

Thermodynamics – Concept, Basic Definitions

Thermodynamics

Thermodynamics is the study of energy and its transformation. Most studies of thermodynamics are primarily concerned with two forms of energy - heat and work. Thermodynamic study includes quantitative analysis of machines and processes for transformation of energy between work and heat. In classical thermodynamics a macroscopic viewpoint is taken regarding such matters. The term 'Thermodynamics', was first introduced by Lord Kelvin in 1849. the term comes from the Greek words *therme* (*heat*) and *dynamis* (*power*).

Objectives of the studies may include the following:

- Improvement of efficiency of processes.
- Making the processes more non-polluting and environment friendly.
- Study and research regarding alternative energy sources or transformation methods.

Working Substance

In thermodynamics a working substance is defined as a fluid (liquid/gas) in which energy can be stored, removed from or transferred through.

eg, Air in an IC engine, Steam in a boiler, Water in a hydraulic turbine.

Pure Substance

A pure substance needs to be –

- Homogeneous in composition (ie. single chemical species)
- Homogeneous and invariable in chemical aggregation (ie. chemically stable)

Here atomic structures of the substances are disregarded and the substances are treated as a continuum with no discontinuities in properties.

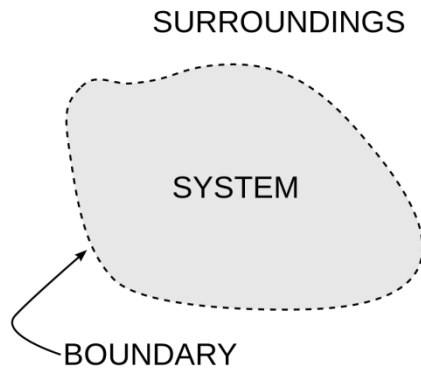
System/Boundary/Surrounding

A system is defined as a region in space containing a quantity of matter whose behavior is being investigated.

The system is separated from its surrounding by a boundary, which may be a real or some imaginary surface enveloping the region. The boundary may be at rest or in motion and may change its size or shape.

The term surrounding is restricted to those portions of matter external to the system which is thermodynamically affected by the changes occurring within the system.

Any thermodynamic analysis begins with the selection of the system, its boundary and the surroundings.



Open and Closed Systems

A closed system (sometimes termed as a control mass) is a system for which no masses cross the boundary i.e. quantity of matter within the system remains fixed throughout the investigation, but energy is allowed to cross the boundary (in the form of heat and work).

An open system (sometimes termed as a control volume) on the other hand is a region in the space defined by a boundary across (in/out/through) which matter may flow in addition to energy (in the form of heat and work).

A system is termed as an Isolated system if neither matter nor energy is allowed to transfer across the boundary. A truly isolated system can only be obtained ideally.

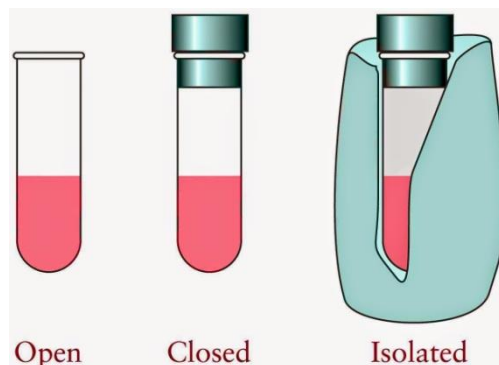
Examples of Closed systems:

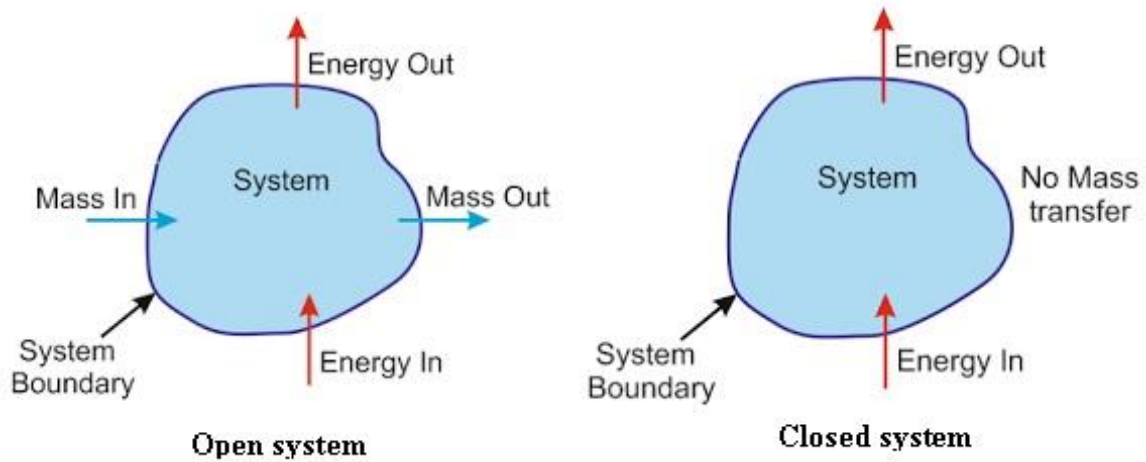
- Mixture of water and steam in a closed vessel.
- Gas expanding in a piston-cylinder

Examples of Open systems:

- Water entering boiler and leaving as steam
- Gases flowing through a turbine
- Gas expanding from a pressurized container, through a nozzle.

Isolated system: A thermo-flask may be considered as approaching an isolated system.





Thermodynamic Properties

These are descriptive characteristics that express the behavior of a system. Any property has a fixed value in a given equilibrium state, regardless how the system has arrived at that state. The change in the value of a property depends on the initial and final states of the system and is independent of the process undergone (path). If the change is dependent on the path of a process then it cannot be considered as a property. Different properties of a system can be inter-related.

State

The state of a system at any instance is its condition characterized by the values of its properties. The state of the system may be completely identified from the knowledge of some of its properties (at least two independent ones for a closed system). These properties are truly defined only when the system is in thermal equilibrium.

Equilibrium State

A system is said to be in thermodynamic equilibrium if it is not capable of a finite spontaneous change to another state, without a finite change in state of the surrounding environment. All properties should be uniform through the system when it is in equilibrium. System in complete equilibrium satisfies – Mechanical (no unbalanced forces), Thermal (no heat transfer) and Chemical (no chemical reactions) equilibrium.

Process – Reversible/Irreversible

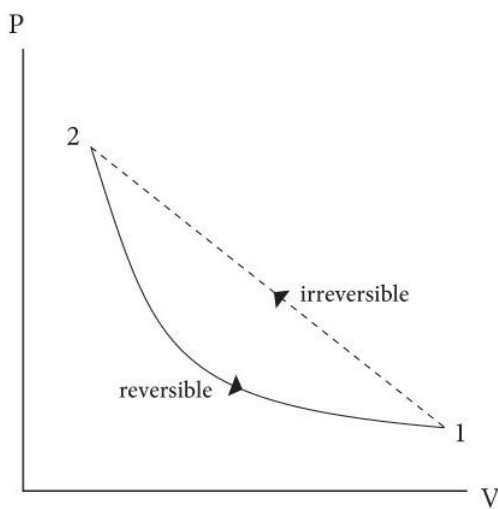
The process is any transformation of a system from one equilibrium state to another. The path of a process refers to the specification of a series of states through which the system passes.

If a system is imagined to pass through a continuous series of equilibrium states – the process is called a reversible process. Here if the process is reversed the initial

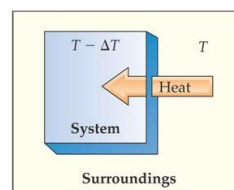
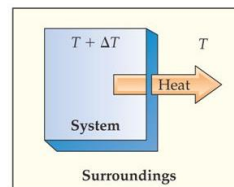
state can be restored without any observed effect on the surrounding. This is possible only if the net heat and work exchange between the system and the surrounding is zero in the combined process. Both the system and the surrounding can come back to the original state. A reversible process is represented by solid line on a diagram.

If the system is not in equilibrium in one or some of the series of intermediate states during a process then it is called an irreversible process. An irreversible process is represented by dotted line on a diagram. Here if the process is reversed the system will not change to its initial state without any effect on the environment. It can be returned to its original state, but this will have some effect on the surrounding. In reality all processes are irreversible. Presence of - temperature gradient, pressure gradient, friction and eddy flows are example of irreversibility. An irreversible process is represented by dotted line on a diagram.

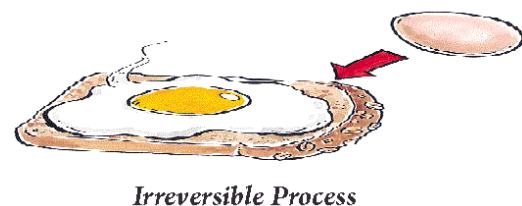
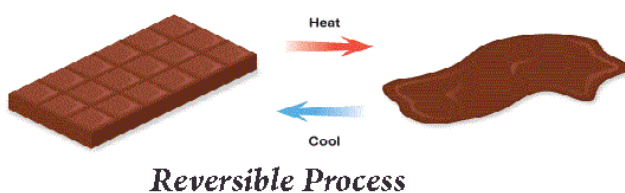
When no irreversibility occurs within the boundaries of the system during a process – it is characterized as **Internally reversible**, eg. quasi-equilibrium expansion of a piston-cylinder. When no irreversibility occurs outside the system boundary during a process - it is characterized as **Externally reversible**, eg. Heat exchange between a reservoir and a system. If a process is both internally and externally reversible, it is called a totally reversible or reversible process.



Reversible Processes

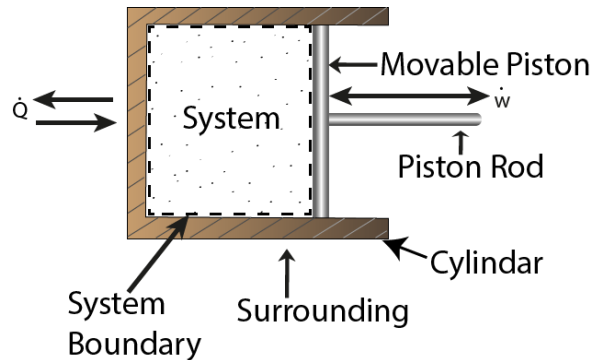


In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.



Process – Flow and Non-flow

The process undergone by the fluid in a closed system is a 'Non-flow Process', while the process in an open system is called a 'Flow Process'.



Properties, Extensive and Intensive Properties

For a closed system six important properties are considered in thermodynamics. These are - pressure, temperature, volume, enthalpy, entropy and internal energy. The first three are measurable quantities, while the last three properties are more like mathematical entities, which behave like a property. For an open system in addition to those mentioned above, mechanical properties are also important eg, - velocity relative to a fixed boundary (K.E), position in the gravitational field (P.E) etc.

Temp, Pressure and Volume or specific volume can be measured using instruments. But we do not have meters for measuring – Internal energy, Enthalpy and Entropy.

Properties which are or when expressed as independent of mass are called Intensive properties, eg. – Temperature, Pressure, Density, Specific enthalpy, Specific entropy etc.

Properties which are or when expressed as dependent on mass are called extensive properties, eg. – total enthalpy, total entropy, total volume etc. Intensive expressions of properties are stated with lower case – h, u, s while extensive expressions are given by uppercase – H, U, S etc.

Internal Energy

The term internal energy was used both by Rudolph Clausius and William Rankine after 1852. Internal energy is defined as - the sum of microscopic energies of all the molecules of a system, which may appear in several complex forms. These forms may include–

- Intermolecular potential energy, associated with the forces between the molecules.
- Molecular K.E. associated with translational and rotational velocity of each molecule.
- Intra-molecular energy within the molecular/atomic structures and related forces.

Internal energy (u, U) is primarily a function of temperature.

Enthalpy

Enthalpy is a mathematical combination of internal energy and pressure energy of the fluid. It is expressed as $H = U + pV$ in extensive or $h = u + pv$ in intensive forms. Common expression in SI system has a unit of kJ/kg (intensive).

Enthalpy was introduced by German scientist R. Mollier, who is also famous for the Mollier charts expressing properties of steam. Initially was called 'Heat Content' but in 1930 it was termed as 'Enthalpy'.

Entropy

Entropy (s, S) represents the disorder or uncertainty of the microscopic level, even yet it is used as a property at macroscopic level. Entropy is specified for every equilibrium state of a pure substance. Entropy is also mainly a function of temperature. In 1865 Rudolph Clausius first introduced the term entropy. Entropy is a measure of molecular disorder, randomness and predictability of motion. As a system becomes more disordered, the position of the molecules become less predictable and the entropy increases. Higher entropy means more uncertainty, entropy is the lowest at solid phase and higher for liquid and gas phases. Note that no entropy is transferred by work. Energy can be transferred by both heat and work, whereas entropy is transferred only by heat. There is no entropy transfer associated with energy transfer as work. However entropy may be generated within a system as work is dissipated into a less useful form of energy.

As the last three properties mentioned are more like mathematical entities having important physical significance, we are more interested in the change of these properties in a process (ie, $ds, du, \Delta S$ etc) rather than the individual values which may depend on reference of calculation.

Cycle

A cyclic process or a cycle is a series of processes which return the system to the initial state. Hence the change in value of any property in a cycle is zero.

Heat

Heat is defined as the form of energy that is transferred between two systems or a system and its surroundings by virtue of temperature difference. Heat energy is associated with the movements of the elements at microscopic level. Heat is energy in transition. It is recognized only as it crosses the system boundary. In thermodynamics we are only concerned with the amount or rate of heat transfer, rather than evaluating the transfer mechanism.

Heat Reservoir

Part of the surrounding, which exchanges energy with the system due to temperature difference, is called a heat reservoir. This may be a source or a sink. Usually the term reservoir is restricted to mean a source or sink of such capacity that the quantity of heat which crosses the boundary during a process is insufficient to change its temperature.

First law of Thermodynamics (Joule 1843)

When any closed system is taken through a cycle the net work delivered to the surrounding is proportional to the net heat taken from the surrounding.

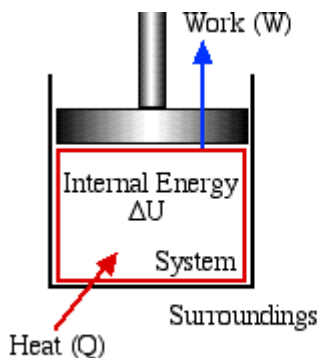
$$\sum \delta Q \propto \sum \delta W \quad \text{also} \quad \sum \delta W \propto \sum \delta Q$$

However heat and work may be expressed in different units and they are related as $W = JQ$, where J is the mechanical equivalent of heat.

$$J = 4.184 \text{ kJ/kcal} \quad \text{or} \quad 427 \text{ Kg-m/kcal} \quad \text{or} \quad 778 \text{ ft-lb/BTU} ;$$

Hence, $J\sum \delta Q - \sum \delta W = 0$ or $\sum \delta Q - \sum \delta W = 0$, if expressed in same unit

Necessarily always Q or W may not be associated with the other form. Energy can neither be created nor destroyed in a process, it can only change forms. For a closed system if there is difference of Q and W then, $Q - W = \Delta U$ change in internal energy.



$$Q - W = \Delta U \quad [\text{kJ}]$$

where: Q is the Heat Transferred to the System

W is the Work Done by the System

ΔU is the Change of Internal Energy

Dividing each term by the system mass m [kg] we obtain the specific form of the Energy Equation:

$$q - w = \Delta u \quad \left[\frac{\text{kJ}}{\text{kg}} \right]$$

Second Law of Thermodynamics (Plank, Clausius 1865)

It is impossible to construct a system which will operate in a cycle, extract heat from a reservoir and do an equivalent amount of work on the surrounding. (Kelvin-Plank statement)

It is impossible to construct a system that operates in a cycle and transfer heat from a lower temperature (cooler) body to a higher temperature (hotter) body, without work being done on the system by the surrounding (Clausius Statement).

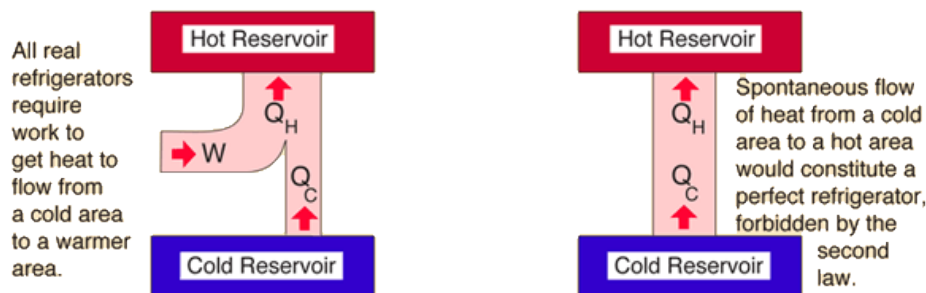
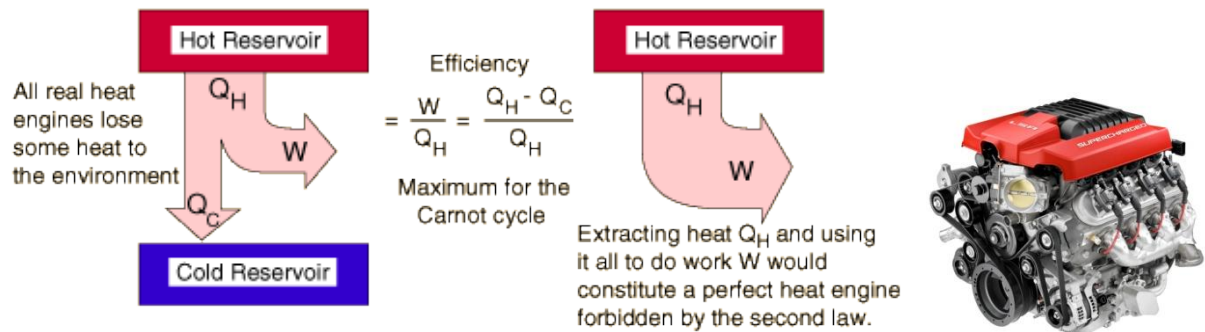
Another summary of 2nd law of thermodynamics –

- If a system is taken through a cycle and produces work, it must be exchanging heat with at least two heat reservoirs at different temperatures.
- If a system is taken through a cycle while exchanging heat with only one reservoir, work done must be either zero or negative.
- Since heat can never be converted continuously and completely in to work, but work can be, so work is a more valuable form of energy transfer.

1st law just states $\sum \delta W \propto \sum \delta Q$, second law states $\sum \delta W < \sum \delta Q$.

An engine which will produce work continuously, while exchanging heat with a single reservoir (perpetual motion machine of the 2nd kind) is not possible.

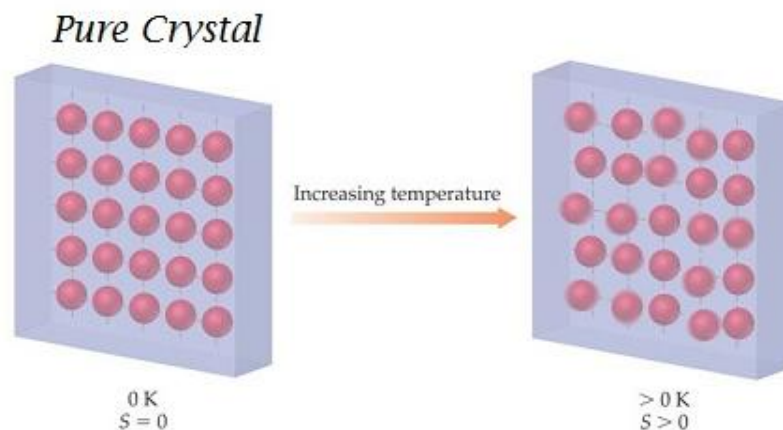
Since all the heat can not be converted to work in a heat engine, the 2nd law introduces efficiency $= W_{net}/Q_{in}$. 2nd law focuses on the quality of energy as well.



Third law of Thermodynamics (W. H Nernst, Max Plank, around 1920)

The entropy of a pure crystalline substance at absolute zero temperature is zero.

There is no uncertainty about the state of the molecules at absolute zero temperature.



FLOW AND NON FLOW PROCESSES

Non-Flow Processes

These are the processes occurring in a closed system, ie. there is energy transfer in the form of heat and work, but no mass transfer is associated.

As stated in 1st law, Non-Flow Energy Equation expresses the relation, $Q - W = \Delta U$

Expression of Non-Flow Energy Equation for particular processes :

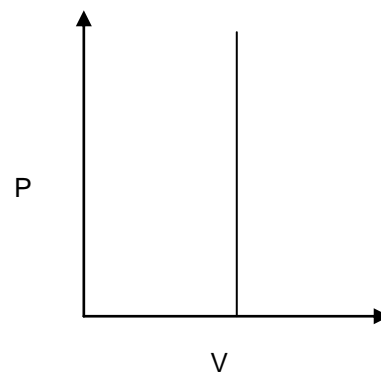
Constant Volume Process

$$Q - W = U_2 - U_1$$

$$Q - \int p dv = u_2 - u_1$$

Since, Δv or $dv = 0$;

$$Q = \Delta u \quad \text{or} \quad dQ = du$$



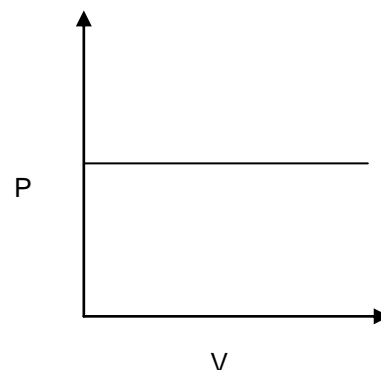
Constant Pressure Process

$$Q - P \int dv = U_2 - U_1$$

$$Q - (pv_2 - pv_1) = u_2 - u_1$$

Since, $h = u + pv$

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



Polytropic Process

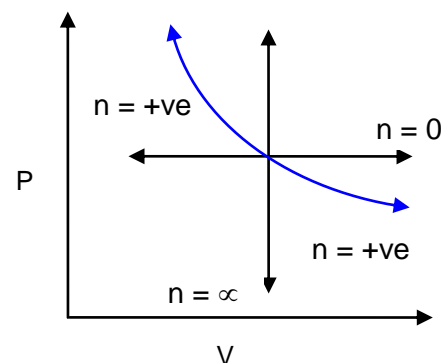
$$pv^n = p_1v_1^n = p_2v_2^n = \text{Constant}$$

$$W = \int p dv = p_1v_1^n \int (dv/v^n)$$

$$= p_1v_1^n (v_2^{1-n} - v_1^{1-n}) / (1-n) = p_2v_2 - p_1v_1 / (1-n)$$

$$Q - (p_2v_2 - p_1v_1) / (1-n) = (u_2 - u_1)$$

n = Index of compression or expansion



Isentropic Process

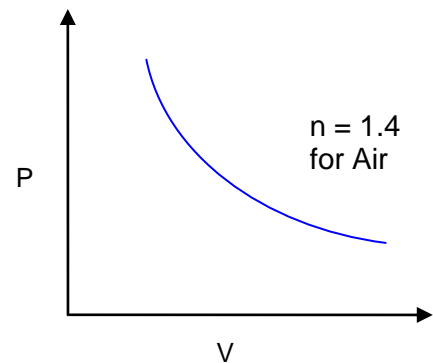
Adiabatic ($Q = 0$) & Frictionless then $s_2 = s_1$

$$W = \int p dv = p_1 v_1^k \int (dv/v^k) = p_2 v_2 - p_1 v_1 / (1-k)$$

as n is replaced by k , $k = c_p/c_v$

$$- (p_2 v_2 - p_1 v_1) / (1-k) = (u_2 - u_1)$$

k = Index of isentropic compression or expansion $k = 1.4$ for Air

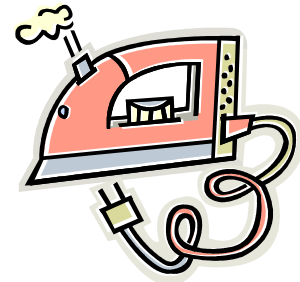


Adiabatic Process

Adiabatic, No heat transfer ($Q = 0$)

May be – High insulation
Not enough time
Not enough area

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

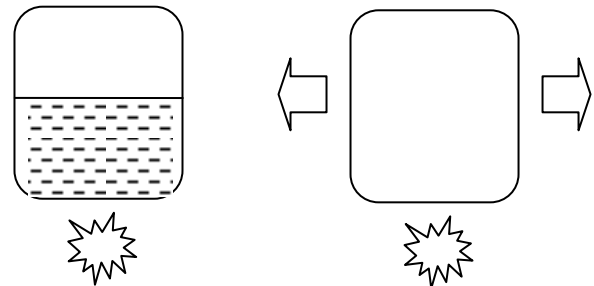


Isothermal Process

$T = \text{Constant}$, $Q = T(s_2 - s_1)$

$$T(s_2 - s_1) - W = (u_2 - u_1)$$

Phase change
Artificially arranged



Steady Flow Processes

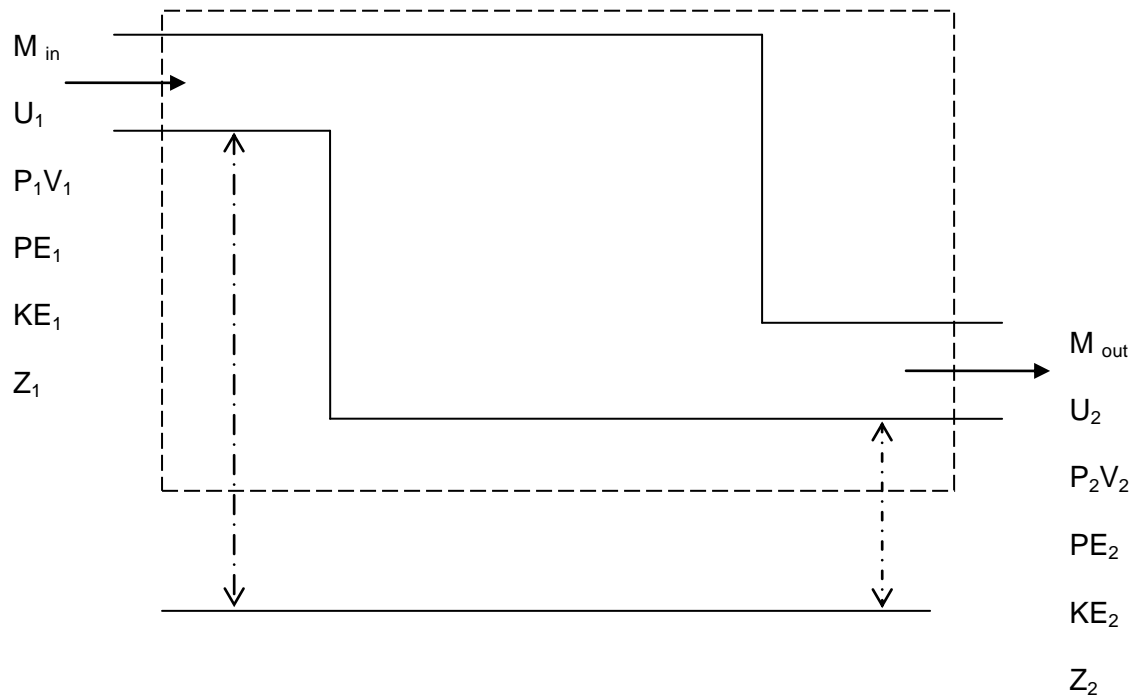
These are the processes occurring in an open system, ie. there is energy transfer in the form of heat and work may occur along with mass transfer is associated.

Assumptions of steady flow process –

1. The mass flow rate at the inlet is constant w.r.t time and equal to the mass flow rate at the outlet.
2. The properties at any point within the open system do not vary with time.
3. Properties are constant over the cross section of the flow at the inlet and outlet.
4. Any heat or work crossing the boundary does so at a uniform rate.

For a steady flow system, energy entering the system must equal the energy leaving the system. The forms of energy considered in thermodynamic analysis include –

Heat **Q**, Work **W**, Internal energy **U**, Flow energy **Pv**, Potential energy **PE**, Kinetic energy **KE**



$$PE_1 + KE_1 + P_1V_1 + U_1 + Q = PE_2 + KE_2 + P_2V_2 + U_2 + W$$

$$Q = \Delta PE + \Delta KE + \Delta H + W \quad \text{or} \quad dQ = dPE + dKE + dH + dW$$

For unit flow rate of mass,

$$Q = g(z_2 - z_1) + \frac{1}{2} (C_2^2 - C_1^2) + (h_2 - h_1) + W$$

This called the steady flow energy equation.

CASE STUDIES:

The steady flow energy equation : $Q = g(z_2 - z_1) + \frac{1}{2} (C_2^2 - C_1^2) + (h_2 - h_1) + W$

For a Boiler or Condenser

$Z_1 = Z_2$, hence $\Delta PE = 0$; C_1, C_2 as both are very small, hence $\Delta KE = 0$;

Nothing moves, No work is done $W = 0$;

$Q = m(h_2 - h_1)$ So heat transferred causes enthalpy change only.

For a Nozzle or Diffuser

$Z_1 = Z_2$, hence $\Delta PE = 0$; No work is done $W = 0$; $Q = 0$, insufficient time;

$$0 = \Delta h + \Delta KE$$

$$m(h_2 - h_1) = \frac{1}{2} m (C_2^2 - C_1^2)$$

For Rotary Compressor or Turbine

$Z_1 = Z_2$, hence $\Delta PE = 0$; $C_1 = C_2$ as direction changes only, hence $\Delta KE = 0$;

$Q = 0$, very high flow velocity, insufficient time;

$$W = m(h_1 - h_2) \quad W = \text{-ve for compressor and +ve for turbine}$$

For Reciprocating Compressor or Turbine

$Z_1 = Z_2$, hence $\Delta PE = 0$; C_1, C_2 as both are very small, hence $\Delta KE = 0$;

In this case lower speed and larger surface area Q occurs.

$$W = Q + m(h_2 - h_1)$$

For Throttling

This process takes place when a sudden abrupt restriction is placed in the flow

$Z_1 = Z_2$, hence $\Delta PE = 0$; C_1, C_2 as both are very small, hence $\Delta KE = 0$;

$Q = 0$, very small surface area for heat transfer

Nothing moves, No work is done $W = 0$;

$$0 = m(h_2 - h_1)$$

$h_1 = h_2$ so this a constant enthalpy process.