**Discipline Course-I
Semester-II
Paper No: Thermal Physics : Physics-IIA
Lesson: Behaviour of real gases
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Behavior of real gases

Learning Objectives:

After studying this lesson, you will be able to understand;

- ✓ how to distinguish between the properties of ideal and real gas?
- ✓ what is the nature of isotherms of CO_2 gas?
- ✓ how to define critical constants?
- ✓ how does CO_2 gas behave below and above the critical point?
- ✓ What are the assumptions of kinetic theory of gases?

1.1 Introduction

It is the intermolecular forces which determine the state of a substance .We are familiar with three states of matter solid, liquid and gas. In the case of a solid the intermolecular distances are small and hence the forces of intermolecular attraction are large. In a liquid, molecules are farther apart than in the solid resulting in weaker force of attraction. In the gaseous state the intermolecular distances are much larger than that of the solid and liquid, hence the intermolecular forces are extremely small. This is an important feature of the particles of the gas which shows its ability to expand.

For a gas at very low pressure the forces of intermolecular attraction are almost negligible and may be ignored hence the gas behaves as an ideal gas, but at ordinary pressure and temperature the gas departs from its ideal behavior and behaves like real gas. Various experiments show that ideal gases differ in their properties from real gases as the ideal gas is one consisting of non-interacting point molecules. Where in case of a real gas the aattractive intermolecular interactions and the size of molecules are significant. There is no such thing as an ideal gas, of course, but many gases behave approximately as if they were ideal even at ordinary working temperatures and pressures.

## 1.2 Deviations from the ideal gas behaviour

Some physicist chose the gaseous state to obtain information about the thermal properties of different states of matter. They developed a mathematical formulation of kinetic theory. The gaseous state was chosen as they are relatively simple to analyze. Usually a gas consists of a large number of identical molecules and it is not possible to keep track of the position and velocities of all of them. Therefore to obtain useful results, say for pressure exerted by a gas, one resorts to statistical averaging. Within the framework of this theory one can also study the **transport phenomena** like viscosity, conduction, diffusion and Brownian motion.

Following are the basic assumption of kinetic theory:

- An infinitely small volume of gas contains a large number of molecules.
- A gas is made up of identical molecules which behave as a rigid perfectly elastic hard sphere.
- The molecules continuously move about in random directions. All direction of motion is equally probable.

Random motion of molecules
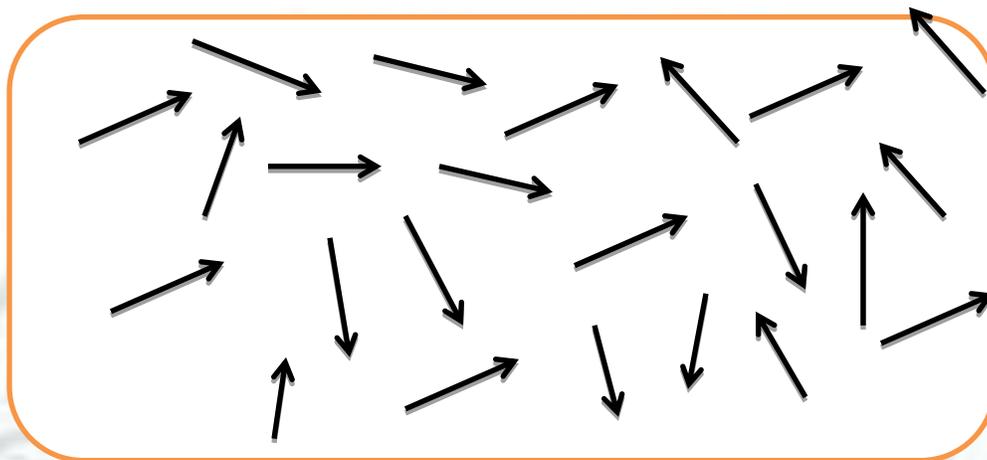
- Collisions between molecules and with the walls are **perfectly elastic** i.e. there is no loss in their kinetic energies in their collision.
- Molecules are distributed uniformly in the absence of external field and there is no preferential direction of motion.
- The molecules move with all possible speeds in all possible directions.
- The time of collision is much less than the time between collisions.
- The size of the molecules is much less than the average distance between them.
- The molecules of a gas exert no forces of attraction or repulsion on each other except when they collide. This means that there are no intermolecular forces.
  The last two points may not be justified always.

Perfectly elastic collision
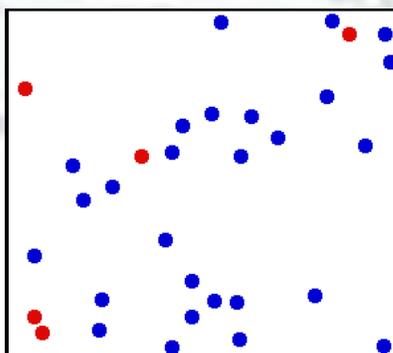
From the kinetic theory of gases following useful laws were deduced:

Boyle's law: The pressure of a given mass of a gas is inversely proportional to its volume. i.e. $PV = constant$

Charles law: The volume of a gas is directly proportional to its absolute temperature at a constant pressure. i.e. $\frac{V}{T} = constant$

Avogadro's law: This law states that at constant temperature and pressure equal volume of all gases contain the same number of molecules.

From the assumptions of kinetic theory of gases, ideal gas model was proposed by making several postulates such as; molecules are mere point masses, there are no forces of attraction between the molecules and the collision between the molecules are perfectly elastic. Based on these assumptions the following equation of state for n moles of an ideal gas was arrived at,

$$PV = nRT - - - - - -(1.1)$$

Double click the following icon to view animation on the ideal gas.

PV=nRT.swf

This animation explains the ideal gas behaviour.

For constant temperature when the weight on the piston increases, the pressure on the gas increases and the volume decreases. Also when the weight on the piston decreases, the pressure decreases and the volume of the gas increases. This activity is depicted in the adjacent PV-indicator diagram. The diagram shows that when the piston goes up, the pressure goes down and the volume goes up. Also when the piston goes down, the pressure goes up and the volume goes down. Thus we conclude that pressure is inversely proportional to volume at constant temperature for an ideal gas.

Let us solve the following problem using ideal gas equation

Problem: A cylinder contains a gas at a pressure of 10 atm and temperature 27^{0}C in a volume of 100 liters. A piston is lowered into the cylinder such that the gas occupies a volume 70 litres and its final temperature becomes 37^{0}C. Calculate the final pressure of the gas if it is assumed to be a perfect gas.

Solution: Since the mass of the gas remains unchanged the perfect gas equation PV=RT gives

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$

Subscript i and f stands for initial and final states.

Here, $P_i = 10\ atm$, $T_i = 27 + 273 = 300K$, $V_i = 100\ litres$

Equation 1.1 is the equation of state that leads to isotherms which are part of rectangular hyperbola almost parallel to each other as plotted in Figure(1.1)[$T_3 > T_2 > T_1$].
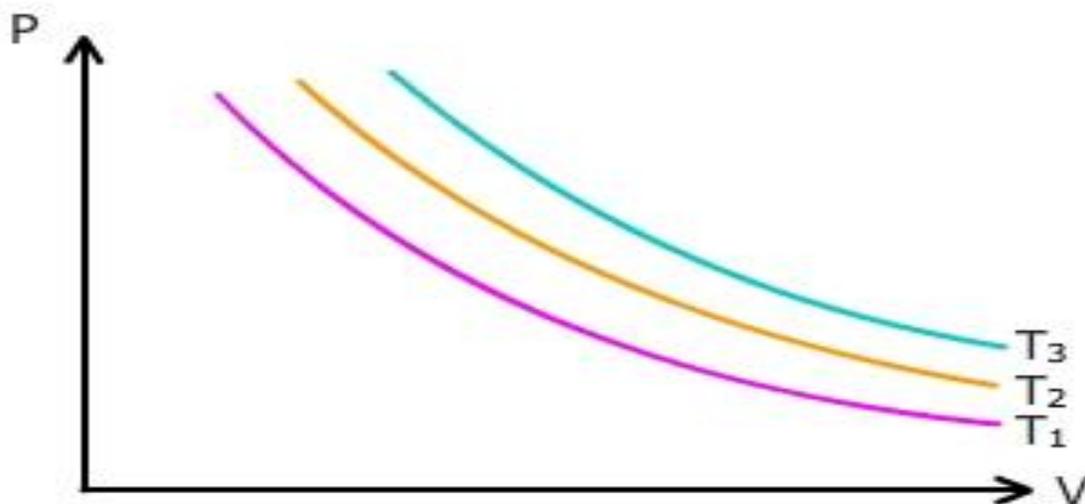
Figure 1.1: Curve between P and V for an ideal gas at different temperatures

However, real gases do not behave quite like this as shown in this Figure (1.1), particularly when the pressure is high and the volume is small. The equation of state for an ideal gas also implies that the product PV is constant for a given temperature. If a graph is plotted between PV and P, it should be a straight line parallel to the pressure axis for the gas, but this is not the case for a real gas as shown in Figure (1.2)
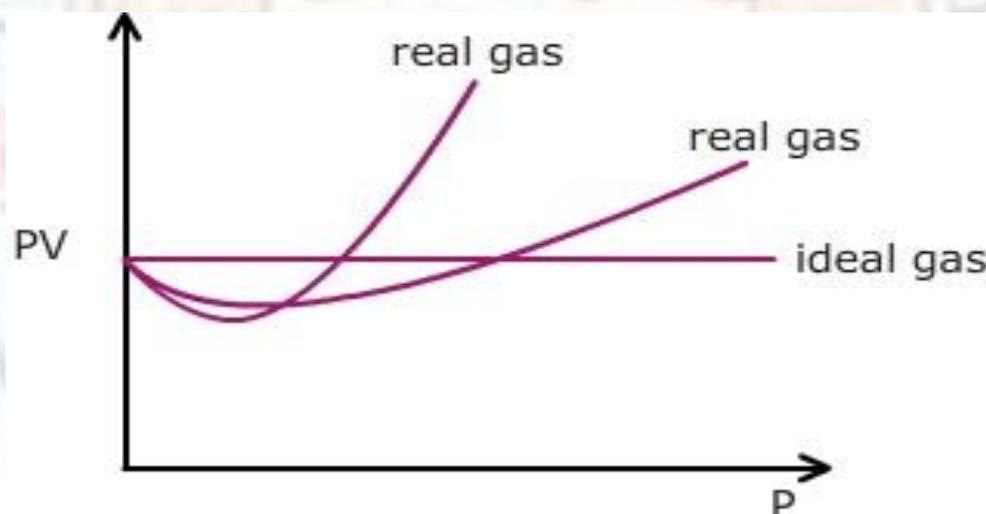

Figure 1.2: Curve between PV and P for real and ideal gases

Real gases can be liquefied at very low temperature and this is something that the ideal gas equation does not predict. So the intermolecular attractions are really significant, which were ignored so far. Hence ideal gas equation cannot be applied to real gases. A real gas shows considerable deviations from the equation of state for a perfect gas even at room temperature. Noble gases show large deviations at high pressure and low temperature.

On account of deviation of real gases from the ideal gases, necessity arose for new equations of state to represent the behaviour of real gases. Of the several equations of state proposed for real gases on empirical or semi empirical basis, two most widely used

are: van der Waal's equation and Virial equation (detailed discussion is proved in the proceeding lesson).

To study the behaviour of real gases some experiments were performed by K. Onnes , Keesom, Holborn and Otto. Such an experimental result for hydrogen gas is shown in Figure (1.3).
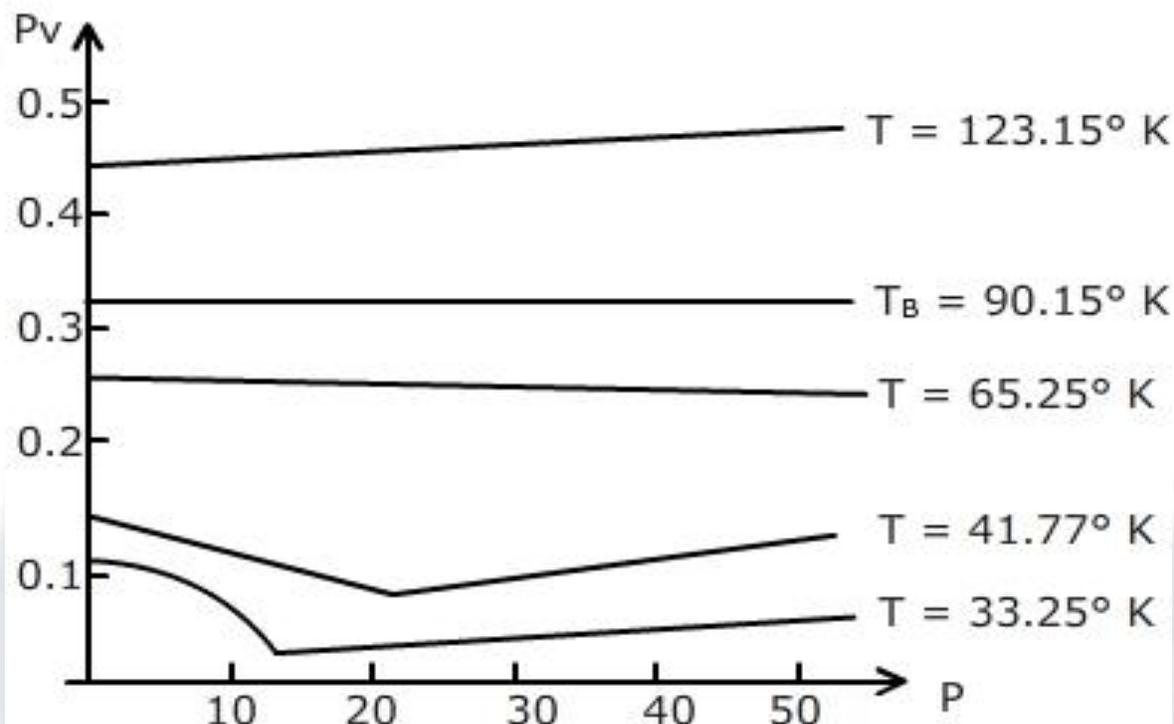

Figure 1.3: Curve between PV and P (atm) for Hydrogen gas at different   temperatures

The observed values of the product PV are plotted against P at specified temperatures. Theses curves do not obey perfect gas equation at a given temperature as PV should remain constant for a given temperature and parallel to the pressure axis. Here, PV does not appear to remain constant particularly at low temperatures.

Deviations from ideality can also be described by the **Compressibility factor**, $Z = \frac{PV}{nRT}$.

For an ideal gas, its value is unity.

1.3 Andrew's experiments on CO_2 gas

The classic experiment on the behaviour of gases was devised by Andrews in 1863.He carried out a number of experiments on the compressibility of gases while attempting to liquefy them. These experiments throw considerable light on the actual behaviour of gases. In his experiment he used carbon dioxide as the test gas. Using the experimental arrangement as shown in Figure (1.4), he plotted a series of **isothermals** (PV curves) to test the validity of Boyle's law over a wide range of pressures. The gases were compressed by tightening the screws and the pressure was estimated using air, assuming that under the conditions of the experiment it still obeyed Boyle's law.

The experimental arrangement for CO_2 gas is shown in the Figure (1.4).
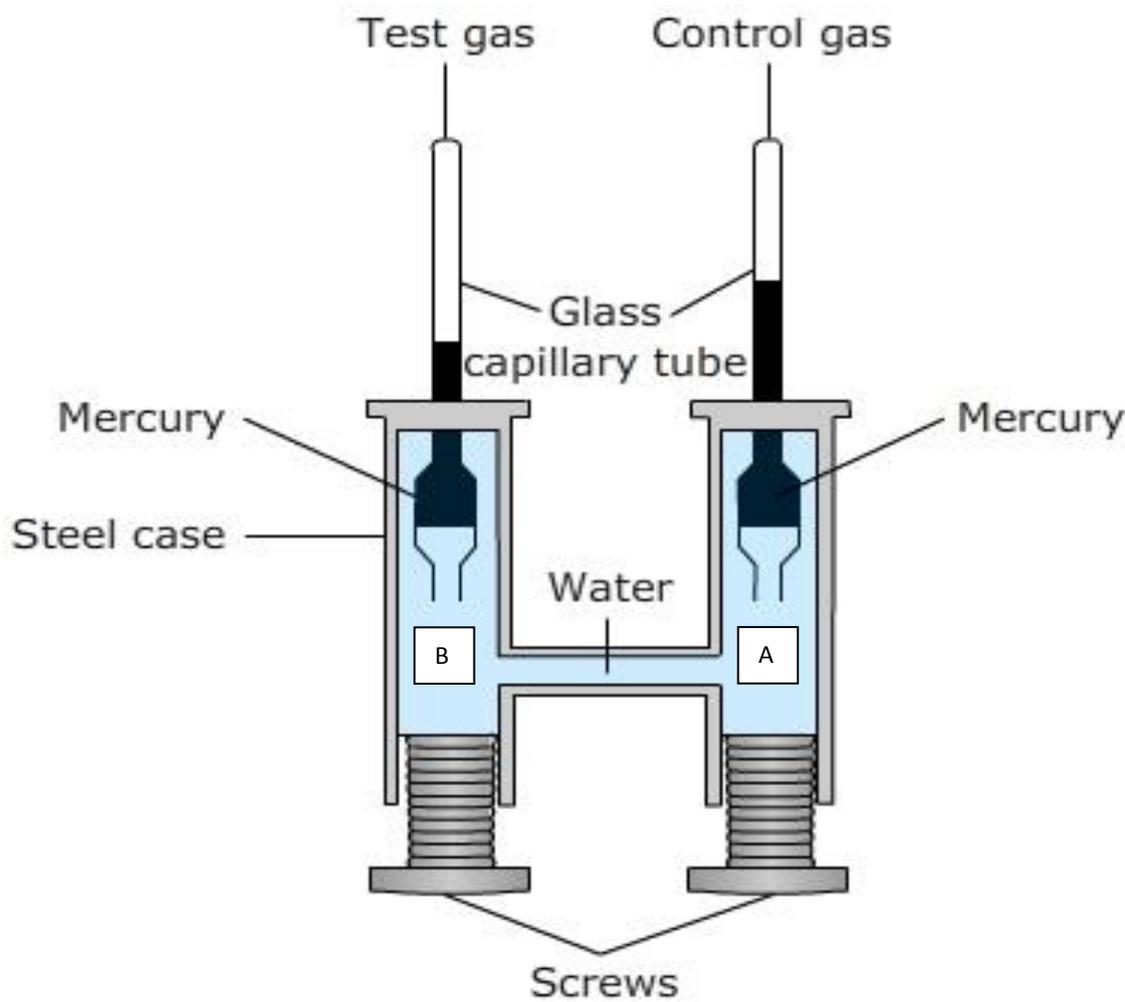

Figure 1.4: The setup for Andrew's experiment

The Experiment:

There are two glass tubes **A** and **B**, having thick capillary tubes at the top and bulbs in the middle. Initially pure dry air as the control gas, is passed through the tube **A** for a long time and then the tube was sealed. Similarly, CO_2 gas is passed through glass tube **B** again for a long time and then sealed. The lower ends of the tubes are dipped in mercury. Small pellet of mercury is drawn in both the tubes by alternately heating and cooling. Both the tubes are fixed in H-shaped steel case having steel stoppers at the ends. The vessel was filled with water. The tube contained water and hence by screwing in, pressure, as high as 400 atmospheres could be applied.

Since the pressure of air in **A** and CO_2 in **B** are the same, from the volume of air in **A**, pressure of CO_2 can be calculated assuming air to obey **Boyle's law**. The volume of CO_2 is read from tube **B** (both the tubes are calibrated to read the volume directly). Air is kept at constant temperature. The temperature of CO_2 could be maintained at any desired temperature between 0°C to 100°C.

Andrews isothermals were drawn at temperatures 13.1^0c, 21.5^0c, 31.1^0c, 32.5^0c, 35.5^0c and 48.1^0c

The experimental result can be depicted in the form of the following graph: Figure (1.5).
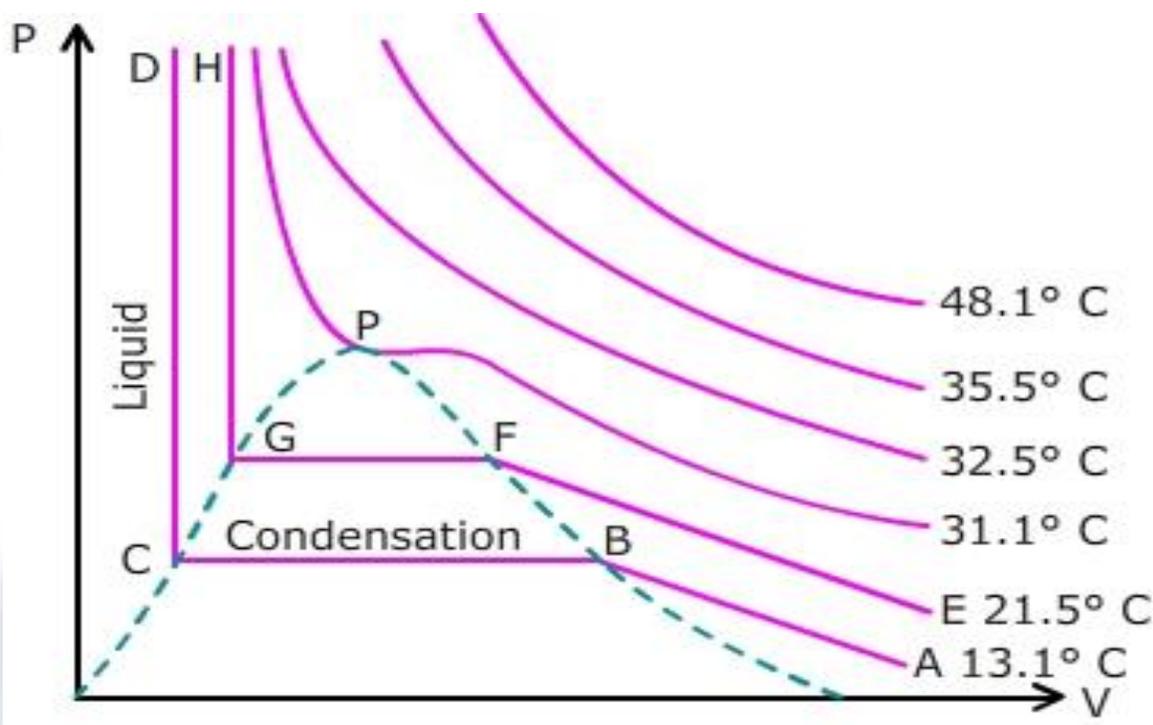

Figure 1.5: The graph between P and V for CO_2 gas.

Explanation of the graph:

The curves obtained by Andrews experiment are shown in the Figure (1.5). We observe that there are two types of isothermals:

(a) Above 31.1°C, the isothermals are almost rectangular hyperbola resembling the behaviour of a perfect gas.

(b) Below 31.1°C, the isothermals are not rectangular hyperbola.

At 13.1°C, the portion **AB** of this curve shows that with the increase of pressure, volume decreases up to the point B showing gaseous behaviour of CO_2 (Boyle's law is obeyed). From **B** to **C**, there is change of state of CO_2 from gaseous to liquid (**condensation**) and the curve becomes parallel to the volume axis. This indicates that volume decreases without appreciable increase in pressure. After the point **C**, the curve is very steep indicating that after **C**, the substance becomes highly incompressible. At **C**, the gas gets liquefied completely. The portion **CD** represents the liquid phase of CO_2.

Conclusions:

(1) Thus the portion **AB** represents the gaseous phase of the substance and **BC** represents the conversion from vapor to liquid state. At **B** conversion starts and at **C,** it gets completed.

(2) At 21.5°C, the curve is similar but only the horizontal portion **BC** has decreased. This shows that compression produces liquefaction.

(3) At 31.1°C, the horizontal portion just disappeared which suggests that gas can be liquefied under compression.

(4) Above this temperature i.e. 32.5^0C, 35.5^0C and 48.1^0C, the horizontal portion vanished and the behaviour of the gas resembles that of a perfect gas.

(5) So, CO_2 cannot be liquefied by exerting pressure alone but also by cooling it below a certain temperature. This temperature is called as the **'critical temperature'**. This behavior is not specific of CO_2 only but it is common to all gases. Thus from experimental curves, it becomes clear that for every gas there exists a temperature above which it can never be liquefied by exerting pressure alone, however great that pressure may be.

1.4 Critical constants

Definitions:

1. Critical Temperature: (T_C)

The temperature at which it just becomes possible to liquefy a gas under compression is known as the 'critical temperature'. Above this temperature the gas cannot be liquefied however large the applied pressure may be. At this temperature the properties of the liquid and its saturated vapour are identical.

2. Critical pressure: (P_C)

It is the pressure necessary to liquefy a gas at critical temperature.

3. Critical Volume: (V_C)

It is the volume which unit mass (or one mole of a gas) of a gas occupies at the critical temperature and pressure.

4. Critical Point:

It is the point on the isothermal for the critical temperature at which the change of state from gaseous to the liquid takes place under constant values of P_C and V_C.

T_C, P_C and V_C are collectively known as 'critical constants'.

For some typical gases, values of critical constants are given in table (1.1).

Gas	T_C (°C)	P_C (atm)	V_C (CC)	RT_C/P_CV_C
He	-268	2.25	154	3.13
H_2	-240	12.8	32.2	3.28
O_2	-119	49.7	2.32	3.42
CO_2	31.0	72.8	2.17	3.48

Table (1.1)

1.5 Continuity of liquid and gaseous states

Earlier it was supposed that the three states of matter (solid, liquid and gas) are non-continuous and are distinctly separate from each other. For a long time it was supposed that the gases like Hydrogen, Carbon dioxide etc. exist only in gaseous state and cannot be liquefied and solidified.

But there exists a **continuity of states** between solid, liquid and gas, as for example, if ice (solid state) is heated ,its molecules become free to move and it changes into water (liquid state).On further heating the intermolecular forces become weaker and at a particular stage the water gets converted into vapour (gaseous state). Thus they are three distinct stages of a continuous physical phenomenon Figure (1.6).

Did you know?

The intermolecular interactions are not always attractive but they become repulsive at very high densities.

In the case of gases at high pressure and low temperature, there are marked deviations from Boyle's law (PV is constant at a given temperature). Also at high pressure the molecules of a gas come close to each other and the forces of intermolecular attraction become appreciable. The distance between two gas molecules becomes so small that it becomes comparable to those of the corresponding liquid and thus the gas gets liquefied [Figure (1.6)(state (c) to state (b)].

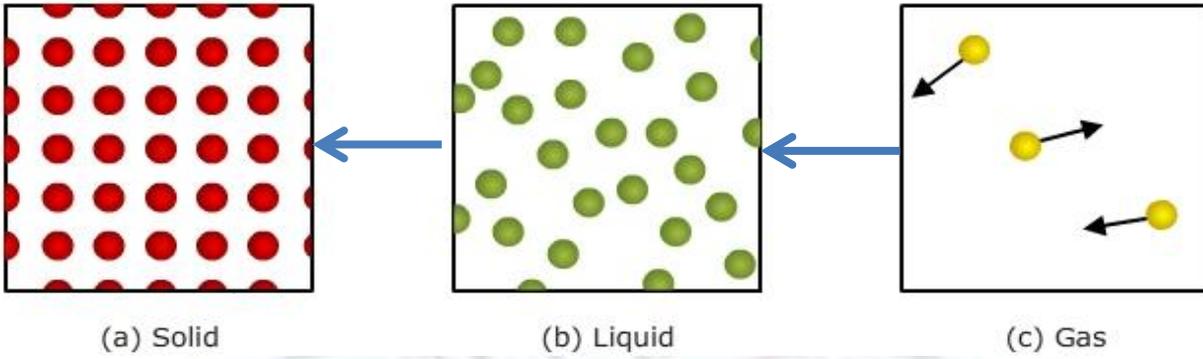(a) Solid   (b) Liquid   (c) Gas

Figure 1.6: Molecular arrangement of the three states

We can also show this continuity for CO_2 gas by considering two isotherms, one below the critical temperature (13.1^0C) and the other above it. For pressure greater than the **critical pressure** ($P>P_C$), an arrow is shown in the diagram which is moving from temperature 50^0C to 13.1^0C .At 50^0C i.e. for temperature greater than the **critical temperature** ($T>T_C$) on the arrow, the substance is purely in gaseous state, but for temperature lower than the critical temperature ($T<T_C$) the substance is purely in liquid state. This means that if we gradually reduce the temperature by keeping pressure constant, the substance changes from gaseous to liquid state without any change in its characteristic properties [Figure (1.7)].
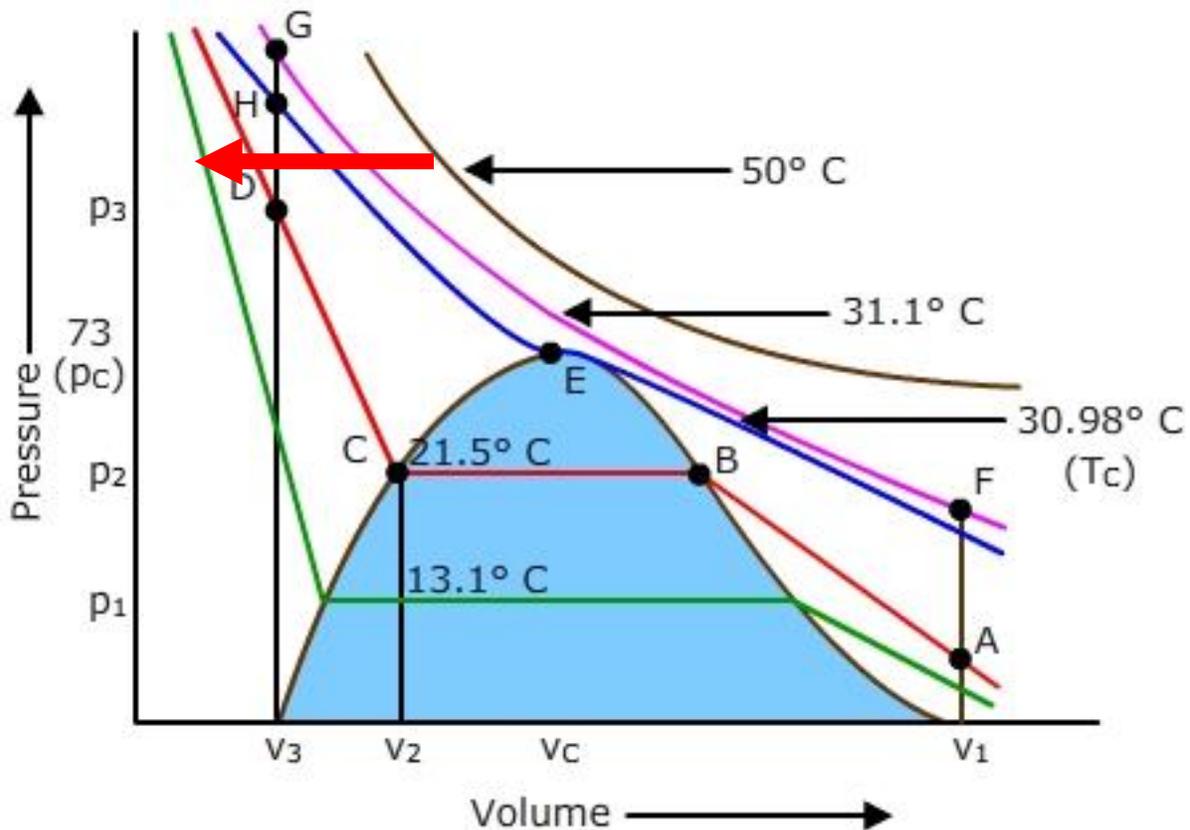
Figure 1.7: Continuity of states

1.6 Summary

✓ Attractive intermolecular interaction and non-zero size of molecules lead to departure from ideal gas behavior.
✓ Deviations from ideality of a real gas can also be measured in terms of the compressibility factor.
✓ From Andrew's experiment on CO_2, it was concluded that the critical temperature, **T_C** of a gas is the temperature above which a gas cannot be liquefied by applying pressure alone.
✓ The minimum pressure which just liquefies the gas at **T_C** is called critical pressure, **P_C** and the volume corresponding to **T_C** and **P_C** is known as the critical volume **V_C**.
✓ Liquefaction is promoted by compression and cooling.
✓ Solid, liquid and gaseous states are the three stages of a continuous phenomenon.
✓ Kinetic theory is based on mainly two postulates:matter is made up of molecules which are in a state of constant random motion and heat can be identified with molecular motion.

1.7 Exercises

I. Fill in the blanks:
1. A gas cannot be liquefied above _____ temperature, however high might be the applied pressure.
2. The forces between the molecules are negligible in case of a _____ gas.

3. According to the ideal gas equation, a gas _____ be liquefied.

4. A real gas may approximately behave as a perfect gas when put to a very low _____.

5. Perfect gas condition is that when P $\rightarrow$ 0, V $\rightarrow$_____ .

II. State true /false for each of the following statements:
1. PV should remain constant at a given temperature for an ideal gas.

2. The plot of PV as a function of P should be a straight line parallel to pressure axis for a real gas.

3. The isotherms of an ideal gas is part of a rectangular hyperbola.

III. Give Reasons:

1. Why isothermals of CO_2 gas are rectangular hyperbola above $31.1°C$?
2. Why the volume of CO_2 in tube B is same as volume of air in tube A in the Andrews Experiment?
3. Why CO_2 can never be liquefied by exerting pressure alone, however great the pressure may be?

IV. Solve the following:

1. A cylinder of volume 120 liters contains a gas at a pressure of 20 atm and temperature 30^0C. A piston is lowered into the cylinder such that the gas occupies a volume of 100 liters and the final temperature becomes 40^0C. Calculate the final pressure of the gas if it is assumed to be perfect.

2. A fixed mass of CO_2 is compressed to 70 atm at 27^0 .It is suddenly released to atmospheric pressure. What is the state of CO_2 before and after being released?

3. Calculate the number of molecules in one litre of an ideal gas at 140^0C temperature and   5atmospheric   pressure.
(hint: If n is the number of molecules per cc
[hint: If n is the number of molecules/cc,n=PN/RT]
[Given: N=6.023×10^{23} and R=8.31×10^7ergs /g mol-K)

4. The pressure exerted by a mixture of gases equals the sum of the pressures exerted by individual gases at the same temperature. Justify the statement.
(hint: The ideal gas law can be expressed in terms of the total number of molecules N. Since the law presumes that we can ignore the detailed structure of the individual   molecules and their interactions. N can represent of any number of non interactive gases.)

5. A cylinder with a tightly fitting but freely sliding piston of mass m contains air compressed by the piston. If initial height of the piston from the bottom of the cylinder is h1,.the entire system is initially in equilibrium at temperature T1. The system is immersed in a water bath whose temperature can be controlled. The temperature of the water bath is gradually increased to a final temperature T2. Calculate the final height h2 of the piston.
(hint: Since the pressure and mass of the gas sample remains constant. Charle's law is applicable and the cylinder has a uniform cross sectional area.)

V. Answer the following :

1. In what way an ideal gas differs from a real gas?

2. Describe Andrew's experiment on CO_2 and discuss the results obtained.

3. Show that the liquid and gaseous states are two distant stages of a continuous phenomenon.

4. Give any five postulates of kinetic theory of gases.

1.8 Glossary

Isotherm: It is a curve on PV indicator diagram at constant temperature.

Continuity of states: Three different stages of a continuous physical phenomenon.

Condensation: This is the process by which gas or vapour changes into liquid.

Compressibility: It is the fractional change in volume $\frac{dV}{V}$ per unit increase in pressure.

Isothermal compressibility, $K_T = -\frac{1}{V}\left(\frac{\delta V}{\delta P}\right)_T$.

Boyle's law: At constant temperature, pressure of an ideal gas is inversely proportional to volume.

Perfectly elastic collision: There is no net conversion of kinetic energy during the collision of molecules.

Transport phenomena: This phenomena occurs only in the non-equilibrium state of a gas. To attain equilibrium states momentum. thermal energy and mass are transported through the molecules from one layer of gas to another.

1.9 References

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Further readings
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