B.Sc. (Honours) Part-I
Paper-IA

Topic: Gaseous State- Van Der Waals Equations and other related terms

UG
Subject-Chemistry

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$$\frac{v_{SO_2}}{v_{CH_4}} = \sqrt{\frac{m_{CH_4}}{m_{SO_2}}}$$

$$= \sqrt{\frac{16}{64}} = \frac{1}{2} \;]$$

4.9 VAN DER WAALS' EQUATION

The gas which conforms to all of the postulates of kinetic theory or which obeys Boyle's law and Charles' law rigidly for all values of temperature and pressure or which strictly follows the general gas equation ($PV = nRT$) is called **ideal** or **perfect gas.** Actually no gas is ideal or perfect in nature. Under ordinary conditions, only those gases nearly behave as ideal or perfect which have very low boiling points such as nitrogen, hydrogen, etc.

At low pressure and moderately high temperature, the real gases approach ideal behaviour (see fig.).

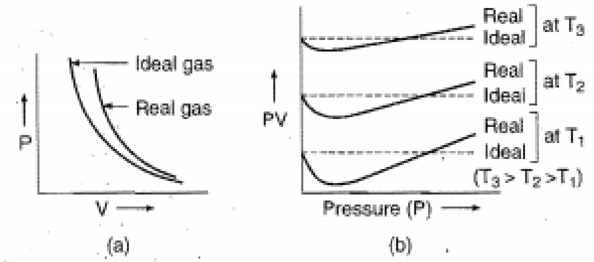


Fig. 4.9 (a) Ideal and real gas, (b) Ideal and real gas (real gas is approaching ideal behaviour with rise in temperature)

It is observed that deviations from gas laws are high under high pressure and low temperature. van der Waals suggested that these deviations are due to the following two faulty assumptions in the kinetic theory of gases:

(i) Actual volume of the gas molecules is negligible as compared to the total volume of the gas.

(ii) Intermolecular attractions are not present in gases.

van der Waals pointed out that in the case of real gases, molecules do have a volume and also exert intermolecular attractions especially when the pressure is high and temperature is low. He applied two corrections:

(a) Volume correction: van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume. Thus, the volume of a real gas, *i.e.*, volume available for compression or movement is, therefore, actual volume minus the volume occupied by gas molecules. If b is the effective volume of the molecules per mol of the gas, the ideal volume for the gas equation is $(V - b)$ and not V, *i.e.*,

corrected volume 'V_i' $= V - b$ for one mole of the gas

and for n mole of the gas, 'V_i' $= V - nb$.

b is termed the excluded volume which is constant and characteristic for each gas. The excluded volume 'b' is actually four times the actual volume of the gas molecules.

$$b = \left[\frac{4}{3}\pi r^3\right] \times 4N$$

where 'r' = radius of gas molecule

N = Avogadro's number

(b) Pressure correction: A molecule in the interior of the gas is attracted by other molecules on all sides. These forces, thus, are not effective, as equal and opposite forces cancel each other. However, a gas molecule which is just going to strike the wall of the vessel experiences an inward pull due to unbalanced attractive forces. Therefore, it strikes the wall with less momentum and the observed pressure will be less than the ideal pressure.

$$P_{\text{ideal}} = P_{\text{obs}} + P'$$

where P' is the pressure correction.

Pressure Correction Depends upon Two Factors

(i) The attractive force exerted on a single molecule about to strike the wall is proportional to the number of molecules per unit volume in the bulk of the gas.

(ii) The number of molecules striking the wall which is also proportional to the number of molecules per unit volume of the gas.

Both these factors are proportional to the density of the gas. Therefore, the attractive force is proportional to the square of the density of the gas.

$$P' \propto \text{total attractive force}$$

$$\propto d^2$$

$$\propto \frac{1}{V^2}$$

or $$P' = \frac{a}{V^2}$$

where 'a' is a constant depending upon the nature of the gas and V is the volume of 1 mole of the gas.

Thus, corrected pressure, $P_{\text{ideal}} = P_{\text{obs}} + \frac{a}{V^2}$

Making both the corrections, the general gas equation $PV = RT$ may be written as:

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

The equation is called van der Waals' equation. van der Waals' equation for n moles of the gas is:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

van der Waals' equation is obeyed by real gases over a wide range of temperature and pressure and hence this equation is called equation of state for the real gases. The constants 'a' and 'b' are called van der Waals' constants and they are characteristic of each gas.

Unit of van der Waals' Constants

a and b are expressed in terms of the units of P and V.

$$\text{Pressure correction } P' = \frac{n^2 a}{V^2}$$

$$a = \frac{P'V^2}{n^2} = \frac{\text{Pressure correction} \times (\text{Volume})^2}{(\text{Mole})^2}$$

Thus, if pressure and volume are expressed in atmosphere and litre respectively, the units of constant 'a' will be atmosphere litre^2 mol^{-2}.

$$\text{SI unit, '}a\text{'} = \text{N m}^4 \text{ mol}^{-2}$$

'b' is the effective volume of the gas molecules in one gram mole of the gas. Thus, the unit of 'b' is the same as for the volume, *i.e.*, litre mol^{-1}.

$$\text{SI unit, '}b\text{'} = \text{m}^3 \text{ mol}^{-1}$$

Boyle temperature: The temperature at which real gas behaves like ideal gas and obeys the gas laws over a wide range of pressure is called Boyle temperature 'T_b'. At this temperature, PV remains constant for an appreciable range of pressure

$$T_b = \frac{a}{Rb} = \frac{1}{2T_i}$$

where, T_i = inversion temperature

a, b = van der Waals' constants

At Boyle temperature, $\frac{\partial PV}{\partial P} = 0$ when P approaches zero.

4.10 CRITICAL PHENOMENON AND LIQUEFACTION OF GASES

During the early part of nineteenth century, a number of gases such as carbon dioxide, sulphur dioxide, ammonia, etc. were liquefied by subjecting the gas to low temperature and high pressure. On cooling, the kinetic energy of the gas molecules decreases. The slow moving molecules come nearer to each other due to forces of attraction and, thus, aggregate and are converted into liquid. The increase of pressure can also bring the gas molecules closer to each other and, thus, is helpful in converting a gas into liquid. The effect of temperature is rather more important than that of pressure. The essential conditions for liquefaction of gases were discovered by **Andrews** in 1869 as a result of his study of Pressure-Volume-Temperature (P-V-T) relationship for carbon dioxide. It was found that above a certain temperature, it was impossible to liquefy a gas whatever the pressure was applied. **The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature** (T_c). The pressure required to liquefy a gas at this temperature is called the **critical pressure** (P_c). The volume occupied by one mole of the substance at the critical temperature and pressure is called **critical volume** (V_c).

The results of Andrews experiments are shown in the following Figure. 4.10(a) in which the pressure is plotted against volume at various temperatures for carbon dioxide. Each pressure-volume plot is called isotherm.

Let us consider an isotherm at 13.1°C. At low pressure, carbon dioxide is entirely gaseous and is represented by the point (A) in the isotherm. On increasing pressure, volume decreases as shown by the portion AX of the isotherm, approximately in accordance with Boyle's law. At X, deviations from Boyle's law begin to appear and the volume decreases rapidly as the gas is converted into liquid. At point Y, carbon dioxide has been completely liquefied. Between X and Y, pressure remains constant and both the gas and liquid phases are in equilibrium. The pressure corresponding to the horizontal portion XY of the isotherm is the vapour pressure of the liquid at the temperature of the isotherm.

The isotherm at 21.5°C shows a similar behaviour except that liquefaction starts at higher pressure and the horizontal portion MN is shorter. As the temperature is raised, the horizontal portion of the isotherm becomes smaller and smaller until at 31.1°C at which it reduces to a point P. Point P is called **critical point;** at this point the boundary between liquid and gas phase (meniscus) disappears indicating that both the phases have identical characteristics. Above 31.1°C, there is no indication of liquefaction. The isotherm at critical temperature 31.1°C is called **critical isotherm.** The tangent at critical point P is horizontal, so that, $\frac{dP}{dV}$ at critical point will be zero. Thus, the point 'P' is also called the **point of inflection.**

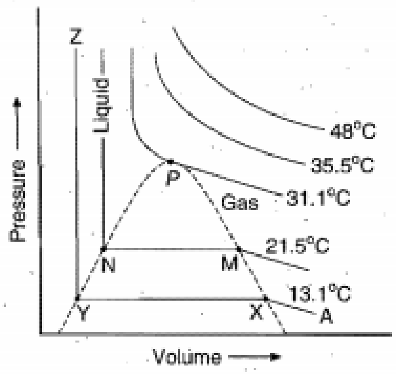


Fig. 4.10 (a) Isotherms of carbon dioxide showing critical region

It may be concluded from this explanation that in the area to the left of the dotted line below the critical isotherm, only liquid carbon dioxide exists. To the right of the dotted line, only gaseous carbon dioxide exists. The horizontal portion, within the dotted line shows the equilibrium between gas and liquid phase.

The van der Waals' Equation and the Critical Constants

The van der Waals' equation for 1 mole of a gas is given by:

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

This equation may be written as,

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

or $$PV^3 + aV - PbV^2 - ab - RTV^2 = 0$$

Dividing above equation by 'P', we get

$$V^3 + \frac{aV}{P} - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0$$

Arranging in descending powers of V, we get

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{aV}{P} - \frac{ab}{P} = 0 \qquad \text{... (i)}$$

Equation (i) is a cubic equation in 'V' and therefore for any value of P and T, it will have three values of V, all of which may be real or one may be real and the other two imaginary. When pressure *versus* volume plots are constructed using equation (i) we get the curves as shown in Fig. 4.10(b).

It is evident from the Fig. 4.10 (b) that the curves at and above the critical temperature are similar to those in Fig. 4.10 (a). However, below critical temperature, the horizontal portion determining the coexistence of gas and liquid is replaced by a (~) shaped curve ABC in Fig. 4.10(b). Thus, this curve predicts that there are three values of V corresponding to the points A, B and C. At the critical point 'P', the three roots of van der Waals' equation are not only real and positive but also identical and equal to the critical value V_c. This condition may be expressed as,

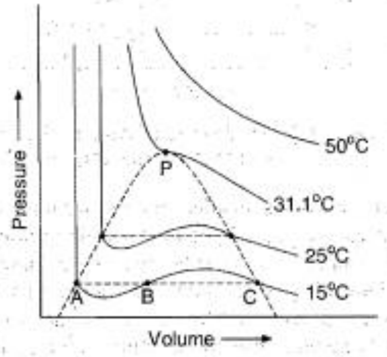


Fig. 4.10 (b) **Isotherms of carbon dioxide according to van der Waals' equation**

$$V = V_c$$

or $$V - V_c = 0$$

$$(V - V_c)^3 = 0$$

$$\therefore \quad V^3 - 3V_cV^2 + 3VV_c^2 - V_c^3 = 0 \qquad \text{... (ii)}$$

At critical point, equations (i) and (ii) must be identical. Comparing and equating the coefficients of like powers of V gives:

$$3V_c = b + \frac{RT_c}{P_c} \qquad \text{... (iii)}$$

$$3V_c^2 = \frac{a}{P_c} \qquad \text{... (iv)}$$

$$V_c^3 = \frac{ab}{P_c} \qquad \text{... (v)}$$

In above equations, $T = T_c$, $P = P_c$ at critical state.

Dividing equation (v) by (iv), we get,

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

i.e., $$V_c = 3b \qquad \text{... (vi)}$$

Substituting the value of V_c from eq. (vi) in (v), we get

$$(3b)^3 = \frac{ab}{P_c}$$

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

Finally, substituting the values of P_c and V_c in eq. (iii), we get

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

We can express the constants a, b and R in terms of critical constants as:

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

$$a = 3P_cV_c^2$$

$$R = \frac{8P_cV_c}{3T_c}$$

$$P_cV_c = \frac{3}{8}RT_c \qquad \text{...(ix)}$$

Equation (ix) is called equation of critical state. Critical compressibility factor of a gas may be calculated as,

$$Z_c = \frac{P_cV_c}{RT_c} = \frac{\left(\frac{a}{27b^2}\right)(3b)}{R\left(\frac{8a}{27Rb}\right)} = 0.375$$

Critical constants of gases

Gas	P_c (atm)	V_c (cm^3 mol^{-1})	T_c (K)
He	2.3	57.8	5.3
H_2	12.8	65	33.2
Ne	26.9	41.7	44.4
N_2	33.6	90.1	126.1
O_2	50.3	74.4	154.5
CO_2	72.7	95.0	304.2
H_2O	218.0	55.6	647.3
NH_3	112.0	72.0	405.5
CH_4	45.8	99.0	191.0
C_2H_6	48.2	139.0	305.5
C_2H_4	50.5	124.0	417.2

4.10.1 EXPERIMENTAL METHODS FOR LIQUEFACTION OF GASES

Discovery of critical phenomenon by Andrews in 1869 showed that gases cannot be liquefied by the application of pressure alone; they must first be cooled below their critical temperatures and then subjected to adequate pressure to cause liquefaction.

Principles involved in liquefaction are:

(1) A gas must be at or below its critical temperature. Lower the temperature below the critical value, easier would be the liquefaction.

(2) The gas is cooled either by doing external work or by expanding against the internal forces of molecular attraction.

Low temperature for liquefaction of gases can be achieved by the following techniques:

(a) Cooling by rapid evaporation of a volatile liquid.

(b) Cooling by Joule-Thomson effect.

(c) Cooling by adiabatic expansion involving mechanical work.

(a) Cooling by Rapid Evaporation of a Volatile Liquid

This method was first employed by **Pictet** and **Cailletet.** An easily volatile liquid is rapidly evaporated to cool and liquefy a less volatile liquid. This is the principle underlying the cascade process [Fig. 4.11(a)] for liquefaction of O_2.

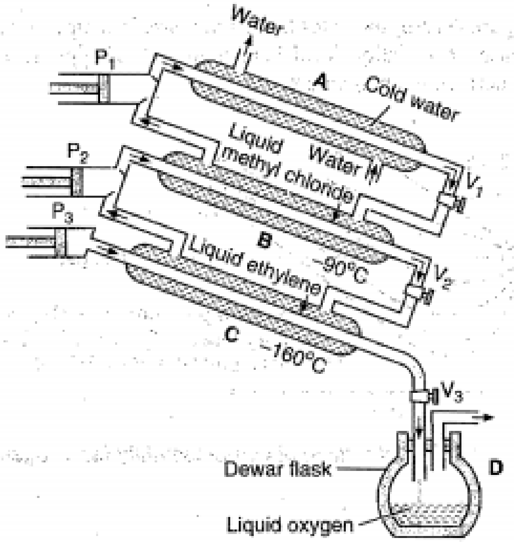


Fig. 4.11 (a) Cascade process for the liquefaction of oxygen

The apparatus consists of three compression pumps P_1, P_2 and P_3 and three compression chambers A, B and C. The compression pumps are joined in series. The pump P_1 compresses methyl chloride gas which is cooled by cold water circulating in outer jacket of A. As the critical temperature of methyl chloride is 143°C, it is liquefied at room temperature. The liquid methyl chloride passes through valve V_1 into the outer jacket of B which is connected to the suction side of P_1. As a result of reduced pressure, the liquid methyl chloride evaporates and the temperature in B reaches −90°C.

The inner tube of B is filled with ethylene gas which is cooled to −90°C. As the critical temperature of ethylene is 10°C, it gets liquefied and passes through valve V_2 into the outer jacket of C. Ethylene liquid is allowed to evaporate under reduced pressure with the help of pump P_2 resulting in a sharp fall in the temperature of oxygen (−118°C) which is filled in the inner tube of C. Oxygen gets liquefied during the compression stroke of pumps P_3 and is collected in the Dewar flask D.

(b) Cooling by Joule-Thomson Effect
(Linde's process for liquefaction of air)

When a compressed gas is allowed to expand into a low pressure or vacuum under adiabatic conditions, a lowering of temperature is observed. This is known as Joule-Thomson effect. In the expansion, molecules of the gas move far apart from one another. Work is done by the gas molecules to overcome intermolecular forces. Work is done at the cost of the kinetic energy of gas molecules. Consequently a cooling effect is observed. For each gas, there is a characteristic temperature above which a gas on expansion shows a heating effect while below it the gas cools on expansion. This temperature is known as **inversion temperature** of the gas. This temperature is related to van der Waals' constant a and b by the expression:

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

where, T_i is the inversion temperature of the gas.

Gases like H_2 and He have low inversion temperatures ($T_{i\,H_2} = 193$ K and $T_{i\,He} = 33$ K) and they show heating effects in Joule-Thomson expansion under ordinary temperature. If these gases are cooled below their inversion temperatures, they also show cooling effects.

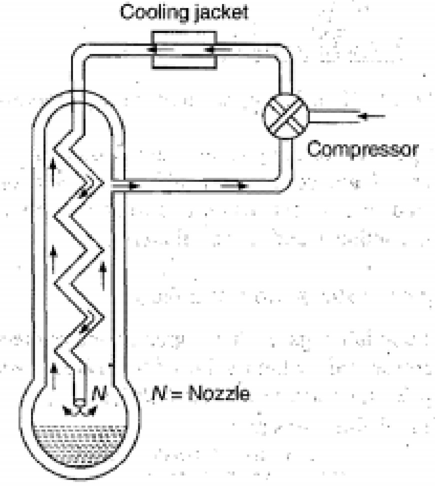


Fig. 4.11 (b) Linde's process for liquefaction of air

Joule-Thomson effect is the basis for liquefaction of air by Linde's process. The apparatus is shown in Fig. 4.11 (b).

Pure and dry air is compressed to a pressure of about 200 atm. Any heat produced during the compression is removed by passing the gas through a cooling jacket. Compressed air is allowed to expand suddenly through a nozzle (N) to a large chamber, where it gets cooled and the pressure reduced to about 1 atmosphere. The cooled air is made to pass through the outer tube and is sent back to the compressor. The incoming air further cools on expansion. The process is continued until air liquefies and is collected at the bottom.

(c) Cooling by Adiabatic Expansion Involving Mechanical Work

When a gas is allowed to expand adiabatically against a pressure, it does some external work at the cost of its kinetic energy, due to which its temperature falls. This principle is used in Claude's process for liquefaction of air. The apparatus is shown in Fig. 4.11 (c).

Pure and dry air is compressed to about 200 atmospheric pressure and then passed through the tube *T*. Compressed air divides itself into two parts at '*A*' and a portion enters through '*C*' fitted with an airtight piston. There, it expands, pushing the piston outward and performs some external work.

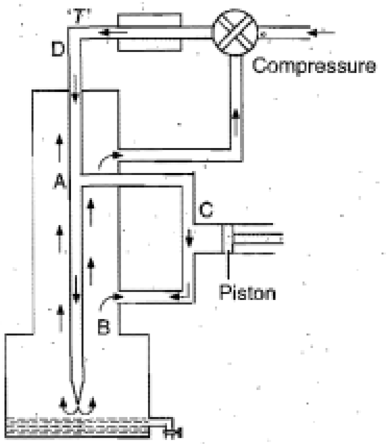


Fig. 4.11 (c) Claude's apparatus for liquefaction of air

The temperature of the gas thus falls. Cooled air then enters the chamber at *B* and cools the incoming air. The temperature of air is also reduced on expansion due to Joule-Thomson effect. The process continues until the air liquefies.

Tendency of Liquefaction of a Gas

Easily liquefiable gases have greater intermolecular force which is represented by high value of '*a*'. *Thus, greater will be the value of 'a' more will be its liquefiability.*

Easily liquefiable gases are:

$$\xrightarrow[\substack{\text{Decreasing value of constant '}a\text{'}\\ \text{(Decreasing tendency of liquefiability)}}]{SO_2 > NH_3 > H_2O > CO_2,\text{ etc.}}$$

Above gases have higher value of '*a*' as compared to the permanent gases O_2, N_2, H_2, He, Ne, etc.

Incompressibility of a Gas

van der Waals' constant '*b*' represents the excluded volume, *i.e.*, four times the volume occupied by the gas per mole. Value of '*b*' remains constant over a wide range of temperature and pressure which implies that gas molecules are incompressible.

Compressibility factor: Mathematically, it may be defined as,

$$Z = \frac{PV}{nRT}$$

The extent to which a real gas departs from ideal behaviour is expressed in terms of compressibility factor.

$$Z = \frac{\text{Molar volume of real gas } (V_m)}{\text{Molar volume of ideal gas } (V_m)} = \frac{PV_m}{RT}$$

When $Z > 1, V_m > 22.4$ L at STP and when $Z < 1, V_m < 22.4$ L at STP.

(i) $Z = 1$ for ideal gas. Deviation from the unity indicates extent of imperfection or non-ideality.

(ii) Real gases have $Z \approx 1$ at low pressure and high temperature. In this case, the real gas behaves like ideal gas.

(iii) $Z > 1$ shows that it is difficult to compress the gas as compared to ideal gas. It is possible at high pressure. In this case, repulsive forces dominate.

(iv) $Z < 1$ shows that the gas is easily compressible as compared to ideal gas. It is possible at intermediate pressure. In this case, attractive forces are dominant.

Plots of Compressibility Factor against Pressure

Figure 4.12(b) indicates that an increase in temperature shows decrease in deviation ideal behaviour, *i.e.*, *Z* approaches unity with increase in temperature.

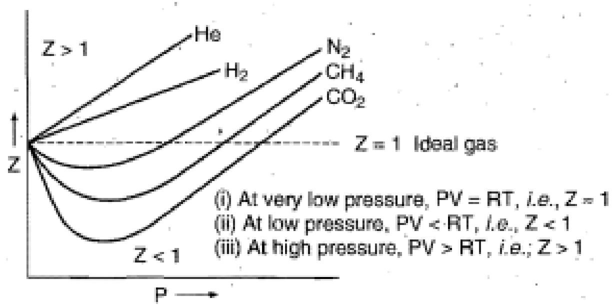


Fig. 4.12(a) Variation of compressibility factor against

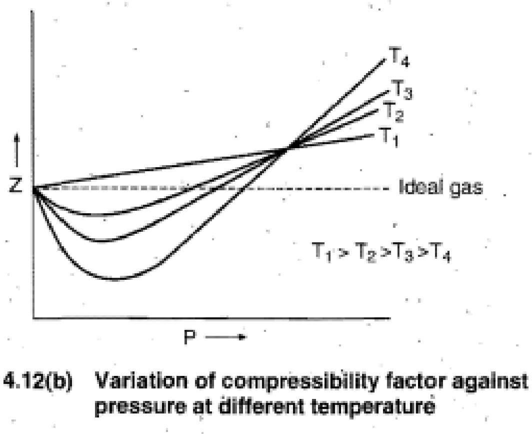


Fig. 4.12(b) Variation of compressibility factor against pressure at different temperature

Note: (i) In case of H_2, $Z > 1$ at 273 K and *Z* increases with the pressure. When temperature is less than 273 K, H_2 has $Z < 1$.

(ii) For gases other than hydrogen, at 273 K there is decrease in '*Z*' at initial stage, with increase in pressure, value of '*Z*' approaches a minimum, with increase in pressure.

(iii) In case of easily liquefiable gas like CO_2, Z dips largely below ideal line in low pressure region, see Fig. 4.12 (a).

Specific Heat of Gases

Amount of heat required to raise the temperature of 1 g of a substance through 1°C is called its specific heat. It can be measured at constant pressure and at constant volume.

Molar specific heat, *i. e.*, heat required to raise 1 gram mole of a substance through 1°C is called heat capacity.

Heat Capacity at Constant Volume

It is denoted by C_V. It may the heat supplied to one mole of a substance to increase the temperature through 1°C at constant volume.

We know from kinetic theory that,

$$PV = \frac{1}{3}mnc^2 \quad \text{or} \quad \frac{1}{2}mnc^2 = \frac{3}{2}RT$$

Thus, kinetic energy $E = \frac{3}{2}RT$

When temperature is raised through 1°C then the increase in kinetic energy may be given as:

$$\text{Increase in kinetic energy} = \frac{3}{2}R(T+1) - \frac{3}{2}RT = \frac{3}{2}R$$

Now, $C_V = \frac{3}{2}R$ since at constant volume, heat supplied to raise the temperature is used up to increase the kinetic energy only.

$C_V = \frac{3}{2}R$ [for monoatomic gases only, since monoatomic gases undergo translational motion only]

$C_V = \frac{3}{2}R + x$ [for di and polyatomic molecules; vibrational and rotational motions also contribute to the total kinetic energy]

where factor 'x' varies from gas to gas and its value is zero for monoatomic gases.

Heat Capacity at Constant Pressure

It is denoted by C_P; it may be defined as heat supplied to 1 mole of a substance in order to increase the temperature through 1°C at constant pressure.

Heat supplied at constant pressure will be used in:

(i) Increasing kinetic energy, which is equal to $\frac{3}{2}R + x$. For monoatomic gas increase in kinetic energy is equal to $\frac{3}{2}R$ when temperature is raised through 1°C.

(ii) Doing work due to volume expansion.

We know that, $PV = RT$ for 1 mole of gas ... (i)

When temperature changes to $(T+1)$, then

$$P(V + \Delta V) = R(T+1) \qquad \text{... (ii)}$$

Subtracting eq. (i) from eq. (ii), we have

$$P\Delta V = R = \text{Work done due to volume expansion}$$

Thus, $C_P = \frac{3}{2}R + R = \frac{5}{2}R$ for monoatomic gases

$$C_P = C_V + R \quad \text{or} \quad C_P - C_V = R \qquad \text{(general equation)}$$

Ratio of Molar Heat Capacity

It is denoted as γ and it represents atomicity of the gas.

$$\text{For monoatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$$

$$\text{For diatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$$

$$\text{For triatomic gas, } (\gamma) = \frac{C_P}{C_V} = \frac{4R}{3R} = 1.33$$

Name	C_P	C_V	$C_P - C_V$	$C_P/C_V = \gamma$	Atomicity
He	5	3.01	1.99	1.661	1
N_2	6.95	4.96	1.99	1.4	2
O_2	6.82	4.83	1.99	1.4	2
CO_2	8.75	6.71	2.04	1.30	3
H_2S	8.62	6.53	2.09	1.32	3

Example 46. *Specific heat of a monoatomic gas at constant volume is 315 $J\ kg^{-1}\ K^{-1}$ and at a constant pressure is 525 $J\ kg^{-1}\ K^{-1}$. Calculate the molar mass of the gas.*

Solution: $C_P = M \times 525$ and $C_V = M \times 315$

where, M is the molecular mass.

$$C_P - C_V = R \ (R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1})$$

$$M \times 525 - M \times 315 = 8.314$$

$$M\ (525 - 315) = 8.314$$

$$M = \frac{8.314}{210} = 0.0396\ \text{kg mol}^{-1} = 39.6\ \text{g mol}^{-1}$$

Example 47. *Calculate the pressure exerted by 16 g of methane in a 250 mL container at 300 K using van der Waals' equation. What pressure will be predicted by ideal gas equation?*

$a = 2.253\ atm\ L^2\ mol^{-2}$, $b = 0.0428\ L\ mol^{-1}$,

$R = 0.0821\ L\ atm\ K^{-1}\ mol^{-1}$

Solution: Given, $16\text{ g } CH_4 = \frac{16}{16} = 1\text{ mole}$

Applying van der Waals' equation,

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)} - \frac{n^2a}{V^2}$$

Substituting $n = 1$,

$R = 0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1}$; $T = 300$ K; $V = 0.250$ L;

$a = 2.253\ \text{atm L}^2\ \text{mol}^{-2}$; $b = 0.0428\ \text{L mol}^{-1}$

$$P = \frac{1\times 0.0821\times 300}{(0.250-1\times 0.0428)} - \frac{1\times 2.253}{(0.250)^2} = 82.822 \text{ atm}$$

The ideal gas equation predicts that,

$$P = \frac{nRT}{V} = \frac{1\times 0.0821\times 300}{0.250} = 98.52 \text{ atm}$$

Example 48. *Calculate the temperature of the gas if it obeys van der Waals' equation from the following data. A flask of 2.5 litre contains 10 mole of a gas under 50 atm. Given $a = 5.46$ atm litre^2 mol^{-2} and $b = 0.031$ litre mol^{-1}.*

Solution: Given that,

$P = 50$ atm; $V = 2.5$ litre, $n = 10$; $a = 5.46$ atm litre^2 mol^{-2};

$b = 0.031$ litre mol^{-1}; $R = 0.0821$ litre-atm K^{-1} mol^{-1}.

Applying van der Waals' equation,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

or

$$T = \frac{\left(P + \frac{an^2}{V^2}\right)(V - nb)}{nR}$$

$$= \frac{\left(50 + \frac{5.46\times 100}{(2.5)^2}\right)(2.5 - 10\times 0.031)}{10\times 0.0821} = 366.4 \text{ K}$$

ILLUSTRATIONS OF OBJECTIVE QUESTIONS

23. At high temperature and low pressure, the van der Waals' equation is reduced to:

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

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

[Ans. (b)]

[Hint: At high temperature and low pressure, V is large in comparison to 'b' and $\left(\frac{a}{V^2}\right)$ is negligible in comparison to P. Hence, the equation reduces to $PV = RT$.]

24. The constant 'a' in van der Waals' equation is maximum in:

(a) He (b) H_2

(c) O_2 (d) NH_3

[Ans. (d)]

[Hint: Intermolecular force of NH_3 is maximum, hence its van der Waals' constant (a) will also be maximum.]

25. The van der Waals' equation for 0.5 mol gas is:

(a) $\left(P + \frac{a}{4V^2}\right)\left(\frac{V - b}{2}\right) = \frac{2RT}{2}$

(b) $\left(P + \frac{a}{4V^2}\right)(2V - b) = RT$

(c) $\left(P + \frac{a}{4V^2}\right)(2V - 4b) = RT$

(d) $\left(P + \frac{a}{4V^2}\right) = \frac{2RT}{2(V - b)}$

[Ans. (b)]

[Hint: $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

For $n = \frac{1}{2}$, $\left(P + \frac{a}{4V^2}\right)\left(V - \frac{b}{2}\right) = \frac{1}{2}RT$

$\left(P + \frac{a}{4V^2}\right)(2V - b) = RT$]

26. van der Waals' constants of two gases X and Y are as given:

	a (litre-atm mol^{-2})	b (litre mol^{-1})
Gas X	5.6	0.065
Gas Y	5.1	0.012

What is correct about the two gases?

(a) $T_c(X) > T_c(Y)$ (b) $T_c(X) = T_c(Y)$

(c) $V_c(X) > V_c(Y)$ (d) $V_c(Y) > V_c(X)$

[Ans. (c)]

[Hint: Gas X Gas Y

$V_c = 3b$ $3\times 0.065 = 0.195$ $3\times 0.012 = 0.036$]

27. Select the correct statements about van der Waals' constant 'b':

1. It is excluded volume
2. Its unit is mol litre^{-1}
3. It depends on intermolecular force
4. Its value depends on molecular size

(a) 2, 3 (b) 1, 2, 4 (c) 2, 3, 4 (d) 3, 4

[Ans. (b)]

28. Gases X, Y, Z, P and Q have the van der Waals' constants 'a' and 'b' (in CGS units) as shown below:

	X	Y	Z	P	Q
a	6	6	20	0.05	30
b	0.025	0.15	0.1	0.02	0.2

The gas with the highest critical temperature is:

[PET (Kerala) 2006]

(a) P (b) Q (c) Y (d) Z

(e) X

[Ans. (e)]

[Hint: Critical temperature, $T_c = \frac{8a}{27Rb}$

$\therefore$ Greater is the value of (a/b), more is the critical temperature of gas.

For gas X, T_c will be maximum.

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

$\frac{a}{b}$ for $X = \frac{6}{0.025} = 240$; for all other gases, $\left(\frac{a}{b}\right)$ is lesser.]

29. At high pressure, van der Waals' equation becomes:

(DPMT 2006)

(a) $PV = RT$ (b) $PV = RT + \frac{a}{V}$

(c) $PV = RT - \frac{a}{V}$ (d) $PV = RT + Pb$

[Ans. (d)]

[**Hint:** $\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ for 1 mol gas}$$

At high pressure, $\left(P + \frac{a}{V^2}\right) = P$

$$\therefore \quad P(V - b) = RT$$

$$PV = RT + Pb]$$

SOME SOLVED EXAMPLES

Example 49. *Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour of gases.*

Given that, $R = 0.082$ *litre − atm* K^{-1} *mol*$^{-1}$. **(IIT 1997)**

Solution:

$$n_{He} = \frac{0.4}{4} = 0.1, \; n_{O_2} = \frac{1.6}{32} = 0.05$$

$$n_{N_2} = 1.4 / 28 = 0.05$$

$$P_{He} \times V = n_{He} \times R \times T$$

$$P_{He} \times 10 = 0.1 \times 0.0821 \times 300$$

$$P_{He} = 0.2463 \text{ atm}$$

$$P \times V = (n_{He} + n_{O_2} + n_{N_2})RT$$

$$P \times 10 = (0.1 + 0.05 + 0.05) \times 0.0821 \times 300$$

$$P = 0.4926 \text{ atm}$$

Example 50. *An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98* g/mL^{-1} *and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.* **(IIT 1998)**

Solution: Mass of liquid = 148 − 50 = 98 g

$$\text{Volume of liquid} = \frac{\text{mass}}{\text{density}} = \frac{98}{0.98} = 100 \text{ mL}$$

Volume of vessel = Volume of liquid

Mass of gas = 50.5 − 50 = 0.5 g

On applying ideal gas equation, we have,

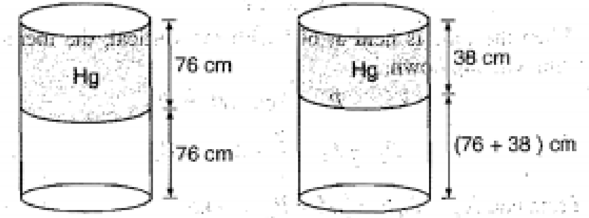
$$PV = \frac{w}{m}RT$$

$$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{m} \times 0.0821 \times 300$$

$$m = 123$$

Example 51. *A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible.*

Solution:



(Initial state) (After heating)

At initial stage:

Pressure of gas = Pressure of Hg + Pressure of atmospheric air

$$= 76 + 76 = 152 \text{ cm}$$

$$T = 300 \text{ K}$$

$$V = V_1 / 2 \text{ where, } V_1 \text{ is volume of cylinder.}$$

At final stage after heating:

Pressure of gas = Pressure of Hg + Pressure of atmospheric air

$$= 38 + 76 = 114 \text{ cm}$$

$$V = \frac{3V_1}{4}, \; T = ?$$

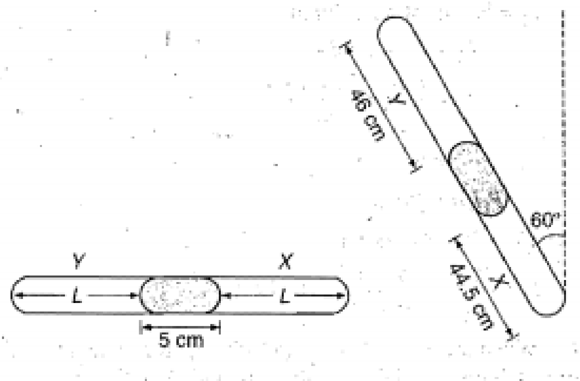
Applying gas equation, we have

$$\frac{152 \times V_1}{2 \times 300} = \frac{114 \times (3V_1/4)}{T}$$

$$T = \frac{114 \times 3 \times 2 \times 300}{4 \times 152}$$

$$= 337.5 \text{ K}$$

Example 52. *A thin tube of uniform cross-section is sealed at both ends. It lies horizontally, the middle 5 cm containing Hg and the two equal ends containing air at the same pressure* P_0. *When the tube is held at an angle 60° with the vertical, the lengths of the air column above and below the mercury are 46 and 44.5 cm respectively. Calculate pressure* P_0 *in cm of Hg. (The temperature of the system is kept at 30°C).*



Solution: At horizontal position, let the length of air column in tube be L cm.

$$\therefore \quad 2L + 5 = 46 + 5 + 44.5 \text{ cm}$$

$$L = 45.25 \text{ cm}$$

When the tube is held at 60° with the vertical, the mercury column will slip down.

$$P_Y + 5\cos 60° = P_X$$

$$P_X - P_Y = \frac{5}{2} = 2.5 \text{ cm Hg} \qquad \text{... (i)}$$

From end X, $\quad P_0 \times 45.25 = P_X \times 44.5$

$$P_X = \frac{45.25}{44.5} P_0 \qquad \text{.... (ii)}$$

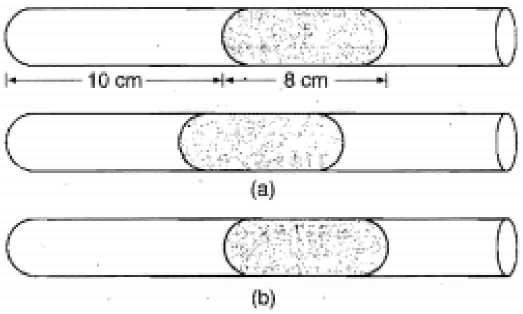
From end Y, $\quad P_0 \times 45.25 = P_Y \times 46$

$$P_Y = \frac{45.25}{46} P_0 \qquad \text{... (iii)}$$

Substituting the values of P_X and P_Y in equation (i) we get

$$P_0 = 75.4$$

Example 53. *A 10 cm column of air is trapped by a column of Hg, 8 cm long, in a capillary tube horizontally fixed as shown below, at 1 atm pressure. Calculate the length of air column when the tube is fixed at the same temperature (a) vertically with open end up (b) vertically with open end down (c) at 45° with the horizontal with open end up.*



Solution: (a) $P_1V_1 = P_2V_2$

or $\quad P_1 l_1 a = P_2 l_2 a$

where, a = area of cross section of tube

l_1, l_2 = length of air column

$$\because \quad P_2 = 76 + 8 = 84 \text{ cm}$$

$$\therefore \quad l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{84}$$

$$= 9.04 \text{ cm}$$

$$P_1 l_1 a = P_2 l_2 a$$

(b) $P_2 = 76 - 8 = 68$ cm

$$\therefore \quad l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{68} = 11.17 \text{ cm}$$

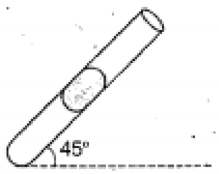
(c) When the tube is held at 45° with open end up, the weight of Hg is borne partially by the gas and partially by the Hg. Vertical height of Hg is a measure of additional pressure on gas, *i.e.,*

$$\therefore \quad l = \frac{8}{\sqrt{2}}$$

Also $\quad P_2 l_2 a = P_1 l_1 a$

$$\therefore \quad l_2 = \frac{P_1 l_1}{P_2}$$

$$= \frac{76 \times 10}{76 + \frac{8}{\sqrt{2}}} = 9.3 \text{ cm}$$



(c)

Example 54. *The stop cock connecting two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure in the two bulbs if the temperature remains the same?*

Solution: $\quad P_1V_1 + P_2V_2 = P_R(V_1 + V_2)$

$$9 \times 5 + 6 \times 10 = P_R(15)$$

$$P_R = 7 \text{ atm}$$

where, P_R = resultant pressure after mixing.

Example 55. *At what temperature is the average velocity of O_2 molecule equal to the root mean square velocity at 27°C?*

(BSE PMT 2005)

Solution: $\quad v_{av} = v_{rms}$

$$\sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{3RT}{M}}$$

$$\frac{8RT}{\pi M} = \frac{3R \times 300}{M}$$

$$T = 353.57 \text{ K}$$

$$t = 80.57° \text{ C}$$

Example 56. *The composition of the equilibrium mixture for the equilibrium $Cl_2 \rightleftharpoons 2Cl$ at 1400 K may be determined by the rate of diffusion of mixture through a pin hole. It is found that at 1400 K, the mixture diffuses 1.16 times as fast as krypton diffuses under the same conditions. Find the degree of dissociation of Cl_2 equilibrium.* **(IIT 1995)**

Solution: Equilibrium of dissociation of Cl_2 may be represented as:

$$\begin{array}{lcc} & Cl_2(g) \rightleftharpoons & 2Cl(g) \\ t=0 & a & 0 \\ t_{eq} & a(1-\alpha) & 2a\alpha \end{array}$$

$$\text{Total moles} = a(1-\alpha) + 2a\alpha = a(1+\alpha)$$

$$M_{mix} = \frac{aM_{Cl_2}}{a(1+\alpha)} = \frac{M_{Cl_2}}{(1+\alpha)}$$

$$\frac{R_{mix}}{R_{Kr}} = \sqrt{\frac{M_{Kr}}{M_{mix}}}$$

$$1.16 = \frac{84(1+\alpha)}{M_{Cl_2}}$$

$$\frac{(1.16)^2 \times 71}{84} - 1 = \alpha; \ \alpha = 0.1374$$