4

Change of State

4·1 Change of State

A substance can exist in three states *viz.*, solid, liquid and gas. The particular state of a substance depends on its temperature. According to the kinetic theory, the molecules of a substance in the solid state have less degrees of freedom than a substance in the liquid or gaseous state. The molecules are more free to move in the gaseous state. The change of state can be brought about by supplying or withdrawing heat from the substance. Ice is the solid state of water. By supplying heat to ice, it can be changed into water. Similarly by supplying heat to water, it can be converted into the gaseous state (steam). The reverse processes occur when heat is withdrawn from steam. This is true for all substances. Even permanent gases like oxygen, nitrogen, hydrogen etc. can be liquefied at low temperatures.

For a given substance, the change of state takes place at a fixed temperature and at a given pressure and *vice versa*. When the substance changes from the solid to the liquid state, the heat supplied at constant temperature (called melting point) is used in overcoming the forces of intermolecular attraction. The mean molecular distance increases and the molecules are more free to move. Similarly, when the substance changes from the liquid to the gaseous state at a fixed temperature (called the boiling point) at standard atmospheric pressure, the heat supplied is used in increasing the mean molecular distance. The molecules become free to move about in the whole space available to them.

4·2 Latent Heat of Fusion

Take small pieces of ice in a beaker. Fix a thermometer to note the temperature of ice in the beaker. Heat the beaker slowly. Ice melts but the thermometer does not show any rise in temperature. When the whole ice has melted the temperature of water rises and

it is indicated by the thermometer. During the processes of conversion from ice to water (change of state from solid to liquid) the heat supplied is used to change the state of ice from solid state to liquid state. This heat is called latent heat. Latent means hidden *i.e.* which is not indicated by the thermometer.

It has been found that one gram of ice takes 80 calories of heat to get itself converted to water. This heat is called latent heat of fusion of ice. Its unit is cals/gram.

Latent heat of fusion of a substance is defined as the amount of heat required to change the state of one gram of a substance from solid to liquid without any change in its temperature.

The melting point of ice is 0°C at a pressure of 76 cm of Hg.

4·3 Laws of Fusion

(1) Every substance changes its state from solid to liquid at a particular temperature (under normal pressure) called the melting point.

(2) As long as the change of state takes place, there is no change in temperature.

(3) One gram of every substance requires a definite quantity of heat for change of state from solid to liquid and it is called the latent heat of fusion of that substance. It is different for different substances.

(4) Some substances show increase in volume on melting *e.g.* wax, ghee etc. while some other substances show decrease in volume on melting *e.g.*, ice.

(5) The melting point of those substances which decrease in volume on melting, is lowered with increase in pressure.

(6) The melting point of those substances which increase in volume on melting, is increased with increase in pressure.

Note. (1) Ice decreases in volume on melting and its melting point is lowered with increase in pressure.

(2) The melting point or solidification point is the same for a substance.

4·4 Practical Applications

(1) Aquatic animals live underneath water in ponds and lakes in winter. Ice is formed on the surface of the pond, and it remains on the surface due to its increase in volume and hence lesser density.

(2) Rocks in the mountains break in frosty weather. Water, which may be locked up in the pores of the rock, may freeze into ice and there is increase in volume. This produces cracks in the rocks.

(3) Fertility of the soil increases due to the splitting of the soil in frosty weather. Water freezes into ice and there is increase

in volume. This increase in volume of ice disintegrates the soil.

(4) Alloys which expand on solidification are used for better casting. The alloy in the liquid form is put into the cast. When it solidifies, there is increase in volume and a sharp casting is obtained. Type metal expands on solidification.

4·5 Effect of Pressure on Freezing Point of Ice—Regelation

Melting point of ice is lowered with increase in pressure. Take a slab of ice. Take a wire and fix two weights (5 kg each) at its two ends. Put the wire over the slab as shown in Fig. 4·1.

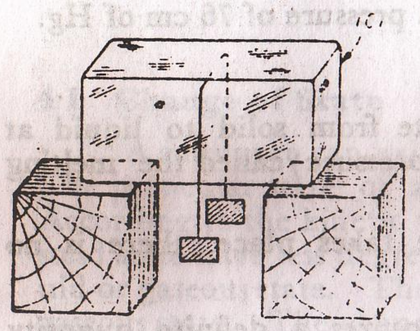


Fig. 4·1

The wire passes through the ice slab. Just below the wire, ice melts at a lower temperature due to increase in pressure. When the wire has passed, the water above the wire freezes again. Thus the wire passes through the slab and the slab does not split. This phenomenon of refreezing is called *Regelation*.

In a similar way it is possible to freeze two pieces of ice by applying pressure and then releasing them.

Examples. (1) Water pipes burst in winter in cold countries due to solidification of water into ice. When water is converted into ice there is increase in volume and the pipes are likely to burst.

(2) When wheels of a cart pass over snow, it melts due to increase in pressure exerted by the wheels. When the wheel passes over, the water formed on the wheel solidifies due to regelation. Due to this reason wheels are covered with snow.

(3) Skating is possible on snow due to the formation of a thin layer of water formed below the skates. The water is formed due to the increase of pressure and it acts as a lubricant.

4·6 Impurities lower Freezing Point

When salt is mixed with ice, some ice melts taking heat from the salt. The temperature of the mixture decreases. Further, the salt dissolves in the water formed and takes latent heat from the mixture. The temperature of the mixture is decreased further. In this way, with a freezing mixture of salt and ice in the ratio 1 : 3, temperatures as low as —13°C can be obtained. A freezing mixture consists of powdered ice, common salt and ammonium nitrate.

Similarly when sugar is dissolved in water, the water is cooled.

4·7 Determination of Melting Point of Wax

Take sufficient quantity of wax in a test tube and fix a cork along with a thermometer. Adjust the test tube in a beaker containing water (Fig. 4·2). Heat the water to its boiling point. The wax in the test tube melts and is in the liquid state. Extinguish the burner and allow the water and wax to cool. Note the temperature of wax after every one minute till the temperature of wax is about 30°C. Draw a graph between temperature and time. The temperature corresponding to the horizontal line in the graph gives the melting point of wax. At this temperature, liquid wax is converted into the solid wax without change of temperature (Fig. 4·3).

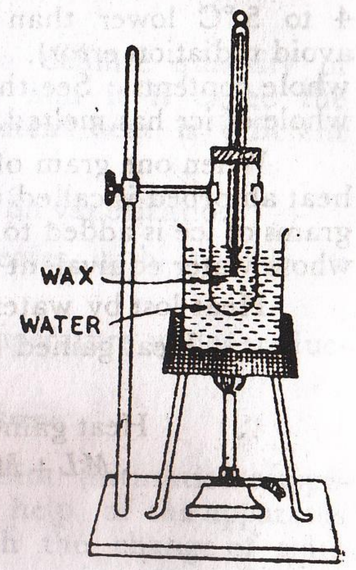


Fig. 4·2

Plot a graph between temperature along the *Y*-axis and time in minutes along the *X*-axis.

The temperature corresponding to the line *BC* gives the melting point of wax. The portion *AB* shows the liquid state of wax and below *C* the graph represents the solid state.

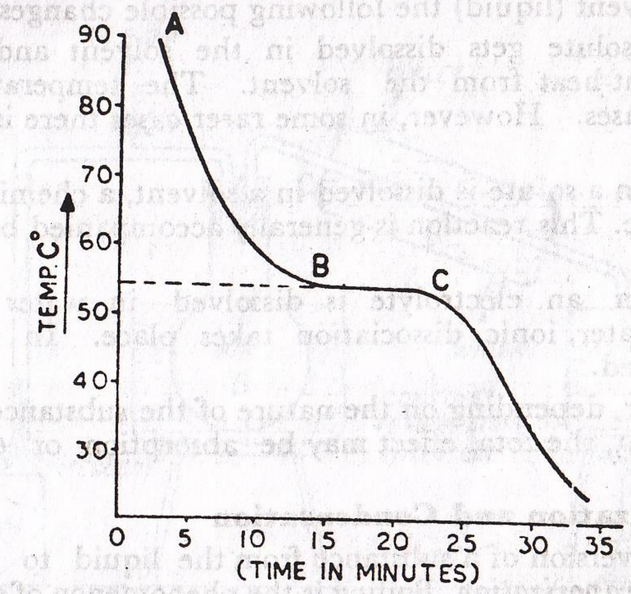


Fig. 4·3

4·8 Determination of Latent Heat of Fusion of Ice

Take a calorimeter. Weigh the calorimeter along with the stirrer. Weigh the calorimeter with stirrer and the lid. Heat some water in a beaker to a temperature of about 10°C higher than t' room temperature. Fill the calorimeter to about half, with hot water. Weigh the calorimeter, hot water, stirrer and lid. Place it

in a wooden box. Note the temperature of water in the calorimeter. It should be about 4 to 5°C higher than the room temperature. Take small pieces of ice in a blotting paper. Add dry pieces of ice gradually into the calorimeter and stir. Continue adding dry pieces of ice into the calorimeter, till the temperature of water is about 4 to 5 °C lower than the room temperature. (This is done to avoid radiation error). Note the final temperature and weigh the whole contents. See that before recording the final temperature the whole of ice has melted.

When one gram of ice melts into water at 0°C, the amount of heat absorbed is called the latent heat of fusion of ice. Suppose M grams of ice is added to m grams of water at t°C in a calorimeter whose water equivalent is W. The final temperature reached $=T$°C.

Heat lost by water and calorimeter $= (m+W)(t-T)$

$\therefore$ Heat gained by ice

$$= ML+MT$$

$\therefore$ Heat gained = Heat lost

$$ML+MT = (m+W)(t-T)$$

$$L = \frac{(m+W)(t-T)}{M} - T$$

Hence latent heat of fusion of ice can be determined.

4·9 Heat Absorbed in Solution

When a solution is formed by dissolving a solute (solid substance) in a solvent (liquid) the following possible changes take place.

(1) The solute gets dissolved in the solvent and takes the necessary latent heat from the solvent. The temperature of the solution decreases. However, in some rarer cases there is absorption of heat.

(2) When a solute is dissolved in a solvent, a chemical reaction may take place. This reaction is generally accompanied by evolution of heat.

(3) When an electrolyte is dissolved in water *e.g.* $CuSO_4$ dissolved in water, ionic dissociation takes place. In this process heat is absorbed.

However, depending on the nature of the substance *i.e.* solute and the solvent, the total effect may be absorption or evolution of heat.

4·10 Vaporization and Condensation

The conversion of a substance from the liquid to the vapour state is called *vaporization*. Boiling is the phenomenon of vaporization accompanied by ebullition *i.e.*, violent ebullition of bubbles. However vaporization can take place without boiling. The water kept on an open plate in summer evaporates and there is a change of state. But there is no boiling. Conversion of water to steam is vaporization. The conversion of the substance from the vapour state to the liquid state is called condensation. Conversion of steam into water is called condensation. Rain is caused due to the condensation of water vapour in the clouds.

4·11 Laws of Ebullition or Boiling

(1) Every liquid changes its state from liquid to its vapour at a particular temperature (under normal pressure) called the boiling point.

(2) As long as the change of state takes place, there is no change in temperature.

(3) One gram of every liquid requires a definite quantity of heat for change of state from liquid to vapour and it is called the latent heat of vaporization of that liquid. Latent heat is different for different substances.

(4) All liquids show increase in volume on vaporization.

(5) The boiling point of a liquid increases with increase in pressure of a liquid.

(6) The liquid can boil at a lower temperature under reduced pressure.

4·12 Change in Boiling Point with Pressure

The effect of pressure on the boiling point (saturation temperature) of a liquid can be studied with the help of the apparatus shown in Fig. 4·4. The temperature at which the change of state from liquid to vapour takes place is called saturation temperature. The saturation temperature increases with increase in pressure. If the pressure is 1 atmosphere, the saturation temperature is called the boiling point. The vessel A contains the liquid (say water). It is

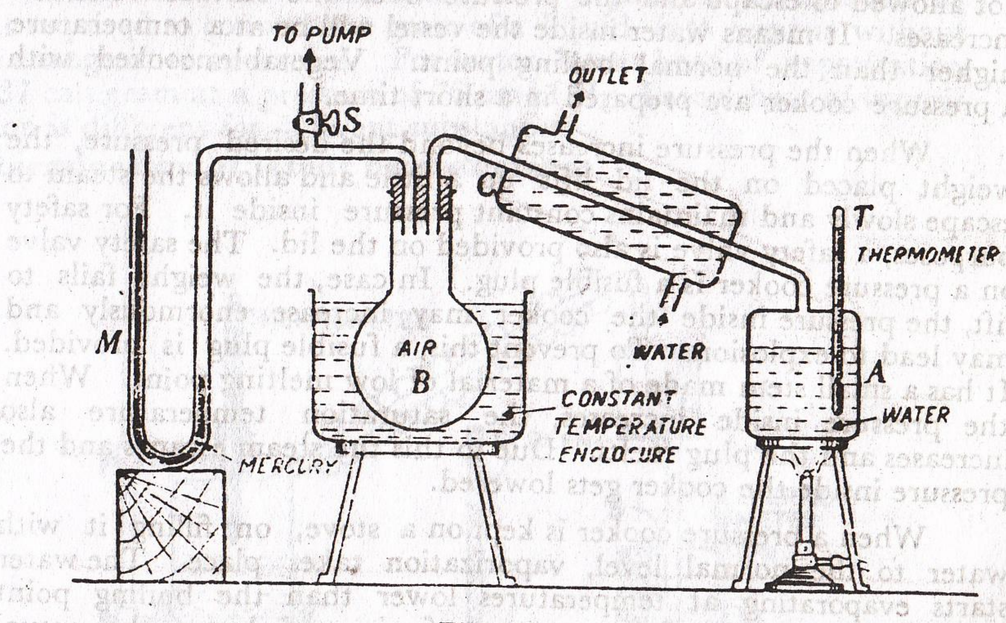


Fig. 4·4

connected to the flask B through a tube C surrounded by a water condenser. To measure the pressure of air over the surface of the liquid in A, a manometer is used.

The pressure of air inside A and B can be changed with the help of the compression pump or evacuation pump.

The stopcock S is opened. With the help of the compression pump, air is compressed into B. The stopcock is closed. Pressure of air in A and B is shown by the manometer. It is more than the atmospheric pressure.

The liquid is heated and the temperature at which it boils is recorded by the thermometer. At the boiling point, the temperature of the liquid remains constant. The condenser through which cold water is circulated prevents steam to enter the vessel B. The steam is condensed and condensed water flows back to A.

In this way at various pressures, the corresponding boiling points of the liquid can be determined. For low pressure, the vacuum pump is used. It is found that the boiling point of a liquid increases with increase in pressure and decreases with decrease in pressure.

The boiling point of water at 76 cm of Hg pressure is 100°C. The boiling point of water at double the normal pressure (*i.e.*, 152 cm of Hg) is about 128°C.

Applications

Papin's Digestor and Pressure cookers are based on the principle that the boiling point of a liquid increases with increase in pressure.

The pressure inside the pressure cooker is much higher than the atmospheric pressure. The steam produced inside the cooker is not allowed to escape and the pressure over the surface of water increases. It means water inside the vessel will be at a temperature higher than the normal boiling point. Vegetables cooked with a pressure cooker are prepared in a short time.

When the pressure increases beyond the desired pressure, the weight placed on the lid lifts up a little and allows the steam to escape slowly and maintains constant pressure inside it. For safety purposes, a safety valve is also provided on the lid. The safety valve on a pressure cooker is a fusible plug. In case, the weight fails to lift, the pressure inside the cooker may increase enormously and may lead to explosion. To prevent this, a fusible plug is provided. It has a small stem made of a material of low melting point. When the pressure inside increases, the saturation temperature also increases and the plug melts. Due to this the steam escapes and the pressure inside the cooker gets lowered.

When a pressure cooker is kept on a stove, on filling it with water to the normal level, vaporization takes place. The water starts evaporating at temperatures lower than the boiling point temperature because of the pressure of air and hence the actual pressure of evaporation is the difference between the atmospheric pressure and the partial pressure of air. As the temperature increases, the rate of evaporation increases and the air is expelled. Gradually, due to the expulsion of air, the vapour pressure of water increases and hence the temperature. After all the air is expelled, boiling takes place. The steam starts rushing out through the opening.

The weight is now placed on the opening. Further, steam that is produced increases the pressure and hence the boiling point is also raised. As soon as the upward force due to the steam pressure is sufficiently high, the weight lifts and allows the steam to escape. This maintains constant pressure and hence constant temperature. If the weight is placed before the expulsion of steam, the partial pressure will not be as high as it ought to be and hence the temperature is not high.

4·13 Franklin's Experiment

Take a flask containing water. Heat it till the water begins to boil. When the water is boiling, the air escapes to the atmosphere. After some time, close the mouth of the flask with an air tight rubber cork. Invert the flask and fix it on the retort stand (Fig. 4·5). Pour cold water over the flask. Due to the condensation of steam, the pressure over the surface of water decreases. Water inside the vessel begins to boil. This experiment shows that water boils at a lower temperature under reduced pressure.

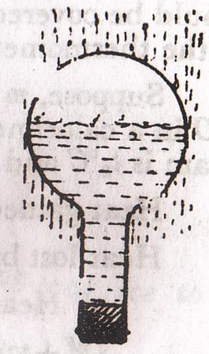


Fig. 4·5

In the laboratory, while preparing steam, the temperature of steam is usually less than 100°C because the atmospheric pressure is less than 76 cm of Hg.

4·14 Latent Heat of Vaporization

latent heat of vaporization of a liquid is the amount of heat required to convert one gram of a liquid into vapour without any change in temperature. For water, latent heat of vaporization is 537 cals/gram at a pressure of 76 cm of Hg. Latent heat of vaporization is different for different substances.

Determination of latent heat of steam

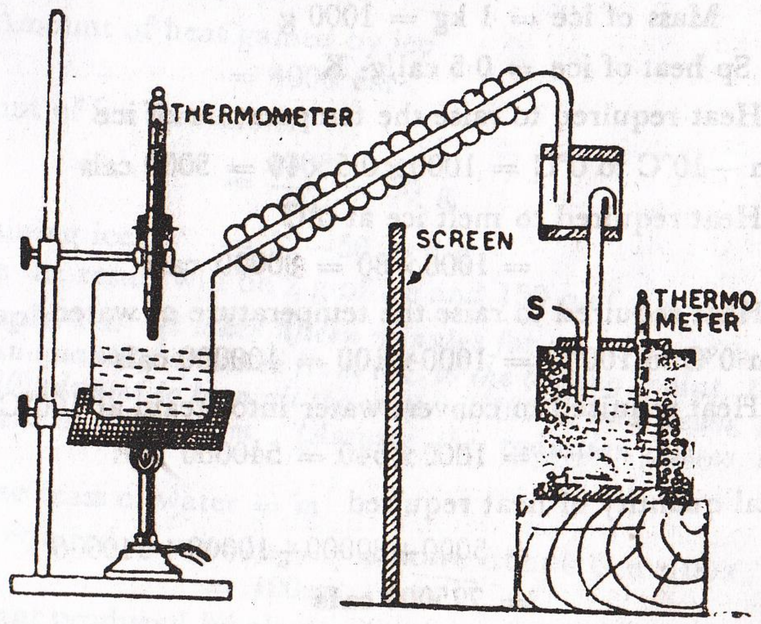


Fig. 4·6

Take a calorimenter. Weigh the calorimeter along with the stirrer. Weigh the calorimeter along with the stirrer and the lid. Fill the calorimeter to about 2/3 with water and weigh along with the stirrer and the lid. Heat the water in the boiler to produce steam. The boiler is fitted with a steam trap as shown in Fig. 4·6. The whole of the delivery tube is covered with wool. When steam starts coming out of the end of the tube, note the temperature of steam. Note the temperature of water in the calorimeter. Now clean the end of the tube with a blotting paper to remove water drops. Insert the tube quickly into the calorimeter and pass steam. When the temperature of water is raised through about 10°C, take out the tube carefully. Continue stirring. Note the final temperature. Remove the thermometer carefully and weigh the calorimeter. The calorimeter should be covered with a lid and no water drops should be sticking to the thermometer.

Suppose, m grams of steam is passed into M grams of water at t_1°C in a calorimeter of water equivalent w. The temperature of steam is t_2°C and final temperature is T°C.

Heat gained by water and calorimeter $= (M+w)(T-t_1)$

Heat lost by steam $= mL+m(t_2-T)$

Heat gained = Heat lost

$$(M+w)(T-t_1) = mL+m(t_2-T)$$

$$L = \frac{(M+w)(T-t_1)}{m} - (t_2-T)$$

Hence, latent heat of steam can be determined.

Example 4·1. *One* kilogram *of ice at* -10°C *is heated until the whole of it evaporates. How much heat is required ? Latent heat of fusion of ice* $= 80$ cals *per* gram *and that of steam* $= 540$ cal *per* gram.

Mass of ice = 1 kg = 1000 g

Sp heat of ice = 0·5 cal/g- K

(1) Heat required to raise the temperature of ice from -10°C to 0°C $= 1000\times0{\cdot}5\times10 = 5000$ cals

(2) Heat required to melt ice at 0°C
$= 1000\times80 = 80000$ cals

(3) Heat required to raise the temperature of water from 0°C to 100°C $= 1000\times100 = 100000$ cals

(4) Heat required to convert water into steam at 100°C
$= 1000\times540 = 540000$ cals

Total quantity of heat required
$= 5000+80000+10000+540000$
$= 725000$ cals

Example 4·2. *One* gram *of steam is passed into a calorimeter containing 100* grams *of ice. Calculate the amount of ice melted.*

Heat given out by one gram of steam when converted from steam into water at 100°C $= mL = 1\times537 = 537$ cal.

Heat given out by one gram of water when cooled from 100°C to 0°C
$= 1\times100 = 100$ cal

∴ Total quantity of heat given out by one gram of steam
$= 537+100 = 637$ cal

Suppose the amount of ice melted
$= m$ grams

Latent heat of ice = 80 cal per gram

Heat absorbed by ice
$= 80\,m$ cal

Heat lost by steam = Heat gained by ice

∴ $637 = 80\,m$

or $m = 7{\cdot}96$ g

Example 4·3. *What will be the result of adding 52 g of ice to 100 g of water at 40°C ?*

Mass of water = 100 g

Temperature of water
= 40°C

∴ Heat lost by water when its temperature falls from 40°C to 0°C $= 100\times40$
$= 4000$ cal

If 52 g of ice melts, heat gained by it should be $52\times80 = 4160$ calories. But water can lose only 4000 calories of heat. Therefore, the whole of ice will not melt.

∴ Amount of heat gained by ice
$= 4000$ cal

Amount of ice that melts
$= \frac{4000}{80} = 50$ g

Remaining ice $= 52-50 = 2$ g

Hence the result will be 2 g of ice and 150 g of water at 0°C.

Example 4·4. *It takes fifteen minutes for an electric kettle to heat a certain quantity of water from 0°C to the boiling point 100°C. It requires 80 minutes to turn all the water at 100°C into steam. Determine the latent heat of steam. (Assume the radiation losses to be negligible).*

Suppose mass of water = m

Heat required to raise its temperature from 0°C to 100°C
$= 100\,m$

∴ Heat produced by electric kettle in 15 minutes = $100\,m$

Heat produced by electric kettle in 1 minute

$$= \frac{100\,m}{15}$$

Heat produced by electric kettle in 80 minutes

$$= \frac{100\,m \times 80}{15} \text{ cal}$$

Suppose latent heat of steam $= L$ cal per gram

Heat required by m grams of water to boil off into steam

$$= mL \text{ cal}$$

$$\therefore \quad mL = \frac{100\,m \times 80}{15}$$

or

$$L = \mathbf{533{\cdot}33\ cal/g}$$

Example 4·5. *A refrigerator converts 50 g of water at 15°C into ice at —20°C in one hour. Determine the quantity of heat removed per* minute. *(Specific heat of ice = 0·5)*

Here $m = 50$ g

Heat removed in cooling water from 15°C to 0°C

$$= 50 \times 1 \times 15 = 750 \text{ cal}$$

Heat removed in converting water into ice at 0°C

$$= 50 \times 80 = 4000 \text{ cal}$$

Heat removed in cooling ice from 0°C to —20°C

$$= 50 \times 0{\cdot}5 \times 20 = 500 \text{ cal}$$

Total heat removed in one hour

$$= 750 + 4000 + 500 = 5250 \text{ cal}$$

Heat removed per minute

$$= \frac{5250}{60}$$

$$\doteq \mathbf{87{\cdot}5\ cal/minute}$$

4·15 Bunsen's Ice Calorimeter

Bunsen's ice calorimeter is used to find the specific heat of a solid or a liquid available in a small quantity. It is based on the principle that when ice melts there is decrease in volume. When one gram of ice melts, the decrease in volume is 0·09 cc.

The apparatus consists of a metal calorimeter C fitted inside a bulb B. The bulb B is connected to the cup A through a glass tube. The cup A is fitted with an air tight lid. A capillary tube EF is fixed whose one end dips inside mercury in the cup A The horizontal portion of the capillary tube is fitted on a graduated scale. The upper portion of the bulb B contains water at 0°C. The lower portion of B, the connecting tubes and the cup A contain mercury.

By adjusting the position of the screw T the position of the mercury meniscus in the capillary tube EF can be suitably adjusted. Th whole apparatus is enclosed in a bath of melting ice.

Working. Ether is poured in the calorimeter C. It evaporates and takes heat for evaporation from the surrounding water in B. As water in B is already at 0°C, a small quantity of water surrounding C freezes into ice.

The substance whose specific heat is to be determined is heated to a desired temperature (θ°C). The position of mercury in the capillary EF is noted on the scale.

The substance is transferred quickly into the calorimeter C. The calorimeter is closed with the rubber cork. The substance loses

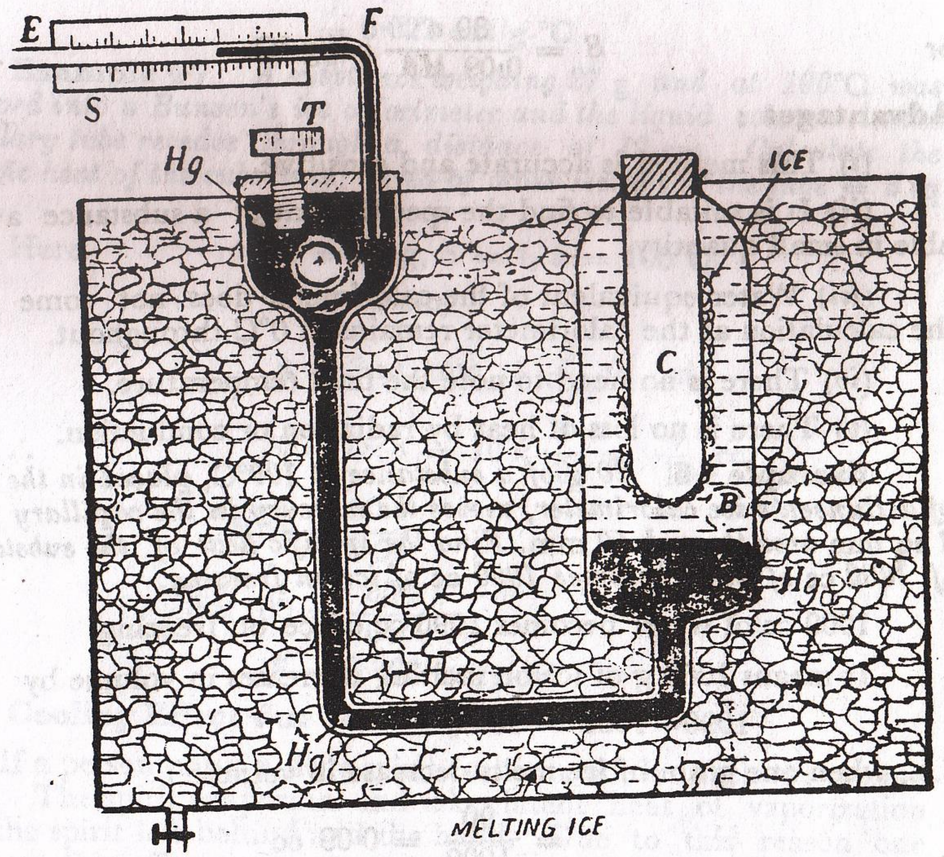


Fig. 4·7

heat to the surrounding ice and cool to 0°C. A small quantity of ice melts and there is decrease in volume. Consequently the mercury in the capillary tube EF recedes. Suppose the length through which mercury has moved $= l$ cm and area of cross-section of the capillary tube $= a$ sq cm.

$\therefore$ Decrease in volume $= v = al$

When decrease in volume is 0·09 cc the amount of ice that melts

$= 1$ gram

When decrease in volume is v cc the amount of ice that melts

$$= m = \frac{v}{0{\cdot}09} \text{ grams}$$

Latent heat of ice $= 80$ cal/g

Heat gained by ice $= 80\,m = \dfrac{80\,v}{0{\cdot}09}$ cal

Heat lost by the substance

$$= MS\,\theta$$

Heat lost = Heat gained

$$\therefore \quad MS\,\theta = \frac{80\,v}{0{\cdot}09}$$

or
$$S = \frac{80\,v}{0{\cdot}09\,M\theta} \text{ cal/g-°C} \qquad \ldots(i)$$

Advantages :

(*i*) This method is accurate and sensitive.

(*ii*) It is suitable to find the specific heat of a substance available in small quantity.

(*iii*) Water equivalent of the calorimeter does not come into the calculation as the calorimeter remains at 0°C throughout.

(*iv*) There is no need to note the final temperature.

(*v*) There is no loss of heat by radiation or conduction.

Example 4·6. *20 g of a substance at 100°C, placed in the tube of a Bunsen's ice calorimeter, moves the mercury in the capillary tube 1 sq mm area through 50 mm. Find the specific heat of the substance if 1000 cc of water becomes 1090 cc of ice on freezing.*

1000 cc of water becomes 1090 cc of ice on freezing.

It means 1000 g of ice on melting decreases in volume by

$$1090 - 1000 = 90 \text{ cc}$$

i.e., when one gram of ice melts decrease in volume

$$= \frac{90}{1000} = 0{\cdot}09 \text{ cc}$$

Mass of the substance

$$= M = 20 \text{ g}$$

$$\theta = 100°\text{C}, \qquad S = ?$$

Area of cross-section $= a = 1$ sq mm

$$= \frac{1}{100} \text{ sq cm}$$

Length of the column through which liquid moves

$$= 50 \text{ mm} = 5 \text{ cm}$$

Decrease in volume $= v = l \times a = 5 \times \dfrac{1}{100}$

$$= \frac{1}{20} \text{ cc}$$

$$MS\theta = \frac{80\,v}{0{\cdot}09}$$

$$S = \frac{80\,v}{0{\cdot}09 \times M \times \theta}$$

$$= \frac{80 \times 1}{20 \times 0{\cdot}09 \times 20 \times 100}$$

$$= \mathbf{0{\cdot}022 \text{ cal/g-°C}}$$

Example 4·7. *A substance weighing 27 g and at 100°C was dropped into a Bunsen's ice calorimeter and the liquid column in the capillary tube recedes through a distance of 10 cm. Calculate the specific heat of the substance. Area of cross-section of the tube = 3 sq mm.*

Here
$$M = 27 \text{ g}, S = ?, \theta = 100°\text{C}$$

$$l = 10 \text{ cm},$$

$$a = 3 \text{ sq mm} = \frac{3}{100} \text{ sq cm}$$

$$\therefore \quad v = l \times a = 10 \times \frac{3}{100} = \frac{3}{10} \text{ cc}$$

$$MS\theta = \frac{80\,v}{0{\cdot}09}$$

$$27 \times S \times 100 = \frac{80 \times 3}{10 \times 0{\cdot}09}$$

$$S = \mathbf{0{\cdot}098 \text{ cal/g-°C}}$$

4·16 Cooling Effect due to Vaporization

If a person pours a little spirit on his hand, he feels a cooling effect. The spirit evaporates and takes latent heat of vaporization from the spirit left behind and the hand. Due to this reason one feels a cooling effect

Thus, whenever evaporation of a liquid takes place, the remaining liquid shows a fall in temperature.

The molecules of a liquid are always in a state of random motion. They collide with each other and they may or may not change their respective kinetic energies. Due to the collision a certain molecule may acquire more energy than the energy with which it is held. As soon as this happens the molecule flies off, *i.e.*, it leaves the liquid surface. This is called evaporation. If no external heat is supplied it is obvious that the mean kinetic energy of the molecules decreases and the temperature of the liquid falls. This explains cooling caused by evaporation. If the moving vapour molecules come near to each other at sufficiently low velocities, they

experience a greater magnitude of force of attraction. The molecules coalesce and this results in condensation. Rate of evaporation increases with increase in temperature of the liquid and decrease in pressure over the liquid surface.

4·17 Cryophorus

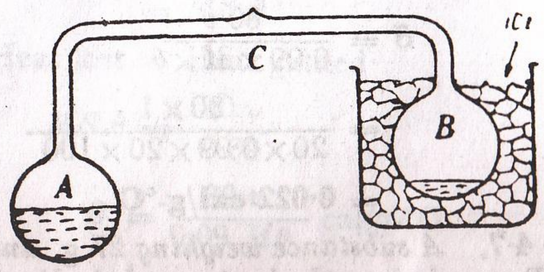


Fig. 4·8.

A cryophorus consists of two glass bulbs *A* and *B* connected through a glass tubing *C* (Fig. 4·8). The bulb *A* contains water.

Air in *B* and the tube is removed with an evacuation pump and the tube is sealed. The space inside *B* and the tube contains water vapour only. The vessel *B* is surrounded by freezing mixtures. Water vapour in *B* condenses and the pressure over the surface of water in *A* falls. Evaporation of water takes place. The process continues at a rapid rate and the temperature of water in *A* decreases. After some time water in *A* begins to freeze.

To prevent any heat from the surroundings to flow into *A*, it is covered with a non-conducting material like cotton or flannel.

4·18 Examples of Cooling Caused by Evaporation

1. In hot weather, we perspire. Water from the body comes out of the fine pores of the skin. Water evaporates and takes heat of vaporization from the body. Due to this reason we feel a cooling sensation.

2. A person wearing wet clothes feels chill. Water evaporates taking the latent heat of vaporization from the body and the person feels chill.

3. Water in an earthen pot remains cool in summer. Water comes out of the pores of the vessel and evaporates. During evaporation, the latent heat is taken from the remaining water. Therefore water remains cool in an earthen vessel.

4. Streets, floors, gardens, lawns etc. are watered in summer. Water evaporates taking the latent heat from them and keeps them cool.

5. Dogs keep their tongues usually out in summer. Water evaporates from the tongue and keeps it cool.

6. *Khas-khas* screens are commonly used in summer. Water is poured on them. Water evaporates and takes heat from them and the air in the room. Due to this reason the room is kept cool.

7. During high fever, a wet cloth soaked in 'Eau de cologne' or ice cold water is kept on the forehead. The liquid evaporates rapidly and takes heat from the head and the body.

8. Hot liquids are poured in a plate to increase the surface area. The rate of evaporation increases and the liquid cools quickly.

9. When a wet muslin piece is wrapped around the bulb of a thermometer, the thermometer records fall of temperature. Water evaporates and takes latent heat from mercury in the bulb.

10. In a packed hall in summer a person feels uneasy. Perspiration from his body does not evaporate. As soon as he comes out of the hall he feels a sudden cooling sensation. Perspiration evaporates rapidly and takes heat from his body.

4·19 Refrigeration

The second law of thermodynamics as given by Clausius gives the principle of working of a refrigerator and ice plants.

"It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance."

This part is applicable in the case of ice plants and refrigerators. Heat itself cannot flow from a body at a lower temperature to a body at a higher temperature. But, it is possible, if some external work is done on the working substance. Take the case of an ammonia ice plant. Ammonia is the working substance. Liquid ammonia at low pressure takes heat from the brine solution in the brine tank and is converted into low pressure vapour. External work is done to compress the ammonia vapour to high pressure. This ammonia at high pressure is passed through coils over which water at room temperature is poured. Ammonia vapour gives heat to water at room temperature and gets itself converted into liquid again. This high pressure liquid ammonia is throttled to low pressure liquid ammonia. In the whole process ammonia (the working substance) takes heat from brine solution (at a lower temperature) and gives heat to water at room temperature (at a higher temperature). This is possible only due to the external work done on ammonia by the piston in compressing it. The only work of electricity in the ammonia ice plant is to move the piston to do external work on ammonia. If the external work is not done, no ice plant or refrigerator will work. Hence, it is possible to make heat flow from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance.

4·20 Ammonia Ice Plant

Ammonia ice plant is commonly used to manufacture ice. It is based on the principle that evaporation causes cooling. Moreover in this plant, heat flows from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance. The schematic sketch of an ammonia ice plant is shown in Fig. 4·9.

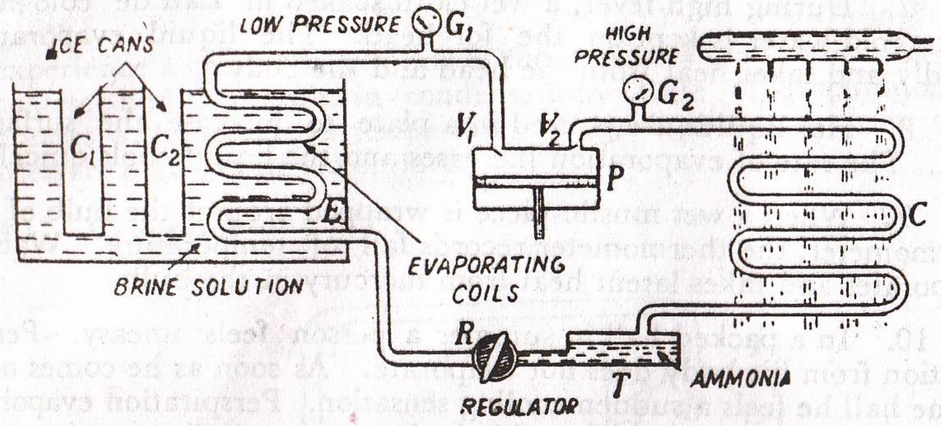


Fig. 4·9

(1) T is a reservoir containing ammonia liquid.

(2) R is a regulator called the expansion valve or throttle valve. High pressure liquid expands towards the low pressure side and with the fall in pressure there is a fall in saturation temperature. Liquid ammonia at low temperature and pressure entering the coils evaporates and takes heat from the surrounding brine solution.

(3) The brine tank contains ice cans C_1 and C_2 containing pure water.

(4) The compression pump P is worked with the help of an electric motor. It has two valves V_1 and V_2. When the piston is moved outwards, valve V_1 opens and V_2 is closed. Ammonia vapour enters the cylinder. When the piston is moved inwards V_1 closes and V_2 opens. Compressed ammonia vapour is passed through the condensing coils C.

(5) G_1 is the low pressure gauge and G_2 is the high pressure gauge. When the pump works, the rate of evaporation of ammonia liquid in the evaporating coils increases and the temperature of the brine solution gradually falls.

(6) The compressed ammonia vapours passing the condensing coils give heat to water falling over the coils. Ammonia vapours get condensed and liquid ammonia is formed. The liquid ammonia enters the reservoir.

The cycle of operations is repeated and the temperature of brine solution in the tank decreases to —8°C. Water in the cans freezes to ice.

(*i*) If the pump stops working, then the cyclic process does not take place and the temperature of the brine tank does not fall.

(*ii*) The function of electricity is to move the piston to and fro with the help of the electric motor and to compress the vapours.

(*iii*) Ammonia is the working substance. It takes heat from the brine solution (at low temperature) and transfers heat to the water falling on the condensing coils at the room temperature. It means heat is transferred from a body at a lower temperature to a body at a higher temperature. Ordinarily it is not possible. But by doing

external work (with the help of the pump) on the working substance this transfer of heat is possible and this is in accordance with the second law of thermodynamics.

4·21 Solid Carbon Dioxide—(Dry Ice)

A cylinder containing liquid CO_2 is taken. A muslin bag is tied to the nozzle. The cylinder is placed in a slanting position (Fig. 4·10). The valve V is opened and the liquid CO_2 enters the muslin bag. The liquid CO_2 evaporates rapidly and takes the latent heat of vaporization from the remaining liquid in the bag. Liquid CO_2 solidifies and solid CO_2 is formed in the muslin bag.

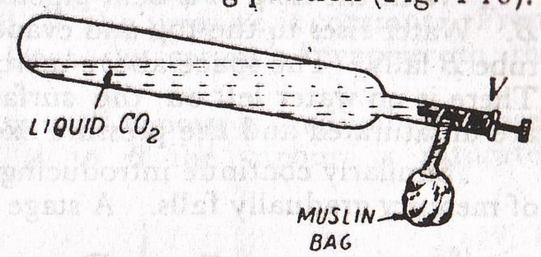


Fig. 4·10

The temperature of solid CO_2 is —78°C and it is also called *dry ice*. It is commonly used by doctors for dressing the wounds. It serves as refrigerant when mixed with ether. Solid CO_2 does not melt when exposed to air. It directly evaporates and forms its vapours.

4·22 Gas and Vapour

Gas and vapour states are the two distant stages of the same continuous phenomenon. These two states have distinct boundary which is governed by a particular temperature called the critical temperature. Above the critical temperature the substance is in the gaseous state and below the critical temperature it is in the vapour state.

A gas cannot be liquefied by mere application of pressure, howsoever high the pressure may be. A vapour can be liquefied by applying pressure. Therefore to liquefy a gas, first it has to be cooled to a temperature lower than its critical temperature. It means it is converted from a gaseous state to the vapour state. Then a high pressure is applied and the vapours get liquefied.

Critical temperature of a gas is that temperature above which the gas cannot be liquefied by mere application of pressure, howsoever large the pressure may be.

TABLE

Critical Temperature

Substance	*Critical temperature °C*
Water	374
Ammonia	132
Carbon dioxide	31
Oxygen	—119
Hydrogen	—240
Helium	—268

4·23 Saturated and Unsaturated Vapours

Take three clean barometer tubes A, B and C as shown in Fig. 4·11. The level of mercury in each tube is up to the same height. The space above mercury in all the tubes is Torricellian vacuum.

With the help of a bent pipette introduce water into the tube B. Water rises to the top and evaporates. Level of mercury in the tube B falls. The space above mercury in B contains water vapours. There is no water left on the surface of mercury. These vapours are unsaturated and the pressure exerted by the vapours is h.

Similarly continue introducing water in the tube C. The level of mercury gradually falls. A stage is reached when no more water

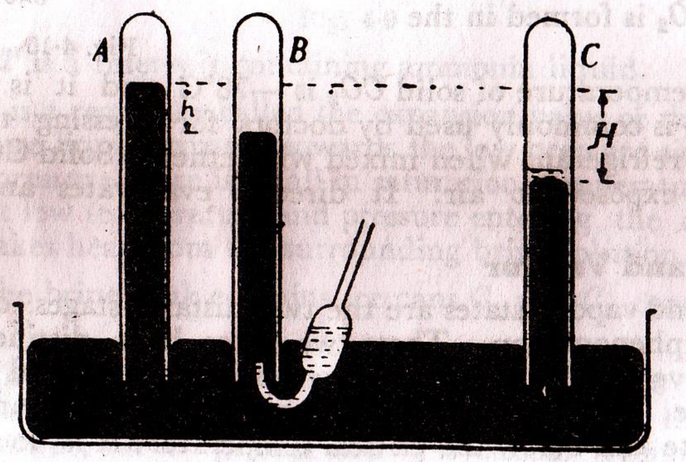


Fig. 4·11

introduced in the tube C evaporaters (Fig. 4·11). It means the space above mercury in C is completely saturated with water vapours. It cannot contain more vapours. The difference in the levels of mercury in A and C is H and it represents the saturated vapour pressure of water at the room temperature.

A space is said to be saturated with water vapours if it cannot contain more vapours. It is unsaturated if it can contain more vapours.

(1) The saturated vapour pressure of a liquid depends on its temperature. The saturated vapour pressure increases with rise in temperature and decreases with fall in temperature.

(2) The saturated vapour pressure depends on the nature of the substance.

(3) The saturated vapour pressure does not depend on the volume occupied by the vapours.

(4) The saturated vapour of a liquid is independent of the presence of the vapours of other liquids present. The vapours should not have any chemical action.

(5) The total pressure exerted by the vapours of all substances is equal to the sum of the pressures exerted by the vapours of individual substances,

$$P = P_1 + P_2 + P_3 + \ldots$$

(6) The saturated vapours do not obey the gas laws whereas unsaturated vapours obey the gas laws.

In Fig. 4·12, the curve AB shows that with decrease in volume the pressure increases. From A to B the vapour is unsaturated and obeys Boyle's law.

At B the vapour is saturated and exerts maximum pressure. With decrease in volume beyond, B, the pressure is constant. From B to C it represents the change from the saturated vapour to the liquid state.

If the temperature of a saturated vapour is gradually increased the pressure increases. From A to B the vapour is saturated

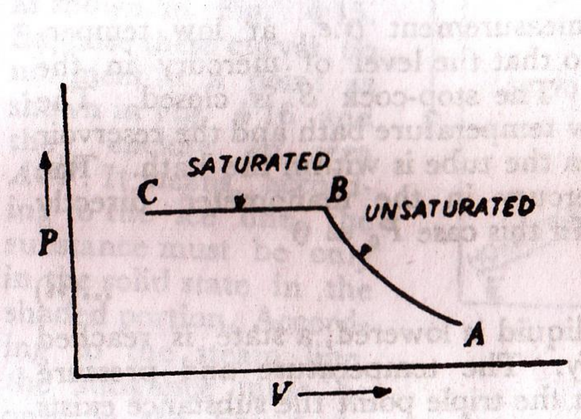


Fig. 4·12

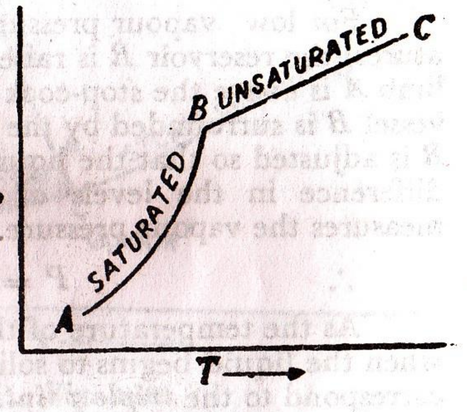


Fig. 4·13

(Fig. 4·13). Beyond B if the temperature is increased, the vapour is unsaturated and pressure increases with temperature. In the region BC, the pressure of the unsaturated vapour is directly proportional to its absolute temperature.

4·24 Vapour Pressure of Liquids

The vapour pressure of a liquid is dependent only on its temperature. The vapour pressure, in general, increases with rise in temperature. The normal boiling point is that temperature at which the vapour pressure of the substance is equal to the normal pressure i.e. 76 cm of Hg. If the atmospheric pressure is lower or higher than the normal pressure, the liquid will boil at a temperature lower or higher than the normal boiling point. Usually the atmospheric pressure in Delhi is less than 76 cm of Hg and water boils at a temperature lower than 100°C. For the measurement of vapour pressure the apparatus shown in Fig. 4·14 is used.

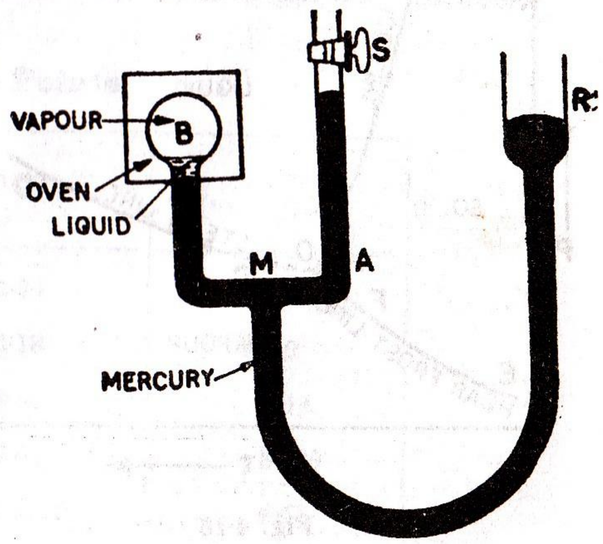


Fig. 4·14

The bulb B contains the vapour in contact with its liquid. M is a manometer limb and R is a reservoir containing mercury. At high temperatures, the stop-cock S is kept open and the tube is filled with a gas at high pressure. Adjust the reservoir R such that the liquid appears in the tube inside the oven. If the pressure of the gas in the limb A is P_0 and the difference in levels of mercury in the manometer limbs is h, then vapour pressure of the liquid at the temperature T is given by

$$P = P_0 + h \qquad \ldots(i)$$

In this way the vapour pressure of the liquid at any temperature can be determined.

For low vapour pressure measurement (*i.e.*, at low temperatures) the reservoir R is raised so that the level of mercury in the limb A is above the stop-cock S. The stop-cock S is closed. The vessel B is surrounded by the low temperature bath and the reservoir R is adjusted so that the liquid in the tube is within the bath. The difference in the levels of mercury in the manometer directly measures the vapour pressure. In this case $P_0 = 0$

$$\therefore \quad P = h \qquad \ldots(ii)$$

As the temperature of the liquid is lowered, a state is reached when the liquid begins to solidify. The temperature and pressure correspond to the *triple point*. At the triple point the substance exists as a solid, liquid and vapour simultaneously.

4·25 Triple Point

(*i*) The melting point of ice decreases with increase in pressure. It means that ice melts at a temperature lower than 0°C at a pressure higher than the normal pressure. The curve AB (Fig. 4·15) represents the relation between pressure and temperature. The curve AB is called the ice line. The substance will exist in the solid state (ice) to the left of the curve AB and in the liquid state to the right of the curve AB. The curve AB represents the equilibrium between the liquid and the solid states.

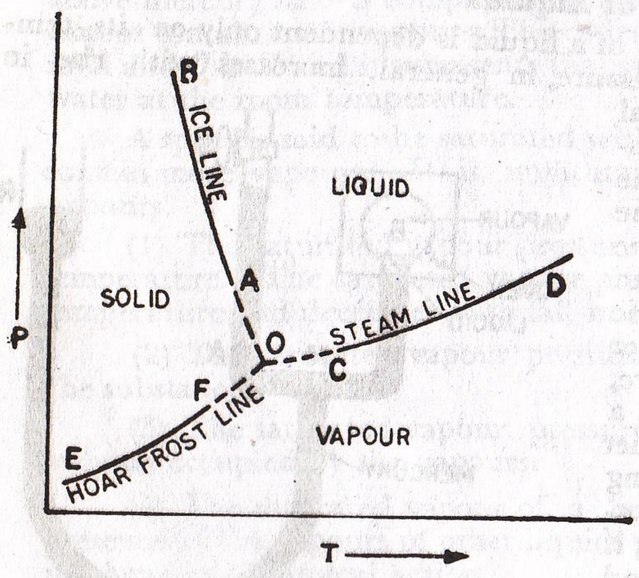


Fig. 4·15

(*ii*) The boiling point of water increases with increase in pressure. The curve CD represents the relation between pressure and temperature and it is called the steam line. Above the curve CD, the substance is in the liquid state and below the curve CD it is in the vapour state. The curve CD represents the equlibrium between the liquid and the vapour states.

(*iii*) The curve EF represents equilibrium between the solid and the vapour states of a substance and is called the *Hoar Frost* line. Above the curve EF, the substance is in the solid state and below the curve EF it is in the vapour state.

These three curves should meet at a point O as shown in Fig. 4·15. Suppose these curves do not meet at a point as shown in Fig. 4·16 and they enclose an area ACF. It means, according to the ice line, the substance must be only in the solid state in the shaded portion. According to the steam line, the substance must be only in the liquid state and according to the hoar frost line the substance must be only in the vapour state. Thus in the shaded portion, the substance must exist simultaneously in the solid, liquid and the vapour states. It is not possible. Therefore, the three curves must meet at a single point O, called the triple point.

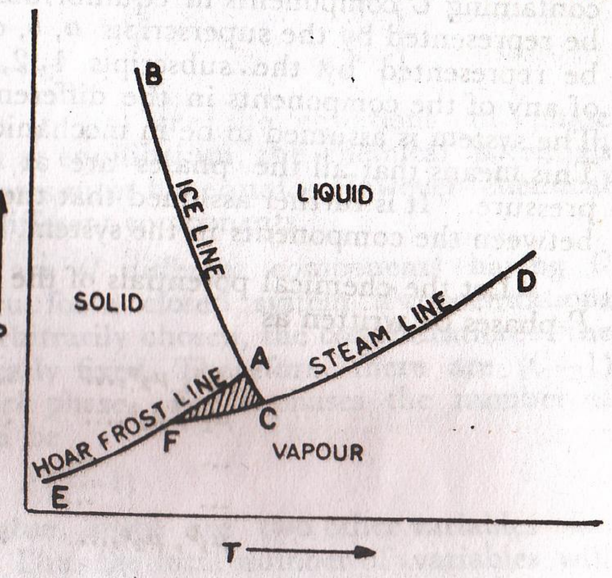


Fig. 4·16

For water, the temperature and pressure corresponding to the triple point are 0·0075°C and 4·58 mm of Hg respectively. The triple point of water is not fixed but is different for different *allotropic forms of ice.*

Triple Points

	T (K)	*Pressure (mm of Hg)*
H_2	13·84	52·8
N_2	63·18	94·0
O_2	54·36	1·14
CO_2	216·65	3·880
H_2O	273·1675	4·58
I	387	90·0

4·26 Gibbs' Phase Rule

Gibbs' phase rule represents the condition of equilibrium between the number of coexisting phases and the components.

Consider a heterogeneous system consisting of P phases and containing C components in equilibrium. Let the different phases be represented by the superscripts a, b, c...p and let the components be represented by the subscripts 1, 2, 3,...C. The concentration of any of the components in the different phases may be different. The system is assumed to be in mechanical and thermal equilibrium. This means that all the phases are at the same temperature and pressure. It is further assumed that there is no chemical reaction between the components in the system.

Let the chemical potentials of the different components in the P-phases be written as

$$\begin{array}{ll} \mu_1^a, \mu_2^a,\ldots & \ldots\mu_C^a \\ \mu_1^b, \mu_2^b,\ldots & \ldots\mu_C^b \\ \ldots \quad \ldots & \ldots \\ \ldots \quad \ldots & \ldots \\ \mu_1^p, \mu_2^p,\ldots & \ldots\mu_C^p \end{array}$$

Now consider that small amounts (dn) of the components are transferred under equilibrium conditions, from one phase to another. It follows that

$$\left.\begin{array}{llll} dn_1^a+dn_1^b+dn_1^c\ldots & & & \ldots dn_1^p = 0 \\ dn_2^a+dn_2^b+dn_2^c\ldots & & & \ldots dn_2^p = 0 \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ dn_C^a+dn_C^b+dn_C^c\ldots & & & \ldots dn_C^p = 0 \end{array}\right\} \quad \ldots(i)$$

From Gibbs-Duhem relation, at equilibrium, the change in Gibbs' potential

$$\left.\begin{array}{rl} & dG = \Sigma\mu\, dn = 0 \\ \therefore \quad \Sigma\mu\, dn = & (\mu_1^a dn_1^a+\mu_1^b dn_1^b+\ldots \quad \ldots\mu_1^p dn_1^p) \\ & +(\mu_2^a dn_2^a+\mu_2^b dn_2^b+\ldots \quad \ldots\mu_2^p dn_2^p) \\ & \ldots \quad \ldots \quad \ldots \quad \ldots \\ & \ldots \quad \ldots \quad \ldots \quad \ldots \\ & +\ (\mu_C^a dn_C^a+\mu_C^b dn_C^b+\ldots\mu_C^p dn_C^p)=0 \end{array}\right\} \quad \ldots(ii)$$

Multiplying the set of equations in (i) by C different multipliers,

$$\left.\begin{array}{llll} \lambda_1, \lambda_2\ldots & \ldots\lambda_C, & & \\ \lambda_1 dn_1^a+\lambda_1 dn_1^b+ & & \ldots+\lambda_1 dn_1^p & = 0 \\ \lambda_2 dn_2^a+\lambda_2 dn_2^b+ & & \ldots+\lambda_2 dn_2^p & = 0 \\ \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \lambda_C dn_C^a+\lambda_C dn_C^b+ & & \ldots\lambda_C dn_C^p & = 0 \end{array}\right\} \quad \ldots(iii)$$

Adding equations (ii) and (iii) and equating the coefficients of dn terms to zero, we get

$$\left.\begin{array}{llll} -\lambda_1 = \mu_1^b = \mu_1^b = \ldots & & & \ldots = \mu_1^p \\ -\lambda_2 = \mu_2^a = \mu_2^b = \ldots & & & \ldots = \mu_2^p \\ \ldots & & \ldots & \ldots \\ \ldots & & \ldots & \ldots \\ -\lambda_C = \mu_C^a = \mu_C^b = \ldots & & & \ldots = \mu_c^p \end{array}\right\} \quad (iv)$$

The set of equations in (iv) are the equations of phase equilibrium. It means that at equilibrium, the chemical potentials of a component in all its phases must be equal. However chemical potentials are different for different components.

In every phase there are C different components having C different concentrations. But for a closed system if concentrations of $(C-1)$ components are arbitrarily chosen, the concentration of the last component is automatically fixed. Therefore, there are $(C-1)$ composition variables in each phase. For P phases the number of composition variables would be

$$P(C-1)$$

In addition to this value, there are two other variables *viz.*, pressure and temperature. Thus the total number of variables will be,

$$= P(C-1)+2 \quad \ldots(v)$$

Further it has been shown that if chemical potential of any one of the P phases is defined then the chemical potential of the remaining $(P-1)$ phases is fixed. Therefore for C components the invariant composition variables will be

$$= C(P-1) \quad \ldots(vi)$$

Therefore the number of independent variables of a system will be given by

$$F = P(C-1)+2-C(P-1) \quad \ldots(vii)$$

Here F represents the number of degrees of freedom.

From equation (vii)

$$F = C-P+2 \quad \ldots(viii)$$

or

$$P+F = C+2 \quad \ldots(ix)$$

Water can exist in three states, *viz.*, solid, liquid and vapour. These are called the three phases of water. A component is defined as a distinct chemical substance different from others. Ice, water and steam refer to the same component *viz.*, water.

In Fig. 4·15, above the curve CD, water exists only in the liquid state. In the space BOD, the pressure or temperature can be changed independently without any change in the phase of a substance. Thus a substance has two degrees of freedom (temperature and pressure) and only one phase (liquid).

Along the curve OD, the substance has two phases (liquid and vapour) but only one degree of freedom (temperature or pressure).

If the pressure is changed the temperature also changes along the curve OD.

At the triple point the substance has three phases (solid, liquid and vapour) and no degree of freedom.

According to Gibbs' phase rule, the sum of the number of phases and the number of degrees of freedom is equal to the number of components plus two.

Let P represent the number of phases, F the number of degrees of freedom and C the number of components. Then

$$P+F = C+2$$

(i) For the liquid state, (region BOD)

$$P = 1, F = 2 \text{ and } C = 1$$

$$1+2 = 1+2$$

(ii) For the liquid-vapour state (curve OD)

$$P = 2, F = 1, C = 1$$

$$2+1 = 1+2$$

(iii) For the solid-liquid-vapour state (triple point)

$$P = 3, F = 0, C = 1$$

$$3+0 = 1+2$$

The phase rule has practical applications when the components involved are more than one, *e.g.*, freezing mixtures (ice and salt).

4·27. Hygrometry

It is that branch of physics which deals with the study of water vapour in the atmosphere.

Relative humidity. It is defined as the ratio of the mass of water vapour (m) actually present in a certain volume of air at room temperature to the mass of water vapour (M) required to saturate the same volume of air at the same temperature.

$$\text{R.H.} = \frac{m}{M}$$

Also $\text{R.H.} = \frac{p}{P}$ where p is the actual vapour pressure and P is the saturated vapour pressure at room temperature.

Dew point. It is the temperature at which the water vapour actually present in the atmosphere is just sufficient to saturate it. It means that the actual vapour pressure at room temperature is equal to the saturated vapour pressure at dew point.

Absolute humidity. It is the amount of water vapour actually present in one cubic metre volume of atmospheric air.

4·28 Deniell's Hygrometer

Daniell's hygrometer consists of two glass bulbs A and B connected by a glass tubing and the space inside is evacuated and sealed (Fig. 4·17). The bulb A contains an evaporating liquid and the space above it, its vapour. The thermometer T_1 fixed on the stand measures the room temperature and the thermometer T_2 fixed inside the glass tubing dips in the liquid of bulb A and measures the dew point temperature.

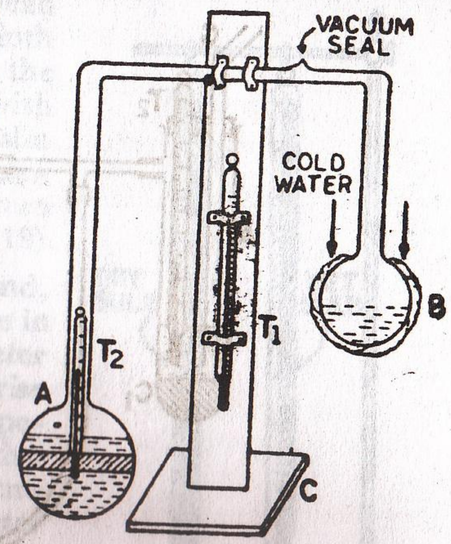


Fig. 4·17

A piece of cotton is tied around B and ether is poured over it. The vapours inside the bulb B condense, some vacuum space is created and the liquid evaporates and this causes cooling of the liquid in the bulb A. When the temperature of the bulb A reaches the dew point, the water vapours present in the atmospheric air condense on the bright metallic ring and it becomes dim. By continuously pouring ether on the bulb B, the temperatures at which dew just appears and disappears are noted and the mean temperature measures the dew point temperature.

From the standard tables the saturated vapour pressures at dew point and room temperature are noted and the relative humidity is calculated.

$$RH = \frac{\text{Saturated vapour pressure at dew point } (T_2)}{\text{Saturated vapour pressure at room temp.} (T_1)}$$

$$\%RH = \left(\frac{\text{Saturated vapour pressure at dew point } (T_2)}{\text{Saturated vapour pressure at room temp. } (T_1)}\right) \times 100$$

4·29 Regnault's Hygrometer

Regnault's hygrometer consists of two glass tubes A and B in which two thermometers T_1 and T_2 are fixed (Fig. 4·18). C_1 and C_2 are two bright silver caps fixed at the bottom of the glass tubes. One of the test tubes say A containing a volatile liquid (ether) is connected to an aspirator and when water is drawn from the aspirator an equal amount of atmospheric air bubbles through the liquid in A and this causes evaporation of the liquid. The temperature of A goes down and when it reaches the dew point temperature dew appears on the metallic cap C_1 and the cap becomes dim. With the help of a telescope kept at a distance, the temperatures at which dew appears and disappears are noted and the mean of these two temperatures measures the dew point. The thermometer T_1 measures the room temperature.

From the standard tables. the saturated vapour pressures of water vapour corresponding to the room temperature and the dew point temperature are noted and relative humidity is calculated.

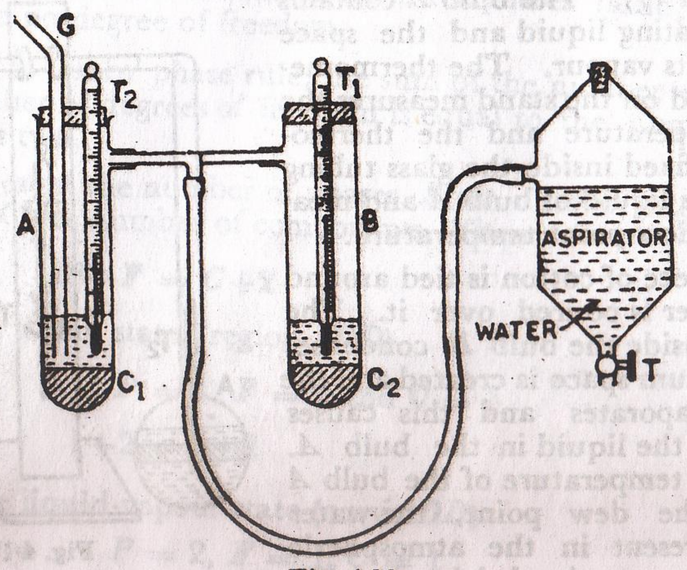


Fig. 4·18

$$\%RH = \left[\frac{\text{Saturated vapour pressure at dew point}}{\text{Saturated vapour pressure at room temp.}}\right] \times 100$$

Advantages of Regnault's hygrometer over Daniell's hygrometer. (1) In the Regnault's hygrometer, the rate of cooling is controlled and is quicker as compared to the Daniell's hygrometer.

(2) In the Regnault's hygrometer, the air bubbling through the whole mass of ether keeps the same temperature throughout the liquid whereas in a Daniell's hygrometer the temperature at the surface of the liquid is less than the interior of the liquid.

(3) Due to the silver caps at the bottom of the tubes in Regnault's hygrometer, temperatures inside and outside are the same. In the Daniell's hygrometer the metal ring is not in direct contact with the liquid due to the glass bulb.

(4) In Regnault's hygrometer, ether is not wasted as in the case of Daniell's hygrometer.

(5) In the case of Regnault's hygrometer, observations are taken at a distance with the help of telescope. Therefore, the breath of the observer and the heat of the body do not affect the humidity. It is not so in the case of the Daniell's hygrometer.

(6) Due to silver caps, the moment when the dew just appears or disappears can be noted very accurately in the case of the Regnault's hygrometer. But it is not so in the case of the Daniell's hygrometer.

4·30 Wet and Dry Bulb Hygrometer

Take two half degree centigrade thermometers. See that both show the same temperature when immersed in water. If they differ, change one of them. Take a piece of clean muslin cloth or wash the muslin cloth with soap. Remove any grease from the muslin piece. Finally wash the piece with clean water. Tie one end of the muslin piece to the bulb of one of the thermometers. Suspend the thermometers from the iron rod of the retort stand (Fig. 4·19).

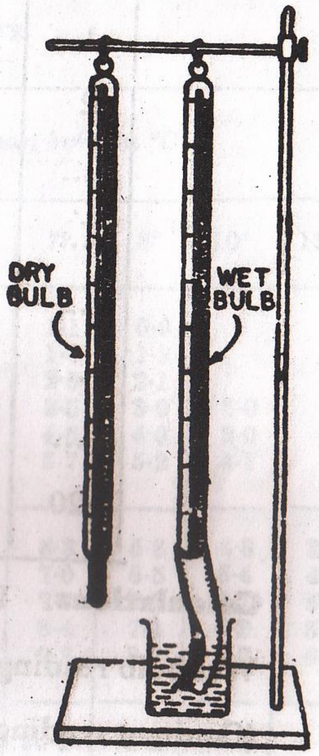


Fig. 4·19

Adjust the height of the iron stand, so that one end of the muslin piece dips in water. The bulb of the thermometer should not dip in water. Water will rise through the muslin piece and will evaporate. Note the temperature of the dry bulb thermometer. Also record the temperature of the wet bulb thermometer (thermometer having muslin piece) after every one minute. Do not place the apparatus near an open window or under a fan. When the wet bulb thermometer shows a constant temperature, record it. Also note the temperature of the dry bulb thermometer after the experiment. Calculate *RH* and dew point with the help of constant tables.

Relative humidity is defined as the ratio of the actual vapour pressure at room temperature to the saturated vapour pressure at room temperature.

$$RH = \frac{\text{Actual } VP \text{ at room temperature}}{SVP \text{ at room temperature}}$$

Dew point is defined as that temperature at which water vapours actually present in the atmosphere are just sufficient to saturate it. The actual vapour pressure at room temperature is equal to the saturated vapour at dew point. Therefore,

$$RH = \frac{\text{Saturated } VP \text{ at dew point}}{\text{Saturated } VP \text{ at room temperature}}$$

Suppose, dry bulb reading before the experiment

$$= t_1°C = \ldots$$

Dry bulb reading after the experiment

$$= t_2°C = \ldots$$

Mean dry bulb reading $= \left(\frac{t_1 + t_2}{2}\right)°C = \ldots$

No.	Wet bulb reading
1	...
2	...
...	
...	
...	
...	
...	
20	...

Calculations. Dry bulb reading A = ...

Wet bulb reading

(Constant reading at the end) B = ...

Difference between the dry and wet bulb readings

$= (A - B)$ = ...

From wet and dry bulb humidity tables :

Saturated vapour pressur [Note the reading for dry bulb temperature (A) under zero column]

$= P$ = ...

Actual vapour pressure [Note the reading for wet bulb temperature (B) under difference column for (A—B)]

$= p$ = ...

$$\%RH = \frac{p}{P} \times 100$$

Dew point (Find the value in the zero column for the value of p, and find the corresponding temperature)

= .....°C

WET AND DRY BULB HUMIDITY TABLE

Temperatures in °C and Saturation Pressures in mm of mercury

Reading in °C Wet bulb	Difference between dry and wet bulb in °C											
	0°	1°	2°	3°	4°	5°	6°	7°	8°	10°	12°	14°
0	4·6	4·1	3·6	3·1	2·6	2·1	1·6	1·1	0·6			
2	5·3	4·8	4·3	3·8	3·3	2·8	2·3	1·8	1·3			
4	6·1	5·6	5·1	4·6	4·1	3·6	3·1	2·6	2·1			
6	7 0	6·5	6·0	5·5	5·3	4·5	4·0	3·5	3·0	2·0		
8	8·0	7·5	7·0	6·5	6·0	5·5	5·0	4·5	4·0	3·0		
10	9·2	8·7	8·2	7·7	7·2	6·7	6·2	5·7	5·2	4·1		
11	9·8	9·3	8·8	8·3	7·8	7·3	6·8	6·3	5·8	4·8	3·8	2·7
12	10·5	10·0	9·5	9·0	8·5	8·0	7·5	7·0	6·5	5·4	4·4	3·4
13	11·2	10·7	10·2	9·7	9·2	8·7	8·2	7·7	7·2	6·1	5·1	4·1
14	12·0	11·5	11·0	10·5	10·0	9·4	8·9	8·4	7·9	6·9	5·9	4·9
15	12·8	12·3	11·8	11·3	10·8	10·2	9·7	9·2	8·7	7·7	6·7	5·7
16	13.6	13.1	12·6	12·1	11·6	11·1	10·6	10·1	9·5	8·5	7·1	6·5
17	14·5	14·0	13·5	13·0	12·5	12·0	11·5	11·0	10·5	9·5	8·4	7·4
18	15·5	15·0	14·5	13·9	13·4	12·9	12·4	11·9	11·4	10·4	9·3	8·3
19	16·5	16.0	15·5	14·9	14·4	13·9	13·4	12·9	12·4	11·4	10·3	9·3
20	17·6	17·1	16·5	16·0	15·5	15·0	14·5	13·9	13·4	12·4	11·4	10·3
21	18·7	18·1	17·6	17·1	16·6	16·1	15·6	15·1	14·6	13·5	12·5	11·5
22	19·8	19·3	18·8	18·3	17·8	17·3	16·8	16·2	15 7	14·7	13·7	12·6
23	21·0	20·6	20·1	19·5	19·0	18·5	18·0	17·5	17·0	15·9	14·9	13·9
24	22·4	21·9	21·4	20·8	20·3	19·8	19·3	18·8	18·3	17·2	16·2	15·2
25	23·8	23·3	22·8	22·3	21·7	21·2	20·7	20·2	19·7	18·6	18·6	16·6
26	25·2	24·7	24·2	23·7	23·2	22·6	22.1	21·6	21·1	21·0	19·0	18·0
27	26·6	26·2	25·7	25·2	24·7	24·2	23·7	23·1	22·6	21·6	20·6	19·5
28	28·4	27·8	27·3	26·8	26·3	25·8	25·3	24·7	24·2	23·2	22·2	21·1
29	30·1	29.8	29.0	28·5	28·0	27·5	27·0	26·4	25·9	24·9	23·9	22·8
30	31·9	31·3	30·8	30·3	29·8	29·3	28·8	28·2	27·7	26·7	25·6	24·6
32	35·7	35·2	34·7	34·1	33·6	33·1	33·6	32·0	31·5	30·5	29·5	28·4
34	39·9	39·4	38·9	38·4	37·9	37·3	36·8	36·3	34·8	34·7	33·7	32·7
36	44·6	44·1	43 6	43·0	42·5	42·0	41·5	40·9	40·4	39·4	38·4	37·3
38	49·7	49·2	48·7	48·2	47·7	47·1	46·6	46·1	45·6	44·5	43·5	42·4
40	55·4	54·9	54·4	53·9	53·8	52·8	52·3	51·7	51·2	50·2	49·1	48·1

4·31 Weather

Dew, rain, clouds, fog, mist, hails, snow, hoar frost etc. are due to the condensation of water vapours present under different conditions in the atmosphere.

Dew. Dew is formed on grass and leaves in the early hours of the morning. The temperature of the atmosphere during the night gradually falls. In the early morning if the temperature of the atmosphere is less than the dew point temperature, formation of dew takes place. The saturated vapours when they come in contact with grass or leaves condense in the form of fine drops of water.

If the night is cloudy, the temperature of the earth does not fall and dew is not formed. A clear sky free from wind is helpful in the formation of dew.

Hoar Frost. If the temperature of the atmosphere falls below 0°C, the dew formed on the leaves and grass freezes and it is called hoar frost.

Fog and Mist. When water vapours present in the atmosphere condense on dust particles in the atmosphere, fog is formed. There is no basic difference between fog and mist. Thick mist is called fog. A clear cold night is favourable for the formation of fog and mist.

Clouds and Rain. When the fog is formed at high altitudes it is called a cloud. When small drops of water in the cloud combine together, bigger water drops are formed and fall in the form of rain.

Snow and Hail. When the cloud suddenly passes through a very cold region, the water drops freeze and fall in the form of snow and hail. Snowfall is common in hill stations because of very low temperature in winter. Hails are caused due to the freezing of rain drops in the atmosphere. Hails are hard and of different sizes whereas snow is quite soft.

Example 4·1. *If the temperature of air is 16·5°C and dew point is 6·5°C, find the % relative humidity of air.*

S.V.P. at 6°, 7°, 16° and 17° are 7·05, 7·51, 13·62 and 14·42 mm *respectively.*

Dew point = 6·5°C

Room temperature = 16·5°C

$$S.V.P. \text{ at } 6{\cdot}5°C = \frac{S.V.P. \text{ at } 6° + S.V.P. \text{ at } 7°}{2}$$

$$p = \frac{7{\cdot}05 + 7{\cdot}51}{2} = 7.28 \text{ mm}$$

$$S.V.P. \text{ at } 165°C = \frac{S.V.P. \text{ at } 16 + S.V.P. \text{ at } 17}{2}$$

$$P = \frac{13{\cdot}62 + 14{\cdot}42}{2} = 14{\cdot}02 \text{ mm}$$

$$R.H. = \frac{p}{P} \times 1000$$

$$= \frac{7{\cdot}28}{14{\cdot}02} \times 100 = \mathbf{51{\cdot}9\%}$$

Example 4·2. *Calculate the dew point when the relative humidity of air at 20°C, is 52%. Given the S.V.P. of water at 20°C, 10°C and 9°C are 17·5, 9·2, 8·6* mm *of* Hg *respectively.*

(Punjab 1966)

$$R.H. = \frac{S.V.P. \text{ at dew point}}{S.V.P. \text{ at room temperature}} = \frac{p}{P}$$

$$0{\cdot}52 = \frac{p}{17{\cdot}5}$$

$$p = 9{\cdot}1 \text{ mm}$$

For 1°C difference = 9·2 − 8·6 = 0·6 mm

∴ Dew point temperature

$$= 9 + \frac{0{\cdot}5}{0{\cdot}6} = \mathbf{9{\cdot}83°C}$$

Exercises IV

1. What do you understand by change of state ?
2. What is triple point ? Show that the steam line, the ice line and the Hoar frost line meet at a single point.
3. Discuss Gibbs' phase rule. What do you understand by phase, degree of freedom and component ?
4. Define hygrometry, relative humidity, dew point and absolute humidity.
5. Describe the construction and working of a Daniell's hygrometer.
6. Describe the construction and working of a Regnault's hygrometer. How is it used to determine the relative humidity ? Compare it with a Daniell's hygrometer.
7. What is the difference between a gas and a vapour ?
8. Distinguish between saturated and unsaturated vapours.
9. What do you understand by relative humidity and dew point ?
10. Describe briefly a wet and a dry bulb hygrometer.
11. Explain briefly the following :

(*i*) Dew (*ii*) Hoar frost (*iii*) Fog (*iv*) Mist (*v*) Clouds (*vi*) Snow (*vii*) Hail (*viii*) Rain.

12. Derive Gibbs' phase rule and discuss the equilibrium of a saturated solution and the solid of the dissolved substance.

[Delhi (Hons) 1976]

13. On a certain day the *RH* is 66·67%. The saturated vapour pressure at room temperature is 18·6 mm. Calculate the saturated vapour pressure at dew point.. [**Ans.** 12·4 mm]

14. On a certain day the dew point is 18·6°C and the room temperature is 23·7°C. The saturated vapour pressures of water at 18°C, 19°C, 23°C, and 24°C are 15·46 mm, 16·46 mm, 21·02 mm and 22 32 mm of Hg respectively. Calculate the relative humidity. [**Ans.** 73·23%]

15. On a certain day the dew pont is 8·5°C and the room temperature is 18·4°C. Find the *RH* if maximum vapour pressure for 8°C, 9°C,18°C, and 19°C are 8·04, 8·61, 15·46 and 16·46 mm of mercury column respectively. [**Ans.** 52·5%]

16. Find the result of mixing 10 g of ice at −10°C with 10 g of water at 10°C. Sp heat of ice = 0·5 and latent heat of ice = 80 cal/g. [**Ans.** A mixture of 9·375 g of ice and 10·625 g of water at 0°C)

17. What will be the result of mixing 400 g of copper chips at 500°C with 500 g of melting ice ? [**Ans.** 250 g of ice melts. Final temperature = 0°C]

18. The density of ice is 0·93 g/cc at 0°C. A piece of metal weighing 1·50 g is heated to 100°C and is then placed in a Bunsen's ice calorimeter. The decrease in volume is found to be 1·876 cc. Calculate the specific heat of the metal. Latent heat of ice = 80 cal/g. [**Ans.** 0·133 cal/g-°C]

19. A solid of mass 20 g is heated to a temperature of 80°C and quickly dropped in a Bunsen's ice calorimeter. The contraction in volume observed is 0·9 cc. The contraction in volume when one gram of ice melts is 0·09 cc. Latent heat of ice = 80 cal/g. Calculate the specific heat of the solid. [**Ans.** 0·5 cal/g°-C]

20. Calculate how much steam from water boiling at 100°C will just melt 200 g of wax at 15°C. (Melting point of wax = 55°C, Sq. heat of wax = 0·7, Latent heat of fusion of wax = 35 cal per g) [**Ans.** 21·54 g]

5

Nature of Heat

5·1 Introduction

In the previous chapters the various effects of heat and its properties have been discussed. At this stage it becomes necessary to formulate a cogent theory to explain the different heat phenomena and to see how far the proposed theory can explain the vast amount of data collected experimentally and otherwise. The theory should satisfactorily explain, primarily the following observed facts : (*a*) thermal expansion, (*b*) conservation of heat energy. When there is transfer of heat between two bodies the heat lost by one body is equal to the heat gained by the other, (*c*) specific heat of bodies, (*d*) thermal capacity of bodies, (*e*) change of state from solid to liquid or liquid to gas, (*f*) propagation of heat radiations in space with the velocity of light.

Two rival theories have been proposed to explain the properties and the effects of heat. The two theories are : (*i*) *Caloric theory of heat* and (*ii*) *Dynamic theory* or the *Kinetic theory of heat*. The caloric theory of heat assumes heat as some fluid and in the course of heat transfer from one body to another, this fluid is transferred. This theory held ground till the end of the eighteenth century.

The experiments of Joule, Rumford and Davy have shown that heat is a form of energy associated with the mechanical motion of material particles. Thus the kinetic theory of matter favoured the dynamical theory in preference to the caloric theory.

5·2 Caloric Theory of Heat

According to this theory heat is considered to be invisible, weightless fluid called *caloric*. This fluid can be produced when substances are burnt and this fluid can flow from a hot body to a cold body. The hot body is assumed to have more of this fluid and the cold body comparatively less. When a hot body is brought

in contact with a cold body, the fluid flows from the hotter to the colder body, just as water flows from higher to lower level. This fluid is supposed to be all-pervading, uncreatable and indestructible. The fluid is highly elastic and the particles of this fluid repel one another very strongly. When this fluid is added to a body its temperature rises and when the fluid is removed its temperature decreases. This fluid occupies the interstices of matter. Just as water can be obtained from a sponge by squeezing, heat can also be obtained from a body by extracting the caloric by friction. The caloric theory could explain in a crude and elementary way, different heat phenomena like conduction, thermal conductivity, latent heat etc.

5·3 Failure of Caloric Theory

The caloric theory held ground till the end of the eighteenth century. The work of Rumford, an artillery engineer began to cast doubts about the validity of the caloric theory. Rumford was engaged in the supervision of boring of cannon for the government of Bavaria. The boring process produced tremendous amount of heat and to prevent this overheating the cannon was immersed in water. Even this water boiled off during the process and the boring process had to be stopped. According to the caloric theory, it was admitted that the caloric had to be supplied to water to raise its temperature to the boiling point. The continuous extraction of caloric during the process of boring was explained on the hypothesis that when matter was finely subdivided its capacity to hold the caloric decreases, and the caloric thus released causes the water to boil.

It was interesting to note that the water surrounding the cannon continued to boil even after the borer became blunt and when there was no further cutting. This proves that even a blunt drill continuously produced an inexhaustible supply of heat which is contrary to the explanation given on the basis of the caloric theory. Further, while explaining the production of heat the conservation principle which is very vital to the concepts of physics has not been kept in mind. During the boring process, mechanical work was continuously expended and caloric was continuously extracted. Rumford's observation gave him an opportunity of eliminating the two cases of non-conservation. This process of elimination is possible only when heat also is considered as a form of energy. What is involved is not the disappearance of the mechanical energy and the appearance of heat energy but it is the transformation of one form of energy into another. Rumford made some measurements regarding the work done and the corresponding heat produced, though his experiments lacked precision. It was later the work of Joule during the years 1843 to 1878, that established the equivalence of heat and work as two forms of energy.

5·4 Mechanical Equivalent of Heat (Joule's Experiments)

James Prescott Joule (1818—1889) performed a series of experiments to prove convincingly that heat is also a form of energy. His findings that there is a definite equivalence between the work done and the corresponding amount of heat and any other form of energy,

put an end to the controversy that existed between the caloric theory and the dynamical theory of heat. The dynamical theory of heat was firmly established.

He developed the argument that if an amount of work W (or any other form of energy) disappears a definite quantity of heat H is produced.

$$W \propto H$$

or

$$W = JH$$

$$J = \frac{W}{H}$$

The constant J is called the mechanical equivalent of heat. The mechanical equivalent of heat (J) is defined as the amount of work done to produce a unit quantity (1 calorie) of heat. The value of J in C.G.S. system is $4{\cdot}18 \times 10^7$ ergs/calorie. In the M.K.S. system its value is 4·18 joules/calorie.

Joule's method for determining the mechanical equivalent of heat. The apparatus consists of a calorimeter with the fixed

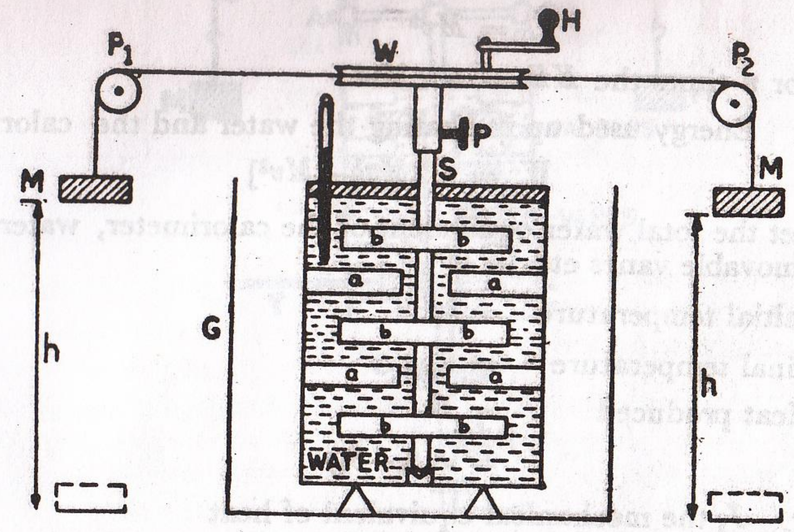


Fig. 5·1

blades a, a etc. fixed to the calorimeter radially. S is a spindle which is fitted with the vanes b, b radially and these vanes are called the movable vanes (Fig. 5·1).

When the spindle rotates, the vanes a, a are stationary and the vanes b, b rotate. The water between any two vanes gets warmed up due to the frictional forces between the two vanes.

W is a wheel with a handle H, which can rotate about a vertical axis. Two strings are wound in the same direction over the drum W and these strings pass over the pulleys P_1 and P_2 and they carry the masses M, M at the other ends.

When the masses are moved up and left free, they move down due to gravity, thus rotating the drum and the spindle. When the masses are moved up the pin P is removed and when the masses

move down the pin P is fixed. This is done because when the masses are moved up, the work done is not taken into calculation.

Let the masses move down by a distance of h cm

Loss of potential energy of the two masses $= 2Mgh$

If the masses fall down n times, the loss of energy

$$= n \times 2Mgh$$

Let the velocity of the masses at the end of the fall be v cm/s

To find v, the time taken by the masses to fall through a height h is noted. The average velocity $= \frac{h}{t}$. Therefore the velocity at the end of the fall will be twice the average velocity because the initial velocity is zero.

$$\therefore \qquad v = 2\left(\frac{h}{t}\right)$$

Kinetic energy of the two masses

$$= 2 \times \tfrac{1}{2}Mv^2$$
$$= Mv^2$$

For n times the $KE = n \times Mv^2$.

$\therefore$ Energy used up in heating the water and the calorimeter,

$$W = n[2Mgh - Mv^2]$$

Let the total water equivalent of the calorimeter, water, fixed vanes, movable vanes etc. be w

Initial temperature $= \theta_1$

Final temperature $= \theta_2$

Heat produced $= H$

$$= w(\theta_2 - \theta_1)$$

$\therefore$ J, the mechanical equivalent of heat

$$= \frac{W}{H}$$

$$= \frac{n[2Mgh - Mv^2]}{w(\theta_2 - \theta_1)}$$

The value of J as a mean of a number of observations is taken. The value of J is $4{\cdot}18 \times 10^7$ ergs/cal.

5·5 Rowland's Experiment

Rowland found the value of J accurately in the year 1879. In the Joule's original experiment there were two main defects. (*i*) The rate of rise of temperature was small [about 0·6°C per hour] and so the loss of heat due to radiation was appreciable and (*ii*) the observed temperatures were not corrected to the standard gas scale.

Rowland's apparatus consists of a calorimeter C fitted with vanes on its inner side (Fig. 5·2). The calorimeter is suspended from a torsion wire. D is a drum over which cords are wound. The ends of the cords are connected to the masses M and M, passing over the pulleys. The cords leave the drum at diametrically opposite points. Thus a couple is applied on the calorimeter. AB is a rod having sliding masses m and m and are used to increase the moment of inertia of the system.

The spindle S has paddles attached to it and it is rotated with a very high speed with the help of a steam engine. The counters C_1 and C_2 are used to measure the number of rotations of the spindle. A sensitive thermometer T already corrected with a standard gas

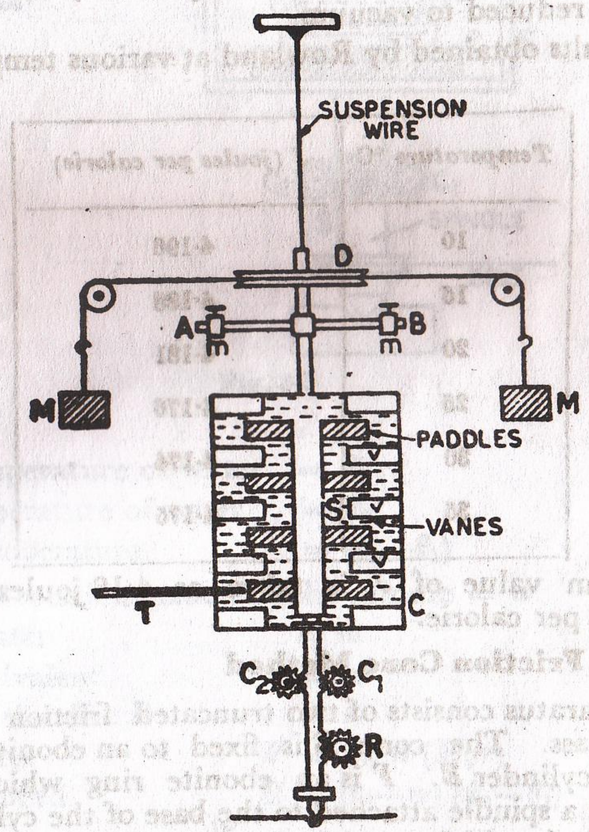


Fig. 5·2

scale is used to measure the temperature of water in the calorimeter. The calorimeter is surrounded by a water jacket in which water is circulated at constant temperature to find the cooling correction.

The initial temperature of water in the calorimeter is noted. The spindle is set rotating and the masses M, M are adjusted quickly so that the calorimeter does not rotate and remains in the equilibrium position. The rotation is continued till there is sufficient rise in temperature. Suppose the initial temperature of water is θ_1 and after n rotations of the spindle, its temperature is θ_2. The rotations are measured with the help of the counters. The couple applied by the masses $= MgD$. Here D is the diameter of the drum.

For n rotations, the work done,

$$W = 2\pi n.Mg\ D$$

Heat produced, $H = (m+w)(\theta_2-\theta_1)$

Here m is the mass of water and w is the water equivalent of the calorimeter, the vanes, the paddles and the spindle.

$$\therefore \quad J = \frac{W}{H}$$

$$= \frac{2\pi n\ MgD}{(m+w)(\theta_2-\theta_1)} \text{ ergs/cal.}$$

Following corrections are to be applied (*i*) cooling correction and (*ii*) correction for the torsional couple, *i.e.*, the weight Mg in air, should be reduced to vacuum.

The results obtained by Rowland at various temperatures were as follows :

Temperature °C	*J (joules per calorie)*
10	4·196
15	4·188
20	4·181
25	4·176
30	4·174
35	4·175

The mean value of J is taken as 4·18 joules per calorie or $4{\cdot}18\times10^7$ ergs per calorie.

5·6 Searle's Friction Cone Method

The apparatus consists of two truncated friction cones A and B made of brass. The cone B is fixed to an ebonite disc C fitted inside a brass cylinder E. F is an ebonite ring which holds B in position. S is a spindle attached to the base of the cylinder E. The spindle is rotated at high speed by hand or with an electric motor. The number of rotations made by the spindle is measured with the help of the counters C_1 and C_2 (Fig. 5·3).

A grooved wooden disc D is fixed to the inner cone A with the help of pins passing through the iron-ring I. The iron ring also provides the necessary weight for the cone A to be in its position. A cord passes around the groove of the disc D and the other end is connected to a mass M. The chord passes over a pulley. A mercury thermometer calibrated to gas scale is used to measure the temperature of water in the cone A.

The outer cone B is rotated with the help of the spindle and it tends to rotate the cone A. The mass M is adjusted quickly so that the cone A does not rotate. A couple Mgr is provided by the mass

in the opposite direction. Due to friction, heat is produced and water in the cone A gets heated.

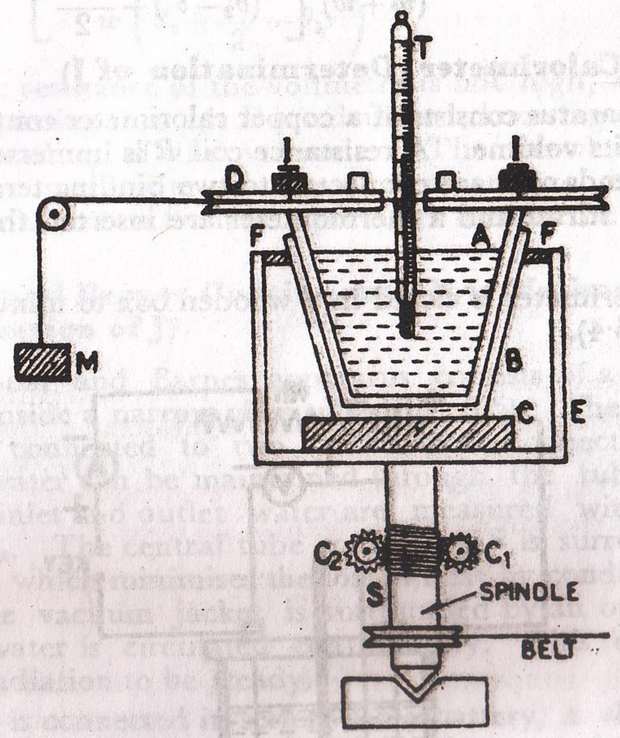


Fig. 5·3

Suppose,

Initial temperature of water $= \theta_1$

Final temperature of water $= \theta_2$

Rise in temperature $= (\theta_2-\theta_1)$

Number of rotations made by the spindle $= n$

Mass of water $= m$

Water equivalent $= w$

Radius of the disc D $= r$

Work done, $W = 2\pi\ n\ (Mgr)$

Heat produced $H = (m+w)\ (\theta_2-\theta_1)$

$$\therefore \quad J = \frac{W}{H}$$

$$= \frac{2\pi n\ Mgr}{(m+w)\ (\theta_2-\theta_1)} \qquad \ldots(i)$$

Radiation Correction. The time for which the spindle is rotated is noted. The fall in temperature is noted for the same time after the experiment. Let $\delta\theta$ be the fall in temperature. Then radiation correction $= (\delta\theta/2)$

$\therefore$ The correct rise in temperature

$$= \left[(\theta_2-\theta_1)+\frac{\delta\theta}{2}\right]$$

$$\therefore \quad J = \frac{2\pi n\, M_2 r}{(m+w)\left[(\theta_2-\theta_1)+\frac{\delta\theta}{2}\right]} \text{ ergs/cal}$$

5·7 Joule's Calorimeter (Determination of J)

The apparatus consists of a copper calorimeter containing water to about $\frac{2}{3}$ of its volume. A resistance coil R is immersed in water and the two ends of R are connected to two binding terminals fixed to the lid. A stirrer and a thermometer are inserted through holes in the lid.

The calorimeter is closed in a wooden box to minimize the loss of heat (Fig. 5·4).

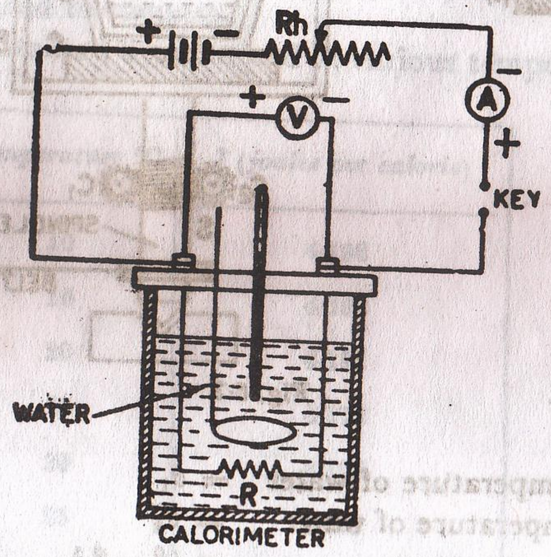


Fig. 5·4

The electrical connections are shown in Fig. 5·4. If a current of I amperes is passed through the resistance coil R at a potential difference of V volts for a time t seconds, then the amount of energy liberated $= VIt \times 10^7$ ergs.

Knowing the total water equivalent w, and the initial and final temperatures of the calorimeter θ_1 and θ_2, the heat produced H can be calculated

$$H = w(\theta_2-\theta_1)$$

To apply the radiation correction, the calorimeter is allowed to cool for the same interval of time t as that of the passage of current, and the fall in temperature θ_3 is noted. Half of this fall in temperature is added to the final observed temperature θ_2.

$$\therefore \text{ Corrected final temperature } = \theta_2+\frac{\theta_3}{2}$$

Mechanical equivalent of heat

$$J = \frac{\text{Work done}}{\text{Heat produced}}$$

$$J = \frac{VIt \times 10^7}{w\left(\theta_2+\frac{\theta_3}{2}-\theta_1\right)} \text{ ergs/cal}$$

In case, the resistance of the voltmeter is not high, the actual value of current passing through R is calculated, knowing the values of R and the reading of the voltmeter. The drawback of this experiment is the small rate of rise of temperature due to low currents that can be drawn from accumulators used as the source of supply.

5·8 Callendar and Barnes Continuous Flow Method (Determination of J)

The Callendar and Barnes apparatus consists of a resistance coil R enclosed inside a narrow glass tube (Fig. 5·5). The two ends of the wire are connected to two thick copper connectors. Continuous flow of water can be maintained through the tube and the temperatures of inlet and outlet water are measured with thermometers T_1 and T_2. The central tube containing R is surrounded by a vacuum jacket which minimises the loss of heat by conduction and convection. The vacuum jacket is surrounded by an outer jacket through which water is circulated continuously. This ensures the loss of heat by radiation to be steady.

The coil R is connected in series with a battery, a rheostat, an ammeter and a key. A voltmeter is connected across the terminals

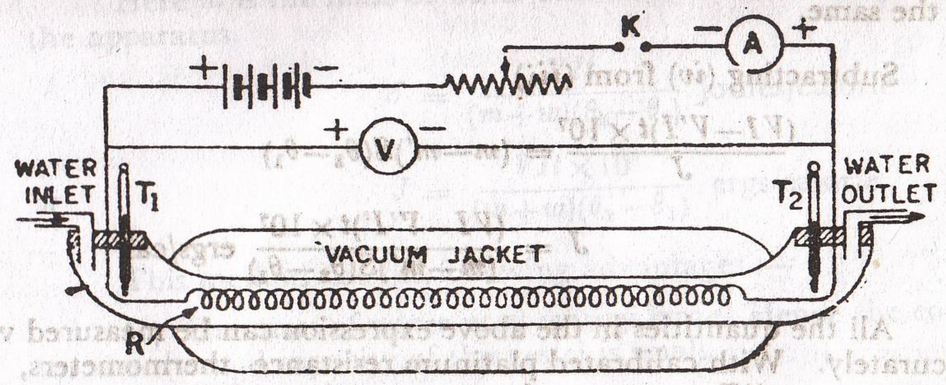


Fig. 5·5. Callendar and Barnes' Continuous Flow Apparatus.

of R. For more accurate work, the current through the coil and the potential difference across its ends are measured using a potentiometer, initially calibrated with a standard cell.

When the rate of flow of water and the current passing through R are maintained constant, a steady state will be reached and the thermometers T_1 and T_2 will show constant readings. At this stage, the temperatures of every part of the apparatus will remain steady. When the thermometers T_1 and T_2 show constant readings, say θ_1 and θ_2, the mass of water (m) flowing in a time t seconds is measured. If S is the mean value of the specific heat of water between the temperatures θ_1 and θ_2 and H the quantity of heat lost by radiation etc., then the amount of heat produced by passage of electric current through the coil

$$= mS(\theta_2-\theta_1)+H \qquad \ldots(i)$$

If V and I are the voltmeter and ammeter readings then the amount of energy liberated in time t seconds $= VIt \times 10^7$ ergs. The corresponding quantity of heat produced

$$= \frac{VIt\times 10^7}{J} \text{ cals} \qquad \ldots(ii)$$

From (i) and (ii)

$$\frac{VIt\times 10^7}{J} = mS(\theta_2-\theta_1)+H \qquad \ldots(iii)$$

To eliminate H, a second set of observations is taken by altering the values of the current and the rate of flow of water such that the difference of temperature $\theta_2-\theta_1$ remains the same after the steady state is reached. If V', I' and m' are the corresponding values for the same time t, then

$$\frac{V'I't\times 10^7}{J} = m'S(\theta_2-\theta_1)+H \qquad \ldots(iv)$$

As the temperature difference $(\theta_2-\theta_1)$ is maintained the same in the two cases, the temperatures of the various parts of the apparatus will be the same and hence the loss of heat by radiation etc. will also be the same.

Subtracting (iv) from (iii)

$$\frac{(VI-V'I)t\times 10^7}{J} = (m-m')S(\theta_2-\theta_1)$$

$$J = \frac{(VI-V'I')t\times 10^7}{(m-m')S(\theta_2-\theta_1)} \text{ ergs/cal}$$

All the quantities in the above expression can be measured very accurately. With calibrated platinum resistance thermometers, the temperature difference can be measured with great precision. Similarly, the values of the current and the potential difference can also be measured very accurately. Thus, this method ensures an accurate determination of the value of J.

5·9 Jaegar and Steinwehr's Method

In 1921 Jaegar and Steinwehr performed an experiment to find the value of J accurately. Their method has an accuracy of 1 in 1,000 The value of J obtained by them is equal to $4{\cdot}186\times 10^7$ ergs per calorie.

The apparatus consists of a large cylinder containing about 50 kg of water. R is a heater coil and T is a sensitive platinum resistance thermometer calibrated to the gas scale. S_1 and S_2 are two electrically rotating stirrers (Fig. 5·6). The cylinder is surrounded by

an outer jacket through which water is circulated at constant temperature. This will help in estimating the cooling correction accurately.

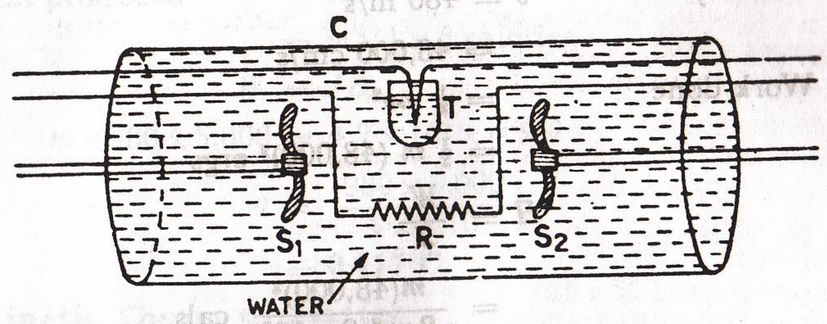


Fig. 5·6

The current is measured with a standard resistance placed in series with the heating resistance R. The potential difference across the standard resistance is obtained with a sensitive potentiometer initially calibrated with a standard cell. The time for which the current is passed is measured accurately with a chronograph.

Let the potential difference across R be V volts and the current flowing for t seconds be I amperes.

Work done $= VIt$ joules

Heat produced $= (m+w)(\theta_2-\theta_1)$

Here m is the mass of water and w is the water equivalent of the apparatus.

$$J = \frac{VIt}{(m+w)(\theta_2-\theta_1)} \text{ joules/calorie}$$

or

$$J = \frac{VIt\times 10^7}{(m+w)(\theta_2-\theta_1)} \text{ ergs/calorie}$$

This method has the following advantages :—

(1) The mass of water used is very large. Hence the correction for the thermal capacity of the vessel is small.

(2) A small rise in temperature of the order of 1·4°C is obtained. This will enable to apply the cooling correction accurately because Newton's law of cooling is applicable.

(3) Efficient stirring of water is provided. Thus the temperature of water and the calorimeter remains uniform.

(4) As the surrounding temperature of the cylinder is kept constant by circulating water at constant temperature, cooling correction can be accurately determined.

Example 5·1 *A lead bullet strikes a target with a velocity of 480* m/s. *If the bullet falls dead, calculate the rise in temperature, assuming that all the heat developed is equally shared between it and the target.* (*Sp. heat of lead* $= 0{\cdot}03$)

Suppose mass of the bullet $= m$ grams
Rise in temperature $= \theta$
Velocity $v = 480$ m/s
$= 48{,}000$ cm/s
Work done $= \frac{1}{2} mv^2$
$= \frac{1}{2} m\,(48{,}000)^2$ ergs

$$H = \frac{W}{J}$$

$$= \frac{m(48{,}000)^2}{2\times 4{\cdot}2\times 10^7} \text{ cals.}$$

Half of this heat energy is used to raise the temperature of the bullet.

$$\therefore \text{ Useful heat } H = \frac{m(48{,}000)^2}{2\times 2\times 4{\cdot}2\times 10^7} \text{ cals}$$

$$ms\theta = \frac{m(48{,}000)^2}{4\times 4{\cdot}2\times 10^7}$$

$$\theta = \frac{48{,}000\times 48{,}000}{0{\cdot}03\times 4\times 4{\cdot}2\times 10^7}$$

$$= 457{\cdot}14°\text{C}$$

Example 5·2 *Calculate the increase in energy per atom of aluminium in ergs when the temperature of a piece of aluminium increases by 1°C (27 g of aluminium contains 6×10^{23} atoms and sp. heat of aluminium = 0·22).*

Heat required to raise the temperature of 27 grams of aluminium by 1°C

$$= 27\times 0{\cdot}22\times 1 \text{ cal}$$

Energy gained by 6×10^{23} atoms of aluminium

$$= 27\times 0{\cdot}22\times 4{\cdot}2\times 10^7 \text{ ergs}$$

Increase in energy per atom of aluminium

$$= \frac{27\times 0{\cdot}22\times 4{\cdot}2\times 10^7}{6\times 10^{23}} \text{ ergs}$$

$$= 4158\times 10^{-19} \text{ ergs}$$

Example 5·3 *What will be the rise in temperature of water if it falls from a height of 50 metres, assuming that all the energy is used in heating the water ?* *(Punjab 1966)*

$h = 50$ metres $= 5{,}000$ cm
Suppose, rise in temperature $= \theta$°C
Mass of water $= m$
Work done $= W = mgh$
$= m\times 980\times 5{,}000$ ergs

Heat produced $= H = ms\theta$
$= m\times 1\times\theta$ calories
$W = JH$
$m\times 980\times 5{,}000 = 4{\cdot}2\times 10^7\times m\times\theta$

$$\theta = \frac{980\times 5{,}000}{4{\cdot}2\times 10^7}$$

$$= 0{\cdot}117°\text{C}$$

5·10 Kinetic Theory of Matter

The experiments on the conversion of work into heat have shown clearly that heat is a form of energy. This energy is connected with the motion of molecules of which the matter is made of. Kinetic theory of matter gives an explanation to the nature of this motion and the nature of heat energy.

According to Kinetic theory of matter, every substance (in the form of solid, liquid or gas) consists of a very large number of very small particles called the molecules. The molecules are the smallest particles of a substance that can exist in free state. The molecules possess the characteristic properties of the parent substance. The molecules are in a state of continuous motion with all possible velocities. The velocity of the molecules increases with rise in temperature.

The energy possessed by the molecules can be of two forms, kinetic or potential. When the stop-cock of an evacuated flask is opened, air rushes in quickly to fill in the space. This shows that the molecules possess rapid motion and hence they possess kinetic energy. When a solid expands on heating, the molecules are pulled apart against the forces of intermolecular expansion. The amount of work done in separating the molecules to larger distances manifests itself as the potential energy of the molecules. Thus the amount of heat given to a solid substance increases the energy of the molecules and this increase in energy is partly kinetic and partly potential.

Thus, the kinetic theory of matter is based on the following three points : (*i*) matter is made up of molecules, (*ii*) molecules are in rapid motion, and (*iii*) molecules experience forces of attraction between one another.

The validity and the soundness of any theory depends on its capability to explain the observed facts, *viz.*, the three states of matter, expansion, change of state and conduction.

5·11 The Three States of Matter

Solid. In the case of a solid the intermolecular distances are small and hence the forces of intermolecular attraction are large. The only motion permissible to a molecule is oscillation or vibration about its mean position which is fixed. Hence a solid has definite size and shape. Heating a solid means giving more energy to the molecules. This will enable the molecules to vibrate more violently about their mean position. The molecules move further apart and

this results in the expansion of the solid. With the supply of more heat to the solid, the amplitude of vibration of the molecules increases to such an extent that the molecules will be free to leave their mean position because the kinetic energy of the molecules is greater than the potential energy due to the forces of intermolecular attraction. Now the molecules are free to move about within the body of the substance and this corresponds to the liquid state of the substance. The amount of heat supplied, which is equivalent to the work done in pulling the molecules apart against the forces of intermolecular attraction, determines the latent heat of fusion of the solid.

Liquid. In a liquid, the molecules are farther apart than the solid. The molecules are not confined to any fixed mean position. They are free to move about within the volume of the liquid. Hence the liquids have their own size but no shape.

The definite size of the liquid is due to the mutual forces of attraction between the molecules. The molecules present on the surface of the liquid experience a resultant downward force due to the presence of the molecules present within the sphere of influence and hence the surface of a liquid behaves as a stretched membrane. This is the phenomenon of surface tension. The volume of the liquid is fixed at a given temperature but the molecular distances are comparatively larger than that of a solid. Therefore the molecules experience less force of attraction and they can occupy any position within the liquid. Hence the liquid occupies the shape of the containing vessel.

The molecules are always in a state of random motion. They collide with each other and they may or may not change their respective kinetic energies. As already explained, every molecule on the surface of the liquid is held in its position as a result of the forces of intermolecular attraction and surface tension. Due to the collisions a certain molecule may acquire more energy than the energy with which it is held. As soon as this happens, the molecule flies off, *i.e.*, it leaves the liquid surface. This is called evaporation. If no external heat is supplied it is obvious that the mean kinetic energy of the molecules decreases and the temperature of the liquid falls. This explains cooling caused by evaporation. If the moving vapour molecules come near to each other at sufficiently low velocities, they experience a greater magnitude of force of attraction. The molecules coalesce and this results in condensation. Rate of evaporation increases with increase in temperature of the liquid and decrease in pressure over the liquid surface.

Gas. In the case of a gas, the inter-molecular distances are much larger than that of a solid or a liquid and the molecules of a gas are free to move about in the entire space available to them. Hence a gas has no shape or size. If the space occupied by a gas is increased, the gas will occupy the whole of the new space uniformly. This is due to the fact that the molecules possess rapid random motion and the force of inter-molecular attraction is negligibly small. The molecules move about independently in straight lines

and the only restriction to this movement is collision with another molecule or collision with the walls of the containing vessel. In a gas the more predominant factor is the movement of the molecules than the force of attraction between the molecules.

5·12 Concept of Ideal or Perfect Gas

At very low pressures, the forces of inter-molecular attraction are negligible. Therefore, at low pressures only, a real gas obeys the equation $PV = RT$. An ideal gas can be defined as a real gas at low pressure. For a real gas the internal energy is a function of pressure and temperature. By definition, the ideal gas should satisfy the equation

$$PV = RT \qquad \ldots(i)$$

and
$$\left[\frac{dU}{dP}\right]_T = 0 \qquad \ldots(ii)$$

$$\left(\frac{dU}{dV}\right)_T = \left[\frac{dU}{dP}\right]_T \left[\frac{dP}{dV}\right]_T$$

From equation (*i*)

$$\frac{dP}{dV} = -\frac{RT}{V^2}$$

$$= -\left[\frac{RT}{V}\right]\left[\frac{1}{V}\right] = -\frac{P}{V}$$

$$\therefore \quad \left(\frac{dU}{dV}\right)_T = \left[\frac{dU}{dP}\right]_T \left[-\frac{P}{V}\right]_T \qquad \ldots(iii)$$

As $\left(-\frac{P}{V}\right)$ is not equal to zero and

$$\left[\frac{dU}{dP}\right]_T = 0$$

$$\therefore \quad \left[\frac{dU}{dV}\right]_T = 0 \qquad \ldots(iv)$$

Since for an ideal gas $\left[\frac{dU}{dP}\right]_T$ and $\left[\frac{dU}{dV}\right]_T$ are both equal to zero, the internal energy of an ideal gas is a function of temperature only.

$$\therefore \quad U = f(T) \qquad \ldots(v)$$

In a large number of calculations, a real gas can be taken approximately as an ideal gas. This involves an error that can be tolerated in the calculations. For all practical purposes, real gases below a pressure of two atmospheres can be considered as ideal gases. A saturated vapour in equilibrium with its own liquid can be considered to have the properties of an ideal gas. The error involved is low.

5·13 Kinetic Theory of Gases

The continuous collision of the molecules of the gas with the walls of the containing vessel and their reflection from the walls results in the change of momentum of the molecules. According to Newton's second law of motion, the rate of change of momentum per unit area of the wall surface corresponds to the force exerted by the gas per unit area. The force per unit area measures the pressure of the gas.

Postulates of the kinetic theory of gases

(*i*) The gas is composed of small indivisible particles called molecules. The properties of the individual molecules are the same as that of the gas as a whole.

(*ii*) The distance between the molecules is large as compared to that of a solid or liquid and hence the forces of inter-molecular attraction are negligible.

(*iii*) The molecules are continuously in motion with varying velocities and the molecules move in straight lines between any two consecutive collisions. The collisions do not alter the molecular density of the gas, *i.e.*, on the average the number of molecules present in a unit volume remains the same. Also, the molecules do not accumulate at any place within the volume of the gas.

(*iv*) The size of the molecules is infinitesimally small as compared to the average distance traversed by a molecule between any two consecutive collisions. The distance between any two consecutive collisions is called free path and the average distance is called the mean free path. The mean free path is dependent on the pressure of the gas. If the pressure is high the mean free path is less and if the pressure is low the mean free path is more.

(*v*) The time of impact is negligible in comparison to the time taken to traverse the free path.

(*vi*) The molecules are perfectly hard elastic spheres and the whole of their energy is kinetic.

5·14 Expression for the Pressure of a Gas

As mentioned earlier, the continuous impact of the molecules on the walls of the containing vessel accounts for the pressure of the gas.

Consider a cubical vessel *ABCDEFGH* of side l cm containing the gas (Fig. 5·7). The volume of the vessel and hence that of the gas is l^3 cc. Let n and m represent the very large number of molecules present in the vessel and the mass of each molecule respectively.

Consider a molecule P moving in a random direction with a velocity C_1. The velocity can be resolved into three perpendicular components u_1, v_1 and w_1 along the X, Y and Z axes respectively. Therefore,

$$C_1^2 = u_1^2 + v_1^2 + w_1^2$$

The component of the velocity with which the molecule P will strike the opposite face $BCFG$ is u_1 and the momentum of the molecule is mu_1. The molecule is reflected back with the same momentum mu_1 in an opposite direction and after traversing a distance l will strike the opposite face $ADEH$.

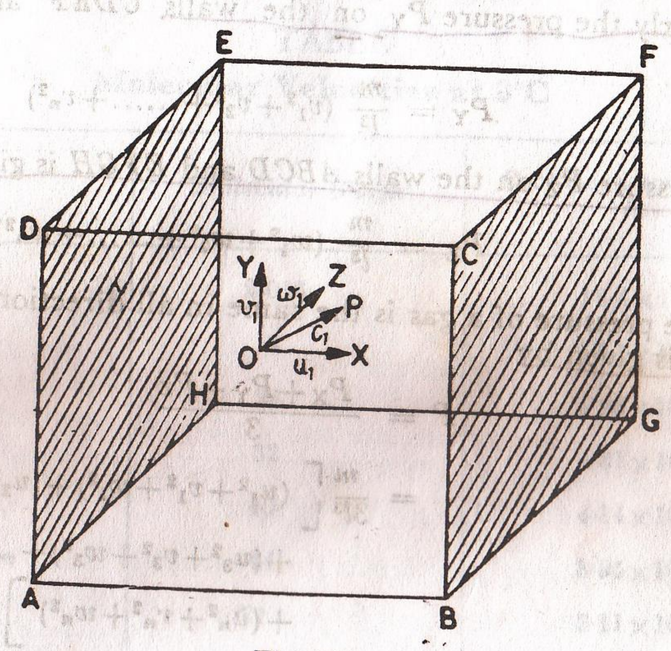


Fig. 5·7

The change in momentum produced due to the impact is

$$mu_1 - (-mu_1) = 2mu_1$$

As the velocity of the molecule is u_1, the time interval between two successive impacts on the wall $BCFG$ is

$$\frac{2l}{u_1} \text{ seconds}$$

$\therefore$ No. of impacts per second

$$= \frac{1}{\frac{2l}{u_1}}$$

$$= \frac{u_1}{2l}$$

Change in momentum produced in one second due to the impact of this molecule is

$$2mu_1 \times \frac{u_1}{2l} = \frac{mu_1^2}{l}$$

The force F_x due to the impact of all the n molecules in one second

$$= \frac{m}{l}\left[u_1^2 + u_2^2 + \ldots + u_n^2\right]$$

Force per unit area on the wall *BCFG* or *ADEH* is equal to the pressure P_X

$$P_X = \frac{m}{l \times l^2}(u_1^2+u_2^2+u_3^2+.....+u_n^2)$$

Similarly the pressure P_Y on the walls *CDEF* and *ABGH* is given by

$$P_Y = \frac{m}{l^3}(v_1^2+v_2^2+.....+v_n^2)$$

and the pressure P_Z on the walls *ABCD* and *EFGH* is given by

$$P_Z = \frac{m}{l^3}(w_1^2+w_2^2+.....+w_n^2)$$

As the pressure of a gas is the same in all directions, the mean pressure P is given by

$$P = \frac{P_X+P_Y+P_Z}{3}$$

$$= \frac{m}{3l^3}\Big[(u_1^2+v_1^2+w_1^2)+(u_2^2+v_2^2+w_2^2)+(u_3^2+v_3^2+w_3^2)+.....+(u_n^2+v_n^2+w_n^2)\Big]$$

$$= \frac{m}{3l^3}\Big[C_1^2+C_2^2+C_3^2+.....C_n^2\Big] \quad ...(i)$$

But volume, $V = l^3$. Let C be the root-mean-square velocity of the molecules (R.M.S. velocity).

Then $$C^2 = \frac{C_1^2+C_2^2+C_3^2+.....C_n^2}{n}$$

or $$nC^2 = C_1^2+C_2^2+C_3^2+.....C_n^2$$

Substituting this value in equation (*i*), we get

$$P = \frac{m.nC^2}{3V} \quad ...(ii)$$

But $M = mn$ where M is the mass of the gas of volume V, m is the mass of each molecule and n is the number of molecules in a volume V.

$$\therefore \quad P = \frac{MC^2}{3V}$$

or $$P = \frac{1}{3}\rho C^2 \quad ...(iii)$$

$$\because \quad \frac{M}{V} = \rho \text{ the density of the gas.}$$

From equation (*iii*)

$$C^2 = \frac{3P}{\rho}$$

or $$C = \sqrt{\frac{3P}{\rho}} \quad ...(iv)$$

[**Note.** R.M.S. velocity C is the square root of the mean of the squares of the individual velocities and it is not equal to the mean velocity of the molecules.]

TABLE

Molecular Velocities at 0°C

Gas	*Molecular Weight*	*Root mean square velocity in* cm/s
Hydrogen	2·016	$18·4\times10^4$
Helium	4	$13·1\times10^4$
Nitrogen	28	$4·95\times10^4$
Oxygen	32	$4·61\times10^4$
Argon	40	$4·14\times10^4$
Carbon dioxide	44	$3·95\times10^4$
Chlorine	71	$3·11\times10^4$

R.M.S. velocity of hydrogen

The density of hydrogen at N.T.P. is 0·000089 g/cc. Therefore C for hydrogen can be calculated as follows :

$$C = \sqrt{\frac{3P}{\rho}}$$

$$= \sqrt{\frac{3\times76\times13·6\times981}{0·000089}}$$

$$= 1·84\times10^5 \text{ cm/s}$$

(*b*) For oxygen the density at N.T.P.

$$= 16\times0·000089$$

$$\therefore \quad C \text{ for oxygen} = \sqrt{\frac{3\times76\times13·6\times981}{16\times0·000089}}$$

$$= 4·6\times10^4 \text{ cm/s}$$

(*c*) For air the density at N.T.P. is 0·001293 g/cc

$$\therefore \quad C \text{ for air} = \sqrt{\frac{3\times76\times13·6\times981}{0·001293}}$$

$$= \mathbf{4·850\times10^4 \text{ cm/s}}$$

Example 5·4 *Calculate the number of molecules in one* c.c. *of oxygen at N.T.P. using the following data :—*

Density of mercury $= 13{\cdot}6$ g/cm³

R.M.S. *velocity of oxygen molecules at* 0°C

$= 4{\cdot}62 \times 10^4$ cm/s

Mass of one molecule of oxygen $= 52{\cdot}8 \times 10^{-24}$ g

$$P = \frac{1}{3}\rho C^2$$

Let the mass of each molecule be m and the number of molecules in one cc $= n$

$$\therefore \quad P = \frac{1}{3} mnC^2$$

$$n = \frac{3P}{mC^2}$$

Here $P = 76 \times 13{\cdot}6 \times 980$ dynes/cm²

$m = 52{\cdot}8 \times 10^{-24}$ g

$C = 4{\cdot}62 \times 10^4$ cm/s

$$\therefore \quad n = \frac{3 \times 76 \times 13{\cdot}6 \times 980}{52{\cdot}8 \times 10^{-24} \times (4{\cdot}62 \times 10^4)^2}$$

$$\mathbf{n = 2{\cdot}697 \times 10^{19}}$$

5·15 Kinetic Energy per Unit Volume of a Gas

$$P = \frac{1}{3}\rho C^2$$

$$= \frac{2}{3} \cdot \frac{1}{2}\rho C^2$$

$$= \frac{2}{3} \cdot E$$

where $E = \frac{1}{2}\rho C^2$ and is equal to the kinetic energy per unit volume of the gas. ρ is the mass per unit volume. Hence, the pressure of a gas is numerically equal to two-thirds of the mean kinetic energy of translation of a unit volume of the molecules.

5·16 Kinetic Interpretation of Temperature

The pressure of a gas, according to the kinetic theory, is

$$P = \frac{1}{3}\rho C^2$$

$$P = \frac{1}{3}\frac{MC^2}{V}$$

$$PV = \frac{1}{3}MC^2$$

Consider 1 gram molecule of the gas at a temperature T K

$$PV = RT$$

$$\therefore \quad \frac{1}{3}MC^2 = RT$$

$$\frac{1}{2}MC^2 = \frac{3}{2}RT \qquad \ldots(i)$$

Let the mass of each molecule be m and Avogadro's number be N.

$$M = m \times N$$

$$\frac{1}{2}mNC^2 = \frac{3}{2}RT$$

$$\frac{1}{2}mC^2 = \frac{3}{2}\frac{R}{N}T$$

$$= \frac{3}{2}kT \qquad \ldots(ii)$$

Here k is called Boltzmann's constant.

Thus, from equation (*ii*), the mean kinetic energy of a molecule is directly proportional to the absolute temperature of a gas. When the temperature of the gas is increased, the mean kinetic energy of the molecules increases. When heat is withdrawn from a gas, the mean kinetic energy of the molecules decreases. Thus, at absolute zero temperature, the kinetic energy should be zero. It means at absolute zero temperature, the molecules are in a perfect state of rest and have no kinetic energy. But before the absolute zero temperature is reached, all gases change their state to liquids and solids.

Also from equation (*ii*), $C^2 \propto T$

It means that the root mean square velocity of the molecules is also directly proportional to the square root of the absolute temperature.

Example 5·5 *At what celsius temperature will oxygen molecules have the same root mean square velocity as that of hydrogen molecules at* −100°C ?

The energy of a gas molecule is,

$$\frac{1}{2}mC^2 = \frac{3}{2}kT$$

For hydrogen molecules

$$\frac{1}{2}m_1C_1^2 = \frac{3}{2}kT_1 \qquad \ldots(i)$$

For oxygen molecules

$$\frac{1}{2}m_2C_2^2 = \frac{3}{2}kT_2 \qquad \ldots(ii)$$

Dividing (*i*) by (*ii*)

$$\frac{m_1C_1^2}{m_2C_2^2} = \frac{T_1}{T_2} \qquad \ldots(iii)$$

Here $C_1 = C_2$

$T_1 = -100$°C

$= -100 + 273$

$= 173$ K

$T_2 = ?$

$\frac{m_2}{m_1} = 16$

From equation (*iii*)

$$T_2 = \frac{m_2 C_2^2 T_1}{m_1 C_1^2}$$

$T_2 = 16 \times 173$

$= 2768$ K

$T_2 = 2768 - 273$

$= \mathbf{2495°C}$

Example 5·6 *Calculate the* RMS *velocity of the oxygen molecules at 27°C.*

First calculate the *RMS* velocity of oxygen at N.T.P.

$$C = \sqrt{\frac{3P}{\rho}}$$

Here $P = 76 \times 13{\cdot}6 \times 980$ dynes/cm^2

$\rho = 16 \times 0{\cdot}000089$

$\therefore \quad C = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 980}{16 \times 0{\cdot}000089}}$

$C = 4{\cdot}6 \times 10^4$ cm/s

Let the *RMS* velocity of the molecules at 27°C be C_1

$$\therefore \quad \frac{C_1}{C} = \sqrt{\frac{T_1}{T}}$$

$$C_1 = C \times \sqrt{\frac{T_1}{T}}$$

Here $C = 4{\cdot}6 \times 10^4$ cm/s

$T = 273$ K

$T_1 = 27°C$

$= 27 + 273$

$= 300$ K

$$C_1 = 4{\cdot}6 \times 10^4 \sqrt{\frac{300}{273}}$$

$$C_1 = \mathbf{4{\cdot}84 \times 10^4 \text{ cm/s}}$$

5·17 Derivation of Gas Equation

From kinetic theory,

$$P = \frac{1}{3} \rho C^2$$

$$P = \frac{1}{3} \frac{M}{V} C^2$$

$$PV = \frac{1}{3} MC^2$$

Consider one gram molecule of a gas at an absolute temperature T. The mean energy of the molecules

$$= \frac{1}{2} MC^2$$

$$= \frac{1}{2} NmC^2$$

$$\therefore \quad PV = \frac{1}{3} NmC^2$$

$$= \frac{2}{3} N \cdot \frac{1}{2} \cdot mC^2$$

Mean kinetic energy of a molecule

$$= \frac{1}{2} mC^2$$

$$= \frac{3}{2} kT$$

$$\therefore \quad PV = \frac{2}{3} N \cdot \frac{3}{2} kT$$

$$PV = NkT$$

But $N \times k = R$

$$\therefore \quad PV = RT \qquad \ldots(ii)$$

Note on the Gas Equation.

In the gas equation

$$PV = RT$$

P is in dynes/sq cm

$R = 8{\cdot}31 \times 10^7$ ergs/g mol-K

T is in K

V is the volume in cc per gram molecule.

Example 5·7 *Calculate the volume occupied by 3·2 grams of oxygen at 76 cm of Hg and 27°C.*

Here $P = 76 \times 13{\cdot}6 \times 980$ dynes/sq cm

$T = 27 + 273$

$= 300$ K

$R = 8{\cdot}31 \times 10^7$ ergs/g mol-K

$PV = RT$

$$V = \frac{8{\cdot}31 \times 10^7 \times 300}{76 \times 13{\cdot}6 \times 980} \text{ cc per g-mol}$$

$V = 24610$ cc per g mol

Volume for 3·2 g of oxygen $= v$

$$= \frac{24610 \times 3{\cdot}2}{32}$$

$$= 2461 \text{ cc}$$

5·18. Derivation of Gas Laws

(i) Boyle's Law

According to the kinetic theory,

$$P = \frac{1}{3} \rho C^2$$

$$P = \frac{1}{3} \frac{M}{V} C^2$$

$$PV = \frac{1}{3} MC^2 \qquad \ldots(i)$$

At a constant temperature T, C^2 is constant. Therefore at a constant temperature

$$\frac{1}{3} MC^2 = \text{constant}$$

Hence $PV = \text{const.}$ —at constant temperature.

(ii) Charles' Law

According to the kinetic theory

$$P = \frac{1}{3} \rho C^2$$

$$P = \frac{1}{3} \frac{M}{V} C^2$$

$$PV = \frac{1}{3} M C^2$$

Consider one gram molecule of a gas at absolute temperature T.

$$M = mN$$

$$PV = \frac{1}{3} NmC^2 \qquad \ldots(i)$$

The mean kinetic energy of a molecule

$$\frac{1}{2} mC^2 = \frac{3}{2} kT$$

$$mC^2 = 3kT$$

Substituting this value in equation (*i*),

$$\therefore \quad PV = NkT \qquad \ldots(ii)$$

where N is the Avogadro's number and k is the Boltzmann's constant.

If P is constant,

$$V \propto T$$

It means that for a given mass of gas, the volume is directly proportional to the absolute temperature provided the pressure remains constant. This is Charles' Law.

(iii) Regnault's Law

From equation (*ii*)

$$PV = NkT$$

When V is constant,

$$P \propto T$$

It means that for a given mass of gas, the pressure is directly proportional to its absolute temperature provided the volume remains constant.

Example 5·8. *Show that n, the number of molecules per unit volume of an ideal gas is given by*

$$n = \frac{PN}{RT}$$

where N is Avogadro's number.

For an ideal gas, for one gram molecule of a gas,

$$PV = RT$$

But $R = Nk$

$$PV = NkT.$$

Let n be the number of molecules per cc. In that case,

$$P = nkT$$

$$\therefore \quad n = \frac{P}{kT}$$

But $k = \frac{R}{N}$

$$\therefore \quad n = \frac{PN}{RT}$$

Example 5·9. *Calculate the number of molecules in one cubic metre of an ideal gas at* N.T.P.

Let the number of molecules per cc be n.

$$n = \frac{PN}{RT}$$

Number of molecules in one cubic metre volume

$$x = n \times 10^6$$

$$x = \frac{PN \times 10^6}{RT}$$

Here $P = 76 \times 13{\cdot}6 \times 980$ dynes/cm^2

$N = 6{\cdot}023 \times 10^{23}$

$R = 8{\cdot}31 \times 10^7$ erg/g

$$T = 273 \text{ K}$$

$$x = \frac{76 \times 13{\cdot}6 \times 980 \times 6{\cdot}023 \times 10^{23} \times 10^{6}}{8{\cdot}31 \times 10^{7} \times 273}$$

$$x = 2{\cdot}688 \times 10^{25}$$

Example 5·10 *Calculate the number of molecules in one litre of an ideal gas at 136·5°C temperature and 3 armospheres pressure.*

Let the number of molecules per cc $= n$

$$n = \frac{PN}{RT}$$

Number of molecules in one litre,

$$x = n \times 10^{3}$$

$$x = \frac{PN \times 10^{3}}{RT}$$

Here

$$P = 3 \times 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$N = 6{\cdot}023 \times 10^{23}$$
$$R = 8{\cdot}31 \times 10^{7} \text{ ergs/g mol-K}$$
$$T = (273 + 136{\cdot}5)$$
$$= 409{\cdot}5 \text{ K}$$

$$\therefore \quad x = \frac{3 \times 76 \times 13{\cdot}6 \times 980 \times 6{\cdot}023 \times 10^{23} \times 10^{3}}{8{\cdot}31 \times 10^{7} \times 409{\cdot}5}$$

$$x = 5{\cdot}376 \times 10^{22}$$

Example 5·11 *The number of molecules per* cc *of a gas is* $2{\cdot}7 \times 10^{19}$ *at* N.T.P. *Calculate the number of molecules per* cc *of the gas.*

(*i*) *at* 0°C *and* 10^{-6} mm *pressure of mercury and*

(*ii*) *at* 39°C *and* 10^{-6} mm *pressure mercury.*

For a unit volume of a gas

$$P = \frac{1}{3} mnC^2$$

(*i*) At 0°C, R.M.S. velocity is equal to C

At N.T.P.

$$P_1 = \frac{1}{3} mn_1 C^2 \qquad \ldots (i)$$

At 0°C and 10^{-6} mm pressure

$$P_2 = \frac{1}{3} mn_2 C^2 \qquad \ldots (ii)$$

From (*i*) and (*ii*)

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

or

$$n_2 = \frac{n_1 \times P_2}{P_1}$$

Here

$$n_1 = 2{\cdot}7 \times 10^{19}$$
$$P_1 = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$P_2 = 10^{-6} \text{ mm of Hg}$$
$$= 10^{-7} \text{ cm of Hg}$$
$$P_2 = 10^{-7} \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$n_2 = \frac{2{\cdot}7 \times 10^{19} \times 10^{-7} \times 13{\cdot}6 \times 980}{76 \times 13{\cdot}6 \times 980}$$

$$n_2 = 3{\cdot}553 \times 10^{10}$$

(*ii*) Let the R.M.S. velocity at 0°C be C_2 and at 39°C be C_3. Number of molecules per cc at 0°C and 10^{-6} mm of Hg pressure

$$= n_2$$

and at 39°C and 10^{-6} mm of Hg pressure

$$= n_3$$

$$P = \frac{1}{3} mnC^2$$

Here pressure is the same in both the cases

$$\therefore \quad \frac{1}{3} mn_2 C_2^2 = \frac{1}{3} mn_3 C_3^2$$

$$\therefore \quad n_2 C_2^2 = n_3 C_3^2$$

$$n_3 = n_2 \frac{C_2^2}{C_3^2}$$

But

$$C \propto \sqrt{T}$$

$$\therefore \quad \frac{C_2^2}{C_3^2} = \frac{T_2}{T_3}$$

$$\therefore \quad n_3 = \frac{n_2 \times T_2}{T_3}$$

Here

$$n_2 = 3{\cdot}553 \times 10^{10}$$
$$T_2 = 0° \text{ C}$$
$$= 273 \text{ K}$$
$$T_3 = 39° \text{ C}$$
$$= 273 + 39$$
$$= 312 \text{ K}$$

$$\therefore \quad n_3 = \frac{3{\cdot}553 \times 10^{10} \times 273}{312}$$

$$n_3 = 3{\cdot}109 \times 10^{10}$$

5·19 Avogadro's Hypothesis

Consider two gases A and B at a pressure P and each having a volume V.

Mass of each molecule of the first gas $= m_1$

Number of molecules of the first gas $= n_1$

Mean square velocity of the molecules of the first gas $= C_1^2$

For the first gas

$$P = \frac{1}{3}\rho_1 C_1^2$$

$$= \frac{1}{3}\frac{m_1 n_1 C_1^2}{V} \quad \ldots(i)$$

Similarly for the second gas

$$P = \frac{1}{3}\rho_2 C_2^2$$

$$= \frac{1}{3}\frac{m_2 n_2 C_2^2}{V} \quad \ldots(ii)$$

where m_2 represents the mass of each molecule, n_2 the number of molecules and C_2^2 the mean square velocity of the molecules.

From (i) and (ii),

$$\frac{1}{3}\frac{m_1 n_1 C_1^2}{V} = \frac{1}{3}\frac{m_2 n_2 C_2^2}{V}$$

or $$m_1 n_1 C_1^2 = m_2 n_2 C_2^2 \quad \ldots(iii)$$

If the two gases are at the same temperature T, the mean kinetic energy of the molecules of both the gases is the same

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2$$

$$\therefore \quad m_1 C_1^2 = m_2 C_2^2 \quad \ldots(iv)$$

From (iii) and (iv),

$$n_1 = n_2$$

Hence, equal volumes of all gases under similar conditions of temperature and pressure have the same number of molecules. This represents Avogadro's hypothesis.

5·20 Graham's Law of Diffusion of Gases

According to the kinetic theory

$$P = \frac{1}{3}\rho C^2$$

or $$C = \sqrt{\frac{3P}{\rho}}$$

$$C \propto \frac{1}{\sqrt{\rho}}$$

It means that the root mean square velocity of the molecules of a gas is inversely proportional to the square root of its density. Consider two gases whose root mean square velocities are C_1 and C_2.

$$\frac{C_1}{C_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

or $$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Here, r_1 and r_2 represent the rates of diffusion of the two gases.

Example 5·12. *Calculate the total random kinetic energy of one gm-molecule of oxygen at 300* K.

Total random kinetic energy per gram-molecule of oxygen

$$= \frac{1}{2} mC^2 \times N$$

$$= \frac{3}{2} kT.N$$

$$= \frac{3}{2} \cdot \frac{R}{N} T.N$$

$$= \frac{3}{2} RT$$

$$= \frac{3}{2} \times 8{\cdot}3 \times 10^7 \times 300$$

$$= 3{\cdot}735 \times 10^{10} \text{ ergs}$$

$$= \mathbf{3735 \text{ joules}}$$

Note. The total random kinetic energy for one gram-molecule of any gas *i.e.*, hydrogen, oxygen, belium, nitrogen, air etc. is the same at the same temperature.

Example 5·13. *Calculate the average kinetic energy of a molecule of a gas at a temperature of 300* K.

Average K.E. of a molecule

$$= \frac{1}{2} mC^2 = \frac{3}{2} kT$$

Here k is Boltzmann's constant.

$$k = 1{\cdot}38 \times 10^{-16} \text{ erg/molecule-deg}$$

Average K.E. of a molecule $= \frac{3}{2} \times 1{\cdot}38 \times 10^{-16} \times 300$

$$= \mathbf{6{\cdot}21 \times 10^{-14} \text{ ergs}}$$

Note. The average kinetic energy of a molecule of any gas *i.e.*, hydrogen, oxygen, helium, nitrogen, air, etc., is the same at the same temperature.

Example 5·14. *Calculate the mean translational kinetic energy per molecule of a gas at 727°C, given R = 8·32* joules/mole-K

(Delhi, 1974)

Avogadro's number,

$$N = 6{\cdot}06 \times 10^{23}$$

$$T = 627 + 273 = 1000 \text{ K}$$

Here $$R = 8{\cdot}32 \text{ joules/mol-K}$$

$$N = 6{\cdot}06 \times 10^{23}$$

$$k = \frac{R}{N} = \left(\frac{8{\cdot}32}{6{\cdot}06 \times 10^{23}}\right) \text{ joules/molecule-K}$$

Mean translational kinetic energy per molecule $= \frac{3}{2} kT$

$$= \frac{3 \times 8{\cdot}32 \times 1000}{2 \times 6{\cdot}06 \times 10^{23}}$$

$$= \mathbf{2{\cdot}059 \times 10^{-20}\ joule}$$

Example 5·15. *Calculate the total random kinetic energy of one gram of nitrogen at 300* K.

Total random energy for one gram molecule of nitrogen

$$= \frac{3}{2} RT$$

Total random energy for 1 gram of nitrogen

$$= \frac{3\ RT}{2\ M}$$

where the molecular weight of nitrogen $M = 28$ g

$$E = \frac{3RT}{2M}$$

$$= \frac{3 \times 8{\cdot}3 \times 10^7 \times 300}{2 \times 28}$$

$$= 133{\cdot}4 \times 10^7 \text{ ergs}$$

$$= \mathbf{133{\cdot}4\ joule}$$

Note. The total random kinetic energy for 1 gram of a gas is different for different gases at the same temperature.

Example 5·16. *Calculate the total random kinetic energy of 2 g of helium at 200* K.

Energy for 1 g of helium

$$= \frac{3RT}{2M}$$

Energy for 2 g of helium

$$= \frac{2 \times 3 \times RT}{2M}$$

$$= \frac{3RT}{M}$$

$$= \frac{3 \times 8{\cdot}3 \times 10^7 \times 200}{4}$$

$$= 1245 \times 10^7 \text{ ergs}$$

$$= \mathbf{1245\ joules}$$

Example 5·17. *Calculate the root mean square velocity of a molecule of mercury vapour at 300* K.

Mean kinetic energy of one molecule of mercury

$$= \frac{1}{2} mC^2 = \frac{3}{2} kT$$

Let N be the Avogadro's number.

Then $$\frac{1}{2} mNC^2 = \frac{3}{2} kNT$$

$$\frac{1}{2} MC^2 = \frac{3}{2} RT$$

$$C = \sqrt{\frac{3RT}{M}}$$

Here the molecular weight of mercury, $M = 221$

$$\therefore \quad C = \sqrt{\frac{3 \times 8{\cdot}3 \times 10^7 \times 300}{221}}$$

$$= \mathbf{1{\cdot}93 \times 10^4\ cm/s}$$

Example 5·18. *With what speed would one gram molecule of oxygen at 300* K *be moving in order that the translational kinetic energy of its centre of mass is equal to the total random kinetic energy of all its molecules ? Molecular weight of oxygen* $(M) = 32$.

Total random kinetic energy of 1 gram-molecule of oxygen

$$= \frac{3}{2} RT = \frac{3}{2} \times 8{\cdot}3 \times 10^7 \times 300$$

$$= 3{\cdot}735 \times 10^{10} \text{ ergs}$$

Kinetic energy of M grams of oxygen moving with a velocity v

$$= \frac{1}{2} Mv^2$$

$$\therefore \quad \frac{1}{2} Mv^2 = 3{\cdot}735 \times 10^{10}$$

$$\frac{1}{2} \times 32 \times v^2 = 3{\cdot}735 \times 10^{10}$$

$$v^2 = \frac{3{\cdot}735 \times 10^{10}}{16}$$

$$\mathbf{x = 4{\cdot}8 \times 10^4\ cm/s}$$

Example 5·19. *Calculate the temperature at which the r.m.s. velocity of a hydrogen molecule will be equal to the speed of the earth's first satellite* (*i.e.* $v = 8$ km/s).

Energy for 1 gram molecule of hydrogen

$$= \frac{1}{2} Mv^2 = \frac{3}{2} RT$$

$$T = \frac{Mv^2}{3R}$$

$$= \frac{2 \times (8 \times 10^5)^2}{3 \times 8{\cdot}3 \times 10^7}$$

$$= \mathbf{5{\cdot}14 \times 10^3\ K}$$

Example 5·20. *At what temperature, pressure remaining constant, will the r.m.s. velocity of a gas be half its value at 0°C ?*

[Delhi (Hons.) 1975]

$$\frac{C_2}{C_1} = \sqrt{\frac{T_2}{T_1}}$$

Here $C_2 = \frac{C_1}{2}$

$T_2 = ?$

$T_1 = 273$ K

$$\therefore \quad \frac{1}{2} = \sqrt{\frac{T_2}{273}}$$

$$\frac{1}{4} = \frac{T_2}{273}$$

$$T_2 = \frac{273}{4} = 68{\cdot}25 \text{ K}$$

or $T_2 = -204{\cdot}75°\text{C}$

5·21 Degrees of Freedom and Maxwell's Law of Equipartition of Energy

A molecule in a gas can move along any of the three co-ordinate axes. It has three degrees of freedom. Degrees of freedom mean the number of independent variables that must be known to describe the state or the position of the body completely. A mono-atomic gas molecule has three degrees of freedom. A diatomic gas molecule has three degrees of freedom of translation and two degrees of freedom of rotation. It has in all five degrees of freedom.

According to kinetic theory of gases, the mean kinetic energy of a molecule at a temperature T is given by

$$\frac{1}{2}mC^2 = \frac{3}{2}kT \qquad \ldots(i)$$

But $C^2 = u^2+v^2+w^2$

As x, y and z are all equivalent, mean square velocities along the three axes are equal

$$\therefore \quad u^2 = v^2 = w^2$$

or $\frac{1}{2}m(u^2) = \frac{1}{2}m(v^2) = \frac{1}{2}m(w^2)$

$$\therefore \quad \frac{1}{2}mC^2 = 3\left[\frac{1}{2}m(u^2)\right] = 3\left[\frac{1}{2}m(v^2)\right]$$

$$= 3\left[\frac{1}{2}m(w^2)\right]$$

$$= \frac{3}{2}kT$$

$$\therefore \quad \frac{1}{2}mu^2 = \frac{1}{2}kT \qquad \ldots(ii)$$

$$\frac{1}{2}mv^2 = \frac{1}{2}kT \qquad \ldots(iii)$$

$$\frac{1}{2}mw^2 = \frac{1}{2}kT \qquad \ldots(iv)$$

Therefore, the average kinetic energy associated with each degree of freedom $= \frac{1}{2}kT$

Thus the energy associated with each degree of freedom (whether translatory or rotatory) is $\frac{1}{2}kT$.

This represents the theorem of equipartition of energy.

5·22 Atomicity of Gases

(*i*) *Mono-atomic gas.* A mono-atomic gas molecule has one atom. Each molecule has three degrees of freedom due to translatory motion only.

Energy associated with each degree of freedom $= \frac{1}{2}kT$

Energy associated with three degrees of freedom

$$= \frac{3}{2}kT$$

Consider one gram molecule of a gas.

Energy associated with one gram molecule of a gas

$$= N \times \frac{3}{2}kT$$

$$= \frac{3}{2}(N \times k)T$$

[But, $N \times k = R$]

$$\therefore \quad U = \frac{3}{2}RT$$

This energy of the gas is due to the energy of its molecules. It is called internal energy U. For an ideal gas, it depends upon temperature only.

$$\therefore \quad C_v = \frac{dU}{dT} = \frac{3}{2}R$$

$\left(\frac{dU}{dT}\right.$ is the increase in internal energy per unit degree rise of temperature$\left.\right)$

But $C_P - C_V = R$

$$C_P = C_V + R$$

$$= \frac{3}{2}R + R = \frac{5}{2}R$$

For a mono-atomic gas

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1{\cdot}67$$

The value of γ is found to be true experimentally for monoatomic gases like argon and helium.

(*ii*) *Diatomic gas.* A diatomic gas molecule has two atoms. Such a molecule has three degrees of freedom of translation and two degrees of freedom of rotation.

Energy associated with each degree of freedom

$$= \frac{1}{2} kT$$

Energy associated with 5 degrees of freedom $= \frac{5}{2} kT$

Consider one gram molecule of gas.

Energy associated with 1 gram molecule of a diatomic gas

$$= N \times \frac{5}{2} kT = \frac{5}{2} RT$$

$$U = \frac{5}{2} RT$$

$$C_V = \frac{dU}{dT}$$

$$= \frac{5}{2} R$$

But $C_P - C_V = R$

$$C_P = C_V + R$$

$$= \frac{5}{2} R + R = 7/2\ R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{\frac{7}{2} R}{\frac{5}{2} R} = 1{\cdot}40$$

The value of $\gamma = 1{\cdot}40$ has been found to be true experimentally for diatomic gases like hydrogen, oxygen, nitrogen etc.

(*iii*) *Triatomic gas.* (*a*) A triatomic gas having 6 degrees of freedom has an energy associated with 1 gram molecule

$$= N \times \frac{6}{2} kT = 3RT$$

$$U = 3RT$$

$$C_V = \frac{dU}{dT} = 3R$$

But $C_P - C_V = R$

$$C_P = C_V + R$$

$$= 3R + R = 4R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{4R}{3R} = 1{\cdot}33$$

(*b*) A triatomic gas having 7 degrees of freedom has an energy associated with 1 gram molecule $= N \times \frac{7}{2} kT = \frac{7}{2} R$

$$U = \frac{7}{2} RT$$

$$C_V = \frac{dU}{dT} = \frac{7}{2} R$$

But $C_P - C_V = R$

$$C_P = C_V + R$$

$$= \frac{7}{2} R + R = \frac{9}{2} R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{9/2\ R}{7/2\ R} = 1{\cdot}28$$

Thus the value of γ, C_P and C_V can be calculated depending upon the degrees of freedom of a gas molecule.

5·23 Maxwell's Law of Distribution of Velocity

At a particular temperature, a gas molecule has a fixed mean kinetic energy. It does not mean that the molecule is moving with the same speed throughout its movement. After each encounter the speed of the molecule changes and due to a large number of collisions, the speed is different at different instants. But the root mean square velocity (r.m.s.) C remains the same at a fixed temperature. At any instant, all the molecules are not moving with the same velocity. Some are moving with a velocity higher than C and the others with a velocity lower than C. But the mean kinetic energy of all the molecules remains constant at a given temperature.

Derivation of Maxwell's law of Distribution of Molecular velocities

The mean square velocity of molecules is defined by the equation

$$C^2 = \frac{1}{N} \int_0^\infty c^2\, dN$$

Here dN is the number of molecules having velocities between c and $c+dc$. If the total number of molecules is N, then a fraction $\frac{dN}{N}$ will have the components of velocities in x direction in the range

u and $u+du$. However, the fraction $\frac{dN_x}{N}$ is a function of U only and is proportional to du.

$$\therefore \quad \frac{dN_x}{N} = f(u)du$$

$$\therefore \quad dN_x = N f(u)\, du$$

The equations for y and z directions are

$$dN_y = Nf(v)dv$$

and

$$dN_z = Nf(w)dw$$

Also the value of N is too large and du is small compared with u but in range u and $u+du$, there are a large number of molecules. The fraction of dN_x molecules whose y components of velocity lie in the range v and $v+dv$ is given by the equation

$$\frac{d^2N_{x,y}}{dN_x} = \frac{dN_y}{N} = f(v)dv$$

$$\therefore \quad d^2N_{x,y} = N f(u)\, f(v) du\, dv$$

The number of molecules represented by $d^2N_{x,y}$ is still large. Suppose that the fraction of these molecules $d^2N_{x,y,z}$ whose components of velocity in Z direction in the range w and $w+dw$ is given by the equation

$$d^3N_{x,y,z} = Nf(u)\, f(v)\, f(w) du\, dv\, dw$$

The density of velocity points is given by the equation

$$\rho = \frac{d^3N_{x,y,z}}{du\, dv\, dw} = Nf(u)\, f(v)\, f(w)$$

As there is no preferred direction of the velocities, the density of velocity points ρ is constant *i.e.*, velocity space is isotropic.

Also $$C^2 = u^2+v^2+w^2$$

$$\therefore \quad Nf(u)\, f(v)\, f(w) = \text{const.} \qquad \ldots(i)$$

when $$u^2+v^2+w^2 = \text{constant} \qquad \ldots(ii)$$

These equations (i) and (ii) must be simultaneously satisfied. Equation (ii) limits the values of the variables in equation (i) and reduces the number of independent variables to two. Therefore it is called an equation of constraint.

Differentiating equations (i) and (ii)

$$f(v)\, f(w) \frac{\partial f(u)}{\partial u} du + f(w)\, f(u) \frac{\partial f(v)}{\partial v} dv + f(u)\, f(v) \frac{\partial f(w)}{\partial w} dw = 0 \qquad \ldots(iii)$$

and

$$2u\, du + 2v\, dv + 2w\, dw = 0 \qquad \ldots(iv)$$

Simplifying equations (iii) and (iv)

$$\frac{1}{f(u)} \frac{\partial f(u)}{\partial u} du + \frac{1}{f(v)} \frac{\partial f(v)}{\partial v} dv + \frac{1}{f(w)} \frac{\partial f(w)}{\partial w} dw = 0 \qquad \ldots(v)$$

and

$$u\, du + v\, dv + w\, dw = 0 \qquad \ldots(vi)$$

As there are only two independent variables, arbitrary values cannot be given to all the three differentials. Suppose the arbitrary values are given to dv and dw. Multiply equation (vi) by $m\beta$ where m is the mass of the molecules and β is an arbitrary, unknown function. The product $m\beta$ is called Langrange undetermined multiplier.

$$\therefore \quad m\beta[udu+vdv+wdw] = 0 \qquad \ldots(vii)$$

Adding equations (v) and (vii)

$$\left[\frac{1}{f(u)} \frac{\partial f(u)}{\partial u} + m\beta u\right] du + \left[\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + m\beta v\right] dv + \left[\frac{1}{f(w)} \frac{\partial f(w)}{\partial w} + m\beta w\right] dw = 0 \qquad \ldots(viii)$$

As the two variables v and w are considered to be independent, their differentials are arbitrary and the values, $dv = 0$ and $dw = 0$ may be assigned to them.

From equation $(viii)$

$$\left(\frac{1}{f(u)} \frac{\partial f(u)}{\partial u} + m\beta u\right) = 0 \qquad \ldots(ix)$$

Taking $dv = 0$, and $dw \neq 0$, we get

$$\frac{1}{f(w)} \frac{\partial f(w)}{\partial w} + m\beta w = 0 \qquad \ldots(x)$$

Taking $dw = 0$ and $dv \neq 0$

$$\frac{1}{f(v)} \frac{\partial f(v)}{\partial v} + m\beta v = 0 \qquad \ldots(xi)$$

To satisfy equations (ix), (x) and (xi), β would either be a constant or a function of the variable in that equation. A constant value of β is the only value that can satisfy all the equations. It is clear from the above equations that the function f satisfies the same differential equation irrespective of the component.

For the x component

$$\frac{d}{du}[\log f(u)] = -m\beta u$$

$$\int d[\log f(u)] = -m\beta \int u\, du$$

$$\log f(u) = -\beta(\tfrac{1}{2}mu^2) + \log A \qquad \ldots(xii)$$

Here A is a constant of integration.

From equation (*xii*)

$$f(u) = Ae^{-\beta(\frac{1}{2}mu^2)} \qquad \ldots(xiii)$$

Similarly $$f(v) = Ae^{-\beta(\frac{1}{2}mv^2)} \qquad \ldots(xiv)$$

and $$f(w) = Ae^{-\beta(\frac{1}{2}mw^2)} \qquad \ldots(xv)$$

From these three equations, the density of velocity points is given by

$$\rho = NA^3 e^{-\beta[\frac{1}{2}m(u^2+v^2+w^2)]}$$

or $$\rho = NA^3\, e^{-\beta[\frac{1}{2}mc^2]} \qquad \ldots(xvi)$$

But $$\rho = \frac{d^3N_{x,\,y,\,z}}{du\,dv\,dw} \qquad \ldots(xvii)$$

i.e. the number of molecules with components of velocity lying in a small cubical volume divided by the volume element. However ρ is constant within the infinitesimal spherical shell within the radii c and $c+dc$. The volume of this element is $4\pi c^2 dc$. This volume element contains dN molecules.

$$\therefore \quad \rho = \frac{dN}{4\pi c^2\, dc} \qquad \ldots(xviii)$$

From equations (*xvi*) and (*xviii*)

$$\frac{dN}{4\pi c^2 dc} = NA^3\, e^{-\beta[\frac{1}{2}mc^2]}$$

or $$\frac{dN}{dc} = 4\pi NA^3 c^2 e^{-\beta[\frac{1}{2}mc^2]} \qquad \ldots(xix)$$

$$\therefore \quad dN = 4\pi NA^3\, e^{-bc^2} c^2 dc \qquad \ldots(xx)$$

where N represents the number of molecules per cc and

$$A = \sqrt{\frac{b}{\pi}} \text{ and } b = \frac{\beta m}{2}$$

and $$b = \frac{m}{2kT},\ \beta = \frac{1}{kT}$$

Here k is Boltzmann's constant.

The graph representing dN/dc and speed is shown in Fig. 5·8.

The shaded area in the figure represents the number of molecules dN having velocities between c and $c+dc$. The number of molecules possessing the root mean square velocity C is maximum.

The number of molecules having very low or very high velocity is small. The total area under the curve represents the tolal number of molecules.

From equation (*xx*)

$$\frac{dN}{dc} = 4\pi N\left[\frac{m}{2\pi kT}\right]^{3/2} c^2\, e^{-\frac{mc^2}{2kT}}$$

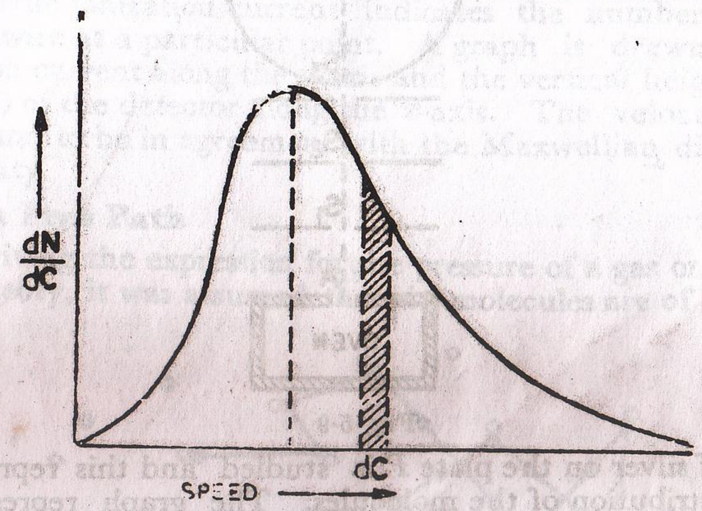


Fig. 5·8

$$\frac{dN}{dc} = \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} c^2\, e^{-\frac{mc^2}{2kT}} \qquad \ldots(xxi)$$

Taking $\frac{1}{2}mc^2 = E$ where E is the mean kinetic energy of a molecule,

$$\frac{dN}{dc} = \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} c^2\, e^{-\frac{E}{kT}} \qquad \ldots(xxii)$$

Thus, Maxwell's law of distribution of velocities shows that the mean kinetic energy of all the molecules of a gas remains constant at a fixed temperature, though at any instant the molecules are moving with different velocities.

5·24 Experimental Verification of Velocity Distribution

Zartman and Ko (1934) performed an experiment to study the distribution of velocity. The apparatus consists of an oven with an opening at A. S_1 and S_2 are two parallel slits. A drum D can be rotated about an axis passing through O. P is a glass surface on which a beam of silver atoms will get deposited (Fig. 5·9).

Metallic silver is melted in the oven. A beam of silver atoms is ejected through A. The drum D is rotated with a speed of 6000 r.p.m. approximately. When the drum is stationary, the silver atoms get deposited at the same point on the glass plate. When the drum is rotated a fine beam of silver molecules enters through the slit S_2. Molecules with very high speeds reach the plate P first, *i.e.*, on the right end of P and moleeules with very low speeds reach the other

end of the plate. After a short time, sufficient quantity of silver is deposited on the plate P. Using a spectro-photometer, the relative

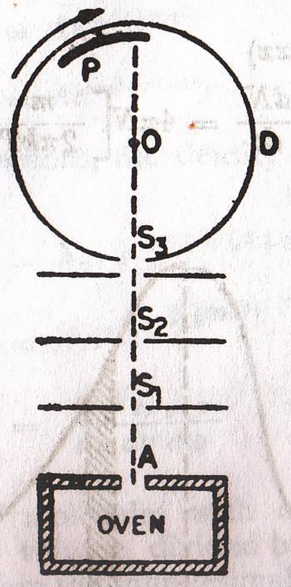


Fig. 5·9

intensity of silver on the plate P is studied and this represents the velocity distribution of the molecules. The graph representing the number of molecules and velocity agrees with Maxwell's distribution of velocity.

In 1947, Estermann, Simpson and Stern designed a more precise apparatus to study the velocity distribution.

Cesium atoms from the oven emerge from the opening A (Fig. 5·10). S is a slit and D is a hot tungsten wire. The whole apparatus is enclosed in an evacuated chamber (pressure 10^{-8} mm of Hg). The opening A and the slit S are horizontal. In the absence of a gravitational field, cesium atoms will strike the wire at D. But due to the gravitational field, the path is a parabola. The atoms

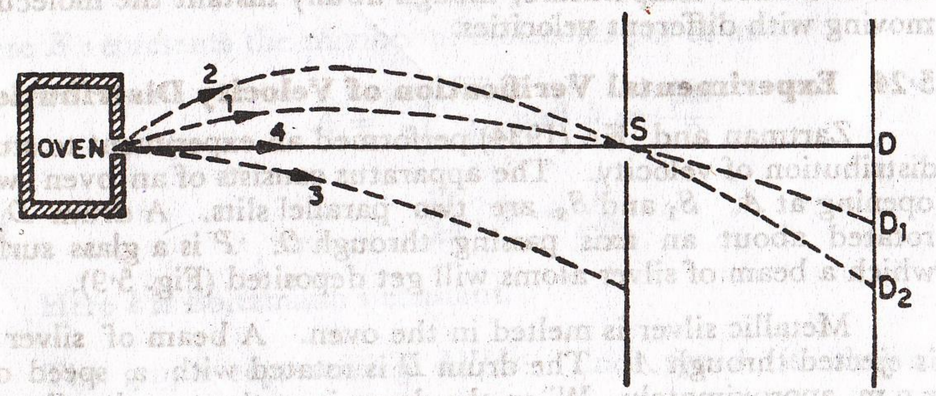


Fig. 5·10

going along the path 3 do not reach the wire. The atoms going along the paths 1 and 2 reach at D_1 and D_2 respectively. The velocity of the atoms in path 1 is higher than the path 2.

When cesium atoms strike the wire they get ionized and re-evaporate. They are collected by a negatively charged detecting cylinder surrounding the tungsten wire. The magnitude of the current indicates the intensity of the atoms at various positions. The detector can be moved to different positions of the wire. The atoms reaching at D_1 have higher velocity than those reaching at D_2. The vertical height of the detector represents the magnitude of the velocity and the ionization current indicates the number of atoms striking the wire at a particular point. A graph is drawn between the ionization current along the y-axis and the vertical height (speed of the atoms) of the detector along the x-axis. The velocity distribution is found to be in agreement with the Maxwellian distribution law of velocity.

5·25 Mean Free Path

In deriving the expression for the pressure of a gas on the basis of kinetic theory, it was assumed that the molecules are of negligible

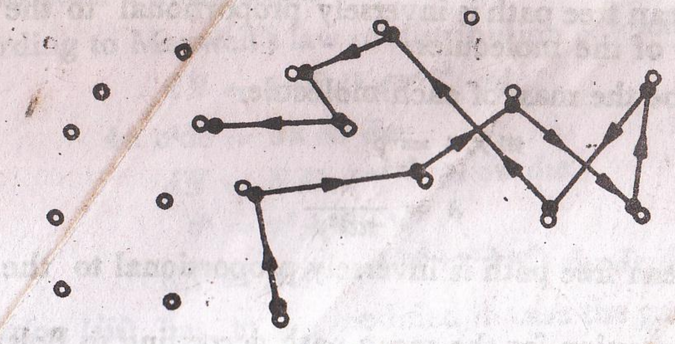


Fig. 5·11

size. They were assumed to be geometrical points. A geometrical point has no dimensions and hence inter-molecular collisions will not be possible. But, a molecule has a finite size (though small) and moves in the space of the vessel containing it. It collides with other molecules and the walls of the containing vessel. The path covered by a molecule between any two consecutive collisions is a straight line, and is called the **free path**. The direction of the molecule is changed after every collision. After a number of collisions, the total path appears to be zig-zag and the free path is not constant (Fig. 5·11). Therefore, a term **mean free path** is used to indicate the mean distance travelled by a molecule between two collisions. If the total distance travelled after N collisions is S, then the mean free path λ is given by

$$\lambda = \frac{S}{N} \qquad \ldots(i)$$

Let the molecules be assumed to be spheres of diameter d. A collision between two molecules will take place if the distance between the centres of the two molecules is d. Collision will also occur if the colliding molecule has a diameter $2d$ and the other molecule is simply a geometrical point. Thus, assuming all other molecules to be geometrical points and the colliding molecule of diameter $2d$, this molecule will cover a volume $\pi d^2 v$ in one second. This corresponds to the volume of a cylinder of diameter $2d$ and length v.

Let n be the number of molecules per cc.

Then, the number of molecules present in a volume $\pi d^2 v$

$$= \pi d^2 v \times n$$

This value also represents the number of collisions made by the molecule in one second.

The distance moved in one second $= v$ and the number of collisions in one second $= \pi d^2 v \times n$.

$$\therefore \quad \text{Mean free path } \lambda = \frac{v}{\pi d^2 v n}$$

$$= \frac{1}{\pi d^2 n} \qquad \ldots(i)$$

This equation was deduced by Clausius.

$$\therefore \qquad \lambda \propto \frac{1}{d^2} \qquad \ldots(ii)$$

The mean free path is inversely proportional to the square of the diameter of the molecules.

Let m be the mass of each molecule.

Then, $\qquad m \times n = \rho$

$$\lambda = \frac{m}{\pi d^2 \rho} \qquad \ldots(iii)$$

The mean free path is inversely proportional to the density of the gas.

The expression for the mean path according to Boltzmann is

$$\lambda = \frac{3}{4\pi d^2 n} \qquad \ldots(iv)$$

He assumed that all molecules have the same average speed.

Maxwell derived the expression,

$$\lambda = \frac{1}{\sqrt{2}.\pi d^2 n} \qquad \ldots(v)$$

He calculated the value of λ on the basis of the law of distribution of velocities

TABLE

Mean Free Path (λ)

Gas	d	λ
Hydrogen	$2{\cdot}47 \times 10^{-8}$ cm	$1{\cdot}83 \times 10^{-5}$ cm
Nitrogen	$3{\cdot}50 \times 10^{-8}$ cm	$0{\cdot}944 \times 10^{-5}$ cm
Helium	$2{\cdot}18 \times 10^{-8}$ cm	$2{\cdot}85 \times 10^{-5}$ cm
Oxygen	$3{\cdot}39 \times 10^{-8}$ cm	$0{\cdot}999 \times 10^{-5}$ cm

Determination of mean free path. As discussed in article 5·27, the relation between coefficient of viscosity and the mean free path of a molecule is given by

$$\eta = \frac{1}{3} mnC\lambda$$

For unit volume,

$$mn = \rho$$

$$\therefore \qquad \eta = \frac{1}{3} \rho C\lambda$$

$$\lambda = \frac{3\eta}{\rho C} \qquad \ldots(i)$$

The root mean square velocity C of a molecule can be calculated knowing pressure, density and temperature. The coefficient of viscosity of the gas is determined experimentally. Hence the value of the mean free path of a molecule can be calculated from equation (i).

5·26 Transport Phenomena

According to Maxwell's law of distribution of velocity

$$dN = 4\pi N A^3 e^{-bc^2} c^2 dc \qquad \ldots(i)$$

But $\qquad 4\pi c^2 dc = du\, dv\, dw$

$$dN = NA^3 e^{-bc^2} du\, dv\, dw \qquad \ldots(ii)$$

Also $\qquad c^2 = u^2 + v^2 + w^2$

$$\therefore \qquad dN = NA^3 e^{-b(u^2+v^2+w^2)} du\, dv\, dw \qquad \ldots(iii)$$

Equation (iii) has to be modified in case the gas as a whole possesses mass motion.

Let u_0, v_0 and w_0 be the components of the mass velocity. Therefore, the actual velocity of a molecule consists of two parts :

(i) the mass velocity components u_0, v_0 and w_0

(ii) the random thermal velocity components

$$u - u_0,\ v - v_0 \text{ and } w - w_0$$

Corresponding to thermal motion without mass motion, similar quantities with mass motion are

$$U = u - u_0$$

$$V = v - v_0$$

and $\qquad W = w - w_0$

From equation (iii), Maxwell's law of distribution of velocity can be written as

$$dN = NA^3 e^{-b(U^2+V^2+W^2)} dU\, dV\, dW \ldots(iv)$$

Equation (iv) holds good only if u_0, v_0, w_0, T and N are constant throughout the gas.

If the gas is not in an equilibrium state, there are three possibilities occurring singly or jointly.

(1) The components of velocity, u_0, v_0, and w_0 may not have the same value in all parts of the gas. This will result in relative motion of the gas layers with respect to one another.

There is relative velocity between different layers of the gas. This gives rise to the phenomena of viscosity.

(2) The temperature of the gas may not be the same throughout. This results in the transference of thermal energy from regions of higher to lower temperature. This gives rise to the phenomenon of conduction.

(3) The number of molecules per cc *i.e.*, N, may not be the same throughout the volume of the gas. This results in the movement of molecules from regions of higher value of N to lower value of N. This gives rise to the phenomenon of diffusion.

From the above disussion it is clear that the transport of momentum, energy and mass represent viscosity, conduction and diffusion respectively. These are called *transport phenomena*. From the thermodynamic point of view, the transport phenomena are irreversible.

The transport phenomena occur due to the thermal agitation of the molecules. The molecules in a particular layer are associated with certain values of velocity components, temperature and molecular density. They tend to minimise the differences in u_0, v_0, w_0, T and N.. The molecules actually possess large velocities whereas these phenomena of viscosity, conduction and diffusion are comparatively slow. This anomaly is explained on the fact that the molecules frequently collide. Therefore the transport phenomena are basically governed by the mean free path λ of a molecule. *A molecule moving through a free path λ is actually transferring momentum, energy and mass through a distance λ.*

The transport phenomena occur only in the non-equilibrium state of a gas.

5·27 Viscosity of Gases

Consider a gas flowing along a horizontal surface. The layer in contact with the wall of the surface is at rest. The velocity of the layer increases with increase in distance from the fixed layer.

Viscosity is defined as the tangential force per unit area required to maintain a unit velocity gradient.

$$F = -\eta A \frac{du}{dx} \qquad \ldots(i)$$

Here η is the coefficient of viscosity and A is the area of the layer and $\frac{du}{dx}$ is the velocity gradient.

The velocity of a molecule at any layer at a height x above the fixed layer $= x \times \frac{du}{dx}$. If the mean free path of a molecule is

λ, then the distance for the first collision to occur $= (x-\lambda)$. The average velocity of these molecules $= (x-\lambda)\frac{du}{dx}$.

The molecules are moving at random in all directions. Approximately it can be assumed that about one-third of the molecules are moving along each axis. As the molecules in a given space will be free to move in any direction, one-sixth can be assumed to be moving in one direction and the other one-sixth in the opposite direction.

Let C be the r.m.s. velocity of the molecules, n the number of molecules per cc and m the mass of each molecule. Then, the number of molecules crossing unit area in one direction in one second $= \frac{1}{6} nC$.

Mass of the molecules $= \frac{1}{6} mnC = M$

Momentum in the forward direction

$$= M\left[(x-\lambda)\frac{du}{dx}\right]$$

Momentum in the opposite direction

$$= M\left[\{x-(-\lambda)\}\frac{du}{dx}\right]$$

Total change in momentum in one second

$$F = M(x-\lambda)\frac{du}{dx} - M(x+\lambda)\frac{du}{dx}$$

$$F = -2M\lambda\frac{du}{dx}$$

$$F = -2\left[\frac{1}{6} mnC\right]\lambda\frac{du}{dx}$$

$$= -\frac{1}{3} mnC\lambda\frac{du}{dx} \qquad \ldots(ii)$$

Comparing (*i*) and (*ii*)

$$\eta A\frac{du}{dx} = \frac{1}{3} mnC\lambda\frac{du}{dx}$$

But $A = 1$ sq cm

$\therefore$ $$\eta = \frac{1}{3} mnC\lambda \qquad \ldots(iii)$$

But $$\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2 n}$$

$$\eta = \frac{1}{3} mnC\frac{1}{\sqrt{2}\,\pi\sigma^2 n}$$

$$\eta = \frac{mC}{3\sqrt{2}\,\pi\sigma^2} \qquad \ldots(iv)$$

But $C \propto \sqrt{T}$

$\therefore$ $\eta \propto \sqrt{T}$ ...(v)

The coefficient of viscosity of a gas is directly proportional to the square root of its temperature in K.

5·28 Thermal Conductivity of Gases

The thermal conductivity of gases can be explained on the basis of kinetic theory of gases. The gas molecules are free to move between the hot end and the cold end. They are also free to move in any direction. Let the temperature gradient be $\frac{d\theta}{dx}$ and the mean free path λ. The temperature decreases from the hot to the cold end and when the steady state is reached, the temperature gradient will be uniform.

The mean temperature of the molecules crossing the layer P from the cold side $= \left(\theta - \frac{d\theta}{dx}\lambda\right)$ and the mean temperature of the molecules crossing the layer P from the hot end $= \left(\theta + \frac{d\theta}{dx}\lambda\right)$.

Let n be the number of molecules per cc, m the mass of each molecule and C the r.m.s. velocity of the molecules. On the aver-

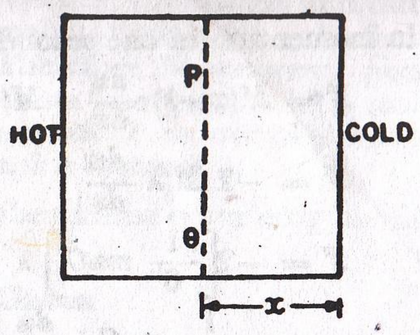


Fig. 5·12

age only $\frac{1}{6}$ of the molecules will be moving from the hot to the cold end and $\frac{1}{6}$ of the molecules will be moving from the cold to the hot end. Consider one sq cm area of cross-section at the layer P (Fig. 5·12).

The mass of the molecules crossing a unit area of cross-section in one second

$$= \frac{1}{6}mnC = M$$

$\therefore$ Heat energy carried by the molecules crossing the unit area of the layer in one second from the hot to the cold end

$$= MC_v\left(\theta + \frac{d\theta}{dx}\lambda\right)$$

Heat carried by the molecules crossing the area of the layer in one second from the cold to the hot end

$$= MC_v\left(\theta - \frac{d\theta}{dx}\lambda\right)$$

Therefore, the net heat conducted per unit area per second from the hot to the cold end

$$H = MC_v\left[\theta + \frac{d\theta}{dx}\lambda\right] - MC_v\left[\theta - \frac{d\theta}{dx}\lambda\right]$$

$$H = 2MC_v\lambda\frac{d\theta}{dx} \quad ...(i)$$

$\therefore$ $$H = 2\left[\frac{1}{6}mnC\right]C_v\lambda\frac{d\theta}{dx}$$

$$H = \frac{1}{3}mnC.C_v\lambda\frac{d\theta}{dx} \quad ...(ii)$$

From the definition of thermal conductivity

$$H = KA.\frac{d\theta}{dx}.t$$

Here $A = 1$ sq cm

$t = 1$ second

$\therefore$ $$H = K.\frac{d\theta}{dx} \quad ...(iii)$$

Comparing (ii) and (iii)

$$K = \frac{1}{3}mnC.C_v.\lambda \quad ...(iv)$$

$$K = \frac{1}{3}mnC.C_v \times \frac{1}{\sqrt{2}.\pi\sigma^2 n}$$

$$= \frac{mC.C_v}{3\sqrt{2}.\pi\sigma^2} \quad ...(v)$$

But $C \propto \sqrt{T}$

$\therefore$ $K \propto \sqrt{T}$

The coefficient of thermal conductivity of a gas is directly proportional to the square root of the absolute temperature.

5·29 Atomic Heat of Solids

A solid is made up of a number of atoms. The atoms can be considered as elastic spheres vibrating about their mean positions. The atoms will have three degrees of freedom in a solid. The kinetic energy for each degree of freedom $= \frac{1}{2}kT$. But an atom has potential energy also. The mean potential energy is equal to the mean kinetic energy. Therefore, the total energy associated for each degree of freedom of an atom $= 2 \times \frac{1}{2}kT$. The total energy associated for three degrees of freedom $= 3kT$. The energy associated with 1 gram molecule

$$= N \times 3kT = 3RT$$

$$U = 3RT$$

$$A_H = \frac{dU}{dT}$$

$$= 3R = 5{\cdot}96 \text{ cals/g-mole K}$$

Thus, the atomic heat of solids (A_H) is $3R$ and this value agrees with the Dulong and Petit's Law.

Example 5·21. *In an experiment, the viscosity of the gas was found to be* $1{\cdot}66 \times 10^{-4}$ dynes/cm^2 *per unit velocity gradient. The R.M.S. velocity of the molecules is* $4{\cdot}5 \times 10^4$ cm/s. *The density of the gas is 1·25* grams *per* litre.

Calculate (i) *the mean free path of the molecules of the gas,* (ii) *frequency of collision and* (iii) *molecular diameter of the gas molecules.*

Here $\eta = 1{\cdot}66 \times 10^{-4}$ units

$C = 4{\cdot}5 \times 10^4$ cm/s

$\rho = 1{\cdot}25 \times 10^{-3}$ g/cc

(i) $$\lambda = \frac{3\eta}{\rho C}$$

$$\lambda = \frac{3 \times 1{\cdot}66 \times 10^{-4}}{1{\cdot}25 \times 10^{-3} \times 4{\cdot}5 \times 10^4}$$

$$\lambda = 9 \times 10^{-6} \text{ cm}$$

(ii) Frequency of collision = number of collisions per second

$$= \frac{R.M.S. \text{ velocity}}{\text{Mean free path}}$$

$\therefore$ $$N = \frac{C}{\lambda}$$

$$N = \frac{4{\cdot}5 \times 10^4}{9 \times 10^{-6}}$$

$$N = 5 \times 10^9$$

(iii) Avogadro's number

$$= 6{\cdot}023 \times 10^{23}$$

Number of molecules per cc $= n$

$$= \frac{6{\cdot}023 \times 10^{23}}{22400}$$

According to Maxwell's relation

$$\lambda = \frac{1}{\sqrt{2} \cdot \pi d^2 n}$$

$\therefore$ $$d = \frac{1}{\sqrt{1{\cdot}414 \times \pi \times n \times \lambda}}$$

$$d = \frac{1}{\sqrt{1{\cdot}414 \times 3{\cdot}142 \times \left(\frac{6{\cdot}023 \times 10^{23}}{22400}\right) \times 9 \times 10^{-6}}}$$

$$d = 3 \times 10^{-8} \text{ cm}$$

Example 5·22. *In an experiment the viscosity of the gas was found to be* $2{\cdot}25 \times 10^{-4}$ CGS *units. The RMS velocity of the molecules is* $4{\cdot}5 \times 10^4$ cm/s. *The density of the gas is 1* gram *per* litre. *Calculate the mean free path of the molecules.*

Here $\eta = 2{\cdot}25 \times 10^{-4}$ CGS units

$C = 4{\cdot}5 \times 10^4$ cm/s

$\rho = 1$ g/litre

$\therefore$ $\rho = 10^{-3}$ g/cc

$$\lambda = \frac{3\eta}{\rho C}$$

$$\lambda = \frac{3 \times 2{\cdot}25 \times 10^{-4}}{10^{-3} \times 4{\cdot}5 \times 10^4}$$

$$\lambda = 15 \times 10^{-6} \text{ cm}$$

Example 5·23. *Calculate the mean free path of a gas molecule, given that the molecular diameter is* 2×10^{-8} cm *and the number of molecule per* cc *is* 3×10^{19}.

$$\lambda = \frac{1}{\pi d^2 n}$$

$$= \frac{1}{3{\cdot}14 \times (2 \times 10^{-8})^2 \times 3 \times 10^{19}}$$

$$\lambda = 3 \times 10^{-5} \text{ cm}$$

Note. The mean free path is less than the wavelength of light in the visible spectrum.

Example 5·24. *Calculate the mean free path of gas molecules in a chamber of* 10^{-6} mm *of mercury pressure, assuming the molecular diameter to be* 2Å. *One gram molecule of the gas occupies* 22·4 litres *at* N.T.P. *Take the temperature of the chamber to be 273* K. (*Agra 1975*)

At 760 mm Hg pressure and 273 K temperature, the number of molecules in 22·4 litres of a gas

$$= 6{\cdot}023 \times 10^{23}$$

Therefore, the number of molecules per cm^3 in the chamber at 10^{-6} mm pressure and 273 K temperature

$$n = \frac{6{\cdot}023 \times 10^{23} \times 10^{-3}}{22400 \times 760}$$

$n = 3{\cdot}538 \times 10^{10}$ molecules/cm^3

$d = 2\text{Å} = 2 \times 10^{-8}$ cm

Mean free path,

$$\lambda = \frac{1}{\pi d^2 n}$$

$$= \frac{1}{3{\cdot}14 \times (2 \times 10^{-8})^2 \times 3{\cdot}538 \times 10^{10}} = 2{\cdot}25 \times 10^4 \text{ cm}$$

5·30 Change of State

The molecules in a liquid have random motion. The average kinetic energy of the molecules depends upon the tempetature. The molecules are held together to occupy a particular volume due to inter-molecular attraction.

Consider water kept in a tray and exposed to the atmosphere. Generally, the atmosphere is not saturated with water vapours. The molecules of the liquid which are in a state of constant random motion collide with each other resulting in exchange of kinetic energies. Thus, there exists the possibility of a particular molecule in the vicinity of water-air interface, acquiring sufficiently high kinetic energy. This energy of the molecule may be high enough to enable the molecule to break away from the forces of attraction of the surrounding molecules. In fact, a molecule on the interface experiences minimum force of attraction. Such a molecule flies off into vapour space. When this molecule leaves the liquid, the mean kinetic energy of the remaining liquid molecules decreases and there is fall in temperature. This explains cooling caused by evaporation. Some vapour molecules in the atmosphere, also coalesce and get absorbed by the water surface. This is called condensation. Evaporation and condensation continue simultaneously but rate of evaporation is higher than the rate of condensation.

An essential pre-condition for cooling due to evaporation is the capacity of air to absorb more moisture.

If the liquid is heated, and if the rise in temperature of the liquid is more than the cooling caused by evaporation, the temperature of the liquid increases in addition to the increase in the rate of evaporation. A stage will come when the rate of heat supply is exactly equal to the energy needed for evaporation. At this stage evaporation takes place without change in temperature. This is boiling. At the boiling point the molecules are pulled further apart and their positions are no longer restricted to the space occupied by the liquid. This explains the change of state from liquid to gas or vapour. The amount of work done in pulling the molecules apart measures the latent heat of vaporisation. At the boiling point, the heat supplied to the liquid is used up only in pulling the molecules apart against the forces of intermolecular attraction and hence no rise in temperature of the liquid is noticed till the whole of the liquid is changed to the gaseous state. 1 cc of water when converted to steam occupies a volume of 1600 cc. This means that the mean inter-molecular distance is approximately 11·7 times more ($\sqrt[3]{1600} =$ 11·7 approximately) in a gas than the corresponding liquid.

5·31 Continuity of State

A substance can exist in three states *viz.*, solid, liquid and gas. For a long time it was supposed that gases like hydrogen, nitrogen, oxygen, helium etc. exist only in the gaseous form. It was also

supposed that liquid and gaseous states are not continuous but are distinctly separate from one another. It was found that at high pressures and low temperatures, there are marked deviations from Boyle's law. At high pressure, the molecules of a gas come close to each other and the forces of inter-molecular attraction become appreciable. If these molecular distances become equal to those of the corresponding liquid, the gas gets liquefied.

The three states of a substance are continuous *i.e.*, solid, liquid and gaseous states are the three different stages of a continuous phenomenon. If ice is heated, its molecules become more free to move and it is converted to the liquid state (water). Further heating increases the molecular movement and when inter-molecular forces become small, at a particular stage it is converted into the gaseous state (steam). The reverse process is also possible by continuously withdrawing heat.

Faraday was able to liquefy chlorine under its own pressure with the help of a freezing mixture.

Cagniard de la Tour's Experiment

The apparatus consists of a tube having a bulb *B*. It contains mercury and above the surface of mercury in *B*, the bulb contains water or alcohol (Fig. 5·13). There is air at the top end of the tube *A*.

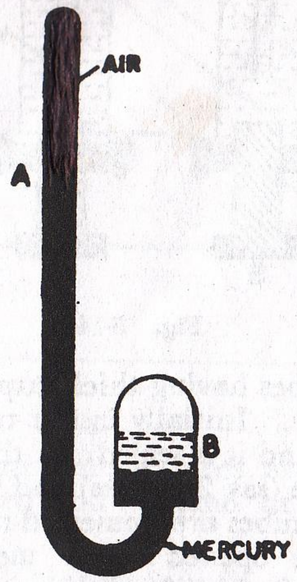


Fig. 5·13

The space above the liquid in the bulb *B* contains only the saturated vapours of the liquid at room temperature. The free surface of the liquid is visible and there is a marked distinction in the boundary of the liquid and its vapour. The bulb *B* is gradually heated. After some time the whole space in the bulb *B* appears foggy though the whole of the liquid has not evaporated. There is no free surface of the liquid at this stage. This shows that there is no distinction in the boundary of the liquid and the gaseous states.

When the bulb is allowed to cool, a cloud appears and it gets condensed. Again the free surface of the liquid is visible. This shows that there is a continuity between the liquid and the gaseous states of a substance. They are two different stages of a continuous phenomenon.

5·32 Andrews' Experiments on Carbon Dioxide

The apparatus used by Andrews to study the isothermals of carbon dioxide at various temperatures is shown in Fig. 5·14. *A* and *B*

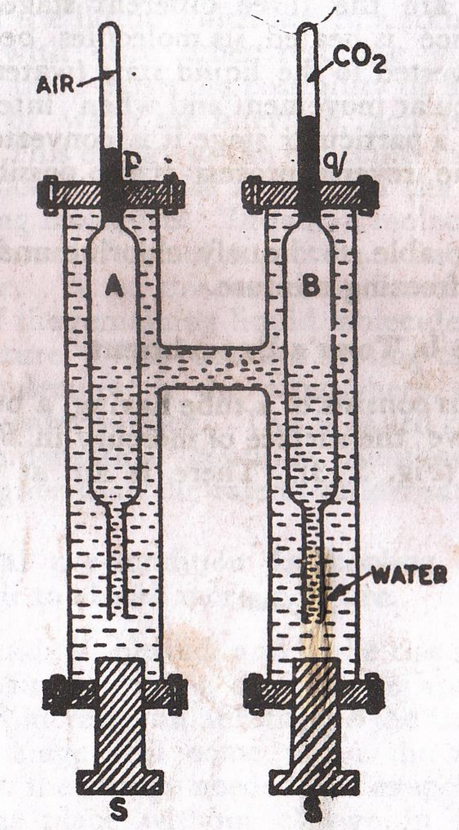


Fig. 5·14

are two similar glass tubes having thick capillary tubes at the top and bulbs in the middle. Initially in the tube *A* pure dry air is passed for a long time and it is sealed. In the bulb *B* carbon dioxide is passed for a long time (say 24 hours) and the ends are sealed. The lower ends of both the tubes are immersed in mercury and the lower ends of the tubes are opened under mercury. A small pellet of mercury is drawn in both the tubes by alternately heating and cooling the tubes. These mercury pellets act as stoppers. Both the tubes are fixed in a *H*-shaded copper vessel having steel stoppers *S*, *S*.

The vessel contains water and the screws are turned so that the mercury pellets in the two tubes appear above the vessel. The capillary tubes of *A* and *B* are calibrated to read volume directly.

Since the pressures of air in *A* and CO_2 in *B* are the same, from the volume of air in *A*, pressure of CO_2 in *B* can be calculated.

The volume of CO_2 is read directly from the tube *B*.

The experiment is performed by maintaining the capillary tube of *A* at a fixed temperature and the capillary tube of *B* at any desired temperature. Different pressures are applied at a fixed temperature of CO_2 and the readings are taken until the volumes are too small. Pressure can be increased by screwing in the plungers *S*, *S*.

The experiment is repeated, maintaining CO_2 at different temperatures. Thus different sets of readings of pressure and volume

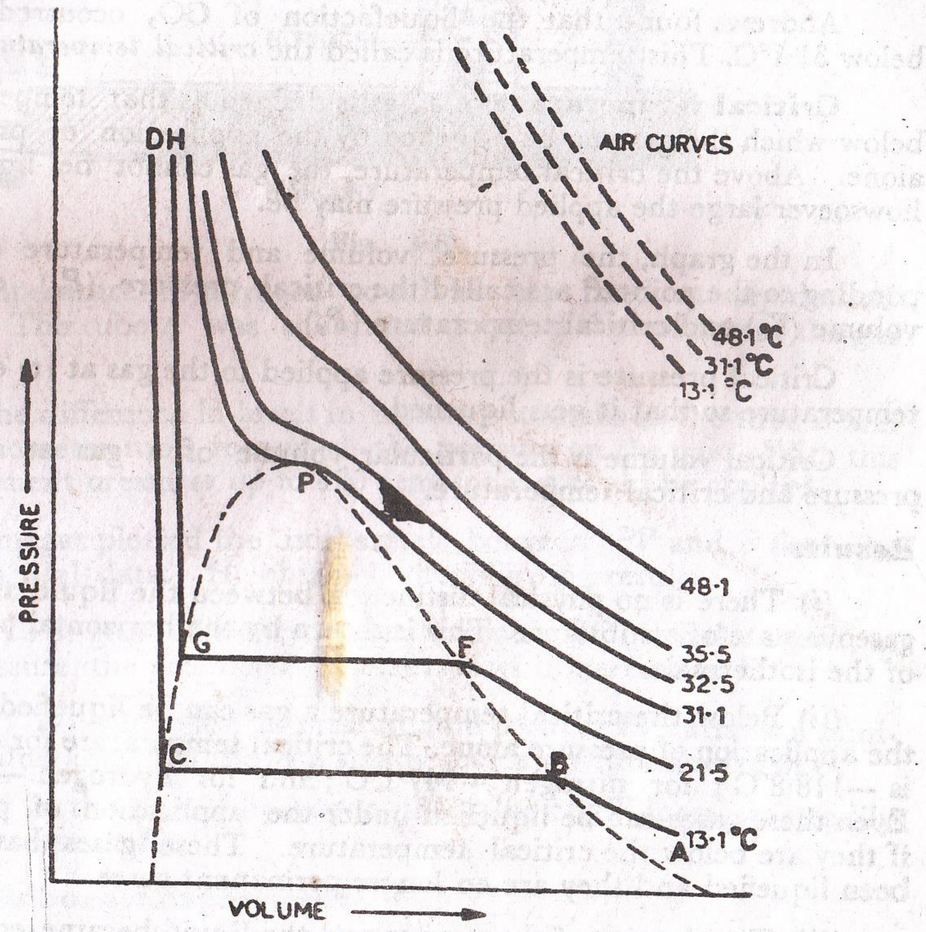


Fig. 5·15

for carbon dioxide at various temperatures are obtained. A graph is plotted between pressure and volume at various temperatures (Fig. 5·15).

The isothermals of CO_2 at various temperatures are shown in Fig. 5 15.

At 13·1°C, the portion *AB* represents the gaseous state of CO_2. Upto the point *B*, it obeys Boyle's law. From *B* to *C* it shows an enormous decrease in volume with slight increase in pressure. The portion *BC* represents the change of CO_2 from the gaseous to the liquid state. At *C* the whole of the gas has been liquefied. The portion *CD* represents the liquid state of CO_2 *i.e.*, there is no appreciable decrease in volume with increase in pressure.

At 21·5°C the curve is similar. The horizontal portion of the curve (FG) has decreased.

At 31·1°C the horizontal portion vanishes. It shows that the gas cannot be liquefied any more and its volume diminishes with increase in pressure.

The isothermals at 32·5°C and 35·5°C show the same behaviour and the portion of large compressibility decreases.

At 48·1°C the curve becomes smooth and it is similar to that of a permanent gas and it obeys Boyle's law.

Andrews found that the liquefaction of CO_2 occurred only below 31·1°C. This temperature is called the *critical temperature.*

Critical temperature of a gas is defined as that temperature below which the gas can be liquefied by the application of pressure alone. Above the critical temperature, the gas cannot be liquefied howsoever large the applied pressure may be.

In the graph, the pressure, volume and temperature corresponding to the point P are called the critical pressure (P_c), critical volume (V_c) and critical temperature (P_c).

Critical pressure is the pressure applied to the gas at its critical temperature so that it gets liquefied.

Critical volume is the particular volume of a gas at critical pressure and critical temperature.

Results

(*i*) There is no physical distinction between the liquid and the gaseous state of a substance. This is shown by the horizontal portions of the isothermals.

(*ii*) Below the critical temperature a gas can be liquefied under the application of pressure alone. The critical temperature for oxygen is −118·8°C; for nitrogen −147·1°C; and for hydrogen −240°C. Even these gases can be liquefied under the application of pressure if they are below the critical temperature. These gases have also been liquefied and they are no longer permanent gases.

(*iii*) The density of the vapour and the liquid became equal at the critical point. At the critical temperature the boundary line between the vapour and the liquid vanishes. Moreover, the compressibility of the vapour is infinite at the critical point.

5·33 Amagat's Experiment

Amagat performed a series of experiments with hydrogen (1878) and nitrogen (1893) to study their behaviour at high pressures. The apparatus consisted of a large metallic cylinder containing mercury having a screw S fitted to its one end. The apparatus was arranged at the base of a mine. A steel manometer tube of length about 300 metres was fixed along the shaft of the coal mine. The manometer tube was open at the top end. A calibrated inverted tube A containing nitrogen (or hydrogen) was fitted to the cylinder containing mercury (Fig. 5·16). An oil bath surrounded the tube A and

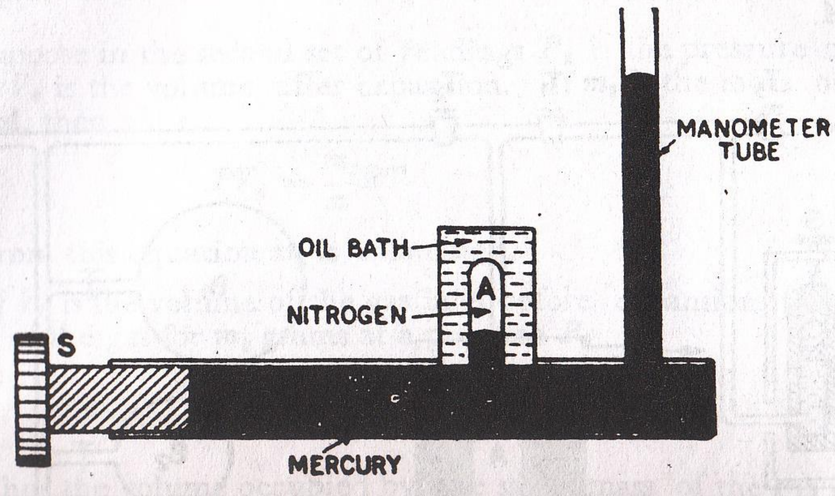


Fig. 5·16

the temperature of nitrogen could be kept fixed at any desired value. The tube A was calibrated to read the volume of the gas directly.

The difference in levels in mercury columns in the tube A and the manometer tube measured the pressure on the gas. With this arrangement pressures up to 420 atmospheres could be applied.

Amagat plotted the isothermals between PV and P from the experimental data. He obtained the following results :

(1) For gases like air, oxygen, nitrogen, CO_2, ethylene etc., at low pressure, the product PV decreases with increase in P.

(2) With increase in pressure, the product PV attains a minimum value and then shows a steady increase with increase in P.

(3) In the case of hydrogen, the value of PV increases steadily with increase in P.

5·34 Holborn's Experiment

In 1915, Holborn and his co-workers performed a series of experiments to study the behaviour of gases at high pressures.

The apparatus consists of a glass bulb A connected to a manometer M, the globes B_1, B_2, B_3 ..., etc., and the pressure balance (Fig. 5·17).

The pressure balance consists of a fixed block E. A piston C fits into the hole in the block E. The piston C balances the pressure exerted by the gas through the oil in the cavity of the block. The piston C is kept at a fixed mark by adjusting the weight W. The total weight exerted on the oil is due to the weight of W, D, S, and C. Let the total weight be Mg and the area of cross-section of the piston C be a. The downward pressure due to the

weight $= \frac{Mg}{a}$. This is also equal to the pressure of the gas in the bulb A.

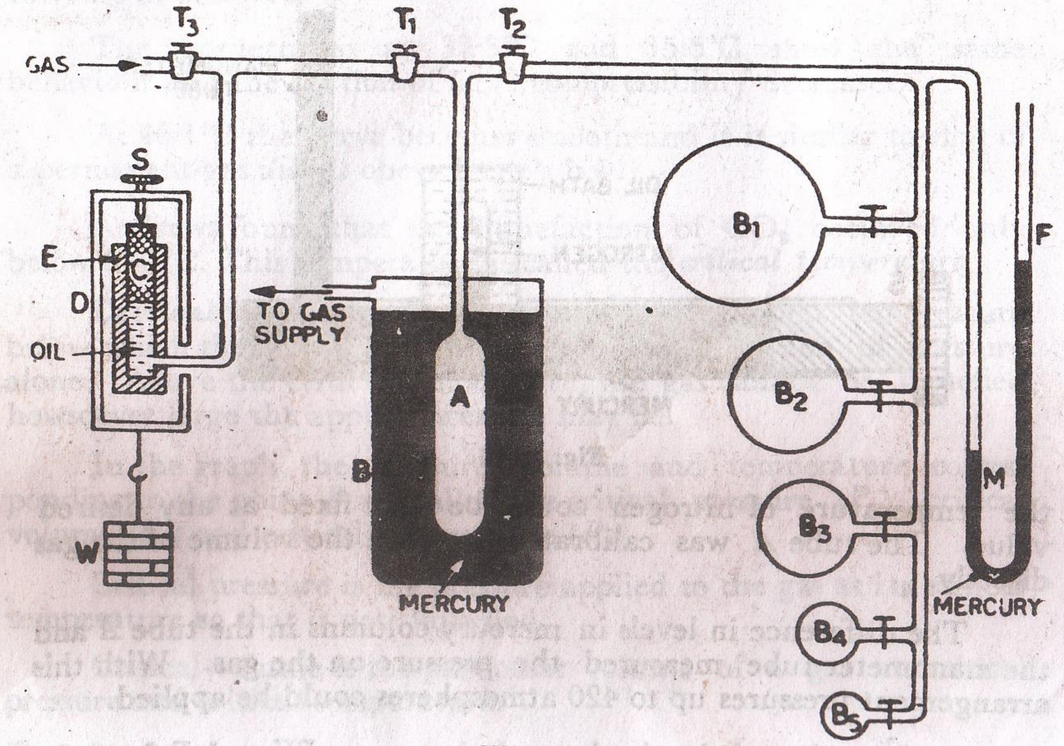


Fig. 5-17.

Initially the bulbs B_1, B_2 and B_3... etc. and A are evacuated. The stop-cock T_2 is closed. Gas at high pressure is admitted by opening the stop-cocks T_2 and T_1. The stop-cock T_2 is closed and the pressure of the gas in A is measured with the help of the pressure balance as explained above.

The stop-cock T_1 is closed and the stop-cock T_2 is opened. The stop-cocks of the bulbs B_1, B_2, etc. are opened one after the other till the pressure of the gas in A and the bulb is approximately equal to the atmospheric pressure. The volume of the bulbs, the connecting tubes and the bulb A is accurately known. The bulb A is enclosed in a bath containing the gas at high pressure to avoid the breakage of the bulb at high pressure.

Let the pressure of the gas as measured with the pressure balance be P_1, where $P_1 = \frac{Mg}{a}$. Let m_1 be the mass of the gas enclosed in A and m be the gram molecular weight of the gas. Then

$$PV_1 = \frac{m_1}{m} . RT$$

Here V_1 is the volume of the gas after expansion.

From this, the value of m_1 is calculated. Here P is the pressure of the gas after expansion and T is the temperature of the gas. If

the volume of the gas admitted initially in the bulb $A = V_0$, then m_1 grams of the gas at a pressure P_1 occupies a volume V_0 at a temperature T.

Suppose in the second set of readings P_2 is the pressure of the gas and V_2 is the volume after expansion. If m_2 is the mass of the gas in A, then

$$PV_2 = \frac{m_2}{m} RT$$

From this equation m_2 is calculated.

If V_0 is the volume of the gas in A before expansion, then the volume of the gas for m_1 grams at a pressure P_2

$$= \frac{V_0 \times m_1}{m_2}$$

Thus the volume occupied by the same mass of the gas for a range of pressures and at different temperatures can be calculated.

5·35 Behaviour of Gases at High Pressure

The isothermals between PV and P for various gases have been drawn and the general nature of the curves is as shown in Fig. 5·18. The general nature of the curves is the same for all gases.

(1) At high temperature, the value of PV increases with increase in P.

(2) At lower temperatures, the value of PV decreases initially with increase in P. It becomes a minimum at a particular pressure and then increases with increase in pressure. The locus of these minima is shown by the dotted curve A.

(3) At temperatures below the critical temperature, there is a sudden decrease in the value of PV with increase in pressure. This corresponds to the change of state from gas to liquid. When the liquefaction is complete, PV gradually increases with increase in P. The shaded area represents the region of liquefaction

Based on the experimental results of Andrews, Amagat and Holborn, K. Onnes suggested an empirical relation

$$PV = A + BP + CP^2 + DP^3 ..... \quad ...(i)$$

Here A, B, C, D etc. are constants depending on the nature of the gas. These constants are called *virial coefficients*. These constants change with temperature. The constant B has a special importance. Its value is negative at low temperatures and its value increases through zero to positive values at higher temperatures. The temperature at which the coefficient B is zero is called the **Boyle temperature**. At the Boyle temperature,

$$PV = A = \text{constant}$$

and

$$B = \frac{d\,[PV]}{dP} = 0$$

Below the Boyle temperature, the gases are highly compressible and this suggests the existence of inter-molecular attractions. Beyond

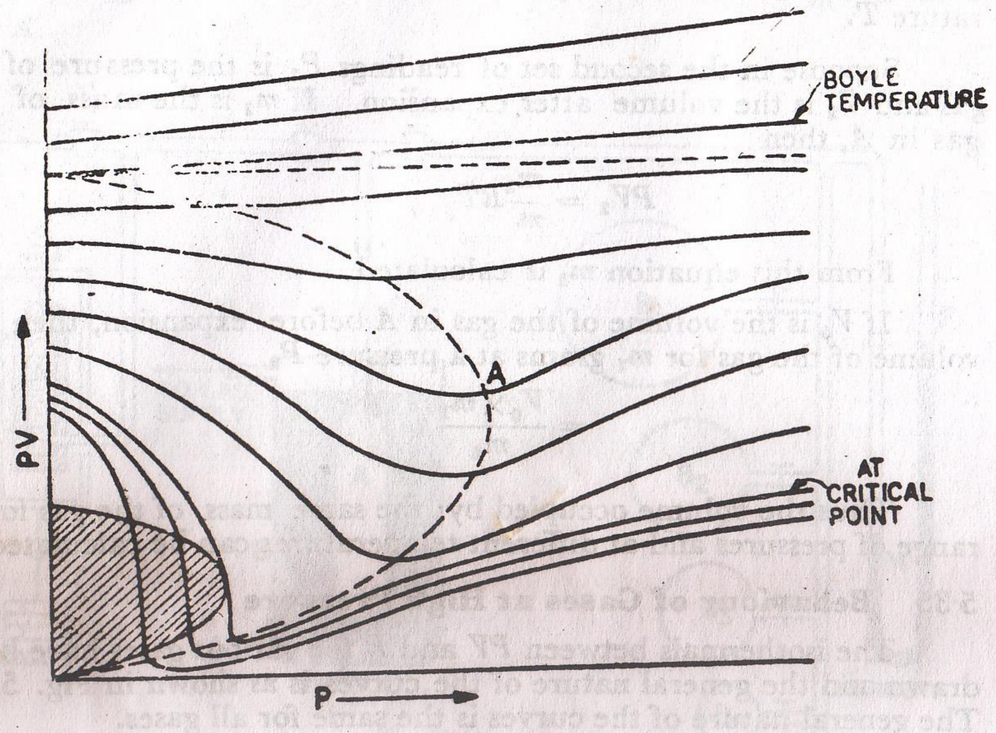


Fig. 5·18.

the Boyle temperature, Boyle's law is obeyed and intermolecular attractions are less significant.

5·36 Van der Waals Equation of State

While deriving the prefect gas equation $PV = RT$ on the basis of kinetic theory, it was assumed that (*i*) the size of the molecule of the gas is negligible and (*ii*) the forces of inter-molecular attraction are absent. But in actual practice, at high pressure, the size of the molecules of the gas becomes significant and cannot be neglected in comparison with the volume of the gas. Also, at high pressure, the molecules come closer and the forces of intermolecular attraction are appreciable. Therefore, correction should be applied to the gas equation.

(*i*) **Correction for Pressure.** A molecule in the interior of a gas experiences forces of attraction in all directions and the resultant cohesive force is zero. A molecule near the walls of the container experiences a resultant force inwards (away from the wall). Due to this reason the observed pressure of the gas is less than the actual pressure. The correction for pressure p depends upon (*i*) the number of molecules striking unit area of the walls of the container per second and (*ii*) the number of molecules present in a given volume. Both these factors depend on the density of the gas.

$$\therefore \quad \text{Correction for pressure } p \propto \rho^2 \propto \frac{1}{V^2}$$

$$p = \frac{a}{V^2}$$

Here a is a constant and V is the volume of the gas

Hence correct pressure

$$= (P+p) = \left(P+\frac{a}{V^2}\right)$$

where P is the observed pressure.

(*ii*) **Correction for Volume.** The fact that the molecules have finite size shows that the actual space for the movement of the molecules is less than the volume of the vessel. The molecules have the sphere of influence around them and due to this factor, the correction for volume is b where b is approximately four times the actual volume of the molecules. Therefore the corrected volume of the gas $= (V-b)$.

Let the radius of one molecule be r.

The volume of the molecule

$$= x = \frac{4}{3}\pi r^3$$

The centre of any two molecules can approach each other only by a minimum distance of $2r$ *i.e.*, the diameter of each molecule. The volume of the sphere of influence of each molecule,

$$S = \frac{4}{3}\pi (2r)^3 = 8x$$

Consider a container of volume V. If the molecules are allowed to enter one by one,

The volume available for first molecule

$$= V$$

Volume available for second molecule

$$= V-S$$

Volume available for third molecule

$$= V-2S$$

.....

Volume available for nth molecule

$$= V-(n-1)\,S$$

Average space available for each molecule

$$= \frac{V+(V-S)+(V-2S)+.....\{V-(n-1)S\}}{n}$$

$$= V-\frac{S}{n}\{1+2+3.....(n-1)\}$$

$$= V-\frac{S}{n}\cdot\frac{(n-1)n}{2}$$

$$= V-\frac{nS}{2}+\frac{S}{2}$$

As the number of molecules is very large $\frac{S}{2}$ can be neglected.

$\therefore$ Average space available for each molecule

$$= V - \frac{nS}{2} \qquad (\text{But } S = 8x)$$

$$= V - \frac{n(8x)}{2}$$

$$= V - 4(nx)$$

$$= V - b$$

$\therefore$ $b = 4(nx)$ = four times the actual volume of the molecules

Thus the Van der Waals equation of state for a gas is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \ldots(i)$$

where a and b are Van der Waals constants.

From the Van der Waals equation of state

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad \ldots(ii)$$

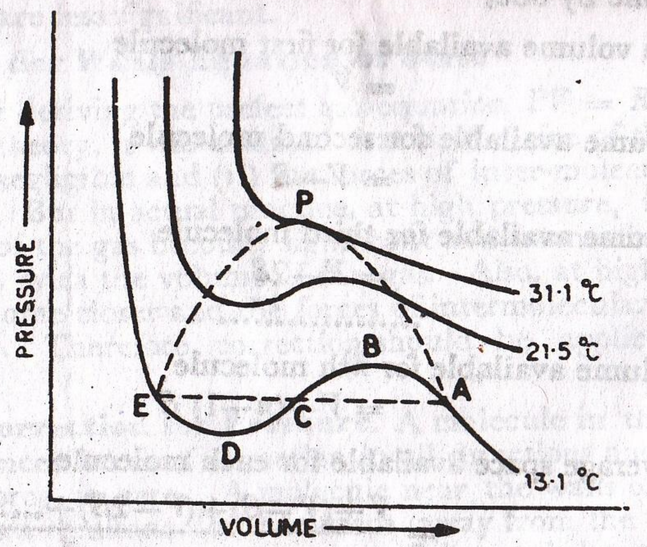


Fig. 5·19

Graphs between pressure and volume at various temperatures are drawn using equation (i). The graphs are as shown in Fig. 5·19. In the graph, the horizontal portion is absent. But in its place, the curve $ABCDE$ is obtained. This does not agree with the experimental isothermals for CO_2 as obtained by Andrews. However, the portion AB has been explained as due to supercooling of the vapours and the portion ED due to super-heating of the liquid. But the portion BCD cannot be explained because it shows decrease in volume with

decrease in pressure. It is not possible in actual practice. The states AB and ED, though unstable, can be realized in practice by careful experimentation. At higher temperatures, the theoretical and experimental isothermals are similar.

Until now as many as 56 different equations of state have been suggested. But no single equation satisfies all the observed facts.

Dicterice (1901) has suggested an equation

$$P(V - b) = RT\, e^{-\frac{a}{RTV}}$$

Berthelot has suggested an equation

$$\left(P + \frac{a}{V^2T}\right)(V - b) = RT$$

5·37 Critical Constants

The critical temperature and the corresponding values of pressure and volume at the critical point are called the critical constants. At the critical point, the rate of change of pressure with volume $\left(\frac{dP}{dV}\right)$ is zero. This point is calledthe point of inflexion.

According to Van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \ldots(i)$$

$$P = \left(\frac{RT}{V - b}\right) - \frac{a}{V^2} \qquad \ldots(ii)$$

Differentiating P with respect to V

$$\frac{dP}{dV} = \frac{-RT}{(V - b)^2} + \frac{2a}{V^3} \qquad \ldots(iii)$$

At the critical point $\frac{dP}{dV} = 0$

$$T = T_c$$

$$V = V_c$$

$$\therefore \quad \frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

or

$$\frac{2a}{V_c^3} = \frac{RT_c}{(V_c - b)^2} \qquad \ldots(iv)$$

Differentiating equation (iii)

$$\frac{d^2P}{dV^2} = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4}$$

At the critical point $\frac{d^2P}{dV^2} = 0$,

$$T = T_c,$$

$$V = V_c$$

$$\therefore \quad \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0$$

$$\frac{6a}{V_c^4} = \frac{2RT_c}{(V_c-b)^3} \qquad \ldots(v)$$

Dividing (*iv*) by (*v*)

$$\frac{V_c}{3} = \frac{V_c-b}{2}$$

or $$2V_c = 3V_c-3b$$

$$V_c = 3b \qquad \ldots(vi)$$

Substituting the value of

$V_c = 3b$ in equation (*iv*)

$$\frac{2a}{27b^3} = \frac{RT_c}{4b^2}$$

or $$T_c = \frac{8a}{27\,Rb} \qquad \ldots(vii)$$

Substituting these values of V_c and T_c in equation (*ii*)

$$P_c = \frac{R \times 8a}{27\,Rb(2b)} - \frac{a}{9b^2}$$

$$P_c = \frac{a}{27b^2} \qquad \ldots(viii)$$

5·38 Corresponding states

Two gases are said to be in corresponding states if the ratios of their actual pressure, volume and temperature and critical pressure, critical volume and critical temperature have the same value. It means

$$\frac{P_1}{P_{c1}} = \frac{P_2}{P_{c2}}$$

$$\frac{V_1}{V_{c1}} = \frac{V_2}{V_{c2}}$$

and $$\frac{T_1}{T_{c1}} = \frac{T_2}{T_{c2}}$$

TABLE

Critical Temperature and Pressure of Common Gases

Substance	*Critical Temperature °C*	*Critical Pressure (atmospheres)*
Helium	—268°C	2·26
Hydrogen	—240°C	12·80
Nitrogen	—146°C	33·50
Air	—140°C	39·00
Argon	—122°C	48·00
Oxygen	—118°C	50·00
Carbon dioxide	31°C	73·00
Ammonia	130°C	15·00
Chlorine	146°C	76·00
Water	374°C	218·00

5·39 Coefficient of Van der Waals Constants

$$V_c = 3b \qquad \ldots(i)$$

$$P_c = \frac{a}{27b^2} \qquad \ldots(ii)$$

$$T_c = \frac{8a}{27\,Rb} \qquad \ldots(iii)$$

From equations (*iii*) and (*ii*)

$$\frac{T_c^2}{P_c} = \frac{64\,a^2}{(27)^2\,R^2b^2} \times \frac{27b^2}{a}$$

$$= \frac{64a}{27\,R^2}$$

$$\therefore \quad a = \frac{27}{64}\,\frac{R^2T_c^2}{P_c} \qquad \ldots(iv)$$

Dividing (*iii*) by (*ii*)

$$\frac{T_c}{P_c} = \frac{8a}{27\,Rb} \times \frac{27b^2}{a}$$

$$= \frac{8b}{R}$$

$$b = \frac{RT_c}{8P_c} \qquad \ldots(v)$$

Also

$$\frac{RT_c}{P_cV_c} = \frac{R\,(8a)\,.\,27b^2}{27\,Rb\,a\,(3b)}$$

$$\frac{RT_c}{P_cV_c} = \frac{8}{3} \qquad \ldots(vi)$$

The quantity $\frac{RT_c}{P_cV_c}$ is called the *critical coefficient* of a gas. Its calculated value $= \frac{8}{3}$ and it is the same for all gases.

The experimental values of the critical coefficient for different gases is given below.

TABLE

Experimental Values of Critical Coefficient $\frac{RT_c}{P_cV_c}$.

Substance	T_c *in* K	P_c *in atm.*	*Specific volume in* cm^3/g	$\frac{RT_c}{P_cV_c}$
Helium	51	2·25	15·4	3·13
Hydrogen	33·1	12·8	32·2	3·28
Nitrogen	125·9	33·5	3·21	3·42
Oxygen	154·2	49·7	2·32	3·42
Carbon dioxide	304	72·8	2·17	3·48
Water	647	218	3·181	4·30

Note. Here V_c = molecular wt × specific volume.

The experimental value of the critical coefficient of all gases is greater than the theoretical value of 2·67.

Example 5·24. *Calculate the Van der Waals constants for dry air, given that*

$T_c = 132$ K, $P_c = 37{\cdot}2$ *atmospheres,*

R per mole $= 82{\cdot}07$ cm^3 *atmos* K^{-1}. *(Delhi 1975)*

Here $P_c = 37{\cdot}2$ atmospheres

$T_c = 132$ K

$R = 82{\cdot}07$ cm^3 atmos K^{-1}

(i) $$a = \frac{27}{64}\,\frac{R^2T_c^2}{P_c}$$

$$a = \left(\frac{27}{64}\right)\frac{(82{\cdot}07)^2(132)^2}{37{\cdot}2}$$

or $$a = \mathbf{13{\cdot}31 \times 10^6\ atmos\ cm^6}$$

(ii) $$b = \frac{RT_c}{8P_c}$$

$$b = \frac{82{\cdot}07 \times 132}{8 \times 37{\cdot}2}$$

or $$b = \mathbf{36{\cdot}41\ cm^3}$$

5·40 Reduced Equation of State

Taking the pressure, volume and temperature of a gas in terms of reduced pressure, volume and temperature,

$$\frac{P}{P_c} = \alpha,\ \frac{V}{V_c} = \beta,\ \frac{T}{T_c} = \gamma$$

$$P = \alpha\,P_c,\ V = \beta\,V_c,\ T = \gamma\,T_c$$

According to Van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \ldots(i)$$

or $$\left(\alpha P_c + \frac{a}{\beta^2 V_c^2}\right)(\beta V_c - b) = R\gamma T_c$$

But $$P_c = \frac{a}{27\,b^2}$$

$$V_c = 3b$$

and $$T_c = \frac{8a}{27\,Rb}$$

$$\therefore \left[\frac{\alpha\,.\,a}{27\,b^2} + \frac{a}{\beta^2\,9b^2}\right][\beta.3b - b] = \frac{R\gamma\,8a}{27\,Rb}$$

$$\left[\alpha + \frac{3}{\beta^2}\right][3\beta - 1] = 8\gamma \qquad \ldots(ii)$$

This is the reduced equation of state for a gas. If two gases have the same values of α, β and γ they are said to be in corresponding states.

5·41 Properties of Matter Near Critical Point

Based on the experiments of Andrews, Amagat and others, the state of matter near the critical point can be summarised as follows :—

(1) The densities of the vapour and the liquid gradually approach each other and their densities are equal at the critical point.

(2) At the critical point or just near the critical point, the line of demarcation between the liquid and the vapour disappears. Consequently, there must exist mutual diffusion between the two phases and the surface tension must be zero. This also means that the forces of inter-molecular attraction in the liquid and vapour states must be equal at the critical point.

(3) The whole mass of the substance exhibits a flickering experience which indicates that there may be variations of density inside the mass. This has been experimentally verified.

(4) The compressibility of the vapour becomes infinite at the critical temperature.

The experiments performed by Callendar and others have shown that the densities of the liquid and vapour are not equal at the critical temperature. The densities are equal at a temperature slightly higher than the critical temperature. The critical temperature of water is 374°C. It was found that the densities are equal at 380°C. At 374°C the latent heat of water was found to be 72·4 calories per gram. At 380°C the latent heat of water is zero.

To conclude, the critical point for any substance is not a particular temperature but it is a narrow region (critical region). **The critical point is that point at which the properties of the two phases become identical.**

5·42 Experimental Determination of Critical Constants

(1) The critical constants can be determined by plotting the isothermals between P and V at different temperatures of the gas. The critical point is found on the graph, where the horizontal portion of the curve (change from gaseous to the liquid state) just vanishes. The pressure, volume and temperature corresponding to the critical point give the *critical constants* of the gas.

(2) With the help of Cagniard de la Tour's apparatus, the temperatures at which the liquid meniscus disappears and reappears

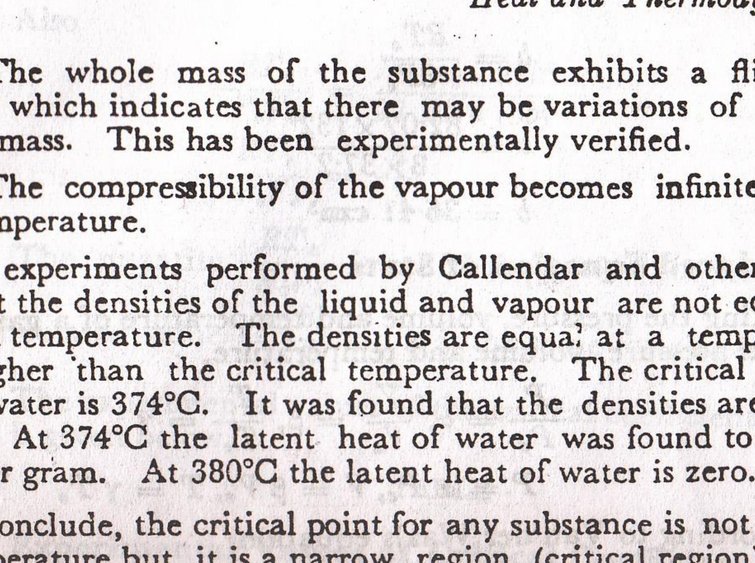


Fig. 5·20

are carefully noted. The mean of these two temperatures gives the critical temperature of the gas. The bulb is surrounded by a bath whose temperature is controlled by a sensitive thermostat and the temperature is varied by small amounts (say 0·1°C). The pressure is read with the help of a manometer. The pressure corresponding

to the critical temperature gives the critical pressure. However, the measurement of critical volume offers a practical difficulty because even if the temperature is slightly below the critical temperature, the change in volume is enormous even for a small change in pressure.

(3) Cailetet and Mathias have suggested a method for the determination of critical volume. Density of the liquid is determined accurately at different temperatures. The density of the saturated vapour is also determined accurately for the same temperature range. A graph is plotted between density and temperature (Fig. 5·20).

The density of the liquid decreases with rise in temperature and that of the saturated vapour increases with rise in temperature. On the graph the points A, B, C and D represent the mean density of liquid and the vapour at temperatures T_1, T_2, T_3, T_4 etc. respectively.

The points lie on a straight line. The line is produced and the curves are extrapolated to meet the line at the point P. The density corresponding to the point P is obtained from the graph. Let this density be ρ.

The specific volume *i.e.* volume per unit mass

$$V_c = \frac{1}{\rho}$$

This represents the critical volume. The temperature corresponding to the point P gives the critical temperature.

5·43 Inter-molecular Attraction

Joule's Experiment. Joule performed an experiment to study the inter-molecular attraction between the molecules of a gas. He designed an apparatus to measure the change in energy of a gas when its pressure and volume are changed.

A and B are two flasks connected by a tube and fitted with a stop-cock S. A was filled with the gas at high pressure and B was perfectly evacuated (Fig. 5·21). The bulbs were surrounded by a water bath and its temperature was noted with a sensitive

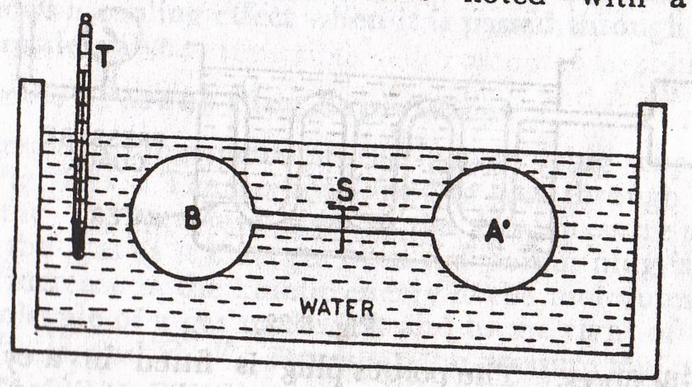


Fig. 5·21

thermometer. The stop-cock was opened and the gas rushed from A to B. If work was done during expansion, cooling was expected.

But in this experiment no cooling was observed. This was puzzling as the work had been done by the gas in overcoming the forces of inter-molecular attractions. Joule was able to explain the drawback in his experiment by assuming that the gas has expanded into vacuum and so no cooling was observed.

In this experiment only the pressure and volume of the gas changed and as the bath did not show any change in temperature, it is evident that the temperature of the gas remained constant.

According to Joule, this experiment also shows that the internal energy of a gas is a function of temperature only, irrespective of the changes in pressure and volume.

The porous plug experiment designad by Joule and Kelvin, however, showed cooling due to the work done by a gas in overcoming the inter-molecular attraction when it was passed from the high pressure to the low pressure side.

5·44 Porous Plug Experiment

The apparatus consists of a porous plug having two perforated brass discs D, D. The space between them is packed with cotton

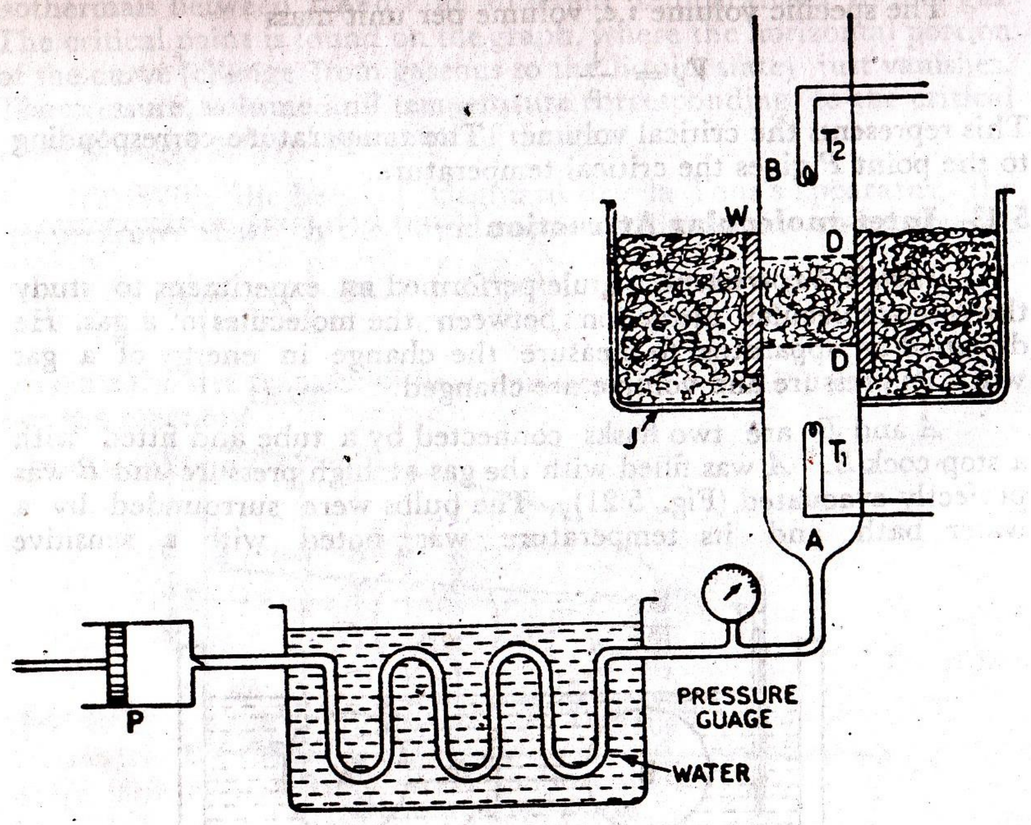


Fig. 5·22.

wool or silk fibres. The porous plug is fitted in a cylindrical box wood tube which is surrounded by a vessel containing cotton wool (Fig. 5·22). This is done to avoid loss or gain of heat from the surroundings. T_1 and T_2 are two sensitive platinum resistance

thermometers and they measure the temperatures of the incoming and the outgoing gas. The gas is compressed to a high pressure with the help of the piston P and it is passed through a spiral tube immersed in a water bath maintained at a constant temperature. If there is any heating of the gas due to compression, this heat is taken by the circulating water in the water bath.

The compressed gas is passed through the porous plug. The gas gets throttled (wire drawn) due to cotton wool. Work is done by the gas in overcoming inter-molecular attraction. The temperature of the outgoing gas is measured with the help of a platinum resistance thermometer T_2. The pressure of the incoming gas is measured with the help of a pressure gauge and the pressure of the outgoing gas is equal to the atmospheric pressure.

The behaviour of a large number of gases was studied at various inlet temperatures of the gas and the results obtained are as follows :

(*i*) At sufficiently low temperatures all gases show a cooling effect.

(*ii*) At ordinary temperatures all gases except hydrogen and helium show cooling effect. Hydrogen shows heating instead of cooling at room temperatue.

(*iii*) The fall in temperature is directly proportional to the difference in pressure on the two sides of the porous plug.

(*iv*) The fall in temperature per atmosphere difference of pressure decreases as the initial temperature of the gas is raised. It becomes zero at a particular temperature and at a temperature higher than this temperature, instead of cooling, heating is observed. This particular temperature at which the Joule-Thomson effect changes sign is called the temperature of inversion.

In the case of hydrogen heating was observed at room temperature because it was at a temperature far higher than its temperature of inversion. The temperature of inversion for hydrogen is —80°C and for helium it is —258°C. If helium is passed through the porous plug at a temperature lower than —258°C it will also show cooling effect. It means any gas below the temperature of inversion shows a cooling effect when it is passed through the porous plug or a throttle valve.

5·45 Theory of Porous Plug Experiment

The simple arrangement of the porous plug experiment is shown in Fig. 5·21. The gas is allowed to pass through the porous plug from the high pressure side to the low pressure side. The velocity of the gas as it emerges from the porous plug is very high and there is increase in the kinetic energy of the molecules. Consider one gram molecule of a gas to the left and to the right of the porous plug. Let P_1, V_1 and P_2, V_2 represent the pressure and volume on the two sides of the porous plug. When the piston A is moved through a certain distance dx, the piston B also moves through the

same distance dx. The work done *on the* gas by the piston $A = P_1 A_1$ $dx = P_1 V_1$. The work done by the gas on the piston B is $P_2 A_2\, dx = P_2 V_2$. Thus, the net external work done by the gas is $P_2V_2 - P_1V_1$.

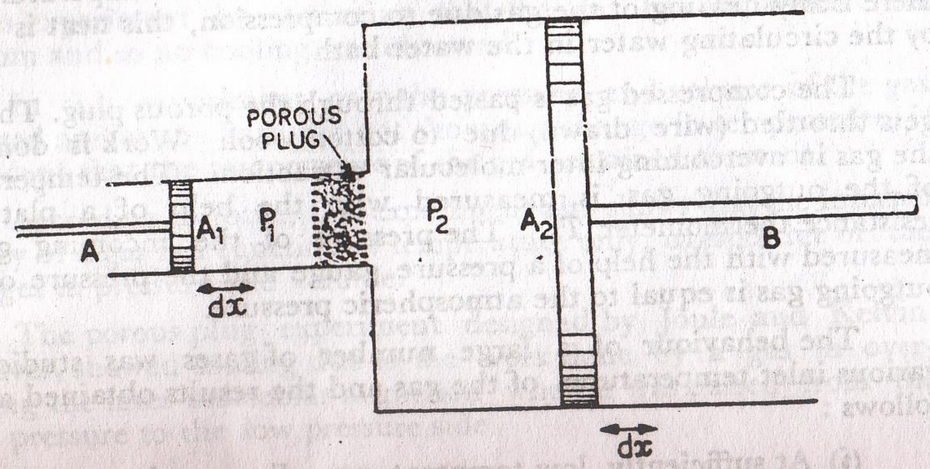


Fig. 5·23

If w is the work done by the gas in separating the molecules against their inter-molecular attractions, the total amount of work done by the gas is

$$(P_2V_2 - P_1V_1) + w$$

No heat is gained or lost to the surroundings. There are three possible cases :

(*i*) Below the Boyle temperature,

$$P_1V_1 < P_2V_2$$

and $P_2V_2 - P_1V_1$ is $+ve$. w must be either positive or zero. Thus a net $+ve$ work is done *by the gas* and there must be cooling when the gas passes through the porous plug.

(*ii*) At the Boyle temperature if P_1 is not very high

$$P_1V_1 = P_2V_2$$

and $$P_2V_2 - P_1V_1 = 0$$

The total work done by the gas in this case is w. Therefore cooling effect at this temperature is only due to the work done by the gas in overcoming inter-molecular attractions.

(*iii*) Above the Boyle temperature

$$P_1V_1 > P_2V_2$$

or $P_2V_2 - P_1V_1$ is $-ve$

Thus, the observed effect will depend upon whether $(P_2V_2 - P_1V_1)$ is greater or less than w.

If $w > (P_1V_1 - P_2V_2)$, cooling will be observed.

If $w < (P_1V_1 - P_2V_2)$, heating will be observed.

Thus, the cooling or heating of a gas due to free expansion through a porous plug from a high pressure to a low pressure side

will depend on (*i*) the deviation from Boyle's law and (*ii*) work done in overcoming inter-molecular attractions.

5·46. Joule-Kelvin Effect—Temperature of Inversion

Assuming that the Van der Waals equation is obeyed, the attractive forces between the molecules are equivalent to an internal pressure $\frac{a}{V^2}$.

When the gas expands from V_1 to V_2, the work done in overcoming inter-molecular attractions

$$w = \int_{V_1}^{V_2} p.\, dV$$

But $$p = \frac{a}{V^2}$$

$$\therefore \quad w = \int_{V_1}^{V_2} \frac{a}{V^2}\, dV$$

$$= -\frac{a}{V_2} + \frac{a}{V_1}$$

If V_1 and V_2 represent the gram molecular volumes on the high and the low pressure sides respectively, the external work done by the gas is

$$(P_2V_2 - P_1V_1)$$

Hence the total work done by the gas

$$W = (P_2V_2 - P_1V_1) + w$$

$$= (P_2V_2 - P_1V_1) - \frac{a}{V_2} + \frac{a}{V_1}$$

Van der Waals equation of state for a gas is

$$\left(P + \frac{a}{V^2}\right)\left(V - b\right) = RT$$

or $$PV + \frac{a}{V} - bP - \frac{ab}{V^2} = RT$$

or $$PV = RT + bP - \frac{a}{V}$$

$$\left[\frac{ab}{V^2} \text{ is negligible}\right]$$

$$W = \left[RT + bP_2 - \frac{a}{V_2}\right] - \left[RT + bP_1 - \frac{a}{V_1}\right] - \frac{a}{V_2} + \frac{a}{V_1}$$

$$= b\left[P_2 - P_1\right] + 2a\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

But

$$V_1 = \frac{RT}{P_1} \text{ and } V_2 = \frac{RT}{P_2}$$

$$\therefore \quad W = b\left[P_2 - P_1\right] + 2a\left[\frac{P_1}{RT} - \frac{P_2}{RT}\right]$$

or $$W = -b\left[P_1 - P_2\right] + \frac{2a}{RT}\left[P_1 - P_2\right]$$

or $$W = \left(P_1 - P_2\right)\left(\frac{2a}{RT} - b\right) \qquad \ldots(i)$$

Suppose the fall in temperature is δT

$$W = JH$$
$$= J\,[MC_P\,\delta T]$$

where M is the gram-molecular weight of the gas

$$\therefore \quad JMC_P\,\delta T = \left(P_1 - P_2\right)\left(\frac{2a}{RT} - b\right)$$

or $$\delta T = \left[\frac{P_1 - P_2}{JMC_P}\right] \times \left(\frac{2a}{RT} - b\right) \qquad \ldots(ii)$$

(*i*) Since $P_1 - P_2$ is +ve

δT will be +ve if $\left(\frac{2a}{RT} - b\right)$ is +ve

i.e. $$\frac{2a}{RT} > b, \quad \text{or} \quad T < \frac{2a}{Rb} \qquad \ldots(iii)$$

Therefore, cooling will take place if the temperature of the gas is less than $\frac{2a}{Rb}$.

(*ii*) For δT to be zero, from equation (*ii*),

$$\frac{2a}{RT} - b = 0$$

or $$T = \frac{2a}{Rb}$$

This temperature is called the temperature of inversion and is represented by T_i

$$T_i = \frac{2a}{Rb} \qquad \ldots(iv)$$

(*iii*) δT will be negative, if

$$\left(\frac{2a}{RT} - b\right) \text{ is } -\text{ve}$$

i.e., $$b > \frac{2a}{RT}$$

or $$T > \frac{2a}{Rb}$$

$$T > T_i$$

Therefore, heating will take place if the temperature of the gas is more than the temperature of inversion.

Results

(*i*) If the gas is at the temperature of inversion, then no cooling or heating is observed when it is passed through the porous plug.

(*ii*) If the gas is at a temperature lower than the temperature of inversion, cooling will take place when it is passed through the porous plug. This is called *regenerative cooling* or *Joule-Kelvin cooling*. This principle has been used in the liquefaction of the so-called permanent gases like nitrogen, oxygen, hydrogen and helium.

(*iii*) If the gas is at a temperature higher than the temperature of inversion, instead of cooling, heating is observed when the gas is passed through the porous plug.

5·47 Relation between Boyle Temperature, Temperature of Inversion and Critical Temperature

Temperature of inversion,

$$T_i = \frac{2a}{Rb} \qquad \ldots(i)$$

Boyle temperature,

$$T_B = \frac{a}{Rb} \qquad \ldots(ii)$$

Critical temperature,

$$T_c = \frac{8a}{27\,Rb} \qquad \ldots(iii)$$

From (*i*) and (*ii*)

$$T_i = 2T_B \qquad \ldots(iv)$$

From (*i*) and (*iii*)

$$\frac{T_i}{T_c} = \frac{2a}{Rb} \cdot \frac{27\,Rb}{8a}$$
$$= \frac{27}{4} = 6{\cdot}75$$

The experimental value of $\frac{T_i}{T_c}$ for actual gases is just less than 6.

It means that the temperature of inversion is very much higher than the critical temperature. For hydrogen $T_i = 190$ K and $T_c = 33$ K. As $T_i \geqslant T_c$, the methods employing regenerative cooling (Joule-Kelvin cooling) are preferred to those employing the initial cooling of the gas below the critical temperature.

Exercises V

1. Describe Andrews' experiments on carbon dioxide. Discuss the results obtained by him. Show that the liquid and the gaseous states are two distant stages of a continuous phenomenon.

2. Derive on the basis of kinetic theory of gases the laws for an ideal gas. *(Agra 1961)*

3. Give the theory of the porous plug experiment. (*Agra 1961*)

4. What are the critical constants of a gas ? State and explain Van der Waals equation. Calculate the critical constants of gas in terms of the constants of this equation. (*Agra 1961*)

5. State the law of equipartition of energy. Prove the law for a perfect gas, whose molecules have n degrees of freedom. Show that for a mono-atomic gas $\gamma = 1{\cdot}66$ and for a diatomic gas $\gamma = 1{\cdot}40$. (*Agra 1963 ; Gorakhpur 1967*)

6. What is Joule-Thomson effect ? Obtain an expression for the cooling produced in a Van der Waals gas. Hence explain why hydrogen and helium show heating effect at ordinary temperatures. [*Delhi (Hons.) 1971, Delhi 1972 ; Agra 1963 ; Lucknow 1964*]

7. Explain what you mean by degrees of freedom. State the law of equipartition of energy. Prove that for a perfect gas whose molecules have n degrees of freedom

$$\frac{C_P}{C_V} = 1 + \frac{2}{n}$$

Hence show that for a mono-atomic gas $\gamma = 1{\cdot}67$, for a diatomic gas $\gamma = 1{\cdot}4$ and for triatomic gas $\gamma = 1{\cdot}33$. (*Agra 1965*)

8. Derive Van der Waals equation. Deduce expressions for the critical constants in terms of a and b. (*Agra 1965 ; Delhi 1969 ; Delhi (Sub) 1966*)

9. Deduce from the kinetic theory of gases, an expression for the pressure of a gas. Also prove that

$$PV = RT$$ (*Delhi 1971 ; Agra 1966*)

10. Explain the corrections introduced by Van der Waals in the gas equation. Show that for a gas obeying Van der Waals equation

$$\frac{RT_c}{P_cV_c} = \frac{8}{3}$$ (*Gorakhpur 1967*)

11. Discuss briefly the considerations which led Van der Waals to modify the gas equation. What are the critical constants of a gas ? Calculate the values of these constants in terms of the constants of the Van der Waals equation. (*Calcutta 1965 ; Delhi 1971, 73*)

12. Show that the pressure exerted by a perfect gas is $\frac{2}{3}$ of the kinetic energy of the gas molecules in a unit volume. (*Calcutta 1966*)

13. Derive and discuss the Van der Waals equation of state of a gas. Mention its defects. (*Rajasthan 1966*)

14. Define mechanical equivalent of heat and give its units in the C.G.S. system. Describe fully Searle's friction-cone method of determining the value of J. Discuss the necessary formula and draw a neat diagram of the apparatus. (*Rajasthan 1966*)

15. Deduce Van dar Waals equation of state. How far does it conform to Andrews' experimental results on carbon dioxide ? What is the importance of Andrews' experiments in the problem of liquefaction of gases ? (*Panjab 1964*)

16. Describe the porous plug experiment. What conclusions have been drawn from it ? (*Delhi 1961*)

17. Describe Joule-Thomson effect and give its theory. (*Delhi 1967*)

18. Derive Maxwell's distribution law of velocities for gas molecules and discuss its experimental verification. (*Delhi 1966*)

19. What is meant by Joule-Kelvin effect ? How is it experimentally established ? How will you interpret the effect ? (*Panjab 1966*)

20. Describe Callendar and Barnes' continuous flow method for finding J.

21. Describe Jaegar and Steinwehr's method for finding the value of J.

22. Describe Holborn's experiments to study the behaviour of gases at high pressure.

23. Describe experiments to find the value of the critical constants of a gas.

24. Derive the relations between the Boyle temperature, temperature of inversion and critical temperature.

25. Derive an expression for the pressure exerted by gas on the basis of kinetic theory. (*Delhi 1969, 72, 73, 76*)

26. Describe the porous plug experiment and derive an expression for the Joule-Thomson cooling of a gas. What is inversion temperature ? (*Delhi 1968, 69, 77*)

27. Derive an expression for the mean free path of a molecule of a gas and describe a method for its determination.

28. Obtain an expression for the pressure of a gas on the basis of the kinetic theory of gases. Show that, according to the law of equipartition of energy the ratio of the two specific heats of ozone is 1·33. (*Delhi 1971*)

29. Distinguish between a perfect gas and a real gas. Derive Van der Waals equation of state and use it to obtain the expressions for the critical constants in terms of the constants of the Van der Waals equation. [*Delhi B.Sc. (Hons.) 1972*]

30. What is the kinetic model of a gas ? How is pressure of a gas explained on this model ? Deduce an expression for the pressure ? (*Delhi B. Sc. (Hons.) 1973*)

31. Describe briefly the porous plug experiment. Deduce a theoretical expression for the Joule-Thomson cooling for 1 gram molecule of a gas obeying Van der Waals equation of state. Why

does hydrogen show a negative Joule-Thomson effect ?
(*Berhampur, 1972, Delhi B.Sc. (Hons.) 1973*)

32. Distinguish between an adiabatic process and Joule-Thomson effect. Prove that for a Van der Waals gas the Joule-Thomson coefficient is given by

$$\left(\frac{\delta T}{\delta P}\right) = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

(*Delhi, 1974, Delhi B.Sc. (Hons.) 1972*)

33. What is Joule-Thomson effect ? Derive an expression for Joule-Thomson cooling. What is temperature of inversion ? Prove that it is equal to $2a/Rb$. (*Delhi 1973*)

34. Show from the kinetic theory of gases that the mean kinetic energy of translation of a molecule of a gas is $3/2\ kT$, where k is the Boltzmann's constant. (*Delhi 1971*)

35. How is the ideal gas equation modified when mutual attraction between molecules and the finite size of the molecules are taken into consideration ? Obtain relations between critical constants and the constants appearing in the Van der Walls equation
(*Delhi 1971*)

36. Derive the reduced equation of state for a gas starting from Van der Waals equation of state. Show that if the two gases have the same reduced pressure and volume, they also have the same reduced temperature ? (*Delhi 1975*)

37. Starting from elementary ideas set up Van der Waals' equation of state and show how the constants of the equation can be expressed in terms of the critical constants. What is the experimental bearing of this equation ? (*Delhi 1975, 1976*)

38. Assuming the various postulates underlying the kinetic theory of gases, show that the mean kinetic energy of translation of a molecule is $3/2\ kT$. (*Delhi 1974*)

39. Derive Van der Waals equation for gases and calculate the theoretical values of the critical constants.
[*Delhi (Hons.) 1974, Delhi 1977*]

40. Show that the pressure exerted by a perfect gas is 2/3 of the mean kinetic energy per unit volume.
[*Madras 1974, Delhi (Hons.) 1975*]

41. On the basis of kinetic theory of gases, derive expressions for the thermal conductivity and viscosity of the gas. Hence obtain the relation between the two. (*Bombay 1974*)

42. Explain the basic principles of the kinetic theory of gases and show that the pressure of an ideal gas is proportional to its density. (*Delhi 1976*)

43. Deduce Van der Waals equation of state and obtain expressions for critical constants in terms of the constants of the equation. (*Kanpur 1975, Delhi 1976*)

44. Describe Andrews' experiments on carbon dioxide. Discuss the results obtained. What is the importance of these results in the liquefaction of gases ? (*Delhi 1976*)

45. How do you interpret (*i*) pressure and (*ii*) temperature on the basis of the kinetic theory of gases. (*Delhi 1976*)

46. What is the meaning of mean free path of the molecules of a gas ? Show that it is equal to $\frac{1}{\eta\pi\sigma^2}$. (*Delhi 1977*)

47. Give a discussion of Maxwellian distribution of speed C amongst N molecules per cm^3 enclosed in a chamber at a temperature T. (*Agra 1975*)

48. Express Maxwell's law of distribution of speeds in terms of the kinetic energy of the molecules. Hence find the most probable and the average energy of the molecules.
[*Delhi (Hons.) 1977*]

49. Derive an expression for the viscosity of a gas on the basis of the kinetic theory and discuss its dependence on temperature and pressure. [*Delhi (Hons.) 1976*]

50. Obtain an expression for the thermal conductivity of an ideal gas on the basis of kinetic theory. Discuss its dependence on pressure and temperature. [*Delhi (Hons.) 1977*]

51. What do you understand by degrees of freedom of a molecule in a thermal system ? State the law of equipartition of energy.

Apply this law to obtain specific heats, C_p and C_v of gases. Compare the values of γ, the ratio of C_p and C_v, so obtained with the experimental results in the case of monoatomic, diatomic and polyatomic gases. Discuss the discrepancies, wherever they occur.
[*Delhi, 1978*]

52. Describe the aim of the porous-plug experiment and its predictions. Outline the important results of this experiment.

53. Derive an expression for the change in the temperature of a gas undergoing Joule-Thomson expansion. Discuss the role of inversion temperature in it. [*Delhi, 1978*]

54. Define viscosity of a fluid. Obtain an expression for the viscosity of an ideal gas on the basis of kinetic theory.
[*Delhi (Hons.), 1978*]

55. Calculate the total random kinetic energy of 1 gram molecule of nitrogen at 300 K. [**Ans.** 3,735 joules]

56. Calculate the average kinetic energy of a hydrogen molecule at 27°C. [**Ans.** $6{\cdot}21 \times 10^{-14}$ ergs]

57. Calculate the total random kinetic energy of 2 grams of nitrogen at 27°C. [**Ans.** 266·8 joules]

58. Calculate the total random kinetic energy of 8 grams of helium at 200 K. [**Ans.** 4,980 joules]

59. Calculate the r.m.s. velocity of a mercury atom at 1,200 K. [**Ans.** $3{\cdot}86 \times 10^4$ cm/s]

60. With what speed would 1 gram molecule of hydrogen at 27°C be moving in order that the translational kinetic energy of

its centre of mass is equal to the total random kinetic energy of all its molecules ? (Molecular weight of hydrogen = 2)

[**Ans.** $1{\cdot}93 \times 10^5$ cm/s]

61. Calculate the temperature at which the r.m.s. velocity of a helium molecule will be equal to the speed of the earth's first satellite *i.e.*, $v = 8$ km/s. [**Ans.** $10{\cdot}28 \times 10^3$ K]

62. Calculate the mean kinetic energy of a molecule of a gas at 1,000°C. Given,

$R = 8{\cdot}31 \times 10^7$ ergs/gram mol-K

$N = 6{\cdot}02 \times 10^{23}$

(*Delhi 1969*) [**Ans.** $2{\cdot}07 \times 10^{-13}$ ergs]

63. If the density of nitrogen is 1·25 g/litre at N.T.P., calculate the R.M.S. velocity of its molecules.

[*Delhi 1972* ; *Delhi* (*Hons.*) *1973*] [**Ans.** $4{\cdot}95 \times 10^4$ cm/s]

64. At what temperature is the R.M.S. speed of oxygen molecules twice their R.M.S. speed at 27°C ?

(*Delhi 1973*) [**Ans.** 927°C]

65. Calculate the R.M.S. velocity of the molecules of hydrogen at 0°C. Molecular weight of hydrogen = 2·016 and

$R = 8{\cdot}31 \times 10^7$ ergs/gram mole °C

(*Delhi 1971*) [**Ans.** $18{\cdot}4 \times 10^4$ cm/s]

66. Calculate the R.M.S. velocity of the hydrogen molecules at room temperature, given that one litre of the gas at room temperature and normal pressure weighs 0·086 g.

(*Delhi 1976*) [**Ans.** $1{\cdot}88 \times 10^5$ cm/s)]

67. Write short notes on :

(*i*) Mean free path [*Agra 1962* ; *Delhi* (*Sub.*) *1966*]

(*ii*) Joule-Thomson Effect (*Agra 1962* ; *Delhi 1974, 75*)

(*iii*) Continuity of state

(*iv*) Rowland's experiment for finding *J*

(*v*) Van der Waals equation of state

(*vi*) Pressure exerted by an ideal gas

(*vii*) Critical constants

(*viii*) Degrees of freedom

(*ix*) Atomicity of gases

(*x*) Maxwell's law of distribution of velocity. (*Delhi 1975*)

(*xi*) Andrews' experiments

(*xii*) Amagat's experiments

(*xiii*) Halborn's experiments

(*xiv*) Behaviour of gases at high pressure

(*xv*) Critical point

(*xvi*) Corresponding states

(*xvii*) Intermolecular attraction

(*xviii*) Temperature of inversion

(*xix*) Reduced equation of state for a gas [*Delhi* (*Hons.*) *1976*]

(*xx*) Porous plug experiment.

6

Thermodynamics

6·1 Thermodynamic System

A thermodynamic system is one which can be described in terms of the thermodynamic co-ordinates. The co-ordinates of a thermodynamic system can be specified by any pair of quantities *viz.*, pressure (P), volume (V), temperature (T) and entropy (S). The thermodynamic systems in engineering are gas, vapour, steam, mixture of gasoline vapour and air, ammonia vapours and its liquid. In Physics, thermodynamics includes besides the above, systems like stretched wires, thermocouples, magnetic materials, electrical condenser, electrical cells, solids and surface films.

Examples : 1. Stretched wire. In a stretched wire, to find the Young's modulus of a wire by stretching, the complete thermodynamic co-ordinates are

(*a*) the stretching force F

(*b*) the length of the stretching wire and

(*c*) the temperature of the wire.

The pressure and volume are considered to be constant.

2. Surface Films. For liquid films, in the study of surface tension, the thermodynamic co-ordinates are

(*a*) the surface tension

(*b*) the area of the film and

(*c*) the temperature.

3. Reversible Cells. The thermodynamic coordinates to completely describe a reversible cell are

(*a*) the E.M.F. of the cell

(*b*) the charge that flows and

(*c*) the temperature.

6·2 Thermal equilibrium and Concept of Temperature [Zeroth Law of Thermodynamics]

A thermodynamic system is said to be in thermal equilibrium if any two of its independent thermodynamic co-ordinates X and Y remain constant as long as the external conditions remain unaltered. Consider a gas enclosed in a cylinder fitted with a piston. If the pressure and volume of the enclosed mass of gas are P and V at the temperature of the surroundings, these values of P and V will remain constant as long as the external conditions *viz.* temperature and pressure remain unaltered. The gas is said to be in thermal equilibrium with the surroundings.

The *zeroth law* of thermodynamics was formulated after the first and the second laws of thermodynamics have been enunciated. This law helps to define the term *temperature* of a system.

This law states that *if, of three systems, A, B and C, A and B are separately in thermal equilibrium with C, then A and B are also in thermal equilibrium with one another.*

Conversely the law can be stated as follows :

If three or more systems are in thermal contact, each to each, by means of diathermal walls and are all in thermal equilibrium together, then any two systems taken separately are in thermal equilibrium with one another.

Consider three fluids A, B and C. Let P_A, V_A represent the pressure and volume of A, P_B, V_B, the pressure and volume of B, and P_C, V_C are the pressure and volume of C.

If A and B are in thermal equilibrium, then

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

or $$F_1[P_A, V_A, P_B, V_B] = 0 \qquad \ldots(i)$$

Expression (i) can be solved, and

$$P_B = f_1[P_A, V_A, V_B] \qquad \ldots(ii)$$

If B and C are in thermal equilibrium

$$\phi_2(P_B, V_B) = \phi_3(P_C, V_C)$$

or $$F_2[P_B, V_B, P_C, V_C] = 0$$

Also $$P_B = f_2[V_B, P_C, V_C] \qquad \ldots(iii)$$

From equations (ii) and (iii) for A and C to be in thermal equilibrium separately,

$$f_1(P_A, V_A, V_B) = f_2[V_B, P_C, V_C] \qquad \ldots(iv)$$

If A and C are in thermal equilibrium with B separately, then according to the zeroth law, A and C are also in thermal equilibrium with one another.

$$\therefore\ F_3[P_A, V_A, P_C, V_C] = 0. \qquad \ldots(v)$$

Equation (iv) contains a variable V_B, whereas equation (v) does not contain the variable V_B. It means

$$\phi_1(P_A, V_A) = \varphi_3(P_C, V_C) \qquad \ldots(vi)$$

In general,

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C) \qquad \ldots(vii)$$

These three functions have the same numerical value though the parameters (P, V) of each are different. This numerical value is termed as *temperature* (T) of the body.

$$\therefore \qquad \phi(P, V) = T \qquad \ldots(viii)$$

This is called the equation of state of the fluid.

Therefore, the temperature of a system can be defined as the property that determines whether or not the body is in thermal equilibrium with the neighbouring systems. If a number of systems are in thermal equiiibrium, this common property of the system can be represented by a single numerical value called the temperature. It means that if two systems are not in thermal equilibrium, they are at different temperatures.

Example. In a mercury in glass thermometer, the pressure above the mercury column is zero and volume of mercury measures the temperature. If a thermometer shows a constant reading in two systems A and B separately, it will show the same reading even when A and B are brought in contact.

6·3 Concept of Heat

Heat is defined as *energy in transit.* As it is not possible to speak of work in a body, it is also not possible to speak of heat in a body. Work is either done on a body or by a body. Similarly, heat can flow from a body or to a body. If a body is at a constant temperature, it has both mechanical and thermal energies due to the molecular agitations and it is not possible to separate them. So, in this case, we cannot talk of heat energy. It means, if the flow of heat stops, the word heat cannot be used. It is only used when there is transfer of energy between two or more systems.

Consider two systems A and B in thermal contact with one another and surrounded by adiabatic walls.

For the system A,

$$H = U_2 - U_1 + W \qquad \ldots(i)$$

where H is the heat energy transferred, U_1 is the initial internal energy, U_2 is the final internal energy and W is the work done.

Similarly for the system B,

$$H' = U_2' - U_1' + W' \qquad \ldots(ii)$$

Adding (i) and (ii)

$$\therefore\ H + H' = (U_2 - U_1) + W + (U_2' - U_1') + W'$$

$$H + H' = [(U_2 + U_2') - (U_1 + U_1')] + (W + W') \qquad \ldots(iii)$$

The total change in the internal energy of the composite system

$$= [(U_2 + U_2') - (U_1 + U_1')]$$

The work done by the composite system $= W+W'$

It means that the heat transferred by the composite system $= H+H'$. But the composite system is surrounded by adiabatic walls and the net heat transferred is zero.

$$\therefore \quad H+H' = 0$$

$$H = -H' \qquad \ldots(iv)$$

Thus, for two systems A and B in thermal contact with each other, and the composite system surrounded by adiabatic walls, the heat gained by one system is equal to the heat lost by the other system.

6·4 Quasistatic Process

A system in thermodynamical equilibrium must satisfy the following requirements strictly :—

(*i*) **Mechanical Equilibrium**. For a system to be in mechanical equilibrium, there should be no unbalanced forces acting on any part of the system or the system as a whole.

(*ii*) **Thermal Equilibrium**. For a system to be in thermal equilibrium, there should be no temperature difference between the parts of the system or between the system and the surroundings.

(*iii*) **Chemical Equilibrium**. For a system to be in chemical equilibrium, there should be no chemical reaction within the system and also no movement of any chemical constituent from one part of the system to the other.

When a system is in thermodynamic equilibrium and the surroundings are kept unchanged, there will be no motion and also no work will be done. On the other hand, if the sum of the external forces is altered, resulting in a finite unbalanced force acting on the system, the condition for mechanical equilibrium will not be satisfied any longer. This results in the following :—

(*i*) Due to unbalanced forces within the system, turbulence, waves etc. may be set up. The system as a whole may possess an accelerated motion.

(*ii*) Due to turbulence, acceleration etc. the temperature distribution within the system may not be uniform. There may also exist a finite temperature difference between the system and the surroundings.

(*iii*) Due to the presence of unbalanced forces and difference in temperature, chemical reaction may take place or there may be movement of a chemical constituent.

From this discussion, it is clear that a finite unbalanced force may cause the system to pass through *non-equilibrium* states. If during a thermodynamic process, it is desired to describe every state of a system by thermodynamic coordinates referred to the system as a whole, the process should not be brought about by a finite unbalanced force.

A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes during a quasistatic process can be considered as equilibrium states.

In actual practice, many processes closely approach a quasistatic process and may be treated as such with no significant error. Consider the expansion of a gas in a closed cylinder fitted with a piston. Initially weights are on the piston and the pressure of the gas inside the cylinder is higher than the atmospheric pressure. If the weights are small and are taken off slowly one by one, the process can be considered quasistatic. If, however, all the weights are removed at once, expansion takes place suddenly and it will be a non-equilibrium process. The system will not be in equilibrium at any time during this process.

A quasistatic process is an ideal concept that is applicable to all thermodynamic systems including electric and magnetic systems. It should be noted that conditions for such a process can never be satisfied rigorously in practice.

6·5 Heat—A Path Function

Heat is a path function. When a system changes from a state 1 to state 2, the quantity of heat transferred will depend upon the intermediate stages through which the system passes *i.e.*, its path. Hence heat is an **inexact differential** and is written as δH.

On integrating, we get

$$\int_{1A}^{2A} \delta H = H_{1A}^{2A}$$

Here, ${}_1H_2$ represents the heat transferred during the given process between the states 1 and 2 along a particular path A.

6·6 Work—A Path Function

Suppose that a system is taken from an initial equilibrium state 1 to a final equilibrium state 2 by two different paths A and B (Fig. 6·1). The processes are quasistatic.

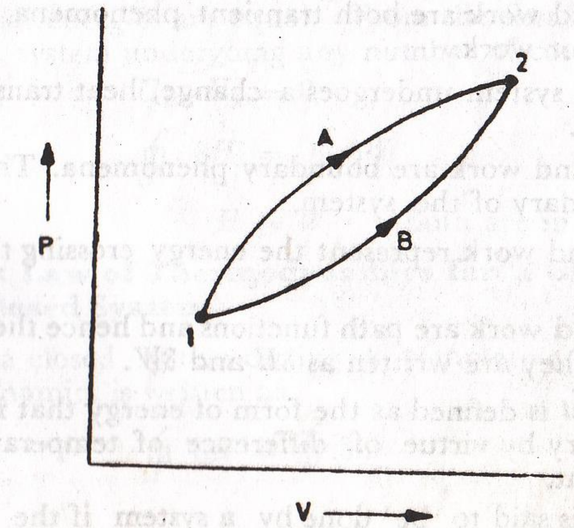


Fig. 6·1

The areas under these curves are different and hence the quantities of work done are also different.

For the path A,

$$W_A = \int_{1A}^{2A} \delta W = \int_{1A}^{2A} P\,dV \qquad \ldots(i)$$

For the path B

$$W_B = \int_{1B}^{2B} \delta W = \int_{1B}^{2B} P\,dV \qquad \ldots(ii)$$

The values of W_A and W_B are not equal. Therefore work cannot be expressed as a difference between the values of some property of the system in the two states. *Therefore, it is not correct to represent*

$$W = \int_{W_1}^{W_2} \delta W = W_2 - W_1 \qquad \ldots(iii)$$

It may be pointed out that it is meaningless to say "work in a system or work of a system". Work cannot be interpreted similar to temperature or pressure of a system.

In terms of calculus δW is an inexact differential. It means that W is not a property of the system and $\int \delta W$ cannot be expressed as the difference between two quantities that depend entirely on the initial and the final states.

Hence, heat and work are **path functions** and they depend only on the process They are not point functions such as pressure or temperature. Work done in taking the system from state 1 to state 2 will be different for different paths.

6·7 Comparison of Heat and Work

There are many similarities between heat and work. These are :—

1. Heat and work are both transient phenomena. Systems do not possess heat or work.

2. When a system undergoes a change, heat transfer or work done may occur.

3. Heat and work are boundary phenomena. They are observed at the boundary of the system.

4. Heat and work represent the energy crossing the boundary of the system.

5. Heat and work are path functions and hence they are inexact differentials. They are written as δH and δW.

6. (*a*) *Heat* is defined as the form of energy that is transferred across a boundary by virtue of difference of temperature or temperature gradient.

(*b*) Work is said to be done by a system if the sole effect on things external to the system could be the raising of a weight.

It is customary to represent, work done by the system as +ve, work done on the system as —ve, heat flowing into the system as +ve, and heat flowing out of the system as —ve.

6·8 First Law of Thermodynamics

Joule's law gives the relation between the work done and the heat produced. It is true when the whole of the work done is used in producing heat or *vice versa*. Here, $W = JH$ where J is the Joule's mechanical equivalent of heat. But in practice, when a certain quantity of heat is supplied to a system the whole of the heat energy may not be converted into work. Part of the heat may be used in doing external work and the rest of the heat might be used in increasing the internal energy of the molecules. Let the quantity of heat supplied to a system be δH, the amount of external work done be δW and the increase in internal energy of the molecules be dU. The term U represents the internal energy of a gas due to molecular agitation as well as due to the forces of inter-molecular attraction. Mathematically

$$\delta H = dU + \delta W \qquad \ldots(i)$$

Equation (*i*) represents the first law of thermodynamics. All the quantities are measured in heat units. The first law of thermodynamics states that the amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done.

For a cyclic process, the change in the internal energy of the system is zero because the system is brought back to the original condition. Therefore for a cyclic process $\oint dU = 0$

and

$$\oint \delta H = \oint \delta w \qquad \ldots(ii)$$

[Both are expressed in heat units].

This equation represents Joule's law.

For a system carried through a cyclic process, its initial and final internal energies are equal. From the first law of thermodynamics, for a system undergoing any number of complete cycles

$$U_2 - U_1 = 0$$

$$\oint \delta H = \oint \delta W$$

$$H = W \qquad \text{[Both are in heat units]}$$

6·9 First Law of Thermodynamics for a Change in State of a Closed System

For a closed system during a complete cycle, the first law of thermodynamics is written as

$$\oint \delta H = \oint \delta W$$

In practice, however, we are also concerned with a process rather than a cycle. Let the system undergo a cycle, changing its

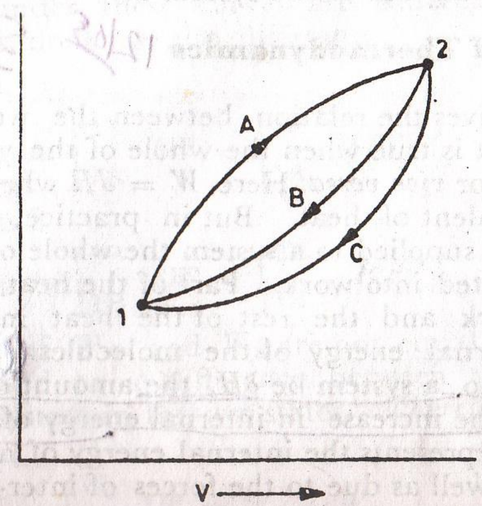


Fig. 6·2

state from 1 to 2 along the path A and from 2 to 1 along the path B. This cyclic process is represented in the P—V diagram (Fig. 6·2).

According to the first law of thermodynamics

$$\oint \delta H = \oint \delta W$$

For the complete cyclic process

$$\int_{1A}^{2A} \delta H + \int_{2B}^{1B} \delta H = \int_{1A}^{2A} \delta W + \int_{2B}^{1B} \delta W \qquad \ldots(i)$$

Now, consider the second cycle in which the system changes from state 1 to state 2 along the path A and returns from state 2 to state 1 along the path C. For this cyclic process

$$\int_{1A}^{2A} \delta H + \int_{2C}^{1C} \delta H = \int_{1A}^{2A} \delta W + \int_{2C}^{1C} \delta W \qquad \ldots(ii)$$

Subtracting (*ii*) from (*i*)

$$\int_{2B}^{1B} \delta H - \int_{2C}^{1C} \delta H = \int_{2B}^{1B} \delta W - \int_{2C}^{1C} \delta W$$

or

$$\int_{2B}^{1B} (\delta H - \delta W) = \int_{2C}^{1C} (\delta H - \delta W) \qquad \ldots(iii)$$

Here B and C represent arbitrary processes between the states 1 and 2. Therefore, it can be concluded that the quantity $(\delta H - \delta W)$ is the same for all processes between the states 1 and 2. The quantity

$(\delta H - \delta W)$ depends only on the initial and the final states of the system and is independent of the path followed between the two states.

Let $$dE = (\delta H - \delta W)$$

From the above logic, it can be seen that

$$\int_1^2 dE = \text{constant and is independent of the path.}$$

This naturally suggests that E is a point function and dE is an exact differential.

The point function E is a property of the system.

Here dE is the derivative of E and it is an exact differential.

$$\therefore \qquad \delta H - \delta W = dE \qquad \ldots(iv)$$

or $$\delta H = dE + \delta W \qquad \ldots(v)$$

Integrating equation (*v*), from the initial state 1 to the final state 2

$$_1H_2 = (E_2 - E_1) + {}_1W_2$$

[Note. $_1H_2$ **cannot be written as** $(H_2 - H_1)$**, because it depends upon the path].**

Similarly, $_1W_2$ cannot be written as $(W_2 - W_1)$, because it also depends upon the path.

Here $_1H_2$ represents the heat transferred,

$_1W_2$ represents the work done,

E_2 represents the total energy of the system in state 2,

E_1 represents the total energy of the system in state 1.

At this point, it is worthwhile discussing what this E can possibly mean. With reference to the system, the energies crossing the boundaries are all taken care of in the form of H and W. For dimensional stability of Eq. (*v*), this E must be energy and this must belong to the system. Therefore,

E_2 represents the energy of the system in state 2

E_1 represents the energy of the system in state 1

This energy E acquires a value at any given equilibrium condition by virtue of its thermodynamic state. The working substance, for example a gas, has molecules moving in all random fashion. The molecules have energy associated by virtue of mutual attraction and this part is similar to the potential energy of a body in macroscopic terms. They also have velocities and hence kinetic energy. This energy E therefore can be visualised as comprising of molecular potential and kinetic energies in addition to macroscopic potential and kinetic energies. The first part, which owes its existence to the

thermodynamic nature is often called the internal energy which is completely dependent on the thermodynamic state and the other two depend on mechanical or physical state of the system.

$E = U + KE + PE +$ Others which depend upon chemical nature etc.

For a closed system (non-chemical) the changes in all others except U are insignificant and

$$dE = dU$$

$\therefore$ From equation (v)

$$\delta H = dU + \delta W \qquad \ldots(vi)$$

Here all the quantities are in consistent units

Example 6·1. *When a system is taken from the state A to the state B, along the path ACB, 80* joules *of heat flows into the system, and the system does 30* joules *of work (Fig. 6·3).*

(a) How much heat flows into the system along the path ADB, if the work done is 10 joules.

(b) The system is returned from the state B to the state A along the curved path. The work done on the system is 20 joules. *Does the system absorb or liberate heat and how much ?*

(c) If $U_A = C$, $U_D = 40$ joules, *find the heat absorbed in the process AD and DB.*

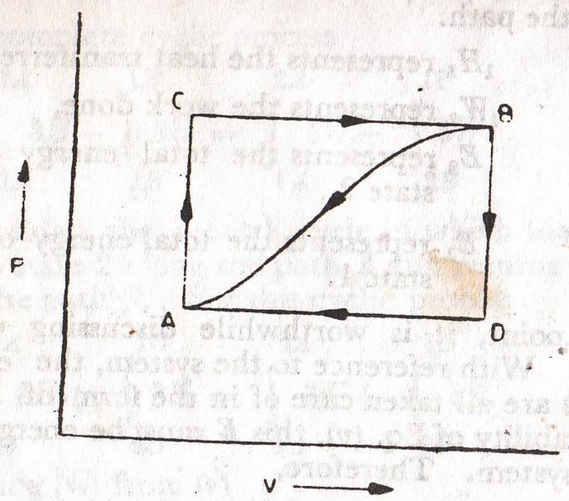


Fig. 6·3

Along the path ACB,

$$H_{ACB} = U_B - U_A + W$$

Here $H = +80$ joules

$W = +30$ joules

$\therefore \quad +80 = U_B - U_A + 30$

$$U_B - U_A = 80 - 30 = \mathbf{50\ joules}$$

(a) Along the path ADB,

$W = +10$ joules

$$H_{ADB} = U_B - U_A + W$$

$$H = 50 + 10 = \mathbf{60\ joules}$$

(b) For the curved path from B to A,

$$W = -20 \text{ joules}$$

$$H = (U_A - U_B) + W$$

$$= -50 - 20 = \mathbf{-70\ joules}$$

(—ve sign shows that heat is liberated by the system)

(c) $U_A = 0, \qquad U_D = 40$ joules

$$U_B - U_A = 50$$

$\therefore \quad U_B = 50$ joules

In the process ADB, 10 joules of work is done. Work done from A to D is +10 joules and from D to B is zero.

For AD,

$$H_{AD} = (U_D - U_A) + W$$

$$= 40 + 10 = 50 \text{ joules}$$

For DB

$$H_{DB} = U_C - U_D + W$$

$$= 50 - 40 + 0 = \mathbf{10\ joules}$$

6·10 Applications of First Law of Thermodynamics

Specific Heat of a Gas (T and V Independent)

The internal energy of a system is a single valued function of the state variables *viz.*, pressure, volume, temperature etc. In the case of a gas, any two of the variables P, V, T are sufficient to define completely its state. If V and T are chosen as the independent variables,

$$U = f(V, T) \qquad \ldots(i)$$

Differentiating equation (i)

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

If an amount of heat δH is supplied to a thermodynamical system, say an ideal gas and if the volume increases by dV at a constant pressure P, then according to the first law of thermodynamics

$$\delta H = dU + \delta W$$

Here $\delta W = P.dV$

$\therefore \quad \delta H = dU + P.dV$

Substituting the value of dU from equation (ii)

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P dV \qquad \ldots(iii)$$

Dividing both sides by dT

$$\frac{\delta H}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + \frac{P.dV}{dT}$$

or $$\left(\frac{\delta H}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{dV}{dT} \quad \ldots(iv)$$

If the gas is heated at constant volume,

$$\left(\frac{\delta H}{\partial T}\right)_V = C_V$$

and $$\frac{dV}{dT} = 0$$

$$\therefore \left(\frac{\delta H}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \quad \ldots(v)$$

When the gas is heated at constant pressure,

$$\left(\frac{\delta H}{dT}\right)_P = C_P$$

$\therefore$ From equation (iv),

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

or $$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{dV}{dT}\right)_P \quad \ldots(vi)$$

From Joule's experiment, for an ideal gas on opening the stop-cock, no work was done and no heat transfer took place.

So $\delta H = 0 = dU + 0$. Therefore, $dU = 0$. Even though the volume changed while the temperature is constant, there is no change in internal energy.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

From the ideal gas equation

$$PV = RT$$

or $$P\left(\frac{\partial V}{\partial T}\right)_P = R \quad \ldots(vii)$$

$$\therefore \quad C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

But $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\therefore C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$\therefore C_P - C_V = R \quad \ldots(viii)$$

Here C_P, C_V and R are expressed in the same units.

From equation (iii)

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad \ldots(ix)$$

For a process at constant temperature

$$dT = 0$$

$$\therefore \quad (\delta H)_T = P(dV)_T + \left(\frac{\partial U}{\partial V}\right)_T (dV)_T \quad \ldots(x)$$

This equation represents the amount of heat energy supplied to a system in an isothermal reversible process and is equal to the sum of the work done by the system and the increase in its internal energy.

For a reversible adiabatic process

$$\delta H = 0,$$

Therefore, from equation (ix),

$$0 = C_V\, dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

or $$C_V dT = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

Dividing throughout by dV,

$$C_V \left(\frac{\partial T}{\partial V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \quad \ldots(xii)$$

The isobaric volume coefficient of expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \alpha V = \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \frac{C_P - C_V}{\alpha V} = P$$

But $$\left(\frac{\partial U}{\partial V}\right)_T = 0 = P - P$$

or $$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{C_P - C_V}{\alpha V}\right) - P \quad \ldots(xiii)$$

or $$-\left(\frac{C_P - C_V}{\alpha V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \quad \ldots(xiv)$$

From equations (*xii*) and (*xiv*)

$$C_V\left(\frac{\partial T}{\partial V}\right) = -\left(\frac{C_P - C_V}{\alpha V}\right)$$

or
$$\left(\frac{\partial T}{\partial V}\right) = \frac{C_V - C_P}{\alpha V C_V} \qquad \ldots(xv)$$

This expression holds good for an adiabatic reversible process.

6·11 Isothermal Process

If a system is perfectly conducting to the surroundings and the temperature remains constant throughout the process, it is called

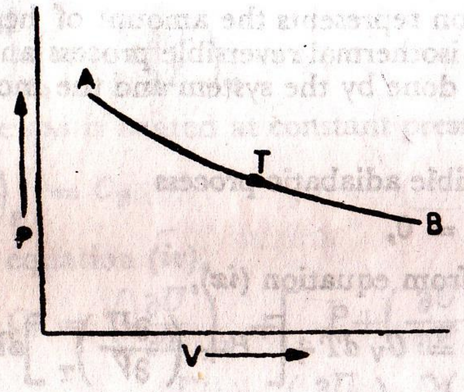


Fig. 6·4

an isothermal process. Consider a working substance at a certain pressure and temperature and having a volume represented by the point *A* (Fig. 6·4).

Pressure is decreased and work is done by the working substance at the cost of its internal energy and there should be fall in temperature. But, the system is perfectly conducting to the surroundings. It absorbs heat from the surroundings and maintains a constant temperature. Thus from *A* to *B* the temperature remains constant. The curve *AB* is called the *isothermal* curve or *isothermal*.

Consider the working substance at the point *B* and let the pressure be increased. External work is done on the working substance and there should be rise in temperature. But the system is perfectly conducting to the surroundings. It gives extra heat to the surroundings and its temperature remains constant from *B* to *A*.

Thus, during the isothermal process, the temperature of the working substance remains constant. It can absorb heat or give heat to the surroundings. The equation for an isothermal process is

$$PV = RT = \text{constant [For one gram molecule of a gas.]}$$

For n gram molecules of a gas $PV = nRT$

6·12 Adiabatic process

During an adiabatic process, the working substance is perfectly insulated from the surroundings It can neither give heat nor take heat from the surroundings. When work is done on the working

substance, there is rise in temperature because the external work done on the working substance increases its internal energy. When work is done by the working substance, it is done at the cost of its internal energy. As the system is perfectly insulated from the surroundings, there is fall in temperature.

Thus, during an adiabatic process, the working substance is perfectly insulated from the surroundings. All along the process, there is change in temperature. A curve between pressure and volume during the adiabatic process is called an adiabatic curve or an adiabatic.

Examples. 1. The compression of the mixture of oil vapour and air during compression stroke of an internal combustion is an adiabatic process and there is rise in temperature.

2. The expansion of the combustion products during the working stroke of an engine is an adiabatic process and there is fall in temperature.

3. The sudden bursting of a cycle tube is an adiabatic process.

Apply the first law of thermodynamics to an adiabatic process, $\delta H = 0$,

$$\delta H = dU + \delta W$$

or
$$0 = dU + \delta W \qquad \ldots(i)$$

The processes that take place *suddenly* or *quickly* are adiabatic processes.

6·13 Isochoric Process

If the working substance is taken in a non-expanding chamber, the heat supplied will increase the pressure and temperature. The volume of the substance will remain constant. Such a process is called an *isochoric process*. The work done is zero because there is no change in volume. The whole of the heat supplied increases the internal energy. Therefore, during the isochoric process $\delta W = 0$.

$$\delta H = dU \qquad \ldots(i)$$

The heat transferred in such a process

$$\delta H = C_v dT$$

$$\therefore \quad C_v dT = dU \qquad \ldots(ii)$$

Hence C_v is the specific heat for one gram-molecule of a gas at constant volume.

6·14 Isobaric Process

If the working substance is taken in an expanding chamber kept at a constant pressure, the process is called an isobaric process. Here, the temperature and volume change. If an amount of heat δH is given to the working substance, it is partly used in increasing the temperature of the working substance by dT and partly used in doing external work. Considering one gram of the working substance,

$$\delta H = 1 \times C_v dT + \frac{P \cdot dV}{J} \quad \ldots(i)$$

But
$$\delta H = C_p dT \quad \ldots(ii)$$
$$P.dV = r.dT$$

$$\therefore \quad C_p dT = C_v.dT + \frac{r.dT}{J}$$

$$C_p - C_v = \frac{r}{J} \quad \ldots(iii)$$

Here C_p and C_v represent the specific heats for 1 gram of a gas and r is the ordinary gas constant.

If C_p and C_v are the gram-molecular specific heats of gas, then

$$C_p - C_v = \frac{R}{J} \quad \ldots(iv)$$

Here R is the universal gas constant.

6·15 Gas Equation During an Adiabatic Process

Consider 1 gram of the working substance (ideal gas) perfectly insulated from the surroundings. Let the external work done by the gas be δW.

Applying the first law of thermodynamics

$$\delta H = dU + \delta W$$

But
$$\delta H = 0$$

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

where P is the pressure of the gas and dV is the change in volume.

$$\therefore \quad 0 = dU + \frac{P.dV}{J} \quad \ldots(i)$$

As the external work is done by the gas at the cost of its internal energy, there is fall in temperature by dT.

$$dU = 1 \times C_v \times dT$$

$$C_v.dT + \frac{P.dV}{J} = 0 \quad \ldots(ii)$$

For an ideal gas

$$PV = rT \quad \ldots(iii)$$

Differentiating,

$$P.dV + V.dP = r \cdot dT$$

Substituting the value of dT in equation (ii),

$$C_v\left[\frac{P.dV + V.dP}{r}\right] + \frac{P.dV}{J} = 0$$

$$C_v[P.dV + V.dP] + r.\left(\frac{P.dV}{J}\right) = 0$$

But,
$$\frac{r}{J} = (C_p - C_v)$$

$$\therefore \quad C_v.P.dV + C_v.V.dP + C_p.PdV - C_v PdV = 0$$

$$C_p.P.dV + C_v.V.dP = 0$$

Dividing by $C_v.PV$,

$$\frac{C_p}{C_v} \cdot \frac{dV}{V} + \frac{dP}{P} = 0$$

But
$$\frac{C_p}{C_v} = \gamma$$

$$\therefore \quad \frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

Integrating, $\log P + \gamma \log V = \text{const.}$

$$\log PV^\gamma = \text{const.}$$

or
$$PV^\gamma = \text{const.} \quad \ldots(iv)$$

This is the equation connecting pressure and volume during an adiabatic process.

Taking
$$PV = rT$$

or
$$P = \frac{rT}{V}$$

$$\left(\frac{rT}{V}\right) . V^\gamma = \text{const.}$$

But r is const.

$$rTV^{\gamma-1} = \text{const.}$$

$$\therefore \quad TV^{\gamma-1} = \text{const.} \quad \ldots(v)$$

Also
$$V = \frac{rT}{P}$$

$$P\left[\frac{rT}{P}\right]^\gamma = \text{const.}$$

or
$$\frac{r^\gamma T^\gamma}{P^{\gamma-1}} = \text{const.}$$

or
$$\frac{P^{\gamma-1}}{T^\gamma} = \text{const.} \quad \ldots(vi)$$

Thus, during an adiabatic process

(i) $PV^\gamma = \text{const.}$

(ii) $TV^{\gamma-1} = \text{const.}$ and

(iii) $\frac{P^{\gamma-1}}{T^\gamma} = \text{const.}$

Example 6·2. *A motor car tyre has a pressure of 2 atmospheres at the room temperature of 27°C. If the tyre suddenly bursts, find the resulting temperature.*

Here, $P_1 = 2$ atmospheres

$T_1 = 27^2+27$

$= 300$ K

$P_2 = 1$ atmosphere

$T_2 = ?$

$\gamma = 1{\cdot}4$

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}}$$

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\left(\frac{1}{2}\right)^{0.4} = \left(\frac{T_2}{300}\right)^{1.4}$$

$$0{\cdot}4 \log (0.5) = 1{\cdot}4\,[\log T_2 - \log 300]$$

$$-0{\cdot}1204 = 1{\cdot}4 \log T_2 - 3{\cdot}4680$$

$$1{\cdot}4 \log T_2 = 3{\cdot}4680 - 0{\cdot}1204$$

$$= 3{\cdot}3476$$

$$\log T_2 = \frac{3{\cdot}3476}{1{\cdot}4}$$

$$= 2{\cdot}3911$$

$$T_2 = 246{\cdot}1 \text{ K}$$

$$= -26{\cdot}9°\text{C}$$

Example 6·3. *A quantity of air at 27°C and atmospheric pressure is suddenly compressed to half its original volume. Find the final (i) pressure and (ii) temperature.*

(i) $P_1 = 1$ atmosphere ; $P_2 = ?$, $\gamma = 1{\cdot}4$

$V_1 = V$; $V_2 = \frac{V}{2}$

During sudden compression, the process is adiabatic

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$P_2 = P_1\left[\frac{V_1}{V_2}\right]^{\gamma}$$

$$= 1[2]^{1.4}$$

$$= 2{\cdot}636 \text{ atmospheres}$$

(ii) $V_1 = V$; $V_2 = \frac{V}{2}$

$T_1 = 300$ K ; $T_2 = ?$

$\gamma = 1{\cdot}4$

$$T_1(V_1)^{\gamma-1} = T_2\,(V_2)^{\gamma-1}$$

$$T_2 = T_1[2]^{1.4-1}$$

$$= 300[2]^{0.4}$$

$$= 395{\cdot}9 \text{ K}$$

$$= 122{\cdot}9°\text{C}$$

Example 6·4. *Air is compressed adiabatically to half its volume. Calculate the change in its temperature.* *(Delhi 1969)*

Let the initial temperature be T_1 K and the final temperature T_2 K.

Initial volume $= V_1$

Final volume $= V_2$

$$= \frac{V_1}{2}$$

During an adiabatic process

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$T_2 = T_1\left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

$$T_2 = T_1[2]^{\gamma-1}$$

But γ for air $= 1{\cdot}40$

$$T_2 = T_1[2]^{1.40-1}$$

$$T_2 = T_1[2]^{0.40}$$

$$T_2 = 1{\cdot}319\,T_1$$

Change in temperature

$$= T_2 - T_1$$

$$= 1{\cdot}319\,T_1 - T_1$$

$$= 0{\cdot}319\,T_1 \text{ K}$$

Example 6·5. *1 gram molecule of a monoatomic ($\gamma = 5/3$) perfect gas at 27°C is adiabatically compressed in a reversible process from an initial pressure of 1 atmosphere to a final pressure of 50 atmospheres. Calculate the resulting difference in temperature.*

[Delhi (Hons.) 1973]

In a reversible adiabatic process

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}}$$

or $$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

Here, $P_2 = 50$,

$P_1 = 1$,

$T_1 = 273+27$

$= 300$ K

$T_2 = ?$

$\gamma = \frac{5}{3}$

$$\therefore \quad (50)^{2/3} = \left(\frac{T_2}{300}\right)^{5/3}$$

or $$\frac{2}{3} \log (50) = \frac{5}{3}\,[\log T_2 - \log 300]$$

$$T_2 = 1{,}434 \text{ K}$$

$$= 1{,}161°\text{C}$$

Example 6·6. *A quantity of dry air at 27°C is compressed (i) slowly and (ii) suddenly to 1/3 of its volume. Find the change in temperature in each case, assuming γ to be 1·4 for dry air.*
[Agra 1969 ; Delhi 71, 75]

(1) When the process is slow, the temperature of the system remains constant. Therefore, there is no change in temperature.

(2) When the compression is sudden, the process is adiabatic.

Here $V_1 = V, \quad V_2 = \frac{V}{3}$

$T_1 = 300$ K, $\quad T_2 = ?$

$\gamma = 1{\cdot}4$

$T_2 (V_2)^{\gamma-1} = T_1 [V_1]^{\gamma-1}$

$$T_2 = T_1 \left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

or $$T_2 = 300 \left[\frac{3V}{V}\right]^{\gamma-1}$$

$$= 300\,[3]^{1.4-1}$$

or $T_2 = 465{\cdot}5$ K

$= 192{\cdot}5$ °C

The temperature of air increases by

$192{\cdot}5 - 27 = \mathbf{165{\cdot}5\ °C}$ or $\mathbf{165{\cdot}5\ K}$

Example 6·7. *A certain mass of gas at* NTP *is expanded to three times its volume under adiabatic conditions. Calculate the resulting temperature and pressure. γ for the gas is 1·40.*
[Delhi (Hons.) 75]

(1) Here, $V_1 = V, \quad V_2 = 3V$

$T_1 = 273$ K $\quad T_2 = ?$

$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

or $$T_2 = T_1 \left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

$$T_2 = 273 \left[\frac{1}{3}\right]^{1.4-1}$$

$$T_2 = \mathbf{176\ K = -97°C}$$

(2) Here, $V_1 = V, \quad V_2 = 3V$

$P_1 = 1$ atmosphere, $\quad P_2 = ?$

$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$$P_2 = P_1 \left[\frac{V_1}{V_2}\right]^{\gamma}$$

or $$P_2 = 1 \left(\frac{1}{3}\right)^{1.4}$$

$$P_2 = \mathbf{0{\cdot}2148\ atmosphere}$$

6·16 Slopes of Adiabatics and Isothermals

In an isothermal process

$$PV = \text{const.}$$

Differentiating,

$$PdV + VdP = 0$$

or $$\frac{dP}{dV} = -\frac{P}{V} \qquad \ldots(i)$$

In an adiabatic process

$$PV^{\gamma} = \text{const.}$$

Differentiating,

$$P\gamma V^{\gamma-1}\,dV + VdP = 0$$

$$\frac{dP}{dV} = -\frac{\gamma P}{V} \qquad \ldots(ii)$$

Therefore, the slope of an adiabatic is γ times the slope of the isothermal.

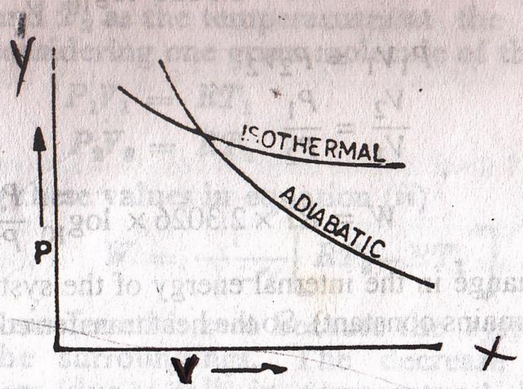


Fig. 6·5

Hence, the adiabatic curve is steeper than the isothermal curve (Fig. 6·5) at a point where the two curves intersect each other.

6·17 Work Done During an Isothermal Process

When a gas is allowed to expand isothermally, work is done by it.

Let the initial and final volumes be V_1 and V_2 respectively. In Fig. 6·6, the area of the shaded strip represents the work done for a small change in volume dV. When the volume changes from V_1 to V_2,

$$\text{Work done} = \int_{V_1}^{V_2} P \,.\, dV = \text{area } ABba \qquad \ldots(i)$$

Fig. 6·6 represents the indicator diagram. Considering one gram molecule of the gas

$$PV = RT$$

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

$$\therefore \quad W = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

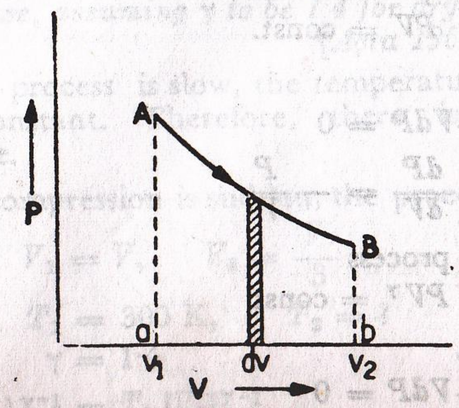


Fig. 6·6

$$= RT \log_e \frac{V_2}{V_1} \quad \ldots (ii)$$

$$W = RT \times 2.3026 \log_{10} \frac{V_2}{V_1} \quad \ldots (iii)$$

Also $P_1V_1 = P_2V_2$

or $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

$$\therefore \quad W = RT \times 2.3026 \times \log_{10} \frac{P_1}{P_2} \quad \ldots (iv)$$

Here, the change in the internal energy of the system is zero (because the temperature remains constant). So the heat transferred is equal to the work done.

6.18 Work Done During an Adiabatic Process

During an adiabatic process, the gas expands from volume V_1 to V_2. As shown by the indicator diagram (Fig. 6.7) the work done for an increase in

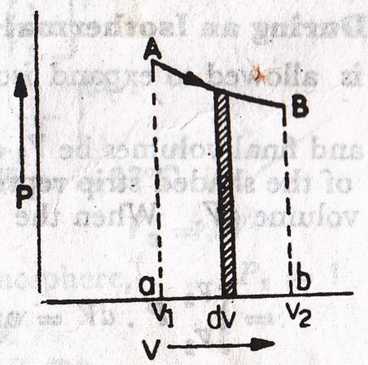


Fig. 6.7.

volume $dV = P.dV$. Work done when the gas expands from V_1 to V_2 is given by,

$$W = \int_{V_1}^{V_2} PdV = \text{Area } ABba$$

During an adiabatic process,

$$PV^\gamma = \text{const} = K$$

or $$P = \frac{K}{V^\gamma}$$

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

$$= \frac{1}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right] \quad \ldots (i)$$

Since A and B lie on the same adiabatic

$$P_1V_1^\gamma = P_2V_2^\gamma = K$$

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

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

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right] \quad \ldots (ii)$$

Taking T_1 and T_2 as the temperatures at the points A and B respectively and considering one gram molecule of the gas

$$P_1V_1 = RT_1$$

and $$P_2V_2 = RT_2$$

Substituting these values in equation (*ii*)

$$W = \frac{1}{1-\gamma}\left[RT_2 - RT_1\right] \quad \ldots (iii)$$

Here, heat transferred is zero because the system is thermally insulated from the surroundings. The decrease in the internal energy of the system (due to fall in temperature) is equal to the work done by the system and *vice versa*.

6·19. Relation Between Adiabatic and Isothermal Elasticities

1. Isothermal Elasticity

During an isothermal process

$$PV = \text{const}$$

Differentiating,

$$PdV + VdP = 0$$

or $$\frac{V.dP}{-dV} = P \quad \ldots (i)$$

From the definition of elasticity of a gas

$$E_{\theta} = \frac{dP}{-dV/V}$$

$$= \frac{VdP}{-dV} \quad \ldots (ii)$$

From (*i*) and (*ii*)

$$E_{iso} = P \qquad \ldots(iii)$$

2. Adiabatic Elasticity

During an adiabatic process

$$PV^{\gamma} = \text{const}$$

Differentiating, $P\gamma V^{\gamma-1}dV + V^{\gamma}dP = 0$

or
$$\frac{VdP}{-dV} = \gamma P \qquad \ldots(iv)$$

From the definition of elasticity of a gas

$$E_{adi} = \frac{dP}{-dV/V}$$

$$= \frac{V.dP}{-dV} \qquad \ldots(v)$$

From (*iv*) and (*v*),

$$E_{adi} = \gamma P \qquad \ldots(vi)$$

Comparing (*iii*) and (*vi*)

$$E_{adi} = \gamma E_{iso}$$

Thus, the adiabatic elasticity of a gas is γ times the isothermal elasticity.

6·20 Clement and Desormes Method—Determination of γ

Clement and Desormes in 1819 designed an experiment to find γ, the ratio between the two specific heats of a gas.

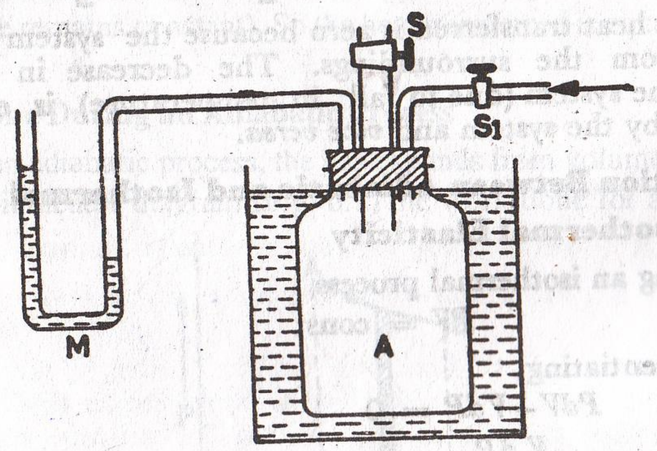


Fig. 6·8

The vessel *A* has a capacity of 20 to 30 litres and is fitted in a box containing cotton and wool. At the top end, three tubes are fitted as shown in Fig. 6·8. Through S_1, dry air is forced into the vessel *A*. The stop cock S_1 is closed when the pressure inside *A* is slightly greater than the atmospheric pressure. Let the difference in level on the two sides of the manometer be *H* and

the atmospheric pressure be P_0. The pressure of air inside the vessel is P_1.

The stop-cock *S* is suddenly opened and closed just at the moment when the levels of the liquid on the two sides of the manometer are the same. Some quantity of air escapes to the atmosphere. The air inside the vessel expands adiabatically. The temperature of air inside the vessel falls due to adiabatic expansion. The air inside the vessel is allowed to gain heat from the surroundings and it finally attains the temperature of the surroundings. Let the pressure at the end be P_2 and the difference in levels on the two sides of the manometer be *h*.

Theory. Consider a fixed mass of air left in the vessel in the end. This mass of air has expanded from volume V_1 (less than the volume of the vessel) at pressure P_1 to volume V_2 at pressure P_0. The process is adiabatic as shown by the curve *AB* (Fig. 6·9).

$$P_1V_1^{\gamma} = P_0V_2^{\gamma}$$

$$\frac{P_1}{P_0} = \left(\frac{V_2}{V_1}\right)^{\gamma} \qquad \ldots(i)$$

Finally the point *C* is reached. The points *A* and *C* are at the room temperature. Therefore *AC* can be considered as an isothermal.

$$P_1V_1 = P_2V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \qquad \ldots(ii)$$

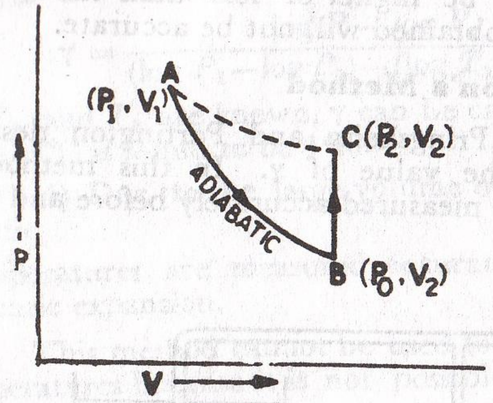


Fig. 6·9

Substituting the value of $\frac{V_2}{V_1}$ in equation (*i*),

$$\frac{P_1}{P_0} = \left(\frac{P_1}{P_2}\right)^{\gamma}$$

Taking logarithms,

$$\log P_1 - \log P_0 = \gamma[\log P_1 - \log P_2]$$

$$\gamma = \frac{\log P_1 - \log P_0}{\log P_1 - \log P_2} \qquad \ldots(iii)$$

But $P_1 = P_0+H$ and $P_2 = P_0+h$

$$\therefore \quad \gamma = \frac{\log(P_0+H)-\log P_0}{\log(P_0+H)-\log(P_0+h)}$$

$$\gamma = \frac{\log\left(\frac{P_0+H}{P_0}\right)}{\log\left(\frac{P_0+H}{P_0+h}\right)}$$

$$= \frac{\log\left(1+\frac{H}{P_0}\right)}{\log\left(1+\frac{H-h}{P_0+h}\right)}$$

Approximately, $$\gamma = \frac{\frac{H}{P_0}}{\frac{H-h}{P_0}} = \frac{H}{H-h}$$

Hence $$\gamma = \frac{H}{H-h} \qquad \ldots(iv)$$

Similarly, γ for any gas can be determined by this method.

Drawbacks. When the stop-cock is opened, a series of oscillations are set up. This is shown by the up and down movement of the liquid in the manometer. Therefore, the exact moment when the stopcock should be closed is not known. The pressure may not be equal to the atmospheric pressure when the stop-cock is closed. It may be higher or less than the atmospheric pressure. Thus the result obtained will not be accurate.

6·21 Partington's Method

Lummer, Pringsheim and Partington designed an apparatus to determine the value of γ. In this method, the pressure and temperature are measured accurately before and after the adiabatic expansion.

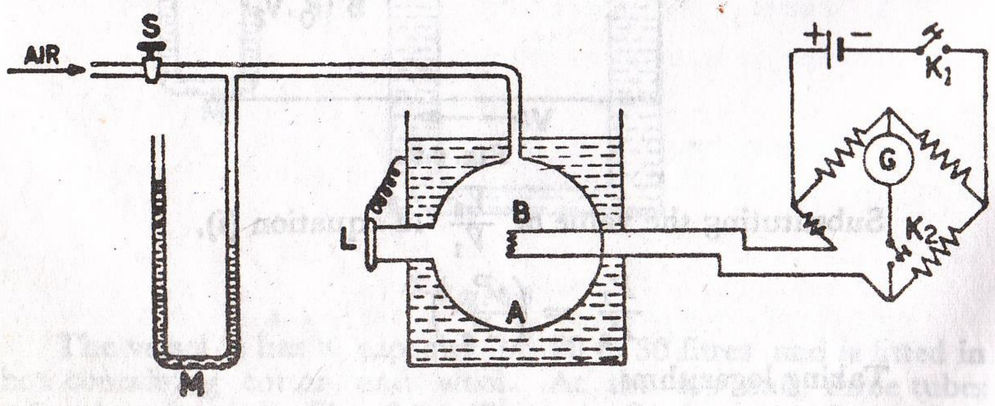


Fig. 6·10

The apparatus consists of a vessel A having a capacity between 130 and 150 litres. The valve L can be opened and closed suddenly

It is controlled by a spring arrangement (Fig. 6·10). Dry air (or gas) at a pressure higher than the atmospheric pressure is forced into the vessel A and the stop-cock S is closed. The oil manometer M is used to measure the pressure of air inside the vessel A. The bolometer B (a platinum wire) and a sensitive galvanometer are used in the Wheatstone's bridge arrangement.

The vessel is surrounded by a constant temperature bath. Let the initial pressure and temperature be P_1 and T_1 (room temperature). The bridge is kept slightly disturbed from the balanced position. The valve L is suddenly opened and closed. The Wheatstones bridge is at once adjusted for balanced position. The temperature of air inside A has decreased due to adiabatic expansion of air. Let the temperature inside be T_0 and the atmospheric pressure P_0. If the apparatus is allowed to remain as such for some time, it will gain heat from the surroundings and the balance point gets disturbed. In order that the balance point remains undisturbed, some pieces of ice are added into the water surrounding the vessel A. When the temperature of water bath is the same as that of air just after adiabatic expansion, the bridge will remain balanced.

The temperature T_0 of the bath represents the temperature of air after the adiabatic expansion.

$$\frac{P_1^{\gamma}}{T_1^{\gamma}} = \frac{P_0^{\gamma-1}}{T_0^{\gamma}}$$

$$\left(\frac{P_1}{P_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^{\gamma}$$

$$(\gamma-1)(\log P_1-\log P_0) = \gamma\,[\log T_1-\log T_0]$$

$$\gamma = \frac{\log P_1-\log P_0}{(\log P_1-\log P_0)-(\log T_1-\log T_0)}$$

As P_1, P_0, T_1 and T_0 are known, γ can be calculated. The value of γ for air at 17°C is found to be 1·4034.

Advantages. (1) Due to the large volume of the vessel, the expansion is adiabatic.

(2) The temperatures are measured accurately just before and after the adiabatic expansion.

Drawbacks. This method cannot be used to find the value of γ at higher temperatures because it is not possible to determine the cooling correction accurately.

6·22 Ruchhardt's Experiment

In 1929, Ruchhardt designed an apparatus to find the value of γ. It is based on the principle of mechanics. Air (or gas) is enclosed in a big jar (Fig. 6·11). A tube of uniform area of cross section is fitted and a ball of mass m fits in the tube just like a piston. In the equilibrium position, the ball is at the point A. The pressure P of air inside the vessel, is given by

$$P = P_0+\frac{mg}{A}$$

where P_0 is the atmospheric pressure and A is the area of cross-section of the tube.

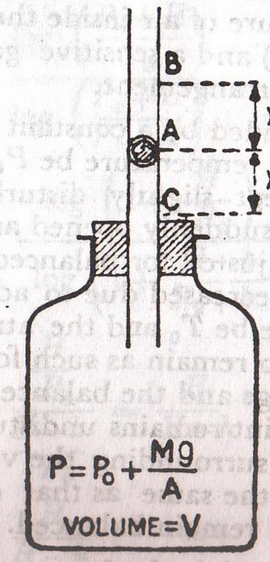


Fig. 6·11

The ball is given a small downward movement through a distance y. It moves up and down and executes simple harmonic motion. Let the change in volume be dV and change in pressure be dP.

$$dV = yA$$

and $$dP = \frac{F}{A}$$

where F is the restoring force

As the ball moves quite rapidly, the process of change in P and V is adiabatic.

$$\therefore \quad PV^\gamma = \text{const}$$

Differentiating, $P\gamma V^{\gamma-1}\,dV + V^\gamma . dP = 0$

$$\gamma P dV + V dP = 0$$

Substituting the values of dV and dP,

$$\gamma P y A + \frac{V . F}{A} = 0,$$

But $$F = M . \frac{d^2y}{dt^2}$$

or $$F = -\frac{\gamma P A^2}{V} . y \qquad \ldots(i)$$

$$\therefore \quad \frac{d^2y}{dt^2} + \frac{\gamma P A^2}{VM} . y = 0 \qquad \ldots(ii)$$

Equation (ii) represents S.H.M.

Let the time period be t

$$t = 2\pi\sqrt{\frac{\text{displacement}}{\text{acceleration}}}$$

$$= 2\pi\sqrt{\frac{y}{-d^2y/dt^2}}$$

$$t = 2\pi\sqrt{\frac{VM}{\gamma PA^2}}$$

$$\gamma = \frac{4\pi^2 VM}{PA^2t^2} \qquad \ldots(iii)$$

As V, M, P and A are already known, only the time period t is to be determined.

Hence γ can be calculated.

This experiment is not very accurate because the ball comes to rest in a short time due to friction and the time period cannot be determined accurately.

Rinkle's Modification. Rinkle suggested a modification in Ruchhardt's experiment. The ball is kept in the equilibrium position where the pressure of air (or gas) is exactly equal to the atmospheric pressure. The ball is allowed to drop and the distance L through which it drops before starting to move up again is noted. This distance is found accurately by taking a series of photographs of the moving ball.

$$\text{Work done} = \int_0^L F\,.\,dy$$

But $$F = \frac{\gamma P_0 A^2 y}{V}$$

$$W = \frac{\gamma P_0 A^2}{V}\int_0^L y\,dy$$

$$= \frac{\gamma P_0 A^2 L^2}{2V} \qquad \ldots(iv)$$

$$\text{Work done} = MgL \qquad \ldots(v)$$

Equating (iv) and (v)

$$\frac{\gamma P_0 A^2 L^2}{2V} = MgL$$

$$\gamma = \frac{2MgV}{P_0 A^2 L} \qquad \ldots(vi)$$

As M, g, V, P_0 and A are known, L is measured from the photographic film. Hence γ can be calculated. The error in the result is due to the following assumptions : (i) that there is no friction, (ii) that the gas is ideal and (iii) the process is completely adiabatic.

6·23 Irreversible Process

The thermodynamical state of a system can be defined with the help of the thermodynamical coordinates of the system. The state of a system can be changed by altering the thermodynamical coordinates. Changing from one state to the other by changing the thermodynamical coordinates is called a *process*.

Consider two states of a system i.e., state A and state B. Change of state from A to B or *vice versa* is a process and the direction of the process will depend upon a new thermodynamical coordinate called **entropy**. All processes are not possible in the universe.

Consider the following processes :

(1) Let two blocks A and B at different temperatures T_1 and T_2 ($T_1 > T_2$) be kept in contact but the system as a whole is insulated from the surroundings. Conduction of heat takes place between the blocks, the temperature of A falls and the temperature of B rises and thermodynamical equilibrium will be reached.

(2) Consider a flywheel rotating with an angular velocity ω. Its initial kinetic energy is $\frac{1}{2}I\omega^2$. After some time the wheel comes to rest and kinetic energy is utilised in overcoming friction at the bearings. The temperature of the wheel and the bearings rises and the increase in their internal energy is equal to the original kinetic energy of the fly wheel.

(3) Consider two flasks A and B connected by a glass tube provided with a stop cock. Let A contain air at high pressure and B is evacuated. The system is isolated from the surroundings. If the stop cock is opened, air rushes from A to B, the pressure in A decreases and the volume of air increases.

All the above three examples though different, are thermodynamical processes involving change in thermodynamical coordinates. Also, in accordance with the first law of thermodynamics, the principl e of conservation of energy is not violated because the total energy of the system is conserved. It is also clear that, with the initial conditions described above, the three processes will take place.

Let us consider the possibility of the above three processes taking place in the reverse direction. In the first case, if the reverse process is possible, the block B should transfer heat to A and initial conditions should be restored. In the second case, if the reverse process is possible, the heat energy must again change to kinetic energy and the fly wheel should start rotating with the initial angular velocity ω. In the third case, if the reverse process is possible the air in B must flow back to A and the initial condition should be obtained.

But, it is a matter of common experience, that none of the above conditions for the reverse processes are reached. It means that the direction of the process cannot be determined by knowing the thermodynamical coordinates in the two end states. To determine the direction of the process a new thermodynamical coordinate has been devised by Clausius and this is called the entropy of the system. Similar to internal energy, entropy is also a function of the

state of a system. For any possible process, the entropy of an isolated system should increase or remain constant. The process in which there is a possibility of decrease in entropy cannot take place.

If the entropy of an isolated system is maximum, any change of state will mean decrease in entropy and hence that change of state will not take place.

To conclude, *processes in which the entropy of an isolated system decreases do not take place or for all processes taking place in an isolated system the entropy of the system should increase or remain constant.* It means a process is irreversible if the entropy decreases when the direction of the process is reversed. A process is said to be irreversible if it cannot be retraced back exactly in the opposite direction. During an irreversible process, heat energy is always used to overcome friction. Energy is also dissipated in the form of conduction and radiation. This loss of energy always takes place whether the engine works in one direction or the reverse direction. Such energy cannot be regained. In actual practice all the engines are irreversible. If electric current is passed through a wire, heat is produced. If the direction of the current is reversed, heat is again produced. This is also an example of an irreversible process. All chemical reactions are irreversible. In general, all natural processes are irreversible.

6·24 Reversible Process

From the thermodynamical point of view, a reversible process is one in which an infinitesimally small change in the external conditions will result in all the changes taking place in the direct process but exactly repeated in the reverse order and in the opposite sense. The process should take place at an extremely slow rate. In a reversible cycle, there should not be any loss of heat due to friction or radiation. In this process, the initial conditions of the working substance can be obtained.

Consider a cylinder, containing a gas at a certain pressure and temperature. The cylinder is fitted with a frictionless piston. If the pressure is decreased, the gas expands slowly and maintains a constant temperature (isothermal process). The energy required for this expansion is continuously drawn from the source (surroundings). If the pressure on the piston is increased, the gas contracts slowly and maintains constant temperature (isothermal process). The energy liberated during compression is given to the sink (surroundings). This is also true for an adiabatic process provided the process takes place infinitely slowly.

The process will not be reversible if there is any loss of heat due to friction, radiation or conduction. If the changes take place rapidly, the process will not be reversible. The energy used in overcoming friction cannot be retraced.

The conditions of reversibility for any heat engine or process can be stated as follows :—

(1) The pressure and temperature of the working substance

must not differ appreciably from those of the surroundings at any stage of the cycle of operation.

(2) All the processes taking place in the cycle of operation must be infinitely slow.

(3) The working parts of the engine must be completely free from friction.

(4) There should not be any loss of energy due to conduction or radiation during the cycle of operation.

It should be remembered that the complete reversible process or cycle of operation is only an ideal case. In an actual process, there is always loss of heat due to friction, conduction or radiation. The temperature and pressure of the working substance differ appreciably from those of the surroundings.

6.23 Second Law of Thermodynamics

A heat engine is chiefly concerned with the conversion of heat energy into mechanical work. A refrigerator is a device to cool a certain space below the temperature of its surroundings. The first law of thermodynamics is a qualitative statement which does not preclude the possibility of the existence of either a heat engine or a refrigerator. The first law does not contradict the existence of a 100% efficient heat engine or a self-acting refrigerator.

In practice, these two are not attainable. These phenomena are recognized and this led to the formulation of a law governing these two devices. It is called second law of thermodynamics.

A new term reservoir is used to explain the second law. A **reservoir** is a device having infinite thermal capacity and which can absorb, retain or reject unlimited quantity of heat without any change in its temperature.

Kelvin-Planck statement of the second law is as follows :

"It is impossible to get a continuous supply of work from a body (or engine) which can transfer heat with a single heat reservoir. This is a negative statement. According to this statement, a single reservoir at a single temperature cannot continuously transfer heat into work. It means that there should be two reservoirs for any heat engine. One reservoir (called the source) is taken at a higher temperature and the other reservoir (called the sink) is taken at a lower temperature.

According to this statement, zero degree absolute temperature is not attainable because no heat is rejected to the sink at zero degree Kelvin. If an engine works between any temperature higher than zero degree Kelvin and zero degree Kelvin, it means it uses a single reservoir which contradicts Kelvin-Planck's statement of the second law. Similarly, no engine can be 100% efficient.

In a heat engine, the engine draws heat from the source and after doing some external work, it rejects the remaining heat to the sink. The source and sink are of infinite thermal capacity and they maintain constant temperature.

First Part. According to Kelvin, the second law can also be stated as follows :

"It is impossible to get a continuous supply of work from a body by cooling it to a temperature lower than that of its surroundings".

In a heat engine the working substance does some work and rejects the remaining heat to the *sink*. The temperature of the source must be higher than the surroundings and the engine will not work when the temperatures of the source and the sink are the same. Take the case of a steam engine. The steam (working substance) at high pressure is introduced into the cylinder of the engine. Steam expands, and it does external work. The contents remaining behind after doing work are rejected to the surroundings. The temperature of the working substance rejected to the surroundings is higher than the temperature of the surroundings.

If this working substance rejected by the first engine is used in another engine, it can do work and the temperature of the working substance will fall further.

It means that the working substance can do work only if its temperature is higher than that of the surroundings.

Second Part. According to Clausius :

"It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance."

This part is applicable in the case of ice plants and refrigerators. Heat itself cannot flow from a body at a lower temperature to a body at a higher temperature. But, it is possible, if some external work is done on the working substance. Take the case of ammonia ice plant. Ammonia is the working substance. Liquid ammonia at low pressure takes heat from the brine solution in the brine tank and is converted to low pressure vapour. External work is done to compress the ammonia vapours to high pressure. This ammonia at high pressure is passed through coils over which water at room temperature is poured. Ammonia vapour gives heat to water at room temperature and gets itself converted into liquid again. This high pressure liquid ammonia is throttled to low pressure liquid ammonia. In the whole process ammonia (the working substance) takes heat from brine solution (at a lower temperature) and gives heat to water at room temperature (at a higher temperature). This is possible only due to the external work done on ammonia by the piston in compressing it. The only work of electricity in the ammonia ice plant is to move the piston to do external work on ammonia. If the external work is not done, no ice plant or refrigerator will work. Hence, it is possible to make heat flow from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance.

Thus, the second law of thermodynamics plays an important part for practical devices *e.g.*, heat engines and refrigerators. The first law of thermodynamics only gives the relation between the

work done and the heat produced. But the second law of thermodynamics gives the conditions under which heat can be converted into work.

6.26 Carnot's Reversible Engine

Heat engines are used to convert heat into mechanical work. Sadi Carnot (French) conceived a theoretical engine which is free from all the defects of practical engines. Its efficiency is maximum and it is an ideal heat engine.

For any engine, there are three essential requisites :

(1) **Source**. The source should be at a fixed high temperature T_1 from which the heat engine can draw heat. It has infinite thermal capacity and any amount of heat can be drawn from it at constant temperature T_1.

(2) **Sink**. The sink should be at a fixed lower temperature T_2 to which any amount of heat can be rejected. It also has infinite thermal capacity and its temperature remains constant at T_2.

(3) **Working Substance**. A cylinder with non-conducting sides and conducting bottom contains the perfect gas as the *working substance*.

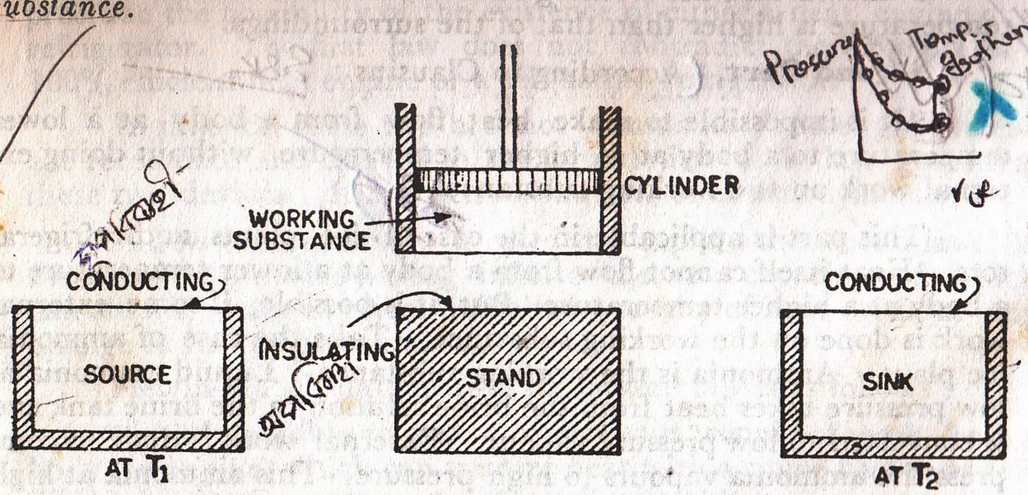


Fig. 6·12

A perfect non-conducting and frictionless piston is fitted into the cylinder. The working substance undergoes a complete cyclic operation (Fig. 6·12).

A perfectly non-conducting stand is also provided so that the working substance can undergo adiabatic operation.

Carnot's Cycle

(1) Place the engine containing the working substance over the source at temperature T_1. The working substance is also at a temperature T_1. Its pressure is P_1 and volume is V_1 as shown by the point A in Fig. 6·13. Decrease the pressure. The volume of the working substance increases. Work is done by the working substance. As the bottom is perfectly conducting to the source at temperature T_1, it absorbs heat. The process is completely isothermal. The temperature remains constant. Let the amount of heat

absorbed by the working substance be H_1 at the temperature T_1. The point B is obtained.

Consider one gram molecule of the working substance.

Work done from A to B (isothermal process)

$$W_1 = \int_{V_1}^{V_2} P.\,dV = RT_1 \log \frac{V_2}{V_1}$$

$$= \text{area } ABGE \qquad \ldots(i)$$

(2) Place the engine on the stand having an insulated top. Decrease the pressure on the working substance. The volume

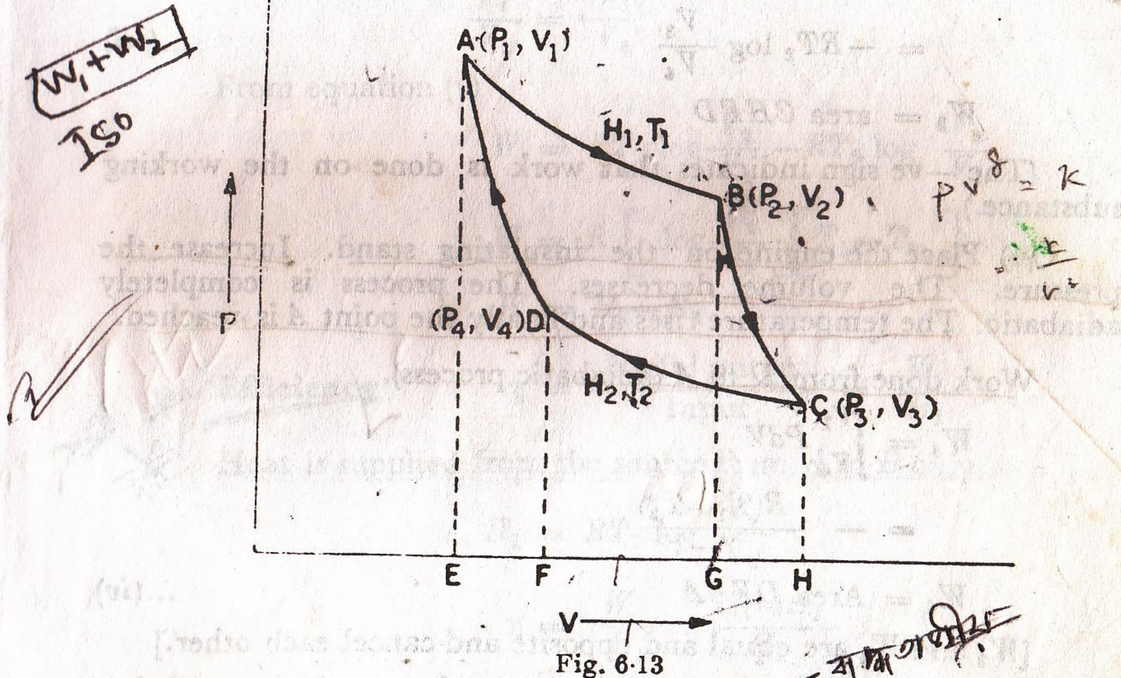


Fig. 6·13

increases. The process is completely adiabatic. Work is done by the working substance at the cost of its internal energy. The temperature falls. The working substance undergoes adiabatic change from B to C. At C the temperature is T_2 (Fig. 6·13).

Work done from B to C (adiabatic process)

$$W_2 = \int_{V_2}^{V_3} P\,.\,dV$$

$$= K\int_{V_2}^{V_3} \frac{dV}{V^\gamma} \quad \because V^{-\gamma}$$

$$= \frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma}$$

$$= \frac{P_3V_3 - P_2V_2}{1-\gamma}$$

$$= \frac{R[T_2 - T_1]}{1-\gamma} = \frac{R[T_1 - T_2]}{\gamma - 1}$$

But PV^γ = constant = K

$P_2V_2 = RT_1$

$P_3V_3 = RT_2$

$P_3V_3^\gamma = P_2V_2^\gamma = K$

W_2 = Area $BCHG$ $\qquad \ldots(ii)$

(3) Place the engine on the sink at temperature T_2. Increase the pressure. The work is done on the working substance. As the base is conducting to the sink, the process is isothermal. A quantity of heat H_2 is rejected to the sink at temperature T_2. Finally the point D is reached.

Work done from C to D (isothermal process)

$$W_3 = \int_{V_3}^{V_4} PdV$$

$$= RT_2 \log \frac{V_4}{V_3}$$

$$= -RT_2 \log \frac{V_3}{V_4} \qquad \ldots(iii)$$

W_3 = area $CHFD$

(The −ve sign indicates that work is done on the working substance.)

(4) Place the engine on the insulating stand. Increase the pressure. The volume decreases. The process is completely adiabatic. The temperature rises and finally the point A is reached.

Work done from D to A (adiabatic process).

$$W_4 = \int_{V_4}^{V_1} PdV$$

$$= -\frac{R(T_1-T_2)}{\gamma-1}$$

W_4 = Area $DFEA$ $\qquad \ldots(iv)$

[W_3 and W_4 are equal and opposite and cancel each other.]

The net work done by the working substance in one complete cycle

= Area $ABGE$ + Area $BCHG$ − Area $CHFD$ − Area $DFEA$

= Area $ABCD$

The net amount of heat absorbed by the working substance

$= H_1 - H_2$

$$\text{Net work} = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \log \frac{V_2}{V_1} + \frac{R(T_1-T_2)}{\gamma-1} - RT_2 \log \frac{V_3}{V_4} - \frac{R[T_1-T_2]}{\gamma-1}$$

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \qquad \ldots(v)$$

The points A and D are on the same adiabatic

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \ldots(vi)$$

The points B and C are on the same adiabatic

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \ldots(vii)$$

From (vi) and (vii)

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

or $$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

or $$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

From equation (v)

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_2}{V_1}$$

$$W = R\left[\log \frac{V_2}{V_1}\right]\left[T_1 - T_2\right]$$

$\therefore$ $$W = H_1 - H_2$$

Efficiency $$\eta = \frac{\text{Useful output}}{\text{Input}} = \frac{W}{H_1}$$

Heat is supplied from the source from A to B only.

$$H_1 = RT_1 \log \frac{V_2}{V_1}$$

$\therefore$ $$\eta = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1}$$

$$= \frac{R[T_1-T_2] \log\left(\frac{V_2}{V_1}\right)}{RT_1 \log\left(\frac{V_2}{V_1}\right)}$$

or $$\eta = 1 - \frac{H_2}{H_1}$$

$$\eta = 1 - \frac{T_2}{T_1} \qquad \ldots(viii)$$

The Carnot's engine is perfectly reversible. It can be operated in the reverse direction also. Then it works as a refrigerator. The heat H_2 is taken from the sink and external work is done on the working substance and heat H_1 is given to the source at a higher temperature.

The isothermal process will take place only when the piston moves very slowly to give enough time for the heat transfer to take place. The adiabatic process will take place when the piston moves

extremely fast to avoid heat transfer. Any practical engine cannot satisfy these conditions.

All practical engines have an efficiency less than the Carnot's engine.

6·27 Carnot's Engine and Refrigerator

Carnot's cycle is perfectly reversible. It can work as a heat engine and also as a refrigerator. When it works as a heat engine, it absorbs a quantity of heat H_1 from the source at a temperature T_1, does an amount of work W and rejects an amount of heat H_2 to the sink at temperature T_2. When it works as a refrigerator, it absorbs heat H_2 from the sink at temperature T_2. W amount of work is done on it by some external means and rejects heat H_1 to the source at a temperature T_1 (Fig. 6·14). In the second case heat flows from a body at a lower temperature to a body at a higher temperature, with the help of external work done on the working substance and it works as a refrigerator. This will not be possible if the cycle is not completely reversible.

Coefficient of Performance. The amount of heat absorbed at the lower temperature is H_2. The amount of work done by the external process (input energy) $= W$ and the amount of heat rejected $= H_1$. Here H_2 is the desired refrigerating effect.

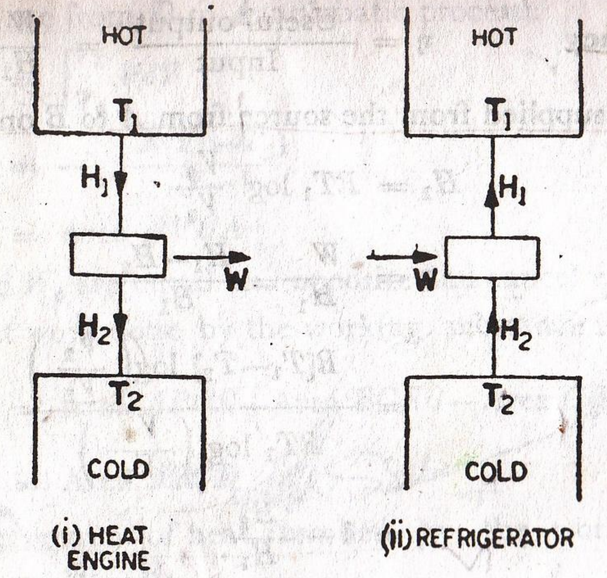


Fig. 6·14

Coefficient of performance

$$= \frac{H_2}{W} = \frac{H_2}{H_1 - H_2}$$

Suppose 200 joules of energy is absorbed at the lower temperature and 100 joules of work is done with external help. Then $200 + 100 = 300$ joules are rejected at the higher temperature.

The coefficient of preformance

$$= \frac{H_2}{W}$$

$$= \frac{H_2}{H_1 - H_2}$$

$$= \frac{200}{300 - 200} = 2$$

Therefore the coefficient of performance of a refrigerator = 2.

In the case of a heat engine, the efficiency cannot be more than 100% but in the case of a refrigerator, the coefficient of performance can be much higher than 100%.

Example 6·8 *Find the efficiency of the Carnot's engine working between the steam point and the ice point.*

$$T_1 = 273 + 100 = 373 \text{ K}$$

$$T_2 = 273 + 0 = 273 \text{ K}$$

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

$$= 1 - \frac{273}{373} = \frac{100}{373}$$

$$\% \text{ efficiency} = \frac{100}{373} \times 100$$

$$= 26{\cdot}81\%$$

Example 6·9. *Find the efficiency of a Carnot's engine working between 127°C and 27°C.*

$$T_1 = 273 + 127 = 400 \text{ K}$$

$$T_2 = 273 + 27 = 300 \text{ K}$$

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

$$= 1 - \frac{300}{400} = 0{\cdot}25$$

$$\% \text{ efficiency} = 25\%$$

Example 6·10. *A Carnot's engine whose temperature of the source is 400 K takes 200 calories of heat at this temperature and rejects 150 calories of heat to the sink. What is the temperature of the sink? Also calculate the efficiency of the engine.*

$H_1 = 200$ cal ; $H_2 = 150$ cal

$T_1 = 400$ K ; $T_2 = ?$

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$T_2 = \frac{H_2}{H_1} \times T_1$$

$$T_2 = \frac{150}{200} \times 400 = 300 \text{ K}$$

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

$$= 1 - \frac{300}{400} = 0{\cdot}25$$

% efficiency = **25%**

Example 6·11. *A Carnot's engine is operated between two reservoirs at temperatures of 450 K and 350 K. If the engine receives 1000 calories of heat from the source in each cycle, calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine and the work done by the engine in each cycle.* (*1* calorie = *4·2* joules).

$T_1 = 450$ K ; $T_2 = 350$ K

$H_1 = 1000$ cal ; $H_2 = ?$

$$\frac{H_2}{H_1} = \frac{T_2}{T_1}$$

$$H_2 = H_1 \times \frac{T_2}{T_1}$$

$$= \frac{1000 \times 350}{450} = \mathbf{777{\cdot}77\ cals}$$

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

$$= 1 - \frac{350}{450} = \frac{100}{450}$$

$$= 0{\cdot}2222$$

% efficiency = **22·22%**

Work done in each cycle

$$= H_1 - H_2$$

$$= 1000 - 777{\cdot}77$$

$$= 222{\cdot}23 \text{ cal}$$

$$= 222{\cdot}23 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{933{\cdot}33\ joules}$$

Example 6·12. *A Carnot's engine working as a refrigerator between 260 K and 300 K receives 500* calories *of heat from the reservoir at the lower temperature. Calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of work done in each cycle to operate the refrigerator.*

[*Delhi (Hons.) 1974*]

$H_1 = ?$ $H_2 = 500$ cal

$T_1 = 300$ K $T_2 = 260$ K

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} ;$$

$$H_1 = H_2 \cdot \frac{T_1}{T_2}$$

$$H_1 = \frac{500 \times 300}{260} = 576{\cdot}92 \text{ cal}$$

$$W = H_1 - H_2 = 76{\cdot}92 \text{ cal}$$

$$= 76{\cdot}92 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{323{\cdot}08\ joules}$$

Example 6·13. *A Carnot's refrigerator takes heat from water at 0°C and discards it to a room at 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat are discarded to the room ? What is the work done by the refrigerator in this process ? What is the coefficient of performance of the machine ?*

[*Delhi 1974*]

$H_1 = ?$

$H_2 = 1000 \times 80 = 80{,}000$ cal

$T_1 = 300$ K

$T_2 = 273$ K

(1) $$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$H_1 = \frac{H_2 T_1}{T_2}$$

$$= \frac{80{,}000 \times 300}{273}$$

$$H_1 = \mathbf{87{,}900\ Cal}$$

(2) Work done by the refrigerator

$$= W = J\,(H_1 - H_2)$$

$$W = 4{\cdot}2\ (87{,}900 - 80{,}000)$$

$$W = 4{\cdot}2 \times 7900$$

or $$W = \mathbf{3{\cdot}183 \times 10^4\ joules}$$

(3) Coefficient of performance,

$$= \frac{H_2}{H_1 - H_2}$$

$$= \frac{80{,}000}{87{,}900 - 80{,}000}$$

$$= \frac{80{,}000}{7900}$$

$$= 10{\cdot}13$$

Example 6·14. *A carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased ?* *(Delhi 1971)*

In the first case

$$\eta = 50\% = 0{\cdot}5, \quad T_2 = 273+7 = 280 \text{ K}.$$

$$T_1 = ?$$

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

or $$0{\cdot}5 = 1 - \frac{280}{T_1}$$

or $$T_1 = 560\ K$$

In the second case

$$\eta' = 70\% = 0{\cdot}7,$$

$$T_2 = 280\ K,$$

$$T_1' = ?$$

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

$$0{\cdot}7 = 1 - \frac{280}{T_1'}$$

or $$T_1' = 840\ K$$

Increase in temperature = 840—560 = **280 K**

6·28 Carnot's Theorem

The efficiency of a reversible engine does not depend on the nature of the working substance. It merely depends upon the temperature limits between which the engine works.

"All the reversible engines working between the same temperature limits have the same efficiency. No engine can be more efficient than a Carnot's reversible engine working between the same two temperatures."

Consider two reversible engines A and B, working between the temperature limits T_1 and T_2 (Fig. 6·15). A and B are coupled. Suppose A is more efficient than B. The engine A works as a heat engine and B as a refrigerator. The engine A absorbs an amount of heat H_1 from the source at a temperature T_1. It does external work W and transfers it to B. The heat rejected to the sink is H_2 at a temperature T_2. The engine B absorbs heat H_2' from the sink at temperature T_2 and W amount of work is done on the working substance. The heat given to the source at temperature T_1 is H_1'.

Suppose the engine A is more efficient than B.

Efficiency of the engine A

$$= \eta = \frac{H_1 - H_2}{H_1} = \frac{W}{H_1}$$

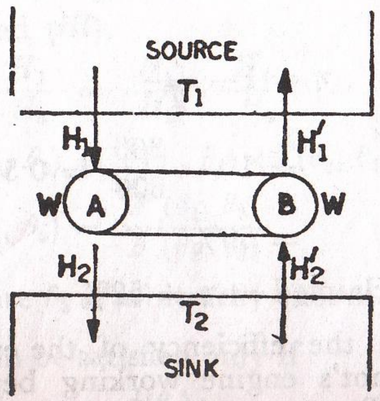


Fig. 6·15.

Efficiency of the engine B

$$= \eta' = \frac{H_1' - H_2'}{H_1'} = \frac{W}{H_1'}$$

Since $$\eta > \eta' ; \ H_1' > H_1$$

Also, $$W = H_1 - H_2 = H_1' - H_2'$$

$$\therefore \quad H_2' > H_2$$

Thus, for the two engines A and B working as a coupled system, $(H_2' - H_2)$ is the quantity of heat taken from the sink at a temperature T_2 and $(H_1' - H_1)$ is the quantity of heat given to the source at a temperature T_1. Both $(H_2' - H_2)$ and $(H_1' - H_1)$ are positive quantities. It means heat flows from the sink at a temperature T_2 (lower temperature) to the source at a temperature T_1 (higher temperature) *i.e.*, heat flows from a body at a lower temperature to a body at a higher temperature. But, no external work has been done on the system. This is contrary to the second law of thermodynamics. Thus, η cannot be greater than η'. The two engines (reversible) working between the same two temperature limits have the same efficiency. Moreover, in the case of a Carnot's engine, there is no loss of heat due to friction, conduction or radiation (irreversible processes). Thus, the Carnot's engine has the maximum efficiency. Whatever may be the nature of the working substance, the efficiency depends only upon the two temperature limits.

In a practical engine there is always loss of energy due to friction, conduction, radiation etc. and hence its efficiency is always lower than that of a Carnot's engine.

Example 6·15. *An inventor claims to have developed an engine working between 600 K and 300 K capable of having an efficiency of 52%. Comment on his claim.*

The efficiency of a Carnot's engine working between 600 K and 300 K,

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

$$= 1 - \frac{300}{600} = 0{\cdot}5$$

$$= 50\%$$

The efficiency claimed $= \eta = 52\%$

It means that the efficiency of the engine is more than the efficiency of a Carnot's engine working between the same two temperature limits. But, no engine can have an efficiency more than a Carnot's engine, so his claim is invalid.

6·29 Thermodynamic (or Work or Absolute) Scale of Temperature

The efficiency of a Carnot's engine does not depend upon the property of the working substance but it depends upon the temperature limits between which the engine works. The scale of temperature based on the working of the Carnot's engine is a standard scale and it does not depend upon the particular property of any substance, as in the case of other thermometric scales. Kelvin worked out the theory of the absolute scale called Kelvin's or thermodynamical scale and also showed that it agrees with the perfect gas scale.

Suppose an engine works between the temperatures θ_1 and θ_2. Here H_1 is the heat absorbed at θ_1 and H_2 is the heat rejected at θ_2

$$\eta = f(\theta_1, \theta_2)$$

$$\eta = \frac{H_1 - H_2}{H_1} = f(\theta_1, \theta_2)$$

$$\therefore \quad 1 - \frac{H_1}{H_2} = f(\theta_1, \theta_2)$$

or
$$\frac{H_1}{H_2} = \frac{1}{1 - f(\theta_1, \theta_2)} = F(\theta_1, \theta_2) \qquad \ldots(i)$$

Similarly, if the engine works between the temperature θ_2 and θ_3 and H_2 is the heat absorbed and H_3 is the heat rejected, then

$$\frac{H_2}{H_3} = F(\theta_2, \theta_3) \qquad \ldots(ii)$$

If the engine works between the temperatures θ_1 and θ_3 and H_1 is the heat absorbed and H_3 is the heat rejected, then

$$\frac{H_1}{H_3} = F(\theta_1, \theta_3) \qquad \ldots(iii)$$

From (*i*), (*ii*) and (*iii*),

$$\frac{H_1}{H_3} = \frac{H_1}{H_2} \times \frac{H_2}{H_3}$$

$$\therefore \quad F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3)$$

$$F(\theta_1, \theta_2) = \frac{F(\theta_1, \theta_3)}{F(\theta_2, \theta_3)}$$

This temperature θ_3 is arbitrarily chosen.

This relation can be satisfied only if

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

$$F(\theta_2, \theta_3) = \frac{\phi(\theta_2)}{\phi(\theta_3)}$$

and
$$F(\theta_1, \theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_3)}$$

where ϕ is another function.

$$\therefore \quad \frac{H_1}{H_2} = F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

The expression on the right hand side represents the ratio of the two Kelvin temperatures and this can be denoted as θ_1/θ_2.

$$\therefore \quad \frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \qquad \ldots(iv)$$

The relation (*iv*) is used to represent a new scale and this does not depend upon the property of the working substance.

Efficiency
$$\eta = \frac{H_1 - H_2}{H_1} = \frac{\theta_1 - \theta_2}{\theta_1} \qquad \ldots(v)$$

$$\eta = 1 - \frac{\theta_2}{\theta_1} \qquad \ldots(vi)$$

6·30 Absolute Zero on Work Scale

Consider an engine working between the steam point and the ice point. The isothermal *AB* is at the steam point and the isothermal *CD* is at the ice point (Fig. 6·16).

$$\eta = 1 - \frac{\theta_{ice}}{\theta_{steam}}$$

$$\eta = \frac{\theta_{steam} - \theta_{ice}}{\theta_{steam}}$$

If the distance between the isothermals AB and CD is divided into 100 equal parts by drawing isothermals parallel to AB or CD, then any isothermal will be at a temperature 1° higher than the isothermal just below it. The difference in temperature between the

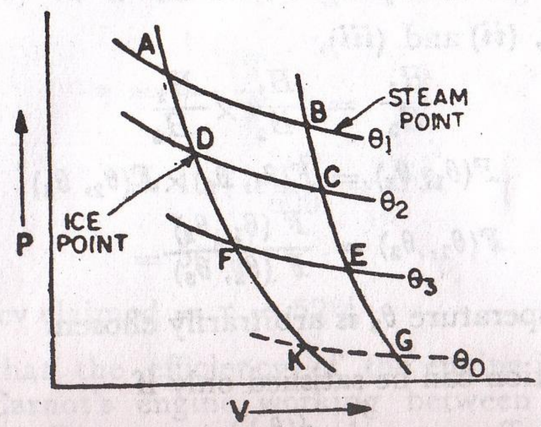


Fig. 6·16

steam point and the ice point is 100 on this scale also. In this way, the work scale (Kelvin) of temperature is fixed. Similarly, isothermals below the ice point can be drawn and an isothermal representing absolute zero can be obtained (Fig. 6·16). The isothermal GK represents absolute zero.

Consider an engine working between the steam point and absolute zero ($\theta_0 = 0$).

$$\eta = 1 - \frac{\theta_0}{\theta_{steam}} = 1$$

i.e., the engine has efficiency equal to 1.

Similarly an engine working between ice point and absolute zero, will have an efficiency

$$\eta' = 1 - \frac{\theta_0}{\theta_{ice}} = 1$$

But efficiency $\eta = \dfrac{H_1 - H_2}{H_1} = 1 - \dfrac{H_2}{H_1}$

If $1 - \dfrac{H_2}{H_1} = 1$, $\dfrac{H_2}{H_1} = 0$ or $H_2 = 0$

It means that if the sink is at the temperature of zero degree absolute, no heat is rejected and the whole of the available energy has been used up in doing useful work and in this case the engine will have 100% efficiency.

Thus the absolute zero temperature on the work scale is defined as the temperature at which a system undergoes a reversible isothermal process without any transfer of heat.

Absolute zero on the work scale can also be defined as that temperature of the sink at which no heat is rejected to it.

According to Kelvin-Planck statement, no engine can have 100 per cent efficiency. Thus the absolute zero temperature is not attainable.

6·31 Work Scale and Ideal Gas Scale

Consider a Carnot's reversible cycle $ABCD$ (Fig. 6·17). The two isothermals are AB and CD. The temperature on the work

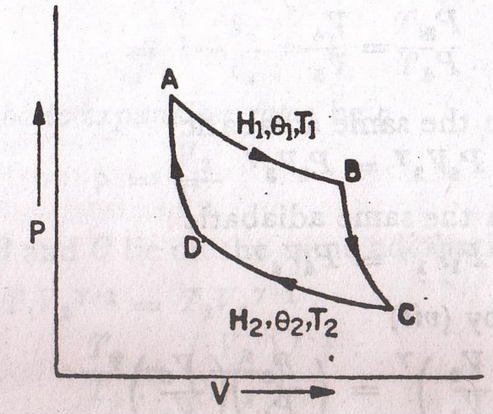


Fig. 6·17

scale is θ_1 and the ideal scale is T_1 for the isothermal AB and the temperature on the work scale is θ_2 and the ideal gas scale is T_2 for the isothermal CD. Let the pressure and volume for the points A, B, C and D be P_1, V_1 ; P_2, V_2 ; P_3, V_3 and P_4, V_4 respectively. Consider that 1 gram of an ideal gas is used as the working substance.

From A to B, the process is isothermal.

$$\text{Work done} = \int_{V_1}^{V_2} P\,dV$$

$$= rT_1 \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\therefore \quad H_1 = rT_1 \log \frac{V_2}{V_1} \qquad \ldots(i)$$

Here r is expressed in heat units.

From C to D, the process is isothermal and a quantity of heat H_2 is rejected by the gas.

$$H_2 = -\int_{V_3}^{V_4} P\,dV$$

$$= -rT_2 \int_{V_3}^{V_4} \frac{dV}{V}$$

$$H_2 = rT_2 \log \frac{V_3}{V_4} \qquad \ldots(ii)$$

Dividing (i) by (ii)

$$\frac{H_1}{H_2} = \frac{rT_1 \log \dfrac{V_2}{V_1}}{rT_2 \log \dfrac{V_3}{V_4}} \qquad \ldots(iii)$$

Also, A and B lie on the same isothermal

$$P_1V_1 = P_2V_2$$

or $$\frac{P_2}{P_1} = \frac{V_1}{V_2} \quad \ldots(iv)$$

C and D lie on the same isothermal

$$P_3V_3 = P_4V_4$$

or $$\frac{P_3}{P_4} = \frac{V_4}{V_3} \quad \ldots(v)$$

B and C lie on the same adiabatic

$$P_2V_2^{\gamma} = P_3V_3^{\gamma} \quad \ldots(vi)$$

A and D lie on the same adiabatic

$$P_1V_1^{\gamma} = P_4V_4^{\gamma} \quad \ldots(vii)$$

Dividing (vi) by (vii)

$$\left(\frac{P_2}{P_1}\right)\left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{P_3}{P_4}\right)\left(\frac{V_3}{V_4}\right)^{\gamma}$$

or $$\left(\frac{V_1}{V_2}\right)\left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{V_4}{V_3}\right)\left(\frac{V_3}{V_4}\right)^{\gamma}$$

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1}$$

or $$\frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \ldots(viii)$$

Substituting this value in equation (iii)

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \quad \ldots(ix)$$

From the work scale of temperature,

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \quad \ldots(x)$$

$$\therefore \quad \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2} \quad \ldots(xi)$$

Special considerations. (i) If θ_1 is zero, T_1 is also zero. It means the two scales are identical at absolute zero temperature.

(ii) Consider that the Carnot's engine works between the steam point and the ice point and there are 100 degrees between the ice point and the steam point on the two scales.

$$\frac{\theta_{steam}}{\theta_{ice}} = \frac{T_{steam}}{T_{ice}}$$

$$\frac{\theta_{ice}+100}{\theta_{ice}} = \frac{T_{ice}+100}{T_{ice}}$$

or $$\theta_{ice} = T_{ice}$$

Therefore, the ice point is the same on the two scales.

Similarly $\theta_{steam} = T_{steam}$

Hence the two scales are completely identical.

Efficiency. The efficiency of a Carnot's engine,

$$\eta = 1 - \frac{H_2}{H_1}$$

$$= 1 - \frac{\theta_2}{\theta_1} = 1 - \frac{T_2}{T_1}$$

Let the *adiabatic expansion ratio* be ρ

$$\rho = \frac{V_3}{V_2}$$

The points B and C lie on the same adiabatic

$$\therefore \quad T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

$$= \left(\frac{1}{\rho}\right)^{\gamma-1}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$$

6·32 Rankine Cycle

In a steam engine, water is used as the working substance. Water is converted into steam in the boiler. The steam is superheated above the boiling temperature. This superheated steam is introduced into the cylinder. For the first part, steam from the boiler enters the cylinder and moves the piston. The inlet valve

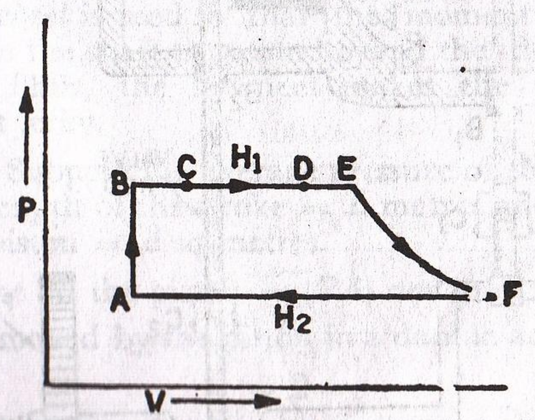


Fig. 6·18

remains open and the steam enters at a constant pressure. In the second part, the inlet valve closes and the steam expands adiabatically. The piston is moved through the rest of the working stroke. As soon as the piston reaches the end of *the stroke* the exhaust valve opens and the steam goes to the condenser. The steam gets condensed in the condenser.

This cycle of operations is known as the Rankine cycle, which is an ideal case. Its working is divided into the following parts :

1. A tc B (Fig. 6·18) represents the compression of water and the boiler pressure is reached.

2. B to C represents the heating of water in the boiler at constant pressure and the boiling point is reached.

3. C to D represents conversion of water into steam at constant pressure.

4. D to E represents superheating of steam beyond its boiling point.

5. E to F represents the adiabatic expansion of steam in doing external work. Steam is cooled and gets condensed.

6. F to A represents the rejection of steam to the condenser where the whole of the steam gets condensed. Finally, the point A is reached.

Efficiency. From B to E, the amount of heat absorbed is H_1 and from F to A, the amount of heat rejected is H_2.

$$\eta = 1 - \frac{H_2}{H_1}$$

6·33 Steam Engine

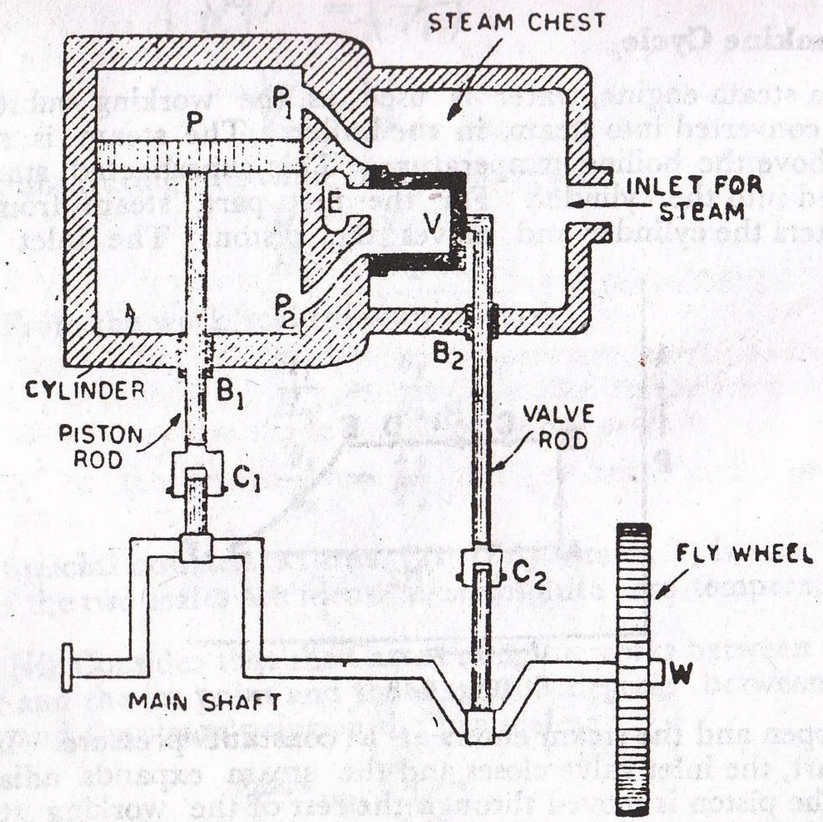


Fig. 6·19

It consists of a steam chest and a cylinder. These are connected by the steam ports P_1 and P_2. P is a piston that moves inside

the cylinder. V is a sliding valve which can also move to and fro such that the port P_1 or P_2 is open to the steam chest. The piston and the sliding valve are connected to the main shaft eccentrically at diametrically opposite points such that when the shaft rotates they move in opposite directions. W is a flywheel attached to thd main shaft. The coupling between the main rod and the piston roe is such that the linear motion of the piston rod is converted to circular motion of the shaft. The machinery to be operated is connected to the main shaft.

Working. 1. Steam at high pressure from the boiler enters the steam chest. The steam enters the cylinder through the port P_1. The piston P is pushed down due to the high pressure of steam (Fig. 6·19). The sliding valve moves up. Both the ports P_1 and P_2 are closed. The steam inside the cylinder expands and moves the piston further in the downward direction. At this position, the port P_1 is connected to the exhaust valve E and P_2 is opened.

2. When steam enters through the port P_2, the piston is pushed up and the sliding valve moves down.

The dead steam in the cylinder is exhausted out to the atmosphere through the exhaust valve E. Both the ports P_1 and P_2 are closed and the steam in the cylinder expands. The piston is pushed further to complete the stroke. Finally the port P_2 is closed and P_1 opens. The process is continuously repeated.

B_1 and B_2 are the stuffing boxes. These boxes allow for the free and smooth sliding of the valve rod and the piston rod. C_1 and C_2 are the cross heads. When the piston moves to and fro, the shaft is rotated and finally the machinery rotates.

Dead centres. Twice in the rotation of the shaft, the force acts at right angles to the shaft. Theoretically a force does not produce any effect when it acts at right angles to the shaft. For this purpose *the flywheel* is used so that the momentum gained by the flywheel enables the shaft to rotate beyond the dead centre in each half rotation. Thus, the flywheel makes the motion of the shaft smooth and not jerky.

Power. Suppose the average pressure of steam = P newtons/metre^2. The length of the stroke = L metres and the area of cross section of the piston = A sq metres.

Total force on the piston = (PA) newtons.

Distance moved by the piston in a double acting steam engine

$$= 2L$$

$\therefore$ Work done for one rotation of the shaft

$$= (PA) \times 2L \text{ joules.}$$

Let the shaft rotate N times per second.

Work done per second $= (PA) \times 2L \times N$ watts

$\therefore$ Power of the engine $= \frac{2PLAN}{1000}$ kilowatts

Efficiency. Most of the heat energy in the steam engine is wasted. Therefore, its efficiency is very low. It is of the order of 8 to 10%. Efficiency is the ratio of the useful mechanical work (W) done by the engine to the amount of heat (H) supplied by the fuel for the same time.

Example 6·16. *In a double acting steam engine, the average pressure of steam is* 10^5 newtons/metre^2. *The length of the stroke is 1 metre and the area of the piston is 0·15 sq metre. Find the power of the engine, if it makes 5 strokes per* second.

Here $P = 10^5$ newtons/metre^2

$L = 1$ metre

$A = 0{\cdot}15$ sq metre

$N = 5$ strokes/second

$$\text{Power} = \frac{2PLAN}{1000}$$

$$\text{Power of the engine} = \frac{2\times10^5\times1\times0{\cdot}15\times5}{1000}$$

$$= 150 \text{ kilowatts.}$$

6·34 Otto Cycle

In the Otto engine (internal combustion engine), air is the

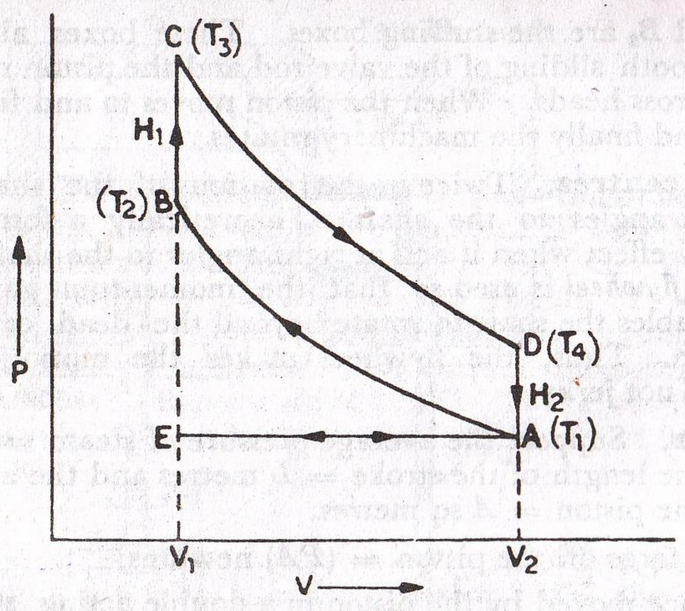


Fig. 6·20

working substance and petrol vapour acts as the fuel. A set of ideal conditions are assumed while discussing an Otto cycle:

1. The working substance is air all the time and it behaves as a perfect gas.

2. There is no friction.

On the basis of these assumptions, Otto cycle can be divided into the following operations :

1. E to A (Fig. 6·20) represents the *charging stroke.* The mixture of air and petrol vapour is allowed to enter at atmospheric pressure. The final volume is V_2 at temperature T_1.

2. A to B represents the *adiabatic compression.* There is no friction and no flow of heat through the walls of the cylinder. The volume changes from V_2 to V_1 and the temperature changes from T_1 to T_2. There is change in pressure also. This represents the *compression stroke.* The compression ratio is nearly 8 *i.e.*, $\frac{V_2}{V_1} = 8$ nearly. The pressure changes from one atmosphere to about 18 atmospheres.

3. B to C represents the *ignition stage.* A spark is produced and the mixture of air and petrol vapour is ignited. The pressure increases from 18 to about 80 atmospheres and the temperature changes from T_2 to T_3 (from 500°C to 2000°C).

4. C to D represents the *working stroke.* The gas expands adiabatically and the engine works. The volume changes from V_1 to V_2. The pressure and temperature decrease.

5. As the point D is reached, the exhaust valve opens. D to A represents the change of pressure to the atmospheric pressure and the temperature changes from T_4 to T_1.

6. A to E represents the *exhaust stroke.* The exhaust gases are completely discharged from the cylinder. Thus, the initial condition of the engine is restored.

Efficiency. Consider that 1 gram of the working substance is used in the process. A quantity of heat H_1 at a higher temperature is absorbed from B to C,

$$H_1 = 1\times C_v(T_3-T_2)$$

A quantity of heat H_2 is rejected at a lower temperature from D to A

$$H_2 = 1\times C_v(T_4-T_1)$$

$$\frac{H_2}{H_1} = \frac{T_4-T_1}{T_3-T_2} \qquad \ldots(i)$$

$$\eta = 1-\frac{H_2}{H_1}$$

$$= 1-\frac{T_4-T_1}{T_3-T_2} \qquad \ldots(ii)$$

The points D and C lie on the same adiabatic

$$\therefore \quad T_4V_2^{\gamma-1} = T_3V_1^{\gamma-1} \qquad \ldots(iii)$$

The points A and B lie on the same adiabatic

$$T_1V_2^{\gamma-1} = T_2V_1^{\gamma-1} \qquad \ldots(iv)$$

Subtracting (iv) from (iii),

$$(T_4-T_1)V_2^{\gamma-1} = (T_3-T_2)V_1^{\gamma-1}$$

$$\frac{T_4-T_1}{T_3-T_2} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \ldots(v)$$

Substituting this value in equation (*ii*),

$$\eta = 1 - \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$= 1 - \left(\frac{1}{(V_2/V_1)}\right)^{\gamma-1}$$

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad \ldots(vi)$$

where ρ is the adiabatic compression ratio.

In an actual petrol engine ρ cannot be made greater than 10. If ρ is more than 10, the mixture gets ignited by itself due to compression much before the sparking takes place.

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$$

If $\rho = 6$ and $\gamma = 1{\cdot}4$

$$\eta = 1 - \left(\frac{1}{6}\right)^{0.4}$$

$$= 0{\cdot}5116 = 51{\cdot}16\%$$

If $\rho = 9$ and $\gamma = 1{\cdot}4$

$$\eta = 1 - \left(\frac{1}{9}\right)^{0.4}$$

$$= 0{\cdot}5847 = 58{\cdot}47\%$$

6·35 Internal Combustion Engine (Petrol Engine)

It consists of a cylinder with an air-tight piston. It has two valves. *I* is the inlet valve and *O* is the outlet valve. The valves are opened and closed at the proper times with a suitable mechanism. The petrol vapours and air from the *carburettor* are admitted into the cylinder through the valve *I*. Here *S* acts as a sparking plug. It is also known as a four-stroke engine.

1. **Charging stroke.** The mixture of petrol vapours and air enters the cylinder. The piston moves down [Fig. 6·21 (*i*)].

2. **Compression stroke.** The inlet valve closes and the piston moves up. The mixture is compressed to a high pressure and the temperature rises to about 500°C [Fig. 6·21 (*ii*)].

3. **Working stroke.** A spark is produced at the sparking plug and the compressed mixture of petrol and air ignites. The temperature rises to about 2000°C and a high pressure of about 15 atmospheres is developed inside the cylinder. The piston is pushed down and the shaft rotates [Fig. 6·21 (*iii*)]. Only in this stroke, work is done by the piston.

4. **Exhaust stroke.** The outlet valve opens and the burnt and unburnt gases are exhausted out to the atmosphere [Fig. 6·21 (*iv*)].

The cycle repeats and the engine works.

Engine Cooling. The internal combustion engine requires cooling, although the efficiency of the engine will be higher without

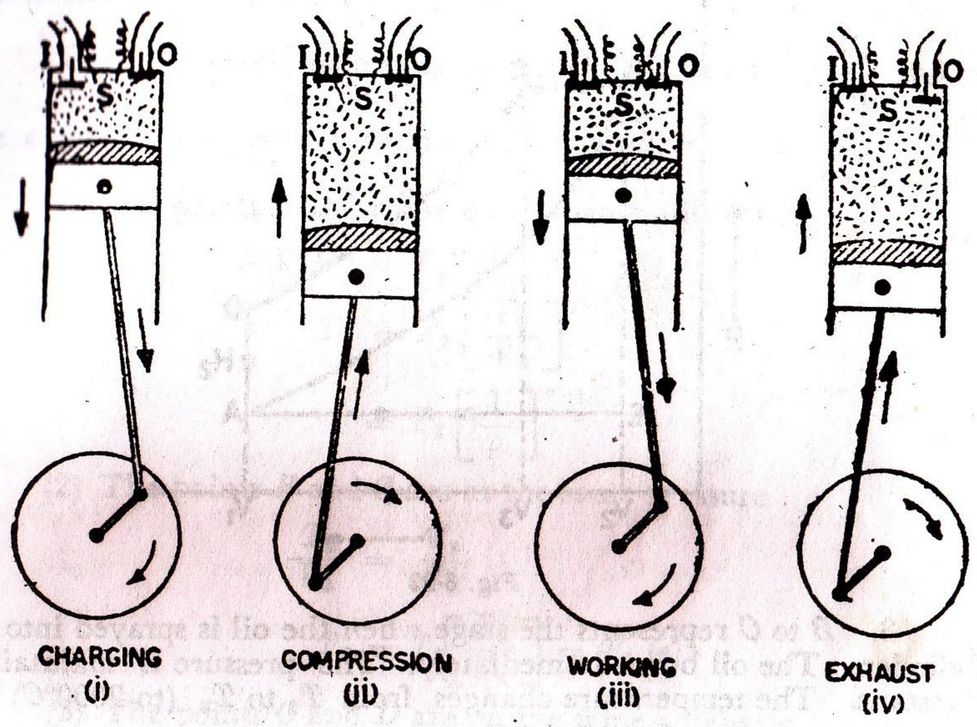


Fig. 6·21

cooling. Temperatures of the order of 2000°C are reached inside the cylinder, although this temperature may last only for a very short interval of time before expansion. If the engine is not cooled the following drawbacks will be present :

(1) Burning of the piston and exhaust valves.
(2) Irregular burning of the fuel.
(3) Seizure of the piston due to expansion.
(4) Burning of the lubricant, and
(5) Melting of the bearing material.

6·36 Diesel Engine

In the case of a diesel engine, air is admitted into the cylinder in the beginning. This air is compressed adiabatically so that the temperature is high enough to ignite the oil sprayed into the cylinder. The ideal conditions are assumed while discussing the complete cycle *viz.* (*i*) the working substance is air all the time and it behaves as a perfect gas and (*ii*) there is no friction. The cycle is called the *diesel cycle*.

1. *E* to *A* (Fig. 6·22) represents the intake of air and its volume changes to V_1. This is the *charging stroke.*

2. *A* to *B* represents the *compression stroke.* Air is compressed adiabatically. The temperature changes from T_1 to T_2 and the

volume changes from V_1 to V_2. The temperature rises to about 1000°C and the pressure to about 40 atmospheres.

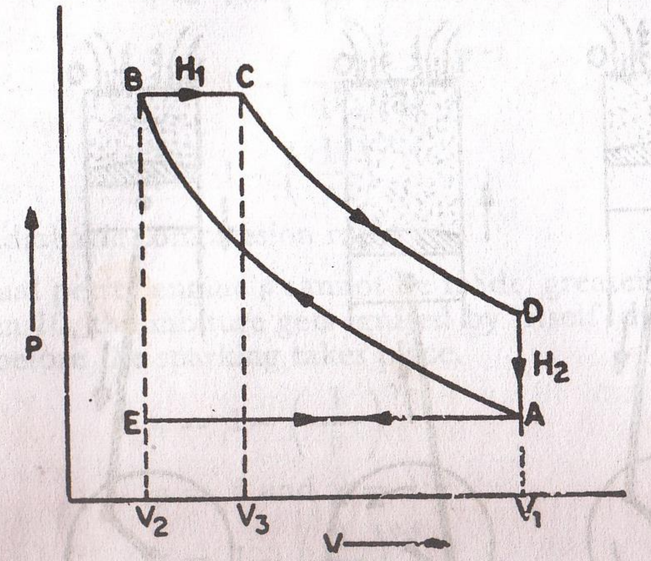


Fig. 6·22

3. B to C represents the stage when the oil is sprayed into the cylinder. The oil burns immediately. The pressure is maintained constant. The temperature changes from T_2 to T_3 (to 2000°C) and the volume changes from V_2 to V_3.

4. C to D represents the *working stroke*. The mixture of air and diesel oil vapour expand adiabatically.

5. As the point D is reached, the exhaust valve opens and the pressure drops to the point A. The volume remains constant, but temperature and pressure decrease.

6. A to E represents the *exhaust stroke*. The unburnt vapours of the oil and the mixture of gases in the cylinder are exhausted out of the cylinder.

Efficiency. From B to C, the pressure remains constant. Considering 1 gram of the working substance, the quantity of heat absorbed,

$$H_1 = 1 \times C_p(T_3 - T_2)$$

From D to A the volume remains constant.

The quantity of heat rejected,

$$H_2 = 1 \times C_v\,(T_4 - T_1)$$

$$\frac{H_2}{H_1} = \frac{C_v}{C_p} \cdot \frac{(T_4 - T_1)}{(T_3 - T_2)}$$

$$= \frac{1}{\gamma} \cdot \frac{T_4 - T_1}{T_3 - T_2}$$

$$\eta = 1 - \frac{H_2}{H_1}$$

$$= 1 - \frac{1}{\gamma}\left(\frac{T_4 - T_1}{T_3 - T_2}\right) \quad \ldots(1)$$

To evaluate $\left(\frac{T_4 - T_1}{T_3 - T_2}\right)$, all the temperatures are to be expressed in terms of T_2.

Let ρ be the adiabatic expansion ratio. Then $\rho = \frac{V_1}{V_2}$ and e the combustion expansion ratio or fuel cut off ratio $= \frac{V_3}{V_2}$.

(1) The points A and B are on the same adiabatic,

$$\therefore \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_1 = T_2\left[\frac{V_2}{V_1}\right]^{\gamma-1}$$

$$= T_2\left[\frac{1}{\rho}\right]^{\gamma-1} \quad \ldots(2)$$

(2) The points B and C are at the same pressure

$$\therefore \quad \frac{T_3}{V_3} = \frac{T_2}{V_2}$$

or $$T_3 = T_2\left[\frac{V_3}{V_2}\right] = T_2\,[e] \quad \ldots(3)$$

(3) The points C and D are on the same adiabatic.

$$\therefore \quad T_4 V_4^{\gamma-1} = T_3 V_3^{\gamma-1}$$

[But $V_4 = V_1$]

$$T_4 = T_3\left[\frac{V_3}{V_1}\right]^{\gamma-1}$$

$$= T_3\left[\frac{V_3}{V_2} \times \frac{V_2}{V_1}\right]^{\gamma-1}$$

$$T_4 = T_3\left[\frac{V_3}{V_2}\right]^{\gamma-1}\left[\frac{V_2}{V_1}\right]^{\gamma-1}$$

$$T_4 = T_3[e]^{\gamma-1}\left[\frac{1}{\rho}\right]^{\gamma-1}$$

$$T_4 = T_2[e][e]^{\gamma-1}\left[\frac{1}{\rho}\right]^{\gamma-1}$$

$$T_4 = T_2[e]^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1} \quad \ldots(4)$$

$$\eta = 1 - \left[\frac{T_4 - T_1}{T_3 - T_2}\right]$$

$$= 1 - \frac{1}{\gamma}\left[\frac{T_2[e]^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1} - T_2\left[\frac{1}{\rho}\right]^{\gamma-1}}{T_2\,[e] - T_2}\right]$$

$$\eta = 1 - \frac{1}{\gamma}\left(\frac{1}{\rho}\right)^{\gamma-1}\left[\frac{e^{\gamma}-1}{e-1}\right] \quad \ldots(5)$$

For the same compression ratio, the efficiency of an Otto engine is more than a diesel engine. In practice, the compression ratio for an Otto engine is from 7 to 9 and for a diesel engine it is from 15 to 20. Due to the higher compression ratio, an actual diesel engine has higher efficiency than the Otto (Petrol) engine. The cylinder must be strong enough to withstand very high pressure.

6·37 Multicylinder Engines

With an engine having one cylinder, the engine works only during the working stroke. The piston moves during the rest of the three strokes due to the momentum of the shaft. In a multicylinder engine (say 4-cylinder engine) the four cylinders are coupled. The working of each cylinder is given below :—

	First	*Second*	*Third*	*Fourth*
First quarter	Working	Exhaust	Compression	Charging
Second quarter	Exhaust	Charging	Working	Compression
Third quarter	Charging	Compression	Exhaust	Working
Fourth quarter	Compression	Working	Charging	Exhaust

In this way, the power of the engine increases and the shaft gets momentum during each quarter cycle.

6·38 Clapeyron Latent Heat Equation

Consider the isothermals $FBAE$ at temperature $T+dT$ and $GCDH$ at temperature T. Here EA and HD show the liquid state

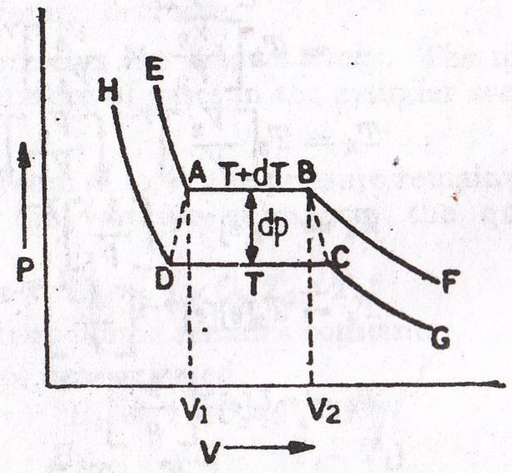


Fig. 6·23

of the substance. At A and D the substance is purely in the liquid state (Fig. 6·23). From A to B or D to C the substance is in transition from the liquid to the gaseous state and *vice versa*. At B and C the substance is purely in the gaseous state. From B to F or C to G the substance is in the gaseous state. Join A to D and B to C by dotted lines.

The cycle $ABCD$ represents a complete cycle and Carnot's theorem can be applied. Suppose the volume at the point A is V_1 and temperature is $T+dT$. The pressure is just below its saturation pressure and the liquid begins to evaporate and at the point B the volume is V_2. The substance is in the vapour state. Suppose the mass of the liquid at B is one gram. The amount of heat absorbed is H_1. Here $H_1=L+dL$, where $L+dL$ is the latent heat of the liquid at temperature $(T+dT)$.

At the point B, the pressure is decreased by dP. The vapour will expand and its temperature falls. The temperature at C is T. At this pressure and temperature T, the gas begins to condense and is converted into the liquid state. At the point D, the substance is in the liquid state. From C to D, the amount of heat rejected (given out) is H_2. Here $H_2 = L$ where L is the latent heat at temperature T. By increasing the pressure a little, the original point A is restored. The cycle $ABCDA$ is completely reversible. Applying the principle of the Carnot's reversible cycle

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

or

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$\frac{H_1-H_2}{H_2} = \frac{T_1-T_2}{T_2}$$

Here, $H_1 = L+dL,\ H_2 = L,$

$T_1 = T+dT,\ T_2 = T$

$H_1-H_2 = L+dL-L = dL$

$T_1-T_2 = T+dT-T = dT$

$$\therefore \quad \frac{dL}{L} = \frac{dT}{T}$$

The area of the figure

$ABCD = H_1-H_2 = dL$

$= dP(V_2-V_1)$

$$\therefore \quad \frac{dP\,(V_2-V_1)}{L} = \frac{dT}{T}$$

$$\frac{dP}{dT} = \frac{L}{T\,(V_2-V_1)} \qquad \ldots(i)$$

This is called the Clapeyron's latent heat equation.

Applications. (1) ***Effect of change of pressure on the melting point.***

When a solid is converted into a liquid, there is change in volume.

(*i*) If V_2 is greater than V_1

$\frac{dP}{dT}$ is a positive quantity. It means that the rate of change of

pressure with respect to temperature is positive. In such cases, the melting point of the substance will increase with increase in pressure and *vice versa*.

(*ii*) If V_2 is less than V_1.

$\frac{dP}{dT}$ is a negative quantity. It means that the rate of change of pressure with respect to temperature is negative. In such cases, the melting point of the substance will decrease with increase in pressure and *vice versa*. In the case of melting ice, the volume of water formed is less than the volume of ice taken. Hence $V_2 < V_1$.

Therefore, the melting point of ice decreases with increase in pressure. Hence ice will melt at a temperature lower than zero degree centigrade at a pressure higher than the normal pressure.

Ice melts at 0°C only at a pressure of 76 cm of Hg.

(2) *Effect of change of pressure on the boiling point.*

When a liquid is converted into a gaseous state, the volume V_2 of the gas is always greater than the corresponding volume V_1 of the liquid *i.e.* $V_2 > V_1$.

Therefore, $\frac{dP}{dT}$ is a +ve quantity.

With increase in pressure, the boiling point of a substance increases and *vice versa*. The liquid will boil at a lower temperature under reduced pressure. In the case of water, the boiling point increases with increase in pressure and *vice versa*. Water boils at 100°C only at 76 cm of Hg pressure. In the laboratories, while preparing steam, the boiling point is less than 100°C because the atmospheric pressure is less than 76 cm of Hg. In pressure cookers, the liquid boils at a higher temperature because the pressure inside is more than the atmospheric pressure.

Example 6·17. *Calculate the depression in the melting point of ice produced by one atmosphere increase of pressure. Given latent heat of ice = 80* cal per gram *and the specific volumes of 1* gram *of ice and water at 0°C are 1·091* cm³ *and 1·000* cm³ *respectively.*

(*Panjab 1963*)

Here

$$L = 80 \text{ cal} = 80 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$
$$T = 273 \text{ K}$$
$$dP = 1 \text{ atmosphere}$$
$$= 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$V_1 = 1{\cdot}091 \text{ cm}^3$$
$$V_2 = 1{\cdot}000 \text{ cm}^3$$
$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$
$$dT = \frac{dP.T.(V_2 - V_1)}{L}$$

$$= \frac{76 \times 13{\cdot}6 \times 980 \times 273(1 - 1{\cdot}091)}{80 \times 4{\cdot}2 \times 10^7}$$
$$= -0{\cdot}0074 \text{ K}$$

Therefore, the *decrease* in the melting point of ice with an increase in pressure of one atmosphere

$$= 0{\cdot}0074 \text{ K} = 0{\cdot}0074°\text{C}$$

Example 6·18. *Find the increase in the boiling point of water at 100°C when the pressure is increased by one atmosphere. Latent heat of vaporisation of steam is 540* cal/gram *and 1* gram *of steam occupies a volume of 1677* cm³.

$$dP = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$T = 100 + 273$$
$$= 373 \text{ K}$$
$$L = 540 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$
$$V_1 = 1{\cdot}000 \text{ cm}^3$$
$$V_2 = 1677 \text{ cm}^3$$
$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$
$$dT = \frac{dP \times T(V_2 - V_1)}{L}$$
$$= \frac{76 \times 13{\cdot}6 \times 980 \times 373 \times 1676}{540 \times 4{\cdot}2 \times 10^7}$$
$$= 27{\cdot}92°\text{C}$$

Therefore, the *increase* in the boiling point of water with an increase in pressure of one atmosphere

$$= 27{\cdot}92°\text{C}$$
$$= 27{\cdot}92 \text{ K}$$

Example 6·19. *Calculate the change in temperature of boiling water when the pressure is increased by 27·12* mm *of* Hg. *The normal boiling point of water at atmospheric pressure is 100°C.*

Latent heat of steam = *537* cal/g

and specific volume of steam = *1674* cm³ (*Delhi 1974*)

$$dP = 2{\cdot}712 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$T = 100 + 273 = 373 \text{ K}$$
$$L = 537 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$
$$V_1 = 1{\cdot}000 \text{ cm}^3$$
$$V_2 = 1674 \text{ cm}^3$$
$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP \times T\,(V_2 - V_1)}{L}$$

$$= \frac{2{\cdot}712 \times 13{\cdot}6 \times 980 \times 373 \times 1673}{537 \times 4{\cdot}2 \times 10^7}$$

$$= \mathbf{1°C \text{ or } 1\ K}$$

Example 6·20. *Calculate the change in the melting point of naphthalene for one atmosphere rise in pressure given that its melting point is 80°C. Latent heat of fusion is 4563* cal/mol *and increase in volume on fusion is 18·7* cm³ *per* mol *and I* calorie $= 4{\cdot}2 \times 10^7$ ergs. *(Delhi 1967)*

$$\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)}$$

dT = 1 atmosphere

$= 76 \times 13{\cdot}6 \times 980$ dynes/cm²

dT = ?

$L = 4563$ cal/mol

$= 4563 \times 4{\cdot}2 \times 10^7$ ergs/mol

$V_2 - V_1 = 18{\cdot}7$ cm³/mol

$T = 80 + 273$

$= 353$ K

$$dT = \frac{dP.T.\,(V_2 - V_1)}{L}$$

$$= \frac{76 \times 13{\cdot}6 \times 980 \times 353 \times 18{\cdot}7}{4563 \times 4{\cdot}2 \times 10^7}$$

$$= \mathbf{0{\cdot}03488\ K}$$

Therefore, the increase in the melting point of naphthalene with an increase in pressure of one atmosphere

$$= \mathbf{0{\cdot}03488\ K}$$

$$= \mathbf{0{\cdot}03488°C}$$

Example 6·21. *Calculate the boiling point of benzene under a pressure of 80* cm *of mercury. The normal boiling point is 80°C. Latent heat of vaporization is 380* joules/g, *density of vapour at the boiling point is 4* g/litre *and that of the liquid 0·9* g/cm³. *(Delhi 1968)*

Here $dP = 80 - 76$

$= 4$ cm of Hg

$= 4 \times 13{\cdot}6 \times 980$ dynes/cm²

$T = 80°C = 80 + 273$

$= 353$ K

$L = 380$ joules/g

$= 380 \times 10^7$ ergs/g

$$V_1 = \frac{1}{0{\cdot}9} = 1{\cdot}11 \text{ cm}^3$$

$$V_2 = \frac{1{,}000}{4} = 250 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T\,[V_2 - V_1]}$$

$$dT = \frac{dP \times T\,[V_2 - V_1]}{L}$$

$$dT = \frac{4 \times 13{\cdot}6 \times 980 \times 353\,[250 - 1{\cdot}11]}{380 \times 10^7}$$

$$= \mathbf{1{\cdot}233\ K}$$

$$= \mathbf{1{\cdot}233°C}$$

$\therefore$ The boiling point of benzene at a pressure of 80 cm of Hg

$$= 80 + 1{\cdot}233$$

$$= \mathbf{81{\cdot}233°C}$$

Example 6·22. *Calculate the change in the boiling point of water when the pressure of steam on its surface is increased from 1 atmosphere to 1·10 atmospheres.*

Latent heat of water at 100°C

$= 537$ cal/g

Volume of one gram of steam at 100°C

$= 1{,}676$ cm³ *(Delhi 1969)*

$dP = 1{\cdot}10 - 1$

$= 0{\cdot}10$ atmosphere

$dP = 0{\cdot}10 \times 76 \times 13{\cdot}6 \times 980$ dynes/cm²

$T = 100 + 273$

$= 373$ K

$L = 537$ cals/g

$= 537 \times 4{\cdot}2 \times 10^7$ ergs/g

$V_1 = 1{\cdot}00$ cm³

$V_2 = 1{,}676$ cm³

$$\frac{dP}{dT} = \frac{L}{T\,[V_2 - V_1]}$$

$$dT = \frac{dP \times T\,[V_2 - V_1]}{L}$$

$$dT = \frac{0{\cdot}1 \times 76 \times 13{\cdot}6 \times 980 \times 373 \times (1{,}675)}{537 \times 4{\cdot}2 \times 10^7}$$

$= 2{\cdot}792$ K

$= 2{\cdot}792°C$

Therefore, the *increase* in the boiling point of water with an increase of 0·1 atmosphere pressure

$= 2{\cdot}792$ K

$= 2{\cdot}792°C$

Example 6·23. *Calculate the change in the melting point of ice when it is subjected to a pressure of 100 atmospheres.*

Density of ice $= 0{\cdot}917$ g/cm³ *and*

Latent heat of ice $= 336$ J/g *(Delhi 1972)*

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$dP = 100-1$

$= 99$ atmospheres

$dP = 99\times76\times13{\cdot}6\times980$ dynes/cm²

$L = 336$ J/g

$= 336\times10^7$ ergs/g

$T = 273$ K

$(V_2-V_1) = 1-\frac{1}{0{\cdot}917}$

$= -\frac{0{\cdot}083}{0{\cdot}917}$

$= -0{\cdot}091$ cm³

$\therefore \quad dT = \frac{T\,dP(V_2-V_1)}{L}$

$dT = \frac{273\times99\times76\times13{\cdot}6\times980\times(-0{\cdot}091)}{336\times10^7}$

$dT = -0{\cdot}7326$ K

$= \mathbf{-0{\cdot}7326°C}$

The decrease in the melting point of ice with a pressure of 100 atmospheres

$= \mathbf{0{\cdot}7326°C}$

Example 6·24 *Calculate the pressure required to lowe melting point of ice by 1°C.*

(L = 79·6 cal/g, specific volume of water at 0°C = 1·000 cm³ specific volume of ice at 0°C = 1·091 cm³ and 1 atmosphere pressure = 1·013 × 10⁶ dynes/cm²). *(Delhi 1973)*

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$dT = -1$ K

$T = 273$ K

$V_2-V_1 = -0{\cdot}091$ cm³

$L = 79{\cdot}6$ cal/g

$= 79{\cdot}6\times4{\cdot}18\times10^7$ ergs/g

$$dP = \frac{L\cdot dT}{T(V_2-V_1)}$$

$$dP = \frac{79{\cdot}6\times4{\cdot}18\times10^7\times1}{273\times0{\cdot}091} \text{ dynes/cm}^2$$

or

$$dP = \frac{79{\cdot}6\times4{\cdot}18\times10^7}{273\times0\,091\times1\,013\times10^6} \text{ atmospheres}$$

$dP = 135{\cdot}2$ atmospheres

∴ Pressure required

$= 135{\cdot}2+1$

$= \mathbf{136{\cdot}2\ atmospheres}$

Example 6·25. *Water boils at a temperature of 101°C at a pressure of 787* mm of Hg. *1 gram of water occupies 1,601* cm³ *on evaporation. Calculate the latent heat of steam. J = 4·2 × 10⁷* ergs/cal. *[Delhi (Hons.) 1971]*

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$dP = 787-760$

$= 27$ mm of Hg

$= 2{\cdot}7$ cm of Hg

$= 2{\cdot}7\times13{\cdot}6\times980$ dynes/cm²

$dT = 1°C = 1K$

$T = 373$ K

$V_2-V_1 = 1,601-1 = 1,600$ cm³

$L = ?$

$$L = \frac{T\,dP\,(V_2-V_1)}{dT}$$

$$L = \frac{373\times2{\cdot}7\times13{\cdot}6\times980\times1,600}{1} \text{ ergs/g}$$

$$L = \frac{373\times2{\cdot}7\times13{\cdot}6\times980\times1,600}{4{\cdot}2\times10^7} \text{ cal/g}$$

$\mathbf{L = 511{\cdot}3\ cal/g}$

Example 6·26. *When lead is melted at atmospheric pressure, (the melting point is 600* K*) the density decreases from 11·01 to 10·65* g/cm³ *and the latent heat of fusion is 24·5* J/g. *What is the melting point at a pressure of 100 atmospheres ?* *[Delhi (Hons.) 1972]*

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

dP = 99 atmospheres

$dP = 99 \times 76 \times 13{\cdot}6 \times 980$ dynes/cm²

L = 24·5 J/g

= $24{\cdot}5 \times 10^7$ ergs/g

$$V_1 = \frac{1}{11{\cdot}01} \text{ cm}^3$$

$$V_2 = \frac{1}{10{\cdot}65} \text{ cm}^3$$

$$V_2 - V_1 = \frac{1}{10{\cdot}65} - \frac{1}{11{\cdot}01}$$

$$= \left(\frac{0{\cdot}36}{10{\cdot}65 \times 11{\cdot}01}\right) \text{cm}^3$$

$$dT = \frac{T\,dP\,(V_2 - V_1)}{L}$$

$$dT = \frac{600 \times 99 \times 76 \times 13{\cdot}6 \times 980 \times 0{\cdot}36}{10{\cdot}65 \times 11{\cdot}01 \times 24{\cdot}5 \times 10^7}$$

dT = **0·7539 K**

= **0·7539°C**

∴ Melting point of lead at 100 atmospheres pressure

= 600 + 0·7539

= **600·7539 K**

Example 6·28. *Calculate under what pressure water will boil at 120°C, if the change in specific volume when 1 gram of water is converted into steam is 1,676* cm³.

Latent heat of steam

= *540* cal/g

J = $4{\cdot}2 \times 10^7$ ergs/cal

1 atmosphere pressure

= 10^6 dynes/cm²

[*Delhi (Hons.) 1972*]

Here $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$

dT = 120—100

= 20 K

T = 373 K

$(V_2 - V_1)$ = 1,676 cm³

L = 540 cal/g

= $540 \times 4{\cdot}2 \times 10^7$ ergs/g

dP = ?

$$dP = \frac{L.dT}{T(V_2 - V_1)}$$

$$dP = \frac{540 \times 4{\cdot}2 \times 10^7 \times 20}{373 \times 1{,}676} \text{ dynes/cm}^2$$

$$dP = \frac{540 \times 4{\cdot}2 \times 10^7 \times 20}{373 \times 1{,}676 \times 10^6} \text{ atmospheres}$$

dP = 0·7254 atmosphere

Pressure required = 1 + 0·7254

= **1·7254 atmospheres**

6·39 Thermionic Emission

The electrical conductivity of metals is due to the free electrons present in the metal and not attached to any particular molecule. These free electrons continuously move within the metal and the velocity of the electrons increases with the increase in temperature of the metal. These electrons exert a pressure similar to that of a gas. However, the electrons cannot escape to the outer space because of the attractive forces at the surface that tend to keep the electrons within the metal. The attractive forces are much greater than the *electron gas pressure.* In order to escape from the surface, an electron has to do a certain amount of work called the work function (ϕ) of the surface and this is different for different metals. This energy is obtained from the kinetic energy of the electrons. At ordinary temperatures the kinetic energy of the electrons is much less than the work function and hence the electrons cannot escape from the surface. With the increase in temperature of the metal surface, the kinetic energy of the electrons increases and if the kinetic energy exceeds the work function, electrons can escape from the surface of the metal. This phenomenon is called *thermionic* emission and the electrons are called *thermo-electrons* or *thermions.* The thermionic current (I) is given by the equation

$$I = AT^2 e^{-\frac{\phi_0}{kT}}$$

where A is a constant, T is the absolute temperature of the metal, ϕ_0 is the work function of the surface at zero degree K and k is the Boltzmann's constant. I measures the thermionic current in amperes per sq cm of the emitting surface. The most commonly used emitters are (*i*) *tungsten* (*ii*) *thoriated tungsten and* (*iii*) *oxide coated cathodes containing barium or strontium.*

6·40 Richardson's Equation

Richardson derived the equtaion for the thermionic emission from a heated metal. He applied Clausius-Clapeyron's latent heat equation for the ejection of electrons from the surface of the metal.

Let the volume for 1 gram molecule of electrons within the metal be v_1 and outside the metal be v_2. The volume v_2 is very high as compared to v_1. The pressure of electrons under equilibrium conditions is P. The energy absorbed by N electrons di ro's number. from the metal surface $= W$. Here N is the Avogad
Applying Clapeyron's latent heat equation

$$\frac{dP}{dT} = \frac{W}{T\,(v_2 - v_1)} \qquad \ldots(i)$$

As $v_2 > > v_1$, v_1 can be neglected

$$\therefore \qquad \frac{dP}{dT} = \frac{W}{T\,v_2}$$

or
$$W = T\,v_2\,\frac{dP}{dT} \qquad \ldots(ii)$$

The energy W consists of two parts : (*i*) The work function of the surface *i.e.*, energy required for ejecting N electrons just outside the metal *i.e.*, in crossing the potential barrier. This energy $= N\phi$ where ϕ is the work function of the surface.

(*ii*) The work done in admitting the ejected electrons into the electron cloud already present outside the metal. This energy is Pv_2. For one gram molecule of electrons

$$Pv_2 = R\,T = N\,k\,T$$

Here k is Boltzmann's constant

$$W = N\,\phi + N\,k\,T \qquad \ldots(iii)$$

From equations (*ii*) and (*iii*)

$$N(\phi + kT) = T\,v_2\,\frac{dP}{dT}$$

But
$$v_2 = \frac{NkT}{P}$$

$$\therefore \qquad N(\phi + kT) = T\left(\frac{NkT}{P}\right) \times \frac{dP}{dT}$$

$$(\phi + kT) = \frac{kT^2}{P} \times \frac{dP}{dT}$$

$$\frac{dP}{P} = \left(\frac{\phi + kT}{kT^2}\right) dT$$

Integrating

$$\int \frac{dP}{P} = \int \frac{\phi}{kT^2}\,dT + \int \frac{dT}{T}$$

$$\log_e P = \int \frac{\phi}{kT^2}\,dT + \log_e T + \text{constant}$$

Let the constant be equal to $\log_e A_1$

$$\log_e P - \log_e T - \log_e A_1 = \int \frac{\phi}{kT^2}\,dT$$

$$\log_e\left(\frac{P}{A_1 T}\right) = \int \frac{\phi}{kT^2}\,dT \qquad \ldots(iv)$$

wo Richardson suggested that ϕ also depends upon T. If ϕ_0 is the
rk function at 0 K, then

$$\phi = \phi_0 + \tfrac{3}{2}kT$$

$$\therefore \qquad \int \frac{\phi}{kT^2}\,dT = \int \frac{\phi_0 + \frac{3}{2}kT}{kT^2}\,dT$$

$$= -\frac{\phi_0}{kT} + \tfrac{3}{2}\log_e T$$

$$= -\frac{\phi_0}{kT} + \log_e T^{\frac{3}{2}}$$

Substituting this value in equation (*iv*)

$$\log_e\left(\frac{P}{A_1 T}\right) = -\frac{\phi_0}{kT} + \log_e T^{\frac{3}{2}}$$

$$\log_e\left(\frac{P}{A_1 T^{\frac{3}{2}}}\right) = -\frac{\phi_0}{kT}$$

or
$$P = A_1\,T^{\frac{3}{2}}\,e^{-\frac{\phi_0}{kT}} \qquad \ldots(v)$$

If the number of electrons per unit volume $= n$ then

$$P = n\,k\,T \qquad \ldots(vi)$$

Equating (*v*) and (*vi*)

$$n\,k\,T = A_1 T^{\frac{3}{2}}\,e^{-\frac{\phi_0}{kT}}$$

$$n = \left(\frac{A_1}{k}\right) T^{\frac{3}{2}}\,e^{-\frac{\phi_0}{kT}} \qquad \ldots(vii)$$

Assuming the perfect gas laws to hold good in the case of an electron cloud, the mean energy of the electron,

$$\tfrac{1}{2}\,m_0\,v^2 = \tfrac{3}{2}\,kT$$

or
$$v = \left(\frac{3kT}{m_0}\right)^{\frac{1}{2}}$$

But Kundsen has shown that the number of electrons passing unit area in one second is,

$$n_0 = \frac{nv}{\sqrt{6\pi}}$$

$$\therefore \qquad n_0 = n \times \left(\frac{3kT}{6\pi m_0}\right)^{\frac{1}{2}}$$

$$= n\left(\frac{kT}{2\pi m_0}\right)^{\frac{1}{2}}$$

Substituting the value of n from equation (*vii*)

$$n_0 = \left[\left(\frac{A_1}{k}\right) T^{\frac{3}{2}}\,e^{-\frac{\phi_0}{kT}}\right]\left[nT^{\frac{1}{2}}\right.$$

$$n_0 = \left[\frac{nA_1}{k} \times \left(\frac{k}{2\pi m_0}\right)^{\frac{1}{2}}\right] T^2 e^{-\frac{\phi_0}{kT}}$$

Taking

$$\frac{nA_1}{k}\left(\frac{k}{2\pi m_0}\right)^{\frac{1}{2}} = A_2 = \text{constant}$$

$$n_0 = A_2 T^2 e^{-\frac{\phi_0}{kT}}$$

Taking the charge on the electron $= e$, the current density due to electron emission,

$$I = n_0 e = A_2 eT^2 e^{-\frac{\phi_0}{kT}}$$

$$I = AT^2 e^{-\frac{\phi_0}{kT}} \qquad \ldots(viii)$$

Here $A = (A_2 e) = \text{constant}$

Equation (*viii*) represents the Richardson's equation for thermionic emission.

The electron emitter can be heated directly or indirectly. In the case of direct heating, the current is passed through the filament which itself serves as the cathode. Tungsten and thoriated tungsten filaments are the commonly used directly heated electron emitters. The indirectly heated electron emitter consists of a heater wire surrounded by a metal sleeve in the form of a cylinder whose surface is coated with electron emitting materials. The most commonly used cathode is the indirectly heated cathode. In both the cases, filaments can be heated either by *DC* or *AC*.

The operating temperatures for tungsten, thoriated tungsten and oxide coated emitters are given below.

Tungsten	2200 to 3000 K
Thoriated Tungsten	1900 K
Oxide coated cathode	1000 to 1150 K

Values of the Emission Constants

Material	ϕ_0 *in eV*	*A in* A/m^2-K	*Melting point in* K
Carbon	4·7	—	—
Nickel	5·0	$2{\cdot}68 \times 10^5$	1725
Platinum	5·32	$3{\cdot}20 \times 10^5$	2047
Tantalum	4·1	$6{\cdot}02 \times 10^5$	3123
Tungsten	4·52	$6{\cdot}02 \times 10^5$	3655

6·41. Clausius Inequality

Before considering entropy, it is necessary to establish the Clausius inequality which states that

$$\oint \frac{\delta H}{T} < 0$$

This relation is between the temperatures of an arbitrary number of heat reservoirs and the amounts of heat transferred (given up or lost).

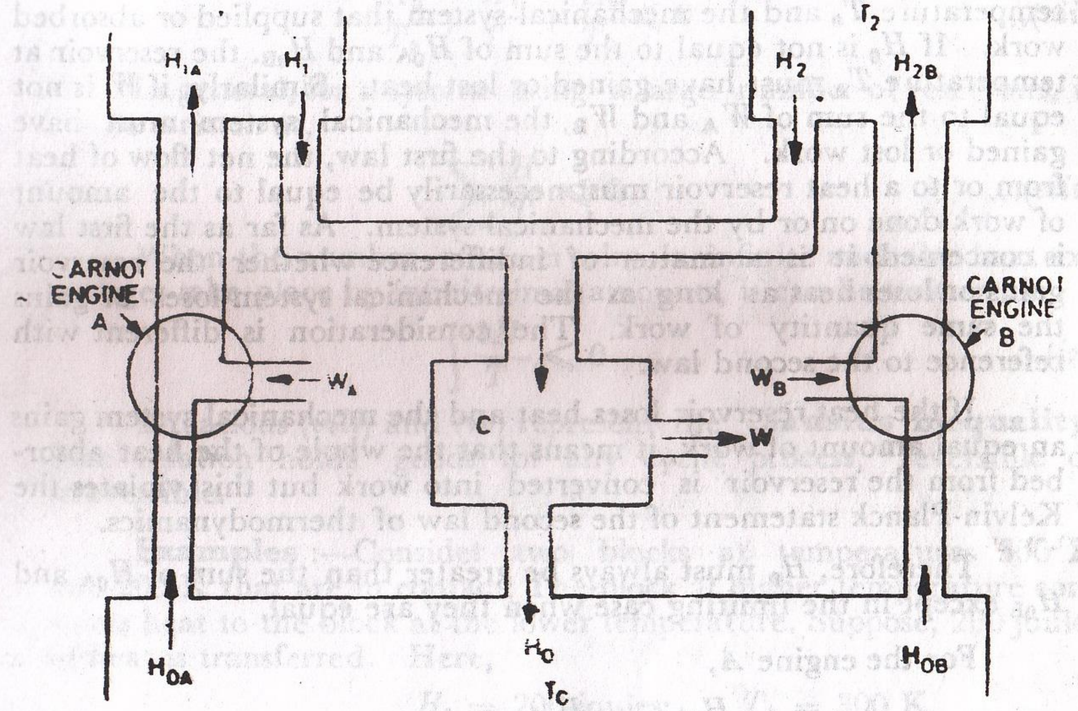


Fig. 6·24.

Consider three heat reservoirs at temperatures T_1, T_2 and T_0 (Fig. 6·24).

The engine C works as a heat engine. It absorbs heat H_1 from reservoir at temperature T_1 and H_2 from reservoir at temperature T_2. The system as a whole does an amount of work W and rejects a quantity of heat H_0 to the reservoir at temperature T_0.

Carnot's engines A and B work as refrigerators. The engine A absorbs heat H_{0A} from the reservoir at temperature T_0, an amount of work W_A is supplied to it and it rejects a quantity of heat H_{1A} to the reservoir at temperature T_1. The engine B absorbs heat H_{0B} from the reservoir at temperature T_0, an amount of work W_B is supplied to it and it rejects a quantity of heat H_{2B} to the reservoir at temperature T_2.

In the general discussion given below, no restriction on the direction of interchanges of the energy is made except that the interchanges must be consistent with the first and the second laws of thermodynamics.

The engine A working as a refrigerator rejects heat H_{1A} to the reservoir at temperature T_1.

Here, $H_{1A}+H_1 = 0$ ...(*i*)

Similarly the engine *B* working as a refrigerator rejects heat H_{2B} to the reservoir at temperature T_2.

Here $H_{2B}+H_2 = 0$ ...(*ii*)

It means that when the three engines work simultaneously, there is no outstanding change in the temperature of reservoirs at temperatures T_1 and T_2.

Thus, there has been no change except for the reservoir at temperature T_0 and the mechanical system that supplied or absorbed work. If H_0 is not equal to the sum of H_{0A} and H_{0B}, the reservoir at temperature T_0 must have gained or lost heat. Similarly, if W is not equal to the sum of W_A and W_B, the mechanical system must have gained or lost work. According to the first law, the net flow of heat from or to a heat reservoir must necessarily be equal to the amount of work done on or by the mechanical system. As far as the first law is concerned it is a matter of indifference whether the reservoir gains or loses heat as long as the mechanical system loses or gains the same quantity of work. The consideration is different with reference to the second law.

If the heat reservoir loses heat and the mechanical system gains an equal amount of work, it means that the whole of the heat absorbed from the reservoir is converted into work but this violates the Kelvin-Planck statement of the second law of thermodynamics.

Therefore, H_0 must always be greater than the sum of H_{0A} and H_{0B} except in the limiting case when they are equal.

For the engine *A*,

$$\frac{H_{1A}}{T_1} = \frac{H_{0A}}{T_0} \qquad ...(iii)$$

For the engine *B*,

$$\frac{H_{2B}}{T_2} = \frac{H_{0B}}{T_0} \qquad ...(iv)$$

Also the quantities, H_1 and H_2 are positive, H_0 is negative, H_{1A} and H_{2B} are negative, H_{0A} and H_{0B} are positive. Mathematically we write all the quantities as positive.

From equation (*iii*)

$$H_{0A} = \frac{T_0\,(H_{1A})}{T_1} = \frac{T_0\,(H_1)}{T_1} = T_0\left(\frac{H_1}{T_1}\right) \qquad ...(v)$$

Similarly, $$H_{0B} = \frac{T_0\,(H_{2B})}{T_2} = \frac{T_0\,(H_2)}{T_2} = T_0\left(\frac{H_2}{T_2}\right) \qquad ...(vi)$$

The net quantity of heat drawn from the reservoir at temperature T_0 is

$$H_0+H_{0A}+H_{0B}$$

According to the second law, this quantity should be less than or equal to zero.

i.e. $$H_0+H_{0A}+H_{0B} \leqslant 0$$

Substituting the values of H_{0A} and H_{0B}

$$H_0+T_0\left(\frac{H_1}{T_1}\right)+T_0\left(\frac{H_2}{T_2}\right) \leqslant 0$$

Dividing by T_0

$$\frac{H_0}{T_0}+\frac{H_1}{T_1}+\frac{H_2}{T_2} \leqslant 0 \qquad ...(vii)$$

In general, for a system using a large number of reservoirs, it can be written as,

$$\sum \frac{H}{T} \leqslant 0 \qquad ...(viii)$$

When the number of reservoirs is infinite and the heat exchanges take place by infinitesimal amounts, it can be written as

$$\int \frac{\delta H}{T} \leqslant 0 \qquad ...(ix)$$

Equations (*viii*) and (*ix*) represent the **Clausius inequality**. The relation holds goods for any cyclic process, reversible or irreversible.

Examples :—Consider two blocks at temperatures 300 K and 200 K that are in contact. The block at higher temperature conducts heat to the block at the lower temperature. Suppose, 200 joules of heat is transferred. Here,

$H_1 = 200$ joules; $T_1 = 300$ K

$H_2 = -200$ joules, $T_2 = 200$ K

$$\therefore \quad \sum \frac{H}{T} = \frac{H_1}{T_1}+\frac{H_2}{T_2}$$

$$= \frac{200}{300}+\frac{(-200)}{200} = -\frac{1}{3}$$

$$= -0{\cdot}33 \text{ joule/degree}$$

(2) Consider an actual heat engine working between the temperatures 500 K and 300 K.

Suppose its efficiency is 20% and it takes 1000 joules of heat from the high temperature reservoir. As the efficiency is 20%.

$$\eta = 1-\frac{H_2}{H_1}$$

$$\frac{20}{100} = 1-\frac{H_2}{100}$$

or $$H_2 = 800 \text{ joules}$$

$$\therefore \quad \sum \frac{H}{T} = \frac{H_1}{T_1}+\frac{H_2}{T_2}$$

Here $H_1 = +1000$ joules

$H_2 = -800$ joules (since heat is rejected)

$T_1 = 500$ K

$T_2 = 300$ K

$$\sum \frac{H}{T} = \frac{1000}{500} + \frac{-800}{300}$$

$$= -\frac{2}{3} \text{ joule/degree}$$

(3) Consider a Carnots reversible engine working between the temperatures 500 K and 300 K. Suppose 1000 joules of heat energy is drawn from the high temperature reservoir.

Here $$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$\frac{1000}{500} = \frac{H_2}{300}$$

$$H_2 = 600 \text{ joules}$$

or $$\sum \frac{H}{T} = \frac{H_1}{T_1} + \frac{H_2}{T_2}$$

Here $H_1 = +1000$ joules

$H_2 = -600$ joules

$T_1 = 500$ K

$T_2 = 300$ K

$$\therefore \quad \sum \frac{H}{T} = \frac{1000}{500} + \frac{(-600)}{300}$$

or $$\sum \frac{H}{T} = 0$$

This example shows $\sum \frac{H}{T} = 0$, only in the limiting case and in no case $\sum \frac{H}{T}$ is greater than zero.

6·42. Entropy and the Second Law of Thermodynamics

Consider a closed system undergoing a reversible process from state 1 to state 2 along the path A and from state 2 to state 1 along the path B (Fig. 6·25). As this is a reversible cyclic process

$$\oint \frac{\delta H}{T} = 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad \ldots(i)$$

Now consider the reversible cycle from state 1 to state 2 along the path A and from state 2 to state 1 along the path C.

For this reversible cyclic process

$$\int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} = 0 \qquad \ldots(ii)$$

From equations (i) and (ii)

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2C}^{1C} \frac{\delta H}{T} \qquad \ldots(iii)$$

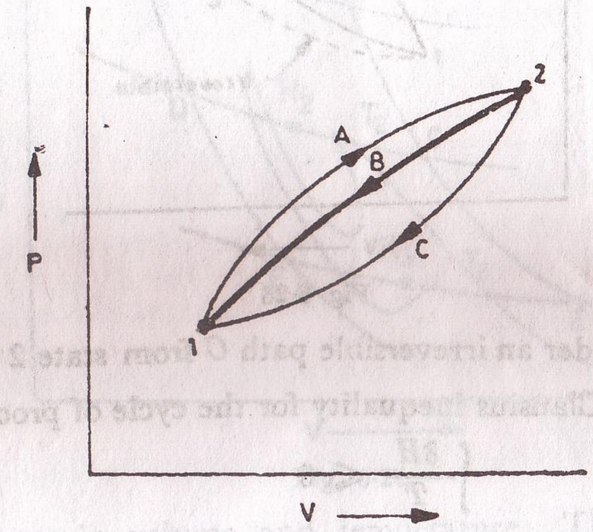


Fig. 6·25

This shows that $\int \frac{\delta H}{T}$ has the same value for all the reversible paths from state 2 to state 1. The quantity $\int \frac{\delta H}{T}$ is independent of the path and is a function of the end states only, therefore it is a property.

This property is called entropy. Entropy is a thermodynamical property and is defined by the relation

$$dS = \frac{\delta H}{T} \qquad \ldots(iv)$$

or $$S_2 - S_1 = \int_1^2 \frac{\delta H}{T} \qquad \ldots(v)$$

The quantity $S_2 - S_1$ represents the change in entropy of the system when it is changed from state 1 to state 2.

6·43 Entropy changes of a Closed System During an Irreversible Process

Consider a reversible cycle where the state is changed from 1 to 2 along the path A and 2 to 1 along the path B (Fig. 6·26).

For a reversible cyclic process

$$\oint \delta H = 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad \ldots(i)$$

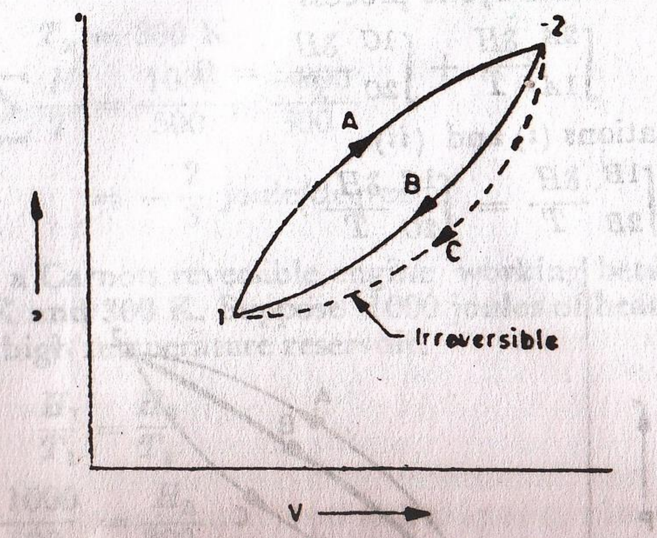


Fig. 6·26

Now consider an irreversible path C from state 2 to state 1.

Applying Clausius inequality for the cycle of processes A and C

$$\int \frac{\delta H}{T} < 0$$

$$\therefore \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} < 0 \qquad \ldots(ii)$$

From equations (i) and (ii)

$$\int_{2B}^{1B} \frac{\delta H}{T} - \int_{2C}^{1C} \frac{\delta H}{T} > 0$$

Since path B is reversible and entropy is a property

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2B}^{1B} dS = \int_{2C}^{1C} dS$$

$$\therefore \quad dS > \frac{\delta H}{T} \qquad \ldots(iii)$$

or $$S_2 - S_1 > \int_1^2 \delta H \qquad \ldots(iv)$$

To conclude,

For a reversible process

$$S_2 - S_1 = \int_1^2 \frac{\delta H}{T}$$

and for an irreversible process

$$S_2 - S_1 > \int_1^2 \frac{\delta H}{T}$$

Equation (iv) shows that the effect of irreversibility is always to increase the entropy of a system.

6.14 Entropy

Consider adiabatics L and M on the $P-V$ indicator diagram (Fig. 6·27). All along the adiabatic L, with change in pressure

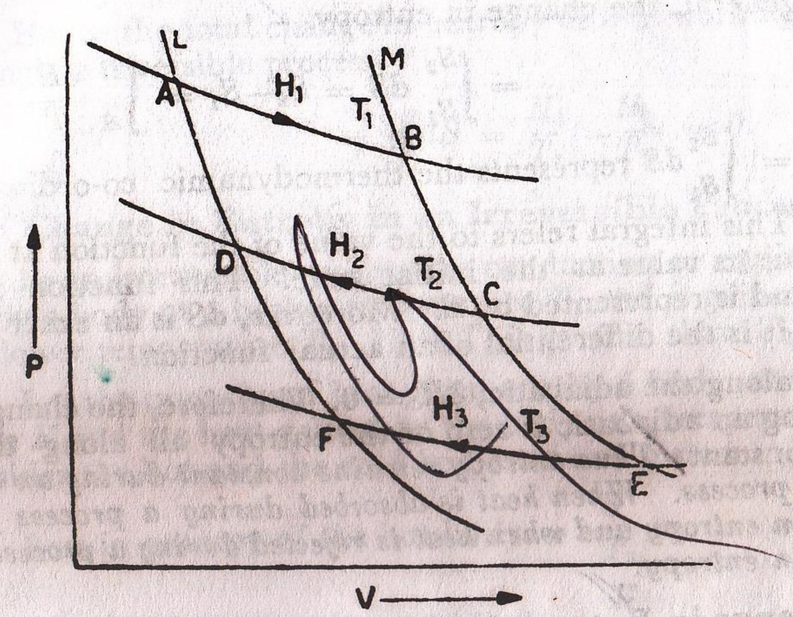


Fig. 6·27

there is change in volume and temperature. This shows that all along the adiabatics L or M, there is change of temperature. Consider the isothermals at temperatures T_1, T_2 and T_3. $ABCD$ represents the Carnot's reversible cycle. From A to B, heat energy H_1 is absorbed at temperature T_1. From C to D, heat energy H_2 is rejected at temperature T_2.

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Similarly considering the cycle $DCEF$

$$\frac{H_2}{T_2} = \frac{H_3}{T_3}$$

$$\therefore \quad \frac{H_1}{T_1} = \frac{H_2}{T_2} = \frac{H_3}{T_3} = \text{constant}$$

From one adiabatic to the other adiabatic, heat energy is either absorbed or rejected. The quantity of heat absorbed or rejected is not constant but it depends upon the temperature. Higher the temperature, more is the heat energy absorbed or rejected and *vice versa*. The quantity H/T between two adiabatics is constant and this is called the change in entropy. Let the entropy for the adiabatics L and M be S_1 and S_2 respectively.

Here S_1 and S_2 are arbitrary quantities.

$$S_2 - S_1 = \frac{H}{T} \text{ constant.}$$

If the adiabatics are very close, and the heat absorbed or rejected is δH at a temperature T,

Change in entropy

$$dS = \frac{\delta H}{T} \qquad ...(1)$$

In general, the change in entropy

$$= \int_{S_1}^{S_2} dS = S_2 - S_1 = \int_A^B \frac{\delta H}{T} \qquad ...(2)$$

$\int_A^B \frac{\delta H}{T} = \int_{S_1}^{S_2} dS$ represents the thermodynamic co-ordinate of a system. This integral refers to the value of the function at the final state minus its value at the initial state. This function is called entropy and is represented by S. Moreover, dS is an exact differential since it is the differential of an actual function.

All along the adiabatic, $\delta H = 0$. Therefore, the change in entropy along an adiabatic is zero or the entropy all along the adiabatic is constant. *Thus entropy remains constant during an adiabatic reversible process. When heat is absorbed during a process there is increase in entropy and when heat is rejected during a process there is decrease in entropy.*

6·45 Change in Entropy in a Reversible Process (Carnot's Cycle)

Consider a complete reversible process [Carnot's cycle] *ABCDA* (Fig. 6·28). From *A* to *B*, heat energy H_1 is absorbed by the working substance at temperature T_1. The gain in entropy of the working substance from *A* to *B* $= H_1/T_1$. (H_1/T_1 is the decrease in entropy of the source from which the amount of heat H_1 is drawn at a temperature T_1). From *B* to *C* there is no change in entropy because *BC* is an adiabatic. From *C* to *D*, heat energy H_2 is rejected by the working substance at a temperature T_2. The loss in entropy of the working substance from *C* to *D* $= H_2/T_2$. (H_2/T_2 is also the gain in entropy of the sink to which the amount of heat H_2 is rejected at a temperature T_2). From *D* to *A* there is no change in entropy. Thus

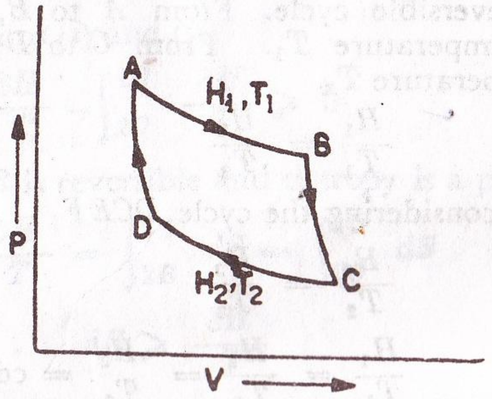


Fig. 6·28

the total gain in entropy by the working substance in the cycle *ABCDA*

$$= \frac{H_1}{T_1} + \frac{H_2}{T_2}$$

But for a complete reversible process

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Hence the total change in entropy of the working substance in a complete reversible process

$$= \oint dS = \frac{H_1}{T_1} - \frac{H_2}{T_2} = 0.$$

6·46 Change in Entropy in an Irreversible Process

In an irreversible process like conduction or radiation, heat is lost by a body at a higher temperature T_1 and is gained by the body at a lower temperature T_2. Here T_1 is greater than T_2.

Let the quantity of heat given out by a body at a temperature T_1 be H and the heat gained by the body at a temperature T_2 be H. Consider the hot and the cold bodies as one system.

Loss in entropy of the hot body $= \frac{H}{T_1}$

Gain in entropy of the cold body $= \frac{H}{T_2}$

Therefore, the total increase in entropy of the system

$$= \frac{H}{T_2} - \frac{H}{T_1}$$

It is a positive quantity because T_2 is less than T_1. Thus the entropy of the system increases in all irreversible processes.

6·47 Third Law of Thermodynamics

In all heat engines, there is always loss of heat in the form o,f conduction, radiation and friction. Therefore, in actual heat engines $\frac{H_1}{T_1}$ is not equal to $\frac{H_2}{T_2}$.

$\therefore \frac{H_1}{T_1} - \frac{H_2}{T_2}$ is not zero but it is a positive quantity. When cycle after cycle is repeated, the entropy of the system increases and tends to a maximum value. When the system has attained the maximum value, a stage of stagnancy is reached and no work can be done by the engine at this stage. In this universe the entropy is increasing and ultimately the universe will also reach a maximum value of entropy when no work will be possible. With the increase in entropy, the disorder of the molecules of a substance increases. The entropy is also a measure of the disorder of the system. With

decrease in entropy, the disorder decreases. *At absolute zero temperature, the entropy tends to zero and the molecules of a substance or a system are in perfect order (well arrenged). This is the third law of thermodynamics.*

Example. The molecules are more free to move in the gaseous state than in the liquid state. The entropy is more in the gaseous state than in the liquid state. The molecules are more free to move in the liquid state than in the solid state. The entropy is more in the liquid state than in the solid. Thus when a substance is converted from a solid to a liquid and then from the liquid to the solid state, the entropy increases and *vice versa*. When ice is converted into water and then into steam, the entropy and disorder of the molecules increase. When steam is converted into water and then into ice, the entropy and disorder of the molecules decrease. *Hence entropy is a measure of the disorder of the molecules of the system.*

By any ideal procedure, it is impossible to bring any system to absolute zero temperature performing a finite number of operations. This is called the principle of unattainability of absolute zero. Thus according to Fowler and Guggenheim, the unattainability principle is called the third law of thermodynamics.

6·48 Temperature-Entropy Diagram

The temperature-entropy diagram is used in engineering and meteorology. Consider the Carnot's cycle *ABCDA* [Fig. 6·29 (*i*)]. From *A* to *B*, heat energy H_1 is absorbed at temperature T_1. The increase in entropy S_1 takes place from *A* to *B* [Fig. 6·29 (*ii*)]. From

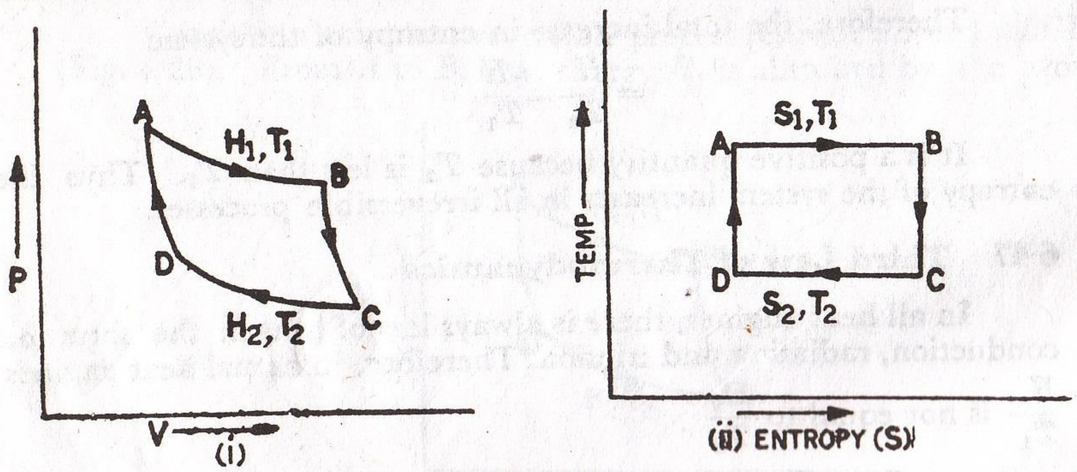


Fig. 6·29

B to *C*, there is no change in entropy. The tempetature decreases at constant entropy. From *C* to *D*, there is decrease in entropy (S_2) at constant temperature T_2. From *D* to *A*, there is no change in entropy but the temperature increases.

The area *ABCD* in the temperature-entropy diagram represents the actual amount of energy converted into work [Fig. 6·29 (*ii*)].

The area $ABCD = S_1 (T_1 - T_2) = S_2 (T_1 - T_2)$

But $S_1 = \frac{H_1}{T_1}$ and $S_2 = \frac{H_2}{T_2}$

Here $S_1 = S_2 = \frac{H_1}{T_1} = \frac{H_2}{T_2} = \frac{H_1 - H_2}{T_1 - T_2}$

$\therefore$ Area $ABCD = \frac{(H_1 - H_2)(T_1 - T_2)}{T_1 - T_2} = H_1 - H_2$

Therefore, the area *ABCD* represents the energy converted to work

Efficiency $= \frac{H_1 - H_2}{H_1} = 1 - \frac{H_2}{H_1} = 1 - \frac{T_2}{T_1}$

Here H_2 is the unavailable energy.

$$H_2 = \frac{H_1}{T_1} \times T_2 = S_1 \times T_2$$

The unavailable energy depends on the change in entropy at temperature T_1 and the temperature T_2.

6·49 Entropy of Perfect Gas

Consider one gram of a perfect gas at a pressure P, volume V and temperature T. Let the quantity of heat given to the gas be δH.

$$\delta H = dU + \delta W$$

$$\delta H = 1 \times C_v \times dT + \frac{PdV}{J} \quad \ldots(i)$$

$$\delta H = TdS$$

$$TdS = C_v dT + \frac{PdV}{J} \quad \ldots(ii)$$

$\therefore$

Also $PV = rT$

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

or

$\therefore$

$$TdS = C_v dT + \frac{rT.dV}{JV}$$

$$dS = C_v \frac{dT}{T} + \frac{r}{J}\frac{dV}{V}$$

Integrating, $\int_{S_1}^{S_2} dS = C_v \int_{T_1}^{T_2} \frac{dT}{T} + \frac{r}{J}\int_{V_1}^{V_2} \frac{dV}{V}$

$$S_2 - S_1 = C_v \log_e \frac{T_2}{T_1} + \frac{r}{J} \log_e \frac{V_2}{V_1} \quad \ldots(iii)$$

$$S_2 - S_1 = C_v \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1} + \frac{r}{J} \times 2{\cdot}3026 \log_{10} \frac{V_2}{V_1} \quad \ldots(iv)$$

The change in entropy can be calculated in terms of pressure also.

$$PV = rT$$

Differentiating

$$PdV + VdP = rdT$$

$$PdV = rdT - VdP$$

or

Substituting the value of PdV in equation (ii)

$$T\,dS = C_V \times dT + \frac{r\,dT}{J} - \frac{V\,dP}{J}$$

$$TdS = \left(C_V + \frac{r}{J}\right) dT - \frac{V\,dP}{J}$$

But $$C_V + \frac{r}{J} = C_P$$

$$\therefore \quad dS = C_P \frac{dT}{T} - \frac{V\,dP}{JT}$$

Also $$PV = rT$$

$$\frac{V}{T} = \frac{r}{P}$$

or

$$\therefore \quad dS = C_P \frac{dT}{T} - \frac{r}{J}\,\frac{dP}{P}$$

Integrating

$$\int_{S_1}^{S_2} dS = C_P \int_{T_1}^{T_2} \frac{dT}{T} - \frac{r}{J} \int_{P_1}^{P_2} \frac{dP}{P}$$

$$S_2 - S_1 = C_P \log_e \frac{T_2}{T_1} - \frac{r}{J} \log_e \frac{P_2}{P_1} \quad \ldots(v)$$

$$S_2 - S_1 = C_P \times 2{\cdot}3026 \times \log_{10} \frac{T_2}{T_1} - \frac{r}{J} \times 2{\cdot}3026 \log_{10} \frac{P_2}{P_1} \quad \ldots(vi)$$

Note. r is the ordinary gas constant and has to be taken in units of work, C_P represents the specific heat for 1 gram of a gas at constant pressure.

If C_P represents gram molecular specific heat of a gas at constant pressure and R the universal gas constant, then

$$S_2 - S_1 = C_P \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1} - \frac{R}{J} \times 2{\cdot}3026 \log_{10} \frac{P_2}{P_1} \quad \ldots(vii)$$

Example 6.29. *Calculate the change in entropy when 10 grams of ice at 0°C is converted into water at the same temperature.* (*Punjab 1963, Delhi 1975*)

Heat absorbed by 10 g of ice at 0°C when it is converted into water at 0°C $= 10 \times 80 = 800$ cal

$$\therefore \quad \delta H = 800 \text{ cal}$$

$$T = 0°C = 273 \text{ K}$$

The gain in entropy

$$dS = \frac{\delta H}{T}$$

$$= \frac{800}{273} = 2{\cdot}93 \text{ cal/K}$$

Example 6.30. *Calculate the change in entropy when 5 kg of water at 100°C is converted into steam at the same temperature.*

Heat absorbed by 5 kg of water at 100°C when it is converted into steam at 100°C

$$= 5000 \times 540$$

$$= 2700000 \text{ cal}$$

$$\therefore \quad \delta H = 2700000 \text{ cal}$$

The gain in entropy

$$dS = \frac{\delta H}{T}$$

$$= \frac{2700000}{373} = 7240 \text{ cal/K}$$

Example 6.31. *Calculate the increase in entropy when 1 gram of ice at −10°C is converted into steam at 100°C. Specific heat of ice = 0·5, latent heat of ice = 80 cal/g, latent heat of steam = 540 cal/g.* (*Bombay 1974; Delhi 1973*)

(1) Increase in entropy when the temperature of 1 gram of ice increases from −10°C to 0°C

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= ms \log_e \frac{T_2}{T_1}$$

$$= ms \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 0{\cdot}5 \times 2{\cdot}3026 \log_{10} \frac{273}{263},$$

$$= 0{\cdot}01865 \text{ cal/K}$$

(2) Increase in entropy when 1 gram of ice at 0°C is converted into water at 0°C.

$$dS = \frac{\delta H}{T}$$

$$= \frac{80}{273} = 0{\cdot}293 \text{ cal/K}$$

(3) Increase in entropy when the temperature of 1 g of water is raised from 0°C to 100°C.

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 1 \times 2{\cdot}3026 \log_{10} \frac{373}{273}$$

$$= 0{\cdot}312 \text{ cal/K}$$

(4) Increase in entropy when 1 g water at 100°C is converted into steam at 100°C

$$dS = \frac{\delta H}{T}$$

$$= \frac{540}{373} = 1{\cdot}447 \text{ cal/K}$$

Total increase in entropy

$$= 0{\cdot}01865 + 0{\cdot}293 + 0{\cdot}312 + 1{\cdot}447$$

$$= \mathbf{2{\cdot}07065 \text{ cal/K}}$$

Example 6·32. *One gram molecule of a gas expands isothermally to four times its volume. Calculate the change in its entropy in terms of the gas constant.*

Work done $= \int_{V_1}^{V_2} P dV$

But $PV = RT$

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

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

$$= RT \log_e \frac{V_2}{V_1}$$

Here $\frac{V_2}{V_1} = 4$

$$W = RT \times 2{\cdot}3026 \log_{10} (4)$$

Here, W and R are in the units of work

Gain in entropy $= \frac{\delta H}{T}$

$$= \frac{W}{JT} = \frac{RT \times 2{\cdot}3026 \log_{10} 4}{JT}$$

$$= \mathbf{1{\cdot}387 \frac{R}{J} \text{ cal/K}}$$

Example 6·33. *50 grams of water at 0°C is mixed with an equal mass of water at 83°C. Calculate the resultant increase in entropy.* (*Punjab 1963*)

(*i*) $m_1 = 50$ g ; $T_1 = 273$ K

$m_2 = 50$ g ; $T_2 = 353$ K

Let the final temperature of the mixture be T K

$$m_1 s \times (T - T_1) = m_2 s (T_2 - T)$$

$$50 \times 1 \times (T - 273) = 50 \times 1 \times (353 - T)$$

$$T = 313 \text{ K}$$

(*ii*) Change in entropy by 50 g of water when its temperature rises from 273 K to 313 K.

$$dS = \int_{T_1}^{T} \frac{\delta H}{T}$$

$$= ms \int_{T_1}^{T} \frac{dT}{T}$$

$$= 50 \times 1 \times \log_e \frac{313}{273}$$

$$= 50 \times 2{\cdot}3026 \times \log_{10} \frac{313}{273}$$

$$= +6{\cdot}829 \text{ cal/K}$$

Here, the +ve sign indicates gain in entropy.

(*iii*) Change in entropy by 50 g of water when its temperature falls from 353 K to 313 K

$$dS = \int_{T_2}^{T_1} \frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$

$$= 50 \times 1 \times \log_e \frac{313}{353}$$

$$= 50 \times 2{\cdot}3026 \times \log_{10} \frac{313}{353}$$

$$= -6{\cdot}023 \text{ cal/K}$$

Here, the —ve sign indicates loss in entropy.

Therefore, the total gain in entropy of the system

$$= 6{\cdot}829 - 6{\cdot}023$$

$$= \mathbf{0{\cdot}806 \text{ cal/K}}$$

Example 6·34. *Calculate the change in entropy when 50 grams of water at 15°C is mixed with 80 grams of water at 40°C. Specific heat of water may be assumed to be equal to 1.* (*Rajasthan 1961*)

(*i*) $m_1 = 50$ g

$T_1 = 15 + 273 = 288$ K

$m_2 = 10$ grams

$T_2 = 40 + 273 = 313$ K

Let the final temperature be T K.

$$m_1 \times s \times (T - T_1) = m_2 \times s \times (T_2 - T)$$
$$50 \times 1 \times (T - 288) = 80 \times 1 \times (313 - T)$$
$$T = 303{\cdot}4 \text{ K}$$

(*ii*) Change in entropy when the temperature of 50 g of water rises from 288 K to 303·4 K

$$= \frac{\delta H}{T} = ms \int_{T_1}^{T} \frac{dT}{T}$$
$$= 50 \times 1 \times 2{\cdot}3026 \times \log_{10} \frac{303{\cdot}4}{288}$$
$$= +2{\cdot}602 \text{ cal/K.}$$

(*iii*) Change in entropy when the temperature of 80 g of water decreases from 313 K to 303·4 K

$$= \frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$
$$= 80 \times 1 \times 2{\cdot}3026 \times \log_{10} \frac{303{\cdot}4}{313}$$
$$= -2{\cdot}487 \text{ cal/K}$$

Therefore, the net change in the entropy of the system

$$= +2{\cdot}602 - 2{\cdot}487$$
$$= +0{\cdot}115 \text{ cal/K}$$

Hence the net increase in the entropy of the system

$$= \mathbf{0{\cdot}115 \text{ cal/K}}$$

Example 6·35. *10 g of steam at 100°C is blown into 90 grams of water at 0°C, contained in a calorimeter of water equivalent 10 grams. The whole of the steam is condensed. Calculate the increase in the entropy of the system.* [*Delhi (Hons.) 1973*]

(*i*)
$$m_1 = 10 \text{ g}$$
$$T_1 = 100°\text{C} = 373 \text{ K}$$
$$m_2 = 90 + 10 = 100 \text{ g}$$
$$T_2 = 273 \text{ K}$$

Let the final temperature be T K

$$10 \times 540 + 10(373 - T) = 100(T - 273)$$
$$T = 331{\cdot}2 \text{ K}$$

(*ii*) Change in entropy when the temperature of water and calorimeter rises from 273 K to 331·2 K

$$= \frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$
$$= 100 \int_{273}^{331{\cdot}2} \frac{dT}{T}$$

$$= 100 \times 2{\cdot}3026 \times \log_{10} \left(\frac{331{\cdot}2}{273} \right)$$
$$= +19{\cdot}32 \text{ cal/K}$$

(*iii*) Change in entropy when 10 grams of steam at 373 K is condensed to water at 373 K

$$= \left(\frac{\delta H}{T} \right) = -\frac{10 \times 540}{373}$$
$$= -14{\cdot}47 \text{ cal/K}$$

(—ve sign indicates decrease in entropy).

(*iv*) Change in entropy when 10 grams of water at 373 K is cooled to water at 331·2 K

$$\frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$
$$= 10 \times 2{\cdot}3026 \log_{10} \left(\frac{331{\cdot}2}{373} \right)$$
$$= -1{\cdot}188 \text{ cals/K}$$

Net change in entropy

$$= 19{\cdot}32 - 14{\cdot}47 - 1{\cdot}188$$
$$= \mathbf{+3{\cdot}662 \text{ cal/K}}$$

Hence the net increase in the entropy of the system

$$= \mathbf{3{\cdot}662 \text{ cal/K}}$$

Example 6·36. *1 g of water at 20°C is converted into ice at −10°C at constant pressure. Heat capacity for 1 g of water is 4·2 J/g-K and that of ice is 2·1 J/g-K. Heat of fusion of ice at 0°C = 335 J/g. Calculate the total change in the entropy of the system.*

(*i*) Change in entropy when the temperature of 1 g of water at 293 K falls to 273 K.

$$dS = \frac{\delta H}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T}$$
$$= 1 \times 4{\cdot}2 \int_{293}^{273} \frac{dT}{T}$$
$$= 4{\cdot}2 \times 2{\cdot}3026 \log_{10} \left(\frac{273}{293} \right)$$
$$= -0{\cdot}2969 \text{ J/K}$$

(*ii*) Change in entropy when 1 g of water at 273 K is converted into ice at 273 K

$$dS = \frac{\delta H}{T} = \frac{-1 \times 335}{273} = -1{\cdot}227 \text{ J/K}$$

(iii) Change in entropy when the temperature of 1 g of ice at 273 K falls to 263 K

$$dS = \frac{\delta H}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= 1 \times 2{\cdot}1 \times 2{\cdot}3026 \log_{10}\left(\frac{263}{273}\right)$$

$$= -0{\cdot}07834 \text{ J/K}$$

Total change in entropy of the system

$$= -0{\cdot}2969 - 1{\cdot}227 - 0{\cdot}07834$$

$$= \mathbf{-1{\cdot}60224 \text{ J/K}}$$

Negative sign shows that there is decrease in entropy of the system.

Example 6·37. *1 kg of water at 273 K is brought in contact with a heat reservoir at 373 K (1) what is the change in entropy of water when its temperature reaches 373 K ?*

(2) What is the change in entropy of (i) the reservoir and (ii) the universe.

(1) Increase in entropy when the temperature of 1000 g of water is raised from 273 K to 373 K

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1000 \times 1 \times 2{\cdot}3026 \log_{10} \frac{373}{273}$$

$$= \mathbf{312 \text{ cal/K}}$$

(2) (i) Change in entropy of the reservoir,

$$dS = \frac{-\delta H}{T}$$

$$= -\frac{1000 \times 1 \times 100}{373} = \mathbf{-268{\cdot}1 \text{ cal/K}}$$

Negative sign shows decrease in entropy

(2) (ii) Change in entropy of the universe

$$= 312 - 268{\cdot}1$$

$$= \mathbf{43{\cdot}9 \text{ cal/K}}$$

Therefore, the net increase in entropy of the universe

$$= \mathbf{43{\cdot}9 \text{ cal/K}}$$

6·50 Zero Point Energy

According to Kinetic theory, the energy of a system at absolute zero should be zero. It means the molecules of the system do not possess any motion. But according to the modern concept, even at absolute zero, the molecules are not completely deprived of their motion and hence possess energy. The energy of the molecules at absolute zero temperature is called **zero point energy.**

6·51 Negative Temperatures

The specific heat of a substance decreases with increase in temperature. However, the specific heat does not tend to zero as the temperature tends to infinity. This shows that the temperature has a +ve sign only.

But recent experiments by Ramsey (1956) have shown that a part of a system *i.e.*, the nucleus of a solid, can have a negative temperature. This sub-system is considered isolated from the main system (*i.e.*, solid lattice). The specific heat of the sub-system tends to zero at high temperature. A small amount of heat energy tends to raise the temperature of the system to infinity. It is possible to add still more energy to the sub-system at infinity and it forces the sub-system into the negative temperature region. It has been shown by microscopic statistical analysis that there is no distinction between the temperature of $+\infty$ and $-\infty$. In thermodynamics, the parameter $1/T$ is more significant than T.

The *negative* temperatures are hotter than the positive temperatures and minus zero (−0) is the hottest temperature and plus zero (+0) is the coldest temperature.

The negative temperature is not possible with the system as a whole and is only an exception to the rule that only positive temperatures exist. The negative temperatures are possible only for isolable sub-systems. For all normal purposes the temperatures are always positive.

6·52 Maxwell's Thermodynamical Relations

From the two laws of thermodynamics, Maxwell was able to derive six fundamental thermodynamical relations. The state of a system can be specified by any pair of quantities *viz.* pressure (P), volume (V), temperature (T) and entropy (S). In solving any thermodynamical problem, the most suitable pair is chosen and the quantities constituting the pair are taken as independent variables.

From the first law of thermodynamics

$$\delta H = dU + \delta W$$

$$\delta H = dU + PdV$$

or $$\delta U = \delta H - PdV$$

From the second law of thermodynamics,

$$dS = \frac{\delta H}{T}$$

or $$\delta H = TdS$$

Substituting this value of δH in the first equation

$$dU = TdS - PdV \qquad \ldots(i)$$

Considering S, U and V to be functions of two independent variables x and y [here x and y can be any two variables out of P, V, T and S],

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values in equation (i)

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right] - P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y\right] dx + \left[T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x\right] dy$$

Comparing the coefficients of dx and dy, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \qquad \ldots(ii)$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \qquad \ldots(iii)$$

Differentiating equation (ii) with respect to y and equation (iii) with respect to x

$$\frac{\partial^2 U}{\partial y \cdot \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y\,\partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \partial x}$$

and

$$\frac{\partial^2 U}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \partial y}$$

The change in internal energy brought about by changing V and T whether V is changed by dV first and T by dT later or *vice versa* is the same.

It means dU is a perfect differential

$$\therefore \quad \frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial x \partial y} \text{ and}$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \partial x}$$
$$= \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \partial y}$$

Simplifying,

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \qquad \ldots(iv)$$

Here x and y can be any two variables out of P, V, T and S.

Derivation of Relations

(1) Taking T and V as independent variables and

$$x = T$$

and

$$y = V$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(v)$$

But

$$dS = \frac{\partial H}{T}$$

$$\therefore \quad \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(vi)$$

(2) Taking T and P as independent variables and

$$x = T$$

and

$$y = P$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} =$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(vii)$$

or $$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(viii)$$

(3) Taking S and V as independent variables and

$$x = S$$

and $$y = V$$

$$\frac{\partial S}{\partial x} = 1, \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots(ix)$$

or $$\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial H}\right)_V \quad \ldots(x)$$

(4) Taking S and P as independent variables and

$$x = S$$

and $$y = P$$

$$\frac{\partial S}{\partial x} = 1, \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial S}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \ldots(xi)$$

or $$\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial H}\right)_P \quad \ldots(xii)$$

(5) Taking P and V as independent variables and

$$x = P \quad \text{and} \quad y = V$$

$$\frac{\partial P}{\partial x} = 1, \frac{\partial V}{\partial y} = 1, \frac{\partial P}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1 \quad \ldots(xiii)$$

(6) Taking T and S as independent variables and

$$x = T \quad \text{and} \quad y = S$$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial S}{\partial y} = 1, \frac{\partial T}{\partial y} = 0, \frac{\partial S}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \quad \ldots(xiv)$$

These are the important thermodynamical relations. While solving a particular problem, the suitable equation is used.

6·53 Helmholtz Function

Helmholtz function F, is the property of a system and is given by the equation

$$F = U - TS \quad \ldots(i)$$

In practice, the primary function of heat engines and other devices is to perform mechanical work. From the first law of thermodynamics, for a system working between two equilibrium states,

$$\delta H = dU + \delta W \quad \ldots(ii)$$

or $$\delta W = \delta H - dU \quad \ldots(iii)$$

It means that the energy converted into work is provided partly by the heat reservoir with which the system is in contact and which gives up a quantity of heat δH and partly by the system whose internal energy decreases by $(-dU)$.

When a system undergoes a process between two equilibrium states, how much maximum work can be done by it ? This can be derived by assuming that the system exchanges heat energy only with a single heat reservoir at a temperature T_0.

From the principle of increase of entropy, it is known that the sum of the increase in entropy of the system and that of the surroundings is equal to or greater than zero. Suppose,

Increase in entropy of the system $= dS$

Increase in entropy of the surroundings (reservoir) $= dS_0$

Heat absorbed by the system from the reservoir $= \delta H$

Temperature of the reservoir $= T_0$

$$\therefore \quad dS + dS_0 \geqslant 0 \quad \ldots(iv)$$

For a reservoir, $dS_0 = \dfrac{-\delta H}{T_0}$ [Since reservoir has given heat]

$$\therefore \quad dS - \frac{\delta H}{T_0} \geqslant 0$$

or $$T_0 . dS \geqslant \delta H \quad \ldots(v)$$

From equations (*iii*) and (*v*)

$$\delta W \leqslant T_0 . dS - dU \quad \ldots(vi)$$

The quantities U and S are the properties of the system and T_0 is a constant. Therefore, for a finite process between state 1 to state 2, by integrating equation (*vi*),

$$W \leqslant T_0 (S_2-S_1)-(U_2-U_1) \quad ...(vii)$$

$$W \leqslant (U_1-U_2)-T_0(S_1-S_2) \quad ...(viii)$$

Suppose that the initial and the final temperatures are equal and are the same as that of the heat reservoir.

$$\therefore \quad T = T_0$$

Here T is the temperature of the system.

Equation (*viii*) can be written as,

$$\therefore \quad W_T \leqslant (U_1-U_2)_T - T(S_1-S_2)_T \quad ...(ix)$$

The Helmholtz function,

$$F = U-TS$$

Therefore for two equilibrium states 1 and 2 at the same temperature T,

$$(F_1-F_2) = (U_1-TS_1)-(U_2-TS_2)$$

$$= (U_1-U_2)-T(S_1-S_2)$$

or $$(F_1-F_2)_T = (U_1-U_2)_T-T(S_1-S_2)_T \quad ...(x)$$

From (*ix*) and (*x*)

$$W_T \leqslant (F_1-F_2)_T \quad ...(xi)$$

Thus the maximum work that can be done in any process between two equilibrium states at the same temperature is equal to the decrease in the Helmholtz function of the system. Here the system exchanges heat with a single heat reservoir at the same temperature. Moreover maximum work is done when the process is reversible. If the process is irreversible, the work done is less than the maximum.

It is to be remembered that the maximum work that can be done is equal to the decrease in the Helmholtz function of a system but the energy converted into work is provided partly by the system and the remaining by the heat taken from the heat reservoir.

6·54 Thermodynamic Potential or Gibbs Function

The Gibbs function G of a system is given by,

$$G = U-TS+PV$$

Consider a system that can do other forms of work, in addition to $P.dV$ work, *e.g.*, a voltatic cell. In the case of a voltaic cell, the electrical work is $-E.dI$. Similarly for a magnetic material, the magnetic work is $-m.dH$. In general, the work will be given by $P.dV$ plus a sum of terms each being the product of intensive variable (such as P, E or m) and the differential of an extensive variable (such as dV, dI and dH). In the case of a voltaic cell, the intensive variable is E and differential of extensive variable is dI.

Suppose, in general, in addition to PdV the intensive variable is y and differential of extensive variable is dx. The work done for any reversible process,

$$\delta W = PdV+ydx$$

$$W = \int_{V_1}^{V_2} PdV + \int_{x_1}^{x_2} ydx$$

Take $$\int_{x_1}^{x_2} ydx = A$$

Consider a process where the system works at constant pressure P_0 and the change in volume is (V_2-V_1)

$$\therefore \quad \int_{V_1}^{V_2} PdV = P_0[V_2-V_1]$$

$$\therefore \quad W = P_0[V_2-V_1]+A \quad ...(i)$$

For a system that exchanges heat with a reservoir temperature

$$W \leqslant (U_1-U_2)-T_0(S_1-S_2) \quad ...(ii)$$

$$P_0[V_2-V_1]+A \leqslant (U_1-U_2)-T_0(S_1-S_2)$$

or $$A \leqslant (U_1-U_2)-T_0(S_1-S_2)+P_0[V_1-V_2] \quad ...(iii)$$

Consider a specific process, where the initial and the final states of the system and the surroundings are at the same temperature (T_0) and pressure (P_0)

$$T_0 = T \quad \text{and} \quad P_0 = P$$

From equation (*iii*)

$$A_{P,T} \leqslant (U_1-U_2)_{P,T}-T(S_1-S_2)_{P,T}+P[V_1-V_2]_{P,T} \quad ...(iv)$$

But, for the Gibbs function,

$$G = U-TS+PV \quad ...(v)$$

Therefore, for two equilibrium states at the same pressure and temperature,

$$[G_1-G_2]_{P,T} = (U_1-U_2)_{P,T}-T[S_1-S_2]_{P,T}+P[V_1-V_2]_{P,T} \quad ...(vi)$$

From equations (*iv*) and (*vi*)

$$A_{P,T} \leqslant (G_1-G_2)_{P,T} \quad ...(vii)$$

Thus the difference between Gribbs function of a system between two equilibrium states sets the maximum limit to the work in addition to PdV work, provided the initial and the final states are at the same pressure and temperature and the system exchanges heat with a single heat reservoir. The work done will be maximum when the process is reversible. The process in this case will be isothermal —isobaric. If the process is irreversible, work done will be less than the maximum.

6·55 Enthalpy

Enthalpy in an extensive thermodynamic property and is given the symbol h. Enthalpy is given by the equation

$$h = U + PV \qquad \ldots(i)$$

Enthalpy is defined as the sum of the internal energy and the product of pressure and volume.

To study the properties of this function, assume that the system undergoes an infinitesimal process from an initial equilibrium state to a final equilibrium state.

From equation (i)

$$dh = dU + PdV + VdP \qquad \ldots(ii)$$

Also

$$\delta H = dU + PdV \qquad \ldots(iii)$$

$$\therefore \quad dh = \delta H + VdP \qquad \ldots(iv)$$

Dividing by dT

$$\frac{dh}{dT} = \frac{\delta H}{dT} + V\frac{dP}{dT} \qquad \ldots(v)$$

At constant pressure (isobaric process),

$$\left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\delta H}{dT}\right)_P$$

But $$\left(\frac{\delta H}{dT}\right)_P = C_P$$

$$\therefore \quad \left(\frac{\partial h}{\partial T}\right)_P = C_P \qquad \ldots(vi)$$

From equation (iv), during isobaric process, $dP = 0$

$$\therefore \quad dh = \delta H$$

or $$h_f - h_i = H \qquad \ldots(vii)$$

Therefore change in enthalpy during an isobaric process is equal to the amount of heat transferred during the process.

In a throttling process, applying first law of thermodynamics

$$H = U_f - U_i + W$$

Here $H = 0$

and $W = P_fV_f - P_iV_i$

$$\therefore \quad 0 = U_f - U_i + P_fV_f - P_iV_i$$

or $$U_i + P_iV_i = U_f + P_fV_f$$

or $$h_i = h_f \qquad \ldots(viii)$$

Therefore in a throttling process, there in no change in enthalpy of the system. The initial and the final enthalpies are equal.

6·56 C_P, C_V and μ

The specific heat at constant pressure C_P, the specific heat at constant volume C_V and the Joule-Kelvin coefficient μ are defined as follows :

$$C_P = \left(\frac{\partial h}{\partial T}\right)_P \qquad \ldots(i)$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \ldots(ii)$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \qquad \ldots(iii)$$

These three quantities are defined in terms of the thermodynamic properties *viz.* pressure, volume, temperature, internal energy and enthalpy. Hence, C_P, C_V and μ are also thermodynamic properties of a substance.

6·57 Maxwell's Equations (Alternative Method)

The properties of pure substances can conveniently be represented in terms of the four functions : internal energy, enthalpy, Helmholtz function and Gibb's function.

Internal energy $= U$

Enthalpy, $h = U + PV$

Helmholtz function $F = U - TS$

Gibb's function $G = h - TS$

or $G = U - TS + PV$

All the above four quantities can be regarded as functions of P, V, T, and S

Now, consider a system undergoing an infinitesimal reversible process from one equilibrium state to another.

(1) The internal energy changes by an amount

$$dU = \delta H - PdV$$

or $$dU = TdS - PdV \qquad \ldots(i)$$

Here U, T and P are supposed to be functions of S and V

(2) The enthalpy changes by an amount

$$dh = dU + PdV + VdP$$

$$dh = (TdS - PdV) + PdV + VdP$$

$$dh = TdS + VdP \qquad \ldots(ii)$$

Here h, T and V are supposed to be functions of S and P

(3) The Helmholtz function changes by an amount

$$dF = dU - TdS - SdT$$

or $$dF = (TdS - PdV) - TdS - SdT$$

or $$dF = -SdT - PdV \quad \ldots(iii)$$

Here F, S and P are supposed to be functions of T and V.

(4) The Gibbs function changes by an amount

$$dG = dh - TdS - SdT$$

$$dG = (TdS + VdP) - TdS - SdT$$

$$dG = -SdT + VdP \quad \ldots(iv)$$

Here G, S and V are supposed to be functions of T and P.

As U, h, F and G are actual functions, their differentials are exact.

For exact differentials

$$dZ = Mdx + Ndy \quad \ldots(v)$$

Here Z, M and N are all functions of x and y

$$\therefore \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \ldots(vi)$$

To derive the Maxwell's equations, equation (vi) can be applied.

(1) From equation (i)

$$dU = TdS - PdV$$

Here $M = T, N = P, x = S, y = V$

From equation (vi)

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots(vii)$$

(2) From equation (ii)

$$dh = TdS + VdP$$

Here $M = T, N = V, x = S, y = P$

From equation (vi)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \ldots(viii)$$

(3) From equation (iii)

$$dF = -SdT - PdV$$

Here $M = S, N = P, x = T, y = V$

From equation (vi)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \ldots(ix)$$

(4) From equation (iv)

$$dG = -SdT + VdP$$

Here $M = S, N = V, x = T, y = P$

From equation (vi)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(x)$$

Note. The equations for dU, dh, dF and dG can be obtained by remembering the sentence, 'Good Physicists have Studied Under Very Fine Teachers'. In this sentence, the letters, G, P, h, S, U, V, F, and T are to be used.

The diagram to be used is shown in Fig. 6·30.

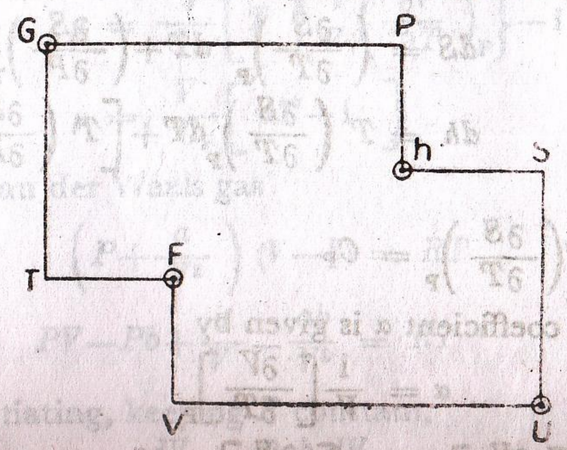


Fig. 6·30

To obtain the expression for dU, note the quantities on the two sides of U, *viz.* they are S and V S is on the +ve direction of y-axis and V is on the —ve direction of x-axis.

$$\therefore dU = +(\quad)\,dS - (\quad)\,dV$$

The quantity associated with dS is T and with dV is P.

$$\therefore dU = TdS - PdV \quad \ldots(i)$$

Similarly for dh

$$dh = (\quad)dS + (\quad)dP$$

$$dh = TdS + VdP \quad \ldots(ii)$$

For dF

$$dF = -(\quad)dT - (\quad)dV$$

$$dF = -SdT - PdV \quad \ldots(iii)$$

For dG

$$dG = -(\quad)dT + (\quad)dP$$

$$dG = -SdT + VdP \quad \ldots(iv)$$

6·58 Joule Kelvin Coefficient

The Joule-Kelvin effect was discussed in the chapter "Nature of heat".

The Joule-Kelvin coefficient is defined as the slope of the isenthalpic curve at any point on the temperature pressure curve.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \quad \ldots(i)$$

From the definition of enthalpy

$$h = U + PV \quad \ldots(ii)$$

or $$dh = dU + PdV + PdV \quad \ldots(iii)$$

Also $$dU = TdS - PdV$$

$$\therefore \quad dU + PdV = TdS$$

$$\therefore \quad dh = TdS + VdP \quad \ldots(iv)$$

Also $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dh = T\left(\frac{\partial S}{\partial T}\right)_P dT + \left[T\left(\frac{\partial S}{\partial P}\right)_T + V\right] dP \quad \ldots(v)$$

But $$T\left(\frac{\partial S}{\partial T}\right)_P = C_P \quad \ldots(vi)$$

The volume coefficient α is given by

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P$$

But $$\left[\frac{\partial V}{\partial T}\right]_P = -\left[\frac{\partial S}{\partial P}\right]_T = \alpha V$$

$$\therefore \quad \left[\frac{\partial S}{\partial P}\right]_T = -\alpha V \quad \ldots(vii)$$

Substituting these values in equation (v),

$$dh = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \quad \ldots(viii)$$

$$dT = \frac{1}{C_P} dh + \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP \quad \ldots(ix)$$

But $$dT = \left(\frac{\partial T}{\partial h}\right)_P dh + \left(\frac{\partial T}{\partial P}\right)_h dP \quad \ldots(x)$$

Comparing the coefficients of equations (ix) and (x),

$$\left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

But $$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

$$\therefore \quad \mu = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

$$\mu C_P = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \quad \ldots(xi)$$

$$\mu C_P = T^2 \frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P \quad \ldots(xii)$$

From equation $(viii)$,

$$\left(\frac{\partial h}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(xiii)$$

From equations (xi) and $(xiii)$

$$\mu C_P = -\left(\frac{\partial h}{\partial P}\right)_T \quad \ldots(xiv)$$

The Joule-Kelvin coefficient,

$$\mu = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \quad \ldots(xv)$$

$$\mu = \frac{V}{C_P}\left[T\left\{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right\} - 1\right] \quad \ldots(xvi)$$

or $$\mu = \frac{V}{C_P}\left[\alpha T - 1\right] \quad \ldots(xvii)$$

For a Van der Waals gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Differentiating, keeping P constant,

$$PdV - \frac{adV}{V^2} + \frac{2ab\,dV}{V^3} = RdT$$

or $$\frac{dV}{dT} = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\frac{RT}{V-b} - \frac{a}{V^2} - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2} \quad \ldots(xviii)$$

Substituting this value in equation (xvi)

$$\mu = \frac{V}{C_P}\left[\frac{RTV^2(V-b)}{RTV^3 - 2a(V-b)^2} - 1\right]$$

$$= \frac{V}{C_P}\left[\frac{RTV^2(V-b) - RTV^3 + 2a(V-b)^2}{RTV^3 - 2a(V-b)^2}\right]$$

$$= \frac{V}{C_P}\left[\frac{2a(V-b)^2 - RTV^2b}{RTV^3 - 2a(V-b)^2}\right] \quad \ldots(xix)$$

From equation $(xvii)$, as V and C_P are always positive, the value of μ and hence the temperature of a Van der Waals gas passing through a porous plug will depend on the value of $\alpha T - 1$.

(1) If $\alpha T > 1$, the temperature of the gas will increase.

(2) If $\alpha T < 1$, the temperature of the gas will decrease.

(3) If $\alpha T = 1$, the temperature will not change.

This temperature at which the inversion takes place is called the temperature of inversion T_i. In this case, from equation $(xvii)$

$\mu = 0$ and from equation (xix)

$$2a(V-b)^2 = RT_iV^2b$$

$$\therefore \quad T_i = \frac{2a(V-b)^2}{RV^2b} \quad \ldots(xx)$$

If $V >> b$

$$T_i = \frac{2a}{Rb} \qquad \ldots(xxi)$$

Ideal Gas. From equation (xii)

$$\mu C_P = T^2\left[\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P\right]$$

$$\therefore \quad \mu = \frac{T^2}{C_P}\left[\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P\right]$$

For an ideal gas $\frac{V}{T} = \frac{R}{P}$

$$\therefore \quad \mu = \frac{T^2}{C_P} \cdot \frac{\partial}{\partial T}\left[\frac{R}{P}\right]_P = 0$$

Thus the Joule-Kelvin coefficient for an ideal gas is zero and the ideal gas passing through the porous gas does not show any change in temperature.

6·59 Equilibrium Between Liquid and its Vapour

Applying Gibbs potential (G), it is possible to investigate the equilibrium between a liquid and its vapour or between any two phases of a substance. Consider a closed system containing a liquid in equilibrium with its saturated vapour. The temperature and pressure are equal in both the phases. As each of the phases is in equilibrium, the temperature and pressure must remain constant throughout the phase and hence the thermodynamical coordinates V, S, U and G will be equal to the product of the specific value and the mass of the substance in that phase.

Suppose m_1 and m_2 are the masses in the liquid and vapour phases and g_1 and g_2 are the specific values of the Gibbs potential in the two phases. Then, for the whole system

$$G = m_1g_1+m_2g_2 \qquad \ldots(i)$$

If a small quantity of liquid changes into vapour, differentiating equation (i)

$$\delta G = \delta m_1\, g_1+\delta m_2\, g_2 \qquad \ldots(ii)$$

As the change takes place at constant temperature and pressure, the process is isothermal and isobaric

$$\therefore \quad \delta G = 0$$

From equation (ii)

$$\delta m_1\, g_1+\delta m_2\, g_2 = 0$$

But $$\delta m_1 = -\delta m_2$$

$$\therefore \quad g_1 = g_2 \qquad \ldots(iii)$$

This shows that the thermodynamical potential per unit mass will be equal in the two phases. Equation (iii) is applicable to the processes of evaporation, fusion and sublimation.

6·60 First order Phase Transitions

Consider an enclosure containing a liquid and its saturated vapour in equilibrium. If this system undergoes an isothermal, isobaric change, then

$$g_1 = g_2 \qquad \ldots(i)$$

Let the temperature of the system be increased from T to $T+dT$. For equilibrium

$$g_1+dg_1 = g_2+dg_2 \qquad \ldots(ii)$$

or $$dg_1 = dg_2 \qquad \ldots(iii)$$

If the condition of saturation is satisfied,

$$\left(\frac{dg_1}{dT}\right)_{sat.} = \left(\frac{dg_2}{dT}\right)_{sat.} \qquad \ldots(iv)$$

The pressure also changes from P to $P+dP$,

$$\therefore \quad dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT+\left(\frac{\partial g_1}{\partial P}\right)_T dP \qquad \ldots(v)$$

or $$\left(\frac{\partial g_1}{\partial T}\right) = \left(\frac{\partial g_1}{\partial T}\right)_P+\left(\frac{\partial g_1}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right) \qquad \ldots(vi)$$

But, for a unit mass,

$$dg = VdP-SdT \qquad \ldots(vii)$$

$$\therefore \quad \left(\frac{\partial g}{dP}\right)_T = V$$

and $$\left(\frac{\partial g}{\partial T}\right)_P = -S$$

Substituting these values in equation (vi)

$$\left(\frac{\partial g_1}{\partial T}\right)_{sat.} = -S_1+V_1\left(\frac{\partial P}{\partial T}\right)_{sat.}$$

Similarly,

$$\left(\frac{\partial g_2}{\partial T}\right)_{sat.} = -S_2+V_2\left(\frac{\partial P}{\partial T}\right)_{sat.}$$

Substituting these values is equation (iv)

$$-S_1+V_1\left(\frac{dP}{dT}\right) = -S_2+V_2\left(\frac{dP}{dT}\right)$$

or $$\left(\frac{dP}{dT}\right)_{sat.} = \left(\frac{S_2-S_1}{V_2-V_1}\right) \qquad \ldots(viii)$$

But $$S_2-S_1 = \frac{\delta H}{T} = \frac{L}{T}$$

Here L is latent heat of vaporization

$$\therefore \quad \left(\frac{dP}{dT}\right) = \frac{L}{T(V_2-V_1)} \qquad \ldots(ix)$$

This is Clausius-Clapeyron latent heat equation.

This equation holds good in the first order phase transitions. In these processes there is transference of heat and hence there is

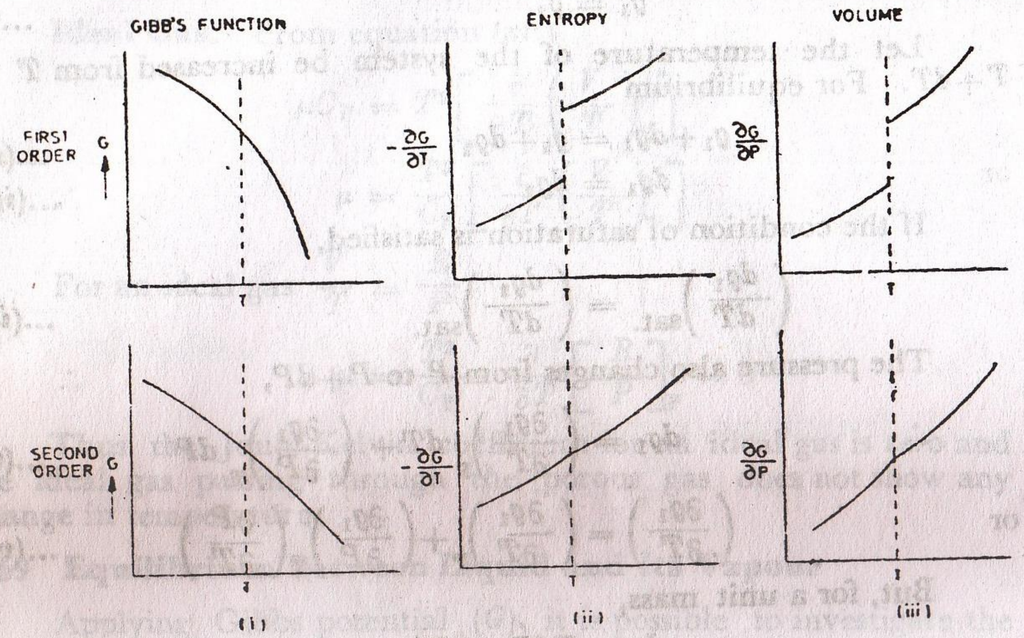


Fig. 6·31

change in entropy and volume. Therefore a first order phase transition can be defined as that one in which the Gibbs function with respect to pressure and temperature change discontinuously at the transition point. However, the value of the Gibbs function is the same in both the phases at equilibrium. These changes are represented graphically in Fig. 6·31.

6·61 Second Order Phase Transitions

Some recent investigations have revealed that during phase change there is no transference of heat and there is no change of volume. It has been found in the case of transition from liquid helium I to liquid helium II, that there is no transfer of heat and no change in volume. Such transitions are called second order phase transitions. Second order phase transitions can be defined as the phenomenon that takes place with no change in entropy and volume at constant temperature and pressure. The examples of second order phase transitions are :

(1) Transition of liquid helium I to liquid helium II.

(2) Transition of a ferromagnetic material to a paramagnetic material at the Curie point.

(3) Transition of a superconducting metal into an ordinary conductor in the absence of a magnetic field.

(4) Order-disorder transitions in chemical compounds and alloys.

In the case of second-order phase transitions there is no discontinuity of $\left(\frac{\partial G}{\partial T}\right)_P$ and $\left(\frac{\partial G}{\partial P}\right)_T$ [Fig. 6·31]. However, the second order derivatives change discontinuously.

For a phase transition,

$$g_1 = g_2$$

or $$g_2 - g_1 = 0 \qquad \ldots(i)$$

$$-\left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial T}\right)_P = S_2 - S_1 = 0 \qquad \ldots(ii)$$

$$\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T = V_2 - V_1 = 0 \qquad \ldots(iii)$$

Also

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\left(\frac{C_P}{T}\right) = \left(\frac{\partial S}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[-\left(\frac{\partial g}{\partial T}\right)_P\right]_P = -\left(\frac{\partial^2 g}{\partial T^2}\right)_P \qquad \ldots(iv)$$

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$KV = -\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_T$$

or $$KV = -\left(\frac{\partial^2 g}{\partial P^2}\right)_T \qquad \ldots(v)$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha V = \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_P$$

or $$\alpha V = \left(\frac{\partial^2 g}{\partial T \partial P}\right) \qquad \ldots(vi)$$

Here K is the isothermal compressibility and α is the volume coefficient of expansion.

From equation (iv)

$$\frac{C_{P1}}{T} = -\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P \qquad \ldots(vii)$$

and $$\frac{C_{P2}}{T} = -\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P \qquad \ldots(viii)$$

Subtracting $(viii)$ from (vii)

$$\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P = \frac{C_{P1} - C_{P2}}{T} \qquad \ldots(ix)$$

Similarly from equations (v) and (vi)

$$\left(\frac{\partial^2 g_2}{\partial P^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial P^2}\right)_T = V(K_1 - K_2) \qquad \ldots(x)$$

and $$\left(\frac{\partial^2 g_2}{\partial T.\partial P}\right)-\left(\frac{\partial^2 g_2}{\partial T.\partial P}\right) = V(\alpha_2-\alpha_1) \quad \ldots(xi)$$

For second order phase transitions, there is no change in entropy and volume.

$\therefore$ $S_1 = S_2$ (at constant temperature T and pressure P)

$\therefore$ $S_1+dS_1 = S_2+dS_2$ (at temp. $T+dT$ and pressure $P+dP$)

$\therefore$ $$dS_1 = dS_2 \quad \ldots(xii)$$

But $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT+\left(\frac{\partial S}{\partial P}\right)_T dP$$

or $$dS = \left(\frac{C_P}{T}\right)dT-\left(\frac{dV}{dT}\right)_P dP$$

$$dS = \left(\frac{C_P}{T}\right)dT-V\alpha\, dP$$

$\therefore$ $$dS_1 = \left(\frac{C_{P1}}{T}\right)dT-V\alpha_1\, dP$$

and $$dS_2 = \left(\frac{C_{P2}}{T}\right)dT-V\,\alpha_2\, dP$$

$\therefore$ $$\left(\frac{C_{P1}}{T}\right)dT-V\alpha_1\, dP = \left(\frac{C_{P2}}{T}\right)dT-V\alpha_2 dP$$

$\therefore$ $$\frac{dP}{dT} = \frac{C_{P2}-C_{P1}}{TV(\alpha_2-\alpha_1)} \quad \ldots(xiii)$$

Similarly by assuming $V_1 = V_2$ for second order phase transition,

$V_1 = V_2$ (at temp. T and pressure P)

$V_1+dV_1 = V_2+dV_2$ (at temp. $T+dT$ and pressure $P+dP$)

$\therefore$ $$dV_1 = dV_2$$

But $$dV = \left(\frac{\partial V}{\partial T}\right)_P dT+\left(\frac{\partial V}{\partial P}\right)_T dP$$

$$dV = V\,\alpha dT-VKdP$$

$\therefore$ $$dV_1 = V\alpha_1 dT-VK_1 dP$$

and $$dV_2 = V\alpha_2 dT-VK_2 dP$$

$\therefore$ $$V\alpha_1 dT-VK_1 dP = V\alpha_2 dT-VK_2 dP$$

$\therefore$ $$\frac{dP}{dT} = \left(\frac{\alpha_2-\alpha_1}{K_2-K_1}\right) \quad \ldots(xiii)$$

Equations (xii) and $(xiii)$ are called **Ehrenfest's Equations.**

Table

Maxwell's Thermodynamical Relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \ldots(i)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(ii)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots(iii)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \ldots(iv)$$

Note. The first four Maxwell's thermodynamical relations need not be memorised. These can be easily written by remembering the word *SP* or $T_f\, V_e$ (sportive). In this *SPTV* represent entropy, pressure, temperature and volume. In derving the first two relations, ∂S is written in the numerator on the left hand side of the equation and the rest of the quantities ∂P, ∂T and ∂V are written (i) in the clockwise order and (ii) in the anticlockwise order. In the clockwise direction, the right hand side expression is with a + sign and for the anticlockwise direction, it is −ve. These equations are

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \ldots(i)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(ii)$$

Similarly to write the other equations, ∂S is written in the denominator of the right hand side of the equation and the other quantities are written (i) in the anticlockwise direction and (ii) in the clockwise direction. These equations are

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \ldots(iii)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \ldots(iv)$$

6·62 The T dS Equations

(1) The entropy S of a pure substance can be taken as a function of temperature and volume.

$\therefore$ $$dS = \left(\frac{\partial S}{\partial T}\right)_V dT+\left(\frac{\partial S}{\partial V}\right)_T dV \quad \ldots(i)$$

Multiplying both sides by T

$$T.dS = T\left(\frac{\partial S}{\partial T}\right)_V dV+T\left(\frac{\partial S}{\partial V}\right)_T dV \quad \ldots(ii)$$

$\therefore$ But $$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

and from Maxwell's relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Substituting these values in equation (*ii*)

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \ldots(iii)$$

Equation (*iii*) is called the first $T\,dS$ equation.

(2) The entropy S of a pure substance can also be regarded as a function of temperature and pressure

$$\therefore \qquad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad \ldots(iv)$$

Multiplying both sides by T

$$T\,.\,dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \qquad \ldots(v)$$

But $$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

and from Maxwell's relations

$$\left(\frac{dS}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Substituting these values in equation (*v*)

$$T\,dS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \ldots(vi)$$

Equation (*vi*) is called the second $T\,dS$ equation.

Example 6·38. *Deduce Clapeyron's latent heat equation from Maxwell's thermodynamical relations.*

From Article 6·52, equation (*vi*)

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(i)$$

Here $\left(\frac{\partial H}{\partial V}\right)_T$ represents the quantity of heat absorbed per unit increase in volume at constant temperature. This quantity of heat absorbed at constant temperature is the latent heat. If ∂H is the latent heat (L), when a unit mass of the substance changes in volume for V_1 to V_2 at constant temperature, then

$$\partial H = L \quad \text{and} \quad \partial V = V_2 - V_1$$

Substituting these values in equation (*i*)

$$\therefore \qquad \left(\frac{L}{V_2 - V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

or $$\frac{L}{V_2 - V_1} = T\frac{dP}{dT}$$

or $$\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)} \qquad \ldots(ii)$$

This is Clapeyron's latent heat equation.

Example 6·39. *Show that for a homogeneous fluid*

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Also show that for a perfect gas $C_P - C_V = R$ *and for a gas obeying Van der Waals equation*

$$C_P - C_V = R\left(1 + \frac{2a}{RTV}\right)$$

Here,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

and $$C_V = \left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Considering S as a function of temperature and volume

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right) + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

But from equation (*v*) [§6·52], $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \qquad C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(i)$$

For a Perfect Gas

$$PV = RT$$

$$\therefore \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

But, $$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = T\left(\frac{R}{V}\right)\left(\frac{R}{P}\right)$$

$$C_P - C_V = \frac{TR^2}{PV} = \frac{R^2T}{RT} = R$$

Hence $C_P - C_V = R$ ...(ii)

[R is in heat units]

For a gas obeying Van der Waals equation

$$\left(P+\frac{a}{V^2}\right)\left(V-b\right) = RT$$

$$\left(P+\frac{a}{V^2}\right) = \frac{RT}{(V-b)}$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

and $$\left(\frac{-2a}{V^3}+\frac{RT}{(V-b)^2}\right)\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b}$$

But $$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \frac{T\left(\frac{R}{V-b}\right)\left(\frac{R}{V-b}\right)}{\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]}$$

$$C_P - C_V = \frac{RT\,(V-b)^2}{RT\,(V-b)^2}\left[\frac{R}{1-\frac{2a\,(V-b)}{V^3\,RT}}\right]$$

Neglecting b as compared to V,

$$C_P - C_V = \frac{R}{\left(1-\frac{2a}{VRT}\right)}$$

Since a is also small as compared to V

$$C_P - C_V = R\left(1+\frac{2a}{VRT}\right) \qquad ...(iii)$$

[R is in heat units.]

Example 6·40. *Derive the specific heat relation or show that*

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

and $$C_P - C_V = -TE\alpha^2V$$

where T is the absolute temperature, E the bulk modulus of elasticity, α the coefficient of volume expansion and V the specific volume,

$$C_P = \left(\frac{\partial H}{\partial T}\right) = T\left(\frac{\partial S}{\partial T}\right)_P$$

and $$C_V = \left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Considering S as a function of temperature and volume,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial T}\right) + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

But from equation (v) of article 6·52,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \quad T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(i)$$

Taking the general equation of state for a gas as

$$P = f(V, T)$$

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

At constant pressure,

$$dP = 0$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

Substituting this value in equation (i)

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P^2 \qquad ...(ii)$$

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T \qquad ...(iii)$$

But $$E = V\left(\frac{\partial P}{\partial V}\right)_T$$

and $$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P$$

Substituting these values in equation (ii)

$$C_P - C_V = -TE\alpha^2V \qquad ...(iv)$$

Example 6·41. *Show that*

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$

where C_1 and C_2 represent the specific heat of a liquid and its saturated vapour and L is the latent heat of the vapour.

For a change of state from liquid to vapour,

$$S_2 - S_1 = \frac{L}{T} \qquad ...(i)$$

Here S_1 and S_2 are the entropies in the liquid and vapour states respectively.

Differentiating equation (i) with respect to T

$$\frac{dS_2}{dT} - \frac{dS_1}{dT} = -L.\frac{1}{T^2} + \frac{1}{T} \cdot \frac{dL}{dT}$$

$$T\left(\frac{dS_2}{dT}\right) - T\left(\frac{dS_1}{dT}\right) = -\frac{L}{T} + \frac{dL}{dT}$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T} \qquad ...(ii)$$

This equation is known an Clausius latent heat equation.

Example 6·42. *Calculate under what pressure water would boil at 150°C if the change in specific volume when 1 gram of water is converted into steam is 1676* cc. *Given latent heat of vaporization of steam = 540* cal *per gram ; $J = 4{\cdot}2 \times 10^7$* ergs/cal *and one atmosphere pressure = 10^6* dynes/cm^2.

Here
$$\delta H = 540 \text{ cal} = 540 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$
$$\partial V = 1676 \text{ cc}$$
$$T = 373 \text{ K, and } 150°\text{C} = 423 \text{ K}$$
$$\partial T = 423 - 373 = 50 \text{ K}$$
$$\partial P = ?$$

Applying these values in the Maxwell's thermodynamical relation

$$\left(\frac{\delta H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{540 \times 4{\cdot}2 \times 10^7}{1676} = 373\left(\frac{\partial P}{50}\right)$$

$$\partial P = \frac{540 \times 4{\cdot}2 \times 10^7 \times 50}{373 \times 1676}$$
$$= 1{\cdot}814 \times 10^6 \text{ dynes/cm}^2$$
$$= 1{\cdot}814 \text{ atmospheres}$$

Therefore, the pressure at which water would boil at 150°C
$$= 1{\cdot}814 + 1{\cdot}000$$
$$= \mathbf{2{\cdot}814 \text{ atmospheres}}$$

Example 6·43. *Calculate under what pressure ice would freeze at −1°C, if the change in specific volume when 1 gram of water freezes into ice is 0·091* cc.

Given latent heat of fusion of ice = 80 cal/g, *$J = 4{\cdot}2 \times 10^7$* ergs/cal *and one atmosphere pressure = 10^6* dynes/cm^2.

Here,
$$\delta H = 80 \text{ cal} = 80 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$
$$\partial V = 0{\cdot}091 \text{ cc}$$
$$T = 273 \text{ K}$$
$$\partial T = 273 - 272 = 1 \text{ K}$$
$$\partial P = ?$$

Applying these values in the Maxwell's thermodynamical relation,

$$\left(\frac{\delta H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{80 \times 4{\cdot}2 \times 10^7}{0{\cdot}091} = \frac{273 \times \partial P}{1}$$

$$\partial P = 135{\cdot}2 \times 10^6 \text{ dynes/cm}^2$$
$$= 135{\cdot}2 \text{ atmospheres}$$

Therefore, the pressure under which ice would freeze = atmospheric pressure + $\partial P = 1 + 135{\cdot}2 =$ **136·2 atmospheres.**

Example 6·44. *Calculate the specific heat of saturated steam given that the specific heat of water at 100°C = 1·01 and latent heat of vaporization decreases with rise in temperature at the rate of 0·64* cal/K. *Latent heat of vaporization of steam = 540* cal.

$$C_1 = 1{\cdot}01 \qquad C_2 = ? \qquad T = 373 \text{ K}$$

$$\frac{dL}{dT} = -0{\cdot}64 \text{ cal/K}$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$

$$C_2 = C_1 + \frac{dL}{dT} - \frac{L}{T}$$

$$= 1{\cdot}01 + (-0{\cdot}64) - \frac{540}{373}$$

$$= \mathbf{-1{\cdot}077 \text{ cal/g}}$$

It shows that the specific heat of saturated steam is negative.

Example 6·45. *Calculate the specific heat of saturated steam at 100°C from the following data :*

L at 90°C = 545·25 cal
L at 100°C = 539·30 cal
L at 110°C = 533·17 cal
Specific heat of water at 100°C = 1·013 cal/g

[Delhi 1975]

Here
$$\frac{dL}{dT} = \frac{533{\cdot}17 - 545{\cdot}25}{20}$$
$$= \frac{-12{\cdot}08}{20} = -0{\cdot}604 \text{ cal/K}$$
$$L = 539{\cdot}3 \text{ cal}$$
$$T = 373 \text{ K}$$

$$C_1 = 1{\cdot}013$$

$$C_2 = ?$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$

$$C_2 = C_1 + \frac{dL}{dT} - \frac{L}{T}$$

$$C_2 = 1{\cdot}013 - 0{\cdot}604 - \frac{539{\cdot}3}{373}$$

$$C_2 = -1{\cdot}036 \text{ cal/g}$$

Example 6·46. *Using Maxwell's thermodynamical relations, prove that for any substance, the ratio of the adiabatic and isothermal elasticities is equal to the ratio of the two specific heats.*

From definition,

Isothermal elasticity $E_T = -V\left(\frac{\partial P}{\partial V}\right)_T$

Adiabatic elasticity $E_S = -V\left(\frac{\partial P}{\partial V}\right)_S$

$$\therefore \quad \frac{E_S}{E_T} = \frac{-V\left(\frac{\partial P}{\partial V}\right)_S}{-V\left(\frac{\partial P}{\partial V}\right)_T}$$

$$= \frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T}$$

$$= \frac{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial V}\right)_T}$$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial S}{\partial V}\right)_T} \quad \ldots(i)$$

But from the first four Maxwell's equations

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$\therefore$ Substituting these values in equation (i)

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial S}{\partial V}\right)_P \left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_V \left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V}$$

$$= \frac{\left(\frac{\partial H}{\partial T}\right)_P}{\left(\frac{\partial H}{\partial T}\right)_V}$$

But $\left(\frac{\partial H}{\partial T}\right)_P = C_P$

and $\left(\frac{\partial H}{\partial T}\right)_V = C_V$

$$\therefore \quad \frac{E_S}{E_T} = \frac{C_P}{C_V} = \gamma \quad \ldots(ii)$$

Example 6·47. *Using Maxwell's thermodynamical relations, prove that the ratio of the adiabatic to the isobaric coefficient of expansion is*

$$\frac{1}{(1-\gamma)}$$

Adiabatic volume coefficient of expansion,

$$\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S \quad \ldots(i)$$

Isobaric volume coefficient of expansion,

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \ldots(ii)$$

$$\therefore \quad \frac{\alpha_S}{\alpha_P} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} \quad \ldots(iii)$$

$$= \frac{\left(\frac{\partial V}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial T}\right)_P}$$

But $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\therefore \quad \frac{\alpha_S}{\alpha_P} = -\frac{1}{\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

$$= \frac{1}{-\left[\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial V}{\partial T}\right)_P\right]}$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_V}{-\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

$$= \frac{T\left(\frac{\partial S}{\partial T}\right)_V}{-T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

But $$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

and $$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\therefore \quad \frac{\alpha_S}{\alpha_P} = \frac{C_V}{-(C_P - C_V)}$$

or $$\frac{\alpha_S}{\alpha_P} = \frac{1}{1-\left(\frac{C_P}{C_V}\right)}$$

or $$\frac{\alpha_S}{\alpha_P} = \frac{1}{1-\gamma} \qquad \ldots(iv)$$

Example 6·48. *Using Maxwell's thermodynamical relations, prove that the ratio of the adiabatic to the isochoric pressure coefficient of expansion is equal to*

$$\frac{\gamma}{(\gamma-1)}$$

Adiabatic pressure coefficient of expansion,

$$\beta_S = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S \qquad \ldots(i)$$

Isochoric pressure coefficient of expansion.

$$\beta_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(ii)$$

$$\therefore \quad \frac{\beta_S}{\beta_V} = \frac{\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S}{\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V} \qquad \ldots(iii)$$

$$= \frac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{1}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial T}\right)_V}$$

But $$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \ldots(iv)$$

$$\frac{\beta_S}{\beta_V} = \frac{1}{\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_V} \qquad \ldots(v)$$

$$= \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{C_P}{C_P - C_V}$$

or $$\frac{\beta_S}{\beta_V} = \frac{\left(\frac{C_P}{C_V}\right)}{\left(\frac{C_P}{C_V} - 1\right)} = \frac{\gamma}{\gamma-1} \qquad \ldots(vi)$$

Example 6·49. *Using Maxwell's thermodynamical relations, show that*

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial V . \partial T}\right) = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

From Maxwell's relations,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(i)$$

Differentiating equation (i) with respect to temperature,

$$\left(\frac{\partial^2 S}{\partial T . \partial V}\right) = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad \ldots(ii)$$

But $$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \ldots(iii)$$

Differentiating equation (*iii*) with respect to volume,

$$\left(\frac{\partial C_v}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial T.\partial V}\right) \qquad ...(iv)$$

From equations (*ii*) and (*iv*)

$$\left(\frac{\partial C_v}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial T.\partial V}\right) = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad ...(v)$$

Example 6·50. *Using Maxwell's thermodynamical relations, show that*

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial P \partial T}\right) = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

From Maxwell's relations,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(i)$$

Differentiating equation (*i*) with respect to temperature

$$\left(\frac{\partial^2 S}{\partial T.\partial P}\right) = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad ...(ii)$$

But $$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad ...(iii)$$

Differentiating equation (*iii*) with respect to pressure,

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial T \partial P}\right) \qquad ...(iv)$$

From equations (*ii*) and (*iv*)

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial T \partial P}\right) = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad ...(v)$$

Example 6·51. *Show that for a perfect gas*

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

From the Maxwell's first equation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{1}{T}\left(\frac{\delta H}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

or $$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

But $$\delta H = dU + PdV$$

$$\therefore \left(\frac{dU+PdV}{dV}\right) = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{dU}{dV} + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

or $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

But from perfect gas equation,

$$PV = RT$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{R}{V}\right) - P$$

or $$\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0$$

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Exercises VI

1. Deduce the adiabatic equation for an ideal gas and give Clement and Desormes' method for determining γ. (*Agra 1960 ; Delhi 1972, 73*)

2. State the Second Law of thermodynamics. Describe Carnot's cycle and deduce the efficiency of an ideal heat engine. (*Agra 1960, 61, 62*)

3. Explain what you understand by thermodynamic scale of temperature. Show that it agrees with an ideal gas scale. What is zero on this scale ? (*Agra 1962*)

4. Derive Clapeyron's latent heat equation.

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$ (*Delhi 1974; Agra 1972*)

5. State and prove Carnot's theorem. (*Agra 1963*)

6. Define Entropy. What is its physical significance ? Show that the entropy of a perfect gas remains constant in a reversible process but increases in an irreversible process. (*Agra 1963 ; Delhi 1971, 73*)

7. Prove that

$$\frac{dL}{dT} - \frac{L}{T} = C_2 - C_1$$

What is the physical significance of negative specific heat ? (*Agra 1963*)

8. Prove that PV^γ = constant in an adiabatic transformation. (*Madras 1974 ; Agra 1972 ; Delhi 1976*)

9. What do you understand by the absolute scale of temperature ? Show that the zero and the size of the degree on this scale and the gas scale are coincident. Is a negative temperature possible on this scale ?

10. Prove the thermodynamic relation

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$$

Hence show that the increase of pressure heats a body that expands with rise of temperature and cools the one that contracts on heating. (*Agra 1964*)

11. Describe with diagrams the working of an Otto engine and deduce an expression for its efficiency.

12. Prove the thermodynamical relation

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

and hence show that

$$L = T(V_2 - V_1)\left(\frac{dP}{dT}\right). \qquad (Agra\ 1965)$$

13. State the two laws of thermodynamics and explain their significance. Derive an expression for the efficiency of a Carnot's engine. (*Delhi 1976, Agra 1966*)

14. Define Kelvin's absolute or thermodynamic scale of temperature. Show how this scale agrees with that of a perfect gas scale. Is a negative temperature possible on this scale ? (*Agra 1966*)

15. Derive the relation between volume and pressure of a gas undergoing adiabatic changes. (*Rajasthan 1960*)

16. Derive an expression for the efficiency of an ideal heat engine, working between the temperatures T_1 and T_2K. Prove that the efficiency of a reversible engine is maximum for the given source and sink. (*Rajasthan 1961 ; Delhi 1972*)

17. Discuss the Second Law of Thermodynamics and the principle of increase of entropy. (*Rajasthan 1964*)

18. Fxplain fully what you understand by entropy. Show that the change in entropy of a substance in a cyclic process is zero. (*Panjab 1964*)

19. Deduce Clapeyron's equation. How does it explain the effect of pressure on (*i*) the melting point of solids and (*ii*) the boiling point of liquids. (*Berhampur 1972 ; Panjab 1963 ; Delhi [Hons.] 1971*)

20. What is a reversible thermodynamic process ? Describe a reversible heat engine and find an expression for its efficiency. (*Lucknow 1963*)

21. State Carnot's theorem. Show how Kelvin used this theorem to define a new scale of temperature which is independent of the nature of the working substance. Compare this temperature scale with the perfect gas scale. (*Berhampur 1972 ; Lucknow 1962, 64*)

22. Describe the absolute scale of temperature. Why is it adopted as the standard scale ? What is the meaning of absolute zero on the scale ? (*Delhi 1961 [Sub] 1966*)

23. Explain the concept of entropy. Deduce the expression for the entropy of a monoatomic gas. (*Delhi 1966*)

24. Derive an expression for the efficiency of a Carnot's engine in terms of the temperatures of the source and the sink. Show how an absolute scale of temperature can be defined with the help of the ideal Carnot's engine. (*Punjab 1966*)

25. Deduce Clausius-Clapeyron's equation. (*Delhi 1967*)

26. Deduce the Clapeyron's latent heat equation from Maxwell's thermodynamical relations.

27. Deduce Maxwell's thermodynamical relations. (*Delhi [Hons.] 1971*)

28. Show that (*Delhi [Hons.] 1976*)

(*i*) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(*ii*) $\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

(*iii*) $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$

(*iv*) $\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial S}\right)_V$

(*v*) $\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial H}\right)_P$

(*vi*) $\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_V\left(\frac{\partial S}{\partial P}\right)_V = 1$

and (*vii*) $\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T\left(\frac{\partial V}{\partial T}\right)_S = 1$

29. Show that for a homogeneous fluid

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_V$$

30. Show from the consideration of Maxwell's thermodynamical relations that

(*i*) for a perfect gas

$$C_P - C_V = R$$

and (*ii*) for a gas obeying Van der Waals equation

$$C_P - C_V = R\left(1 + \frac{2a}{RTV}\right).$$

31. Derive the specific heat relation

$$C_P - C_V = -TE\alpha^2 V$$ [*Delhi (Hons) 1971*]

32. What do you understand by the internal energy of a system. State the first law of thermodynamics and use it to derive a relation between the volume and temperature of a perfect gas undergoing an adiabatic change of state. (*Delhi 1969*)

33. Deduce Clausius-Clapeyron's equation and discuss the effect of change of pressure on the melting and boiling points of a substance. (*Delhi 1968, 71, 76*)

34. Deduce the Clausius-Clapeyron's equation for the change of equilibrium pressure of two phases with temperature. (*Delhi 1969, 1972*)

35. Describe Partington's method for the determination of the ratio of the two specific heats of a gas. (*Delhi 1971*)

36. What are isothermal and adiabatic changes ? Derive the equation PV^γ = constant, for an ideal gas. (*Delhi 1971*)

37. What is meant by a reversible process ? Describe Carnot's cycle and show that all reversible engines working between the same two temperatures have the same efficiency.
[*Madras 1974 ; Delhi 1971*]

38. Calculate the work done in a Carnot's cycle of operations. Deduce the efficiency of a Carnot's engine in terms of the temperatures between which it works. (*Delhi 1973*)

39. Define entropy. State and prove the principle of increase of entropy.

40. Define work scale of temperature. Show that the ideal gas scale and the work scale are identical. [*Delhi 1971*]

41. Show that

$$\int_A^B \frac{\delta Q}{T}$$ is independent of the path for a reversible change. [*Delhi (Hons) 1977*]

42. Calculate the change in entropy when m grams of a liquid of specific heat S is heated from T_1 K to T_2 K and then converted into vapour without raising its temperature. Latent heat of vaporisation at T_2 is L. [*Delhi (Hons) 1961*]

43. Show that

$$\frac{\left[\frac{\partial P}{\partial T}\right]_S}{\left[\frac{\partial P}{\partial T}\right]_V} = \frac{\gamma}{\gamma - 1}$$

[*Delhi (Hons) 1971, 1976*]

44. What is meant by thermodynamical equilibrium ? Discuss the equilibrium between a liquid and its vapour and hence deduce Clausius-Clapeyron's equation. [*Delhi (Hons) 1972*]

45. Explain the concepts of reversible and irreversible processes. Obtain an expression for the efficiency of a reversible Carnot engine with a perfect gas as the working substance. Show that for the same pair of working temperatures, the efficiency of all reversible engines is the same and is the maximum value attainable.
[*Delhi 1975, Delhi (Hons) 1973*]

46. Show how the second law of thermodynamics enables us to define a scale of temperature independent of the properties of any working substance. How is the scale realised in practice ?
[*Delhi (Hons) 1973*]

47. Derive Maxwell's thermodynamical equations and show that

$$C_P - C_V = -T\left[\frac{\partial V}{\partial T}\right]_P^2 \left[\frac{\partial P}{\partial V}\right]_T$$

[*Delhi (Hons) 1972*]

48. Describe in detail Clement and Desorme's method of finding the ratio of the two specific heats of air giving the simple theory of the method. What are the objections to the method and what modifications and improvements have been proposed ?
[*Delhi 1975, 76, 77*]

49. Establish the relation connecting the temperature and the volume of a gas undergoing adiabatic compression. [*Delhi 1975*]

50. Establish the latent heat equation,

$$\frac{dL}{dT} - \frac{L}{T} = C_2 - C_1$$

where C_1 and C_2 are the specific heat of the liquid and the saturated vapour respectively. [*Delhi 1975, 1976*]

51. Explain the terms entropy and isentropics. Show that the entropy of a system tends to a maximum. Represent the Carnot's cycle on a temperature-entropy diagram and prove that its area represents available energy. Establish directly from the above considerations that the efficiency of the engine is

$$\frac{T_1 - T_2}{T_1}$$

[*Delhi 1975*]

52. Define entropy. What is its physical significance ? Show that the entropy remains constant in a reversible process. What happens in case the process is an irreversible one ?
[*Delhi 1975*]

53. Enunciate the second law of thermodynamics. Define a temperature scale without making use of the peculiarities of any selected thermometric substance. Show that Kelvin's work scale is such a scale and that the ratio of the two temperatures as measured on the Kelvin scale is identical with the ratio of the same two temperatures on a perfect gas scale. [*Delhi 1975*]

54. State the first law of thermodynamics and use it to derive a relation between pressure and temperature of a perfect gas undergoing an adiabatic change. [*Delhi, 1974*]

55. Under suitable conditions the Joule-Thomson effect results in cooling and so does an adiabatic expansion of a gas.

Distinguish between these two types of cooling.
[*Delhi, 1974 ; Rajasthan 1975*]

56. Deduce the following Maxwell's relations

(*i*) $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

(*ii*) $$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

[*Delhi (Hons.) 1974*]

57. With the help of appropriate Maxwell's relations, show that for a substance

$$C_P - C_V = TVE\,\alpha^2$$

[*Rajasthan, 1975 ; Delhi (Hons.) 1974*]

58. State Carnot's theorem and deduce it from the second law of thermodynamics. [*Kanpur, 1975 ; Delhi (Hons) 1974*]

59. Derive the Clausius Clapeyron's latent heat equation for first order phase changes.

$$\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)}$$

[*Agra, 1975 ; Delhi (Hons.) 1974 ; Delhi 1976*]

60. Distinguish between isothermal and adiabatic changes. Show that for an adiabatic change in a perfect gas

$$PV^\gamma = \text{constant.}$$

[*Delhi (Hons) 1975*]

61. What do you understand by the Kelvin's thermodynamic scale of temperature ? Prove that the ratio of two temperatures on the thermodynamic scale is identical with the ratio of the same two temperatures measured on the perfect gas scale.
[*Delhi, 1977 ; Delhi (Hons.) 1975, 1977*)

62. Explain what you mean by entropy of a substance. Show that the entropy remains constant in a reversible process but increases in an irreversible process.
[*Kanpur, 1975 ; Delhi (Hons.) 1975*]

63. Prove that

$$\frac{E_S}{E_T} = \gamma$$

[*Delhi (Hons.) 1975*]

64. State the first law of thermodynamics. Express it mathematically and explain its physical significance.
[*Delhi (Additional Physics) 1975*]

65. Deduce the first latent heat equation. Discuss how the boiling point of a liquid and the melting point of a solid are affected by change of pressure. [*Bombay, 1974*]

66. Describe Carnot's cycle and obtain an expression for the efficiency of an ideal heat engine in terms of temperatures.
[*Bombay, 1974*]

67. Derive the relation between the volume and temperature of a perfect gas undergoing adiabatic compression. [*Delhi, 1976*]

68. Explain what you mean by entropy of a substance. Show that for any reversible cyclic change of a system, the total change of entropy is zero. Show that this statement is not true for an irreversible change. [*Delhi, 1977*]

69. Discuss the equilibrium between a liquid and its vapour and hence deduce Clausius-Clapeyron's equation. Explain, how the boiling point of a liquid and the melting point of a solid are affected by change of pressure. [*Delhi (Hons.) 1977*]

70. Derive Maxwell's first and second thermodynamical relations and deduce the Clausius-Clapeyron's latent heat equation from Maxwell's second relation. [*Kanpur 1975*]

71. Define Carnot's cycle. Explain the working of a Carnot's heat engine. Calculate its efficiency when a perfect gas is the working substance. [*Rajasthan, 1975*)

72. What is meant by the order of a phase change ? Discuss it giving examples. [*Delhi (Hons.), 1977*]

State and discuss Zeroth law of thermodynamics. [*Delhi, 1978*]

73. Define isothermal and adiabatic transformations. Give examples.

Obtain equation of state for an ideal gas undergoing (*i*) an isothermal transformation and (*ii*) an adiabatic transformation.
[*Delhi, 1978*]

74. Dry air at N. T. P. (normal temperature and pressure) is compressed adiabatically to one-third of its original volume. Calculate the resulting pressure. Given that the ratio C_p/C_v of air is 1·40. [*Delhi, 1978*]

75. What is the importance of Clausius-Clapeyron latent heat equation ? Derive this equation and outline its applications.
[*Delhi, 1978*]

76. For a quasi-static adiabatic process of an ideal gas, prove

$$\frac{T}{(P)^{(\gamma-1)/\gamma}} = \text{constant.}$$

[*Delhi (Hons.), 1978*]

77. State Carnot's Theorem and show that it is a necessary consequence of Second Law of Thermodynamics. Prove that the efficiency of a Carnot engine using an ideal gas as a working substance is $\eta = \frac{T_1 - T_2}{T_1}$. [*Delhi (Hons.), 1978*]

78. Derive the following relations :

(*a*) $$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

(*b*) $$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

(*c*) $$\frac{(\partial P/\partial T)_S}{(\partial P/\partial T)_V} = \frac{\gamma}{\gamma - 1}.$$ [*Delhi (Hons.), 1978*]

79. Write short notes on :

(*i*) Isothermal Process
(*ii*) Adiabatic Process
(*iii*) Isochoric Process
(*iv*) Carnot's engine
(*v*) Carnot's theorem [*Delhi, 1975*]
(*vi*) Second Law of thermodynamics
(*vii*) Clement and Desormes' method
(*viii*) Ruchhardt's experiment for γ
(*ix*) Absolute gas scale
(*x*) Rankine cycle
(*xi*) Diesel engine
(*xii*) Steam engine
(*xiii*) Otto cycle
(*xiv*) Entropy is a measure [illegible]
(*xv*) Entropy tends to a max[illegible]n
(*xvi*) Third Law of thermodynamics
(*xvii*) Absolute zero temperature
(*xviii*) Entropy of a perfect gas [*Delhi (Hons.) 1977*]
(*xix*) Temperature-Entropy diagram
(*xx*) Thermodynamic system
(*xxi*) Thermal Equilibrium
(*xxii*) Concept of Temperature
(*xxiii*) Concept of Heat
(*xxiv*) Zeroth Law in Thermodynamics.
(*xxv*) Phase changes of the second order. [*Delhi (Hons.) 75*]

80. A motor car tyre has a pressure of 3 atmospheres at the room temperature of 27°C. If the tyre suddenly bursts what is the resulting temperature ? [**Ans.** 218·6 K = −54·4°C]

81. A quantity of air ($\gamma = 1{\cdot}4$) at 27°C is compressed suddenly to $\frac{1}{4}$ of its original volume. Find the final temperature.
[**Ans.** 522·3 K = 249·3°C]

82. A quantity of air at 27°C and atmospheric pressure is suddenly compressed to $\frac{1}{5}$ of its original volume. Find (*i*) the final pressure and (*ii*) the final temperature.
[**Ans.** (*i*) 8·29 atmospheres (*ii*) 571·1 K = 298·1°C]

83. Find the efficiency of the Carnot's engine working between 150°C and 50°C. [**Ans.** 23·64%]

84. Find the efficiency of a Carnot's engine working between 227°C and 27°C. [**Ans.** 40%]

85. A Carnot's engine whose temperature of the source is 400 K takes 500 calories of heat at this temperature and rejects 400 calories of heat to the sink. What is the temperature of the sink ? Calculate the efficiency of the engine.
[**Ans.** (*i*) 320 K, (*ii*) 20%]

86. A Carnot's engine is operated between two reservoirs at temperatures of 500 K and 400 K. If the engine receives 2000 calories of heat from the source in each cycle, calculate (*a*) the amount of heat rejected to the sink in each cycle, (*b*) the efficiency of the engine and (*c*) the work done by the engine in each cycle in (*i*) joules (*ii*) kilo-Watt hours.
[**Ans.** (*a*) 1600 calories, (*b*) 20%, (*c*) (*i*) 1780 joules, (*ii*) $4{\cdot}944 \times 10^{-4}$ kWh]

87. A Carnot's engine working as a refrigerator between 250 K and 300 K receives 1000 calories of heat from the reservoir at the lower temperature. (*i*) Calculate the amount of heat rejected to the reservoir at the higher temperature. (*ii*) Calculate also the amount of work done in each cycle to operate the refrigerator.
[**Ans.** (*i*) 1200 cal, (*ii*) 840 joules]

88. Calculate the depression in the melting point of ice produced by 2 atmospheres increase of pressure. Given latent heat of ice = 80 cal/g and the specific volumes of 1 gram of ice and water at 0°C are 1·091 cm^3 and 1·000 cm^3 respectively.
[**Ans.** 0·0148 K or 0·0148°C]

89. Find the increase in the boiling point of water at 100°C when the pressure is increased by 2 atmospheres. Latent heat of vaporisation of steam is 540 cal/g and 1 g of steam occupies 1677 cm^3 volume. [**Ans.** 55·84 K or 55·84°C]

90. Calculate the change in the melting point of naphthalene for 2 atmospheres rise in pressure, given that its melting point is 80°C. Latent heat of fusion is 4563 cal/mol and increase in volume on fusion is 18·7 cm^3/mol. 1 cal = $4{\cdot}2 \times 10^7$ ergs.
[**Ans.** −0·06976 K or −0·06976°C]

91. Calculate the temperature at which ice will freeze if the pressure is increased by 135·2 atmospheres. The change in specific volume when 1 gram of water freezes into ice is 0·091 cm^3. One atmospheric pressure = 10^6 dynes/cm^2. Latent heat of fusion of ice = 80 cal/g. and $J = 4{\cdot}2 \times 10^7$ ergs/cal. [**Ans.** −1·0°C]

92. Calculate the temperature at which water will boil if the pressure is increased by 1·814 atmospheres. Given that the change in specific volume when one gram of water is converted into steam is 1676 cm^3. Latent heat of vaporization of steam = 540 cal/g. $J = 4{\cdot}2 \times 10^7$ ergs/cal and one atmosphere pressure = 10^6 dynes/cm^2.
[**Ans.** 150°C]