

Vacuum Science and Technology

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Vacuum Science and Technology

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Preface

In 2000 the Dutch Vacuum Society NEVAC published our "Basisboek Vacuümtechniek" (BBVT) for the benefit of the vacuum technology courses offered under the auspices of NEVAC. The content not only successfully supported lectures on vacuum technology at universities and colleges, but also provided a solution for the need of an extended Dutch-language reference work. Without exaggeration we may state that the book has since become a standard work in the fields of vacuum physics and technology. After two reprints in 2003 and 2008, it is justified to speak of a "Dutch bestseller". This was not unexpected, because the book contains a wealth of information presented in a clear and concise way.

As Dutch universities and high tech industries are more and more populated by PhD students in physics and chemistry from foreign countries and highly skilled foreign employees, the requirement of an English translation arose. In addition, there was a growing call from home and abroad to produce an English language book suited for world-wide distribution. Thus, the seed of an idea for a translation was born. The subsequent road map to the English version of our book was however a long and difficult one. Not only did the translation of such a specialist technical work give several expected and unexpected problems for Dutch authors, but, in addition, after more than a decennium the book needed a serious revision and update. For example, recent developments in vacuum pump design in answer to demanding physical problems, like within the semiconductor manufacturing industry, were missing. Furthermore, substantial updates were necessary in the field of (partial) pressure measurement, leak detection and cleaning and working discipline.

As a result, the English version 'Vacuum Science and Technology' (VST) presented here covers all the currently relevant vacuum topics and can really be classified as a contemporary book in the field of vacuum physics and technology.

In order to get an impression of how the book has been updated to current state of the art, a brief overview is given of the main innovations with respect to the Dutch version of 2000. The large chapter 4 about pumps and pumping systems contains some major changes and significant innovations with respect to the Dutch book. First of all, we added a separate

paragraph about compression. Furthermore, the chapter is extended with attention to the multi-stage Roots pump, which in the past decade has rapidly developed into a valuable alternative to the claw pump and is able to discharge to atmospheric pressure. In the paragraph about the claw pump, new insights are incorporated about the use of an integrated combination of Roots and claw stages. Concerning the screw pump, attention is paid to the tapered pitch as a solution to reduce the heat generated by isochoric compression. The section 'Molecular pumps' is extended with a paragraph on the combination 'Molecular drag pump (MDP) + side channel pump', consisting of a Holweck type molecular drag pump and a multiple stage miniature type of side channel blower. This pump combination appears to be able to discharge against atmospheric pressure. The required knowledge regarding the side channel blower is added as a separate paragraph to the section 'Dry rotary pumps'. The section 'Sputter-ion pumps' is supplemented with information on the so-called 'Galaxy' and 'StarCell' cathode structures to increase the pumping speed for noble gases.

Chapter 5, which deals with total pressure measurement, is extended with the quartz crystal friction pressure gauge and a Bourdon variant with electronic readout.

In the overview on ion sources in chapter 6, about partial pressure measurement and gas analysis, the axial and gas tight ion sources are added. The section on the quadrupole mass spectrometer (QMS) is provided with a short piece about a special focusing method whereby electron-stimulated desorption (ESD) can be identified and suppressed. Furthermore, the chapter includes a section on the autoresonant trap mass spectrometer (ARTMS). The expectation is that this residual gas analyzer (RGA) is going to be a serious competitor of the QMS in the pressure range 10^{-3} - 10^{-9} Pa. The setup of the section 'spectrum analysis' has changed substantially, while error rates get more attention.

The layout of chapter 8 about leak detection has been completely revised. As concerned to helium leak detectors, the emphasis has moved to the counterflow principle. The maximum achievable sensitivity of counterflow leak detectors has become comparable with that of main flow detectors in the past decade. This circumstance, added to the user-friendliness of counterflow detectors, has now meant that main flow detectors are no longer commercially available. Two inside-out leak detection methods are added, namely the atmosphere method and the bombing method. In a separate paragraph a quantitative analysis of the sensitivities of both methods and their usefulness in specific circumstances is discussed. The arsenal of available leak detection instruments has been extended with multigas sniffer systems (e.g. infrared leak detector), the hydrogen leak detector and the quartz window sensor.

In Chapter 10, about material selection, lubrication, cleaning and working discipline, the section 'Cleaning procedures' has been adapted to the changed views in this area and more focused on complete vacuum systems.

By keeping the overall framework of the Dutch book, VST can not only be considered as an excellent reference book, but is also a unique double-level textbook for both high and middle graduates. Text meant for high graduates is placed behind margin lines. Omitting this text gives a clearly structured textbook for middle graduates. Both with and without the margin texts the volume shows the desired internal coherence for the associated training level. Several chapters are provided with exercises, divided in two levels of difficulty. Exercises with/without asterisk are appropriate respectively for high and medium graduates. Short answers have been added at the end of the book. The "two books in one" format makes the work perfectly suited for self-study and (combined) high and medium level trainings. A multi-level training approach will be particularly useful in the common case of a group of course participants with a wide range of (academic and medium) preparation and/or experience.

After publication of the 1st edition hardcover in february 2016, the E-book version has been supplemented or amended on some points. A substantial update is the inclusion of all fully worked solutions to the chapter exercises. This to further enhance the book's quality as an excellent course manual with his unique integrated two-level setup.

A noteworthy addition to chapter 5 'Pressure measurement' concerns a new type of ionization gauge, based on the Bayard-Alpert design: the so-called "Belt Bent-Beam" (3B) gauge. A brand new concept, in terms of objective akin to the classic extractor gauge: Keep the gauge ion collector as far away as possible from all radiation and desorption effects. The X-ray limit of the 3B-gauge is in the low 10^{-12} Pa range. This extremely low limit is achieved through a combination of material choice (low heat radiation and outgassing) and a smart geometry (low flux of soft X-rays and ESD in the collector area). Furthermore, the number of pressure zones below 1 atmosphere has been expanded from four to five. In more recent vacuum literature and advertisements from vacuum manufacturers, for the sake of distinction and convenience, in line with the well-known ultra-high vacuum pressure range 10^{-4} - 10^{-7} Pa, the term "extreme high vacuum" (XHV) is increasingly used to denote the pressure range below 10^{-7} Pa. We've the whole book conformed to this additional vacuum terminology; see figure 5.1.

The authors would like to respond to criticism (comments) by some official reviewers and respondents to the 1st edition regarding the lack of literature references in the book. On this point they hold a clear opinion: although their decision to not include references in VST may perhaps slightly affect its value as a reference book, they nevertheless believe this disadvantage does not outweigh the advantage of a textbook where the flow of reading is not disturbed by excessive well-intended references. Furthermore, in the authors' opinion online facilities meanwhile guarantee an inexhaustible, ever-renewing and growing source of information for those who want to "dig deeper" into a specific subject. For example, the

free encyclopedia Wikipedia.org offers up-to-date information and literature references on nearly all vacuum topics. Viewed in this light, it seems reasonable to argue that including references becomes less essential.

Attentive readers will also note that source references are missing for a lot of the graphs, drawings and illustrations. For clarity and as accountability, it's therefore worthwhile mentioning that in more than half of all figures the authors themselves acted as sources with measurements, graphs, etc. obtained in their own research. Sources of approximately 40% of the figures are unfortunately no longer traceable. They were initially used in our earlier Dutch books and lecture notes and originate from scientific papers, books and catalogs of around the mid-last century when vacuum technology was still being practiced with scientific ambitions by a relatively small "inner circle" of fellow scientists. Undoubtedly the use of these figures at that time would informally be agreed, but written agreements have unfortunately been lost or even may never have been made. All more recent figures (about 10%) are provided with a source acknowledgement.

The authors are indebted to Dick van Langeveld for his valuable contribution to the new set-up of the section on spectrum analysis in chapter 6, useful discussions on various relevant topics (piezo electricity, equations of motion of the quartz crystal in a quartz crystal friction gauge) and initiating useful contacts of various kinds. Our thanks also goes to Dr Masahiro Hirata (National Institute of Advanced Industrial Science and Technology, Japan) for useful email correspondence concerning the physics of a quartz crystal friction gauge. We express our gratitude to Harold Zandvliet (University Twente, Enschede, NL) for critically reading section 8.9.2 dealing with the hydrogen leak detector. His comments have contributed significantly to our understanding of the physics of this detector. We are very grateful to Norbert Koster (TNO Science and Industry, Semiconductor Equipment, Delft, NL) and Peter van der Heijden (VDL Enabling Technologies Group, Eindhoven, NL) for their contributions to the update of the section on cleaning in chapter 10. For incorporating the ceramic bead blasting cleaning technique in chapter 10, the information in the prospectus 'Ceramic bead blasting of stainless steel' from Vecom, a company based in Maassluis, NL, was very helpful to us.

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Special thanks are due to Sam Jimenez for his excellent book review. He really has managed, using his own words, "To aim for language that is grammatically 100% correct but which sounds slightly international, which is what I tend to find when I read published literature from non-native speakers. It could always be rewritten in more depth to make it sound like it was completely written by a British English speaker but I think that it would take away from the fact that it is a collection of Dutch expertise". This wise view and all his help as a reviewer have undoubtedly contributed to the confidence of the authors in their aim to come to a valuable English translation of their Dutch book.

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Peize (NL)
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1

Basic concepts

1.1 INTRODUCTION

In Latin, vacuum means 'void of air'. However, when we speak about 'vacuum' we usually do not mean 'void of air' in this strict sense. If the total pressure of a gas or a mixture of gases in an enclosed chamber is lower than the 1 atmosphere air pressure surrounding us, we say 'there is vacuum in the chamber'.

Even though it is not usual to speak of 'vacuum' in situations where the pressure is only a little less than 1 atmosphere (e.g. in the high mountains), this natural limit of 1 atmosphere has been chosen in order to clearly demarcate the vacuum range at the high-pressure end. The other extreme of vacuum, the complete absence of gas particles, will in practice never be attained. The closest one can get to this condition is in the low pressure regions of intergalactic space, where the gas density is estimated to be in the order of 10^4 hydrogen atoms per m^3 . If based on astrophysical grounds a 'temperature' of 10^4 K is assumed for this hydrogen gas, this density corresponds to a pressure of approximately 10^{-20} (!) atmospheres. In enclosed volumes on Earth gas densities down to 10^9 particles per m^3 are achievable nowadays, corresponding to a room temperature pressure of about 5×10^{-17} atmosphere.

The term 'vacuum technique' refers to methods and techniques used to obtain and measure pressures below 1 atmosphere. Vacuum technique plays a crucial role in today's science and industry; we only need to think of examples like vacuum packaging, light bulbs, degassing, freeze drying, TV and computer monitors, the manufacture of thin films, pure metals, semiconductors, and closely related to this the research on solid state surfaces. It's not too much to say that without the ability to evacuate large and small volumes, our society would remain at the technological level of the early 20th century.

After a brief historical review, we will discuss in the following paragraphs the fundamental physical laws which govern the behaviour of vacuum and play a role in the technique of evacuation. To this end, it is necessary to have some insight in the characteristics and structure of gases, but also of liquids and solids. The properties of rarefied gases at

different pressures and temperatures are quite well explained by the kinetic theory of gases. The basic principles of this theory will be discussed, including topics such as the thermal motion of gas particles, the mean free path, rate of incidence, vapour pressure, evaporation rate etc. Also the empirical gas laws of Boyle/Gay-Lussac, Avogadro and Dalton have their formal basis in the kinetic gas hypothesis. Finally, we will focus on some non-equilibrium properties of gases at high and low pressures (thermal conductivity, viscosity, diffusion). The reasonably good agreement between the kinetic transport laws and experimental practice evidences the validity and usefulness of the kinetic gas theory.

1.2 HISTORICAL OVERVIEW

For the first ideas around the concept of 'vacuum' we must go back to the time of the Greek philosophers. Even before our era, in particular, Aristotle (382-322 BC) dealt with the question of whether a vacuum could exist. He argued that nature would abhor vacuum and therefore not allow the existence of empty space. This view, known as the 'Horror Vacui', lasted for twenty centuries.

Renaissance brought a change of views on many subjects. Through experimental observations, Copernicus, Kepler and Galilei discovered the earth to revolve around the Sun. This put a new trend in thinking. The philosophical approach was increasingly abandoned to make way for more rationalism, the search for an explanation of physical phenomena by conducting experiments.

The immediate reason for research on 'vacuum' came from the inability to pump water out of deep wells. Initially it was assumed that the applied pumps simply were not 'good enough'. One didn't yet recognise that the actual cause was a 'lack of air pressure'. Nevertheless, based on these and other observations, Baliani built in 1639 an instrument that today would be termed as a 'water barometer'. Then, Torricelli in 1644 filled a long glass tube with mercury and placed it upside down in a container with mercury. The mercury inside the tube dropped to a height of about 76 cm above the mercury level in the container. While he believed, above the mercury column an 'empty space' had been created, a clear explanation was not forthcoming. Through an extensive correspondence with other scientists this new knowledge spread all over Europe.

In this way also Blaise Pascal was informed about 'Torricelli's experiment' and repeated the test several times. To prove that the mercury column in the tube was held up by the prevailing atmospheric pressure, he asked his brother-in-law Perier in 1648 to repeat the experiment on the Puy de Dome, a 1465 m high mountain near ClermontFerrand. On top of the mountain the mercury column only came to a height of 65 cm! 'Horror vacui' anyway seemed to be different on top of the mountain. In honour of this 'evidence' today's standard unit of pressure is named 'Pascal'.

More or less parallel to these facts, Otto von Guericke in Magdeburg designed a pump by which a beer barrel, first filled with water and then sealed, could be evacuated. Shortly thereafter he replaced the leaky wooden beer barrel by two copper hemispheres placed against each other to form a single enclosed sphere, which could withstand the outside air pressure. To demonstrate the force of this air pressure, he did an experiment in which he evacuated the sphere and subsequently tried to pull both hemispheres from each other with two teams of eight horses. This 'Test of the Magdeburg hemispheres' drew a lot of attention during the Reichstag in Regensburg (1657). The Jesuit Father Caspar Schott repeated these experiments and described them in detail. In this way the new knowledge about this 'vacuum set-up' quickly spread. In The Netherlands, the phenomenon drew the attention of scientists like Christiaan Huygens, 's Gravensande and Peter van Musschenbroek; in England Robert Boyle and Robert Hooke were involved. The experiments of Boyle eventually led to the famous 'law of Boyle'.

After this period, the phenomenon of 'vacuum' remained for some time in the ambiance of 'Physique Amusante', until in the mid-19th century a new phase down to much lower pressures was initiated by the invention of mercury-filled pumps by Geißler (1857), Töpler (1862) and Sprengel (1865). At the same time pressure measurement also became possible. The measuring range of the meanwhile well-known U-tube mercury manometer was expanded with the compression manometer of McLeod (1874). Edison's invention of the light bulb in 1879 was possible thanks to the low pressure he could achieve with a Sprengel pump.

A common disadvantage of the aforementioned pumps was their low pumping speed. However, a breakthrough took place in 1905 with the invention of the mercury filled rotary pump by Gaede. Using Bunsen's water jet pump (1870) as a roughing pump, Gaede achieved a pressure of about 10^{-3} Torr in a short pump time. In 1908 Gaede came up with an improved design for an oil-lubricated rotary pump, developed some years before by the Siemens employee Hoffman (1904). From that moment on, this improved version became known world-wide as the 'Gaede pump' and in fact can be considered as the forerunner of the current rotary-vane pump.

In 1911 Gaede designed the molecular pump: a fast-moving wall transfers momentum to gas particles colliding with it. This gives the gas particles an extra velocity component in the direction in which they should be discharged. Unfortunately however, the mechanical industry at the beginning of the 20th century was not yet sufficiently advanced for mass-production of this pump with the required accuracy.

In 1913 Gaede invented the mercury diffusion pump, improved by Langmuir in 1916 and later made to run on oil by Burch. These inventions came precisely at a time when the rapidly emerging light bulb and radio tube industry felt the need for well-functioning high vacuum pumps. Parallel to these developments in the field of hardware, researchers like

4 BASIC CONCEPTS

Knudsen, Langmuir and also Gaede progressed with the implementation of the kinetic theory of gases, while Clausing and Knudsen came up with a more detailed description of how gas flows under rarefied gas (molecular flow) conditions.

Although through all these developments vacuum in the period after 1910 found more and more application in such areas as the chemical industry, the pumping of vapours remained a problem associated with the condensation that occurs during compression. Only when Gaede conceived the gas ballast principle in 1935, did the problem come to the end.

The disadvantage of the intermittent pressure measurement with the McLeod compression manometer was overcome in 1906 by Pirani's thermal conductivity gauge, followed in 1916 by Buckley's ionization gauge, derived from the triode radio tube. In 1937 the Philips employee Penning invented the cold cathode ionization gauge. Although it became readily clear that this so-called 'Penning gauge' possessed a pumping action, it would take until 1958 before this principle was used in the so-called sputter-ion pump. The low-pressure range of the conventional hot cathode ionization gauge was improved in 1950 by the American researchers Bayard and Alpert. Today their 'Bayard-Alpert (B&A) ionization gauge' is still the most widely used high vacuum gauge.

In 1954 the arsenal of vacuum pumps expanded with the Roots pump: a dry rotary pump based on the principle of the air blower, developed by the Roots brothers already in 1868 to evenly boost a forge!

Between 1956 and 1959 Gifford and MacMahon developed a new method to achieve low temperatures: by compression and expansion of helium it appeared possible to cool a solid surface down to 10-20 K. It then took until 1974 before the first cryo pump based on this principle became commercially available.

A well-known disadvantage of the diffusion pump - the backflow of oil vapour to the high vacuum side - received new interest with the rise of surface science in the fifties. The predominant adsorption of oil vapour molecules flowing back to high vacuum rendered measurement on really clean surfaces an impossible goal. In 1958 Becker made an attempt to eliminate this problem by mounting a rotating baffle in the form of a fan on top of a diffusion pump. This turned out to be an effective tool, especially when a multiple stage fan was used. Since the baffle not only reduced the back-streaming of oil vapour, but also gave a considerable increase in pumping speed, Becker decided to further refine this 'rotating baffle' and build it as a stand-alone unit: the turbomolecular pump was born. The extensive mechanical and electronic developments since the beginning of the 20th century made this pump, unlike the former molecular pump of Gaede, become a successful design. Currently, the turbomolecular pump is considered as the 'workhorse' in high vacuum technology.

The same trends made it possible in 1977 to turn a theory of Knudsen dating from 1920 into a new manometer based on the phenomenon of gas friction: the spinning rotor gauge.

This vacuum gauge with a 'floating steel ball' has since proven to be the most accurate and reliable contemporary pressure gauge and, once self-calibrated, can be effectively used as a calibrator.

The rise of the semiconductor industry in the 1980's sharply increased the demand for dry-running roughing pumps. The vacuum industry was faced with new challenges, leading to the development of the claw pump, scroll pump and screw pump. In the 1990's, due to increasingly stringent environmental regulations for the semiconductor industry as well as other industrial fields (especially the chemical industry), these dry rotary pumps became an attractive alternative for the hitherto used wet pumps.

At the end of this brief historical overview we conclude that the concept of 'vacuum', as developed in ancient times, has matured into a widely applied technological field only in the 20th century. The vacuum technique has provided appropriate experimental conditions for a variety of scientific discoveries in physics and chemistry. In addition, many industrial developments and innovations would have been inconceivable without the application of vacuum conditions.

1.3 MOLECULES AND ATOMS

All solids, liquids and gases are made up of molecules and atoms. A 'molecule' is defined as the smallest particle of a substance that still has the same properties as the substance itself. Each substance consists of a large number of identical molecules. There are millions of different species of pure substances and just as many different types of molecules.

Molecules are further split into even smaller particles called 'atoms'. (Keep in mind that by separating a molecule into its constituent atoms, the properties of the molecular substance are lost!) Atoms are the smallest particles of an element (examples of elements are: hydrogen, nitrogen, mercury, copper, silver). There are just as many types of atoms as atomic elements: a total of about 90. Molecules are made up of the atoms of these elements. Molecules of an element are simply individual atoms of that element (e.g. helium and argon) or pairs of atoms (e.g. hydrogen, oxygen, nitrogen). In the case where molecules consist of atoms of different elements, we speak of a compound. Examples are natural gas, water and iron oxide. The question now arises: what precisely is an atom and in what sense do different types of atoms (elements) differ from each other?

To answer this question think that in one way or another electrons can be released from all substances. Electrons are very small negatively charged particles. All atoms must therefore contain electrons. However, since all substances are electrically neutral, the negative electron charge has to be compensated by a positive charge. The next question is, what are the carriers of this positive charge and where are they located in the atom? The answer to this question was first given in 1911 by the famous English scientist

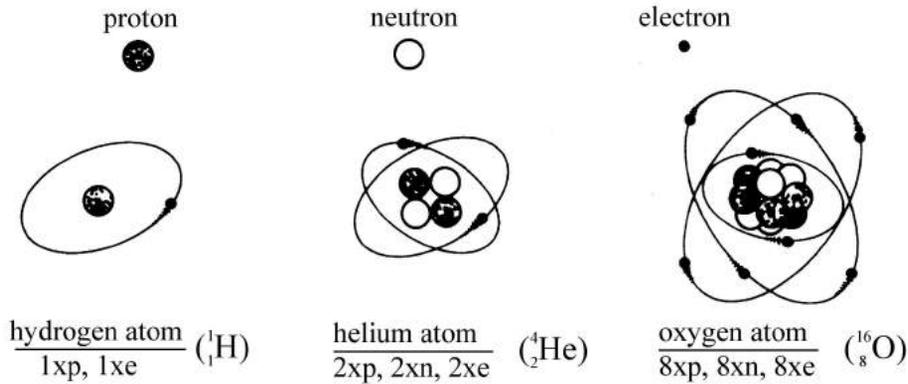


Figure 1.1
The structure of some atoms.

Rutherford. From experiments Rutherford concluded that atoms had to be very 'empty' structures with a small nucleus (core) in the centre. The positive charge and by far most of the atomic mass is concentrated in this nucleus. The negative electrons as it were form a 'cloud' around the nucleus and, according to Rutherford, move in closed orbits around it (cf. motion of the planets orbiting around the Sun).

The structure of the atomic nucleus and in particular the magnitude of its positive charge determine the type of atom. Each nucleus consists of one or more particles with approximately the same mass, called *nucleons*. Two types of nucleons can be distinguished:

1. *Protons*: positively charged particles, the charge being equal in magnitude, but just opposite to that of a (negative) electron. For each proton in the nucleus there is one electron around it. Consequently, the total positive and negative charges exactly cancel each other, thus making an atom as a whole to be electrically neutral.
2. *Neutrons*: uncharged particles, electrically neutral.

The proton and neutron masses are (approximately) equal: 1.67×10^{-27} kg. The mass of an electron is 1836 times smaller: 9.1×10^{-31} kg. Thus, the contribution of the electrons to the total mass of the atom is negligible, i.e. the atomic mass is almost entirely determined by the number of protons and neutrons in the nucleus.

In figure 1.1, the structure of some types of atoms is shown schematically. Note that the ratio of the diameters of nucleons and electron orbits is a lot smaller than pictured.

The left hand atom in figure 1.1 represents the hydrogen atom. This is the most simple atom: the nucleus consist of only one single proton and one electron revolves around it. As a matter of course, this atom has the smallest possible mass, approximately equal to the

proton mass: 1.67×10^{-27} kg. Atomic masses are always (approximately) a multiple of the hydrogen mass. Therefore, instead of expressing the mass in kg, it is easier to introduce a new unit called *atomic mass unit*, abbreviation amu (or in short u). 1 amu is (approx) equal to the mass of a proton. Thus, expressed in amu the mass of a hydrogen atom equals 1. Expressed in units amu the atomic mass is usually called *mass number*. Thus, the mass number of hydrogen is 1.

The central atom helium has a nucleus with two protons and two neutrons. Consequently, the mass number of helium is 4. The right atom, consisting of 8 protons and 8 neutrons, represents oxygen with a mass number 16.

The existence of a nucleus with only two or more protons is not possible; bringing them together creates problems because similar charges repel each other. However, the presence of neutrons leaves this possibility open and allows protons to be in each other's vicinity. Thus, for a stable nucleus to contain more than one proton, the addition of neutron 'couplers' is an essential necessity. For larger atoms, the number of neutrons required to form a stable nucleus, is slightly larger than the number of protons.

The number of protons (in a neutral atom equal to the number of electrons) in the nucleus is called the *atomic number*. Accordingly, the atomic number of hydrogen is 1, the helium atom contains 2 protons and has an atomic number 2, while the atomic number of oxygen equals 8.

Atoms having a specific atomic number (= number of protons) may differ in their number of neutrons. We speak in this case of *isotopes*. Isotopes are atoms of the same type (= element), but with different mass.

Example

All chlorine nuclei have 17 protons. However, the number of neutrons can be 18 or 20. Consequently, there are two stable chlorine isotopes to distinguish with mass numbers 35 and 37. Their respective notations are ${}_{17}^{35}\text{Cl}$ (75%) and ${}_{17}^{37}\text{Cl}$ (25%). The numbers in brackets represent the natural abundances of the two isotopes.

From experiments atomic diameters have been calculated to be in the order of 10^{-10} m, while the diameters of the nuclei are in the order of 10^{-15} m. The atomic nucleus is therefore 100.000 times smaller than the atom itself.

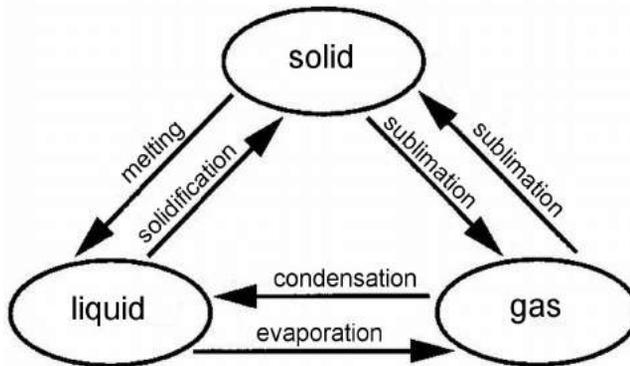
Different atomic species do not greatly differ in diameter; the largest atom is not more than roughly 5 times as large as the smallest one.

If we know the atomic composition of a molecule and the masses of all its composing atoms, we can easily calculate its molecular mass.

1.4 PHYSICAL STATES OF MATTER

Most substances have three different physical states or phases:

- a. Solid phase (e.g. ice)
- b. Liquid phase (e.g. water)
- c. Gaseous phase (e.g. water vapour)



In a solid the atoms (or molecules) are in a close packed structure at fixed positions relative to each other. They are held together by interatomic or intermolecular attraction forces, collectively called cohesive forces or van der Waals forces (see also chapter 2). The thermal energy in a solid manifests itself in vibrations of the atoms or molecules around their equilibrium positions. Normally, these vibrations are not strong enough to break up interatomic bonds. However, if the solid is heated, these vibrations strongly increase. At sufficiently high temperatures, the regular atomic or molecular bonds will eventually break up, the solid melts and forms a liquid. By cooling the liquid will *solidify* again and thus returns to the solid phase. Some solids turn directly into vapour when heated without passing the liquid phase. This phenomenon is known as *sublimation* and forms the basis of, for example, the vacuum freeze-drying process.

In the liquid phase the atoms (or molecules) are also close to each other. Their relative positions however are not fixed. They move at random and more or less freely in the fluid, but are still held together by interatomic (or intermolecular) bonding forces. When the liquid is heated, their movement can become so violent that at a certain temperature they overcome their binding forces and escape from the surface. This happens for instance, when the liquid boils and turns into gas (or vapour). The transition from liquid to gas is called *evaporation*. Conversely, if a gas particle, in collision with the liquid surface, under

influence of the van der Waals forces returns into the liquid phase, then we speak of *condensation*. The stronger the bond strength, the stronger the thermal motion must be in order to evaporate the liquid. The boiling point of a liquid therefore is a measure of the magnitude of the bonding forces.

In the gaseous phase the particles move freely with respect to each other at relatively large distances. In atmospheric air at room temperature, for example, all molecules together occupy only 0.01% of the available space. In a solid this fraction is usually well above 50%. Although interatomic forces no longer have any effect, the gas particles collide with each other and with the walls of their container, and thus scatter in all directions. A key result of this chaotic motion is that a gas will always evenly spread over the available space.

1.5 KINETIC THEORY OF GASES

Since in a gas we usually have to deal with a very large number of particles - even at the currently lowest achievable pressure of about 5×10^{-17} atm 1 m^3 gas at room temperature still contains about 10^9 molecules - it will be understood that a description of the individual behaviour of all these particles is not possible. We must therefore be content with a description of the macroscopic behaviour of a gas, such as we perceive it. The kinetic theory of gases is a statistical model that allows us to predict this macroscopic behaviour of a gas. The theory is based on two fundamental assumptions:

1. The gas is composed of a large number of molecules which, for a particular type of gas, are completely identical in size, shape and mass.
2. The molecules are in a continuous chaotic motion. Their mutual collisions and collisions with the wall of their enclosure are fully elastic.

A gas that meets these conditions is called an *ideal* gas. Real gases under vacuum conditions (< 1 atm) to a good approximation appear to behave as ideal gases.

The kinetic theory enables us to calculate the probability that a random gas particle is found in 'a certain state'. This state (or property) may be, for example, its velocity, energy or specific location in space. This probability multiplied by the total number of particles in a given volume of gas yields the number of molecules that *on average* will be in a particular state (or have a particular property). We write here 'on average' because the actual number will in fact vary from moment to moment. This variation is however very limited when dealing with large numbers of particles. The mathematical formula used to calculate the probability for a gas particle to be in a particular state is called the *distribution function*.

Suppose the state of a gas particle to be completely determined by s position coordinates q_1 to q_s and s momenta p_1 to p_s (for a monatomic gas $s = 3$: $q_1 = x$, $q_2 = y$, $q_3 = z$, $p_1 = p_x$, $p_2 = p_y$, $p_3 = p_z$). We are able then to introduce a statistical distribution function $f(q_1, q_2, \dots, q_s, p_1, p_2, \dots, p_s)$ according to the usual definition: