Chapter Two

Gases

3.1 Real gases and reasons for their deviation from ideal behavior

The kinetic theory of ideal gases explains the behavior of gases using the ideal gas laws. An ideal gas is a hypothetical model that does not exist, and a number of real gases obey the ideal gas laws well when the temperature is relatively high and the pressure is relatively low.

Why can't kinetic theory be applied to the behavior of real gases?

A: Because at low temperatures and high pressures, all gases deviate from ideal behavior.

The laws of ideal gases were derived from kinetic theory based on two important assumptions:

(1) Neglecting the size of the molecules compared to the total volume of the gas.

(2) Neglecting the forces of attraction between the molecules.

To measure the deviation from ideal behavior, we plot the compressibility factor (Z) of the gas against pressure. If we start with the ideal gas equation

$$PV = nRT$$

we can represent the compressibility coefficient for one mole of gas

$$Z=\frac{PV}{RT}, \quad n=1$$

where V represents the molar volume of the gas or the volume of one mole of gas at specific conditions of temperature and pressure.

3.2 Compressibility factor

The compressibility factor (Z) is defined as a measure of the deviation of a real gas from the behaviour of an ideal gas. The value of Z for an ideal gas is equal to one (Z=1) at all values of (P) and at low pressures (≤10 atm).

Therefore, Z=1 for an ideal gas and Z>1 or Z<1 for a real gas.

The relationship between compressibility coefficient and pressure (p):

As pressure increases, compressibility increases (direct relationship).

The relationship between compressibility coefficient and temperature (T):

As temperature decreases, compressibility coefficient increases (inverse relationship).

3.3 Van der Waals equation

Van der Waals discovered that the relationship (PV = nRT) failed when applied to real gases and attributed this to the neglect of both the size of the molecules and the forces of attraction between them. If (m) moles of a given gas are placed in a container of volume V, the volume in which the molecules move freely is equal to V in one case, which is when the size of the molecules themselves is neglected. However, the existence of molecules with no size indicates the existence of a certain volume in which the molecules cannot move freely, called the excluded volume, symbolized by (σ).

$$\sigma = 2\mathrm{r}$$

The correction to the Van der Waals equation is as follows:

(1) The first correction factor is related to the excluded volume (exclusion) - the effect of particle size.

$$P\,(V-b) = n\,R\,T$$

Where:

V: Volume of the container

b: Excluded volume, defined as (the volume in which the molecule is not free due to the presence of other molecules and collisions between them).

(2) The second correction factor is related to the internal attractive forces between molecules:

As a result of the proximity of molecules to each other at low temperatures, internal attraction will occur, leading to collisions and generating additional pressure (p). This additional pressure is directly proportional to the square of the number of moles (m^2) and inversely proportional to the square of the volume (V^2). The Van der Waals equation for real gases is defined as follows:

$$P \propto \frac{n^2}{V^2}$$

$$P = a\frac{n^2}{V^2} \quad \because PV=nRT$$

$$\left(P + a\frac{n^2}{V^2}\right)(V - n\,b) = n\,R\,T$$

Where:

(P) represents the measured pressure,

($a\frac{n^2}{V^2}$) represents the correction limit for the pressure.

(V) represents the volume of the vessel.

($n\,b$) represents the correction factor for volume.

(n) represents the number of moles.

(a) and (b) represent constants. The value of (b) (the excluded volume of one mole of gas) is calculated as follows: $b = 4\,V_m\;N$

Where:

Vm: particle volume (molecular volume: the volume shared between particles inside the container).

N: Avogadro's number (6.022×10^{23}).

Where a and b depend on the nature of the gas and the temperature, and as the size of the molecule increases, a and b increase because the excluded volume increases and collisions increase.

Therefore, the Van der Waals equation for one mole of gas is:

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

The excluded volume is defined as: (the volume in which the two particles cannot move freely because their movement causes them to collide).
Since:

the radius of the circle = the molecular diameter

then:

The excluded volume for each pair of molecules is equal to the volume of the sphere and is equal to:

$$\frac{4}{3}\pi\times(2r)^3=\frac{4}{3}\pi\times\sigma^3$$

Ball size = radius^3 × constant ratio

Assuming that the particles are spherical and their diameter is then: $\sigma=2r$

Ball size = $\dfrac{\frac{4}{3}\pi \times (2r)^3}{\frac{4}{3}\pi \times \sigma^3}$

Example (7): Calculate the molar volume of CH_4 gas in units of (cm^3) at 0 °C and a pressure of (50 atm) using:

(a) the ideal gas equation **(b)** the Van der Waals equation

Note that the values of a, b

a=2.25 lit^2. atm. mole^{-2} , b= 0.0428 lit. mole^{-1}

Since the volume of one mole = one mole of gas

a-

$$V = \frac{n\,R\,T}{P}$$

$$V = \frac{1 \times 0.082 \times 273}{50} = 0.448\,\text{lit} = 0.448 \times 1000 = 448\text{cm}^3$$

b-

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

$$\left(P+\frac{2.25}{V^2}\right)(V-0.0428)=R\,T$$

$$\left(50+\frac{2.25}{V^2}\right)(V-0.0428)=0.082\times 273$$

$$V=0.391\text{ lit}$$

$$\because 1\text{ lit} = 1000\text{ ml} = 1000\text{ cm}^3$$

$$\therefore V = 391\text{ cm}^3$$

It is a real gas.

3.4 Using gas laws in storing biofuels and green hydrogen

Gas laws are a fundamental part of the design and operation of alternative fuel systems such as biofuels and green hydrogen. Understanding these laws enables us to calculate the pressure, volume, and temperature of gases in storage tanks, ensuring the efficiency and safety of the systems.

- Green hydrogen is a clean fuel produced through the electrolysis of water using renewable energy. Due to its light and volatile nature, it requires very high pressure or very low temperatures for storage.

- Biofuel is methane gas **(**CH_4) (biogas) produced from the anaerobic decomposition of organic matter. For its design, we mainly rely on the ideal gas law, which relates pressure (P), volume (V), number of moles (n), ideal gas constant (R), and absolute temperature (T) with the formula:

Ideal gas law: $PV = nRT$

In order to store these gases safely and efficiently, we must understand how pressure and volume change with temperature**.**

- If the pressure increases, the volume decreases.

- If the temperature rises, the pressure inside the tank increases.

Example(8) : We have 5 kilograms of methane (CH_4) stored at 25°C and 10 bar. What is the order volume?

Mass = 5 kilograms

M.wt (CH_4) = 16g/mol **»»»** M.wt (CH_4) =0.016 kg/mol

n=5000÷16=312.5mol

T=25°C+273=298 K

P=10bar×10^5Pa/bar=1×10^6Pa

$$PV = nRT$$

$$V = \frac{n R T}{P}$$

$$V = \frac{312.5 \times 8.314 \times 298}{10^6}$$

$$V = \frac{774241.25}{10^6}$$

V≈ 0. 774m^3 ,So, the required tank volume is 0.773 cubic meters.

Example(9) : We want to store 100 kilograms of green hydrogen in a tank at a pressure of 700 bar and a temperature of 25°C. What is the required volume for this tank? (The molar mass of hydrogen (H_2) is 2.016 g/mol.)

Note that the van der Waals constants for hydrogen (H2) are:

a=0.02476 $L^2 \cdot bar/mol^2$

b=0.02661 L/mol

These constants must be converted to SI units (cubic meter and pascal):

a=$0.02476\times (0.001\ m^3/L)^2\times 10^5$ Pa/ bar

a $\approx 2.476\times10^{-3}$ $Pa\cdot m^6/mol^2$

b=$0.02661\times (0.001\ m^3/L) = 2.661\times10^{-5}\ m^3/mol$

P=$700\ bar\times10^5\ Pa/bar = 7\times10^7$ Pa

T=25+273.15=298.15 K

n= (100 kg×1000 g/kg)/2.016 g/mol≈ 49603 mol

R= 8.314 J/mol. K

Note: Since the pressure in the question is 700 bars, which is very high, the hydrogen molecules are very close together, and the attractive forces between them affect their behavior. Therefore, the ideal gas equation will

$$\left(P + a\frac{n^2}{V^2}\right)(V - n\,b) = n\,R\,T$$

Since this is a cubic equation in V, solving it is complicated. We can use approximation or an iterative solution.

Approximating the solution: Let's start by calculating the volume using the ideal gas equation as a first approximation, then use this volume in the van der Waals equation.

V_{ideal}=nRT/ P

V_{ideal} =49603×8.314×298/ 700×10^5 ≈1.758 m^3

Now we use this volume as an initial value and solve for the van der Waals equation (by substituting V into the correction factors).

$$\left(P + a\frac{n^2}{V^2}\right)(V - n\,b) = n\,R\,T$$

$$(700 \times 10^5 + \frac{(2.476\times10^{-3})(49603)^2}{(1.758)^2})(V - 49603 \times 2.661 \times 10^{-5}) = 49603 \times 8.314 \times 298.15$$

$$(7 \times 10^7 + 1.95 \times 10^6)(V - 1.319) = 1.23 \times 10^8$$

$$(7.195 \times 10^7)(V - 1.319) = 1.23 \times 10^8$$

$$V - 1.319 = \frac{1.23\times10^8}{7.195\times10^7} \approx 1.709$$

$$V = 1.709 + 1.319 = 3.028 \text{ m}^3$$

Note: This second approximation shows that the actual required volume is approximately 3.028 cubic meters. In precise engineering calculations, we can use computer programs to solve the van der Waals equation to obtain a more accurate value, but this method gives us a clear understanding of the difference between an ideal gas and a real gas.

Conclusion: The required volume of the tank is 3.028 cubic meters based on the van der Waals equation. This demonstrates that using the ideal gas equation (which yielded 1.758 cubic meters) would be a significant error that could lead to design problems.

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What can we learn from these examples?

Storing gas requires precise pressure and volume calculations.

Green Hydrogen: Requires very high pressure and robust tanks, so we use:

Special pressurized tanks (350–700 bar).or storing it as a liquid at very low temperatures.

Biogas: Easier to store at lower pressures (5–20 bar) and is easier to handle.

3.5 Hydrogen storage calculations

1. Compressed storage:

- Hydrogen is typically stored in steel tanks at pressures exceeding 700 bar (70 MPa).

- The use of the Van der Waals equation becomes necessary to accurately estimate the pressure.

- **Example**: At a pressure of 70 MPa, the volume of the gas is much smaller than predicted by the ideal gas law due to the attractive forces between the molecules.

2. Refrigerated storage (liquid hydrogen):

- Hydrogen is cooled to -253°C (20 Kelvin) to convert it into a liquid, which significantly reduces its volume.

- In this state, hydrogen becomes a condensed state, and the laws of gases do not apply to it.

- This process requires excellent thermal insulation to prevent the liquid from evaporating.

Note: Applying gas laws, whether idealized for biofuels or realistic for hydrogen, is the cornerstone of clean energy system design. These precise calculations ensure that tanks can safely and efficiently withstand operating conditions, contributing to the transition to a more sustainable energy future.