

UNIT - III

HEAT

Specific Heats

Heat is a form of energy. This energy is connected with motion of molecules. According to Kinetic theory.

1. Matter is made up of molecules,
2. Molecules are in rapid motion and
3. Molecules experience forces of attraction between one another.

In cases of gases, the inter molecular distances are much larger than that of a solid or a liquid. Also 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.

Van der Waals Equation of State

While deriving the perfect 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 force 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.

Correction for pressure $p \propto p^2 \propto 1/v^2$

$$P = p + \frac{a}{v^2}$$

Here a is 'a' constant and V is the volume of the gas.

Hence correct pressure.

$$P = p + \frac{a}{V^2}$$

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 = $(V-b)$.

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Let the radius of one molecule be 'r'.

The volume of the molecules = $x = 4/3\pi r^3$

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.

$$S = 4/3\pi(2r)^3 = 8x$$

Consider a container volume V . If the molecules are allowed to enter one by one,

$$\text{The volume available for first molecule} = V$$

$$\text{Volume available for second molecule} = V - S$$

$$\text{Volume available for third molecule} = V - 2S$$

$$\text{Volume available for } n^{\text{th}} \text{ molecule} = V - (n-1)S$$

Average space available for each molecule

$$= \frac{V + (V - S) + (V - 2S) + \dots + \{V - (n-1)S\}}{n}$$

$$= V - \frac{S}{n} \{1 + 2 + 3 + \dots + (n-1)\}$$

$$= V - \frac{S}{n} \cdot \frac{(n-1)n}{2}$$

$$= V - \frac{nS}{2} + \frac{S}{2}$$

As the number of molecules is very large so $S/2$ can be neglected.

Average space available for each molecule.

$$= V - \frac{nS}{2} \quad (\text{But } S = 8x)$$

$$= V - \frac{n(8x)}{2}$$

$$= V - 4(nx)$$

$$= V - b$$

$b = 4(nx)$ = four times the actual volume of the molecules

Thus the Van der Waals equation of state for a gas is

$$P + \frac{a}{V^2} (V - b) = RT \quad \text{-(i)}$$

Where a and b are Van der Waals constants.

From the Van der Waals equation of state

$$P + \frac{a}{V^2} (V - b) = RT$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \text{-(ii)}$$

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 is zero. This point is called point of inflexion.

According to Vander Waals equation

$$\left[P + \frac{a}{V^2 T} \right] (V - b) = RT \quad \text{-(i)}$$

$$P = \left[\frac{RT}{V - b} \right] - \frac{a}{V^2} \quad \text{-(ii)}$$

Differential P with respect to V

$$\frac{dP}{dV} = \frac{-RT}{(V - b)^2} + \frac{2a}{V^3} \quad \text{-(iii)}$$

At the critical point $dP/dV = 0$

$$T = T_c$$

$$V = V_c$$

$$\frac{-RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

$$\text{Or} \quad \frac{2a}{V_c^3} = \frac{RT_c}{(V_c - b)^2} \quad \text{-(iv)}$$

Differential equation (iii)

$$\frac{d^2P}{dV^2} = \frac{2RT}{(V - b)^3} = \frac{6a}{V^4}$$

At the critical point $\frac{d^2P}{dV^2} = 0$

$$T = T_c$$

$$V = V_c$$

$$\frac{2RT_c}{(V_c - b)^3} + \frac{6a}{V_c^4} = 0$$

$$T = T_c$$

$$V = V_c$$

$$\frac{6a}{V_c^4} = \frac{2RT_c}{(V_c - b)^3} \quad \text{-(v)}$$

Dividing (iv) by (v)

$$\frac{V_c}{3} = \frac{V_c - b}{2}$$

$$\text{Or} \quad 2V_c = 3V_c - 3b$$

$$V_c = 3b \quad \text{-(vi)}$$

Substituting the value of

$$V_c = 3b \text{ in equation (iv)}$$

$$\frac{2a}{27b^3} = \frac{RT_c}{4b^2}$$

$$T_c = \frac{8a}{27Rb} \quad \text{-(vii)}$$

Substituting these value of V_c and T_c in equation (ii)

$$P_c = \frac{R \times 8a}{27Rb(2b)} - \frac{a}{9b^2}$$

$$P_c = \frac{a}{27b^2} \quad \text{-(viii)}$$

Co-efficient Van der Waals constants

$$V_c = 3b \quad \text{-(i)}$$

$$P_c = \frac{a}{27b^2} \quad \text{-(ii)}$$

$$T_c = \frac{8a}{27Rb} \quad \text{-(iii)}$$

From equation (iii) and (ii)

$$\frac{T_c^2}{P_c} = \frac{64a^2}{(27)^2 R^2 b^2} \times \frac{27b^2}{a}$$

$$= \frac{64a}{27R^2}$$

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad \text{-(iv)}$$

Dividing (iii) by (ii)

$$\frac{T_c}{P_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a}$$

$$= \frac{8b}{R}$$

$$b = \frac{RT_c}{8P_c} \quad \text{-(v)}$$

Also

$$\frac{RT_c}{P_c V_c} = \frac{R(8a) \cdot 27b^2}{27Rba(3b)}$$

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} \quad \text{-(vi)}$$

The quantity $RT_c/P_c V_c$ is called the critical coefficient of gas.

Its calculated value = 8/3 and it is the same for all gases.

Problem

Calculate the Van der Waals constants for dry air given that

$$T_c = 132\text{K},$$

$$P_c = 37.2 \text{ atmosphere},$$

$$R \text{ per mole} = 82.07 \text{ cm}^3 \text{ atmos K}^{-1}$$

Here

$$P_c = 37.2 \text{ atmospheres}$$

$$T_c = 132\text{F}$$

$$R = 82.07 \text{ cm}^3 \text{ atmos K}^{-1}$$

$$(i) \quad a = \frac{27}{64} \frac{R^2 T_c^2}{P_c}$$

$$a = \frac{27}{64} \frac{(82.07)^2 (132)^2}{37.2}$$

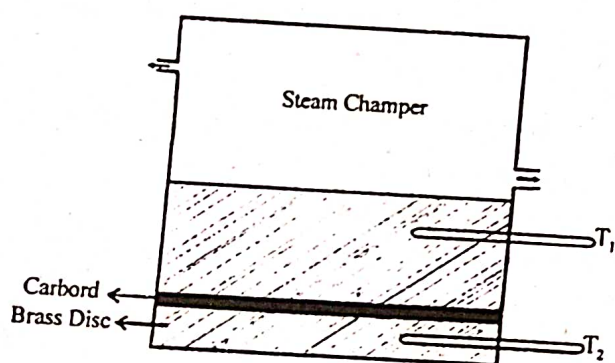
$$\text{Or } a = 13.31 \times 10^6 \text{ atmos cm}^6$$

$$(iii) \quad b = \frac{RT_c}{8P_c}$$

$$b = \frac{82.07 \times 132}{8 \times 37.2}$$

$$b = 36.41 \text{ cm}^3$$

Lee's Disc Method - Determination of the Thermal Conductivity of bad Conductor



The thermal conductivity of a bad conductor like ebonite can be determined by using Lee's disc method. The experimental arrangement is as shown in figure.

Description of apparatus

A is a thick brass disc. It is suspended in a stand using three strings. Over this an ebonite disc is placed. The diameter of this ebonite disc is the same as that of brass disc A. B is a cylindrical steam chest and its lower part is thick. The steam chest is placed over the ebonite disc. The diameter of the chamber is as that of ebonite disc. There are two opening in the steam chamber. Through the opening in the upper part, steam is passed and the steam come out through the opening in the lower part. There are holes in the steam chamber and also in the brass disc A. Thermometers T_1 and T_2 are inserted through the holes.

Experiment

Steam is passed through the steam chamber. The heat is conducted from the steam chamber to brass disc through the ebonite disc. Due to this the temperature indicated by T_1 and T_2 increases. After some time, there will be no increase in the temperature. Now it is in the steady state. The steady temperature θ_1 and θ_2 are noted. If d is the thickness of the ebonite disc, the temperature gradient is $= (\theta_1 - \theta_2)/d$.

If r is the radius of the ebonite disc, the area of the ebonite disc is πr^2 .

At the steady, state the heat conducted through the ebonite disc is

$$Q = \frac{K\pi r^2(\theta_1 - \theta_2)}{d} \text{ Joule} \quad - (1)$$

Where K is the thermal conductivity which is to be determined.

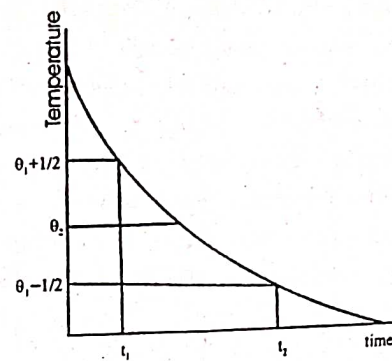
Now the ebonite disc is removed and the brass disc is directly heated. The temperature indicated by T_2 increases. When the temperature reaches $(\theta_2 + 10)^\circ\text{C}$, the steam chamber is removed. The ebonite disc is placed over the brass disc and it is allowed to cool. When the temperature reaches $(\theta_2 + 5)^\circ\text{C}$, a stop clock is started. Time is recorded for each degree fall of temperature continuously until the temperature reaches $(\theta_2 - 5)^\circ\text{C}$.

A graph is drawn by taking the time in X- axis and the temperature at Y - axis. The graph will be as shown. In figure. At the steady temperature, the rate of cooling is calculated from the graph.

$$\text{Rate of cooling } R = d\theta/dt$$

Let M be the mass of the brass disc, t be thickness of the disc and S be the specific heat capacity of the material of the disc.

At the steady state, quantity of heat lost by radiation per second by the flat surfaces and one curved surface of the brass disc = M S R Joule.



Hence the quantity of heat lost only one flat surface and curved surface.

$$= \frac{MSR(\pi r^2 + 2rt)}{(2\pi r^2 + 2rt)} = \frac{MSR}{(r + 2t)(2r + 2t)} \quad - (2)$$

At the steady state, the quantity of heat conducted through the ebonite disc is equal to the quantity of heat lost per second by the brass disc.

$$\frac{k\pi r^2(\theta_1 - \theta_2)}{d} = \frac{MSR(r + 2t)}{(2r + 2t)}$$

$$K = \frac{MSR d (r + 2t)}{\pi^2(2r + 2t)} \text{ } \text{wm}^{-1}\text{K}^{-1} \quad - (3)$$

Using a screw gauge and Vernier calipers, the thickness of the ebonite disc (d), the thickness of the brass disc (t) and radius of the disc (r) can be measured. Hence using relation (3), the thermal conductivity of bad conductor can be calculated.

Joule - Thomson effect (Joule - Kelvin effect)

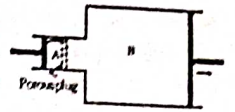
If a gas is allowed to expand through a fine hole or a porous plug, so that it issues from a region at a higher pressure to a region at a lower pressure there will be a fall in temperature of the gas, provided the initial temperature of the gas is below its inversion temperature. This phenomenon is called Joule - Thomson effect. Joule Thomson effect proved the existence of inter molecular attraction. It is very important in the liquefaction of gases.

Theory

Consider a cylinder with non-conducting walls having a porous plug of a porous material like cotton, wool, etc. with a number of fine holes or pores in it. Consider two light frictionless pistons A and B on either side of the porous plug. Let us assume that the unit mass of high compressed gas is enclosed between the piston A and the porous plug. Let the volume of this gas be V_1 and the pressure be P_1 .

Let the piston B be on the low pressure side of the plug and be initially in contact with the plug. Due to this large pressure difference the gas flows through the pores and becomes throttle or wire drawn. That is the molecules of the gas are further drawn apart from one another. The piston A is slowly moved inward so as to keep the pressure P_1 constant as the gas escapes. Similarly the piston B will move slowly outward to keep the pressure on the other side constant at P_2 . Let the volume of the gas be V_2 when it has been completely expelled through the plug to the low pressure side.

When the piston A has pushed the gas into the low pressure side completely through the plug an amount of work $P_1 V_2$ has been done on the gas. When the gas enters the low pressure side and pushes the piston B back an amount of work $P_2 V_2$ has been done by the gas.



Network done by the gas is

$$W = - P_2 V_2 - P_1 V_1 \quad - (1)$$

No heat energy is supplied to the gas from outside since the entire apparatus is thermally insulated. Also the piston A is not pushed by any external agency. As the gas in the lower part issues through the plug the piston A merely moves forward to keep the pressure P_1 constant. So there is no supply of mechanical energy to the system from outside. Therefore the energy required for doing the work W is drawn by the gas from its own internal energy content. If the internal energy of the gas below (Piston A side) is E_1 and the above (Piston B side) is E_2 we must have $E_2 < E_1$ so that the decrease $(E_1 - E_2)$ in the internal energy is equal to the energy used up by the gas for doing the work W .

$$W = E_1 - E_2 = P_2 V_2 - P_1 V_1 \quad - (2)$$

$$E_1 + P_1 V_1 = E_2 + P_2 V_2$$

$$E + PV = \text{Constant}$$

The quantity $E + PV$ is called the total heat or the enthalpy of unit mass of the gas. In the porous plug experiment the enthalpy of the gas remains constant so that the expansion of the gas is an isenthalpic process.

The internal energy E consists of two parts.

1. The kinetic energy K.E. whose value depends on the temperature of the gas.
2. The potential energy P.E. due to intermolecular forces.

The value of potential energy depends on the separation of the molecules and therefore on the volume of the gas.

$$E = \text{K.E.} + \text{P.E.}$$

The internal energy of the gas below (Piston A side)

$$E_1 = (\text{K.E.})_1 + (\text{P.E.})_1$$

The internal energy of the gas (Piston B side)

$$E_2 = (\text{K.E.})_2 + (\text{P.E.})_2$$

Substituting the values of E_1 and E_2 in equation (2).

$$P_2V_2 - P_1V_1 = [(\text{K.E.})_1 + (\text{K.E.})_2] + [(\text{P.E.})_1 - (\text{P.E.})_2]$$

$$(\text{K.E.})_1 + (\text{K.E.})_2 = (P_2V_2 - P_1V_1) + [(\text{P.E.})_2 - (\text{P.E.})_1] \quad (3)$$

If $\text{K.E.}_1 > \text{K.E.}_2$, then there will be a decrease in kinetic energy and hence there will be a decrease in temperature of the gas. The

decrease in temperature is due to increase in the value of PV and/or due to the increase in the potential energy of the molecules.

Case 1:

For a perfect gas which obeys Boyle's law

$$P_2V_2 = P_1V_1$$

Further there are no intermolecular forces in a perfect gas so that

$$(\text{P.E.})_2 - (\text{P.E.})_1 = 0$$

$$\text{Therefore } (\text{K.E.})_1 - (\text{K.E.})_2 = 0$$

There will be no change of temperature or no cooling effect.

Case : 2

For a real gas, in which there are intermolecular attractive forces, the potential energy increases when the molecules are pulled apart to greater distances during the expansion of the gas through the porous plug.

- (i) Each gas has Boyle temperature T_B at which Boyle's law is obeyed. That is the product PV is constant with respect to pressure at that temperature. Below the Boyle temperature of the gas, PV increases as P decreases (Provided P_1 is not too high).

$$\text{So that } P_2V_2 > P_1V_1$$

Therefore from equation (3), we get

$$(K.E.)_1 > (K.E.)_2$$

Hence there is a decrease in kinetic energy of the gas and a consequent fall in temperature.

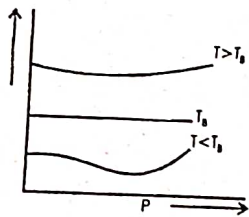
- (ii) Above the Boyle temperature of the gas PV decreases as P decreases so that $P_2V_2 < P_1V_1$

$$(K.E.)_1 + (K.E.)_2 = (P_1V_1 - P_2V_2) + [(P.E.)_2 - (P.E.)_1]$$

Since $(P_1V_1 - P_2V_2)$ is positive, the cooling produced due to decrease of kinetic energy becomes less.

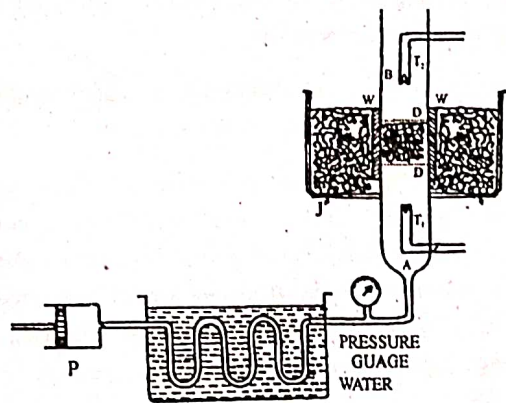
- iii. As the initial temperature of the gas is increased, the rate of increase of PV with P becomes equal to $[(P.E.)_2 - (P.E.)_1]$ so that $[(K.E.)_1 - (K.E.)_2] = 0$. At that temperature there will be no change in the temperature of the gas when it issues from the porous plug. This temperature is called the inversion temperature of the gas.

- iv. If the initial temperature of the gas is still higher, $(P_1V_1 - P_2V_2)$ will be greater than $[(P.E.)_2 - (P.E.)_1]$ so that $[(K.E.)_1 - (K.E.)_2]$ is negative. Therefore there is an increase in the kinetic energy of the gas and hence the temperature of the gas increases when it passes through the porous plug.



Porous plug experiment

The apparatus consists of a porous plug having two perforated brass discs D_1 and D_2 . The space between them is packed with cotton wool or silk fibers. The porous plug is fitted in a cylindrical box wood tube which is surrounded by a vessel containing cotton wool (figure). 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, the 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 temperature of the gas and the results obtained are as follows:

- (i) At sufficiently low temperatures all gases show a cooling effect.
- (ii) At ordinary temperature all gases except hydrogen and helium show cooling effect. Hydrogen shows heating instead of cooling at room temperature.
- (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 as 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 was observed at room temperature because it was at a temperature for 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 below the temperature of inversion shows a cooling effect when it is passed through the porous plug or a throttle valve.

Temperature of inversion

In molecular which obeys Vanderwalls equations, the pressure a/V^2 is equal to V .

Whenever the volume of gases increases from V_1 to V_2 , the workdone opposes to the force between the molecules is

$$w_1 = \int_{V_1}^{V_2} PdV$$

ಅಭ್ಯಂತರ $P = \frac{a}{V^2}$

$$\begin{aligned} \therefore w_1 &= \int_{V_1}^{V_2} \frac{a}{V^2} dV = a \left(-\frac{1}{V} \right)_{V_1}^{V_2} \\ &= a \left(-\frac{1}{V_2} + \frac{1}{V_1} \right) = a \left(\frac{1}{V_1} - \frac{1}{V_2} \right) \end{aligned} \quad (1)$$

The volume of gases at low and high pressure is V_1 and V_2 respectively, then external workdone by the gases.

$$w_2 = (P_2 V_2 - P_1 V_1) \quad (2)$$

Therefore total workdone by gases

$$\begin{aligned} w &= \text{External work} + \text{Internal work} \\ &= w_2 + w_1 \end{aligned}$$

$$= P_2 V_2 - P_1 V_1 + \left(\frac{a}{V_1} - \frac{a}{V_2} \right) \quad (3)$$

Vander Walls equation of gases.

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

$$PV + \frac{a}{V} - bP - \frac{ab}{V^2} = RT$$

$$PV = RT + bP - \frac{a}{V}$$

Because (ab/V^2) is able to reject by above equation.

$$\begin{aligned} w &= \left(RT + bP_2 - \frac{a}{V_2} \right) - \left(RT + bP_1 - \frac{a}{V_1} \right) + \frac{a}{V_1} - \frac{a}{V_2} \\ &= b(P_2 - P_1) + 2a \left(\frac{1}{V_1} - \frac{1}{V_2} \right) \end{aligned}$$

But $V_1 = \frac{RT}{P_1}$ and $V_2 = \frac{RT}{P_2}$

$$w = b(P_2 - P_1) + 2a \left(\frac{P_1}{RT} - \frac{P_2}{RT} \right)$$

$$w = -b(P_1 - P_2) + \left(\frac{2a}{RT} \right) (P_1 - P_2)$$

$$w = (P_1 - P_2) \left(\frac{2a}{RT} - b \right) \quad (4)$$

δT in decrease of temperature

$$w = JH$$

$$= J [M C_p \delta T]$$

(5)

M - Molecular weight of gases

From (4), (5)

$$J M C_p \delta T = P_1 - P_2 \left(\frac{2a}{RT} - b \right)$$

$$\delta T = \frac{P_1 - P_2}{J M C_p} \left(\frac{2a}{RT} - b \right) \quad (6)$$

Cases :

i. $(P_1 - P_2)$ is positive

$\frac{2a}{RT} - b$ is positive, δT also positive.

i.e. $\frac{2a}{RT} > b$ or $T < \frac{2a}{Rb}$ then the gas is cooled

ii. " δT " is at zero

$$\frac{2a}{RT} - b = 0$$

$$T = \frac{2a}{Rb}$$

(7)

This is called temperature of increasing T_i .

$$\text{i.e. } T_i = \frac{2a}{Rb}$$

iii. " δT " is negative.

$$2a$$

$$-b \text{ is negative}$$

$$RT$$

" δT " is negative.

$$b > \frac{2a}{RT}$$

$$T > \frac{2a}{Rb}$$

$$T > T_i$$

(8)

From the above equation, we know that whenever the temperature is higher than temperature of inversion, the gas would be heated.

Liquefaction of Gases

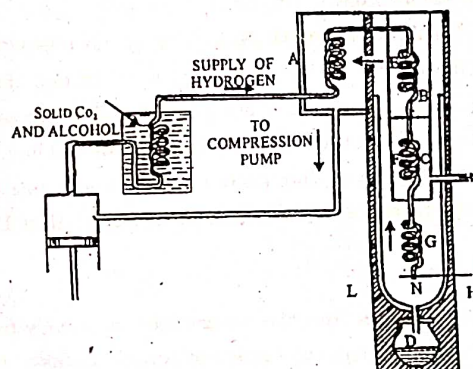
Introduction

For a long time it was thought that air remains in the gaseous state at all temperatures. Gases like oxygen, nitrogen, hydrogen, helium etc., were termed as permanent gases. Freezing mixture could liquefy chlorine, hydrogen sulphide, sulphur dioxide, ammonia, hydrochloric acid etc. under high pressure. Andrew's experiment on CO_2 in 1862 showed that below the critical temperature, a gas can be liquefied by mere application of pressure but it cannot be liquefied above the critical temperature, however large the applied pressure may be. Below the critical the gas is termed as vapour and above the critical temperature it is called a gas.

In 1877, Pictet liquefied by Cascade process. Linde was able to liquefy air in 1896 by Joule-Kelvin effect. Using the principle of Joule-Kelvin effect, hydrogen and helium were also liquefied.

	Critical Temp.	Boiling Point
CO_2	-31.1°C	-78.6°C
Oxygen	-118.8°C	-183°C
Nitrogen	-146°C	-195.8°C
Hydrogen	-240°C	-252.8°C
Helium	-267.8°C	-269.8°C

Liquefaction of Hydrogen



Hydrogen cannot be liquefied by Cascade process because its critical temperature is -240°C . Linde's ordinary apparatus used for the liquefaction of air cannot be used for hydrogen because the temperature of inversion for hydrogen is -83°C . The gas must initially be cooled to a temperature lower than the temperature of inversion for the cooling to take place due to Joule-Kelvin effect.

The original apparatus designed by Dewar (1898) was improved later by Travers, Olszewski, Nernst and others (Fig. 3-9) To have complete insulation the whole apparatus is enclosed in an outer Dewar flask L.

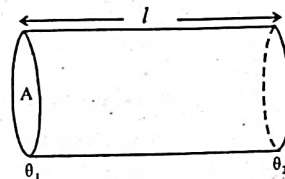
Hydrogen under a pressure of 200 atmosphere is passed through a coil immersed in solid CO_2 and alcohol. It enters the coil in the chamber A where it is further cooled by the outgoing hydrogen. The chamber B contains liquid air and cools hydrogen in the coil E. In the chamber C liquid air is allowed to boil under reduced pressure (10 cm of Hg) and hydrogen in the coil F is cooled to a temperature of -200°C . This cooled hydrogen passed through the regenerative coil G and the nozzle N. Hydrogen is cooled further due to Joule-Kelvin effect. The cooled hydrogen coming from the nozzle N is allowed to circulate back to the pump as shown in figure. The process of regenerative cooling continues and after some time hydrogen gets liquefied and is collected in the Dewar flask D.

Conduction

The transfer of heat from the hotter region of a body to its colder region without actual movement of particle is called heat conduction.

When one end of the rod is heated, the heat is conducted to the other end by the process of conduction. In metals heat is conducted by conduction.

a. Thermal conductivity



Consider a uniform rod of area of cross section A and length l . One end of the rod is heated to a steady temperature. Let θ_1 and θ_2 be the temperature at the ends of the rod. θ_1 is greater than θ_2 . Heat is conducted from the region of higher temperature to the region of lower temperature. Let Q be the quantity of heat conducted in t seconds. The quantity of heat Q conducted is

1. Directly proportional to the area of cross section ($Q \propto A$).
2. Directly proportional to the temperature difference between the ends ($Q \propto (\theta_1 - \theta_2)$)
3. Inversely proportional to the length of the rod ($Q \propto 1/l$) and
4. Directly proportional to the time of conduction ($Q \propto t$).

Quantity of heat conducted

$$Q \propto A(\theta_1 - \theta_2) t/l$$

$$\text{or } Q = K. A(\theta_1 - \theta_2) t/l$$

Where K is a constant called the co-efficient of thermal conductivity or simply thermal conductivity. $(\theta_1 - \theta_2)/l$ is the change of temperature with distance and is called temperature gradient.

If $A = 1\text{m}^2$, $(\theta_1 - \theta_2)/l = 1$ and $t = 1$ sec, then from this we can define the thermal conductivity.

The thermal conductivity of a material is defined as the heat energy conducted across unit area of cross-section in unit time. When the temperature gradient is unity.

Unit : $\text{J s}^{-1}\text{m}^{-1}\text{K}^{-1}$ or $\text{W.m}^{-1}\text{K}^{-1}$.

b. Good conductors and bad conductors

Based on the thermal conductivity or materials, it can be divided into two types.

1. Good conductor
2. Bad or poor conductor

Good Conductors

Material which have large thermal conductivity are called good conductors. Through this heat is conducted easily. All metals are good conductor of heat.

Bad or poor conductor

Material which have small thermal conductivity are called bad or poor conductors. Through this heat is conducted very slowly. Wood, glass, ebonite etc are examples for bad conductors.

Problems

1. Calculate the drop in temperature produced by adiabatic throttling process in the case of oxygen when the pressure is reduced by 50 atmosphere. Initial temperature of the gas is 27°C . Given that the gas obeys Vander Waal's equation and

$$a = 1.32 \times 10^{12} \text{cm}^4 \text{ dynes mole}^{-2}$$

$$b = 31.2 \text{cm}^3 \text{mole}^{-1}$$

$$\text{and } C_p = 7 \text{ cal } \text{K}^{-1} \text{ mole}^{-1}$$

$$a = 1.32 \times 10^{12} \text{cm}^4 \text{ dynes mole}^{-2}$$

$$= 13.2 \times 10^{-2} \text{Nm}^4 \text{ mole}^{-2}$$

$$b = 31.2 \text{cm}^3 \text{mole}^{-1}$$

$$= 31.2 \times 10^{-6} \text{m}^3 \text{mole}^{-1}$$

$$R = 8.3 \text{ JK}^{-1} \text{ mole}^{-1}$$

$$C_p = 7 \text{ Cal } \text{K}^{-1} \text{ mole}^{-1}$$

$$= 7 \times 4.168 \text{ JK}^{-1} \text{ mole}^{-1}$$

$$\delta P = 50 \text{ atmosphere}$$

$$= 50 \times 10^{-5} \text{Nm}^{-2}$$

$$\delta T = \left[\frac{\delta P}{C_p} \right] \left[\frac{2a}{RT^{-b}} \right]$$

$$= 12.93 \text{ K}$$

2. The Vander Waal's constants a and b for 1 gram molecule of hydrogen are $a = 0.245 \text{ atm. litre}^2/\text{mole}^2$, $b = 2.67 \times 10^{-2} \text{ litre/mole}$.
 $R = 8.31 \text{ J/K-mole}$

$$a = 0.245 \text{ atm. litre}^2/\text{mole}^2$$

$$a = 0.245 \times 10^5 \times 10^{-6} \text{ Nm}^4 \text{ mole}^{-2}$$

$$= 0.245 \times 10^{-1} \text{ Nm}^4 \text{ mole}^{-2}$$

$$b = 2.67 \times 10^{-2} \text{ litre / mole}$$

$$b = 2.67 \times 10^{-2} \times 10^{-3} \text{ m}^3 \text{ mole}^{-1}$$

$$b = 2.67 \times 10^{-5} \text{ m}^3 \text{ mole}^{-1}$$

$$R = 8.3 \text{ JK}^{-1} \text{ mole}^{-1}$$

$$T_B = \frac{a}{Rb}$$

$$= \frac{0.245 \times 10^{-1}}{8.31 \times 2.67 \times 10^{-5}}$$

$$= 110.4 \text{ K}$$

$$T_i = \frac{2a}{Rb} = 2T_B$$

$$= 2 \times 110.4$$

$$= 220.8 \text{ K}$$

$$T_c = \frac{8}{27} \frac{a}{Rb}$$

$$= \frac{8}{27} T_B$$

$$= (8 \times 27) \times 110.4$$

$$= 32.72 \text{ K}$$

3. Calculate the Boyle temperature, inversion temperature and the critical temperature of He. Given $a = 0.0341 \text{ atm. litre}^2/\text{mole}^2$, $b = 0.0237 \text{ litre/mole}$. $R = 8.3 \text{ Joule/k-mole}$.

$$a = 0.0341 \text{ atm litre}^2/\text{mole}^2$$

$$a = 0.0341 \times 10^{-1} \text{ Nm}^4 \text{ mole}^{-2}$$

$$b = 0.0237 \text{ litre / mole}$$

$$b = 0.0237 \times 10^{-3} \text{ m}^3 \text{ mole}^{-1}$$

$$R = 8.3 \text{ JK}^{-1} \text{ mole}^{-1}$$

$$T_B = \frac{a}{Rb}$$

$$= \frac{0.03412 \times 10^{-1}}{8.31 \times 0.0237 \times 10^{-3}}$$

$$= 17.34 \text{ K}$$

$$T_i = \frac{2a}{Rb} = 2T_B$$

$$= 2 \times 17.34$$

$$= 34.68 \text{ K}$$

$$T_c = \frac{8}{27} \frac{a}{Rb}$$

$$= \frac{8}{27} T_B$$

$$= (8 \times 27) \times 17.34$$

$$= 5.137 \text{ K}$$

University Questions

2 Mark questions

1. State van der Waals equation of state.
2. What are critical constants.
3. Explain Joule - Thomson effect.
4. What are the behaviours of gases?
5. Write the results of temperature of inversion.
6. What means Boyle temperature?
7. Write the equation for relation between Boyle temperature, temperature of inversion and critical temperature.
8. What is liquefaction of gases?
9. What is absolute zero temperature?
10. What is temperature of inversion?

5 Mark questions

1. Derive expressions for critical constants.
2. Discuss determination of the thermal conductivity of bad conductor using Less disc method.
3. Give the theory of porous plug experiment.
4. Discuss Boyle temperature.
5. Give the process of the liquefaction of hydrogen.

10 Mark questions

1. Describe Vander Waals equation of state.
2. Discuss Joule - Thomson effect.
3. Derive equation for the fall in temperature of a Vander Waals gas by Joule - Thomson effect.