1 Elements and Periodicity

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The elements are found in various states of matter and define the independent constituents of atoms, ions, simple substances, and compounds. Isotopes with the same atomic number belong to the same element. When the elements are classified into groups according to the similarity of their properties as atoms or compounds, the periodic table of the elements emerges. Chemistry has accomplished rapid progress in understanding the properties of all of the elements. The periodic table has played a major role in the discovery of new substances, as well as in the classification and arrangement of our accumulated chemical knowledge. The periodic table of the elements is the greatest table in chemistry and holds the key to the development of material science. Inorganic compounds are classified into molecular compounds and solid-state compounds according to the types of atomic arrangements.

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1.1 The origin of elements and their distribution

All substances in the universe are made of elements. According to the current generally accepted theory, hydrogen and helium were generated first immediately after the Big Bang, some 15 billion years ago. Subsequently, after the elements below iron (Z = 26) were formed by nuclear fusion in the incipient stars, heavier elements were produced by the complicated nuclear reactions that accompanied stellar generation and decay.

In the universe, hydrogen (77 wt%) and helium (21 wt%) are overwhelmingly abundant and the other elements combined amount to only 2%. Elements are arranged below in the order of their abundance,

$$ {}^{1}_{1}\mathrm{H} > {}^{4}_{2}\mathrm{He} >> {}^{16}_{8}\mathrm{O} > {}^{12}_{6}\mathrm{C} > {}^{20}_{10}\mathrm{Ne} > {}^{28}_{14}\mathrm{Si} > {}^{27}_{13}\mathrm{Al} > {}^{24}_{12}\mathrm{Mg} > {}^{56}_{26}\mathrm{Fe} $$

The **atomic number** of a given element is written as a left subscript and its **mass number** as a left superscript.

1.2 Discovery of elements

The long-held belief that all materials consist of atoms was only proven recently, although elements, such as carbon, sulfur, iron, copper, silver, gold, mercury, lead, and tin, had long been regarded as being atom-like. Precisely what constituted an element was recognized as modern chemistry grew through the time of alchemy, and about 25 elements were known by the end of the 18th century. About 60 elements had been identified by the middle of the 19th century, and the periodicity of their properties had been observed.

The element technetium (Z = 43), which was missing in the periodic table, was synthesized by nuclear reaction of Mo in 1937, and the last undiscovered element promethium (Z = 61) was found in the fission products of uranium in 1947. Neptunium (Z = 93), an element of atomic number larger than uranium (Z = 92), was synthesized for the first time in 1940. There are 103 named elements. Although the existence of elements Z = 104-111 has been confirmed, they are not significant in inorganic chemistry as they are produced in insufficient quantity.

All trans-uranium elements are radioactive, and among the elements with atomic number smaller than Z = 92, technetium, prometium, and the elements after polonium are also radioactive. The half-lives (refer to Section 7.2) of polonium, astatine, radon, actinium, and protoactinium are very short. Considerable amounts of technetium ^{99}Tc are obtained from fission products. Since it is a radioactive element, handling ^{99}Tc is problematic, as it is for other radioactive isotopes, and their general chemistry is much less developed than those of manganese and rhenium in the same group.

Atoms are equivalent to alphabets in languages, and all materials are made of a combination of elements, just as sentences are written using only 26 letters.

1.3 Electronic structure of elements

Wave functions of electrons in an atom are called **atomic orbitals**. An atomic orbital is expressed using three quantum numbers; the **principal quantum number**, n; the **azimuthal quantum number**, l; and the **magnetic quantum number**, m_l. For a principal quantum number n, there are n azimuthal quantum numbers l ranging from 0 to n-1, and each corresponds to the following orbitals.

l : 0, 1, 2, 3, 4, …
s, *p*, *d*, *f*, *g*, …

An atomic orbital is expressed by the combination of n and l. For example, n is 3 and l is 2 for a 3*d* orbital. There are $2l+1$ m_l values, namely $l, l-1, l-2, ..., -l$. Consequently, there are one *s* orbital, three *p* orbitals, five *d* orbitals and seven *f* orbitals. The three aforementioned quantum numbers are used to express the distribution of the electrons in a hydrogen-type atom, and another quantum number m_s (1/2, -1/2) which describes the direction of an electron spin is necessary to completely describe an electronic state. Therefore, an electronic state is defined by four quantum numbers (n, l, m_l, m_s).

The wave function ψ which determines the orbital shape can be expressed as the product of a radial wavefunction R and an angular wave function Y as follows.

$$\psi_{n,l,ml} = R_{n,l}(r)Y_{l,ml}(\theta,\phi)$$

R is a function of distance from the nucleus, and Y expresses the angular component of the orbital. Orbital shapes are shown in Fig. 1.1. Since the probability of the electron's existence is proportional to the square of the wave function, an electron density map resembles that of a wave function. The following conditions must be satisfied when each orbital is filled with electrons.

[The conditions of electron filling]

Pauli principle: The number of electrons that are allowed to occupy an orbital must be limited to one or two, and, for the latter case, their spins must be anti-parallel (different direction).

Hund's rule: When there are equal-energy orbitals, electrons occupy separate orbitals and their spins are parallel (same direction).

The order of orbital energy of a neutral atom is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p \ldots$$

and the electron configuration is determined as electrons occupy orbitals in this order according to the Pauli principle and Hund's rule. An *s* orbital with one m_l can accommodate 2 electrons, a *p* orbital with three m_l 6 electrons, and a *d* orbital with five m_l 10 electrons.

Exercise 1.1 Describe the electron configuration of a C atom, an Fe atom, and a Au atom.

[Answer] Electrons equal to the atomic number are arranged in the order of orbital energies. Since the electrons inside the valence shell take the rare gas configuration, they may be denoted by the symbol of a rare gas element in brackets.

C: $1s^2 2s^2 2p^2$ or [He]$2s^2 2p^2$
Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$ or [Ar]$3d^6 4s^2$
Au: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^1$ or [Xe]$4f^{14} 5d^{10} 6s^1$

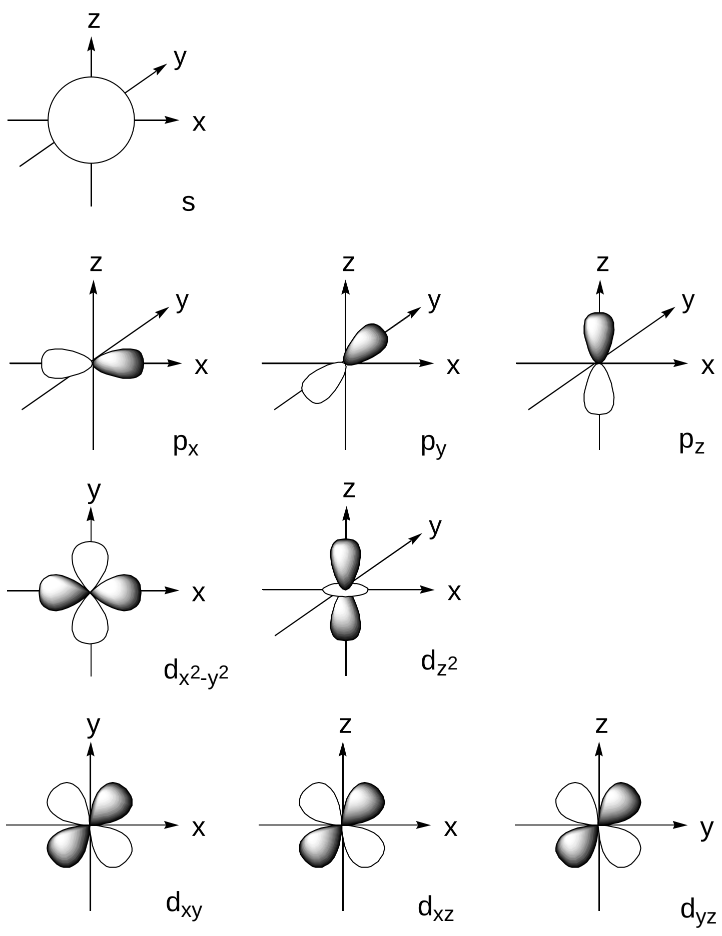

Fig. 1.1 Shapes of *s*, *p*, and *d* orbitals.

Table 1.1 Periodic table of elements. The values are atomic weights.

	1	2	3	4	5	6	7	8	9
1	1.008 $_{1}$H								
2	6.941 $_{3}$Li	9.012 $_{4}$Be							
3	22.99 $_{11}$Na	24.31 $_{12}$Mg							
4	39.10 $_{19}$K	40.08 $_{20}$Ca	44.96 $_{21}$Sc	47.87 $_{22}$Ti	50.94 $_{23}$V	52.00 $_{24}$Cr	54.94 $_{25}$Mn	55.85 $_{26}$Fe	58.93 $_{27}$Co
5	85.47 $_{37}$Rb	87.62 $_{38}$Sr	88.91 $_{39}$Y	91.22 $_{40}$Zr	92.91 $_{41}$Nb	95.94 $_{42}$Mo	(99) $_{43}$Tc	101.1 $_{44}$Ru	102.9 $_{45}$Rh
6	132.9 $_{55}$Cs	137.3 $_{56}$Ba	Lantha- noid	178.5 $_{72}$Hf	180.9 $_{73}$Ta	183.8 $_{74}$W	186.2 $_{75}$Re	190.2 $_{76}$Os	192.2 $_{77}$Ir
7	(223) $_{87}$Fr	(226) $_{88}$Ra	Acti- noid						
Lanthanoid			138.9 $_{57}$La	140.1 $_{58}$Ce	140.9 $_{59}$Pr	144.2 $_{60}$Nd	(145) $_{61}$Pm	150.4 $_{62}$Sm	152.0 $_{63}$Eu
Actinoid			(227) $_{89}$Ac	232.0 $_{90}$Th	231.0 $_{91}$Pa	238.0 $_{92}$U	(237) $_{93}$Np	(239) $_{94}$Pu	(243) $_{95}$Am

10	11	12	13	14	15	16	17	18
								4.003 $_{2}$He
			10.81 $_{5}$B	12.01 $_{6}$C	14.01 $_{7}$N	16.00 $_{8}$O	19.00 $_{9}$F	20.18 $_{10}$Ne
			26.98 $_{13}$Al	28.09 $_{14}$Si	30.97 $_{15}$P	32.07 $_{16}$S	35.45 $_{17}$Cl	39.95 $_{18}$Ar
58.69 $_{28}$Ni	63.55 $_{29}$Cu	65.39 $_{30}$Zn	69.72 $_{31}$Ga	72.61 $_{32}$Ge	74.92 $_{33}$As	78.96 $_{34}$Se	79.90 $_{35}$Br	83.80 $_{36}$Kr
106.4 $_{46}$Pd	107.9 $_{47}$Ag	112.4 $_{48}$Cd	114.8 $_{49}$In	118.7 $_{50}$Sn	121.8 $_{51}$Sb	127.6 $_{52}$Te	126.9 $_{53}$I	131.3 $_{54}$Xe
195.1 $_{78}$Pt	197.0 $_{79}$Au	200.6 $_{80}$Hg	204.4 $_{81}$Tl	207.2 $_{82}$Pb	209.0 $_{83}$Bi	(210) $_{84}$Po	(210) $_{85}$At	(222) $_{86}$Rn
157.3 $_{64}$Gd	158.9 $_{65}$Tb	162.5 $_{66}$Dy	164.9 $_{67}$Ho	167.3 $_{68}$Er	168.9 $_{69}$Tm	173.0 $_{70}$Yb	175.0 $_{71}$Lu	
(247) $_{96}$Cm	(247) $_{97}$Bk	(252) $_{98}$Cf	(252) $_{99}$Es	(257) $_{100}$Fm	(258) $_{101}$Md	(259) $_{102}$No	(262) $_{103}$Lr	

1.4 Block classification of the periodic table and elements

Starting from hydrogen, over 100 elements are constituted as electrons are successively accommodated into 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, and 3*d* orbitals one by one from lower to higher energy levels. When elements with similar properties are arranged in columns, the periodic table of the elements is constructed. The modern periodic table of the elements is based on one published by D. I. Mendeleev in 1892, and a variety of tables have since been devised. The long periodic table recommended by IUPAC is the current standard, and it has the group numbers arranged from Group 1 alkali metals through Group 18 rare gas elements (Table 1.1).

Based on the composition of electron orbitals, hydrogen, helium and Group 1 elements are classified as ***s*-block elements**, Group 13 through Group 18 elements ***p*-block elements**, Group 3 through Group 12 elements ***d*-block elements**, and lanthanoid and actinoid elements ***f*-block elements**. (Fig. 1.2). *s*-Block, *p*-block, and Group 12 elements are called **main group elements** and *d*-block elements other than Group 12 and f-block elements are called **transition elements**. The characteristic properties of the elements that belong to these four blocks are described in Chapter 4 and thereafter. Incidentally, periodic tables that denote the groups of *s*-block and *p*-block elements with Roman numerals (I, II, ..., VIII) are still used, but they will be unified into the IUPAC system in the near future. Since inorganic chemistry covers the chemistry of all the elements, it is important to understand the features of each element through reference to the periodic table.

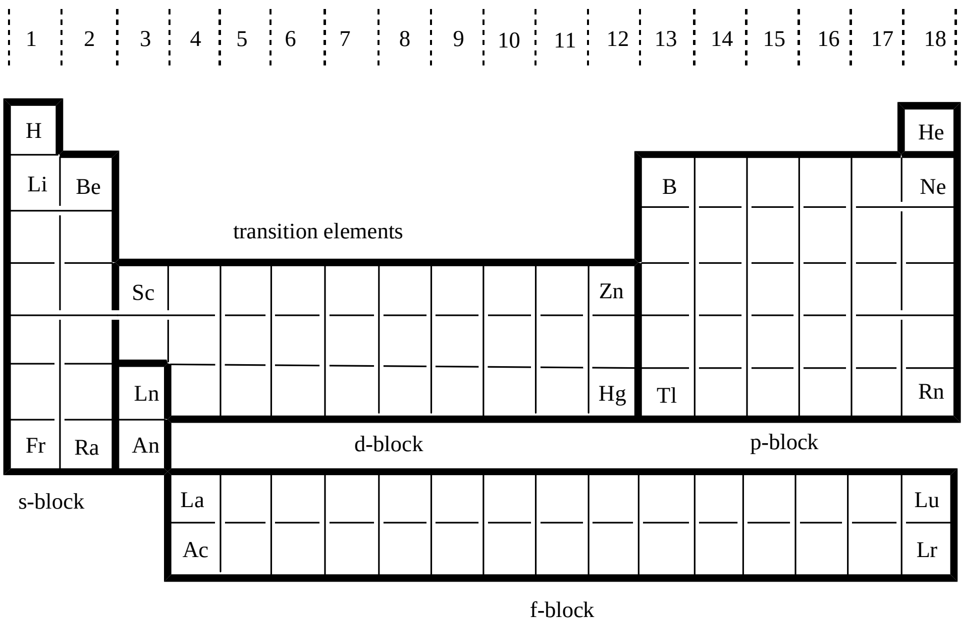

Fig. 1.2 Block classification of elements in the periodic table.

1.5 Bonding states of elements

Organic compounds are molecular compounds that contain mainly carbon and hydrogen atoms. Since inorganic chemistry deals with all compounds other than organic ones, the scope of inorganic chemistry is vast. Consequently, we have to study the syntheses, structures, bondings, reactions, and physical properties of elements, molecular compounds, and solid-state compounds of 103 elements. In recent years, the structures of crystalline compounds have been determined comparatively easily by use of single crystal X-ray structural analysis, and by through the use of automatic diffractometers. This progress has resulted in rapid development of new areas of inorganic chemistry that were previously inaccessible. Research on higher dimensional compounds, such as **multinuclear complexes**, **cluster compounds**, and solid-state inorganic compounds in which many metal atoms and ligands are bonded in a complex manner, is becoming much easier. In this section, research areas in inorganic chemistry will be surveyed on the basis of the classification of the bonding modes of inorganic materials.

(a) Element

Elementary substances exist in various forms. For example, helium and other rare gas elements exist as single-atom molecules; hydrogen, oxygen, and nitrogen as two-atom molecules; carbon, phosphorus, and sulfur as several solid allotropes; and sodium, gold, *etc*. as bulk metals. A simple substance of a metallic element is usually called **bulk metal**, and the word "metal" may be used to mean a bulk metal and "metal atom or metal ion" define the state where every particle is discrete. Although elementary substances appear simple because they consist of only one kind of element, they are rarely produced in pure forms in nature. Even after the discovery of new elements, their isolation often presents difficulties. For example, since the manufacture of ultra high purity silicon is becoming very important in science and technology, many new purification processes have been developed in recent years.

Exercise 1.2 Give examples of allotropes.

[Answer] carbon: graphite, diamond.

Phosphorus: white phosphorus, red phosphorus.

(b) Molecular compounds

Inorganic compounds of nonmetallic elements, such as gaseous carbon dioxide CO_2, liquid sulfuric acid H_2SO_4, or solid phosphorus pentoxide P_2O_5, satisfy the valence requirements of the component atoms and form discrete molecules which are not bonded together. The compounds of main group metals such as liquid tin tetrachloride $SnCl_4$ and solid aluminum trichloride $AlCl_3$ have definite molecular weights and do not form infinite polymers.

Most of the molecular compounds of transition metals are metal complexes and organometallic compounds in which ligands are coordinated to metals. These molecular compounds include not only **mononuclear complexes** with a metal center but also multinuclear complexes containing several metals, or cluster complexes having metal-metal bonds. The number of new compounds with a variety of bonding and structure types is increasing very rapidly, and they represent a major field of study in today's inorganic chemistry (refer to Chapter 6).

(c) Solid-state compounds

Although solid-state inorganic compounds are huge molecules, it is preferable to define them as being composed of an infinite sequence of 1-dimensional (chain), 2-dimensional (layer), or 3-dimensional arrays of elements and as having no definite molecular weight. The component elements of an inorganic solid bond together by means of ionic, covalent, or metallic bonds to form a solid structure. An ionic bond is one between electronically positive (alkali metals *etc*.) and negative elements (halogen *etc*.), and a covalent bond forms between elements with close electronegativities. However, in many compounds there is contribution from both ionic and covalent bonds (see Section 2.1 about bondings).

Exercise 1.3 Give examples of solid-state inorganic compounds.
[Answer] sodium chloride NaCl, silicon dioxide, SiO_2, molybdenum disulfide, MoS_2.

The first step in the identification of a compound is to know its elemental composition. Unlike an organic compound, it is sometimes difficult to decide the empirical formula of a solid-state inorganic compound from elemental analyses and to determine its structure by combining information from spectra. Compounds with similar compositions may have different coordination numbers around a central element and different structural dimensions. For example, in the case of binary (consisting of two kinds of elements) metal iodides, gold iodide, AuI, has a chain-like structure, copper iodide, CuI, a zinc blende type structure, sodium iodide, NaI, has a sodium chloride structure, and cesium iodide, CsI, has a cesium chloride structure (refer to Section 2.2 (e)), and the metal atoms are bonded to 2, 4, 6 or 8 iodine atoms, respectively. The minimum repeat unit of a solid structure is called a **unit lattice** and is the most fundamental information in the structural chemistry of crystals. X-ray and neutron diffraction are the most powerful experimental methods for determining a crystal structure, and the bonds between atoms can only be elucidated by using them. **Polymorphism** is the phenomenon in which different kinds of crystals of a solid-state compound are obtained in which the atomic arrangements are not the same . Changes between different polymorphous phases with variations in temperature and/or pressure, or **phase transitions**, are an interesting and important problem in solid-state chemistry or physics.

We should keep in mind that in solid-state inorganic chemistry the elemental composition of a compound are not necessarily integers. There are extensive groups of compounds, called **nonstoichiometric compounds**, in which the ratios of elements are non-integers, and these non-stoichiometric compounds characteristically display conductivity, magnetism, catalytic nature, color, and other unique solid-state properties. Therefore, even if an inorganic compound exhibits non-integral stoichiometry, unlike an organic compound, the compound may be a thermodynamically stable, orthodox compound. This kind of compound is called a non-stoichiometric compound or **Berthollide compound**, whereas a stoichiometric compound is referred to as a **Daltonide compound**. The law of constant composition has enjoyed so much success that there is a tendency to neglect non-stoichiometric compounds. We should point out that groups of compounds in which there are slight and continuous changes of the composition of elements are not rare.

Problem 1.1 Express the isotopes of hydrogen, carbon, and oxygen using the symbols of the elements with atomic and mass numbers and write the number of protons, neutrons, and electrons in parenthesis.

Superheavy elements

The last element in the ordinary periodic table is an actinoid element lawrencium, Lr, (Z = 103). However, elements (Z = 104 – 109) "have already been synthesized" in heavy ion reactions using nuclear accelerators. These are 6*d* elements which come under the 5*d* transition elements from hafnium, Hf, to iridium, Ir, and it is likely that their electronic structures and chemical properties are similar. As a matter of fact, only the existence of **nuclides** with very short lives has been confirmed. The trouble of naming the super heavy elements is that the countries of their discoverers, the United States, Russia and Germany, have proposed different names. The tentative names of these elements are:

unnilquadium Une (Z = 104), unnilpentium Unp (Z = 105), unnilhexium Unh (Z = 106), unnilseptium Unq (Z = 107), unniloctium Uno (Z = 108) and unnilennium Une (Z = 108). It has recently been settled that they be named: Rutherfordium $_{104}$Rf, Dubnium $_{105}$Db, Seaborgium $_{106}$Sg, Bohrium $_{107}$Bh, Hassium $_{108}$Hs, and Meitnerium $_{109}$Mt.

"Synthesis" of the element (Z = 110), which should come under platinum, was considered the technical limit, but there is a recent report that even the element (Z = 112) "was synthesized". In any case, the superheavy elements will run out shortly. It is natural that complications are caused by naming of a new element, because it is a great honor for a scientist to have a new element named after him or her.
