

Raffles Institution Year 5 H2 Chemistry 2022 Lecture Notes 4 – The Gaseous State

Content

- Ideal gas behaviour and deviations from it
- pV = nRT and its use in determining a value for M_r
- Dalton's Law and its use in determining the partial pressures of gases in a mixture

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. Introduction
- 2. Gas Laws
- 3. The Ideal Gas Equation
- 4. Sketching of Graphs Using Ideal Gas Equation
- 5. The Kinetic Theory of Gases
- 6. Real Gases and Ideal Gases
- 7. Mixture of Gases
- 8. Vapour Pressures

Resources

- 1. Chemistry The Molecular Nature of Matter and Change, Silberberg
- 2. Chemistry, Cann and Hughes
- 3. Chemistry Principles and Practice, Reger, Goode and Ball
- 4. <u>https://phet.colorado.edu/en/simulation</u> /gas-properties

1. INTRODUCTION

Gases are made up of particles that are separated by large distances (due to weak intermolecular forces between the particles) and these particles are constantly moving around.

These constant movements in a container result in constant collisions with the walls of the container, giving rise to the phenomenon known as the "**pressure**" of the gas.



The gas particles are constantly moving as they possess kinetic energy (K.E.). The amount of K.E. depends on the temperature of the gas.

In summary, the gaseous state is characterised by the following physical properties:

- Gases do not have a fixed shape and volume, i.e. gases assume the volumes and shapes of their containers.
- Gases are highly compressible and gas volume changes greatly with pressure.
- Gases exert pressure equally in all directions.
- Gases mix evenly and completely when confined to the same container.
- Gases have much lower densities than solids or liquids.
- Gases are poor heat conductors, i.e. good insulators.

2. GAS LAWS

Over the past few centuries, scientists performed multiple experiments to understand the common behaviors of gases. They have observed that a gas's physical condition depends on four measurable macroscopic properties:

| | SI units |
|--|----------------|
| p = pressure exerted by the gas | Pa |
| V = volume occupied by the gas | m ³ |
| T = temperature of the gas | к |
| n = amount of the gas | mol |

Through a series of experimental studies, the relationships between these four variables are expressed in the following gas laws.

2.1 Avogadro's Law

Avogadro's hypothesis states that at constant T and p, gases of the same volume contain the same number of particles. This means that one mole of any gas occupies the same volume as another gas at the same T and p.

| The volume occupied by 1 mol of any gas, V_m , is called the molar gas volume . | | | |
|--|---|--|--|
| At s.t.p. | V _m = 22.7 dm ³ mol ⁻¹ | at 10 ⁵ Pa [1 bar] and 273 K [0 °C] | |
| At r.t.p. | V _m = 24 dm ³ mol ⁻¹ | at 101325 Pa [1 atm] and 293 K [20 °C] | |

*Information can be found in the data booklet.

This means that 1 mol of neon gas occupies the same volume as 1 mol of ammonia gas under the same temperature and pressure. Under r.t.p., 1 mol of either gas will occupy 24 dm³.

Stemming from Avogadro's hypothesis, Avogadro's Law states that "for a gas at constant temperature and pressure, the volume of the gas is directly proportional to the number of moles of the gas."

V oc n



Ne NH₃ (same number of moles)

This means that $\frac{V}{2}$ = constant. The effect of changing number of moles on the volume for a gas at

constant T and p can be deduced using:

At constant T and p,

 $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

Example 1

4.00 g of methane, CH₄, occupies a volume of 6.25 dm³ at a particular temperature and pressure. Find the volume of the same mass of hydrogen under the same conditions.

Note: Constant T & p.

Applying Avogadro's Law, $n_{1} = \frac{4.00}{16.0} = 0.25 \text{ mol} \qquad V_{1} = 6.25 \text{ dm}^{3}$ $n_{2} = \frac{4.00}{2.0} = 2.00 \text{ mol} \qquad V_{2} = ?$ $\therefore \text{ volume of } H_{2} = \frac{50.0 \text{ dm}^{3}}{2.0} = 50 \text{ odm}^{3}$

2.2 Gay-Lussac's Law

Gay-Lussac's Law states that "for a fixed mass of gas at constant volume, the pressure of the gas is directly proportional to its absolute temperature", i.e. temperature in Kelvin.

At constant V and n.



This means that $\frac{p}{r}$ = constant. The effect of changing temperature on the pressure for this fixed

mass of gas at constant V can be deduced using:



2.3 Charles' Law

Charles' Law states that "for a fixed mass of gas at constant pressure, the volume of the gas is directly proportional to its absolute temperature", i.e. temperature in Kelvin.

At constant p and n, $V \propto T$



This means that $\frac{V}{T}$ = constant. The effect of changing temperature on the volume for this fixed mass

of gas at constant p can be deduced using:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Example 2

A sample of gaseous argon, maintained at constant pressure, is found to have a volume of 10.5 m³ at 25 °C. If the system is heated to 250 °C, what is the resulting volume?

Note: Constant p for the same sample of gas.

Applying Charles' Law, $\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_1}{T_1} \times T_2 = \frac{10.5}{298} \times 523$ $V_1 = 10.5 \text{ m}^3$ $V_2 = ?$ T_K = T ₀_C+273 $T_1 = 25 + 273 = 298 \text{ K}$ $T_2 = 250 + 273 = 523 \text{ K}$ \therefore resulting volume = $\frac{18 \cdot 4}{M^3}$

2.4 Boyle's Law

Boyle's Law states that "for a fixed mass of gas at *constant temperature*, the *volume* of the gas is *inversely proportional* to the *pressure*."

At constant T and n,
$$V \propto \frac{1}{p}$$

This means that pV = constant. The effect of changing pressure on the volume for this fixed mass of gas at constant T can be deduced using:

$$p_1V_1 = p_2V_2$$



Example 3

A sample of a gas has a pressure of 2.00 atm and a volume of 45.0 dm³. Find its pressure if it is compressed to 10.0 dm³ at constant temperature.

Note: Constant T for the same sample of gas.

$$p_1 = 2.00 \text{ atm}$$

 $v_1 = 45.0 \text{ dm}^3$
 $p_2 = ?$
 $v_2 = 10.0 \text{ dm}^3$
 $\therefore \text{ pressure when volume is 10.0 \text{ dm}^3 = 9.00\text{ Atm}$

3. THE IDEAL GAS EQUATION

Candidates should be able to

 \square state and use the general gas equation pV = nRT in calculations, including the determination of $M_{\rm r}$.

3.1 Ideal Gas Equation

The four gas laws are all inter-related. Putting all the gas laws together:

| Boyle's Law | Charles' Law | Gay-Lussac's Law | Avogadro's Law | |
|-------------------------|---------------------|---------------------|---------------------|--|
| at constant T and n | at constant p and n | at constant V and n | at constant p and T | |
| $V \propto \frac{1}{p}$ | V∝T | p∝T | V∝n | |
| | | | | |

Combining these individual effects into one relationship, we get $pV \propto nT$

By introducing a constant of proportionality known as **R**, the **molar gas constant**, into the relationship above, the ideal gas equation is obtained:

Ideal gas equation:

pV = nRT

In the Data Booklet, the value of the molar gas constant R is stated as 8.31 J K⁻¹ mol⁻¹.



| Note the useful | $1 \text{ dm}^3 = 1000 \text{ cm}^3$ | 1 atm = 101325 Pa |
|-----------------|--|-------------------------------|
| conversions: | $1 \text{ dm}^3 = 10^{-3} \text{ m}^3$ | 1 bar = 1 x 10⁵ Pa |
| | $1 \text{ cm}^3 = 10^{-6} \text{ m}^3$ | $T_{K} = T_{\circ_{C}} + 273$ |

Example 4

Calculate the amount of nitrogen gas with a volume of 200 cm³, at a temperature of 100 °C and pressure of 10 atm.

$$V = 200 \text{ cm}^{3} \qquad pV = nRT$$

= 2.00 x 10⁻⁴ m³ 1013250 x 2.00 x 10⁻⁴ = n x 8.31 x 373
T = 100 °C
= (100 + 273) K = 373 K
$$n = \frac{(1013250)(2.00 \times 10^{-4})}{(8.31)(373)}$$

= 0.0654 mol
p = 10 atm = (10 x 101325) Pa
= 1013250 Pa

Example 5

A 1.00 dm³ balloon filled with helium gas is released at sea-level where the temperature is 29 °C and the pressure is 1.00 atm. What will be its volume when it reaches a height where the temperature is 27 °C and the pressure is 0.98 atm?



Determining the molar mass of a gas 3.2

Through a rearrangement of the ideal gas equation, an expression involving the molar mass M of the gas can be obtained.

Using the ideal gas equation, pV = nRT

$$pV = \frac{m}{M}RT$$
 where n = amount of gas (in mol) = $\frac{m}{M}$
m = mass of the gas (in g)

M = molar mass of the gas (in g mol⁻¹)

Rearranging,

mRT M = pV

Note:

Molar mass M has the same numerical value as the relative molecular mass, Mr. It is important to note that while M has the units of g mol⁻¹, M_r is dimensionless (no units).

Example 6

•

Compound X is a volatile liquid. In order to determine the relative molecular mass of X, an experiment involving the apparatus shown below was used.



Calculate the relative molecular mass of X using the experimental data above.

Solution

 $\overline{\mathbf{X}}$ is a volatile liquid (i.e. \mathbf{X} easily vaporises). Assume the increase in volume in the gas syringe is due entirely to gaseous \mathbf{X} ,

m = 20.476 - 20.252 = 0.224 g; p = 1.00 x 10⁵ Pa; T = 99.6 + 273 = 372.6 K

 $V = 96.8 - 1.4 = 95.4 \text{ cm}^3 = 9.54 \times 10^{-5} \text{ m}^3$; Molar mass. M = ?



Example 7

A large flask is evacuated and found to weigh 134.6 g. It is then filled to a pressure of 98 kPa at 31 °C with a gas of unknown molar mass and then reweighed; its mass is 137.5 g. The evacuated flask is then filled with water and again weighed. Its mass is now 1067.9 g. Assuming that the gas behaves ideally, what is the molar mass of the unknown gas?

(The density of water at 31 °C is 0.997 g cm⁻³.)

From pV = nRT, $pV = \frac{m}{M}RT$ $M = \frac{mRT}{pV}$ $M = \frac{mRT}{pV}$ $M = \frac{79.9 \text{ g mol}^{-1}}{1067.9 - 134.6}$ $= \frac{1067.9 - 134.6}{0.997}$ $= 936.1 \text{ cm}^3$ $= 9.361 \times 10^{-4} \text{ m}^3$

3.3 Determining the density of a gas

The ideal gas equation can be rearranged to give an expression involving the density of a gas. Using the ideal gas equation, pV = nRT

$$pV = \frac{m}{M}RT$$
 where n = amount of gas (in mol) = $\frac{m}{M}$
m = mass of the gas (in g)
M = molar mass of the gas (in g mol⁻¹)
V = volume of the gas (in m³)
$$p = \left(\frac{m}{V}\right)\frac{RT}{M} = \rho \frac{RT}{M}$$

where ρ = density of gas (in g m⁻³) = $\frac{m}{V}$

Example 8

A sample of an organic compound of molar mass *M* is vapourised in a gas syringe and occupies $V \text{ cm}^3$ at *T* K and *p* atm.

What is the density of the compound?

A
$$\frac{p \times M \times (T + 273)}{24000 \times 293}$$
 C $\frac{M \times T}{p \times 24000 \times 293}$
B $\frac{p \times M \times 293}{24000 \times T}$ D $\frac{M \times (T + 273)}{p \times 24000 \times 293}$

Solution:

By observation, R does not appear in any of the options. Instead, the number 24000 indicates that the value of R can be derived by using V, T and p of 1 mol of gas at r.t.p. conditions: T = 293 K, V = 24000 cm³ and p = 1 atm.

 $pV = nRT = \frac{m}{M}RT$ $p \ge 101325 \ge V \ge 10^{-6} = \frac{m}{M} \ge R \ge 7$ $1 \ge 101325 \ge 24 \ge 10^{-3} = 1 \ge R \ge 293$ $p = \frac{m}{V} = \frac{p \ge M \ge 293}{24000 \ge T}$ (Answer B)

4. SKETCHING OF GRAPHS USING IDEAL GAS EQUATION

The ideal gas equation can be used to generate graphical plots for a fixed amount of ideal gas.

Some useful mathematics knowledge on graph plotting:



Type 1: y = *k*x

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| Oranh to Skotch | Manipulation of Ideal Gas Equation | Graph |
|---|---|---|
| (1) p against V for a fixed mass of gas at constant T | pV = nRT p = $\frac{nRT}{V}$ Since n, R and T are constants, p = $\frac{k}{V}$ Hence graph is Type 3: $y = \frac{k}{x}$ | o constant T |
| (2) pV against p for a fixed mass of gas at two constant temperatures T_1 and T_2 where $T_1 > T_2$ | pV = nRT Since n, R and T constants, pV = constant at a particular T. Hence graph is of Type 4: y = c (horizontal line) Since T ₁ is greater than T ₂ , pV is larger at T ₁ . | $ \begin{array}{c} \rho V & T_1 > T_2 \\ \hline & & T_1 \\ \hline & & & T_2 \\ \hline & & & T_1 \\ \hline & & & & T_2 \\ \hline & & & & T_2 \\ \hline & & & & & P \end{array} $ |
| (3) p against $\frac{1}{V}$ for a fixed mass of gas at two constant temperatures T ₁ and T ₂ where T ₁ > T ₂ | $pV = nRT$ $p = \frac{1}{V}(nRT)$ Since n, R and T are constants, $p = \frac{1}{V}(k)$ Hence graph is Type 1: $y = kx \text{ (straight line that passes through origin)}$ Since T ₁ is greater than T ₂ , the graph at T ₁ has a steeper gradient. | $P = T_1 > T_2$ $T_1 > T_2$ T_2 T_2 |

| (4) V against T/K for a fixed mass of gas at constant p | pV = nRT $V = \frac{nR}{p}(T)$ | Constant p |
|---|--|--|
| | Since n, R and p are constants, V = k(T) | |
| | Hence graph is Type 1: | |
| | y = kx (straight line that passes through origin | 0 TIK |
| (5) V against T/°C for a fixed mass of gas at two constant pressures p_1 and p_2 in which $p_1 > p_2$ | Let $T_K = T$ in K; $T \circ_C = T$ in °C. $pV = nRT_K$ $= nR(T \circ_C + 273)$ $V = \frac{nR}{p}(T \circ_C + 273)$ $V = \frac{nR}{p}(T \circ_C) + \frac{nR}{p}(273)$ Since n, R and p are constants, $V = k(T \circ_C) + k(273)$ Hence graph is of Type 2: y = kx + c (straight line with a y -intercept; y -intercept = $k \times 273$) Since $p_1 > p_2$, graph at p_1 has a gradient which is less steep. | $P_{1} > p_{2}$ $P_{1} > p_{2}$ P_{1} P_{2} P_{1} P_{2} P_{1} P_{2} P_{3} P_{3} P_{4} P_{5} P_{7} P_{7 |

Example 9



5. THE KINETIC THEORY OF GASES

Candidates should be able to

state the basic assumptions of kinetic theory as applied to an ideal gas.

The Kinetic Theory of Gases is a mathematical model that is used to study the behavior of gases. It is an attempt to explain the macroscopic properties (e.g. p, V, T, n) of a gas in terms of its molecular behaviour.

In reality, an ideal gas does not exist; it is a hypothetical gas that allows us to gain a better understanding of real gases by simplifying their complexities so that behavior of gases can be more easily understood. The kinetic theory therefore considers various assumptions as applied to an ideal gas.

Basic assumptions of the Kinetic Theory as applied to an Ideal Gas:





- (b) The gas particles exert negligible attractive forces on one another.
 - (c) The gas particles are in constant random motion, colliding with one another and with the walls of the container. Between collisions, they move in straight lines.
 - (d) Collisions between the gas particles are perfectly elastic i.e. there is no loss of overall kinetic energy upon collision, though kinetic energy can be transferred between colliding particles.
 - (e) The average kinetic energy of particles in a gas is constant at constant temperature. The average kinetic energy is **proportional** to the **absolute temperature** (i.e. temperature in K). At the same temperature, all gases have the same average kinetic energy.

6. REAL GASES AND IDEAL GASES

Candidates should be able to

☑ explain qualitatively in terms of intermolecular forces and molecular size:

- (a) the conditions necessary for a gas to approach ideal behaviour;
- (b) the limitations of ideality at very high pressures and very low temperatures.

6.1 Concept of an Ideal Gas

An ideal gas is one that obeys the ideal gas equation (i.e. pV = nRT) under all conditions of pressure and temperature.

An ideal gas is assumed to be one where:

- 1. the gas particles have negligible volume and
- 2. the gas particles exert negligible attractive forces on one another.

6.2 Real Gases and Non-Ideal Gas Behavior

As mentioned in section 5, ideal gases do not exist in real life. All **real gases** deviate from ideal gas behaviour because they do not follow the above two assumptions entirely.

In a real gas,

- · the gas particles have a finite volume and size, and
- there are attractive forces between the gas particles.

For a real gas to approach ideality, the conditions have to allow for these two main assumptions to be met as far as possible, i.e.

- low pressure
- high temperature

| 1. At Low Pressure | 2. At High Temperature |
|--|--|
| At low pressure, the gas particles are very far apart. As such, the volume occupied by the gas particles can be considered to have negligible volume compared to the volume of the container. In addition, the intermolecular attractive forces between the widely spaced gas particles are peoligible. | At high temperature, the gas particles possess sufficiently <u>high kinetic</u> <u>energy</u> to overcome the intermolecular attractive forces. Hence the <u>intermolecular attractive forces</u> can be considered <u>negligible</u> . |
| <u>Conclusion:</u> A gas approaches ideal gas behavior at <u>low press</u> | sure and high temperature. |

Conversely, a real gas deviates most from ideality under very high pressure and very low temperature:

| 1. | At High Pressure | 2. | At Low Temperature |
|------------------|---|-----|--|
| • | At high pressure, the gas particles are much closer together and the gas occupies a smaller volume. As such the volume of the gas particles is not negligible as compared to the volume of the container. | • | At low temperature, the gas particles possess <u>less kinetic energy</u> and hence the <u>intermolecular attractive</u> forces are significant. |
| • | In addition, the <u>intermolecular attractive forces</u> between the closely spaced gas particles are <u>significant.</u> | | |
| <u>Co</u> A (| <u>nclusion:</u> gas <i>deviates</i> from ideal gas behavior at <u>high pr</u> | ess | ure and <u>low temperature.</u> |

Low pressure

- Gas particles are far apart
- Volume of gas particles is negligible compared to volume of container
- Intermolecular attractive forces are negligible



Comparison between low pressure and high pressure

High pressure

- Gas particles are close together
- Volume of gas particles is <u>not negligible</u> compared to volume of
- container
 Intermolecular attractive forces between gas particles are <u>significant</u>

| F | Features of an Ideal Gas | Features of a Real Gas | |
|-----|---|--|--------------------------------|
| (a) | The particles have negligible volume. | (a) The particles have a finite size and volume . | |
| (b) | There are negligible forces of attraction between the particles. | (b) There are forces of attraction between the particles. The forces of attraction of some gases are stronger than others, e NH ₃ molecules form stronger intermolecular hydrogen bondir while H ₂ molecules form weaker instantaneous dipole–induced dipole interactions at the same temperature and pressure. | The e.g ing ced |
| (c) | When the particles collide, the collision is perfectly elastic . This means that the particles bounce apart when they collide, with no loss in total kinetic energy. | (c) When particles collide, the collision may not be elastic . | |
| (d) | An ideal gas obeys the gas laws and the ideal gas equation perfectly under all conditions. | (d) A real gas approaches ideality under the conditions of: (i) Low pressure: The particles are far apart. Hence the volume occupied by the gas particles is negligible compared to the volume of the container and the intermolecular forces of attraction a negligible as the particles are far apart. (ii) <u>High temperature:</u> The gas particles have large kinetic energy to overcom attractive forces so that intermolecular forces of attractive between them are negligible. | the the are me ion |

6.3 Comparison between an Ideal Gas and a Real Gas

6.4 Deviation from Ideal Gas Behavior



Example 10

The volume of 1 mole of CO_2 was measured at various pressures but at a constant temperature of 285 K. The following results were obtained. Complete the calculations for the 3rd column.

| P/Pa | V / m ³ | pV / m³Pa |
|------------|-------------------------|-----------|
| 4.0 x 10⁵ | 5.80 x 10 ⁻³ | 2320 |
| 8.0 x 10⁵ | 2.85 x 10 ⁻³ | 2280 |
| 15.0 x 10⁵ | 1.46 x 10 ⁻³ | 2175 |
| 20.0 x 10⁵ | 1.07 x 10 ⁻³ | 2140 |

The ideal gas behavior predicts that pV is a constant at constant T and n. In this case, the values of pV seem to vary with p.

Based on your understanding from Chemical Bonding, what could have accounted for the trend of pV versus p, as observed in this example?

In general, real gases deviate from ideal gas behavior as the intermolecular attractive forces between the gas particles are significant and the volume occupied by the gas particles is not negligible as compared to the volume of the container.

However, it is observed that real gases experience negative and positive deviations as pressure increases. The deviations can be accounted for by two factors:

1. intermolecular attractive forces

2. intermolecular repulsive forces

Note that both intermolecular attractive forces and intermolecular repulsive forces are affected by molecular size. In general, the greater the molecular size, the <u>larger the electron cloud</u> which result in <u>stronger intermolecular attractive and repulsive forces</u>. This will be discussed further in part (2) below.

(1) Graph of $\frac{pV}{RT}$ against p/atm for 1 mole of a real gas at constant temperature

The $\frac{pV}{RT}$ curve shown on the right is typical of that for 1 mole of a real gas: it decreases below the ideal gas value at moderately high pressures and then rises above it as pressure increases further.





(2) Graphs of $\frac{pV}{BT}$ against p/atm for 1 mole of H₂, N₂ and NH₃ at constant temperature



(i) Comparing NH₃ and N₂/H₂:

NH₃ molecules form stronger intermolecular hydrogen bonding while H₂ and N₂ molecules form weaker instantaneous dipole-induced dipole interactions. Hence, NH₃ deviates more from ideal gas behavior than H₂ and N₂.

(ii) <u>Comparing N₂ and H₂:</u>

At moderately high pressure, negative deviation is observed for N₂. Both N₂ and H₂ molecules form instantaneous dipole-induced dipole interaction. N₂ has more electrons and a larger electron cloud which is more easily polarised, thus N₂ molecules form stronger instantaneous dipole-induced dipole interactions. N₂ deviates more from ideality than H₂.

At very high pressure, positive deviation is observed. The intermolecular repulsive force between N₂ molecules is more significant than that of H₂ as the molecular size and thus the size of electron cloud of N₂ molecules is larger than that of H₂ molecules. Hence, N₂ deviates more from ideality than H₂.

In general, deviation is greatest for polar molecules with strong intermolecular forces of attraction and smallest for small, non-polar molecules.

e.g. deviation of $NH_3 > HCl > CO_2 > O_2 > N_2 > H_2$

7. MIXTURE OF GASES

Candidates should be able to

use Dalton's Law to determine the partial pressures of gases in a mixture

7.1 Partial Pressure of a Gas

- In a mixture of gases that <u>do not react with each other</u>, each gas behaves as if it were the only gas present.
- For such a mixture, under the same physical conditions (e.g. temperature and volume), each
 gas exerts its own pressure that is equal to the pressure it would exert when it occupies the
 container alone. This pressure is known as the partial pressure of the gas.

7.2 Dalton's Law of Partial Pressures

- Dalton's law of partial pressures states that the total pressure of a mixture of non-reacting
 gases is equal to the sum of the partial pressures of the individual gases in the mixture.
- For a mixture of non-reacting gases containing gases A, B and C, the total pressure of the
 mixture is given as P_{total} = P_A + P_B + P_c where P_A is the partial pressure of gas A etc.



7.3 Mole Fraction and Partial Pressure

• The mole fraction of a component A, x_A, in a non-reacting gas mixture is the ratio of the number of moles of gas A to the total number of moles of all gaseous components present in the mixture.

Mathematically, $x_A = \frac{\text{number of moles of component A}}{\text{total number of moles of all components in mixture}} = \frac{n_A}{n_{\text{total}}}$

• The partial pressure of a gas A in a mixture of non-reacting gases is the product of the mole fraction of A in the mixture and the total pressure of the mixture.

Mathematically, $P_A = x_A P_{total}$

The equation P_A = x_A P_{total} can be derived as follows:

Consider a mixture of non-reacting gases A, B and C in a container of volume V at temperature T. The partial pressure of a gas A in a mixture of non-reacting gases is the product of the mole fraction of A in the mixture and the total pressure of the mixture.

Assuming ideal gas behaviour and applying the ideal gas equation,

 $p_{total}V = n_{total}RT \qquad(1)$ $p_AV = n_ART \qquad(2)$

Dividing (2) by (1),

 $\frac{p_A}{p_{total}} = \frac{n_A}{n_{total}} = x_A$

which can be rearranged to give

$$p_{A} = \frac{n_{A}}{n_{total}} \times p_{total}$$

n

Hence

$$p_A = X_A \times p_{total}$$

 $p_{\rm B} = X_{\rm B} \times p_{\rm total}$

 $p_{c} = X_{c} \times p_{total}$

Similarly,

Note: $x_A + x_B + x_C = 1$

Example 11

A mixture of 1 mole of N_2 , 2 moles of O_2 and 2 moles of CO_2 exert a total pressure of 10.0 atm. Calculate the mole fraction and hence partial pressure of each gas in the mixture.

Solution
 $P_{total} = 10.0 \text{ atm}$ $p_{N2} = \text{partial pressure of } N_2 = x_{N2} P_{total} = (0.2)(10.0)$
= 2.00 atmTotal amount of gases = 5 mol $p_{O2} = \text{partial pressure of } O_2 = x_{O2} P_{total} = (0.4)(10.0)$
= 4.00 atm $x_{N2} = \text{mole fraction of } N_2 = \frac{1}{5} = 0.2$
 $x_{O2} = \text{mole fraction of } O_2 = \frac{2}{5} = 0.4$ $p_{CO2} = \text{partial pressure of } CO_2 = x_{CO2} P_{total} = (0.4)(10.0)$
= 4.00 atm $x_{CO2} = \text{mole fraction of } CO_2 = \frac{2}{5} = 0.4$ $p_{CO2} = \text{partial pressure of } CO_2 = x_{CO2} P_{total} = (0.4)(10.0)$
= 4.00 atm

Example 12

A 5 dm³ flask containing a gas X at a pressure of 8 atm is connected to another flask containing a gas Y at a pressure of 2 atm and having a volume of 10 dm³ as shown in the diagram on the right.

What is the final pressure in the flasks if the valve between the 2 flasks is opened and pressures allowed to equilibrate, assuming that the 2 gases do not react and the temperature remains constant?



Solution

After the valve is opened, the gases will equilibrate and the new volume = 15 dm³

| Method 1 | Method 2 |
|---|---|
| Let the final pressure be p _{final} . | Let the partial pressures of X and Y after the valve |
| Assume ideal gas behaviour. | respectively. |
| From pV = nRT, | Since temperature and amount of <u>each gas</u> remain constant Boyle's law (i.e. $p_1V_1 = p_2V_2$) can be |
| $(p_{final})(V) = (n_{total})RT$ = $(n_x + n_v)RT$ | applied for each gas. |
| = n _x RT + n _y RT | For gas X, |
| = $p_{x(initial)}V_{x(initial)} + p_{y(initial)}V_{y(initial)}$ | $(8)(5) = (p_{X(final)})(15)$ |
| Thus, | $\Rightarrow p_{x(\text{final})} = \frac{40}{15}$ |
| $(p_{\text{final}})(V) = p_{x(\text{initial})}V_{x(\text{initial})} + p_{y(\text{initial})}V_{y(\text{initial})}$ | = 2.67 atm |
| | For gas Y, |
| $(p_{final})(15) = 8 \times 5 + 10 \times 2$ | $(2)(10) = (p_{Y(final)})(15)$ |
| = 60 | $\Rightarrow p_{Y(final)} = \frac{20}{15}$ |
| 60 | = 1.33 atm |
| Final pressure, $p_{final} = \frac{30}{15} = \frac{4.00 \text{ atm}}{15}$ | Final pressure = p _{X(final)} + p _{Y(final)} = <u>4.00 atm</u> |
| 8. VAPOUR PRESSURES | |

Consider a system where a liquid is enclosed in a <u>closed</u> container:



Some of the more energetic particles on the surface of the liquid can possess sufficient energy to escape from the attractive forces holding the liquid together. In other words, they evaporate.

There is constant evaporation from the surface but in a closed container, these particles are trapped in the space above the liquid.

The pressure exerted by the gaseous particles on the liquid surface and on the walls of the container is known as the <u>vapour pressure</u>.

A dynamic equilibrium will be rapidly set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it. In this equilibrium at a particular temperature, there will be a fixed number of the gaseous particles in the space above the liquid.

Liquid ⇒ Vapour

The vapour pressure exerted is called the saturated vapour pressure at that temperature.

7.1 Relating Intermolecular Forces, Boiling Points and Vapour Pressures

Boiling occurs when the saturated vapour pressure becomes equal to the external pressure exerted on the liquid.

The boiling point of a liquid gives an indication of the strength of its intermolecular forces, i.e. the stronger the intermolecular forces, the higher its boiling point.

Similarly, for a liquid with strong intermolecular forces, it will be more difficult for its particles to escape from the surface of the liquid. This translates into a lower saturated vapour pressure (and lower volatility), i.e. the stronger the intermolecular forces of a liquid, the lower its volatility and saturated vapour pressure, but the higher its boiling point.

Example 13

×.

Consider the following five alkanes:

C₅H₁₂ C₆H₁₄ C₇H₁₆ C₈H₁₈ C₉H₂₀

For which property of the alkanes does the numerical value decrease?

- A Density
- B Strength of intermolecular forces
- C Boiling point
- D Vapour pressure

| | D |
|---------|---|
| Answer: | 9 |
| | |

Explanations:

- As the size of the alkanes increases, the number of electrons increases, the electron cloud becomes more polarisable ⇒ increasing strength of instantaneous dipole-induced dipoles (id-id) between molecules (option B is wrong).
- Since the strength of intermolecular forces increases, molecules are held closer together, i.e. more molecules per unit volume ⇒ density increases from C₅H₁₂ to C₉H₂₀ (option A is wrong)
- Since the strength of intermolecular forces increases, more energy is required to overcome the intermolecular forces of attraction ⇒ increasing boiling points (*option C is wrong*)
- With stronger id-id between alkanes, it becomes increasingly harder for molecules to escape from the liquid surface into the vapour state ⇒ decreasing vapour pressure (*option D is correct*).

Summary of the Gas Laws

| Gas Laws | Mathematical Expressions | Graphical Representations |
|--|--|---|
| Boyle's Law states that | At constant T and n, | At constant T and n, |
| at constant temperature, | | n ≜ D. |
| the volume of a fixed | $V \propto \frac{1}{2}$ | |
| mass of gas is inversely | р | |
| proportional to its | | |
| pressure. | From Ideal Gas Equation, | |
| | | gradient = nk r |
| | pv = nR i | |
| | $p = \frac{m(r)}{N}$ | \downarrow \downarrow \downarrow \downarrow |
| | constant | 0 V |
| | $p = \frac{1}{V}$ | |
| | 1 | pv |
| | p∝ <u>v</u> | -87 |
| | Similarly $V \propto \frac{1}{2}$ | |
| | p | |
| | Note: pV = constant | |
| | or $p_1/(1 = p_2)/2$ | n n |
| | | 0 |
| | At constant p and p | |
| charles' Law states that | At constant p and n, | At constant p and n, |
| volume of a fixed mass | V∝T | v. |
| of gas is directly | | v v |
| proportional to its | From Ideal Gas Equation, | |
| absolute temperature. | pV = nRT | |
| | $V = (\frac{nR}{m})T$ | |
| Note: | р | nR |
| I _K = I ⁰ _C +2/3 | V = constant x I | gradient =i |
| | V∝I | gradient = |
| | Noto: V = constant | |
| | | |
| | $V_1 V_2$ | |
| | or $\frac{1}{T_1} = \frac{1}{T_2}$ | |
| | | |
| Gay-Lussac's Law | At constant V and n, | At constant V and n, |
| states that at constant | | p |
| volume, the pressure of | p∝T | ∧ v |
| a fixed mass of gas is | From Ideal Gas Equation | |
| directly proportional to | FIUIT Ideal Gas Equation, | |
| its absolute temperature. | pV = nRT | |
| | $n = \langle nR \rangle T$ | andiont _ nR |
| | $p = \left(\frac{1}{V}\right)^{n}$ | gradient – V |
| | Note: $\frac{p}{d} = \text{constant}$ | gradient = V |
| | <u> </u> | |
| | or $\frac{p_1}{p_2} = \frac{p_2}{p_2}$ | 0 1/0 |
| | $T_1 T_2$ | |
| | | |

| Gas Laws | Mathematical Expressions | Graphical Representations |
|--|---|--|
| Avogadro's law states that at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of the | At constant T and p, V ∝ n From Ideal Gas Equation, pV = nRT RT | At constant T and p, |
| gas. For example, doubling the number of moles of the gas will cause the volume to double if T and p remain constant. | $V = n(\frac{n}{p})$ $V = \text{constant } x \text{ n}$ $V \propto n$ Note: $\frac{V}{n} = \text{constant}$ or $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ | $radient = \frac{RT}{p}$ |
| Avogadro's law states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. | It follows from Avogadro's particles must be the same The volume occupied by o gas. Molar volume of gas a o Molar volume of gas a | law that the volume occupied by one mole of gas e for all gases. one mole of a gas is termed the molar volume of the at s.t.p. (273 K and 10 ⁵ Pa [1 bar]) = 22.7 dm ³ mol ⁻¹ at r.t.p. (293 K and 101325 Pa [1 atm]) = 24 dm ³ mol ⁻¹ |
| A combination of the gas laws gives the combined gas laws , which applies to the situation when two of the three variables (p, V, T) change and the effect on the third variable is to be determined. | At constant n, $\frac{pV}{T} = nR = constant$ or $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ | $ \begin{array}{c} \frac{pV}{T} \\ nR \\ 0 \end{array} \rightarrow p \end{array} $ |

•



Tutorial 4 - The Gaseous State

Self-check questions

1 N2005/1/32

Which equations apply to an ideal gas? [p = pressure, V = volume, M = molar mass, ρ = density, c = concentration, R = gas constant, T = temperature]

1
$$p = \frac{\rho RT}{M}$$
 2 $pV = MRT$ **3** $pV = \frac{cRT}{M}$

- A 1, 2 and 3
- B 1 and 2
- C 2 and 3
- D 1 only

2 CJC Y62017Prelim/1/8

Use of the Data Booklet is relevant to this question.

Gas canisters used in camping stoves contain partially liquified hydrocarbon. A canister was connected to a gas syringe and the valve opened slightly to allow some gas into the syringe. 0.200 g of the gas occupied a volume of 96.0 cm³ at a temperature of 30.0 °C and a pressure of 101 kPa.

What is the average M_r of the gas mixture?

| Α | 31.0 | С | 479.0 |
|---|------|---|-------|
| В | 52.0 | D | 519.0 |

3 N2009/1/7

Which expression gives the pressure exerted by 1.6 X 10^{-3} mol of N₂ in a container of volume 3.0 dm³ at 273°C.

- A $\frac{1.6 \times 10^{-3} \times 8.31 \times 273}{3.0 \times 10^{-6}}$ Pa B $\frac{1.6 \times 10^{-3} \times 8.31 \times (273+273)}{3.0 \times 10^{-6}}$ Pa
- C $\frac{1.6 \times 10^{-3} \times 8.31 \times 273}{3.0 \times 10^{-3}}$ Pa
- D $\frac{1.6 \times 10^{-3} \times 8.31 \times (273+273)}{3.0 \times 10^{-3}}$ Pa

4 J2001/3/6

A small spacecraft of capacity 10 m³ is connected to another of capacity 30 m³. Before connection, the pressure inside the smaller craft is 50 kPa and that inside the larger is 100 kPa.

If all measurements are made at the same temperature, what is the pressure in the combined arrangement after connection?

A 75 kPa
B 87.5 kPa
C 100 kPa
D 125 kPa

5 N2013/1/6

Under which conditions will the behaviour of a gas be most ideal?

| | pressure | temperature |
|-------|----------|-------------|
| A | high | high |
| В | high | low |
| C low | | high |
| D | low | low |

6 N2014/1/4

A given mass of an ideal gas occupies a volume V and exerts a pressure p at 27°C.

At which temperature will the same mass of the ideal gas occupy the same volume V and exert a pressure 2p?

- A 54°C
- **B** 54 K
- C 600°C
- D 600 K

7 RI 2016 Y5CT1/1/8

The value of pV is plotted against p for three gases: an ideal gas and two real gases, **B** and **C**.

[*p* is the pressure and *V* is the volume of the gas.]



Which of the following pairs of gases could be B and C?

| | В | С |
|---|------------------------------------|---------------------------------|
| A | CH ₄ | NH ₃ |
| B | HF | HBr |
| С | CH ₃ CH ₂ Cl | CH ₃ CH ₃ |
| D | O ₂ | H ₂ |

8 RI 2014 Y5CT1/1/8

A mixture containing 32.1 g of SO_2 and 25.5 g of NH_3 in a container at 300 K has a total pressure of 0.369 atm. What is the partial pressure of SO_2 in the mixture?

- A 0.0935 kPa
- B 9.36 kPa
- C 20.8 kPa
- D 28.0 kPa

9 HCI 2018 Promo/1/6

Each of the following graphs represents plots for an ideal gas at two different temperatures. Which graph shows the correct relationship where temperature T_1 is lower than T_2 ?



10 You may check out this website to visualize the relationships between the variables p, V, n, and T for an ideal gas.

https://phet.colorado.edu/en/simulation/gas-properties

For a constant number of moles of an ideal gas, sketch the following graphs:

| (a) | At constant T | (i) | p vs V | (ii) | p vs $\frac{1}{V}$ |
|-----|---------------|-------|-----------|------|--------------------|
| | | (iii) | pV vs p | (iv) | pV vs V |
| (b) | At constant p | (i) | V vs T/ºC | (ii) | density vs T/K |
| (c) | At constant n | (i) | pV vs T/K | (ii) | pV ⊤ vs p |



Gas Laws and Related Concepts

11 A glass of cola is fizzy because carbon dioxide, CO₂, has been dissolved in it under pressure. When the cola is poured out of the can, CO₂ is gradually released as bubbles of gas. The cola will eventually go flat, as the concentration of dissolved CO₂ decreases to its saturation level. A saturated solution of CO₂ at room temperature has a concentration of 1.50 g dm⁻³.

A 500 cm³ can of cola has 2.00 g of CO_2 dissolved in it under pressure. Calculate the volume of CO_2 that is released to the atmosphere as it goes flat, assuming CO_2 behaves as an ideal gas at room temperature and pressure.

Deviation from Ideal Gas Behaviour

12 N2015/3/2(e)

The volume of 0.40 mol of hydrogen chloride gas was measured at a temperature of 300 K, when various pressures were applied. The following results were obtained.

| pressure, p / Pa | volume, V / dm ³ | pressure x volume, pV / Pa dm ³ |
|----------------------|-----------------------------|--|
| 5.0×10^{5} | 1.924 | 9.62 × 10 ⁵ |
| 10.0×10^{5} | 0.926 | |
| 15.0×10^{5} | 0.592 | |

- (a) State how the value of pV should change with pressure for an ideal gas at constant temperature.
- (b) Calculate the volume of 0.40 mol of an ideal gas at a temperature of 300 K and a pressure of 12.0 × 10⁵ Pa.
- (c) Complete the third column of the table. Use your values of pV to estimate the value of pV when $p = 12.0 \times 10^5$ Pa. Use your estimated value of pV to calculate the value of V when $p = 12.0 \times 10^5$ Pa.
- (d) Suggest an explanation of the difference in the values of V you have obtained in (b) and (c) in terms of the properties of HC*l* molecules.

1

- 13 (a) State the two main assumptions of the kinetic theory as applied to an ideal gas.
 - (b) Sketch a graph of pV/nT against p for an ideal gas.
 - (c) Under what conditions of temperature and pressure is the behaviour of real gases most nearly ideal? Give reasons for your answers.
 - (d) On the same axes in (b), sketch the graph for O₂ gas and explain your answer.
- 14 (a) The graph on the right illustrates the behaviour of 1 mol each of two different gases, CO₂ and H₂, at 298K.

(Given: R = 8.31 J K⁻¹mol⁻¹)

- (i) Calculate the value of X.
- (ii) Give two reasons why CO₂ shows a greater deviation from ideality than H₂.



(b) Sketch, using the axes above, the corresponding graph for 1 mol of HF at 298 K and explain your answer.

Dalton's Law of Partial Pressure

- 15 A vessel contains 120 g of oxygen at a pressure of 3.00 atm at 25°C.
 - (a) What is the final pressure if 5.00 g of hydrogen are added at the same temperature without changing the volume of the container?
 - (b) If the mixture in (a) is then exploded and allowed to cool back to 25°C, what will be the pressure of the gas in the vessel?
- 16 Xenon and fluorine were mixed in a 1:1 ratio by volume and sealed in a vessel attached to a barometer. After some time, crystals were found to have formed on the walls of the vessel and the barometer showed that the pressure had dropped to 70% of its original pressure. Analysis of the gases remaining indicated 4 parts xenon to 3 parts fluorine. Assuming that the temperature remained constant and only one crystal product was formed, construct a balanced equation with state symbols for the reaction.