

Preparation and Properties of Hydrocarbons-I

37

26.1 INTRODUCTION

Hydrocarbons are an important series of organic compounds. They are used as domestic fuels, as well as fuels in space crafts. Petroleum, which is a major source of hydrocarbons, has national and international importance. The products obtained from distillation of petroleum are used almost in every sphere of life. They are used as fuels, lubricants, dry cleaning agents, ingredients in medicines and in dyes etc. Hydrocarbons are considered to be the parent organic compounds, from which other organic compounds can be derived by replacing one or more hydrogen atoms with oxygen, sulphur, nitrogen, halogen, etc. All these types of compounds are very useful to us. In this lesson we will study about their preparation and important physical properties.

Due to their vast uses these compounds are very much needed in our daily life. Thus we must know their methods of preparation and properties.

26.2 OBJECTIVES

After reading this lesson you will be able to:

- describe the importance of hydrocarbons,
- list different methods to prepare hydrocarbons,
- differentiate between saturated and unsaturated hydrocarbons,
- list the various reasons responsible for variations in physical properties of different hydrocarbons,
- describe the mechanism of dehydration of alcohols,
- differentiate between cis and trans isomers of alkenes,
- list the various fractions of coal obtained during destructive distillations of coal,
- differentiate between Gem and vicinal dihalo alkanes,
- differentiate between aliphatic and aromatic hydrocarbons and
- apply the idea of resonance to explain the stability of different organic and inorganic compounds.

26.3 PREPARATION OF HYDROCARBONS

26.3.1 Alkanes (Paraffins):

Important methods of preparation of alkanes are as follows;

A. From Alkyl Halides : The organic compounds in which one hydrogen atom has been replaced by a halogen atom are called alkyl halides. Alkyl halides can be converted to alkanes by three different methods.

a) **The Reduction of Alkyl Halides:** The process of replacement of halogen atom of alkyl halides with hydrogen is called the reduction of alkyl halides.

Alkyl halides can be reduced to alkanes by using:

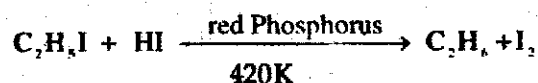
(i) A suitable metal and an acid e.g. zinc and dilute HCl

(ii) HI in the presence of red phosphorous

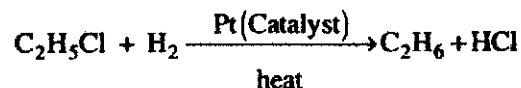
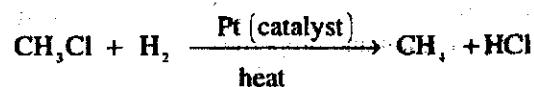
(iii) Catalytic reduction.



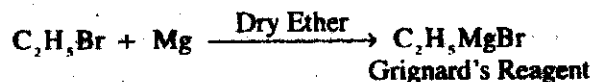
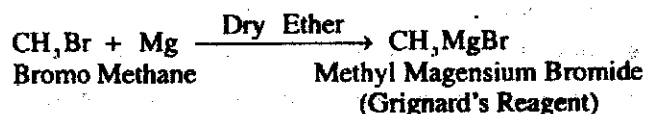
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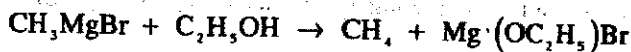
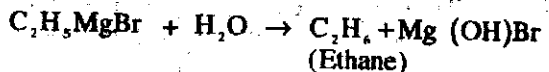
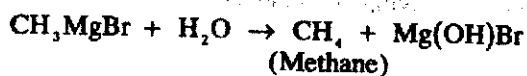


b) **By using Grignard's Reagent :** Grignard reagent is prepared by reacting alkyl halide with magnesium metal in the presence of dry ether. Grignard's reagent is used to prepare a large number of organic compounds like hydrocarbons, ether, alcohols, carboxylic acids, etc. This reagent is also called as a tool in the hands of a chemist.

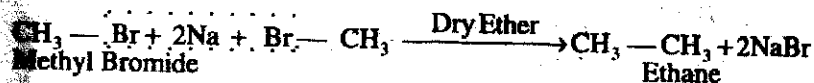


Grignard's reagent so formed reacts with the compounds containing active hydrogen and form alkanes. Easily replaceable hydrogen present in the compounds is called active

hydrogen. Active hydrogen can be obtained from (i) alcohols (ii) water.

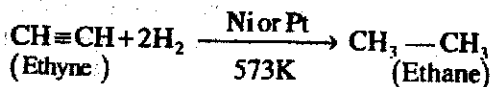
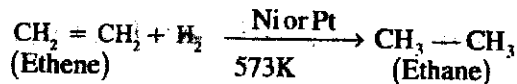


• **By Wurtz's Reaction:** The reaction, in which an alkyl halide when reacted with sodium metal in the presence of dry ether forms higher alkanes, is called Wurtz's Reaction.



1) From Unsaturated Hydrocarbons

The unsaturated hydrocarbons (Alkenes and alkynes) can be converted to alkanes by adding hydrogen to them in the presence of a catalyst like Nickel or Platinum.

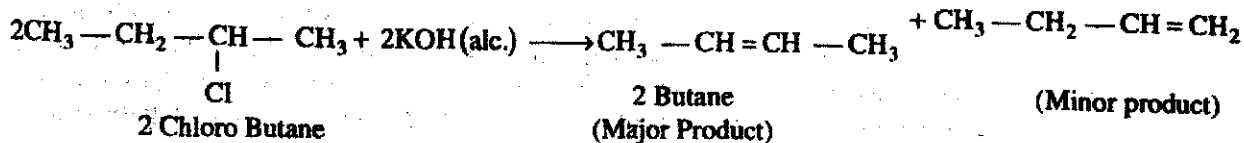
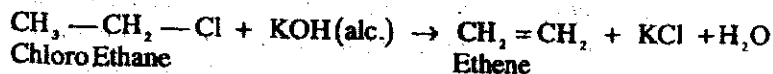


This reaction is called hydrogenation, and it is used to prepare vegetable ghee from edible oils.

26.3.2 Alkanes (Olefins)

They are unsaturated hydrocarbons containing at least one double covalent bond between two carbon atoms. In the laboratory alkenes are generally prepared either from alkyl halides or alcohols.

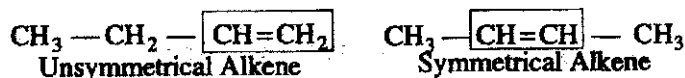
(i) **From Alkyl Halides:** Alkyl halides are converted to alkenes by dehydrohalogenation. The process of removal of halogen acid like HCl, HBr and HI from the adjacent carbon atoms of alkyl halides, when reacted with alcoholic solution of potassium hydroxide, is called dehydrohalogenation.



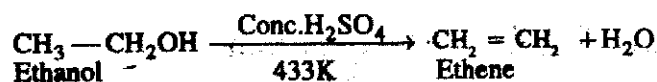
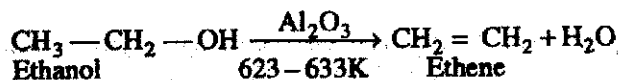
Saytzeff's Rule: It states that when an alkyl halide is reacted with alcoholic solution of potassium hydroxide and if two alkenes are possible, then the one which is more symmetrical will be the major product.

If in an alkene the number of hydrogen atoms attached with both the carbon atoms of double bond are the same, then it is a symmetrical alkene.

e.g.



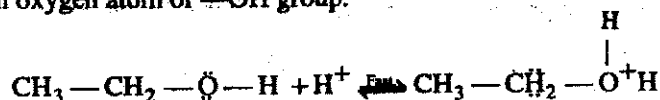
ii) **From Alcohols** : Alkenes can be prepared from alcohols by the method of dehydration in the presence of a suitable dehydrating agent, such as: (1) Al_2O_3 (2) Concentrated H_2SO_4



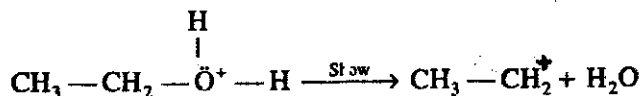
Let us explain the process of occurrence (mechanism) of this reaction.

Mechanism: The dehydration of alcohols takes place in three steps.

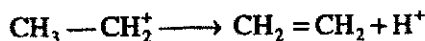
1. In the first step a proton is added to the alcohol because alcohols have a lone pair of electrons on oxygen atom of $-\text{OH}$ group.



2. The presence of positively charged hydrogen on oxygen which is more electronegative, weakens the bond between carbon and oxygen due to which water molecule is eliminated.



3. The proton is lost from the adjacent carbon atom to that having positive charge.



As second step is the slowest step of the mechanism, so this is the rate determining step.

Laboratory Preparation of Ethene

It is prepared in the laboratory by heating ethyl alcohol and conc. H_2SO_4 at a temperature of 443K (Fig. 26.1). The mixture of ethyl alcohol and conc. H_2SO_4 is taken in the ratio of 1:2 in a round bottom flask fitted with a thistle funnel and a delivery tube whose other end is in water through which ethylene is collected by the downward displacement of water. Small amount of anhydrous aluminium sulphate and sand are added. Aluminium Sulphate catalyses the reaction and sand avoids frothing during heating process. Ethene prepared by this method generally contains impurities of SO_2 and CO_2 . The impurities can be removed by passing through caustic soda solution.

found to be 0.065 atm. Suppose, further a sample of argon is pumped into a second 1 litre box and its pressure is found to be 0.027 atm. If both samples are now transferred to a third 1 litre box, the pressure is observed to be 0.092 atm for the general case, Dalton's Law can be written as

$$P_{\text{total}} = p_A + p_B + p_C + \dots$$

Where p_A, p_B, p_C, \dots are the partial pressures of gases A, B, C, respectively. The gas laws provide a simple way of calculating the partial pressure of each component, given the composition of the mixture and the total pressure. First we introduce the mole fractions X_A and X_B . These are defined as

$$X_A = \frac{n_A}{n} \text{ and } X_B = \frac{n_B}{n}$$

Where n_A and n_B are the number of moles of gas A and B respectively and $n = n_A + n_B$.

Since $p_A = n_A RT/V$, $p_B = n_B RT/V$ and $p = n RT/V$, it follows that

$$P_A = X_A p \text{ and } P_B = X_B p$$

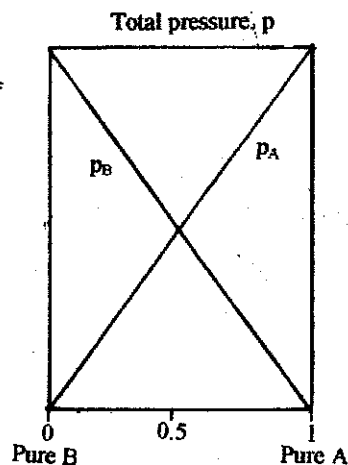


Fig. 4.6: Dependence of partial pressures on the composition

This dependence of the partial pressures on the composition is illustrated in Fig. 4.6.

This is an exceptionally useful (and simple) way of arriving at partial pressures when the composition and total (measured) pressure of a mixture of gas is known.

Example 4.6: Atmosphere is often considered mainly as a mixture of nitrogen and oxygen: 76.8% by mass of nitrogen and 23.2% by mass of oxygen. Calculate the partial pressure of each gas when the total pressure is 1 atm.

Solution: The number of moles of each component is

$$n_{N_2} = 76.8 \text{ g} / 28 \text{ g mol}^{-1} = 2.74 \text{ mol}$$

$$n_{O_2} = 23.2 \text{ g} / 32 \text{ g mol}^{-1} = 0.725 \text{ mol}$$

The mole fractions of the components are therefore

$$X_{N_2} = (2.74) / (2.74 + 0.725) = 0.791; X_{O_2} = (0.725) / (2.74 + 0.725) = 0.209$$

The partial pressures are therefore given by

$$p_{N_2} = 0.791 \times 1 \text{ atm} = 0.791 \text{ atm}$$

$$p_{O_2} = 0.209 \times 1 \text{ atm} = 0.209 \text{ atm}$$

INTEXT QUESTIONS 4.2

1. State and give the mathematical expression for:

(a) Avogadro's Law

.....

(b) Dalton's Law of partial pressures.

2. Explain why Dalton's Law is not applicable to a system of hydrogen and oxygen.

3. Give three different values of R in the ideal gas equation.

4.7 KINETIC MOLECULAR THEORY OF GASES (ACCOUNTING FOR THE GAS LAWS)

To explain the behaviour of the gases theoretically, Clausius, Maxwell and Boltzmann made the following assumptions:

- (1) Gases consist of large number of tiny particles called molecules.
- (2) The gas molecules are so small and so far apart that the total volume of the molecules is a negligible fraction of the total volume occupied by the gas.
- (3) The molecules are in a state of constant rapid random motion colliding with one another and with the walls of the container.
- (4) There are no attractive or repulsive forces between the molecules of the gas.
- (5) The collisions of the molecules among themselves and with the walls of the containing vessel are perfectly elastic, so that there is no loss of energy during collisions.
- (6) The pressure exerted by a gas is due to the bombardment of the molecules on the walls of the containing vessel.
- (7) The kinetic energy of a gas is a measure of Kelvin temperature of the gas.

On the basis of this model, it is possible to derive the following expression for a gas:

$$pV = \frac{1}{3} mN\bar{c}^2$$

Where p denotes pressure, V denotes volume, m is the mass of a gas molecule, N is the total number of molecules, and \bar{c} is the velocity of the gas molecules. It is not just the mean value of velocities. It is the root mean square velocity (RMS velocity).

4.7.1 Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically,

$$\text{RMS Velocity} = \sqrt{(c_1^2 + c_2^2 + \dots + c_N^2) / N}$$

Where c_1, c_2, \dots, c_N are the molecular velocities.

4.8 GRAHAM'S LAW OF DIFFUSION

If we open a bottle of perfume in one corner of a room or burn an essence stick we can feel the smell of the perfume or the essence stick all over the room also. The smell of perfume or essence stick spreads from one point of the room to the other. This free intermingling of gases when placed in contact with each other is known as **diffusion**.

Diffusion occurs in liquids as well as in gases. Effusion is the escape of a gas through a small hole, as in a puncture in a tyre.

The experimental observation of the rate of effusion of gases through a small hole in the side of the containing vessel led Graham (1829) to formulate the following law:

At constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density. Graham's law is applicable to both diffusion and effusion.

If the time for a given volume of gas A to escape is t_A , while the time for the same volume of gas B to escape is t_B , it follows, that

$t_A/t_B = (\text{rate})_B / (\text{rate})_A = \sqrt{d_A/d_B}$ where d_A and d_B are the densities of gases A and B respectively.

The ratio of the densities of the molecules is the same as the ratio of the molecular masses of the gases at the same temperature and pressure.

Hence, $t_A/t_B = (\text{rate})_B / (\text{rate})_A = \sqrt{M_A/M_B}$ where M_A and M_B are the molecular masses of gases A and B respectively.

4.9 REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

In case of one mole of an ideal gas $pV/RT = 1$ for every value of p . Measured values of pV/RT are plotted in Fig 4.7. In some cases (generally at low pressures) the value of pV/RT is less than 1, while at higher pressures it is greater than 1. Can you explain why?

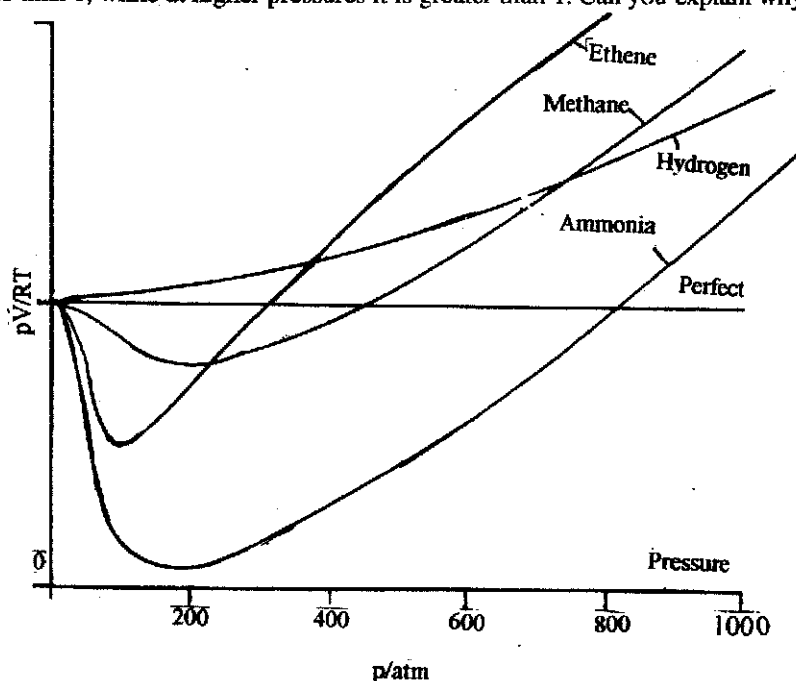


Fig. 4.7 The dependence of pV/RT on the pressure for real gases

In 1873 van der Waals pointed out two reasons why the value of pV for a gas varies with the pressure at a fixed temperature. At high pressures the molecules are close together and the volume taken up by the molecules is no longer negligible. Thus, if V is the volume of

the gas and the space occupied by the molecules is b , the compressible part of the total volume is only $V-b$. (Fig. 4.8).

Again, if the molecules of a gas attract each other, a molecule in the interior will be attracted equally on all sides by other molecules, but this will not be true for a molecule on the walls (Fig. 4.9). The pressure of a gas is due to molecular impacts on the walls of the container. The velocity of a molecule just about to make an impact will be reduced by the attraction of molecules towards the interior of the gas. For a given mass of gas the number of molecules striking the walls in unit time is inversely proportional to the volume V . also the number of molecules which exert an attraction on a molecule just before impact is again inversely proportional to V . We should therefore add to the observed pressure a term depending on the reciprocal of V^2 . Hence, we can write the law for gases in the form suggested by van der Waals, that is, for 1 mole of gas

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

Where a and b are constants.

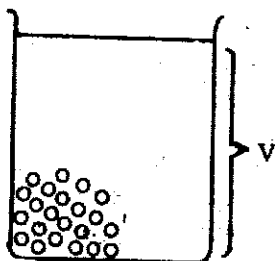


Fig. 4.8: Volume occupied by compressed molecules of a gas

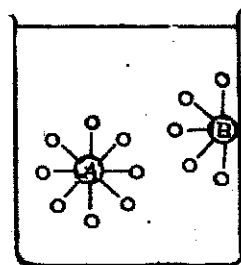


Fig. 4.9: Force of attraction between molecules in a gas

4.10 LIQUIFACTION OF GASES

Any gas can be liquified at atmospheric pressure if it is cooled sufficiently. Many gases (but not all) can be liquified at ordinary temperatures by compressing them.

The conditions of temperature and pressure under which gases liquify were first investigated by Andrews in 1869.

Andrews subjected CO_2 to various pressures at different temperatures and plotted the effect of pressure on volume (Fig. 4.10). The curve obtained at a given temperature is called an *isotherm*. As can be seen in the figure, at 48°C the volume of the gas decreased with the increased pressure approximately in accordance with the Boyle's Law. At 21°C , however, the volume first

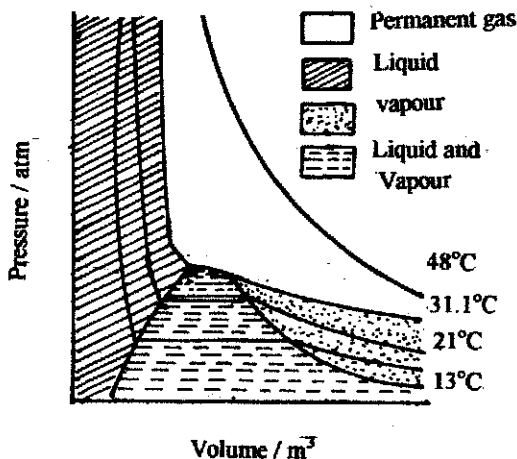


Fig. 4.10: Isothermals of carbon dioxide

decreases in accordance with Boyle's Law until the pressure was increased to about 60 atm. At this pressure there was a sudden break in the curve and liquid carbon dioxide appeared. The pressure remained constant until all the gas had been converted into liquid. Subsequent increase of pressure caused practically no change in volume. In accordance with the general rule that extremely high pressures are required to compress liquids appreciably.

Similar changes took place when the isotherms were constructed for temperatures below 21°C, except that the pressure required to liquify the gas became smaller as the temperature decreased. Andrews found that liquifaction could be brought about at all temperatures below 31.1°C, but above this temperature no liquifaction occurred no matter how much the pressure was increased. This temperature was therefore called the **critical temperature** for CO₂. The pressure required to liquify the gas at the critical temperature was called the **critical pressure**, and the volume of 1 mole of the substance at the critical temperature and pressure, the **critical volume**.

The temperature above which a gas cannot be liquified, however large the pressure may be is known as critical temperature.

The table 4.2 contains values of the critical temperature and pressure for some common substances.

TABLE 4.2

Substance	Critical Temperature (K)	Critical Pressure (atm)
Water, H ₂ O	647	217.7
Sulphur dioxide, SO ₂	430	77.7
Ammonia, NH ₃	406	112.5
Hydrogen Chloride, HCl	324	81.6
Carbon dioxide, CO ₂	304	73.0
Oxygen, O ₂	154	49.7
Nitrogen, N ₂	126	33.5
Hydrogen, H ₂	33	12.8

INTEXT QUESTIONS 4.3

1. State the postulates of Kinetic theory of gases.
.....
2. Define critical temperature and critical volume.
.....

4.11 WHAT YOU HAVE LEARNT

- Matter exists in three states, namely, solid, liquid and gases.
- The three states of matter differ in the relative closeness of the molecules constituting them.
- There exists a definite relationship between the pressure, volume and temperature of a gas. The gases obeying gas laws are known as ideal gases.

- Most of the gases deviate from the ideal behaviour. The deviations of gases from ideal behaviour is due to the wrong assumptions.
- Gases can be liquified by increasing pressure only below the critical temperature.

4.12 TERMINAL EXERCISE

1. Draw the graphs of the following:
 - a) P vs V at constant T
 - b) $1/V$ vs p at constant T
 - c) T vs V at constant p
2. What is the volume occupied by one mole of a gas at STP?
.....
3. The volume of a sample of a gas is 500 mL at a pressure of 1.5 atm. If the temperature is kept constant, what will be the volume of that gas at
 - (a) 1 atm.....
 - (b) 5.0 atm?.....
4. List the wrong assumption of kinetic theory of gases which led to vander Waals equation.
.....
5. What is the standard temperature and pressure?
.....
6. What is the lowest possible temperature.
.....
7. CO_2 can not be liquified at 35°C , however large the pressure may be, Why?
.....
8. A sample of nitrogen gas weighing 9.3 g at a pressure 0.99 atm occupies a volume of 12.4 litres when its temperature is 55K. What do you expect its volume when the temperature is 220 K? Assume pressure stays constant.
.....
9. Calculate the volume of one mole of oxygen at 27°C and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.
.....

CHECK YOUR ANSWERS

INTEXT QUESTIONS: 4.1

1. (a) Please refer to section 4.4.1
(b) Please refer to Section 4.4.2
2. At higher altitudes, the atmospheric pressure decreases. Thus the relative pressure inside the balloon increases and so the volume of the weather balloon increases.
3. Please refer to section 4.4.3.

INTEXT QUESTIONS: 4.2

- (a) Please refer to section 4.4.4
(b) Please refer to section 4.5
- Dalton's law is not applicable to a system of hydrogen and oxygen because it is only applicable to a mixture of non-reacting gases.
- The three different values of R are:
0.082057 L atm/mol K; 8.314 J mol⁻¹ K⁻¹; 1.987 cal mol⁻¹ K⁻¹.

INTEXT QUESTIONS: 4.3

- Please refer to Section 4.7
- Please refer to Section 4.10

TERMINAL EXERCISE

- (a) Please refer to Section 4.4.1
(b) Please refer to section 4.4.1
(c) Please refer to Section 4.4.2

2. 22.4 litres

3. $V_1 = 500$ ml $V_2 = ?$

$p_1 = 1.5$ atm $p_2 = 1$ atm and 5 atm

Substitute the values of p and V in the equation $p_1 V_1 = p_2 V_2$

(a) $p_1 V_1 = p_2 V_2$

$$1.5 \times 500 = 1 \times V_2$$

$$\text{or } V_2 = 1.5 \times 500 = 750 \text{ mL}$$

(b) $p_1 V_1 = p_2 V_2$

$$1.5 \times 500 = 5 \times V_2$$

$$\text{or } V_2 = \frac{1.5 \times 500}{5}$$

$$= 150 \text{ mL}$$

- The following wrong assumptions of kinetic theory of gases led to van der Waals equation:
 - The gas molecules are so small and far apart that the total volume of the molecules is negligible fraction of the total volume occupied by the gas.
 - There are no attractive or repulsive forces between the molecules of the gas.
- Standard temperature is 273.15 K and standard pressure is 760 mm Hg or 1 atm.
- The lowest possible temperature is zero kelvin.
- A gas cannot be liquified above its critical temperature, however large the pressure may be. The critical temperature of CO₂ is 31.1°C and so CO₂ can not be liquified at 35°C.

8. $V_1 = 12.4 \text{ L}$ $V_2 = ?$

$T_1 = 55 \text{ K}$ $T_2 = 220 \text{ K}$

Substitute the value of V and T in the eqn. $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{12.4 \text{ L}}{55 \text{ K}} = \frac{V_2}{220 \text{ K}}$$

or $V_2 = \frac{12.4 \text{ L} \times 220 \text{ K}}{55 \text{ K}} = 4.9 \text{ L}$

9. $V_1 = ?$ $T_1 = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$ $p_1 = 2 \text{ atm}$

$V_2 = 22.4 \text{ L}$ $T_2 = 273 \text{ K}$ $p_2 = 1 \text{ atm}$

Substitute the value of p, V and T in the equation

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$\frac{2 \times V_1}{300} = \frac{1 \times 22.4}{273}$$

or $V_1 = \frac{1 \times 22.4 \times 300}{2 \times 273} = 12.3 \text{ L}$