CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

1

Atoms, molecules and the forces between them

1.1 Atoms and molecules

1.1.1 *The evidence for atoms and molecules*

Matter is not a continuum of uniform density, but consists of discrete particles or, if one wishes to be more up to date, of localized regions of very high density separated by regions of almost zero density. The particulate nature of matter has been known to us since the time of the Greeks and the idea of atoms (units which could not be further cut or divided) is generally attributed to Democritus (*c.* 460–370 BC). Many of his concepts have a surprisingly modern ring and constitute a tribute to the immense power, as well as the originality, of the Greek approach to logical inference and abstract reasoning. Much of his work was, indeed, the result of thought rather than of direct experiment. One must not, however, read too much modern science into these early ideas. For example in a passage quoted by Theophrastus, *De Sensu*, 61–2, Democritus states, 'Hard is what is dense, and soft what is rare . . . Hard and soft as well as heavy and light are differentiated by the position and arrangement of the voids. Therefore iron is harder and lead heavier.' But it would be wrong from this to attribute to Democritus a knowledge of dislocations and point defects.

The first real attempt to get to grips with the basic 'atoms' of matter had to wait until more quantitative measurements and generalizations had been made. The law of multiple proportions, largely due to the work of J. Dalton (1766–1844) was one of these. It stated that if two elementary substances combined chemically to form more than one compound the weights of one which combine with a fixed weight of the other are in a simple ratio to one another. For example nitrogen and oxygen combine to form nitrous oxide, nitric oxide, nitrogen sesquioxide and nitrogen

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

dioxide; three of these oxides were, in fact, amongst the compounds which Dalton first studied in the course of his investigation. In these compounds 14 unit masses of nitrogen combine respectively with 8, 16, 24 and 32 unit masses of oxygen: i.e. the ratio is 1:2:3:4. This fits in naturally with the concept of unit masses which can combine in simple multiples with one another.

We consider a simpler case, the reaction of hydrogen and oxygen to form water. Quantitatively we find 1 unit mass of hydrogen combines with 8 unit masses of oxygen to form 9 unit masses of water. According to Dalton's atomic theory (Dalton 1808) we should write

1 atom hydrogen + 1 atom oxygen → 1 atom water

or

$$H + O \rightarrow HO.$$

When these reactions are studied in the gaseous state and the volumes are measured at a standard temperature and pressure, the equation becomes

2 volumes hydrogen + 1 volume oxygen →
2 volumes water vapour.

The next step in the argument depends on the hypothesis put forward by A. Avogadro in 1811 that at a specified temperature and pressure a given volume of any gas contains the same number of unit masses.

2 unit masses of hydrogen + 1 unit mass of oxygen →
2 unit masses of water.

This statement makes sense only if the 'unit mass' of oxygen is itself divisible into two equal parts each of which goes into one of the unit masses of water. Arguments along these lines lead finally to chemical equations of the type

$$2H_2 + O_2 \rightarrow 2H_2O,$$

where H_2, the smallest quantity of hydrogen which can exist in the free state, is called the molecule whilst H, the smallest quantity of hydrogen to enter into chemical combination, is called the atom. Avogadro's 'unit masses' are therefore molecules.

1.1.2 *Avogadro's law*

This is still called a hypothesis but deserves to be promoted to the status of a law. It states that at a specified temperature and pressure a fixed volume of any gas or vapour contains the same number of unit masses, i.e. molecules or atoms if the free molecule is monatomic. If we redefine the atom of hydrogen as 1 unit mass, the molecule of hydrogen

© Cambridge University Press www.cambridge.org

CAMBRIDGE

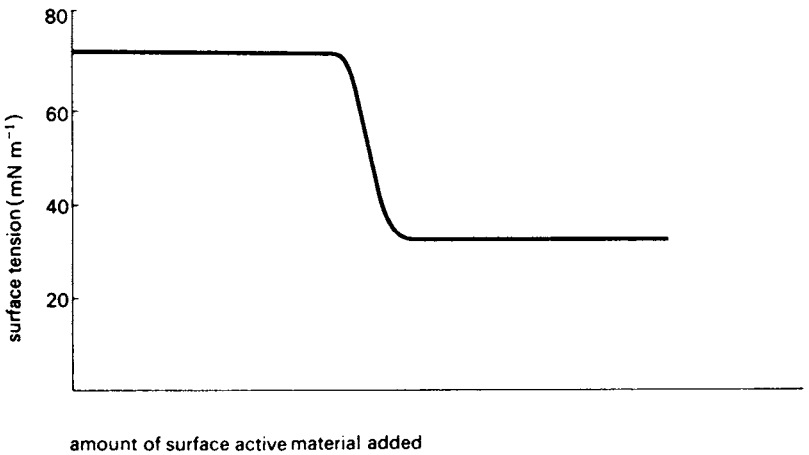
Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

consists of 2 unit masses. In the older literature these quantities in grams were called the gram-atom or gram-molecule respectively. In SI units the standard is no longer hydrogen but carbon-12: the gram-atom and gram-molecule are replaced by the mole (and the unit is written 'mol'). It is defined as the 'amount of substance of a system which contains as many elementary particles as there are atoms in 0.012 kg of carbon-12. We can only regard this definition in terms of 12 grams of carbon as a failure of nerve on the part of physical chemists. The logic of SI units demands the use of 12 kg of carbon-12 as the unit and indeed some physicists use the kilomole in this way. We shall not, however, introduce such units into this book. One mole of any gas at a pressure of 760 mm Hg (101 325 Pa) and a temperature of 273 K fills approximately 0.0224 m^3. The number of molecules in a mole of any substance is called Avogadro's number (N_A) and has the value of 6.02×10^{23}. For example (N_A) molecules of hydrogen weigh approximately 2 g: these constitute the mole-mass of these materials to the nearest integer.

1.1.3 *First experimental deduction of the size of molecules*

Pioneer work by Fraülein Pockels in 1891 showed that certain organic molecules with polar end groups such as oleic acid which are insoluble in water in bulk will spread over the surface of clean water.

Figure 1.1. Schematic diagram showing the surface tension of water as small quantities of surface-active material are added. The surface tension remains fairly high until a critical amount, corresponding approximately to a complete monolayer of surfactant, has been added; it then falls rapidly to a constant lower value.



© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

Lord Rayleigh experimented further with this and showed in 1899 that if the amount of acid added to the water surface is less than a certain amount there is practically no reduction in surface tension of the water. If, however, the amount added exceeds a certain critical value the surface tension falls rapidly. This is shown schematically in figure 1.1. Rayleigh assumed that this change occurred when there was a continuous monomolecular layer of fatty acid on the surface. He was thus able to determine the weight of acid per m^2 of surface at which the monolayer was formed. Assuming the monolayer to have the same density as the acid in bulk, the thickness of the monolayer was calculated and found to be about 10^{-9} m, i.e. 10 Å. This was the first direct indication that atomic and molecular dimensions are of the order of angstroms.

1.1.4 *Determination of Avogadro's number* N_A

We shall mention three very different ways of determining N_A. They are all of historic interest but only the last two provide reasonably accurate values.

1.1.4.1 *Radioactive disintegration.* Radium disintegrates to give off α particles and leave radon gas. Radon disintegrates to give off α particles and leave behind polonium. Further stages in the disintegration are not, in the present context, of great importance. The α particles emitted can be counted by allowing the particles emitted within a small known solid angle to strike a fluorescent screen. Each particle may be counted since it produces an individual scintillation on the screen. From the size of the solid angle chosen the total emission over a solid angle of 4π can be deduced. Lord Rutherford in 1909 showed that the α particle is a helium atom which has lost its two orbital electrons (see below). These electrons are picked up by the particles so that each α particle becomes a helium atom, and since helium is a monoatomic gas each α particle thus becomes a gas atom. The volume of the helium gas produced in this way can be measured. By extrapolation Rutherford found that, in one year, one kilogram of radium would emit a total of 11.6×10^{20} particles which would turn into 43×10^{-6} m^3 of helium gas at s.t.p.

Consequently 43×10^{-6} m^3 He contains 11.6×10^{20} atoms.
Therefore 22.4×10^{-3} m^3 He contains 6×10^{23} atoms.

This derivation is of interest since it showed for the first time that atoms are individual particles.

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

1.1.4.2 *Electrolysis.* If a quantity of electricity known as a faraday is used to electrolyse a dilute acid, exactly 1 gram of hydrogen is liberated. Since the faraday is equal to 96 500 coulombs, this means that 96 500 coulombs are involved in converting N_A ions of hydrogen into N_A atoms of hydrogen gas. The charge on the hydrogen ion is due to the loss of a single electron, hence

$$96\ 500 \text{ coulomb} = \text{charge of } N_A \text{ electrons} = N_A e.$$

The next step is to determine e. This was carried through successfully by R. Millikan in 1909. He produced very fine droplets of oil between the plates of a parallel plate condenser, the plates being set in a horizontal plane. The particles gradually fall because of gravity. If, however, the air surrounding them is subjected to ionizing radiation the particles will pick up charge of say q. It then becomes possible to apply an electrostatic field E which is able just to hold the drop in equilibrium in a stationary position. In this state

$$Eq = mg.$$

Therefore as m, g and E were known, q was calculated and found always to be an integral number of some fundamental unit charge. This was assumed to be the charge e of the electron. The current value of e found in this way is very nearly

$$e = 1.6 \times 10^{-19} \text{ coulomb.}$$

Hence

$$N_A = \frac{96\ 500}{1.6 \times 10^{-19}} = 6.03 \times 10^{23}.$$

1.1.4.3 *X-rays.* X-rays are electromagnetic waves of short wavelength (about 10^{-10} m). M von Laue was the first to suggest, in 1912, that since the spacing of crystal planes in a simple inorganic crystal is of this order, it ought to be possible to use the crystal as a diffraction grating for X-rays. The wavelengths λ of the X-rays may be determined accurately by diffracting them with a conventional ruled grating, at glancing incidence. The X-rays may then be used to find the lattice spacing in the crystal. If, for example, a collimated beam of X-rays strikes a crystal plane at an angle θ_1, it is first refracted through an angle θ_2, but since the refractive index for X-rays is almost unity one may take $\theta_1 = \theta_2 = \theta$. The condition for reinforcement is then that $2d \sin \theta = n\lambda$, where d is the distance between scattering planes and n is an integer. By observing the angles for which strong diffracted beams are obtained, the various scattering planes and

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

their separation may be found. In this way the crystal structure and the lattice spacings may be deduced.

As an example, consider the sodium chloride crystal. This has a cubic structure with sodium and chloride ions at alternate sites (see figure 1.2). The distance a between each site is found by X-ray analysis to be 0.2818 nm. Consider one of the unit cubes of side a. Each of these cubes has 4 sodium and 4 chloride ions, i.e. 4 NaCl molecules. But each corner of the cube is shared by eight contiguous cubes. Consequently each volume a^3 contains one-eighth of four molecules of NaCl $=\frac{1}{2}$ molecule of NaCl. If M = molecular weight, ρ = density, the volume occupied by the half-molecule is $\frac{1}{2}(M/N_A)(1/\rho)$. Consequently

$$a^3 = \frac{1}{2}\frac{M}{N_A}\frac{1}{\rho}.$$

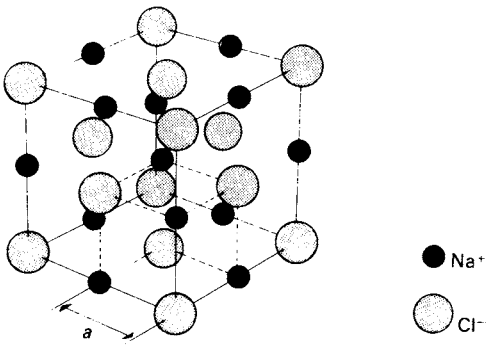
Inserting $M = 0.0585$ kg, $\rho = 2170$ kg m^{-3}, $a = 0.2818$ nm,

$$N_A = 6.02 \times 10^{23}.$$

1.1.5 *Energy states in atoms: the earliest evidence for quantization*

By the turn of the century the work of J. J. Thomson and others had shown that the atom consists of a positively charged massive nucleus and several very light negatively charged particles – the electrons. The problem that perplexed physicists for the next 25 years was the way in which the electrons were linked to the nucleus and the factors that determined the energies of the electrons.

Figure 1.2. Structure of sodium chloride crystal. The sodium and chloride ions are arranged alternately on a cubic lattice, the separation between ions being 0.2818 nm. The sodium fluoride structure is identical except that $a = 0.231$ nm. The unit cell size is $2a$.



© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

The following argument concerning the energy of electrons within the atom has been given by Sir Neville Mott,† and brings out very simply the need for quantization. Consider the thermal properties of a monatomic gas such as neon. The atom has 10 electrons interacting in some way with the nucleus. Careful calorimetric measurements show that the thermal energy per atom of neon is exactly $\frac{3}{2}kT$ where k is Boltzmann's constant (1.380×10^{-23} J K^{-1}) and T is the absolute temperature. If we increase the temperature of the gas by 1 degree the energy increase per atom (at constant volume) is exactly $\frac{3}{2}k$. Now the kinetic theory of gases shows that $\frac{3}{2}kT$ is the kinetic energy of a single particle in equilibrium with its surroundings at temperature T. This means that the only energy which is changed when we heat a neon atom is its kinetic energy as a single entity. If anything within the atom is moving it is not speeded up by the addition of heat, i.e. no energy has been transferred to the constituent parts of the atom.

This has an important consequence for if the electronic energies were continuous they would have to share in the thermal energy of the atom as a whole. They do not do so. This implies two things. First, the electronic energy states are discontinuous: they are at certain specific levels and no energies between these levels can exist. Secondly the gap between these energy levels must be very large compared with normal thermal energies: for this reason electrons cannot be promoted to higher levels at ordinary temperatures.‡ In fact the gaps between the electron energy levels are of order 5 eV which is very much greater than the thermal energy per atom, about $\frac{1}{40}$ eV at room temperature.

This argument provides, with some hindsight, the simplest and most basic evidence for the existence of quantized energy states within the atom.

1.1.6 *Basic structure of the atom*

It is not the purpose of this book to provide a full account of atomic structure. This would involve the wave properties of matter and other concepts used in describing electronic configurations. We shall very briefly fall back on the simple Bohr model: for although this has been superseded by the ideas of orbitals and the uncertainty principle it provides a very convenient model on which to base many order-of-magnitude calculations.

† N. Mott, *Contemporary Physics*, vol. 5 (1964), p. 401.

‡ This has a bearing not only on the specific heat of a gas but also on the Langevin treatment of diamagnetism described on pp. 387–90.

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

If the nucleus has a charge Ze and a specified electron of mass m, charge $-e$, describes a circular orbit of radius r at a speed v, we may balance the centrifugal force mv^2/r with the Coulombic attraction between electron and nucleus. Assuming that there is no shielding of charge by other electrons we may write

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2}\frac{1}{4\pi\varepsilon_0}, \tag{1.1}$$

where ε_0 is the permittivity of free space. The kinetic energy of the electron is

$$\tfrac{1}{2}mv^2 = \frac{1}{2}\frac{Ze^2}{r}\frac{1}{4\pi\varepsilon_0}. \tag{1.2}$$

The potential energy is the work done in carrying the electron from infinity to a distance r from the nucleus. This is given by

$$\int_{\infty}^{r} \frac{Ze^2}{r^2}\frac{1}{4\pi\varepsilon_0}\,\mathrm{d}r = -\frac{Ze^2}{r}\frac{1}{4\pi\varepsilon_0}. \tag{1.3}$$

Note that attractive forces always give negative potential energies. The total energy W of the electron, which is the sum of the potential and kinetic energies, is the sum of equations (1.2) and (1.3) so that

$$W = -\frac{1}{2}\frac{Ze^2}{r}\frac{1}{4\pi\varepsilon_0}. \tag{1.4}$$

The major defects of this model are twofold. First, an electron rotating about a nucleus should, if treated classically, radiate electromagnetic energy and spiral into the nucleus. Secondly, even if such orbits were stable all possible values of W should be possible corresponding to all possible values of r.

When the wave nature of the electron is incorporated into this model both these difficulties disappear. The idea of a crisp orbit is now replaced by a somewhat fuzzy orbital describing the probability of locating the electron. Such an orbital is found to correspond to a stable energy state and no energy is radiated by the electron. Further, a whole series of stable orbitals are permitted as determined by certain (integral) quantum numbers. For example the angular momentum, which in the simple Bohr model has a value mvr, must be quantized to be $n(h/2\pi)$, where n is an integer and h is Planck's constant (6.626×10^{-34} J s). We may pursue this

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

a little further. We write

$$mvr = n(h/2\pi) \tag{1.5}$$

so that

$$mv^2 = \frac{v}{r} mvr = nh(v/2\pi r). \tag{1.6}$$

But $2\pi r$ is the circumference of the orbit (or the orbital) so that $v/2\pi r$ is the frequency ν with which the electron orbits the nucleus. Comparing equations (1.4) and (1.2) we see that the total energy W is equal to $-\frac{1}{2}mv^2$. We thus obtain

$$W = -\tfrac{1}{2}nh\nu = -\frac{1}{2}\frac{nZe^2}{r}\frac{1}{4\pi\varepsilon_0}. \tag{1.7}$$

For the hydrogen atom, where $Z = 1$, the frequency ν becomes

$$h\nu = \frac{e^2}{r}\frac{1}{4\pi\varepsilon_0}, \tag{1.8}$$

a result we use later in this chaper in deriving van der Waals forces.

Of course equations (1.7) and (1.8) still contain r. For each integral value of n in equation (1.5) there will be an associated radius r and if this is fed into equation (1.4) we shall obtain a whole series of permitted energy levels. The result is

$$W = -\frac{1}{n^2}\frac{Z^2e^4m}{2(4\pi\varepsilon_0)^2}\left(\frac{2\pi}{h}\right)^2. \tag{1.9}$$

Using known values of e, m and h we find that for the hydrogen atom ($Z = 1$) the deepest energy level ($n = 1$) has a value of -24×10^{-19} J or -15 eV; the next level ($n = 2$) has a value of -3.75 eV so that there is a gap of over 11 eV. With larger atoms containing more electrons, higher values of n are involved for the lowest energy states but Z is also larger, even if we allow for the effect of screening of the nuclear charge by some of the orbital electrons. In general, the gap between the lowest energy level and the next highest level is of order 5 eV.

Quantum mechanics gives a slightly more complicated picture. The energy levels remain quantized and are still given by equation (1.9), where n is the principal quantum number and can have any value from 1 upwards. The angular momentum, however, is no longer given by $n(h/2\pi)$: it has a value $l^{\frac{1}{2}}(l+1)^{\frac{1}{2}}(h/2\pi)$, where l is an integer which can be either positive or negative but numerically cannot be greater than $n-1$.

© Cambridge University Press www.cambridge.org

CAMBRIDGE

Cambridge University Press
0521406676 - Gases, Liquids and Solids: And Other States of Matter, Third Edition - D. Tabor
Excerpt
More information

This has an unexpected consequence. The lowest energy state is $n=1$: to this corresponds $l=0$. This means that the lowest energy state (the S orbital) has zero angular momentum – the electron does not move in a circle, it moves in and out radially. There is no simple classical analogue although one might regard the smeared electron cloud as pulsing in and out.

An orbiting electron behaves like a circulating current and its interaction with an applied magnetic field determines the magnetic properties of the atom or molecule. For this reason the quantization of angular momentum is of great importance in explaining atomic magnetism. The detailed behaviour is very complicated since the angular momentum must itself follow further quantization rules when exposed to a magnetic field. However, as we shall see in a later chapter, many of the basic magnetic properties of atoms may be understood in terms of the simplest models.

1.1.7 *Charge, mass and configuration of atoms: the periodic table*

We may now summarize the main features of atomic structure and establish the basis on which the periodic table of elements may be constructed.

1. An atom consists of a minute nucleus, which is positively charged and contains the main mass of the atom.

2. The nucleus consists of protons and neutrons. These are of equal mass but each proton carries a positive charge whilst the neutron carries no charge. The resultant positive charge (referred to the proton as unit charge) is called the atomic number Z, i.e. Z is equal to the number of protons in the nucleus.

3. As a crude approximation, valid especially for smaller atoms of atomic number less than 20, there are about equal numbers of protons and neutrons so that the mass of the nucleus, referred to the proton as unit mass, is about twice the atomic number. This is known as the mass number and in practice is the integer nearest to the mass of the atom, referred to the carbon-12 atom as 12.000. In the older literature the mass number is sometimes loosely referred to as the atomic weight.

4. The nucleus is surrounded by electrons. These have a mass only $\frac{1}{1840}$ of the mass of the H atom (i.e. of a proton or neutron) and they have a unit negative charge.

5. Since the atom is electrically neutral the number of orbital electrons is equal to the atomic number.

6. The chemical properties of the atom are determined by the configuration of the electrons, especially of the outermost ones.

© Cambridge University Press www.cambridge.org