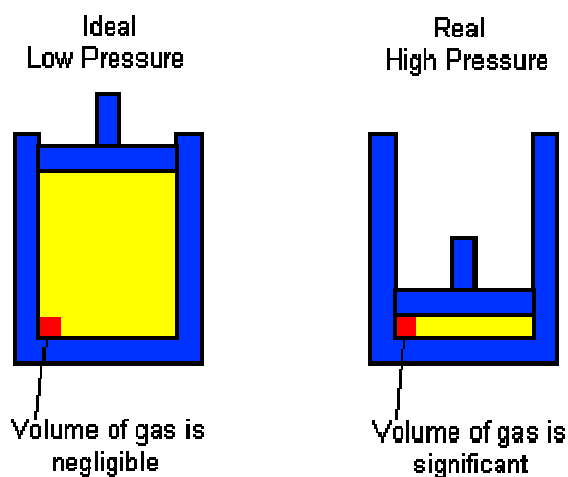


Deviation From Ideal gas Behavior:

A gas which obeys the gas laws and the gas equation $PV = nRT$ strictly at all temperatures and pressures is said to be an ideal gas. The molecules of ideal gases are assumed to be volume less points with no attractive forces between one another. But no real gas strictly obeys the gas equation at all temperatures and pressures. Deviations from ideal behavior are observed particularly at high pressures or low temperatures.

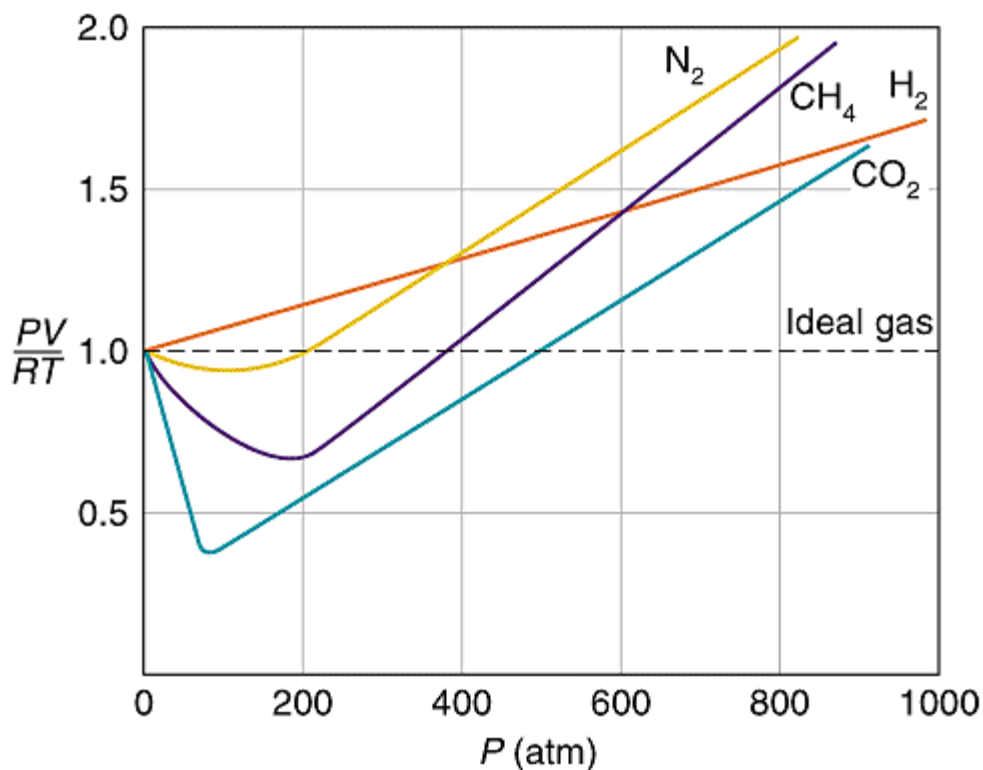


The deviation from ideal behaviour is expressed by introducing a factor Z known as **compressibility factor** in the ideal gas equation. Z may be expressed as $Z = PV / nRT$

- In case of ideal gas, $PV = nRT \therefore Z = 1$
- In case of real gas, $PV \neq nRT \therefore Z \neq 1$

Thus in case of real gases Z can be < 1 or > 1

- When $Z < 1$, it is a negative deviation. It shows that the gas is more compressible than expected from ideal behavior.
- When $Z > 1$, it is a positive deviation. It shows that the gas is less compressible than expected from ideal behavior.

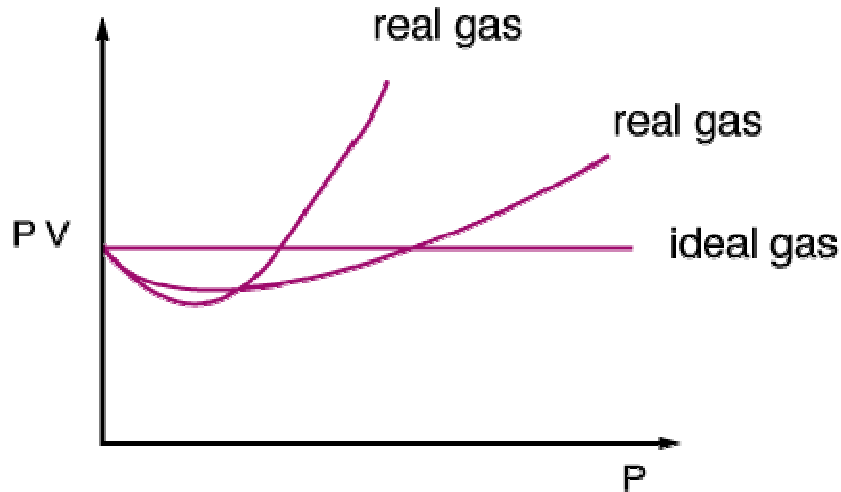


Causes of deviation from ideal behavior:

The causes of deviations from ideal behavior 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.

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 incompressible the volumes of molecules are no more negligible as compared to the total volume of the gas.

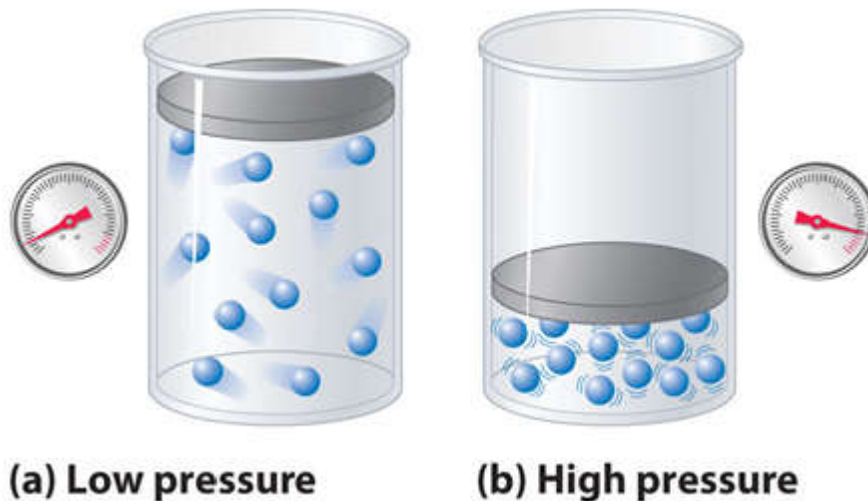


The second assumption is not valid when the pressure is high and temperature is low. But at high pressure or low temperature when the total volume of gas is small, the forces of attraction become appreciable and cannot be ignored.

Van der Waals' Equation of State for a Real Gas:

This equation can be derived by considering a real gas and 'converting' it to an ideal gas.

Volume correction:



We know that for an ideal gas $PV = nRT$. Now in a real gas the molecular volume cannot be ignored and therefore let us assume that 'b' is the volume excluded (out of the volume of container) for the moving gas molecules per mole of a gas. 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

$$V_i = V - nb \dots\dots\dots(i)$$

n = Number of moles of real gas

V = Volume of the gas

b = A constant whose value depends upon the nature of the gas

The Van der Waals constant b (the excluded volume) is actually 4 times the volume of a single molecule.

$b = 4 \times \text{volume of a single molecule} = 4 \times 6.023 \times 10^{23} \times (4/3)\pi r^3$, where r is the radius of a molecule.

Pressure correction:

Let us assume that the real gas exerts a pressure P . 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.

It can be seen that the pressure the real gas exerts would be less than the pressure an ideal gas would have exerted. The real gas experiences attractions by its molecules in the reverse direction. Therefore if a real gas exerts a pressure P , then an ideal gas would exert a pressure equal to $P + p$ (p is the pressure lost by the gas molecules due to attractions).

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)

$P \propto n/v$ (concentration of molecules which are attracting these molecules) $\Rightarrow p \propto n^2/v^2$

$P = an^2/v^2$ 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

$$P_i = (P + an^2 / V^2) \dots\dots\dots(ii)$$

Here,

n = Number of moles of real gas

V = Volume of the gas

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 is obtained as

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

The constants a & b

Vander Waals constant for attraction (a) and volume (b) are characteristic for a given gas. Some salient features 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 $a = \text{litre}^2 \text{ atm mole}^{-2}$ & that of $b = \text{litre mole}^{-1}$
- 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.

Different forms of Van der Waal's equation

- **At low pressures:**

'V' is large and 'b' is negligible in comparison with V.

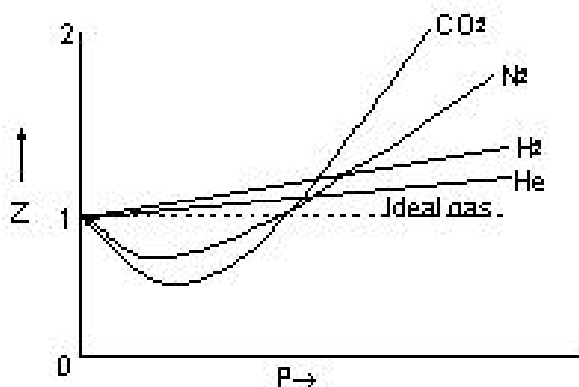
The Vander Waals equation reduces to:

$$(P + a/V^2)V = RT;$$

$$PV + a/V = RT$$

$$PV = RT - a/V \text{ or } PV < RT$$

This accounts for the dip in PV vs P isotherm at low pressures.



- **At fairly high pressures**

a/V^2 may be neglected in comparison with P.

The Vander Waals equation becomes

$$P(V - b) = RT$$

$$PV - Pb = RT$$

$$PV = RT + Pb \text{ or } PV > RT$$

This accounts for the rising parts of the PV vs P isotherm at high pressures.

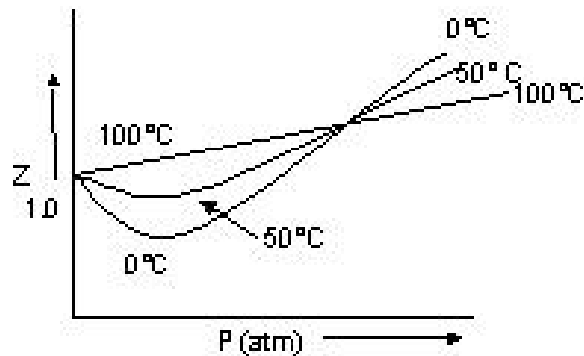


Johannes Diederik van der Waals

Johannes Diederik van der Waals was a physicist born on November 23, 1837, in Leiden, Netherlands.

He won the Nobel prize in 1910 for his research on the gaseous and liquid states of matter. His work made the study of temperatures near absolute zero possible and also led Sir James Dewar of England and Heike Kamerlingh Onnes of The Netherlands to the determination of the necessary data for the liquefaction of hydrogen and helium. He is well known for the Van-der Waal's equation which is also known as equation of state. It explains the properties of real gas.

He died in Amsterdam on March 8, 1923.



- **At very low pressures:**

V becomes so large that both b and a/V^2 become negligible and the Vander Waals equation reduces to $PV = RT$. This shows why gases approach ideal behavior at very low pressures.

- **Hydrogen and Helium:**

These are two lightest gases known. Their molecules have very small masses. The attractive forces between such molecules will be extensively small. So a/V^2 is negligible even at ordinary temperatures.

Thus $PV > RT$. Thus Vander Waals equation explains quantitatively the observed behavior of real gases and so is an improvement over the ideal gas equation. Vander Waals equation accounts for the behavior of real gases.

At low pressures, the gas equation can be written as,

$$(P + a/v_m^2) (V_m) = RT$$

or

$$Z = V_m / RT = 1 - a/V_m RT$$

Where Z is known as compressibility factor. Its value at low pressure is less than 1 and it decreases with increase of P . For a given value of V_m , Z has more value at higher temperature.

At high pressures, the gas equation can be written as

$$P (V_m - b) = RT$$

$$Z = PV_m / RT = 1 + Pb / RT$$

Here, the compressibility factor increases with increase of pressure at constant temperature and it decreases with increase of temperature at constant pressure. For the gases H_2 and He , the above behavior is observed even at low pressures, since for these gases, the value of ' a ' is extremely small.

$$\overbrace{p + a\left(\frac{n}{v}\right)^2}^{\text{Ideal Pressure}} \overbrace{(v - nb)}^{\text{Ideal Volume}} = nRT$$

Measured pressure

Correction factor to account for intermolecular attractions

Measured volume

Correction factor to account for the finite size of the molecules

Some other important definitions

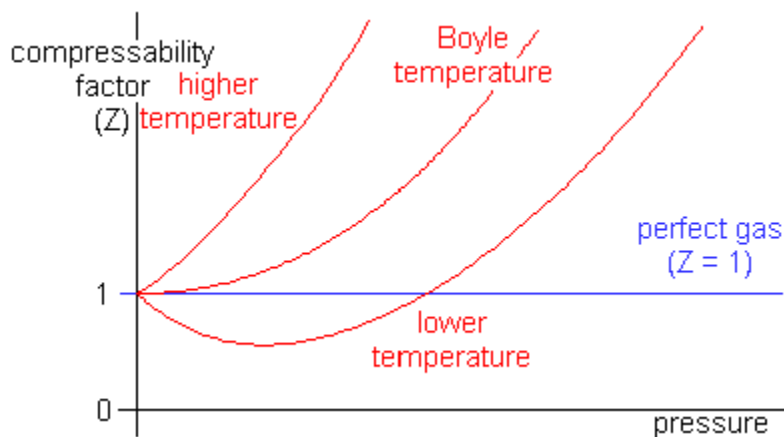
- Relative Humidity (RH)**

At a given temperature it is given by equation

$$RH = (\text{partial pressure of water in air}) / (\text{vapor pressure of water})$$

- Boyle's Temperature (T_b)**

Temperature at which real gas obeys the gas laws over a wide range of pressure is called Boyle's Temperature. Gases which are easily liquefied have a high Boyle's temperature [T_b (O_2)] = 46 K] whereas the gases which are difficult to liquefy have a low Boyle's temperature [T_b (He) = 26K].



Critical temperature is the maximum temperature at which a gas can be liquefied i.e. the temperature above which a gas can't exist as liquid.

$$\text{Boyle's temperature } (T_b) = a / Rb = 1/2 T_i$$

Where T_i is called Inversion Temperature and a , b are called van der Waals constant.

- Critical Temperature (T_c):**



It (T_c) is the maximum temperature at which a gas can be liquefied i.e. the temperature above which a gas can't exist as liquid.

$$T = 8a / 27Rb$$

- **Critical Pressure (P_c):**

It is the minimum pressure required to cause liquefaction at T_c

$$P_c = a/27b^2$$

- **Critical Volume:**

It is the volume occupied by one mol of a gas at T_c and P_c

$$V_c = 3b$$

Molar heat capacity of ideal gases:

Specific heat c , of a substance is defined as the amount of heat required to raise the temperature of 1 g of substance through 1°C , the unit of specific heat is $\text{calorie g}^{-1} \text{K}^{-1}$. (1 cal is defined as the amount of heat required to raise the temperature of 1 g of water through 1°C)

Molar heat capacity C , is defined as the amount of heat required to raise the temperature of 1 mole of a gas through 1°C . Thus,

Molar heat capacity = Sp. Heat molecular wt. Of the gas

For gases there are two values of molar heats, i.e., molar heat at constant pressure and molar heat at constant volume respectively denoted by C_p and C_v . C_p is greater than C_v and $C_p - R = 2 \text{ cal mol}^{-1} \text{K}^{-1}$

From the ratio of C_p and C_v , we get the idea of atomicity of gas.

For monatomic gas $C_p = 5 \text{ cal}$ and $C_v = 3 \text{ cal}$

$$\therefore (\gamma = 5/3 = 1.67 \quad (\gamma \text{ is poisson's ratio} = C_p / C_v))$$

For diatomic gas $C_p = 7 \text{ cal}$ and $C_v = 5 \text{ cal}$

$$\gamma = 7/5 = 1.40$$

For polyatomic gas $C_p = 8 \text{ cal}$ and $C_v = 6 \text{ cal}$

$$\gamma = 8/6 = 1.33$$

also $C_p = C_v + R$,

where, C_p and C_v are specific heat and m , is molecular weight.

Question 1: When $Z < 1$, it shows

- a. a negative deviation
- b. a positive deviation.
- c. that the gas is showing ideal behavior
- d. that the gas is less compressible than expected from ideal behavior

Question 2: A real gas behaves ideally at

- a. high temperature and low pressure
- b. high temperature and high pressure
- c. low temperature and high pressure
- d. low temperature and low pressure

Question 3: Which of the following equations represents the correct form of Vander waal's equation at very low pressure?

- a. $PV = RT - a/V$
- b. $pV = nRT$
- c. $P(V_m - b) = RT$
- d. $P(V - b) = RT$

Question 4: The maximum temperature at which a gas can be liquefied is called

- a. Boiling point.
- b. melting point
- c. Boyle's temperature
- d. critical temperature