

Chemical Engineering (GATE & PSUs)

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GATE & Public Sectors

## THERMODYNAMICS

### GATE 2015 Top Results

### Chemical Engineering



**1<sup>st</sup> Rank**  
Archhit Trichal



**2<sup>nd</sup> Rank**  
Keval Pareta

GATE 2015 Result

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Registration Number	<input type="text" value="CH8804151135"/>	Gender	<input type="text" value="Male"/>		
Examination Paper	<input type="text" value="Chemical Engineering (CH)"/>				
Marks out of 100 <sup>†</sup>	<input type="text" value="65.67"/>	All India Rank in this paper	<input type="text" value="1"/>		
Qualifying Marks <sup>‡‡</sup>	<input type="text" value="27.52"/> General	<input type="text" value="24.77"/> OBC (NCL)	<input type="text" value="18.34"/> SC/ST/PwD	GATE Score	<input type="text" value="947"/>

**Highest Result in GATE 2015**

**Rank 1, 2, 7, 8.....**

**Total 39 Ranks under AIR 100**

### GATE 2014 Topper

### Chemical Engineering



**1<sup>st</sup> Rank**  
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### GATE 2015 Cut-off Marks

BRANCH	GENERAL	SC/ST/PD	OBC(Non-Creamy)	Total Appeared
Chemical Engineering	27.52	18.34	24.77	15874

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## CHAPTER-1 INTRODUCTION

The Word “Thermodynamics” originates from Therme (means heat) + dynamic (means force). The subject is concerned with the interrelation between energy and change of state of any real world system.

- Thermodynamics forms the basis for the study of a vast variety of devices such as refrigerators, air conditioners, aircraft, power plant etc the application of which is involved in the everyday life of almost every individual
- Every thermodynamics equipment / device makes use of a working substance on which the processes are executed.
- Most commonly utilized working substances are water & air.
- H<sub>2</sub>O is the working substance in steam power plant; air is the working substance in petrol and diesel engines, etc.
- The subject of thermal sciences deals with relations between the relevant properties of working substances energy interactions & inter conversions in the form of ‘work’ & ‘heat’.
- It is the science of relations between heat, work & the properties of the system.

**Thermodynamic system:** It is defined as a quantity of matter or region in space chosen for study.

For the purpose of thermodynamic analysis, it is necessary to define a ‘system’

**Surrounding:** The mass or region outside the system is said to be the surrounding. For all practical purposes, in any thermodynamic analysis of a system it is necessary to include only the immediate surroundings in which the effects are felt.

**Boundary:** The real or imaginary surface that separates the system from its surroundings. It may change in shape as well as in size over time, i.e., increase or decrease

**Universe:** A system and its surrounding together comprise a universe.

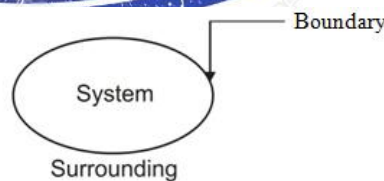


fig: Thermodynamic system

A question arises at this point of time!

How does one characterize the changes that occur in the system during any thermodynamic process. This can be done if one could measure the change in terms of some properties of the system

A thermodynamic system is, thus, characterized by its properties, which are the descriptors of state of system.

### **Properties of system:**

Any characteristic of a system is known to the property such as pressure P, temperature T, volume V & mass m.

- Properties are supposed to be either intensive or extensive
- Intensive properties are those that are independent of the mass of the system eg. Temperature, pressure & density
- Extensive properties are those whose value depends on the size of the system. E.g. total mass, total volume etc.

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- The ratio of two extensive properties of a homogeneous system is called intensive property. e.g. specific volume
- If an extensive property is divided by the mass or number of moles of a substance forming a system, then intensive property is called a specific property. e.g. specific volume.
- The ratio of an extensive property to the number of moles of the substance in the system is called molar property.

### Three classes of system:

- Closed system
- Open system
- Isolated system

Closed system: It is a system of fixed mass. There is no mass transfer across the system boundary.

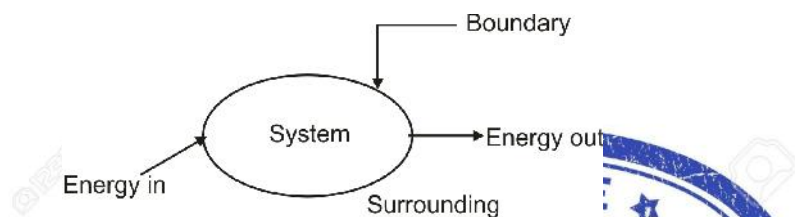
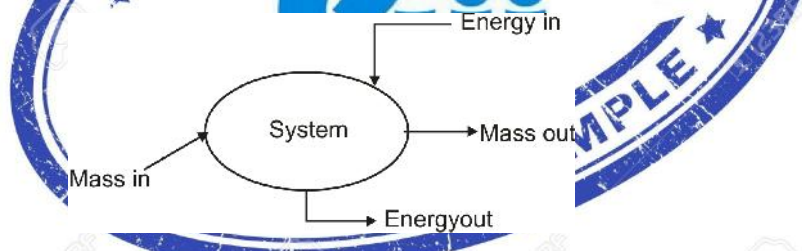


fig: Closed system

e.g. A certain quantity of fluid in a cylinder bounded by a piston

The open system: in which mass crosses the boundary of the system.



e.g. An air compressor in which air enters at low pressure & leaves at high pressure.

In either closed or open system, energy transfer can occur across the system boundary in any form (e.g. heat, work, electrical| magnetic energy, etc)

However, we chemical engineers are interested in only HEAT and WORK for most of the real world systems.

The isolated system: It is one in which there is no interactions between the system & the surroundings.

Here is neither mass transfer nor energy transfer across the system boundary.

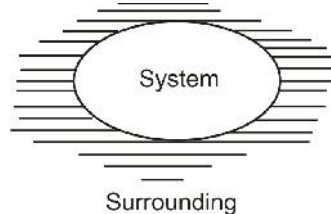


fig: An isolated system

### Thermodynamic Properties, processes & cycles:

State: When all the properties (pressure, volume, temperature) of a system have definite values, the system

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is known to be at a definite state.

Following figure a system shown at two diff. states.

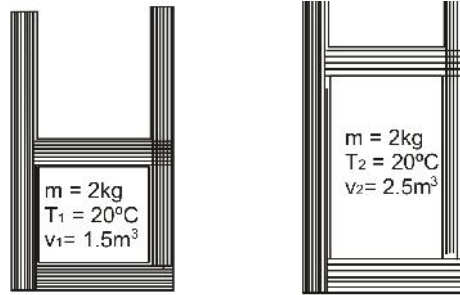


fig: (a) State 1

fig: (b) State 2

**Path:** The succession of states passed through at the time of a change of state is said to be the path of the change of state.

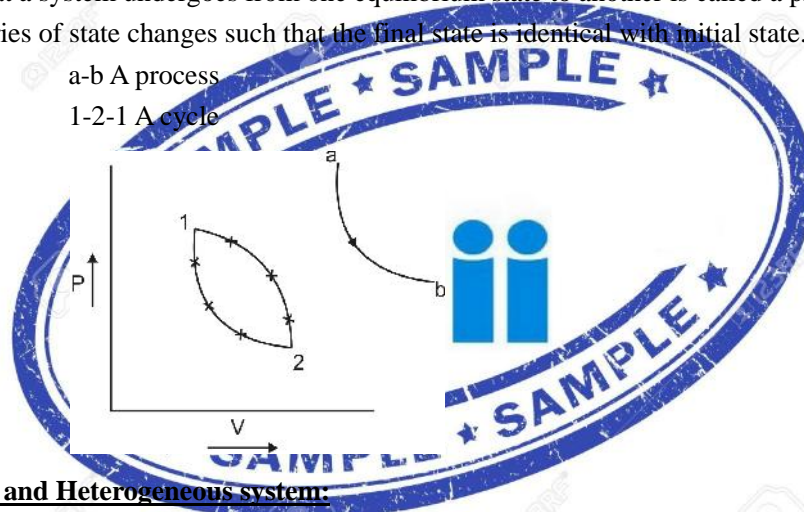
**Process:** when the path is fully specified, the change of state is known as process.

e.g. constant pressure process, constant volume process

or

Any change that a system undergoes from one equilibrium state to another is called a process.

**Cycle:** As a series of state changes such that the final state is identical with initial state. As shown in figure.



a-b A process

1-2-1 A cycle

### Homogeneous and Heterogeneous system:

**Phase:** A quantity of matter homogeneous throughout in chemical composition & physical structure is said to be phase. viz, solid, liquid and gas

**Homogeneous system:** A system including of single phase is called homogenous system.

**Heterogeneous system:** A system consisting of greater than one phase is said to be a heterogeneous system.

**Thermodynamic equilibrium:** A system is known to exist in a state of thermodynamic equilibrium when no change in any macroscopic property is registered, when the system isolated from its surroundings.

Change of state of a thermodynamic system results from existence of gradients of various types within or across its boundary

Pressure gradient result in heat transfer, temperature gradient result in mass transfer, concentration gradient results in mass transfer, as long as these gradients exist, system will undergo a change of state. The result of all such changes is to nullify the gradients.

The ultimate limit where all gradients are non – existent and system undergoes no further changes is the 'state of thermodynamic equilibrium'.

\* For a system in thermodynamic equilibrium, it thus needs to also satisfy the criteria for mechanical, chemical and thermal equilibrium.

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- (a) Mechanical equilibrium
- (b) Chemical equilibrium
- (c) Thermal equilibrium

- A. Absence of any unbalanced force within the system itself & between the surroundings and the system.
- B. If its chemical composition does not change with time, that is no chemical reaction happen
- C. When there is no spontaneous change in any property of the system.

### Quasi – static process:

A quasi – static process is one in which

- The deviation from thermodynamic equilibrium is very small
- All states of the system passes through are equilibrium states.
- In the system (as shown in figure), if the weights are removed slowly. One at a time, and the system is allowed to come to equilibrium after every removal of weight, the system could be supposed as undergoing a quasi – equilibrium or quasi – static process as shown in following figure.

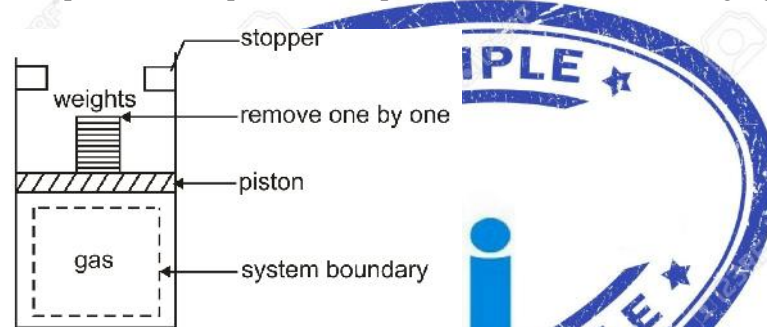


fig: Carrying out a quasi - equilibrium process on a gas by removal of weights in infinitesimal steps.

- If, whereas, all the weights are removed suddenly, the piston will jump up & strike the stoppers.
- Therefore quasi – static process is supposed to take place very slowly in each step.

### Zeroth Law of thermodynamics:

When a body x is thermal equilibrium with a body Y, and also separately with a body Z, then Y & Z will be in thermal equilibrium with each other.

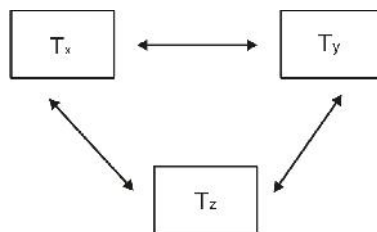


fig: Zeroth law of thermodynamics

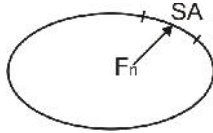
- The zeroth law provides the basis for the measurements of temperature.

**Classical thermodynamics:** the study of thermodynamics that does not require knowledge of the behavior of individual particle.

**Statistical thermodynamics:** Based on average behavior of large groups of individual particles.

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**Pressure:** It is the normal force exerted by a system against unit area of the boundary surface.



**Power:** The rate of energy transfer is said to be power. Unit: Watt (w), kW, MW.

**Ideal gas:** It is theoretical gas composed of a set of randomly – moving, non – interacting point particles.

It obeys the ideal gas law  $\bar{P}\bar{V} = \bar{R}T$

$$\bar{V} = \frac{V}{n}$$

Where V – total volume

n = number of moles of the gas

Therefore equation of ideal gas, we can write

$$\bar{P}\bar{V} = n\bar{R}T$$

$$\boxed{PV = mRT} \quad \left[ \because n = \frac{m}{M} \right]$$

The ideal gas law is a limiting law that is valid primarily for gaseous systems at low pressure.

For practical purposes, it is observed to remain valid at atmospheric pressures also.

Hence, it serves as a useful approximation for the estimation of all real fluid thermodynamic properties of practical interest.

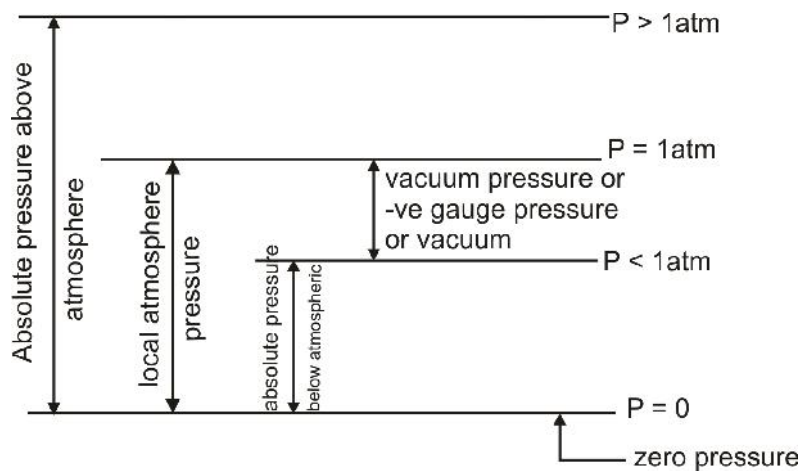
**Pressure:** Unit in SI system Pascal (pa), which is the force of one Newton acting on an area of  $1m^2$ .

$$\boxed{1pa = 1N / m^2}$$

→  $1 \text{ bar} = 10^5 \text{ Pascal} = 100\text{kPa} = 0.1\text{MPa}$ , and standard atmospheric pressure,  $1 \text{ atm} = 101.325\text{kPa}$ .

→ **Gauge Pressure:** The pressure relative to the atmosphere is said to be gauge pressure.

**Atmosphere pressure:** The atmospheric air exerts a normal pressure upon all surfaces with which it is in contact.



$$\boxed{1\text{mm of Hg} = 1\text{torr} = 133\text{ Pascal}}$$

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### The phase Rule

The phase rule determines the number of independent variables that must be specified to establish the intensive state of any system at equilibrium.

$$F = C - P + 2 - r$$

F: Degrees of freedom of thermodynamic system.

C: Number of components

P: Number of co-existing phases

r: Number of independent reactions that may occur between the system components.

For a non – reactive system

$$F = C - P + 2$$

Phase refers to solid, liquid or gas.

\* Various phases can coexist, but they must be in equilibrium for the phase rule to apply.

Component refers to the number of pure substances present in system.

⇒ Consider a biphasic system of a pure component – say water and steam

There comes only 1 degree of freedom.

i.e. either temperature or pressure may be specified to fix all other intensive properties of the system.

Example: Calculate the number of degrees of freedom when a liquid solution of alcohol in water is in equilibrium with its vapour.

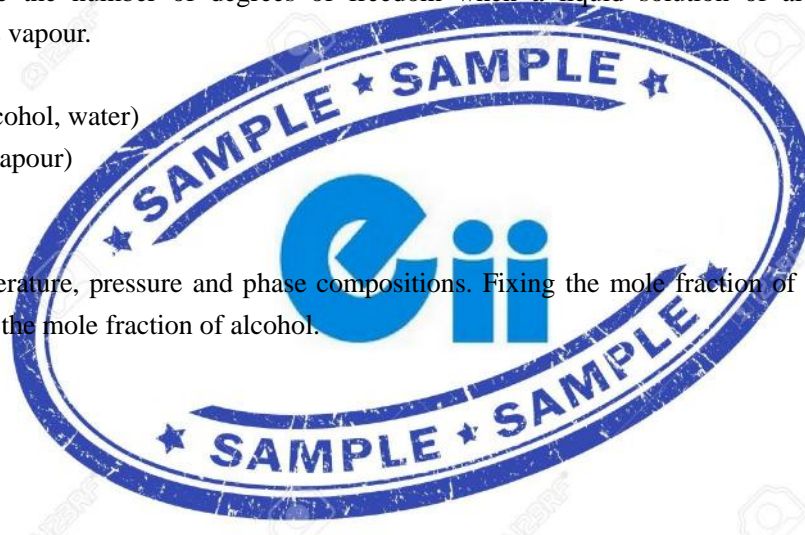
$$F = C - P + 2$$

Component = 2 (alcohol, water)

Phase = 2 (liquid, vapour)

$$\therefore F = 2$$

Variables are temperature, pressure and phase compositions. Fixing the mole fraction of water in liquid phase automatically fixes the mole fraction of alcohol.





## CHAPTER-2

### WORK AND HEAT TRANSFER

Types of energies associated with thermodynamic processes:

A thermodynamic system containing a fluid possess both potential energy and kinetic energy which constitute macroscopic, mechanical forms of energy

Another is the microscopic forms of energy which is due to

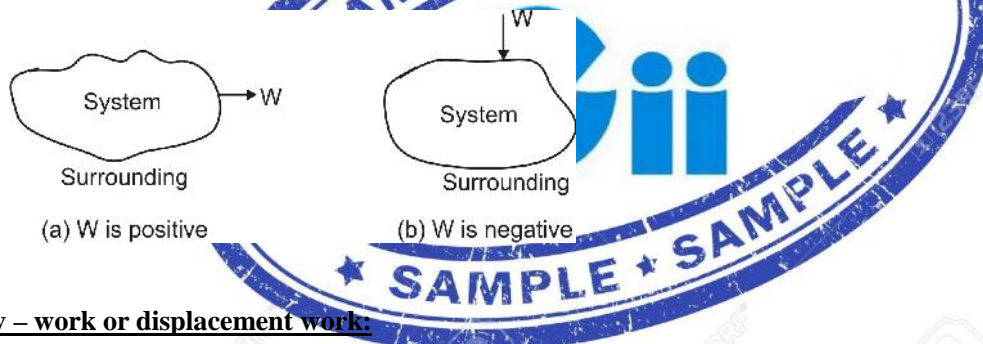
- Translation, Rotation and vibration of atoms/ molecules (INTRAMOLECULAR)
- INTERMOLECULAR interactions
- Motion, spin of electrons, nucleus – electron or nucleus – nucleus interactions (INTRATOMIC)

The energy possessed by matter due to the microscopic modes of motion is referred to as the internal energy of matter. Thus, when a thermodynamic system undergoes change of state, the change in internal energy is responsible for the energy leaving or entering the system. This exchange is done by heat or work.

A closed system and surrounding can interact in following ways

- (a) By work transfer
- (b) By heat transfer

→ If work is done by the system, it is taken to be positive and when is done upon the system, it is taken negative.



#### Pdv – work or displacement work:

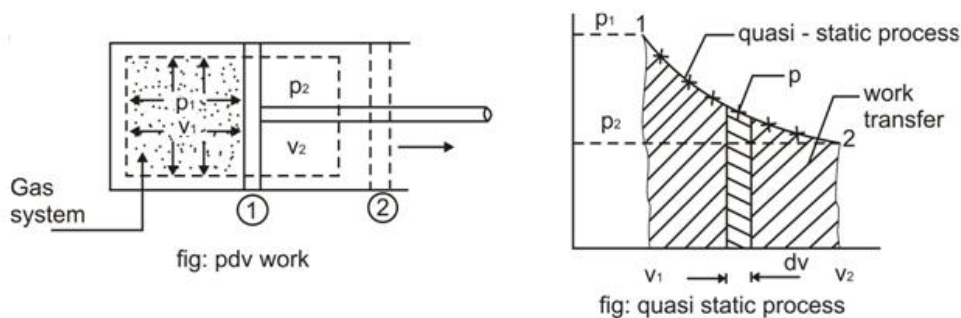
Work refers to a form of energy transfer which results due to changes in external macroscopic physical constraints on a thermodynamic system. Mechanical work is most commonly encountered in real thermodynamic systems. Such work results from the energy applied to expand the volume of the system against an external pressure.

Force is applied on the system boundary due to which it either contracts or expands.

→ Consider gas in the cylinder (as shown in figure) be a system

→ Initial pressure  $p_1$  & volume  $V_1$

→ The system is in thermodynamic equilibrium, the state of which is denoted by the coordinate's  $p_1, V_1$ .



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- The piston is the only boundary which moves because of gas pressure.
- Suppose the piston move out to final position 2, this new position also a thermodynamic equilibrium state described by  $p_2, V_2$ .
- Any intermediate point in the travel of the piston, pressure is  $p$  & volume  $V$ .
- If the piston moves on infinitesimal distance  $dl$ , & if 'a' be the area of the piston
- Force  $F$  acting on the piston  $F = p.a$ .
- The infinitesimal amount of work done by the gas on the piston

$$dw = F \cdot dl = P \cdot a \cdot dl = P dV \text{ [If piston area } a \text{ is constant]}$$

$$\boxed{dw = P dv} \quad [adl = dv]$$

- Hence, we can say that when work is done by the system (EXPANSION), volume increases and work done is positive. The reverse is true when work is done on the system (COMPRESSION), volume decreases and hence work done is negative.
- If the piston moves out from state 1 to state 2 with volume changing from  $V_1$  to  $V_2$ .
- The amount of work  $w$  done by

$$\boxed{W = \int_{V_1}^{V_2} p dV}$$

- The integration  $\int p dV$  can be performed only on a quasi-static path.
- Work is path function and  $dw$  is an inexact or imperfect differential.
- Thermodynamic properties are point function; there is definite value for each property.
- For cyclic process, the change in any property is zero

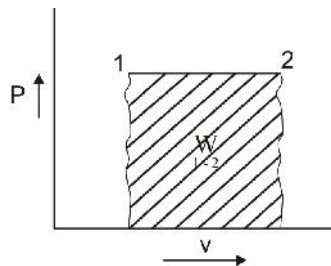
$$\oint dV = 0, \quad \oint dp = 0, \quad \oint dT = 0$$

Where  $\oint$  stands for the cyclic integral for the closed path.

### Pdv – work in several quasi-static processes:

- (1) Isobaric process (constant pressure process or isopiestic process)

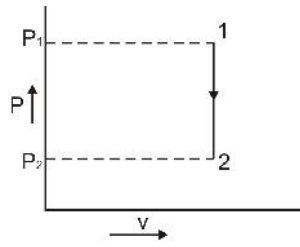
$$\begin{aligned} W &= \int_{V_1}^{V_2} p dV \\ &= p(V_2 - V_1) \end{aligned}$$



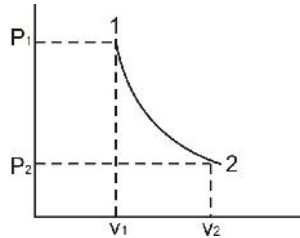
- (2) Constant volume process (isochoric process)

$$W = \int_{V_1}^{V_2} p dV = 0$$

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(3) Isothermal process (constant temperature process):



$$p_2 V_2 = pV = p_1 V_1 = c$$

$$W_{1-2} = \int_{v_1}^{v_2} p dV$$

$$W_{1-2} = p_1 V_1 \int_{v_1}^{v_2} \frac{dV}{V} = p_1 V_1 \ln \frac{V_2}{V_1}$$

$$W_{1-2} = p_1 V_1 \ln \frac{p_1}{p_2} = p_1 V_1 \ln \frac{V_2}{V_1}$$

(4) Process in which  $pV^n = c$

$$pV^n = p_1 V_1^n = p_2 V_2^n = c$$

$$P = \left( \frac{p_1 V_1^n}{V^n} \right)$$

$$W_{1-2} = \int_{v_1}^{v_2} p dV = \int_{v_1}^{v_2} \frac{p_1 V_1^n}{V^n} dV$$

$$= p_1 V_1^n \left[ \frac{V^{-n+1}}{-n+1} \right]_{V_1}^{V_2}$$

$$= \frac{p_1 V_1^n}{1-n} [V_2^{1-n} - V_1^{1-n}]$$

$$= \frac{p_2 V_2^n \cdot V_2^{1-n} - p_1 V_1^n \times V_1^{1-n}}{1-n}$$

$$= \frac{p_2 V_2 - p_1 V_1}{1-n}$$

$$= \frac{p_1 V_1 - p_2 V_2}{n-1}$$

Likewise, for process in which  $pV^r = c$ ,  $r = \frac{c_p}{c_v}$

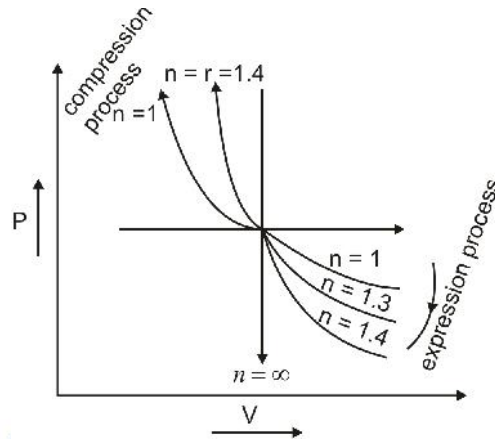
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$$W_{1-2} = \frac{p_1 V_1 - p_2 V_2}{r - 1}$$

All the above processes can be captured in the form of a single P – V relation which can be reduced to yield all forms of processes. (For different values of n)

$$PV^n = \text{Constant} \quad \text{or} \quad TV^{n-1} = \text{Constant}$$

$$\text{or} \quad TP^{(1-n)/n} = \text{Constant}$$



Depending upon value n

$n = 0$	$p = c$ (Isobaric)
$n = 1$	$T = c$ (Isothermal)
$n = \infty$	$V = c$ (Isochoric)
$n = 1.3$	adiabatic process
$n = 1.4$	polytropic process
$n = r$	reversible adiabatic process

**Flow Work:** it is the work required to move a fluid into or out of a system.

Let an element of fluid of mass  $dm$  & volume  $dV$ . It is necessitate to push this fluid of mass  $dm$  & volume  $dV$  into the control volume of an open system through a duct or a passage of cross – sectional area  $A$  against an existing pressure  $p$ .

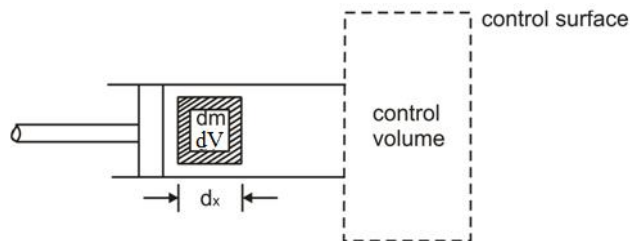


fig: flowing fluid

- Consider the fluid, fluid behind this element acts as piston, and pushes the fluid into the control volume.
- To determine the work required, suppose that an imaginary piston is placed behind this elemental fluid as shown in figure.
- The distance travelled by the piston is  $dx$  if the fluid with volume  $dV$  has been pushed into the control volume.

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→ The required flow work

$$\begin{aligned}
 u w_{flow} &= \text{force} \times \text{distance} \\
 &= (P \times A) \times dx \quad \left[ \begin{array}{l} P - \text{pressure} \\ A - \text{Area} \end{array} \right] \\
 &= PA \left( \frac{dV}{A} \right) = p dv
 \end{aligned}$$

The flow work per unit mass of the fluid is

$$\begin{aligned}
 W_{flow} &= \frac{u W_{flow}}{dm} = p \frac{dV}{dm} = pv \\
 W_{flow} &= pv \quad \text{since } \frac{dV}{dm} = v
 \end{aligned}$$

Non Flow Process: A process undergone by a closed system of fixed mass is said to be non – flow process:

Flow process: A change of state of a substance taking place while flowing through a control volume in an open system is called flow process:

Work done in non – flow process

$$W_{non\ flow} = \int_1^2 p dV$$

Work done in flow process

$$W_{flow} = - \int_1^2 V dp$$

Specific Heat: it is defined as the energy required to raise the temperature of a unit mass of substance by one degree. It is denoted by symbol  $c$ .

$$c = \frac{Q}{m \Delta T} \text{ J / kgK}$$

### Heat

Heat is that form of energy that is exchanged between system and its surrounding owing to a temperature differential between the two. Heat always flows down the gradient of temperature.

Heat flow is regarded to be positive for a thermodynamic system, if it enters the system and negative if it leaves. Like work, heat is a form of energy that exists only in transit between a system and its surrounding. So after transit, both work and heat can only transform into the kinetic and potential energy of the constituent atoms and molecules.

### Units of Heat:

British Thermal Unit (Btu)

1/180<sup>th</sup> quantity of heat which when transferred to one pound mass of water raised its temperature from 32°F (ICE POINT) to 212°F (STEAM POINT) at standard atmosphere pressure

### Calorie (cal)

1/100<sup>th</sup> quantity of heat which when transferred to one kilogram mass of water raised its temperature from 0°C to 100°C at standard atmospheric pressure.

Relation between Temperature scales

- 1)  $t (^{\circ}\text{C}) = T (\text{K}) - 273.15$
- 2)  $t (\text{R}) = 1.8T(\text{K})$
- 3)  $t (^{\circ}\text{F}) = T(\text{R}) - 459.67$
- 4)  $t (^{\circ}\text{F}) = 1.8 t(^{\circ}\text{C}) + 32$

## Sample Problems

### CHAPTER-3

### FIRST LAW OF THERMODYNAMICS

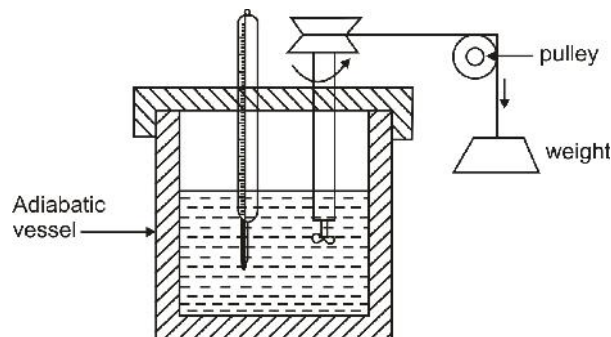
#### Laws of Thermodynamics

The extent of change of state of system due to transfer of energy to or from the system is captured through the basic equations of thermodynamics which are derived starting from a set of fundamental observations known as “Laws of thermodynamics”

The laws are the postulates that govern the nature of interaction of real systems and energy. These are human observations to which no exceptions have been found so far and so are considered to be “Laws”. The laws are applicable from microscopic to macroscopic order.

Note: All the processes taking place in universe, whether in non – living or living system, are subjected to the laws of thermodynamics.

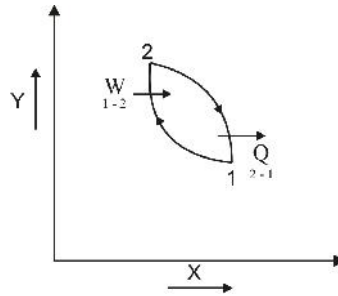
- Work and heat are different forms of the same entity, known as energy, which is conserved.
- Energy which enters a system as work may leave the system as heat, otherwise which enters the system a heat may leave as work.
- Suppose a closed system which includes of a known mass of water contained in an adiabatic vessel having a paddle wheel and a thermometer. (Joule’s experiment)



- Consider a certain amount of work  $W_{1-2}$  be done on the system with the help of paddle wheel.
- The quantity of work is determined by the fall of weight which drives the paddle wheel through a pulley

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- The system was stating at temperature  $t_1$ , the same as that of atmosphere, and after work transfer then the temperature rise to  $t_2$ , but the pressure is 1 atmospheric
- The process 1-2 undergone by the system in generalized thermodynamics coordinates



- Now, the insulator be removed, the system and the surroundings interact by heat transfer till the system come back to the initial temperature  $t_1$ , attaining the condition of thermal equilibrium with atmosphere.

## Sample Study Materials



**Classroom GATE Coaching**  
**Postal Correspondence Coaching**  
**All India Test Series-ONLINE**