Anderson Serangoon Junior College H2 Chemistry THE GASEOUS STATE

Learning Outcomes

Candidates should be able to:

- (a) state the basic assumptions of the kinetic theory as applied to an ideal gas
- (b) explain qualitatively in terms of intermolecular forces and molecular size:
 (i) the conditions necessary for a gas to approach ideal behaviour
 - (ii) the limitations of ideality at very high pressures and very low temperatures
- (c) state and use the general gas equation pV = nRT in calculations, including the determination of M_r
- (d) use Dalton's Law to determine the partial pressures of gases in a mixture

Lecture Outline

- 1. Kinetic Theory of Matter
 - 1.1 Introduction
 - 1.2 Kinetic Theory and their Assumptions as applied to an Ideal Gas
- 2. Gas Laws: Boyle's Law, Charles's Law, Gay-Lussac's Law and Avogadro's Law
 - 2.1 Boyle's Law
 - 2.2 Charles's Law
 - 2.3 Gay-Lussac's Law
 - 2.4 Combined Gas Law
 - 2.5 Avogadro's Law
 - The Ideal Gas Equation
 - 3.1 Calculation of molar gas constant, R
 - 3.2 Other useful forms of Ideal Gas Equation
- 4. Dalton's Law of Partial Pressures
- 5. Deviation from Ideal Behaviour Real Gases
 - 5.1 Conditions for real gas to approach ideal behaviour
 - 5.2 Graphical representations of deviation from ideal behaviour

References

3.

- 1. Chemistry for Advanced Level, Peter Cann & Peter Huges
- 2. Understanding Advanced Physical Inorganic Chemistry, Jeanne Tan, Kim Seng Chan
- 3. Chemistry, The Central Science (10th edition), Brown, LeMay & Bursten
- 4. A-Level Chemistry, E.N. Ramsden
- 5. Chemistry in Context, Graham Hill & John Holman

Additional Readings

- 1. Real Gases Deviations from Ideal Behaviour
- (Adapted from intro.chem.okstate.edu and www.chemguide.co.uk)
- 2. The Ideal Gas Law at the Center of the Sun, David B. Clark, Pennsylvania College of Technology
- 3. The Chemistry Behind the Air Bag, Andreas Madlung, Oregon State University

1. Kinetic Theory of Matter *Quick recap from 'O' level Chemistry:*

1.1 Introduction

- The Kinetic Theory of Matter describes the particles in solids, liquids and gases and the movement of these particles.
- The bulk characteristics (i.e. physical properties) of matter can be explained by the **arrangement** and **movement** of the particles.
- Many pure substances can exist in all of the three states of matter, depending on the conditions of the **temperature** and **pressure**.

	Solids	Liquids	Gases
Volume	definite (fixed)	definite (fixed)	take the volume of the container
Shape	definite (fixed)	take the shape of the container, but do not necessarily occupy all of it	occupy the whole of the container
Relative compressibility	nil	almost nil	large
Relative density	large	large	small
Arrangement of particles	packed closely together in an orderly manner	packed closely together, not in orderly manner	far apart (gas consists mainly of empty space) and random
Movement of particles	vibrate and rotate about fixed positions	vibrate, rotate and move as clusters throughout the liquid (translational)	vibrate, rotate and translate <i>freely and</i> <i>randomly anywhere</i> within the container

Bulk characteristics

- 1.2 Kinetic Theory and their Assumptions as applied to an Ideal Gas
- It can be observed from the table above that the bulk characteristics of gases differ from that of solids and liquids.
- The *Kinetic Theory* was put forward to *explain* the behaviour of gases, based on the following assumptions:

	Basic Assumptions of the Kinetic Theory as applied to an Ideal Gas
1	Gases consist of rigid, spherical molecules that are in continuous, random motion.
☆ 2	The volume of the gas molecules is <u>negligible</u> compared to the volume of the container.
☆ 3	The forces of attraction between the gas molecules as well as between the gas molecules and walls of the container are negligible.
☆ 4	All molecular collisions are perfectly elastic . There is no loss of the kinetic energy during collision.
5	The average kinetic energy of the molecules is proportional to the absolute temperature (measured on the Kelvin scale).

In summary,

- An ideal gas is a hypothetical gas whose pressure, volume and temperature is completely described by the **ideal-gas equation**.
- Note that ideal gases do <u>NOT</u> exist in real life! Section 5 discusses how gases deviate from ideality.

2. Gas Laws: Boyle's Law, Charles's Law, Gay-Lussac's Law and Avogadro's Law

• All the four gas laws are discovered *experimentally* and they express the mathematical relationships among T, *p*, V and n.



Types of mathematical graphs



Graphical plots to represent ideal gas behaviour

- 1. Manipulate the ideal gas equation to make the term shown on the y axes of the plot, the subject of the equation.
- 2. For all terms that are kept constant, replace by k.
- 3. Replace the term shown on the x-axes of the plot by "x".
- 4. Choose the appropriate mathematical graph.

2.1 <u>Boyle's Law: pressure-volume relationship</u>

 Boyle's Law states that the <u>volume</u> of a <u>fixed amount of gas</u> (n is constant) is <u>inversely</u> proportional to its pressure under <u>constant temperature</u>.



(constant n and T)

This diagram shows the exponential relationship between pressure and volume involving the same no. of moles of gaseous molecules and keeping temperature constant.

Using the relationship above,

 $\boldsymbol{\rho}_{i} \mathbf{V}_{i} = (4)(\vee)$ = (2)(2\neq) = $\boldsymbol{\rho}_{f} \mathbf{V}_{f}$



- Application of Boyle's Law:
 - o Scuba diving



Scuba divers should not hold their breath whilst ascending to the water surface. For every 10 m of depth that a scuba diver descends, he will experience an additional 1 atm of pressure due to the weight of the water above him. When a diver inhaled a lungful of air at a pressure of 3 atm, and swam quickly to the surface of the water whilst holding his breath, the pressure would decrease by a factor of 3, the volume of air would increase by a factor of 3, causing severe damage to his lungs.

 Shaking a sealed can of fizzy drink results in a great "explosion" when opened



The fizz in the drink is actually dissolved carbon dioxide gas, CO_2 . Under high pressure, CO_2 molecules are forced into the drink in an amount that is greater than what would ordinarily dissolve under atmospheric conditions. Shaking the unopened can of fizzy drink causes bubbles of CO_2 to line the walls inside the can. As soon as the can is opened, the pressure in the can decreases and the volume of each bubble increases, most of the excess gas escapes into the room.

Tapping the top of the can would dislodge the bubbles from the wall and bottom of the can so that they can float to the top of the can (since gas is lighter than liquid). Once the bubbles are at the top of the can, there will only be a small amount of liquid blocking their escape when the can is opened. As a result, the fizzy drink doesn't spray.

- 2.2 Charles's Law: temperature-volume relationship
- Charles's Law states that the <u>volume</u> of a <u>fixed amount of gas</u> (*n* is constant) maintained at <u>constant pressure</u> is <u>directly proportional</u> to its <u>absolute temperature</u> (*in Kelvin*).



• Comparing the temperature and volume of a given amount of a gas **under two different sets of conditions** at <u>constant pressure</u>, the following equation is applicable.



A hot air balloon floats as the air inside the balloon is less dense than the air outside. According to Charles's Law, warming the air in the balloon with a burner will cause an increase in its volume and lowering its density, causing the balloon to float in the colder and denser surrounding air.

2.3 <u>Gay-Lussac's Law: temperature-pressure relationship</u>

• Gay-Lussac's Law states that the <u>pressure</u> of a <u>fixed amount of gas</u> (n is constant) maintained at <u>constant volume</u> is <u>directly proportional</u> to its <u>absolute temperature</u> (in Kelvin).



(constant n and V)

• Comparing the temperature and pressure of a given amount of a gas **under two different sets of conditions** at **constant volume**, the following equation is applicable.



• Graphical representations (at fixed V):



- Application of Gay-Lussac's Law:
 - Shooting of a gun

As gunpowder burns, it creates superheated gas, which forces the bullet out of the gun barrel.

• Pumping Car Tires



In temperate countries, car tire pressures need to be checked in winter. This is because with the low temperatures in the winter months, car tires could be underinflated due to a drop in gas pressure. Driving under such conditions could reduce tire durability and fuel economy of the car.

Similarly, in tropical countries, car tires should only be pumped or checked in the morning and not after a long drive. This is because after travelling for some time, the temperature of the tires will increase, causing an increase in gas pressure.

2.4 Combined Gas Law

• Mathematically, in combining Boyle's Law ($V \propto \frac{1}{p}$), Charles's Law ($V \propto T$) and Gay-Lussac's Law ($p \propto T$):

$$V \propto \frac{T}{p}$$
 (constant n)
 $V = k \frac{T}{p}$
 $\frac{pV}{T} = k$ where k is a constant

• Comparing the properties of a gas under all three conditions of pressure, volume and temperature, the following equation is applicable when the <u>amount of</u> <u>gaseous particles remains unchanged</u>.

$$\frac{p_i V_i}{T_i} = \frac{p_f V_f}{T_f}$$

• Hence, the quantitative effect of the gas can be calculated *when two quantities* of the gas are varied at the same time.

2.5 Avogadro's Law: quantity-volume relationship

 Avogadro's Law states that at <u>constant temperature and pressure</u>, the <u>volume</u> of a gas is <u>directly proportional</u> to the <u>number of moles</u> of the gas.

Mathematically, Vαn $V = constant \times n$ or

• It then follows that *equal volumes of gases contain the same number of gas particles* under constant T and *p* (Avogadro's Hypothesis).

Therefore,

- \Rightarrow 1 mole of <u>**any</u>** gas will occupy the same volume!</u>
- \Rightarrow Recap: molar gas volume, V_m
- At 0 °C (273 K) and 1 bar or 1 x 10⁵ Pa (s.t.p.), 1 mole of any gas occupies a volume of 22.7 dm³.
- At 20 °C (293 K) and 1 atm or 101325 Pa (r.t.p.), 1 mole of any gas occupies a volume of 24.0 dm³.
- Application of Avogadro's Law:

When blowing a balloon, its size increases because more gaseous particles are being introduced into the balloon at constant external pressure and temperature.

3. Ideal Gas Equation

• The gas laws are:

Boyle's law:	$V \alpha \frac{1}{p}$	(constant n, T)
Charles's law:	$V \alpha T$	(constant n, <i>p</i>)
Gay-Lussac's law:	ραΤ	(constant n, V)
Avogadro's law:	$V \alpha n$	(constant p, T)

• Combining these relationships:

$$\Rightarrow \qquad \forall \alpha \frac{nT}{p}$$
$$\Rightarrow \qquad \forall e R \frac{nT}{p}$$

Rearranging,



where $p = \text{pressure of gas in Pascal (Pa) or Nm^{-2}}$ $V = \text{volume of gas in cubic metres (m^3)}$ n = number of moles of gas $R = \text{molar gas constant} = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ T = temperature in Kelvin (K)

This equation is known as the *ideal gas equation*.

Take note of the units!

- The ideal gas equation describes **how** gases behave as experimental conditions like temperature and pressure changes.
- 3.1 Other useful forms of Ideal Gas Equation
- Since $n = \frac{m}{M}$ where m = mass of gas in grams and M = molar mass of gas

$$pV = \frac{m}{M} RT$$

$$(1)$$

$$M = \frac{mRT}{pV}$$

$$(2) useful in calculating Mr of the gas$$

• Rearranging above equation (1):
$$p = \left(\frac{m}{V}\right) \frac{RT}{M}$$

 $\Rightarrow \boxed{p = \rho\left(\frac{RT}{M}\right)}$ (3) where ρ = density of gas in **g** m⁻³
• Rearranging ideal gas equation: $p = \left(\frac{n}{V}\right)RT$

- (4)

where c = gas concentration in **mol m⁻³**

 \Rightarrow

p = cRT

3.2 Calculation of molar gas constant, R



<u>Note:</u> You **must** convert the units of *p* into **Pa**, V into \mathbf{m}^3 and T into **K** whenever you use molar gas constant, R = 8.31 J mol⁻¹ K⁻¹.

Schema for selecting gas laws for calculations



Example 1 (N98/II/2)

0.080 g of a liquid compound **X** was vapourised in a gas syringe at 127 °C and a pressure of 1 atmosphere, 81 cm³ of vapour was produced.

(i) Calculate the relative molecular mass of the liquid.

Take note of units! Remember to convert T to K, p to Pa and V to m³!!!Using ideal gas equation, pV = nRT $M = \frac{mRT}{pV}$ m = 0.080 g $V = 81 \times 10^{-6} \text{ m}^3$ $T = = ___K$ p = 101325 Pa $M = = 32.4 \text{ g mol}^{-1}$ Thus, the relative molecular mass of X is 32.4 (no units).

(ii) The liquid used was pure methanol (CH₃OH). Suggest a reason why there is a difference between the theoretical value and the value obtained in (i).

The difference is due to the fact that methanol is assumed to be an _____gas when we perform the calculation. Methanol has strong intermolecular forces of attraction (______bonds) and deviates from ideal gas behaviour. Hence, the calculated value is different from the theoretical value.

Example 2

With the aid of the *Data Booklet*, determine the density, in g cm⁻³, of SO₂ gas at 20 °C and 1 atm. (M_r of SO₂ = 64.1)

pV = nRT $pV = \frac{m}{M}RT$ = **2.67 x 10⁻³ g cm⁻³** (3 s.f.)

Example 3

A sample of gas has a volume of 30 dm³ at a pressure of 5 atm and a temperature of 28 °C.

(i) Find the new pressure if the gas is compressed to 20 dm³ at a constant temperature.

Approach: Read the question carefully to decide which of the variables are changing: p, V, n or T. T and n are constant. Use the ideal gas equation and simplify it by grouping all the constants together to derive a new expression (in this case, Boyle's Law).

Using the ideal gas equation, pV = nRTSince n, R and T are constant, pV = constant (Boyle's Law) \Rightarrow where p_f is the new pressure

Substituting the values,

*p*₂ = <u>7.5 atm</u>

(ii) At what temperature, in °C, will the volume of the gas be 50 dm³ if the pressure is kept constant?

Using the ideal gas equation,	pV = nRT
Since n, R and <i>p</i> are constant,	$\frac{V}{T} = \frac{nR}{P}$ = constant (Charles's Law)
\Rightarrow	$\frac{V_i}{T_i} = \frac{V_f}{T_f}$ where T _f is the new temperature
\Rightarrow	
\Rightarrow	T _f =K = <u>229 °C</u>

(iii) When the temperature is doubled from 28 °C to 56 °C under constant p, the volume will also be doubled from 30 dm³ to 60 dm³.

True / False

Example 4

The volume of nitrogen gas collected at a temperature of 18 °C and a pressure of 98.5 kPa measures 47.0 cm³. What volume will the gas occupy at s.t.p.?



4. Dalton's Law of Partial Pressure (For Gas Mixtures)

The pressure of a gas is due to the force exerted by the gas molecules when they strike the walls of its container.



H₂ only

 $p_{\text{total}} = p_{\text{H2}}$

(partial pressure of He)

- **Partial pressure** of a gas (usually annotated with small *p*) is equal to the pressure that the gas would exert <u>as if it alone occupied the container</u>.
- Dalton's Law of Partial Pressure states that in a mixture of gases (which do not react chemically), the <u>total pressure</u> (p_{total}) is the <u>sum of the partial pressures</u> (p) of <u>all the constituent gases</u> at the same temperature.

 $p_{\text{total}} = p_{\text{A}} + p_{\text{B}} + p_{\text{C}} + p_{\text{D}} + \dots$

(where p_A is the partial pressure of gas **A**, p_B is the partial pressure of gas **B**..... in the mixture)

Let n_A , n_B , n_c , n_D and so forth be the number of moles of each gas in the mixture and n_{total} be the total number of moles of gas ($n_{total} = n_A + n_B + n_C + n_D + ...$)

• Assuming a mixture containing non-reacting gases behave ideally,

From above equation (1), $p_{\text{total}} = \frac{n_{\text{total}} RT}{V}$

 $p_{\text{total}} V = n_{\text{total}} RT$ (2)

For constituent gas A present,

 $p_{A}V = n_{A}RT$ (3)

Dividing (3) by (2) under the same conditions of T and V,

. .

$$\frac{\rho_{A}V}{\rho_{total}V} = \frac{n_{A}RT}{n_{total}RT}$$

$$\Rightarrow \qquad \frac{\rho_{A}}{\rho_{total}} = \frac{n_{A}}{n_{total}} \Rightarrow \qquad \rho_{A} = \left(\frac{n_{A}}{n_{total}}\right)\rho_{total} = \chi_{A}\rho_{total}$$

Mole fraction (χ) and its relation to partial pressure

The **mole fraction** of a constituent gas A, χ_A , in a gas mixture is the **ratio** of number of moles of gas A to the total number of moles of gas components present.

 $\Rightarrow \qquad \qquad \chi_{A} = \frac{n_{A}}{n_{total}} \text{ (no units)}$

Example 5

(a) Calculate the mole fractions of nitrogen, argon and oxygen in a gas mixture containing 0.3 mol of N_2 , 0.5 mol of Ar and 0.7 mol of O_2 .

 $n_{\text{total}} = = 1.5 \text{ mol}$ $\chi_{N2} = \frac{n_{N2}}{n_{\text{total}}} = = \frac{0.200}{200} \qquad \chi_{Ar} = \frac{n_{Ar}}{n_{\text{total}}} = = \frac{0.333}{200}$ $\chi_{O2} = \frac{n_{O2}}{n_{\text{total}}} = = \frac{0.467}{200}$ Note: all the mole fractions should add up to 1.

(b) Calculate the partial pressure of nitrogen if the total pressure of the gas mixture is 20 atm.

 $p_{N2} = \chi_{N2} p_{total} = = \underline{4 \text{ atm}}$

Example 6

A gaseous mixture containing 8.0 g of hydrogen and 64.0 g of oxygen has a total pressure of 300 kPa. Calculate the partial pressures of each gas.

Approach: In order to find the partial pressure, the mole fraction of each gas has to be calculated first.

n _{O2} =	= 2 mol	n _{H2} =	= mol
n _{total} =	= mol		
<i>p</i> ₀₂ =	= <u>100 kPa</u>	<i>р</i> _{H2} =	= <u>200 kPa</u>

$rac{l}{l}$ Example 7

Flask X contains 1 dm³ of helium at 2 kPa and flask Y contains 2 dm³ of neon at 1 kPa. If the flasks are connected at constant temperature, what is the final pressure?



Approach : Upon connection, the gases from each flask will equilibrate and the new volume is $1 + 2 = 3$ dm ³ . Treat each flask as a system on its own and apply the ideal gas equation to each flask.				
For He in Flask X,				
Using the ideal gas equation, $pV = nRT$				
with n, R and T constant, (2000)(1 x 1	$p_1 V_1 = p_2 V_2$ $ 0^{-3}) = p_2 (3 \times 10^{-3})$ $p_2 = 666.67 \text{ Pa}$	where p ₂ is the partial pressure of He after connection and V ₂ is the new volume after connection		
For Ne in Flask Y,	$p_3 V_3 = p_4 V_4$			
	<i>p</i> ₄ = 666.67 Pa	where p₄ is the partial pressure of Ne after connection and V₄ is the new volume after connection		
Using Dalton's Law,				
Total (final) pressure = <i>p</i> ₂ + <i>p</i> ₄ = 666.67 + 666.67 = <u>1.33 kPa</u>				

5. Deviations from Ideal Behaviour – Real Gases

- An ideal gas is a **hypothetical** gas whose pressure, volume and temperature behaviour is completely described by the ideal gas equation, *p*V = nRT.
- Recall the **three** <u>main</u> basic assumptions of an ideal gas (from page 3):
 - $\frac{1}{10}$ 1. The volume of the gas molecules is <u>negligible</u> compared to the volume of the container.
 - ☆ 2. The forces of attraction between the gas molecules as well as between the gas molecules and walls of the container are negligible.
 - 3. All molecular collisions are **perfectly elastic**. There is **no loss of the kinetic energy** during collision.

(State the third assumption only if the question asks for the three assumptions.)

• However, ideal gas does <u>not</u> exist in real life!

(Try compressing a gas in a sealed syringe, you will reach a point where you will feel strong resistance and you can no longer compress it further! That's the volume of the gas molecules.)

- Real gases have <u>finite volumes</u> and the gas molecules <u>attract</u> one another. Hence, the two basic assumptions are not entirely true and <u>real gases deviate from ideality (or ideal behaviour)</u>.
- However, real gases can still <u>approach ideal behaviour</u> by changing the conditions such that the two main basic assumptions above can still be applied.

5.1 <u>Conditions for real gas to approach ideal behaviour:</u>

1. Low Pressure

Gases behave more ideally at low pressures because when pressure is low, the gas <u>molecules</u> are <u>far apart</u>. The <u>volume of the gas molecules</u> therefore becomes <u>insignificant</u> compared to the volume of the container. Similarly, the intermolecular forces of attraction are negligible.

2. <u>High Temperature</u>

Gases behave more ideally at high temperatures because when the temperature is high, the gas <u>molecules</u> <u>move faster</u> (higher kinetic energy) and the <u>intermolecular</u> <u>forces of attraction become negligible</u>.

5.2 Graphical representations of deviation from ideal behaviour

• For an ideal gas, $pV = nRT \implies \frac{pV}{RT} = n$ For **1 mol** of an ideal gas, $n = 1 \implies \frac{pV}{RT} = 1$

A graph of pV/RT against p for 1 mol of ideal gas should be a <u>horizontal line</u> with value of 1.



Graphs of pV/RT against p for 1 mol of N_2 at three different temperatures

Refer to "Additional Reading" for explanation on positive and negative deviation from ideality.



Graphs of pV/RT against p for 1 mol of N₂, H₂ and NH₃ at 300 K

 Different gases deviate to a different extent from ideality, depending on the nature of the gas, the <u>strength</u> of the intermolecular forces of attraction and the molecular volume.

With reference to the graph above:

(i) Suggest reasons as to why the deviation from ideality for the 3 gases are as follow: $NH_3 > N_2 > H_2$, when the pressure is low to moderate.

At Low to Moderate Pressure

 Generally, the <u>stronger</u> the intermolecular forces of attraction, the <u>greater</u> the deviation from ideal behaviour since the <u>forces of attraction between</u> <u>the gas molecules</u> will be more significant.

gas	nature of intermolecular forces of attraction	relative strength of intermolecular forces of attraction	Deviation from ideal behaviour
H_2	Instantaneous dipole – induced dipole (id – id)		Least deviation
N ₂	id – id	more electrons than H ₂ , hence stronger than that between H ₂ molecules but weaker than bonds between NH ₃ molecules	
NH₃	hydrogen bonding		Highest deviation

 Polar molecules such as NH₃ and H₂O have stronger forces of attraction between the molecules compared to the non-polar molecules such as H₂ and N₂. Thus, the extent of deviation is greater for polar molecules. (ii) Suggest reasons as to why N_2 deviates more from ideality as compared to H_2 when the pressure is high.

At very High Pressure

- Generally, the <u>larger</u> the volume of the gas molecules, the <u>greater</u> the deviation from ideal behaviour since the volume of the gas molecules will be significant as compared to the volume of the container.
- The molecular volume of N₂ is greater than H₂, hence N₂ deviate more from ideality as compared to H₂ when the pressure is high.

Application: Bubble-jet printer



The ejection of ink from a thermal bubble-jet printer deduced from the ideal gas equation.

$$\frac{\text{pV}}{\text{T}} = \text{constant}$$

Ink is fed into thousands of tiny reservoirs in the print-head of the ink cartridge. The ink is heated rapidly by a tiny resistor and then boils, forming bubbles. As temperature increases (T increases), the bubbles expand (V increases) and coalesce to form an air pocket. The increase in temperature increases the pressure within the air pocket (P increases). The increased air pressure is sufficient to eject the ink bubble from the pore of printer head and onto a page. This pressure-activated ejection is similar to spitting.



Adapted from:

Monk, P. (2008). Properties of Gases and the Gas Laws. In Physical Chemistry: Understanding our Chemical World (p 26-28). John Wiley and Sons

Additional Reading: Real Gases - Deviations from Ideal Behaviour

Although the ideal gas equation is a very useful description of gases, most gases do not obey this relationship. Gases which do not obey the ideal gas equation are called **real gases**.

To see how real gases behave, we will consider plotting the quotient $\frac{pV}{RT}$ versus *p* for the gas.

The quotient is also known as the *compression factor* of a gas.

For <u>1 mol of an ideal gas</u>, a plot of this quotient against pressure is a constant (horizontal straight line) in Figure 1. This is because increasing the pressure decreases the volume, according to Boyle's law.

However, with real gases we observe deviation from this plot. Let's consider carbon dioxide and observe how this quotient changes as we increase the pressure.



Graphs of pV/RT against p for 1 mol of N_2 , CH_4 , H_2 and NH_3 at 300 K

We observe that initially the quotient for carbon dioxide deviates negatively (pV/RT < 1). However, as pressure continues to increase, we observe that the quotient starts to deviate positively (pV/RT > 1). The reason for such deviations is because real gases do not obey the assumptions of the Kinetic Theory of gases.

Positive Deviation - The Volume Effect

In Figure 1, carbon dioxide starts to exhibit a positive deviation, (pV/RT > 1) at about 500 atm. This is because unlike ideal gas, the molecules of real gases have significant volume. As the pressure on the gas increases, the gas molecules are packed more closely together as the volume of the container decreases. The volume of the gas molecules is no longer negligible compared to the volume of the container.

Since molecules of real gases have significant volume, the actual volume (free space volume) which is available for the gas molecules is smaller than the volume of the container as seen in Figure 2 ($V_{container} > V_{actual}$).



For ideal gas, V = V_{container} – V_{gas molecules} ≈ V_{container} (since V_{gas molecules} is negligible)

For real gas, $V = V_{container} - V_{gas molecules} < V_{container}$ (since $V_{gas molecules}$ is not negligible.)

If you worked out the quotient $\frac{pV}{RT}$, by putting the total volume of the container (V_{container}) into the formula, **the product of** *p***V is greater than it should be**. Hence, we see a **positive deviation**.

Negative Deviation - The Pressure Effect

We also see that carbon dioxide exhibit a negative deviation (pV/RT < 1) initially. This is because unlike ideal gas, the intermolecular forces of attraction for real gases are significant. As the pressure increases, the gas molecules are forced closer together. When this happens, they experience attraction to adjacent molecules.

Now, imagine a gas molecule approaching the wall of a container. The force of impact by this molecule on the wall of the container decreases, due to the attraction of the neighbouring molecules (Figure 3). Since gas pressure measures the force exerted by the molecules when they strike the container wall, the real pressure is less than the ideal pressure.



If you put the measured pressure into the quotient $\frac{pV}{RT}$, the product *pV* is now less than is expected and we observe a negative deviation.

$$p_{real} < p_{ideal} \implies \frac{p_{real}V}{RT} < \frac{p_{ideal}V}{RT}$$
$$\implies \frac{p_{real}V}{RT} < 1$$

Negative deviation from ideality can also be observed at low temperatures (Graph on pg 18). At low temperatures, average kinetic energy of gas molecules decreases and the gas molecules move slowly and hence unable to overcome the attractive forces between them. Thus, the intermolecular forces of attraction become significant. As a result, the force with which the molecules strike the wall is reduced, resulting in lower pressure. The molecules also tend to "stick" to each other and the collisions are no longer elastic.

The degree of the negative deviation is thus a good measure of the strength of the attraction between the molecules. Hydrogen exhibits no negative deviation as the forces of attraction between the hydrogen molecules are very weak. Hence, the attraction between molecules is not as significant for hydrogen as compared to carbon dioxide.

The van der Waals Equation

The **van der Waals equation** corrects for the volume of, and attractive forces between, gas molecules:

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

There are two corrective factors in van der Waals equation. The first alters the pressure in the ideal gas equation. It accounts for the intermolecular attractive forces between gas molecules. The magnitude of 'a' is indicative of the strength of the intermolecular attractive forces. The factor 'nb' accounts for the volume occupied by the gas molecules.

Source: Adapted from intro.chem.okstate.edu and www.chemguide.co.uk