UNIT - 1

ZEROTH & FIRST LAW OF THERMODYNAMICS

Thermodynamics:

Thermodynamics comes from the Greek words "therme" which means heat and "dynamikos" which means force or power. So, it is the study of forces due to heat or heat due to forces.

In simple words, thermodynamics is a branch of physics that deals with heat, work, temperature and energy.

Thermodynamic System:

A thermodynamic system refers to a certain portion of universe selected for investigation. (It is imagined to be distinct and set apart from everything else). This means that a thermodynamic system is essentially macroscopic.

Example: (i) Gases ~~such~~ as helium
(ii) Vapours such as steam
(iii) Mixture such as phenol-water mixture.
(iv) Thermocouples, magnetic materials, etc.

Surroundings and Boundary:

Everything outside the system that can influence the behaviour of a system constitutes surroundings and the envelope which encloses a system and seperates it from its surroundings is called the boundary of the system.

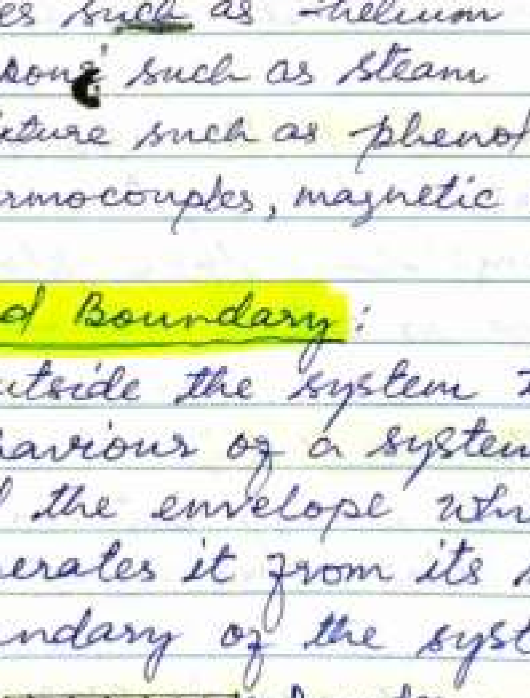


Fig: The gas in the enclosure is a thermodynamic system

Isolating boundary and Isolated system:

The boundary of a system may or may not allow it to interact with the surroundings. A boundary which prevents any exchange of energy and matter between the system and the surroundings is termed as Isolating boundary, and the system is then said to be an Isolated system.

Open and closed system:

If the surface of a system permits exchange of matter between the system and its surroundings, the system is said to be an open system. On the other hand, if exchange of energy only and no matter occurs, the system is said to be a closed system.

Adiabatic wall: An ideal wall or partition seperating two systems such that no-heat exchange can take place between the systems is called adiabatic wall.

Diathermic wall: A wall that allows exchange of heat energy between two systems is said to be diathermic wall.

Thermodynamic variables:

In thermodynamics, the state of a system at any instant represents its condition at that time. It is specified by a set of experimentally measureable quantities called thermodynamic variables, such as temperature, pressure, volume, electric field, surface area, etc. In other words, thermodynamic variables are the quantities that describe the state of a physical system and can be used to characterize it.

Thermodynamic variables may be devided into two categories: Intensive and Extensive.

(i) Intensive variables:

The variables of a system in a given state that are independent of its mass or the number of particles are called intensive variables.
Example: Pressure, surface tension, electric field and temperature are some of the intensive variables.

(ii) Extensive variables:

The variables that are proportional to the mass and to the number of particles in the system belong to the category of extensive variables.

Table: Intensive and extensive variables:

System	Intensive	Extensive
Hydrostatic system	Pressure, p	Volume$^+$, V
Paramagnetic substance	Flux density, B	Magnetic dipole moment, m
Electric cell	Potential difference, V_d	Charge, Z
Surface film	Surface tension, σ	Area, A
Stretched wire	Tension, F	Length, L
Dielectric Solid	Electric field, E	Electric dipole moment, p_e.

The Zeroth law and the concept of temperature.

The Zeroth law of thermodyanamics deals with systems in thermal equilibrium. This law enables us to give a precise meaning to temperature. It can be stated as follows:

If two systems are seperately in thermal equilibrium with a third system, they will also be in thermal equilibrium with one another.

According to thermodynamics, temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems. So, two bodies in thermal equilibrium will be at the same temperature.

Equation of state;

Consider three isolated systems 1, 2 and 3 each of them are equilibrium individually. Let pressure(P) and volume(V) be used as independent variables to describe their equilibrium states.

We choose system 3, defined by p_3 and V_3 as the reference system.

Then, the condition for thermal equilibrium between systems 1 and 3 may be expressed in the functional form as

$$f_{13}(p_1, V_1, p_3, V_3) = 0 \longrightarrow ①$$

This equation implies that once p_3, V_3 and p_1 are fixed, V_1 will be uniquely determined. Out of the four variables, only three are independent.

Similarly, for thermal equilibrium between systems 2 and 3, we have

$$f_{23}(p_2, V_2, p_3, V_3) = 0 \longrightarrow ②$$

Equations ① and ② can be solved for say p_3 and the solution can be expressed as

$$p_3 = F_{13}(p_1, V_1, V_3) \longrightarrow ③$$

and $$p_3 = F_{23}(p_2, V_2, V_3) \longrightarrow ④$$

On equating these values of p_3, we get

$$F_{13}(p_1, V_1, V_3) = F_{23}(p_2, V_2, V_3) \rightarrow ⑤$$

This may be solved for p_1 to give

$$p_1 = G(V_1, p_2, V_2, V_3) \longrightarrow ⑥$$

But, according to Zeroth law, if systems 1 and 2 are seperately in thermal equilibrium with system 3, they will also be in thermal equilibrium with one another. This requires

$$f_{12}(p_1, V_1, p_2, V_2) = 0 \longrightarrow ⑦$$

Again, we can solve this for p_1 to obtain

$$p_1 = F_{12}(V_1, p_2, V_2) \longrightarrow ⑧$$

Equation ⑧ states that under given conditions, p_1 is uniquely determined by V_1, p_2 and V_2. V_3 must drop out in equation ⑥. For this happen, the functions F_{13} and F_{23} must be of the general form

$$F_{13} = \phi_1(p_1, V_1)\,\eta(V_3) + \xi(V_3) \longrightarrow ⑨$$

and $$F_{23} = \phi_2(p_2, V_2)\,\eta(V_3) + \xi(V_3) \longrightarrow ⑩$$

This implies that eqn. ⑤ should be in this form.

$$\phi_1(p_1, V_1) = \phi_2(p_2, V_2) \longrightarrow ⑪$$

This is the condition for thermal equilibrium between systems 1 and 2. In general, we can write

$$\phi_1(p_1, V_1) = \phi_2(p_2, V_2) = \phi_3(p_3, V_3).$$

This equation shows that when two or more systems are in thermal equilibrium, for each system, state variables p and V define a single valued function which has a common numerical value for all of them known as empirical temperature.

Thus for thermal equilibrium between the system of interest and the reference system, we can write as.

$$\phi(p, V) = T \longrightarrow$$ ⑬

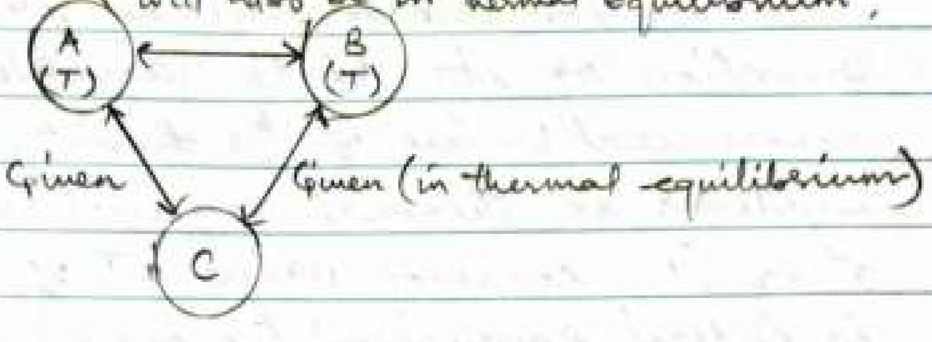
This equation may be rearranged in the more general form as

$$\phi(p, V, T) = 0 \longrightarrow$$ ⑭

This equation is called the equation of state. Note that ϕ is a single valued function of pressure and Volume at temperature T. Where T is empirical temperature.

The Zeroth Law of Thermodynamics :

If two systems A and B are in thermal equilibrium with a third system C, then they all are in equilibrium with each other.



From the statement it is clear that three systems must have some property in common, it is identified as temperature. The condition under which system A and system C are in thermal equilibrium is expressed ~~as~~ by the equation

$$\phi_1 (P_A, V_A, P_C, V_C) = 0$$

$$\text{or} \quad P_C = F_1 (P_A, V_A, V_C) \longrightarrow ①$$

Where F_1 is another function.

Similarly, system B is in thermal equilibrium with system C, then

$$\phi_2 (P_B, V_B, P_C, V_C) = 0$$

$$\text{or} \quad P_C = F_2 (P_B, V_B, V_C) \longrightarrow ②$$

Hence, $F_1 (P_A, V_A, V_C) = F_2 (P_B, V_B, V_C) \longrightarrow ③$.

Then, the Zeroth law may be expressed as

$$\phi_3 (P_A, V_A, P_B, V_B) = 0 \longrightarrow ④$$

In terms of the law, equation ③ and ④ are equivalent. So, F_1 and F_2 must contains V_C. Then, equation ③ may reduce to

$$\phi_1 (P_A, V_A) = \phi_2 (P_B, V_B) \longrightarrow ⑤$$

Applying the same argument, since system A and system C are seperately in equilibrium with system B, it follows that

$$\phi_1(P_A, V_A) = \phi_3(P_C, V_C) \longrightarrow ⑥$$

Therefore, $\phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C) = T \longrightarrow$

Thus, for every system there exists a function of its state variables such that the numerical value of the function is same for all systems in thermal equilibrium with each other. The common value T of these functions is called empirical temperature.

Temperature may be defined as a function of state of a system such that it takes the same value for all systems in thermal equilibrium with one another.

For a simple system,

$\phi(P, V) = T$ is called the equation of state.

Thermodynamic equilibrium ;

It is a state of a physical system in which the system is in thermal, mechanical, electrical and chemical equilibrium and there is no tendency for spontaneous change.

(i) Thermal equilibrium : It denotes uniformity of temperature or absence of temperature gradient or heat flow.

(ii) Mechanical equilibrium ; It denotes uniformity of pressure or absence of unbalanced force.

(iii) Electrical equilibrium : It denotes equality of electrical potential and absence of current flow.

(iv) Chemical equilibrium; It denotes absence of phase change or chemical reaction and there is no mass diffusion.

First law of Thermodynamics:

The first law of thermodynamics is the statement of the principle of conservation of energy. Heat is a form of energy and energy is conserved.

The first law of thermodynamics states that when a system is constrained to undergo a change by mechanical, diffusive or thermal interactions, its internal energy changes by an amount equal to the heat transferred to it, work done on it and matter exchanged.

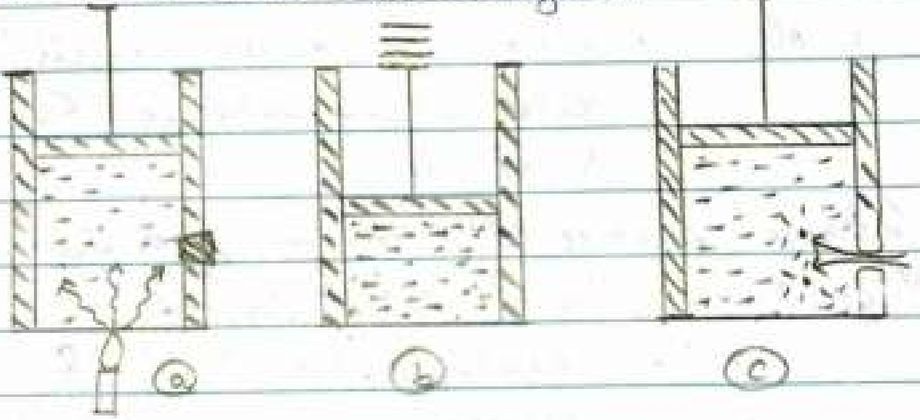


Figure: Illustration of processes by which internal energy of a system can change.

Let dU be the change in internal energy of a system when δQ amount of heat is added to it, δW work is done by it and dN is the change in the number of particles.

Then, the first law of thermodynamics can mathematically be written as,

$$dU = \delta Q - \delta W + \mu dN \longrightarrow ①$$

Where μ is chemical potential.

By convention, the heat flow into the system (δQ) is taken as positive, whereas workdone by a system (δW) is considered negative.

If more than one kind of work is done by the system, δW is replaced by $\Sigma_j \delta W_j$. Similarly, if there are several kinds of particles in the system, μdN is replaced by $\Sigma_i \mu_i dN_i$. On the other hand, a system in diffusive equilibrium may undergo thermal and mechanical interactions.

Then, the first law takes the form

$$dU = \delta Q - \delta W \longrightarrow ②$$

This is the differential form of the first law of thermodynamics for a non-diffusively interacting system.

Note: d denotes changes in internal energy.
δ denotes changes in heat added and work done.

Internal energy of a system is a function of a state rather than the path followed.

$dU \rightarrow$ exact differential, δ is used for inexact differential.

Significance of the first law of thermodynamics:

① It defines 'internal energy' as a function of state of the system.

② It highlights the heat is energy in transit.

③ It rules out the possibility of constructing a machine which can work on its own, without any input.

General relation between C_p and C_V:

For an infinitesimal quasistatic process performed by one mole of a chemical system,

$$\cancel{\delta Q}\ \delta Q = dU + p\,dV. \longrightarrow ①.$$

δQ is not exact differential. U and V are functions of coordinates defining the equilibrium state of the system.

In general, U is a function of the independent variables T and V of the system.

$$\therefore U = U(T, V).$$

A small change in U can then be expressed as

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \longrightarrow ②$$

Substituting eqn. ② in ①, we get,

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} dV \longrightarrow ③$$

We now introduce the concept of heat capacity, C_V. For an isochoric process, where V = constant, dV = 0. So, the second term in eqn. ③ will vanish.

Then,
$$C_V = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \longrightarrow ④ \quad \left\{ \because \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \frac{\partial T}{\partial T} + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} \frac{\partial V}{\partial T} \right\}$$

Where C_V is the heat capacity at constant volume. Since we have taken 1 mole, C_V is also the molar specific heat at constant volume.

Similarly, For an isobaric process, we can write the expression for heat capacity at constant pressure (C_p) as,

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left\{p + \left(\frac{\partial U}{\partial V}\right)_T\right\} \left(\frac{\partial V}{\partial T}\right)_p \longrightarrow ⑤.$$

here also, C_p is the molar specific heat at constant pressure.

Combining equation ④ and ⑤, we get.

$$C_p = C_V + \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\left(\frac{\partial V}{\partial T}\right)_P.$$

So that. $C_p - C_V = \left\{\left(\frac{\partial U}{\partial V}\right)_T + P\right\}\left(\frac{\partial V}{\partial T}\right)_P \rightarrow$ ⑥.

Here, $\frac{\partial U}{\partial V}$ the first term of RHS tells us how internal energy changes with volume at constant temperature. The second term tells us how much work is done in pushing back the surroundings at constant pressure,

Special cases;

① For an ideal gas, $pV = RT$.

So, that $p\left(\frac{\partial V}{\partial T}\right)_P = R$. Since, there is no intermolecular attraction, its internal energy is wholly kinetic ~~energy~~ and remains unchanged in free expansion. Thus, $\left(\frac{\partial U}{\partial V}\right)_T = 0$.

Then, eqn. ⑥ will become,

$$C_p - C_V = R \rightarrow ⑦ \quad ; \left\{ P\left(\frac{\partial V}{\partial T}\right)_P = R \right.$$

For n mole, eqn. ⑦ becomes as $pV = RT$ for

$$C_p - C_V = nR, \quad \text{perfect gas} \}.$$

This is known as Mayer's Formula.

It may also be defined as the rate at which the temperature of an air parcel changes in response to expansion or compression associated with altitude change.

Adiabatic lapse rate:

It is the variation of temperature in the atmosphere with height above sea level. This arises mainly due to convection currents in the troposphere - the lowest and most dense region of the earth's atmosphere. When air from the sea level rises to the upper regions of lower pressure, it expands and we may consider this ~~low~~ expansion as an adiabatic.

Adiabatic equation of an ideal gas is given by,

$$\frac{T^{\gamma}}{p^{\gamma-1}} = \text{constant}$$

$$\Rightarrow \quad T^{\gamma} p^{1-\gamma} = \text{constant}(k) \longrightarrow ①$$

To, calculate the change in temperature with height, the logarithmic form of eqn. ① can be written as,

$$\ln T = \frac{\gamma-1}{\gamma} \ln p = \ln k . \longrightarrow ②$$

On differentiating this equation ②, we get

$$\frac{dT}{T} - \frac{\gamma-1}{\gamma} \frac{dp}{p} = 0.$$

or

$$\frac{dp}{p} = \frac{\gamma}{\gamma-1} \frac{dT}{T} \longrightarrow ③$$

If we assume that pressure decreases by dp as we go up a distance dh in the atmosphere, we can write

$$dp = -\rho g \, dh \text{ ——}$$

Where ρ is the density of air and g is acceleration due to gravity.

On dividing both sides by p and using the equation of state, we obtain

$$\frac{dp}{p} = -\frac{gM}{RT} dh. \longrightarrow ④$$

Where M ($= 28.88u$) is the average molecular weight of air.

Comparing eqn. ③ and ④, we get,

$$\frac{dT}{dh} = -\left(\frac{\gamma - 1}{\gamma}\right)\frac{Mg}{R} \longrightarrow ⑤$$

This is the required expression of adiabatic lapse rate. The negative sign implies that temperature decreases with height.

This result holds good for dry air, but there is a lot of moisture in the air. The lapse rate decreases in the presence of vapours. The decrease in temperature with height under static condition and morning air is shown below:

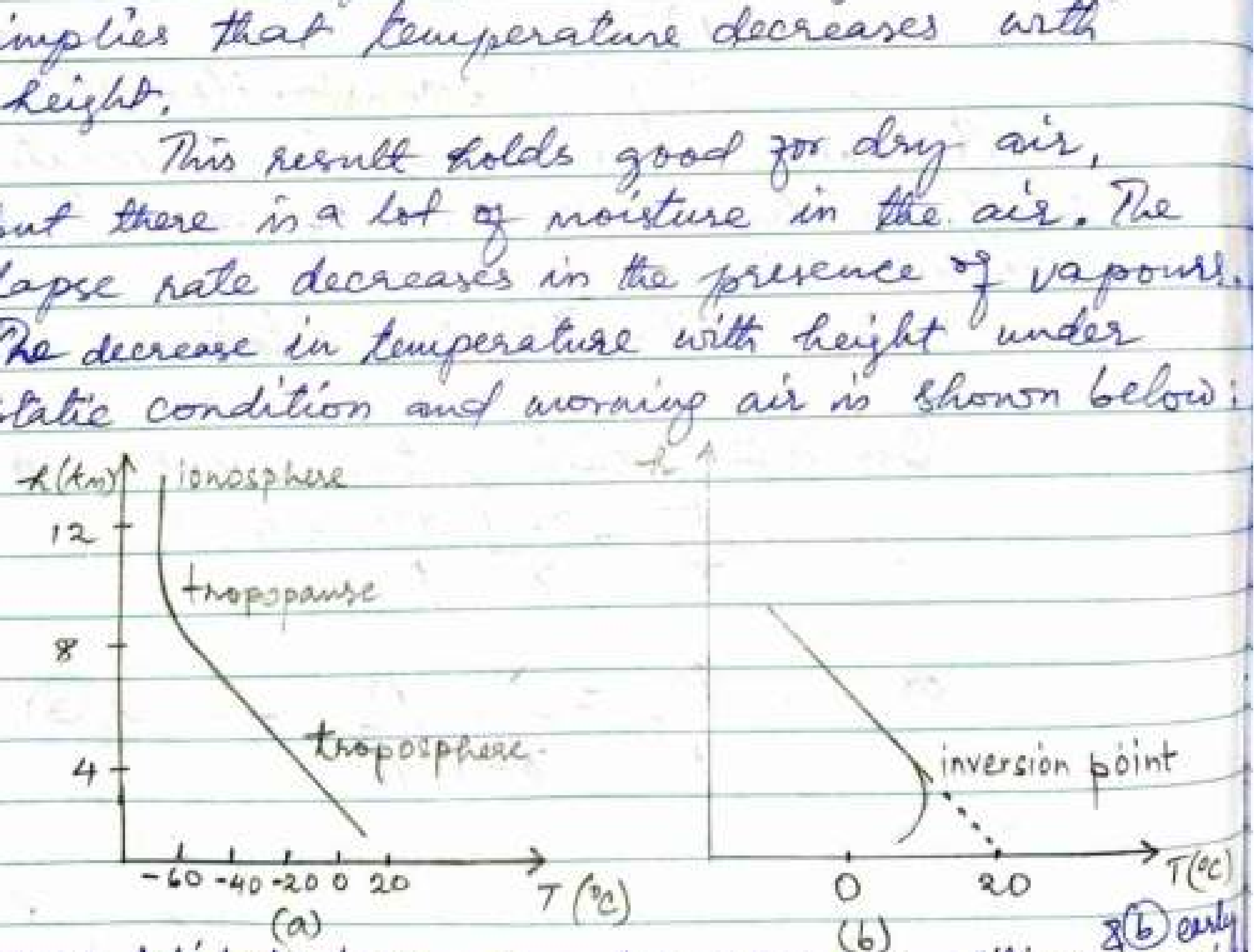


Figure: Adiabatic lapse rate under ⓐ steady conditions & ⓑ early mornin

If we take $\gamma = 1.4$, $g = 9.81\,m\,s^{-2}$, $R = 8.31\,J\,mol^{-1}\,K^{-1}$ and $M = 0.029\,kg\,mol^{-1}$. Then, the adiabatic lapse rate is given by

$$\frac{dT}{dh} = -\frac{0.4}{1.4} \times \frac{(0.029\,kg\,mol^{-1}) \times 9.81\,m\,s^{-2}}{8.31\,J\,mol^{-1}\,K^{-1}}$$

$$= -9.78 \times 10^{-3}\,K\,m^{-1}.$$

This shows that temperature drop over 1 km will be about 10°C. This value is somewhat higher than the observed lapse rate of 5 to 6.5°C per km. The difference may be attributed to the effect of water vapours in the expanding mass of air. The exact value of the adiabatic lapse rate will be determined by the amount of water vapour in the atmosphere. In addition, some modification to the vertical temperature gradient are also caused by mountains, glaciers, volcanoes and industrial/vehicular exhaust.

Date:

Adiabatic expansion of an ideal gas:

The word 'adiathermal' means 'without flow of heat. A system bounded by adiathermal walls is said to be 'thermally isolated'. We define a change to be adiabatic if it is both adiathermal and reversible.

In an adiabatic expansion, there is no flow of heat and so, we have,

$$\partial Q = 0, \longrightarrow ①.$$

The first law of thermodynamics therefore implies that, $dU = \delta W. \longrightarrow ②$.

For an ideal gas, $dU = C_V dT$ and using $\delta W = -pdV$ for a reversible change. For 1 mole of ideal gas,

$$C_V dT = -pdV = -\frac{RT}{V}dV, \longrightarrow ③.$$

So, that

$$\ln\frac{T_2}{T_1} = -\frac{R}{C_V}\ln\frac{V_2}{V_1} \longrightarrow ④.$$

Here, Cv here is per mole, since we are dealing with 1 mole of ideal gas.

Now, $C_p = C_V + R$, and dividing this by C_V yields $\gamma = C_p/C_V = 1 + R/C_V$ and, therefore,

γ = specific heat ratio.

$-\left(\frac{R}{C_V}\right) = 1-\gamma$, so that eqn ④ becomes

$$TV^{\gamma-1} = \text{Constant} \longrightarrow ⑤,$$

or equivalently (using $pV \propto T$ for an ideal gas)

$$p^{1-\gamma}T^{\gamma} = \text{Constant} \longrightarrow ⑥.$$

and

$$\boxed{pV^{\gamma} = \text{Constant}} \longrightarrow ⑦$$

For an expansion, $V_2 > V_1$ and so $\Delta Q > 0$. The internal energy has stayed the same, but the volume has increased so that the energy density has gone down. The energy density and the pressure are proportional to one another, so that pressure also decrease.

: Concept of Work and Heat ;

Heat: It is a thermal energy transferred between systems due to a temperature difference and it is denoted by Q.

Workdone: The workdone on an object is the amount of energy transferred to an object through work.

For eg. When you are exerting a force on an object that causes its position to change in the same direction, So you are doing work on that object. So, Work (W) is, $W = F \times d$.

$\forall$ F = force, d = distance.

Equivalence of Heat & Work ;

Acc^n to thermodynamics, heat is a form of energy. Therefore, it can be converted ~~from~~ into mechanical work and vice versa.

Eg: Heat is produced by rubbing of hands.

Spark produced when a stone is hammered.

Work is the energy exchanged btw ~~and~~ a system and surroundings due to change in volume of the system, Date:___.___._____

Any device which converts heat energy into mechanical work is known as a heat engine.

For eg. Steam engine, petrol engine, etc.

Joule established a relation btw workdone W and heat produced Q. Acc^n to him,

Whenever work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.

$$W \propto Q.$$

$$\text{or } W = JQ. \longrightarrow ①.$$

Where J is a constant known as Joule's mechanical equivalent of heat.

If Q is measured in calories and W in Joule, then $J = 4.18$ Joule/calories.

In SI unit both W and Q are measured in Joules. then $W = Q$. ⟶ ②

Workdone by a thermodynamic system:

The term work refer to an interchange of energy between system and its surroundings.

If F produces an infinitesimal displacement dx, then workdone by the force is

$$dW = F.dx. \longrightarrow ①.$$

If a force is exerted by the system as a whole on its surroundings and displacement takes place, the workdone either by or on the system is called External work.

Suppose the gas is expanding against the piston as shown in figure. The workdone by the gas in displacing the piston through an infinitesimal displacement dx is given by,

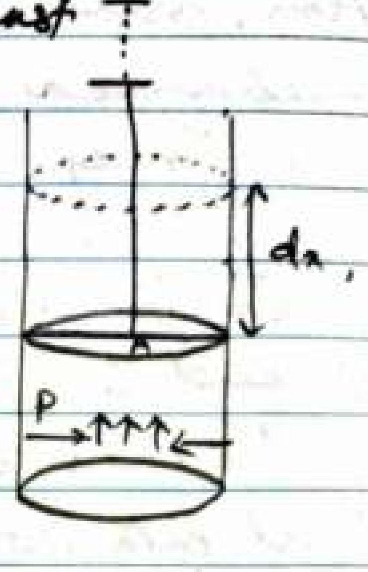


Fig: Expansion of gas.

$$dW = Fdx \cdot \longrightarrow \textcircled{2}$$

Where F is the force exerted by the gas on the piston.

If A is area of the piston and P is the pressure of that instant when displacement dx is taking place.

$$dW = PAdx = PdV \longrightarrow \textcircled{3}$$

Then, the total workdone by the ~~piston~~ gas on the piston is found by integration,

$$W = \int dW = \int_{V_i}^{V_f} PdV \,. \longrightarrow \textcircled{4}\,,$$

Workdone in Certain process;

1. Isothermal Process;

In a isothermal process, the temperature of the system remains constant throughout the change.

In this process, work is done by a gas when it is allowed to expand isothermally.

Let V_1 and V_2 be the initial and final volumes respectively. The workdone for a small change in volume dV is given by.

$$dW = PdV \longrightarrow ①$$

When gas expands from V_1 to V_2,

$$W = \int_{V_1}^{V_2} PdV \longrightarrow ②$$

Since, the expansion is isothermal,

$$PV = RT \quad (\text{for 1 mole of gas}).$$

$$P = \frac{RT}{V}$$

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

or $W = 2.3026\, RT \log_{10} \frac{V_2}{V_1}. \longrightarrow ③$

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2. Isobaric Process; In this process, the pressure of the system remains constant throughout the process.

Let V_1 and V_2 be the initial and final volumes of one gm mole of a perfect gas enclosed in an expanding chamber in a constant pressure.

The workdone for a very small change in volume, dV is $dW = PdV \longrightarrow ①$.

When the gas expands from V_1 to V_2

∴ Workdone, $W = \int_{V_1}^{V_2} PdV$

or $W = P(V_2 - V_1) \rightarrow ②$.

Here P is kept in constant.

3. Adiabatic process : In adiabatic process, the system is not allowed to exchange heat with its surroundings during the change of state.

This can be done by thermally insulating the system from the surroundings by using thermal insulating materials or by performing the process so rapidly, so that gas does not find time to exchange heat.

The internal energy of the gas remains constant in this process.

Suppose one gram mole of a perfect gas is enclosed in a cylinder having perfectly insulating walls.

Let the gas expands adiabatically from initial pressure P_1 and volume V_1 (at point A) to final pressure P_2 and final volume V_2 (at point B) as shown in figure.

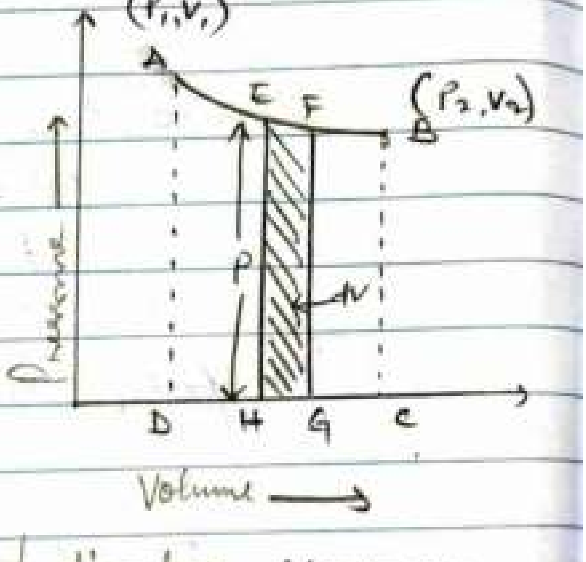


Fig : Indicator diagram.

Then the workdone by the gas during this expansion is given by,

$$W = \int_{V_1}^{V_2} P\,dV = \text{Area } ABCD \;\longrightarrow ①$$

During an adiabatic process, we have the relation, $PV^\gamma = K$ (Constant).

$$P = \frac{K}{V^\gamma} \; B. \longrightarrow ②$$

Substituting this value in eqn. ①, we get

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

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

But A and B lie on the same adiabatic curve,
So, $P_1V_1^\gamma = P_2V_2^\gamma = K$.

$$\therefore W = \frac{1}{1-\gamma}\left[\frac{P_2V_2^\gamma}{V_2^{\gamma-1}} - \frac{P_1V_1^\gamma}{V_1^{\gamma-1}}\right]$$

$$\boxed{W = \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]}$$

If $P_2V_2 = nRT_2$ and $P_1V_1 = nRT_1$ (for n no. of moles of gas.

$$\therefore W = \frac{1}{1-\gamma}\left[nRT_2 - nRT_1\right]$$

4. Isochoric Process: In isochoric process, the state of gas changes in such a manner that its volume remains constant during the process. There is a change in the pressure of the gas when heat is given to it or taken from it, no ~~wo~~ external work is done.

The isochoric process is represented by a parallel line to the pressure axis in the P-V diagram.

So, as $dV = 0$,

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

No area is enclosed by the P-V diagram (indicator diagram).

1. <u>First law of thermodynamics:</u>

In simple terms, Accn to first law of thermodynamics, if heat is recognized as a form of energy, then the total energy of a system plus its surroundings is conserved. In other words, the total energy of the universe remains constant.

① The change in an internal energy $^{(U)}$ of the system is equal to the difference between heat added (Q) to the system from its surroundings and work done (W) by the system on its surroundings.

$$dU = dQ - dW.$$

The idea of 1st law is similar to that we pay for energy in the form of electricity, gas, oil, etc to have heat, the amount of heat that we get is proportional to the amount of energy that we pay for. <u>Heat</u> is generated by doing <u>work</u> on the system.

Eg. Work is given by using force × displacement. It is being identified as Pressure $(P) = F/A$ (Force per unit area)

and displacement is being identified as change in volume. (= displacement of surface area × area = $A.dx$).

Eg. Another example of work involves electricity.

The Force is identified as EMF (electromotive force), and Displacement as the charge transferred (= electric current × time).

Simply, the 1st law is that the net flow of <u>energy</u> across the boundary of a system is equal to the <u>change in energy</u> of the system.

Note: In thermodynamics, it is to consider that how energy flow across a boundary of a system.

① One is workdone on a system or
Workdone by the system.

② Other is Flow of heat is either by conduction or radiation.

Consider quantity dQ of heat supplied to the system. Then, this heat supplied is generally spend in three ways.

① Some partial of heat is spent in raising the temperature of a body, it is equivalent ~~to~~ of increasing its internal KE.

② A part ~~x~~ of heat is spent in doing internal work against molecular attractions, which is equivalent ~~to~~ of increasing the internal P.E.

③ The remaining heat energy is spent in expanding the system against external pressure. i.e. in doing external work.

If dU_K is the change in internal KE and dU_P is the change in internal P.E. and dW is the external workdone.

Since, energy can neither be created nor destroyed, but only converted from one form to another. We have,

$$dQ = dU_K + dU_P + dW.$$

But $dU_K + dU_P = dU$, So,

$$dQ = dU + dW. \longrightarrow ②$$

This equation② represents the differential form of 1st law.

In all transformations, the heat energy supplied to the system must be balanced/ equal by external workdone plus the increase in internal energy.

So, the 1st law of thermodynamics establishes an exact relationship between heat and work.

Conclusions :-

(i) As U is a state function, in a cyclic process,

$$\oint dU = 0,$$

$$\therefore \oint dQ = \oint dU + \oint dW = \oint dW.$$

∴ Therefore, total work~~done~~ obtained is same as the net heat supplied and no excess work is produced.

(ii) In isothermal ~~ch~~ process, there will be no change in internal energy as at constant temperature, internal energy is constant.

i.e. $dU = 0$,

So, $dQ = dW$. This means all the heat supplied to the system is spent to external work.

(iii) In adiabatic process, there will be no exchange of heat between the body and the surroundings.

i.e. $dQ = 0$, So, $dW = -dU$.

So, work is done by the system at the expense of its own internal energy.

— x —

Date:

Applications of First law of Thermodynamics:

① Isothermal process:

When a change in pressure and volume of a substance takes place but the temperature remains constant, the change (process) is said to be isothermal.

Thus, in an isolated change the temperature is kept constant by adding heat or taken from the substance. As temperature is constant, there is no change Internal Energy. $dU = 0$.

Accn to 1st law,

$$dQ = dU + dW$$

$$\therefore dQ = dW.$$

So, In isothermal process, heat added (or subtracted) is equal to workdone on (or by) the gas.

For perfect gas isothermal change is represented by Boyle's law,

$$PV = \text{constant}$$

Accn to Boyle's law, at fixed temperature, the volume of the gas (V) is inversely proportional to the pressure (P) exerted by the gas.

② Adiabatic change:

In adiabatic change the temperature does not remains constant and no heat from outside is supplied to the system or taken away from it. It does not mean that the heat of the system remains constant.

$$\therefore dQ = 0.$$

Accn to 1st law,

$$dQ = dU + dW$$

$$0 = dU + dW.$$

$$dU = -dW$$

$\therefore$ In adiabatic process,

Increase (or decrease) of U = External workdone on (or by) the system;

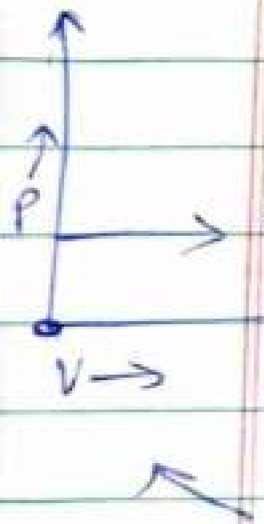
③. **Isobaric Process**: A thermodynamic process, which takes place at constant pressure is called isobaric process. So, Acc^n to 1st law,

$$dQ = dU + dW,$$

So, the amount of heat supplied is partly used in doing external work due to increase in temperature.

If pressure remains constant, P and increase in volume dV, then external workdone

$$dW = PdV$$



In P-V diagram -

④ **Isochoric process**: A thermodynamic process in which volume of the system remains constant is known as an isochoric process.

Accn. to first law of thermodynamics

$$dQ = dU + dW.$$

Since, the volume remains constant, $dV = 0$.

So, $dW = PdV = 0$.

$$\therefore\ dQ = dU. \longrightarrow ①$$

Thus, ~~the~~ whole of the heat supplied to the system is used to increase its internal energy only.

P-V diagram for an isochoric process is.

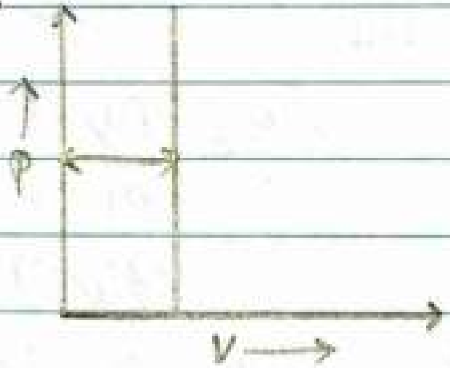


Figure: P-V diagram of isochoric process.