Chapter II

Thermodynamic properties of pure substances

I-Introduction:

A pure substance is a substance with a homogeneous and stable chemical composition. It can exist in different phases (solid, liquid, gas), but its chemical composition remains the same in all phases. Water, nitrogen, helium, and carbon dioxide are examples of pure substances. A mixture of various chemical elements or components is also considered a pure substance as long as the mixture is homogeneous.

The thermodynamic properties of pure substances generally include six properties: Temperature (T); Pressure (P); Mass volume (V); Enthalpy (H); Internal Energy (U); Entropy (S).

II-Ideal gas:

An ideal gas is an ideal thermodynamic model that describes the behavior of real gases at low pressure .It is consists of point-like particles with zero diameter and insignificant volume compared to their surroundings. This eliminates attraction and repulsion between gas molecules.

II-1.Ideal gas laws:

The ideal gas rigorously obeys the three laws: MARIOTTE, GAY LUSSAC and CHARLES.

II-1.1. BOYLE-MARIOTTE law: At constant temperature 'T', the product of the pressure 'P' of a gaseous mass and its volume 'V' is constant: P.V = Cte

We have: $P.V = n.R.T$; $T = Cte \Longrightarrow P.V = Cte \Longrightarrow V \alpha \frac{1}{P} \Longrightarrow V = \frac{Cte}{P} \Leftrightarrow P = \frac{Cte}{V}$

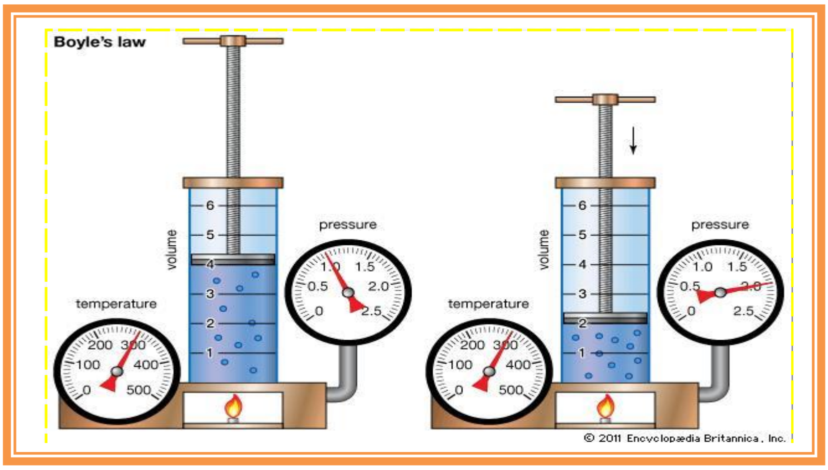
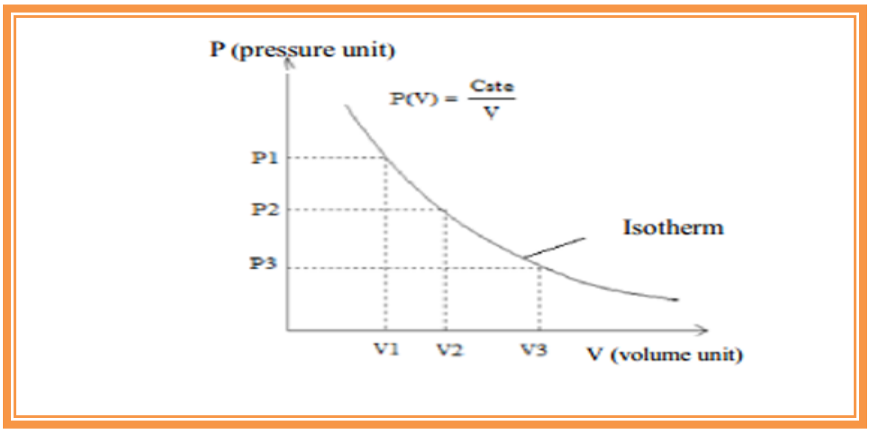
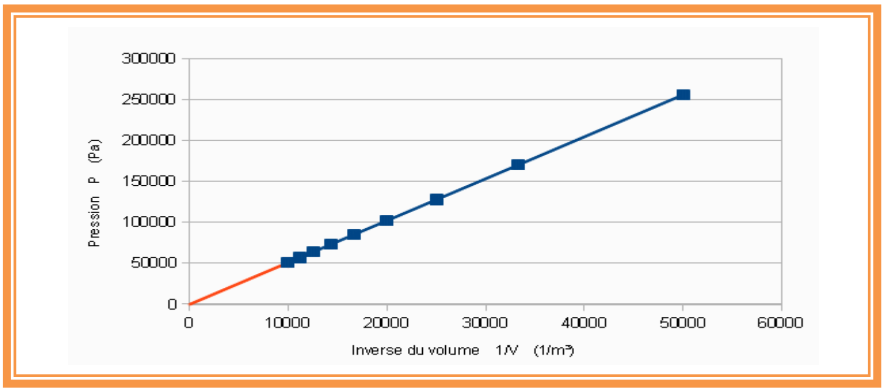


Figure: **Boyle-Mariotte Law.**



Figure



Figure

$$V \propto \frac{1}{P} \Longrightarrow V=K\times\frac{1}{P} \Longrightarrow P\times V= K(Cte) \Longrightarrow P_1\,V_1 = P_2$$

II-1.2- GAY-LUSSAC law: At constant volume, the pressure of a quantity of gas is directly proportional to its temperature.

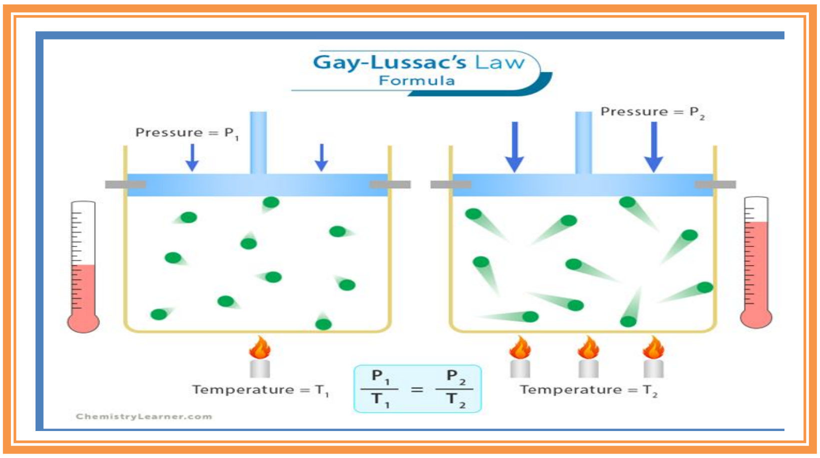
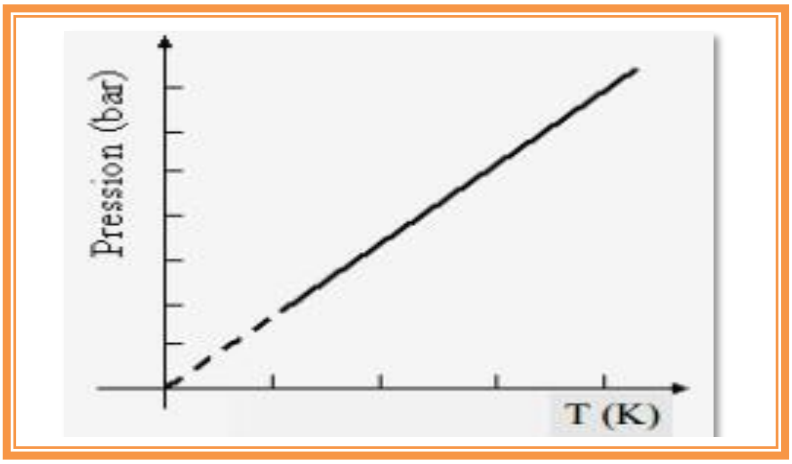


Figure: **GAY-LUSSAC law**

We have: P.V = n.R.T; V = Cte $\Longrightarrow P = \frac{nRT}{V}$ =Cte. T $\Longrightarrow$P $\propto$ T

$$P \propto T \Longrightarrow P=K\times T \Longrightarrow \frac{P_1}{T_1}= K(Cte) \Longrightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2}=\frac{P_n}{T_n}$$



Figure

II-1.3- CHARLES law: At constant pressure, the volume occupied by a quantity of gas is directly proportional to its absolute temperature.

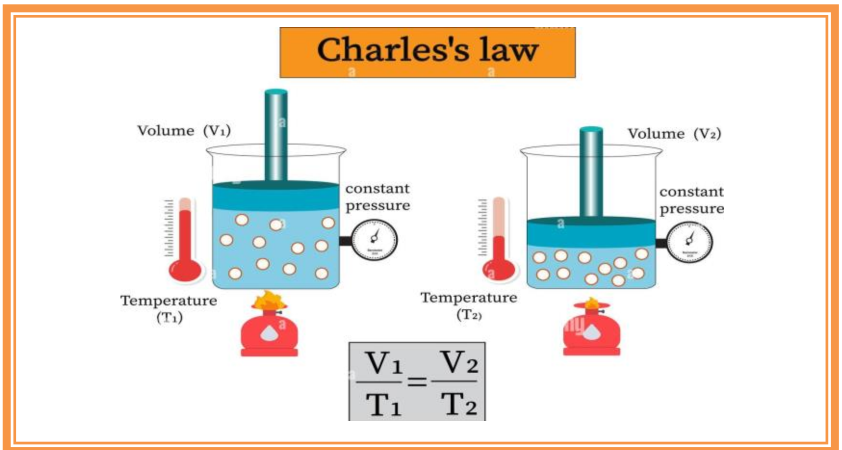


Figure: **CHARLES law.**

We have: P.V = n.R.T; P = Cte $\Longrightarrow$V= $\frac{nRT}{P}$ = Cte. T$\Longrightarrow$ V $\propto$ T

$$V \propto T \Longrightarrow V=K\times T \Longrightarrow \frac{V_1}{T_1} = K(Cte) \Longrightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_n}{T_n}$$

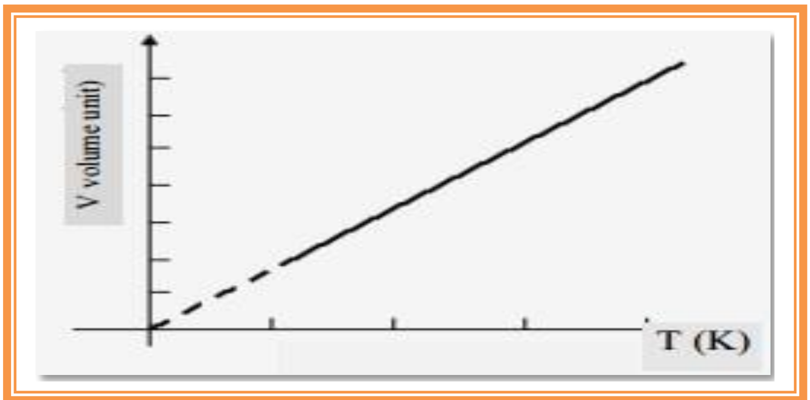


Figure:

II.1.4- AFOGADRO'S Law: Avogadro's law, a statement that under the same conditions of temperature and pressure, equal volumes of different gases contain an equal number of molecules. Since equal numbers of molecules means equal number of moles, the number of moles of any gas is proportional to its volume, so **$V \propto n$**.

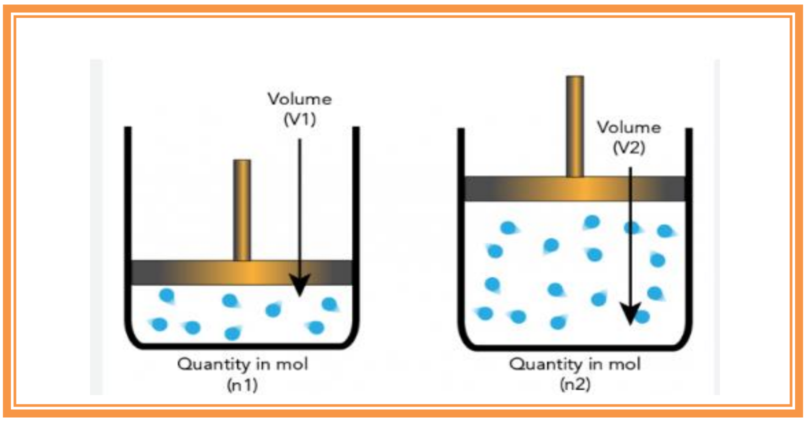


Figure: **AFOGADRO'S Law.**

The specific number of molecules in one gram-mole of a substance, defined as the molecular weight in grams, is $6.02214076 \times 10^{23}$, a quantity called Avogadro's number, or the Avogadro constant.

The volume occupied by one gram-mole of gas is about 22.4 liters at standard temperature and pressure (0°C, 1 atmosphere) and is the same for all gases, according to Avogadro's law.

II.1.5-Equation of state for perfect gas:

So far we have discussed three relationships of volume to which the perfect gas is subject

$$\left.\begin{array}{ll} \text{MARIOTTE Law :} & V \propto \frac{1}{P} \\ \text{CHARLES law:} & V \propto T \\ \text{Avogadro Law:} & V \propto n \end{array}\right\}$$

According to the laws of proportionality in mathematics:

$$\left.\begin{array}{l} V \propto \frac{1}{P} \\ \text{and} \\ V \propto T \end{array}\right\} \Rightarrow \left.\begin{array}{l} V \propto \frac{1}{P} \times T \\ \text{and} \\ V \propto n \end{array}\right\} \Rightarrow V \propto T \times n \times \frac{1}{P} \Rightarrow V = Cte \times T \times n \times \frac{1}{P} \Rightarrow Cte = R$$

$$P.V = nRT \Leftrightarrow V = \frac{nRT}{P}$$

This is the ideal gas law.

Where:

P: gas pressure;

V: volume of the gas;

n: number of moles of the gas;

R: perfect gas constant;

T: gas temperature.

- ***Calculate the value of the perfect gas constant "R":***

For one mole of gas occupying a volume of 22.4L, under standard conditions (T= 0°C =273,15 K° and P = 1atm).

We have: P.V= n.R.T⇒ $R = \frac{P.V}{n.T}$

P = 1atm = 1,01325. 10^5 pa; V=22,4L = 22,4.10^{-3} m^3; T= 0+273,15= 273,15 K°; n= 1mol.

$R = \frac{P.V}{n.T} = \frac{1,0325 .10^5 .\ 22,4.10^{-3}}{1.\ 273,15}$ ⇒ R=8,314 J.mol^{-1}.k^{-1}

R= 8,314 J/mol.K

1Cal = 4,18J⇒ $R = \frac{8,314}{4,18}$ = 1,987 Cal.mol^{-1}.K^{-1}

R= 2 Cal/mol.K

When V=22,4L and P= 1atm: $R = \frac{1.\ 22,4}{1.\ 273,15}$ ⇒ R=0,082 l. atm. mol^{-1}.k^{-1}.

R= 0,082 l.atm/mol.K

II.1.6-Dalton's law: Dalton's law (also called **Dalton's law of partial pressures**) states that in a mixture of non- reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases. This empirical law was observed by John Dalton in 1801 and published in 1802. Dalton's law is related to the ideal gas laws. Mathematically, the pressure of a mixture of non-reactive gases can be defined as the summation:

$$P_{tot} = \sum_{i=1}^{n} P_i = P_1 + P_2 + P_3 \dots\dots P_n$$

Where p_1, p_2, ..., p_n represent the partial pressures of each component.

- ***Mole fraction:***

In chemistry, the **mole fraction** or **molar fraction**, also called **mole proportion** or **molar proportion**, is a quantity defined as the ratio between the amount of a constituent substance, n_i (expressed in unit of moles, symbol mol), and the total amount of all constituents in a mixture, n_{tot} (also expressed in moles):

$$xi = \frac{n_i}{n_{tot}}$$

It is denoted $\boldsymbol{x_i}$ (lowercase Roman letter x), sometimes $\boldsymbol{\chi_i}$ (lowercase Greek letter chi). (For mixtures of gases, the letter y is recommended.)

The relationship between partial pressure and molar fraction:

We have:

$x_i = \frac{n_i}{n_{tot}}$ And $\sum x_i = 1$

$P_T.V=n_T.R.T$ ……….**(1)**

$P_i.V=n_i.R.T$………....**(2)**

Dividing **1** by **2**, we find:

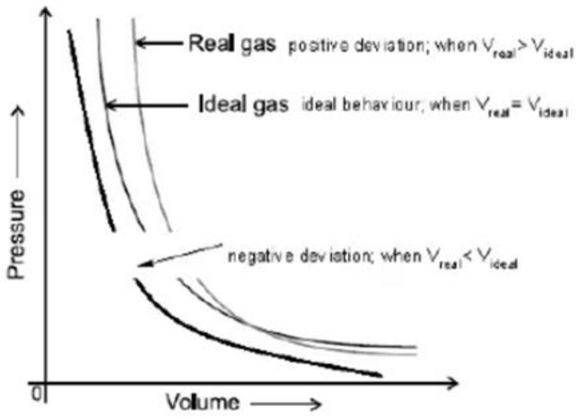
$$P_i = x_i . P_T$$

Behavior of real gases

Real gases are non-ideal gases with molecules that occupy space and interact between themselves, and thus do not obey the ideal gas law. The ideal gas law does not apply to Real gases because of such intermolecular interactions of gas particles.

Real gases do not obey ideal gas equation under all conditions. They nearly obey ideal gas equation at higher temperatures and very low pressures. However they show deviation from ideality at low temperatures and high pressures.

The deviations from ideal gas behaviour can be illustrated as follows:



V_{real}= volume of the real gas.
V_{ideal} = volum of the gas calculated by idel gas equation at given pressure.

Figure: Plot of pressure vs volume for idel and real gas

The isotherms obtained by plotting pressure against volume V for real gases do not coincide with that of ideal gas, as show below.

It is clear from above graphs that the volume of real gas is more than or less than expected in certain cases. The deviation from ideal gas behavior can also be expressed by compressibility factor Z.

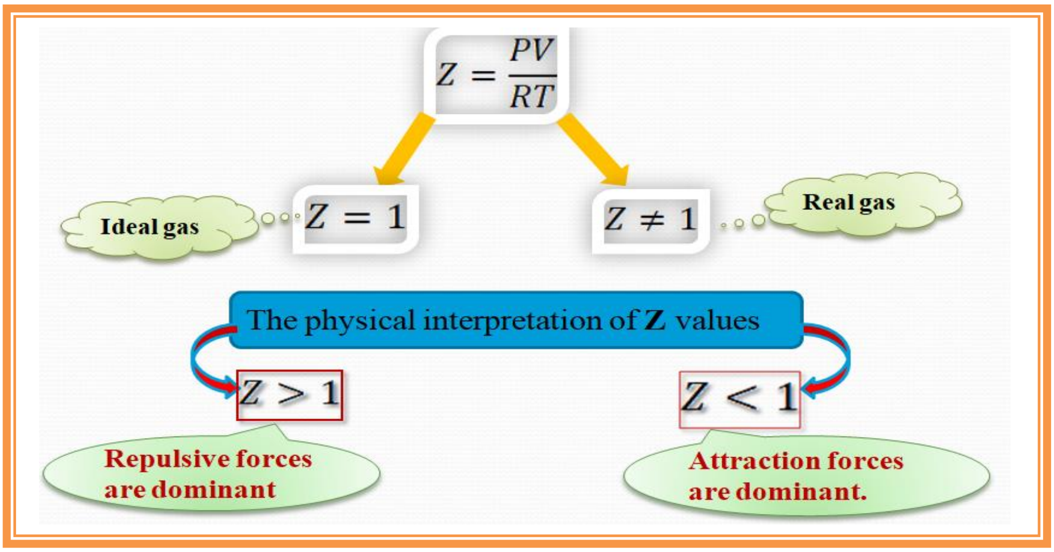
Compressibility factor Z: The ratio of PV to nRT is known as compressibility factor. Or the ratio of volume of real gas V_{real} to the ideal volume of that gas, $V_{perfect}$ calculated by ideal gas equation is known as compressibility factor.

$$Z = \frac{P.V_{real}}{nRT}$$

But from ideal gas equation: $P.V_{perfect} = nRT$ or $V_{perfect} = \frac{nRT}{P}$

Therefore: $Z = \frac{\mathbf{P.V_{real}}}{\mathbf{nRT}} = \frac{\mathbf{V_{real}}}{\mathbf{V_{perfect}}}$.

For ideal or perfect gases, the compressibility factor **Z=1,** but for real gases $\mathbf{Z \neq 1}$.



Case I: if Z>1:

- $V_{real} > V_{ideal}$.
- The repulsion forces become more significant than the attractive forces.
- The gas cannot be compressed easily.
- Usually the Z>1 for so called permanent gases like He, H_2.

Case I: if Z<1:

- $V_{real} < V_{ideal}$.
- The attractive forces are more significant than the repulsive forces.
- The gas can be liquefied easily.
- Usually the Z<1 for gases like NH_3, CO_2, SO_2.

The isotherms for one mole of different gases, plotted against the Z value and pressure P at 0 C° are shown below:

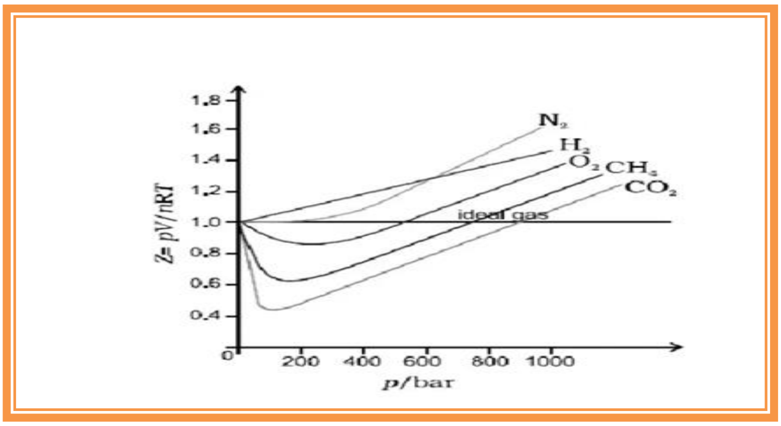


Figure: variation of compressibility factor for some gases

For gases like He, H_2 the Z value increases with increase in pressure (positive deviation); it is because, the repulsive forces become more significant and the attractive force become less dominant. Hence these gases are difficult to be condensed.

For gases like CH_4, CO_2, NH_3, etc…the Z value decreases initially (negative deviation) but increases at higher pressures, it is because: at low pressure the attraction forces are more dominant over the repulsion forces, whereas at higher pressures the repulsion forces become significant as the molecules approach closer to each other.

But for all the gases, the Z value approaches one at very low pressures, indicating the ideal behavior.

The graph below shows the values of **Z** for different gases.

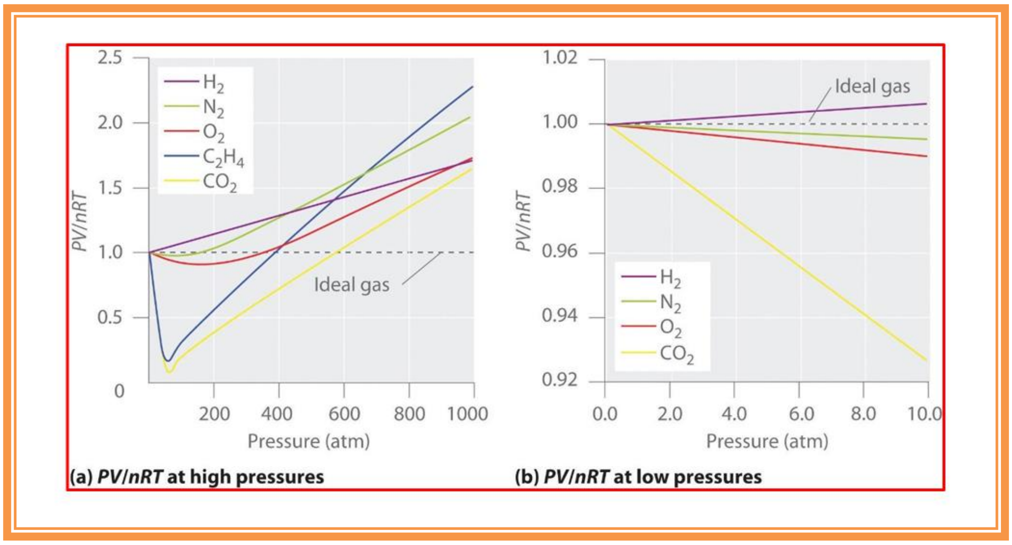


Figure: Real Gases, (a) at High Pressures, (b) at Low Pressures.

To study the effect of intermolecular forces, we examine the variation in the compressibility factor of a given gas, at different temperatures.

In the case of nitrogen, for temperatures T between 300 K and 400 K and for a pressure below 200 bar, the curve tends to resemble that which would be expected for an ideal gas. When the temperature is lowered to 200 K and 100 K, the curve is much further from that of an ideal gas. In particular, at low pressures, it can be seen that Z for real gases is substantially less than 1 for T=200 K, and this effect is even more pronounced at 100 K.

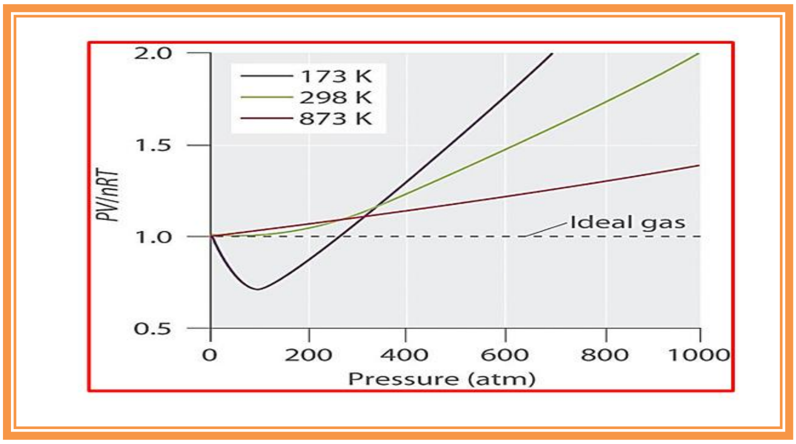


Figure: The Effect of Temperature on the Behavior of Real Gases.

What happens at low temperatures? Imagine the gas molecules bouncing all over the container. The pressure that is measured comes from the force with which the gas molecules hit the walls of the container. The forces of attraction between the molecules will allow them to be brought a little closer to each other, which will slightly slow down each molecule before it hits the wall of the container.

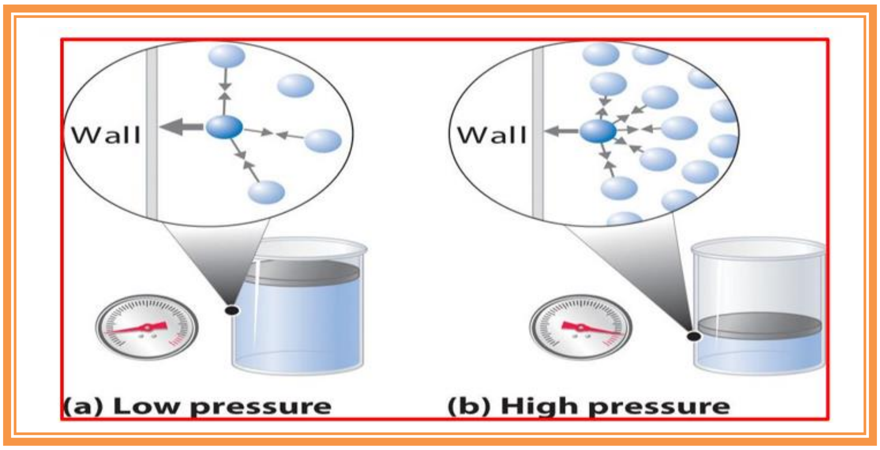


Figure: The Effect of Intermolecular Attractive Forces on the Pressure a Gas Exerts on the Container Walls.

Intermolecular forces and real gas behavior:

Intermolecular forces play a critical role in the actual behavior of gases, differentiating their behavior from that of ideal gases. Unlike the ideal gas model, where molecules are considered point and without interaction, molecules in a real gas have a finite volume and are subject to attractive or repulsive forces, mainly van der Waals forces. These intermolecular forces influence the pressure exerted by the gas and modify its behavior, especially at high pressure and low temperature. At short distances, repulsive forces dominate, preventing molecules from overlapping, while at greater distances, attractive forces act, reducing the effective pressure compared to that predicted by the ideal gas model. To take these effects into account, the ideal gas equation is corrected, for example, by the Van der Waals equation, which introduces two parameters:

- A term **b** which corrects the available volume by accounting for the excluded volume (covolume) occupied by the molecules themselves,

- A term **a** that corrects the pressure by taking into account the attractive forces between molecules. Thus, the Van der Waals equation is written:

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

Where ***P*** is the pressure, ***V*** the volume, ***n*** the quantity of matter in moles, ***R*** the constant of the ideal gases, and ***T*** the temperature.

These corrections explain why real gases deviate from the laws of ideal gases, in particular by showing a compressibility factor other than 1, which varies with temperature and pressure. At low pressure and high temperature, real gases behave almost like ideal gases because the molecules are far apart and the interactions are weak.

Note: **a** and **b** are determined experimentally and are characteristic of the substance under consideration.

Corresponding states, residual deviations:

The principle of corresponding states, formulated by van der Waals, states that all pure bodies in the fluid state exhibit similar thermodynamic behavior when compared to reduced conditions, i.e. normalized with respect to their critical properties. More precisely, at the same reduced temperature and reduced pressure, the substances have very similar compressibility factors, and deviate from the behavior of the ideal gas in a comparable way. This allows the use of dimensionless universal equations of state to predict the behavior of real gases from their critical properties.

Reduced state variables are numbers (without units) that give the ratio of a real variable to that of a reference state. For example, a reduced pressure is the ratio of a pressure to a reference pressure.

$$Tr = \frac{T}{Tc} \qquad Pr = \frac{P}{Pc} \qquad V_{m,r} = \frac{V}{V_{m.c}}$$

Where: T_c critical temperature; P_c critical pressure; $V_{m,c}$**:** critical molar volume.

T_r**:** reduced temperature; P_r**:** reduced pressure; $V_{m,r}$: reduced molar volume.

Note: When two gases have the same reduced temperature $\mathbf{T_r}$ and reduced pressure $\mathbf{P_r}$, their behaviour is similar regardless of the type of gas.

The reduced Van Der Waals equation becomes:

$$\left(p_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r$$

Principle of corresponding states: If two Van Der Waals gases have two equal reduced state variables, then the third reduced state variable is also equal. The two gases are said to be in corresponding states.

Example: Consider **helium** (Critical point: Tc = 5.2 K, Pc = 2.3 bar and Vc = 0.233 m^3/kg) at a temperature of 10.4 K (i.e. Tr = 2) and pressure of 2.3 bar (i.e. Pr = 1), and **hydrogen** (Critical point: Tc = 33.2 K, Pc = 13 bar and Vc = 0.52 m^3/kg) at a temperature of 66.4 K (i.e. Tr = 2) and pressure of 13 bar (i.e. Pr = 1), these two gases occupy the same reduced volume.

Residual differences

Residual deviations are the difference between the actual thermodynamic properties of a gas and those calculated assuming an ideal gas. For example, for a thermodynamic property M, the residual deviation is defined as:

$$M^{résiduel} = M^{réel} - M^{gaz\,parfait}$$

Example: $G^R = G^{real} - G^{ideal}$; $H^R = H^{real} - H^{ideal}$; $U^R = U^{real} - U^{ideal}$; $S^R = S^{real} - S^{ideal}$

These differences reflect the effects of molecular interactions and finite molecular volume, which are not accounted for in the ideal gas model. They are essential for correcting thermodynamic calculations and obtaining accurate results for real gases, especially at high pressure or low temperature.