Thermodynamics.

The branch of physics which deals with the study of transformation of heat energy into other forms of energy and vice-versa is called thermodynamics.

Thermodynamic Terms.

In order to understand these transformation we need to understand the terms given below.

Thermodynamical System

An assembly of an extremely large number of particles which is capable of exchange of energy with its surroundings is called thermodynamic system.

Thermodynamic system is classified into the following three systems

(i) Open System :- It exchange both energy and matter with surroundings.

(ii) Closed System :- It exchange only energy (not matter) with surroundings

(iii) Isolated System :- It exchages neither energy nor matter with the surroundings.

Thermodynamic Parameter or Coordinates or Variables.

The State of thermodynamic system can be described by specifying pressure, volume, temperature, internal energy and number of moles, etc. These are called thermodynamic parameters or coordinates or variables.

The state variables may be extensive or intensive in nature.

Extensive State Variable :- Extensive state variable depends on the size of the system eg volume total mass, internal energy etc.

Intensive State variables :- These are State variable that donot depend on the size of the system eg pressure, temperature and density

Thermal Equilibrium

A thermodynamic system is said to be in thermal equilibrium when macroscopic variables (like pressure, volume, temperature mass, composition etc) that characterise the system do not change with time.

Adiabatic wall

It is an insulating wall (can be movable) between two thermodynamic systems that does not allow flow of energy (or heat) from one system to another system.

Diathermic wall

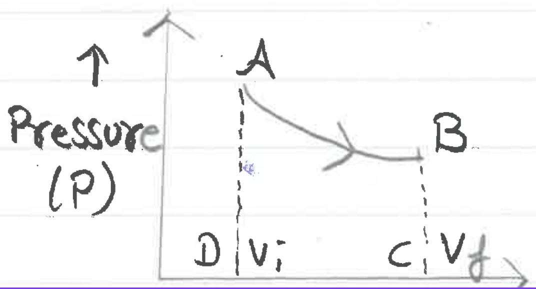
It is a conducting wall between two thermodynamic systems that allows energy flow (or heat) from one system to another system

Work done :-

Work done by a thermodynamic system is given by

$$W = P \times \Delta V$$

where p = pressure
and ΔV = change in volume.



Work done by a thermodynamic system is equal to the area enclosed between the P–V curve and the volume axis.

work done in process A-B = $\int_{V_i}^{V_f} p\,dV$ = Area ABCDA

Work done by a thermodynamic system depends not only upon the initial and final states of the system but also depend upon the path followed by process.

Work done by the Thermodynamic System is taken as

positive → as volume increases
Negative → as volume decreases.

Internal Energy (U).

The total energy possessed by any ~~stem~~ system due to molecular motion and molecular configuration is called its internal energy

Internal energy of a thermodynamic system depends on temperature.

Zeroth Law of Thermodynamics.

According to this law, two system in thermal equilibrium with a third system separately are also in thermal equilibrium with each other. Thus if A and B are separately in equilibrium with C i.e if $T_A = T_C$ and $T_B = T_C$, then this implies that $T_A = T_B$ ie, the system A and B are also in thermal equilibrium.

First Law of Thermodynamics

Heat given to a thermodynamic System (ΔQ) is partially utilised in doing work (ΔW) against the surrounding and the remaining part increases the internal energy (ΔU) of the system.

Therefore $\Delta Q = \Delta U + \Delta W$

First law of thermodynamics is a restatement of the principle of conservation of energy.

Thermodynamic Processes

A thermodynamical process is said to take place when some changes occur in the state of a thermodynamic System i.e. the thermodynamic parameters of the system change with time.

(i) **Quasi-Static Process** :— Quasi-Static is a thermodynamic process which proceeds extremely slowly such that at every instant of time, the temperature and pressure are the same in all parts of the system.

(ii) **Isothermal Process** :— A process taking place in a thermodynamic system at constant temperature is called an isothermal process.

Isothermal processes are very slow processes.

This process follow's Boyles law, according to which

$$pV = \text{constant}.$$

From $dU = nC_v dT$ as $dT = 0$ so $dU = 0$ ie internal energy is constant.

From first law of thermodynamic $dQ = dW$ ie heat given to the system is equal to the work done by the system surroundings.

$$\text{work done } W = 2.303 nRT \log_{10}\left(\frac{V_f}{V_i}\right)$$

$$= 2.303 nRT \log_{10}\left(\frac{P_i}{P_f}\right)$$

where n = number of moles
R = ideal gas constant
T = absolute temperature

After differentiating

PV = constant we get.

$$\frac{dP}{dV} = \frac{-P}{V} \quad \text{and} \quad \frac{-dP}{dV/V} = P$$

i.e. bulk modulus of gas in isothermal process $K = P$.

(iii) **Adiabatic Process** :- A process taking place in a thermodynamic system for which there is no exchange of heat between the system and its surroundings.

Adiabatic processes are very fast processes.

This process follows Poisson's law, according to which

$$PV^{\gamma} = TV^{\gamma-1} = \frac{T^{\gamma}}{P^{\gamma-1}} = \text{constant}.$$

from $dQ = nC\,dT$, $C_{adi} = 0$ as $dQ = 0$ i.e. molar heat capacity for adiabatic process is zero.

From first law $dU = -dW$ ie work done by the system is equal to decrease in internal energy, when a system expands adiabatically work done is positive and hence internal energy decrease ie the system cools down and vice-versa.

work done in an adiabatic process is

$$W = nR(T_i - T_f) = \frac{P_iV_i - P_fV_f}{\gamma - 1}$$

where T_i and T_f are initial and final temperatures

(iv) Isobaric Process A process taking place in a thermodynamic system at constant pressure is called an isobaric process.

process equation is $\frac{V}{T}$ = constant.

Molar heat capacity of the process in C_p and $dQ = nC_pdT$

Internal energy $dU = nC_vdT$

From the first law of thermodynamics $dQ = dU + dW$

$$dW = PdV = nRdT$$

P-V curve is a straight line parallel to volume axis.

(V) Isochoric Process :- A process taking place in a thermodynamic system at constant volume is called an isochoric process

Process equation is $\frac{P}{T}$ = Constant

$dQ = nC_v dT$, molar heat capacity for isochoric process is C_v

Volume is constant so $dW = 0$

From the first law of thermodynamics

$$dQ = dU = nC_v dT$$

P-V curve is a straight line parallel to pressure axis

(VI) Cyclic Process :- When a thermodynamic system returns to its initial state after passing through several states, then it is called a cyclic Process.

For cyclic process

$$dU = 0$$

or $dQ = dW$

Efficiency of the cycle is given by

$$\eta = \frac{\text{work done}}{\text{Heat supplied}}$$

work done by the cycle can be computed from area enclosed by cycle on P-V curve

Second Law of Thermodynamics.

The Second law of thermodynamics gives a fundamental limitation to the efficiency of a heat engine and the coefficient of performance of a refrigerator. It says that efficiency of a heat engine can never be unity (or 100%). This implies that heat released to the cold reservior can never be made zero.

Kelvin Statement.

It is impossible to obtain a continuous supply of work from a body by cooling it to a temperature below the coldest of its surroundings.

Clausius Statement

It is impossible to transfer heat from a lower temperature body to a higher temperature body without use of a external agency.

Planck's Statement.

It is impossible to construct a heat engine that will convert heat completely into work. All these statements are equivalent as one can be obtained from the other.

Reversible and Irreversible Processes.

Reversible Process :- A process which could be reserved in such a way that the system and its surrounding returns exactly to their initial states with no other changes in the universe is known as reversible process.

Irreversible Process :- Any process which is not reversible exactly is an irreversible process.

Heat Engine

A heat engine is a device which converts heat energy into mechanical energy. A heat engine consists of three parts.

(i) Source of heat at higher temperature
(ii) working substance
(iii) Sink of heat at lower temperature

Thermal efficiency of a heat engine is given by.

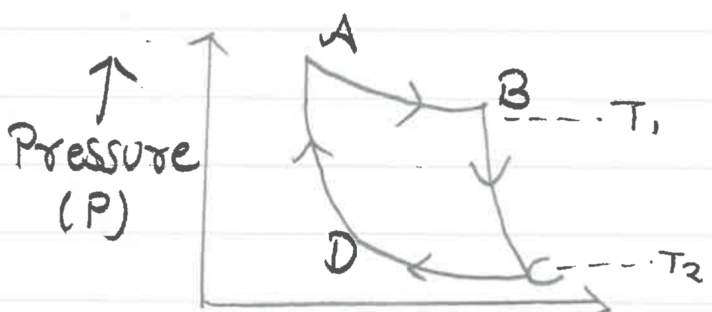
$$\eta = \frac{\text{work done / cycle}}{\text{Total amount of heat absorbed / cycle}}$$

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

where Q_1 is heat absorbed from the source Q_2 is heat rejected to the sink and T_1 and T_2 are temperatures of source and sink.

Carnot's cycle.

Carnot devise an ideal cycle of operation for a heat engine called Carnot's cycle.



A carnot's cycle contains the following four processes.

(i) Isothermal expansion (AB)

(ii) Adiabatic expansion (BC)

(iii) Isotheramal compression (CD)

(iv) Adiabatic compression (DA)

The net work done per cycle by the engine is numerically equal to the alea of the loop representing the carnot cycle.

After doing the calculation's for different processes we can show that

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

Therefore efficiency of the cycle is

$$\eta = 1 - \frac{T_2}{T_1}$$

Efficiency of carnot engine is maximum (not 100%) for given temperature T_1 and T_2 But still carnot engine is not a pratical engine because many ideal situations have been assumed while designing this engine which can ~~pat~~ practically not be obtained

Carnot Theorem.

According to carnot theorem.

(i) A heat engine working between the two given temperature T_1 of hot reservior ie source and T_2 of cold reservior ie sink cannot have efficiency more that that of the carnot engine.

(ii) The efficiency of the carnot engine is independent of the nature of working substance.

Refrigerator.

A refrigerator is a device used for cooling things. It absorbs heat from sink at lower temperature and rejects a large amount of heat to source at higher temperature.

Coefficient of performance of refrigerator is given by

$$\beta = \frac{Q_2}{\ } = \frac{Q_2}{\ } = \frac{T_2}{\ }$$

where Q_2 is heat absorbed from the sink Q_1 is heat rejected to source and T_1 and T_2 are temperature of source and sink.

Relation between efficiency (η) and coefficient of performance (β)

$$\beta = \frac{1-\eta}{\eta}.$$