freezing point of water.

➢Then : Absolute temperature = Thermometer reading in °C + 273.15.

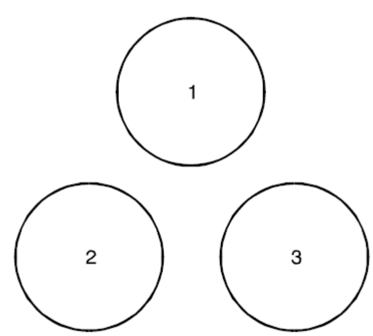
- Absolute temperature is degree centigrade is known as degrees kelvin, denoted by K (SI unit).

ZEROTH LAW OF THERMODYNAMICS

- **'Zeroth law of thermodynamics'** *states that if two systems are each equal in temperature to a third, they are equal in temperature to each other*.

Example. System '1' may consist of a mass of gas enclosed in a rigid vessel fitted with a pressure gauge.

- If there is no change of pressure when this system is brought into contact with system '2' a block of iron, then the two systems are equal in temperature (assuming that the systems 1 and 2 do not react each other chemically or electrically).
- Experiment reveals that if system '1' is brought into contact with a third system '3' again with no change of properties then systems '2' and '3' will show no change in their properties when brought into contact provided they do not react with each other chemically or electrically.
- Therefore, '2' and '3' must be in equilibrium.



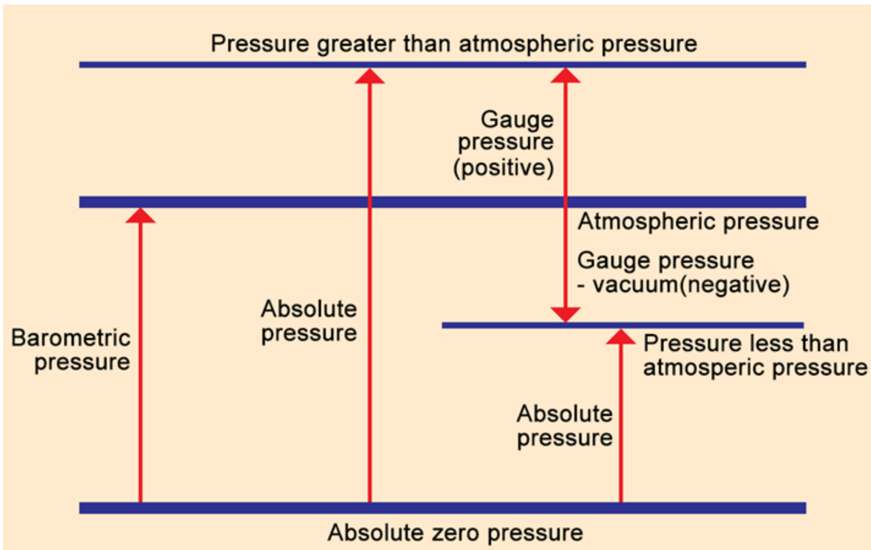
PRESSURE

- Pressure is defined as a *force per unit area*.
- Pressures are exerted by gases, vapours and liquids.
- The instruments that we generally use, however, record pressure as the difference between two pressures. Thus, it is the *difference between the pressure exerted by a fluid of interest and the ambient atmospheric pressure.*
- Such devices indicate the pressure either above or below that of the atmosphere. When it is ***above*** *the atmospheric pressure*, it is termed *gauge pressure* and is *positive*. When it is ***below*** atmospheric, it is *negative* and is known as *vacuum*.
- Vacuum readings are given in millimetres of mercury or millimetres of water below the atmosphere.

PRESSURE

- It is necessary to establish an absolute pressure scale which is independent of the changes in atmospheric pressure.
- A pressure of absolute zero can exist only in complete vacuum.
- *Any pressure measured above the absolute zero of pressure* is termed an '*absolute pressure*'.
- A schematic diagram showing the *gauge pressure, vacuum pressure* and the *absolute pressure* is given in the following Fig.

PRESSURE



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PRESSURE

- Mathematically :

(*i*) Absolute pressure = Atmospheric pressure + Gauge pressure

$$P_{abs.} = P_{atm.} + P_{gauge.}$$

(*ii*) Vacuum pressure = Atmospheric pressure – Absolute pressure.

- *Vacuum* is defined as the *absence of pressure*.
- A *perfect vacuum* is obtained when *absolute pressure is zero*, at this instant *molecular momentum is zero*.
- Atmospheric pressure is measured with the help of barometer.

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PRESSURE

- The fundamental SI unit of pressure is N/m^2 (sometimes called *pascal*, Pa) or bar.
- 1 bar = 10^5 N/m^2 = 10^5 Pa.
- Standard atmospheric pressure = 1.01325 bar = 0.76 m (or 760 mm) Hg.
- Low pressures are often expressed in terms of mm of water or mm of mercury. This is an abbreviated way of saying that the pressure is such that which will support a liquid column of stated height.

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SPECIFIC VOLUME

- The *specific volume* of a system is the volume occupied by the unit mass of the system.
- The symbol used is v and units are; for example, m^3/kg.
- The symbol V will be used for volume. (Note that specific volume is *reciprocal of density*).

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Ideal Gas

- From experimental observations it has been established that an ideal gas (to a good approximation) behaves according to the simple equation

$$pV = mRT$$

where p, V and T are the pressure, volume and temperature of gas having mass m and R is a constant for the gas known as its ***gas constant*.**

- This equation can be written as

$$pv = RT$$

(where v = V/m)

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Ideal Gas

- In reality there is no gas which can be qualified as an ideal or perfect gas. However *all gases tend to ideal or perfect gas behavior at all temperatures as their pressure approaches* ***zero***
- For two states of the gas $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$$\frac{T_2}{T_1} = \frac{p_2}{p_1} \times \frac{V_2}{V_1}$$

With the help of this eqn. ($pV = mRT$), the temperatures can be measured or compared.

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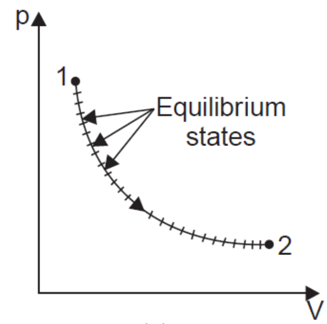
REVERSIBLE AND IRREVERSIBLE PROCESSES

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



Reversible process

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REVERSIBLE AND IRREVERSIBLE PROCESSES

- Reversible process has the following *characteristics* :
  1. It must pass through the same states on the reversed path as were initially visited on the forward path.
  2. This process when undone will leave no history of events in the surroundings.
  3. It must pass through a continuous series of equilibrium states.
- No real process is truly reversible but some processes may approach reversibility, to close approximation.

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REVERSIBLE AND IRREVERSIBLE PROCESSES

- Reversible process **Examples**

Some examples of nearly reversible processes are:

(*i*) Frictionless relative motion.

(*ii*) Expansion and compression of spring.

(*iii*) Frictionless adiabatic expansion or compression of fluid.

(*iv*) Polytropic expansion or compression of fluid.

(*v*) Isothermal expansion or compression.

(*vi*) Electrolysis.

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REVERSIBLE AND IRREVERSIBLE PROCESSES

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

1. Combustion
2. Diffusion
3. Free expansion
4. Throttling
5. Heat transfer
6. Plastic deformation.
7. Relative motion with friction
8. Electricity flow through a resistance

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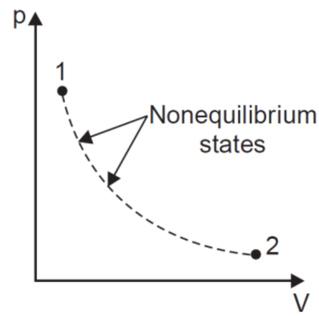
REVERSIBLE AND IRREVERSIBLE PROCESSES

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



Irreversible process

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REVERSIBLE AND IRREVERSIBLE PROCESSES

- Irreversibilities are of *two types* :

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

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

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

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

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ENERGY, WORK AND HEAT
Energy

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

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ENERGY, WORK AND HEAT
Energy

- In a ***non-flow process*** *usually there is no change of potential or kinetic energy and hence change of mechanical energy will not enter the calculations*.
- In a ***flow process***, however, *there may be changes in both potential and kinetic energy and these must be taken into account while considering the changes of stored energy.*
- ***Heat and work*** are *the forms of energy in transition*.
- These are the only forms in which energy can cross the boundaries of a system.
- *Neither heat nor work can exist as stored energy.*

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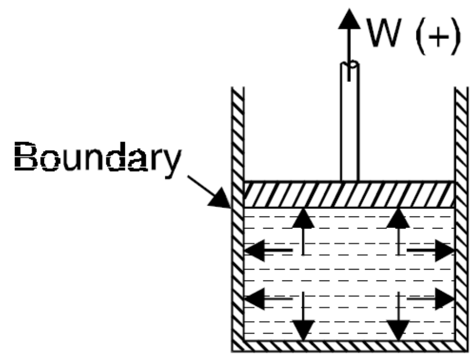
ENERGY, WORK AND HEAT
Work

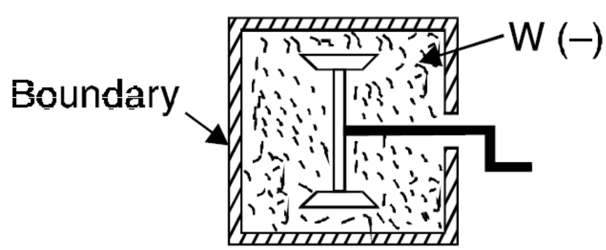
- Work is said to be done when a *force moves through a distance*.
- If a part of the boundary of a system undergoes a displacement under the action of a pressure, the work done *W* is the product of the force (pressure × area), and the distance it moves in the direction of the force.
- Fig. (*a*) illustrates this with the conventional piston and cylinder arrangement, the heavy line defining the boundary of the system.



(a)

ENERGY, WORK AND HEAT
Work

- Fig. (*b*) illustrates another way in which work might be applied to a system.
- A force is exerted by the paddle as it changes the momentum of the fluid, and since this force moves during rotation of the paddle work is done.



(b)

ENERGY, WORK AND HEAT
Work

- *Work is a transient quantity which only appears at the boundary while a change of state is taking place within a system.*
- *Work is 'something' which appears at the boundary when a system changes its state due to the movement of a part of the boundary under the action of a force*.
- **Sign convention :**
- If the work is done *by* the system *on* the surroundings, *e.g.,* when a fluid expands pushing a piston outwards, the work is said to be *positive*.

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

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

i.e., Work input to system = – *W*

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ENERGY, WORK AND HEAT
Heat

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

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

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ENERGY, WORK AND HEAT
Heat

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

$$\int_1^2 \delta W = W_{1-2} \text{ or } {}_1W_2 \text{ (or } W\text{), and}$$

$$\int_1^2 \delta Q = Q_{1-2} \text{ or } {}_1Q_2 \text{ (or } Q\text{)}$$

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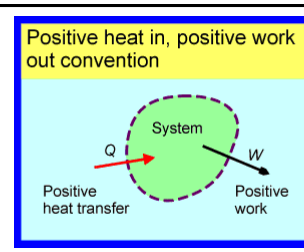
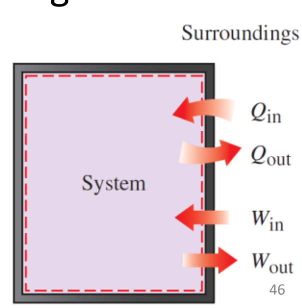
ENERGY, WORK AND HEAT
Heat



- **Sign convention :**
- If the heat flows ***into*** a system *from* the surroundings, the quantity is said to be ***positive***
- If heat flows ***from*** the system to the surroundings it is said to be ***negative***.
- In other words :
  - *Heat received by the system = + Q*
  - *Heat rejected or given up by the system = – Q.*



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ENERGY, WORK AND HEAT

Comparison of Work and Heat

- ***Similarities :***

1. Both are *path functions and inexact differentials*.
2. Both are boundary phenomenon *i.e.,* both are recognized at the boundaries of the system as they cross them.
3. Both are associated with a process, not a state. Unlike properties, work or heat has no meaning at a state.
4. Systems possess energy, but not work or heat.

Dissimilarities :

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

REVERSIBLE WORK

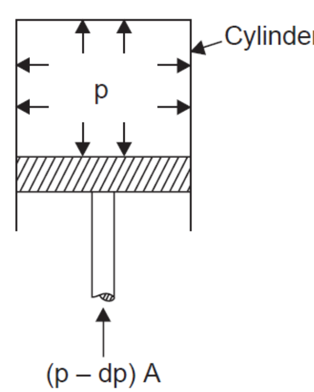
- Let us consider an ideal frictionless fluid contained in a cylinder above a piston.
- *Assume that the pressure and temperature of the fluid are uniform and that there is no friction between the piston and the cylinder walls*. Let:

A = Cross-sectional area of the piston,

p = Pressure of the fluid at any instant,

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

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



REVERSIBLE WORK

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

i.e.,

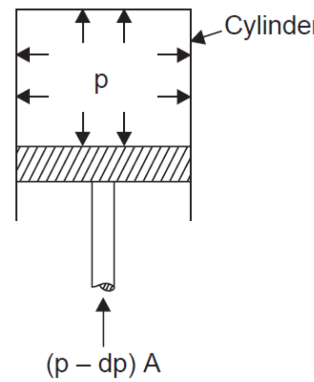
- Work done by the fluid = $(pA) \times dl = pdV$

(where dV = a small increase in volume)

Or considering unit mass

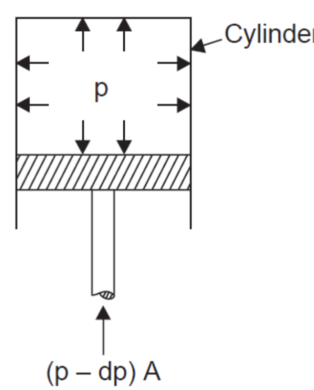
- Work done = pdv

(where v = specific volume)



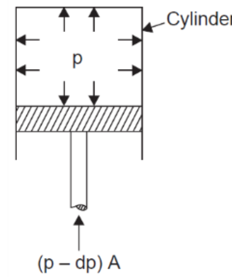
REVERSIBLE WORK

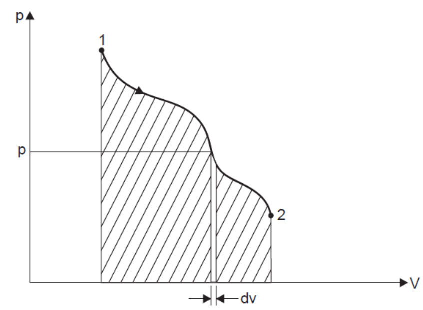
- This is only *true* when (*a*) the *process is frictionless and (b) the difference in pressure between the fluid and its surroundings during the process is infinitely small*.
- Hence when a reversible process takes place between state 1 and state 2, we have
- Work done by the unit mass of fluid = $\int_1^2 pdv$



REVERSIBLE WORK

- When a fluid undergoes a reversible process a series of state points can be joined up to form a line on a diagram of properties.
- The work done by the fluid during any reversible process is therefore given by the area under the line of process plotted on a *p*-*v* diagram.
- *i.e.*, Work done = Shaded area = $\int_1^2 pdv$
- When *p* can be expressed in terms of *v* then the integral, $\int_1^2 pdv$ can be evaluated.





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