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Ch. 1. Reactions in gase phase

THE air we all breathe contains numerous gases, such as oxygen, nitrogen, or carbon dioxide. Some of these gases are indeed essential for life. As an example, plants take up carbon dioxide to give off oxygen, and water is produced by the reaction of oxygen and hydrogen gas. Other gases are dangerous for life. An example is carbon monoxide, which results from gas stoves, heating systems, and fire. This is a colorless, odorless, and tasteless gas that can bind to the blood displacing oxygen. As a consequence, carbon monoxide can build up in closed environments causing death. This chapter deals with the properties of gases. You will learn how to calculate the volume or pressure of a gas, characterizing its state. You will also learn how to work with mixtures of gases and for example predict the pressure of oxygen in an atmosphere containing numerous gases.

1.1 Gases and its properties

Gases contain atomic or molecular particles. They have very different properties than liquids or solids. The particles of a gas are spread and far away from each other. Liquids, on the other hand, are made of loose particles that interact through weak forces. Solids, on the other hand, are packed materials, and their particles, atoms, or molecules, are closer together. This section covers the different properties of gases.

Gases in the periodic table Some of the elements in the periodic table are molecular gases, resulting from the combination of two atoms of the same element. For example, molecular oxygen (O_2) is a gas. Similarly, molecular nitrogen (N_2), molecular hydrogen (H_2), molecular chlorine (Cl_2), or molecular fluorine (F_2) are all diatomic gases–they contain two atoms of the same element. Other gases result from the combination of two different non-metals. Examples are carbon monoxide (CO) or dioxide (CO_2), and nitrogen monoxide (NO) or dioxide (NO_2). The noble gases (Ne, He, Ar) also exist in the gas state.

Characteristics of gases Gases have different properties compared to solids or liquids:

- Gases assume the volume and shape of their container. As they expand, they have no shape different than their container's shape.
- Gases are compressible: they can be compressed, reducing their volume. Differently, liquids and solids are incompressible.
- The density of gases is small, compared to the one for solids and liquids.

`Volume, V` The volume of a gas (V) is the amount of space it occupies, and gases fully occupy the volume of their container. Liters (L) and milliliters (mL) are units of volume. A liter is a cubic unit and one litter equals a cubic decimeter (dm^3).

`Temperature, T` The temperature (T) of a gas is related to the speed (the average velocity) of its particles. The higher the temperature the higher the particles' speed. Although there are different units of temperature such as Kelvin (K) or celsius (C°), in this chapter many formulas require the use of Kelvin temperature (T_K), that related to celsius (T_C) by the formula

$$\boxed{T_K = T_C + 273}$$

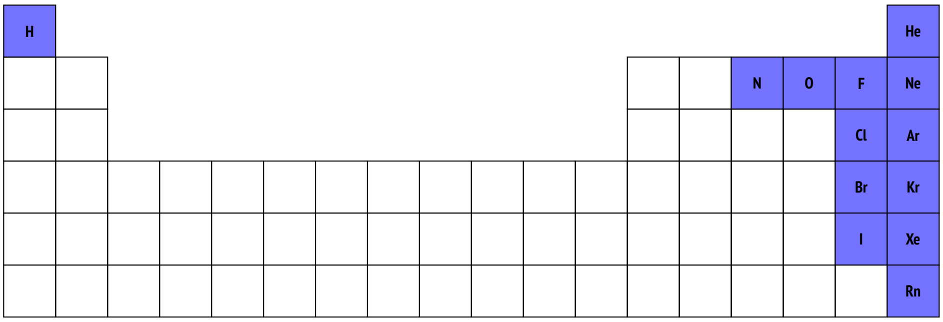

Figure 1.1 All gas elements

▼Chlorine reactive is a gas

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▼Hydrogen is a flammable gas used to power some cars

© wikipedia

`Amount of gas, n` The amount of a gas (n) refers to the number of gas particles. The larger the amount of gas, the larger the number of gas particles. The amount of gas is measured in moles or grams. Figure 1.1 displays a list of all gas elements.

`Pressure, P` In general, pressure is defined as force divided by surface. In the international system, the unit of force is the Newton (N) and the unit of area (A) is the m^2. One newton is $1\text{kg} \cdot \text{m/s}^2$.

$$\boxed{P = \frac{F}{A}}$$

The particles of a gas are constantly moving. On their movement, they frequently hit the walls of their container, like raindrops hitting the ceiling when it rains. When they hit the walls they exert pressure, and pressure is defined as the force acting on a certain area. The larger pressure the stronger the collisions with the walls and the higher the frequency of collision–the stronger the force applied to the walls. Imagine you are driving a motorcycle. While you drive you can feel the collision of the air's particles with your face. The faster you go the higher pressure. The value of air pressure is measured with a barometer and depends on your location on the earth–in particular your altitude–as well as the weather. If you are at sea level the atmospheric pressure is one unit of pressure (one atm), due to the air that you have on top of you. If you climb a mountain, the pressure decreases, as there is less air on top of you. The higher you are from the sea level, the lower the air pressure. The weather also affects pressure, and on hot days the pressure of air is higher, whereas on cold days pressure is lower.
Units of pressure are bars, atmospheres (atm), torr, pascals (Pa), or millimeters of mercury (mmHg). To covert pressure units, you can use the following conversion factors:

$$\boxed{\frac{1\text{ atm}}{1.01325\text{ bar}}} \quad \boxed{\frac{1\text{ atm}}{760\text{ mmHg}}} \quad \boxed{\frac{1\text{ torr}}{1\text{ mmHg}}} \quad \boxed{\frac{1\text{ atm}}{101325\text{ Pa}}}$$

one millimeter of mercury (mmHg) is the same as 1 torr. As a note, the name torr acknowledges the person who invented the barometer: Torricelli, an Italian physicist.

Sample Problem 1

An oxygen sample has a pressure of 2 atm. Convert this value to: (a) mmHg and (b) Pascals.

SOLUTION

(a) we start by placing the given data (2 atm) and using the conversion factor between atm and mmHg, with the atm unit on the bottom, so that the units cancel

$$2\,\cancel{\text{atm}} \times \frac{760\text{ mmHg}}{1\,\cancel{\text{atm}}} = 1520\text{mmHg}$$

(b) we proceed as in (a) but using the conversion between atm and Pa:

$$2\,\cancel{\text{atm}} \times \frac{101325\text{ Pa}}{1\,\cancel{\text{atm}}} = 2.02 \times 10^5\text{Pa}$$

STUDY CHECK

An oxygen sample has a pressure of 730 mmHg. Convert this value to atmospheres.

▼A barometer used to measure the atmospheric pressure

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▼A manometer used to measure gas pressures

© wikipedia

▼A pressure gauge

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Figure 1.2 Pressure measuring devices

Measuring pressure Two different devices are used to measure pressure, barometers, and manometers. Barometers are used to measure specifically the atmospheric pressure and historically, they consist of a glass tube filled with mercury (Hg), inverted on a plate containing more mercury. At sea level, the height of the mercury columns should be close to 760mmHg. Manometers, on the other hand, are used to measure the pressure of any gas. Manometers consist of a u-shaped tube filled with mercury. There are two types of manometers: open-tube and closed-tube manometers. The pressure exerted by a gas changes the level of mercury on both sides of the tube and the height difference measured as the right minus the left side ($\Delta h = h_{right} - h_{left}$) is related to the gas pressure. For closed-tube manometers–normally used to measure pressure below the atmospheric pressure–when the gas pressure increases the left column of the barometer is reduced and the right column increases. The difference between both columns is related to the gas pressure through:

$$\boxed{\text{P}^{closed} = \text{hdg}} \qquad \boxed{\text{P}^{open} = \text{hdg} + \text{P}_{atm}} \tag{1.1}$$

where:

P is the pressure of the gas in Pa

Δh is the height difference in m, measured as $h_{right} - h_{left}$

d is the density of mercury 13593 kg/m^3

g is gravity, 9.8 m/s^2

P$_{atm}$ is the atmospheric pressure close to 101325 Pa

For the open-tube manometer, normally used to measure pressure above the atmospheric pressure, we need to take into account the atmospheric pressure to the gas pressure. For this type of manometer, if the left column is below the right column ($\Delta h = h_{right} - h_{left} < 0$), this means that the pressure in the gas is below the atmospheric pressure.

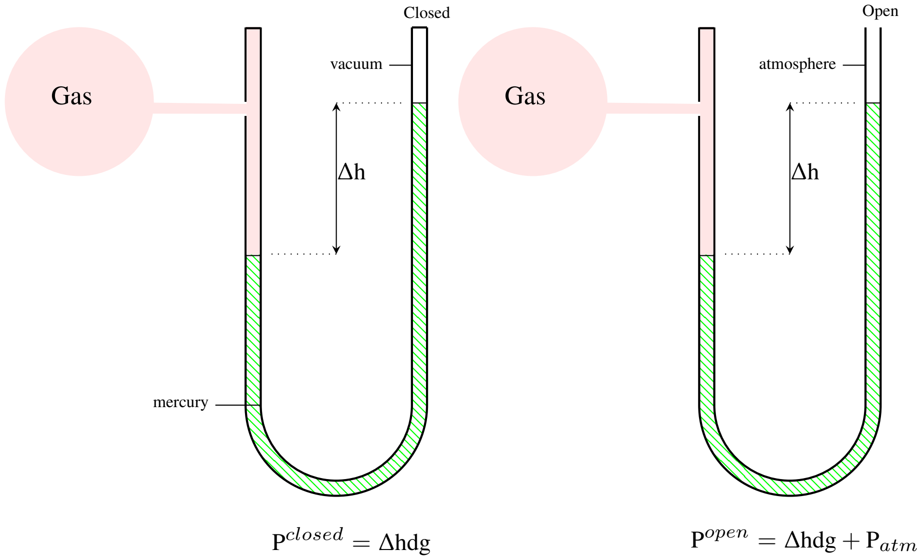

Figure 1.3 Two types of manometers: open-tube and closed-tube manometer

1.2 Ideal gas law

Ideal gases are gases made of particles without a size (very tinny) that do not interact with each other. The temperature, pressure, volume, and number of moles of a gas are not independent. They are related through the ideal gas law. In this section, we will introduce this law in two different forms: in terms of volume and terms of density.

`Ideal gas law in terms of moles` The ideal gas law says:

$$\boxed{PV = nRT} \quad \text{Ideal Gas Law}$$

where:

P is the pressure of the gas in atm

V is the volume of the gas in L

n is the number of moles of the gas

T is the temperature of the gas in K

R is the constant of the gas $0.082 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}$

Imagine for example that you inflate a balloon with your mouth, introducing air particles into the balloon. While the number of particles inside the balloon grows, its volume will grow too. More particles will collide with the walls of the balloon and hence, the pressure inside the balloon will also increase.

Sample Problem 2

Helium gas is used to inflate blimps, scientific balloons and party balloons. What is the volume in litters of a 0.2 moles Helium balloon at 300K and 2 atm.

SOLUTION

Analyze the Problem	Given	Asking
	$T = 300K$ $P = 2atm$ $n = 0.2mol$ $R = 0.082\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}$	V

Using now the ideal gases formula: $PV = nRT$, we have

$$2\cancel{\text{atm}} \cdot V = 0.2\cancel{\text{mol}} \cdot 0.082\frac{\cancel{\text{atm}} \cdot \text{L}}{\text{mol} \cdot \cancel{\text{K}}} \cdot 300\cancel{K}$$

All units but L cancel out. Solving for V we have 2.46 L.

STUDY CHECK

What is the pressure in atmospheres of a 1 L balloon containing 3 moles of Helium at 40C°.

Ideal gas law in terms of density The ideal gas law in terms of density is:

$$\boxed{P \cdot MW = DRT} \quad \text{Ideal Gas Law in terms of D}$$

where:

P is the pressure of the gas in atm

MW is the molecular weight (or atomic weight, AW) of the gas in g/mol

D is the density in $g \cdot L^{-1}$

T is the temperature of the gas in K

R is the constant of the gas $0.082\frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}$

We use this formula when we are questioned about the molar mass or density of the gas.

Sample Problem 3

What is the density of a Helium balloon at 400K and 3 atm.

SOLUTION

Besides the data in the problem, as the gas is He we already know its atomic mass from the periodic table:

Given	Asking

Analyze the Problem		
	$T = 400K$ $P = 3atm$ $AW = 4g \cdot mol^{-1}$ $R = 0.082 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}$	D

Using now the ideal gases formula in terms of density: $P \cdot MW = DRT$, we have

$$3\cancel{\text{atm}} \cdot 4\frac{g}{\cancel{\text{mol}}} = D \cdot 0.082\frac{\cancel{\text{atm}} \cdot \text{L}}{\cancel{\text{mol}} \cdot \cancel{\text{K}}} \cdot 400\cancel{K}$$

Solving for D we have 0.36 $g \cdot L^{-1}$.

STUDY CHECK

What is the molecular mass of a 4 $g \cdot L^{-1}$ density gas at 30C° and 5 atm.

`STP conditions` STP conditions refer to standard temperature (273K) and pressure (1 atm) conditions. Working at STP conditions means the pressure will be fixed at 1 atm and temperature at 273K.

$\boxed{\text{1 atm and 273K}}$ STP Conditions

Sample Problem 4

Calculate the volume in litters of 5 moles of nitrogen at STP conditions.

SOLUTION

From the problem we have the following data:

	Given	Asking
Analyze the Problem	$n = 5moles$ $P = 1atm$ $T = 273K$	V

We need to apply the ideal gas formula with the set of given variables:

$$1\cancel{\text{atm}} \cdot V = 5\cancel{\text{mol}} \cdot 0.082\frac{\cancel{\text{atm}} \cdot \text{L}}{\text{mol} \cdot \cancel{\text{K}}} \cdot 273\cancel{K}$$

and solving for V we have a final volume of 112L.

STUDY CHECK

Calculate the grams in 4L of N_2 at STP conditions.

1.3 Change of gas properties

The previous section addressed the properties of an ideal gas. However, as all properties of a gas are related, if we modify one the others will change too. This section covers situations in which one of the gas properties changes (e.g. V changes) and you need to predict the change of another gas property (e.g. P). For example, imagine you compress a balloon with your hand. The temperature and number of moles of the gas inside the balloon are constant, as the balloon is closed and in contact with the atmosphere. Differently, the pressure and volume will change. In particular, the volume will decrease and the pressure will increase. This means that the gas particles will hit the balloon harder and with more frequency.

`Solving problems with an initial and final state` To solve problems in which two of the gas variables are kept fixed and the other two are fixed, one needs to apply the ideal gas law at the initial and final state to then divide both formulas. Imagine a situation in which you have a 1L hot air balloon with 1 mole of gas and you add gas to a total of 5 moles. You want to calculate the final volume after you inflate the volume, knowing the temperature and pressure are kept constant. The initial state corresponds to 1L and 1 mole of gas and the final estate corresponds to an unknown volume and 5 moles. Using the ideal gas formula twice you have:

$$\left.\begin{array}{l} PV_1 = n_1RT \\ \\ PV_2 = n_2RT \end{array}\right\} \quad \frac{PV_1}{PV_2} = \frac{n_1RT}{n_2RT} \tag{1.2}$$

as some of the variables the cancel out:

$$\frac{\cancel{P}V_1}{\cancel{P}V_2} = \frac{n_1\cancel{RT}}{n_2\cancel{RT}} \tag{1.3}$$

and you end up with Avogadros' law. If you plug the numbers into the formula:

$$\frac{1L}{V_2} = \frac{1\text{ mol}}{5\text{ mol}} \tag{1.4}$$

and you get a final volume of 5L.

Sample Problem 5

A 3L gas sample has a pressure of 5 atm. If the pressure increases to 10 atm at fixed temperature and number of moles, calculate the final volume of the gas.

SOLUTION

From the problem we have the following data:

Analyze the Problem	Given	Asking
	$V_1 = 3L$ $P_1 = 5atm$ $P_2 = 10atm$	V_2

We need to apply the ideal gas formula to the initial state and final state and divide both formulas. The number of moles and the temperature are constant and will cancel out from both equations:

$$\left.\begin{array}{l} P_1V_1 = nRT \\ \\ P_2V_2 = nRT \end{array}\right\} \quad \frac{P_1V_1}{P_2V_2} = \frac{nRT}{nRT} \tag{1.5}$$

Plugging the values:

$$\frac{P_1V_1}{P_2V_2} = \frac{nRT}{nRT} \tag{1.6}$$

and solving:

$$\frac{3 \cdot 5}{10 \cdot V_2} = 1 \tag{1.7}$$

the final volume will be 1.5 L.

STUDY CHECK

A 4 atm gas sample has a temperature of 300K. If we decrease its temperature to 200K at fixed volume and number of moles, calculate the final pressure of the gas.

`Pressure-Volume change` If temperature and the number of moles of gas are kept constant the product of pressure and volume will remain constant too. This is the case of the balloon-pressing example. We call this Boyle's Law:

$$\boxed{\frac{P}{V} = c \quad or \quad P_1 \cdot V_1 = P_2 \cdot V_2} \quad \text{Boyle's law}$$

where:

P_1, V_1 are the initial pressure and volume

P_2, V_2 are the final pressure and volume

c is a constant

`Volume-Temperature change` Imagine you cool down a balloon at a fixed pressure (under the atmosphere). What would happen to the balloon's volume? Based on Charle's law, its volume will decrease:

$$\boxed{\frac{V}{T} = c \quad or \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}} \quad \text{Charle's law}$$

where:

V_1, T_1 are the initial volume and temperature

V_2, T_2 are the final volume and temperature

c is a constant

`Volume-Temperature change` Imagine you cool down a balloon at a fixed pressure (under the atmosphere). What would happen to the balloon's volume? Based on Charle's law, its volume will decrease:

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where:

V_1, T_1 are the initial volume and temperature

V_2, T_2 are the final volume and temperature

c is a constant

`Volume-Moles change` Imagine a hot air balloon. Air comes in and out of the balloon as the balloon is not closed. Hence the pressure inside the balloon is just the atmospheric pressure. Also as the balloon is in contact with the air, its temperature will be constant, resulting from the thermal equilibrium between the inside of the balloon and the atmosphere. If you inflate the balloon with hot air, the volume of the balloon and the number of moles are related by Avogadro's law:

$$\boxed{\frac{V}{n} = c \quad or \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}} \quad \text{Avogadro's law}$$

where:

V_1, n_1 are the initial volume and number of moles

V_2, n_2 are the final volume and number of moles

c is a constant

Relating the different variables of a gas The question is now if we increase the pressure at a fixed number of moles and pressure, how do we know if the volume will increase or perhaps decrease? Similarly, if for example, the number of gas moles increases at fixed pressure and volume, will the temperature of the gas increase or perhaps decrease? We can answer these questions by employing the ideal gas law. If the variables that we need to relate are on the same side of the equation (e.g. P and V) then if one of the variables increases the other will decrease. Differently, If the gas variables to relate are located on opposite sides of the gas law (e.g. P and T) then both will change in the same direction. For example, let us consider the changes of P and V (at fixed n and T). As they are on the same side of the ideal gas law ($PV = nRT$) if P increases V will decrease. Differently, for the change of P and T (at fixed V and n), as both variables are on opposite sides of the ideal gas law ($PV = nRT$), if P increases, T will increase as well.

1.4 Mixtures of gases and gas stoichiometry

The air is a mixture of different gases. It contains oxygen (O_2) and nitrogen (N_2) as well as other gases such as carbon dioxide, argon, or water vapor. Only 21% of the air is made of oxygen and 78.2% of nitrogen. The other gases represent 0.8% of the air. The atmospheric pressure is 1 atm and results from the pressure of all the components of the air. Each gas exerts a partial pressure and all combined exert the total atmospheric pressure. In this section, you will learn how to work with mixtures of gases. This section also covers the use of the molar volume to relate moles and volume at standard conditions.

Molar volume If we work at STP conditions the volume of one mole of gas equals 22.4L, and we refer to this relationship as the molar volume.

$$\boxed{\frac{1\text{mol}}{22.4\text{ L at STP}}} \quad \text{Molar Volume}$$

This relationship allows us to carry out stoichiometric calculations in a chemical reaction involving gases.

Stoichiometry and gases If you encounter chemical reactions with gases, the molar volume relation allows you to carry out stoichiometric calculations. Why is this important? Imagine you have this reaction:

$$\underset{3L}{2\,H_2(g)} + O_2(g) \longrightarrow \underset{xL}{2\,H_2O(g)}$$

Gases are measured using their pressure and are more convenient to speak about liters of hydrogen than moles of hydrogen or grams of hydrogen, as hydrogen is a gas. This way, if we start by mixing 3L of H_2 we would like to know how much water is being produced. To calculate this, we will use the stoichiometric coefficients. In previous chapters, we saw that these numbers represent moles and the units of these numbers are mol. If the reaction deals with gases you want to interpret the stoichiometric coefficients in terms of liters. This way:

$$x = 3\,\cancel{\text{L of H}_2} \times \frac{2\text{ L of H}_2\text{O}}{2\,\cancel{\text{L of H}_2}} = 3\text{ L of H}_2\text{O}.$$

Overall, if we mix three liters of hydrogen we obtain 3L of water. In case we know the litters of any of the reactants and we need to calculate the moles of product, then we have to add an extra step to transform litters into moles.

Sample Problem 6

Hydrogen gas reacts with oxygen gas to produce water vapor according to the following equation:

$$\underset{}{2\,H_2(g)} + \underset{2L}{O_2(g)} \longrightarrow \underset{x\text{ mol}}{2\,H_2O(g)}$$

Calculate the number of moles of water produced from 2L of oxygen at STP conditions.

SOLUTION

We will solve the problem in a single line, first relating the liters of oxygen and litters of water produced and finally converting litters of water into moles of water using the molar volume. Remember when there are gases in the reaction, the stoichiometric coefficients can be interpreted in terms of liters:

$$x = 2L\,\cancel{\text{L of O}_2} \times \frac{\cancel{2\text{ L of H}_2\text{O}}}{2\,\cancel{\text{L of O}_2}} \times \frac{1\text{ mol of H}_2\text{O}}{22.4\cancel{\text{L of H}_2\text{O}}} = 0.178\text{ mol of H}_2\text{O}.$$

We have that two liters of oxygen produce four liters of water. At the same time, 22.4L of water–or any other gas–is 1 moles of that gas. So four L of water are 0.17moles of water.

STUDY CHECK

Hydrogen gas reacts with nitrogen (MW=28 g/mol) gas to produce ammonia (MW=17 g/mol) at STP conditions according to the following equation:

$$3\,H_2(g) + \underset{0.5L}{N_2(g)} \longrightarrow \underset{x\text{ g}}{2\,NH_3(g)}$$

Calculate the number of grams of ammonia produced from 0.5L of nitrogen.

`Partial and total pressure` Imagine you have a container with 1atm of Ar and another container of the same volume containing 1 atm of Ne. If you combine the containers into a single container (and the temperature does not change), hence the pressure in the container will result from both gases and will be 2 atm. Inside the mixed container, 2 atm will the total pressure (P_{Total}), whereas the partial pressure of each gas (p_1 and p_2) will be 1 atm. Dalton's Law says that the total pressure results from adding the partial pressure of each gas. For a gas mixture with n components:

$$\boxed{P_{Total} = p_1 + p_2 + \ldots p_n} \quad \text{Dalton's Law}$$

Sample Problem 7

Medical Air is a odorless gas made mostly of nitrogen and oxygen, administer by ventilator in hospital settings with an operating gauge pressure of 3 atm. If the oxygen pressure inside a container is 2.37 atm, calculate the partial pressure of nitrogen in the mixture.

SOLUTION

The problem gives the total pressure of the mixture and the partial pressure of one of the components. By using Dalton's law, we know that if the total pressure is 3atm and the partial pressure of oxygen is 2.37, hence the partial pressure of the other component has to be 0.63 atm.

STUDY CHECK

Entonox is a medicinal mixture of dinitrogen oxide (N_2O) and oxygen (O_2). The pressure N_2O in a entonox container is 2 atm and the oxygen pressure is 1520 mmHg as well. Calculate the total pressure in atm in a Entonox container.

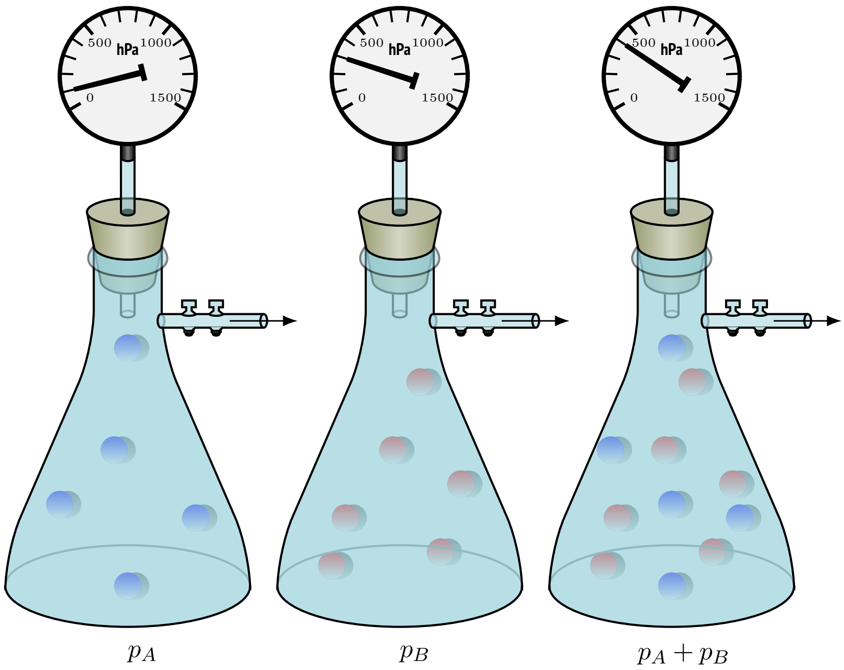

Figure 1.4 A visual representation of Dalton's law of partial pressure: after adding two different gases with different partial pressured, the final pressure is the result of adding both partial pressures.

`Partial pressure of a gas in a mixture` For a mixture with different gases, the partial pressure of a given gas (A) will depend on the number of moles of that particular gas and the overall volume of the mixture

$$\boxed{p_A = \frac{n_A RT}{V}}$$

`Mole fraction` The mole fraction (X_A) of a gas (A) in a mixture of gas is just the number of moles of this gas over the total number of moles in the mixture. The larger the mole fraction of a gas in a mixture the more molecules of that specific gas are there in the mixture. One can express the morel fraction in terms of partial pressures also, as the pressure of a given gas over the total pressure. For a mixture with n components:

$$\boxed{X_A = \frac{n_A}{n_A + n_B + \cdots + n_n} \quad or \quad \frac{p_A}{p_A + p_B + \cdots + p_n}}$$

For a mixture of gases, the partial pressure of a gas (p_A) is related to the mole fraction of that gas (X_A) and the total pressure of the mixture of gases (P_{Total}):

$$\boxed{p_A = X_A \cdot P_{Total}}$$

Sample Problem 8

A mixture of gases with a total pressure of 2 atm contains 3 moles of Ar, 3 moles of He and 1 moles of Ne. Calculate the partial pressure of each component on the mixture.

SOLUTION

We calculate first the mole fraction for each component of the mixture. As the total number of moles if 7 moles and there are 3 moles of Ar, its mole fraction is 0.43. Similarly, the mole fraction for He is 0.43 and for Ne is 0.14. To calculate the partial pressure of each gas you just need to multiply its mole fraction by the total pressure (2 atm). Hence: p_{Ar}=0.86atm, p_{He}=0.86atm and p_{Ne}=0.28atm

STUDY CHECK

A mixture of gases with a total pressure of 5 atm contains 1 mol of Ar and 1 mol of He. Calculate the partial pressure of each component on the mixture.

1.5 Collecting gas over water

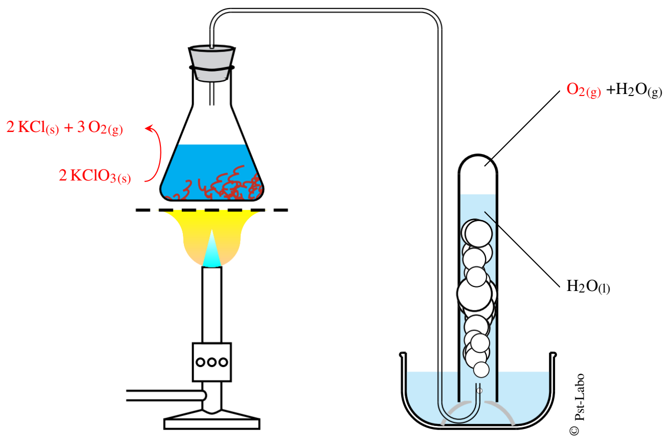

Figure 1.5 Apparatus for measuring the amount of gas produced by a reaction over water.

Table 1.1 Vapor pressure, partial water pressure as a function of temperature

T°C	P(atm)	T°C	P(atm)	T°C	P(atm)	T°C	P(atm)	T°C	P(atm)
5	0.0086	25	0.0313	45	0.0946	65	0.2469	85	0.5706
10	0.0121	30	0.0419	50	0.1218	70	0.3077	90	0.6920
15	0.0168	35	0.0555	55	0.1555	75	0.3806	95	0.8342
20	0.0231	40	0.0728	60	0.1967	80	0.4675	100	1.0000

`Collecting gas over water: use of partial pressures`

Numerous reactions produce gases. As an example, potassium chlorate decomposes to produce oxygen gas:

$$2\,KClO_{3(s)} \longrightarrow 2\,KCl_{(s)} + 3\,O_{2(g)}$$

The volume of gas produced by a chemical reaction is collected often over water. Gas bubbles go through water being collected in an apparatus similar to the one represented in Figure 1.5.

As the gas is collected over water, with the gas produced by the reaction, we will also find water molecules that will exhibit a certain partial pressure. In other words, we will collect a mixture of two gases, the gas produced by the reaction and water. The partial pressure of the gas produced will be:

$$\boxed{P_{gas} = P_{total} - P_{\mathrm{H_2O}}}$$

The partial pressure of water, also called the vapor pressure of water, depends on temperature and its values can be found in Table 1.1. For example, at 25°C, the vapor pressure of water in the atmosphere is 0.0313 atm and at 100°C is equal to 1atm. When liquids boil, their vapor pressure is equal to the atmospheric pressure, which is the reason behind the vapor pressure of water being 1 atm at 100°C, the boiling point of water.

Sample Problem 9

Oxygen is collected over water in the decomposition of potassium chlorate:

$$2\,KClO_{3(s)} \longrightarrow 2\,KCl_{(s)} + 3\,O_{2(g)}$$

Given that 20mL of gas are collected at 30°C at a pressure of 0.9atm, and that the vapor pressure of water at that temperature is 0.0419 atm, calculate the number of moles of oxygen collected.

SOLUTION

In order to calculate the number of moles of oxygen collected we need the partial pressure of oxygen, the temperature and the volume. We have that as the total pressure is 0.9atm and the partial pressure of water is 0.0419 atm, then the partial pressure of oxygen should be $0.9 - 0.0419$ atm, that is 0.481 atm. As we have the temperature (303K) and the volume (0.02L), we can calculate the number of moles of oxygen:

$$n_{\mathrm{O_2}} = \frac{P_{\mathrm{O_2}}V}{RT} = \frac{0.481 \cdot 0.02}{0.082 \cdot 303} = 3.8 \times 10^{-4} \text{moles of } \mathrm{O_2}$$

STUDY CHECK

Oxygen is collected over water in the decomposition of potassium chlorate:

$$2\,KClO_{3(s)} \longrightarrow 2\,KCl_{(s)} + 3\,O_{2(g)}$$

Given that 10mL of gas are collected at 35°C at a pressure of 0.5atm, and that the vapor pressure of water at that temperature is 0.0555 atm, calculate the number of moles of $KClO_3$ decomposed.

1.6 Kinetic molecular theory of gases

At this point, we know enough about the properties of gases to be able to condense all these pieces of information into a quantitative model that could generate numerical predictions. The kinetic model of gases can predict among other properties the particle average velocity–this is technically called root mean square velocity, v_{RMS}.

Kinetic theory of gases The kinetic theory of gases is a model that explains the properties of gases. This theory envisions a gas in the form of a set of moving particles. Some of the ideas behind this model are:

- The particles of a gas are in constant motion and move very fast.
- On its movement, gas particles collide with each other changing paths and colliding with the walls of their container exerting pressure.
- Gas particles are far apart from each other, barely interacting.
- The average kinetic energy of the particles of gas (this is the energy of the particles due to movement) is proportional to the temperature of the gas.

Using the kinetic theory we can rationalize the different properties of a gas. As the particles of a gas are in constant motion and apart from each other they fill and occupy the same volume of their container. The temperature of a gas is related to its kinetic energy, that is, the average speed of the gas particles. Also, as the gas particles collide with the container's wall, they exert pressure. The kinetic theory of gases explains for example how room fresheners work. As you spray the room, the molecules of the perfume in a gas state move fast and occupy the room. The kinetic molecular theory of the gases gives a molecular-based description of the temperature of a gas–among other properties. The ideal gas law is experimental; this means is a law that comes from measuring and carrying experiments. However, this law does not provide any reasons behind the behavior of gases, ideal or real. The kinetic molecular theory provides a molecular description of temperature. In particular one of the outcomes of this theory is that the average velocity of a gas particle depends on the square root of the temperature of the gas. More precisely, the way this theory describes velocity is in the form of a *root mean square velocity* v_{RMS}, that is, as an average of the velocity of each particle. The formula that connects the root mean square velocity with temperature is:

$$\boxed{v_{RMS} = \sqrt{\frac{3000RT}{MW}}}$$ root mean square velocity formula

where:

MW is the molecular weight of the gas in g/mol

T is the temperature of the gas in K

R is the constant of the gas in energy units 8.314 $J \cdot K^{-1} \cdot \text{mol}^{-1}$

v_{RMS} is the root mean square velocity in m/s

It is important to notice that the root mean square velocity depends on temperature–the more temperature the more velocity– and is inversely proportional to the molecular weight of the gas–the heavier the mass the lower velocity.

Sample Problem 10

Order the following molecules in increasing order of root mean square velocity: Ne, CO_2 and H_2O.

SOLUTION

Root mean square velocity is inversely proportional to the molecular weight of the gas; hence, the larger the mass the lower velocity. If we compare the molecular weight of the gases: Ne(MW=20g/mol), CO_2(MW=44g/mol) and H_2O(MW=18g/mol). The root mean square velocity of water is the largest and the root mean square velocity of carbon dioxide is the smallest.

STUDY CHECK

Calculate the root mean square velocity of the molecules of water at 25C°.

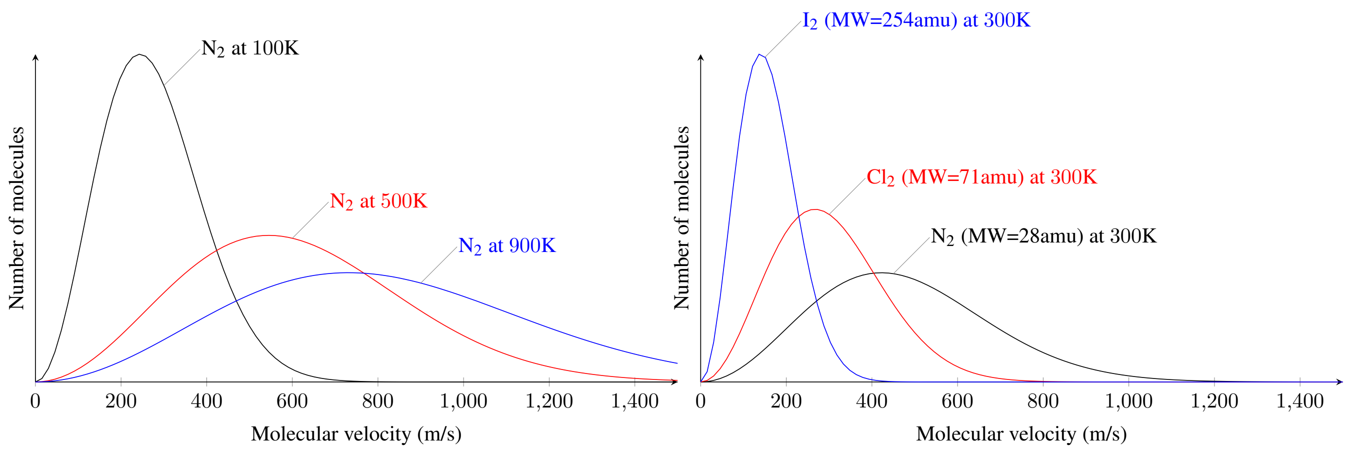

Figure 1.6 Effect of temperature and mass on the distribution of molecular speeds

`Distribution of velocities` The root means square velocity v_{RMS} is just an average of the square velocities of the gas particles. Still, some particles will have faster velocity than v_{RMS}, and others will have slower velocity. The molecular velocities of the particles of gas follow a distribution that is mass and temperature dependent. As shown in Figure 1.6, the higher temperature the larger the root square velocity, with a wider distribution of velocities. At the same time, the larger the molar mass of the gas, the smaller the root square velocity with a thinner distribution of velocities.

1.7 Real gases

Until now we have discussed ideal gases. These simplistic representations of gases represent very dilute gases in which the gas particles are apart. The particles of an ideal gas are also considered to be very minute without a volume. At the same time, the collisions between the particles and the walls of the container are elastic–this means the molecules do not lose any energy. As you can imagine, no gas is an ideal gas, as this is just an ideal model. This section will cover the properties of real gases, in which the gas particles interact among themselves and the collisions are inelastic and energy is lost.

Van der Waals equation for real gases When we take into account the fact that the particles of a gas interact with each other the formula of the ideal gases does not work anymore. Instead, we can use the Van der Waals equation for real gases that functions in a very similar way.

$$\boxed{P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}}$$ Van der Waals equation

where:

P is the pressure of the gas in atm

V is the volume of the gas in L

n is the number of moles of the gas

T is the temperature of the gas in K

R is the constant of the gas $0.082 \frac{\mathrm{atm \cdot L}}{\mathrm{mol \cdot K}}$

a and b are the Van der Waals constants in units of $\mathrm{atm \cdot L^2 \cdot mol^{-2}}$ and $\mathrm{L \cdot mol}$

Table 1.2 Van der Waals constants for several gases

gas	a ($\mathrm{atm \cdot L^2/mol^2}$)	b (L/mol)	gas	a ($\mathrm{atm \cdot L^2/mol^2}$)	b (L/mol)
NH_3	4.225	0.0371	Ar	1.355	0.03201
C_6H_6	18.24	0.1154	CO	3.640	0.04267
CH_4	2.283	0.0427	CH_3OH	9.649	0.06702
CS_2	11.77	0.0768	Cl_2	6.579	0.05622
Ne	0.2135	0.01709	NO	1.358	0.02789
N_2	1.370	0.0387	NO_2	5.354	0.04424

The meaning of the Van der Waals constants There are two Van der Waals constants: a and b (see Table 1.2). The Van der Waals constant a represents the degree of interaction between the molecules of a gas. The larger these values the more interactions exist between the gas particles. For example, for He we have $a = 0.0341 \mathrm{atm \cdot L^2/mol^2}$, whereas for H_2O we have $a = 5.46\ \mathrm{atm \cdot L^2/mol^2}$. Comparing the values of a for both gases, we can conclude that the interaction between the particles of He is very weak and in contrast, the interactions between the particles of H_2O are stronger. The Van der Waals constant b is related to the molecular size, however, the relationship is not as straightforward as in the case of the a constant.

Sample Problem 11

Calculate the pressure of 0.2 moles of water vapor at 500K occupying a volume of 0.1L, using: (a) the ideal gas formula and (b) the Van der Waals formula $a = 5.46 \mathrm{atm \cdot L^2/mol^2}$ and $b = 0.0305 \mathrm{L/mol}$.

SOLUTION

We will use the ideal gas formula first, given the number of moles (n=0.2 mol), temperature (T=500K), pressure (p=6 atm) and the volume (V=0.1L).

$$P = \frac{nRT}{V} = \frac{0.2 \times 0.083 \times 500}{0.1} = 82atm$$

Now, using the Van der Waals formula:

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2} = \frac{0.2 \times 0.083 \times 500}{0.1 - 0.2 \times 0.0305} - \frac{0.2^2 \times 5.46}{0.1^2} = 65atm$$

Both values are very different and this is consistent with the fact that water vapor does not behave as an ideal gas.

STUDY CHECK

Calculate the pressure of 0.9 moles of ammonia gas at 900K occupying a volume of 0.1L, using: (a) the ideal gas formula and (b) the Van der Waals formula $a = 4.17\text{atm} \cdot \text{L}^2/\text{mol}^2$ and $b = 0.0371\text{L}/\text{mol}$.