

FUNDAMENTAL CONCEPT

- **Macroscopic Vs Microscopic Viewpoint**
- **Thermodynamic System**
- **Surroundings**
- **Closed system**
- **Open system**
- **Isolated system**
- **Thermodynamic properties,**
- **Processes and Cycles**
- **Intensive properties**
- **Extensive properties**
- **Homogeneous and Heterogeneous Systems**
- **Thermodynamic Equilibrium**
- **Temperature (t)**
- **Absolute temperature (T)**
- **pressure**
- **Absolute volume**
- **Specific Volume and Density**
- **Power**
- **Reversible & Irreversible Processes**
- **Zeroth Law of Thermodynamics**
- **Energy, Work and Heat**
- **Internal energy (u)**
- **Work energy (W)**

1) FUNDAMENTAL CONCEPT

Thermodynamics is the science of energy transfer and its effect on the physical properties of substances. It is based upon observations of common experience which have been formulated into thermodynamic laws.

➤ **Macroscopic Vs Microscopic Viewpoint** There are two points of view from which the behavior of matter can be studied: the macroscopic and the microscopic. In the macroscopic approach, a certain quantity of matter is considered. without the events occurring at the molecular level being taken into account From the microscopic point of view, matter is composed of millions of molecules. The behaviour of the gas is described by summing up the behavior of each molecule. Such a study is made in microscopic or statistical approach.

➤ **Thermodynamic System** A thermodynamic system is defined as a quantity of matter or a region in space upon which attention is concentrated in the analysis of a problem.

➤ **Surroundings** Everything external to the system is called the surroundings or the environment. The system is separated from the surroundings by the system boundary.

➤ **There are three classes of systems:**

(a) closed system

(b) open system

(c) isolated system

(a) closed system

The closed system is a system of fixed mass. There is no mass transfer across the system boundary. There may be energy transfer into or out of the system. A certain quantity of fluid in a cylinder bounded by a piston constitutes a closed system.

(b) open system

The open system is one in which matter crosses the boundary of the system. There may be energy transfer also. Most of the engineering devices are generally open systems, e.g., an air compressor in which air enters at low pressure and

leaves at high pressure and there are energy transfers across the system boundary.

(c) isolated system

The isolated system is one in which there is no interaction between the system and the surrounding. It is of fixed mass and energy, and there is no mass or energy transfer across the system boundary.

➤ **Thermodynamic properties, Processes and Cycles**

Every system has certain characteristics by which its physical condition may be described, e.g., volume, temperature, pressure, etc. Such characteristics are called properties of the system. These are all macroscopic in nature. When all the properties of a system have definite values, the system is said to exist at a definite state. Thermodynamics properties are the coordinates to describe the state of a system. They are the state variables of the system.

- **State** Any operation in which one or more of the properties of a system changes is called a change of state. The succession of states passed through during a change of state is called the path of the change of state.
- **Processes** When the path is completely specified, the change of state is called a process, e.g., a constant pressure process. A thermodynamic cycle is defined as a series of state changes such that the final state is identical with the initial state
- **Properties** may be of two types.
- **Intensive properties** are independent of the mass in the system, e.g., pressure, temperature, etc. **Extensive properties** are related to mass, e.g., volume,

energy, etc. If mass is increased, the values of the extensive properties also increase.

➤ **Homogeneous and Heterogeneous Systems** A quantity of matter homogeneous throughout in chemical composition and physical structure is called a phase. Every substance can exist in any one of the three phases, viz., solid, liquid and gas. A system consisting of a single phase is called a homogeneous system, while a system consisting of more than one phase is known as a heterogeneous system.

➤ **Thermodynamic Equilibrium** A system is said to exist in a state of thermodynamic equilibrium when no change in any macroscopic property is registered, if the system is isolated from its surroundings. thermodynamic equilibrium, if the conditions for the following three types of equilibrium are satisfied

(a) **Mechanical equilibrium** (b) **Chemical equilibrium** (c) **Thermal equilibrium** In the absence of any unbalanced force within the system itself and also between the system and the surroundings, the system is said to be in a state of mechanical equilibrium.

If an unbalanced force exists, either the system alone or both the system and the surroundings will undergo a change of state till mechanical equilibrium is attained.

if there is no chemical reaction or transfer of matter from one part of the system to another, such as diffusion or solution, the system is said to exist in a state of chemical equilibrium.

if there is no spontaneous change in any property of the system, the system is said to exist in a state of thermal equilibrium

➤ **Temperature (t)** It determines the level of heat intensity or thermal energy of a body/system. The difference in temperature of two bodies shows that the body with higher temperature is hotter than the body with lower temperature or the body with lower temperature is colder than the body with higher temperature. It is measured with the help of a thermometer which may be of many types.

The commonly used unit of temperature is Celsius (C) 1°C is $1/100^{\text{th}}$ of the difference between boiling point & freezing point of water where freezing point is taken as 0°C . Another unit of temperature used in English speaking countries is Fahrenheit.

$$\text{Temperature in F} = 1.8 \times \text{Temperature in C} + 32$$

In SI system of units the unit of temperature used is Kelvin (K), which is actually the unit of absolute temperature as mentioned below:

➤ **Absolute temperature (T)**

The zero chosen on Celsius or Fahrenheit scale is quite arbitrary and these scales are useful only when we have to consider the change in temperature or we have to compare the temperature of two different bodies. Otherwise these scales of temperature do not show the absolute value of thermal energy inside the body i.e. 0 °C temperature does not mean that the body has zero value of thermal energy or zero intensity of heat. The absolute zero temperature shown on the Kelvin scale means the temperature at which there is no heat intensity or thermal energy in the body. It is the temperature at which a gas will not occupy any volume and it occurs at -273.15 °C. Thus, 0 °C equals to 273.15 K.

Thus absolute zero temperature (0 K) is that temperature, below which the temperature of any substance cannot fall and the temperature measured above this zero is called absolute temperature given in K. One degree on Celsius scale and Kelvin scale is same.

$$\text{Temperature in K} = 273.15 + \text{Temperature in C}$$

➤ **Pressure (P)**

It is defined as the force per unit area exerted by a body/matter/system on its surface in a direction normal to the surface. When a force is exerted on a fluid this force is transmitted throughout the fluid and is exerted in all direction with equal intensity. It is measured by pressure gauge which shows the pressure above the atmospheric pressure because atmospheric pressure always acts on the pressure gauge when it shows zero on the pressure scale. And any value shown on the scale is always the pressure above atmospheric pressure, which is called gauge pressure.

Thus Absolute pressure = Atmospheric Pressure + Gauge Pressure.

$$\text{Or } P_{\text{abs}} = P_{\text{atm}} + P_g$$

For pressure below atmospheric, gauge pressure would be negative and is termed as vacuum.

$$\text{Thus, } P_{\text{abs}} = P_{\text{atm}} - \text{Vacuum.}$$

In SI system of units the units of pressure is Pascal (Pa) such that

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

$$1 \text{ bar} = 10^5 \text{ N/m}^2$$

Pressure can also be measured in terms of height of column of a liquid. For example, the pressure exerted by a height h of column of a liquid of density ρ filled in a tube/pipe over the area A of the bottom end of the tube will be weight of liquid column upon area, A , if top end of tube is closed. In this case pressure can be calculated by knowing the weight of liquid and area A of tube:

$$\left[p = \frac{\rho(A \cdot h) \cdot g}{A} = \rho g h \right]$$

As the value of density, ρ for a given liquid is constant and g is also an absolute constant, the pressure can indirectly be indicated in terms of height of column of a specified liquid. One commonly used unit of pressure in terms of height of mercury (Hg) column is given as:

$$1 \text{ mm of Hg} = 1 \text{ Torr} = 0.001 \text{ m of Hg}$$

$$= 0.001 \times 13600 \times 9.81 = 133.41 \text{ Pa}$$

$$\text{Standard Atmospheric Pressure} = 760 \text{ mm of Hg}$$

$$= 760 \times 133.41 \text{ Pa}$$

$$= 101300 \text{ Pa}$$

$$= 1.013 \text{ bar}$$

➤ **Absolute volume (V)** It is defined as three dimensional space occupied by matter i.e. gas or liquid. It is measured in m^3 .

➤ **Specific Volume and Density** Volume is the space occupied by a substance and is measured in m^3 The specific volume (v) of a substance is defined as the volume per unit mass and is measured in m^3/kg .

Density (p) is the mass per unit volume of a substance,

➤ **Power** The rate of energy transfer or storage is called power. The unit of power is watt (W), kilowatt (kW) or megawatt (MW). $1 \text{ W} = 1 \text{ J/s} = 1 \text{ Nm/s}$

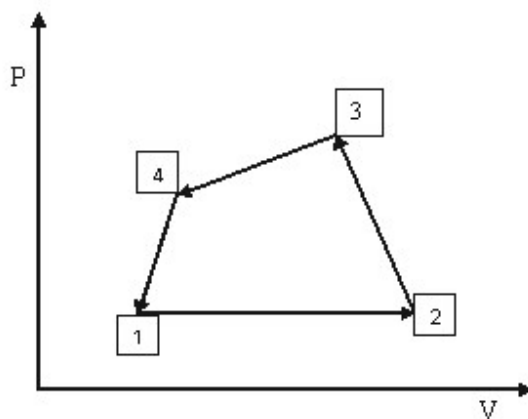


Fig Thermodynamic cycle

A **reversible process** also known as quasi-static process is one which can be reversed at any stage to the same initial condition and also leaving no effect on the surroundings.

That means after completely reversing the process, the system and surroundings are exactly restored to their initial condition. Hence a reversible process has following characteristics:

- 1) It must pass through the same states on the reversed path as were initially visited on the forward path.
- 2) This process when undergoes will leave no history of events in the surroundings.
- 3) It must pass through a continuous series of equilibrium states.

No real process is truly reversible but some processes may approach reversibility to close approximation.

An **irreversible process** is one which cannot be reversed or which is not reversible e.g. heat transferred through a finite temperature difference or work done on a gas enclosed in cylinder piston arrangement etc.

➤ **Reversible & Irreversible Cycles**

A cycle containing all the reversible processes is reversible cycle.

A cycle containing one or more irreversible process is known as irreversible cycle.

In reality, a reversible cycle is not possible and is only of theoretical importance. In real practice, every thermodynamic device is based on any irreversible cycle.

➤ **Zeroth Law of Thermodynamics**

Temperature Equality and Inequality: When two bodies or system come in contact with each other and if their thermal equilibrium is disturbed i.e. there is some change in properties then it is said that they have unequal temperature or temperature inequality. But after a substantial long time the change in properties is no more and the systems are again in thermal equilibrium then it can be said that now they have equal temperature i.e. temperature equality.

On this concept of temperature equality & inequality & thermal equilibrium, *Zeroth law of Thermodynamics* states that when two systems A and B have thermal equilibrium separately with a third system C then A and B also must be in thermal equilibrium with each other. It is clearly shown in figure

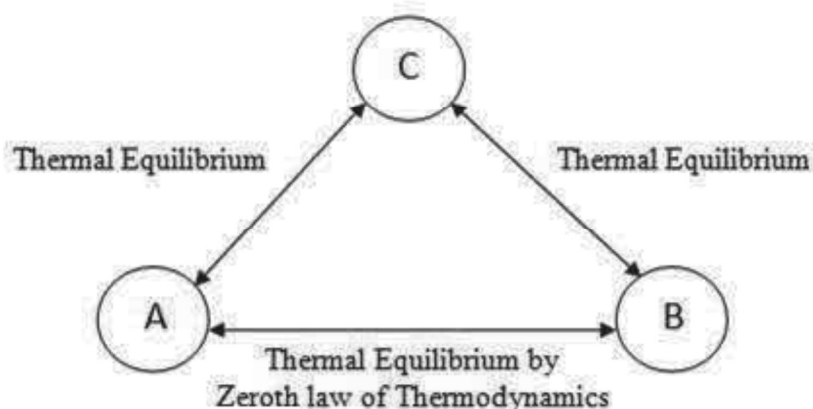


Fig Zeroth Law of Thermodynamics

➤ **Energy, Work and Heat**

(b) Energy is a general term and in a very simple way, it is defined as the capacity of an agent to do work. In general we feel energy when it is in transition i.e. being transferred from one medium to other medium. E.g. heat transferred from one body to other body or work done on a gas to compress it to a lower volume or moving of wheels of car by its engine etc. The other phase of energy is stored energy which cannot be visible or felt e.g. chemical energy of fossil fuel, potential energy of a body placed at some height etc. In this way broadly, energy can be classified in two forms as (i) Transit energy and (ii) Stored energy, which can transform into each other.

In thermodynamics, we deal with both types of energies possessed or transformed by the working substance and their types are as given below:

- (i) Stored Energy Internal Energy
- (ii) Transit Energy Heat & work

➤ **Internal energy (u)**

Internal energy is that energy which remains stored in the working substance in the form of thermal energy, which is due to molecular activity or lattice vibrations etc. and it is measured or indicated by the temperature of substance. Internal energy is directly proportional to temperature of substance, which is also called Joules Law. So it is a quantity depending on the state of the system.

$$U \propto T$$

$$\Delta U \propto \Delta T$$

$$\Delta U = m C_v \Delta T$$

Where, ΔU = Change in internal energy in Joules of the working medium in the system due to change in its temperature, ΔT

m = Mass of the working medium in kg

C_v = Specific heat at constant volume of the medium in J/ kg.K

Heat energy (Q)

It actually means thermal energy in transit i.e. heat exchanged by the system with its surroundings. The word heat alone is seldom used and commonly used term is heat exchanged or heat absorbed or heat liberated etc. This exchange of heat between system and surroundings may be by any mode of heat transfer i.e. conduction, convection or radiation. Its intensity is directly proportional to difference in temperature of system and surrounding. The heat absorbed by the system is taken as positive and heat liberated by the system is taken as negative. It is a quantity, which depends on the process or path followed by the system.

Work energy (W)

It is the energy in transit and occurs when a body is moving some distance under some force. Mathematically, it is force multiplied by displacement. In thermodynamics, work is there when there is some displacement on the boundaries of the system. When the boundaries of the system expand i.e. displace the surroundings, the work is taken as positive and when by some external pressure the boundaries of the system contracts, the work is taken as negative. Thus positive work means system is producing or doing work and negative work means work is being done on the system by some external agency or surroundings. In real thermodynamic application, mechanical work is exchanged through a rotating shaft crossing the boundary of system. It is also a quantity depending on the process or path followed by the system.

Units: In MKS system of units, unit of heat is Calorie (Cal) which is defined as amount of heat (thermal energy) required in raising the temperature of 1 gram of water by 1C. And unit of work is kgf-m, which occurs, when one kg force moves a body by a distance of one meter. But in SI system of units, the units of heat and work are not different as both are different form of energies and also interchangeable. Here unit of heat is taken same as unit of work and it is Joule. One Joule (J) = One Newton x Meter (N-m)

Conversion factor of heat energy to work energy as given by Joules (from MKS to SI) is 1 Cal = 4.187 J.

Laws of perfect gases

- Boyle's law
- Charles's law
- Gay-Lussac's law
- Avogadro's law
- General Gas Equation
- Equation of State of a Perfect Gas
- Universal Gas Constant (R_u)
- Specific Heat
- Molar specific heats

1) Boyle's law

In 1662 Robert Boyle studied the relationship between volume and pressure of a gas of fixed amount at constant temperature. He observed that volume of a given mass of a gas is inversely proportional to its pressure at a constant temperature. Boyle's law, published in 1662, states that, at constant temperature, the product of the pressure and volume of a given mass of an ideal gas in a closed system is always constant. It can be verified experimentally using a pressure gauge and a variable volume container. It can also be derived from the kinetic theory of gases: if a container, with a fixed number of molecules inside, is reduced in volume, more molecules will strike a given area of the sides of the container per unit time, causing a greater pressure.

A statement of Boyle's law is as follows:

The volume of a given mass of a gas is inversely related to pressure when the temperature is constant. $V \propto 1/P$ (Temp. $T = C$)

11) Charles's law

Charles's law, or the law of volumes, was found in 1787 by Jacques Charles. It states that, for a given mass of an ideal gas at constant pressure, the volume is directly proportional to absolute temperature, assuming in a closed system.

The statement of Charles's law is as follows: the volume (V) of a given mass of a gas, at constant pressure (P), is directly proportional to its temperature (T). As a mathematical equation, Charles's law is written as either: $V \propto T$ (Pressure $P = C$)

111) Gay-Lussac's law

Gay-Lussac's law, Amontons' law or the pressure law was found by Joseph Louis Gay-Lusaac law in 1809. It states that, for a given mass and constant volume of an ideal gas, the pressure exerted on the sides of its container is directly proportional to its absolute temperature

$P \propto T$ (Volume = C)

iv) Avogadro's law

Avogadro's law states that the volume occupied by an ideal gas is directly proportional to the number of molecules of the gas present in the container. This gives rise to the molar volume of a gas, which at STP (273.15 K, 1 atm) is about 22.4 L

V) Ideal gas law

The Combined gas law or General Gas Equation is obtained by combining Boyle's Law, Charles's law, and Gay-Lussac's Law. It shows the relationship between the pressure, volume, and temperature for a fixed mass (quantity) of gas $P_1V_1/T_1 = P_2V_2/T_2 = \text{Constant}$

V1) Equation of State of a Perfect Gas

By combining the Boyle's law and Charles' s law, the equation of state for a perfect gas can be derived.

For example: consider a perfect gas initially at a state of absolute pressure P_1 , absolute temperature T_1 and specific volume v_1 . Let it be expanded or compressed at constant temperature to a new state of absolute pressure P_2 and specific volume v_1' . Then by Boyle' s law

$$P_1v_1 = P_2v_1' \quad [\text{Sub Eq. (i)}]$$

Let after this state, the gas is further expanded or compressed such that the pressure P_2 remains constant. Let the new state is of specific volume v_2 and absolute temperature T_2 . Then by Charles' s Law:

$$\frac{v_1'}{T_1} = \frac{v_2}{T_2} \quad v_1' = v_2 \frac{T_1}{T_2} \quad \text{Sub Eq. (ii)}$$

Now, putting the value of v_1' in *sub-equation (i)*

$$P_1v_1 = \frac{P_2v_2T_1}{T_2}$$

$$\text{Or} \quad \frac{P_1v_1}{T_1} = \frac{P_2v_2}{T_2}$$

$$\text{Or} \quad \frac{Pv}{T} = \text{constant} = R$$

Where, R is known as characteristics gas constant.

Above equation can be re-written as

$$Pv = RT$$

$$\text{Or } PV = mRT \text{ (Eq. 3.3)}$$

It is called the equation of state of a perfect gas.

From the equation of state, the units of R are J/ kg K.

For atmospheric air, value of R is 287 J/ kg K.

V11) Universal Gas Constant (R_u)

We know that one kg-mole of a gas is equal to M kg of the gas where M = molecular weight of gas

Let mass m contains n no. of kg moles, then $m = n \cdot M$

From the equation of state we know that

$$\frac{PV}{T} = mR$$

$$\text{Or } \frac{PV}{T} = nMR \text{ (Eq. 3.4)}$$

Now by Avogadro Law, equal volume of different perfect gases at the same temperature and pressure contain equal number of molecules or equal number of kg-moles. Thus by this rule if we see the equation of state given above for two different gases at same pressure, volume and temperature and so the same number of moles, the value of MR will also be same for these two gases. So the product of M & R , molecular weight and characteristics gas constant of any perfect gas is always constant and is named as universal gas constant (R_u).

It is found that $R_u = M \cdot R = 8314$ J/ kg mole K

Thus equation of state can be re-written in terms of number of kg moles as

(Eq. 3.5)

This is called as universal gas equation

V111) Specific Heat

The specific heat of a substance is defined as the quantity of heat required to raise the temperature of a unit mass of the substance through a unit degree. It is denoted as C .

If the unit mass of substance is a gas then specific heat is of two types: as specific heat at constant pressure C_p and specific heat at constant volume, C_v .

Specific heat at constant volume, C_v for a gas is the heat energy required to be supplied to unit mass of gas for unit degree rise in its temperature by keeping it at constant volume in a fixed volume container.

specific heat at constant pressure, C_p for a gas is the heat energy required to be supplied to unit mass of gas for unit degree rise in its temperature by keeping it at constant pressure in a

container, one boundary of which can move to allow for expansion of gas and hence to keep its pressure at a constant level.

C_p is always more than C_v and for a particular gas the ratio of C_p and C_v i.e. γ ($\gamma = C_p/C_v$) remains constant. By Regnault's law, both types of specific heats remain constant with varying temperature and pressure. But this is only approximately true. In actual practice value of specific heats vary with varying temperature. Also for real gases C_p & C_v increases considerably with increase in temperature.

Thus to calculate the quantity of heat exchanged only for a small temperature change, the following formula can be used

$$Q = m C \Delta t$$

Where, Q = Heat Exchanged

m = Mass of gas

C = Specific heat of gas

Δt = Temperature change of gas

C_p for air = 1.004 kJ/kg K

C_v for air = 0.7178 kJ/kg K

V111) Molar specific heats

The molar specific heat of a substance is defined as the quantity of heat required to raise the temperature of one mole of a substance through a unit degree. Now the mass of one mole is M kg where, M is molecular weight of the substance.

Thus $C_{p-mol} = M.C_p$ and $C_{v-mol} = M.C_v$

3.THERMODYNAMIC PROCESSES

- Isothermal process:
temperature is constant $T=C$
- Isobaric process: pressure is
constant, $P=C$
- Isentropic process: entropy is
constant, $s=C$
- Constant-volume process,
 $v=C$
- Adiabatic process: no heat
transfer, $Q=0$

Constant temperature process (Isothermal Process)

The beauty of isothermal expansion or compression process is that the internal energy remains constant and so whole of the heat exchange by system is converted to work and vice versa. However the process is difficult to visualize while thinking that when the system (gas filled behind piston in the cylinder) absorbs heat, its temperature should always increase. But what happens in the isothermal process that while absorbing heat, simultaneously the gas expands thus decrease in its pressure and temperature takes place and the net change in temperature is zero. While expanding, the gas gives positive work equal to the heat supplied. Conversely also if the gas is compressed by doing extra work on the gas, its pressure and temperature tends to increase, but simultaneously if the gas is cooled in such proportion that the net change in temperature remains zero, the compression process becomes isothermal. In this isothermal compression process, again the work supplied to the gas is given away by the system in the form of heat.

Applying first law of thermodynamics to this isothermal process in which $dU=0$, because $dT=0$,

$$\delta Q = \delta W = P.dV$$

From gas law

$$\frac{PV}{T} = \text{constant}$$

At $T = \text{constant}$

Gas law reduces to $PV = \text{constant}$ or $P_1V_1 = P_2V_2 = PV$

$$\begin{aligned} Q = W &= \int_1^2 \frac{P_1V_1}{V} \cdot dV = P_1V_1 \int_1^2 \frac{dV}{V} \\ &= P_1V_1 \log_e \frac{V_2}{V_1} \end{aligned}$$

By using this equation we can calculate the work exchange or heat exchange during isothermal process if we know the change in volume

Constant volume heating/cooling process

Let the piston is fixed at one point in the walls of cylinder such that volume $V = \text{Constant}$

So the ideal gas law $PV/T = \text{Constant}$ will reduce to

$$\frac{P}{T} = \text{Constant}$$

Now let a small increment of heat δQ is supplied to the gas. As per 1st law of thermodynamics

$$\delta Q = \delta W + dU$$

$$\delta Q = P.dV + dU$$

As $V = \text{Constant}$, $\delta W = P.dV = 0$

$$\text{So } \delta Q = \Delta U = mC_v \Delta T$$

Thus knowing the values of δQ and C_v , ΔT (Increase in temperature) can be calculated and so ΔP can also be calculated. By measuring the small increment in temperature and pressure of system, the quantity δQ & ΔU can also be calculated.

Constant pressure process

Let the piston is free to move in the cylinder and force, F or pressure, P on the piston remains constant. So now the boundaries of the system can move and so the gas can expand or can be compressed i.e. the system is able to exchange work.

Now let a small quantity of heat, δQ is supplied to the gas through the walls of cylinder.

On absorbing this heat, the temperature of gas will tend to increase and simultaneously the gas will tend to expand against force F on the piston. Applying 1st law of thermodynamic to this process.

$$\delta Q = \delta W + dU$$

$$\text{or } \delta Q = P.dV + mC_v dT$$

$$\text{or } mC_p dT = mRdT + mC_v dT \quad \left[\because \frac{P.dV}{dT} = mR \right]$$

$$\text{or } C_p = R + C_v$$

$$\text{or } C_p - C_v = R$$

Thus characteristic gas constant of an ideal gas is the difference between specific heat at constant pressure (C_p) and at constant volume (C_v).

The ratio of specific heats C_p/C_v is denoted as γ .

The physical meaning of R or γ can be taken as the characteristic of an ideal gas to expand under the influence of heat or we can say the increase in product of pressure and volume PV with increase in T .

Also by ideal gas law, $\frac{PV}{T} = \text{Constant} = mR$

As pressure, $P = \text{Constant}$, the gas law reduce to $V/T = \text{Constant}$

Thus the increase in volume of gas due to expansion and increase in temperature are interrelated and if one can be measured the other can be found and the quantities W , ΔU and so Q can be calculated from equation 4.7 as

$$Q = P(V_2 - V_1) + mC_v(T_2 - T_1)$$

Adiabatic process

$$\begin{aligned}P_1 V_1^n &= P_2 V_2^n = P V^n \\W &= \int_1^2 P dV = \int_1^2 (P_1 V_1^n) V^{-n} dV \\&= (P_1 V_1^n) \int_1^2 V^{-n} dV = \frac{(P_1 V_1^n)}{1-n} (V_2^{1-n} - V_1^{1-n}) = \frac{P_2 V_2 - P_1 V_1}{1-n}\end{aligned}$$

Laws of thermodynamics

1st Law of thermodynamics

2nd Law of thermodynamics

3rd Law of thermodynamics

1st Law of thermodynamics **FIRST LAW OF THERMODYNAMICS & NON FLOW PROCESSES**

Introduction

The first law of thermodynamics is basically a form of law of conservation of energy i.e. energy can neither be created nor be destroyed and only it can be transformed from one form to the other.

It is actually a precise statement of law of conservation of energy in particular reference to heat energy and work energy which are our subject of study in thermodynamics. So whenever a thermodynamic system undergoes a thermodynamic process or cycle first law of thermodynamics is always to be followed. This law actually justifies or gives answer to any difference coming between heat exchange and work exchange of a system. Thus the calculation of any energy exchange in a thermodynamic process or cycle is based on this law.

First Law of Thermodynamics

Applied to a thermodynamic cycle

It states that when a system undergoes a cycle, then the net heat supplied to the system from its surroundings is equal to net work done by the system on its surroundings or net work done on the system is equal to the net heat rejected by the system.

$$\oint \delta Q = \oint \delta W \text{ or Cyclic Integral of Heat Exchange} = \text{Cyclic Integral of Work Exchange}$$

Corollary

A device or machine is impossible, which can produce work continuously without absorbing energy from its surroundings.

Applied to a thermodynamic process

If the first law is applied to a thermodynamic process in which initial and final state of the system are different, then it can be stated that the net heat exchange between system and surroundings is equal to the sum of net work exchange between system and surrounding and change in its internal energy (U).

$$Q_{1-2} = W_{1-2} + (U_2 - U_1)$$

Or $Q = W + \Delta U$

Heat Exchanged in a process = Work Exchange + Change in Internal Energy

As shown in figure , the quantity Q is taken as positive if the systems absorbs or takes heat from its surroundings and negative if the system rejects heat to the surroundings. Unlike to that, the quantity W is taken as positive if the system is doing work on its surroundings and negative if the work is being done on the system by some external agency. The quantity ΔU , change in internal energy of the system is taken as positive or negative depending on its increase or decrease.

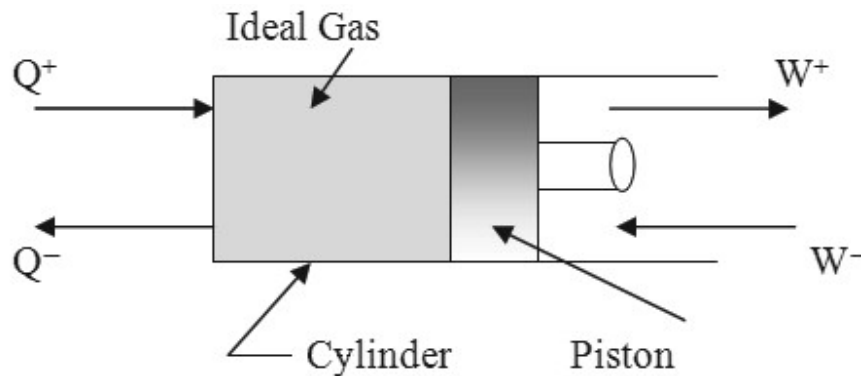


Fig. Closed System

For a cycle, initial state is same as final state and as internal energy is a point function depending on state only, so net change in internal energy in a complete cycle is zero.

By putting $\Delta U = 0$ in equation 4.2, it is reduced to equation 4.1 which is applicable to a cycle. **Internal Energy (U)**

It has already been discussed in the first chapter that the internal energy is a property of the system and depends on temperature only. From the first law of thermodynamics as discussed in previous article

$$Q = W + dU$$

If there is a case when heat is supplied to a fix volume of gas (thermodynamic system) confined in fix boundary of the system i.e. there is no change in volume of gas during supplying of heat, then there will not be any work. So

$$W = 0 \text{ and } dU = Q$$

As Q is heat supplied to gas keeping it at constant volume, it can be calculated as $mC_v dt$. Thus change in internal energy is heat exchanged at constant volume and can be calculated as

$$dU = Q = mC_v dt$$

Change in internal energy per unit mass i.e.

$$\text{Specific Internal Energy} = \frac{dU}{m} = du = C_v dt$$

Thus internal energy is a property derived from first law of thermodynamics. It accounts for the difference between heat exchange and work exchange and shows that energy cannot be created nor be destroyed. Change in specific internal energy of a system is always calculated as $C_v dt$ i.e. as a function of temperature change.

Enthalpy (H)

It is also a property of thermodynamic system which is calculated in terms of other properties. It is defined as the sum of internal energy and product of pressure and volume of a thermodynamic system. Thus it is a calculated property and loosely defined as total heat content of the system. It is denoted by H.

$$H = U$$

$$\text{And } dH = dU + d(PV)$$

$$dH = dU + P.dV + V.dP$$

Enthalpy like internal energy is also a mass dependent property and enthalpy per unit mass is named as specific enthalpy and denoted as h.

$$h = \frac{H}{m}$$

Where m = mass of the system

If we consider a fixed mass m of a gas confined in closed boundaries and remaining at constant pressure P, while absorbing heat Q. The temperature of gas will increase and simultaneously it will expand from initial volume V_1 to final volume V_2 . So, by first law of thermodynamics.

$$Q = W + \Delta U$$

Or

$$mC_p(T_2 - T_1) = (U_2 - U_1) + P(V_2 - V_1) \quad (i)$$

Also enthalpy change during this constant pressure process 1- 2

$$(H_2 - H_1) = (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$=(U_2 - U_1) + P_2(V_2 - V_1) \quad (ii)$$

[∵ $P_1 = P_2$ in constant pressure process]

From (i) & (ii)

$$H_2 - H_1 = mC_p(T_2 - T_1)$$

$$\text{or } \Delta H = mC_p\Delta T$$

$$\text{or } \Delta h = C_p\Delta T$$

Thus change in enthalpy is also dependent on temperature only and is always calculated as $C_p\Delta T$.

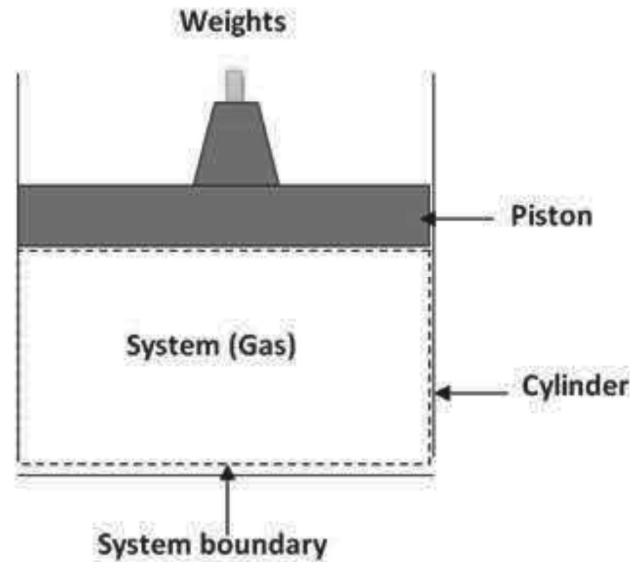


Fig. Closed system of gas filled in metallic cylinder

When infinitely small heat δQ is supplied to gas from outside through the wall of cylinder, the gas tends to expand and forces the piston weight F to move up. Let piston moves by a short distance, dl . Then the infinitesimal work done can be calculated as

$$\delta W = F \times dl$$

$$= \frac{F}{A} \times dl \times A$$

$$= P \cdot dV$$

= Pressure * Change in volume

Total work during a non-flow process 1-2 i.e. compression or expansion of gases can be calculated as taking integral of $P \cdot dV$

All these reversible processes of heat exchange (Heating or Cooling) and work exchange (compression or expansion) by a system of ideal gas with its surroundings can take place in various ways as discussed below:

Constant volume heating/cooling process

Let the piston is fixed at one point in the walls of cylinder such that volume $V = \text{Constant}$

So the ideal gas law $PV/T = \text{Constant}$ will reduce to

$$\frac{P}{T} = \text{Constant}$$

Now let a small increment of heat δQ is supplied to the gas. As per 1st law of thermodynamics

$$\delta Q = \delta W + dU$$

$$\delta Q = P \cdot dV + dU$$

As $V = \text{Constant}$, $\delta W = P \cdot dV = 0$

$$\text{So } \delta Q = \Delta U = mC_v \Delta T$$

SECOND LAW OF THERMODYNAMICS, ENTROPY, CARNOT CYCLE

Introduction

In the last chapter we studied that heat and work are different forms of energy and are convertible in to each other. During this conversion, law of conservation of energy i.e. first law of thermodynamics is followed. But this law has limitation in depicting the fraction of heat energy of a system or supplied to system which can be converted to work. Also it does not specify the conditions under which conversion of heat in to work is possible. Second law of thermodynamics removes this limitation and tells under what conditions, in what direction of heat flow and how much of it can maximum be converted in to work.

Statements of Second Law of Thermodynamics Kelvin-Planck statement

It is impossible to construct a thermodynamic system or device which operates in a cycle and produce no effect other than the production of work by exchange of heat with a single reservoir. Or in simple terms it states that all the heat from a single heat reservoir cannot be converted to work.

In detail, the meaning of statement is that there is no such device possible which can continuously take heat from heat reservoir on one side and convert all of it into work on the other side. But only a part of heat energy while flowing from high temperature reservoir to low temperature reservoir can be converted to work and the remaining part must be rejected to low temperature reservoir i.e. atmosphere. Therefore only a part of heat energy while in transition from high temperature to low temperature is possible to be converted in to work.

Classius statement

This statement is regarding the conversion of work in to heat and it states that *(it is impossible to construct a thermodynamic system or device which, while operating in cycle (i.e. working continuously), transfers heat from low temperature reservoir to high temperature reservoir without taking help or absorbing work from some external agency.)*

In detail, the meaning of statement is that heat can be made to flow from low temperature to high temperature only by applying external work.

Heat Engine

It is a thermodynamic system or device which can continuously convert heat energy into work energy or we can say thermal energy in to mechanical energy. We know that to work continuously, anything has to operate in a cycle. Therefore heat engine is also a thermodynamic device operating in a cycle. The performance of a heat engine is measured in terms of its thermal efficiency which is the ratio of work output to heat absorbed by engine, i.e.

$$\eta_{th} = \frac{W}{Q} ;$$

Where W = Rate of mechanical work done by engine

Q = Heat absorbed by engine or rate of heat supplied to engine.