BPSC

ASSISTANT ENGINEER

PRELIMINARY EXAMINATION 2018

THERMODYNAMICS AND HEAT TRANSFER

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UNIT-1

BASIC CONCEPTS OF THERMODYNAMICS

Thermodynamic System

Thermodynamic system is defined as a quantity of matter or region in space upon which is selected for thermodynamic analysis.

Surroundings: Everything outside the thermodynamic system can be said to be surroundings.

System + Surrounding = Universe

System Boundary

The system and surrounding are separated by system boundary. The boundary of system may be either fixed or moving. It may also be either real or imaginary. The boundary has zero thickness & thus it can neither contain any mass nor occupy any volume in space.

Thermodynamic systems are divided in three types namely,

(1) Closed System (2) Open system. (3) Isolated System.

(1) **Closed System (Control Mass) :** It is a system of fixed mass i.e. mass can not change or cross the system boundary but energy in the form of heat and work can cross. The volume of closed system may change and thus the system boundary may also move. Ex. Pressure Cooker, Piston cylinder assembly.

(2) **Open System (Control Volume) :** In this system the energy as well as mass can cross the system boundary. Generally boundary is fixed and a specific region or space of system is selected for analysis purpose. Example: Compressor, pump, turbine etc.

(3) **Isolated System :** This system has no interaction with surrounding i.e. neither mass nor energy can transfer the system boundary. It is a fixed mass and fixed energy system e.g. coffee in an insulated thermo flask, universe is itself an isolated system. This is a special case of closed system.

Ex. Bomb calorimeter, manual ice cream freezer, hot coffee stored in a well insulated thermos flask, ice kept in a well insulated thermos flask.

System	Mass transfer	Energy Transfer
Open system	Yes	Yes
Closed	No	Yes
Isolated	No	No

Note: The identification of system and thereby surroundings depends on our choice. It is similar to the free body diagram concept used in mechanics.

Homogeneous and Heterogeneous Systems

Any substance in single phase e.g. mixture of air and water vapour, water and nitric acid is called homogeneous system and if a system has more than one phase, it is called heterogeneous system.

Thermodynamic States, Properties, Processes and Cycles

Thermodynamic state: The state of a system is described by its properties. But we do not need to specify all the properties in order to fix state. Once a sufficient number of properties are specified, the rest of the properties assume certain values automatically. That is specifying a certain number of properties is sufficient to fix a state.

Thermodynamics properties are observable characteristics of the system. A thermodynamic property refers to a characteristic which is concerned with interaction of energy in the form of heat and work between a system and its surroundings. When all the properties have definite value, the system is said to exist in definite state.

There are two types of thermodynamic properties:

(1) **Intensive property** : These are independent of mass or size of system e.g. pressure, temperature, density, thermal conductivity, dielectric constant, thermal expansion coefficient etc.

(2) **Extensive Property** : These properties depend on mass or size of system. e.g. volume, kinetic energy, potential energy etc.

If we divide a homogeneous substance into many parts, the intensive thermodynamic property has the same value for the system as a whole as well as each subdivision.

The ratio of two extensive properties of a homogeneous system is an intensive property. Specific properties are intensive e.g. [extensive property per unit mass]. Energy per unit mass, volume per unit mass etc. But work and heat are not properties.

To completely define the state of a system, certain minimum number of properties are required to be known. These are called independent properties. Thus, either p and v or p and t or t and v become two independent properties of the system. The values of the remaining properties can be determined in terms of the values of the independent properties. These other properties are called dependent properties.

Thermodynamic Process

Any operation which brings change in one or more properties is called change of state. Whenever, one or more of the thermodynamic properties of a system change, we say that there is a change in state of the system. This change of state of a system is referred to as thermodynamic process.

The state of a system can be defined only when it is in equilibrium hence we say that process is any transformation of a system from one equilibrium state to the other. The path followed in a process may or may not be clearly identifiable.

A process occurs due to heat and work interaction between system and surroundings when they are not in the same intensive state.

Thermodynamic state of a system at any given instant of time is its condition as characterised by certain observable thermodynamic properties, i.e. the set of properties completely determine the state of a system.

Isobaric–constant pressure

Isochoric–constant volume

Isothermal–constant temperature

Adiabatic–No heat transfer takes place during the process–PV^{γ} = constant

Polytropic–PV^{n} = Constant

Reversible and Irrevesible Processes

Reversible process means one which can be completely reversed. It implies that when carried out in the opposite direction, the system follows the same succession of states it followed in the forward direction. Thus, the system is restored to its initial conditions.

Not only the system, but the surroundings are also restored to their initial conditions. Thus, if a process is reversible then when it is reversed, the system and surroundings both come back to the original states and no trace of the history of the forward process is left.

Quasi-static process is an infinitely slow process since all the potential differences viz. temp & pr. differences acting on the system are infinitely small. Quasistatic process becomes reversible when it is frictionless. Thus, all the reversible processes are quasi-static but all quasi static processes are not reversible.

A reversible process is an infinite succession of equilibrium states. Every point on the path can be traced. The process can be stopped at any point and made to proceed in the opposite direction at that point by infinitesimal potential difference. A non-equilibrium process can't be exactly reversed and the system can't be brought back to the initial state without leaving a net change in the surroundings.

A reversible process should fulfill the following conditions:

(i) Process should not involve friction.

(ii) Heat transfer should not take place with finite temp difference.

(iii) No free expansion.

(vi) No mixing of fluids.

(v) Process must proceed in a series of equilibrium states. Ex. Frictionless adiabatic expansion/compression, Frictionless isothermal expansion/compression condensation & boiling.

Causes of Irreversibility

(i) Friction, viscous forces, electric resistance and inelastic collision converts high grade energy into law grade energy, hence causes irreversibility.

(ii) Heat transfer through temperature difference causes irreversibility and as the temperature difference for heat transfer tends to zero the process tends to be reversible.

(iii) Heat transfer processes for a gas with the source at constant temperature should be treated as irreversible except for isothermal process.

Any heat transfer process can be made reversible if carried out with the help of infinite reservoirs.

(iv) Phase change process like boiling, evaporation etc. are considered as internally reversible process.

(v) Free expansion of a gas, expansion of a material beyond elastic region and mixing of fluid causes irreversibility. If the mixing fluid are same and the initial condition is also some and the initial condition is also same then the mixing is considered reversible.

Note: How can we describe the intermediate states of a system along the path of a process since the process takes place only when equilibrium is disturbed. The solution is quasi-static process. In quasi-static, deviation from equilibrium is infinitesinal. Thus, all the states passed through the system can be considered as succession of equilibrium states. Thus, the path of the process can be plotted and each state is an equilibrium state. Quasi-static process can also be called quasi-equilibrium process.

What is thermodynamic cycle?

When a system in a given initial state undergoes a series of processes and returns to the initial state then the system is said to have undergone a thermodynamic cylce. The change in the value of any property for a cyclic process is zero. $\oint dp = 0$ & $\oint dv = 0$

A cycle is said to be reversible only when each process of the cycle is reversible.

Point function & path function

Point Function—Change in the value of a property between any two given states is the same irrespective of the path followed to reach that state. The state and properties are point functions.

These are also exact differentials because $\int_1^2 dp = p_2 - p_1$ or, $\int_1^2 dv = v_2 - v_1$ the value in this case depends on the path followed by the process during the change of state. Path functions are inexact differentials because $\int_1^2 dW \neq W_2 - W_1$. The value of path function depends upon the path followed to reach the final state.

Thermodynamic Equilibrium

If two systems or the system and surrounding are in the same intensive state, then they are in thermodynamic equilibrium. The difference of intensive properties vis-a-vis another system or surroundings acts as a potential difference to drive a system towards a change of state.

A system is in thermodynamic equilibrium if it is not capable of a finite spontaneous change to another state. All thermodynamic properties have the same value at all points of the system in a thermodynamic equilibrium. For complete thermodynamic equilbrium, the system should be in all of three.

(i) Thermal equilibrium
(ii) Mechanical equilibrium
(iii) Chemical equilibrium

Thermal equilibrium—For this, temp of system & surroundings must be same.

Mechanical equilibrium—For this, pressure of system & surroundings must be same.

Chemical equilibrium—In this the system can't undergo a chemical reaction. It means the matter in the system stays as inert. For chemical equilibrium, chemical potential between system & surroundings must be same.

When any of the above three conditions are not satisfied, the system is considered to be in a non-equlibrium state. For example if a non equilibrium state is due to unbalanced pressure difference, there is no single pressure which characterises the pressure of the system as a whole.

Thus, when there is equilibrium in the system, then only the state of the system is specified by its properties.

Pure Substance

A substance is pure if,

- Homogeneous in composition–Chemical composition of each part of system is same.
- Homogeneous in chemical aggregation – Chemical compound in the system must be combined in the same way in every part of the system.
- Invariable in chemical compostion – Chemical doesn't change in time.
  Change in phase is possible here.
- A pure substance does not have to be of a single chemical element or compound, so a mixture of various chemical compounds also qualify as pure substance.

Examples of pure substances

Atmospheric air, steam–water mixture, combustion products of fuel.

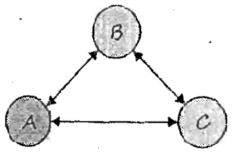
But mixture of air and liquid air is not pure substance because relative proportion of oxygen and nitrogen are different in two phases.

Temperature Concept

- Temperature is the property which differentiate between hot and cold body.
- The basis of temperature measurement is Zeroth law of thermodynamics.

Zeroth Law of Thermodynamics

"If a body A is in thermal equilibrium with body B and body B is in thermal equilibrium with body C, then A and C will be in thermal equilibrium".



It is used as a basis for temperature measurement.

UNIT-2

FIRST LAW THERMODYNAMICS

Thermodynamic Work

In mechanics, work is defined as the product of a force F and the resulting displacement dx measured in the direction of the force. $W = \int_1^2 Fdx = \int_1^2 pAdx = \int_1^2 pdv$. In thermodynamics, force is not much relevant, hence we calculate work due to the pressure. In thermodynamics, work is done by a system if the sole effect on the surrounding could be reduced to the raising of a weight. Note that the definition does not call for the actual raising of the weight but rather the possibility of raising a weight.

Work is a boundary phenomenon i.e. the work transfer must cross the system boundary or the control surface.

By convention, work done by system– +ve

work done on system– –ve

When a system does some +ve work, the surroundings do an equal amount of negative work and vice-versa. Thus, in any process, $W_{system} + W_{surrounding} = 0$.

Work is manifest at the system boundary only during any interaction between sysem and surroundings. Before interaction, no work is present and after interaction, no work is present.

$\int pdv$ work is applicable to non-flow reversible processes and quasi-static processes. Thus, thermodynamic work is the product of an intensive thermodynamic property and the differential of an extensive property. However, work is not a property.

Path function is an inexact differential.

Whereas property is an exact differential.

Property
- Intensive → doesn't depend on amount of substance
- Extensive → depends on amount of substance.

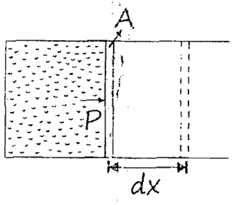
Intensive property—Pressure, temp., sp.vol., sp. energy, density, sp. heat capacity.

Extensive properties—Energy, entropy, length, mass, volume, momentum etc.

Type of work transfer

Work transfer in a Thermodynamic Process

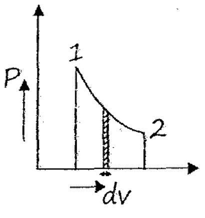
For a non-flow, reversible or quasi-static process,



$$\delta W = P(A.dx) = pdv$$

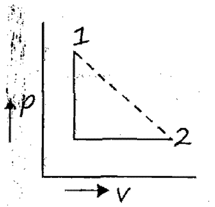
$$\delta w = pdv \Rightarrow w = \int_{V_1}^{V_2} pdv$$

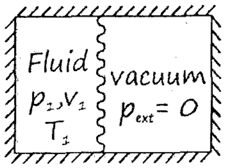
Work done = area under the curve in p-v diagram

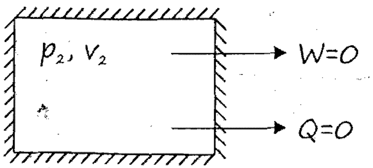


In a quasi-static process, each state is an equilibrium state in an infinitely slow process. It is an idealised hypothesis. Interpration $\int pdv$ can be performed only on a quasi-static path. Since, areas under different curves would be different, so work done is a path function i.e. it's value depends on the path travelled in the p-v diagram.

Free Expansion







Membrane ruptured

Free expansion is a non-equilibrium adiabatic process in which the volume of a closed system increases, yet no work is done.

Let first consider, the fluid and vacuum together as the system. No work is done, volume constant.

Now, let us consider only the compartment containing fluid as system. Then the system boundary moves and volume increases. However, it is a non-quasistatic process, and $p_{ext} = 0$ Hence, no work done.

$$\cancel{\delta Q}^{0} = du + \cancel{W}^{0} \Rightarrow du = 0$$

$U_i = U_f$ for any gas in free expansion.

but $T_i = T_f$ only for ideal gas in free expansion.

$h_i = h_f$ only for ideal gas in free expansion.

$T_i = T_f$ does not mean free expansion is an isothermal process, rather only initial & final for equal but temp not constant theroughout the process. Initially during expansion temp decreases but finally when molecules rub against wall of container temp increases.

In free expansion, $dv \neq 0$, work is zero because pdv is applicable only for reversible processes.

Free expansion

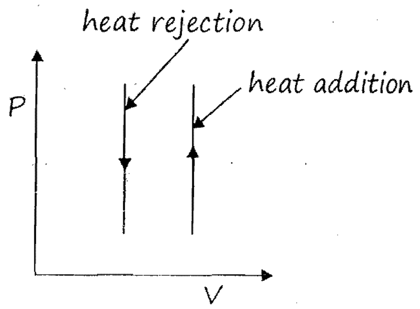
Ideal Gas eqn for Various Process

1. Constant volume process

$$V = \text{constant}$$
$$PV = mRT$$
$$\text{or } P \propto T$$
$$\frac{p_2}{p_1} = \frac{T_2}{T_1}$$

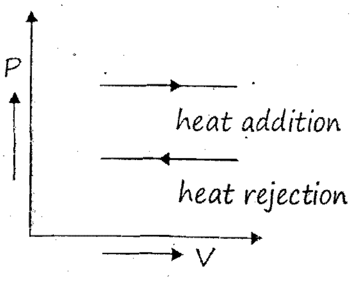
As T↑ ⇒ P↑ ⇒ heat addition

As T↓ ⇒ P↓ ⇒ heat rejection



2. Constant pressure process

$$P = \text{constant}$$
$$pv = mRT$$
$$V \propto T$$
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$



As T↑ ⇒ V↑ ⇒ heat addition

As T↓ ⇒ V↓ ⇒ heat rejection

3. Isothermal process

$$T = \text{constant or } pv = mRT = \text{constant}$$

$$p_1v_1 = p_2v_2$$

or,

$$\frac{p_1}{p_2} = \frac{v_2}{v_1}$$

4. Adiabatic process

$$pv^{\gamma} = C \text{ but } pv = mRT \text{ or } P = \frac{mRT}{v}$$

$$\therefore \quad \frac{mRT}{v}\cdot v^{\gamma} = C \text{ or } \boxed{Tv^{\gamma-1} = C}$$

$$P\left(\frac{mRT}{P}\right)^{\gamma} = C \text{ or } \frac{T^{\gamma}}{P^{\gamma-1}} = C$$

5. Polytropic process

$$PV^{n} = C$$

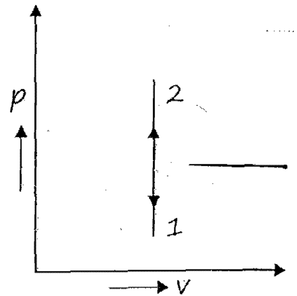
$$TV^{n-1} = C \rightarrow \frac{T^{n}}{P^{n-1}} = C$$

Pdv Work in Various Processes

Pdv Work in various closed/non-flow processes

1. Constant volume/Isochoric

$$W = \int pdv \Rightarrow W = 0, \text{ since } v = \text{constant}$$



In case of a rigid container of constant volume, work = 0

2. Constant pressure/Isobaric

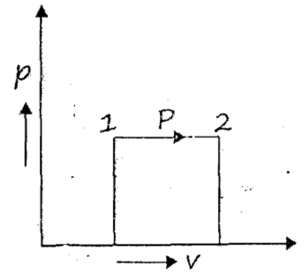
$$\text{work} = \int pdv = p(v_2 - v_1)$$

i.e

$$P_{gas} = P_{atm} + P_{piston}$$

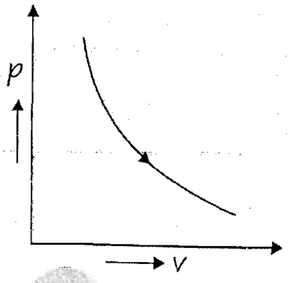
$$= p_{atm} + \frac{W}{A}$$

$$\Rightarrow \quad P_{gas} = \text{constant}$$



3. Constant temperature/Isothermal

$$pv = \text{constant} = C = mRT$$



$$W = \int p\,dv = \int_1^2 \frac{C}{v}dv = C\ln\frac{v_2}{v_1}$$

$$= mRT\ln\frac{v_2}{v_1}$$

$$= mRT\ln\frac{p_1}{p_2} = p_1v_1\ln\frac{v_2}{v_1}$$

4. Adiabatic process

$$pv^n = \text{constant} = c$$

$$w = \int p\,dv = \int cv^{-\gamma}dv = c\left|\frac{v^{1-\gamma}}{1-\gamma}\right|_1^2$$

$$= \frac{c}{1-v}\left(v_2^{1-\gamma} - v_1^{1-\gamma}\right) = \frac{p_2v_2 - p_1v_1}{1-\gamma} = \frac{p_1v_1 - p_2v_2}{\gamma - 1}$$

5. Polytropic process

$Q \neq 0$, $pv^n = c$, n = polytropic index

Generally, $1 < n < \gamma$

$$W = \frac{p_1v_1 - p_2v_2}{n-1}$$

In polytropic process, there is both heat and work transfer, whereas in adiabatic process, there is only work transfer.

If we take a general condition

$$pv^k = c$$

then, for isobaric process, $k = 0$

for isothermal process, $k = 1$

for polytropic process, $k = n$

for adiabatic process, $k = \gamma$

for constant volume process $k = \infty$

Since, $pv^k = c \Rightarrow p^{1/k}.v = c^{1/k}$

Hence $k \to \infty$, then v = constant

Representation of Various Processes on p-v Diagram