THERMODYNAMICS

Fundamental Concepts and Definitions

THERMODYNAMICS:

- It is the science of the relations between heat, Work and the properties of the systems.

- How to adopt these interactions to our benefit?

Thermodynamics enables us to answer this question.

Analogy

All currencies are not equal

Eg: US$ or A$ or UK£ etc. Have a better purchasing power than Indian Rupee or Thai Baht or Bangladesh Taka similarly,all forms of energy are not the same.

Human civilization has always endeavoured to obtain

- Shaft work
- Electrical energy
- Potential energy to make life easier

Examples

If we like to

- Rise the temperature of water in kettle
- Burn some fuel in the combustion chamber of an aero engine to propel an aircraft.
- Cool our room on a hot humid day.
- Heat up our room on a cold winter night.

What is the smallest amount of electricity/fuel we can get away with?

Examples (Contd…)

On the other hand we burn,

- Some coal/gas in a power plant to generate electricity.
- Petrol in a car engine.

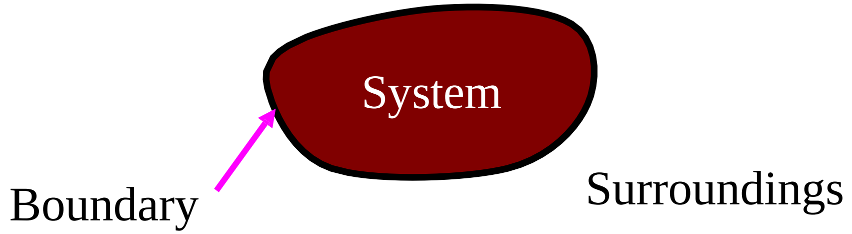
What is the largest energy we can get out of these efforts?

Thermodynamics allows us to answer some of these questions

Definitions

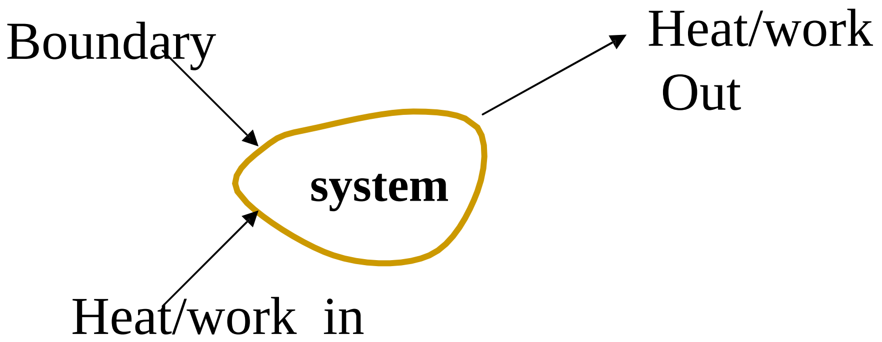
- In our study of thermodynamics, we will choose *a small part of the universe* to which we will apply the laws of thermodynamics. We call this subset a SYSTEM.
- The thermodynamic system is analogous to the free body diagram to which we apply the laws of mechanics, (i.e. Newton's Laws of Motion).
- The system is a macroscopically identifiable collection of matter on which we focus our attention (eg: the water kettle or the aircraft engine).

- The rest of the universe outside the system close enough to the system to have some perceptible effect on the system is called the surroundings.
- The surfaces which separates the system from the surroundings are called the boundaries as shown in fig below (eg: walls of the kettle, the housing of the engine).



Types of System

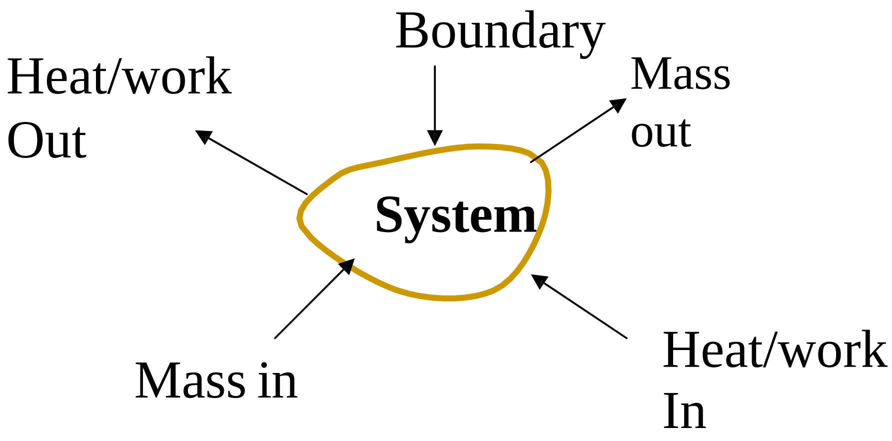
- Closed system - in which no mass is permitted to cross the system boundary i.e. we would always consider a system of constant mass.We do permit heat and work to enter or leave but not mass.



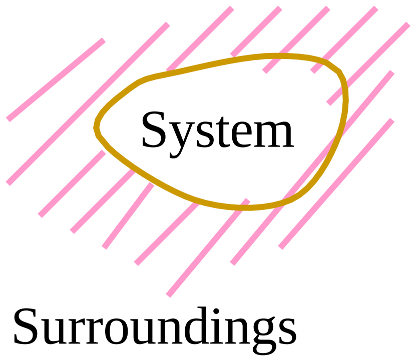
No mass entry or exit

- Open system- in which we permit mass to cross the system boundary in either direction (from the system to surroundings or *vice versa*). In analysing open systems, we typically look at a specified region of space, and observe what happens at the boundaries of that region.

Most of the engineering devices are open system.



- Isolated System - in which there is no interaction between system and the surroundings. It is of fixed mass and energy, and hence there is no mass and energy transfer across the system boundary.



Choice of the System and Boundaries Are at Our Convenience

- We must choose the system for each and every problem we work on, so as to obtain best possible information on how it behaves.
- In some cases the choice of the system will be obvious and in some cases not so obvious.
- Important: you must be clear in defining what constitutes your system and make that choice explicit to anyone else who may be reviewing your work.

Choice of the System and Boundaries Are at Our Convenience (contd…)

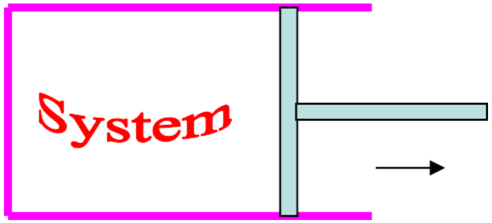
- The boundaries may be real physical surfaces or they may be imaginary for the convenience of analysis.

eg: If the air in this room is the system,the floor,ceiling and walls constitutes real boundaries.the plane at the open doorway constitutes an imaginary boundary.

Choice of the System and Boundaries Are at Our Convenience (contd…)

- The boundaries may be at rest or in motion.

eg: If we choose a *system* that has a certain defined quantity of mass (such as gas contained in a piston cylinder device) the *boundaries* must move in such way that they always enclose that particular quantity of mass if it changes shape or moves from one place to another.



Macroscopic and Microscopic Approaches

Behavior of matter can be studied by these two approaches.

- In macroscopic approach, certain quantity of matter is considered,without a concern on the events occurring at the molecular level. These effects can be perceived by human senses or measured by instruments.

- eg: pressure, temperature

Microscopic Approach

- In microscopic approach, the effect of molecular motion is Considered.

eg: At microscopic level the pressure of a gas is not constant, the temperature of a gas is a function of the velocity of molecules.

Most microscopic properties cannot be measured with common instruments nor can be perceived by human senses

Property

- It is some characteristic of the system to which some physically meaningful numbers can be assigned without knowing the history behind it.
- These are macroscopic in nature.
- Invariably the properties must enable us to identify the system.
- eg: Anand weighs 72 kg and is 1.75 m tall. We are not concerned how he got to that stage. We are not interested what he ate!!.

Examples (contd...)

We must choose the most appropriate set of properties**.**

- For example: Anand weighing 72 kg and being 1.75 m tall may be a useful way of identification for police purposes.
- If he has to work in a company you would say Anand graduated from IIT, Chennai in 1985 in mechanical engineering.
- Anand hails from Mangalore. He has a sister and his father is a poet. He is singer. ---If you are looking at him as a bridegroom!!

Examples (contd…)

- All of them are properties of Anand. But you pick and choose a set of his traits which describe him best for a given situation.
- Similarly, among various properties by which a definition of a thermodynamic system is possible, a situation might warrant giving the smallest number of properties which describe the system best.

Categories of Properties

- Extensive property:

whose value depends on the size or extent of the system (upper case letters as the symbols).

eg: Volume, Mass (V,M).

If mass is increased, the value of extensive property also increases.

- Intensive property:

whose value is independent of the size or extent of the system.

eg: pressure, temperature (p, T).

Property (contd..)

Specific property:

- It is the value of an extensive property per unit mass of system. (lower case letters as symbols) eg: specific volume, density (*v*, ρ).
- It is a special case of an intensive property.
- Most widely referred properties in thermodynamics:
- Pressure; Volume; Temperature; *Entropy; Enthalpy; Internal energy*

(Italicised ones to be defined later)

- State:

It is the condition of a system as defined by the values of all its properties.

It gives a complete description of the system.

Any operation in which one or more properties of a system change is called a change of state.

- Phase:

It is a quantity of mass that is homogeneous throughout in chemical composition and physical structure.

e.g. solid, liquid, vapour, gas.

Phase consisting of more than one phase is known as heterogenous system .

Path And Process

The succession of states passed through during a change of state is called the *path of the system*. A system is said to go through a process if it goes through a series of changes in state. Consequently:

- **A** system may undergo changes in some or all of its properties.
- A process can be construed to be the locus of changes of state

Processes in thermodynamics are like streets in a city

eg: we have north to south; east to west; roundabouts; crescents

Types of Processes

- As a matter of rule we allow one of the properties to remain a constant during a process.
- Construe as many processes as we can (with a different property kept constant during each of them)
- Complete the cycle by regaining the initial state

- Isothermal (T)
- Isobaric (p)
- Isochoric (v)
- Isentropic (s)
- Isenthalpic (h)
- Isosteric (concentration)
- Adiabatic (no heat addition or removal

Quasi-static Processes

The processes can be restrained or unrestrained We need restrained processes in practice.

A quasi-static process is one in which

- The deviation from thermodynamic equilibrium is infinitesimal.
- All states of the system passes through are equilibrium states.

Quasi-static Processes (contd…)

- If we remove the weights slowly one by one the pressure of the gas will displace the piston gradually. It is quasistatic.
- On the other hand if we remove all the weights at once the piston will be kicked up by the gas pressure.(This is unrestrained expansion) but we don't consider that the work is done - because it is not in a sustained manner
- In both cases the systems have undergone a change of state.
- Another eg: if a person climbs down a ladder from roof to ground, it is a quasistatic process. On the other hand if he jumps then it is not a quasistatic process.

Equilibrium State

- A system is said to be in an equilibrium state if its properties will not change without some perceivable effect in the surroundings.
- Equilibrium generally requires all properties to be uniform throughout the system.
- There are mechanical, thermal, phase, and chemical equilibria

Equilibrium State (contd)

Nature has a preferred way of directing changes. eg:

- water flows from a higher to a lower level
- Electricity flows from a higher potential to a lower one
- Heat flows from a body at higher temperature to the one at a lower temperature
- Momentum transfer occurs from a point of higher pressure to a lower one.
- Mass transfer occurs from higher concentration to a lower one

Types of Equilibrium

Between the system and surroundings, if there is no difference in

- Pressure → Mechanical equilibrium
- Potential → Electrical equilibrium
- Concentration of species → Species equilibrium
- Temperature → Thermal equilibrium

No interactions between them occur.
They are said to be in equilibrium.

Thermodynamic equilibrium implies all those together.
A system in thermodynamic equilibrium does not deliver anything.

Definition Of Temperature and Zeroth Law Of Thermodynamics

- Temperature is a property of a system which determines the degree of hotness.
- Obviously, it is a relative term.

eg: A hot cup of coffee is at a higher temperature than a block of ice. On the other hand, *ice is hotter than liquid hydrogen.*

Thermodynamic temperature scale is under evolution. What we have now in empirical scale.

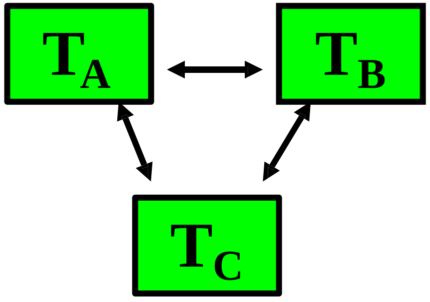
Zeroth Law Of Thermodynamics (Contd…)

- Two systems are said to be equal in temperature, when there is no change in their respective observable properties when they are brought together. In other words, “when two systems are at the same temperature they are in thermal equilibrium” (They will not exchange heat).

Note:They need not be in thermodynamic equilibrium.

Zeroth Law

- If two systems (say A and B) are in thermal equilibrium with a third system (say C) separately (that is A and C are in thermal equilibrium; B and C are in thermal equilibrium) then they are in thermal equilibrium themselves (that is A and B will be in thermal equilibrium



Explanation of Zeroth Law

- Let us say T_A,T_B and T_C are the temperatures of A,B and C respectively.
- A and c are in thermal equilibrium. $T_a = t_c$
- B and C are in thermal equilibrium. $T_b = t_c$

Consequence of of '0'th law

- A and B will also be in thermal equilibrium $T_A = T_B$
- Looks very logical
- All temperature measurements are based on this LAW.