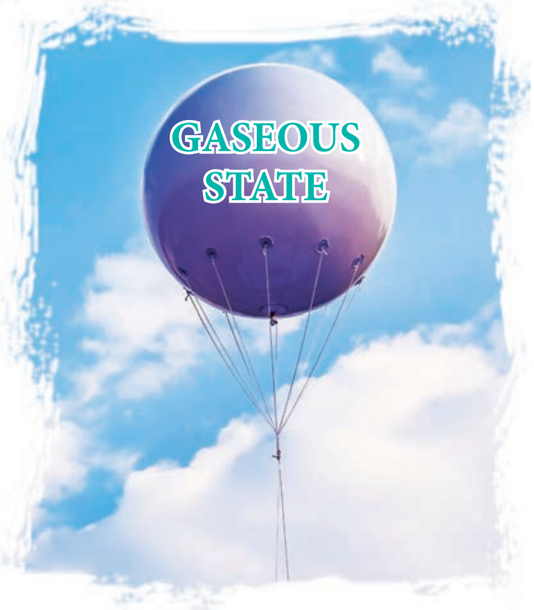
Unit 6

GASEOUS STATE

> So many properties of properties of matter, especially when in gaseous form, can be deduced from hypothesis that their minute parts are in rapid motion, the velocity increasing with temperature, that the precise nature of this motion becomes a subject of rational curiosity.
>
> James Clerk Maxwell



Jacques Charles
(1746-1823)

Learning Objectives

After studying this unit, students will be able to

- State the laws governing an ideal gas
- Demonstrate gas laws in various real life situations
- Derive ideal gas equation and perform calculations using it.
- State the deviations from ideal behavior
- Derive van der Waals equation.
- Define Graham's law of diffusion
- Define compressibility factor
- Explain critical phenomena
- Derive critical constants in terms of van der Waal's constants
- Explain Andrew's isotherms of carbon dioxide
- Describe Joule – Thomson effect and liquefaction of gases.

DECHM

6.1. Introduction

We can survive for weeks without food, days without water, but only minutes without air. Thus, we inhale a lungful of air every few seconds, keep some of the molecules for our own end, and some of the molecules that our body no longer needs, and exhale the mixture back into the surrounding air. The air around us is in the gaseous state, which is the simplest of the states of matter. Although the chemical behaviour of gases depends on their composition, all the gases have remarkably similar physical behaviour.

DO YOU KNOW?

Do you know the difference between gas and vapour?

Gas is a substance that is normally in a gaseous state at room temperature and 1 atm pressure, while vapour is the gaseous form of any substance that is a liquid or solid at room temperature and 1 atm pressure.

Earth is surrounded by an atmosphere of air whose composition in volume percentage is roughly 78 % nitrogen, 21 % oxygen and 1 % other gases. Of the known elements, only eleven are gases under normal atmospheric conditions. The elements hydrogen (H_2), nitrogen (N_2), oxygen (O_2), fluorine (F_2) and chlorine (Cl_2) exist as gaseous diatomic molecules. Another form of oxygen, namely, ozone (O_3) is also a gas at room temperature. The noble gases, namely, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) of 18th group are monatomic gases. Compounds such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen dioxide (NO_2) and nitric oxide (NO) also exist in gaseous state under normal atmospheric conditions. In this unit you will learn the properties of gases and other related phenomena.

6.2. The Gas Laws

The gas laws have played a major role in the development of chemistry. The physical properties of all gases are governed by the gas laws that were formulated based on the studies of the properties like pressure, volume, etc., as a function of temperature. Before studying the gas laws in detail, let us understand an important parameter, namely, the pressure.

Pressure is defined as force divided by the area to which the force is applied. The SI unit of pressure is pascal which is defined as 1 Newton per square meter (Nm^{-2}). There are other units that are commonly used and their relation with the SI unit is as follows.

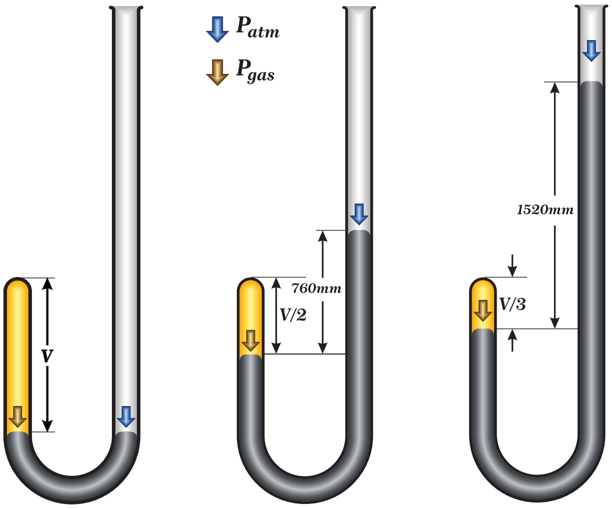
$$\text{Pressure} = \frac{\text{Force (N or kg m s}^{-2}\text{)}}{\text{Area (m}^2\text{)}}$$

Table 6.1 Units of pressure

Unit	Symbol	Value (Nm^{-2} or $kgm^{-1}s^{-2}$)
pascal	Pa	1 Pa = 1 Nm^{-2}
atmosphere	atm	1 atm = 101325 Pa
millimeter of mercury	mmHg	1 mmHg = 133.322 Pa
bar	bar	1 bar = 10^5 Pa
torr	Torr	1 Torr = 133.322 Pa
pound per square inch	psi	1 psi = 6894.76 pa

6.2.1 Boyle's Law: Pressure-Volume Relationship

Robert Boyle performed a series of experiments to study the relation between the pressure and volume of gases. The schematic of the apparatus used by him is shown in figure 6.1.



(a) (b) (c)

Figure. 6.1 Boyle's law experiment

Mercury was added through the open end of the apparatus such that the mercury level on both ends are equal as shown in the figure 6.1(a). Add more amount of mercury until the volume of the trapped air is reduced to half of its original volume as shown in figure 6.1(b). The pressure exerted on the gas by the addition of excess mercury is given by the difference in mercury levels of the tube. Initially the pressure exerted by the gas is equal to 1 atm as the difference in height of the mercury levels is zero. When the volume is reduced to half, the difference in mercury levels increases to 760 mm. Now the pressure exerted by the gas is equal to 2 atm. It led him to conclude that at a given temperature the volume occupied by a fixed mass of a gas is inversely proportional to its pressure.

Mathematically, the Boyle's law can be written as

$$V \alpha \frac{1}{P} \text{ ------- } (6.1)$$

(T and n are fixed, T-temperature, n- number of moles)

$$V = k \times \frac{1}{P} \text{ ------- } (6.2)$$

k – proportionality constant

When we rearrange equation 6.2.

$PV = k$ ------ (6.2a)(at constant temperature and mass)

Boyle's law is applicable to all gases regardless of their chemical identity (provided the pressure is low). Therefore, for a given mass of a gas under two different sets of conditions at constant temperature we can write

$$P_1V_1 = P_2V_2 = k \text{ ------ } (6.3)$$

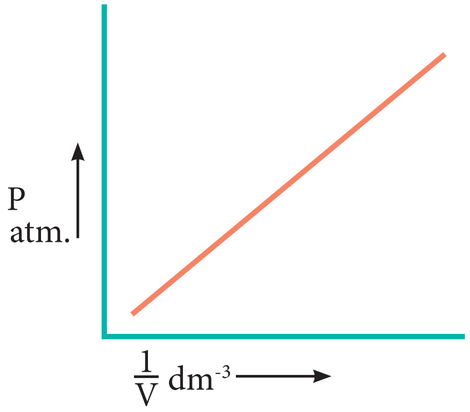


Figure. 6.2 a Graphical representation of Boyle's law (equation 6.2)

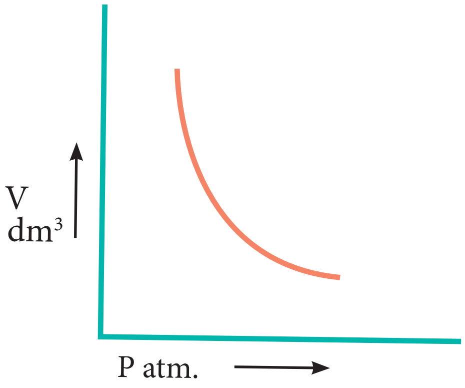


Figure. 6.2 b Graphical representation of Boyle's law (equation 6.2 a)

The PV relationship can be understood as follows. The pressure is due to the force of the gas particles on the walls of the container. If a given amount of gas is compressed to half of its volume, the density is doubled and the number of particles hitting the unit area of the container will be doubled. Hence, the pressure would increase twofold.

Consequence of Boyle's law

The pressure-density relationship can be derived from the Boyle's law as shown below.

$$P_1V_1 = P_2V_2 \quad \text{(Boyle's law)}$$

$$P_1\frac{m}{d_1} = P_2\frac{m}{d_2}$$

where "m" is the mass, d_1 and d_2 are the densities of gases at pressure P_1 and P_2.

$$\frac{P_1}{d_1} = \frac{P_2}{d_2} \quad \text{------ (6.4)}$$

In other words, the density of a gas is directly proportional to pressure.

All the passenger aeroplane cabins have to be artificially pressurised. do you know why?

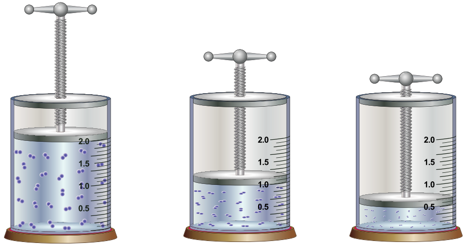
Most commercial aeroplanes fly at about 30,000 feet altitude. The pressure decreases with the increase in altitude as there are fewer molecules per unit volume of air. Hence, while at air, the pressure around the aeroplane will be so low that one could pass out for lack of oxygen. For this reason aeroplanes cabins are artificially pressurized.

Similarly, the effect of drop in pressure is felt as a little pain in the ears by a person while ascending a mountain in a plain. Though the external pressure drops, the internal pressure within the ear cavities remains the same. This creates an imbalance. The greater internal pressure forces the eardrum to bulge outward causing pain. The excess air within the ear cavities escapes after some time and with the help of yawning and thereby equalizing the internal and external pressure to relieve the pain.

Underwater divers are advised not to hold the breath unnecessarily while diving. Do you know why?

In figure (6.3) let us find the missing parameters (volume in 6.3 (b) and pressure in 6.3(c))

Fig. 6.3(a) Fig. 6.3 (b) Fig. 6.3(c)



$P_1 = 1$ atm. $V_1 = 1\ dm^3$ T = 298 K

$P_2 = 2$ atm. $V_2 = ?\ dm^3$ T = 298 K

$P_3 = ?$ atm. $V_3 = 0.25 dm^3$ T = 298 K

Figure. 6.3 Effect of pressure on volume of the gas to verify Boyle's law

Solution:

According to Boyle's law, at constant temperature for a given mass of gas at constant temperature,

$$P_1V_1 = P_2V_2 = P_3V_3$$

$$1\ \text{atm} \times 1\ \text{dm}^3 = 2\ \text{atm} \times V_2 = P_3 \times 0.25\ \text{dm}^3$$

$$\Psi\ 2\ \text{atm} \times V_2 = 1\ \text{atm} \times 1\ \text{dm}^3$$

$$V_2 = \frac{\cancel{1\ \text{atm}} \times 1\ \text{dm}^3}{\cancel{2\ \text{atm}}}$$

$$\boxed{V_2 = 0.5\ \text{dm}^3}$$

and $P_3 \times 0.25\ \text{dm}^3 = 1\ \text{atm} \times 1\ \text{dm}^3$

$$P_3 = \frac{1\ \text{atm} \times 1\ \cancel{\text{dm}^3}}{0.25\ \text{dm}^3}$$

$$\boxed{P_3 = 4\ \text{atm}}$$

Evaluate Yourself

1. Freon-12, the compound widely used in the refrigerator system as coolant causes depletion of ozone layer. Now it has been replaced by eco-friendly compounds. Consider 1.5 dm^3 sample of gaseous Freon at a pressure of 0.3 *atm*. If the pressure is changed to 1.2 *atm*. at a constant temperature, what will be the volume of the gas increased or decreased?

2. Inside a certain automobile engine, the volume of air in a cylinder is 0.375 dm^3, when the pressure is 1.05 *atm*. When the gas is compressed to a volume of 0.125 dm^3 at the same temperature, what is the pressure of the compressed air?

6.2.2 Charles Law (Volume-temperature relationship)

The relationship between volume of a gas and its temperature was examined by J. A. C. Charles. He observed that for a fixed mass of a gas at constant pressure, the volume is directly proportional to its temperature (K). Mathematically it can be represented as (at constant P and n)

$$V = kT \quad \text{-------}\ (6.5)$$

$$\text{or} \qquad \frac{V}{T} = \text{Constant}$$

If the temperature of the gas increases, the volume also increases in direct proportion, so that $\frac{V}{T}$ is a constant. For the same system at constant pressure, one can write

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \ \text{Constant -----}\ (6.6)$$

For example, if a balloon is moved from an ice cold water bath to a boiling water bath, the temperature of the gas increases. As a result, the gas molecules inside the balloon move faster and gas expands. Hence, the volume increases.

Ice water Boiling water

Figure. 6.4 Air filled balloon in ice cold and hot water

Variation of volume with temperature at constant pressure

The plot of the volume of the gas against its temperature at a given pressure is shown in the figure 6.5. From the graph it is clear that the volume of the gas linearly increases with temperature at a given pressure. Such lines are called isobars. It can be expressed by the following straight line equation.

V = mT + C where T is the temperature in degree Celsius and m & C are constants.

When T= 0 °C the volume becomes V_0. Hence, V_0 = C and slope of the straight line m is equal to ΔV / ΔT. Therefore the above equation can be written in the following form.

$$V = \left(\frac{\Delta V}{\Delta T}\right) T + V_0 \quad \text{-------} \ (6.7)$$

(n, P are constant)

Divide the equation 6.7 by V_o

$$\frac{V}{V_0} = \frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right) T + 1 \quad \text{--------} \ (6.8)$$

Charles and Gay Lussac found that under constant pressure, the relative increase in volume per degree increase in temperature is same for all gases. The relative increase in volume per ° C (α)is equal to $\frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right)$.

Therefore

$$\frac{V}{V_0} = \alpha T + 1$$

$$V = V_0 (\alpha T + 1) \quad \text{------} \ (6.9)$$

Charles found that the coefficient of expansion is approximately equal to 1/273. It means that at constant pressure for a given mass, for each degree rise in temperature, all gases expand by 1/273 of their volume at 0 °C

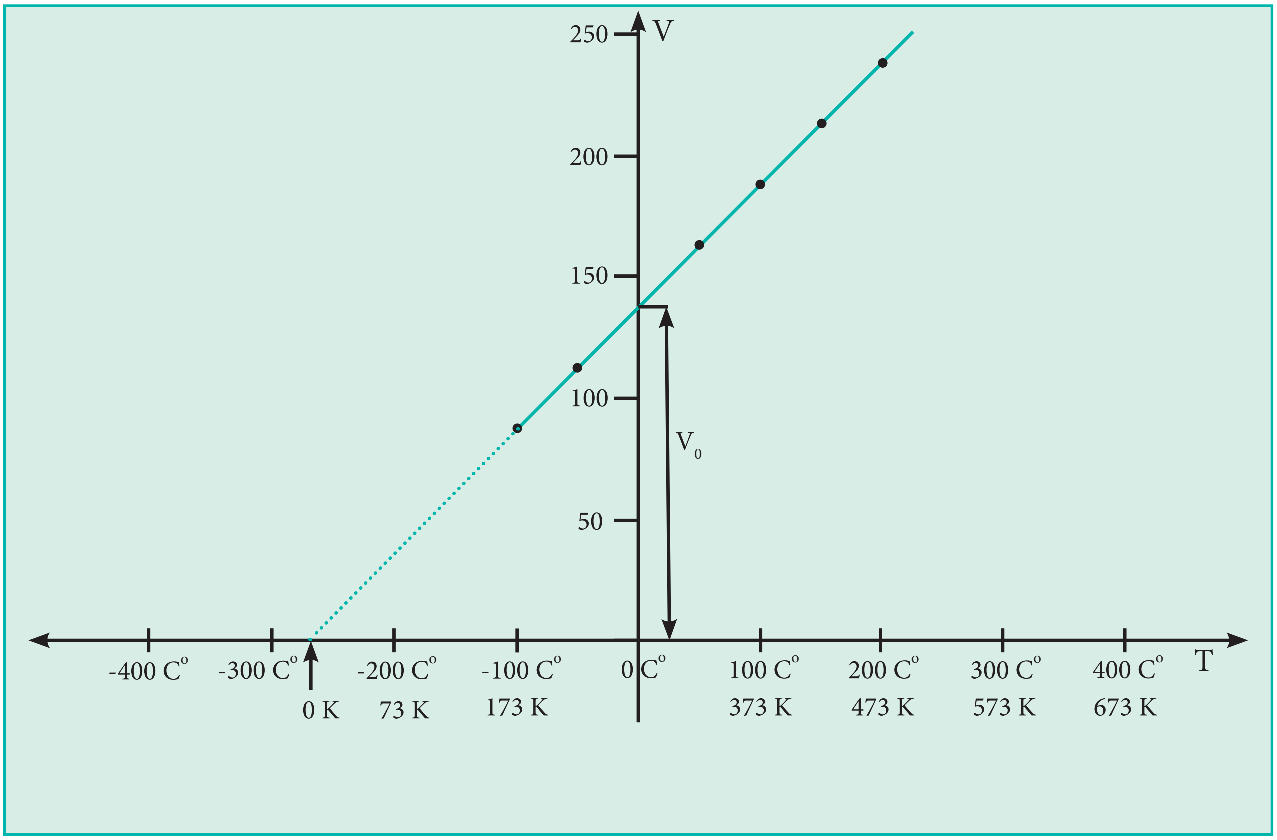


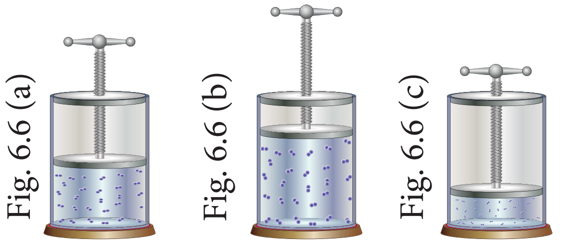
Figure. 6.5 Plot of volume vs temperature for an ideal gas

If we extrapolate the straight line in the figure 6.5 beyond the experimental measurements, the straight line intersects the temperature axis (x-axis) at -273⁰ C. This shows that the volume of the gas becomes zero at -273⁰ C, more precisely this temperature is -273.15⁰ C. Beyond this temperature the gas would have a negative volume which is physically impossible. For this reason, this temperature was defined as absolute zero by Kelvin and he proposed a new temperature scale with absolute zero as starting point which is now called Kelvin scale. The only difference between the Kelvin scale of temperature and Celsius scale of temperature is that the zero position is shifted. The boiling and freezing point of water in both scales are given below.

	Kelvin Scale	Celsius scale
Absolute Zero	0 K	-273.15 °C
Freezing point of water	273.15 K	0 °C
Boiling point of water	373.15 K	100 °C

Example:

In figure 6.6 let us find the missing parameters (volume in 6.6 (b) and temperature in 6.6(c))



P = 1 atm.
$V_1 = 0.3\ dm^3$
$T_1 = 200\ K$

P = 1 atm.
$V_2 = ?\ dm^3$
$T_2 = 300\ K$

P = 1 atm.
$V_3 = 0.15\ dm^3$
$T_3 = ?\ K$

Fig. 6.6. Effect of temperature on volume of the gas to verify Charles law

Solution:

According to Charles law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3}$$

$$\frac{0.3\ dm^3}{200\ K} = \frac{V_2}{300\ K} = \frac{0.15\ dm^3}{T_3}$$

$$\frac{V_2}{300\ K} = \frac{0.3\ dm^3}{200\ K}$$

$$V_2 = \frac{\overset{1.5}{\cancel{300\ K}} \times 0.3\ dm^3}{\cancel{200\ K}}$$

$V_2 = 0.45\ dm^3$ and

$$\frac{0.15 dm^3}{T_3} = \frac{0.3\ dm^3}{200\ K}$$

$$T_3 = \frac{\overset{0.5}{\cancel{0.15 dm^3}} \times 200\ K}{\cancel{0.3\ dm^3}}$$

$T_3 = 100\ K$

Evaluate Yourself

3. A sample of gas has a volume of $3.8\ dm^3$ at an unknown temperature. When the sample is submerged in ice water at 0 °C, its volume gets reduced to $2.27\ dm^3$. What is its initial temperature?

6.2.3 Gay-Lussac's Law (Pressure-temperature relationship)

Joseph Gay-Lussac stated that, at constant volume the pressure of a fixed mass of a gas is directly proportional to temperature.

$P \alpha T$

$$\text{or} \quad \frac{P}{T} = \text{Constant } k$$

If P_1 and P_2 are the pressures at temperatures T_1 and T_2, respectively, then from Gay Lussac's law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Activity -1

The table below contains the values of pressure measured at different temperatures for 1 mole of an ideal gas. Plot the values in a graph and verify the Gay Lussac's law. [Lines in the pressure vs temperature graph are known as iso chores (constant volume) of a gas.]

Temperature (in deg celcius)	32	69	94	130	154	191
Pressure in 50 L container (atm)	0.51	0.56	0.6	0.66	0.7	0.76
Pressure in 75 L container (atm)	0.34	0.37	0.40	0.44	0.47	0.51

6.2.4 Avogadro's Hypothesis

Avogadro hypothesised that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. The mathematical form of Avogadro's hypothesis may be expressed as

$$V \propto n,$$

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \text{constant} \text{ -------- } (6.10)$$

where V_1 & n_1 are the volume and number of moles of a gas and V_2 & n_2 are a different set of values of volume and number of moles of the same gas at same temperature and pressure.

Evaluate Yourself

4. An athlete in a kinesiology research study has his lung volume of 7.05 dm^3 during a deep inhalation. At this volume the lungs contain 0.312 mole of air. During exhalation the volume of his lung decreases to 2.35 dm^3. How many moles of air does the athlete exhale during exhalation? (assume pressure and temperature remain constant)

6.3. Ideal gas equation

The gaseous state is described completely using the following four variables T, P, V and n and their relationships were governed by the gas laws studied so far.

$$\text{Boyle's law} \quad V \propto \frac{1}{P}$$

$$\text{Charles law} \quad V \propto T$$

$$\text{Avogadro's law} \quad V \propto n$$

We can combine these equations into the following general equation that describes the physical behaviour of all gases.

$$V \propto \frac{nT}{P}$$

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

where, R is the proportionality

constant called universal gas constant.

The above equation can be rearranged to give the ideal gas equation

PV = nRT. ------ (6.11)

We already know that pressure is expressed in many different units (Table 6.1) hence it is important to know the values of gas constant R in different units as well.

We can calculate R using the equation,

$$R = \frac{PV}{nT}$$

For Conditions in which P is 1 *atm*., volume 22.414 dm^3. for 1 mole at 273.15 K.

$$R = \frac{1\,atm. \times 22.414\,dm^3}{1\,mol. \times 273.15\,K}$$

$$= \mathbf{0.0821\ dm^3\ atm.\ mol^{-1}\ K^{-1}}$$

Under standard conditions (STP) Where P = 1 bar (10^5 pascal), V= 22.71 × 10^{-3} m^3 for 1 mole of a gas at 273.15 K

$$R = \frac{10^5\ Pa \times 22.71 \times 10^{-3}\ m^3}{1\,mol. \times 273.15\,K}$$

$$= \mathbf{8.314\ Pa\ m^3\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314 \times 10^{-5}\ bar\ m^3\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314 \times 10^{-2}\ bar\ dm^3\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314 \times 10^{-2}\ bar\ L\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314\ J\ K^{-1}\ mol^{-1}}$$

The ideal gas equation is a relationship between four variables (P, V, T, n). Since it describes the state of any gas, it is referred to as the equation of state of gases.

Let us calculate the pressure exerted by 2 moles of sulphur hexafluoride in a steel vessel of volume 6 dm^3 at 70 °C assuming it is an ideal gas.

We will use the ideal gas equation for this calculation as below:

$$P = \frac{nRT}{V} = \frac{\begin{array}{c}2\ mol \times \\ 0.0821\ \ L\ atm.\ K^{-1}.mol^{-1} \times \\ (70 + 273\ K)\end{array}}{6\ dm^3}$$

= 9.39 atm.

Evaluate Yourself

5. A small bubble rises from the bottom of a lake where the temperature and pressure are 8° C and 6.4 *atm.* to the water surface, where the temperature is 25°C and pressure is 1 *atm*. Calculate the final volume in (mL) of the bubble, if its initial volume is 2.1 mL.

6.4 Mixture of gases - Dalton's law of partial pressures

Studies of non-reacting gaseous mixtures showed that in a gaseous mixture each component behaves independently. For a gaseous mixture, it is important to know, how the pressure of individual component contributes to the total pressure of the mixture.

John Dalton stated that "the total

pressure of a mixture of non-reacting gases is the sum of partial pressures of the gases present in the mixture" where the partial pressure of a component gas is the pressure that it would exert if it were present alone in the same volume and temperature. This is known as *Dalton's law of partial pressures.*

i.e., for a mixture containing three gases 1, 2 and 3 with partial pressures p_1, p_2 and p_3 in a container with volume V, the total pressure P_{total} will be give by

$$P_{total} = p_1 + p_2 + p_3 \text{ ------- } (6.12)$$

Assuming that the gases behave ideally,

$$p_1 = n_1 \frac{RT}{V} ; p_2 = n_2 \frac{RT}{V} ; p_3 = n_3 \frac{RT}{V}$$

$$P_{Total} = n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V}$$

$$P_{Total} = n_{Total} \left(\frac{RT}{V} \right) \text{------} (6.13)$$

The partial pressure can also be expressed as

$$\left(\frac{RT}{V} \right) \text{ can be expressed as } \frac{p_1}{n_1} \text{ or } \frac{p_2}{n_2} \text{ or } \frac{p_3}{n_3}$$

or in general $\frac{p_i}{n_i}$

Therefore

$$P_{Total} = n_{Total} \frac{p_i}{n_i} = \frac{n_{Total}}{n_i} p_i$$

$$\Rightarrow p_i = \frac{n_i}{n_{Total}} P_{Total} = x_i P_{Total} \text{ ------- } (6.14)$$

where x_i is the mole fraction of the i^{th} component.

Application of Dalton's law

In a reaction involving the collection of gas by downward displacement of water, the pressure of dry vapor collected can be calculated using Dalton's law.

$$P_{\text{dry gas collected}} = p_{total} - p_{\text{water vapour}}$$

$p_{\text{water vapour}}$ is generally referred as aqueous tension and its values are available for air at various temperatures.

Let us understand Dalton's law by solving this problem. A mixture of gases contains 4.76 mole of Ne, 0.74 mole of Ar and 2.5 mole of Xe. Calculate the partial pressure of gases, if the total pressure is 2 *atm*. at a fixed temperature.

Solution:

$$p_{Ne} = x_{Ne} P_{Total}$$

$$x_{Ne} = \frac{n_{Ne}}{n_{Ne} + n_{Ar} + n_{Xe}}$$

$$= \frac{4.76}{4.76 + 0.74 + 2.5} = 0.595$$

$$x_{Ar} = \frac{n_{Ar}}{n_{Ne} + n_{Ar} + n_{Xe}}$$

$$= \frac{0.74}{4.76 + 0.74 + 2.5} = 0.093$$

$$x_{Xe} = \frac{n_{Xe}}{n_{Ne} + n_{Ar} + n_{Xe}}$$

$$= \frac{2.5}{4.76 + 0.74 + 2.5} = 0.312$$

$$P_{Ne} = x_{Ne} P_{Total} = 0.595 \times 2$$

$$= 1.19 \text{ atm.}$$

$$P_{Ar} = x_{Ar}\,P_{Total} = 0.093 \times 2$$

$$= 0.186 \text{ atm.}$$

$$P_{Xe} = x_{Xe}\,P_{Total} = 0.312 \times 2$$

$$= 0.624 \text{ atm.}$$

Evaluate Yourself

6. (a) A mixture of He and O_2 were used in the 'air' tanks of underwater divers for deep dives. For a particular dive 12 dm^3 of O_2 at 1 *atm*. and 46 dm^3 of He, at 1 *atm*. were both pumped into a 5 dm^3 tank. Calculate the partial pressure of each gas and the total pressure in the tank at 298 K

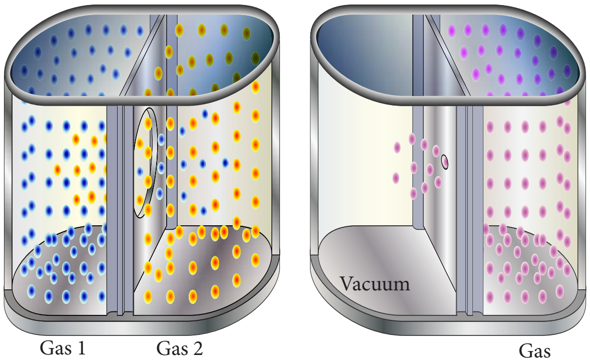
(b) A sample of solid $KClO_3$ (potassium chlorate) was heated in a test tube to obtain O_2 according to the reaction

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

The oxygen gas was collected by downward displacement of water at 295 K. The total pressure of the mixture is 772 mm of Hg. The vapour pressure of water is 26.7 mm of Hg at 300K. What is the partial pressure of the oxygen gas?

6.4.1 Graham' s Law of Diffusion

Gases have a tendency to occupy all the available space. When two non -reactive gases are allowed to mix, the gas molecules migrate from region of higher concentration to a region of lower concentration. This property of gas which involves the movement of the gas molecules through another gases is called diffusion. Effusion is another process in which a gas escapes from a container through a very small hole.



Diffusion Effusion

Figure. 6.7 Diffusion and effusion of gases

The rate of diffusion or effusion is inversely proportional to the square root of molar mass. This statement is called Graham's law of diffusion/effusion.

$$\text{Mathematically, rate of diffusion } \alpha \frac{1}{\sqrt{M}}$$

Otherwise

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \text{ -------- } (6.15)$$

When diffusing gases are at different pressures (P_A, P_B),

$$\frac{r_A}{r_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}} \text{ -------}(6.16)$$

where r_A and r_B are the rates of diffusion of A and B and the M_A and M_B are their respective molar masses.

DO YOU KNOW?

Graham's Law forms the basis of the process of enriching the isotopes of U^{235} from other isotopes.

Example:

1. An unknown gas diffuses at a rate of 0.5 time that of nitrogen at the same

temperature and pressure. Calculate the molar mass of the unknown gas

Solution:

$$\frac{\text{rate}_{\text{unknown}}}{\text{rate } N_2} = \sqrt{\frac{M_{N_2}}{M_{\text{unknown}}}}$$

$$0.5 = \sqrt{\frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}}$$

Squaring on both sides

$$(0.5)^2 = \frac{28 \text{ g mol}^{-1}}{M_{\text{unknown}}}$$

$$\Rightarrow M_{\text{unknown}} = \frac{28}{0.25} = 112 \text{ g mol}^{-1}$$

Evaluate Yourself

7. A flammable hydrocarbon gas of particular volume is found to diffuse through a small hole in 1.5 minutes. Under the same conditions of temperature and pressure an equal volume of bromine vapour takes 4.73 min to diffuse through the same hole. Calculate the molar mass of the unknown gas and suggest what this gas might be.

   (Given that molar mass of bromine = 159.8 g/mole)

6.5 Deviation from ideal gas behaviour

The kinetic theory of gases (postulates of kinetic theory of gases are described in physics text book) which is the basis for the gas equation (PV=nRT), assumes that the individual gas molecules occupy negligible volume when compared to the total volume of the gas and there is no attractive force between the gas molecules. Gases whose behaviour is consistent with these assumptions under all conditions are called ideal gases. But in practice both these assumptions are not valid under all conditions. For example, the fact that gases can be liquefied shows that the attractive force exists among molecules. Hence, there is no gas which behaves ideally under all conditions. The non-ideal gases are called real gases. The real gases tend to approach the ideal behaviour under certain conditions.

6.5.1 Compressibility factor Z

The deviation of real gases from ideal behaviour is measured in terms of a ratio of PV to nRT. This is termed as compressibility factor. Mathematically,

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

For ideal gases PV = nRT, hence the compressibility factor, Z = 1 at all temperatures and pressures. For these gases the plot of Z vs P should be a straight line parallel to the pressure axis. When a gas deviates from ideal behaviour, its Z value deviates from unity. For all gases, at very low pressures and very high temperature the compressibility factor approaches unity and they tend to behave ideally. The plot of the compressibility factor vs pressure for some common gases are shown in Figure 6.8.

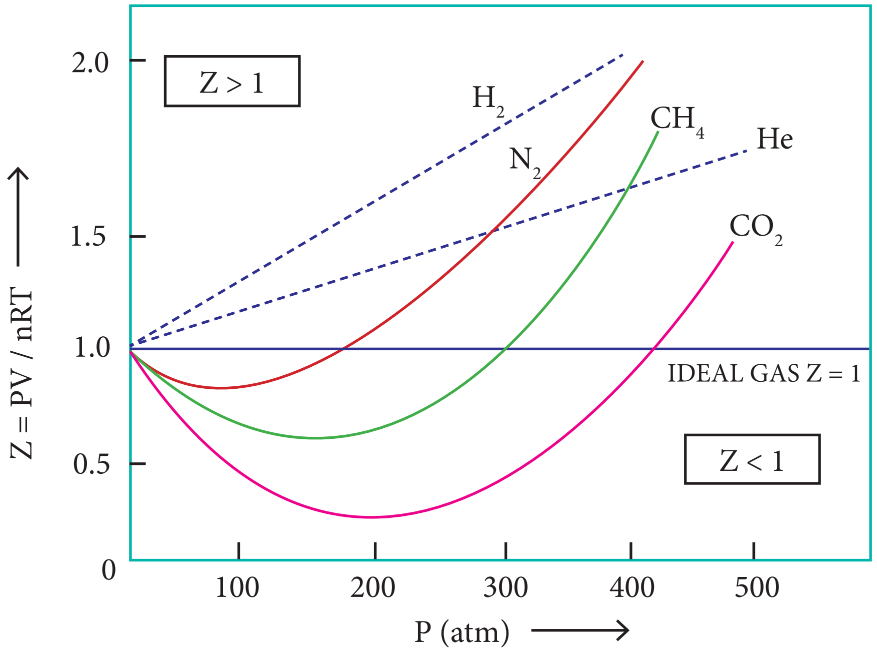


Figure. 6.8 Plot of compressibility factor(Z) vs pressure for some common gases

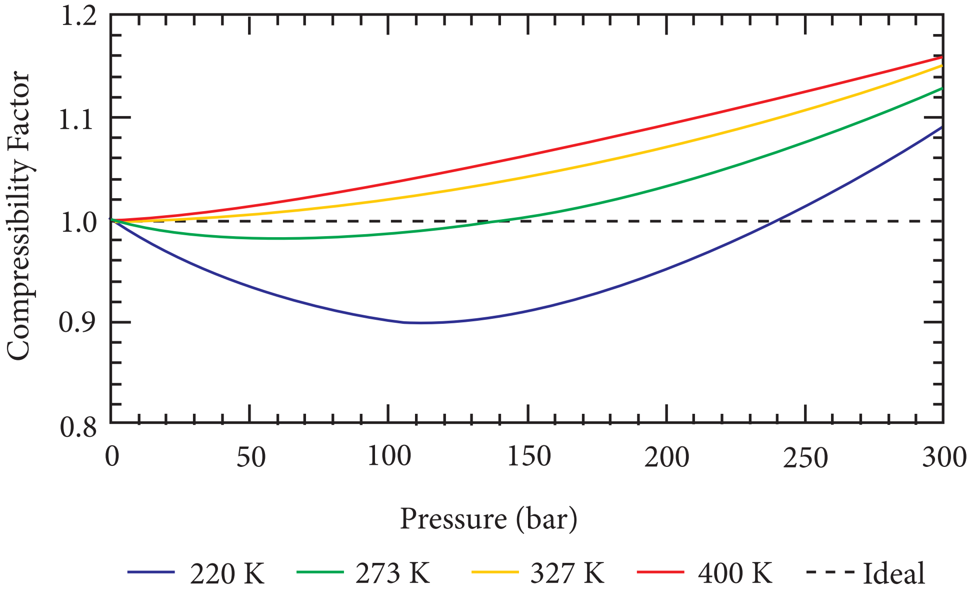


Figure. 6.9 Compressibility factor vs pressure at different temperatures for Nitrogen

When the pressure is low, the volume of the container is very large compared to the volume of the gas molecules so that individual volume of the gas molecules can be neglected. In addition, the molecule in a gas are far apart and attractive forces are negligible. As the pressure increases, the density of gas also increases and the molecules are much closer to one another. Hence, the intermolecular force becomes significant enough to affect the motion of the molecules and the gas will not behave ideally.

At high temperatures the average kinetic energy of the molecules is very high and hence inter moleclular attractions will become insignificant. As the temperature decreases, the average kinetic energy of molecules also decreases, hence the molecular attraction is enhanced. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point. The Boyle point varies with the nature of the gas. Above the Boyle point, for real gases, Z > 1, ie., the real gases show positive deviation. Below the Boyle point, the real gases first show a decrease for Z, reaches a minimum and then increases with the increase in pressure. So, it is clear that at low pressure and at high temperature, the real gases behave as ideal gases.

6.5.2 Compressibility factor for real gases

The compressibility factor Z for real gases can be rewritten

$$Z = \frac{PV_{real}}{nRT} \qquad ------(6.17)$$

$$V_{ideal} = \frac{nRT}{P} \qquad -------(6.18)$$

Substituting 6.18 in 6.17

$$Z = \frac{V_{real}}{V_{ideal}} \quad ----------- \quad (6.19)$$

Where V_{real} is the molar volume of the real gas and V_{ideal} is the molar volume of it when it behaves ideally.

6.5.3 Van der Waals Equation

J. D. Van der Waals made the first mathematical analysis of real gases. His treatment provides us an interpretation of real gas behaviour at the molecular level. He modified the ideal gas equation PV = nRT by introducing two correction factors, namely, pressure correction and volume correction.

Pressure Correction:

The pressure of a gas is directly proportional to the force created by the bombardment of molecules on the walls of the container. The speed of a molecule moving towards the wall of the container is reduced by the attractive forces exerted by its neighbours. Hence, the measured gas pressure is lower than the ideal pressure of the gas. Hence, van der Waals introduced a correction term to this effect.

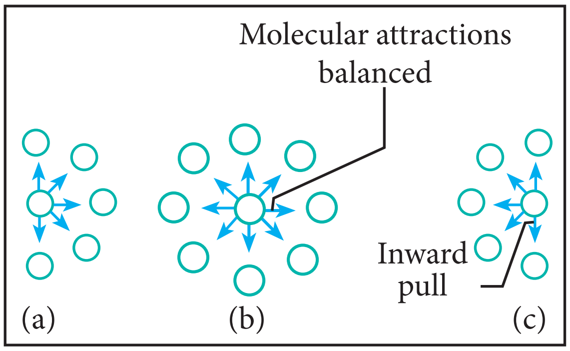


Figure. 6.10 Inter-molecular forces of attraction

Van der Waals found out the forces of attraction experienced by a molecule near the wall are directly proportional to the square of the density of the gas.

$$P' \alpha \, \rho^2$$

$$\rho = \frac{n}{V}$$

where n is the number of moles of gas and V is the volume of the container

$$\Rightarrow P' \alpha \frac{n^2}{V^2}$$

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

where a is proportionality constant and depends on the nature of gas

Therefore,

$$P_{ideal} = P + \frac{an^2}{V^2} \text{ ------ } (6.20)$$

Volume Correction

As every individual molecule of a gas occupies a certain volume, the actual volume is less than the volume of the container, V. Van der Waals introduced a correction factor V' to this effect. Let us calculate the correction term by considering gas molecules as spheres.

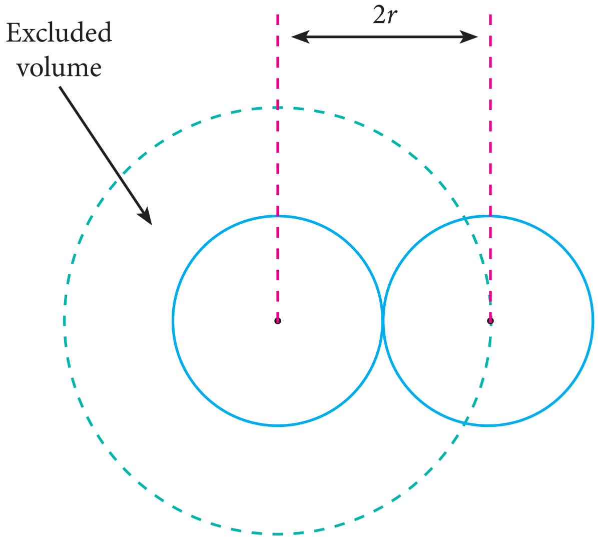


Figure. 6.11 Excluded volume

V = excluded volume

Excluded volume for two molecules

$$= \frac{4}{3}\pi(2r)^3$$

$$= 8\left(\frac{4}{3}\pi r^3\right) = 8\,V_m$$

where v_m is a volume of a single molecule

Excluded volume for single molecule

$$= \frac{8\,V_m}{2} = 4\,V_m$$

Excluded volume for n molecule

$$= n\,(4\,V_m) = nb$$

Where b is van der waals constant whch is equal to $4\,V_m$

$$\Rightarrow V' = nb$$

$$V_{ideal} = V - nb - - - - - (6.21)$$

Replacing the corrected pressure and volume in the ideal gas equation PV=nRT we get the van der Waals equation of state for real gases as below,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ . ----}(6.22)$$

The constants *a* and *b* are van der Waals constants and their values vary with the nature of the gas. It is an approximate formula for the non-ideal gas.

6.6 Pressure-Volume isotherms of Carbon dioxide

Andrew's isotherm

Thomas Andrew gave the first complete data on pressure-volume-temperature of a substance in the gaseous and liquid states. He plotted isotherms of carbon dioxide at different temperatures which is shown in Figure. 6.12. From the plots we can infer the following.

At low temperature isotherms, for example, at 13⁰ C as the pressure increases, the volume decreases along AB and is a gas until the point B is reached. At B, a liquid separates along the line BC, both the liquid and gas co-exist and the pressure remains constant. At C, the gas is completely converted into liquid. If the pressure is higher than at C, only the liquid is compressed so, there is no significant change in the volume. The successive isotherms shows similar trend with the shorter flat region. i.e. The volume range in which the liquid and gas coexist becomes shorter. At the temperature of 31.1 ⁰C the length of the shorter portion is reduced to zero at point P. In other words, the CO_2 gas is liquefied completely at this point. This temperature is known as the liquefaction temperature or critical temperature of CO_2. At this point the pressure is 73 atm. Above this temperature CO_2 remains as a gas at all pressure values. It is then proved that many real gases behave in a similar manner to carbon dioxide.

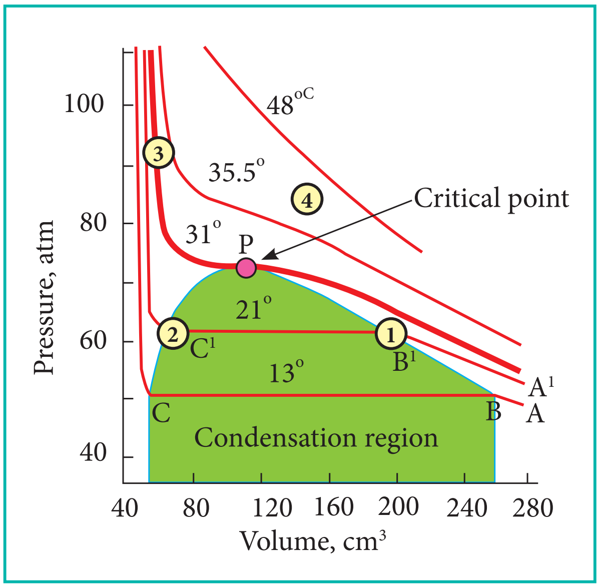


Figure. 6.12 Isotherms of Carbon dioxide at different tempeartures

Though the nature of isotherm remains similar, the critical temperature, the corresponding pressure and volume are characteristics of a particular gas.

Now we can define the critical constants as follows. Critical temperature (T_c) of a gas is defined as the temperature above which it cannot be liquefied even at high pressure. Critical pressure (P_c) of a gas is defined as the minimum pressure required to liquefy 1 mole of a gas at its critical temperature. Critical volume (V_c) is defined as the volume occupied by 1 mole of a gas at its critical temperature and critical pressure. The critical constants of some common gases are given in Table 6.2

Table 6.2 Critical constants of some gases

Name of the Gas	Critical Temperature (T_c) in K	Critical Pressure (P_c) in atm	Critical Volume (V_c) $cm^3\ mol^{-1}$
Helium (He)	5.2	2.26	57.8
Carbon dioxide (CO_2)	304.2	72.9	94.0
Oxygen (O_2)	154.8	50.14	78.0
Nitrogen (N_2)	126.3	33.54	90.1
Hydrogen (H_2)	33.2	12.80	65
Water (H_2O)	647.4	218.3	55.3
Ammonia (NH_3)	405.5	111.3	72.5
Hydrogen Chloride (HCl)	324.7	81.5	81.0
Methane (CH_4)	190.6	45.6	98.7
Ethylene (C_2H_4)	283.1	50.50	124

Evaluate Yourself

8. Critical temperature of H_2O, NH_3, and CO_2 are 647.4, 405.5 and 304.2 K, respectively. When we start cooling from a temperature of 700 K which will liquefy first and which will liquefy finally?

6.6.1 Derivation of critical constants from van der Waals constant:

The van der Waals equation for n moles is

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ ---------- } (6.22)$$

For 1 mole

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ ---------- } (6.23)$$

From the equation we can derive the values of critical constants P_c, V_c and T_c in terms of a and b, the van der Waals constants, On expanding the above equation

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT = 0 \text{ ------- } (6.24)$$

Multiply equation (6.24) by V^2 / P

$$\frac{V^2}{P}\left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2} - RT\right) = 0$$

$$V^3 + \frac{aV}{P} + - bV^2 - \frac{ab}{P} - \frac{RTV^2}{P} = 0 \text{ --- } (6.25)$$

When the above equation is rearranged in powers of V

$$V^3 - \left[\frac{RT}{P} + b\right]V^2 + \left[\frac{a}{P}\right]V - \left[\frac{ab}{P}\right] = 0 \text{ --- } (6.26)$$

The equation (6.26) is a cubic equation in V. On solving this equation, we will get three solutions. At the critical point all these three solutions of V are equal to the critical volume V_C. The pressure and temperature becomes P_c and T_c respectively

i.e., $V = V_C$

$$V - V_C = 0$$

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

$$V^3 - 3V_CV^2 + 3V_C^2V - V_C^3 = 0 \text{ ---- } (6.27)$$

As equation (6.26) is identical with equation (6.27), we can equate the coefficients of V^2, V and constant terms in (6.26) and (6.27).

$$-3V_CV^2 = -\left[\frac{RT_C}{P_C} + b\right]V^2$$

$$3V_C = \frac{RT_C}{P_C} + b \text{ ---- } (6.28)$$

$$3V_C^2 = \frac{a}{P_C} \text{ ---- } (6.29)$$

$$V_C^3 = \frac{ab}{P_C} \text{ ---- } (6.30)$$

Divide equation (6.30) by equation (6.29)

$$\frac{V_C^3}{3V_C^2} = \frac{ab / P_C}{a / P_C}$$

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

i.e. $V_C = 3b$ ------- (6.31)

when equation (6.31) is substituted in (6.29)

$$3V_C^2 = \frac{a}{P_C}$$

$$P_C = \frac{a}{3V_C^2} = \frac{a}{3(3b^2)} = \frac{a}{3 \times 9b^2} = \frac{a}{27\,b^2}$$

$$P_C = \frac{a}{27b^2} \quad \text{------ (6.32)}$$

substituting the values of V_c and P_c in equation (6.28),

$$3V_C = b + \frac{R\,T_C}{P}$$

$$3\,(3\,b) = b + \frac{R\,T_C}{\left(a/27\,b^2 \right)}$$

$$9\,b - b = \left(\frac{R\,T_C}{a} \right) 27\,b^2$$

$$8\,b = \frac{T_C\,R\,27b^2}{a}$$

$$\therefore \quad T_C = \frac{8\,a\,b}{27\,R\,b^2} = \frac{8\,a}{27\,R\,b}$$

$$T_C = \frac{8\,a}{27\,R\,b} \quad \text{------ (6.33)}$$

The critical constants can be calculated using the values of van der waals constant of a gas and vice versa.

$$a = 3\,V_C^2\,P_C \quad \text{and} \quad b = \frac{V_C}{3}$$

6.7 Liquefaction of gases

For important commercial operations such as LPG and rocket fuels, we require gases in their liquid state. The liquefication methods are based on the Joule-Thomson effect. He observed appreciable cooling when the compressed gas is forced through an orifice plug into a low-pressure region. This phenomenon of lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect. This effect is observed only below a certain temperature, which is a characteristic one for each gas. This temperature below which a gas obeys Joule-Thomson effect is called inversion temperature (T_i). This value is given using van der waals constants *a* and *b*.

$$T_i = \frac{2a}{Rb} \quad \text{--------- (6.34)}$$

Gases like O_2, He, N_2 and H_2 have very low T_c, hence Joule-Thomson effect can be applied for cooling effectively. At the inversion temperature, no rise or fall in temperature of a gas occurs while expanding. But above the inversion temperature, the gas gets heated up when allowed to expand through a hole.

There are different methods used for liquefaction of gases:

1) In **Linde's method,** Joule-Thomson effect is used to get liquid air or any other gas.

2) In **Claude's process,** the gas is allowed to perform mechanical work in addition to Joule-Thomson effect so that more cooling is produced.

3) In **Adiabatic process,** cooling is produced by removing the magnetic property of magnetic material such as gadolinium sulphate. By this method, a temperature of 10^{-4} K i.e. as low as 0 K can be achieved.

SUMMARY

The state of a gas is defined by a relationship between the four independent variables pressure (P), volume (V), temperature (T) and number of moles (n). The relationship between these parameters is governed by different gas laws as summarised below.

LAW	Expression	Conditions	Expression for two differnt states
Boyle's law	$PV = \text{constant}$	n and T are constant	$P_1V_1 = P_2V_2$
Charle's law	$\frac{V}{T} = \text{constant}$	P and n are constant	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay Lussac's law	$\frac{P}{T} = \text{constant}$	V and n are constant	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Combined gas law	$\frac{PV}{T} = \text{constant}$	n is constant	$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
Avogadro's Hypothesis	$\frac{V}{n} = \text{constant}$	T and P are constant	$\frac{V_1}{n_1} = \frac{V_2}{n_2}$
Dalton's law of partial pressure	$P_{Total} = p_1+p_2+p_3+....$	T and V are constant	
Graham's law of diffusion	$r \alpha \frac{1}{\sqrt{M}}$	T and P are constant	$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

Gases that obey the equation PV=nRT under all conditions are called ideal gases. But in practice there is no ideal gas. Gases tend to behave ideally at high temperatures and at low pressures. For real gases, van der Waals modified the ideal gas equation as

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

Critical temperature (T_c) of a gas is defined as the temperature above which it cannot be liquefied at any pressure. Critical pressure (P_c) of a gas is defined as the minimum pressure required to liquefy 1 mole of a gas at its critical temperature. Critical volume (V_c) is defined as the volume occupied by 1 mole of a gas at its critical temperature and critical pressure.

The critical constants are related to Van der Waals constants as follows

$$T_C = \frac{8\,a}{27\,R\,b}, \quad P_C = \frac{a}{27b^2} \quad \text{and} \quad V_C = 3b$$

When a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, the temperature of the gas is reduced rapidly and this is known as Joule-Thomson effect. This effect is used in the liquefication of gases.

EVALUATION

I. Choose the best answer

1. Gases deviate from ideal behavior at high pressure. Which of the following statement(s) is correct for non-ideality?

   a) at high pressure the collision between the gas molecule become enormous

   b) at high pressure the gas molecules move only in one direction

   c) at high pressure, the volume of gas become insignificant

   d) at high pressure the intermolecular interactions become significant

2. Rate of diffusion of a gas is

   a) directly proportional to its density

   b) directly proportional to its molecular weight

   c) directly proportional to its square root of its molecular weight

   d) inversely proportional to the square root of its molecular weight

3. Which of the following is the correct expression for the equation of state of van der Waals gas?

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

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

4. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules

   a) are above inversion temperature

   b) exert no attractive forces on each other

   c) do work equal to the loss in kinetic energy

   d) collide without loss of energy

5. Equal weights of methane and oxygen are mixed in an empty container at 298 K. The fraction of total pressure exerted by oxygen is

   (a) $1/3$ (b) $1/2$ (c) $2/3$ (d) $1/3 \times 273 \times 298$

6. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called

a) Critical temperature
b) Boyle temperature
c) Inversion temperature
d) Reduced temperature

7. In a closed room of 1000 m^3 a perfume bottle is opened up. The room develops a smell. This is due to which property of gases?

a) Viscosity
b) Density
c) Diffusion
d) None

8. A bottle of ammonia and a bottle of HCl connected through a long tube are opened simultaneously at both ends. The white ammonium chloride ring first formed will be

a) At the center of the tube
b) Near the hydrogen chloride bottle
c) Near the ammonia bottle

d) Throughout the length of the tube

9. The value of universal gas constant depends upon

a) Temperature of the gas
b) Volume of the gas
c) Number of moles of the gas
d) units of Pressure and volume.

10. The value of the gas constant R is

a) 0.082 dm^3*atm*.
b) 0.987 cal mol^{-1} K^{-1}
c) 8.3 J $mol^{-1}K^{-1}$
d) 8 erg $mol^{-1}K^{-1}$

11. Use of hot air balloon in sports and meteorological observation is an application of

a) Boyle's law
b) Newton's law
c) Kelvin's law
d) Brown's law

12. The table indicates the value of van der Waals constant 'a' in $(dm^3)^2$*atm*. mol^{-2}

Gas	O_2	N_2	NH_3	CH_4
a	1.360	1.390	4.170	2.253

The gas which can be most easily liquefied is

a) O_2
b) N_2
c) NH_3
d) CH_4

13. Consider the following statements

i) Atmospheric pressure is less at the top of a mountain than at sea level

ii) Gases are much more compressible than solids or liquids

iii) When the atmospheric pressure increases the height of the mercury column rises
Select the correct statement

a) I and II b) II and III c) I and III d) I, II and III

14. Compressibility factor for CO_2 at 400 K and 71.0 bar is 0.8697. The molar volume of CO_2 under these conditions is

a) 22.04 dm^3 b) 2.24 dm^3 c) 0.41 dm^3 d) 19.5dm^3

15. If temperature and volume of an ideal gas is increased to twice its values, the initial pressure P becomes

a) 4P b) 2P c) P d) 3P

16. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of n ?

a) 8 b) 4 c) 3 d) 1

17. Equal moles of hydrogen and oxygen gases are placed in a container, with a pin-hole through which both can escape what fraction of oxygen escapes in the time required for one-half of the hydrogen to escape. (NEET phase I)

a) $3/8$ b) $1/2$ c) $1/8$ d) $1/4$

18. The variation of volume V, with temperature T, keeping pressure constant is called the coefficient of thermal expansion ie $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. For an ideal gas α is equal to

a) T b) $1/T$ c) P d) none of these

19. Four gases P, Q, R and S have almost same values of 'b' but their 'a' values (a, b are Vander Waals Constants) are in the order Q < R < S < P. At a particular temperature, among the four gases the most easily liquefiable one is

a) P b) Q c) R d) S

20. Maximum deviation from ideal gas is expected from (NEET)

a) CH_4 (g) b) NH_3 (g) c) H_2 (g) d) N_2 (g)

21. The units of Vander Waals constants 'b' and 'a' respectively

a) mol L^{-1} and L atm^2 mol^{-1} b) mol L and L atm mol^2
c) mol^{-1}L and L^2 atm mol^{-2} d) none of these

22. Assertion : Critical temperature of CO_2 is 304K, it can be liquefied above 304K.

Reason : For a given mass of gas, volume is to directly proportional to pressure at constant temperature

a) both assertion and reason are true and reason is the correct explanation of assertion

b) both assertion and reason are true but reason is not the correct explanation of assertion

c) assertion is true but reason is false

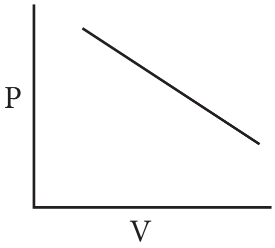
d) both assertion and reason are false

23. What is the density of N_2 gas at 227°C and 5.00 atm pressure? (R = 0.082 L atm K–1 mol^{-1})

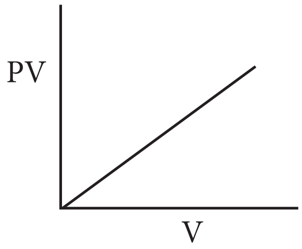
a) 1.40 g/L b) 2.81 g/L c) 3.41 g/L d) 0.29 g/L

24. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas ? (T is measured in K)

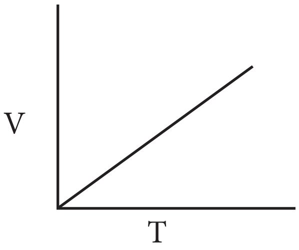
a)



b)



c)



d) All of these

25. 25g of each of the following gases are taken at 27°C and 600 mm Hg pressure. Which of these will have the least volume ?

a) HBr b) HCl c) HF d) HI

II. Write brief answer to the following questions:

26. State Boyle's law.
27. Name two items that can serve as a model for Gay Lusaac' law and explain.
28. Give the mathematical expression that relates gas volume and moles.
29. What are ideal gases? In what way real gases differ from ideal gases.
30. Can a Van der Waals gas with a=0 be liquefied? explain.
31. Suppose there is a tiny sticky area on the wall of a container of gas. Molecules hitting this area stick there permanently. Is the pressure greater or less than on the ordinary area of walls?
32. Explain the following observations
    a) Aerated water bottles are kept under water during summer
    b) Liquid ammonia bottle is cooled before opening the seal
    c) The tyre of an automobile is inflated to slightly lesser pressure in summer than in winter
    d) The size of a weather balloon becomes larger and larger as it ascends up into larger altitude
33. Give suitable explanation for the following facts about gases.
    a) Gases don't settle at the bottom of a container
    b) Gases diffuse through all the space available to them
34. Suggest why there is no hydrogen (H_2) in our atmosphere. Why does the moon have no atmosphere?
35. Explain whether a gas approaches ideal behavior or deviates from ideal behaviour if
    a) it is compressed to a smaller volume at constant temperature.
    b) the temperature is raised while keeping the volume constant
    c) more gas is introduced into the same volume and at the same temperature
36. Which of the following gases would you expect to deviate from ideal behaviour under conditions of low temperature F_2, Cl_2 or Br_2? Explain.
37. Distinguish between diffusion and effusion.
38. Aerosol cans carry clear warning of heating of the can. Why?
39. Would it be easier to drink water with a straw on the top of Mount Everest?
40. Write the Van der Waals equation for a real gas. Explain the correction term for pressure and volume
41. Derive the values of critical constants in terms of van der Waals constants.
42. Why do astronauts have to wear protective suits when they are on the surface of moon?
43. When ammonia combines with HCl, NH_4Cl is formed as white dense fumes. Why do more fumes appear near HCl?

44. A sample of gas at 15 °C at 1 atm. has a volume of 2.58 dm^3. When the temperature is raised to 38 °C at 1 atm does the volume of the gas increase? If so, calculate the final volume.

45. A sample of gas has a volume of 8.5 dm^3 at an unknown temperature. When the sample is submerged in ice water at 0 °C, its volume gets reduced to 6.37 dm^3. What is its initial temperature?

46. Of two samples of nitrogen gas, sample A contains 1.5 moles of nitrogen in a vessel of volume of 37.6 dm^3 at 298K, and the sample B is in a vessel of volume 16.5 dm^3 at 298K. Calculate the number of moles in sample B.

47. Sulphur hexafluoride is a colourless, odourless gas; calculate the pressure exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 dm^3 at 69.5 °C, assuming ideal gas behaviour

48. Argon is an inert gas used in light bulbs to retard the vaporization of the tungsten filament. A certain light bulb containing argon at 1.2 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure in atm.

49. A small bubble rises from the bottom of a lake where the temperature and pressure are 6°C and 4 atm. to the water surface, where the temperature is 25°C and pressure is 1 atm. Calculate the final volume in (mL) of the bubble, if its initial volume is 1.5 mL.

50. Hydrochloric acid is treated with a metal to produce hydrogen gas. Suppose a student carries out this reaction and collects a volume of 154.4×10^{-3} dm^3 of a gas at a pressure of 742 mm of Hg at a temperature of 298 K. What mass of hydrogen gas (in mg) did the student collect?

51. It takes 192 sec for an unknown gas to diffuse through a porous wall and 84 sec for N_2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

52. A tank contains a mixture of 52.5 g of oxygen and 65.1 g of CO_2 at 300 K the total pressure in the tanks is 9.21 atm. Calculate the partial pressure (in atm.) of each gas in the mixture.

53. A combustible gas is stored in a metal tank at a pressure of 2.98 atm at 25 °C. The tank can withstand a maximum pressure of 12 atm after which it will explode. The building in which the tank has been stored catches fire. Now predict whether the tank will blow up first or start melting? (Melting point of the metal = 1100 K).

CONCEPT MAP

Gaseous State

IDEAL GASES

obey following gas laws under all conditions

1. Boyle's Law $P \propto \frac{1}{V}$
   (T, n constant)
2. Charles Law - $V \propto T$
   (P, n constant)
3. Gay Lusaac - $P \propto T$
   (V, n constant)
4. Avogadro's Hypothesis - $V \propto n$
   (T, P constant)
5. Ideal gas equation
   $PV = nRT$

REAL GASES

obey Van der Waals equation

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

↓

Critical constant

$$T_C = \frac{8a}{27Rb}, \quad P_C = \frac{a}{27b^2}$$

and $V_C = 3b$

Gases

Diffusion

↓

Graham's Law of diffusion

Critical phenomenon

↓

Critical temperature
Critical volume
Critical pressure

Liquefaction of gases

↓

Joule-Thomson effect