A Matter

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➤ Why do you need to know this material?

Because chemistry is about matter and the changes that it can undergo, both physically and chemically, the properties of matter underlie the entire discussion in this book.

➤ What is the key idea?

The bulk properties of matter are related to the identities and arrangements of atoms and molecules in a sample.

➤ What do you need to know already?

This Topic reviews material commonly covered in introductory chemistry.

The presentation of physical chemistry in this text is based on the experimentally verified fact that matter consists of atoms. In this Topic, which is a review of elementary concepts and language widely used in chemistry, we begin to make connections between atomic, molecular, and bulk properties. Most of the material is developed in greater detail later in the text.

A.1 Atoms

The atom of an element is characterized by its **atomic number**, Z, which is the number of protons in its nucleus. The number of neutrons in a nucleus is variable to a small extent, and the **nucleon number** (which is also commonly called the *mass number*), A, is the total number of protons and neutrons in the nucleus. Protons and neutrons are collectively called **nucleons**. Atoms of the same atomic number but different nucleon number are the **isotopes** of the element.

(a) The nuclear model

According to the **nuclear model**, an atom of atomic number Z consists of a nucleus of charge $+Ze$ surrounded by Z electrons each of charge $-e$ (e is the fundamental charge: see inside the front cover for its value and the values of the other fundamental constants). These electrons occupy **atomic orbitals**, which are regions of space where they are most likely to be found, with no more than two electrons in any one orbital. The atomic orbitals are arranged in **shells** around the nucleus, each shell being characterized by the **principal quantum number**, $n = 1, 2, \ldots$. A shell consists of n^2 individual orbitals, which are grouped together into n **subshells**; these subshells, and the orbitals they contain, are denoted s, p, d, and f. For all neutral atoms other than hydrogen, the subshells of a given shell have slightly different energies.

(b) The periodic table

The sequential occupation of the orbitals in successive shells results in periodic similarities in the **electronic configurations**, the specification of the occupied orbitals, of atoms when they are arranged in order of their atomic number. This periodicity of structure accounts for the formulation of the **periodic table** (see the inside the back cover). The vertical columns of the periodic table are called **groups** and (in the modern convention) numbered from 1 to 18. Successive rows of the periodic table are called **periods**, the number of the period being equa to the principal quantum number of the **valence shell**, the outermost shell of the atom.

Some of the groups also have familiar names: Group 1 consists of the **alkali metals**, Group 2 (more specifically, calcium, strontium, and barium) of the **alkaline earth metals**, Group 17 of the **halogens**, and Group 18 of the **noble gases**. Broadly speaking, the elements towards the left of the periodic table are **metals** and those towards the right are **non-metals**; the two classes of substance meet at a diagonal line running from boron to polonium, which constitute the **metalloids**, with properties intermediate between those of metals and non-metals.

The periodic table is divided into s, p, d, and f **blocks**, according to the subshell that is last to be occupied in the formulation of the electronic configuration of the atom. The members of the d block (specifically the members of Groups 3–11 in the d block) are also known as the **transition metals**; those of the f block (which is not divided into numbered groups) are sometimes called the **inner transition metals**. The upper row of the f block (Period 6) consists of the **lanthanoids** (still commonly the 'lanthanides') and the lower row (Period 7) consists of the **actinoids** (still commonly the 'actinides').

(c) Ions

A monatomic **ion** is an electrically charged atom. When an atom gains one or more electrons it becomes a negatively charged **anion**; when it loses one or more electrons it becomes a positively charged **cation**. The charge number of an ion is called the **oxidation number** of the element in that state (thus, the oxidation number of magnesium in Mg^{2+} is +2 and that of oxygen in O^{2-} is −2). It is appropriate, but not always done, to distinguish between the oxidation number and the **oxidation state**, the latter being the physical state of the atom with a specified oxidation number. Thus, the oxidation number *of* magnesium is +2 when it is present as Mg^{2+}, and it is present *in* the oxidation state Mg^{2+}.

The elements form ions that are characteristic of their location in the periodic table: metallic elements typically form cations by losing the electrons of their outermost shell and acquiring the electronic configuration of the preceding noble gas atom. Nonmetals typically form anions by gaining electrons and attaining the electronic configuration of the following noble gas atom.

A.2 Molecules

A **chemical bond** is the link between atoms. Compounds that contain a metallic element typically, but far from universally, form **ionic compounds** that consist of cations and anions in a crystalline array. The 'chemical bonds' in an ionic compound are due to the Coulombic interactions between all the ions in the crystal and it is inappropriate to refer to a bond between a specific pair of neighbouring ions. The smallest unit of an ionic compound is called a **formula unit**. Thus $NaNO_3$, consisting of a Na^+ cation and a NO_3^- anion, is the formula unit of sodium nitrate. Compounds that do not contain a metallic element typically form **covalent compounds** consisting of discrete molecules. In this case, the bonds between the atoms of a molecule are **covalent**, meaning that they consist of shared pairs of electrons.

> *A note on good practice* Some chemists use the term 'molecule' to denote the smallest unit of a compound with the composition of the bulk material regardless of whether it is an ionic or covalent compound and thus speak of 'a molecule of NaCl'. We use the term 'molecule' to denote a discrete covalently bonded entity (as in H_2O); for an ionic compound we use 'formula unit'.

(a) Lewis structures

The pattern of bonds between neighbouring atoms is displayed by drawing a **Lewis structure**, in which bonds are shown as lines and **lone pairs** of electrons, pairs of valence electrons that are not used in bonding, are shown as dots. Lewis structures are constructed by allowing each atom to share electrons until it has acquired an **octet** of eight electrons (for hydrogen, a *duplet* of two electrons). A shared pair of electrons is a **single bond**, two shared pairs constitute a **double bond**, and three shared pairs constitute a **triple bond**. Atoms of elements of Period 3 and later can accommodate more than eight electrons in their valence shell and 'expand their octet' to become **hypervalent**, that is, form more bonds than the octet rule would allow (for example, SF_6), or form more bonds to a small number of atoms (see *Brief illustration* A.1). When more than one Lewis structure can be written for a given arrangement of atoms, it is supposed that **resonance**, a blending of the structures, may occur and distribute multiple-bond character over the molecule (for example, the two Kekulé structures of benzene). Examples of these aspects of Lewis structures are shown in Fig. A.1.

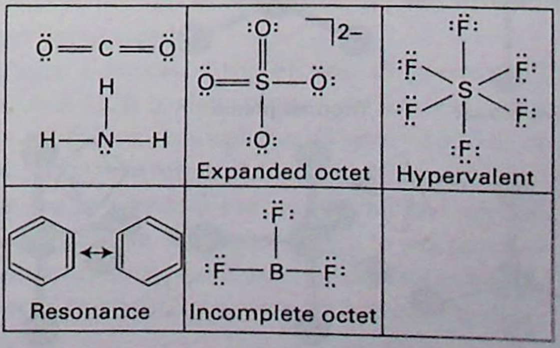
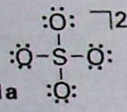


Figure A.1 Examples of Lewis structures.

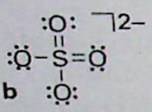
Brief illustration A.1 Octet expansion

Octet expansion is also encountered in species that do not necessarily require it, but which, if it is permitted, may acquire a lower energy. Thus, of the structures (**1a**) and (**1b**) of the SO_4^{2-} ion, the second has a lower energy than the first. The actual structure of the ion is a resonance hybrid of both structures (together with analogous structures with double bonds in different locations), but the latter structure makes the dominant contribution.



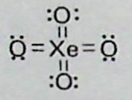
$\left[:\ddot{O}-\overset{\overset{:\ddot{O}:}{|}}{\underset{\underset{:\ddot{O}:}{|}}{S}}-\ddot{O}:\right]^{2-}$

1a



$\left[:\ddot{O}-\overset{\overset{:O:}{\|}}{\underset{\underset{:\ddot{O}:}{|}}{S}}=\ddot{O}\right]^{2-}$

1b



$\ddot{O}=\overset{\overset{:O:}{\|}}{\underset{\underset{:O:}{\|}}{Xe}}=\ddot{O}$

2

Self-test A.1 Draw the Lewis structure for XeO_4.

Answer: See 2

(b) VSEPR theory

Except in the simplest cases, a Lewis structure does not express the three-dimensional structure of a molecule. The simplest approach to the prediction of molecular shape is **valence-shell electron pair repulsion theory** (VSEPR theory). In this approach, the regions of high electron density, as represented by bonds—whether single or multiple—and lone pairs, take up orientations around the central atom that maximize their separations. Then the position of the attached atoms (not the lone pairs) is noted and used to classify the shape of the molecule. Thus, four regions of electron density adopt a tetrahedral arrangement; if an atom is at each of these locations (as in CH_4), then the molecule is tetrahedral; if there is an atom at only three of these locations (as in NH_3), then the molecule is trigonal pyramidal, and so on. The names of the various shapes that are commonly found are shown in Fig. A.2. In a refinement of the theory, lone pairs are assumed to repel bonding pairs more strongly than bonding pairs repel each other. The shape a molecule then adopts, if it is not determined fully by symmetry, is such as to minimize repulsions from lone pairs.

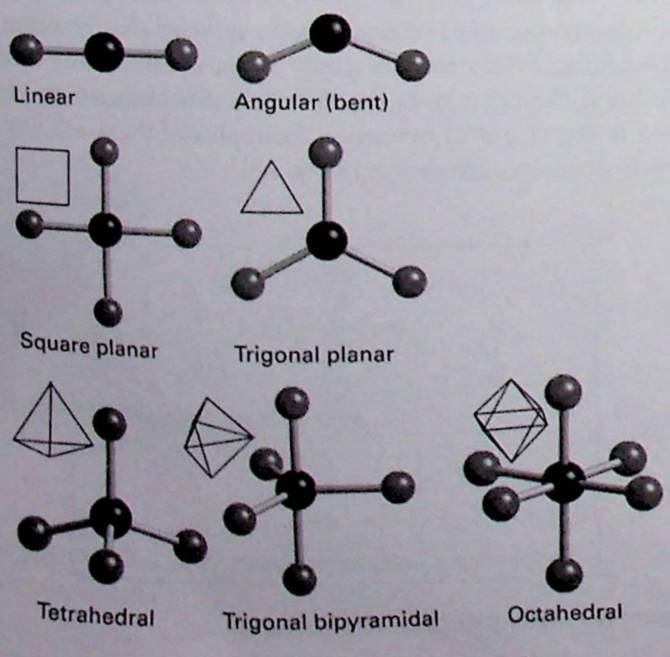


Figure A.2 The shapes of molecules that result from application of VSEPR theory.

Brief illustration A.2 Molecular shapes

In SF_4 the lone pair adopts an equatorial position and the two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule (Fig. A.3).

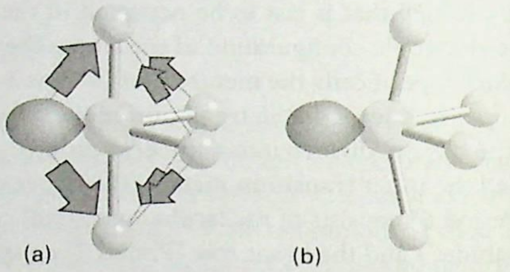


Figure A.3 (a) In SF_4 the lone pair adopts an equatorial position. (b) The two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule.

Self-test A.2 Predict the shape of the SO_3^{2-} ion.

Answer: Trigonal pyramid

(c) Polar bonds

Covalent bonds may be **polar**, or correspond to an unequal sharing of the electron pair, with the result that one atom has a partial positive charge (denoted δ+) and the other a partial negative charge (δ−). The ability of an atom to attract electrons to itself when part of a molecule is measured by the **electronegativity**, χ (chi), of the element. The juxtaposition of equal and opposite partial charges constitutes an **electric dipole**. If those charges are $+Q$ and $-Q$ and they are separated by a distance d, the magnitude of the **electric dipole moment**, μ, is

$$\mu = Qd \qquad \textit{Definition} \quad \text{Magnitude of the electric dipole moment} \qquad \text{(A.1)}$$

Brief illustration A.3 Nonpolar molecules with polar bonds

Whether or not a molecule as a whole is polar depends on the arrangement of its bonds, for in highly symmetrical molecules there may be no net dipole. Thus, although the linear CO_2 molecule (which is structurally OCO) has polar CO bonds, their effects cancel and the molecule as a whole is nonpolar.

Self-test A.3 Is NH_3 polar?

Answer: Yes

A.3 Bulk matter

Bulk matter consists of large numbers of atoms, molecules, or ions. Its physical state may be solid, liquid, or gas:

> A **solid** is a form of matter that adopts and maintains a shape that is independent of the container it occupies.
>
> A **liquid** is a form of matter that adopts the shape of the part of the container it occupies (in a gravitational field, the lower part) and is separated from the unoccupied part of the container by a definite surface.
>
> A **gas** is a form of matter that immediately fills any container it occupies.

A liquid and a solid are examples of a **condensed state** of matter. A liquid and a gas are examples of a **fluid** form of matter: they flow in response to forces (such as gravity) that are applied.

(a) Properties of bulk matter

The state of a bulk sample of matter is defined by specifying the values of various properties. Among them are:

> The **mass**, m, a measure of the quantity of matter present (unit: 1 kilogram, 1 kg).
>
> The **volume**, V, a measure of the quantity of space the sample occupies (unit: 1 cubic metre, 1 $\mathrm{m^3}$).
>
> The **amount of substance**, n, a measure of the number of specified entities (atoms, molecules, or formula units) present (unit: 1 mole, 1 mol).

Brief illustration A.4 Volume units

Volume is also expressed as submultiples of 1 $\mathrm{m^3}$, such as cubic decimetres ($1\,\mathrm{dm^3}=10^{-3}\,\mathrm{m^3}$) and cubic centimetres ($1\,\mathrm{cm^3}=10^{-6}\,\mathrm{m^3}$). It is also common to encounter the non-SI unit litre ($1\,\mathrm{L}=1\,\mathrm{dm^3}$) and its submultiple the millilitre ($1\,\mathrm{mL}=1\,\mathrm{cm^3}$). To carry out simple unit conversions, simply replace the fraction of the unit (such as 1 cm) by its definition (in this case, $10^{-2}\,\mathrm{m}$). Thus, to convert 100 $\mathrm{cm^3}$ to cubic decimetres (litres), use $1\,\mathrm{cm}=10^{-1}\,\mathrm{dm}$, in which case $100\,\mathrm{cm^3}=100\,(10^{-1}\,\mathrm{dm})^3$, which is the same as 0.100 $\mathrm{dm^3}$.

Self-test A.4 Express a volume of 100 $\mathrm{mm^3}$ in units of $\mathrm{cm^3}$.

Answer: 0.100 $\mathrm{cm^3}$

An **extensive property** of bulk matter is a property that depends on the amount of substance present in the sample; an **intensive property** is a property that is independent of the amount of substance. The volume is extensive; the mass density, ρ (rho), with

$$\rho=\frac{m}{V}\qquad\text{Mass density}\qquad\text{(A.2)}$$

is intensive.

The **amount of substance**, n (colloquially, 'the number of moles'), is a measure of the number of specified entities present in the sample. 'Amount of substance' is the official name of the quantity; it is commonly simplified to 'chemical amount' or simply 'amount'. The unit 1 mol is currently defined as the number of carbon atoms in exactly 12 g of carbon-12. (In 2011 the decision was taken to replace this definition, but the change has not yet, in 2014, been implemented.) The number of entities per mole is called **Avogadro's constant**, N_A; the currently accepted value is $6.022\times10^{23}\,\mathrm{mol^{-1}}$ (note that N_A is a constant with units, not a pure number).

The **molar mass of a substance**, M (units: formally kilograms per mole but commonly grams per mole, $\mathrm{g\,mol^{-1}}$) is the mass per mole of its atoms, its molecules, or its formula units. The amount of substance of specified entities in a sample can readily be calculated from its mass, by noting that

$$n=\frac{m}{M}\qquad\text{Amount of substance}\qquad\text{(A.3)}$$

A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units $\mathrm{kg\,mol^{-1}}$). *Relative* molecular masses of atoms and molecules, $M_r=m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant (see inside front cover), are still widely called 'atomic weights' and 'molecular weights' even though they are dimensionless quantities and not weights (the gravitational force exerted on an object).

A sample of matter may be subjected to a **pressure**, p (unit: 1 pascal, Pa; $1\,\mathrm{Pa}=1\,\mathrm{kg\,m^{-1}\,s^{-2}}$), which is defined as the force, F, it is subjected to divided by the area, A, to which that force is applied. A sample of gas exerts a pressure on the walls of its container because the molecules of gas are in ceaseless, random motion, and exert a force when they strike the walls. The frequency of the collisions is normally so great that the force, and therefore the pressure, is perceived as being steady.

Although 1 pascal is the SI unit of pressure (*The chemist's toolkit* A.1), it is also common to express pressure in bar ($1\,\mathrm{bar}=10^5\,\mathrm{Pa}$) or atmospheres ($1\,\mathrm{atm}=101\,325\,\mathrm{Pa}$ exactly), both of which correspond to typical atmospheric pressure. Because many physical properties depend on the pressure acting on a sample, it is appropriate to select a certain value of the pressure to report their values. The **standard pressure** for reporting physical quantities is currently defined as $p^{\ominus}=1$ bar exactly.

The chemist's toolkit A.1 Quantities and units

The result of a measurement is a **physical quantity** that is reported as a numerical multiple of a unit:

$$\text{physical quantity} = \text{numerical value} \times \text{unit}$$

It follows that units may be treated like algebraic quantities and may be multiplied, divided, and cancelled. Thus, the expression (physical quantity)/unit is the numerical value (a dimensionless quantity) of the measurement in the specified units. For instance, the mass m of an object could be reported as $m=2.5\,\mathrm{kg}$ or $m/\mathrm{kg}=2.5$. See Table A.1 in the *Resource section* for a list of units. Although it is good practice to use only SI units, there will be occasions where accepted practice is so deeply rooted that physical quantities are expressed using other, non-SI units. By international convention, all physical quantities are represented by oblique (sloping) symbols; all units are roman (upright).

Units may be modified by a prefix that denotes a factor of a power of 10. Among the most common SI prefixes are those listed in Table A.2 in the *Resource section*. Examples of the use of these prefixes are:

$$1\,\mathrm{nm}=10^{-9}\,\mathrm{m} \qquad 1\,\mathrm{ps}=10^{-12}\,\mathrm{s} \qquad 1\,\mu\mathrm{mol}=10^{-6}\,\mathrm{mol}$$

Powers of units apply to the prefix as well as the unit they modify. For example, $1\,\mathrm{cm}^3=1\,(\mathrm{cm})^3$, and $(10^{-2}\,\mathrm{m})^3=10^{-6}\,\mathrm{m}^3$. Note that $1\,\mathrm{cm}^3$ does not mean $1\,\mathrm{c(m^3)}$. When carrying out numerical calculations, it is usually safest to write out the numerical value of an observable in scientific notation (as $n.nnn\times 10^n$).

There are seven SI base units, which are listed in Table A.3 in the *Resource section*. All other physical quantities may be expressed as combinations of these base units (see Table A.4 in the *Resource section*). *Molar concentration* (more formally, but very rarely, *amount of substance concentration*) for example, which is an amount of substance divided by the volume it occupies, can be expressed using the derived units of $\mathrm{mol\,dm^{-3}}$ as a combination of the base units for amount of substance and length. A number of these derived combinations of units have special names and symbols and we highlight them as they arise.

To specify the state of a sample fully it is also necessary to give its **temperature**, T. The temperature is formally a property that determines in which direction energy will flow as heat when two samples are placed in contact through thermally conducting walls: energy flows from the sample with the higher temperature to the sample with the lower temperature. The symbol T is used to denote the **thermodynamic temperature** which is an absolute scale with $T=0$ as the lowest point. Temperatures above $T=0$ are then most commonly expressed by using the **Kelvin scale**, in which the gradations of temperature are expressed as multiples of the unit 1 kelvin (1 K). The Kelvin scale is currently defined by setting the triple point of water (the temperature at which ice, liquid water, and water vapour are in mutual equilibrium) at exactly 273.16 K (as for certain other units, a decision has been taken to revise this definition, but it has not yet, in 2014, been implemented). The freezing point of water (the melting point of ice) at 1 atm is then found experimentally to lie 0.01 K below the triple point, so the freezing point of water is 273.15 K. The Kelvin scale is unsuitable for everyday measurements of temperature, and it is common to use the **Celsius scale**, which is defined in terms of the Kelvin scale as

$$\theta/{}^\circ\mathrm{C} = T/\mathrm{K} - 273.15$$

Definition Celsius scale (A.4)

Thus, the freezing point of water is 0 °C and its boiling point (at 1 atm) is found to be 100 °C (more precisely 99.974 °C). Note that in this text T invariably denotes the thermodynamic (absolute) temperature and that temperatures on the Celsius scale are denoted θ (theta).

> *A note on good practice* Note that we write $T=0$, not $T=0\,\mathrm{K}$. General statements in science should be expressed without reference to a specific set of units. Moreover, because T (unlike θ) is absolute, the lowest point is 0 regardless of the scale used to express higher temperatures (such as the Kelvin scale). Similarly, we write $m=0$, not $m=0\,\mathrm{kg}$ and $l=0$, not $l=0\,\mathrm{m}$.

(b) The perfect gas equation

The properties that define the state of a system are not in general independent of one another. The most important example of a relation between them is provided by the idealized fluid known as a **perfect gas** (also, commonly, an 'ideal gas'):

$$pV = nRT$$

Perfect gas equation (A.5)

Here R is the **gas constant**, a universal constant (in the sense of being independent of the chemical identity of the gas) with the value $8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Throughout this text, equations applicable only to perfect gases (and other idealized systems) are labelled, as here, with a number in blue.

> *A note on good practice* Although the term 'ideal gas' is almost universally used in place of 'perfect gas', there are reasons for preferring the latter term. In an ideal system the interactions between molecules in a mixture are all the same. In a perfect gas not only are the interactions all the same but they are in fact zero. Few, though, make this useful distinction.

Equation A.5, the **perfect gas equation**, is a summary of three empirical conclusions, namely Boyle's law ($p \propto 1/V$ at constant temperature and amount), Charles's law ($p \propto T$ at constant volume and amount), and Avogadro's principle ($V \propto n$ at constant temperature and pressure).

Example A.1 Using the perfect gas equation

Calculate the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 cm^3 at 20 °C.

Method To use eqn A.5, we need to know the amount of molecules (in moles) in the sample, which we can obtain from the mass and the molar mass (by using eqn A.3) and to convert the temperature to the Kelvin scale (by using eqn A.4).

Answer The amount of N_2 molecules (of molar mass 28.02 g mol^{-1}) present is

$$n(\mathrm{N_2})=\frac{m}{M(\mathrm{N_2})}=\frac{1.25\,\mathrm{g}}{28.02\,\mathrm{g\,mol^{-1}}}=\frac{1.25}{28.02}\,\mathrm{mol}$$

The temperature of the sample is

$$T/\mathrm{K}=20+273.15,\ \text{so}\ T=(20+273.15)\,\mathrm{K}$$

Therefore, after rewriting eqn A.5 as $p=nRT/V$,

$$p=\frac{\overbrace{(1.25/28.02)\,\mathrm{mol}}^{n}\times\overbrace{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}^{R}\times\overbrace{(20+273.15)\,\mathrm{K}}^{T}}{\underbrace{(2.50\times10^{-4})\,\mathrm{m^3}}_{V}}$$

$$=\frac{(1.25/28.02)\times(8.3145)\times(20+273.15)}{2.50\times10^{-4}}\,\frac{\mathrm{J}}{\mathrm{m^3}}$$

$$\overset{1\,\mathrm{J\,m^{-3}}=1\,\mathrm{Pa}}{\widehat{=}}\quad 4.35\times10^{5}\,\mathrm{Pa}=435\,\mathrm{kPa}$$

A note on good practice It is best to postpone a numerical calculation to the last possible stage, and carry it out in a single step. This procedure avoids rounding errors. When we judge it appropriate to show an intermediate result without committing ourselves to a number of significant figures, we write it as *n.nnn…*.

Self-test A.5 Calculate the pressure exerted by 1.22 g of carbon dioxide confined in a flask of volume 500 dm^3 (5.00 × 10^2 dm^3) at 37 °C.

Answer: 143 Pa

All gases obey the perfect gas equation ever more closely as the pressure is reduced towards zero. That is, eqn A.5 is an example of a **limiting law**, a law that becomes increasingly valid in a particular limit, in this case as the pressure is reduced to zero. In practice, normal atmospheric pressure at sea level (about 1 atm) is already low enough for most gases to behave almost perfectly, and unless stated otherwise, we assume in this text that the gases we encounter behave perfectly and obey eqn A.5.

A mixture of perfect gases behaves like a single perfect gas. According to **Dalton's law**, the total pressure of such a mixture is the sum of the pressures to which each gas would give rise if it occupied the container alone:

$$p=p_A+p_B+\cdots \qquad \text{Dalton's law} \qquad (A.6)$$

Each pressure, p_J, can be calculated from the perfect gas equation in the form $p_J=n_JRT/V$.

Checklist of concepts

☐ 1. In the **nuclear model** of an atom negatively charged electrons occupy atomic orbitals which are arranged in shells around a positively charged nucleus.

☐ 2. The **periodic table** highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties.

☐ 3. **Covalent compounds** consist of discrete molecules in which atoms are linked by covalent bonds.

☐ 4. **Ionic compounds** consist of cations and anions in a crystalline array.

☐ 5. **Lewis structures** are useful models of the pattern of bonding in molecules.

☐ 6. The **valence-shell electron pair repulsion theory** (**VSEPR theory**) is used to predict the three-dimensional shapes of molecules from their Lewis structures.

☐ 7. The electrons in **polar covalent bonds** are shared unequally between the bonded nuclei.

☐ 8. The physical states of bulk matter are solid, liquid, or gas.

☐ 9. The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature.

☐ 10. The **perfect gas equation** is a relation between the pressure, volume, amount, and temperature of an idealized gas.

☐ 11. A **limiting law** is a law that becomes increasingly valid in a particular limit.

Checklist of equations

Property	Equation	Comment	Equation number
Electric dipole moment	$\mu = Qd$	μ is the magnitude of the moment	A.1
Mass density	$\rho = m/V$	Intensive property	A.2
Amount of substance	$n = m/M$	Extensive property	A.3
Celsius scale	$\theta/°\mathrm{C} = T/\mathrm{K} - 273.15$	Temperature is an intensive property; 273.15 is exact.	A.4
Perfect gas equation	$pV = nRT$		A.5
Dalton's law	$p = p_A + p_B + \cdots$		A.6

B Energy

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➤ **Why do you need to know this material?**

Energy is the central unifying concept of physical chemistry, and you need to gain insight into how electrons, atoms, and molecules gain, store, and lose energy.

➤ **What is the key idea?**

Energy, the capacity to do work, is restricted to discrete values in electrons, atoms, and molecules.

➤ **What do you need to know already?**

You need to review the laws of motion and principles of electrostatics normally covered in introductory physics and concepts of thermodynamics normally covered in introductory chemistry.

Much of chemistry is concerned with transfers and transformations of energy, and from the outset it is appropriate to define this familiar quantity precisely. We begin here by reviewing **classical mechanics**, which was formulated by Isaac Newton in the seventeenth century, and establishes the vocabulary used to describe the motion and energy of particles. These classical ideas prepare us for **quantum mechanics**, the more fundamental theory formulated in the twentieth century for the study of small particles, such as electrons, atoms, and molecules. We develop the concepts of quantum mechanics throughout the text. Here we begin to see why it is needed as a foundation for understanding atomic and molecular structure.

B.1 Force

Molecules are built from atoms and atoms are built from subatomic particles. To understand their structures we need to know how these bodies move under the influence of the forces they experience.

(a) Momentum

'Translation' is the motion of a particle through space. The **velocity**, $\boldsymbol{v}$, of a particle is the rate of change of its position $\boldsymbol{r}$:

$$\boldsymbol{v}=\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} \qquad \textit{Definition} \quad \text{Velocity} \qquad \text{(B.1)}$$

For motion confined to a single dimension, we would write $v_x=\mathrm{d}x/\mathrm{d}t$. The velocity and position are vectors, with both direction and magnitude (vectors and their manipulation are treated in detail in *Mathematical background* 5). The magnitude of the velocity is the **speed**, v. The **linear momentum**, $\boldsymbol{p}$, of a particle of mass m is related to its velocity, $\boldsymbol{v}$, by

$$\boldsymbol{p}=m\boldsymbol{v} \qquad \textit{Definition} \quad \text{Linear momentum} \qquad \text{(B.2)}$$

Like the velocity vector, the linear momentum vector points in the direction of travel of the particle (Fig. B.1); its magnitude is denoted p.

The description of rotation is very similar to that of translation. The rotational motion of a particle about a central point is described by its **angular momentum**, $\boldsymbol{J}$. The angular