

Sauermann

Barke

**Chemistry
for Cross Entries**

Volume 1

Structural chemistry and
particle systematicity

Chemistry for cross entries

Volume 1: Structural chemistry and particle systematicity

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Preface

It can be read in any encyclopaedia: "Chemistry is the science of the substances and their transformations." The non-initiate shudders upon hearing this, nowadays even reacts with rejection. At school **chemistry is almost bottom in the rankings of the favourite subjects**, it is considered being difficult and unfathomable. For the novice, even when being really curious and eager to learn, chemistry becomes increasingly difficult after the first acquaintance, although there exist beginner's chemistry textbooks in wide abundance.

What is the reason that pupils of secondary schools feel that chemistry is a subject of horror? **What are the reasons** for students of mechanical engineering, electrical engineering or civil engineering possibly failing the subject chemistry? This question has accompanied the authors during almost thirty years of teaching in industry and universities as well as pupils in secondary state schools.

The answer can be found looking at the history of chemistry and looking back for a moment. The corrosion of iron or the burning of coal are very old experiences of humankind. A substance changes or seems to disappear completely. Due to those and other experiences alchemists and chemists have planned and evaluated experiments, have sorted their observations into systems and even described those with secret and unfathomable formulas and symbols. In former times every chemist and every layman alike could perceive substances only in the form which was available for humankind: a much sought after gold nugget, red-brown copper crystals, clear water in a glass, white sugar or salt crystals. Today we call this the **macroscopic apparition of the substances**. The corrosion of iron and the burning of coal therefore show changes in the macroscopic characteristics of those substances.

However, an unambiguous description, order, overview and systematicity of the substances and their conversions based alone on the macroscopic apparition is not possible. Therefore the modern science of chemistry with its systematicity has its **roots not in the chemical art of cooking in the laboratory but in philosophy!** The tragedy of the subject of chemistry is due to the fact that this insight has been totally lost for the teaching at university and chemistry lessons at schools.

What is now the core of this philosophy underlying chemistry? Some Greek philosophers had an age-old dream. They wanted to explain unambiguously the world and its manifold

apparitions based upon the **combination of basic building blocks**. They wanted to assemble the world like a child building today with his Lego blocks. This building block kit philosophy was taken over by the chemists at the beginning of the 19th century because it was the best system to be applied to successfully interpret the observation of many materials and their conversions.

As basic building blocks today spherical atoms and ions are assumed and substances are described as combinations of an uncountable amount of atoms or ions in particle aggregates. In doing this the modern chemist carries on the tradition of the old philosophy. Insofar he has to interpret and converse his substances from a macroscopic world into a microscopic world: He has to imagine a piece of gold, iron or coal as being a systematic combination of smallest particles. Regardless of the experiments and observations carried out in the laboratory - the chemist does not see the smallest particles! He normally does not see anything that is important for him - **therefore the smallest particles always have to accompany the chemist in his imagination when carrying out experiments**.

Also the beginner has to submerge into this imaginative world of the tiny, invisible particles. Then he will be able to answer consistently many questions of everyday experiences and technology, even to foresee them. Why does corrosion at the car appear under the coating as a bump? Why cannot gold be manufactured chemically from lead? Why does ice swim on top of water? How does the binding of gypsum work? Nowadays many substances are specially manufactured based on the philosophy of the macroscopic particles in order to achieve certain characteristics of the materials: beginning with glasses with certain characteristics of refraction, continuing with corrosion-resistant materials with a certain hardness, up to pharmaceuticals. In every case imagination is important.

This bears the greatest difficulty for the beginner. Insofar this book shall develop, strengthen and train the power of imagination and the imagination needed for chemistry. In order to achieve this for the time being substances will only be presented and transferred into a microscopic way of viewing. The systematic order and combination of particles within space belongs to this field. Such particle combinations within space are called **chemical structures**. For the learning process it is now absolutely vital to understand those structures with the aid of **structural models**: the best way is for the beginner to build them with balls commercially available or with the pre-built building blocks of a model building kit.

It is decisive for the beginner and cross entry alike that the **chemical symbolism**, which is used by the chemist for his substances in form of formulas and reaction equations, can be

directly developed and derived from the structure. This will be shown consistently for all substances treated so that the novice can acquaint himself fast and with certainty with the chemical language of symbols.

The question how far one tries to deduce and to justify the **bonding forces between the building blocks** from causes will be totally in the background at the beginning - only the **effects** of forces are primarily of importance. Descriptive calculations of wave and quantum mechanics are not used in this framework for good reasons.

Since at the beginning of this introduction of the subject of chemistry knowingly no questions concerning the chemical bonding but preferentially questions concerning structures are treated we call this concept **structural oriented**. Based on the structure in a second step the chemical reaction is interpreted as a rearrangement of the particles.

The excerpt of substances out of the about 12 million substances, which have been known and synthesised until today, is exemplary. The substances chosen by us are supposed to show the most important basics of particle combination and particle rearrangement. In order to answer special questions with regard to characteristics of certain substances and the whole "chemistry of the materials" we only refer to the known encyclopaedias of chemistry.

This book sequence is made for everyone who, coming from the macroscopic knowledge of many substances, would like to enter the modern microscopic chemistry or who want to "cross enter" from other subjects. A **cross entry** therefore is possible into any volume of this sequence, because the structure of the materials treated can be reproduced and therefore be "understood". This concept has been primarily developed for students of technical vocations: mechanical engineers, civil engineers, electrical engineers, public utility engineers. It also is supposed to appeal to interested and motivated pupils and anyone who is interested in chemistry as a minor subject. We further hope, that many teachers, who want to optimise the success of teaching their subject, can take any useful stimuli from this sequence of books.

In the first volume the periodic table will be presented as a "particle building kit" with the corresponding common combination rules. The special particle combinations leading to metal crystals, molecule crystals and ion crystals will be found in the further volumes.

After the structures of important groups of materials have been studied in a first section, then in a second section the chemical reaction is to be interpreted as a rearrangement of structures.

If the structures from the first section, which take part in the reactions, are known, then a cross entry into the world of chemical reactions is possible.

In this sense enjoy the studies of chemistry on a structural oriented pathway.

Muenster and Munich in January 1997

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Introduction

Chemistry as the offspring of philosophy

For millennia people have wondered how our world had come into existence, which regularities govern it and which "sorting hand" had created those regularities. The question of the "sorting hand" stems directly from the religious domain and from this source arise the questions modern chemistry is still dealing with. For the time being this may sound strange when thinking about modern laboratories with their complicated equipment. Chemistry, as often said, is the classical science about materials, the substances and their transformations, therefore chemistry is based upon the experiment like no other science, laboratory and the experiment come in first place for all work to be done.

Undoubtedly in chemistry extensive experiments are carried out in a large number. However, the experiment always contains a strictly intellectual background, it has to help to decide about theories, to prove or disprove them. The decisive factor in the chemist's work is therefore not the experiment alone, but still the corresponding theoretical construct of ideas.

For millennia people have carried out experiments with many substances. Fire, ceramics, the production of copper and bronze, the dyeing with crimson are some examples. From ancient Egypt there is even known a galvanisation method for the gold-plating of copper figures. But still all those skilful people, who possessed those manufacture skills, were no chemists: they lacked the extensive intellectual system of thoughts.

This system started to mature with a range of excellent thinkers, the Greek philosophers during the era of about 600 - 350 BC. These philosophers of nature are also called "pre-Socratics", among them are Thales, Anaximenes, Heraklith, Empedokles, Leukipp, Demokrit. All of them have wondered about the variety of nature; they have watched and investigated. The basic question was always, whether the great variety of substances and phenomena could be assembled by using a few things.

Tales saw the origin of matter in the picture of water and considered everything as being made out of it; in analogy Anaximenes considered everything being made out of air and Heraklith

out of fire. To solve this difficult problem Empedokles took even four basic principles into consideration: water, fire, air and earth, he called them elements. By combination of those elements Empedokles wanted to create his cosmos: "Out of the first mixture of the elements air has separated and has spread out all around in circles. But after the air fire has broken out." And one can further read at the philosophers of nature: "The mixture of elements in the manner of Empedokles has to be an organisation like a wall built out of bricks; and this mixture will be made out of elements, which will not be altered as such, but which will be joined together in small pieces, and this is also the case with the substance of flesh and every other material."

Demokrit developed a system of building blocks which he refined together with his teacher Leukipp in such a way that he based the construction of matter upon small undividable particles, the "atoms": "They consider the atoms as matter of things and they let everything else arise from their differences. However, there are three of them: form, position, order."

This building block system was later discarded by the most influential philosopher of this time, Aristotle. His pupils have fought against the system, later on it was forgotten. Only after almost two thousand years, after the influence of Aristotle's teaching had ceased, scientists again were concerned with the question about the building block system of nature. The number of different kinds of atoms, the elements, was enlarged in the course of experimental findings, the position of the atoms within space could actually be made empirically accessible.

Nowadays every chemist has to know the availability of building blocks and how to combine them. Therefore the modern chemist is the successor of the old philosophers of nature. This is documented by the fact, that in the first quarter of our century chemistry belonged to the philosophical faculties of the universities. In these days and nowadays likewise the chemist is forced to bring his thoughts and theories into line with the phenomena and observations of nature. Interpretations of substances and reactions which contradict the observation of nature are not permitted.

In the following chapters the system of combination of the particles will be described, this system provides the basis and the leitmotif how the chemists nowadays argue and how they interpret observations. In doing this the description of the substances and the system of description are predominant rather than the experiment. When knowing the systematic chemistry which is still called by the great chemist Leopold Gmelin "the pure, theoretical, philosophical chemistry" (1817) the experimental chemistry is easily accessible: "The

philosophical chemistry is the science, the experimental chemistry is the art" according to Gmelin.

Chemistry as science is based upon a large number of philosophical statements. In his work "A new system of Chemical Philosophy" the English chemist John Dalton gave 1808 the following statements about atoms being the smallest particles of matter:

1. All same particles behave in the same manner within the universe.
2. No particles get lost; neither can they come into existence out of nothing, nor can they dissolve into nothing.
3. The manner in which the particles are combined is reproducible in a lawful way and leads to certain substances.
4. Substances differ from each other in type and order of their smallest building blocks.

We will have to deal with many more philosophical theses and reflections within the following chapters.

I. The structure of crystalline solids

1. The basic building blocks

1.1 Atoms and ions

We are constantly surrounded by a vast number of different substances. Metals such as iron, copper, zinc, chromium, silver and gold are well known to us, we encounter rocks of all kind in nature or in the household: Examples are gypsum and marble, gems such as sapphire and diamond. Coal and oil are used for heating, air and water are essential for our lives, we prepare our meals with sugar and salt: substances upon substances, the chemist also calls them materials.

All substances are composed of an uncountable number of **smallest particles**, which are imagined as being spherical building blocks. They are so small that we cannot perceive them with our senses as individuals. However, many characteristics and conversions of substances, which we will get to know later on, indicate the existence of those particles. When investigating many substances using experiments, one can get two **different types of smallest particles differing in their qualities**. They differ in the way how they react towards "force transmitters".

Let us make this situation clear when looking at similar examples: Everyone knows a magnet and its property. If one moves a piece of iron towards a magnet, then a force will be perceptible which attracts the iron towards the magnet. The metals cobalt and nickel behave like iron. Other metals such as aluminium, copper or lead, other materials like wood or salt do not react to the magnet's mysterious offer of attraction. Obviously the magnet has a property which answers to a special feature of iron, cobalt and nickel. In order to observe an effect of force over a distance two things are needed: Firstly there must be a "force transmitter" with the characteristic of supplying the force, on the other hand the material, to which the force is to be applied, has to have the property to perceive the force. The spatial area, in which the force effects are perceivable, is called "field" by the physicist. A magnet possesses a magnetic field around itself.

An analogous situation provides the attraction of mass. The very large mass of the earth transmits perceivable force effects over a wide distance and other materials have the characteristic of perception. We notice the resulting force effects on all material things: all objects fall down in direction of the earth. The physicist calls the area around the earth in which the force effects on matter are noticeable, a field of gravity. Gravity and matter therefore belong to each other like magnetic force and iron.

A third, almost mundane phenomenon is given by the electrical force field: When combing dry, freshly washed hair blue sparks can be observed, when walking across a synthetic floor covering one charges himself, plastic sheets and paper "are glued" to each other. A plastic foil rubbed with paper therefore possesses the ability of a force effect, an electrical field. This effects paper, which is in the vicinity, and strongly attracts the paper. The paper has to show a special characteristic in order to "answer" the electrical field of the foil: This characteristic is called electrical charge. The corresponding terms are set side by side in table 1.1.

Field	corresponding property	quality of force
magnetic field	magnetism	magnetic force
gravitational field	mass	gravity
electrical field	charge	electric force

Table 1.1: Different force fields, properties and force effects.

If we now produce those three different force fields and imagine to hold a small test ball into the field, the area of force, we can then test whether the small test ball possesses one of the properties belonging to force fields. If the property is present then a force effect has to appear, if there is no effect, the ball does not possess the property.

In this manner we now test the types of building blocks of our materials. The result is the following:

1. None of the many particles types reacts primarily to a magnetic field.
2. All particle types react to the gravitational field, therefore they possess a mass.
3. A large number of particles reacts in the electric field, they possess an electric charge.

4. Other particles do not react in the electric field, they are electrically uncharged.

This differentiation of the particles regarding their quality of force is essential. Therefore the particle types with different qualities of force have been called differently.

The uncharged basic building blocks are called **atoms**. The basic building blocks with the property of an "electric charge" are called **ions**. Atoms naturally possess force effects among each other, ions also exert forces on each other, but not in the same sense. Further details about this will be presented later (3.1.).

We would like to explain the experimental result of the physicist via an experiment of ideas. We take any ion as a "test ion" and fix it in a place. Now we take from our substances one ion after the other and bring it slowly into the vicinity of the test ion and watch the electric force effect between the two. Some ions are strongly attracted by the test ion, the other ions are strongly repulsed.

Those different characteristics of ions are marked with the plus symbol "+" or the minus symbol "-". All ions which repulse each other and which are marked positively are called **cations**, the ones which repulse each other and which are marked negatively are called **anions**. Anions and cations are therefore those ions which attract each other.

During the investigation of the substances a lot of building block types have been found. There are e.g. iron atoms, copper atoms, chlorine atoms, sulphur atoms and many more. At the same time there have also been found iron ions, copper ions, chlorine ions and sulphur ions. At first glance it may seem strange that the chemists were naming atoms and ions in the same way, e.g. iron atoms and iron ions. The reason for this is that corresponding atoms and ions can be converted into each other quite easily and therefore they are assigned to the same family of particles. However, this should not mislead about the fact that an ion has totally different characteristics than its directly related atom, that therefore the **chlorine ion** shows different characteristics than the **chlorine atom**.

Maybe we can make this clear with the following example: A car, e.g. a BMW, has a certain driving characteristic. If we remove a tyre, then the driving characteristic changes dramatically! However, everyone will still identify the car as a BMW. The BMW character did not change, but in contrast the driving characteristics are totally different. Until which point one can alter a thing and still calls it by the same name, is an old philosophical question. We will meet it more often when describing our substances.

Chemical name	language of origin	German	English	French	symbol of element
Argentum	Latin	Silber	silver	argent	Ag
Aurum	"	Gold	gold	or	Au
Bismutum	"	Bismut	bismuth	bosmuth	Bi
Carbon	"	Kohle	carbon	charbon	C
Cuprum	"	Kupfer	copper	cuiivre	Cu
Ferrum	"	Eisen	iron	fer	Fe
Hydrogenium	Greek	Wasserstoff	hydrogen	hydrogene	H
Hydrargyrium	"	Quecksilber	mercury	mercure	Hg
Nitrogenium	"	Stickstoff	nitrogen	nitrogene	N
Oxygenium	"	Sauerstoff	oxygen	oxygene	O
Plumbum	Latin	Blei	lead	plomb	Pb
Sulfur	"	Schwefel	sulphur	soufre	S
Stannum	"	Zinn	tin	étain	Sn

Table 1.2: Some element names and element symbols

In any case it remains to be emphasised that the characteristics of atoms and corresponding ions have to be carefully watched and determined individually. One cannot deduce the characteristics of an atom based upon the characteristics of the corresponding ion and vice versa.

Under natural conditions ions are in general more stable than the corresponding atoms. For this reason we mostly find the ions in nature and not the atoms. Out of 97 stable basic building block types only 17 can be found as atoms (**noble** metals, **noble** gases), all the other 80 basic building block types occur as ions. A basic building block type, atom and corresponding ion, is generally called **element**. The many millions natural and synthetically produced substances are composed of those few elements!

1.2 Naming and symbols

Until today many experiments have produced about 103 basic building block types and the physicists continue working in their laboratories to produce new types of atoms. Such new additional atoms do not play a role for the chemist since they exist only for fractions of seconds.

In table 1.2. some basic building block types and their names are presented in alphabetical order. The naming took place over centuries, sometimes over millennia when thinking of gold or copper. Normally the discoverer had free choice to find a suitable name. However, it is important to know that Greek or Latin names form the basis for the longest known elements. In many cases for those foreign names English terms are used nowadays, but the original names must be known by the chemist. It is advisable to learn the German and French terms as well.

Each basic building block type has a symbol which, in most cases, stems from the abbreviation of the name, very often the first two letters. This symbol is used for information about an atom of those basic building block types, therefore it is also called **atomic symbol**. If there should be given information about more than one discrete (non-connected) atom, then the corresponding number can precede the atomic symbol. Scheme 1.1 shows some examples.

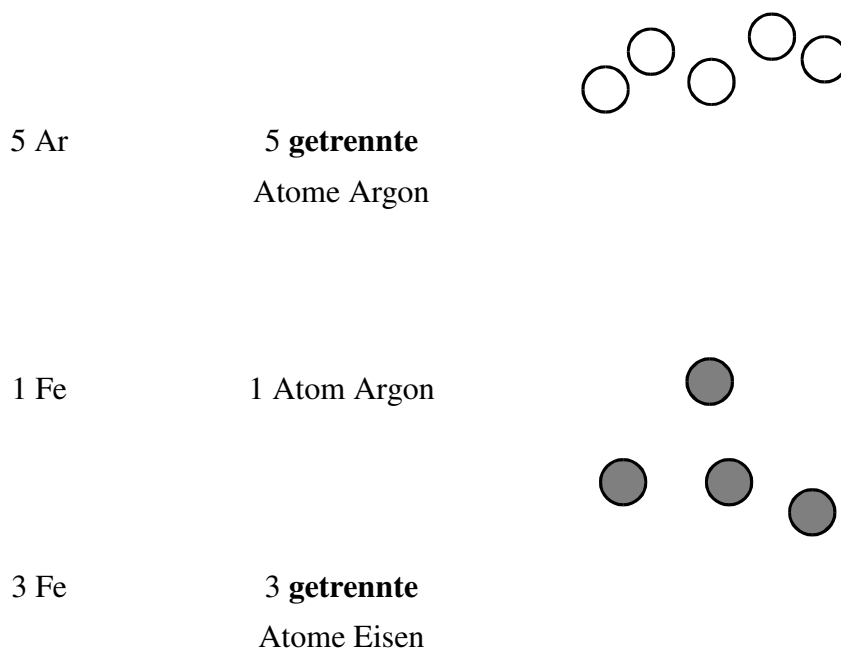
1 Ar or Ar	1 argon atom
5 Ar	5 discrete argon atoms
1 Fe or Fe	1 iron atom
3 Fe	3 discrete iron atoms

Scheme 1.1: Examples for the use of atomic symbols.

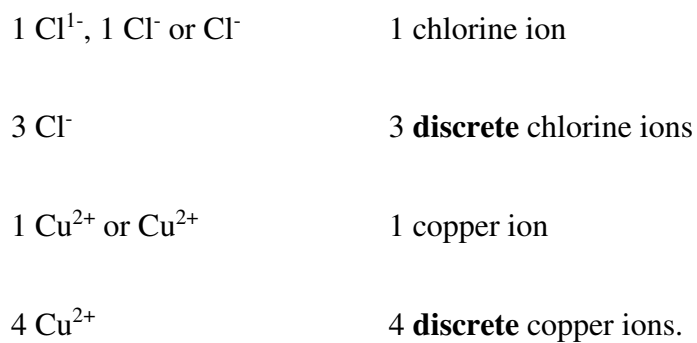
Ar oder Ar

1 Atom Argon

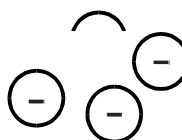


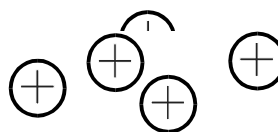


In principle information about type and number of ions is given in the same manner, in order to do this **ionic symbols** are used. They differ from the atomic symbols by the additional feature of the **charge number**. Cations receive in the upper right-hand corner of the symbol the sign for the positive charge (1+, 2+, 3+, and so on), anions receive the sign for the negative charge (1-, 2-, 3-, and so on). Scheme 1.2 shows some examples. The value of the charge number will occupy us in the next chapter.



Scheme 1.2: Examples for the use of ionic symbols





1.3 Basic building blocks and the macroscopic substance

All samples of the materials which surround us including the substance of our body consist of a for us unimaginable large number of connected basic building blocks. According to the building block type and to the internal spatial particle architecture different materials result, which differ from each other in their external physical and chemical properties, e.g. colour, density, hardness, possibility of shaping, electrical conductivity, heat conductivity, refraction and solubility.

If, for instance, copper building blocks are connected, the result is copper. It can be in the shape of a sheet, a cube, a crystal, a vase or a penny, the physical and chemical properties are always the same. Connected nickel particles therefore result in nickel, maybe known from the nickel plated screw. Our coins from the 50 Pf coin up to the 5 DM coin consist of a copper-nickel alloy, therefore a combination of copper and nickel particles. The 5 and 10 Pf coins consist of a iron core which is covered by brass: This copper-zinc alloy is made out of copper and zinc particles.

Each of these alloys has special characteristics regarding colour, density, and so on. How strongly the spatial arrangement of the particles can affect the characteristics of a material should be explained via the example of graphite and diamond. Both materials are commonly known, the sparkling diamond as a much sought-after gem and the black graphite as the main ingredient of pencil leads. Table 1.3 shows apart from the difference in colour some other significantly different properties.

	Hardness (acc. to Mohs)	density (g/cm³)	colour	electrical conductivity
diamond	10	3.52	colourless	bad (insulator)
graphite	1	2.25	black	very good

Table 1.3: Comparison of some properties of diamond and graphite

Both materials differ totally in their characteristics, but consist of the same building blocks, namely of carbon atoms. The great difference can therefore only be explained by the fact that the arrangements of the carbon atoms are different for diamond and graphite. We will get to know those different structures more closely later on.

In summary it should be emphasised what matters for the chemist, if he wants to produce substances via connection of particles, is:

1. the type of the particles connected,

2. the spatial arrangement within the association of particles.

For the chemist one substance is identical with another one if the particles and the spatial arrangement are the same. When comparing extremely exact, then at the same temperature the distances between the corresponding particles have to be identical.

atomic symbol	element name	ordinal number	atomic symbol	element name	ordinal number	atomic symbol	element name	ordinal number
Ac	actinium	89	Ge	germanium	32	Pr	praseodymium	59
Ag	silver	47	H	hydrogen	1	Pt	platinum	78
Al	aluminium	13	He	helium	2	Pu	plutonium	94
Am	americium	95	Hf	hafnium	72	Ra	radium	88
Ar	argon	18	Hg	mercury	80	Rb	rubidium	37
As	arsenic	33	Ho	holmium	67	Re	rhenium	75
At	astatine	85	I	iodine	53	Rh	rhodium	45
Au	gold	79	In	indium	49	Rn	radon	86
B	boron	5	Ir	iridium	77	Ru	ruthenium	44
Ba	barium	56	K	potassium	19	S	sulphur	16
Be	beryllium	4	Kr	krypton	36	Sb	antimony	51
Bi	bismuth	83	La	lanthanum	57	Sc	scandium	21
Bk	berkelium	97	Li	lithium	3	Se	selenium	34
Br	bromine	35	Lr	lawrencium	103	Si	silicon	14
C	carbon	6	Lu	lutetium	71	Sm	samarium	62
Ca	calcium	20	Mg	magnesium	12	Sn	tin	50
Cd	cadmium	48	Mn	manganese	25	Sr	strontium	38
Ce	cerium	58	Mo	molybdenum	42	Ta	tantalum	73
Cf	californium	98	Md	mendelevium	101	Tb	terbium	65
Cl	chlorine	17	N	nitrogen	7	Tc	technetium	43
Cm	curium	96	Na	sodium	11	Te	tellurium	52
Co	cobalt	27	Nb	niobium	41	Th	thorium	90
Cr	chromium	24	Nd	neodymium	60	Ti	titanium	22
Cs	caesium	55	Ne	neon	10	Tl	thallium	81
Cu	copper	29	Ni	nickel	28	Tm	thulium	69
Dy	dysprosium	66	No	nobelium	102	U	uranium	92
Er	erbium	68	Np	neptunium	93	V	vanadium	23
Es	einsteinium	99	O	oxygen	8	W	tungsten	74
Eu	europium	63	Os	osmium	76	Xe	xenon	54
F	fluorine	9	P	phosphorus	15	Y	yttrium	39
Fe	iron	26	Pa	protactinium	91	Yb	ytterbium	70
Fm	fermium	100	Pb	lead	82	Zn	zinc	30
Fr	francium	87	Pd	palladium	46	Zr	zirconium	40

Ga	gallium	31	Pm	promethium	61
Gd	gadolinium	64	Po	polonium	84

Table 2.1: Atomic symbols in alphabetic order, element names and ordinal numbers

2. The order of the basic building blocks

2.1 The periodic table of the elements

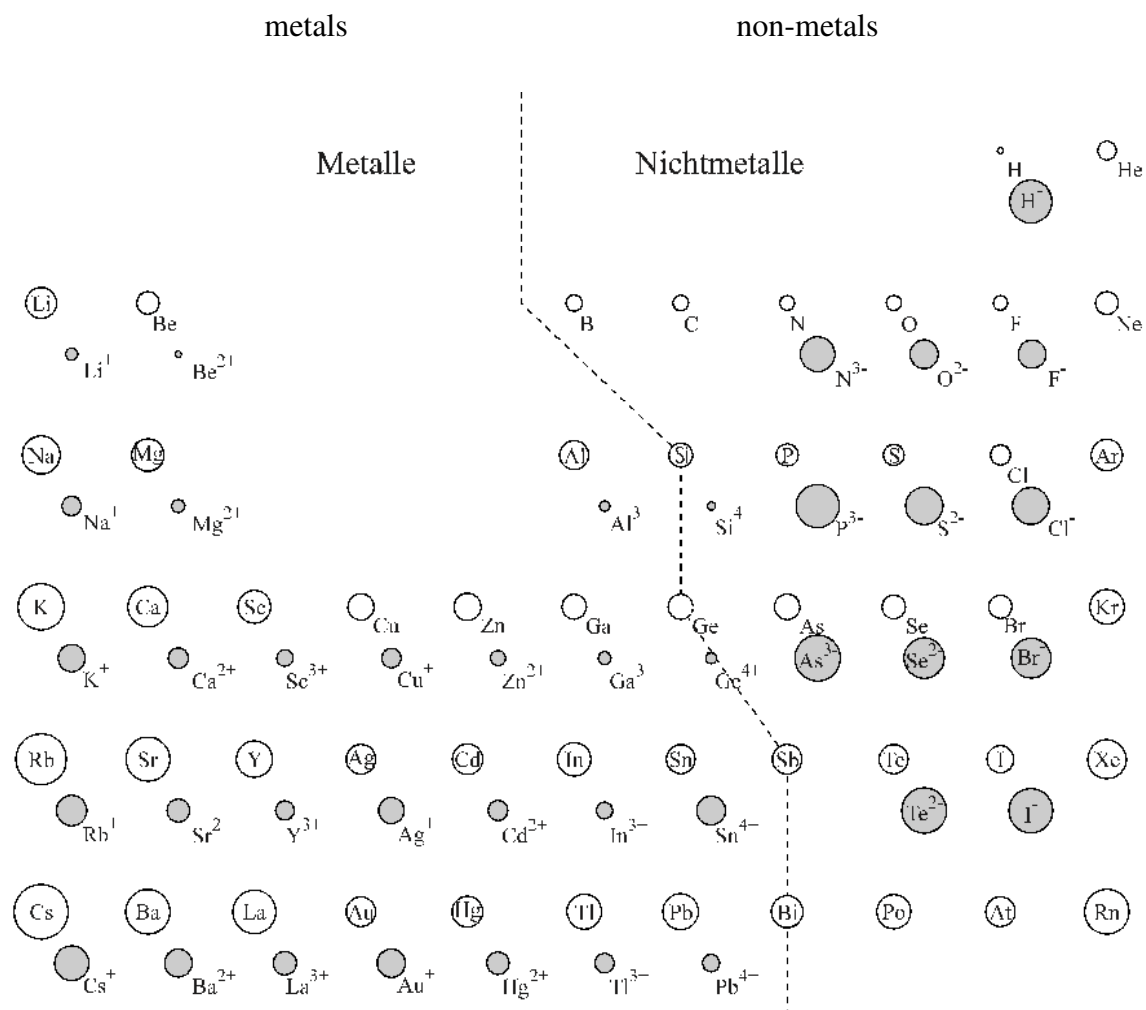
In table 2.1 some basic building block types are listed in alphabetic order. However, this does not give us any indication which particles can be joined easily with other particles or maybe which particles cannot be combined at all. But this is the concern of the chemist. Therefore, the particles were sorted based on their similar behaviour towards other particles.

For example the combination of lithium, sodium or potassium particles respectively with chlorine particles leads to similar salt-like substances in which the particles are joined in the ratio of 1:1. If magnesium or calcium particles are combined, then they will join with chlorine particles in the ratio of 1:2. If oxygen, sulphur or selenium particles are combined with hydrogen then one will get substances which are similar to each other and which are joined in the ratio of 1:2 particles. The combination of hydrogen and oxygen particles results in the substance of water, the other two substances behave similarly to water.

Those few examples should give a clue about the question which provided the basis for the experimental research of the chemists until the middle of the last century. All ratios of particles which had been found were compared and due to similarities different types of particles were ordered correspondingly. Particles which are very similar to each other are called related by the chemist, e.g. lithium, sodium and potassium particles belong to one **element family**. Those relations and other ordering factors are presented in the "**periodic table of the elements**".

Scheme 2.1 shows a part of the periodic table, scheme 2.2 shows the complete periodic table, but only schematically and without giving the element names and symbols. In table 2.1 all currently known elements are given and ordered alphabetically regarding their atomic symbols.

A first glance at the shortened periodic table of the elements in scheme 2.1 shows circles, marked with atomic and ionic symbols. They are supposed to portray the **basic building block types as spheres**. Obviously atoms and corresponding ions have a different size. Also the atoms and ions of one element family are different: the atomic and ionic radii increase from top to bottom.



Scheme 2.1: Periodic table of the elements and basic building blocks of matter (excerpt)

The portrayed circles in the periodic table reflect the relative size of the particles. The absolute diameters of the particles are in the range of 50 - 250 pm (unit picometer: $1 \text{ pm} = 10^{-12} \text{ m}$). However, at the beginning of our work we do not need these numbers and will bring them up when they play a role.

In addition atoms and ions are not rigid like wooden balls but rather elastic like rubber balls: the distance shortens with an increasing binding force between the particles, the measurement of the radii depends on a specific association of particles. Due to this reason it is difficult to give absolute numbers for the diameter of particles. Since the distance between the particles

are not important for our first basic ideas, within a model we can assume the atoms and ions being rigid wooden balls.

Let us imagine all basic building blocks are kept in shelves with drawers which exactly resemble, when viewed from the front, the periodic table. Let us assume a chemical store would possess such filled shelves, then we could easily buy any number of building blocks and assemble them to get the desired substances.

However, in the drawers there would be not only atoms but also ions, maybe separately in two compartments of the drawer. In this way atoms and ions can be called upon independently, in order to combine them independently.

periods

main groups

d-block elements

Scheme 2.2: Schematic filling of the groups and periods within the periodic table

Let us follow in scheme 2.1 the atomic radii within a period: They decrease from left to right, only the last particle of the period does not fit into this rule. Basically the same applies to the ions. However, we have to take care that anions and cations have to be considered individually. All positively charged cations are standing on the left-hand side of the periodic table, all negatively charged anions on the right-hand side. Furthermore it has to be noticed that cations are smaller and anions are larger than their corresponding atoms.

The particles in the middle of scheme 2.2 have been left out for clarity - they can be gathered from the overview of scheme 2.2.

2.3 The groups

The particles which stand vertically in a column are put together in so-called groups. Scheme 2.2 shows all groups in the complete periodic table. Viewing them in this picture, eight groups can be seen, which, when viewed from the bottom of the table, protrude the forth period: those are called **main groups**. The first six main groups start with the second period, the seventh and eighth main group start with the first period. The seventh main group starts with the element hydrogen, being a non-metal it is filed here. There exist other presentations which put the element hydrogen at the beginning of the first main group.

The groups that start with the fourth period are called *d*-block elements. Their numbering seems to be quite unconventional, particularly as three groups are summarised in group eight.

When looking in scheme 2.1 at the change of the particle radii within a group, it can be seen an increase from top to bottom for atoms as well as ions. Therefore in the periodic table the largest atom can be found in lower left-hand corner and the smallest atom in the upper right-hand corner.

Within the groups of the periodic table the element families can be found: the particles within a group are related to each other, they behave in a similar manner. Therefore some main groups were given their own names. The first main group, led by lithium, is called the group of the alkali metals, the second main group beginning with beryllium is called the group of the alkaline-earth metals. Sometimes the term chalcogens is used for the sixth main group with oxygen as its first element and halogens for the seventh main group, starting with fluorine (and not with hydrogen!). The noble gases with helium at the beginning form the eighth main group. All elements with their atomic symbols and ordinal numbers are given in table 2.1.

3. Bonding power of basic building blocks

3.1 Different qualities of force

If a substance is said to be composed of many basic building blocks then the particles have to possess certain individual force effects with which they affect each other and therefore keep themselves together. First of all one can assume that each particle of any particle type would be able to be easily joined with a particle of any other kind.

However, this is not the case. For example zinc atoms and sulfur atoms do not join in general, the same applies to copper atoms and fluorine atoms. A large number of examples could be added here. It is only important to notice that the characteristics of particles with regard to their joining abilities are investigated in the laboratory. An infinite number of experiments was necessary in order to find out the binding behaviour of the particles. This has been worked stepwise into the periodic table.

Based on how we encounter the particles during the built-up of substances within the laboratory we can assign to the particles different force qualities. In chapter 1.1 the different qualities of gravity, magnetic and electric force effects have already been listed as principal examples. In a similar manner we have to imagine the different quality of particles with their ability to affect other particles forcewise. The experiment of ideas is practically the same as the one given in chapter 1.1. A test particle is imaginatively fixed then one particle after the other approaches and the force effect is observed. The result of the observations is the following: if force effects are present then the quality of force of the particles, which were brought close, must be the same. If there is no force effect then the quality of force has to be different.

In this manner three different qualities have been found. The magnetic quality is not among them, also gravity does not play a role, it is too small for joining the particles. However, the electric force quality can be assigned to the ions among themselves as has been already stated in chapter 1.1. A further unique quality is held by the metal atoms among themselves, a third force quality has to be assigned to the non-metallic atoms among themselves: The carbon atoms of the diamond therefore do not affect neither gold atoms nor iron ions with their bonding power, nor does the bonding power of sulfur atoms affect silver atoms or copper ions.

The experimental result of the investigation of the force qualities of particles recommends an **organisation of the particles into three classes:**

1. metal atoms
2. non-metal atoms
3. ions

The use of the terms metal atoms, non-metal atoms and ions therefore includes the force quality towards other particles. As a result of the experiments and the classification the following sentence can be formulated: In general only particles with the same force quality can be combined.

3.2 Spatially undirected bonding power (borderline type)

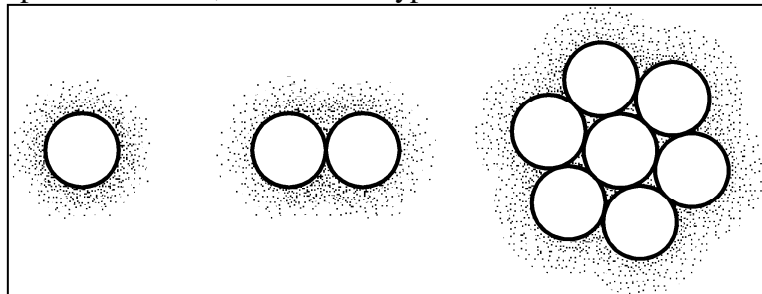
It is commonly known how variably one can build with bricks - only the brick does not possess any noticeable bonding power! Stacked bricks are held together by the gravity of the earth. Mortar or cement are just serving as "glue". However, if a building block possesses its own bonding power then the question is which part of the building block this bonding power comes from and how this power carries its effect into space.

The simplest case is if the bonding power of a spherical building block is evenly distributed around the sphere, if each smallest part of the surface possesses the same force effect directed vertically into space. A vivid model of such a particle is given by the earth. All over the surface we can take a walk or go by boat, everywhere on earth we are attracted vertically to the surface with same force of gravity. From the outside every body, an aeroplane or a satellite can be tied on and joined with any point of the earth's surface.

A difficulty arises if one attempts to show these facts graphically in order to give information about the spatial arrangement of the bonding power of the sphere. It is not possible to see this bonding power or to make it visible, **only the effects can be noticed**. Of this effect it is now measurable that it

1. is evenly distributed around the sphere and that it
2. decreases with increasing distance.

We therefore draw "something" evenly around a projected ball, a circle, with the "something" decreasing towards the outside. This can somehow look like scheme 3.1. Since the whole bonding power of this particle evenly fills the surrounding space with no preference for any spatial direction, we call this type of force distribution around a particle "spatially not directed



towards a special direction" or a little bit shorter: "**spatially undirected**".

Scheme 3.1: Model drawing of particles with spatially undirected bonding power.

Such a particle with spatially undirected bonding abilities operates its force effects towards all directions. If one joins two such particles we then say that they are bound at the area where they touch each other. The total further bonding power around the particle is still available for bonding purposes. Using imagination one could imagine that the moon had slowly joined with the earth. At other places of the surface the earth could tie on many more moons, it would only be a question of space, of geometry.

This formulation of the question can be made more vivid with table-tennis balls, paper balls or wooden balls. If we assume that the balls, which we want to be joined spatially undirected, are all of the same size, then within a plane one ball can be joined with six other balls (cf. scheme 3.1). Each outer ball is connected with its neighbours, it therefore has the space to tie on three other balls within the plane.

3.3 Spatially directed bonding power (borderline type)

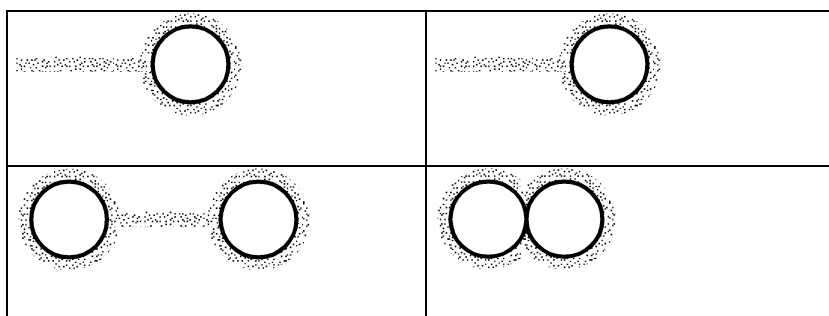
Many particles are known of which the force effects are not evenly distributed around the particle. With a different force quality this phenomenon is also known with many magnets. For example a bar magnet does not possess the same force effect everywhere around itself. One can prove this by probing with a nail. Starting at a pole the force effect is the strongest, it decreases significantly towards the middle of the magnet and increases towards the other pole. If the strength of the force was to be depicted by an arrow, one would achieve a picture like the one in scheme 3.2. The line which connects the arrow points would describe the distance where the nail would always be attracted with the same force. Again we will undergo an

experiment of ideas. We scan all around a hydrogen atom, which is present as one of two hydrogen atoms bound in a hydrogen molecule, with regard to its force effects. It can be shown that almost the whole force effect is vertically directed outwards from a certain spot on the surface. Only in this direction the hydrogen atom binds forcewise with another hydrogen atom. The rest of the surface only possesses a minimal remainder of the bonding power.

Graphically we can present the information about those facts as given in scheme 3.3. The "beak" in this model drawing is supposed to symbolise the direction and the force which is made available for bonding. The dots around the larger part of the model molecule symbolise a minimal remaining spatially undirected bonding power, which cannot be used under many conditions because it is too weak. Since the whole bonding power is focused in one direction into space we call it "**spatially directed bonding power**".

before coupling

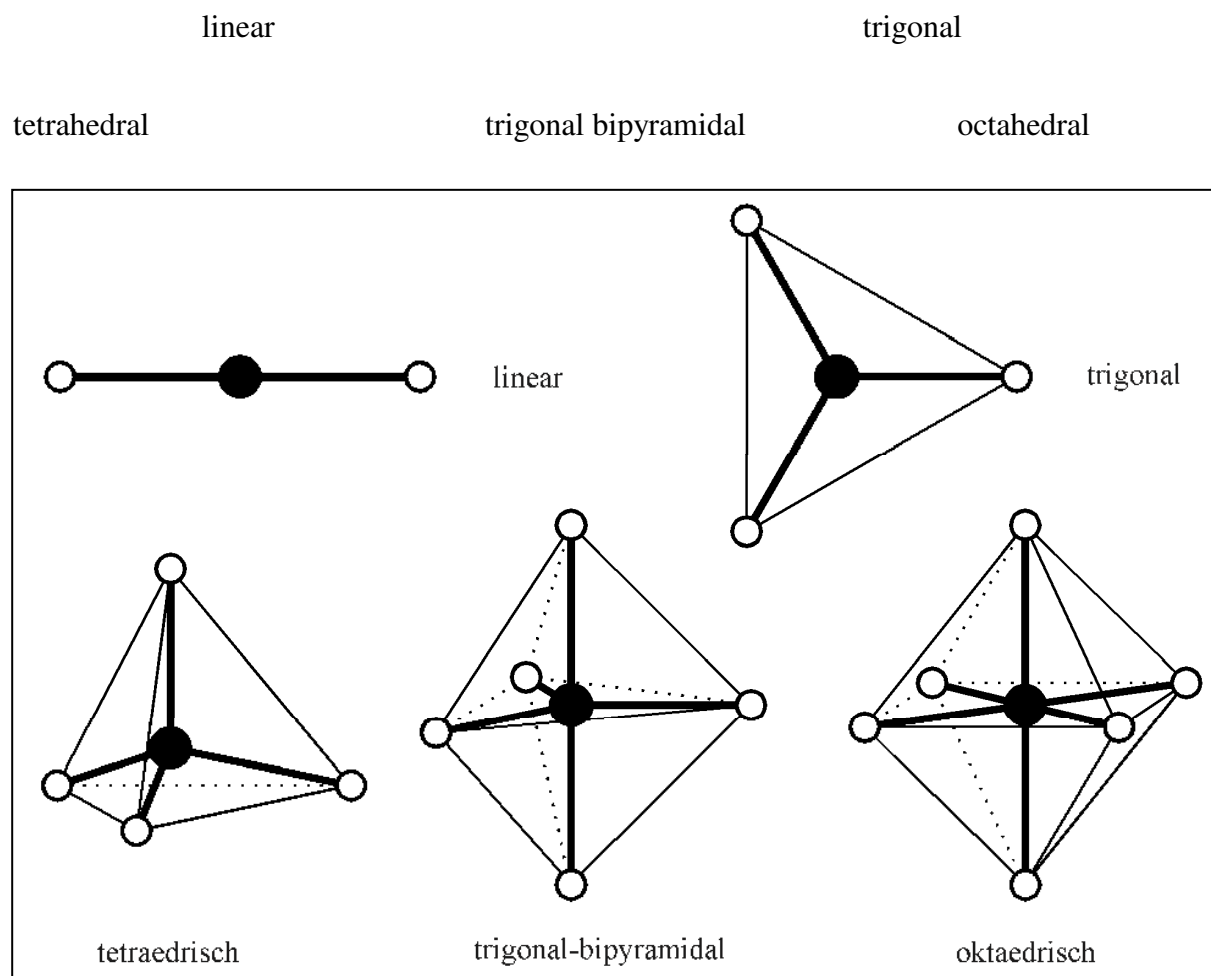
after coupling



Scheme 3.3: Model drawing of spatially directed bonding power.

It is decisive for the combination of e.g. two hydrogen atoms that the bonding stems from certain areas of both atoms in the hydrogen molecule. After this bonding a further base for bonding with other hydrogen atoms does not exist. This is the consequence of this spatially directed bonding power.

To such a bonding capacity which is already taken up by another atom is also said: "the bonding is saturated". In the model the force effects of spatially directed bonding power are drawn in a symbolic length. In reality one particle is naturally situated directly next to the other particle. The point of contact symbolises the area of the spatially directed bonding power (scheme 3.3).



Scheme 3.4: Spatially directed bonding power of atoms

The examination of the particle types with spatially directed bonding power led to the result that not always the whole bonding power has to be focused into one direction. The bonding power can be directed into space in more than one direction. Some examples are shown by the models in scheme 3.4.

The manner in which particles behave in certain cases is reserved for later chapters. For the depiction in models it proved to be worthwhile to attach snap fasteners to the model balls in the direction of the bonding power. In this way it is possible to join spatially directed with spatially directed bonding power within the model. We will often use this kind of modelling since in this manner many building principles of substances can be shown with a large enough accuracy.

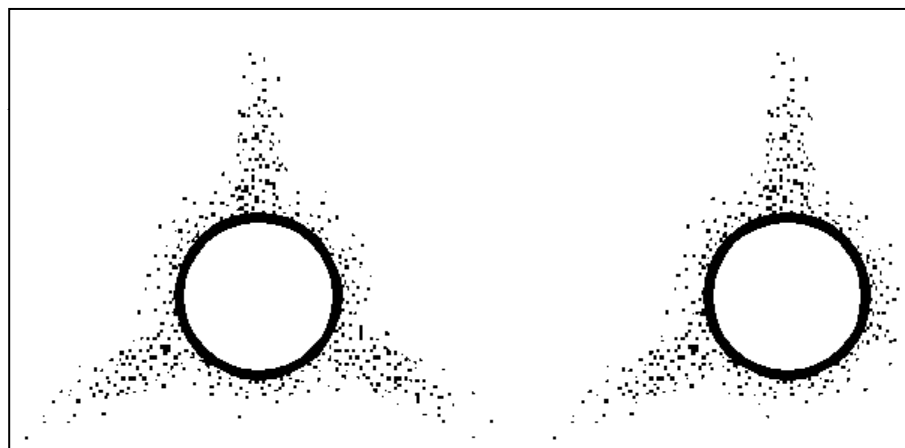
3.4 Simultaneously spatially directed and undirected bonding power (transitional case)

We have to bear in mind that we did not invent the directed and undirected bonding power, but that they were observed in many particles of the substances. 100 types of atoms and some million substances: it has always been attempted to divide the bonding power either as directed or as undirected. A different classification was not taken into consideration. But this bears a difficulty in any natural science, because nature does not go by our desired way of classification. It is especially not easy for botanists and zoologists.

Like the botanist we often use the terms tree and shrub. Those are terms with which we describe nature. We probably stood in front of a plant and asked ourselves whether it was a tree or a shrub. In order to be a tree too small and bushy and in order to be a shrub too high and not bushy enough. Finally we decide to use term which comes closest to the plant. But what would we say about the flower aster, which - as has been observed in a national park in Uganda - suddenly grew to a height of 15 meters?

Every one of us differentiates a bird from a mammal. This seems to be straightforward. A bird has feathers, a beak and lays eggs. A mammal normally has fur, teeth and nurses its offspring. This classification has proven to be worthwhile. What is a researcher supposed to do who suddenly discovers in Australia the platypus? It has fur, a beak, lays eggs and nurses the hatching young ones. The systematicity only includes birds or mammals. Therefore, one can call the platypus bird or mammal. This ambiguity is not the fault of this strange animal, it is rather our systematicity in which we have to call this animal a transitional case. Transitional case that is neither the one nor the other but something in-between.

It is the same case with our classification of the bonding types into spatially directed and undirected. Many particles have both bonding types, within our systematicity they are hermaphrodite. The model drawing in scheme 3.5 tries to illustrate this.



cted bonding power of

This model shows particles with a strong undirected bonding force and two or three weak directed bonding abilities respectively. Since we do not have an own term for this transitional case we remain with the twofold systematicity of spatially directed and spatially undirected. We will first examine those particle types which embody the purest types in the best way and from this we will draw our consequences for the substances. After that we will draw our attention to the transitional cases.

3.5 Strength and standardisation of spatially directed bonding power

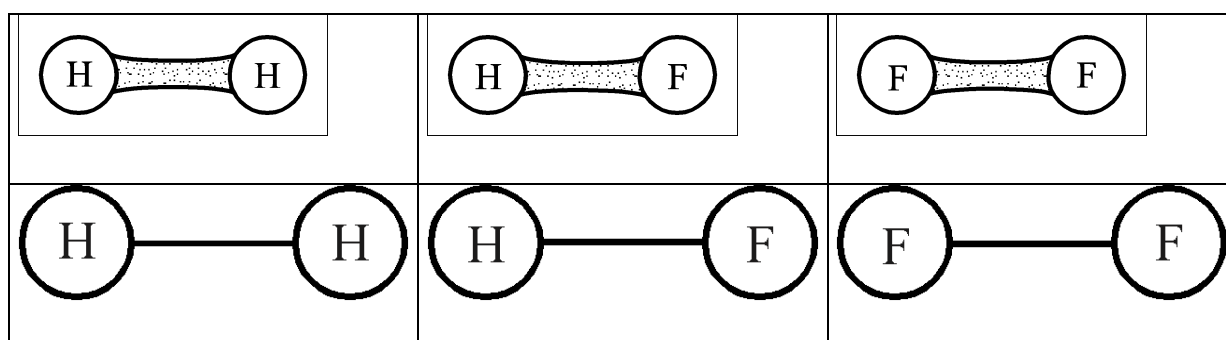
3.5.1 Standardisation and degree of bonding

It is our goal to find a rule for combination of particles with the spatially directed bonding type. This is countered by the fact that many particles possess a different number of bonding abilities.

In order to sort out clearly this variety, the standardisation based on the bonding ability of the hydrogen or fluorine atom has been proven worthwhile. With regard to this we knowingly ask only for the ability to tie on a particle but not for the physical background of chemical bonding. In order to assist this standardisation a huge number of experiments has been carried out since the beginning of the last century. We want to summarise all those experimental results in a large experiment of ideas.

A hydrogen atom can be easily joined with another hydrogen atom in a stable manner. The same applies to two fluorine atoms, also to one hydrogen atom and one fluorine atom. The directed bonding power of the atoms tie each other on, in a model we can imagine this like depicted in scheme 3.6.

Scheme 3.6: Model drawings and structural symbols for the combination of hydrogen and fluorine atoms



This leads to the conclusion that the combination abilities are the same for the hydrogen and the fluorine atom. It can be repeated that the ability is the same, we are not talking about forces and similar accompanying physical quantities. An analogous example could be drawn upon: The lawful bonding ability of a man to a woman is one within European countries, in oriental countries the man's ability could be four, the woman's ability remains one. The bonding ability is therefore only to be understood as an assigning quantity, it does not imply anything about force and beauty or attraction and repulsion. Here the bonding ability is also only a sorting, legal quantity which states the possibilities of bonding.

It is now decisive that this bonding ability can be expressed in numbers as we have done before. We assign the bonding ability of one to the hydrogen and the fluorine atom. Within the symbol we can portray this as a hyphen, which can be deduced from the drawing of the directed bonding power.

As shown in scheme 3.6 two joined balls look like dumb-bells in sports. For this reason here one talks about a hydrogen dumb-bell, a fluorine dumb-bell or a fluorohydrogen dumb-bell.

If one uses the corresponding letters for the atoms respectively then the **structural symbols** of the molecules result. With constant remembrance that it is an arrangement between the chemists we want to call this bonding ability of the hydrogen and fluorine **standard bonding ability**.

The combination based on standard bonding abilities which fit each other is called **standard bond**, to achieve a standard bond both particles have to contribute their standard bonding ability. If we give the hyphen, which depicts the standard bonding ability of one (H-, F-) with the atomic symbol, then even an amateur can find the combinations shown in scheme 3.7. In a model construction kit those standard bonding abilities are symbolised by snap fasteners or stick-like joints.

The transition of this standard onto all other particles which apply the spatially directed bonding ability is possible due to the fact that we can test experimentally with different compounds of hydrogen and fluorine how many atoms are joined with each other. In a model we examine an atom unknown regarding its bonding ability for the maximum number of fluorine or hydrogen atoms which can be bound with the atom. The number of connected

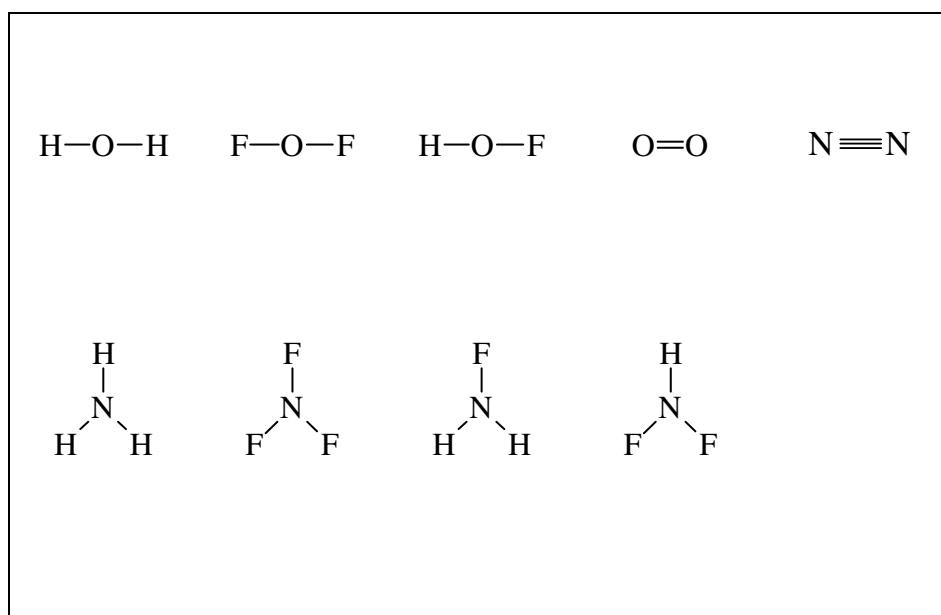
fluorine or hydrogen atoms gives directly the standard bonding ability of the particle examined.

For example an oxygen atom binds two fluorine or hydrogen atoms. Regardless of the spatial structure, to which we will give our attention later on, this particle combination can be given in the symbolism of standard bonding abilities without any problems. The oxygen atom therefore has two standard bonding abilities and the nitrogen atom has three.

Two oxygen atoms can now be combined in a way that the two bonding abilities saturate each other to form the bond. Therefore this oxygen dumb-bell possesses between the two oxygen atoms a bond which is given by two standard bonding abilities. We call such a bond also a **double bond** in contrast to the **single bond** of the hydrogen dumb-bell. If we combine two nitrogen atoms according to this method than the three standard bonding abilities are united between the two nitrogen atoms. We achieve a nitrogen dumb-bell, of which the bond can be described by three standard bonding abilities. We call it a **triple bond**.

Whether the new combinations given in scheme 3.8, which we achieved with relative ease, exist in reality one has to decide in the laboratory. In this case they have actually been found or produced by an experiment.

Scheme 3.8: Examples for the combination of atoms with the standard bonding ability of two and three



If we now compare the dumb-bells of hydrogen, oxygen and nitrogen, they differ in their bond by the number of standard bonding abilities. The number of standard bonding abilities which is used for a bond is called **bond order**. This bond order, which normally should be called standard bond order due to the standard bonding abilities, does not have to be a whole number. The bonding abilities can be distributed around a particle in a quite unconventional manner. However, the sum of the standard bonding abilities, i.e. the whole bonding power of the atoms, remains. This guarantees the functioning of the combination method. Let us make this clear with some examples.

bond order

Bindungsgrad		
Einfachbindung	$\text{H}-\text{H}$	1
Doppelbindung	$\text{O}=\text{O}$	2
Dreifachbindung	$\text{N}\equiv\text{N}$	3

single bond

double bond

triple bond

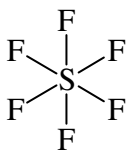
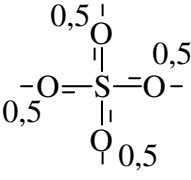
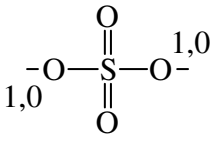
Scheme 3.9: Standard bonding abilities and bond order

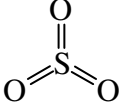
A sulfur atom usually builds directed bonds with the oxygen atoms, many experiments have shown that the sum of the directed standard bonding abilities of the sulfur atom is six.

Therefore, six fluorine atoms can be tied on a sulfur atom. The fluorine atoms are evenly distributed around the sulfur atom: in front, behind, left, right, on top, under. If one would connect the fluorine atoms positioned around the sulfur by drawing straight lines, then the result would be the spatial body of an octahedron. It is shown as a body in scheme 3.4 and in table 3.1 it is symbolised in entry (1).

structure **number of** **number of bonds** **bond order**
 standard bonds

Table 3.1: The connection between bond order and standard bonds as in the sulfur atom

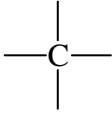
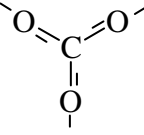
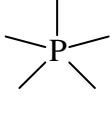
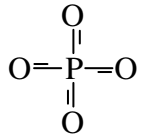
Struktur	Anzahl der Normbindungen	Anzahl der Bindungen	Bindungsgrad
	6	6	1,0
	6	4	1,5
	6	2	2,0
		2	1,0

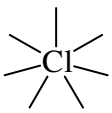
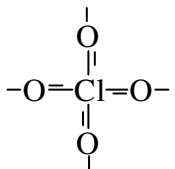
				
(4)	6	3	2,0	

Difficulties arise with the depiction of fractional bond orders within a symbol. One could certainly define the length of a standard hyphen, let's say at 1 cm. Then the bond order could be portrayed as 1.33 cm or 1.75 cm as can be seen in table 3.2. However, this can not be carried out in practice, neither when writing the symbols, nor when reading them. Because of this the bond order, if it is of interest, is given as a number or it can be calculated if the standard bonding ability of the central particle is known.

symbol of standard bond **number of standard bonds** **symbol of association** **number of bonds** **bond order**

Table 3.2: Some examples regarding the number of standard bonds and the bond order

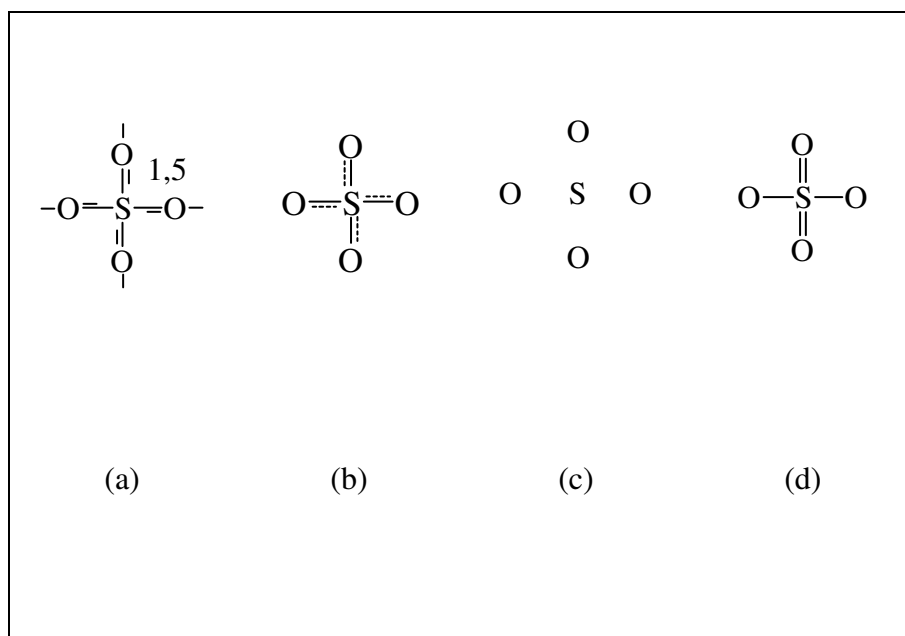
Normbindungs-symbol	Anzahl der Normbindungen	Verknüpfungssymbol	Anzahl der Bindungen	Bindungsgrad
	4		3	1,33
	5		4	1,25

	7		4	1,75
---	---	---	---	------

A fractional bond order cannot be portrayed with a model building kit which symbolises standard bonding abilities with snap fasteners, though. 0.33 snap fasteners do not exist!

In the course of the following chapters we will have to deal more and more with the symbolism with which information can be given about the structure of particle associates. One major difficulty for the beginner is given by the fact that the trained chemist abbreviates his information the more, the clearer the facts are for him. This we will make us clear based on scheme 3.10 with different symbols for the combination of four oxygen atoms around a sulfur atom distributed in a tetrahedron.

Scheme 3.10: Content of information of different symbols for the same particle



The content of information of the symbol decreases from left to right. From the symbol (a) not only the bond order can be gathered but also the standard bonding ability of the sulfur atom, therefore the experimentally proven fact that all four oxygen atoms are evenly tied to the sulfur atom. From information (b) can be gathered that the four atoms are bound to the sulfur

atom in the same manner, however, the bond order cannot be discerned. Symbol (c) contains the lowest degree of information and allows for individual interpretations regarding the standard bonding ability of the sulfur atom. From symbol (d) the standard bonding ability of six can be gathered, however, it supposes different bonding of the oxygen atoms. Nevertheless very often such a factually wrong symbol is used, because it is preferred to work with whole rather than fractional bond orders.

Here it applies to chemistry as to everywhere: The more the person to be informed knows the less precise the information supplied has to be. The less the person knows the more precise the information has to be. The more one knows his way around in a certain area the less a good map is needed. However, who does not know his way around in an area needs very good information, i.e. a very good map.

3.5.2 Standard bond and bond length

We consider the atoms with spatially directed bonding power being balls. We can approach rigid wooden balls until they touch each other. This is the simplest model-like portrayal of a bond. In some cases, however, it is recommendable to make the bonding behaviour of atoms clear by using soft tennis balls in order to describe the experimental results from the laboratory in a better way.

The tennis ball differs from the wooden ball by its elasticity. If two wooden balls touch we cannot bring them closer by pressing with our two hands. With tennis balls this is possible. The point where they touch is pressed flat and the distance from centre to centre shortens. Therefore this distance results from the interaction of two forces: on the one hand the force with which one ball pushes the other away due to the internal pressure, on the other hand the force of our hand which is in objection to the internal pressure.

Also with atoms bound to each other a certain distance or bond length will appear which results from the attraction and the repulsion of both atoms. The physical chemists can measure those **bond lengths** and **bond angles** quite exact with the modern equipment. But the difficulty herein is to change the distances of the bonds into diameters and radii of particles, i.e. to assign to each atoms its part of the bond length.

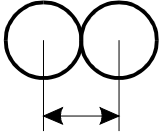
It is simplest with the combination of two identical particles. Then the radius of each atom equals half of the bond length. This distance varies somewhat with regard to the atoms which

are additionally joined with the atom pair which is to be considered. Decisive is now the distance at a certain bond order. Table 3.3 contains some values for single bonds.

mean distance [pm]

radius [pm]

Table 3.3: Bond lengths for some single bonds

	mittlerer Abstand [pm]	Radius [pm]
C—C	154	77
N—N	148	74
O—O	148	74
P—P	220	110
S—S	208	104

It is now the aim of the determining of the atomic radii to predict the distances of the different combinations of particles. Those distances should be the sum of the radii of the two particles joined. As can be seen in table 3.4 this method does not function as well as it was hoped to.

The force effects of the individual particles can obviously be influenced in many ways and they are dependent on the conditions provided by the other particle so that only a first estimate can be gathered from this method. Even calculated corrections which take the force quality of the bond into closer consideration only come into close proximity of the measurement. Nevertheless the bond length is a valuable complementary quantity in order to describe particle associates more systematically. An increase in the bond order between two particles should lead to a decrease in the bond length according to our theories. In reality this has been proven true in experiments as shown in table 3.5.

**bond lengths calculated from
the atomic radii [pm]** **bond length
measurements [pm]**

Table 3.4: Comparison between calculated and measured bond lengths

	errechnete Abstände aus den Radien [pm]	gemessene Abstände [pm]
C—N	$77 + 74 = 151$	147
C—O	$77 + 74 = 151$	143 - 146
N—O	$74 + 74 = 148$	143 - 147
P—O	$110 + 74 = 184$	160 - 175

The standard bond order is, as has been pointed out before, not always a whole number. For example within graphite the carbon atoms are arranged in a honeycomb structure so that each

carbon atom is surrounded and bound by three other carbon atoms in a regular fashion. Since four standard bonding abilities have to be assigned to each carbon atom, those four bonding abilities have to be distributed to three bonds. The resulting bond order is $4/3 = 1.33$. The corresponding bond length was measured as 142 pm (cf. scheme 3.11).

Table 3.5: Bond lengths for the bond orders 1, 2 and 3 (examples)

C—C 154 pm	C=C 133 pm	C≡C 121 pm
C—O 143 pm	C=O 119 pm	C≡O 107 pm
N—O 145 pm	N=O 117 pm	N≡O 107 pm

A similar hexagonal construction is present in the benzene molecule as shown in scheme 3.11: Six carbon atoms are joined to form a regular planar ring, in which one hydrogen atom is bound to each carbon atom. Between the carbon and the hydrogen atoms functions a single bond. If four standard bonding abilities are again assigned to each carbon atom, then each carbon atom has three bonding abilities left for its two neighbours, therefore the bond order between two carbon atoms in benzene molecules is 1.5. The measured bond length between two neighbouring carbon atoms is 140 pm, it is shorter than the bond length between two carbon atoms within graphite.

Graphite

142 pm

1.33 bond order

or

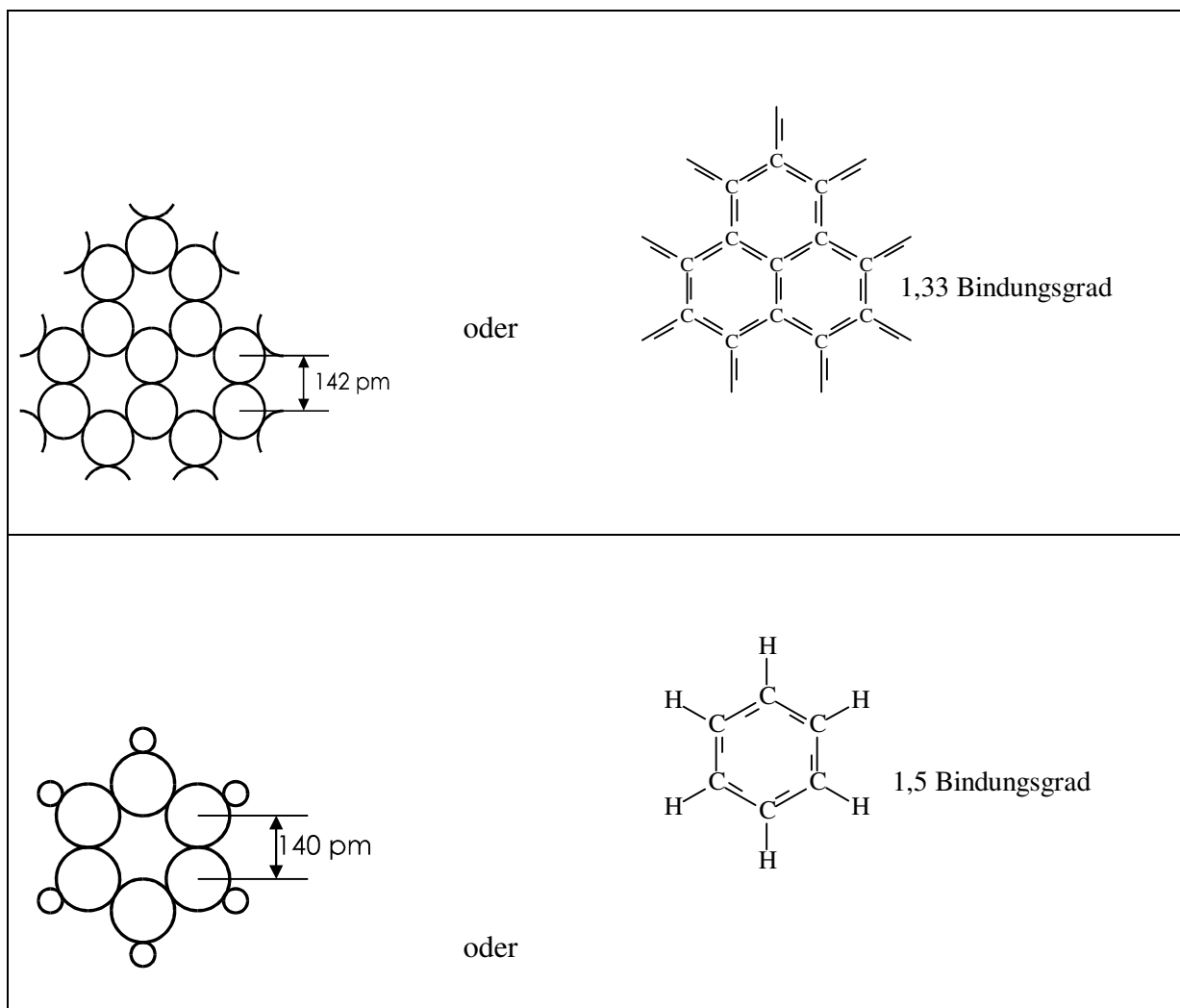
Benzene

140 pm

1.5 bond order

or

Scheme 3.11: Bond order and bond length of C atoms in the graphite lattice and the benzene molecule

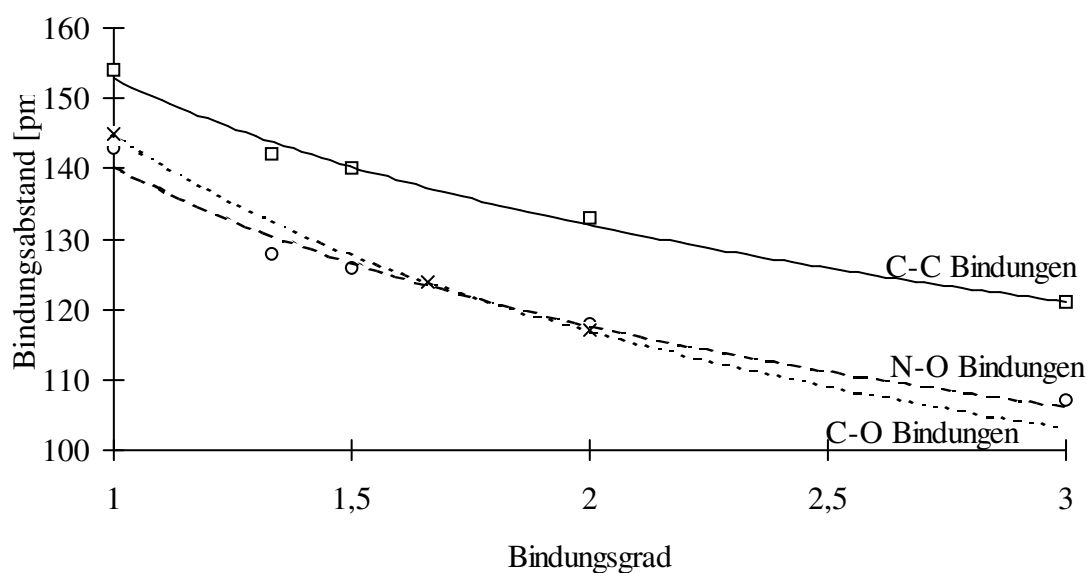


If the bond order is plotted against the bond length in a diagram then a mutual dependence for the bonds between two carbon atoms can be gathered, from which a useful relation of bond order and length can be seen. Scheme 3.12 shows this interrelation.

bond length [pm]

C-C bonds

Scheme 3.12: Interdependence of bond length and bond order in specific atomic combinations



bond order

As further examples of the dependency of the bond length on the bond order the measurement of the distances within particle associates between nitrogen and oxygen atoms or between carbon and oxygen atoms are to be considered. There exist planar triangular constructions as shown in scheme 3.13.

There are to be assigned four standard bonding abilities to the carbon atoms and five standard bonding abilities to the nitrogen atom. If the bonding abilities are evenly distributed to three bonds respectively, then the resulting bond order for C-O bonds is $4/3 = 1.33$ and for the N-O bond $5/3 = 1.66$. The measured bond lengths are 129 pm (C-O) and 124 pm (N-O). If two oxygen atoms and one carbon atom are bound around a carbon atom within a plane, then the

result is again a planar triangle. The bond between the carbon atoms is of the length of a single bond, so that three bonding abilities are left for the bonding of the carbon atom to the two oxygen atoms. This results in the bond order of $3/2 = 1.5$, the bond length is 131 pm and the bond angle is 130° (see scheme 3.13).

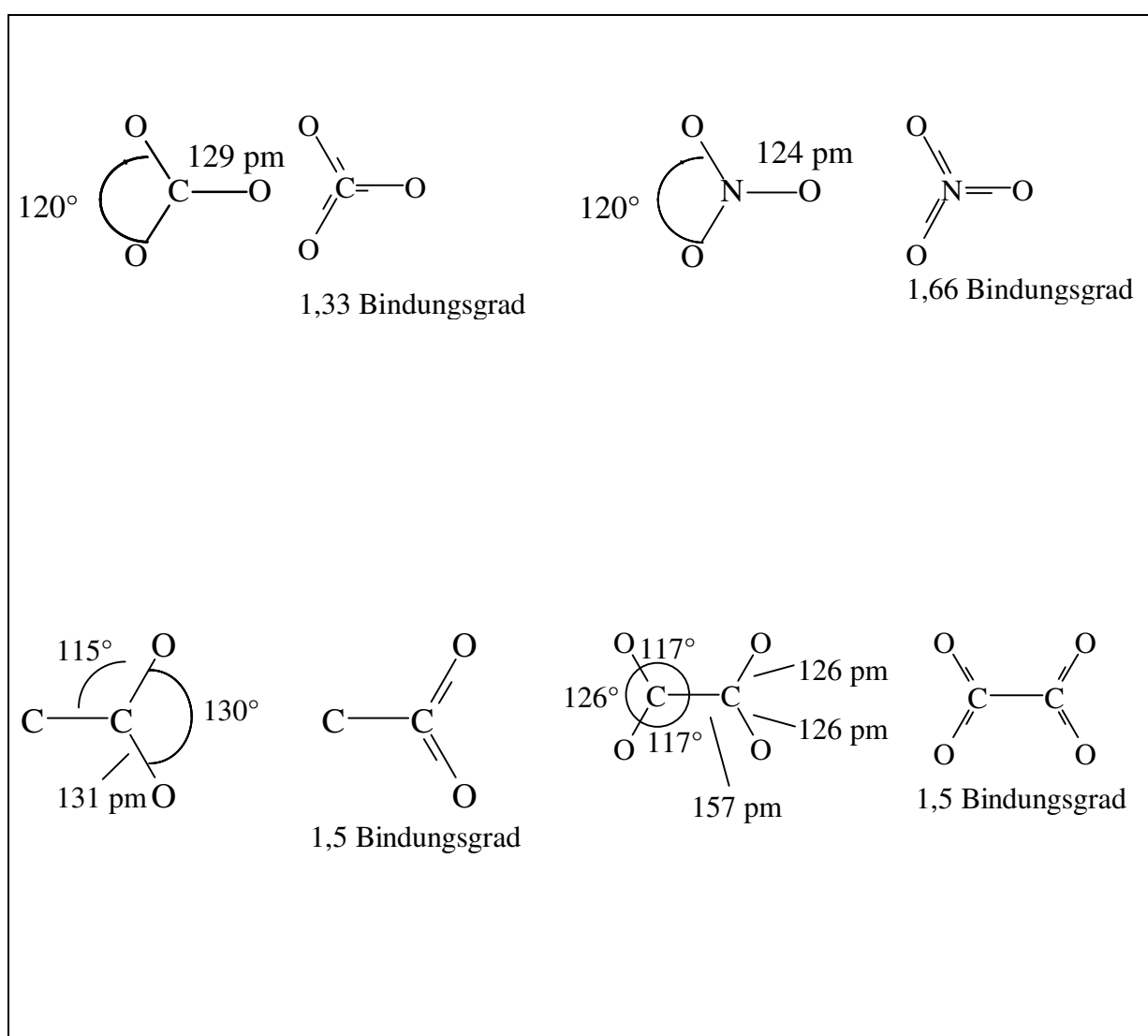
1.33 bond order

1.66 bond order

1.5 bond order

1.5 bond order

Scheme 3.13: Bond lengths and fractional bond orders



At closer inspection the triangle in which the bound particles associate is not equilateral any more, but only isosceles. It was equilateral in the combination of three oxygen atoms around a carbon atom. If now two further oxygen atoms are attached to the lone carbon atom within this

formation then the result is a highly symmetrical construction, which can serve as an additional example how exact particle constructions can be measured with regard to their distances and angles (cf. scheme 3.13).

In the example cited above the bond length for the C-O bond order of 1.5 was 131 pm, in this example now it is at the same bond order 126 pm. Here the limitations of this too simple description can already be seen. Nevertheless, a clear interdependence between bond length and bond order is still obvious. In fact we cannot derive the bond order from the distance between the particles and vice versa not the distances from the bond order, but we gain useful hints in which directions both quantities move. The following conclusions are admitted in any case:

1. If particles of the same type are joined and the distances are all the same, as given in the example of the carbon atoms within the benzene molecule or the graphite lattice, then the bond order between the particles must be the same.
2. If the bond order and the further environment of the particles are the same, as in the example of the carbon atom surrounded by three oxygen atoms, then the distances have to be the same.
3. If a particle associate only changes the bond order, then with increasing bond order the distances have to decrease and with decreasing bond order the distances have to increase.
4. If a bond order is not a whole number, then the bond length is between the two distances of the bond orders rounded up and down. Therefore, the bond order 1.4 will have a bond length between the bond length of the bond orders 1 and 2.
5. If a bond length is measured, which lies between the corresponding bond lengths of two whole bond orders, then the corresponding bond order will be within those limits.
6. The sum of the bond orders, which are used for binding a particle, gives its standard bonding ability and facilitates statements about its combination ability. In complicated particle associates the structural information is not given by the chemist via the bond order but only via the bond lengths and bond angles. In doing this the information about the bonding abilities and the combination abilities with other particles are eliminated.

3.5.3 Bond order and stability

With an increase in the bond order the distance between the particles bound shortens because the force effect is greater. However, this does not necessarily mean that the bond is more stable. "Stable" is a term which has nothing to do whatsoever with the force effective between the particles. It only describes how a bond reacts towards any "disturbances".

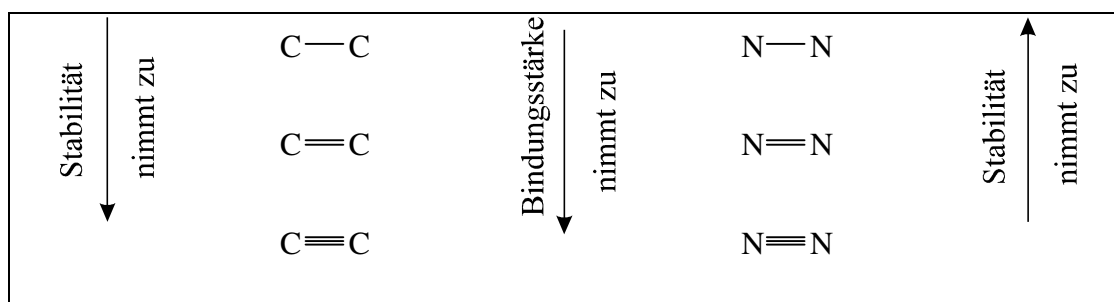
A mechanical picture can make this clear in the best way possible. We attach a spring between two balls and tension it. The more we move the balls apart the more the spring tensions, it causes a greater force. But whether the system of balls and spring is stable depends on how the spring is attached to the balls. Good hooks which do not allow the spring to detach make the system stable. Open hooks in which the spring just dangles lead to instability.

The instrument for testing the stability is to be a small hammer. If the spring is tensioned between the two balls and one knocks slightly with the hammer on the spring, then the spring will detach immediately out of a frail anchoring. If the spring is well anchored then even a strong blow with a hammer does not do any harm. This fact is also known with mouse and rat traps. Both the mouse trap and the rat trap with its much greater effective force must be set up with the springs tensioned and in a frail adjustment. They have to react to the slightest "knock". Otherwise no rats or mice can be caught with this device.

The measure for stability therefore is the strength of the "hammer blow" in order to detach the bond from its "anchoring" and not the tension of the spring. The same applies to joined particles. We will consider later what could be used as a hammer for the small particle associates.

stability	bond strength	stability
increases	increases	increases

Scheme 3.14: Bond order and stability (examples)



Since stability and bond strength are quantities independent from each other there exists the whole range possible of bonds:

strong and stable *strong and frail*

weak and stable *weak and frail*

As an example let us consider bonds between nitrogen and carbon atoms respectively, from the single bond to the triple bond. In both cases the bond strength increases from the single bond to the triple bond. In case of the nitrogen molecule the triple is even the most stable, the third bond is "anchored" especially well. In case of the carbon atom the reverse is true, the triple bond is the frailest.

However, with those model comparisons it has to be considered exactly how far the possibilities of illustration work, how far the model fits. The bonding model of the balls and spring illustrates the chemical bond according to experimental results only if the balls are not separated from each other. If the balls are separated slowly they have to be pulled apart. If the bond is portrayed by a spring then the force would increase constantly and then it would detach with a sudden jerk. This does not fit the observations. The force necessary to separate particles of a substance is greater at the beginning and decreases until the balls are separated. In this case the picture of two connected magnets which are to be separated fits better.

In order to illustrate the behaviour of the particles the chemist must have a great store of pictures or models available. The art is in the right choice and in the useful application of the models. If there is no suitable model at hand then it is up to the intuition of the chemist to come up with a suitable picture. Here the philosophical approach to chemistry appears again.

3.6 Strength and standardisation of spatially undirected bonding power

3.6.1 Standardisation of the bonding power of ions

The ions as for example given in the periodic table can be combined in an amazing variety. This variety of experimental observation leads to the question of a sorting principle according to which the ions can be combined with each other.

To find this order is much more difficult than with the directed bonding power. Considering spatially undirected bonding ability the number of particles which can be tied on is in principle unlimited, because it depends on the space available, on the geometry.

Ions possess the characteristic of attracting or repulsing each other. Cations among themselves and anions among themselves repulse each other. No other particle type does this. Atoms with directed bonding power do not do this, nor atoms with undirected bonding power: With all those particles only attractive forces are employed.

If ions are joined then the attractive and repulsive principle must be balanced. In this case the ionic charge serves as a descriptive quantity. Firstly we will carry out an experiment of ideas, which will show the force effect of ions in analogy to the attraction of masses (compare (1) and (2) in scheme 3.15).

Let us take the earth as the standard mass and let us hang two balls of different weight on a spring balance. If the spring balance shows the double force for the second ball, then the mass of this ball can be labelled with e.g. 2 kg and the mass of the first ball with 1 kg. Now we take something with a constant electric field, which is negatively charged (e.g. a rubbed foil, cf. (2) in scheme 3.15), and measure the force with which a positively charged lithium ion is attracted. We repeat the same with source of force, which is effective over a distance, and measure the force effect on a negatively charged fluorine ion. The result of the measurements is that the forces effective on both ions, the lithium ion and the fluorine ion, are exactly of the same quantity. Now we measure all the other ions in the distantly effective electric field and evaluate their force effects. We take the positive lithium ion and the negative fluorine ion as a standard and note how much stronger the "test ion" is attracted in the electric field than the lithium or fluorine ion. Picture (2) symbolises a Ca^{2+} ion which shows the double strength of the force effect.

force effective
over a distance

(1) Standard mass, e.g. the earth

(2) standard charge, e.g. foil

(gravitational field)

(electric field)

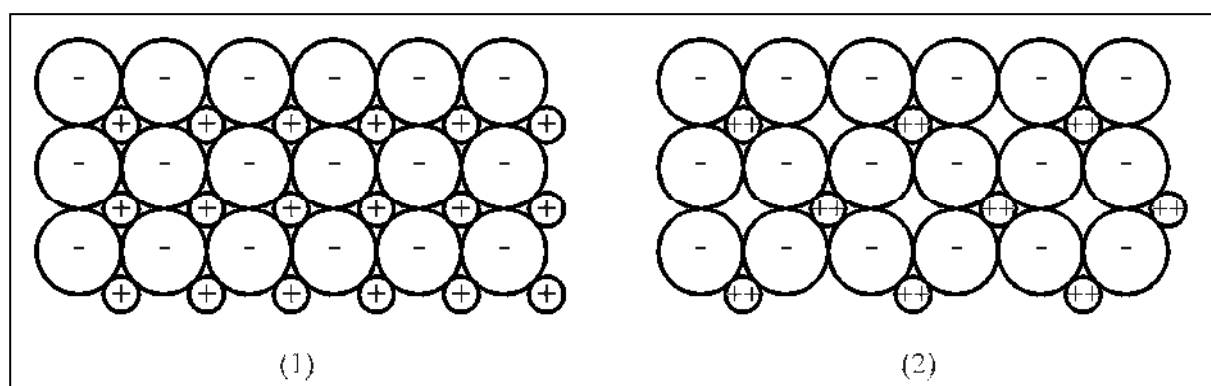
Scheme 3.15: Ionic charges as a standard of force effects

Li^+	Mg^{2+}	Al^{3+}	N^{3-}	O^{2-}	F^-
Na^+	Ca^{2+}	Fe^{3+}	P^{3-}	S^{2-}	Cl^-
K^+	Ba^{2+}	Cr^{3+}			Br^-
Ag^+	Zn^{2+}				I^-

Out of the positively charged ions sodium, potassium and silver ions show the same force effect like a lithium ion. Magnesium, calcium and zinc ions have double, aluminium, some iron or chromium ions triple, some lead ions even four times the force effect of a lithium ion.

These force effects can also be shown in an experiment. Following this the size of the electric charge has been labelled: 1+, 2+, 3+ or 4+. Some examples of positively charged ions with the corresponding **ionic symbols** are shown in (3) in scheme 3.15.

The standardisation of negatively charged ions is carried out analogously in a positive electric field. The force effects of the negatively charged ions are measured and compared with the force effect of the fluorine ion, which has been given the standard charge of 1-. The charges of ions are given as a multiple of the charge of the fluorine ion. Scheme 3.15 also shows some examples.



With the charge numbers of the ions we describe the electric bonding forces around the ion. If we join a few ions then the ions with distantly effective forces take their places in a way so that with an equal number and a balanced distribution of positive and negative charges attraction and repulsion are in balance and stable. Such a particle associate is also said to be electrically balanced or electrically neutral.

Scheme 3.16 shows two-dimensional models of ion associates, which are called "electrically neutral". The pictures within this scheme are excerpts of areas of any size and they give the building principle after which the ions are to be combined within the associate.

In picture (1) each positively charged ion with the charge number $1+$ is surrounded by four negatively charged ions with the charge number $1-$ and at the same time each ion with the charge number $1-$ is surrounded by four other ions: Each ion with the charge number $1-$ is therefore surrounded by the charge $4+$ and each ion with the charge number $1+$ by the charge $4-$.

In picture (2) each " $2+$ ion" is surrounded by four " $1-$ ions" and at the same time each " $1-$ ion" by two " $2+$ ions". Therefore each ion with the charge number $1-$ is also surrounded by the charge $4+$ and each " $2+$ ion" by the charge $4-$.

The standardisation of the ionic charge based on the Li^+ and F^- ions carries the advantage that we can sort and use the ions according to their equal electrical force effect. Furthermore the requirement of electric neutrality when combining ions leads to the prediction of the ratio in which we have to make the anions and cations available. In the case of (1) the ratio of the ions $\text{A}^+ : \text{B}^-$ has to be $1 : 1$, in the case of (2) $\text{A}^{2+} : \text{B}^- = 1 : 2$. However, about the number of countercharged ions which have to be joined with a single ion no common statement is possible.

3.6.2 Standardisation of spatially undirected, non ionic bonding ability

Undirected, non ionic bonding power is employed by the metal atoms. The number of bonding partners, which can be tied on a metal atom, cannot, as it was the case with the ions, be standardised due to the spatially undirected bonding ability. Metal atoms also do not repulse each other. Therefore for metal atoms there result no clues for the standardisation of the bonding power. Due to this fact there is also no prospect for a combination systematicity of the metal atoms. The physical chemists, physicists and metallographers work feverishly to solve this problem.

Therefore the chemist is forced to synthesise and investigate each combination of metal atoms which is of interest. It is an arduous and not very popular field. However, we can still work out some common basic facts about the chemistry of metals.

4. Possibilities of variation in the combination of basic building blocks

4.1 Selection of particle quality and bonding type

We remember the large number of basic building blocks which is summarised in the periodic table. They build by appropriate combination the substances known to us. We now know from many element types two qualities, the atoms and the ions. Which quality should we take for the combination, i.e. which quality are we allowed to take? For the combination of nitrogen and fluorine particles should ions or atoms be used, which particle qualities for the combination of sodium and chlorine particles or for the combination of copper and gold particles? This question has to be answered in the chemical laboratory.

At the same time the question remains which bonding type is to be employed, because we have to decide between the spatially directed and the spatially undirected bonding ability. Nitrogen and fluorine particles, sodium and chlorine particles, copper and gold particles: which bonding type will they make use of? Let us compile which possibilities are given theoretically, if we consider both particle qualities and both bonding types in the combination technique of the particles.

As has been explained in 3.1

- a) metal atoms with undirected bonding ability
 - b) non-metal atoms with directed bonding ability
 - c) ions with undirected bonding ability
- each lead to their own force qualities due to their force effects.

If we assume that only particles with the same force quality can be joined, then this is directly translated into action in the variations 1-3. These three variations are in fact the most important combination types within the great framework.

	particle quality	bonding type
1.	atoms-atoms	spatially undirected
2.	atoms-atoms	spatially directed
3.	ions-ions	spatially undirected
4.	ions-ions	spatially directed

5.	ions-atoms	spatially undirected
6.	ions-atoms	spatially directed

Table 4.1: Theoretical possibilities of particle combination and bonding types

The variations 4-6 also exist. However, in their reciprocal force effect including the corresponding combination system they are much more difficult to describe than the variations 1-3 and they concern complicated particle combinations, which are exemplary presented in chapter 5.

4.2 Combination rules based on the periodic table

We now come to the question where in the periodic table the individual particles with the particle and bonding qualities can be met. In order to find an easy way to orientate ourselves within the periodic table, we divide it into two parts, left and right (cf. scheme 2.1).

We start setting the boundary from top to bottom, beginning with beryllium (Be) and boron (B), continue the line diagonally along silicon (Si) in the third period and germanium (Ge) in the fourth period. The further course of our boundary line leads us diagonally in direction of the lower right hand corner to antimony (Sb) in the fifth period and then vertically downwards to bismuth (Bi) in the sixth period. This strange boundary line is dictated by results from the laboratory.

Of the 103 element types cited 77 types are therefore on the left side of the periodic table, those are the **metals**. On the right side 22 particle types are at home, which are no metals, they are therefore called **non-metals**. Four particle types are on the borderline, they are "hermaphrodites" which cannot be counted neither to the metals nor to the non-metals or which are part of both.

Now we can set up three easy rules for the combination of particles which are shown in a shortened schematic version in table 4.2:

1. If we want to combine particles from the left hand side of the periodic table then we have to take the atoms and join them spatially undirected.
2. With particles from the left hand side we choose the atoms and join them spatially directed.

3. The combination of particles from the left hand side with particles from the right hand side demands the use of the corresponding ions which are joined spatially undirected.

Some examples are to explain those rules: If we combine only Mg particles which each other then rule 1 is valid. All particles are on the left hand side of the periodic table. Therefore we have to join Mg atoms with spatially undirected bonding ability. We can also find Cu and Zn particles on the left hand side. When combining in order to achieve brass Cu atoms and Zn atoms are joined spatially undirected.

place of the particles within the periodic table	particle quality	bonding type
left + left	atoms	spatially undirected
right + right	atoms	spatially directed
left + right	ions	spatially undirected

Table 4.2: Possibilities of combination of particles and bonding types

If we now want to combine S atoms with each other, then we find those on the right hand side of the periodic table: rule 2 applies here, S atoms are joined with spatially directed bonds. The same applies if we combine P and O atoms.

If we want to set up ions then we always have to use at least two types, because we need cations and anions, e.g. Mg^{2+} ions and Br^- ions. They are joined spatially undirected as it is the case with Ca^{2+} and O^{2-} or Na^+ and Cl^- ions.

In chapter 5 the most important constructions which result from these basic rules will be explained.

One word about the placing of hydrogen within the periodic table: There exist many representations in which the corresponding author sets the hydrogen particles at the beginning of the first main group. A few reasons support doing it this way. But hydrogen is a typical non-metal, H atoms carry out directed bonds and the corresponding ions are hydride ions (H^-) which can be joined with positively charged ions: Insofar hydrogen belongs on the right hand side of the periodic table, here it fits best into the combination system present.

4.3 Naming of special particle associates

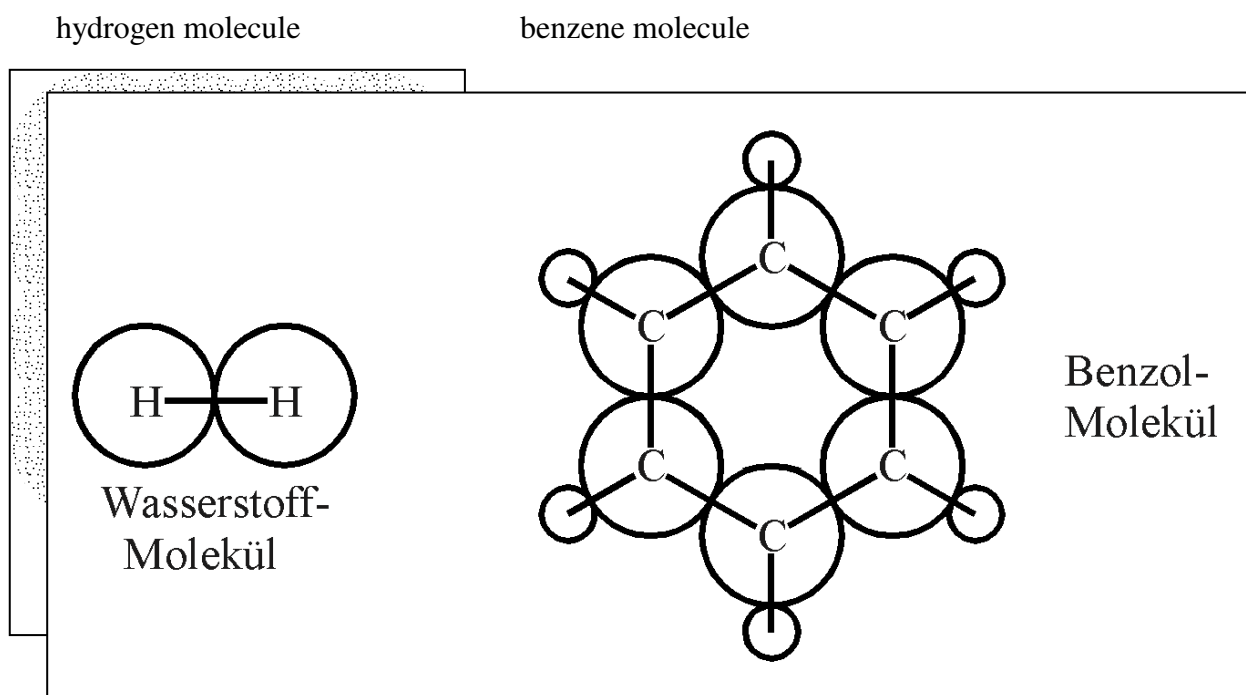
The building with particles, which possess undirected bonding power, leads to totally different constructions than the building with particles, which employ spatially directed bonding power. This has led to individual terms.

If particles, which possess spatially **undirected** bonding power, are joined, then it is a major characteristic that the corresponding construction will never be "finished". One can use as many particles as he wishes, on the edges and boundary surfaces there are always particles with unused bonding power. If the particles are combined according to a regular scheme then this is called a spatial lattice or simply **lattice**. These lattices are realised in **crystals**. Scheme 4.1 make this clearer showing a surface of a lattice.

In the case of particles which possess spatially **directed** bonding power it is characteristic that relatively small building groups are already saturated with regard to the bonding ability. Such an atom associate, which is finished due to the directed bonding ability, is called a **molecule**. Examples are shown in scheme 4.2.

bonding abilities are not used up

Scheme 4.1: Two-dimensional model of a lattice



The terms **lattice and molecule** as well as the terms **atom and ion** serve as a help to describe materials microscopically regarding the particle structure. Two other terms which are often used in chemistry, but which for the time being have nothing to do with the particles, are **element and compound**.

These terms stem from a time when substances in their outer apparition were seen, felt and described only macroscopically. Only in later times these terms were given a meaning based on particles: Any amount of joined or free basic building blocks of the same type of atoms is named a chemical **element**. Any amount of joined or free molecules which are built from only one type of atoms also signifies an element. Turning back this sentence and saying then an element is any amount of joined or free molecules built out of only one type of atoms is wrong because an element does not always have to contain molecules: Elements such as iron or copper consist of the corresponding atoms. The turning back sentence is wrong due to the fact that originally the term element was not invented in order to describe particles.

A compound consists of at least **two types of atoms or ions**. Atoms can be combined to metal associates or molecules, ions to ion associates in corresponding salt structures. Any amount of joined or free molecules which are composed out of different atom types therefore is called a compound - this statement is right. The turning back statement that a compound describes any amount of joined or free molecules built out of different atom types is wrong: a compound can also consist of ions.

In summary the following information can be noted:

An **element** is built out of atoms of only one atom type, the atoms can occur free, they can be combined spatially undirected to give lattices, or they can be combined spatially directed to give molecules.

A **compound** is built out of atoms or ions made out of at least two different atom types: Atoms can be combined to give lattices or molecules or even in a different manner, ions occur free or combined to give lattices.

Dear reader:

After the presentation of our concept in the present first volume we will start in a second volume to combine in a concrete way metal atoms to give metal associates. We want to show which different possibilities exist to combine **metal atoms** of only one atom type to **elementary metal crystals** and how to combine metal atoms of two or more types to give **alloy crystals**. We kindly invite you to undertake this tour into the fascinating world of metals and alloys!

In all further volumes the titles including a short description of which can be found in the appendix, other **principal possibilities for the combination of particles** to give large particle aggregates are to be described. Those description will be this exact so that you can join the particles in your imagination or even build on your own with balls and glue the corresponding structural models. Whether you build the structures of different materials in your imagination or in reality - we hope you enjoy and we wish you every success with the **cross entry into chemistry!**

"Chemistry for cross entries"

Volume 1: Structural chemistry and systematicity of particles

Atoms and ions as basic building blocks of matter; undirected and directed bonding power of particles; periodic table of the elements; combination rules for atoms and ions based on the periodic table; lattices and molecules as fundamentally different structures.

Volume 2: Structure of metals and alloys

Combination of metal atoms to give metal lattices; building principles in spherical packing; filling of holes in close-packed structures, substitutional and interstitial mixed crystals; connection between characteristics and structure in alloys.

Volume 3: Molecules and molecular structures

Combination of non-metal atoms to give molecules; directed bonding power in molecules; standard bond; bond length and bond order; graphite and diamond; molecules of elements and compounds; isomerism; nomenclature and symbolism in molecules.

Volume 4: Ionic crystals with simple lattice building blocks

Combination of ions to give ionic lattices, undirected bonding power of ions within lattices, spherical packing and filling of holes according to the rule of ratio of radii; spatial lattices as models for crystal structures; complex ions; nomenclature and symbolism

Volume 5: Ionic crystals with assembled lattice building blocks

Combination of particles to give chains, bands, layers and three dimensional networks; tetrahedra and octahedra as building units of associated particles; silicates, zeolithe, feldspar, gypsum and alaun.

Volume 6: Classification, symbolism and nomenclature

Summarising overview of the formulate description and nomenclature; form and symmetry of crystalline solids; non-crystalline solids; overview of structures and characteristics.