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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 exchanges both energy and matter with surroundings.

(ii) **Closed System** It exchanges only energy (not matter) with surroundings.

(iii) **Isolated System** It exchanges neither energy nor matter with the surroundings.

Thermodynamic Parameters 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 Variables Extensive state variables depend on the size of the system, *e.g.* volume, total mass, internal energy etc.

Intensive State Variables These are state variables that do not depend on the size of the system, *e.g.* pressure, temperature and density.

Thermal Equilibrium

A thermodynamical 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

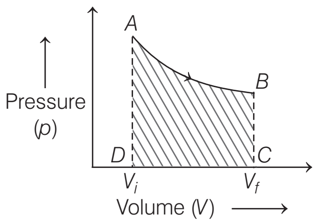
It is a conducting wall between two thermodynamic systems that allows energy flow (or heat) from one system to another system.

Work Done

Work done by a thermodynamic system is given by

$$W = p \times \Delta V$$

where, $p =$ pressure and $\Delta V =$ 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 in the process.

Work done by the Thermodynamic System is taken as

Positive $\rightarrow$ as volume increases.

Negative $\rightarrow$ as volume decreases.

Internal Energy (U)

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

Internal energy of a thermodynamic system depends on temperature.

It is the characteristic property of the state of the system.

Zeroth Law of Thermodynamics

According to this law, two systems 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 $T_A = T_B$, *i.e.* the systems 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, $\Delta Q = \Delta U + \Delta W$

In differential form,

$$dQ = dU + dW$$

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 follows **Boyle's law**, according to which

$$pV = \text{constant}$$

From $dU = nC_V dT$ as $dT = 0$ so $dU = 0$, *i.e.* internal energy is constant.

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

$$\text{Work done } W = 2.3026\mu RT \log_{10}\left(\frac{V_f}{V_i}\right)$$

$$= 2.3026\,\mu RT \log_{10}\left(\frac{p_i}{p_f}\right)$$

where, μ = number of moles, R = ideal gas constant, T = absolute temperature and V_i, V_f and p_i, p_f are initial and final volumes and pressures, respectively.

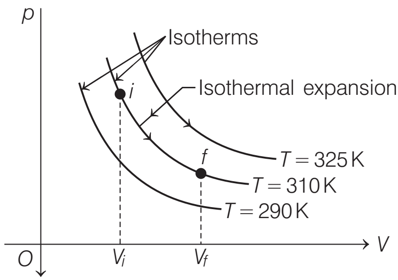
After differentiating pV = constant, we have

$$\frac{dp}{dV} = -\frac{p}{V} \text{ and } -\frac{dp}{\frac{dV}{V}} = p$$

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

p-V Diagram

p-V curve for this process is a rectangular hyperbola as shown below



Examples

(a) Melting process is an isothermal change, because temperature of a substance remains constant during melting.

(b) Boiling process is also an isothermal operation.

(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 $dQ = nCdT, C_{adi} = 0$ as $dQ = 0$, *i.e.* molar heat capacity for adiabatic process is zero.

From first law, $dU = -dW$, *i.e.* 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 decreases, *i.e.* the system cools down and *vice-versa*.

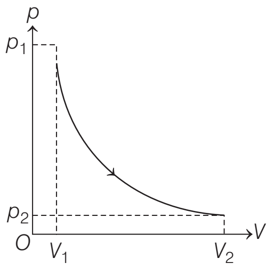
Work done in an adiabatic process is

$$W = \frac{nR(T_i - T_f)}{\gamma - 1} = \frac{p_i V_i - p_f V_f}{\gamma - 1}$$

where, T_i and T_f are initial and final temperatures.

p-V Diagram

In p-V curve of this process, pressure decreases exponentially with increase in volume as shown below



pV^{γ} = Constant

Examples

(a) Sudden compression or expansion of a gas in a container with perfectly non-conducting wall.

(b) Sudden bursting of the tube of a bicycle tyre.

(c) Propagation of sound waves in air and other gases.

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

Process equation is $\frac{V}{T} = \text{Constant}$.

Molar heat capacity of the process is C_p and $dQ = nC_p dT$.

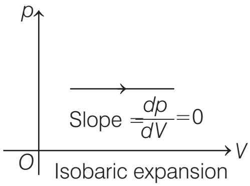
Internal energy $\quad dU = nC_V \, dT$

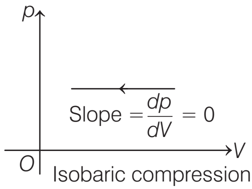
From the first law of thermodynamics,

$$dQ = dU + dW$$

$$dW = pdV = nRdT$$

p-V curve is a straight line parallel to volume axis as shown below





(v) **Isochoric Process** A process taking place in a thermodynamic system at constant volume is called an **isochoric process**.

Process equation is $\frac{p}{T} = \text{Constant.}$

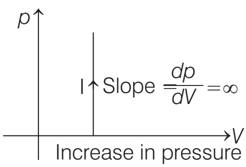
$dQ = nC_V dT$, molar heat capacity for isochoric process is C_V.

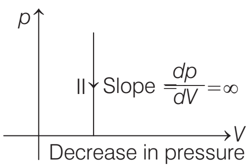
Volume is constant, so $dW = 0$.

From the first law of thermodynamics,

$$dQ = dU = nC_V dT$$

p-V curve is a straight line parallel to pressure axis as shown below.





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

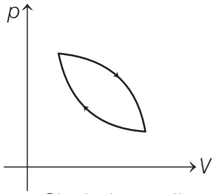
For cyclic process, $\quad dU = 0$

or $\quad dQ = dW$

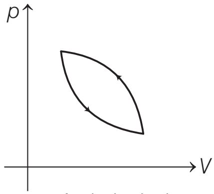
Efficiency of the cycle is given by

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

Work done by the cycle can be computed from area enclosed by cycle on p-V curve.



Clockwise cyclic process



Anti-clockwise cyclic process

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 reservoir can never be made zero.

Kelvin's 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 an 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.

Entropy

Entropy is related to the disorderness of molecular motion of the system. Greater the randomness or disorderness, greater the entropy.

Change in entropy is given by $dS = \frac{dQ}{T}$

where, dQ = heat supplied to the system

and T = absolute temperature.

Entropy of a system never decreases, *i.e.* $dS \geq 0$.

Entropy is a physical quantity that remains constant during a reversible adiabatic change.

Entropy of a system increases in an irreversible process.

Change in Entropy for Solids and Liquids

(i) When heat is supplied to a solid and its state changes such that temperature remains constant, then

Change in entropy, $\Delta S = \frac{\Delta Q}{T}$

$$\Rightarrow \quad dS = \frac{dQ}{T} = \frac{\pm |mL|}{T}$$

Positive sign is used for heat absorption and negative sign is used for heat rejection.

(ii) When temperature of a substance changes from T_1 to T_2, then

$$dS = \int \frac{dQ}{T} = mS \int_{T_1}^{T_2} \frac{dT}{T} = ms \ln\left(\frac{T_2}{T_1}\right)$$

$$= 2.303\, mS \log_{10}\left(\frac{T_2}{T_1}\right)$$

where, m = mass of the substance

and s = specific heat of the substance.

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.

Heat engine are of two types

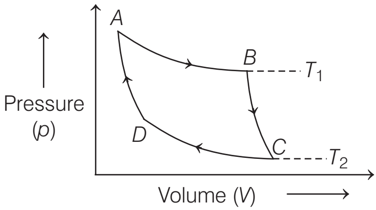
(i) **External Combustion Engine** In this engine, fuel is burnt in a chamber outside the main body of the engine, *e.g.* steam engine. In practical life, thermal efficiency of a steam engine varies from 12% to 16%.

(ii) **Internal Combustion Engine** In this engine, fuel is burnt in inside the main body of the engine, *e.g.* petrol and diesel engine.

In practical life, thermal efficiency of a petrol engine is 26% and for a diesel engine is 40%.

Carnot's Cycle

Carnot devised 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) Isothermal compression (CD)

(iv) Adiabatic compression (DA)

The net work done per cycle by the engine is numerically equal to the area of the loop representing the Carnot's cycle.

After doing the calculations 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 temperatures T_1 and T_2. But still Carnot engine is not a practical engine because many ideal situations have been assumed while designing this engine which can practically not be obtained.

Carnot Theorem

According to Carnot theorem,

(i) A heat engine working between the two given temperatures T_1 of hot reservoir *i.e.*, source and T_2 of cold reservoir *i.e.*, sink cannot have efficiency more than 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

$$\beta = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

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

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

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