THERMODYNAMICS

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CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The word THERMODYNAMICS means “Heat in Motion”.

“THERMODYNAMICS is basically a branch of science which focuses on the study of energy transfer and its effect on various physical properties of the system.”

“THERMODYNAMICS is the study of three E’s i.e. Energy, Entropy and Equilibrium.”

“THERMODYNAMICS is a science that governs following:

- Energy and its transformation.
- Feasibility of a process involving transformation of energy.
- Feasibility of a process involving transfer of energy.
- Equilibrium process.

Thus, we can say that THERMODYNAMICS deals with energy conversion, energy exchange and the direction of exchange.

Thermodynamics is the branch of science that embodies the principles of energy transformation in macroscopic systems. The general restrictions which experience has shown to apply to all such transformations are known as the laws of thermodynamics. These laws are primitive; they cannot be derived from anything more basic. The first law of thermodynamics states that energy is conserved; that although it can be altered in form and transferred from one place to another, the total quantity remains constant. Thus, the first law of thermodynamics depends on the concept of energy; but, conversely, energy is an essential thermodynamic function because it allows the first law to be formulated. This coupling is characteristic of the primitive concepts of thermodynamics.

THERMODYNAMIC SYSTEM

- System is that part of universe which is under investigation or under the study of observer.
- Properties of the system are observed when the exchange of energy i.e. work or heat, takes place.
- There is no arbitrary rule for selection of system but proper selection makes the calculations easy.

SURROUNDINGS

- The remaining portion of universe which is external to the system is called as surrounding.
- The exchange of energy takes place between system and surroundings; hence surroundings may be influenced by the changes taking place in system.

UNIVERSE

- System and surroundings together constitutes Universe i.e.
  System + Surroundings = Universe.

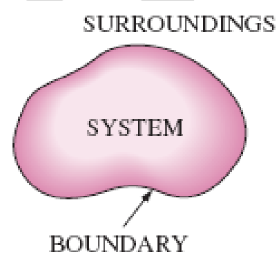


Figure 1.1

SYSTEM BOUNDARY

- System and surroundings in the universe are separated by System boundary.
- A system boundary has **zero thickness**.
- Boundary may be Real or Hypothetical and Fixed or Moving.
- It is a surface, and since a surface is a two-dimensional object, it has zero volume. Thus, **it attains neither mass nor volume**.

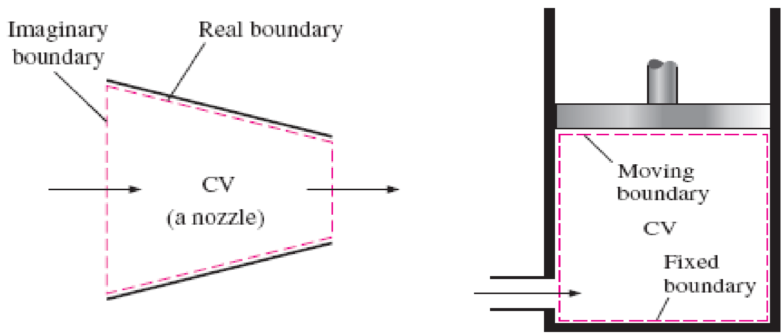


Figure 1.2

If heat (energy) exchange doesn't take place across body it is called adiabatic boundary otherwise it will be diathermic boundary.

DIFFERENCE BETWEEN SURROUNDINGS, IMMEDIATE SURROUNDINGS AND ENVIRONMENT

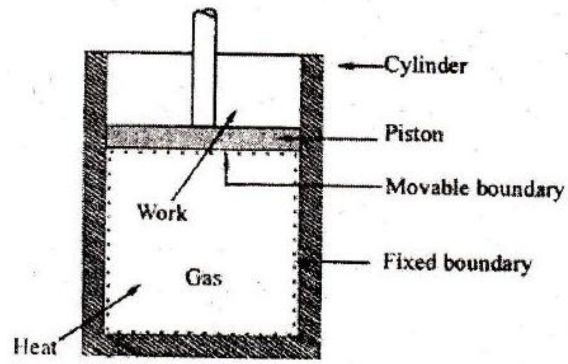
- **Surroundings** are everything outside the system boundaries.
- The **immediate surroundings** refer to the portion of the surroundings that is affected by the process, and
- **Environment** refers to the region beyond the immediate surroundings whose properties are not affected by the process at any point.

1.2 CLASSIFICATION OF THERMODYNAMIC SYSTEM

On the basis of mass and energy transfer across / through the system boundaries, a thermodynamic system can be classified as follows:

1.2.1 CLOSED SYSTEM (OR NON FLOW SYSTEM)

The system which can exchange energy with surroundings but which cannot transfer matter across the boundaries are known as *closed system.*



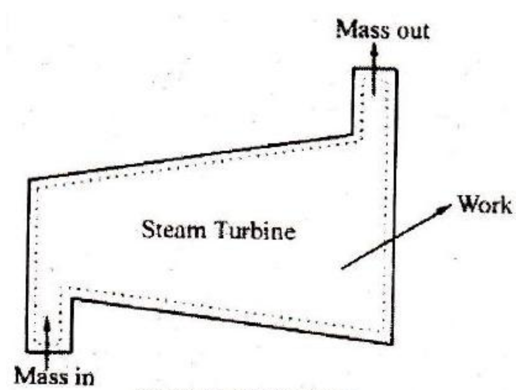
[CLOSED SYSTEM]

Closed System

- Heat and work (energy) crosses the boundary.
- No mass transfer takes place i.e. mass of system is fixed, hence it is also called as NON FLOW SYSTEM.
- Due to fixed mass, we also define closed system as CONTROL MASS.
- Boundary of the system is not fixed but arbitrarily selected.
- Since boundary may change, volume of the system is not necessarily fixed.
- Energy transfer can be experienced only at boundaries.
- e.g. Piston cylinder arrangement, gas being compressed by a piston in a closed cylinder.
  The fluid contained in the cylinder can receive or reject heat, can expand or contract, hence changing the volume, but no matter (fluid) can flow out or into the cylinder, i.e. mass remains fixed.

1.2.2 OPEN SYSTEM (OR FLOW SYSTEM)

The system that can exchange both energy and matter with their environment.



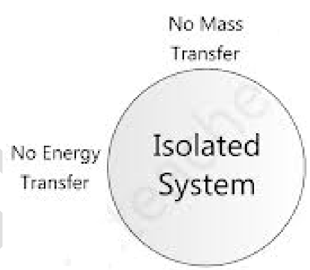
[OPEN SYSTEM]

- Heat and work crosses the boundary.
- Mass transfer also takes place i.e. mass of system is not fixed; hence it is also called as FLOW SYSTEM.
- System boundary is known as CONTROL SURFACE which always remains fixed.
- Volume of the system does not change; hence open system is also defined as CONTROL VOLUME.
- e.g. Steam generator or boiler

  A steam generator converts water into steam by gaining heat from furnace. Hence water flows into the system and steam flows out of the system; hence matter is crossing the boundary of system.

1.2.3 ISOLATED SYSTEM

An isolated system exchanges neither matter nor energy with its surroundings.



Isolated System

- Heat and work does NOT cross the boundary.
- Mass of the system remains fixed i.e. No mass transfer takes place.
- e.g. Thermos flask.
- Neither heat flows into/out of the system nor the matter flows.

Classify the following as open, close or isolated system with suitable reasons:

- Cooling system of engine of a car
- Pressure cooker
- Air compressor

Thus, a special type of closed system that does not interact with its surroundings is called an Isolated System.

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Open system

- Heat and work crosses the boundary. Mass transfer also takes place i.e. mass of system is not fixed
- Known as FLOW SYSTEM.
- Volume of the system does not change.

Closed System

- Heat and work (energy) crosses the boundary. No mass transfer takes place.
- Known as NON FLOW SYSTEM.
- Volume of the system change.

Isolated System

Heat and work does not cross the boundary. No mass transfer takes place.

Past GATE Questions on GATE Tip

Q.1 A closed thermodynamic system is one in which

(a) There is no energy or mass transfer across the boundary
(b) There is no mass transfer, but energy transfer exists
(c) There is no energy transfer, but mass transfer exists
(d) Both energy and mass transfer take place across the boundary, but the mass transfer is controlled by valves

Q.2 Which of the following statements are true?

(a) A closed system is necessarily an isolated system
(b) An isolated system is necessarily a closed system
(c) A system cannot be both closed and isolated.
(d) The concepts of closed and isolated in regards to a system are independent concepts.

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Q.3 Which of these Cases would be best suited for using a control volume approach in the thermodynamic analysis of the system?
(a) Compression of air in a cylinder
(b) Expansion of gases in a cylinder after combustion
(c) Air in a balloon
(d) Air Filling in a Cycle tyre from any compressor

Solutions

1) (b) As we know that In closed system only energy transfer will happen.

2) Statement (b) is true. Because for isolated system ,system should be a closed system at first.

3) All Systems (a) to (c) are closed systems, so we can't use control mass for these cases. Only system (d) is an open system with a fixed boundary because here mass flow and energy transfer both are taking place so option (d) will be answer.

1.3 BASIC TERMINOLOGIES

There are some basic terms one should know for the good study of thermodynamics:

1.3.1 HOMOGENEOUS AND HETEROGENEOUS SYSTEM

- A **phase** is defined as the quantity of matter which is homogeneous throughout in chemical composition i.e. chemical composition does not vary within system; and physical structure i.e. solid, liquid or gas.
- The system consisting of single phase is called a ***homogeneous system***. e.g. air, mixture of water and sugar etc.
- The system which consists of more than one phase is called ***heterogeneous system***. e.g. mixture of water and oil etc.

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MACROSCOPIC AND MICROSCOPIC VIEWPOINT

Macroscopic Viewpoint	Microscopic Viewpoint
1. A certain quantity of matter is under investigation without focusing on the events taking place at molecular level.	1. The behaviour of matter is described by summing up behaviour of each molecule.
2. Properties that define the system can be measured and can be felt by human senses.	2. Since properties are concerned with individual molecule, they cannot be felt by human senses.
3. Observations are based on assumption (properties are average values) since structure of matter is not considered at all.	3. Exact observations are carried out by considering the structure of matter.
4. The analysis of this approach requires simple mathematical formula.	4. The analysis of approach requires a large no. of molecules so behaviour of the molecules is studied by using advanced statistical and mathematical methods.

- **Macroscopic viewpoint is an engineering approach while microscopic viewpoint is a scientific approach.**

1.3.2 THERMODYNAMIC EQUILIBRIUM

When a system is in equilibrium with regard to all possible changes in state, the system is in *thermodynamic equilibrium*. For example, if the gas that comprises a system is in thermal equilibrium, the temperature will be the same throughout the entire system.

1.3.3 CONTROL VOLUME

A *control volume* is a fixed region in space chosen for the thermodynamic study of mass and energy balances for flowing systems. The boundary of the control volume may be a real or imaginary envelope. The control surface is the boundary of the control volume.

1.3.4 STEADY STATE

Steady state is that circumstance in which there is no accumulation of mass or energy within the control volume, and the properties at any point within the system are independent of time.

1.3.5 THERMODYNAMIC PROCESS

Whenever one or more of the properties of a system change, a change in the state of the system occurs. The path of the succession of states through which the system passes is called the thermodynamic process. One example of a thermodynamic process is increasing the temperature of a fluid while maintaining a constant pressure. Another example is increasing the pressure of a confined gas while maintaining a constant temperature.

1.3.5.1 CYCLIC PROCESS

When a system in a given initial state goes through a number of different changes in state (going through various processes) and finally returns to its initial values, the system has undergone a cyclic process or cycle. Therefore, at the conclusion of a cycle, all the properties have the same value they had at the beginning. Steam (water) that circulates through a closed cooling loop undergoes a cycle.

1.3.5.2 REVERSIBLE PROCESS

A reversible process for a system is defined as a process that, once having taken place, can be reversed, and in so doing leaves no change in either the system or surroundings. In other words the system and surroundings are returned to their original condition before the process took place. In reality, there are no truly reversible processes; however, for analysis purposes, one

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uses reversible to make the analysis simpler, and to determine maximum theoretical efficiencies. Therefore, the reversible process is an appropriate starting point on which to base engineering study and calculation. Although the reversible process can be approximated, it can never be matched by real processes.

One way to make real processes approximate reversible process is to carry out the process in a series of small or infinitesimal steps. For example, heat transfer may be considered reversible if it occurs due to a small temperature difference between the system and its surroundings. For example, transferring heat across a temperature difference of 0.00001 °F "appears" to be more reversible than for transferring heat across a temperature difference of 100 °F. Therefore, by cooling or heating the system in a number of infinitesimally small steps, we can approximate a reversible process.

1.3.5.3 IRREVERSIBLE PROCESS

An irreversible process is a process that cannot return both the system and the surroundings to their original conditions. That is, the system and the surroundings would not return to their original conditions if the process was reversed. For example, an automobile engine does not give back the fuel it took to drive up a hill as it coasts back down the hill. There are many factors that make a process irreversible. Four of the most common causes of irreversibility are friction, unrestrained expansion of a fluid, heat transfer through a finite temperature difference, and mixing of two different substances. These factors are present in real, irreversible processes and prevent these processes from being reversible.

1.3.5.4 ADIABATIC PROCESS

An adiabatic process is one in which there is no heat transfer into or out of the system. The system can be considered to be perfectly insulated.

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1.3.5.5 ISENTROPIC PROCESS

An isentropic process is one in which the entropy of the fluid remains constant. This will be true if the process the system goes through is reversible and adiabatic. An isentropic process can also be called a constant entropy process.

1.3.5.6 POLYTROPIC PROCESS

When a gas undergoes a reversible process in which there is heat transfer, the process frequently takes place in such a manner that a plot of the Log P (pressure) vs. Log V (volume) is a straight line. Or stated in equation form PV^n = constant. This type of process is called a polytropic process. An example of a polytropic process is the expansion of the combustion gasses in the cylinder of a water-cooled reciprocating engine.

1.3.5.7 THROTTLING PROCESS

A throttling process is defined as a process in which there is no change in enthalpy from state one to state two, $h_1 = h_2$; no work is done, W = 0; and the process is adiabatic, Q = 0. To better understand the theory of the ideal throttling process let's compare what we can observe with the above theoretical assumptions.

1.4 PROPERTIES OF A SYSTEM

- Properties are the descriptive and measurable characteristics of the system.
- Properties **describe** the state of a system i.e. has a definite value when system is in a particular state.
- These are macroscopic in nature and hence, can be **measured** very easily.
- Their differential is exact i.e. value can be determined by simply integrating from one state to another.
- They depend only upon the state of system but not on the path followed by the process, hence are **Point function or State function**.

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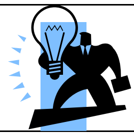
- Temperature, pressure, volume energy etc. are the various properties of system.



GATE Tip

Thus, Properties are macroscopic characteristics of a system such as mass, volume, energy, pressure and temperature etc. to which numerical values can be assigned at a given time without knowledge of the past history of the system.

Check for a property:

- An expression is a property of the system if its differential is exact.
  e.g. Expression $p\,dv + v\,dp$ is an exact differential of $d(pv)$, hence is a property. But $p\,dv$ or $v\,dp$ alone are not exact differential, hence are not the property of system.
- Expression $dP = M\,dx + N\,dy$ is exact differential if

$$\left[\frac{\partial M}{\partial y}\right]_x = \left[\frac{\partial N}{\partial x}\right]_y$$

INTENSIVE AND EXTENSIVE PROPERTIES

- Properties of system may be classified as Intensive or Extensive properties.

- **INTENSIVE PROPERTIES** are those which are independent of mass of system.
- Property of small portion of the system defines the property of whole of the system.
- Intensive properties are expressed in lower case letters except Pressure (P), temperature (T).
- All the specific properties are intensive properties.
- e.g. Pressure (P), temperature (T), density(ρ) etc.

- **EXTENSIVE PROPERTIES** are mass dependent. Hence their value depends upon the size of the system.

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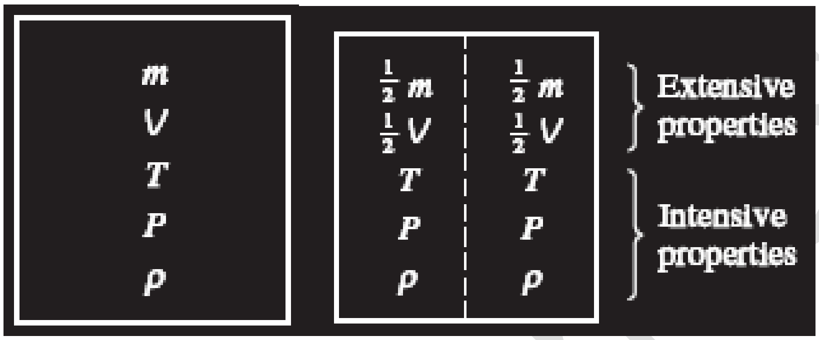
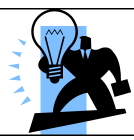
- An extensive property when expressed as per unit mass becomes an intensive property (**Specific property**).
- Extensive properties are expressed in upper case letter except mass.
- e.g. mass (m), energy (E), enthalpy (H), entropy (S) etc.
- $.\frac{\text{Extensive}}{\text{Extensive}} = \text{intensive}$





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Intensive properties are those which will be unchanged by any process, whereas those properties whose values are increased or decreased in proportion to the enlargement or reduction of the system are called extensive properties.

If the system consists of mixture of different phases, the phases are separated from each other by phase boundary. The thermodynamic properties change abruptly at the phase boundary, even though the intensive properties like temperature and pressure are identical.

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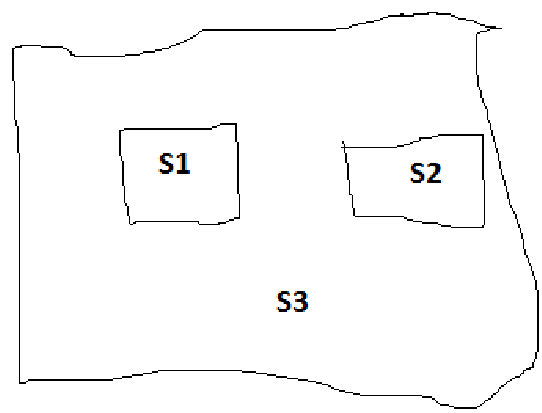
Past GATE Questions on Concept

Q.1 Here two systems S1 and S2 as shown in figure. Both the systems are in similar states. S3 is the combined system of S1 and S2. Is the value of property for S3 same as that for S1 and S2 or will have some other value?



Ans 1: If property is intensive then S3 will also have same value as S1 and S2 and if property is extensive then it will not have same value as S1 and S2.

Q.2 Which of the following are intensive properties?
1. Kinetic energy 2. Specific enthalpy
3. Pressure 4. Entropy
Select the correct answer using the code given below:
(a) 1 and 3
(b) 2 and 3
(c) 1, 3 and 4
(d) 2 and 4

Ans. 2**:** Specific Enthalpy is defined as enthalpy per unit mass so it will not depend on mass and Pressure will not depend on mass also. Thus both Specific Enthalpy and Pressure both will be treated as intensive property.

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STATE OF A SYSTEM

- State of a system is the condition of system at any point of time.
- **The state of a simple compressible system can be completely specified by two independent, intensive properties. (**This is also called two property rule or state postulates) Gibb's phase rule

$$F = C - P + 2$$

- When one or more than one property of system changes, then a **change of state of system** takes place.

Note:

- A system is called a **simple compressible system** in the absence of electrical, magnetic, gravitational, motion, and surface tension effects. (These effects are nearly negligible in the most of the engineering problems)

- Two properties are **independent** if one property can be varied while the other one is held constant.

- Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system

Dialogue box....
Temperature and pressure, however, are independent properties for single-phase systems, but are dependent properties for multiphase systems. Explain.

THERMODYNAMIC PROCESS, PATH AND CYCLE

- Any change that a system undergoes from one equilibrium state to another is called a **process**
- The series of states through which a system passes during a process is called the **path** of the process

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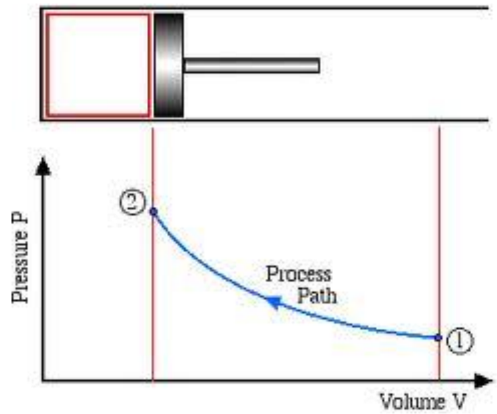
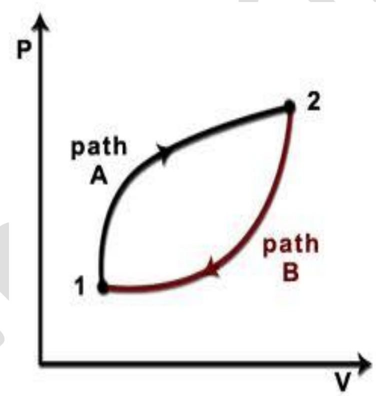


- When change of state takes place in such a way that the initial and final states of system are identical, then the process is called **thermodynamic cycle.**



THERMODYNAMIC EQUILIBRIUM

- A system is said to be in thermodynamic equilibrium if the conditions are satisfied for:
  - Mechanical equilibrium
  - Chemical equilibrium
  - Thermal equilibrium
  - Phase equilibrium

Mechanical equilibrium in system exists when there is no change in pressure at any point of system with time i.e. uniformity of pressure. It also means that there is no any unbalanced force. In other words, there is no pressure gradient within the system.

- *The variation of pressure as a result of gravity in most thermodynamic systems is relatively small and usually disregarded.*
- *Still water contained in a tank is also considered to be in mechanical equilibrium, though the pressure increases as one move downward from free water surface.*

- **Chemical equilibrium** in a system exists when there is no change in chemical composition with time i.e. no chemical reaction takes place.
- **Thermal equilibrium** in a system exists when there is no temperature differential within system.
    - Temperature is same throughout the entire system.
    - Fluids comprising the system are not chemically reactive since it may raise temperature of system by chemical reaction.
- **Phase equilibrium** in a multiphase system exists when the mass of each phase reaches an equilibrium level and stays there.

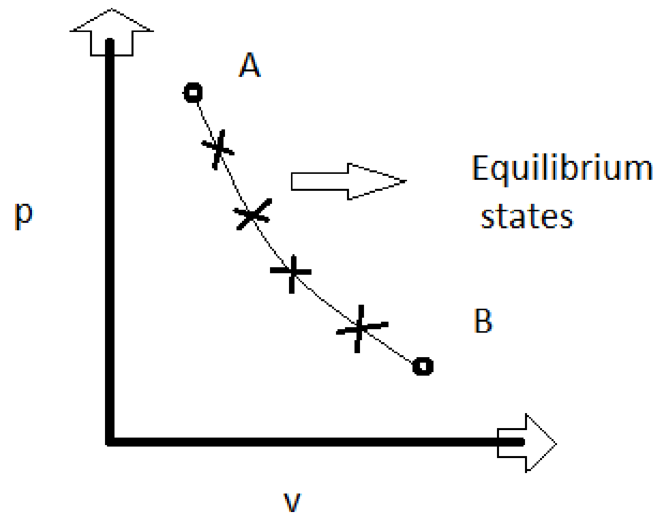
Note:

- A system is said to be in non-equilibrium state if any one of the above condition is not satisfied by the system.
- In non-equilibrium, states passed by the system cannot be described by thermodynamic properties which represent the system as a whole.

When a system remains in equilibrium state, it should not undergo any changes on its own.

QUASI-STATIC PROCESS

- When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a **quasi-static,** or **quasi-equilibrium, process.**
- Thus, clear state properties (pressure, temperature etc.) can be assigned to the system at every moment. A quasi-static process can thus be represented by a set of continuous points on a state-space diagram (e.g., a p − V diagram or a T − v diagram).

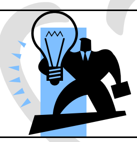


Quasi-static process

Features of Quasi-Static Process

- A quasi-equilibrium process is a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.

- Frictionless quasi-static processes are reversible.
- These are idealized process and not the true representation of actual process.
- Every state passed may be regarded as equilibrium state.
- Infinite slow process and easy to analyze.
- All work producing devices work on this principle.



GATE Tip

A process is said to be reversible if the system and its surroundings are restored to their respective initial states by reversing the direction of the process. A reversible process has to be quasi-static, but a quasi – static process is not necessarily reversible.

Examples:

Quasi-static: Slow expansion of a piston and cylinder system such that pressure and volume can be clearly defined at every point in time.

Non quasi-static: Sudden expansion of the piston-cylinder system. Pressure in the system cannot be specified at every point in time.

Quasi-static: Two bodies exchanging energy in the form of heat such that the temperature of each body is clearly defined at every point of time.

Non quasi-static: Rapid removal of energy from one surface of a reasonably large system such that there is no unique temperature for the system.

Reversible Process

A process in which an infinitesimal change in the driving potential can reverse the direction of the process.

Example: A piston expanding against an external pressure. The driving potential is the pressure difference which is infinitesimal. At any stage, if the external pressure is increased infinitesimally, the piston should start moving the opposite way.

Or Else: Heat transfer occurring due to a temperature difference between two bodies. The temperature difference between the two bodies is infinitesimal. If the temperature of body receiving energy is changed infinitesimally, the direction of heat transfer also changes.

NOTE: A reversible process is necessarily quasi-static though the opposite is not true. For example, consider heat exchange between a really well insulated vessel at temperature T1 and the surroundings which are at T2 far lesser than T1. Changing either T1 or T2 does not reverse the direction of the process, though it is slow enough to be quasi-static.

Q.3 Which Of The Following Is/Are Reversible Process(es)?

1. Isentropic expansion
2. Slow heating of water from a hot source
3. Constant pressure heating of an ideal gas from a constant temperature source
4. Evaporation of a liquid at constant temperature

Select the correct answer using the code given below:

(a) 1 Only
(b) 1 And 2
(c) 2 And 3
(d) 1 And 4

Ans:
(d) Isentropic expansion and evaporation of a liquid at constant temperature. Isentropic expansion is also known as reversible adiabatic process (which will be discussed in later chapter).

CONCEPT OF CONTINUUM

Despite the large gaps between molecules, a substance can be treated as a continuum because of the very large number of molecules even in an extremely small volume.

It assumes a continuous distribution of mass within the matter or system with no empty space, instead of the actual conglomeration of separate molecules.

If the mean free path is very small as compared with some characteristic length in the flow domain (i.e., the molecular density is very high) then the gas can be treated as a continuous medium. If the mean free path is large in comparison to some characteristic length, the gas cannot be considered continuous.

- The continuum idealization allows us
  - to treat properties as point functions and
  - to assume the properties vary continually in space with no jump discontinuities.

- This idealization is valid as long as the size of the system we deal with is large relative to the space between the molecules.

PATH FUNCTION AND POINT FUNCTION

Point Functions

- They depend only upon the initial and final condition (state) of the system but not on the path followed by the system.
- They have exact differential i.e. their integration can be carried out simply.

- Differential amount is represented by symbol "d" i.e. small change in volume will be expressed as dV.
- Change in value can be expressed as the difference between initial and final value.

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

- **Thermodynamic properties** are point functions since for a given state there is a definite value for each property and is independent of the path the system follows during the change of state.
- In a cycle, since initial and final states are identical, the cyclic integral of a property (point function) is always zero i.e. $\oint V = 0, \oint P = 0, \oint T = 0$.

Path Functions

- They depend upon the path followed by the system.
- They have inexact differential.
- Differential amount is represented by symbol δ i.e. for small work done δW and small heat transfer δQ
- **Work and heat** are the path functions.
- Change in the value can **NOT** be expressed as the difference between initial and final value.

$$\int \delta W \neq W_2 - W_1 \neq \Delta W$$
$$= W_{1\text{-}2} \text{ (but not } \Delta W)$$

- Before integration, multiplication with integrating factor is required.

WORKING SUBSTANCE

- A working substance refers to a fluid in thermodynamic devices to serve as a medium for transport of energy between the system and surroundings.
- Fluid may be gas, vapour, liquid or any nonreactive mixture of these constituents.
- Working substance may change their phase during processes occurring in the system.
- Example – **refrigerants** used in refrigeration and air-conditioners, **water vapour** used in steam power plants.

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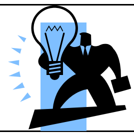

GATE Tip

Intensive Property

- Independent of mass

Extensive Property

- mass dependent.
- value depends upon the size of the system.

Specific property

- An extensive property when expressed as per unit mass becomes an intensive property.

Point Functions

- They depend only upon the initial and final condition
- not on the path followed by the system.
- exact differential
- Cyclic integral of a property (point function) is always zero

Path Functions

- Depend upon the path followed by the system.
- Inexact differential.

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