

# 1

## Reactions in gase phase

THE air we all breath 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 by means of weak forces. Solids on the other hand are packed materials and its 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 of the combination of two atoms of the same element. For example, molecular oxygen ( $O_2$ ) is 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 of 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 nobel gases (Ne, He, Ar) also exist in gas state.

*Characteristics of gases* Gases has different properties compared to solids of liquids:


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



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#### GOALS

- 1 Use the ideal and real gas law
- 2 Calculate partial pressures
- 3 Compute gas-property changes
- 4 Carry stoichiometric calculations with volumes
- 5 Compute root square mean velocities

 **Discussion:** Explain why a hot air balloon rises up. Furthermore, why a He-filled birthday balloon rises while if you fill it with air it does no?

one millimeters 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



▼ A manometer used to measure gas pressures



▼ A pressure gauge



**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 the sea level, the height of the mercury columns should be close to 760 mmHg. 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 level of mercury on both sides of the tube and the difference in height measured as the right minus the left side ( $\Delta h = h_{\text{right}} - h_{\text{left}}$ ) is related to the gas pressure. For closed-tube manometers—normally used to measure pressured 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 by means of:

$$P^{\text{closed}} = \text{hdg} \quad P^{\text{open}} = \text{hdg} + P_{\text{atm}} \quad (1.1)$$

where:

P is the pressure of the gas in Pa

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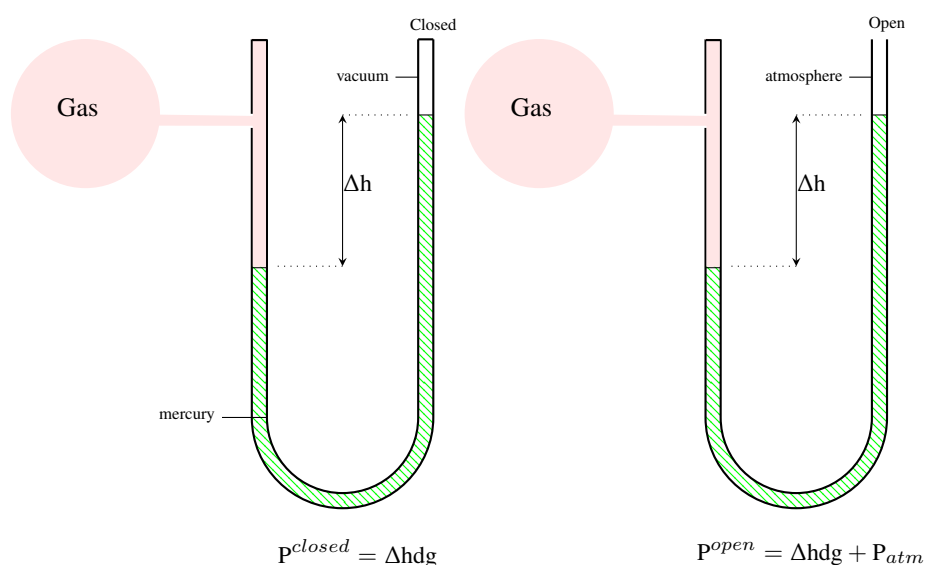
$\Delta h$  is the height difference in m, measured as  $h_{right} - h_{left}$

$d$  is the density of mercury  $13593 \text{ kg/m}^3$

$g$  is gravity,  $9.8 \text{ m/s}^2$

$P_{atm}$  is the atmospheric pressure close to  $101325 \text{ Pa}$

65 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 manometers, if the left column is below the right column ( $\Delta h = h_{right} - h_{left} < 0$ ), this means that the pressure of in the gas is below the atmospheric pressure.



70 **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 by the ideal gas law. In this section we will introduce this law in two different forms: in terms of volume and in terms of density.

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

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

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.

85

## Sample Problem 2

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

**SOLUTION**

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

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

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

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 40°C.

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

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

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

90

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

$T$  is the temperature of the gas in K

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

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

95

## Sample Problem 3

What is the density of 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	$T = 400K$ $P = 3atm$ $AW = 4g \cdot mol^{-1}$ $R = 0.082 \frac{atm \cdot L}{mol \cdot K}$	$D$

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

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

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  $30C^{\circ}$  and 5 atm.

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

1 atm and 273K

STP Conditions

#### Sample Problem 4

Calculate the volume in liters 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:

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

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* In order 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 the situation in which you have a 1L hot air balloon with 1 moles of a 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 moles of gas and the final state corresponds to an unknown volume and 5 moles. Using the ideal gas formula twice you have:

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

as some of the variables of the cancel out:

$$\frac{\cancel{P}V_1}{\cancel{P}V_2} = \frac{n_1\cancel{RT}}{n_2\cancel{RT}} \quad (1.3)$$

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

$$\frac{1L}{V_2} = \frac{1 \text{ mol}}{5 \text{ mol}} \quad (1.4)$$

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:

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

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:

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

Plugging the values:

$$\frac{P_1V_1}{P_2V_2} = \frac{nRT}{nRT} \quad (1.6)$$

and solving:

$$\frac{3 \cdot 5}{10 \cdot V_2} = 1 \quad (1.7)$$

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 a 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:

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

where:

125  $P_1, V_1$  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 fixed pressure (under the atmosphere). What would happen to the balloon's volume? Based on Charle's law, its volume will decrease:

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

where:

130  $V_1, T_1$  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 balloon. 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:

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

where:

135  $V_1, n_1$  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 questions is now, if we increase the pressure at 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 increase at fixed pressure and volume, will the temperature of the gas increase or perhaps decrease. We can answer these questions by means of the ideal gas law. If the variables that we need to relate are in the same side of the equation (e.g. P and V) then if one of the variables increase the other will decrease. Differently, If the gas variables to relate are located in 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 in 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 in 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<sub>2</sub>) and nitrogen (N<sub>2</sub>) 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 to 22.4L, and we refer to this relationship as the molar volume.

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

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

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



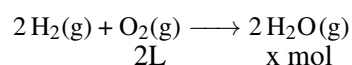
Gases are measured by means of their pressure and is more convenient to speak about liters of hydrogen than moles of hydrogen or grams of hydrogen, as hydrogen is a gas. This way, if we start by mixing 3L of H<sub>2</sub> we would like to know how much water is being produced. In order to calculate this, we will use the stoichiometric coefficients. In previous chapters we saw that these numbers represent moles and the units of these numbers is 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 liters of any of the reactants and we need to calculate the moles of product, then we have to add an extra step to transform liters into moles.

## Sample Problem 6

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



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

**SOLUTION**

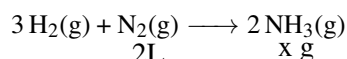
We will solve the problem in a single line, first relating the liters of oxygen and liters of water produced and finally converting liters of water into moles of water using the molar volume. Remember when there are gases in the reaction, the stoichiometric coefficients can be interpreted in terms of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

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

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 at STP conditions according to the following equation:



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 nother container of the same volume containing 1 atm of Ne. If you combine the containers into a single container (and 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 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:

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

## 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 ( $\text{N}_2\text{O}$ ) and oxygen ( $\text{O}_2$ ). The pressure  $\text{N}_2\text{O}$  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 pressures, the final pressure is the result of adding both partial pressures.

170

*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

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

*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 with respect to all components. One can express the mole fraction in terms of partial pressures also, as the pressure of a given gas over the total pressure. For a mixture with  $n$  components:

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

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 ( $P_{Total}$ ):

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

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 is 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:  $p_{Ar}=0.86\text{atm}$ ,  $p_{He}=0.86\text{atm}$  and  $p_{Ne}=0.28\text{atm}$

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.

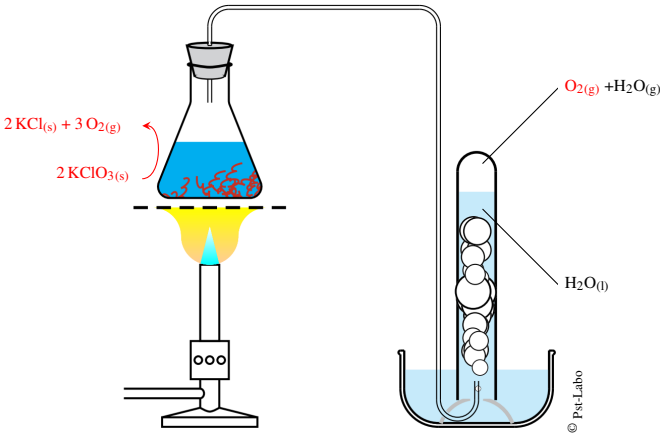
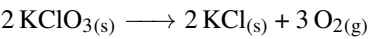


Figure 1.5 Apparatus for measuring the amount of gas produced by a reaction over water.

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



The volume of gas produced by a chemical reaction is collected often times 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 another words, we

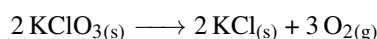
will collect a mixture of two gases, the gas produced by the reaction and water. The partial pressure of the gas produced will be:

$$P_{\text{gas}} = P_{\text{total}} - P_{\text{H}_2\text{O}}$$

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 1 atm. When liquids boil, their vapor pressure is equal to the atmospheric pressure, that is the reason behind the vapor pressure of water being 1 atm at 100°C, the boiling point of water. 185

#### Sample Problem 9

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



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

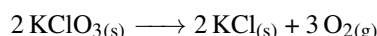
#### SOLUTION

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 0.9 atm 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 (303 K) and the volume (0.02 L), we can calculate the number of moles of oxygen:

$$n_{\text{O}_2} = \frac{P_{\text{O}_2} V}{RT} = \frac{0.481 \cdot 0.02}{0.082 \cdot 303} = 3.8 \times 10^{-4} \text{ moles of O}_2$$

#### STUDY CHECK

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



Given that 10 mL of gas are collected at 35°C at a pressure of 0.5 atm, and that the vapor pressure of water at that temperature is 0.0555 atm, calculate the number of moles of  $\text{KClO}_3$  decomposed.

## 1.5 Real gases and the kinetic molecular theory of 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. 190 195

*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 do

not work anymore. Instead, we can use the Van der Waals equation for real gases that functions in a very similar way.

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{V^2}$$

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  $0.082 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}}$
- $a$  and  $b$  are the Van der Waals constants in units of  $\text{atm}\cdot\text{L}^2\cdot\text{mol}^{-2}$  and  $\text{L}\cdot\text{mol}$

Table 1.2 Van der Waals constants for several gases					
gas	a (atm · L <sup>2</sup> /mol <sup>2</sup> )	b (L/mol)	gas	a (atm · L <sup>2</sup> /mol <sup>2</sup> )	b (L/mol)
NH <sub>3</sub>	4.225	0.0371	Ar	1.355	0.03201
C <sub>6</sub> H <sub>6</sub>	18.24	0.1154	CO	3.640	0.04267
CH <sub>4</sub>	2.283	0.0427	CH <sub>3</sub> OH	9.649	0.06702
CS <sub>2</sub>	11.77	0.0768	Cl <sub>2</sub>	6.579	0.05622
Ne	0.2135	0.01709	NO	1.358	0.02789
N <sub>2</sub>	1.370	0.0387	NO <sub>2</sub>	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  $a$  represent the degree of interaction between the molecules of a gas. The larger these values the more interactions exists between the gas particles. For example, for He we have  $a = 0.0341\text{atm}\cdot\text{L}^2/\text{mol}^2$ , whereas for H<sub>2</sub>O we have  $a = 5.46\text{atm}\cdot\text{L}^2/\text{mol}^2$ . Comparing the values of  $a$  for both gases, we can conclude that the interaction between the particles of He are very weak and in contrast, the interactions between the particles of H<sub>2</sub>O 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 10

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  $a = 5.46\text{atm}\cdot\text{L}^2/\text{mol}^2$  and  $b = 0.0305\text{L}/\text{mol}$ .

SOLUTION

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

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

Now, using the Van der Waals formula:

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

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  $b = 0.0371 \text{ L/mol}$ .

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,  $v_{RMS}$ .

220

*Kinetic theory of gases* The kinetic theory of gases is a model that explain 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 collide with the walls of its container exerting pressure.
- Gas particles are far apart from each other, barely interacting.
- The average kinetic energy of the particles of a gas (this is the energy of the particles due to movement) is proportional to the temperature of the gas.

225

By means of 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 its 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 explain 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 an experimental law; 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 describe 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 the root mean square velocity with temperature is:

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

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  $8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

250

$v_{RMS}$  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 11

Order the following molecules in increasing order of root mean square velocity: Ne, CO<sub>2</sub> and H<sub>2</sub>O.

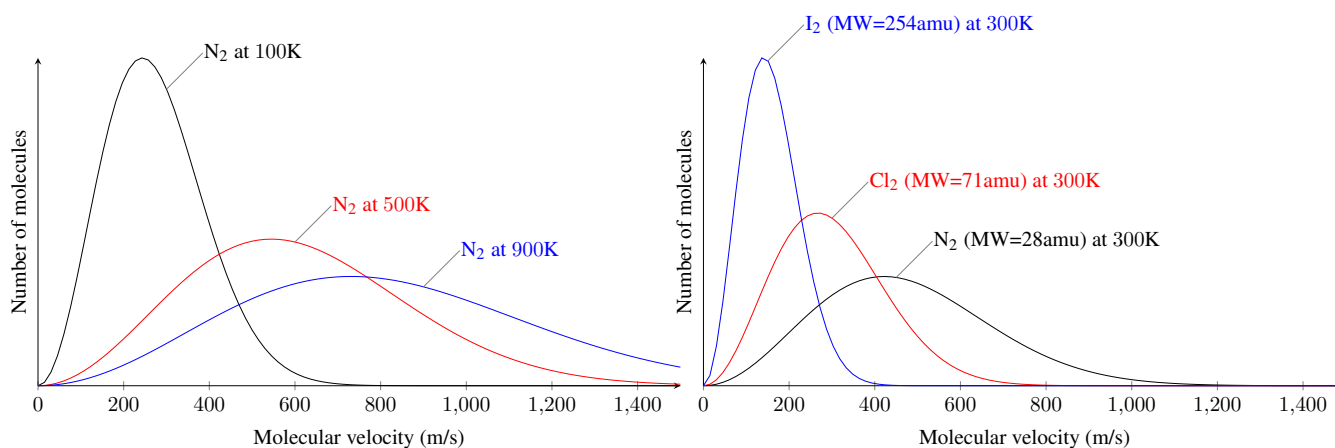
#### SOLUTION

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<sub>2</sub>(MW=44g/mol) and H<sub>2</sub>O(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 25°C.

255



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

260

*Distribution of velocities* The root mean 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 other will have slower velocity. The molecular velocities of the particles of a gas follow a distribution which 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.





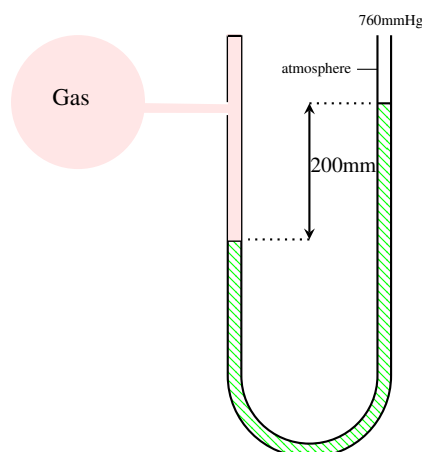
# CHAPTER 1

## GASES AND ITS PROPERTIES

**1.1** Convert the following properties: (a) A pressure value of 2 atm into mmHg (b) A pressure value of 3000 Pa into atm (c) A temperature value of 25°C into K

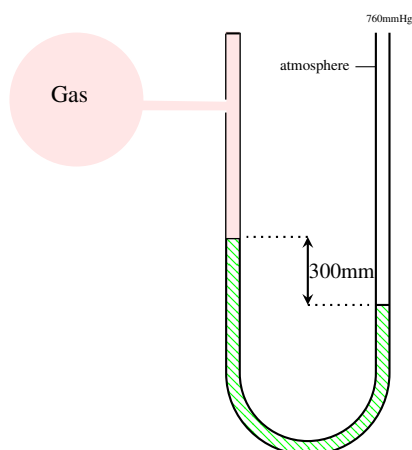
**1.2** Convert the following properties: (a) A pressure value of 900 mmHg into torr (b) A temperature value of 400K into °C

**1.3** An open-tube manometer is used to measure the pressure of a given gas. When there is no gas in the container, the mercury levels are equal in both sides of the u-tube.



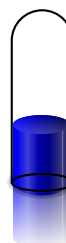
(a) Would the gas pressure be lower or higher than the atmospheric pressure? (b) Calculate the gas pressure in MPa. (c) Calculate the gas pressure in Torr.

**1.4** An open-tube manometer is used to measure the pressure of a given gas. When there is no gas in the container, the mercury levels are equal in both sides of the u-tube.



(a) Would the gas pressure be lower or higher than the atmospheric pressure? (b) Calculate the gas pressure in MPa. (c) Calculate the gas pressure in Torr.

**1.5** A barometer is a device used to measure the atmospheric pressure. It is made of a glass tube filled with a liquid, inverted on a dish of the same liquid. When inverting the tube, liquid will remain on the tube. The filled height of the column is proportional to the pressure. The liquid used is normally mercury with density 13593 kg/m<sup>3</sup>.



(a) Given that the height of the column is 750mm, calculate the atmospheric pressure in MPa. (b) Calculate the atmospheric pressure in atm if you use a barometer containing a liquid of density 1000 kg/m<sup>3</sup> and the liquid height is 9cm. (c) What are the benefits of building a barometer with a lighter liquid than mercury? (d) What are the drawbacks of building a barometer with a lighter liquid than mercury?

## IDEAL GAS LAW

**1.6** A gas contained in a 3L tank has a pressure of 5 atm at a temperature of 400 K. Calculate the number of moles in the tank.

**1.7** Dinitrogen oxide, used in dentistry, is an anesthetic also called laughing gas. What is the pressure in atm of 0.35 moles of N<sub>2</sub>O at 22°C in a 5L container?

**1.8** A 4 moles sample of gas at 400K has a pressure of 10 atm. Calculate the volume of the sample.

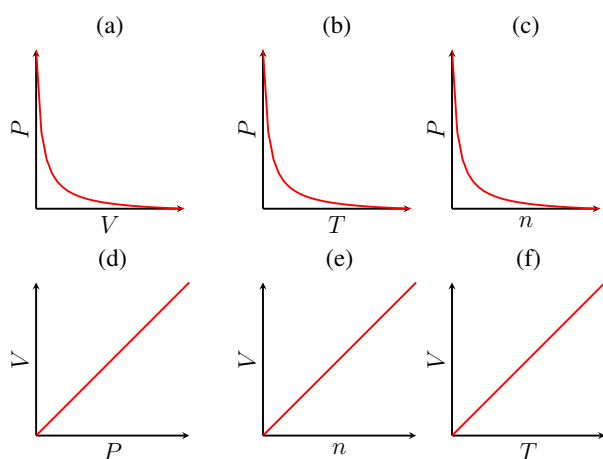
**1.9** A 3 grams sample of Ar at 40°C is placed in a 3L container. Calculate the pressure inside the container.

**1.10** Eighteen moles of a gas in a 11L container at 400K exert a pressure of 3 atm. Calculate the molar mass of the gas.

**1.11** What is the molar mass of a gas if a 3.16 g sample at 0.75 atm and 45°C occupies a volume of 2L.

**1.12** Answer the following questions: (a) Calculate the volume of a 4 moles of Ar at STP conditions. (b) Calculate the volume of a 4 moles of Ne at STP conditions. (c) Calculate the moles of gas in 3L of Ar at STP conditions. (d) Calculate the volume of 64 g of O<sub>2</sub> gas at STP (273K, 1atm)

**1.13** Indicate what plot (or plots) below best represent the following gas laws: (a) Boyle's law (b) Charles's law (c) Avogadro's law



#### CHANGE OF GAS PROPERTIES

**1.14** A sample of a gas at 400K and 12 atm is cooled in the same container to 200K. Calculate the new pressure.

**1.15** In a storage area where the temperature has reached 300K, the pressure of oxygen gas in a 15 L steel cylinder is 1 atm. Calculate the volume if the pressure is reduced to 0.5 atm.

**1.16** A H<sub>2</sub> sample has a volume of 5 L and a pressure of 1 atm. What is the new pressure if the volume is decreased to 2L with no change in temperature and the amount of gas.

**1.17** A sample of Ne in a closed, expandable container, has a volume of 3L at 40°C. Calculate the new volume if the container is cooled to 25°C.

**1.18** If the pressure of a gas increases, at fixed temperature and moles, its volume....

**1.19** If the temperature of a gas increases, at fixed volume and moles, its pressure....

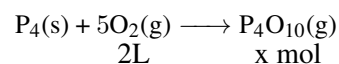
#### MIXTURE OF GASES AND GAS STOICHIOMETRY

**1.20** A tank contains Ne gas at 700 mmHg, Ar at 2 atm, and Kr at 700 torr. What is the total pressure of the mixture in atm?

**1.21** An anesthetic consist of a mixture of cyclopropane gas and oxygen gas. If the mixture has a total pressure of 2 atm and the partial pressure of cyclopropane is 0.5atm, what is the partial pressure of O<sub>2</sub>?

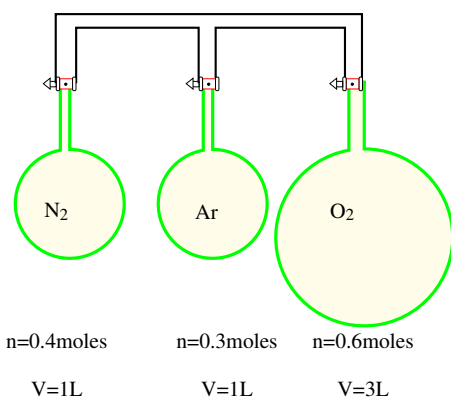
**1.22** The atmospheric pressure on a hot day is 780 mmHg. Given that the air is made of 78% of nitrogen and 22% of oxygen, calculate the partial pressure of each gas in the air.

**1.23** Phosphorus reacts with oxygen gas to produce tetraphosphorus decaoxide according to the following equation:

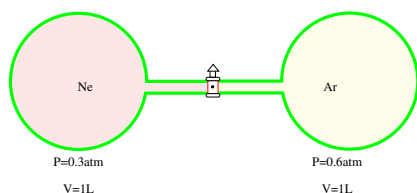


Calculate the number of moles of phosphorus that react with 2L of oxygen at STP conditions.

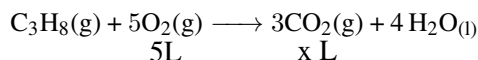
**1.24** Consider the set up below with three different gases in three different closed containers at 300K. Assuming that the connecting tubes have zero volume, once the flasks are connected, calculate: (a) The partial pressure of each gas in the mixture (b) The total gas pressure



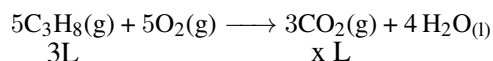
**1.25** Consider the set up presented below, where the connecting tubes have negligible volume. Calculate the partial pressure of each gas after the connection between the flasks is open.



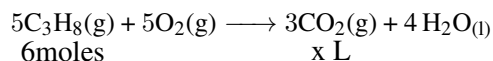
**1.26** For the following reaction, calculate the unknown  $x$  at STP conditions:



**1.27** For the following reaction, calculate the unknown  $x$  at STP conditions:



**1.28** For the following reaction, calculate the unknown  $x$  at STP conditions:



### REAL GASES AND THE KINETIC MOLECULAR THEORY OF GASES

**1.29** What is the pressure in atm of 1 mol of  $He$  at 600K in a 1L container: (a) Using the ideal gas law (b) Using the real gas law given  $a = 0.0342 \text{ atm} \cdot L^2/\text{mol}^2$  and  $b = 0.0237 \text{ L/mol}$

**1.30** Calculate the pressure  $p$  in atm exerted by 2 moles of methane ( $CH_4$ ) in a 0.5L container at 300K. (a) Using the ideal gas law  $p^{ideal}$  (b) Using the real gas law  $p^{real}$ , given  $a = 2.283 \text{ atm} \cdot L^2/\text{mol}^2$  and  $b = 0.04278 \text{ L/mol}$  (c) Calculate the percent error in the ideal gas law using  $|p^{ideal} - p^{real}|/p^{real} \times 100$ .

**1.31** Use the Van der Waals constant  $a$  to compare which of the gases exhibit stronger intermolecular interactions between its particles for the following pair of gases: (a)  $Ar$  or  $Ne$  (b)  $CO$  or  $NO$

**1.32** Without consulting the values of the Van der Waals constant  $b$  indicate which of the gases of the following pair would exhibit a larger  $b$  value: (a)  $C_2H_6$  or  $CH_4$  (b)  $H_2$  or  $CH_4$

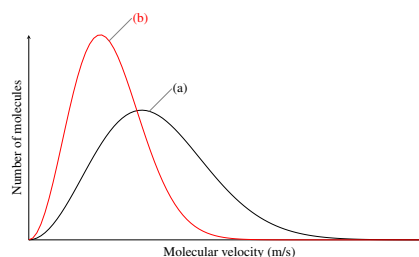
**1.33** What is the rms speed of  $O_2$  at STP?

**1.34** Order the following molecules in increasing order of root-mean square velocity:  $Ne$ ,  $CO_2$ ,  $H_2O$ ,  $CH_4$ .

**1.35** The kinetic molecular theory of gases assumes that:

- (a) gas particles interact with each other
- (b) gas particles have large sizes
- (c) particles move slowly
- (d) gas particles move randomly

**1.36** For the velocity distribution curve below: (a) The plots represent the distribution of velocity of two gases  $Ne$  or  $Ar$  at STP conditions in a fixed volume. What line represents each gas? (b) The plots represent the distribution of velocity of a gas at two different temperatures 300K and 500K at fixed pressure and volume conditions. What line represents each temperature?



**Answers** **1.1** (a) 1520 mmHg (b)  $2.96 \times 10^{-2}$  atm (c) 298K **1.3** (a) higher (b) 0.127MPa (c) 960mmHg  
**1.5** (a) 0.09MPa (b)  $8.7 \times 10^{-3}$ atm (c) it would be more sensitive to pressure changes (d) it would have to be taller than a  
barometer based on mercury **1.7** 1.7atm **1.9** 0.64 atm **1.11** 21 *g/mol* **1.13** (a) (a) (b) (f) (c) (e) **1.15** 30L **1.17** 2.8 L  
**1.19** increases **1.21** 1.5atm **1.23** 0.017 mol **1.25** (a)  $p_{\text{Ne}}=0.15\text{atm}$ ,  $p_{\text{Ar}}=0.3\text{atm}$  **1.27** 1.8L **1.29** (a) 49.2 atm (b) 50.36  
atm **1.31** (a) Ar (b) CO **1.33** 481.9 m/s **1.35** gas particles move randomly