deviations from Boyle's law. At high pressure, the molecules of a gas come close to each other and the forces of intermolecular attraction becomes appreciable. The distance between two gas molecules become so small that it is comparable or equal to those of the corresponding liquid, the gas gets *liquefied*.

If ice is heated, its molecules become more free to move and acquires a liquid state *i.e.*, water. Further heating, the intermolecular forces become so small, that at a particular temperature the water gets converted in gaseous (*i.e.*, vapour) state Fig. 2.1. The reverse process is also possible by withdrawing heat continuously. Thus all the three states of matter are continuous. In other words, solid, liquid and gaseous states are the three different stages of a continuous phenomenon Fig. 2.2.

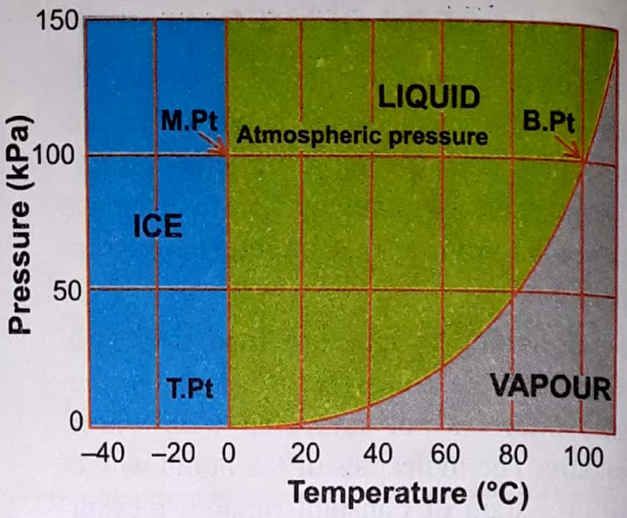


Fig. 2.2

2.3 Andrew's Experiments on Carbon Dioxide

Fig. 2.3 shows the apparatus used by Andrew in 1869, to study the isothermals of carbon dioxide at different temperatures.

The apparatus consists of two similar glass tubes *A* and *B*, having thick capillary tubes at the top and bulbs in the middle. Initially in tube *A* pure dry air is passed for a long time and then sealed at both the ends. Similarly, in tube *B*, carbon dioxide is passed for a long time (nearly 24 hours) and then both the ends are sealed. The lower ends of both the tubes are immersed in mercury. A small pellet of mercury is drawn in both the tubes by alternately heating and cooling the tubes. Both the tubes are fixed in *H* shaped copper vessel having steel stoppers *S* and *S*′. The vessel is filled with water. By screwing in the plunger, the water is compressed and the pressure is transmitted to the enclosed gases. Pressures of the order of 400 atmospheres can thus be applied.

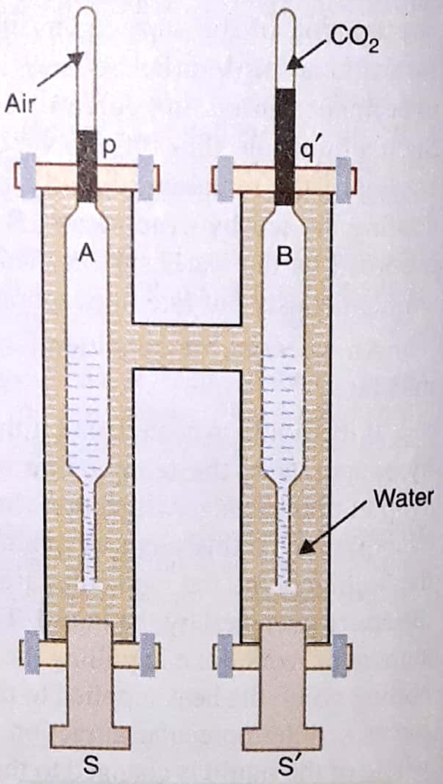


Fig 2.3

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 can be calculated assuming air to obey Boyle's law. The volume of CO_2 is read from tube *B*, as it is calibrated to read the volume directly. Both the tubes are surrounded by water baths (not shown). Air is kept at constant temperature. The temperature of CO_2 could be maintained at any desired temperature between 0°C to 100°C. In Andrew's actual experiments, isothermals were drawn at temperatures 13.1°C, 21.5°C, 31.1°C, 32.5°C, 35.5°C and 48.1°C as shown in Fig. 2.4.

Discussion of Results

From the isothermals of CO_2 at various temperatures (Fig 2.4), following conclusions can be drawn.

1. At 13.1°C, the portion *AB* represents the gaseous states of CO_2 up to the point *B*, it obeys Boyle's law from *B* to *C*, volume decreases suddenly (enormous decrease) with slight increase in

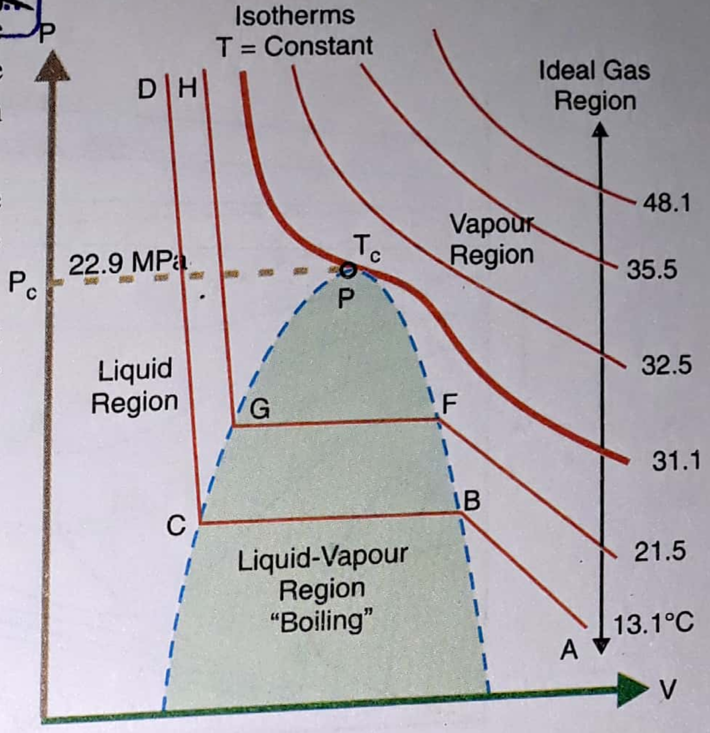


Fig 2.4 Isothermals of CO_2 and air

pressure. The portion BC represents the change of CO_2 from the gaseous to liquid state. At C, the gas has been liquefied completely. The portion CD represents the liquid state of CO_2.

2. At 21.5°C, the curve is similar. The horizontal portion BC has decreased further to FG.

3. At 31.1°C, the horizontal portion is just vanished. This is called critical isothermal for CO_2. Above this temperature *i.e.*, 35.5°C and 48.1°C the horizontal portion does not appear at all and the gas obeys Boyle's law from one end to the other. This isothermals are similar to the isothermals for air as shown in Fig. 2.4.

4. Thus, for CO_2, the critical isothermal divides into two regions. Above the critical isothermal, the CO_2 gas cannot be liquefied howsoever large the applied pressure may be. Below the critical isothermal, CO_2 gas can be liquefied by the application of pressure alone. The dotted curve whose highest point *P* is called the critical point and the temperature 31.1°C of the isothermal is called the critical temperature.

2.4 Critical Constants

1. **Critical temperature (T_c):** It is defined as the maximum temperature at which a gas can be liquefied by the increase of pressure alone. Above this temperature, the gas cannot be liquefied howsoever large the applied pressure may be.

2. **Critical pressure (P_c):** The pressure necessary to liquefy a gas at critical temperature is called the critical pressure.

3. **Critical volume (V_c):** It is the volume which unit mass of a gas occupies at the critical temperature and critical pressure.

These three quantities, T_c, P_c and V_c are called critical constants of a gas.

4. **Critical point:** It is that point on the isothermal for the critical temperature at which the change of state from the gaseous state to the liquid state takes place under constant values of P_c and V_c.

2.5 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. 2.5.

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 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.

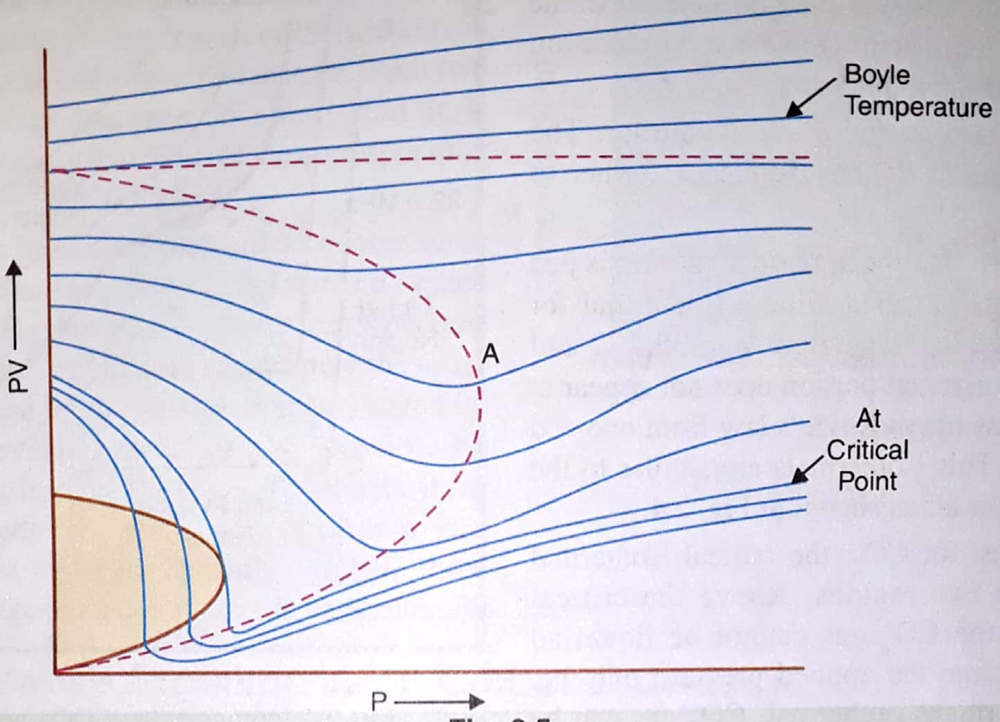


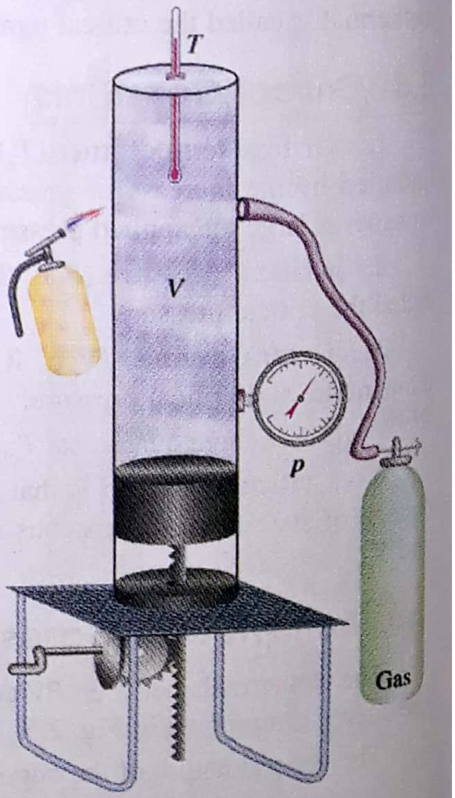
Fig. 2.5

Thus, the Boyle's law $PV = RT$ is obeyed only under ideal conditions, *i.e.*, at high temperature and low pressure.

Attempts were made to modify Boyle's law. Based on the experimental results of Andrew, Amagat and Holborn, K. Onnes suggested for all real gases at high pressure and at constant temperature, an empirical relation

$$PV = A + BP + CP^2 + DP^3 + \ldots\ldots \tag{2.1}$$

where A, B, C, D, etc. are constants for a given temperature depending on the nature of the gas and are called **virial coefficients**. A is called the first virial coefficient, B the second virial coefficient, C the third virial coefficient, and so on. These coefficients are in decreasing order of magnitude, *i.e.*, $A > B > C > D$ and so on. The ratio B/A is of the order of 10^{-3} while C/A is of the order of 10^{-5}. A is simply equal to RT because as $P \to 0$, equation (*ii*) reduces to $PV = RT$. The second, third and fourth terms become negligible in comparison to first at very low pressure and then gases obey Boyle's law accurately– lower the pressure, higher is the degree of accuracy.



2.6 Boyle Temperature

The coefficient B has a special importance. For all gases, it varies in a similar manner. Its value is negative at low temperatures, but gradually increases to zero and becomes positive as the temperature is increased. The temperature at which coefficient B is zero is called the **Boyle temperature**, represented by T_B. At this temperature Boyle's law holds good over a wide range of pressure provided the constants C, B, ... are all negligible. Thus, at Boyle temperature.

$$B = \frac{d}{dP}(PV) = 0 \qquad \text{...}(i)$$

and

$$PV = A = \text{constant.} \qquad (ii)$$

From Van der Waals' equation of state for a real gas

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

where a and b are Van der Waals' constants.

Solving eq. (*iii*), we get

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

or

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \qquad \text{...}(iv)$$

we can write approximately,

$$V = \frac{RT}{P} \qquad \text{...}(v)$$

Putting this value of V in equation (*iv*), we get

$$PV = RT + Pb - \frac{a}{RT}P + \frac{ab}{R^2T^2}P^2$$

$$= RT + \left(b - \frac{a}{RT}\right)P + \frac{ab}{R^2T^2}P^2 \qquad \text{...}(vi)$$

Comparing this with equation (2.1), we have

$$A = RT, B = b - \frac{a}{RT} \quad \text{and} \quad C = \frac{ab}{R^2T^2} \qquad \text{...}(vii)$$

At Boyle Temperature $T = T_B$ and $B = 0$, therefore, we have

$$0 = b - \frac{a}{RT_B}$$

or

$$T_B = \frac{a}{Rb} \qquad \text{...(2.2)}$$

This equation gives the value of Boyle's temperature for all gases obeying Van der Waals' equation of state. Clearly Boyle temperature (T_B) depends upon a and b which are different for different gases. Hence **Boyle temperature is different for different gases.** For nitrogen T_B is 50°C, for hydrogen it is −169°C while for helium it is – 254°C.

The behaviour of gases above, below and at Boyle temperature is expressed by plotting the product PV against P for different temperatures (Fig. 2.6). The general nature of the curves is the same for all gases. Following conclusions can be drawn:

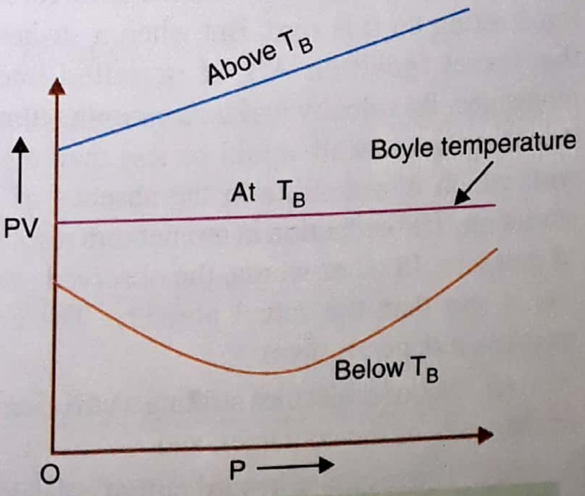


Fig. 2.6

1. **Below Boyle Temperature, ($T < T_B$) :** The value of PV first decreases (as B is –ve) with increase in P, reaches a minimum at a particular pressure and then begins to increase. This is because at high pressures the terms CP^2, DP^3 etc. of equation (2.1)

become more effective and are positive and thus PV increases with increase in P after reaching a minimum. This suggests the existence of intermolecular attraction because below T_B, the gases are highly compressible.

2. Above Boyle Temperature ($T > T_B$) : Above Boyle temperature, PV continuously increases with increase in P. This is because, the coefficient B is +ve above Boyle temperature and thus the terms on R.H.S. of equation (2.1) are positive. It now indicates that the intermolecular attraction is now less significant.

3. At Boyle temperature ($T = T_B$) : The product PV is almost constant for a long range of pressure. Thus, Boyle's law is obeyed over a wide range of pressures.

Thus, below the Boyle temperature, the gases are highly compressible and this suggests the existence of intermolecular attraction. Beyond Boyle temperature, Boyle's law is obeyed and inter-molecular attractions are less significant.

Definition: Boyle temperature is that temperature above which a real gas behaves like an ideal gas and obeys Boyle's law.

2.7 Reasons for Modification of Gas Equation

The perfect gas equation $PV = RT$ is not obeyed by real gases, particularly at high pressure and low temperature. At ordinary temperatures and pressures, the deviation is small but at high pressures and low temperatures the deviations are very large. In the derivation of the perfect gas equation, on the basis of kinetic theory of gases, the following assumptions have been made, which do not hold true in case of real gases. These are (*i*) the size of the molecule of the gas is negligible, and (*ii*) the forces of intermolecular attraction are absent. But in actual practice, at high pressure the size of the molecule 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 molecular attraction are appreciable. Hence, a perfect gas equation needs modification.

2.8 Van der Waals Equation of State

In 1879 Van der Waals modified the perfect gas equation $PV = RT$ by applying corrections for

1. Intermolecular force of attraction and
2. Finite size of molecules.

1. Correction for Pressure:

Consider a molecule A of the gas, well inside the vessel as shown in Fig. 2.7. It is attracted by other molecules in all directions with the same force and the net force acting on it is zero. But when it strikes the wall of the vessel (position A′), it is pulled back by other molecules. Its velocity and hence momentum with which it will strike the wall would be less than the momentum with which it will strike in the absence of the force of attraction. This reduction in momentum results in decrease of pressure. In other words, the observed pressure of the gas is less than the actual pressure. The correction for pressure p depends upon

(*i*) No. of molecules striking a unit area per unit time of the walls of the container, and

(*ii*) The resultant inward pull of cohesion on each of the striking molecules.

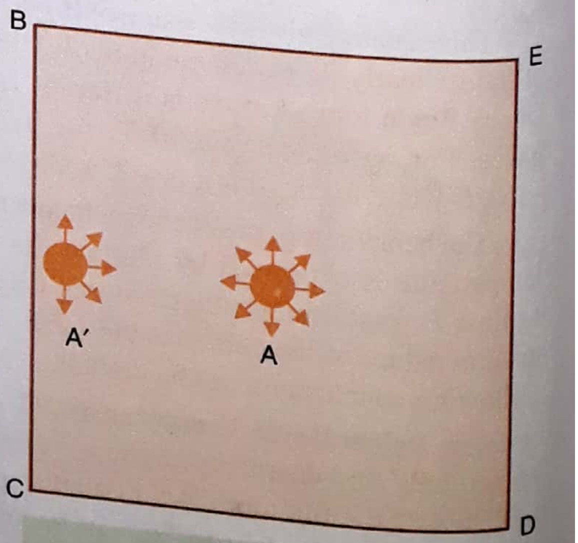


Fig. 2.7

Each of these factors is proportional to the density of the gas.

$\therefore$ Correction for pressure $p \propto \rho^2 \propto \dfrac{1}{V^2}$

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

$\therefore$

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

Therefore, the corrected or real pressure

$$= P + p = \left(P + \frac{a}{V^2}\right) \qquad \text{...(2.3)}$$

where P is the observed pressure.

2. Correction for Volume :

Due to the finite size of gas molecules, the actual space available for the movement of the molecules is less than the volume of the vessel. The molecules have the sphere of influence (Fig. 2.8) around them of radius $(2r)$, within which no other molecule can penetrate.

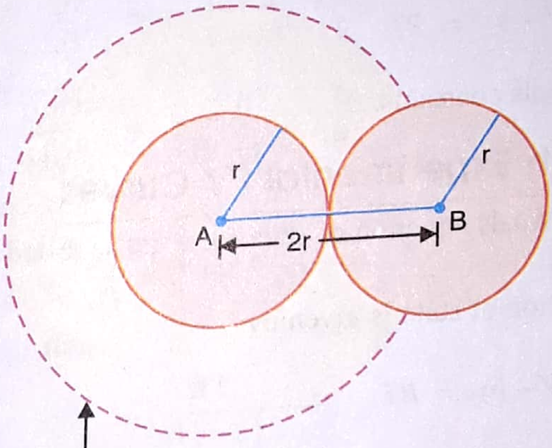


Fig. 2.8

Here r is the radius of each gas molecule.

Volume of the molecule $= \quad x = \dfrac{4}{3}\pi r^3$

The centre of any two molecules can approach each other only by a minimum distance of $2r$. The volume of sphere of influence of each molecule

$$s = \frac{4}{3}\pi\,(2r)^3 = 8 \times \frac{4}{3}\pi r^3 = 8\,x$$

Let us fill the whole space of the volume V with n molecules one by one.

The volume available for the first molecule $= V$

The volume available for the second molecule $= V - 8x$

$= V - s$

The volume available for nth molecule $= [V - (n-1)\,s]$.

$\therefore$ Average space available for each molecule

$$= \frac{V + (V-s) + (V-2s) + \ldots\ldots\ldots + [V-(n-1)\,s]}{n}$$

$$= \frac{n\,V}{n} - \frac{s}{n}\,\{1 + 2 + 3 + \ldots\ldots\ldots + (n-1)\}$$

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

$$= V - \frac{ns}{2} + \frac{s}{2}$$

As the number of molecules is very large $\frac{s}{2}$ can be neglected.

∴ Average space available of each molecule

$$= V - \frac{ns}{2}$$

$$= V - \frac{n\,(8x)}{2} \qquad (\because\ s = 8x)$$

$$= V - 4\,(n\,x)$$

$$= V - b$$

Where $b = 4\,(n\,x)$ = four times the actual volume of the molecules.

Thus, the Van der waals equation of state for a gas is

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

where a and b are Van der waals constants.

2.9 Comparison with Experimental PV Curves

The validity of Van der Waals equation of state for a gas is tested by comparing its PV c with the experimental results.

The Van der Waals equation of state is given by

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

or

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

we see that if $V \to \infty$, $P \to 0$. Again if V is very small and $V \to b$, then $P \to \infty$.

A family of plots *i.e.*, curves between pressure and volume at various temperatures are drawn using equation 2.5. The curves are as shown in Fig. 2.9. In the graph, the horizontal portion is absent. But in place of it, the curve *ABCDE* is obtained. This does not agree with the experimental isothermals for CO_2 as obtained by Andrew. However, the portion *AB* has been explained as due to super cooling of the vapours and the portion *ED* is due to super-heating of the liquid. But the portion *BCD* cannot be explained because it shows decrease in volume with decrease in pressure, which is not true in actual practice. At higher temperatures, however, both theoretical and practical *PV* curves are similar.

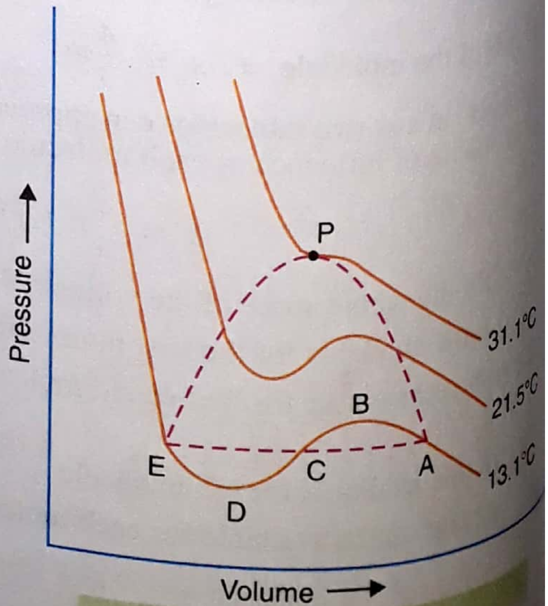


Fig. 2.9

2.10 Estimation of Critical Constants

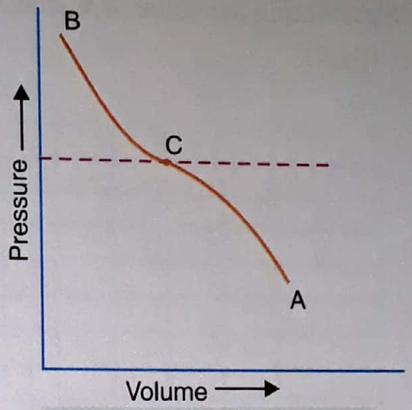


Fig. 2.10

Consider the critical isothermal ACB as shown in Fig. 2.10. At the critical point C, the curve is horizontal. Therefore, at point C, $\left(\frac{dP}{dV}\right) = 0$. At this point, the tangent also crosses the curve. Therefore, the tangent at such a point is said to be stationary and the point is called **'the point of inflexion'**. At the point of inflexion, we have

$$\frac{d^2P}{dV^2} = 0$$

Hence, at critical point C, we have $\frac{dP}{dV} = 0$ and $\frac{d^2P}{dV^2} = 0$.

The Van der Waals equation is

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

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

and

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

At the critical point C, we have

$$T = T_c,\ P = P_c,\ V = V_c,\ \frac{dP}{dV} = 0 \text{ and } \frac{d^2P}{dV^2} = 0$$

Substituting in the above equations,

$$P_c = \frac{RT_c}{(V_c-b)} - \frac{a}{V_c^2} \qquad \text{...}(iv)$$

$$\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3} \qquad \text{...}(v)$$

and

$$\frac{2RT_c}{(V_c-b)^3} = \frac{6a}{V_c^4} \qquad \text{...}(vi)$$

Dividing (v) by (vi),

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

$$\therefore \quad \boxed{V_c = 3b} \qquad \text{...(2.7)}$$

Substituting the value of V_c in equation (v), we get

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

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

$$\therefore \quad \boxed{T_c = \frac{8a}{27bR}} \qquad \text{...(2.8)}$$

Substituting the value of V_c and T_c in equation (*iv*), we get

$$P_c = \frac{8aR}{27bR(3b-b)} - \frac{a}{(3b)^2}$$

$$= \frac{8a}{27\times 2b^2} - \frac{a}{9b^2}$$

$$= \frac{a}{9b^2}\left[\frac{8}{6}-1\right] = \frac{a}{9b^2}\times\frac{1}{3}$$

$$\boxed{P_c = \frac{a}{27b^2}} \qquad \text{...(2.9)}$$

TABLE 2.1 Critical Temperature and Pressure of Common Gases

Substance	*Critical Temperature °C*	*Critical Pressure (atmosphere)*
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

2.11 Constants of Van der Waals Equation

From equation (2.8),

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

$$\therefore \qquad \frac{a}{b} = \frac{27RT_c}{8} \qquad \text{...(vii)}$$

But

$$P_c = \frac{a}{27b^2}$$

$$\therefore \qquad \frac{a}{b^2} = 27P_c \qquad \text{...(viii)}$$

Dividing (*vii*) by (*viii*),

$$\frac{a}{b}\times\frac{b^2}{a} = \frac{27RT_c}{8}\times\frac{1}{27P_c}$$

$$\therefore \qquad b = \frac{RT_c}{8P_c} \qquad \text{...(2.10)}$$

	C6 H6	SO2	Cl2	C2 H6	H2O	C2 H4	H2 S	Xe	NH3	CO2	Kr	CH4	CO	N2	O2	Ar	H2	Ne	He
🟥 a (atm ltr²/mol²)	18.24	6.803	6.579	5.562	5.536	4.53	4.49	4.25	4.225	3.64	2.346	2.283	1.505	1.408	1.378	1.363	0.2476	0.2155	0.0346
🟩 b (0.01 ltr/mol)	11.54	5.636	5.622	6.38	3.049	5.714	4.287	5.105	3.707	4.267	3.978	4.278	3.985	3.913	3.183	3.219	2.661	1.709	2.37

Fig. 2.11. Vander Waals coefficients

Substituting for b in equation (vii), we get

$$\frac{a}{\dfrac{RT_c}{8P_c}} = \frac{27\,RT_c}{8}$$

$$\therefore \qquad a = \frac{RT_c}{8\,P_c} \times \frac{27\,RT_c}{8}$$

$$\text{or} \qquad a = \frac{27\,R^2\,T_c^{\,2}}{64\,P_c} \qquad \text{...(2.11)}$$

Equation (2.10) and (2.11) gives the value of constants a and b respectively.

2.12 Critical Coefficient

The quantity $\dfrac{RT_c}{P_c V_c}$ is called the critical coefficient. Its value is obtained by substituting the values of P_c, V_c and T_c.

$$\therefore \qquad \text{Critical coefficient} = \frac{RT_c}{P_c V_c} = \frac{R \times \dfrac{8a}{27\,bR}}{\dfrac{a}{27\,b^2} \times 3b}$$

$$= \frac{8\,a}{27\,b} \times \frac{27\,b^2}{3\,ab} = \frac{8}{3}$$

$$= 2.667 \qquad \text{...(2.12)}$$

The calculated value of critical coefficient $\dfrac{RT_c}{P_c V_c}$ is $\dfrac{8}{3}$ and it is the same for all gases.

The experimental values of critical coefficient for different gases are given in Table 2.2.

TABLE 2.2 Experimental values of Critical Coefficient $\frac{RT_c}{P_c V_c}$

Substance	T_c *in K*	P_c *in atm.* in cm^3/g	*Specific Volume*	$\frac{RT_c}{P_c V_c}$
Helium	5.1	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 2.667.

2.13 Limitations of Van der Waals Equation

1. The values of constants 'a' and 'b' obtained by different methods differ considerably. Although Van der Waals theory assumes them to be constant. The value of a is found to depend on the temperature. At very high temperatures, it tends to zero.

2. According to theory, $V_c = 3b$, but it is found to depend on the nature of gas. Experimentally, it is found that $V_c \cong 2b$.

3. The theoretical value of critical coefficient $\frac{RT_c}{P_c V_c}$ is 2.667 for all gases. However, it varies from gas to gas with an average value of 3.7 for most of the gases. This constant appears to depend on the molecular structure of the gas.

Thus no gas obeys Van der Waals equation closely in the vicinity of the critical point.

2.14 Reduced Equation of State

When the actual pressure, volume and temperature of a fixed mass of a gas are divided by the critical values of these quantities, the resulting ratios are called the reduced pressure (P_r), reduced volume (V_r) and reduced temperature (T_r) respectively.

Thus, we have

$$P_r = \frac{P}{P_c},\quad V_r = \frac{V}{V_c} \quad \text{and} \quad T_r = \frac{T}{T_c}$$

$$\therefore \quad \begin{aligned} P = P_c P_r &= \frac{a}{27b^2} P_r \\ V = V_c V_r &= 3b\, V_r \\ T = T_c T_r &= \frac{8a}{27\,Rb} T_r \end{aligned}$$

At ordinary temperatures, all gases except hydrogen show cooling effect on passing through the porous plug, but hydrogen shows a heating effect. At sufficiently low temperatures all gases show a cooling effect.

2.21 Joule-Thomson Porous Plug Experiment

The experimental set up for the porous plug experiment to study the Joule-Thomson effect is shown in Fig. 2.15. It consists of the following main parts:

1. The apparatus consists of a porous plug having two perforated brass discs *D, D*.
2. The space between *D, D* is packed with cotton wool or silk fibers.
3. The porous plug is fitted in a cylindrical box-wood *W* which is surrounded by a vessel containing cotton wool (Fig. 2.15). This is done to avoid loss or gain of heat from the surroundings.

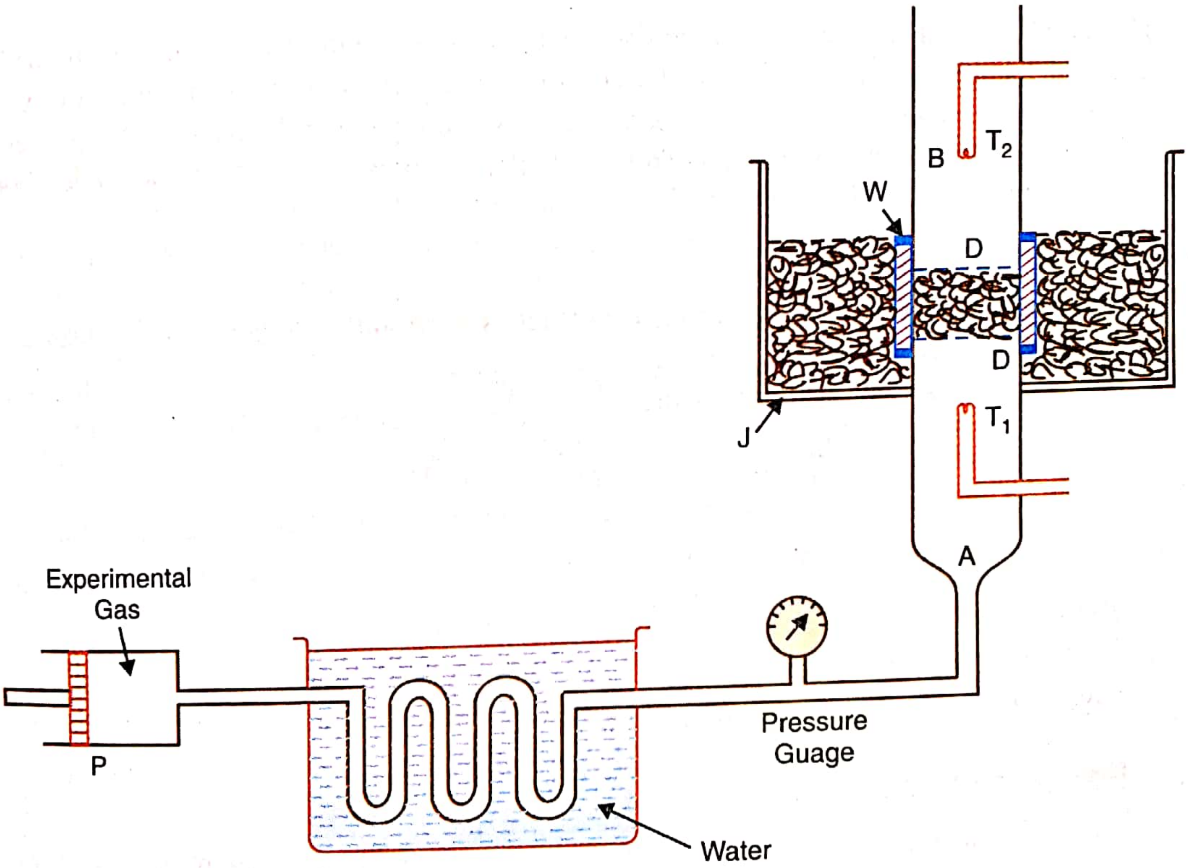


Fig 2.15 J-T Porous Plug Experiment

4. T_1 and T_2 are two sensitive platinum resistance thermometers and they measure the temperatures of the incoming and outgoing gas.
5. The gas is compressed to a high pressure with the help of piston *P* and it is passed through a spiral tube immersed in water bath maintained at a constant temperature. If there is any heating of the gas due compression, this heat is absorbed by the circulating water in the water bath.

Experimental procedure

By means of the compression pump *P*, the experimental gas is passed slowly and uniformly through the porous plug keeping the high pressure constant, read by pressure gauge. During its passage through the porous plug, the gas is throttled, *i.e.* the separation between the molecules increases. On passing through the porous plug, the volume of the gas increases against the atmospheric pressure. As there is no loss or gain of heat during the whole process, the expansion of the gas takes place adiabatically.

The initial and final temperatures are noted by means of the platinum resistance thermometers T_1 and T_2.

Experimental Results

Inversion Temperature

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 and helium show 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 for a given difference of pressure decreases with rise in the initial temperature of the gas. It was found that the cooling effect decreased with the increase of initial temperature and became zero at a certain temperature and at a temperature higher than this temperature, instead of cooling, heating was observed. This particular temperature at which the Joule-Thomson effect changes sign is called the *temperature of inversion.*

Definition

The temperature at which Joule-Thomson effect is zero and changes sign is known as the temperature of inversion.

It is denoted by T_i and at this temperature

$$\frac{2a}{RT_i} = b$$

or

$$T_i = \frac{2a}{Rb} \qquad ...(2.15)$$

when $T < T_i$, cooling takes place, and

$T > T_i$, heating takes place.

for helium $T_i = 35$ K, and for hydrogen $T_i = 193$ K.

2.22 Regenerative Cooling

In case of hydrogen and helium, 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 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 its temperature of invession shows a cooling effect when it is passed through the porous plug or a throttle valve. This is called regenerative cooling or Joule-Kelvin cooling. This principle is used in the liquefaction of the so called permanent gases like nitrogen, oxygen, hydrogen and helium.

2.23 Estimates of *J-T* Cooling (Theory of Porous Plug Experiment)

Theory

The simple arrangement of the Joule-Thomson porous plug experiment is shown in Fig. 2.16. The gas is allowed to pass through the porous plug from the high pressure side to the low pressure side. Due to this large difference of pressure, the gas flows through the fine pores and becomes throttled or wire drawn, *i.e.* the molecules of the gas are further drawn apart from one another.

2.25 Relation between Boyle Temperature, Temperature of Inversion and Critical Temperature

Temperature of inversion,

$$T_i = \frac{2a}{Rb} \qquad \text{...(2.16)}$$

Boyle temperature,

$$T_B = \frac{a}{Rb} \qquad \text{...(2.17)}$$

Critical temperature,

$$T_c = \frac{8a}{27\,Rb} \qquad \text{...(2.18)}$$

From (2.16) and (2.17), we have

$$T_i = 2\,T_B$$

From (2.16) and (2.18), we have

$$\frac{T_i}{T_c} = \frac{2a}{Rb} \cdot \frac{27\,Rb}{8a}$$

$$= \frac{27}{4} = 6.75 \qquad \text{...(2.19)}$$

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.

Since ratio $\frac{T_i}{T_c}$ is a number (*i.e.*, 6.75) from equation 2.19, the ratio of temperature of inversion and critical temperature does not depend upon the nature of the gas.

between Joule Expansion, Joule