Deviation of Real Gases from Ideal Gas Behaviour

Ideal and Real Gas

An ideal gas is composed of randomly moving minute particles, which undergo elastic collisions. Although there is no such thing as an ideal gas, genuine gases are known to behave in ideal ways under certain circumstances. An ideal gas obeys the ideal gas equation PV=nRT at all pressures and temperatures. The molecules of ideal gases are assumed to be volume less points with no attractive forces between one another.

Real gases are the ones which do not follow the ideal relations of gas law. The deviation of real gases from ideal gas behaviour occurs due to the assumption that if pressure increases the volume decreases. The volume will approach a smaller number but will not be zero because the molecules will occupy some space that cannot be compressed further. Almost all gases vary in some manner from the ideal behavior. Non-ideal or actual gases, such as H_2, N_2, and CO_2, do not obey the ideal-gas equation. Deviations from ideal behaviour are observed particularly at high pressures or low temperatures

Compressibility Factor

A new function called the Compressibility factor, denoted by Z, can be used to quantify the degree to which real gas deviates from ideal behaviour. It's described as

$$Z = PV/RT$$

- The plot of the compressibility factor, Z, vs. P, reveals the degree of departure from optimum behaviour.
- For, ideal gases, Z= 1 at all temperature and pressures.
- Temperature and pressure have no effect on an ideal gas, which has a Z value of 1 at all temperatures and pressures
- For non-ideal or real gases, **Z>1 or Z< 1.**
- Thus, the value of Z determines the difference between ideal and real gas behaviour.
- The degree of gas non-ideality is represented by the difference between unity and Z.
- Pressure and temperature cause deviations from optimal behaviour in a real gas.
- When $Z < 1$, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behaviour.
- When $Z > 1$, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behaviour.

## Effect of Pressure Variation on Deviations

In the graph below, the compressibility factor, Z, for **H_2, N_2, and CO_2** at constant temperature is plotted against pressure.
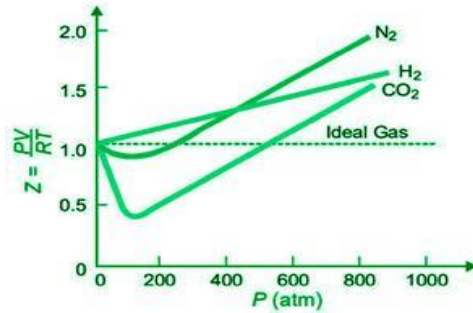
- For all of these gases, Z is practically equal to one at very low pressure.
- Real gases behave almost perfectly at low pressures (up to 10 atm).
- As the pressure rises, H_2 exhibits a steady increase in Z (from Z=1). As a result, the H_2 curve is higher than the ideal gas curve at all pressures.
- For N_2 and CO_2, Z decreases at first (Z<1), then reaches a minimum, and finally increases with increasing pressure (Z>1).
- Because CO_2 is the most easily liquefied gas, it has the greatest drop in the curve.

Effect of Temperature on Deviations

The graph below shows plots of Z or PV/RT against P for N_2 at various temperatures.
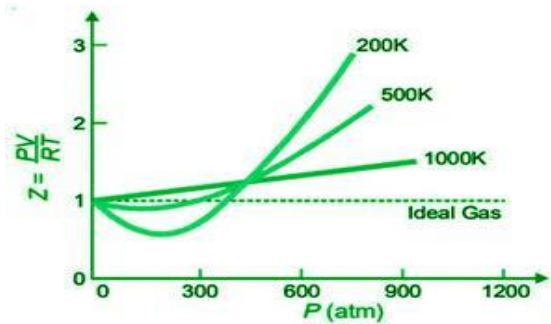
- As the temperature rises, the deviations from ideal gas behaviour become smaller and smaller, as shown by the shape of the graphs.
- At lower temperatures, the curve dips significantly, and the slope of the curve is negative. In this situation, Z<1.
- As the temperature rises, the dip in the curve decreases. The curve's minimum vanishes at a certain temperature and remains horizontal for a wide range of pressures.
- At this temperature, PV/RT is nearly equal, thus Boyle's law is satisfied. As a result, Boyle's temperature refers to the temperature of the gas.
- Each gas has its own Boyle temperature, such as 332K for N_2.

Important facts:

- **Real gases perform approximately ideal at low pressures and relatively high temperatures, and the ideal-gas equation is obeyed.**
- **A real gas deviates greatly from ideality at low temperatures and sufficiently high pressures, and the ideal-gas equation is no longer valid.**
- **As the gas approaches the liquefaction point, the departure from ideal behaviour grows.**

Causes of Real Gas Behaviour

The causes of deviations from ideal behaviour may be due to the following two assumptions of kinetic theory of gases-

- **The volume occupied by gas molecules is negligibly small as compared to the volume occupied by the gas.**
- **The forces of attraction between gas molecules are negligible**.

- **Volume of gas molecules:** The first assumption is valid only at low pressures and high temperature, when the volume occupied by the gas molecules is negligible as compared to the total volume of the gas. But at low temperature or at high pressure, the molecules being in compressible the volumes of molecules are no more negligible as compared to the total volume of the gas. This means that the actual volume occupied by the gas is slightly less than the volume of the container.
- **Intermolecular forces:** The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored. Thus, in real gases, there are attractive and repulsive forces between gas molecules, which affect the behavior of the gas. The attractive forces between gas molecules cause the gas molecules to be attracted to each other, which reduces the pressure of the gas. The repulsive forces between gas molecules cause the gas molecules to repel each other, which increases the pressure of the gas.

Van der Waals Equation

The equation is named after Dutch physicist Johannes Diderik van der Waals, who proposed it in 1873.

The Van der Waals equation is an equation of state that describes the behavior of real gases, taking into account the volume of the gas molecules and the attractive and repulsive forces between them. The Van der Waals equation is based on the two above mentioned assumptions about real gases and it provides a more accurate description of the behavior of real gases, particularly at high pressures and low temperatures, where the ideal gas law breaks down.

The Van der Waals equation is:

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

Where, P is the pressure, V is the volume, n is the number of moles of gas, R is the gas constant, T is the temperature, **a** is a measure of the attractive forces between gas molecules, and **b** is a measure of the

volume of the gas molecules. The term n^2a/V^2 is related to pressure correction term and nb is related to volume correction term.

Volume Correction

The volume of a gas is the amount of free space in the container where molecules can move about. The volume V of an ideal gas is equal to the volume of the container. Because ideal gas molecules have no volume, they can freely move around inside the container.
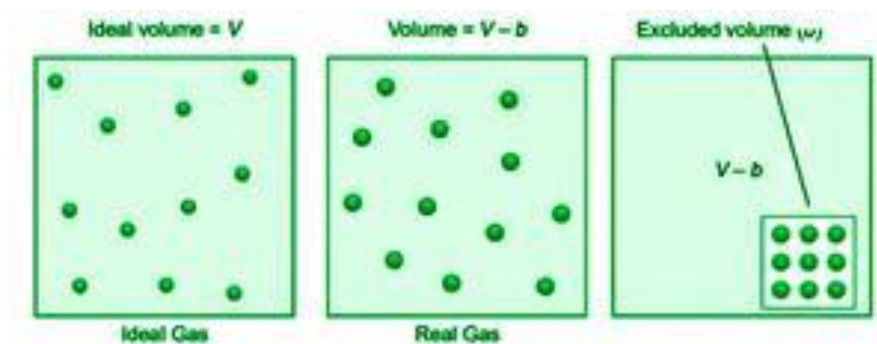
In a real gas, the molecular volume cannot be ignored. Van der Waals thought of molecules in a genuine gas as rigid spherical objects with a fixed volume. As a result, the volume of a real gas is ideal volume minus gas molecule volume. If b is the effective volume of molecules per mole of gas, the volume b will be excluded from total volume (out of the volume of container).

Therefore due to n moles of a gas the volume excluded would be nb. A real gas in a container of volume V has only available volume of (V - nb) and this can be thought of as an ideal gas in container of volume (V - nb).

Hence, Ideal volume
$V_i = V - nb$ …............(i)
n = Number of moles of real gas
V = Volume of the gas
b = A constant whose value depends upon the nature of the gas.

[**Note:** The Van der Waals constant b (the excluded volume) is actually 4 times the volume of a single molecule

b = 4 × volume of a single molecule = 4 × 6.023 × 10^{23} ×(4/3) πr^3, where r is the radius of a molecule.]

Pressure Correction

A molecule in the interior of gas is attracted by molecules on all sides. The molecules that exert the force on the container will get attracted by molecules of the immediate layer which are assumed not to be exerting pressure. These appealing characteristics cancel each other out. A molecule poised to impact the vessel's wall, on the other hand, is drawn only by molecules on one side. It feels forced to go

inside as a result. As a result, it hits the wall with less force, and the real gas pressure, P, is less than the ideal pressure.
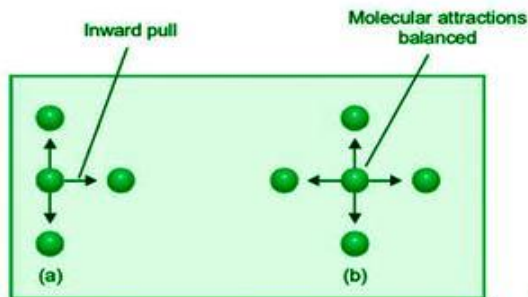
 If the actual pressure P is smaller than the ideal pressure P_{ideal} by a factor p, we've got

$P = P_{ideal} - p$

$P_{ideal} = P + p$

This small pressure p would be directly proportional to the extent of attraction between the molecules which are hitting the container wall and the molecules which are attracting these.

Therefore $p \propto n/V$ (concentration of molecules which are hitting the container's wall), and
$\qquad p \propto n/V$ (concentration of molecules which are attracting these molecues)
Thus, $\qquad p \propto n^2/V^2$
Or, $\qquad p = an^2/V^2$
Where **a** is the constant of proportionality which depends on the nature of gas. A higher value of 'a' reflects the increased attraction between gas molecules.
Hence ideal pressure
$\qquad P_i = (P + an^2/V^2)$ ….............(ii)
Here, n = Number of moles of real gas, V = Volume of the gas and, a = A constant whose value depends upon the nature of the gas.

Substituting the values of ideal volume and ideal pressure in ideal gas equation i.e. PV=nRT, the modified equation (Van der waals equation) is obtained as

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

Some salient feature of a & b are:

- For a given gas Vander Waal's constant of attraction 'a' is always greater than Vander Waals constant of volume b.
- The gas having higher value of 'a' can be liquefied easily and therefore H_2 & He are not liquefied easily.
- The units of a = $litre^2$ atm $mole^{-2}$ & that of b = litre $mole^{-1}$
- The numerical values of a & b are in the order of 10^{-1} to 10^{-2} & 10^{-2} to 10^{-4} respectively.
- Higher is the value of 'a' for a given gas, easier is the liquefaction.
-

Question 1: Define ideal gas and real gas.

Answer: An ideal gas obeys the ideal gas equation PV = nRT at all pressures and temperatures. No gas, on the other hand, is excellent. Almost all gases vary in some manner from the ideal behaviour. Non-ideal or actual gases, such as H2,N2, and CO2, do not obey the ideal-gas equation.

Question 2: What is the compressibility factor?

Answer: The degree to which real gas deviates from ideal behaviour can be expressed using a new function called the Compressibility factor, indicated by Z.

Z=PV/RT

Question 3: What is the ideal behaviour of gases?

Answer: An ideal gas obeys the ideal gas equation PV=nRT at all pressures and temperatures. However, no gas is ideal. Almost all gases vary in some manner from the ideal behaviour.

Question 4: What is the behaviour of real gases?

Answer: Gases that depart from ideal behaviour are known as real gases. The degree to which real gas deviates from ideal behaviour can be expressed using a new function called the Compressibility factor, indicated by Z.

Z=PV/RT

A plot of the compressibility factor, Z, vs P can reveal the degree of divergence from ideal behaviour. Z=1 for an ideal gas, and it is unaffected by temperature or pressure.

Question 5: What are the causes of real gas behaviour? Derive Van der Waals Equation.

Answer: According to Van der Waals (1873), the deviations of real gases from ideal behaviour are attributable to two faulty kinetic theory postulates. The following are some of them:

1. In a gas, the molecules have no volume and have point masses.

2. There are no intermolecular attractions in a gas.

As a result, the ideal gas equation PV=nRT developed from kinetic theory could not be applied to real gases. Van der Waals pointed out that both the pressure (P) and volume (V) elements of the ideal gas equation needed to be modified to make it applicable to real gases.

Van der Waals changed the ideal gas equation to make it applicable to all gases. The Van der Waals equation for n moles of gases,

$(P + an^2/V^2)(V–nb) = nRT$

Question 6: What is the Boyle temperature? Give an example.

Answer: The compressibility factor, Z, of a gas depends on the temperature also.
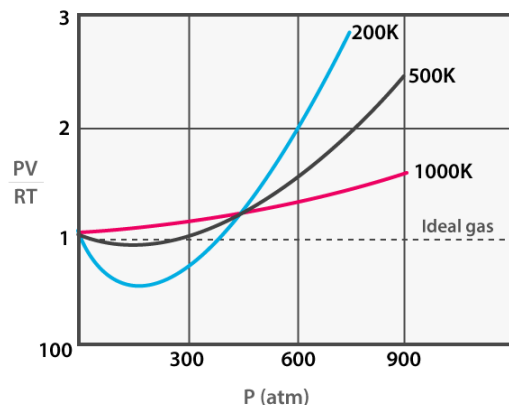
The compressibility factor is inversely proportional to temperature. So, an increase in temperature decreases the deviation from ideal behaviour. Every real gas has a certain temperature, where the compressibility factor shows little changes and comes close to one. Some gases obey ideal gas laws at high pressures at a certain temperature.

The temperature at which a real gas behaves like an ideal gas over a long range of pressure is Boyle's temperature for the gas. For example, nitrogen has a Boyle temperature of 323 K.

Question 7: What is the significance of the Van der Waals constants?

Answer: The Van der Waal constant 'a' signifies the magnitude of attraction between the gas molecules, and the constant 'b' signifies the effective volume occupied by the gas molecules.

Question 8: What are the conditions under which gasses deviate from ideality?

Answer: At high pressure and low temperature, gasses deviate from ideality.

2. Choose the correct option.

a) Increasing temperature increases the distribution of molecular velocities.

b) Larger the mass lesser the distribution of velocities.

c) Most probable velocity is the velocity that most of the molecules have at that temperature.

d) All the above

Answer: All the options are correct, and hence, 'd' is the correct option.