

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.

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 a purification processes have been developed in recent years.

? Exercise 1.5.2

Give examples of allotropes.

Answer

- Carbon: graphite, diamond.
- Phosphorus: white phosphorus, red phosphorus.

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' inorganic chemistry (see [Chapter 6](#)).

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 1.5.3

Give examples of solid-state inorganic compounds.

Answer

- Sodium chloride NaCl
- Silicon dioxide, SiO₂
- Molybdenum disulfide, MoS₂

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 6d elements which come under the 5d 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 ₁₀₄Rf, Dubnium ₁₀₅Db, Seaborgium ₁₀₆Sg, Bohrium ₁₀₇Bh, Hassium ₁₀₈Hs, and Meitnerium ₁₀₉Mt.

"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 a scientist to have a new element named after him or her.

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