



The behaviour of real gases is different from ideal gases. You will learn the differences between these gases when you study this unit. (Picture source:

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UNIT 1

IDEAL AND REAL GASES

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STUDY GUIDE

In this unit, you will learn basic concepts of kinetic theory of gases and use the expression for pressure to obtain kinetic interpretation of temperature and deduce gas laws. The elementary kinetic theory fails to explain the behaviour of real gases under different temperatures and pressures. This problem was overcome by van der Waals. It is possible that you are familiar with some of these concepts from your +2 physics classes. In that case, you will find it easier to follow the content and begin your journey through this course on a positive note. Therefore, we would like you to refresh your earlier knowledge by referring to your school textbook. Then it will be a perfect launch pad into the core of kinetic theory.

"Life is a relationship between molecules."

Linus Pauling

1.1 INTRODUCTION



Rudolf Julius Emmanuel Clausius (1822-1888) was a German physicist and mathematician who is considered to be one of the founders of kinetic theory of gases and thermodynamics. Beginning with his famous paper in 1850 entitled "On the mechanical theory of heat", he formulated the statements of first and second laws of thermodynamics. He interpreted the free heat of the system as the kinetic energy of gas molecules.

In your school science curriculum, you have learnt that matter is made up of atoms and a few atoms combine to form a molecule. A molecule is the smallest entity that can exist in free state and exhibit all characteristic properties of a substance. You may recall that these building blocks are identical in size, mass and chemical properties. When Clausius supplemented this hypothesis by laws of mechanics for molecular motion, a new area of knowledge – **the kinetic theory of gases** – was born. You may recall that elementary kinetic theory has been used successfully to explain even large-scale physical phenomena. Some of these include distribution of gases with altitude in the Earth's lower atmosphere and adiabatic lapse rate (which refers to the change in temperature of air as we move upwards), etc.

Broadly speaking, kinetic theory of gases is based on two basic postulates: (i) Matter is made up of identical molecules, and (ii) thermal energy can be identified with molecular motion. Based on these postulates, a few assumptions are made about the nature of molecules, interactions among them and their movement. To describe this motion, simple laws of mechanics are used. This helps us to obtain elegant explanations of the laws governing the behaviour of ideal gases in equilibrium.

In Sec. 1.2, you will learn the assumptions of kinetic theory of gases. We have given justifications for their appropriateness as far as possible. In Sec. 1.3, you will learn an expression for the pressure exerted by a gas on the walls of a container and use it to correlate temperature with molecular properties. In particular, you will discover that *Absolute Zero* is that temperature at which all molecular motion ceases to exist. You will also apply this to deduce gas laws and calculate the magnitude of molecular speeds for different gases. These help us to explain the observed distribution of gases in our atmosphere. In Sec. 1.4, we have discussed the behaviour of real gases – how van der Waals' equation helps us in explaining their observed properties.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ discuss the basic assumptions of kinetic theory of gases;
- ❖ use the expression for pressure to deduce gas laws;
- ❖ interpret temperature in terms of molecular properties;
- ❖ discuss deviations shown by a real gas from an ideal gas behaviour; and
- ❖ explain how van der Waals' equation of state satisfactorily explains the behaviour of real gases.

To develop understanding of elementary kinetic theory, we first state its basic assumptions as a convenient starting point.

1.2 ASSUMPTIONS OF KINETIC THEORY

The basic assumptions of kinetic theory of ideal gases are:

1. **A gas consists of a very large number of identical molecules.** This assumption is quite justified. The number of molecules in a kilomole is 6.023×10^{26} . (This is commonly known as Avogadro number.) It means that 1 cm^3 of an ideal gas at standard temperature and pressure (STP) contains nearly 3×10^{19} molecules. (This number is almost six billion times the population of the world as of now.)
2. **The gas molecules can be regarded as point masses.** Experiments show that the diameter of a gas molecule is about $2 - 3 \times 10^{-10} \text{ m}$. The distance between any two neighbouring gas molecules at STP, on an average, is about $3 \times 10^{-9} \text{ m}$, which is an order of magnitude bigger than their diameter.
3. **The gas molecules are in a state of constant random motion.** This is shown in Fig. 1.1. (The motion of gas molecules resembles the motion of honeybees disturbed from their hive.) In essence, it means that molecules of an ideal gas can move in all possible directions and all positions are equally probable. The support for this assumption came from Brownian motion.

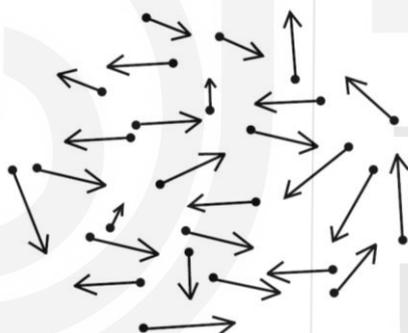


Fig. 1.1: Depiction of random motion of molecules of a gas.

4. **In the absence of any external force field, the molecules are distributed uniformly in the container.** It means that an ideal gas behaves as an isotropic medium. In practice, however, some randomness in the direction of the velocities may arise because of irregularities in the walls of the container.
5. **The molecules of a gas experience force only during collisions.** This assumption implies that there are no intermolecular forces (of mutual attraction) or any forces between the molecules and the walls of the container. That is, molecule of a gas can be thought of as moving about freely unaware of the presence of other molecules. It means that molecules of an ideal gas possess only kinetic energy.
6. **The molecules of a gas behave as perfectly elastic hard spheres.** It means that the molecules undergo perfectly elastic collisions, i.e. they do not deform in collisions among themselves or with the walls of the container.

Standard Temperature and Pressure (STP)

refer to commonly agreed sets of conditions under which experimental measurements are reported.

Internationally, two standards are in use: International Union of Pure and Applied Chemistry (IUPAC) and the National Institute of Standards and Technology (NIST). The IUPAC's standard refers to a temperature of 0°C (273.15 K) and an absolute pressure of 100 kPa (0.986 atm) while NIST's standard is a temperature of 20°C (293.15 K) and an absolute pressure of 101.325 kPa (1 atm). In this course, we shall use IUPAC standards, unless stated otherwise.

7. **The duration of collision is negligible compared to the time interval between successive collisions.**
8. **All molecules do not move with the same speed.** That is, there is a spread of molecular speeds about a mean value. This is depicted in Fig. 1.2. An indirect justification for this assumption lies in the finite width of spectral lines.
9. **All molecules move in a straight line between successive collisions. The authenticity of this assumption was validated by Brown.**

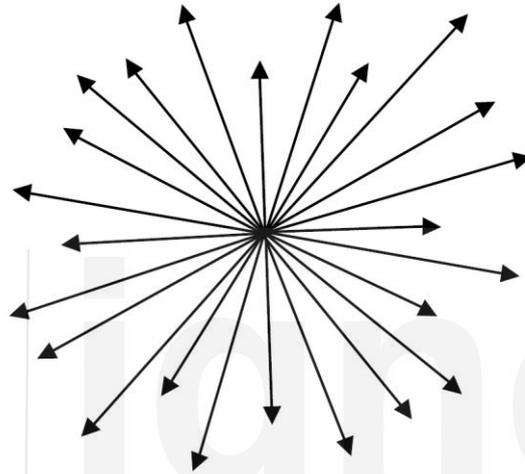


Fig. 1.2: Distribution of molecular velocities at a given temperature.

You now know the basic assumptions of kinetic theory of gases. Using these assumptions, an expression for pressure exerted by the molecules of a gas on the walls of a container can be derived. You must have learnt it in your school physics. So, we will just quote the result and use it to obtain gas laws and some other useful results. The correctness of its various predictions put faith in the kinetic theory model in its initial stages.

You may now like to answer the following SAQ.

***SAQ 1* – Validity of assumptions**

Write down the assumptions which are not justified for real gases.

1.3 PRESSURE EXERTED BY AN IDEAL GAS

Consider μ kilomole of a gas confined in a container (Fig. 1.3). For generality, we denote the total number of molecules in volume V by N . So we can say that there are $n(= N/V)$ molecules per m^3 . We assume that mass of each molecule is m . Since gas molecules are moving randomly with finite speeds, these will collide with the walls of the container and recoil. This will cause change in their momentum. Using Newton's second law of motion, it can be related to force and force exerted per unit area leads to following expression for pressure:

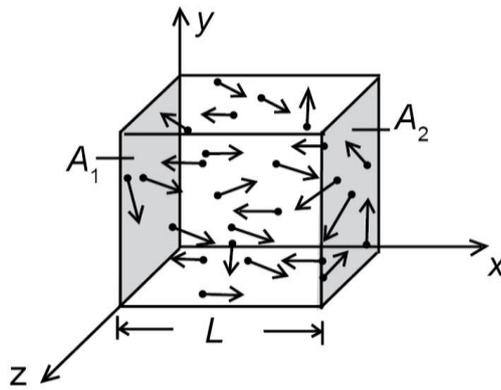


Fig. 1.3: Schematics of motion of molecules of a gas in a cubical container

$$\begin{aligned}
 p &= \frac{1}{3} mn\overline{v^2} \\
 &= \frac{1}{3V} mN\overline{v^2} = \frac{1}{3} \rho \overline{v^2}
 \end{aligned} \quad (1.1)$$

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

In the instant case,
Mass of gas = mN .

where $n = N/V$ is number density, ρ is density of the gas and $\overline{v^2}$ is mean square speed of gas molecules. This is an important result. You will note that it relates macroscopic properties (p and V) with the microscopic properties (m and v) of individual molecules making up the system. Moreover, it is independent of the shape of container.

Before proceeding further, we summarise the result of this section.

EXPRESSION FOR PRESSURE

The pressure exerted by the molecules of an ideal gas on the walls of the container is given by

$$p = \frac{1}{3} mn\overline{v^2} = \frac{1}{3} \rho \overline{v^2}$$

where m is the mass of a molecule, n is the number of molecules per cubic metre, ρ is the density of the gas and $\overline{v^2}$ is the mean square speed of gas molecules. Note that in this prescription, gas molecules are regarded as randomly moving point masses devoid of inter-molecular forces.



Don't forget!

You will agree that we started from a purely mechanical picture of a gas as a collection of randomly moving molecules. But we have obtained an expression for pressure in terms of the microscopic properties of individual molecules. Let us now discover kinetic interpretation of temperature and learn to use Eq. (1.1) to deduce gas laws.

1.3.1 Kinetic Interpretation of Temperature

To seek kinetic interpretation of temperature, we first rewrite Eq. (1.1) as

$$pV = \frac{2}{3} N \left(\frac{1}{2} m\overline{v^2} \right) = \frac{2}{3} N\epsilon \quad (1.2)$$

where $\varepsilon = \frac{1}{2} m \overline{v^2}$ is average kinetic energy of a gas molecule.

For one mole of a gas, N equals Avogadro's number, N_A . And from ideal gas equation, we recall that

$$pV = \mu RT$$

where $\mu = N/N_A$ is the number of kilomole of the gas, T is absolute temperature and R is *kilomolar gas constant*. Its value is $8314 \text{ J kmol}^{-1} \text{ K}^{-1}$. By combining ideal gas equation with Eq. (1.2), we can connect ε to temperature through the relation

$$\frac{2}{3} \mu N_A \varepsilon = \mu RT$$

or
$$\varepsilon = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} k_B T \quad (1.3)$$

In text books, Boltzmann constant is denoted by k .

$$1.6 \times 10^{-19} \text{ J} = 1 \text{ eV}$$

where $k_B = R/N_A$ is *Boltzmann constant*. Its value is $1.38 \times 10^{-23} \text{ JK}^{-1}$. At 300 K, kinetic energy of a molecule is about $6 \times 10^{-21} \text{ J}$ or 0.04 eV (see SAQ 2). Therefore, even if all this energy could be absorbed in a head-on collision between molecules moving in opposite directions, it is too small to increase the internal energy of either molecule. This justifies why it is reasonable to treat gas molecules as perfect hard spheres.

Note that in arriving at Eq. (1.3), we have connected a purely mechanical quantity – the average kinetic energy of a molecule – to temperature. This is a big step as it relates molecular (microscopic) and macroscopic viewpoints through Boltzmann constant. (In Block 4, you will learn that Boltzmann constant appears in the relation that bridges the statistical and the thermodynamic viewpoints for a system in equilibrium.) This assigns a completely new and deeper meaning to temperature:

- Temperature is linearly proportional to average (kinetic) energy of molecules of an ideal gas.
- At a given temperature, the (kinetic) energy of the molecules of all gases, irrespective of the differences in their masses, will be the same.
- The motion of gas molecules will become more vigorous as temperature increases. However, **at absolute zero of temperature, the gas molecules will be devoid of all motion**. So kinetic theory predicts that at absolute zero, all molecules will behave as if frozen in space. (In Block 4 on Statistical Mechanics, you will learn that due to quantum effects, a few typical systems possess finite energy even at absolute zero.)

Activity 1

We cannot see gas molecules. But to get a feel of increased molecular motion, observe the motion of potassium permanganate (KMnO_4) molecules in water kept in a glass beaker. As you heat water, motion of KMnO_4 molecules will gradually become more and more vigorous.

KINETIC INTERPRETATION OF TEMPERATURE

Temperature is linearly proportional to average (kinetic) energy of molecules. It means that the motion of gas molecules will become more lively as temperature increases. However, at absolute zero, all molecules will behave as if frozen in space, devoid of all motion.



Before proceeding further, you should solve the following SAQ.

SAQ 2 – Average kinetic energy of an ideal gas

Calculate the average kinetic energy of molecules of an ideal gas at STP.

Take $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

Do you think that we have developed a reliable model of gaseous state? As a first check of this model, let us use it to calculate the value of molecular speed. Thereafter, we shall calculate some other numbers of physical interests.

1.3.2 Molecular Speeds

To know how fast the molecules in a gas move, we equate expressions for kinetic energy expressed in terms of mean square speed and temperature as

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T = \frac{3}{2} \frac{R}{N_A} T$$

so that

$$\overline{v^2} = \frac{3k_B T}{m} = \frac{3RT}{M}$$

where $M = mN_A$ is molecular weight of the gas.

The square root of mean square speed is usually denoted as v_{rms} and is called **root mean square speed**. It is given by

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}} \quad (1.4)$$

From this expression we note that v_{rms} is inversely proportional to the molecular weight of a gas. It implies that at a given temperature, lighter gas molecules would move faster. For a few gases found in our atmosphere, the values of v_{rms} at STP are given in Table 1.1.

Table 1.1: Values of v_{rms} for different gases at 273 K

Gas	v_{rms} (ms ⁻¹)	Gas	v_{rms} (ms ⁻¹)
H ₂	1840	O ₂	450
He	1300	Ar	410
H ₂ O	615	CO ₂	393
N ₂	493	Benzene vapour	290
Air	485	Mercury vapour	180

The fact that lighter molecules move faster has an interesting consequence for existence of life on our planet. Gases like hydrogen, helium, nitrogen and water vapour move upward in the Earth's atmosphere, whereas oxygen and carbon dioxide are available near the Earth's surface. This provided an indirect evidence in favour of kinetic theory.

Further, from your school physics, you will recall that an object having radially outward velocity more than 11.2 km s^{-1} can escape from the influence of gravity of Earth. ($v_e = \sqrt{2gR}$, where R is radius of the Earth.) Since no gas molecule has speed greater than v_e , there is little chance of their escaping from the Earth instantaneously. For the Moon, Jupiter and the Sun, the values of escape velocity are 2.3 km s^{-1} , 60 km s^{-1} and 600 km s^{-1} , respectively. This explains why over a period of time, all gases have escaped from the surface of the Moon, whereas even hydrogen is held back by the Sun.

The ever widening ozone holes in the upper atmosphere over the North Arctic as well as Antarctica are together of the size of Australia and pose a serious threat to the existence of life on our planet.

The vertical distribution of gases in our atmosphere can also be used to understand the ill-effects of pollution of air and greenhouse effect caused by gases such as carbon monoxide and nitrogen oxide, which combine with atmospheric oxygen and get converted into carbon dioxide, chlorofluorocarbons (CFCs) and oxides of nitrogen. These chemicals are discharged by vehicular/air traffic, air conditioners and refrigerators in our atmosphere. This highlights why we should plant more trees and push for eco-friendly systems. Moreover, it is important to get our vehicles regularly checked for pollution. (In fact, in metropolitan cities, the central and state governments have made pollution check for all vehicles mandatory. Now-a-days, these agencies are recommending the use of CNG gas. But some experts are of the view that even the use of CNG is not devoid of harmful effects, since benzene vapour tends to stay close to the ground level. The emission standards for vehicles are also being reviewed periodically and Govt proposes to move to Bharat VI compliant vehicles.) In the upper layers of the atmosphere, these gases are breaking up ozone, which is so vital for absorbing ultraviolet radiations and stopping them from entering the biosphere.

The correct prediction of vertical distribution of gases in our atmosphere provided indirect but sound evidence in its favour and boosted the confidence of physicists in it. The next step was to deduce gas laws from the expression for pressure. You will now learn to deduce the gas laws.

1.3.3 Deduction of Gas Laws

By combining Eqs. (1.2) and (1.3) for a given mass of a gas, we can write

$$pV = Nk_B T \quad (1.5)$$

Since the right-hand side in the above relation will remain constant at a fixed temperature, we can write

$$pV = \text{constant} \quad (1.5a)$$

From this result we note that *pressure exerted by a given mass of a gas varies inversely with its volume, when temperature remains constant*. This is **Boyle's law**.

For constant volume, Eq. (1.5) implies that

$$\frac{p}{T} = \text{constant} \quad (1.5b)$$

That is, *at constant volume, pressure exerted by a given mass of a gas is directly proportional to its temperature.* This is **Gay-Lussac's law**.

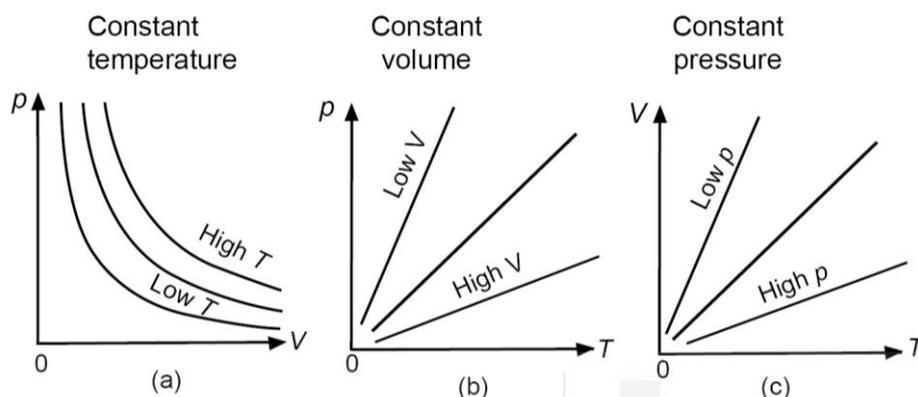


Fig. 1.4: Graphical depiction of a) Boyle's law; b) Gay-Lussac's law; c) Charles' law.

When pressure remains constant, Eq. (1.5) implies that

$$\frac{V}{T} = \text{constant} \quad (1.5c)$$

That is, *the volume of a given mass of a gas changes linearly with temperature.* This is **Charles' law**. Fig. 1.4 illustrates these three laws graphically.

Note that the straight lines in Figs. 1.4b and c seem to merge towards origin. The trend is only indicative, as absolute zero is unattainable. Therefore, these curves can be obtained only for finite values of temperature.

Note that these laws are strictly valid only for ideal gases.

Next, we consider two different gases at the same temperature and pressure. Then, from Eq. (1.1) we can write

$$\begin{aligned} p &= \frac{1}{3} m_1 n_1 \overline{v_1^2} \\ &= \frac{1}{3} m_2 n_2 \overline{v_2^2} \end{aligned} \quad (1.6)$$

where $\overline{v_1^2}$ and $\overline{v_2^2}$ are respectively the mean squared speeds of the molecules of two gases.

Recall that at constant temperature, the mean kinetic energies of both gases will be equal. So, we can write

$$\frac{1}{2} m_1 \overline{v_1^2} = \frac{1}{2} m_2 \overline{v_2^2}$$

On combining this result with Eq. (1.6), we get

$$n_1 = n_2 \quad (1.7)$$

This is mathematical statement of **Avogadro's law**, which states that *at constant temperature and pressure, equal volume of all gases contains the same number of molecules.*

Before proceeding further, you should answer the following SAQ.

SAQ 3 – Gas laws

When we blow air in a balloon, both pressure and volume increase simultaneously. Does it violate Boyle's law? Explain.

To get a feel of these results you should go through the following example carefully.

EXAMPLE 1.1: DENSITY OF A GAS

Calculate the number density of oxygen at $1 \text{ atm} = 1.013 \times 10^5 \text{ Nm}^{-2}$ and $T = 300 \text{ K}$. Also calculate its density using the data given in Table 1.1. Take $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$.

SOLUTION ■ By combining Eq. (1.1) with the equation of state for an ideal gas, we can write

$$p = \frac{1}{3} mn \overline{v^2} = nk_B T$$

so that

$$n = \frac{p}{k_B T}$$

On substituting the given numerical values, we get

$$\begin{aligned} n &= \frac{1.013 \times 10^5 \text{ Nm}^{-2}}{(1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K})} \\ &= \frac{1.013 \times 10^{26}}{4.14} \text{ m}^{-3} = 2.45 \times 10^{25} \text{ m}^{-3} \end{aligned}$$

Using the value of $\overline{v^2}$ given in Table 1.1, we can write

$$\rho = \frac{3p}{\overline{v^2}} = \frac{3 \times 1.013 \times 10^5 \text{ Nm}^{-2}}{(450 \text{ ms}^{-1})^2} = 1.5 \text{ kg m}^{-3}$$

You will agree that motion of extremely large number of molecules can be described in terms of simple laws which can be verified by experiments up to a fairly reasonable degree of correctness. The remarkable elegance of kinetic theory brings out its aesthetic appeal. The success proved an important milestone in the growth of the kinetic theory. However, this theory was put to litmus test when it was applied to real gases.

1.4 DEVIATIONS FROM IDEAL GAS BEHAVIOUR

You now know that ideal gas model is simple and widely applicable. However, it does not hold universally. The concept of ideal gas breaks down for common gases at high pressures and low temperatures. That is, *the ideal gas equation does not apply at high pressures and low temperatures*. Another major drawback of ideal gas model is its inability to predict liquefaction of gases, which is technologically important. You will now definitely like to know the reasons responsible for these limitations. The following paragraphs will serve this purpose.

1. **Regnault's Experiments:** Regnault performed a series of experiments by applying pressure up to 30 atmosphere and varying the temperature from 273 K to 373 K. His results for hydrogen, oxygen, nitrogen and carbon dioxide for $T = 273\text{K}$ and pressure in the range 0-10 atm are shown in Fig. 1.5, where we have plotted pV as a function of p . The straight line (dotted curve) parallel to the p -axis corresponds to a perfect gas. On closely examining the curves, you will note that for real gases:

- The curves are straight lines inclined to the p -axis.
- The product pV increases with p for hydrogen and decreases for nitrogen, oxygen and carbon dioxide.
- All the curves converge to the same point ($2.271 \times 10^3 \text{ J mol}^{-1}$) on the pV -axis at 273 K. This value corresponds to $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ for $T = 273 \text{ K}$. This is the accepted value of Universal gas constant. Therefore, we can say that real gases deviate from perfect gas behaviour, except for $p \rightarrow 0$.

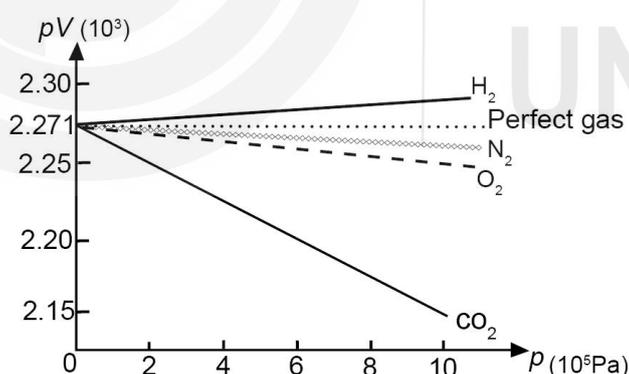


Fig. 1.5: Variation of pV versus p for hydrogen, oxygen, nitrogen and carbon dioxide in the range 0-10 atm. The dotted horizontal line indicates the values for an ideal gas.

2. **Andrews' Experiments:** Andrews carried out detailed experiments on the compressibility of gases while trying to liquefy them. For CO_2 , his results are shown on the p - V diagram at various temperatures in Fig. 1.6. We can draw the following conclusions:

- At 321 K and above, the behaviour of CO_2 resembles that of a perfect gas.

- ii) At 304.4 K, a kink appears in the isotherm. It signifies that CO₂ gas has begun to condense. The point *P* is called point of inflexion.
- iii) At 294.5 K, the kink has spread into a horizontal line. It signifies coexistence of liquid and gaseous phases. Physically, it implies a discontinuous change in the density of the material for a particular range of values of pressure and temperature.
- iv) For $T < 294.5$ K, this trend continues.

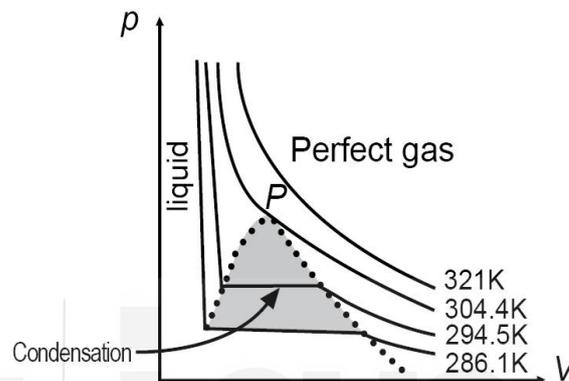


Fig. 1.6: Andrews' curves for CO₂.

The set of values of temperature (T_c) and pressure (p_c) at the point of inflexion are called **critical values**.

You may ask: Are the gaseous and liquid phases identical at this point? Note that the dotted curve in Fig. 1.6 passes through the extremities of horizontal portions of different isotherms indicating vapour state on the right and liquid state on the left. The area within the dotted curve marks co-existence of vapour – liquid phase in equilibrium.

The values of T_c and p_c for some common gases are given in Table 1.2.

You will note that each gas has its characteristic critical temperature and pressure. Furthermore, the pressure required for liquefaction is less for a gas having lower value of critical temperature.

Table 1.2: Critical temperature and pressure for some common gases

Gas	T_c (K)	p_c (10^5 Pa)
He	5.2	2.3
H ₂	33	13
Ar	151	49
O ₂	155	51
CO ₂	304	74
NH ₃	405	113

Critical temperature (T_c): of a gas is defined as that temperature below which the gas can be liquefied by the application of pressure alone. Above the critical temperature, the gas cannot be liquefied howsoever large the applied pressure may be.

Critical pressure (p_c): is the pressure applied to the gas at its critical temperature so that it gets liquefied.

From Fig. 1.6, we can say that

- a) A gas can be liquefied only if it is cooled up to or below its characteristic critical temperature. It is therefore clear that the increase in pV for hydrogen observed by Regnault (Fig. 1.5) arises because its critical temperature is much below the room temperature.
 - b) There exists a continuity of liquid and gaseous states. That is, these are two distinct stages of a continuous physical phenomenon. It means that it is possible to move from the gas to the liquid phase by compressing the gas to a high pressure and then cooling it gradually.
3. Amagat and other experimentalists investigated the behaviour of several gases at various temperatures and up to 3000 atm pressure. Their work lent support to the findings of Regnault and Andrews.

Before proceeding further, let us recapitulate what you have learnt in this section.

REAL GASES

Recap

The work of Andrews, Regnault, Amagat and other experimental physicists on real gases showed that

- Real gases do not obey ideal gas equation of state, except for low pressures.
- It is easier to liquefy a gas at lower temperatures. No liquefaction can occur above critical temperature, however high the pressure may be.
- Compression promotes liquefaction.

Before proceeding further, you may like to answer an SAQ.

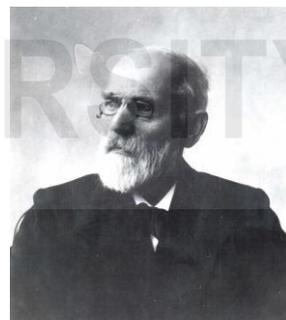
SAQ 4 – Liquefaction of gases

In Table 1.2 we have given values of T_c and p_c for some common gases. Which of these gases cannot be liquefied by compression alone at room temperature?

So far, we have discussed the observed behaviour of a few gases under different conditions of temperature and pressure. A satisfactory theoretical explanation of these results was provided by van der Waals.

1.5 VAN DER WAALS' EQUATION OF STATE

In order to explain experimental results, theoretical physicists revisited the assumptions of elementary kinetic theory with a view to modify the ideal equation of state. Accordingly, several equations of state were put forward to describe the behaviour of real gases. But the most elegant effort in this



Johannes Diderik van der Waals (1837 – 1923) was a Dutch theoretical physicist. He is credited for his equation of state to understand the behaviour of real gases, concept of molecular size and intermolecular forces. He received the Nobel Prize in 1910 for this work.

direction was made by van der Waals. He made reasonable assumptions regarding the size of gas molecules and nature of intermolecular forces. It is therefore pertinent to first know the assumptions made by him.

Assumptions

1. Gas molecules have finite size and behave as incompressible rigid spheres.
2. Gas molecules attract each other with a weak force which is a function of distance between them. (This implies that molecules of a real gas have kinetic as well as potential energies.) However, only nearest neighbour interactions are important.
3. The number of collisions with the walls of the container remain the same for point and finite size molecules.

For one mole of the gas, he obtained the following equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (1.8)$$

This equation is known as **van der Waals' equation of state**. The constants a and b are known as van der Waals' constants. Their values are assumed to depend only on the nature of the gas. For some common gases, we have listed the values of van der Waals' constants in Table 1.3. (a/V^2) is termed as cohesive pressure and arises due to presence of inter-molecular interactions.

Table 1.3: van der Waals' Constants for Some Common Gases

Gas	a ($10^{-6} \text{ atm m}^6 \text{ mol}^{-2}$)	b ($10^{-6} \text{ m}^3 \text{ mol}^{-1}$)
H ₂	0.244	26.6
He	0.034	23.7
N ₂	1.39	39.1
O ₂	1.36	31.8
Ar	1.35	32.2
Ne	0.210	17.1
H ₂ O	5.46	30.5
NH ₃	4.17	37.1
CO ₂	3.59	42.7
CH ₄	2.25	42.8

A p - V diagram is also referred to as an indicator diagram.

For μ moles of the gas, van der Waals' equation takes the form

$$\left(p + \frac{\mu^2 a}{V^2}\right)(V - \mu b) = \mu RT \quad (1.9)$$

Note that for a rarefied gas, $p \gg a/V^2$ and $V \gg \mu b$, van der Waals' equation

reduces to the equation of state for an ideal gas. For a given temperature, plot of Eq. (1.8) on the indicator diagram is shown in Fig. 1.7. The contribution of self-attracting term is shown separately.

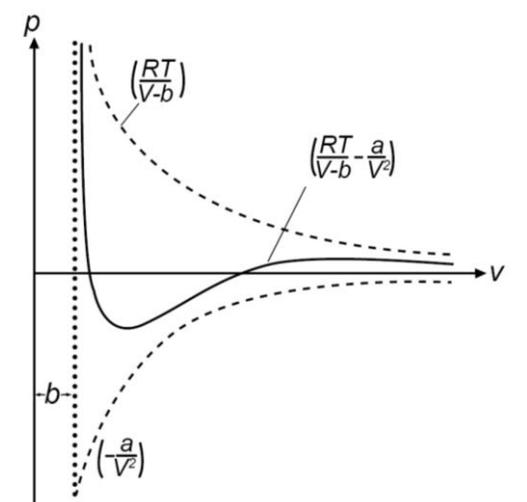


Fig. 1.7: Plot of Eq. (1.8) on p - V diagram.

We now give a solved example. It should give you an idea about the magnitude of various terms occurring in Eq. (1.8). You should go through it carefully.

EXAMPLE 1.2: VAN DER WAALS' EQUATION

One mole of CO_2 occupies 192 cm^3 at 32.5°C and 70 atm . Calculate the pressure exerted by CO_2 molecules, if we assume that it obeys (i) perfect gas equation, and (ii) van der Waals' equation. Given $a = 3.59 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2}$, $b = 42.7 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ and $R = 8.2 \times 10^{-5} \text{ atm m}^3 \text{ K}^{-1} \text{ mol}^{-1}$.

SOLUTION ■ Volume of $\text{CO}_2 = 192 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$,
 $T = 273 + 32.5 = 305.5 \text{ K}$

i) In case CO_2 behaves as a perfect gas, we have

$$p = \frac{RT}{V} = \frac{(8.2 \times 10^{-5} \text{ atm m}^3 \text{ K}^{-1} \text{ mol}^{-1}) \times (305.5 \text{ K})}{(192 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})} = 131 \text{ atm}$$

ii) If CO_2 obeys van der Waals equation, the pressure exerted by CO_2 molecules is given by

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{(8.2 \times 10^{-5} \text{ atm m}^3 \text{ K}^{-1} \text{ mol}^{-1}) \times (305.5 \text{ K})}{(192 \times 10^{-6} - 42.7 \times 10^{-6}) \text{ m}^3 \text{ mol}^{-1}} - \frac{3.59 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2}}{(192 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})^2} = 70.4 \text{ atm}$$

You will note that in this case, (a) the pressure calculated for a van der Waals' gas is close to the observed value of 70 atm , and (b) it is much less than that calculated by assuming CO_2 to be an ideal gas. It means that the cohesive pressure and co-volume account for nearly 60.6 atm .

Before proceeding further, we recapitulate what you have learnt about it so far.

Recap

VAN DER WAALS' EQUATION

- van der Waals modified the ideal gas assumptions on the size of molecules and inter-molecular forces.
- Based on these assumptions, for one mole of the gas he obtained the equation

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

where a and b are constant for a gas.

- b is referred to as **co-volume**.
- Due to intermolecular forces, the pressure exerted by the molecules of a real gas is less than that exerted by an ideal gas. This drop is known as **cohesive pressure**.

1.5.1 Comparison with Experimental Results

We now discuss how van der Waals' equation explains experimental results. To do so, we first rewrite Eq. (1.8) as

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \quad (1.10)$$

In expanded form, this equation can be rewritten as

$$pV^3 - (pb + RT)V^2 + a(V - b) = 0 \quad (1.11)$$

From this we note that:

1. van der Waals' equation is cubic in V . It means that for given values of p and T , V will have three values, which become equal at the point where condensation begins ($T = T_c$).
2. For large values of V , p would be small and van der Waals' equation reduces to an ideal gas equation. On the other hand, when $V \rightarrow b$ for finite temperatures, $p \rightarrow \infty$. Further, V cannot be less than b as this will lead to negative values of p , which is physically unacceptable. Obviously, a gas cannot occupy volume less than that of molecules, which are assumed to be incompressible rigid hard spheres.
3. For CO_2 , the plot of theoretical curves obtained on the basis of van der Waals' equation at various temperatures is shown in Fig. 1.8. Note that the qualitative shape of the curves resembles the experimental isotherms of Andrews (Fig. 1.6). However, there are differences in details, particularly at low temperatures. For instance, van der Waals' equation predicts wave-like pattern in the straight-line region of Andrews' curves obtained for $T \leq 294.5$ K. This is depicted as shaded portion in this figure. For $T = 286.1$ K, the portions AB and FG respectively represent gaseous and liquid states. However, the portion BC represents supersaturated

vapour and portion EF represents a superheated liquid. These correspond to meta-stable states and are not observed in the experimental results obtained by Andrews, which represent only the states of stable equilibrium. The portion CDE of the theoretical curve indicates that as we move from the state of supersaturated vapour towards superheated liquid, the volume and pressure decrease simultaneously. This corresponds to a *collapsible state*, which is unnatural and can never be realised in practice.

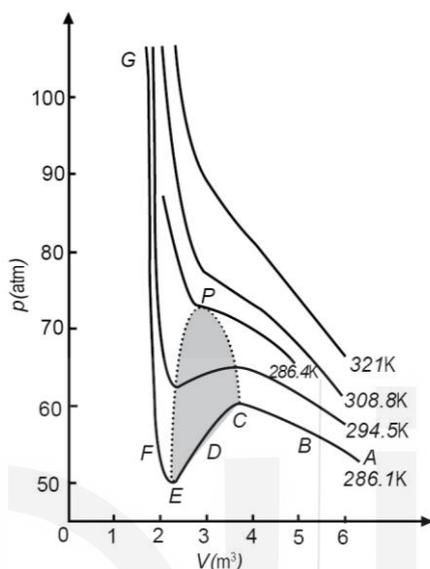


Fig. 1.8: Theoretical isotherms for CO_2 .

We thus find that proper interpretation of van der Waals' curves helps to resolve the apparent discrepancy with observed results.

Let us now sum up what you have learnt in this unit.

1.6 SUMMARY

Concept	Description
Pressure exerted by gas molecules	<ul style="list-style-type: none"> The pressure exerted by the molecules of a gas on the walls of a container is given by $p = \frac{1}{3} mn\overline{v^2} = \frac{1}{3} \rho \overline{v^2}.$
Root mean square speed	<ul style="list-style-type: none"> The root mean square speed of a gas molecule is given by $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}}$ <ul style="list-style-type: none"> At absolute zero temperature, gas molecules are devoid of all motion.
Van der Waals' equation for real gases	<ul style="list-style-type: none"> Ideal gas equation fails to explain observed behaviour of real gases, except at low temperatures. van der Waals' equation of state for one mole of a real gas is $\left(p + \frac{a}{V^2}\right)(V - b) = RT$

- Here (a / V^2) arises due to the presence of intermolecular interactions and is called cohesive pressure. b is known as co-volume and has its origin in the finite size of the gas molecules.
- van der Waals' equation reduces to perfect gas equation at low pressures.

1.7 TERMINAL QUESTIONS

1. Calculate v_{rms} for helium atoms at 300K. At what temperature will oxygen molecules have the same value of v_{rms} ?
Take $m_{He} = 6.67 \times 10^{-27}$ kg.
2. A cubical box of side 0.1 m contains 3×10^{22} molecules of a gas at 300 K. Calculate the average pressure exerted by it on the walls of the cube.
3. Calculate the temperature at which the root mean square speed of hydrogen and oxygen molecules will be equal to their escape velocities from the Earth's gravitational field. The radius of the Earth is 6400 km.

$$N_A = 6 \times 10^{26} \text{ mol}^{-1}, \quad g = 9.8 \text{ ms}^{-2}, \quad k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

4. Calculate the average kinetic energy of neutrons at 300 K. Take the mass of the neutron as 1.675×10^{-27} kg.
5. 210 g of N_2 gas at 8 atm pressure occupies $24 \times 10^{-3} \text{ m}^3$ of volume. Assuming that the gas obeys van der Waals' equation of state with $a = 1.39 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2}$ and $b = 39.1 \times 10^{-6} \text{ atm m}^3 \text{ mol}^{-1}$, calculate its temperature.

1.8 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. The assumptions made about point size of molecules and lack of intermolecular attraction will not be valid for real gases. The equation of state for real gases is more accurately described by van der Waals' equation.
2. We know that the average kinetic energy of a molecule is given by

$$\begin{aligned} \varepsilon &= \frac{3}{2} k_B T = \frac{3}{2} \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times 300 \text{ K} \\ &= 6.21 \times 10^{-21} \text{ J} = 3.88 \times 10^{-2} \text{ eV} = 39 \text{ meV} \end{aligned}$$

since $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

3. Boyle's law is not violated because in this case the mass of the gas does not remain constant inside the balloon.
4. We know that a gas can be liquefied by compression when its temperature is below its critical temperature. So, we cannot liquefy helium, argon, hydrogen and oxygen at room temperature.

Terminal Questions

1. We know that

$$v_{rms}(\text{He}) = \sqrt{\frac{3k_B T}{m_{\text{He}}}}$$

On inserting the numerical data, we get

$$\begin{aligned} v_{rms} &= \sqrt{\frac{3 \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K})}{6.67 \times 10^{-27} \text{ kg}}} \\ &= 1365 \text{ ms}^{-1} \end{aligned}$$

You can also write

$$\begin{aligned} 1 &= \frac{v_{rms}(\text{O}_2)}{v_{rms}(\text{He})} \\ &= \sqrt{\frac{T_{\text{O}_2}}{M_{\text{O}_2}} \times \frac{M_{\text{He}}}{T_{\text{He}}}} \end{aligned}$$

so that the temperature at which the root mean square speed of oxygen will become equal to that of helium is given by

$$\begin{aligned} T_{\text{O}_2} &= \frac{M_{\text{O}_2} T_{\text{He}}}{M_{\text{He}}} = \frac{8 M_{\text{He}} T_{\text{He}}}{M_{\text{He}}} \\ &= 8 T_{\text{He}} = 2400 \text{ K} \end{aligned}$$

2. Here $N = 3 \times 10^{22}$ molecules, $T = 300 \text{ K}$ and $V = 10^{-3} \text{ m}^3$. On inserting these values in the ideal gas equation

$$p = \frac{N}{V} k_B T$$

we get

$$\begin{aligned} p &= \frac{3 \times 10^{22}}{10^{-3} \text{ m}^3} \times (1.38 \times 10^{-23} \text{ JK}^{-1}) \times (300 \text{ K}) \\ &= 1.24 \times 10^5 \text{ Nm}^{-2} \end{aligned}$$

3. The average kinetic energy of a gas molecule of mass m and moving with root mean square speed, v_{rms} is equal to $\frac{1}{2} m \overline{v^2}$ or $\frac{3}{2} k_B T$. We know that the escape velocity from the surface of the Earth is given by

$$v_{es} = \sqrt{2gR_0}$$

where g is acceleration due to gravity and R_0 is the radius of the Earth.

Since kinetic energy of a molecule moving with escape velocity will be equal to $\frac{1}{2} m v_{es}^2$ we can write

$$\frac{3}{2} k_B T = mgR_0$$

so that $T = \frac{2}{3} \frac{mgR_0}{k_B}$

a) For hydrogen molecules

$$T_{\text{H}_2} = \frac{2}{3} \frac{m_{\text{H}_2} g R_0}{k_B}$$

$$\text{Here } m_{H_2} = \frac{2}{N_A} = \frac{2}{6 \times 10^{26}} \text{ kg, } g = 9.8 \text{ ms}^{-1}, R_0 = 6.4 \times 10^6 \text{ m}$$

$$\text{and } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}.$$

$$\therefore T_{H_2} = \frac{2}{3} \times \left(\frac{2}{6 \times 10^{26}} \text{ kg} \right) \times \left(\frac{(9.8 \text{ ms}^{-2}) \times (6.4 \times 10^6 \text{ m})}{1.38 \times 10^{-23} \text{ JK}^{-1}} \right) = 1.1 \times 10^4 \text{ K}$$

b) For oxygen molecules

$$\begin{aligned} T_{O_2} &= \frac{2}{3} \frac{m_{O_2} g R_0}{k_B} = \frac{2}{3} \times \frac{16 m_{H_2}}{k_B} g R_0 = 16 T_{H_2} \\ &= 1.62 \times 10^5 \text{ K} \end{aligned}$$

4. The average kinetic energy of an ideal gas molecule is given by

$$\varepsilon = \frac{3}{2} k_B T$$

We consider that assembly of neutrons behaves as an ideal gas.

Therefore, on substituting the values of $k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}$ and

$T = 300 \text{ K}$, we get

$$\varepsilon = \frac{3 \times 1.38 \times 10^{-23} \times 300}{2} = 6.21 \times 10^{-21} \text{ J} = 0.04 \text{ eV}$$

Such neutrons are known as thermal neutrons and are very effective in inducing fission reaction in isotopes of uranium and plutonium. A controlled fission reaction is used to produce electricity in a nuclear power plant. Nuclear energy also finds important uses in agriculture, industry and medicine, among others.

5. Since mass of the gas taken is 210 g and its molecular weight is 28, the number of moles is $210 \text{ g} / 28 \text{ g} = 7.5$.

Volume of the gas $V = 24 \times 10^{-3} \text{ m}^3$

External pressure $p = 8 \text{ atm}$

Now, van der Waals' equation of state for μ moles reads

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

We rewrite it as

$$T = \frac{1}{\mu R} \left(p + \frac{\mu^2 a}{V^2} \right) (V - \mu b)$$

Substituting various values, we get

$$\begin{aligned} T &= \left(\frac{1}{7.5 \text{ mol} \times (8.2 \times 10^{-5} \text{ atm m}^3 \text{ mol}^{-1} \text{ K}^{-1})} \right) \times \\ &\quad \left(8 \text{ atm} + \frac{(7.5)^2 \text{ mol}^2 \times (1.39 \times 10^{-6} \text{ atm m}^6 \text{ mol}^{-2})}{(24 \times 10^{-3} \text{ m}^3)^2} \right) \times \\ &\quad (24 \times 10^{-3} \text{ m}^3 - 7.5 \text{ mol} \times 39.1 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \\ &= 313.2 \text{ K} \end{aligned}$$