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## Introduction to Thermodynamics

### Thermodynamics

It is that branch of science that deals with the conversion of heat energy into other forms of energy and to study those conversions quantitatively.

### Continuum Model

Techniques of statistical mechanics and kinetic theory are used to describe matter at molecular level. However for engineering purposes averaged information i.e. macroscopic description of any material is required. There are two reasons for it:

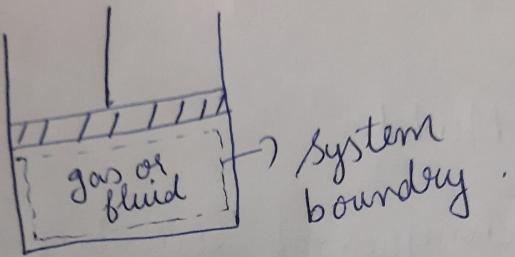
- 1) Microscopic description of an engineering device will generate too much information to manage.
- 2) Microscopic ~~to~~ positions and velocities are generally not very useful for determining how macroscopic systems act.

Therefore, this model neglects the fact that real substances are composed of ~~discrete~~ ~~to~~ discrete molecules and consider it to be smoothed-out continuum i.e. the microscopic information is averaged over a volume.

## Principle concepts of Thermodynamics

### ① System

A thermodynamic system is a quantity of fixed identity, around which boundary can be drawn as shown below.



The boundaries can be fixed or moveable. Work and heat can be transferred across the system boundary.

~~as~~ everything outside the boundary is the surroundings.

A closed system is a special case of system with boundaries across which matter cannot cross, also called control system. In this case principle of conservation of mass is automatically satisfied.

### ② State:-

The thermodynamic state of a system defined by specifying values of a set of physically measurable properties that are sufficient to determine all other properties. For example, in case of gaseous or fluid systems these properties are temperature, volume and pressure.

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These properties can either be extensive ~~or~~ or intensive.

(3)

extensive properties are those that depend upon the mass or quantity of matter or either on its size i.e. volume. Examples - Volume.

Intensive properties are those that depend upon the nature of the material instead of quantity of matter. Examples - Temperature, Pressure.

(3) equilibrium:-

The state of a system in which properties have definite unchanged values as long as external conditions ~~are~~ remain unchanged is called an equilibrium state.

A thermodynamic system is said to be in equilibrium if it is simultaneously in mechanical equilibrium (no unbalanced forces), thermal equilibrium (no temperature differences) and chemical equilibrium.

(4) Process:-

If a system undergoes a change from one equilibrium state to other ~~is~~ then it is undergoing a process and the successive states through which the system passes during this change is called the path of the process.

If after the completion of the process the ideal properties of the system return to their original values then it is a cyclic process or cycle. However, during this process (cycle) the state of the surroundings definitely changes.

### Quasi-equilibrium processes

When a process is carried out in such a way that at every instant, the system deviation from thermodynamic equilibrium is infinitesimal then the process is known as quasi-static or quasi-equilibrium process and each state in the process can be considered as an equilibrium state. It is also known as reversible process which means the process can be reversed in direction and the system retraces the same equilibrium states.

### ⑤ Equation of state :-

It is relation which

equation of state is the relation which shows how the various properties required to specify a system are related and in general can be expressed as  $f(P, V, T) = 0$ , where  $P$  = pressure,  $V$  = volume,  $T$  = temperature if pressure ( $P$ ), volume ( $V$ ) and temperature ( $T$ ) are the properties defining a particular system.

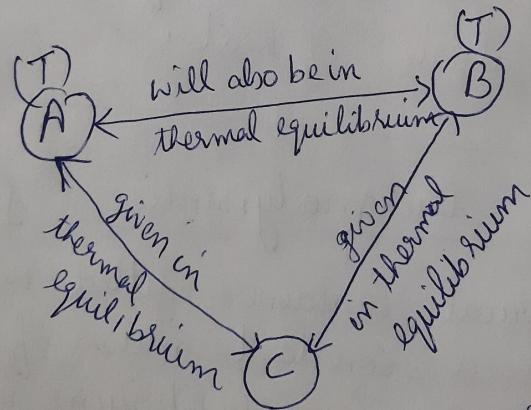
④ Ideal gas equation is one such equation of state defining an ideal gas.

$$TPV = m RT$$

[where  $m$  is no. of moles  
of gas]

### Thermal equilibrium or Zeroth Law of Thermodynamics

It states that if two systems A and B are in thermal equilibrium with a third system C, then all the three systems (A, B and C) are in thermal equilibrium with each other.



This law is simply based upon the fact of experience. From statement it is clear that all the three systems in thermal contact have same property in common and was called as temperature.

## Equivalence of Heat and Work

According to thermodynamics, heat is a form of energy and can be converted into mechanical work and vice-versa. Joule established a relation between work done  $W$  and heat produced  $Q$ . According to him whenever work is transformed into heat or heat into work then the two are equivalent.

$$W \propto Q$$

$$W = J Q$$

Where,  $J$  is constant of proportionality called Joule's constant or mechanical equivalent of heat.

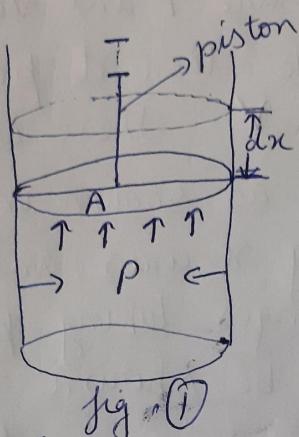
It is defined as the amount of work done in producing 1 Calorie of heat.

## Work done by a thermodynamic System

Consider a cylindrical container fitted with a movable piston filled with a constant mass of gas. Let initially the system be in equilibrium with its surroundings and has pressure  $P_i$  and volume  $V_i$ . Heat can flow in and out of the system through walls of the container.

Let the system interacts by some process with the surroundings and acquires final equilibrium state having pressure  $P_f$  and volume  $V_f$ .

6 At the gas undergoes expansion against the piston 7  
and is shown as



The workdone by the gas in displacing the piston through an infinitesimal displacement  $dx$  is

$$dW = F dx \quad \text{--- (1)}$$

Where  $F$  is the force exerted by the gas on the piston. If  $A$  is the area of piston and  $P$  is the pressure of the gas at that instant when displacement  $dx$  takes place then eqn. (1) can be written as

$$dW = PA dx$$

$$\text{or } dW = P dV$$

where  $dV (= Adx)$  is the infinitesimal increase in the volume of the gas.

∴ Total work done (enclosed) by the gas on the piston is

$$W = \int dW = \int_{V_i}^V P dV$$

## Indicator Diagram

The thermodynamic state of a system can be represented by its pressure  $P$  and volume  $V$ . If a gaseous system undergoes a change then it passes through various values of  $P$  and  $V$ . These changes can be represented on a  $PV$  graph as shown in fig (2) in which volume  $V$  is taken along  $x$ -axis and pressure  $P$  along  $y$ -axis. The entire changes taking place in the system during a process can be shown by a curve in  $P-V$  graph and is called indicator diagram for the system for that particular process.

The physical significance of indicator diagram is that it helps in calculating the workdone in a process for which there is no direct mathematical relation between  $P$  and  $V$  and is given by the area enclosed by the  $P-V$  diagram and the volume axis.

To determine the workdone involved in the process shown by the indicator diagram in fig(2) let us consider a strip  $EFGH$  of infinitesimal width  $dV$ . Since  $E$  and  $F$  are infinitesimally close thus  $EFGH$  can be considered as a rectangle i.e. pressure  $P$  at  $E$  and  $F$ . The area of this strip is  $PdV$  and is equal to the work done in small change in volume  $dV$ .

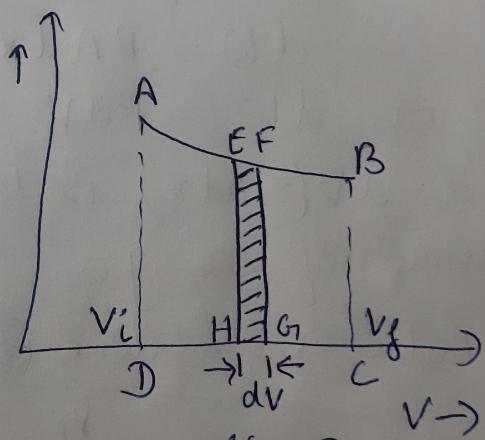


fig - (2)

Indicator diagram

(9)

Thus area of fine strip EFGH represents the amount of workdone in infinitesimal change  $dV$  in volume, & entire indicator diagram can be divided into large number of infinitesimally narrow strips. The sum of the areas of all these narrow strips will be equal to the total work done when system changes from state A to state B.

$\therefore W = \text{sum of the areas of infinitesimal narrow strips}$

$$= \sum_{V_i} P dV = \text{Area ABCD}$$

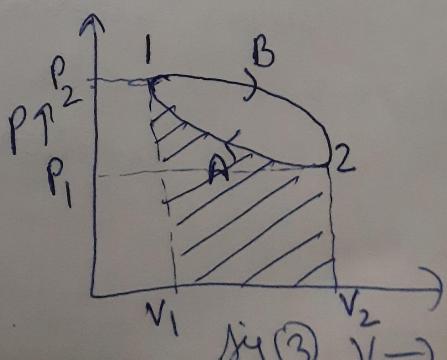
or  $W = \int_{V_i}^V P dV = \text{Area of } \cancel{PV \text{ graph}} \text{ indicator diagram on P-V graph}$

### Heat and Work - Path functions

Thermodynamics properties like pressure, volume, temperature and entropy are point functions i.e they have definite values corresponding to a particular state. The differentials of point functions are exact differentials.

Let  $P_1$  and  $V_1$  be the pressure and volume of a gas in initial state 1 and  $P_2$  and  $V_2$  are the corresponding values in final state 2 as shown in fig. (3). The change in volume is given as

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



i.e. The change in volume depends only upon the values  $V$  in initial and final states and is independent of the paths.

On the other hand work is a path function i.e. the work done in a quasistatic process between two states depends upon the path followed and is given by an exact differential.

From fig. ③, the workdone during the process along Path A is equal to the area  $\int_{V_1}^{V_2} P dV$  and along Path B the workdone is equal to the area

$$\text{ie. } W_A = \int_{V_1}^{V_2} P dV = \int_{A_1}^{A_2} P dV$$

$$\text{and } W_B = \int_{V_1}^{V_2} P dV = \int_{B_1}^{B_2} P dV$$

Values of  $W_A$  and  $W_B$  are not equal though initial and final states involved between the two processes are same, hence work cannot be expressed as the difference between values of some property of the system in initial and final states.

Now, according to Joule's law both work and heat involved in the process are equivalent thus if work is path function then heat is also a path function.

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## Work done in certain Processes

### (1) Isothermal Process

In this process the temperature of the system remains constant throughout the conversion.

Let ~~the~~<sup>1 mole of</sup> gas be allowed to expand isothermally such that  $V_1$  and  $V_2$  are its initial and final volumes respectively. Then work done ( $W$ ) during this process is given as

$$W = \int_{V_1}^{V_2} P dV \quad \text{--- (1)}$$

For isothermal expansion

$$PV = RT \quad \text{--- (2)}$$

where  $T$  is the temperature of the gas at pressure  $P$  and  $R$  is the universal gas constant.

equ. (2) can be written as

$$P = \frac{RT}{V} \quad \text{--- (3)}$$

using equ. (3) in equ. (1)

$$W = \int_{V_1}^{V_2} \frac{RT}{V} dV$$

$$W = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$W = RT \log_e \frac{V_2}{V_1}$$

$$\text{or } W = 2.303 RT \log_{10} \frac{V_2}{V_1}$$

(A)

[for 1 mole gas]

$$\text{or } W = 2.303 n RT \log_{10} \frac{V_2}{V_1}$$

[for  $n$  moles of gas]

$$\text{Also } P_1 V_1 = P_2 V_2 \\ \text{or } \frac{V_2}{V_1} = \frac{P_1}{P_2} \quad \text{--- (9)}$$

using equ. (9) in equ. (8)

$$W = 2.303 RT \log_{10} \frac{P_1}{P_2} \quad [\text{for 1 mole}]$$

$$\text{or } W = 2.303 mRT \log_{10} \frac{P_1}{P_2} \quad [\text{for } m \text{ moles}]$$

## (2) Adiabatic Process

An adiabatic process is the one in which the system is not allowed to exchange heat with the surroundings.

Let 1 mole of ~~gas~~ perfect gas be enclosed in a cylinder having perfectly insulating walls. Let the gas expands adiabatically from initial pressure  $P_1$  and volume  $V_1$  to final pressure  $P_2$  and volume  $V_2$  respectively.

$\therefore$  Work done during the process

$$W = \int_{V_1}^{V_2} P dV \quad \text{--- (1)}$$

For adiabatic Process

$$PV^\gamma = K \quad \text{--- (2)}$$

where  $\gamma$  is the ratio of specific heat at constant pressure ( $C_p$ ) and specific heat at constant volume ( $C_v$ ) and  $K$  is some arbitrary constant.

Eqn. ② can be written as

(13)

$$P = \frac{K}{V^\gamma} \quad \text{--- (3)}$$

Using eqn. ③ in eqn. ①

$$W = \int_{V_1}^{V_2} K \frac{dV}{V^\gamma} = K \int_{V_1}^{V_2} V^{-\gamma} dV$$

$$\text{or } W = K \left[ \frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2}$$

$$W = \frac{K}{1-\gamma} \left[ \frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right] \quad \text{--- (4)}$$

Also for adiabatic process

$$P_1 V_1^\gamma = P_2 V_2^\gamma = K \quad \text{--- (5)}$$

∴ using eqn. ⑤ eqn. ④ can be written as

$$W = \frac{1}{1-\gamma} \left[ \frac{P_2 V_2^\gamma}{V_2^{\gamma-1}} - \frac{P_1 V_1^\gamma}{V_1^{\gamma-1}} \right]$$

On Solving

$$\boxed{W = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1]}$$

### (3) Isobasic Process

In this process the pressure of the system always remains ~~not~~ constant.

Let 1 mole of perfect gas undergoes isobaric expansion at pressure  $P$ , and its volume changes from  $V_1$  in ~~not~~ initial state to  $V_2$  in final state.

! work done during this process,  $w = \int_{V_1}^{V_2} P dV$

$$\boxed{w = P(V_2 - V_1)}$$

(since  $P$  is constant)

#### ④ Isochoric Process

In this process when system change from one state to another then during this change volume remains constant.

∴ Total work done during this process

$$W = \int P dV = 0$$

since volume is constant in this process

$$\therefore dV = 0$$

$$\Rightarrow \boxed{W=0}$$

Thus, no work is done during an ~~isochoric~~ <sup>isochoric</sup> process  
Also no area is enclosed by the indicator diagram  
on ~~P-V~~ PV-graph.

#### ⑤ Cyclic Process

A cyclic process is the one in which the system return to its initial state after undergoing a series of changes.

In fig. ④ ABCDA is a cyclic process in which the system ~~starts~~ starts from initial state A reaches state C via path ABC and then returns to initial state A via path CDA

(2)

Work done when system goes from A  $\rightarrow$  C (charge ABC)

$$W_{A \rightarrow C} = \text{Area of curve } ABC$$

$$= \text{Area of } ABCC'A'A$$

Similarly when system goes from C  $\rightarrow$  A (charge CDA)

$$W_{C \rightarrow A} = \text{Area of curve } CDA$$

$$= \text{Area of } CDAA'C'C$$

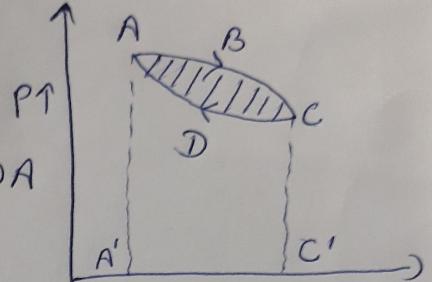


fig (4)

$\therefore$  Net work done during complete cycle

$$W = W_{A \rightarrow C} - W_{C \rightarrow A}$$

$$= \text{Area } ABCC'A'A - \text{Area } CDAA'C'C$$

$$\boxed{W = \text{Area } ABCDA} \quad (\text{Shaded region in fig (4)})$$

Thus, work done during a cyclic process is equal to the area enclosed by its indicator diagram in the PV-graph.

During a cyclic change if traced in clockwise direction then the net amount of work done is positive and if it is traced in anti-clockwise direction then net amount of work done is negative.

(15)