

6 GASES

Gases are one of the three states of matter, and while this state is indispensable for chemistry's study of matter, this chapter mainly considers the relationships between volume, temperature and pressure in both ideal and real gases, and the kinetic molecular theory of gases and thus, is not directly very chemical. The treatment is primarily about physical change, and chemical reactions are not discussed.

However, the physical properties of gases depend on the structures of their gaseous molecules and the chemical properties of gases also depend upon their structures. The behavior of gases that exists as single molecules is a good example of the dependence of the macroscopic properties of matter on microscopic structure.

6.1 The ideal gas law

(a) Properties of gases

The properties of gases can be summarized as below.

Property of gases

- (1) Gases are transparent.
- (2) Gases distribute uniformly in a vessel whatever shape it may have.
- (3) Gases in a container exert **pressure** on its walls.
- (4) The volume of a given amount of gas is equal to the volume of its container. If a gas is not confined in a vessel, the volume of the gas will become infinitely large, and its pressure will become infinitely small.
- (5) Gases diffuse in all directions regardless of the presence or absence of external pressure.
- (6) When two or more gases mix, they distribute uniformly.
- (7) Gases can be compressed by external pressure. If the pressure is reduced, the gas will expand.
- (8) Gases will expand if heated, and will shrink if cooled.

Of the properties described above, the most significant is the pressure of a gas. Suppose a liquid fills a vessel. If the liquid is cooled and its volume is reduced, the liquid cannot fill the vessel completely any more. However, a gas fills the container regardless of the change in temperature. However, the pressure the gas exerts on the wall will change.

A device to measure the pressure of a gas is called a **manometer**. The prototype is the barometer invented by Torricelli to measure the atmospheric pressure.

Pressure is defined as force per unit area; thus

$$\text{pressure} = \text{force/area}$$

In SI, the unit of force is the Newton (N), the unit of area is m^2 , and that of pressure is Pascal (Pa). 1 atm is *ca.* 1013 hPa.

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa} = 1013.25 \text{ hPa}$$

However, the non-SI unit, Torr, *i.e.*, $1/760$ of 1 atm, is frequently used to record pressure during chemical experiments.

(b) Volume and pressure

The fact that the volume of a gas changes with changes in pressure was noticed as early as the 17th century by Torricelli and the French philosopher/scientist Blaise Pascal (1623-1662). Boyle observed, by applying pressure with a mercury column, that the volume of a gas confined in a glass tube sealed at one end decreases. In this experiment, the volume of the gas was measured at

pressures higher than 1 atm.

Boyle constructed a vacuum pump using the highest techniques of his day, and he observed that the gas at pressures below 1 atm expanded. After he carried out a wide range of experiments, Boyle proposed Eq. (6.1) to describe the relation between the volume V and the pressure P of a gas. This equation is called **Boyle's law**.

$$PV = k \text{ (a constant)} \quad (6.1)$$

The graphical presentation of Boyle's experiments can be done in two ways. If P is plotted as ordinate and V as abscissa, a hyperbola is obtained (Fig. 6.1(a)). If V is plotted against $1/P$, a straight line is obtained (Fig. 6.1(b)).

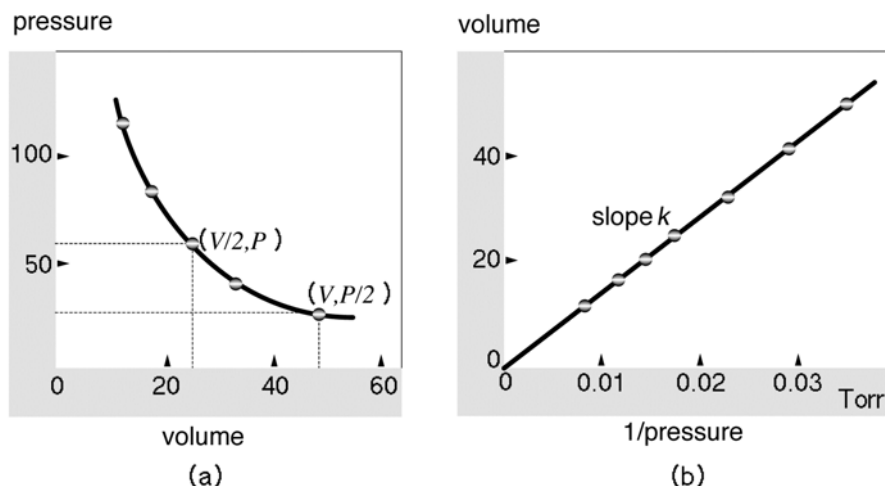


Figure 6.1 Boyle's law.

- (a) Plot of the results of an experiment; pressure vs. volume
 (b) Plot of the results of an experiment; volume vs. $1/\text{pressure}$. Note the slope k is constant.

(c) Volume and temperature

It was more than a century after Boyle that scientists began to take interest in the relation between the volume and the temperature of a gas. It was probably because thermal balloons became the talk of the town at that time. The French chemist Jacques Alexandre César Charles (1746-1823), a famous balloon navigator at that time, recognized that, at constant pressure, the volume of a gas increased as the temperature increased. This relation was called **Charles's law**, though his data were not necessarily quantitative. Gay-Lussac later plotted the volume of a gas against the temperature and obtained a straight line (Fig. 6.2). For this reason Charles's law is sometimes called **Gay-Lussac's law**. Both Charles' law and Gay-Lussac's law held approximately well for all gases so long as liquefaction did not take place.

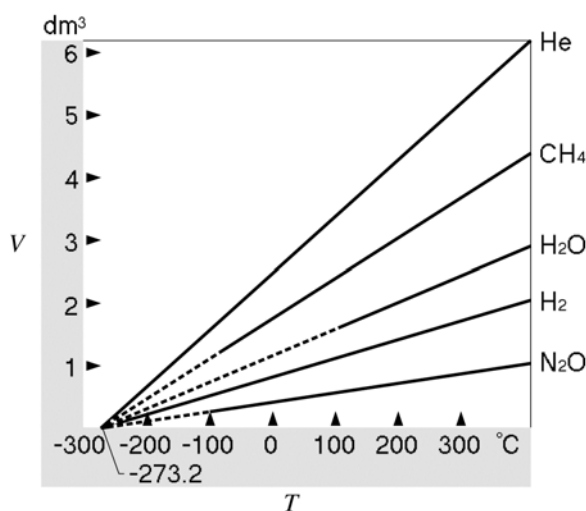


Figure 6.2 Charles's law.

Plot of the volume of several gases against temperature. Solid lines are based on experimental data and the dotted lines are obtained by extrapolating the experimental values. The amount of gas varies.

An interesting discussion can be drawn from Charles's law. By extrapolating the plot of the volume of gases against temperature, the volumes became zero at a certain temperature. It is interesting that the temperature at which the volumes become zero is *ca.* -273°C (the exact value is -273.2°C) for all gases. This indicates that at a constant pressure, two straight lines obtained by plotting the volume V_1 and V_2 of two different gases 1 and 2 against the temperature will intersect at $V = 0$.

The British physicist Lord Kelvin (William Thomson (1824-1907)) proposed that at this temperature the molecules of gases become essentially motionless and hence its volume becomes negligible as compared with that at ambient temperatures, and he proposed a new scale of temperature, the **Kelvin temperature** scale, which is defined by the following equation.

$$273.2 + ^{\circ}\text{C} = \text{K} \quad (6.2)$$

Today the Kelvin temperature K is called the **absolute temperature**, and 0 K is called the **absolute zero point**. Using the absolute temperature scale, Charles's law may be expressed by a simple equation as shown below.

$$V = bT(\text{K}) \quad (6.3)$$

where b is a constant independent of the type of gas.

According to Kelvin, temperature is a measure of molecular motion. In this regard, absolute zero is particularly interesting since at this temperature, molecular motion of gases would cease. Absolute zero has never been realized by experiments. The lowest temperature ever attained is believed to be *ca.* 0.000001K .

Avogadro thought that for all gases compared under conditions of equal temperature and pressure, equal volumes would contain the same number of molecules (Avogadro's law; Ch. 1.2(b)). This is equivalent to assuming that the real volume of any gas is negligibly small as compared with the volume that the gas occupies. If this assumption is correct, the volume of a gas is proportional to the number of molecules of the gas contained in that volume. Hence, the relative mass, *i.e.*, the atomic weight or molecular weight of a gas, can easily be obtained.

(d) Equations of state for ideal gases

The essence of the three gas laws is summarized below. By the three laws, the relation between

temperature T , pressure P and volume V of n mols of gas is clearly shown.

Three gas laws

Boyle's law

$$V = a/P \text{ (at constant } T, n)$$

Charles's law

$$V = bT \text{ (at constant } P, n)$$

Avogadro's law

$$V = cn \text{ (at constant } T, P)$$

Thus, V is proportional to T and to n , and is inversely proportional to P . The relation can be combined into one equation Eq. (6.4) or (6.5).

$$V = RTn/P \quad (6.4)$$

or

$$PV = nRT \quad (6.5)$$

where R is a new constant. The above equation is called the **equation of state of ideal gases** or simply the ideal **equation of state**.

The value of R when $n = 1$ is called the **gas constant**, which is one of the fundamental physical constants. The value of R is various depending on the unit used. In the metric system, $R = 8.2056 \times 10^{-2} \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$. Today, the value $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ is more frequently used.

Sample Exercise 6.1 The ideal equation of state

A sample of 0.06 g of methane CH_4 has a volume of 950 cm^3 at a temperature of 25°C . Calculate the pressure (Pa or atm).

Answer

Since the molecular weight of CH_4 is 16.04, the amount of substance n is given as;

$$n = 0.06 \text{ g} / 16.04 \text{ g mol}^{-1} = 3.74 \times 10^{-2} \text{ mol}$$

Then,

$$\begin{aligned} P &= nRT/V = (3.74 \times 10^{-2} \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) / 950 \times 10^{-6} \text{ m}^3 \\ &= 9.75 \times 10^4 \text{ J m}^{-3} = 9.75 \times 10^4 \text{ N m}^{-2} \\ &= 9.75 \times 10^4 \text{ Pa} = 0.962 \text{ atm} \end{aligned}$$

With the aid of the gas constant, the unknown molecular weight of a gas can easily be determined if the mass w , the volume V and the pressure P are known. If the molar mass of the gas is M (g mol^{-1}), Eq. (6.6) is obtained because $n = w/M$.

$$PV = wRT/M \quad (6.6)$$

Then

$$M = wRT/PV \quad (6.7)$$

Sample Exercise 6.2 Molecular weight of a gas

The mass of an evacuated container with a volume of 0.500 dm^3 is 38.7340 g, and the mass increases to 39.3135 g after it is filled with air at a temperature of 24°C and a pressure of 1 atm. Assuming air is an ideal gas (*i.e.*, Eq. (6.5) can be applied), calculate the apparent molecular weight of air.

Answer

28.2. Since this is such an easy exercise, the details of the solution are not given. You can obtain the same value from the composition of air (approximately $N_2:O_2 = 4:1$)

(e) Law of partial pressures

In many cases you will be dealing not with pure gases but with **mixed gases** containing two or more gases. Dalton was concerned with humidity and was thus interested in wet air, that is, mixtures of air and water vapor. He derived the following relation by assuming that each gas in the mixture behaved independently of the other.

Suppose a mixture of two kinds of gases A (n_A mol) and B (n_B mol) has a volume of V at a temperature T . The following equations can be obtained for each gas.

$$p_A = n_A RT/V \quad (6.8)$$

$$p_B = n_B RT/V \quad (6.9)$$

where p_A and p_B are called the **partial pressures** of gas A and gas B, respectively. The partial pressure is the pressure that a component in the mixed gas would exert if it were alone in the container.

Dalton proposed the **law of partial pressures** which states that the **total pressure** P that the gas exerts is equal to the sum of the partial pressures of the two gases. Thus,

$$P = p_A + p_B = (n_A + n_B)RT/V \quad (6.10)$$

This law indicates that in a mixed gas each component gas exerts pressure completely independently. Though several gases are present, the pressure each gas exerts is not influenced by the presence of other gases.

If the molar fraction of gas A, x_A , in the mixture is defined as $x_A = n_A/(n_A + n_B)$, then p_A can be expressed in terms of x_A .

$$p_A = [n_A/(n_A + n_B)]P \quad (6.11)$$

In other words, the partial pressure of each component gas is the product of the molar fraction, in this case x_A , and the total pressure P .

The **saturated vapor pressure** (or simply **vapor pressure**) of water is defined as the maximum value of partial pressure that can be exerted by water vapor at a given temperature in a mixture of air and water vapor. If more vapor is present, all the water cannot remain as a vapor and part of it condenses.

Sample exercise 6.3 Law of partial pressures

A 3.0 dm^3 flask contains carbon dioxide CO_2 at a pressure of 200 kPa, and another 1.0 dm^3 flask contains nitrogen N_2 at a pressure of 300 kPa. The two gases are transferred into a 1.5 dm^3 flask. Calculate the total pressure of the mixed gas. The temperature is kept constant throughout the experiment.

Answer

The partial pressure of CO_2 will be 400 kPa since the volume of the new flask is 1/2 of the previous flask while that of N_2 is $300 \times (2/3) = 200$ kPa since the volume is now 2/3. Then the total pressure is $400 + 200 = 600$ kPa.

6.2 Ideal gases and real gases

(a) Equation of state of van der Waals

Gases which follow Boyle's law and Charles' law, that is, the ideal equation of state (Eq. (6.5)), are called **ideal gases**. It was found, however, that gases that we encounter, *i.e.*, real gases, do not strictly follow the ideal equation of state. The lower the pressure of the gas at constant temperature, the smaller the deviation from ideal behavior. The higher the pressure of the gas, or in other words, the smaller the intermolecular distances, the larger the deviation.

At least two reasons may account for this deviation. First, the definition of the absolute temperature is based on the assumption that the real volume of gases is negligibly small. Molecules of gases should have some actual volume even though if it may be extremely small. Furthermore, as the intermolecular distances become smaller, some kind of intermolecular interaction should arise.

The Dutch physicist Johannes Diderik van der Waals (1837-1923) proposed an equation of state for real gases, which is known as the **van der Waals equation** or the **van der Waals equation of state**. He modified the equation of state for an ideal gas (Eq. 6.5) in the following ways: added to the pressure term P a correction to compensate for intermolecular interaction; subtracted from the volume term V a correction to account for the real volume of the gas molecules. Thus,

$$[P + (n^2 a/V^2)] (V - nb) = nRT \quad (6.12)$$

where a and b are experimentally determined values for each gas and called **van der Waals constants** (Table 6.1). Smaller values for a and b indicate that the behavior of the gas should be closer to the behavior of an ideal gas. The magnitudes of a values are also related to the relative ease of liquefying the gas.

Table 6.1 Values of van der Waals constants for some common gases

gas	a (atm dm ⁶ mol ⁻²)	b (dm ³ mol ⁻¹)	gas	a (atm dm ⁶ mol ⁻²)	b (dm ³ mol ⁻¹)
He	0.0341	0.0237	C ₂ H ₄	4.47	0.0571
Ne	0.2107	0.0171	CO ₂	3.59	0.0427
H ₂	0.244	0.0266	NH ₃	4.17	0.0371
N ₂	1.39	0.0391	H ₂ O	5.46	0.0305
CO	1.49	0.0399	Hg	8.09	0.0170
O ₂	1.36	0.0318			

Sample exercise 6.4 Ideal gas and real gas

A sample of 10.0 mols of carbon dioxide is contained in a 20 dm³ container and vaporized at a temperature of 47°C. Calculate the pressure of carbon dioxide (a) as an ideal gas and (b) as a real gas. The experimental value is 82 atm. Compare this value with your results.

Answer

The pressure as an ideal gas can be calculated as follows:

$$P = nRT/V = [10.0 \text{ (mol)} 0.082(\text{dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) 320(\text{K})]/(20 \text{ dm}^3) = 131 \text{ atm}$$

The value obtained by using Eq. 6.11 is 82 atm which is identical with the experimental value. The results seem to indicate that a polar gas such as carbon dioxide will not behave ideally at a high pressure.

(b) Critical temperature and critical pressure

Since water vapor easily condenses into water, it was long expected that all gases could be liquefied if cooled and a pressure applied. However, it turned out that gases existed which could not be liquefied no matter what pressure was applied so long as the temperature of the gas was above a certain temperature called the **critical temperature**. The pressure required to liquefy a gas at the critical temperature was called the **critical pressure**, and the state of matter in which the

temperature and the pressure have their critical values is called the **critical state**.

The critical temperature is determined by the intermolecular attractions between gaseous molecules. Accordingly the critical temperature of nonpolar molecules is generally low. Above the critical temperature, the kinetic energy of gaseous molecules is much larger than the intermolecular attraction and hence liquefaction does not take place.

Table 6.2 Critical temperature and critical pressure of some common gases

gas	critical temperature(K)	critical pressure(atm)	gas	critical temperature(K)	critical pressure(atm)
H ₂ O	647.2	217.7	N ₂	126.1	33.5
HCl	224.4	81.6	NH ₃	405.6	111.5
O ₂	153.4	49.7	H ₂	33.3	12.8
Cl ₂	417	76.1	He	5.3	2.26

(c) Liquefaction of gases

Among the pressure correction terms a of van der Waals constants, H₂O, ammonia and carbon dioxide have large values, while oxygen and nitrogen and other gases have intermediate values. The value for helium is very small.

It was once known that liquefying nitrogen and oxygen was difficult. In the 19th century, it was found that such newly discovered gases such as ammonia were liquefied relatively easily. This finding prompted attempts to liquefy other gases. Liquefaction of oxygen or nitrogen by cooling under pressure was not successful. Such gases were regarded as “**permanent gases**” which could never be liquefied.

Later the existence of the critical temperature and critical pressure was discovered. That meant there should not be any permanent gases. Some gases are easily liquefied and others not. In the liquefaction of gases on an industrial scale, the **Joule-Thomson effect** is employed. When a gas confined in a well-insulated vessel is rapidly compressed by pushing down a piston, the kinetic energy of the moving piston increases the kinetic energy of the molecules in the gas, raising its temperature (since this is an adiabatic process, no kinetic energy is transferred to the wall of the vessel, *etc.*). This process is called **adiabatic compression**. If the gas then is expanded rapidly through an orifice, the temperature of the gas decreases. This is **adiabatic expansion**. It is possible to cool a gas by alternatively repeating rapid adiabatic expansions and compressions till liquefaction takes place.

In a chemical laboratory, ice, or a mixture of ice and salt, or a mixture of dry ice (solid CO₂) and acetone are used as coolants. When lower temperatures are required, liquid nitrogen is appropriate because it is stable and relatively cheap.

6.3 Kinetic molecular theory of gases

The problem, why gas laws are valid for all gases, was explained by physicists at the end of the 19th century by the atomic theory. The crucial point of their theory was that the origin of the pressure of gases is the movement of gaseous molecules. Hence the theory is called the **kinetic molecular theory of gases**.

According to this theory, the gas exerts pressure by its molecules colliding against the walls of the vessels. The larger the number of gaseous molecules in a unit volume, the larger the number of molecules that collide against the walls of the vessel, and as a result, the higher the pressure of the gas. The assumptions of this theory are as follows.

Assumptions of kinetic molecular theory

- (1) Gases are composed of molecules moving randomly.
- (2) There is neither attraction nor repulsion among the gaseous molecules.
- (3) Collisions between molecules are perfect elastic collisions, *i.e.*, no kinetic energy is lost.
- (4) As compared with the volume that the gas occupies, the real volume of the gaseous molecules is negligible.

Based on these assumptions, the following equation can be derived for a system composed of n molecules with a mass of m .

$$PV = nm\bar{u}^2/3 \quad (6.13)$$

where \bar{u}^2 is the mean square velocity. It is clear that the form of Eq. 6.13 is identical with that of Boyle's law. Indeed, if \bar{u}^2 is a constant at constant temperature, the equation is a variation of Boyle's law

Eq. 6.13 indicates that the velocity of the gas molecule is a function of PV . Since the value of PV for a given amount of gas is constant, it is possible that the velocity of the gas molecule is related to the mass of the gas, *i.e.*, molecular weight. For 1 mol of a gas, the following equation can be derived.

$$PV_m = N_A m \bar{u}^2 / 3 \quad (6.14)$$

where V_m is the molar volume and N_A is the Avogadro constant. By substituting $PV_m = RT$ in Eq. 6.14, the following equation is obtained.

$$\frac{1}{2} N_A m \bar{u}^2 = \frac{3}{2} RT \quad (6.15)$$

The left side of the equation corresponds to the kinetic energy of the gas molecules. From this equation, the **root mean square velocity** of gases $\sqrt{\bar{u}^2}$ can be obtained.

$$\sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{N_A m}} = \sqrt{\frac{3RT}{M}} \quad (6.16)$$

Sample exercise 6.5 Root mean square velocity of gases

Determine the root mean square velocity of a hydrogen molecule H_2 at S.T.P. (= standard temperature and pressure; 25°C, 1 atm).

Answer

The molar mass of hydrogen is 2.02 g mol⁻¹. Then

$$\sqrt{\bar{u}^2} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 298}{2.02 \times 10^{-3}}} = 1.92 \times 10^3 \text{ m s}^{-1}$$

If the root mean square velocity of gas molecules can be approximately proportional to the diffusion velocity as determined by experiment, it may be possible to determine the molecular weight of a gas A whose molecular weight is not yet known by comparing the diffusion velocity of

A with that of a gas B whose molecular weight is already known.

If you reverse the left side and right side of Eq. 6.15, you will obtain the following equation.

$$\frac{3}{2}RT = \frac{1}{2}N_A m \bar{u}^2 \quad (6.17)$$

This equation clearly indicates that in terms of kinetic molecular theory, the temperature is a measure of the intensity of molecular motion.

Exercise

6.1 Boyle's law and Charles's law

A sample of methane CH_4 has a volume of 7.0 dm^3 at a temperature of 4°C and a pressure of 0.848 atm . Calculate the volume of methane at a temperature of 11°C and a pressure of 1.52 atm .

6.1 Answer

$$V = [0.848 \text{ (atm)} \times 7.0 \text{ (dm}^3\text{)} \times 284\text{(K)}] / [1.52 \text{ (atm)} \times 277\text{(K)}] = 4.0 \text{ dm}^3$$

6.2 Law of gaseous reactions

The molecular formula of a gaseous hydrocarbon is C_3H_x . When 10 cm^3 of this gas was reacted with excess oxygen at a temperature of 110°C and a pressure of 1 atm , the volume increased to 15 cm^3 . Estimate the value of x .

6.2 Answer

The equation for the perfect combustion of hydrocarbons is as follows.



The volume of oxygen required for the perfect combustion of 10 cm^3 of hydrocarbon is $(30 + (5x/2)) \text{ cm}^3$ and the volume of CO_2 and vapor generated is 30 cm^3 and $5x \text{ cm}^3$, respectively. Then the total balance of gases is given below where a is the volume of excess oxygen.

$$30 + 5x + a = 5 + 10 + (5x/2) + a \quad \therefore x = 6$$

The hydrocarbon is propene C_3H_6 .

6.3 Gas constant

1 mol of an ideal gas occupies 22.414 dm^3 at the temperature of 0°C and the pressure of 1 atm . Using this data, calculate the gas constant in $\text{dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$ and in $\text{J mol}^{-1} \text{ K}^{-1}$.

6.3 Answer

$$0.0821 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}, \quad 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

6.4 Equation of state

A 0.2000 dm^3 flask contains 0.3000 mol of helium at a temperature of -25°C . Calculate the pressure of helium in two ways.

(a) With the aid of the equation for an ideal gas

(a) With the aid of the equation for a real gas

6.4 answer

(a) 30.6 atm , (b) 31.6 atm . For gases such as helium, the error involved in treating it as an ideal gas is very small (3 % in this case).

6.5 Velocity of gases

It can be assumed that the velocity of the diffusion of gases is determined by the root mean

square velocity. How fast can He diffuse as compared with a molecule of NO_2 ?

6.5 Answer

By using Eq. 6.16, you can obtain the following relation.

$$\sqrt{M_{\text{He}}/M_{\text{NO}_2}} = \text{velocity}_{\text{NO}_2}/\text{velocity}_{\text{He}}$$

The ratio is 0.295, which means that He can diffuse *ca.* 3.4 times as fast as NO_2 .

6.6 General problem for gases

Suffix 1 and 2 correspond to gas 1 and gas 2. Choose the larger one for each question.

- (a) u_1 or u_2 when $T_1 = T_2$ and $M_1 > M_2$
- (b) N_1 or N_2 when $P_1 = P_2$, $V_1 = V_2$, $T_1 = T_2$ and $M_1 > M_2$
- (c) V_1 or V_2 when $N_1 = N_2$, $T_1 = T_2$ and $P_1 > P_2$
- (d) T_1 or T_2 when $P_1 = P_2$, $V_1 = V_2$ and $N_1 > N_2$
- (e) P_1 or P_2 when $V_1 = V_2$, $N_1 = N_2$, $u_1 = u_2$ and $M_1 > M_2$

where P is the pressure, V the volume, T the temperature, M the molar mass, u the root mean square velocity and N is the number of molecules in the volume V .

6.6 Answer

- (a) $u_1 < u_2$ (b) $N_1 = N_2$ (c) $V_1 < V_2$ (d) $T_1 < T_2$ (e) $P_1 > P_2$