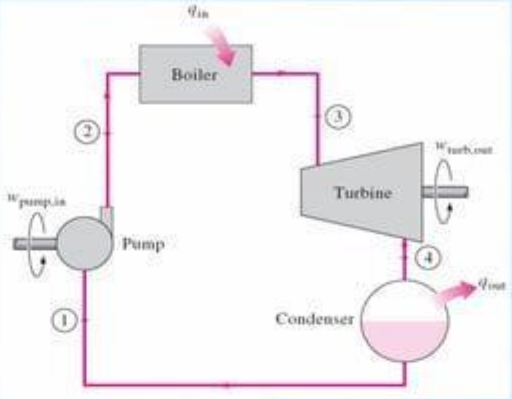
THERMODYNAMICS

What is Thermodynamics?

- The science of energy, that concerned with the ways in which energy is stored within a body.
- Energy transformations – mostly involve heat and work movements.
- The Fundamental law is the conservation of energy principle: energy cannot be created or destroyed, but can only be transformed from one form to another.

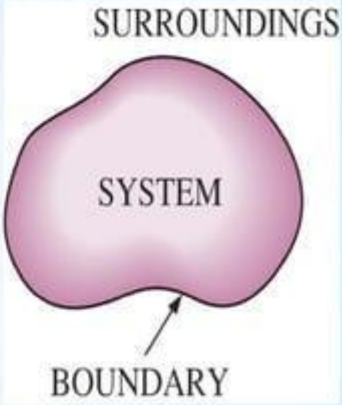


System, surroundings and boundary

- **System**: A quantity of matter or a region in space chosen for study.

- **Surroundings**: The mass or region outside the system

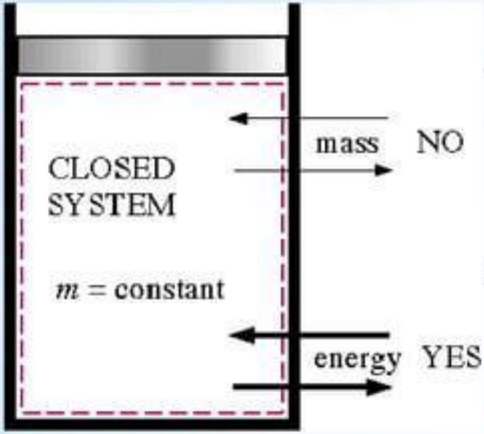
- **Boundary**: The real or imaginary surface that separates the system from its surroundings.



Type of system
(isolated system)

- Isolated system – neither mass nor energy can cross the selected boundary
- Example (approximate): coffee in a closed, well-insulated thermos bottle

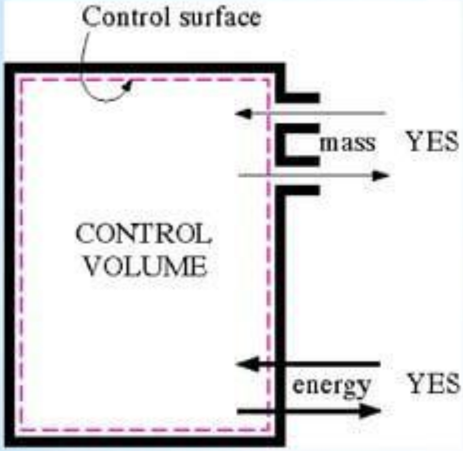
Type of system
(Closed system)



- Closed system – only energy can cross the selected boundary

- Examples: a tightly capped cup of coffee

Type of system
(Open system)



- ❖ Open system – both mass and energy can cross the selected boundary
- ❖ Example: an open cup of coffee

Properties of a system

Properties of a system is a measurable characteristic of a system that is in equilibrium.

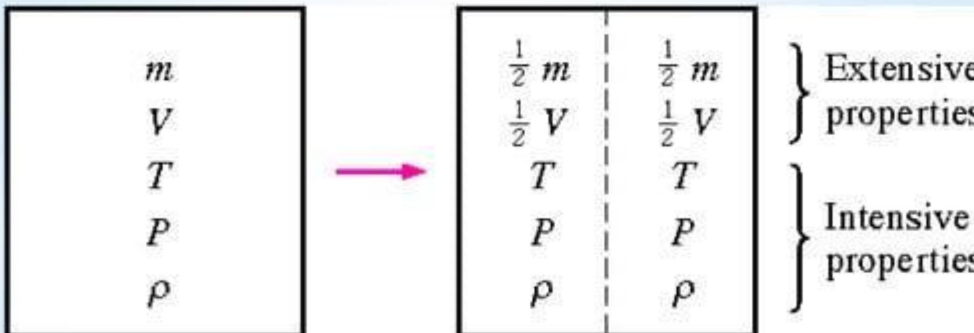
Properties may be intensive or extensive.

- **Intensive – Are independent of the amount of mass:**

e.g: Temperature, Pressure, and Density,

- **Extensive – varies directly with the mass**

  e.g: mass, volume, energy, enthalpy



Properties of a system

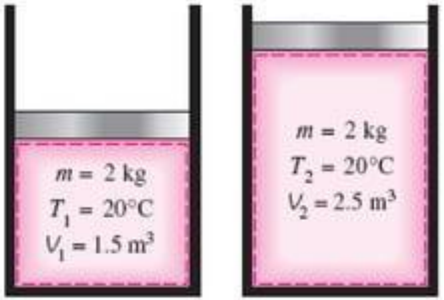
Specific properties – The ratio of any extensive property of a system to that of the mass of the system is called an average specific value of that property (also known as intensives property)

Specific Volume	$V/m = v$	m^3/kg
Total Energy	$E/m = e$	J/kg
Internal Energy	$U/m = u$	J/kg

State, Equilibrium and Process

- State – a set of properties that describes the conditions of a system. Eg. Mass m, Temperature T, volume V

- Thermodynamic equilibrium - system that maintains thermal, mechanical, phase and chemical equilibriums.

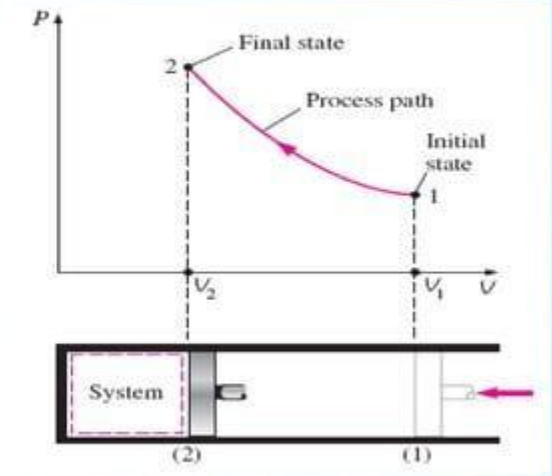


(a) State 1 (b) State 2

State, Equilibrium and Process

- Process – change from one equilibrium state to another.

Process	Property held constant
isobaric	pressure
isothermal	temperature
isochoric	volume
isentropic	entropy

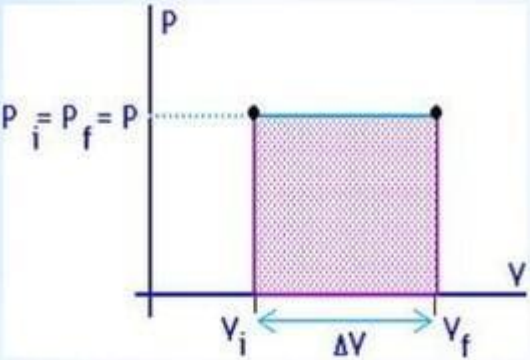


State, Equilibrium and Process

The prefix iso- is often used to designate a process for which a particular property remains constant.

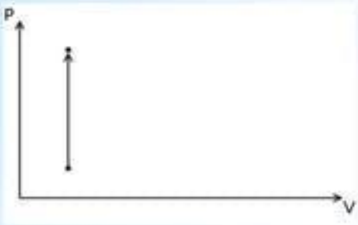
Isobaric process: A process during which the pressure *P* remains constant.

Pressure is Constant (**ΔP = 0**)

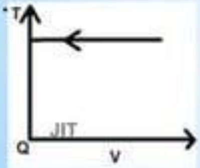


State, Equilibrium and Process

Isochoric (or isometric) process: A process during which the specific volume *v* remains constant



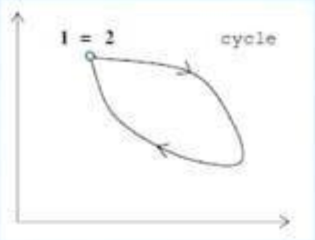
Isothermal process: A process during which the temperature *T* remains constant.



Process	Property held constant
isobaric	pressure
isothermal	temperature
isochoric	volume
isentropic	entropy

Types of Thermodynamics Processes

- **Cyclic process** - when a system in a given initial state goes through various processes and finally return to its initial state, the system has undergone a cyclic process or cycle.



- **Reversible process** - it is defined as a process that, once having take place it can be reversed. In doing so, it leaves no change in the system or boundary.

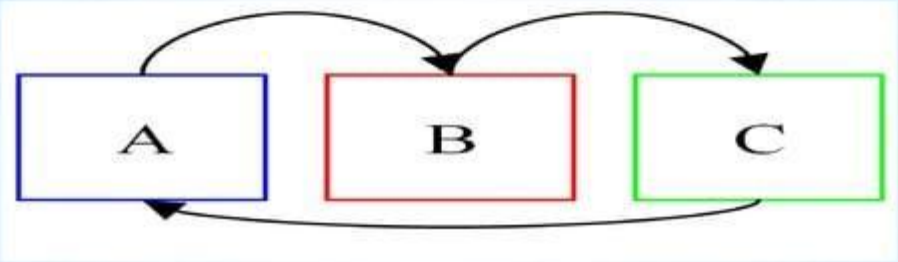
- **Irreversible process** - a process that cannot return both the system and surrounding to their original conditions

Types of Thermodynamics Processes

- **Adiabatic process** - a process that has no heat transfer into or out of the system. It can be considered to be perfectly insulated.
- **Isentropic process** - a process where the entropy of the fluid remains constant.
- **Polytropic process** - when a gas undergoes a reversible process in which there is heat transfer, it is represented with a straight line, PV^n = constant.
- **Throttling process** - a process in which there is no change in enthalpy, no work is done and the process is adiabatic.

Zeroth Law of Thermodynamics

" If two bodies are in thermal equilibrium with a third body, there are also in thermal equilibrium with each other."



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

Point Function

When two co-ordinates are located on the graph, They define a point and the two properties on the graph define state. These properties (p, T, v) are called point function.

Path Function

There are certain quantities like heat and work can not be located on a graph by a point but there are represented by the area. It is not a state or point function, rather it depends on the path of the process. Such quantities are called path function and they are inexact differentials

Process

- If any one or more properties of the system undergo a change due to energy or mass transfer we say that the system has undergone a change of state
- The successive change of state of the system due to energy or mass transfer defined by definite path is called a process.
- The curve joining the successive state represents the process path
- If a system undergoes two or more processes and returns to its original state after conclusion of processes, the system is said to have undergone a cycle

Thermodynamic equilibrium

- A system is said to be in thermodynamic equilibrium which is incapable of any spontaneous change of its macroscopic properties (p, v, t) and it is in complete balance with its surroundings.
- A system will be in thermodynamic equilibrium if it satisfies the condition of mechanical, thermal and chemical equilibrium

1.Mechanical equilibrium :- No unbalance forces

2.Thermal Equilibrium :- Uniformity of temp. inside with surrounding

3.Chemical Equilibrium :- Absence of any chemical reaction

Quasi Static Process / Reversible

- A quasi static process is defined as a process in which the properties of the system depart infinitesimally (extremely small) from the thermodynamic equilibrium path
- If the properties of the system has finite departures from thermodynamic equilibrium path the process is said to be non quasi static
- Quasi static process is the succession of thermodynamic equilibrium state while in case of non-quasi static process the end states only represent the thermodynamic equilibrium.

Condition for reversible process are

1. No Friction

2. Heat transfer is through infinitely temperature difference.

3. There are no spontaneous changes in the system.

- All processes in nature are irreversible.

Work done in moving boundary of close system in quasi-static process displacement work

- Force Exerted on piston, F = P A

- Small work done, δw = F dl

δw = P A dl

δw = P dV

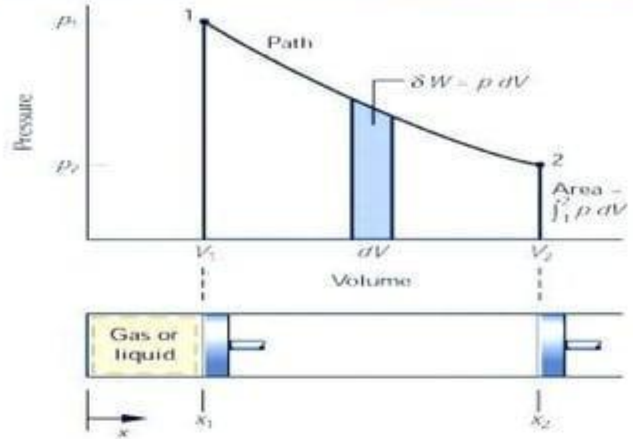


Fig. Work of a quasi-equilibrium expansion or compression process.

$W = \int_1^2 \delta w = \int_1^2 P\, dV$ • In non-quasi-static process, $W \neq \int_1^2 P\, dV$ because there is non unique value of ‘P’

• We conclude that the equation $W = \int_1^2 P\, dV$ is valid for quasi-static & reversible process only.

Heat

- Heat is the form of energy which transfer without transfer of mass, from one body to another body (or between system and surroundings) from higher temperature to lower temperature by virtue of temperature difference between two bodies.
- Abbreviated as 'Q' and Unit is J (Joule)
- Heat Addition into system :- Positive (+Q)
- Heat Rejection from system :- Negative (-Q)
- Extensive Property and Path Function (Inexact Differential)

Work

- Analogous to heat, work is also a transient form of energy which is observed when it crosses the boundaries of the system without transfer of mass
- It is Path Function
- Small work done due to displacement ds

$$\delta W = F \cdot \mathrm{ds}$$

Total Work done, $W = \int_1^2 F \cdot \mathrm{ds}$

Difference between heat and work

1. Heat can only transfer when there is difference of temperature between the system and surrounding, while work transfer can take place even without the change in temperature

2. In constant volume process though work can not take place, however heat can be transferred.

3. In case of work transfer, its sole effect could be raising or lowering a weight in the surrounding but in case of heat transfer other effects are also observed.

Similarities between heat and work

1. Both heat and work exist in transit and these are never possessed or contained in a system.

2. Both heat and work refer to boundary phenomena.

3. Both heat and work are path function and do not represent as the properties of system (Inexact difference, □□)

Enthalpy

- It is total energy of the system
- Specific Enthalpy,
- U, p, V are point function, so H is point function and property of system
- Unit of Enthalpy (H) is kJ
- Unit of Specific Enthalpy (h) is kJ/kg

$$H = U + pV$$

$$h = u + pv$$

First law of thermodynamic (Energy conservationlaw)

- " Energy can neither be created nor-destroyed but it can be converted from one form to another."

First law of thermodynamic applied to close System, Cyclic Process If a close system goes through a cycle, the algebraic sum of total energy transfer to it as heat and work is zero.

$$\oint \delta Q - \delta W = 0$$

Limitations of the first law of thermodynamics

1. No restriction on the direction of the flow of heat: the first law establishes definite relationship between the heat absorbed and the work performed by a system. The first law does not indicate whether heat can flow from a cold end to a hot end or not. For example: we cannot extract heat from the ice by cooling it to a low temperature. Some external work has to be done.

2. Does not specify the feasibility of the reaction: first law does not specify that process is feasible or not for example: when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.

3. Practically it is not possible to convert the heat energy into an equivalent amount of work.