INORGANIC CHEMISTRY

FOR TECHNOLOGISTS

KNUTD Textbook Series
for International Training Programmes

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Ministry of Education and Science of Ukraine
Kyiv National University of Technologies and Design

T.M. Derkach

Inorganic Chemistry for Technologists

It is recommended by the Academic Council of
the Kyiv National University of Technology and Design
as a textbook for students of higher education
in the fields of chemical technology & engineering,
biotechnology & bioengineering, and pharmacy & industrial pharmacy

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T.M. Derkach.
D36 Inorganic Chemistry for Technologists. Textbook for students of technological specialities. Kyiv: KNUTD, 2019, 336 pages.
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The book introduces to the basic concepts of inorganic chemistry, such as atomic-molecular theory, classes of inorganic compounds, atomic structure, the periodic law, chemical bonds, equilibrium and kinetics of chemical reactions, properties of solutions, the structure of complex compounds, as well as basic chemical properties of elements. It provides some examples of problem solving, as well as tasks and exercises for independent work.

The book is intended for undergraduate students majoring in chemical technologies & engineering, biotechnology & bioengineering, and pharmacy & industrial pharmacy.

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Content

Abbreviations and reference designations

am – ammonia
aq – aqueous
boil – boiling
conc – concentrated
const. – constant
diam – diamond
dil – dilute
EDTA – ethylenediaminetetraacetato
en – ethylenediamine
g – gas
graph – graphite
freez – freezing
ini – initial
IUPAC – the International Union of Pure and Applied Chemistry
l – liquid
MO and MMO – molecular orbitals and method of molecular orbitals
prod – product
s – solid
soln – solution
SI – International System of Units
sub(subs) – substance
3D – three-dimensional

a – the activity
A_r – the relative atomic mass
C – the molarity (or molar concentration)
C_f – the normality (or equivalent concentration)
C_m – the molality (or molal concentration)
c.n. – the coordination number
E_a – the activation energy
E_b – the binding energy of an electron
E^0 – the standard reduction potential
f – the coefficient of activity
$f_{equ} = 1/z$ – the equivalence factor
G and ΔG – the free energy of Gibbs and its change
H and ΔH – the enthalpy and its change
I – the energy of ionisation
i – the isotonic coefficient
k (or K) – the constant of the reaction rate
K_a – the acid ionisation constant
K_b – the base ionisation constant

K_c – the cryoscopic constant
K_d – the dissociation constant
K_{eb} – the ebullioscopic constant
K_h – the hydrolysis constant
K_e – the equilibrium constant
K_w (or K_{H2O}) – the ion product of water
K_{in} – the instability constant
K_{sp} – the solubility product constant
K_{st} – the stability (or formation) constant
M – the molar (mol) mass
M_f – the equivalent mass
M_r – the relative molecular mass
n, m_l, l, s – quantum numbers
pH – the hydrogen index
pOH – a measure of hydroxide ion (OH^-) concentration
P_{osm} – the osmotic pressure
Q_V (Q_p) – the heat under constant volume (pressure)
s p d f – electron energy sublevels (orbitals)
S°_{298} and ΔS – the standard entropy and its change
U and ΔU – the internal energy of the system and its change
v – the rate of reaction
V_f – the equivalent volume
Z – the charge of a nucleus or the element number in the periodic table
z – the equivalent number

α – the valence angle
α – the degree of dissociation
α, β, γ – types of irradiation
γ – the temperature coefficient of reaction rate
ΔH_f – the heat (enthalpy) of formation
δ_i – the effective charge of an ion of element i
$\bar{e}$ – the electron charge
λ – the length of wave
μ – the solution ionic strength
ν – the amount of substance
σ, δ, π – types of chemical bonds
τ – time
χ – the electronegativity of an atom
ψ – the wave function
ω – the mass fraction of the element in a compound

Introduction

The educational process should provide fundamental scientific training for students, as well as consolidate their skills for independent work and the desire for continuous updating of knowledge.

In the preparation of future technologists of different industries, an extremely important role belongs to the study of a block of basic chemical disciplines. Among these disciplines, inorganic chemistry forms the basis for further mastering of other chemical subjects as it provides mastery of basic concepts and laws of chemistry. In the course of inorganic chemistry learning, students develop a dialectical way of thinking, the ability to analyse phenomena and understand processes at the molecular level. Besides, the perception of the world is formed, and scientific ideas about matter, structure and properties of substances are expanded and deepened.

Inorganic chemistry is a methodological basis for mastering special disciplines by future technologists. For many technical specialities, such as biotechnology, chemical technology and engineering, industrial pharmacy, organisation and implementation of technological processes require knowledge of the chemical composition of raw materials and finished products. During production, a complex of chemical, biochemical, microbiological, and physicochemical processes is carried out that results in the transformation of raw materials into finished products. Understanding all of these processes will not be possible without knowledge of the basics of inorganic chemistry.

One of the reasons for the lack of cognitive activity of students is the lack of scientifically substantiated textbooks and manuals which are written with a glance of the profile of future specialists. Existing books are not designed for independent study of material, too voluminous, overloaded with facts instead of interpreting the laws that determine these facts. This current issue is intended to help students in mastering the program material independently.

The book consists of six chapters. Each chapter provides examples of solutions to typical tasks, as well as problems, exercises, and tasks for self-control.

The first chapter is devoted to the formulation of basic concepts and laws of chemistry. The basics of the atomic-molecular theory are explained, which will be used in the future. The classification of the main classes of inorganic compounds is given.

In chapter 2, the concepts of the structure of the atom in its historical development are introduced. The concepts of quantum mechanics regarding quantum numbers, the dualistic nature of electrons, and the rules for filling electronic orbitals are introduced. On this basis, the periodicity in changes of chemical and physical properties of elements, principles of construction of the periodic system and the periodic table of elements are considered. The basic types of chemical bonding are analysed.

The third chapter deals with chemical reactions. The main postulates and laws of thermodynamics are formulated, as well as the basic laws governing the equilibrium and kinetics of chemical reactions are described.

Chapter 4 deals with hydrolysis and redox reactions. The behaviour of these processes are illustrated by a detailed analysis of a large number of practical examples

Chapter 5 deals with complex compounds. The main types of coordination compounds, their nomenclature, the available types of chemical bonds, and the stability of coordination compounds are considered. The basic types of isomers, as well as the types and examples of important ligands, are provided.

The chemical properties of the elements are analysed in chapter 6. According to the degree of filling of the electronic shells, all chemical elements are divided into three blocks — s-block (groups 1 and 2), p-block (groups 13–18) and d-block (groups 3–12) elements. In each block, the properties of the elements are considered in terms of groups of the periodic table. The basic regularities for changes in the properties of the elements from lightest to heaviest in the groups are given. For each group, critical redox and acid-base reactions, as well as complexing properties of the elements of each group, are described. Also, examples of the application of the most important elements, and technological processes and reactions used to their preparation are discussed.

The textbook is designed to work within the frames of a credit-module system of the organisation of the educational process. The amount of information provided is adapted to teach the course material in 32 lecture hours and completing relevant homework.

Chapter 1. Basic concepts and laws of chemistry. Classification and nomenclature of inorganic compounds

Even in the times of ancient Greek philosophers, it was believed that substances consist of microscopic indivisible particles — atoms. However, they could not confirm it experimentally. Scientific ideas about the atom arose much later, as a result of the development of experimental physics and chemistry.

In the XVII century, English scientist Robert Boyle (1627–1691), whose chemical ideas were based on atomism, explained all the chemical changes in terms of unification and separation of atoms. In the XVIII century, Russian scientist M. Lomonosov (1711–1765) formulated the basic provisions of atomic-molecular theory.

The quantitative basis of atomic-molecular theory was created thanks to the rapid development of chemistry in the works of many scientists at the end of the XVIII – the beginning of the XIX century.

English scientist John Dalton (1766–1844) formulated the law of multiple proportions and first introduced the concept of atomic mass.

French chemist and physicist Joseph Louis Gay-Lussac (1778–1850) discovered the law of combining volumes.

Italian scientist Amedeo Avogadro (1776–1856) in 1811 proposed the definition of a molecule as the smallest part of a substance that is capable of independent existence and consists of atoms. He also discovered the law that got his name.

At the beginning of the XIX century, French chemists Joseph-Louis Proust (1754–1826) and Claude Louis Berthollet (1748–1822) identified and differentiated the concept of "chemical substance" and "mechanical mixture".

Proust in 1808 formulated the law of definite proportions. A clear definition of the concepts of "atom" and "molecule" was given by Italian Stanislao Cannizzaro (1826–1910) in 1858. All these definitions were adopted at the First International Congress of Chemists in the city of Karlsruhe in 1860.

Thus, the foundations of the atomic-molecular theory were created, which were later confirmed and developed in a series of outstanding discoveries of the late XIX century. So, in 1869, D.I. Mendeleev (1834–1907), a Russian chemist, formulated the periodic law of chemical elements. In 1860, Russian chemist A.M. Butlerov (1828–1886) developed a theory of the chemical structure of organic substances. In 1873, Dutch scientist Johannes Diderik van der Waals (1837–1923), a Nobel Prize winner, formulated the principle of continuity of the liquid and gaseous states of matter. Dutch chemist Jacobus Henricus van't Hoff (1852–1911) made an outstanding contribution to the field of chemical kinetics.

1.1. Basic concepts and laws of chemistry

1.1.1 Highlights of atomic-molecular theory

1. Substances have a discrete structure. They consist of particles (structural elements – molecules, atoms or ions).
2. Parts of matter are continuous, randomly moving.
3. The forces of mutual attraction and repulsion act between the constituent particles of matter.
4. Gaps exist between the constituent particles of matter.
5. The molecules consist of atoms.
6. Molecules remain intact during physical phenomena and are destroyed during chemical processes.
7. Atoms remain intact during chemical reactions; at the same time, their rearrangement occurs, which leads to the formation of new substances.
8. Diversity of substances is due to different combinations of atoms.

1.1.2 Basic concepts

The basic concepts of the atomic-molecular theory are the molecule, atom, chemical element, and substance.

A molecule (from the Latin moles – mass) is the smallest proportion of matter that retains the properties of this substance and is capable of independent existence.

An atom (from the Greek atomos – indivisible) is a chemically indivisible electroneutral component of a substance consisting of a positively charged nucleus and negatively charged electrons.

A chemical element is a kind of atoms with the same charge of the nucleus.

The substance is a type of matter characterised by specific physical and chemical properties under these conditions.

1.1.3 Physical quantities used in chemistry

Since the absolute values of the masses of atoms and molecules are very small quantities, it is very uncomfortable to use them in chemical calculations. In connection with this, it was necessary to introduce their relative values.

The relative atomic mass of a chemical element (A_r) is a physical quantity, which is determined by the ratio of the mass of an atom (m_a) of the element to one-twelfth of the mass of an atom of the isotope of carbon ^{12}C.

$$A_r = \frac{m_m}{{}^1\!/_{12}\, m_a(^{12}C)} \qquad (1.1)$$

The relative molecular mass (M_r) is a physical quantity determined by the ratio of the mass of the molecule (m_m) to one-twelfth of the mass of the carbon atom isotope ^{12}C.

$$M_r = \frac{m_m}{{}^1\!/_{12}\, m_a(^{12}C)} \qquad (1.2)$$

The relative molecular mass can be calculated as a sum of the relative atomic masses of all elements that are parts of the molecule:

$$M_r = n_1A_r^{/} + n_2A_r^{//} + \ldots + nA_r. \qquad (1.3)$$

The mass fraction of the element included in the molecule is determined by the formula:

$$\omega(E) = \frac{nA_r}{M_r} \cdot 100\% \,. \qquad (1.4)$$

Amount of substance (ν) is a physical quantity, which is determined by the number of particles – the structural elements of matter: molecules, atoms, ions, ion associates.

The following ratio determines the amount of substance:

$$\nu = \frac{N}{N_A}\,, \qquad (1.5)$$

where N is the number of structural elements in a certain portion of the substance. If $N= N_A$, then $n = 1$. This unit in the International System of Units is called mole and designated as mol.

A mole is a unit of measurement of the amount of substance, as well as a kilogram (kg), is a unit of measurement of the mass.

Mole is the amount of substance that contains the number of particles (structural elements – molecules, atoms, ions) equal in value to the number of atoms in the carbon isotope ^{12}C weighing 0.012 kg.

The number of atoms or molecules contained in a substance of 1 mol is called Avogadro number.

$$N_A = \frac{m(^{12}C)}{m_a(^{12}C)} = \frac{0.012\ \text{kg}}{1\ \text{mol}\cdot 1.9927\cdot 10^{-26}\ \text{kg}} = 6.02\cdot 10^{23}\,\text{mol}^{-1} \quad (1.6)$$

The molar (or mol) mass (M) is the mass of 1 mol expressed in g/mol.

$$M = m_a N_A \quad (1.7)$$

The values of M_r and M are the same in magnitude, but the molar mass, unlike the dimensionless relative molecular mass, has its dimension. If $\nu = 1$ mol, then the mass of the substance is equal to the molar mass $m = M$, and if we increase ν, then the mass of matter m also increases, that is

$$m = \nu M \text{ or } \nu = m / M. \quad (1.8)$$

For gases, molar volume is an important value. The molar volume is the volume of a gaseous substance in the amount of 1 mol.

Under normal conditions (P = 101.3 kPa, t = 0°C or T = 273 K), the molar volume of any gaseous substance is $V_M = 22.4$ L/mol.

Thus, the amount of substance can be determined by the formula

$$\nu = V/V_M \quad (1.9)$$

1.1.4 Fundamental laws of chemistry

The basic laws of chemistry were discovered in the late XVIII – early XIX century and served as the base for the transformation of chemistry into a science that uses mathematical methods.

1. Law of conservation of mass of substances.

This law was discovered and experimentally substantiated by M.V. Lomonosov in 1748 and then by French chemist Antoine Lavoisier (1743–1794) in 1789:

The mass of substances entering the chemical reaction is equal to the total mass of substances formed as a result of the reaction.

If the chemical reaction is expressed in the general form as A + B = C + D, then the law can be written as m(A + B) = m(C + D)

For example:

$$\underbrace{\underset{2\cdot 2}{2H_2} + \underset{32}{O_2}}_{36} = \underbrace{\underset{2\cdot 18}{2H_2O}}_{36}$$

2. The law of definite proportions.

This law was formulated by J.-L. Proust in 1808:

Each chemical compound, regardless of the method of its extraction, consists of the same elements, and the ratio of the masses of constituent elements is constant, and the ratio of the number of their atoms is expressed by integers.

Later, in connection with the development and implementation of experimental methods that allow ones to determine the elemental composition of compounds more precisely, the limited validity of the laws of Dalton and Proust was found: They are valid only for liquid and gaseous compounds with a molecular structure (for example, SO_2, SO_3, NH_3, or CH_4). Such compounds in honour of Dalton are called daltonides.

Besides daltonides, there are non-stoichiometric compounds known as berthollides. Berthollides are crystalline phases of variable composition in which the ratio of the numbers of different atoms cannot be precisely expressed by small integers.

The stoichiometric indices in the berthollides formulas may not be integers. Berthollides are often found among binary compounds (hydrides, oxides, nitrides, or carbides) of transition metals. For example, ferrous oxide belongs to berthollides, the composition of which can be represented by the formula $Fe_{1-x}O$, where $x < 1$. In other words, depending on the conditions, oxides of $Fe_{0.93}O$ or $Fe_{0.89}O$ can be obtained.

3. The law of combining volumes.

French chemist and physicist J.-L. Gay-Lussac formulated it in 1808:

Under conditions of invariable pressure and temperature, the ratio between the volumes of the reactant gases and the gaseous products can be expressed in simple integers.

For example, in the reaction $N_2 + 3H_2 = 2NH_3$

the ratio of volumes is equal to:

$$V(N_2) : V(H_2) : V(NH_3) = 1 : 3 : 2.$$

4. The law of Avogadro.

Amedeo Avogadro formulated it in 1811:

Equal volumes of different gases under identical conditions contain identical numbers of molecules. In symbolic form, it is written as follows: $N = \text{const.}$ if $P, V, T = \text{const.}$

Avogadro's law obtained evidence in the molecular-kinetic theory of gases.

The Avogadro law, the Gay-Lussac and Boyle-Mariotte gas laws belong to the laws of ideal gases. For ideal gases, intermolecular interaction and volume of molecules can practically be neglected.

The dependence of the volume of gas on the external conditions (pressure and temperature) is expressed by the law of Jacques Charles (1746–1823) and Gay–Lussac.

$$V = \frac{V_0 T}{T_0} \qquad (1.10)$$

and by the law of Robert Boyle and Edme Mariotte (1620–1684):

$$pV = \text{const.} \qquad (1.11)$$

The relationship between pressure, volume and temperature (p, V, T) is expressed by the equation of the state of ideal gases. Typically, measurements of gas volumes are carried out under physical conditions other than normal. It is convenient to use the equation combining the laws of Boyle-Mariotte and Charles – Gay-Lussac to bring the volume of gas to normal conditions:

$$\frac{pV}{T} = \frac{p_0 V_0}{T_0}\,. \qquad (1.12)$$

When calculating the correction for water vapour, pressure should be taken into account. The pressure of the saturated water vapour has a certain value at each temperature and is characterised, like every gas in the mixture, by its partial pressure by the law of partial pressure. Dalton established this law and formulated it in the following way: **The pressure of a mixture of gases, which do not chemically interact with each other, is equal to the sum of their partial pressures**.

We associate the equation (1.12) with the molar mass (M) of gas. Then, according to Avogadro's law, for the same physical conditions, volumes of 1 mol of all gases should be the same because they contain the same number of molecules equal to the Avogadro's number N_A. Then, the value p_0V_0/T_0 will have a constant value of R = 8.31 J/mol K (universal gas constant). Equation (1.12) for 1 mol will take the form:

$$PV = RT,$$

and the following form for ν (mol) = m/M:

$$pV = \nu RT \text{ or } pV = \frac{m}{M}RT. \qquad (1.13)$$

This equation is called the Mendeleev-Clapeyron equation.

Consequences of Avogadro's law:

1) at the normal pressure and temperature, 1 mol of any gas takes the volume of 22.4 litres;

2) the densities of two gases at the same pressure and temperature are directly proportional to their molar mass:

$$\frac{\rho_1}{\rho_2} = \frac{M_1}{M_2} = D \qquad (1.14)$$

The relative gas density (D) is equal to the ratio of the molar mass of gas to the molar mass of another gas taken as a reference.

5. The law of equivalent proportions or reciprocal proportions.

German chemist Jeremias Benjamin Richter (1762–1807) formulated it in 1792. Before defining the law, one should introduce the concepts of equivalent, equivalence factor and molar mass of the equivalent.

The solving of several computational tasks in chemistry is greatly simplified if we use the concept of chemical equivalents. This concept played a revolutionary role in the chemistry of the last century when the concept of atoms, molecules, atomic masses and valences was formed.

Based on the equation of chemical reaction $2H_2 + O_2 = 2H_2O$,

it can be argued that 2 molecules of hydrogen (their mass is $2 \times 2 = 4$) and 1 molecule of oxygen (its mass is equal to $1 \times 32 = 32$) enter the reaction Thus, the ratio of the number of hydrogen molecules to the number of oxygen molecules is 2:1, and the mass ratio $m(H_2):m(O_2) = 4:32 = 1:8$. This mass ratio is steady for the given reaction.

Thus, it can be argued that ¼ oxygen molecules (their mass is $\frac{1}{4} \times 32 = 8$) react with ½ molecules of hydrogen (their mass is equal to $\frac{1}{2} \times 2 = 1$). In this case, the ratio of the number of hydrogen molecules to the number of oxygen molecules is also equal to ½ : ¼ = 2 : 1.

According to modern concepts, chemical equivalents are conditional particles of matter; they are z times less than real particles corresponding to a particular chemical formula.

The real particles are H_2, O_2 and H_2O.

Chemical equivalents are $1/2H_2$, $1/4O_2$ and $1/2H_2O$.

The number z is called an equivalent number, $z \geq 1$. The value of z is determined by the chemical reaction in which the substance is involved. The inverse value of the equivalent number 1/z is called the equivalence factor (f_{equ}).

The equivalent is a real or conditional particle of a substance which is equivalent to one cation of hydrogen in the given acid-base reaction or equivalent to one electron in the given oxidation-reduction reaction.

The number that determines, which fraction of a real particle of a substance is equivalent to one hydrogen cation in this acid-base reaction or one electron in this oxidation-reduction reaction, is called the equivalence factor – f_{equ}. The equivalence factor has no dimension.

The equivalence factor is calculated based on the stoichiometric coefficients of the given reaction. For example,

a) $H_2S + 2NaOH = Na_2S + 2H_2O$

The reaction involves two cations of hydrogen of each molecule of hydrogen sulfide. Thus, two cations of hydrogen are equivalent to one particle (molecule) of hydrogen sulfide, and one cation H^+ is equivalent to a ½ molecule of H_2S. That is, $f_{equ}(H_2S) = ½$.

b) $H_2S + NaOH = NaHS + H_2O$

Only one hydrogen cation of each molecule H_2S is involved in the reaction. Thus, one molecule of hydrogen sulfide is equivalent to one hydrogen cation. That is, $f_{equ}(H_2S) = 1$.

The oxidation-reduction reaction:

c) $2H_2S + 3O_2 = 2H_2O + 2SO_2$

The degree of oxidation of sulfur varies from −2 to +4. The molecule H_2S gives 6 electrons, that is, one H_2S molecule is equivalent to 6 electrons, and one electron is equivalent to 1/6 molecules of hydrogen sulfide. That is, $f_{equ}(H_2S) = 1/6$.

So:

1) The equivalent of the same substance can be different depending on the reaction in which this substance is involved; that is, to calculate the equivalent and the equivalence factor, it is necessary to indicate which reaction is being discussed.

2) The equivalence factor can be equal to 1 and can be less than 1.

The number of equivalents is measured in moles, as well as any other amount of substance.

The molar mass of equivalents (M_f) is the mass of equivalents of 1 mol, which equals to the product of the equivalence factor and the molar mass of the substance:

$$M_f = f_{equ} \cdot M \tag{1.15}$$

By analogy with the molar mass, we can write:

$$M_f = \frac{m}{\nu_{equ}}, \text{ g/mol}$$

For the reactions discussed above:

a) $M_f(H_2S)$ = 1/2·34 = 17 g/mol;

b) $M_f(H_2S)$ = 1·34 = 34 g/mol;

c) $M_f(H_2S)$ = 1/6·34 = 5.68 g/mol.

The molar masses of the equivalents of such substances as hydrogen and oxygen are constant values:

$M_f(H_2) = M(1/2H_2)$ = (2 g/mol)/2 = 1 g/mol;

$M_f(O_2) = M(1/4O_2)$ = (32 g/mol)/4 = 8 g/mol.

Now we can formulate the law of equivalent proportions:

The masses (volumes) of the reactants are proportional to the molar masses (volumes) of their chemical equivalents:

$$\frac{m(A)}{m(B)} = \frac{M_f(A)}{M_f(B)}; \qquad \frac{m(A)}{V(B)} = \frac{M_f(A)}{V_f(B)},$$

where V_f is the equivalent volume of a gaseous substance.

$$V_f = \frac{V}{\nu_{equ}}, \text{ L/mol.}$$

Under normal conditions, the equivalent volume equals:

$V = f_{equ} \cdot 22.4$, L/mol.

$V_f(H_2)$ = 1/2·22.4 = 11.2 L/mol;

$V_f(O_2)$ = 1/4·22.4 = 5.6 L/mol.

From the law of equivalent proportions, substances enter chemical reactions in the equivalent proportions:

$$\nu_{equ}(A) = \nu_{equ}(B).$$

To determine the molar masses of the equivalents of complex compounds, it is necessary to take into account the chemical reaction in which the substance is involved and the class to which this substance belongs (see Table 1.1).

Table 1.1 Determination of molar masses of equivalents of compounds

Compound (element)	Formula of compounds	The molar mass of equivalents
Element (in compound)	A^{b+} (A_aB_b)	$\frac{M(A)}{b}$
Oxide	A_2O_b	$\frac{M(A_2O_b)}{2b} = M_f(A) + M_f(O) = M_f(A) + 8$
Acid	H_aB	$\frac{M(H_aB)}{a} = M_f(H) + M_f(B^{a-}) = 1 + \frac{M(B)}{a}$
Base	$A(OH)_b$	$\frac{M[A(OH)_b]}{b} = M_f(A) + M_f(OH) = 17 + \frac{M(A)}{b}$
Salt	A_aB_b	$\frac{M(A_aB_b)}{a \cdot b} = \frac{M(A)}{b} + \frac{M(B)}{a}$

In summary

The key concepts, definitions, laws and formulas:

1. The law of conservation of mass of substances allows one to calculate the quantitative ratios of reagents and reaction products.

2. Calculations of the quantities of reagent substances and reaction products can be greatly simplified if we use the law of equivalent proportions.

3. The law of bulk proportions allows us to calculate the bulk proportions of gaseous substances which participate in a reaction or form during a reaction.

4. Definitions and formulas:

$\omega(E) = \frac{nA_r}{M_r} \cdot 100\%$ – the mass fraction of the element in a compound;

$\nu = \frac{N}{N_A} = \frac{m}{M} = \frac{V}{V_m}$ – the amount of substance;

$pV = \frac{m}{M}RT$ – Mendeleev-Clapeyron equation;

$D_2(1) = \frac{M_1}{M_2}$ – the relative density of gas 1 to gas 2;

$M_f(H_2) = M(1/2H_2) = (2\ g/mol)/2 = 1\ g/mol$ – the molar mass of hydrogen equivalents;

$M_f(O_2) = M(1/4O_2) = (32\ g/mol)/4 = 8\ g/mol$ — the molar mass of oxygen equivalents;

$M_f(A_aB_b) = \frac{M(A_aB_b)}{a \cdot b} = \frac{M(A)}{b} + \frac{M(B)}{a}$ – the molar mass of equivalents of a complex substance;

$V_f = \frac{V}{\nu_{equ}}$ – the equivalent volume;

$\frac{m(A)}{m(B)} = \frac{M_f(A)}{M_f(B)}$ or $\frac{m(A)}{V(B)} = \frac{M_f(A)}{V_f(B)}$ – the equivalent proportions law.

Necessary practical skills:

1. To determine the relative molecular and molar masses of substances; number of particles in a certain amount of substance, mass of matter, and volume of gas; the volume of this mass or quantity of gas matter under normal conditions; relative gas density by another gas; the mass fraction of an element in the compound according to its formula.
2. To establish a chemical formula of a substance in terms of the mass fraction of the elements included in its composition.
3. To determine the molar masses of gaseous substances by molar volume, by relative density or by the equation of Mendeleev-Clapeyron.
4. To calculate the mass, volume and amount of substance by known mass and amount of substance of one of the reagents or reaction products according to the chemical reaction equations.
5. To implement the transition from normal to experimental conditions based on gas laws.
6. To calculate molar masses of equivalents of different substances.
7. To perform calculations using the law of equivalent proportions.

1.2 Main classes of inorganic compounds

1.2.1 Classification of inorganic compounds

All inorganic compounds in the composition are divided into elementary and complex (Fig. 1.1). Among the elementary substances, there are metals and nonmetals.

Metals consist of atoms of chemical elements – metals (sodium Na, potassium K, iron Fe, magnesium Mg, silver Ag, etc.).

Nonmetals consist of, as a rule, molecules of chemical elements – nonmetals (chlorine Cl_2, sulfur S_8, phosphorus P_4, oxygen O_2, nitrogen N_2, etc.).

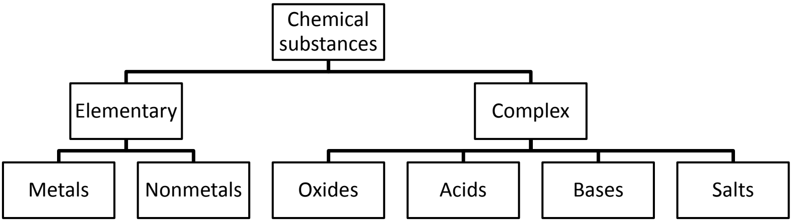


Figure 1.1 Classification of inorganic compounds

Metals and nonmetals have different chemical properties. The difference is explained by the electronic structure of their atoms. We will get acquainted with the properties of these elementary compounds later.

Complex substances are divided into the following classes: oxides, bases, acids, and salts. The division of complex substances into classes is based on the similarity of chemical properties.

1.2.2 Oxides

Oxides are substances that consist of two elements, one of which is oxygen with an oxidation degree -2. In oxides, the atoms of oxygen are joined to the atoms of other elements but are not interconnected.

$$C{=}O,\ O{=}C{=}O,\ O{=}B{-}O{-}B{=}O$$

Compounds of elements with oxygen, which have a bond between oxygen atoms, are called peroxides (H_2O_2 – hydrogen peroxide H–O–O–H). Metal peroxides belong to a class of salts; hydrogen peroxide reveals acidic properties.

Nomenclature. The names of oxides, according to the new systematic nomenclature, can be constructed in two ways:

1) using numeric prefixes;

2) indicating the degree of oxidation of the element in the form of the cation.

A cation is named first, and then you give the name of an anion:

Examples: N_2O_5 – dinitrogen pentaoxide, or nitrogen (V) oxide, Sb_2O_3 – distibium trioxide, or antimony (III) oxide, Na_2O – disodium oxide, sodium oxide.

Transition metals may form more than one ion. Therefore, one needs to specify which particular ion we are talking about. This is indicated by assigning a Roman numeral after the metal. The Roman numeral denotes the charge and the oxidation state of the transition metal ion. For example, iron can form two common ions, Fe^{2+} and Fe^{3+}. To specify the difference, Fe^{2+} would be named iron (II) and Fe^{3+} would be named iron (III).

Several exceptions apply to the Roman numeral assignment: aluminium, zinc, and silver. Although they belong to the transition metal category, these metals do not have Roman numerals written after their names because these metals only exist in one ion. Instead of using Roman numerals, the different ions can also be presented in plain words. The metal is changed to end in -ous or -ic.

-ous ending is used for the lower oxidation state:

-ic ending is used for the higher oxidation state.

If the element forms only one oxide or single oxide in the usual valency, then its name may consist only of the name of the element and the word “oxide”: BaO — barium oxide, B_2O_3 — boron oxide, K_2O — potassium oxide.

Oxygen compounds with more electronegative element fluorine must be called fluorides: OF_2 — oxygen fluoride, O_2F_2 — dioxygen difluoride.

The general rule is as follows: for the name of any complex inorganic compound, initially call cation and then anion.

By chemical properties, oxides are divided into salifiable (salt-forming) and neutral oxides. Oxides that do not form salts are called neutral: NO — nitrogen (II) oxide, N_2O — nitrogen (I) oxide, SiO — silicon (II) oxide. There are very few neutral oxides. Oxides, which form salts during the chemical reactions, are salifiable. They include most oxides. Salt-forming oxides are divided into basic, acidic and amphoteric.

Basic oxides. Oxides that give a base in water are known as basic oxides. This kind of oxides includes only metal oxides: alkali (Li, Na, K, Rb, Cs), alkaline earth elements (Mg, Ca, Sr, Ba, Ra), lanthanum, and all other metals in lower oxidation levels (CrO, MnO, PbO).

Acidic oxides. An oxide that combines with water to give an acid is termed as an acidic oxide. Acidic oxides are also called acid anhydrides.

This family includes oxides of nonmetals, as well as metals in higher oxidation states: SO_2, SO_3, CO_2, CrO_3, Mn_2O_7.

Amphoteric oxides. Amphoteric are called oxides, which, depending on the conditions, exhibit the properties of basic and acidic oxides. Amphoteric oxides are formed by some light metals of groups 2 and 3 (beryllium, aluminium – BeO, Al_2O_3) and also many other metals in intermediate oxidation states (MnO_2, Fe_2O_3).

Physical and chemical properties of oxides are given in Table 1.2.

Table 1.2 Physical and chemical properties of oxides

Properties	Basic oxide	Acidic oxide	Amphoteric oxide
Aggregate state	Solid	Solid, liquid, gaseous	Solid
Type of chemical bond	Ionic	Covalent polar	Ion-covalent
Hydroxide nature	Base	Acid	Both acid and base properties
Interaction: with water	Some: alkali and alkaline earth metal oxides $CaO + H_2O = Ca(OH)_2$	Most oxides $SO_3 + H_2O = H_2SO_4$	Do not react
With acids	All with formation of salts $Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O$	Do not react	$ZnO + 2HCl = ZnCl_2 + H_2O$
With bases	Do not react	With alkalis: $2NaOH + SiO_2 = Na_2SiO_3 + H_2O$	$ZnO + 2NaOH + H_2O = Na_2[Zn(OH)_4]$
With oxides: Basic	Do not react	React with the formation of salts $CO_2 + CaO = CaCO_3$	$ZnO + CaO \xrightarrow{t^\circ} CaZnO_2$
Acidic	$CaO + SiO_2 = CaSiO_3$	Do not react	$ZnO+SiO_2 \xrightarrow{t^\circ} ZnSiO_3$
Amphoteric	$Li_2O+Al_2O_3 = 2LiAlO_2$	$SO_3 + Al_2O_3 = Al_2(SO_4)_3$	Do not react

1.2.3 Bases

Bases are compounds which consist of a metal atom or an ammonium group (NH_4^+) and one or more OH^- groups.

From the theory of electrolytic dissociation: the bases are electrolytes, which form hydroxide anions during dissociation.

Examples: NaOH, $Ca(OH)_2$, $Mg(OH)_2$, $La(OH)_3$.

The group OH^- is a hydroxide ion, its charge is −1. The number of hydroxide ions in the base is determined by the degree of oxidation of the metal.

Nomenclature. The names of the bases and amphoteric hydroxides are formed from the name of the cation and the words "hydroxide", indicating the degree of oxidation or adding the corresponding numerical prefixes. If metal forms only one hydroxide, then the degree of its oxidation is not indicated: $Fe(OH)_2$ — iron (II) hydroxide, ferrous hydroxide, or ferrum dihydroxide; $Al(OH)_3$ — aluminium hydroxide, or aluminium trihydroxide.

The acidity of the base. The number of hydroxyl groups bound to the metal atom determines the acidity of the base. For example, LiOH, NaOH — single-acid base; $Ca(OH)_2$, $Ba(OH)_2$ — two-acid; $Cr(OH)_3$, $Bi(OH)_3$ — tri-acid.

Physical properties. Bases are solids. By solubility in water, they are divided into two groups: soluble (alkali) and insoluble. Alkalis are alkali metal hydroxides (elements of group 1 of the periodic table) and alkaline earths (elements of group 2, except beryllium and magnesium).

Alkalis are ionic compounds. Metal ions and hydroxide ions occupy the lattice sites of solid crystalline alkalis. In other bases, the chemical bond has an ion-covalent character.

Chemical properties. The chemical properties of the bases are given in Table 1.3. As can be seen from the table, only soluble in water bases (alkalis), being strong electrolytes in aqueous solutions, almost completely dissociate with the formation of hydroxide ions:

$$NaOH \leftrightarrow Na^+ + OH^-.$$

Thus, they have some common properties due to the presence of hydroxide ions; for example, they affect the colour of many acid-base indicators.

Insoluble in water bases do not change the colour of the indicators, do not interact with acidic and amphoteric oxides, as well as salts because they, as weak electrolytes, are insoluble in water.

Insoluble in water bases weakly dissociate into ions. A small amount of hydroxide ions, contained in their saturated solutions, is not sufficient to ensure the flow of these reactions. Insoluble in water bases give only two reactions.

Table 1.3 Chemical properties of bases

Property	Soluble bases	Insoluble bases	Amphoteric hydroxides
Dissociation in aqueous solution	$Ba(OH)_2 \leftrightarrow Ba^{2+} + 2OH^-$ Change the colour of the indicators: litmus on blue, phenolphthalein on crimson and methyl orange on yellow	Very weakly dissociate into ions, weak electrolytes	weak electrolytes
Interaction with acids (neutralisation reaction)	$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$; $Ca(OH)_2 + HCl \rightarrow Ca(OH)Cl + H_2O$; $Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2H_2O$	$Mn(OH)_2 + 2HCl \rightarrow MnCl_2 + 2H_2O$	$Al(OH)_3 + 3HNO_3 \rightarrow Al(NO_3)_3 + 3H_2O$
Interaction with water-soluble bases	Do not react	Do not react	fusion with alkalis: $NaOH + Al(OH)_3 \rightarrow NaAlO_2 + 3H_2O$; $3NaOH + Al(OH)_3 \rightarrow Na_3AlO_3 + 3H_2O$; the effect of water solutions: $NaOH + Al(OH)_3 \rightarrow Na[Al(OH)_4]$; $3NaOH + Al(OH)_3 \rightarrow Na_3[Al(OH)_6]$
Interaction with acidic oxides	$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$	Do not react	Do not react
Interaction with amphoteric oxides during fusion	$6NaOH + Cr_2O_3 \rightarrow Na_2CrO_3 + 3H_2O$	Do not react	Do not react
Interaction with soluble salts	if hydroxide or salt is formed, insoluble in water, or weak electrolyte: $CuCl_2 + 2NaOH \rightarrow Cu(OH)_2\downarrow + 2NaCl$; $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$	Do not react	Do not react
Under heating	Hydroxides of alkali metals do not decompose, and alkaline earths decompose $Ca(OH)_2 \rightarrow CaO + H_2O$	$Mg(OH)_2 \rightarrow MgO + H_2O$	$2Cr(OH)_3 \rightarrow Cr_2O_3 + 3H_2O$

Amphoteric hydroxides are hydroxides that exhibit basic and acidic properties depending on the conditions, namely the nature of the second component, which is involved in the acid-base interaction.

Amphoteric hydroxides include hydroxides of beryllium, aluminium, and zinc, as well as many metals in intermediate oxidation states: $Be(OH)_2$, $Al(OH)_3$, $Zn(OH)_2$, $Cr(OH)_3$.

The type of bond between metal atoms and hydroxyl groups is covalent. All amphoteric hydroxides are weak electrolytes. Since the polarity of the covalent bonds of Me–O and O–H in their molecules is similar, amphoteric hydroxides can dissociate both as a base and as an acid:

$$\begin{gathered} Al(OH)_3 \leftrightarrow [Al(OH)_2]^+ + OH^- \leftrightarrow [Al(OH)]^{2+} + 2OH^- \leftrightarrow Al^{3+} + 3OH^-; \\ \Updownarrow \\ H_3AlO_3 \leftrightarrow 3H^+ + AlO_3^{3-} \leftrightarrow HAlO_2 + H_2O \leftrightarrow H^+ + AlO_2^- + H_2O \end{gathered}$$

Amphoteric hydroxides do not change the colour of the indicators.

1.2.4 Acids

Compounds known as acids contain hydrogen atoms, which can be replaced by metal atoms. Possible classification of acids is illustrated in Fig. 1.2.

From the theory of electrolytic dissociation, acids are electrolytes, which during the dissociation form only one type of positively charged ions, namely cations of hydrogen.

Nomenclature. A quick way to identify acids is to check if there is an H (denoting hydrogen) in front of the molecular formula of the compound. To name binary acids, the prefix hydro- is placed in front of the nonmetal modified to end with –ic. The state of acids is aqueous (aq) because acids are found in water.

Some common binary acids include:

$HF_{(g)}$ = hydrogen fluoride → $HF_{(aq)}$ = hydrofluoric acid;

$HBr_{(g)}$ = hydrogen bromide → $HBr_{(aq)}$ = hydrobromic acid;

$HCl_{(g)}$ = hydrogen chloride → $HCl_{(aq)}$ = hydrochloric acid;

$H_2S_{(g)}$ = hydrogen sulfide → $H_2S_{(aq)}$ = hydrosulfuric acid.

It is important to include (aq) after the acids because the same compounds can be written in the gas phase (denoted as (g)) with hydrogen named first followed by the anion ending with –ide.

$HCl_{(l)}$ = hydrochloric acid whereas $HCl_{(g)}$ = hydrogen chloride (l = liquid, g = gas)

Exception: $HCN_{(l)}$ = hydrocyanic acid (prefix hydro- although it is a ternary compound; it is an oxygen-free acid).

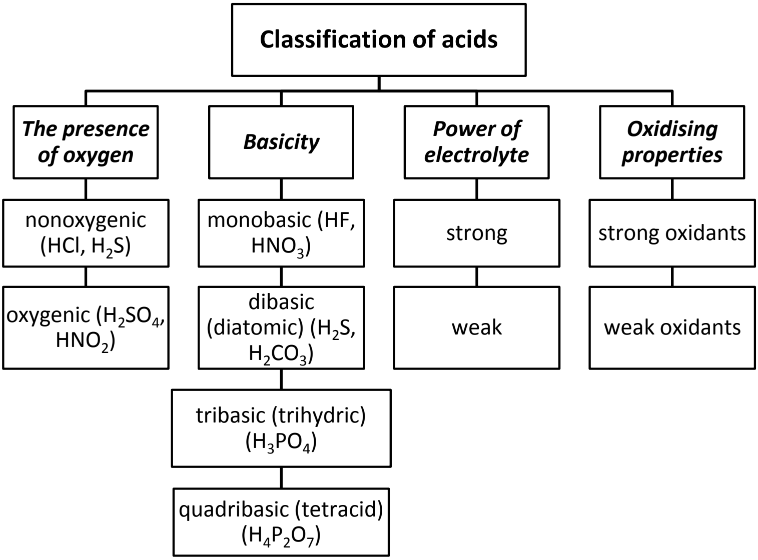


Figure 1.2 Classification of acids

The oxygen-containing acids have polyatomic ions. Such acids include sulfuric acid (H_2SO_4) or carbonic acid (H_2CO_3), for example. To name them, follow these quick, simple rules:

1. If the ion ends in -ate and is added with an acid, the acid name will have an -ic ending. Examples: nitrate ion (NO_3^-) + H^+ (denoting the formation of acid) = nitric acid (HNO_3)

2. If the ion ends in -ite and is added with an acid, then the acid name will have an -ous ending. Example: nitrite ion (NO_2^-) + H^+ (denoting the formation of acid) = nitrous acid (HNO_2)

For example, H_2CO_3 = carbonic acid (its anion = carbonate, so the suffix for acid must be -ic).

HClO = hypochlorous acid (anion = hypochlorite) Cl^{1+};
$HClO_2$ = Chlorous acid (anion = chlorite) Cl^{3+};
$HClO_3$ = Chloric acid (anion = chlorate) Cl^{5+};
$HClO_4$ = (Hy)perchloric acid (anion = perchlorate) Cl^{7+}.

The prefixes hypo- (= under) and per- (or hyper- = above) are used if more than two oxidation states are formed by a central atom (e.g. all halogens).

Oxygenic acids are hydrates (products of coupling with water) of oxides of nonmetals, as well as oxides of certain metals in higher oxidation states (+5, +6, +7). For example, carbonic acid H_2CO_3 is the product of aggregation of CO_2 with water, sulfuric acid H_2SO_4 – SO_3, chromic acid H_2CrO_4 – CrO_3.

The number of hydrogen atoms, which can be replaced by metal atoms with the formation of a salt, determines the basicity of the acid. So, HC1, HBr, HNO_3, CH_3COOH – are monobasic acids; H_2S, H_2SO_4, H_2CO_3, H_3PO_3 – dibasic; H_3PO_4, H_3AsO_4 – tribasic.

Negative ions, which are formed as a result of the separation of one or more hydrogen ions from the acid molecule, are called acid residues. The value of the negative charge of the ion of the acid residue is determined by the number of hydrogen ions that have been detached.

The presence of hydrogen atoms in the acid residues is denoted by the word “hydrogen” with the corresponding prefix — for example, HSO_4^- — hydrogen sulfate, $H_2PO_4^-$ — dihydrogen phosphate.

Physical properties. Acids can be solid (H_3BO_3, H_2SiO_3) or liquid (H_2SO_4, HNO_3). Most of them are well soluble in water. Aqueous solutions of gaseous hydrogen compounds of some nonmetals (HCl, HBr, H_2S, HCN, HCNS) also belong to the acid family. In acid molecules, hydrogen atoms are bound to acid residues by a covalent, polar bond.

Chemical properties.

1. Acids in aqueous solutions dissociate into ions: strong acids dissociate completely, weak acids dissociate little:

$$HC1 \leftrightarrow H^+ + Cl^-;$$

$$H_2SO_4 \leftrightarrow H^+ + HSO_4^-;$$

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-.$$

Therefore, acids have some common properties due to the presence of hydrogen-ions H^+. For example, they change the colour of many indicators (see Table 1.4).

2. Acids react with bases. Interaction of the acid with the base, which results in the formation of salt and water, is called the neutralisation reaction: $NaOH + HCl \rightarrow NaCl + H_2O$.

Reactions with acids of insoluble bases and amphoteric hydroxides are also neutralisation reactions. Under such conditions, an amphoteric hydroxide reveals basic properties.

If polyacid bases or polybasic acids are involved in the reaction of neutralisation, medium, acid and basic salts may be formed.

$$Fe(OH)_3 + HCl \rightarrow Fe(OH)_2Cl + H_2O;$$

$$Fe(OH)_3 + 3HCl \rightarrow FeCl_3 + 3H_2O;$$

$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O.$$

Table 1.4 Intervals of transitions of indicators

Indicator	pH value				
	0 1 2 3 4	5 6 7 8	9 10 11	12 13	14
Litmus	Red		Transition interval	Blue	
Phenolphthalein	Colourless			Transition interval	Crimson
Methyl orange	Pink	Transition interval	Yellow		

3. Acids interact with basic and amphoteric oxides to form salt and water.

$$CaO + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O;$$

$$Fe_2O_3 + 6HNO_3 \rightarrow 2Fe(NO_3)_3 + 3H_3O.$$

4. Acids react with metals. As a result of the reaction, a salt is formed and hydrogen is released:

$$Zn + H_2SO_{4(dil)} \rightarrow ZnSO_4 + H_2\uparrow.$$

Metals, which are to the left of hydrogen in the range of standard electrode potentials, displace hydrogen from acids; those located to the right of hydrogen (Cu, Hg, Ag, Au, Pt) do not displace.

5. Acids interact with salts. In this case, the following compounds can be formed:

A) A new acid and salt (medium or acidic):

$$2NaCl_{(s)} + H_2SO_{4(conc)} \rightarrow Na_2SO_4 + 2HCl\uparrow;$$

$$2NaNO_{3(s)} + H_2SO_{4(conc)} \rightarrow Na_2SO_4 + 2HNO_3\uparrow;$$

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S\uparrow.$$

If the acid being formed is unstable, it can decompose with the formation of acidic oxides:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow.$$

B) An acidic salt only:

$$Na_2S + H_2S \rightarrow 2NaHS;$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2.$$

C) A few salts and water:

$$NaAlO_2 + 4HCl \rightarrow NaCl + A1C1_3 + 2H_2O;$$

$$2NaAl(OH)_4 + 4H_2SO_4 \rightarrow Na_2SO_4 + A1_2(SO_4)_3 + 8H_2O.$$

6. During heating, oxygenic acids are decomposed into water and an acidic oxide:

$$H_2SO_4 \xrightarrow{t^\circ} 4H_2O + SO_3;$$

$$4HNO_3 \xrightarrow{t^\circ} 2H_2O + 4NO_2 + O_2.$$

1.2.5 Salts

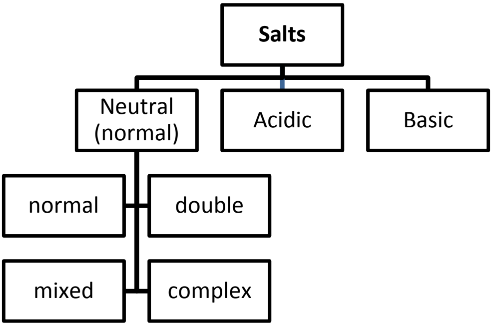
Definition. Salts are the products of substitution of acid hydrogens with metals or with products of the exchange of hydroxyl groups of metal hydroxides with acid residues.

$$H_2SO_4 + Zn = ZnSO_4 + H_2;$$

Acid Salt

$$NaOH + HC1 = NaCl + H_2O.$$

Base Salt



From the theory of electrolytic dissociation, the salts are electrolytes, which, during dissociation, form cations of the base residue and anions of the acid residue (Fig. 1.3).

Figure 1.3 Classification of acids

Nomenclature. The name of the salt consists of the name of the metal (the Roman numeral indicates the valence of the metal if the metal exhibits several valences) and the name of the acid residue.

For example: NaCl — sodium chloride; solution of $CaSO_4$ — solution of calcium sulfate; $Fe(NO_3)_2$ — iron (II) nitrate.

Physical properties. Salts are solid crystalline substances. The residues of the bases and acids in the salts are interconnected, usually by an ion bond. Salts have different colours and are characterised by different solubility in water.

Medium salts are products of complete replacement of acid hydrogen with a metal or a complete exchange of hydroxyl groups of the base to acid residues, for example

$$Na_2SO_4, Ca(NO_3)_2: 2Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2\uparrow;$$

$$Fe(OH)_3 + 3HClO_4 \rightarrow Fe(C1O_4)_3 + 3H_2O.$$

Normal salts contain ions of one metal only. Normal salts are: Na_2SO_4, $Ca(NO_3)_2$ etc.

If atoms of hydrogen in acid are replaced by atoms of various metals, then such salts are called **double**. Example: $KAl(SO_4)_2$.

If the hydroxyl groups of the bases are exchanged for different acid residues, then **mixed** salts are formed (for example, Ca(OCl)Cl).

Complex salts contain complex ions. For example, salts $K_4[Fe(CN)_6]$, $Na[Al(OH)_4]$, $Na_3[Al(OH)_6]$ are complex because they contain complex ions $Fe(CN)_6^{4-}$, $Al(OH)_4^{-}$, $Al(OH)_6^{3-}$.

Acidic salts are products of incomplete substitution of hydrogen with polyhydric acid, for example, $NaHSO_4$, $Ca(HCO_3)_2$ are acidic salts.

Basic salts are products of incomplete exchange of hydroxyl groups of polyacid bases with acid residues, for example, MgOHCl, $Al(OH)_2C1$ are basic salts:

$$Mg(OH)_2 + HCl \rightarrow MgOHCl + H_2O;$$

$$A1(OH)_3 + HC1 \rightarrow A1(OH)_2C1 + H_2O.$$

Chemical properties.

1. The salts react with alkalis or ammonium hydroxide. As a result, new salts (medium, acidic, basic) and hydroxide or a basic salt (depending on the molar ratio of reagents) are formed.

$$MgCl_2 + NaOH \rightarrow Mg(OH)Cl + NaCl;$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCl;$$

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O;$$

$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O.$$

2. Salts interact with acids if a precipitate or a weak electrolyte is formed. In this case, various compounds (depending on the molar ratio of reagents) can be formed.

i) A new acid and a new salt: $FeS + 2HCl \rightarrow FeCl_2 + H_2S$.

ii) Acidic and medium salts:

$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 + 2CaSO_4$.

iii) An acidic salt: $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$.

iv) One or two medium salts, a basic salt:

$Fe(OH)_2Cl + HCl \rightarrow Fe(OH)C1_2 + H_2O$;

$CuOHCl + HCl \rightarrow CuCl_2 + H_2O$.

3. The salts interact with each other if a precipitate forms. As a result, new salts are formed:

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$.

A medium salt can react with the acidic or basic salts of the same metal if an acid or base salt of an intermediate composition exists between the reagents. Such an intermediate salt will be the product of the following reaction:

$$Na_3PO_4 + NaH_2PO_4 \rightarrow 2Na_2HPO_4;$$

$$FeCl_3 + Fe(OH)_2Cl \rightarrow 2FeOHCl_2.$$

4. Salts interact with metals to form a new salt and metal:

$$CuSO_4 + Fe \rightarrow FeSO_4 + Cu.$$

Each metal can displace from the solutions of salts any metals, which are characterised by higher values of the standard electrode potential. Otherwise, it does not displace metals with lower electrode potentials, and the reaction does not start. For example: $FeSO_4 + Cu$ (no reaction).

Metals located to the left of magnesium (K, Ba, Ca, Na, etc.) are not used to displace metals out of solutions of their salts because they react with water to form hydrogen and alkali, which, in turn, interacts with the salt with the formation of insoluble hydroxide:

$$CuSO_4 + 2Na + 2H_2O \rightarrow Cu(OH)_2\downarrow + Na_2SO_4 + H_2\uparrow.$$

5. Salts interact with oxides (acidic or amphoteric) during heating with the formation of a salt and an acid oxide if the new oxide is more volatile than the original:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2\uparrow;$$

$$4LiNO_3 + 2A1_2O_3 \rightarrow 4LiA1O_2 + 4NO_2\uparrow + O_2\uparrow.$$

6. Salts decompose during heating. Depending on the nature of the metal and acid, various products are formed:

$$CaCO_3 \xrightarrow{t^\circ} CaO + CO_2\uparrow;$$

$$2NaNO_3 \xrightarrow{t^\circ} 2NaNO_2 + O_2\uparrow.$$

1.2.6 Genetic affinity between classes of inorganic compounds

The following scheme in Fig. 1.4 illustrates the genetic (from the Greek "genesis" — the origin) relationship between the various classes of compounds:

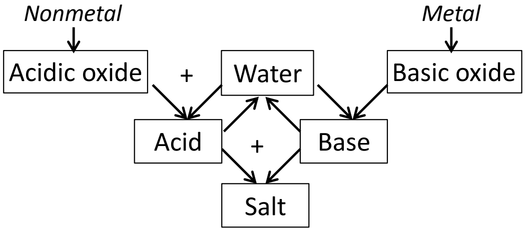
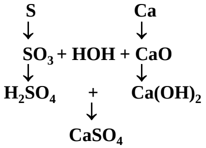


Figure 1.4 Genetic links between the main classes of inorganic compounds

Here (see on the right side) is an example that reflects such a connection by writing the formula of water in the form of HOH:



Comparing the formulas of acid and water, we can conclude that the acid is formed by replacing the hydroxyl group in water to the acid residue. Similarly, the base is formed by replacing the hydrogen atom in water to the metal. The salt is formed by replacing the hydrogen atoms in the acid with the metal, or the hydroxyl group in the base with the acid residue, or the hydroxyl group of water to the acid residue, and the hydrogen atom to the metal.

In summary

The key concepts, definitions, laws and formulas:

1. Inorganic substances are divided into elementary and complex.
2. Complex substances include oxides, acids, bases, and salts.
3. The name of the complex substance consists of the names of cations and anions.

Necessary practical skills:

1. To distinguish classes of inorganic compounds.
2. To write the equations of chemical reactions, characterising the properties of different classes of inorganic compounds.
3. To name inorganic compounds using the actual nomenclature.
4. To write chemical formulas of compounds using their names.
5. To understand genetic links between the main classes of inorganic compounds.

1.3 Problem solving

1.3.1 Examples

Example 1.1 The mass of the carbon atom is $1.993 \cdot 10^{-26}$ kg; the mass of the sulfur atom is $5.3238 \cdot 10^{-26}$. Calculate the relative atomic mass of sulfur

$$1/12\ m_a(^{12}C) = 1.66 \cdot 10^{-27}\ \text{kg};$$

$$A_r(S) = \frac{5.3238 \cdot 10^{-26}}{1.66 \cdot 10^{-27}} = 32.0599\,.$$

Example 1.2 Calculate the molar mass of sulfur if the average mass of its molecule is equal to $5.3238 \cdot 10^{-23}$ g.

$$M(S) = m_a \cdot N_A = 5.3238 \cdot 10^{-23}\ \text{g} \cdot 6.022 \cdot 10^{23}\ \text{mol}^{-1} = 32.0599\ \text{g/mol}.$$

Example 1.3 Determine the equivalent numbers for chlorine, nitrogen, carbon and phosphorus using the mass ratios shown in the table:

Reaction H_2 + A	$m(H_2) : m(A)$	Reaction A + O_2	$M(A) : m(O_2)$
$H_2 + Cl_2 = 2HCl$	1 : 35.5	$2H_2 + O_2 = 2H_2O$	1 : 8
$3H_2 + N_2 = 2NH_3$	1 : 4.7	$C + O_2 = CO_2$	3 : 8
$2H_2 + C = CH_4$	1: 3	$P_4 + 5O_2 = P_4O_{10}$	6.2 : 8

For chlorine Cl_2, the real particle (molecule) has a mass of 71; in our reaction, $m(Cl_2) = 35.5$; therefore, it is twice less than the real particle.

Thus, $z(Cl_2) = 2$.

For nitrogen $M(N_2) = 28$; $28/4.7 = 6$; therefore, $z(N_2) = 6$.

$M(C) = 12$; $12/3 = 4$; $z(C) = 4$.

$M(O_2) = 32$; $32/8 = 4$; $z(O_2) = 4$.

$M(P_4) = 124$; $124/6.2 = 20$; $z(P_4) = 20$.

Example 1.4 Determine the mass fraction of carbon in methane.

$$\omega = \frac{nA_r}{M_r} \cdot 100\%; \qquad \omega(C) = \frac{A_r(C)}{M_r(CH_4)} \cdot 100\%;$$

$$A_r(C) = 12; \qquad M_r(CH_4) = 12 + 4 \cdot 1 = 16;$$

$$\omega(C) = \frac{12}{16} \cdot 100\% = 75\%.$$

Thus, the mass fraction of carbon in methane is 75%.

Example 1.5 Determine the number of oxygen atoms contained in 320 g of oxygen.

$$\nu(O_2) = \frac{m}{M}\text{; } \nu(O_2) = (320\text{ g}) / (32\text{ g/mol}) = 10\text{ mol;}$$

$$\nu(O) = 2\nu(O_2) = 2\cdot 10\text{ mol} = 20\text{ mol;}$$

$$N(O) = \nu(O)\cdot N_A = 20\text{ mol}\cdot 6.02\cdot 10^{23}\text{ mol}^{-1} = 1.204\cdot 10^{25}.$$

Thus, the number of atoms of oxygen is $1.204\cdot 10^{25}$.

Example 1.6 The density of the vapour of the substance relative to the air is 2. Determine the molar mass of this substance.

$$D_{air} = \frac{M}{M(air)}; \quad M = D_{air}\cdot M(air)\,.$$

$$M(air) = 29\text{ g/mol; } M = 2\cdot 29\text{ g/mol} = 58\text{ g/mol.}$$

Thus, the molar mass of this substance is 58 g/mol.

Example 1.7 How many molecules and atoms are contained in 11.2 litres of hydrogen sulfide under normal conditions?

$$N(H_2S) = \nu(H_2S)\cdot N_A\text{; } \nu(H_2S) = \frac{V}{V_m}\text{ ;}$$

$$\nu(H_2S) = \frac{11.2L}{22.4L/mol} = 0.5\text{ mol.}$$

$N(H_2S) = 0.5\text{ mol}\cdot 6.02\cdot 10^{23}\text{ mol}^{-1} = 3.01\cdot 10^{23}$ molecules

Each molecule of hydrogen sulfide contains two atoms of hydrogen and one sulfur atom, that is, the number of atoms in the molecule is three times greater.

$$N_{atom}(H, S) = N(H_2S)\cdot 3 = 3\cdot 3.01\cdot 10^{23} = 9.03\cdot 10^{23}\text{ atoms.}$$

The number of molecules is $3.01\cdot 10^{23}$; the number of atoms is $9.03\cdot 10^{23}$.

Example 1.8 Determine the relative density for a gas mixture with respect to hydrogen. The mixture consists of 56 litres of nitrogen and 28 litres of neon. The volumes of gases are reduced to normal conditions.

$$D_{H_2} = \frac{M(mixture)}{M(H_2)};$$

The molar mass of the mixture is determined as follows:

$$M(\text{mixture}) = \frac{m(\text{sum})}{\nu(\text{sum})} = \frac{m(N_2) + m(\text{Ne})}{\nu(\text{sum})} =$$

$$\frac{\nu(N_2)M(N_2) + \nu(\text{Ne})M(\text{Ne})}{\nu(\text{sum})} = \frac{V(N_2)M(N_2) + V(\text{Ne})M(\text{Ne})}{V(\text{sum})}$$

$$M(\text{sum}) = \frac{56 \cdot 28 + 28 \cdot 20}{56 + 28} = 25.3\ (\text{g/mol});$$

$$D_{H_2} = \frac{25.3}{2} = 12.7\,.$$

Example 1.9 Determine the atomic mass of the divalent metal and determine what this metal is if 8.34 g of the metal is oxidised by 0.680 litres of oxygen (normal conditions).

According to the law of equivalents:

$$\frac{m(\text{Me})}{V_o(O_2)} = \frac{M_f(\text{Me})}{V_f(O_2)}\,.$$

We can find the molar mass of the metal equivalent as follows:

$$M_f(\text{Me}) = \frac{m(\text{Me}) \cdot V_f(O_2)}{V_o(O_2)} = \frac{8.34 \cdot 5.6}{0.680} = 68.7\ \text{g/mol}\,.$$

Since the metal is divalent, we find its atomic mass by the formula $A = M_f(\text{Me}) \cdot 2$.

Thus the atomic mass of the metal is equal to 68.7·2=137. This metal is barium.

Example 1.10 Determine the molar mass of matter if 600 mL of its steam at 87°C and 83.2 kPa of pressure is 1.30 g.

From the Mendeleev-Clapeyron equation, one can express the molar mass of matter as follows:

$$M = \frac{mRT}{PV} = \frac{1.3 \cdot 8.31 \cdot (87 + 273)}{83.2 \cdot 0.6} = 78\ \text{g/mol}\,.$$

Example 1.11 Write the equation of reactions characterising the following transformations:

$$SO_2 \rightarrow Na_2SO_3 \rightarrow NaHSO_3 \rightarrow Na_2SO_3 \rightarrow Na_2SO_4.$$

When SO_2 is passed through an excess sodium hydroxide solution, sodium sulfite is formed:

$$SO_2 + 2NaOH \rightarrow Na_2SO_3 + H_2O.$$

When excess SO_2 is passed through a sodium sulfite solution, sodium hydrogen sulfite is formed:

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3.$$

Sodium hydrogen sulfite decomposes with heating:

$$2NaHSO_3 \rightarrow SO_2\uparrow + Na_2SO_3 + H_2O.$$

Sulfuric acid displaces sulfurous acid from sulfites:

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2\uparrow + H_2O.$$

1.3.2 Problems

1. Calculate the amount of substance (normal conditions): a) nitrogen weighing 14 g; b) oxygen weighing 48 g; c) iron weighing 112 g; d) phosphorus weighing 31 g.

2. Determine the molar mass of gas, if 5 g of it occupies a volume of 4 litres under normal conditions.

3. The relative density of gas with respect to hydrogen is 17. Find the mass of 1 litre (normal conditions) of this gas and calculate its relative density with respect to the air.

4. A gas occupies the volume of 600 m^3 at 7 $^\circ$C and 100 kPa. Determine the volume of gas at 13 $^\circ$C and 80 kPa.

5. Determine how many molecules of nitrogen atoms are contained in 16 g of ammonium nitrate.

6. Determine the molar mass of acetone if the mass of 500 mL of its vapour at 87 $^\circ$C and a pressure of 96 kPa is equal to 0.93 g.

7. The mass of 2 litres (normal conditions) of ozone is 4.286 g. Determine its molar mass and density relative to the air.

8. Determine the temperature at which the mass of 1 litre of carbon (IV) oxide will be 1 g if the pressure is equal to 152 kPa.

9. A gasometer with a volume of 20 litres is filled with gas. The relative density of this gas with respect to the air is 0.40, pressure 103.3 kPa, and temperature 17°C. Calculate the mass of this gas.

10. Aluminium with a weight of 0.376 g, when in contact with acid, displaced 0.468 L of hydrogen (normal conditions). Determine the equivalent volume of hydrogen if the molar mass of the equivalent of aluminium is 8.99 g/mol.

11. Calculate the molar mass equivalent of a metal and sulfur if 3.24 g of this metal makes 3.48 g of oxide and 3.72 g of sulfide.

12. The mass of 14.7 g of sulfuric acid is required to dissolve 16.8 grams of metal. Determine the molar mass of the equivalent of the metal and the volume of hydrogen released (normal conditions).

13. Hydrogen with a volume of 250 mL was collected above water at 260°C and a pressure of 98.7 kPa. The pressure of the saturated vapour at this temperature is 3.4 kPa. Calculate the volume and mass of hydrogen under normal conditions.

14. A metal of 0.2 g was displaced from acid by 197 mL of hydrogen collected over water at 200°C and a pressure of 104 kPa. The saturated vapour pressure at this temperature is 2.32 kPa. Determine the molar mass of the equivalent of the metal.

15. For reduction of 1.80 g of a metal oxide, 883 mL of hydrogen was consumed, measured under normal conditions. Determine the molar masses of the oxide and the metal equivalent.

16. Write the formulas of the anhydrides of the acids listed below: H_2SO_4, H_3BO_3, H_3PO_4, $HClO$, $HMnO_4$.

17. Name the substances by the following formulas: $MgSO_4$, $KHCO_3$, H_2SO_4, $CaOHCl$, $Cu(OH)_2$, Fe_2O_3, $KAl(SO_4)_2$. What classes of compounds do they belong to?

18. Work out the equations of reactions corresponding to the following transformation schemes:

a) $Ba \rightarrow BaO \rightarrow BaCl_2 \rightarrow Ba(NO_3)_2 \rightarrow BaSO_4$;

b) $S \rightarrow ZnS \rightarrow H_2S \rightarrow SO_2 \rightarrow BaSO_3 \rightarrow SO_2$;

c) $P \rightarrow P_2O_5 \rightarrow H_3PO_4 \rightarrow Ca_3(PO_4)_2 \rightarrow H_3PO_4$.

19. Which of the substances: orthophosphate acid, zinc chloride, iron (II) chloride — with the addition of alkali forms a precipitate that dissolves in excess of alkali? Work out the equations of the corresponding reactions.

20. Work out the molecular equations of the reactions by which one can realise the following transformation scheme: sodium chloride → sodium → sodium hydroxide → sodium sulfate → sodium nitrate → sodium nitrite.

Chapter 2. Structure of matter

Modern concepts of an elementary substance, elements, atoms, and molecules as a set of connected atoms formed relatively recently. However, the atomic theory of the structure of matter, namely the doctrine that all substances consist of the smallest particles, has passed a long and difficult path.

The assumptions of the ancient, based only on reflections, in principle, are not so distant from the present ideas: There are certain types of atoms (elements) that can be interconnected in different ways, giving a huge variety of substances with dissimilar properties. Such an idea was the greatest achievement of the human mind.

Very amusingly, American physicist Nobel Prize winner Richard Feynman said: "If, as a result of some kind of global catastrophe, all the accumulated scientific knowledge would have been destroyed, and only one phrase would come to the coming generations of living beings, then what kind of statement, composed of as few words as possible, would bring the most information? I believe that this is an atomic hypothesis (it can be called not a hypothesis, but a fact, but it does not change anything): all bodies consist of atoms — small bodies that are in a continuous motion, are attracted at a small distance, but repel if one from them more densely pressed to the other. This small phrase contains an incredible amount of information about the world, and it is only necessary to add a little imagination and some reasoning to it."

Till the end of the XIX century, researchers believed that the atom is the smallest particle of a simple substance and is indivisible and unchanged. Such an idea was confirmed by chemical reactions in which the substances react in certain ratios (the laws of stoichiometry).

After completion of the atomic theory based on the indivisibility of the atom, a problem of its internal structure arose. The hypothesis that atoms are linked with electric charges has been firmly established in the minds of scientists in the course of accumulation of new scientific discoveries and their generalisation.

2.1 Atom structure

2.1.1 Complexity of atom structure

The metaphysical perception of the atom prevailed in chemistry by the end of the XIX century. It was believed that the atom is the smallest indivisible particle of an elementary substance. However, the results of some research of many scientists gave evidence that the atom is divisible and is a complex system. The discovery of electrons and radioactivity was the most important step for further development of the atomic theory.

The first data on the complexity of the atomic structure was obtained in the study of cathode radiation generated as a result of the propagation of electric current through rarefied gases. Cathodic radiation occurs in a glass vessel, from which the air is removed and into which the metal cathode and anode (Fig. 2.1) are welded.

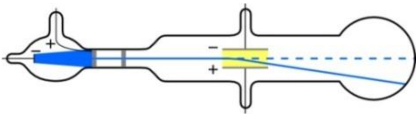


Figure 2.1 Scheme of a cathode tube

If you connect these electrodes to a high voltage current source and switch on the current, then the cathode produces an invisible beam, which, passing through a narrow hole on the anode, causes the greenish glow of glass. This glow does not depend on the nature of the cathode. Creating an electric field between the plates causes the moving of a glow toward the positive pole of the external field. A similar deviation is observed if a magnet is brought to the beam.

Based on these facts, English physicist and chemist William Crookes (1832–1919) in 1880 suggested that cathode radiation is a stream of negatively charged particles which are moving very fast.

The study of cathode radiation, especially the measurement of its deviation in the electric and magnetic fields, has shown that this is the flow of the smallest particles that carry the smallest electric charge. These particles were called electrons. The charge of an electron ($1.602 \cdot 10^{-19}$ coulombs) and the charge-to-mass ratio were calculated, and then the electron mass ($9.1094 \cdot 10^{-28}$ g) was estimated.

Free electrons are formed not only when the electric current is passing through rarefied gases but also during the heating of metals or irradiation of metals by ultraviolet rays. All these phenomena give evidence that electrons are a part of substances and can be detached from atoms under certain conditions.

The discovery and study of radioactivity also played an important role in establishing the complex nature of atoms.

French physicist Antoine Henri Becquerel (1852–1908) noticed in 1896 that uranium salt acts on a photographic plate without its prior lighting. Also, he found that uranium compounds emit an invisible beam that causes blackening of the photographic plate, passing through not only black paper but also through the wooden or thin metal plates.

Various scientists were interested in experiments of Becquerel. In particular, Marie Sklodowska-Curie (1867–1934) found that thorium acts on the photographic plate like compounds of uranium. In 1898, M. Sklodowska-Curie and her husband Pierre Curie (1859–1906) discovered two more elements (polonium and radium) in the uranium ore which similarly act on the photographic plate.

The ability of some elements to irradiate invisible beam, which causes the blackening of photographic plates, passes through the substance and ionises the air, is called **radioactivity;** the relevant elements are called **radioactive**.

Experiments showed that the radioactivity is determined only by the content of the radioactive element and does not depend on the nature of the compound and external conditions. All these facts indicate that radioactivity is due to the spontaneous decay of atoms of radioactive elements.

When studied the nature of radioactivity, the prominent English physicist Ernest Rutherford (1871–1937), a Nobel Prize winner, found in 1899 that it is heterogeneous. He found three types of radiation were emitted from a radium source by separating the beam by a magnetic field (Fig. 2.2).

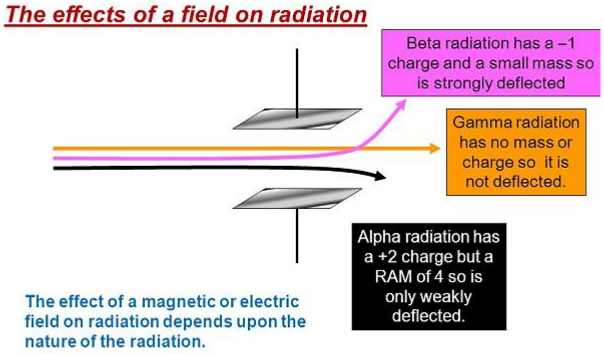


Figure 2.2 Effect of a magnetic field on alfa, beta and gamma radiation

Alfa and beta particles are deflected in opposite directions due to their opposite charges. Alfa particles are positively charged helium nuclei. Beta particles are negatively charged electrons. Due to their much larger mass, alfa particles are deflected far less than beta. Gamma rays are not deflected because they are not charged. Gamma-ray is electromagnetic radiation, which is characterised by high penetrability.

2.1.2 First models of atoms

The study of cathode radiation and radioactivity showed that the atoms of the elements contain electrons. Since the atoms are electroneutral, they must contain as many positive charges as the electrons are contained in them. How are the electrons and positive charges placed in the atom?

The first model of the atom was proposed by Englishman J.J. Thomson (1856–1940), a Nobel Prize-winning physicist, in 1903. According to his hypothesis, the atom has the form of a continuous, positively charged sphere. This sphere contains negatively charged electrons, which are small in size (as compared to atoms). Based on the placement of elements in the periodic table of elements and the periodic change in their chemical properties, Thomson suggested that the electrons in the atom are placed in layers. The chemical properties of the elements depend on the outer layer of electrons. Such an atom model could explain only some of its properties (radiation, scattering, absorption of light). Many experimental data and, in particular, the experiments of E. Rutherford, however, could not be explained by the Thomson model.

Ernest Rutherford conducted a series of experiments with α-particles to test Thompson's model and determine the internal structure of the atom more accurately. He directed α-particles to thin metal plates, monitoring their movement (Fig. 2.3). It was found that the vast majority of α-particles penetrate through metal plates, some of them deviate from the original direction of motion, and only a small amount of particles (1 part per 10,000) is thrown back to its original position.

It is impossible to explain both the penetration through a metal plate and a reflection of α-particles from the Thomson atom model. An α-particle has a double positive charge and a massive mass. During its rapid motion, such a particle can only be rejected in its original position when it encounters another particle with a much greater positive charge on its way. Also, the penetration of a large number of α-particles through a metal plate gives evidence that the atom is almost "empty" and has a discrete structure. Based on his experiments, Rutherford proposed a nuclear model of an atom in 1911.

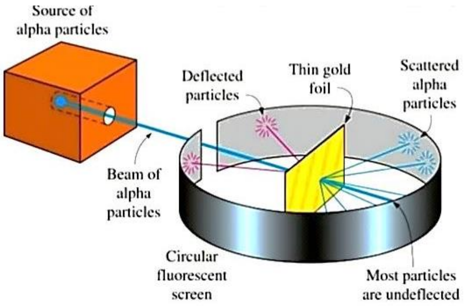


Figure 2.3 Rutherford experiment scheme

According to his nuclear model, a positively charged nucleus, the mass of which is almost equal to the mass of the atom, is located in the centre of the atom. Electrons, the number of which is equal to the positive charge of the nucleus, are moving around the nucleus. Electrostatic (Coulomb) forces, interacting between the nucleus and electrons, are balanced by the centrifugal force arising from the motion of electrons. If the force of Coulomb attraction to the nucleus is e^2/r and the centrifugal force is mv^2/r, then

$$\frac{mv^2}{r} = \frac{e^2}{r} , \tag{2.1}$$

where m is the electron mass; v is the velocity of an electron; e is the electron charge; r is the radius of the orbital along which the electron moves.

Experiments with α-particles allowed Rutherford to estimate the charge size of the nuclei of different atoms. The results of the calculations showed that the charge of the atomic nucleus is numerically equal to the ordinal number of the element in the periodic table of elements. The atoms of elements are neutral, and therefore, the number of electrons in each of them is also equal to the corresponding ordinal number of an element.

The research of former Rutherford’s student, English physicist Henry Moseley (1887–1915) was of great significance for determining the charge of the atomic nucleus.

2.1.3 Atomic spectra

The nuclear model of the Rutherford atom, which was confirmed by a large number of experimental data, was a significant step forward in the process of knowing the structure of the atom. However, it could not explain some of the facts. If the sun's ray passes through the prism, it decomposes. As a result, a coloured strip that contains all the colours of the rainbow in a continuous sequence appears on the screen set behind the prism. Such a phenomenon is explained by the fact that the white ray consists of electromagnetic waves of different lengths. The waves, passing through the prism, are refracted unequally and fall into different places of the screen. Such a spectrum is called continuous and is generated by a high-temperature solid body or liquid.

The light emitted by the heated gas or vapour consists of electromagnetic waves of a certain length. Therefore, instead of a continuous coloured strip, several individual colour lines appear, and they are separated by dark spaces. For example, in the visible part of the emission spectrum of hydrogen, there are seen five lines: red, green, blue and two violets (Fig. 2.4). In absorption spectra, the luminous lines are replaced by black lines located at the same places in the spectrum. Such spectra are called line (atomic) spectra. Each chemical element is characterised by its atomic spectrum, which differs from the spectra of other elements.

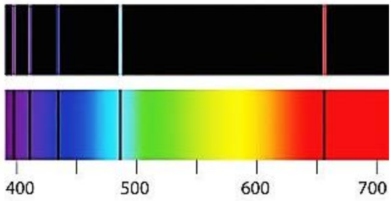


Figure 2.4 Emission (top) and absorption (bottom) atomic spectra of hydrogen in the visible region

The Rutherford atom model could not explain the nature of the line spectra, contradicting them. According to the laws of classical electrodynamics, if an electron rotates around the nucleus, it must continuously emit electromagnetic energy in the form of light waves. The electron velocity will decrease over time, and the electron will “fall” into the nucleus. As a result, the atom will cease to exist.

Such a conclusion contradicts the real properties of atoms, which are stable formations and can exist without destruction continually. Also, with the continuous emission of energy by an electron, the spectrum of an atom must be continuous rather than line-shaped.

Consequently, the model of the Rutherford atom could not explain either the existence of stable atoms or the presence of line spectra.

2.1.4 Quantum theory of light

In 1900, German physicist Max Planck (1858–1947), a Nobel Prize winner, studying the nature of the radiation of heated solids, suggested that energy is emitted and absorbed not continuously, but discretely, in certain portions. These portions are quanta, which are proportional to the frequency of oscillations. In other words, the transition from one energy state to the next one is accompanied by radiation or absorption of energy in the form of certain portions — quanta of energy.

The magnitude of the energy quantum can be calculated from a relation called the Planck equation:

$$E=h\nu\,, \tag{2.2}$$

where E is the amount of energy with oscillation frequency ν; h is the constant of proportionality, or Planck's constant equal to $6.626\cdot10^{-34}$ J s.

As follows from Planck's equation, the quantum energy is the larger, the larger the oscillation frequency or, the smaller the wavelength.

Planck's postulate was corroborated by Nobel Prize winner Albert Einstein (1879–1955). In 1905, analysing the phenomenon of the photoelectric effect, that is, the ability of metals to radiate electrons under the influence of light, he came to the conclusion that the electromagnetic (radiant) energy exists only in the form of quanta and the radiation is the flow of indivisible material "particles" (photons) whose energy is determined by Planck's equation.

From the standpoint of the classical mechanics, rotation of an electron with a mass m around the atomic nucleus is determined by the moment of the amount of motion, the product mvr, where r is the radius of the circle; v — the velocity of the electron. It is assumed that the values r and v can vary arbitrarily and continuously.

In quantum mechanics, the energy of the moving electron can vary only by quanta. Therefore, the values r and v, on which the energy value and the movement moment value (mvr) depend, must also change in leaps and bounds (unevenly). In quantum mechanics, the moment of movement is written by the expression $h/2\pi$ and can be equal to $h/2\pi n$, where n = 1, 2, 3, 4, that is, any integers:

$$mvr=\frac{h}{2\pi}n\,. \tag{2.3}$$

2.1.5 The Bohr model of atoms

Taking into account the quantum theory of light, the linear nature of atomic spectra and the nuclear model of Rutherford, Danish physicist Niels Bohr (1885–1962), a Nobel Prize winner, in 1913 formulated the basic ideas of his theory of the structure of a hydrogen atom in the form of postulates.

First Bohr postulate. An electron rotates around the nucleus without emitting energy, only in some precise circular orbits, which are called stationary or quantum ones.

Based on the quantum theory, Bohr assumed that the momentum of the motion of the electron, mvr, could vary in a jump-like manner according to equation (2.3).

Substituting the value of v from (2.3) into equation (2.1), one can find the radii of stable quantum orbitals, in which the electron motion is possible without irradiation of energy:

$$r_n = \frac{h^2 n^2}{4\pi^2 m e^2} . \qquad (2.4)$$

Substituting in equation (2.4) all known values of h, m, e, π, we obtain:

$$r_n = 0.529 \cdot 10^{-8}\, n^2 \text{ cm} = 0.0529\, n^2 \text{ nm}, \qquad (2.5)$$

where n = 1,2,3,...

As follows from equation (2.5), the radii of orbitals are referred to as squares of small integers:

$$r_1 : r_2 : r_3 : r_4 : \ldots r_n = 1^2 : 2^2 : 3^2 : 4^2 : \ldots : n^2 . \qquad (2.6)$$

From equations (2.1) and (2.3) we can find an expression for determining the electron velocity at any quantum level:

$$v_n = \frac{2\pi e^2}{h} \cdot \frac{1}{n} . \qquad (2.7)$$

Substituting all known values, we get:

$$v_n = 2.18\ 10^{-8} \cdot \frac{1}{n} \text{ cm/s} = 2.187 \cdot 10^{-6} \cdot \frac{1}{n} \text{ m/s.}$$

Consequently, the velocity of the electrons is inversely proportional to the numbers of the natural series:

$$v_1 : v_2 : v_3 : \ldots : v_n = \frac{1}{1} : \frac{1}{2} : \frac{1}{3} : \ldots : \frac{1}{n} .$$

Second Bohr postulate. An electron can jump from one stationary orbital to another. Such a transition is accompanied by either emission or absorption of a quantum of electromagnetic radiation. The energy of this quantum is equal to the energy difference between the final and initial states of an atom.

The energy of an electron, which rotates around the nucleus, depends on the radius of its orbital. The electron has the least energy when it is located on the nearest to the core orbital. The state corresponding to the lowest energy is called the main one. To transfer an electron to a more distant orbital from the nucleus, it is necessary to overcome the attraction of an electron to a positively charged nucleus that requires energy to be consumed. This process is accompanied by the absorption of a quantum of light. The energy of an atom at such an electron transition increases, and it moves into an excited state. The transition of an electron to the initial state causes a decrease in the energy of the atom. At the same time, energy is emitted in the form of a quantum of electromagnetic radiation. If we denote the electron energy at a more distant orbital through E_2, and the electron energy in the ground state through E_1, then the energy of the quantum E emitted by the electron in the transition will be as follows:

$$E = E_2 - E_1 . \quad (2.8)$$

Taking into account the Planck equation, we obtain:

$$h\nu = E_2 - E_1 ; \quad (2.9)$$

$$\nu = \frac{E_2 - E_1}{h} . \quad (2.10)$$

Equation (2.10) allows one to calculate the possible frequencies of radiation that absorbs or irradiates an atom.

Based on his theory, Bohr calculated the spectrum of the hydrogen atom. The calculated locations of the spectral lines in the visible part of the spectrum coincide with the experimental values.

The set of all possible transitions of electrons in an atom corresponds to the atomic spectrum of this atom. During the transition of an electron from any more distant orbital to another one closer to the nucleus, a spectral series arises. Each transition of an electron to a certain orbital corresponds to a certain spectral line.

Consequently, the Bohr theory of the atomic structure not only explains the physical nature of the atomic spectra as a consequence of transitions of electrons from one orbital to another but also allows one to calculate the spectra.

Bohr believed that the electrons were moving along the circular orbits. In studying the fine structure of the spectral lines, German physicist Arnold Sommerfeld (1868–1951) in 1916 substantiated the possibility of the motion of electrons along elliptical orbits, which are differently located in space.

The Bohr theory was quite clear and convenient. However, its successes were limited only to the hydrogen atom. The hydrogen atom is a one-electron system where only the Coulomb forces of attraction of an electron to the positively charged nucleus are operative. The spectrum of the helium atom, as well as any spectra of more complex atoms, cannot be calculated based on Bohr's representations. Electrostatic forces of repulsion, which act between electrons in more complex (multi-electron) systems in addition to the forces of attraction, are not taken into account by the Bohr theory. Also, some issues related to the very postulates were unclear. For example, the transition of an electron from one orbital to another, separated by some distance from the original, occurs for a certain time. In this case, the electron must be somewhere between the original and the final orbitals. However, such an intermediate state of the theory is "forbidden", since the electron in accordance with the Bohr postulates should be limited to certain stationary quantum orbits.

Creating his atom model, Bohr considered the electron as a classical material particle. However, based on the Planck–Einstein theory of light quanta (photons), it has been proved that the laws of nature, which are valid for large bodies (objects of the macrocosm), cannot be automatically extended to extremely small bodies (objects of the microworld — atoms, electrons, photons). Since the masses and sizes of microparticles are very small in comparison with the masses and the sizes of macroscopic bodies, the properties and patterns of motion of individual microparticles qualitatively differ from the properties and regularities of the motion of macroscopic bodies subject to the laws of classical physics. There was a need to develop a new physical theory for describing the properties and behaviour of objects in the microworld.

Thus, it was necessary to improve the atomic theory of Bohr–Sommerfeld, understand the wave nature of microparticle motion and develop methods of describing micro-objects based on the wave-mechanical ideas about the quantisation of energy.

2.1.6 Wave nature of light. Electron clouds

In the ‘20s of the XX century, thanks to the works of three Nobel Prize winners, Frenchman L. de Broglie (1892–1987), Austrian E. Schrödinger (1887–1961) and German W. Heisenberg (1901–1976), as well as other scientists, the foundations of the wave theory of the dual corpuscular-wave nature of light radiation were developed. As was noted, Albert Einstein proved that radiation is the flow of indivisible material "particles" (photons) whose energy is determined by Planck's equation.

The equation $h\nu = mc^2$ follows from the equations of M. Planck ($E = h\nu$) and A. Einstein ($E = mc^2$). Taking into account that $\nu = c/\lambda$ and the velocity of photons v is equal to the speed of light c, we obtain the basic equation of wave mechanics, so-called de Broglie equation:

$$\lambda = \frac{h}{mv}. \tag{2.11}$$

Therefore, a particle with a mass m moving at a velocity v corresponds to a wave of length λ. Equation (2.11) can be used to characterise the motion of not only a photon but also of other material particles: electrons, neutrons, protons, etc.

Consequently, the electron is both a particle and a wave at the same time. In 1925, Heisenberg proposed the principle of uncertainty, according to which the exact position of an electron in space cannot be established simultaneously with its speed or momentum.

A new representation of the electron forced researches to abandon the atomic models previously adopted, in which the electron moves over precise circular or elliptical orbits. The electron can be in any part of the space that surrounds the atomic nucleus, but the probability of its stay in one or another part of it is not the same.

The motion of an electron has a wave character. Therefore, quantum mechanics describes this motion in an atom using the wave function ψ, which is different in value at different points of the atomic space. The location of a point in space is determined by its coordinates x, y, z that is mathematically written by the dependence $\psi = f(x,y,z)$.

Since the motion of an electron is wavy, the determination of the wave function reduces to finding the amplitude of the electron wave.

The motion of an electron wave is quantitatively characterised by the amplitude ψ, which can be calculated from the Schrödinger differential equation. This equation binds the wave function ψ to the potential and total electron energy. For a one-electron hydrogen atom, the Schrödinger equation has the following form:

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-U)\psi=0, \qquad (2.12)$$

where m is the electron mass, h is the Planck constant; E is the total electron energy, and U is the potential electron energy.

For atoms with several electrons, one can use the approximate Schrödinger equation. Permissible solutions of equation (2.12) are possible only for some discrete values of the electron energy. Each of the functions ψ_1, ψ_2, ψ_3,..., ψ_n, which are solutions of the wave equation, corresponds to a certain energy value E_1, E_2, E_3, ..., E_n.

Equation (2.12) allows one to calculate the ψ-wave amplitude (wave function). The square of the amplitude ψ^2 expresses the probability of an electron being present at a certain point in the atomic space, and the value ψ^2dV is the probability of an electron being in the volume element dV.

The concept of an electron cloud is adopted in quantum mechanics as a model of an electron in an atom. The density of corresponding sections of the cloud is proportional to the probability of the electron being there. The electron is "smeared" around the nucleus in a sphere remote from the nucleus at a certain distance. One of the possible forms of an electron cloud of the atom is shown in Fig. 2.5.

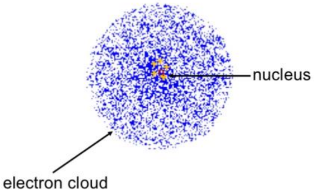


Figure 2.5 Illustration for electron cloud of the 1s electron

The maximum electron density corresponds to the highest probability of electron stay that is determined by the value of ψ^2. Obviously, the stronger the electron-nucleus bond, the electron cloud is smaller in size and more compact in terms of the charge distribution.

The space around the nucleus, in which the electron is most likely to be, is called the orbital. This interpretation of the orbital is somewhat simplistic. Orbital is a mathematical notion, the content of which follows from the wave equation. Therefore, we can assume that the wave function, which is the solution of the Schrödinger equation, is called an orbital.

So, instead of Bohr's orbitals, the nucleus of an atom is surrounded by electron clouds. The main characteristics that determine the motion of an electron around the nucleus are its energy and spatial features of the corresponding orbitals.

The evolution of concepts of the structure of an atom is illustrated in Fig. 2.6.

At the beginning of the XIX century, an atom was considered as an indivisible unit of matter, but by the end of the century, a complex internal structure of the atom universally recognised.

Later, the developments were focused on the description of the behaviour of electrons, and they took final shape in the late 20s – early 30s of the XX century.

The critical change consisted in the transition from ideas about orbital movements of individual electrons to quantum concepts of wave-particle duality based on the uncertainty principle.

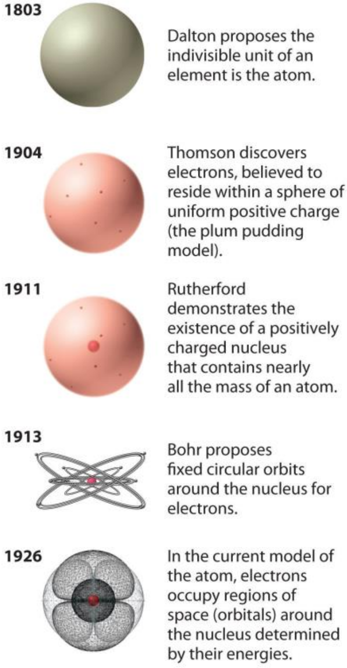


Figure 2.6 Evolution of atom structure models

2.1.7 Quantum numbers

According to the quantum-mechanical theory, the state of an electron in an atom is characterised by the values of four quantum numbers: n – main (or principal), l — orbital, m_l — magnetic, s — spin.

The main quantum number n. The main characteristic of the electron, which rotates around the nucleus, is its energy. In a real atom, the electron energy is quantised, that is, it acquires not any, but some discrete values corresponding to the theory of quanta. The transition of an electron from one quantum state to another is associated with a jump-like change in its energy.

The main quantum number determines the radius of a shell (the average distance from the nucleus to an area of elevated electron density) or the total electron energy at a certain level. The main quantum number can have positive integer values of 1, 2, 3, and up to ∞. The electron has the smallest energy at $n = 1$. The quantum state of an atom with the lowest energy E is called the ground (or nonexcited) one. As the value of n increases, the total electron energy increases. The quantum state of an atom with higher energies E_2, E_3, ..., E_n is called excited. The electron in the ground state is strongly connected to the nucleus; the connection with the nucleus weakens in excited states. Therefore, the state of an electron, which is characterised by a certain value of the main quantum number, is called the energy level of an electron in an atom. For energy levels with different values of n, the designations are taken in large Latin letters:

Main quantum numbers: 1 2 3 4 5 6 7; energy levels: K L M N O P Q.

The maximum number of energy levels that an atom can have in the ground state corresponds to the number of the period in which a certain chemical element is located. Energy is required to transfer the electron from a lower energy level to a higher one. This value determines the binding energy of the electron E_b, which is inversely proportional to the square of the principal quantum number:

$$E_b = \frac{-2.18 \cdot 10^{-18}}{n^2} \text{ (in J).}$$

The main quantum number determines the size of the electron cloud. Quantum transitions of an electron correspond to a jump-like change in the average size of an electron cloud: the decrease in the binding energy of an electron with a nucleus corresponds to an increase in the volume of the cloud and vice versa. According to quantum-mechanical calculations, the radii with the highest probability of staying an electron in the hydrogen atom are 0.053 nm ($n = 1$), 0.212 nm ($n = 2$), 0.477 nm ($n = 3$), etc. The values of these radii are referred to as squares of integers (the main quantum numbers), that is, $1^2 : 2^2 : 3^2$, etc. Consequently, the maximum electron densities in the hydrogen atom are concentrated at such distances from the nucleus that correspond to the radii of orbits in the theory of Bohr. However, the agreed conclusions of the Bohr and quantum-mechanical theories are obtained only for the hydrogen atom, but they also have different interpretations.

Orbital quantum number l. Linear spectra corresponding to the transition of an electron from one energy level to another, when viewed in a high-resolution spectroscope, mainly consist of several closely spaced individual lines. Such a fine structure of spectra (multiplicity) indicates various quantum states of electrons at a certain energy level due to differences in the shapes of electron orbitals. Consequently, the main energy levels consist of a certain number of energy sublevels that appear in the fine structure of the spectra.

An orbital quantum number l is introduced, which is also called azimuthal quantum number, to characterise the energy of an electron on a sublayer or shapes of electron orbitals. It corresponds to the value of the orbital momentum of the electron motion.

An orbital quantum number can range from 0 to $n - 1$. Each value l corresponds to a certain sublevel. Numbers and small Latin letters indicate energy sublevels:

Orbital quantum numbers: 0 1 2 3; energy sublevels: s p d f.

The possible number of sublevels for each energy level is equal to the number of the level, that is, the magnitude of the main quantum number. Thus, at the first energy level, characterised by the main quantum number $n = 1$, there can be only one sublevel with an orbital quantum number $l = 0$. At the second energy level ($n = 2$) there can be two sublevels corresponding to the orbital quantum numbers $l = 0; 1$. The third energy level ($n = 3$) has three sublevels with their corresponding orbital quantum numbers 0; 1; 2. At the fourth energy level ($n = 4$) there can be four sublevels, each of which has its orbital quantum number value: 0; 1; 2; 3.

According to the letters of the energy sublevels, the electrons in them are called s electrons, p electrons, d electrons and f electrons. At the first energy level, there can be only s electrons; on the second — s and p electrons; on the third — s, p and d electrons. At a given value of the main quantum number n, the s electrons have the smallest energy, then the p, d and f electrons.

By quantum-mechanical calculations, s orbitals have the shape of a sphere (spherical symmetry), p orbitals possess the shape of dumbbells, and more complex forms characterise d and f orbitals. Under the words "shape of the orbital", one must understand the spatial geometric model within which the electron is most likely to be located. Shapes of boundary surfaces of s, p and d orbitals are shown in Fig. 2.7.

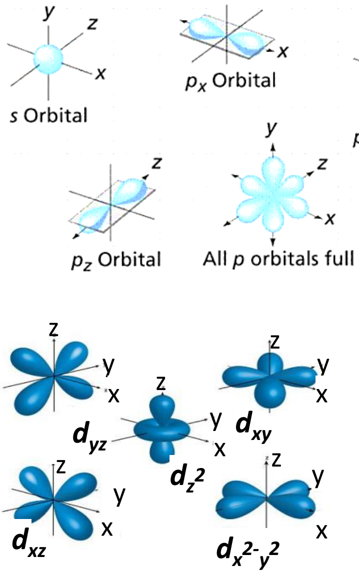


Figure 2.7 Forms and spatial orientation of s, p and d orbitals

The state of an electron in an atom corresponding to a certain value of n and l is written as follows: first, the number denotes the main quantum number, and then the letter describes the orbital quantum number.

For example, the designation 3s characterises an electron, which has the main quantum number n = 3 and the orbital quantum number l = 0 (the orbital has the shape of a sphere); the notation 4p means that the electron is characterised by the main quantum number n = 4 and the orbital p = 1 (the orbital has the shape of a dumbbell).

Magnetic quantum number m_l. In the magnetic field, the spectral lines of the atoms become wider or split, that is, new, closely spaced lines appear. Such a phenomenon is explained by the fact that an electron in an atom at all sublevels, except for the s sublayer, behaves like a magnet and, therefore, is also characterised by magnetic moment in addition to orbital moment. The energy changes, which occur in this electron, can be explained by the different placement of the electron orbitals in space relative to one another.

The spatial placement of electron orbitals relative to the direction of the magnetic field is characterised by a third quantum number m_l, which is called a magnetic number. The magnetic quantum number can take on integer values (positive and negative) from +l to −l. The number of values of the magnetic number depends on the orbital quantum number and shows how many orbitals can exist with a certain value of l.

So, for s electrons only one value $m_l = 0$ ($2{\cdot}0+1=1$) is possible; for p electrons (l=1) three values of m_l (−1; 0; +1) are possible; for d electrons (l = 2) the magnetic quantum number m_l can possess five values (−2; −1; 0; +1; +2); for f electrons (l = 3) there can be seven values of m_l (−3; −2; −1; 0; +1; +2; +3). A certain value of l corresponds to (2l + 1) possible values of the magnetic quantum number. Orbitals with the same energy are called degenerate orbitals. The p state degenerates three times, the d state is fivefold, and the f state is sevenfold.

Unlike spherical s orbital, p, d and f orbitals exhibit some preferential directions in space (Fig. 2.7). Depending on the orientation in space, p orbitals can be extended along the axes xx', yy', zz' and denoted as p_x, p_y, p_z, respectively. The directions of the d orbitals not only coincide with the coordinate axes but also lie between them. The d orbitals, oriented along the coordinate axes, are designated as d_{x2-y2} (elongated along the axes xx' and yy') and dz^2 (elongated along the axis zz'). The d orbitals, oriented between the coordinate axes, are denoted by d_{xy}, d_{yz}, d_{xz} (located along the bisectors between the axes). The f orbitals possess a more complex shape.

Sometimes, orbitals are depicted as power cells (or quantum cells) in the form of squares. For s electrons, there can be only one orbital, or one power cell, □; for p electrons — three cells, □□□; for d electrons — five □□□□□; for f electrons – seven □□□□□□□. The number of cells is determined by the value of the magnetic quantum number.

Spin quantum number s. Based on studying the fine structure of atomic spectra, it was established that the state of electrons in an atom, in addition to rotation around the nucleus, which is determined by the quantum numbers n, l, m_l, also depends on their own motion — spin. The sake of simplicity, spin (from the English spin — torsion, rotation) can be imagined as the motion of an electron around its axis. Such motion of an electron is characterised by a spin quantum number s. The spin quantum number describes the angular momentum of an electron. Because angular momentum is a vector, the spin quantum number has both a magnitude (1/2) and direction (+ or −). Spin is often represented by arrows: ↑↑ , ↑↓. The electron spins, directed in one direction, are called parallel, and in the opposite — antiparallel. Each orbital can only hold two electrons. One electron will have a +1/2 spin, and the other will have a −1/2 spin, *id est* they will spin in opposite directions.

2.1.8 Pauli exclusion principle

The values of four quantum numbers characterise electron motion in an atom but do not give a complete picture of the distribution of electrons in it.

Based on the analysis of atomic spectra and taking into account the position of elements in the periodic system, Austrian physicist Wolfgang Pauli (1890–1958), a Nobel Prize winner, formulated in 1925 the principle that allowed ones to determine such combinations of quantum numbers that correspond to the real distribution of electrons in an atom. According to the Pauli exclusion principle (or Pauli principle), there cannot be two electrons with the same values of all four quantum numbers in the atom.

For example, two electrons, having the same values of three quantum numbers m_l, l and n, differ in the value of the fourth quantum number s. The essence of the Pauli principle is that no more than two electrons with antiparallel spins can occupy one orbital, which is characterised by certain values of n, l and m_l.

The distribution of electrons at energy levels/sublevels is written as follows: a large Arabic number indicates the number of energy levels. The lower Latin letters are sublevels, and the number of electrons in the sublevel is a small Arabic number in the upper right index. For example, the distribution of electrons at the third level is written as $3s^2 3p^6 3d^{10}$.

2.1.9 Rules for filling orbitals in multi-electron atoms

The development of the modern theory of atomic structure allowed researchers to establish an electronic structure of all elements.

The most stable is the state of the atom in which the electrons are in the lowest energy states. In other words, an electron in the stable state is placed on the energy levels nearest to the nucleus. The electron energy is determined by the quantum numbers n and l.

The sequence of filling electron orbitals, as a function of the principal and orbital quantum numbers, was studied by Russian scientist V. Klechkovsky (1900–1972). He found that the electron energy increases with an increase in the sum of these two quantum numbers, that is, the quantities (n + l). Accordingly, he formulated so-called the first rule of Klechkovsky (also known as E. Madelung's rule in honour of Erwin Madelung (1881–1972), German physicist). **When the atomic nucleus charge increases, the successive filling of electron orbitals**

occurs from orbitals with a lower value of the sum of the main and orbital quantum numbers (n + 1) to orbitals with a greater value of this sum. With the same values of the sum (n + 1), the electron energy is the higher, the greater the value of the main quantum number n. Therefore, in such cases, the filling of electrons with energy sublevels is determined by the second rule of Klechkovsky: **At the same values of the sum (n + 1), the orbitals are filled successively in the direction of increasing the value of the principal quantum number n.**

When the energies of close sublevels differ very little from each other, the order of filling the neighbouring sublayers is complicated, and the electrons can be on both one and another sublevel.

In multi-electron atoms, the filling of energy levels and sublevels with electrons depends on their energy in the following sequence: 1s→2s→2p→3s→3p→4s→3d→4p→5s→4d→5p→6s→5d→4f→6p→7s →6d→5f→7p.

Following the above scheme, the sequence of filling energy levels with electrons will also change the energy of the electrons. At each next energy level, the energy of electrons is greater than that at the previous one, and the connection with the nucleus is weaker in value. Within the limits of a certain energy level, the energy of electrons increases with the transition from s to p orbital and from p to d orbital.

The filling of electrons of equivalent orbitals takes place by Hund's rule which was named after German physicist Friedrich Hund (1896–1997) and formulated as follows:

1. Every orbital in a sublevel is singly occupied before any orbital is doubly occupied.
2. All of the electrons in singly occupied orbitals have the same spin (to maximise total spin).

For example, if an atom has three electrons in the p level, they are placed on p_x, p_y, p_z orbitals, that is, there will be one electron located on each orbital. With another placement of electrons (two on one orbital and a third on another), the total spin number will be smaller than in the first variant.

In other words, the electrons of a certain sublayer occupy the maximum possible number of equivalent orbitals. At the same time, electrons with parallel spins are first placed on orbitals, after which the orbitals are filled with electrons with antiparallel spins.

In summary

The key concepts, laws, definitions and formulas:

1. Microscopic objects are characterised by the unity of certain (fixed) and uncertain properties.
2. Atom has a complex structure.
3. An electron may be in any part of the space that surrounds the atomic nucleus, but the probability of its stay in one or another part of it is not the same.
4. By the quantum-mechanical theory, the state of an electron in an atom is completely characterised by the values of four quantum numbers: n — main (principal), l — orbital (azimuthal), m_l — magnetic, s — spin.
5. Orbitals that have the same value of principal quantum number form a shell. Orbitals within the shells are divided into subshells, which differ in the values of orbital and magnetic quantum numbers
6. Two electrons with the same values of all four quantum numbers cannot exist simultaneously in the atom (Pauli principle).
7. The rules of electron orbital filling in multi-electron atoms.
8. Value and physical interpretation of quantum numbers.

Necessary practical skills:

1. To record the electronic and graphic formulas of atoms and their simple ions (cations and anions) as well as atoms of non-metallic elements in excited states.
2. To determine the composition of electron shells (energy levels and sublevels) of atoms of elements of the first to third periods.

2.2 Periodic law

2.2.1 The periodic table of elements

Analysing the data on the internal relationship between groups of substances with similar properties, Dmitry Mendeleev concluded that the chemical and physical properties are determined by the fundamental and general characteristics of chemical elements. The atomic mass of an element was taken as one of such characteristics. He wrote that the whole essence and nature of elements is expressed in their masses.

Having located the known at that time 63 elements in the order of growth of their atomic masses from left to the right, that is, having made the first version of its table, D. Mendeleev noticed that the chemical properties of the elements naturally change. Elements with identical properties are periodically repeated through a certain number of elements, and their chemical and physical properties are a periodic function of the atomic mass. The idea of the periodic law was published in 1869. In 1871, the following wording was given to this law: **the properties of elements, as well as the properties of simple and complex bodies formed by them, are periodically dependent on the magnitude of atomic masses of elements.**

The merit of Dmitry Mendeleev is that he considered the revealed periodical dependence as an objective pattern of nature, while his predecessors could not do it. He believed that the composition of compounds, their chemical properties, the temperature of boiling and melting, the structure of crystals, reactivity, etc. exhibit the periodic dependence on the atomic mass.

D.I. Mendeleev replaced the atomic masses of almost 20 elements for the construction of a periodic table based on the similarity of their chemical properties. Thus, beryllium, which was considered as a trivalent metal at that time, was referred to the divalent elements; its atomic mass was corrected from 13.7 to 9.4. He replaced the valence of indium from two to three that resulted in the correction of its atomic mass from 75.4 to 113.1. Modern values of atomic masses of Be (9.01) and In (114.8) are close to the values proposed by D.I. Mendeleev.

D.I. Mendeleev predicted the existence of approximately 20 new elements on the base of the revealed periodicity and provided for them empty cells in the periodic table. So, the properties of three elements that Dmitry Mendeleev denoted with the prefix "eka" (one) (eka-boron, eka-aluminium and eka-silicium) were predicted with amazing accuracy.

The triumph of the periodic law became evident after the discovery of a new element called gallium by Frenchman Lecoq de Boisbaudran (1838–1902) in 1875. The properties of gallium, determined experimentally, completely corresponded to the properties of eka–aluminium which were predicted by D.I. Mendeleev. In 1879, Swedish scientist Lars Fredrik Nilson (1840–1899) discovered eka-boron and called it scandium. In 1886, German Clemens Winkler (1838–1904) discovered eka-silicon and named it germanium. Thus, during the fifteen years, Mendeleev’s predictions were confirmed. Since that time, the periodic law has gained universal recognition.

At the end of the XIX century, noble gases were discovered (He, Ne, Ar, Kr, He), which, according to the values of atomic masses, Mendeleev located between typical nonmetals (halogens) and typical metals (alkaline), creating for them a new zero group in his version of the periodic system.

The central structural units of the periodic table of elements are periods and groups. Each row of the periodic table is called a period, and each column of the periodic table is called a group (or family). Many variants of the periodic table have been developed till now, which differ in the numbers of periods and groups and arrangements of components of the table.

Seven periods are available in virtually all variants whereas the number of groups is different for short and extended versions of the periodic table. As a rule, short-form patterns include eight groups of chemical elements; these groups are usually denoted with Roman numerals. The long form of the periodic table contains 18 groups. In this book, we will use the long form of the periodic table (see Attachment A), which has been favoured by the International Union of Pure and Applied Chemistry (IUPAC) since 1990.

2.2.2 Classification of elements by electronic structures of atoms

Some issues were not resolved at the time of the creation of the periodic table. For example, the numbers of elements that can be located between hydrogen and helium, and hydrogen and uranium, were unknown. The location of rare earth metals and the placement of noble gases, as well as the possibility of discovering new elements, were not defined. The reasons for periodicity in changing the properties of elements were also not disclosed. It seemed unreasonable to place in the same group of the short-form table such different elements as, on the one hand, halogens and, on the other hand, Mn, Tc, Re; chalcogens and refractory Cr, Mo, W; alkali metals and Cu, Ag, Au. It was also unclear why periods contain different numbers of elements. Some inconsistencies were observed between maximum valency of some elements and their positions in the periodic table (for example, for fluorine, oxygen, copper, gold, etc.). With progress in the atomic structure theory, all these problems were solved.

When the correct values of serial numbers of elements were defined in the periodic table, it turned out that the elements are arranged in order of increasing their serial numbers rather their masses. Therefore, the serial numbers are those quantitative characteristics, which determine the chemical nature of elements, and they correspond to the magnitude of the positive charge of the atomic nuclei. The periodic law acquired a new formulation: **the properties of elements, as well as the form and features of their compounds, are periodically dependent on the charge of the nuclei of their atoms.**

The new formulation confirmed the correctness of placement of some elements in the periodic system. For example, Mendeleev placed six elements (three pairs of elements) not in order of magnitude of their atomic masses: Ar (39.95) – K (39.10), Co (59.93) – Ni (58.71), Te (127.6) – I (126.9). Since the charge of the nucleus of a potassium atom is greater than the charge of the nucleus of an argon atom, the latter is placed in the system before potassium.

Based on the theory of atomic structure, the cause of the periodic change in the properties of elements in the periodic system was established, namely: **the properties of elements change periodically because similar electronic structures are formed and repeated periodically with the development of atomic structures.**

The modern form of the periodic table by IUPAC is shown in Appendix A. The actual layout of the periodic table is based on the grouping of elements according to their chemical properties.

If an energy level with the same principal quantum number is being filled in a sequence of elements, such elements compose a period in the periodic table. In this case, the period number coincides with the value of the principal quantum number n of the external energy level.

When a first electron appears at a new s sublevel, a new period starts to build-on. Hydrogen and alkali metals are located at the beginning of each period. When all p orbitals at an external energy level are occupied with electrons, the formation of a period is completed. Noble gases are located at the end of each period.

The study of the structure of atoms showed that each period, except for the first, has elements, whose electronic configurations are intermediate between the structures of two successive noble gases with electronic configurations $(n-1)s^2np^6$.

The structure of electron levels and sublevels in atoms is different depending on the position of an element in the periodic system. In the first three periods, external energy levels are being filled by electrons with an increase in charge of the nucleus of elements.

The first period consists of two elements. In the hydrogen atom (Z = 1), one electron is placed on the s sublevel of the K level (n = 1): $_1$H: $1s^1 n = 1$.

Helium atom (Z = 2) has two electrons. By Pauli principle, they are characterised by antiparallel spins: $_2$He: $1s^2 n = 1$. Such placement of electrons forms a very stable configuration, which determines the relative inertia of helium in reactions with other elements. In a helium atom, the filling of the nearest to nucleus K level is completed.

Elements, whose atoms are filled with s orbital electrons, are called s elements.

The second and third periods contain eight elements each. Among elements of the second period, an occupation of the L level (n = 2) takes place. In atoms of the first two elements (Li and Be), 2s orbitals are filled, and in B and Ne, sequentially the 3p orbitals are filled.

Examples of the electronic structure of atoms of the second-period elements are shown below:

(Z = 5) B: $1s^2 2s^2 2p^1$ (Z = 8) O: $1s^2 2s^2 2p^4$

The occupation of 2p orbitals is completed in a neon atom. As a result, the second energy level is filled by the maximum possible number of electrons that forms a highly symmetric structure: Ne $1s^2 2s^2 2p^6$. The neon atom completes the second period of the periodic system and closes the second L-energy level.

Elements, whose atoms are filled by electrons of p orbitals, are called p elements.

Consequently, the second period consists of two s elements and six p elements.

Elements of the third period are filled with electrons of the M level (n = 3), which consists of 3s, 3p and 3d orbitals. Atoms of the first two elements Na and Mg are filled with electrons of 3s orbitals; in Al–Ar, 3p orbitals are being filled, and 3d orbitals are vacant.

Here are examples of electronic configurations and schemes of the structure of atoms of some elements of the third period:

$_{11}$Na $1s^2 2s^2 2p^6 3s^1$ or can be written as [Ne]$3s^1$

$_{15}$P $1s^2 2s^2 2p^6 3s^2 3p^3$ or can be written as [Ne]$3s^2 3p^3$

$_{18}$Ar $1s^2 2s^2 2p^6 3s^2 3p^6$ or can be written as [Ne]$3s^2 3p^6$

Argon is the last element of the third period; it has completely filled 3s and 3p orbitals. Therefore, the external energy level consists of four pairs of paired electrons.

Thus, the third period contains two s elements and six p elements. The structure of the external energy levels of the corresponding elements of the second and third periods is similar.

There are 18 elements in the fourth and fifth periods. Atoms of the fourth period are sequentially closing the N level ($n = 4$). In the first two elements (K and Ca), 4s orbitals are under construction. Vacant 3d orbital is shielded by an electron layer of $3s^2 3p^6$. Due to the repulsion of the 19th electron in potassium atom and the 20th electron in calcium atom from the $3s^2 3p^6$ layer, the 4s orbital is more energy-efficient than the 3d. Also, for 3d orbitals ($n = 3$, $l = 2$) the sum of $n + 1$ is 5, and for the 4s orbitals ($n = 4$, $l = 0$), the sum is equal to 4. Therefore, following the first rule of Klechkovsky, the 4s orbital should be filled before 3d orbital that is observed in reality:

$_{19}K$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or can be written as $[Ar]4s^1$

$_{20}Ca$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or can be written as $[Ar]4s^2$

With a further increase in the effective charge of the nucleus in elements, which are located after calcium, the energy of 3d orbital is more favourable than 4p. Therefore, starting with scandium, the element of the fourth period and the third group, the 3d orbital is being filled, and this process ends with the atom of copper. Here are examples of electronic formulas for some elements of the fourth period:

$_{21}Sc$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$ or can be written as $[Ar]4s^2$

$_{24}Cr$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ or can be written as $[Ar]3d^5 4s^1$

$_{29}Cu$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ or can be written as $[Ar]3d^{10} 4s^1$

$_{30}Zn$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$ or can be written as $[Ar]3d^{10} 4s^2$

Elements, whose atoms are filled with d orbital electrons, are called d elements.

After filling 3d and 4s orbitals in the atoms of Ga–Cr elements, the 4p orbitals are being built up. The fourth period ends with noble gas krypton, which atom has all the paired electrons:

$_{36}Kr$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ or can be written as $[Ar]3d^{10} 4s^2 4p^6$.

Thus, the fourth period begins with s elements (two elements) and ends with p elements (six); between them, there are ten d elements.

In the fifth period, the filling of energy levels and sublevels occurs in a similar way to the fourth period. Namely, the 5s orbitals are filled for Rb and Sr, the first two elements of the period. For Y–Cd series, 4d orbitals are filled and for In–Xe sequence — 5f orbitals. Thus, the fifth period contains two s elements, six p elements and ten d elements.

The sixth period, containing thirty-two elements, begins with two s elements (Cs and Ba), where 6s orbitals are being closed. For the atom of La, the filling of 5d orbitals (one electron) begins, and in the atoms of Ce–Lu series of elements, the 4f orbital is more energy-efficient than the 5d orbital. Therefore, 4f orbitals are being filled in the atoms of these elements. In addition to lanthanum, gadolinium and lutetium have one electron each on the 5d orbitals. Then, the 5d orbital in the atoms of the elements Hf–Au continues to be filled, and this period ends with the elements Tl–Rn, where 6p orbitals are being built up.

Elements, whose atoms are filled with f orbital electrons, are called f elements and known as lanthanides.

Thus, the sixth period consists of two s elements, six p elements, ten d elements and fourteen f elements.

The seventh period consists of 32 elements as well; it is considered as that completed recently. As a rule, period 7 elements fill their 7s shells first, then their 5f, 6d, and 7p shells, in that order. However, there are exceptions, such as plutonium. All elements of period 7 are radioactive. This period contains the actinides (fourteen f elements), which contains the heaviest naturally occurring element, plutonium; subsequent elements can be synthesised artificially.

A group (also known as a family) of the periodic system is a vertical series, which contains similar elements in properties. The modern numbering "group 1" to "group 18" has been recommended by the IUPAC since about 1990. The f-block columns (between groups 3 and 4) are not numbered in this system. The new IUPAC replaces two older incompatible naming schemes (both were based on eight groups), used by the Chemical Abstract Service (more popular in the U.S.), and by IUPAC before 1990 (more popular in Europe).

The elements in a group have similar physical or chemical characteristics of the outermost electron shells of their atoms (i.e., the same core charge), as most chemical properties are dominated by the orbital location of the outermost electron.

Groups 15–18 are often identified by their topmost element or have specific names. For example, group 16 is variously described as the "oxygen family" or as the "chalcogens".

As you know, the external energy level is being filled in s and p elements, and the penultimate level is being filled in d elements. The third from the top outer level is built-up in f elements. Therefore, the difference in properties is most manifested in the neighbouring s and p elements. In d elements and especially in f elements, the difference in properties is not obvious. The third external energy level has little effect on the chemical properties of the elements, so lanthanides and actinides are very similar to each other in their properties.

Since the electronic configurations are similar but not identical in the rows of analogous elements, then not just repetition but more or less clearly expressed logical changes in properties are observed in the transition from an element to an element in groups and periods.

2.2.3 Periodicity of properties of elements

Ionisation energy. All properties of the elements, determined by the electronic structure of the atom, naturally change in periods and groups of the periodic system.

The chemical nature of an element is determined by the ability of its atom to lose or acquire electrons. This ability can be quantified by the energy of ionisation of an atom and its affinity to an electron.

The energy of ionisation, I, is the amount of energy that is needed to separate an electron from an unexcited atom:

$$E^{\circ} + I = E^{+} + \bar{e}\,.$$

The energy of ionisation is expressed in kJ/mol or eV/atom. The value of ionisation energy in eV/atom is numerically equal to the ionisation potential in Volts.

For multi-electron ions, ionisation energies I_1, I_2, I_3, ... correspond to the separation of the first, second, and other electrons. At the same time, $I_1 < I_2 < I_3$ since increasing the number of detached electrons leads to an increase in the positive charge of the resulting ion.

The energy of ionisation of an atom strongly depends on its electronic configuration. So, complete electron layers demonstrate an increased level of stability. The smallest values of ionisation energy I_1 have s elements of the first group in the modern IUPAC classification (Li, Na, K). The values of ionisation energies I_2 in these elements sharply increase that corresponds to the removal of the electron from the completed layer (ns^2np^6 and $2s^2$ for Li). In the s elements of group 2 (Be, Mg, Ca), removal of an electron from a completed layer (ns^2np^6 and $2s^2$ for Be) similarly leads to a sharp increase in ionisation energy I_3.

The s elements of group 1 demonstrate the smallest ionisation energy (3–5 eV), whereas the s and p elements of group 18 possess the highest ionisation energy. The growth of ionisation energy in the transition from s elements of group 1 to p elements of group 18 is determined by the growth of the charge of the nucleus.

In the transition from s elements of group 1 to p elements of group 18, the ionisation energy changes nonmonotonously with the manifestation of internal periodicity. The relatively large value of ionisation energy is typical for elements of group 2 (Be, Mg, Ca) and group 15 (N, P, As). At the same time, elements of groups 13 (B, Al, Ga) and 16 (O, S, Se) are characterised by smaller values of ionisation energy.

Electron affinity. Electronegativity. The energy effect F of the process of joining the electron to a neutral atom E with its transformation into a negative ion E^- is called the electron affinity:

$$E + \bar{e} = E^- \pm F.$$

The electron affinity can be expressed in kJ/mol or eV/atom. The electron affinity is numerically equal but opposite in the sign, to the ionisation energy of a negatively charged ion E^-.

Reliable electron affinity values were found only for a small number of elements. It is clear that electron affinity depends on the electron configuration of the atom; a pronounced periodicity in the nature of its change is observed with an increase in the serial number of the element.

The p elements of group 17 have the greatest values of electron affinity. The least and even negative values are observed for atoms with the configuration s^2 (Be, Mg, Zn) and s^2p^6 (Ne, Ar, Kr) or with a half-filled p orbital (N, P, As). Such behaviour gives additional proof of the stability of electronic configurations.

The addition of one electron to the atoms of oxygen, sulfur, carbon and some others is accompanied by the energy release. Thus, for these elements, the force of binding of an additional electron to the nucleus is greater than the repulsion forces between the additional electron and the electron shell of the atom.

The addition of further electrons to an atom, e.g., two, three, or more electrons, is impossible according to quantum mechanical calculations.

The concept of electronegativity is conditional. It allows one to estimate the ability of an atom of the element to attract the electron density in comparison with the atoms of other elements in the compounds. This ability depends on the ionisation energy of the atom and its electron affinity. According to one of the definitions given by Robert S. Mulliken (1896–1986), the electronegativity of an atom χ can be expressed as a half-sum of its ionisation energy and electron affinity: $\chi = 1/2(I+F)$. There are about 20 scales of electronegativity. The values of electronegativity of different scales vary, but the relative arrangement of elements in different electronegativity series is the same. In the scale of electronegativity by Pauling, for example, the electronegativity of fluorine is 4.0.

A general tendency of growth of electronegativity of elements in periods and its reduction in groups are observed. The smallest values of electronegativity characterise s elements of group 1, and the largest are p elements of group 17.

Strictly speaking, it is impossible to attribute a steady electronegativity to each chemical element. Its value depends on many factors, in particular on the valence state of an element, the type of compound involved, etc. However, this concept of electronegativity is useful for a qualitative explanation of the properties of chemical bonding in compounds.

Atomic radii. The radii of atoms and ions are very important. Using this geometric parameter, a large number of experimental facts and properties of chemical elements and their compounds were explained. The atomic radii of chemical elements vary periodically depending on the element's serial number. Decreasing from alkali metal to halogen, the atomic radius of the next alkali metal increases again and exceeds the radius of the atom of the previous alkali metal. Thus, the sodium atom has a radius of 0.186 nm, magnesium — 0.16 nm, chlorine — 0.099 nm, and the radius of the potassium atom is again increased and becomes equal to 0.231 nm.

Thus, the general regularity in the change of radii, as a rule, consists in decreasing the radius with electron filling of s, p, d or f sublevels. Such behaviour can be explained by the fact that as the charge increases, the attraction force between the nucleus and electrons plays a greater role than the mutual repulsion of the electrons.

Usually, atomic radii increase considerably in groups of the periodic system from top to bottom. Such a dependence is observed, for example, in alkaline and alkaline earth metals, in halogens, and others. As a result of the presence of ten 3d elements between the 4s-element calcium and the 4p-element gallium, the radius of the gallium atom (0.122 nm) is less than the radius of the aluminium atom (0.143 nm). The radius of the atom of the d-element scandium (0.16) is greater than the radius of the aluminium atom. Therefore, the chemical properties of gallium fall out the B – Al – Ga series. In contrast, the properties of scandium fit well the B – Al – Sc series, even though B, Al, Ga are p elements and scandium is a d element.

The second exception to the general pattern of increasing atomic radii in groups is observed in the elements following the lanthanides. Reducing the radii of atoms of lanthanides with an increase in the atomic mass is called lanthanide compression. The reason for this is the same: with an increasing charge of the nucleus, the attraction of electrons increases. The number of electron layers within the same period does not increase. As a result of lanthanide compression, the atomic radius of hafnium (0.157) is equalised with the zirconium radius (0.157) that results in very similar properties of zirconium and hafnium, niobium and tantalum. In addition to lanthanide compression, there is actinide compression for 5f elements.

In the transition from left to a neighbouring right cell, the radii of atoms and ions decrease as much as they increase in the transition from top to down along a group.

Thus, the radii of neighbouring elements located diagonally, for example, Li and Mg, as well as Be and Al, are close. D.I. Mendeleev noted such a rule. It is the basis of the law, called diagonal. According to this law, lithium in some properties is more like magnesium than other alkali metals. Lithium, like magnesium, gives marginally soluble phosphate and carbonate. Lithium and magnesium relatively easily interact with molecular nitrogen with the formation of nitrides.

Thus, knowing the position of an element in the periodic system, one can predict the properties of its compounds using the following information.

1. The composition of higher oxides of saliferous elements is determined by the number of the group (Table 2.1).

2. Hydrogen-containing volatile compounds of a certain composition are formed only by nonmetals, that is, elements of only the 14–17 groups (Table 2.1). It is necessary to distinguish the general concept of "hydrides of elements" and specific "volatile hydrogen–containing compounds". Hydrides are compounds with hydrogens of various composition and nature, which are formed by almost all elements, while volatile hydrogen-containing compounds are formed by nonmetals only.

Table 2.1 Formulas of higher saliferous oxides and volatile hydrogen-containing compounds of chemical elements depending on IUPAC group numbers

Compounds by groups	1	2	13	14	15	16	17	18
Higher saliferous oxides	E_2O	EO	E_2O_3	EO_2	E_2O_5	EO_3	E_2O_7	EO_4
Volatile hydrogen-containing compounds of the element	–	–	–	EH_4	EH_3	EH_2	EH	–

3. Along periods, chemical properties change from metallic (elements at the beginning of periods) through the intermediate between metallic and nonmetallic to nonmetallic (elements at the end of periods).

4. Metallic properties enhance, and nonmetallic ones reduce with the growth of atomic masses. In particular, densities of simple substances increase, melting temperatures of simple metals decline, and melting temperatures of nonmetallic substances usually increase. These phenomena are explained based on the electronic structure of atoms.

5. Properties of each element are expressed as the average between the properties of four elements that surround it in the periodic system from every quarter.

In summary

The key definitions concepts, laws and formulas

1. Formulation of the periodic law.
2. Definitions of structural elements of the periodic table.
3. Periodic change of basic atomic characteristics of elements
4. Properties of chemical elements, as well as compounds formed by them, are dependent on the electronic structure of their atoms.

5. A graphic representation of the periodic system of chemical elements is the periodic table.

6. The basic regularities of the periodic system are the natural weakening of the metallic properties in periods from left to right and their amplification in groups from top to bottom.

7. Each element of the periodic system in its properties is similar to the elements surrounded it.

Necessary practical skills:

1. To distinguish periods and groups in the periodic system.
2. To use the information from the periodic system to characterise elements, simple substances.
3. To analyse changes in the properties of simple substances depending on the placement of elements in the periodic system.

2.3 Chemical bond

The concept of atoms, as the smallest particles of matter, was created by Greek philosophers, but a scientifically based atomic-molecular theory was formed only when the development of physical experiments allowed chemists to conduct precise experiments.

Investigation of chemical transformations and substances from the quantitative point of view allowed us to understand the nature of chemical compounds and draw a clear lane line between them and mechanical mixtures.

The first attempt to answer the question, why and how the atoms are interconnected, made Swedish chemist Jöns Jacob Berzelius (1779–1848), who believed that the bases of chemical phenomena are electrical processes, that is, the connection of atoms of two different elements occurs due to the presence of different charges.

From this viewpoint, all elements were divided into two large groups — metals (positively charged) and nonmetals (negatively charged), and chemical reactions were reduced to the interaction of metal atoms with nonmetal atoms.

At the same time, Avogadro introduced the notion of the molecular structure of simple substances to explain the "abnormal" nature of the interaction of hydrogen with chlorine, when one volume of hydrogen, coupled with one volume of chlorine, gives rise to two volumes of HCl. The Avogadro notation did not contradict the experiment because, instead of $H + Cl = HCl$, he proposed to write $H_2 + Cl_2 = 2HCl$.

Contemporaries did not perceive Avogadro's revolutionary views because they contradicted the theory of Berzelius on the nature of the chemical bond.

Indeed, how can the atoms of the same type, that is, one element, be interconnected since they have an absolutely identical charge and should be repulsed?

The reconciliation of the antagonistic views of Berzelius and Avogadro became possible after creating clear ideas about the structure of atoms.

The analysis of the nature of changes in the chemical activity of various elements, depending on the electron filling of their outer (valence) shells, allowed American chemist Gilbert N. Lewis (1875–1946), a Nobel Prize winner, and German chemist Walther Kossel (1888–1956) to express the assumption that the most stable of possible combinations is the octet electronic configuration. Therefore, those atoms which have an octet on an outer shell (Ne, Ar, etc.) are inert, while other atoms are trying to achieve the stable octet configuration. Thus, the electronic theory of chemical bond was created, according to which atoms, in the process of interatomic interaction, acquire the outer shell filled with an octet of electrons.

The completion of outer shell is achieved either by the loss of excess or by the addition of the required amount of electrons, when the atoms become ions with an octet periphery, or by the so-called socialisation of external electrons when the created octet belongs to two involved atoms. The authors of the electronic theory of chemical bonding also believed that atoms interact with each other by pairing existing unpaired valence electrons.

As we can see, the theory of Berzelius is a special case of the theory of Lewis and Kossel. Moreover, in the theory of Berzelius, the result of a certain type of chemical interaction, which ends with the creation of charged atoms (ions), is considered as the very interaction.

The electronic theory of chemical bonds had been improving and supplementing for several decades, but its limitation eventually became apparent with time. In particular, it was impossible to explain:

– why is the energy of the spin-spin interaction of electrons substantially (several orders of magnitude) less than the energy of the chemical bond formed by the pairing of electrons?

– Why do unpaired electrons exist in the oxygen molecule?

– Why do H^{2+} ions exist? Etc.

The huge number of accumulated issues and the failure of the Lewis–Kossel theory to answer them forced scientists to move forward. For understanding the nature of chemical bonds, they were forced to assume that the laws, which consider atoms as a construction of a positively charged nucleus and negatively charged electrons, remain operative when constructing multi-atom molecules.

The theory of molecular orbitals (MO) appeared on the light. According to modern concepts of the MO theory, the chemical bond is identified with the so-called bonding molecular orbital. Any bonding MO differs from other types of MOs because its energy is much smaller than the sum of energies of the initial atomic orbitals on which the electrons were located. The energy advantage of the transition of electrons from atomic orbits to a bonding MO is the driving force that forces the atoms to interact with each other and join the molecule.

The types of chemical bonds, such as σ, π, δ, were distinguished by the type of MO.

2.3.1 Ionic bond

In multi-electron atoms, the outer (valence) electrons are attracted by the nucleus with varying force. This force will be the smaller, the larger the radius of the atom and the more electrons are located between the nucleus and the valence electrons.

Quantitatively, the interaction of valence electrons with the nucleus is estimated by electronegativity χ. The ion bond is formed if the difference in the electronegativity of the interacting atoms exceeds 1.9 (in the lithium electronegativity scale).

For example, in the interaction of sodium ($\chi_{Na} = 0.9$) with chlorine ($\chi_{Cl} = 3.0$), the difference is $\Delta\chi_{NaCl} = \chi_{Cl} - \chi_{Na} = 3.0 - 0.9 = 2.1$ and is greater than 1.9; therefore, in this case, the ionic compound is formed, such as sodium chloride.

In ionic compounds, atoms localise a significant amount of electric charge and are considered as self-charged particles — ions.

It should be noted that in a substance, the electric charge, which is localised on atoms, is always less than one. It is true even in the case of the formation of a compound with a maximum difference in the electronegativity of the constituent elements. An example of such a compound is CsF, where $\Delta\chi_{CsF} = \chi_{Cs} - \chi_F = 3.3$. In this salt, the charge of ions caesium is +0.89, and ions of fluorine are −0.89, respectively.

Monatomic multiply charged ions O^{2-}, S^{2-}, N^{3-}, C^{4-} do not have a charge higher than one unit because joining of two or more electrons to atoms is practically impossible from the energy considerations as follows from quantum-chemical calculations. Thus, in the oxide of CaO, the charge of calcium ions is +0.8, oxygen ions are −0.8.

At the same time, the existence of multi-atomic ions, such as CO_3^{2-}, PO_4^{3-}, whose charge exceeds one unit, is possible because the excess of electron density in them is distributed among all the atoms forming the group.

By definition, **the ionic bond is the electrostatic interaction of cations and anions. Characteristic features of an ionic bond are: non-directional and unsaturated**.

The non-directional ion bond is because the electric field of a charged particle extends in space in all directions.

The absence of physical constraints for the interaction of a charged particle with any number of other charged particles causes the unsaturation of the ionic bond.

As a result, each particle of a certain charge surrounds itself to the maximum possible number of particles that have the charge of the opposite sign.

Thus, in NaCl crystals, each sodium ion directly contacts as much as six anions of chlorine. Each anion Cl^- contacts with the same number of Na^+ cations.

The ability to attract a certain number of ions with an opposite charge is estimated by the coordination number (c.n.). In the case of NaCl, the coordination number for the ions of $C1^-$ and Na^+ is the same and equal to 6. The value of c.n. depends on the ratio of radii of cations and anions: R(cat)/R(an).

If R(cat)/R(an) is in the range of $1.37 \div 0.73$, then c.n. = 8, which corresponds to the cubic structure of the crystalline lattice. If R(cat)/R(an) is between $0.73 \div 0.41$, the octahedral structure with c.n. = 6 is realised; and if R(cat)/R(an) < 0.41, the tetrahedral environment of ions is observed with c.n. = 4.

The peculiarity of the ordered arrangement of cations and anions in the crystalline lattice causes some specific properties of crystals with ionic chemical bonds, such as hardness and brittleness.

The significant hardness of crystalline substances is because each ion, interacting with a large number of ions with an opposite charge, is firmly held in its lattice site, and a tremendous effort is required to shift one layer of ions relative to others. However, if it succeeds, then each ion gets particles with the same name and charge. The ions are sharply repulsed, and the crystal breaks down. As a result of repeated intensive mechanical action, the crystal fractures and separates into a large number of small crystals.

2.3.2 Covalent bond

If the nucleus of each of two atoms in a molecule acts on external electrons with a force of similar magnitude, an equilibrium system is created, in which an attraction of oppositely charged particles is balanced with the repulsion of equally charged. In this case, the so-called covalent bond is realised.

For the first time, German physicists Walter Heitler (1904–1981) and Fritz London (1900–1954) considered such variant of the interaction of atoms on an example of hydrogen. The proposed scheme of total interactions of protons and electrons in two hydrogen atoms and the formation of a hydrogen molecule is illustrated in Fig. 2.8.

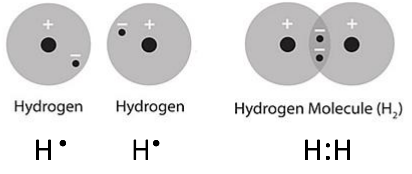
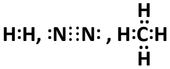


Figure 2.8 Scheme of interactions of protons and electrons in two hydrogen atoms and molecule H:H

In each hydrogen atom, the single electron is held in its orbital by its attraction to the proton in the nucleus. When two hydrogen atoms approach each other, the electron of each atom is also attracted to the proton in the other nucleus. The valence orbitals overlap, and the two electrons with opposite spins become shared in a covalent bond forming an H_2 molecule. As can be seen from the scheme above, the generated electron pair is localised and fixed between the nuclei. The covalent bond is characterised as saturated and directed based on, on the one hand, the fixation of a combined pair of electrons in the internuclear space, and, on the other hand, fixing the nuclei by a combined pair of electrons,

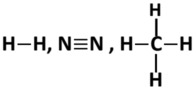
The concept of W. Heitler and F. London on the mechanism of formation of covalent bond in the hydrogen molecule was later extended to more complex molecules.

Based on this scheme, the covalent bond was first depicted in the form of two points between the symbols of the atoms that chemically interact with each other, as illustrated on the right side scheme.



$\mathrm{H{:}H,\ {:}N\vdots\vdots N{:},\ H{:}\overset{\displaystyle H}{\underset{\displaystyle H}{\ddot{\underset{\cdot\cdot}{C}}}}{:}H}$

These pairs of dots correspond to the combined pairs of electrons. Later, the dots were replaced by risks that made it possible to depict the spatial structure of molecules.



$\mathrm{H-H,\ N\equiv N,\ H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-H}$

Depending on which orbitals (s, p, d, f) are considered, and how they interact with each other, different types of covalent bonding can be formed: σ, π or δ bonds. Some examples of σ, and π bonds are illustrated in Fig. 2.9. In the case of σ bond, electron clouds have only one overlapping area. When π bond is formed, electron clouds can have two overlapping zones. Such interaction option is possible for p, d and f electrons because of understandable geometric considerations.

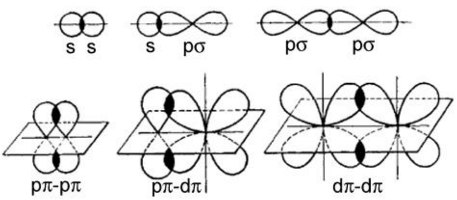


Figure 2.9 Formation of σ bonds and π bonds

The electron clouds of d and f electrons are complex in shape, and they can form δ bond with four overlapping zones. Delta bonds are covalent chemical bonds, where four lobes of one involved atomic orbital overlap four lobes of the other involved orbital. An example is shown in Fig. 2.10. This overlap leads to the formation of a bonding molecular orbital with two nodal planes which contain the internuclear axis and go through both atoms.

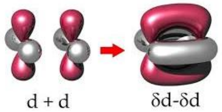


Figure 2.10 Formation of δ bonds between d electrons

If the covalent bond is formed by the same atoms, the combined electron pair is symmetrically and evenly spaced between their nuclei (see left scheme for H_2 in Fig. 2.11), and such a bond is nonpolar.

When the atoms of various elements interact, the valence electrons involved in the formation of a bond are attracted by the nuclei with different forces, which results in the displacement of the electron pair toward the more active atom (Fig. 2.11, the molecule of HCl). Such a bond assumes a polar character.

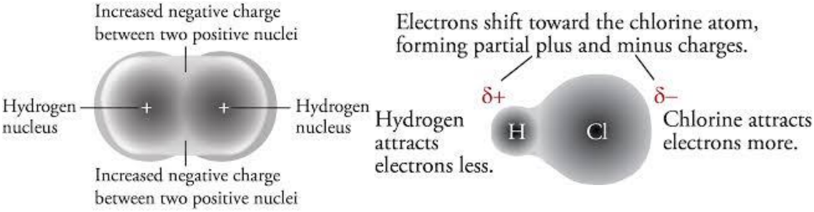


Figure 2.11 Distribution of charge of paired electrons in molecules H_2 and HCl

The degree of polarity of a covalent bond is quantitatively estimated, on the one hand, by the magnitude of excessive electron charge acquired by the atoms, and, on the other hand, by its deficit. The following expression, known as an effective charge, is used:

$$\delta = \frac{q_i - q_e}{q_e} .$$

In the case of HCl molecule, $\delta_H = +0.17$ and $\delta_{Cl} = -0.17$. In the transition from HCl to H_2S molecule, the polarity of the single covalent bond H–S decreases, while the effective charge of the sulfur atom compared to chlorine atom increases: $\delta_H = +0.1$, $\delta_S = -0.2$.

The polarity of the covalent bond affects, and sometimes very significantly, the geometry of the molecule if there are more than two atoms in the molecule. Those atoms, which acquire the same charge in sign, repulse each other, like petals in an electrometer (Fig. 2.12). The greater the charge is localised to them, the greater the repulsion force and the greater the valence angle α.

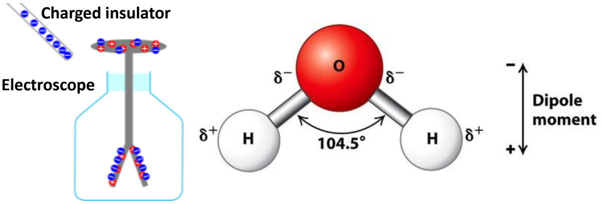


Figure 2.12 The effect of electrostatic interaction in an electroscope and a water molecule

Thus, in the series of H_2Te, H_2Se, H_2S, H_2O molecules, the value of α increases from 90° to 104.5° in proportion to the increase of the effective charge on the hydrogen atoms (Table 2.2).

In the given group of molecules, the atoms of the central element (Te, Se, S, and O) use two valence p electrons for the interaction with the hydrogen atoms. These electrons are known to be located at 90° in space. Thus, if the atoms of hydrogen would not be repulsed from each other, then the valence angle in molecules of type H_2E would be 90°. Concerning this angle, one can calculate the increase α and compare $\Delta\alpha$ with the value of δ_H.

Table 2.2 Value of valence angles

Compound	H_2Te	H_2Se	H_2S	H_2O
α, degrees	90	91	92.2	104.5

It is worthy to note that repulsion of atoms in complex molecules not only increases the valence angle but also affects the energy and the geometry of the bonding molecular orbitals, that is, σ bonds.

Sometimes deformation is so significant that the shape of the final molecular orbital is completely different from the original one. Such an effect is called the hybridisation of σ bonds.

The hybridisation effect can be demonstrated in the classic example of a methane molecule (Fig. 2.13).

Figure 2.13 Methane molecule

Here, the carbon atom for interaction with the hydrogen atoms in an excited state uses one s and three p-valence electrons. In the absence of repulsion of the polar fragments in the CH_4 molecule, three σ(s,p) bonds and one σ(s,s) bond would have formed, which have a fundamentally different shape (see Fig. 2.9). Instead, four equivalent bonds of the new form are formed.

The type of hybridisation is characterised by type and number of valence electrons involved.

Thus, sp^3 hybridisation is observed in the CH_4 molecule, sp^2 hybridisation in BF_3 molecule and sp hybridisation in BeF_2 molecule. It is possible to establish the fact of hybridisation by the value of the valence angle (Table 2.3).

Table 2.3 Hybridisation types

Hybridisation type	sp^3	sp^2	sp
valence angle	109°28′	120°	180°
Structure	tetrahedral	plane triangular	linear
Example	CH_4, NH_4^+	BF_3, H_3O^+	BeF_2, CO_2

If the valence angle is closer to that specified in Table 2.3, then the hybridisation of bonds occurs. For example, in the ammonia molecule (Fig. 2.14), α = 107°29′.

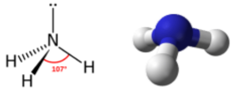


Figure 2.14 Ammonia molecule (NH_3)

The valence angle is rather close to that in Table 2.3 that allows one to characterise the ammonia molecule as a tetrahedral structure, in which the fourth fragment is a pair of s electrons of a nitrogen atom.

In the molecule of PH_3, α =94°, indicating some deformation of the σ bonds. However, such deformation is not so strong to talk about their hybridisation. Therefore, the phosphine molecules are attributed to the pyramidal structure.

In summary

The key concepts, definitions, laws and formulas:

1. Ion bond is the electrostatic interaction of ions. It is unsaturated and non-directional.

2. The ion bond is formed between atoms, the difference in electronegativity of which exceeds 1.9.

3. The same atoms form a nonpolar covalent bond; different atoms form a polar bond.

4. Repulsion of equally charged atoms in molecules leads to an increase in the valence angle; a strong repulsion is completed by the hybridisation of the σ bonds.

5. The polarity of the covalent bond is estimated by the magnitude of the effective charges of the atoms $\delta = \frac{q_i - q_e}{q_e}$.

6. The type of hybridisation is determined by the type and number of valence electrons involved in the formation of σ bonds.

Necessary practical skills:

1. To determine the types of chemical bond: ionic and covalent.

2. To determine types of hybridisation

2.4 Problem solving

2.4.1 Examples

Example 2.1 In what sequence are the atomic orbitals 3p, 3d, 4s and 4p filled with electrons?

Determine the value of the sum of the principal and orbital quantum numbers for each orbital:

3p: $(n+l) = 3+1 = 4$

3d: $(n+l) = 3+2 = 5$

4s: $(n+l) = 4+0 = 4$

4p: $(n+l) = 4+1 = 5$

So, we have the following sequence: 3p, 4s, 3d, 4p.

Example 2.2 The oxide of a chemical element of the third group of the periodic system has a relative molecular mass of 70. Name the chemical element and make up the formula of its hydroxide.

Let $A_r(E) = X$, since the element is in Group III, then the formula of this oxide E_2O_3, then

$M_r(E_2O_3) = 2x + 3\cdot16$; $70 = 2x + 48$; $22 = 2x$; $x = A_r(E) = 11$.

Thus, the element is boron; its hydroxide is boric acid (H_3BO_3).

Example 2.3 Write the electronic formula of the element of chlorine. Specify the molecular weight of its compound with hydrogen.

An electronic formula shows the distribution of electrons by orbitals. 17 electrons of chlorine are distributed as follows:

$${}_{17}Cl\ 1s^2 2s^2 2p^6 3s^2 3p^5$$

The valence of chlorine in compounds with elements having a lower electronegativity is 1. Therefore, the formula of its compounds with hydrogen is HCl. The molecular weight of this compound is M = 36.5 g/mol.

Example 2.4 Make an electronic formula and an abbreviated electronic formula of the element with serial number 19.

In an atom, there are 19 electrons. This element is potassium. The electronic formula has the form $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.

Example 2.5 Write electronic formulas of a sulfur atom and sulfur ions in degrees of oxidation 0, −2, +4, +6. Indicate the distribution of the electrons of the external energy level by orbitals.

Sulfur has element number 16. The electronic formula of the sulfur atom, corresponding to the oxidation level 0, has the form: $1s^2 2s^2 2p^6 3s^2 3p^4$.

Distribution of electrons of the external energy level by orbitals:

3s	3p		
↑↓	↑↓	↑	↑

At oxidation −2, the sulfur atom has 2 electrons more. These electrons are placed on the 3p sublevel of $1s^22s^22p^63s^23p^6$.

3s	3p		
↑↓	↑↓	↑↓	↑↓

In going to oxidation +4, the sulfur atom loses four electrons from the 3p sublevel: $1s^22s^22p^63s^23p^0$,

3s	3p		
↑↓			

At oxidation +6, it loses 6 electrons from 3s and 3p sublevels: $1s^22s^22p^63s^03p^0$.

Example 2.6 Name the element according to the following data: it is in group I, the relative molecular weight of hydroxide is 40.

The element of the first group corresponds to the hydroxide with the general formula EON.

$$M_r(EOH) = A_r(E) + 16 + 1;\ M_r(EOH) = 40;\ M_r(EOH) = A_r(E) + 17;$$

$$40 = A_r(E) + 17$$

$$A_r(E) = 40 - 17 = 23$$

Sodium (Na) has the relative atomic mass of 23.

Example 2.7 Make an electronic formula of an atom that has four energy levels, and the last one contains 6 electrons.

If the atom has 6 electrons at the outer level, then this element is located in group 16 of the periodic table. Since the atom has four energy levels, it belongs to the fourth period. This element is selenium: $_{34}Se\ 1s^22s^22p^63s^23p^63d^{10}4s^24p^4$.

Example 2.8 How many unpaired electrons have chlorine in an unexcited state?

Chlorine belongs to group 17 of the third period. Therefore, the valence level has the following form: $_{17}Cl...3s^23p^5$.

Distribution of electrons of the external energy level for orbitals:

3s	3p		
↑↓	↑↓	↑↓	↑

In an unexcited state, the atom has one unpaired electron.

Example 2.9 Determine the total number of electrons in an N^{3-} ion.

Nitrogen in the periodic system has a serial number 7. At a degree of oxidation −3, an atom has 3 electrons more. Their total number is 10.

Example 2.10 The acid has the formula H_2EO_3. The acid-forming element has the highest degree of oxidation. The element is located in the 4th period and belongs to p elements. Name the acid and make a formula of oxide which corresponds to the acid.

Determine the valence of the acid-forming element $\overset{I}{H_2}\,\overset{IV}{E}\,\overset{II}{O_3}$.

So, this is an element of group 14. Now the element is known to be located in the 4th period, group 14. Such a position in the periodic system occupies germanium.

Thus, the desired element is germanium, oxide — GeO_2.

Example 2.11 Write the equation of reaction between simple substances, formed by elements, if the electronic formulas of atoms of these elements have the ending $...3s^2$; $...3s^2\ 3p^5$. Indicate the oxidiser and reducing agent, and the type of chemical bond in the formed compound.

The valence formula of the atom ($...\ 3s^2$) indicates that this element is located in the 3rd period, group 2. This is magnesium.

If the valence formula of the atom has the ending $...\ 3s^23p^5$, this means that the element is in the 3rd period, group 17 ($2 + 5 = 7$) and belongs to the p elements. This element is chlorine. The reaction equation between these simple substances has the form

$Mg^o + Cl_2^o = Mg^{+2}Cl_2^-$

Magnesium is a reducing agent, and chlorine is an oxidiser. The chemical bond between metal and nonmetal is ionic.

Example 2.12 The atom of the element has 3 electrons more than the sodium ion. Name an element, and compile the electronic formulas of its atom and ion.

Sodium-ion Na^+ is an electrically charged particle formed from a neutral atom due to the removal of one electron: $Na^0 - 1\bar{e} \rightarrow Na^+$.

$11\bar{e} - 1\bar{e} = 10\bar{e}$. We calculate the number of electrons in the electron shell of an unknown element: $10\bar{e} + 3\bar{e} = 13\bar{e}$

The unknown element is aluminium. The electronic formula for the aluminium atom is $1s^22s^22p^63s^23p^1$, the electronic formula for the aluminium ion is $1s^22s^22p^6$. Thus, the desired element is aluminium.

Example 2.13 Determine the type of chemical bond in the molecules KCl, N_2, SiO_2. Justify your answer.

KCl is an ionic type of bond since it is formed between two atoms, which differ greatly in their electronegativity values (metal and nonmetal);

N_2 is a molecule formed between the atoms of the same element. Thus the bond is covalent nonpolar;

In SiO_2, the bond is formed between atoms of the same nature (nonmetals), and therefore, it is a covalent, polar bond. Electronegativity of oxygen is greater than the electronegativity of silicon.

2.4.2 Problems

1. Name the element and compile the electronic formula of its atom and ion, if the atom of the element has 7 electrons more than the sodium ion.

2. Find out how many values of the magnetic quantum number are possible for electrons in the energy sublevel, whose orbital quantum number is a) l = 2; b) l = 3.

3. Indicate impossible variants among the following electronic configurations and prove the reason why their existence is impossible: a) $1p^3$; b) $3p^6$; c) $3s^2$; d) $2d^1$; e) $5f^4$; f) $2p^1$; g) $3p^8$; h) $4d^{12}$; i) $5f^{12}$.

4. Write the electronic formulas of the following ions: Fe^{2+}; Se^{2-}; Cl^-; Al^{3+}; Mn^{2+}.

5. Determine the elements in accordance with the electronic structure of the external energy level: a) $3s^23p^4$; b) $4s^24p^6$; c) $2s^22p^1$; d) $5s^25p^3$; e) $6s^26p^2$; f) $5s^25p^5$; g) $3d^64s^2$; h) $3d^54s^1$.

6. Describe the form of orbitals and electron clouds, the state of which is characterised by the following quantum numbers: a) $n = 3$, $l = 0$, $m_l = 0$; b) $n = 3$, $l = 1$, $m_l = 0, \pm1$; c) $n = 3$, $l = 2$, $m_l = 0, \pm1, \pm2$.

7. Determine which of the atoms has the largest radius in the ground state: C, Si, Ge, Cr, Sn, Pb.

8. Place the following atoms in order of increasing their electronegativity: a) F, Sn, O, Te, K, N; b) Pb, Br, I, F, S, P.

9. Compare the electronic graphic configurations of Fe^{2+} and Fe^{3+} ions. Which of the ions has the most stable configuration, and why?

10. Define the energy of electron affinity. Explain the change of this characteristic: a) by a period; b) by a group.

11. Define electronegativity. Explain the change of this characteristic: a) by a period; b) by a group.

12. An element forms a gaseous compound with hydrogen, a mass fraction of hydrogen in which is 12.5%. Name the unknown element if its higher salifiable oxide has the formula EO_2.

13. At the interaction of the unknown metal with a mass of 2 grams of water, 1.12 litres (normal conditions) of hydrogen were released. Metal belongs to the second group of the periodic system of chemical elements. Identify the metal and explain what the compounds interact with its oxide.

14. Determine the molecular formula of the hydroxide if the relative molecular weight of this compound is 121, and the element, included in its composition, belongs to the 3rd group of the periodic system.

15. One of the elements predicted by D.I. Mendeleev forms an oxide, a mass fraction of oxygen in which is 30.5%. The chemical formula of the compound of this element with hydrogen is EH_4. Determine the unknown element E, compile the formula of its hydroxide, and indicate its character.

16. The acid has the formula H_2EO_3, in which the acid-forming element exhibits a higher degree of oxidation. The element belongs to the IV period of the p elements. Name the acid, make a formula of the oxide corresponding to the acid mentioned above and write the electronic configuration of the atom of the element.

17. When 5.2 g of the hydroxide of an element, belonging to the third group of the periodic system, was heated, water was obtained in the amount of substance sufficient to dissolve calcium oxide with a mass of 5.6 g completely. Identify an unknown element and indicate the nature of its oxide.

18. Specify the type of chemical bond in the following compounds: NaI, F_2, MgO, SO_3, CH_4. Justify your answer.

19. Formulate the equation of reaction between simple substances formed by elements with sequence numbers 1 and 9. What type of chemical bond has the compound formed?

20. Hydrogen compounds whose elements are not able to form hydrogen bonds: a) iodine; b) carbon; c) nitrogen; d) silicon; e) oxygen; e) phosphorus. Explain why?

Chapter 3. Chemical reactions

3.1 Chemical thermodynamics

Chemical thermodynamics is a part of general thermodynamics that studies the transformation of energy from one form to another, as well as the ways of energy transition from one object to another. The word "thermodynamics" comes from the Greek word thermos (heat) and dynamos (force).

Chemical thermodynamics studies the transformation of energy during chemical reactions and the ability of chemical systems to perform useful work. It is an important part of chemistry. The subject of chemical thermodynamics is:

1) prediction of the possibility of a chemical reaction;

2) determination of the amount of energy that is theoretically necessary for the reaction or, conversely, can be released during its spontaneous flow;

3) prediction of the degree to which the reaction will occur before it reaches a state of equilibrium.

3.1.1 Thermal effects. Internal energy and enthalpy

Chemical reactions occur with the release or absorption of energy. Energy effects in reactions are manifested in various forms: thermal, mechanical, electrical and light.

So, the energy is released in the form of heat and light in the reactions of combustion of substances. The reaction of magnesium combustion can serve as an example. On the contrary, the reaction of the thermal decomposition of calcium carbonate to calcium and carbon oxides occurs with the absorption of heat, and the reaction of the decomposition of the silver bromide to the simple substances in the photographic process or the photosynthesis in plants takes place with the absorption of light quanta. The work of a galvanic element or accumulator is an example of the release of electric energy due to the course of chemical reactions. The processes of electrolysis, on the contrary, are examples of the absorption of electrical energy during the reaction. In the case of the explosion of trinitrotoluol (trotyl) or dynamite, the energy of the chemical reaction is released in the form of mechanical work and heat. Reactions of combustion of phosphorus, sulfur, as well as the decay of ozone, occur with the release of heat. The formation of ozone from oxygen, and decay of $KMnO_4$, KNO_3, HgO, and others, on the contrary, consume energy.

Consequently, all chemical processes are accompanied by the conversion of chemical energy into other forms of energy.

The law of conservation of energy points to the equivalence of various forms of energy. Therefore, different energy effects can be reduced to one kind of energy to quantify the energy of chemical reactions. The thermal form of energy is associated with the chaotic motion of the particles of substances, whereas the work is connected with the directed movement of bodies (for example, their lifting in the field of gravity), with the directed motion of electrons (electric current), with the expansion of a gas, etc. The total value of different kinds of energy composes the thermal effect of the reaction.

The amount of energy that is released or absorbed during the reaction is called the thermal effect of the reaction.

In the International System of Units (SI), the main unit of energy is Joule (J). To express a higher amount of energy, one can use kiloJoule (kJ).

The energy effects of reactions are studied by a section of chemistry called thermochemistry.

Consider the reasons for the occurrence of thermal effects in chemical reactions. It is known that chemical transformations are the destruction of chemical bonds between atoms in the starting materials and the formation of new bonds in the reaction products. Since the energy of chemical bonds in the starting materials and reaction products is not the same, the energy difference is released or absorbed in the form of heat. It should be noted that the thermal effect of the reaction is also influenced by the change in the energy of intermolecular interaction and some other factors.

The energies of chemical bonds and intermolecular interactions are constituent parts of the internal energy of the system.

The internal energy of the system (U) is a thermodynamic function, which is equal to the sum of the kinetic and potential energy of all particles in the system.

Kinetic energy is the energy that is associated with the movement of bodies. Potential energy is the position energy, which depends on the location of the bodies.

The chemical system may consist of atoms, molecules and ions, or any combinations thereof. All particles have kinetic and potential energy. Kinetic energy is determined by the different kinds of motion of particles: translational, oscillating, and rotating. The potential energy of the particles is determined by the electrostatic forces of attraction between the particles and inside the particles.

The absolute value of internal energy is unknown; only its change can be determined. The difference between the final and initial states of the system, which will be denoted by the indices "2" and "1" respectively, is written as follows:

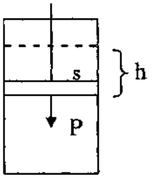
$$\Delta U = U_2 - U_1. \qquad (3.1)$$

As follows from the law of conservation of energy, which is also called the first law of thermodynamics, **energy is not created and does not disappear in all processes occurring in the surrounding world; it is transmitted from one object to another or transformed from one form to another.**

By this law, the internal energy of the system U remains stable, unless there is a heat exchange between the system and the environment ($\Delta U = 0$). In the case of bringing into the system of heat Q, this heat will be spent on changing the internal energy of the system and working against external forces. Equation (3.2) is a mathematical expression of the first law of thermodynamics.

$$Q = \Delta U + A. \qquad (3.2)$$

For a visual representation of the physical content of this equation, let us consider a system which consists of gas, contained in a cylinder and closed by a piston. If the piston is fixed, then the system volume will not change. The work of expansion (A) will be zero, and the whole heat brought to the system of the fixed volume (Q_v) will be spent on increasing the internal energy:



$$Q_v = \Delta U. \qquad (3.3)$$

If the system absorbs the heat (Q_p) under constant pressure and allows the piston to move freely, then the system will do the work A during the expansion:

$$A = Fh = PSh,$$

where F is the force applied to the piston; h is the length of piston movement, P – is the pressure and S is the square of the piston.

Since the product of the values of S and h is equal to the change of the volume ΔV, then one can write:

$$A = P\Delta V = P(V_2 - V_1). \tag{3.4}$$

In this case, equation (3.2) takes the form

$$Q_p = \Delta U + P(V_2 - V_1) = U_2 - U_1 + P(V_2 - V_1) = (U_2 + PV_2) - (U_1 + PV_1). \tag{3.5}$$

We introduce a new thermodynamic function, called enthalpy, or heat content, of system H, which is equal to the sum of the internal energy of the system and the product PV:

$$H = U + PV. \tag{3.6}$$

Then, one can write from equations (3.5) and (3.6):

$$Q_p = H_2 - H_1 = \Delta H. \tag{3.7}$$

Consequently, the change in the enthalpy of the system corresponds to the thermal effect of the reaction, measured under constant pressure and temperature.

In exothermic processes, heat is released by reducing the internal energy of the system; therefore:

$$U_2 < U_1,\ \Delta U < 0. \tag{3.8}$$

Similarly, for processes that occur under constant pressure, we have

$$H_2 < H_1,\ \Delta H < 0. \tag{3.9}$$

On the contrary, the system absorbs heat in the endothermic processes, the value of its energy increases and therefore:

$$U_2 > U_1,\ \Delta U > 0. \tag{3.10}$$

$$H_2 > H_1,\ \Delta H > 0. \tag{3.11}$$

Since the vast majority of chemical reactions occur precisely at constant pressure (in an open flask), the enthalpy change ΔH is used to characterise the energy effects.

The equation of chemical reactions, in which the thermal effect is indicated, is called thermochemical. The values of the thermal effect refer to the number of moles of reactants and reaction products corresponding to stoichiometric coefficients.

Thermal effects depend on the aggregate state of substances and conditions under which the reaction takes place. That is why, the aggregate state of substances is indicated in thermochemical equations; if not stipulated specifically, the thermal effects are indicated for standard conditions.

Standard conditions are considered to be 298 K and partial pressure of gaseous substances 101.3 kPa, for solutions — concentration of 1 mol/L.

For example: $2H_{2(g)} + O_{2(g)} = 2H_2O_{(l)}$, $\Delta H = -571.66$ kJ/mol,

The **first law of thermochemistry** was formulated by Frenchmen Antoine Lavoisier and Pierre-Simon Laplace (1749–1827):

The heat of decomposition of the given compound is numerically equal to the heat of its formation but has the opposite sign.

The second law of thermochemistry was discovered by German chemist Henri Hess (1802–1850) in 1840:

The thermal effect of the chemical reaction depends on the type and condition of the reactants and reaction products but does not depend on the path (intermediate stages), on which the process takes place.

The essence of the Hess law will be demonstrated by the example of the reaction of carbon with oxygen, which can occur in different ways.

The first way:

$$C_{(graph)} + 1/2O_{2(g)} = CO_{(g)},\ \Delta H_1 = -110.5 \text{ kJ/mol}; \quad (3.12)$$

$$CO_{(g)} + 1/2O_{2(g)} = CO_{2(g)},\ \Delta H_2 = -283.0 \text{ kJ/mol}. \quad (3.13)$$

The second way:

$$C_{(graph)} + O_{2(g)} = CO_{2(g)},\ \Delta H_3 = -393.5 \text{ kJ/mol}. \quad (3.14)$$

In fact, according to the Hess law, the thermal effect in both cases is the same: if you add the thermal effects corresponding to the steps of the method I, we get the same thermal effect as in the second way of conducting the process. It is obvious that adding equations (3.12) and (3.13), we obtain the total reaction of the formation of CO_2 (3.14).

In this connection, we can formulate some consequences of the Hess law.

1) The thermal effect of the chemical reaction is equal to the sum of the thermal effects of its intermediate stages.

2) The thermochemical equations can be multiplied by any number, added or subtracted with their thermal effects as algebraic equations.

The condition or type of the initial material affects the value of the thermal effect of the reaction. So, if different allotropic modifications of carbon, such as graphite and diamond, come into reaction with oxygen, then the thermal effects will be different:

$$C_{(graph)} + O_{2(g)} = CO_{2(g)},\ \Delta H_3 = -393.5\ \text{kJ/mol};$$

$$C_{(diam)} + O_{2(g)} = CO_{2(g)},\ \Delta H_4 = -395.3\ \text{kJ/mol}. \qquad (3.15)$$

Interestingly, in the case of subtracting the equation (3.15) from (3.14) and the reduction of similar terms, we can obtain:

$$C_{(graph)} - C_{(diam)} = 0,\ \Delta H_3 - \Delta H_4 = 1.8\ \text{kJ/mol}.$$

Thus,

$$C_{(graph)} \rightarrow C_{(diam)},\ \Delta H = 1.8\ \text{kJ/mol}.$$

We received the heat of the polymorphic transformation. Thus, using the Hess law and its consequences, it is possible to calculate the thermal effects of reactions for cases when ΔH cannot be measured experimentally.

The thermal effect of the reaction of the formation of 1 mol of any compound from simple substances, stable under standard conditions, is called the heat (enthalpy) of formation (ΔH_f).

For example, the heat of the calcium carbonate formation is ΔH of the following reaction:

$$Ca_{(s)} + C_{(graph)} + 3/2O_{2(g)} = CaCO_{3(s)}\,,$$

where simple substances, stable under standard conditions (graphite rather than diamond and oxygen rather than ozone), are used as initial ones.

The heat of formation of simple substances, stable under standard conditions, is equal to zero. The values of ΔH_f under standard conditions are given in reference tables.

3) The consequence of the Hess law: The thermal effect of the chemical reaction is equal to the difference between the sum of the heat of formation of the reaction products and the sum of the heat of formation of the initial substances, taking into account the number of moles of these substances.

$$\Delta H = \Sigma\Delta H_{f(prod)} - \Sigma\Delta H_{f(ini)}.$$

For example, $2NaOH_{(s)} + CO_{2(g)} = Na_2CO_{3(s)} + H_2O_{(l)}$.

$$\Delta H = [\Delta H(Na_2CO_3) + \Delta H(H_2O)] - [2\Delta H(NaOH) + \Delta H(CO_2)] =$$
$$[-1129.3 - 285.8] - [2\cdot(-426.6) - 393.6] = -168.3\ \text{kJ}.$$

3.1.2 Direction of processes. Entropy. Gibbs potential

According to the first law of thermodynamics, or the law of energy conservation, in all processes occurring in the surrounding world, energy is not created and does not disappear; it is transmitted from one object to another or transformed from one form to another. However, based on this law, we cannot reach any conclusions about the possibility of a particular process. In other words, it is impossible to determine in which direction the process may go spontaneously.

Under certain conditions (T, P, C), a spontaneous process will occur on its own. For example, a ball will roll down an incline, water will flow downhill, ice will melt into the water at room temperature, radioisotopes will decay, and iron will rust in the air medium.

For each of these phenomena, one can imagine a reverse process, but in reality, these reverse processes do not occur. Therefore, spontaneous processes go in a certain direction only.

What is the driving force behind spontaneous processes? Summarising many other similar examples, first of all, one can conclude that all of them occur with the release of energy. The final state of the system has lower energy than the initial state because the state with less energy is a more stable one.

Consequently, the energy (enthalpy) factor directs processes toward the least energy of the system, which is the most stable.

In fact, under normal conditions, most spontaneous processes are exothermic, but the tendency to achieve minimal energy is not the only factor in determining the direction of the process. We know many processes, including chemical ones, which occur with the absorption of heat. The energy of the system increases as a result of such processes. Mainly many endothermic processes occur spontaneously at elevated temperatures.

To determine another factor, in addition to the energy, which affects the direction of spontaneous processes, consider some of the phenomena that are not accompanied by a noticeable thermal effect — for example, the process of mixing different gases, which do not chemically interact with each other.

Thus, the molecules of nitrogen and oxygen filled two vessels, separated by a membrane. After removing the partition, the gases are spontaneously mixed until a homogeneous gas mixture is formed. Spontaneous separation of the gas mixture into its separate parts does not occur. Other similar examples can be cited: equalisation of gas pressure in two connected vessels, the uniform distribution of the substance in the whole volume of the solution, etc. Reverse processes are difficult to imagine.

What determines the direction of the process of mixing gases or the distribution of gas or dissolved substance in the entire volume of a vessel? The direction of these processes is not connected with the change in the energy of the system. In all cases, the driving force is a disorderly, chaotic movement of molecules, and the final state of the system is characterised by greater randomness compared to the initial state. A thermodynamic function, entropy, which is denoted by the Latin letter S, characterises the degree of disorder of the system. The greater the chaos in the disordered system, the greater is the entropy value. In the examples mentioned above, such as the processes of mixing gases, distributing gas or dissolved matter in the whole volume, the entropy of the system is increasing.

Disorder or disarray of the systems can be characterised by thermodynamic probability. M. Planck substantiated the postulate according to which **the entropy of crystalline bodies is equal to zero at zero absolute temperature.**

Physically, this means that at 0 K in the ideal crystal, the motion of atoms is absent; the atoms are located in certain precisely defined positions relative to each other.

Consequently, the Planck postulate allows one to determine the starting point from which the count of absolute values of the entropy of chemical compounds begins.

As the temperature rises, the oscillatory motion of the atoms begins to intensify, resulting in a change in their mutual arrangement and a gradual increase of entropy.

During the melting of a crystal, translational motion of particles is added to the oscillatory. Long-range order in the placement of particles changes to short-range order, and an abrupt increase in the entropy value is observed. A similar jump in the entropy occurs during the evaporation of a liquid when the short-range order disappears.

The growth of entropy during heating is associated with an increase in the intensity of the thermal motion of particles or, in other words, with the amount of heat brought to the system. The amount of the heat can be measured experimentally with the use of a special device (calorimeter) or calculated on the base of heat capacity values. After that, the change of entropy is determined by the following ratio:

$$dS = \frac{dH}{T}. \qquad (3.16)$$

Unlike enthalpy, whose absolute values are unknown, the absolute values of entropy were determined for many substances. The entropy, S (J/mol K), refers to a certain amount of matter and to certain conditions in the same way as enthalpy. The reference tables show the standard entropy S°_{298}. For transformations of different types, it is important to know not the absolute value of entropy, but its change ΔS, which will characterise the probability of the process.

The positive value of ΔS indicates that the spontaneous process occurs in the system, and the negative ΔS shows that the process can only occur when consuming a certain amount of energy.

In general, the positive values of ΔS characterise all processes that increase the disorder in the location and movement of molecules and atoms. Increasing the temperature and volume of the system leads to an increase in entropy. An increase in the entropy is also caused by the rise in the number of particles in the system.

The change in entropy in the case of a chemical reaction (the reaction entropy) is equal to the difference between the amount of entropy of the reaction products and the amount of entropy of the starting substances, taking into account the number of moles of substances that are involved in the reaction. For example, in the reaction

$$aA + bB + ... \leftrightarrow pP + qQ + ...$$

the complete change of entropy is equal to:

$$\Delta S=(pS(P)+qS(Q)+...)-(aS(A)+bS(B)+...) \text{ or } \Delta S=\Sigma S(prod)-\Sigma S(ini). \qquad (3.17)$$

The ΔS sign can be evaluated qualitatively (i.e. without calculations) by comparing the number of particles, as well as the aggregate states of the reactants and reaction products. An increase in the number of moles of gaseous substances due to the reaction usually causes an increase in entropy ($\Delta S > 0$). On the contrary, with a decrease in the number of moles of gases, the value of $\Delta S < 0$.

Thus we can conclude that the direction of the processes is determined by two factors, namely entropy and enthalpy.

They act independently of each other and can direct processes in opposite directions. Therefore, to determine the true direction of the process, a third thermodynamic function should be introduced that would include both of these factors. This function is called the isobaricisothermal potential or the free energy of Gibbs (or Gibbs thermodynamic potential), in the name of American scientist Josiah Willard Gibbs (1839–1903), who first proposed to use it.

Free energy is associated with enthalpy and entropy by the following ratio:

$$G = H - TS. \tag{3.18}$$

The change in the free energy in processes occurring under constant pressure and temperature is determined by the expression:

$$\Delta G = \Delta H - T\Delta S. \tag{3.19}$$

The physical meaning of function G consists of describing the ability of the system to perform useful work. In spontaneous processes, this ability decreases; therefore, the criterion for the spontaneous flow of the process at constant pressure and constant temperature is the reduction of free energy, that is, $\Delta G < 0$. If $\Delta G > 0$, the process cannot occur spontaneously in the forward direction. If ΔG is positive, then the reaction is not feasible, and it cannot happen. It is necessary to work under the system from the outside to initiate such a process. If $\Delta G = 0$, then the system is in a state of equilibrium.

Absolute values of the Gibbs free energy are unknown. Equation (3.19) can be used to calculate the change of free energy for chemical reactions. To do this, first, using the reference data, calculate the values of ΔH° and ΔS°, which are then substituted to equation (3.19). The values of the standard Gibbs energies are given in the reference tables. The change in the free energy of the reaction under standard conditions can be defined as the difference between the sum of the Gibbs energy of the reaction products and the sum of the Gibbs energy of the initial substances:

$$\Delta G = \Delta G^\circ_{(prod)} - \Delta G^\circ_{(ini)}.$$

The change in temperature, concentration and other parameters causes the change ΔG and, thus, causes a change in the conclusions about the possibility of the reaction. Large positive values of the Gibbs energy indicate that the reaction is impossible under any conditions. If the positive values of free energy are small (up to 40 kJ/mol), then the reaction can be carried out by changing the concentration.

By signs of changes in enthalpy and entropy, it is possible to predict the course of the reaction, that is, the sign of the change in the energy of Gibbs (Table 3.1).

Table 3.1 Determination of the course of the chemical reaction by values of ΔH and ΔS

Sign of function change			Feasibility of spontaneous reactions
ΔH	ΔS	ΔG	
−	+	−	The reaction is possible at any temperature
+	−	+	Impossible at all temperatures
−	−	±	Possible at fairly low temperatures (enthalpy factor)
+	+	±	Possible at sufficiently high temperatures (entropy factor)

In summary

The key concepts, definitions, laws and formulas:

1. Chemical reactions occur with the release or absorption of energy. Energy effects in reactions appear in various forms: thermal, mechanical, electrical, and light.
2. Change in the enthalpy of the system corresponds to the thermal effect of the reaction, measured at constant pressure and temperature.
3. The energy (enthalpy) factor directs processes toward the least energy of the system.
4. In isolated systems, only processes, accompanied by an increase in entropy, can be carried out spontaneously.
5. The criterion for the spontaneous flow of a process under constant pressure and temperature is a reduction in the free energy of Gibbs.
6. Conditions of the spontaneous flow of chemical processes
7. Laws of thermochemistry.
8. The physical meaning of thermodynamic functions (enthalpy, entropy, Gibbs energy).

Necessary practical skills:

1. To conduct the calculations of the change in enthalpy of the chemical reaction.
2. To determine the sign of entropy change by the equation of the chemical reaction.
3. To conclude the possibility of the flow of chemical processes on the base of calculations of Gibbs energy changes.

3.2 Chemical kinetics and equilibrium

The freshly cut slice of apples is quickly covered with a brown film in the air, and the bronze monument in the wet air is slowly covered with a bloom of green colour. Gold decorations retain their beauty and glitter in the air for centuries. Petard, thrown into the flames, explodes instantly.

However, from thermodynamics, all these processes are possible, even the oxidation of gold. Simply they have different speeds.

To understand the course of a chemical reaction correctly, in addition to the energy characteristics (ΔH, ΔS), it is also necessary to know the basic laws of its flow for a certain time, that is, to have data on the speed and mechanism of the processes involved.

3.2.1 The subject of chemical kinetics

The chemistry section, which studies the course of chemical processes for a certain time, is called the chemical kinetics.

The study of the kinetics of chemical processes has not only theoretical but also practical interest. The need to consider the kinetic factor in consideration of chemical reactions can be seen on the example of the interaction of oxygen and hydrogen:

$$2H_{2(g)} + O_{2(g)} = 2H_2O_{(g)},\ \Delta G = -456.4\ \text{kJ}.$$

Although the reaction is characterised by a significant reduction in the energy of Gibbs, giving evidence to the possibility of spontaneous process, however, under normal conditions, hydrogen and oxygen do not interact with each other, and their mixture can be stored for a long time. In the presence of a catalyst or when heated to $\approx 700^{\circ}C$ ($\Delta G_{1000} = -495.3$ kJ), the mixture reacts very quickly, and sometimes even with an explosion. In both cases, the Gibbs energy of the system is almost identical, while the kinetic features are different.

In this way, the negative value of the Gibbs energy change is a necessary but not sufficient condition.

There are many branches of technology, production, and science, where the speed of reactions plays a leading role. For example, at what speed does fuel burn in a car engine? How quickly does concrete or varnish, which coats the floor, harden? What determines the speed of metal corrosion?

The study of factors that influence the velocity of processes, and the determination of optimal conditions for proceeding reactions to obtain a given substance, is the subject of chemical kinetics.

Before considering the question of how fast the reaction is, let us note that chemical reactions can occur in homogeneous and heterogeneous (inhomogeneous) systems. A homogeneous system consists of one phase, and heterogeneous contains several phases.

The phase is the homogeneous part of the system, the same in composition and properties and separated from other phases by the separation surface (or interphase).

Homogeneous reactions occur throughout the volume of the system, heterogeneous — on the surface of phase separation. Examples of homogeneous reactions are reactions in gas mixtures, solutions, heterogeneous – the interaction of metals with oxygen, solutions of acids, salts, etc.

3.2.2 Rate of chemical reactions

Chemical transformations occur in the event of a collision of molecules, if, as a result of the collision, the chemical bonds are rebuilt, that is, the bonds in the parent molecules break, and new bonds are formed. The rate of chemical reactions characterises the intensity of the chemical process, that is, the number of elementary acts of interaction or decomposition in a unit of time in a unit of volume (for homogeneous actions) or per unit of the surface of the phase separation (for heterogeneous reactions).

For homogeneous processes, which are carried out without changing the volume, the rate of a chemical reaction is determined as the change in the concentrations of the reactants or reaction products per unit time.

The change in concentration is equal to the difference between the concentration C_2, which corresponds to the time τ_2, and the initial concentration of C_1 at time τ_1. Then the average reaction rate is:

$$v = \pm\frac{\Delta C}{\Delta \tau} = \frac{C_2 - C_1}{\tau_2 - \tau_1}. \qquad (3.20)$$

The concentration of substances in the reaction process changes all the time, and this affects the reaction rate. Therefore, the instantaneous reaction rate (the speed at a given moment) should be considered. For homogeneous reactions, this is the time derivative of concentration.

$$v = \pm \frac{dC}{d\tau}. \qquad (3.21)$$

Since the rate of chemical reactions is always positive and characterised by a change in the concentrations of the reactants ($C_2 < C_1$), the value of $\Delta C(dC)$ will be negative and the ratio $\Delta C/\Delta\tau$ $(dC/d\tau)$ must be taken with the minus sign (Fig. 3.1, a). If the reaction rate is determined by changing the concentration of one of the reaction products, then the value of ΔC is positive and the ratio $\Delta C/\Delta\tau$ $(dC/d\tau)$ must be taken with the plus sign (Fig. 3.1, b). The rate of the chemical reaction equals the tangent of the inclination angle of a tangent line to the concentration-time curve: $v = \mathrm{tg}\,\alpha$.

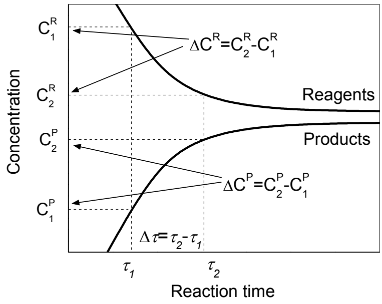


Figure 3.1 Changes in concentrations of initial reagents and reaction products as a function of reaction time

The rate of chemical reactions depends on the nature of the reactants, their concentrations, temperature, the presence of the catalyst and some other external factors.

3.2.3 Effect of concentration on the reaction rate. Mass action law

A necessary condition for the chemical reactions between two substances is the collision of their molecules. The rate of the chemical reaction depends on the number of such collisions per unit volume. The probability of a collision of interacting molecules for a homogeneous reaction is proportional to the concentrations of the reactants.

Thus, the rate of the chemical reaction is proportional to the product of the concentrations of the reactants in degrees, which are equal to the coefficients located in front of the formulas of substances in the corresponding equation of the reaction.

This rule was established experimentally by Norwegian chemists C.M. Guldberg (1836–1902) and P. Waage (1833–1900) in 1867 and is called the mass action law. At that time, the concentration of substances was called active masses.

For the interaction of two molecules, for example, hydrogen and iodine by equation

$$H_2 + I_2 = 2HI,$$

in an elementary act of which one molecule is involved, the mass action law can be expressed as

$$v = kC(H_2)C(I_2). \qquad (3.22)$$

For reaction

$$2NO + Cl_2 = 2NOCl$$

the rate is $v = kC^2(NO)C(I_2)$.

For the reaction in general form

$$aA + bB = cC + dD,$$

the rate is:

$$v = kC^a(A)C^b(B) = k[A]^a[B]^b. \qquad (3.23)$$

The value k is the coefficient of proportionality between the rate and concentration and is called the constant of the reaction rate. It is numerically equal to the reaction rate if the concentration of the corresponding substances is equal to one. The constant of the reaction rate is a constant magnitude at a steady temperature and characterises the nature of the reactants.

The rate constant is the reaction rate provided that the concentrations of reactants are equal to 1 mol/L.

The equation linking the reaction rate with the concentrations of reagents is called the rate equation, or the kinetic equation of the reaction.

For most chemical reactions, the total stoichiometric equation does not reflect an actual mechanism of the process (intermediate stages) but is a general expression for the starting materials and reaction products. In this case, the degrees in the equation of the mass action law do not equal the stoichiometric coefficients and have a formal character.

Consider a simple example. The photochemical dissociation of a gaseous HBr runs along with the following stoichiometric equation

$$2HBr_{(g)} = H_{2(g)} + Br_{2(g)}.$$

A stage of the interaction between two molecules HBr is not included in this reaction. In fact, this photochemical reaction is carried out by the following mechanism:

$$HBr + hv = H + Br;$$

$$H + HBr = H_2 + Br;$$

$$Br + Br = Br_2.$$

Thus, there is no relation between the stoichiometry of the equation and the mechanism of the reaction, as well as between stoichiometric coefficients and degree indices in the kinetic equation. The similarity observed for some reactions has a random character.

The course of most chemical reactions is such that the formation of products occurs through a series of intermediate elementary stages (sequential or parallel), which can be considered as elementary reactions. Each of these reactions is described by its kinetic equation. In such cases, the dependence of reaction rate on the concentration can be very complex. The situation is simplified if any of these stages runs much more slowly than others.

Then one of the important principles of kinetics, namely the principle of the limiting stage, comes into force: the speed of a complex reaction is determined by the speed of the slowest (limiting) elementary stage.

This principle is also called the principle of "bottle throat", "bottleneck", "narrow bridge", etc.

The sum of the degree indices in the rate equation of the chemical reaction (the kinetic equation) is an essential characteristic of the mechanism of the process and is called the order of a chemical reaction. Separate indicators of the levels of reagent concentrations determine the order of reaction for a given substance.

An elementary act of reaction occurs as a result of the collision of molecules. The concept of molecularity of the reaction is used to characterise the reaction mechanism.

The number of molecules involved in an elementary reaction act is called the molecularity of a reaction.

The reaction, for which only one molecule is required, is called a monomolecular reaction. This is a reaction of dissociation or regrouping, for example:

$$I_2 = 2I;$$

$$N_2O_5 = 2NO_2 + 1/2O_2.$$

In a bimolecular reaction, the presence of two particles (molecules, ions, atoms) for an elementary act is required:

$$H_2 + I_2 = 2HI.$$

Three molecules react simultaneously in a three-molecule reaction (these reactions occur very rarely):

$$2NO + O_2 = 2NO_2.$$

Reactions, the molecularity of which is more than three, do not happen since simultaneous collisions of four or more molecules at one point are unlikely. All elementary chemical reactions are monomolecular or bimolecular. In other words, all the real chemical reactions are very simple if we do not take into account the complexity of some total stoichiometric equations. Thus, the total form of the equation of a chemical reaction does not reflect the complexity and multi-stage process, which can consist of several elementary reactions of a different order.

3.2.4 Effect of temperature on the reaction rate. Activation energy

As already noted, the condition of an elementary act of interaction is a collision of reacting particles. However, not every collision can lead to chemical interaction. In fact, chemical interaction involves the redistribution of electron density, the formation of new chemical bonds and the rearrangement of atoms. Thus, in addition to the collision, the energy of the reacting particles should be greater than the repulsion energy (energy barrier) between their electron shells.

As a result of the redistribution of energy, a part of the molecules in the system always have certain excess energy compared to the average energy of the molecules. Therefore, they can overcome the energy barrier and engage in chemical interactions. Such reactive molecules are called active molecules.

The difference between the average energy of the system and the energy required for the reaction is called the activation energy of the reaction. This energy is necessary to overcome the energy barrier.

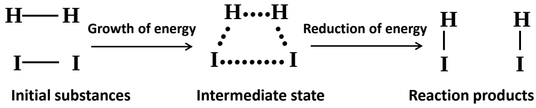
The presence of an energy barrier leads to the fact that many reactions, the course of which is completely possible, does not start at all. For example, coal, wood, and oil, able to oxidise and burn in the air, do not ignite under normal conditions. Such behaviour is due to the high activation energy of the corresponding oxidation reactions. Increasing the temperature increases the number of active molecules, and therefore, more and more molecules of oxygen, coal, wood and oil acquire the necessary energy content to start the reaction. At a certain temperature, the reaction rate reaches a certain value, and the combustion reaction begins.

Before new chemical bonds are formed, the bonds between atoms in the initial molecules must be weakened or broken. To do this, you need to spend energy. So, in the reaction of hydrogen with iodine

$$H_2 + I_2 = 2HI$$

the bonds of H–H and I–I begin to extend in the course of collisions of molecules. They weaken, and only after that new bonds H–I begin to form. As a result, a group, which is called an activated complex or a transition state, appears. After the formation of a transition state, the process of a further build-up of new bonds and the final break of the initial bonds are occurring.

The process of chemical transformation can be represented by the following scheme of interaction between hydrogen and iodine:



The change in the energy of the reacting particles during chemical transformations can be illustrated by the energy diagram (Fig. 3.2). The OX axis is the coordinate of reaction, which is related to the interatomic distances.

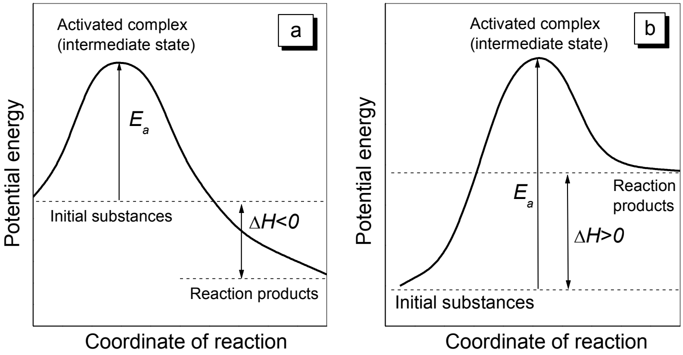


Figure 3.2 Energy diagrams for exothermic (a) and endothermic (b) reactions

Thus, during the chemical process, the transition of the system of starting materials from the energy state of E_{ini} to the energy state of E_{prod} is carried out through an energy barrier equal to the activation energy of the system E_a. At the same time, the thermal effect of the reaction is $\Delta H = E_{prod} - E_{ini}$.

For an endothermic reaction, the energy of the reaction products is greater than the energy of the initial substances (see Fig. 3.2b); for exothermic, on the contrary, the energy of the reaction products is less than the energy of the starting substances (see Fig. 3.2a). However, in both cases, an activated complex having increased energy is formed between the starting materials and the reaction products.

The difference in the energies of the transition state and of the initial substances is called the activation energy or the potential barrier of the reaction.

Consequently, not all molecules can participate in the chemical transformation, but only so-called active ones, that is, those having energy sufficient for the formation of a transition state.

The activation energy is an important characteristic of chemical transformations which holds back or makes it impossible for many reactions that, from thermodynamics, can run arbitrarily.

Thus, the existence of most molecules, crystalline substances, and even living cells is possible because the processes of their transformation and destruction are associated with overcoming a significant energy barrier.

The increase in the temperature of the reacting particles due to the increase in the velocity of molecules leads to an increase in the total energy of the system and, accordingly, an increase in the relative content of active molecules that is equivalent to the growth of the chemical reaction rate. The influence of temperature and activation energy on the rate of chemical reactions can be expressed by the dependence of the reaction rate constant k on the temperature T and the activation energy E_a:

$$k = A\exp(-\frac{E_a}{RT}) \text{ or in logarithmic form } \ln k = \ln A - \frac{E_a}{RT},$$

where A is the Arrhenius factor or the frequency factor proportional to the number of collisions of molecules.

If the concentrations of the reactants are 1 mol/L, the Arrhenius equation (named after Swedish chemist Svante Arrhenius (1859–1927)) gives the possibility of expressing the temperature dependence of the reaction rate v:

$$v = A\exp(-\frac{E_a}{RT}). \tag{3.24}$$

Since the temperature is included in the degree indicator of the equation, the rate of chemical reactions to a large extent depends on the change in temperature.

It has been experimentally established that the temperature dependence of the reaction rate can be expressed in the form of the empirical rule of van't Hoff: the reaction rate increases 2–4 times with a temperature increase of every 10 degrees.

In the mathematical form, the van't Hoff rule is written as follows:

$$\frac{v_{t_2}}{v_{t_1}} = \gamma^{\frac{t_2 - t_1}{10}}, \qquad (3.25)$$

where $\Delta t = t_2 - t_1$ is the difference (growth) of temperatures; v_{t1} and v_{t2} are the reaction rates at temperatures t_1 (before temperature rise) and t_2 (after temperature rise); γ is the temperature coefficient of reaction rate ($\gamma = 2 \ldots 4$).

The temperature coefficient shows how many times the reaction rate increases if the temperature rises by 10 degrees.

3.2.5 Catalysis

A catalyst is a substance, which participates at intermediate stages of the reactions and changes the reaction rate, but does not form a part of the reaction products and remains after the reaction in an unaltered amount.

Catalysts increase the rate of reactions. They are of great importance in industrial and laboratory chemical processes, as well as in chemical reactions occurring in living organisms, the atmosphere and the oceans.

So, in green leaves of plants under the influence of special catalysts (enzymes), various complex organic compounds are synthesised from carbon dioxide and water with the absorption of sunlight. In the human body, complex processes of the transformation of chemical compounds that provide vital functions of an organism occur with the participation of enzymes. Enzymes play an important role in the food industry; in some cases, they carry out or help to carry out many technological processes, while in others they complicate their carrying out. For example, the conversion of raw materials into such branches of the food industry as the production of wine, beer, alcohol, bread, cheese, several sour-milk products, is carried out with the direct participation of enzymes.

The reaction rate essentially depends on the activation energy, and the reduction of the activation energy (potential barrier) provides the growth of reaction speed. In general, the effect of catalysts is explained by the fact that they reduce the activation energy. The catalyst takes part in the intermediate stages of the reaction and changes the path of the reaction. The difference between the activation energies of the catalytic process and the same process without a catalyst is illustrated in Fig. 3.3. In the presence of a catalyst, other activated complexes appear.

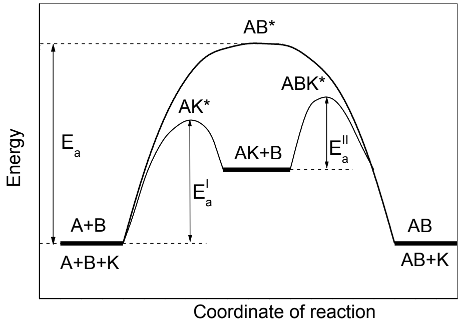


Figure 3.3 Change of activation energy of a catalytic process

The formation of such new catalyst-induced activated complexes requires less energy than that of complexes without a catalyst.

For example, there is a reaction with a certain activation energy E_a:

$$A + B = AB\ (E_a).$$

If we add a catalyst K to this reaction, then substance A initially forms an unstable compound with the catalyst:

$$A + K = A...K\ (E'_a).$$

Later, the unstable compound reacts with substance B with the release of the catalyst K and the formation of the final product AB:

$$A...K + B = AB + K\ (E''_a).$$

The values of the activation energy of the intermediate stages (E'_a and E''_a) are less than the activation energy of the reaction that occurs without a catalyst. Therefore, a large proportion of the molecules will have sufficient energy to form activated complexes that arise in the presence of a catalyst.

There are two types of catalysis – homogeneous and heterogeneous. In homogeneous catalysis, the catalyst and the substances involved in the reaction form a single-phase (gas or solution).

In heterogeneous catalysis, the catalyst is in the system in the form of an independent phase.

The reaction of $2H_2O_2 = 2H_2O + O_2$, which occurs in an aqueous solution, is accelerated in the case of addition of OH-ions (alkaline solution), free Br_2 or solid MnO_2. Therefore, both homogeneous and heterogeneous catalyses are possible for the same reaction.

3.2.6 Chemical equilibrium

In studying the basic laws of equilibrium processes, primarily the concept of reversible and irreversible reactions, the inversion of chemical processes is considered.

Chemical reactions that run only in one direction are called irreversible. The irreversible reactions include, for example, the reaction of the decay of potassium permanganate when heated:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

or interaction of alkali metals with water

$$2K + 2H_2O = 2KOH + H_2.$$

Reversible are reactions that can run in the forward and reverse directions.

Reversible reactions include, for example, the interaction of oxygen with hydrogen:

$$2H_2 + O_2 \leftrightarrow 2H_2O.$$

In fact, at temperatures of 800–1500°C, oxygen with hydrogen form water and interact very violently. At temperatures of 3000–4000°C, on the contrary, water decomposes with the formation of H_2 and O_2. Interaction of iodine with hydrogen

$$H_2 + I_2 \leftrightarrow 2HI$$

occurs at temperatures 300–400°C. At the same temperature, the opposite reaction of the decomposition of hydrogen iodide is also possible.

Most chemical reactions are reversible. For some reactions, the reverse reaction is impossible under certain conditions (interaction of H_2 and O_2); for others, the flow of both direct and inverse reaction is possible (interaction of H_2 and I_2). In both of these examples, one can detect a reciprocal reaction and even determine the rates of the direct and reverse reactions. There are some conditions under which both direct and reverse reactions occur simultaneously. However, there are known some processes for which it is impossible to determine the speed of the reciprocal reaction. Therefore, we can only talk about the reversibility of such processes. To what extent this or that reverse process depends on the nature of the reactants and the conditions under which the reaction runs?

Let us consider in more detail reversible reactions, which simultaneously run in two directions under certain conditions:

$$aA + bB \leftrightarrow cC + dD.$$

At the first moment, the rate of direct reaction is determined by the initial concentrations of the initial substances:

$$v_1 = k_1[A]^a[B]^b .$$

The speed of the reciprocal reaction is zero. In the course of interaction of A and B and the formation of C and D, the rate of the direct reaction will decrease, and the rate of the reciprocal reaction will rise:

$$v_2 = k_2[C]^c[D]^d .$$

After some time, the rates of direct and reverse reactions are equalised (Fig. 3.4). In this case, the number of formed molecules C and D will be equal to the number of molecules C and D, which have already reacted and turned into A and B.

The state of the reaction system, when the speed of direct and reverse reactions is the same, is called chemical equilibrium.

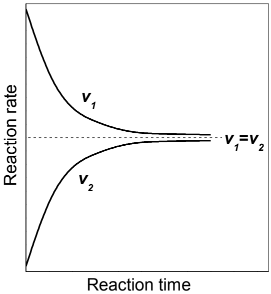


Figure 3.4 Rate of a reversible reaction

At chemical equilibrium, the amount and concentration of both initial substances reaction products, do not change (they are equilibrium).

In other words, the chemical equilibrium is dynamic. That is why the chemical equilibrium also has the name of dynamic equilibrium.

At the moment of chemical equilibrium, when the rates of the direct and the reverse reaction are the same, we can write:

$$v_1 = v_2$$

or $k_1[A]^a[B]^b = k_2[C]^c[D]^d$; then $\dfrac{k_1}{k_2} = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$.

At this temperature, the values of the rate constants k_1 and k_2 are constants; therefore, their relationship $K = \frac{k_1}{k_2}$ is also constant. Then the equilibrium constant is written as follows:

$$K = \frac{C_C^c C_D^d}{C_A^a C_B^b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}. \tag{3.26}$$

This equation is a mathematical expression of the mass action law for the state of equilibrium. The equilibrium constant depends on temperature and the change in enthalpy and entropy but does not depend on the activation energy, which affects only the time of equilibration. Therefore, a catalyst, reducing the activation energy and increasing the entropy of the activation of direct and reciprocal reactions, accelerates the establishment of equilibrium, without changing its constant.

By changing the conditions, one can transfer the system from one equilibrium state to another one, which corresponds to new conditions. The equilibrium is shifted because the change in conditions does not affect the rates of direct and reverse reactions. The nature of the equilibrium shift, depending on external factors, can be determined by the principle of Le Chatelier (1884):

if the system, which is in a state of equilibrium, is influenced from the outside, then the equilibrium moves towards the reaction that weakens this influence.

According to the principle of Le Chatelier, named after French chemist Henry Louis Le Chatelier (1850–1934):

1) Heat promotes the flow of endothermic and cooling favours exothermic reactions.

2) Increasing the pressure causes the balance to move towards the formation of those substances that occupy a smaller volume, and pressure reduction — in the opposite direction. If the volume of the system does not change during the reaction, then the pressure does not affect the state of equilibrium.

3) The introduction of additional quantities of any of the reagents into the system causes an equilibrium shift in the direction in which its concentration decreases. That is why, the introduction into the system of raw materials displaces the equilibrium towards the formation of

reaction products, and an increase in the concentration of reaction products acts in the direction of the formation of starting substances.

4) Equally accelerating both direct and reverse reactions, the catalyst promotes the rapid establishment of equilibrium, without affecting the equilibrium concentration of substances.

The value of the principle of Le Chatelier in chemistry is very large since it allows us to predict the direction of the reaction under different conditions, and, therefore, control the flow of reactions. The principle of Le Chatelier is valid not only for chemical processes; it has general scientific significance and extends to all processes that are in a state of dynamic equilibrium.

The principle of Le Chatelier is of great practical importance. Determining the equilibrium position for different temperatures and pressures, you can choose the most favourable conditions for the technological process which allow you to achieve the maximum possible output (shift of chemical equilibrium) at the highest speed of its formation.

In summary

The key concepts, definitions, laws and formulas:

1. The mass action law.
2. Rule of van’t Hoff.
3. Le Chatelier's principle.
4. For the correct understanding of the course of the chemical reaction, in addition to the energy characteristics (ΔH, ΔS), it is also necessary to know the basic laws of its flow with time, to have data on the speed and mechanism of the process.
5. The rate of chemical reactions depends on the nature of the reactants, their concentrations, temperature, the presence of a catalyst and some other external factors.
6. The activation energy E_a is an important characteristic of chemical transformations because it holds back or makes it impossible for many reactions that, from thermodynamics, can run arbitrarily.
7. The chemical equilibrium is shifted because the change in conditions affects the rate of direct and reverse reactions in different ways.

Necessary practical skills:

1. To calculate the rates of chemical reaction according to the mass action law.

2. To determine the dependence of the rate of the chemical reaction on temperature, using the empirical rule of van't Hoff.

3. To determine the nature and direction of shifts of chemical equilibrium under the influence of external factors.

3.3 Problem solving

3.3.1 Examples

Example 3.1 Calculate the rate of chemical reaction $2NO + O_2 \leftrightarrow 2NO_2$ if the concentration of nitrogen monoxide decreases from 0.2 to 0.1 mol/L for 10 minutes.

$$v = \pm\frac{\Delta C}{\Delta t} = -\frac{(C_2 - C_1)}{\Delta t}.$$

What will be the rate of the chemical reaction?

$$v = -\frac{(0.1\,mol/L - 0.2\,mol/L)}{10\,min} = 0.01\,mol/L\cdot min\ .$$

Thus, the average reaction rate is ±0.01 mol/L·min.

Example 3.2 How many times does the rate of the direct reaction $NO + CO_2 \leftrightarrow NO_2 + CO$ change if the nitrogen monoxide concentration is increased by two times, and the carbon dioxide — three times?

On the basis of the action mass law we determine the reaction rates at C_1 and C_2:

The reaction rate at C_1 is $v_1 = k[NO][CO_2]$; $v_1 = k[1][1] = k$.

The reaction rate at C_2 is $v_2 = k[2][3] = k6$.

The speed of the direct reaction will increase by $\frac{v_2}{v_1} = \frac{k6}{k1} = 6$ times.

Example 3.3 The reaction rate at 180°C is 0.02 mol/L min. Calculate the rate of this reaction at 210°C if the temperature coefficient of reaction is 2.7?

$$v(t_2) = v(t_1)\cdot\gamma^{\frac{t_2 - t_1}{10}}\ .$$

$$v(t_2) = 0.02\cdot 2.7^{\frac{210^\circ - 180^\circ}{10}} = 0.02\cdot 2.7^3 = 0.3936\ \ mol/L\cdot min\ .$$

Consequently, the reaction rate at 210°C is 0.3936 mol/L·min.

Example 3.4 At 30°C, the reaction rate is 0.15 mol/L·min, and at 50°C – 2.4 mol/L·min. Calculate the temperature coefficient of the reaction.

$$v(t_2) = v(t_1) \cdot \gamma^{\frac{t_2 - t_1}{10}} ;$$

$$2.4 = 0.15 \cdot \gamma^{\frac{50-30}{10}} = 0.15 \cdot \gamma^2 ;$$

$$2.4 = 0.15 \cdot \gamma^2 ;$$

$\gamma = 4$.

Thus, the temperature coefficient is equal to 4.

Example 3.5 How does the equilibrium of the reaction $2CO_2 \leftrightarrow 2CO + O_2$ change with increasing pressure?

$$\longleftarrow$$

$$2CO_2 \leftrightarrow 2CO + O_2$$

2V 3V

When solving the problem, we use the consequence of the principle of Le Chatelier. Since all the substances are in a gaseous state when the pressure is raised, the chemical equilibrium will shift towards smaller volumes, that is, to the left. Thus, the chemical equilibrium will shift toward CO_2 because three volumes are on the right side of the equation, and two volumes are on the left-hand side.

Example 3.6 When a mixture of carbon monoxide with chlorine is heated in a closed vessel, the equilibrium is established $CO + Cl_2 \leftrightarrow COCl_2$. How do the rates of the direct and reverse reactions change if we increase the pressure of the gas mixture twice at constant temperature? Will the change in the pressure cause the shift of the chemical equilibrium?

To find the relation between the rates of the direct and the reciprocal reactions in the state of equilibrium and the ratio of the velocities of the same reaction at elevated and initial pressures, we write the expression for the action mass law: $v = K \cdot C^A(A) \cdot C^B(B)$.

Let the equilibrium concentrations of reagents make $C(CO) = a$ mol/L; $C(Cl_2) = b$ mol/L, $C(COCl_2) = c$ mol/L. Then the reaction rate in equilibrium is equal to:

$v(\text{direct}) = K \cdot a \cdot b$; $v(\text{reverse}) = K \cdot c$.

With an increase in the pressure of the reacting system twice, the concentration of all reagents will also be doubled. Then the reaction rates will be equal to:

$$v'(\text{direct}) = K\cdot 2a\cdot 2b = 4K\cdot a\cdot b; \qquad v'(\text{reverse}) = 2K\cdot c.$$

Comparing the obtained expressions of rates, we find, how many times the speed of direct and reciprocal reaction will increase:

$$\frac{v'(\text{direct})}{v(\text{direct})} = \frac{K4ab}{Kab} = 4; \quad \frac{v'(\text{reverse})}{v(\text{reverse})} = \frac{K2c}{Kc} = 2\,.$$

Thus, with a double increase in the pressure in the system, the speed of the direct reaction will increase four times, and the speed of the reverse will double. Consequently, the equilibrium of the reaction will shift towards the formation of phosgene $COCl_2$.

3.3.2 Problems

1. Based on the thermal effect of the reaction $3CaO_{(s)} + P_2O_{5(s)} = Ca_3(PO_4)_{2(s)}$; $\Delta H° = -739$ kJ, determine the standard enthalpy of formation ($\Delta H°_{298}$) of calcium phosphate.

2. Determine the enthalpy of the formation of ozone from molecular oxygen based on the heat of the oxidation reaction of As_2O_3 with oxygen and ozone:

$As_2O_{3(s)} + O_{2(g)} = As_2O_{5(s)}$; $\Delta H° = -271$ kJ;

$As_2O_{3(s)} + \frac{2}{3} O_{3(g)} = As_2O_{5(s)}$; $\Delta H° = -365$ kJ.

3. Based on the thermal effect of the reaction, calculate the enthalpy of the formation of calcium carbide CaC_2:

$CaO_{(s)} + 3C_{(graph)} = CaC_{2(s)} + CO_{(g)}$; $\Delta H° = 460$ kJ;

4. Based on the reactions:

$KClO_{3(s)} = KCl_{(s)} + \frac{3}{2} O_{2(g)}$; $\Delta H° = -49.4$ kJ;

$KClO_{4(s)} = KCl_{(s)} + 2O_{2(g)}$; $\Delta H° = 33$ kJ;

calculate ΔH of the reaction $4KClO_{3(s)} = 3KClO_{4(s)} + KCl_{(s)}$.

5. Determine, using the reference data, the change in the entropy of reactions under standard conditions:

a) $MgO_{(s)} + H_{2(g)} = Mg_{(s)} + H_2O_{(l)}$;

b) $FeO_{(s)} + CO_{(g)} = Fe_{(s)} + CO_{2(g)}$.

6. Without calculations, determine, in which chemical reactions ΔS^0_{298} will be positive, negative, or equal to zero:

a) $2NH_{3(g)} = N_{2(g)} + 3H_{2(g)}$;
b) $CO_{2(s)} = CO_{2(g)}$;
c) $CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)}$;
d) $4Fe_{(s)} + 3O_{2(g)} = 2Fe_2O_{3(s)}$;
e) $N_2O_{4(g)} = 2NO_{2(g)}$;
f) $2H_{2(g)} + O_{2(g)} = 2H_2O_{(l)}$.

7. Determine which of the above reactions is thermodynamically more probable under standard conditions:

a) $2H_2S_{(g)} + 3O_{2(g)} = 2H_2O_{(g)} + 2SO_{2(g)}$;
b) $2H_2S_{(g)} + O_{2(g)} = 2H_2O_{(g)} + 2S_{(s)}$.

8. Determine the decomposition temperature of the following substances:

a) $NH_4NO_{3(s)} = N_2O_{(g)} + 2H_2O_{(g)}$;
b) $(NH_4)_2CO_{3(s)} = 2NH_{3(g)} + CO_{2(g)} + H_2O_{(g)}$.

9. Determine how many times the chemical reaction rate $2A_{(g)} + B_{(g)} \rightarrow A_2B_{(g)}$ changes if the concentration of substance A is doubled, and the concentration of substance B is halved.

10. In the system $CO_{(g)} + Cl_{2(g)} \rightarrow COCl_{2(g)}$, the concentration of carbon (II) oxide increased from 1.2 mol/L to 1.5 mol/L and chlorine — from 1.2 mol/L to 2 mol/L. Determine how many times the reaction rate has increased.

11. Determine the initial concentrations of substances A and B for the reaction $3A_{(g)} + B_{(g)} \rightarrow 2C_{(g)} + D_{(g)}$, if in some time after the beginning of the reaction, the concentrations of the substances were: [A] = 0.03 mol/L, [B] = 0.01 mol/L, [C] = 0.008 mol/L.

12. Explain how the equilibrium state changes in the above reactions in the event of a pressure increase:

a) $H_{2(g)} + Cl_{2(g)} \leftrightarrow 2HCl_{(g)}$;
b) $CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$;
c) $PCl_{3(g)} + Cl_{2(g)} \leftrightarrow PCl_{5\,(g)}$;
d) $CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$.

13. Explain how the equilibrium state changes in the above reactions in the event of an increase in temperature:

a) $2SO_{2(g)} + O_{2(g)} \leftrightarrow 2SO_{3(g)}$; $\Delta H < 0$;
b) $N_{2(g)} + O_{2(g)} \leftrightarrow 2NO_{(g)}$; $\Delta H > 0$.

14. Calculate how many degrees it is necessary to raise the temperature in the system so that the reaction rate increases: a) 81 times ($\gamma = 3$); b) 243 times ($\gamma = 3$); c) 64 times ($\gamma = 4$).

15. Determine the temperature coefficient of reaction rate, if the reaction rate increases 15.6 times when the temperature increases by 30°C.

16. At 150°C, some reaction ends in 16 minutes. Given that the temperature coefficient of the reaction rate is equal to 2.5, determine the time after which this reaction will end if it proceeds at the temperature: a) 200°C; b) 80°C.

17. The initial concentrations of nitrogen and hydrogen in the mixture to produce ammonia were respectively 4 mol/L and 10 mol/L. At the moment of equilibrium, 25% of nitrogen was reacted.

Calculate a) the equilibrium concentrations of nitrogen, hydrogen and ammonia; b) the equilibrium constant.

18. At a certain temperature, the equilibrium in the system $2NO_{2(g)} \leftrightarrow 2NO_{(g)} + O_{2(g)}$ was established at the following concentrations: $[NO_2] = 0.006$ mol/L; $[NO] = 0.024$ mol/L.

Determine the initial concentration of NO_2 and the equilibrium constant of the reaction.

19. The reaction between substances A and B occurs according to the equation $A_{(g)} + B_{(g)} \leftrightarrow C_{(g)} + 2D_{(g)}$. The molecules A, B, C and D, each in the amount of 1 mol, were mixed. After the equilibrium was detected, 1.8 mol of substance C was detected in the mixture.

Calculate the value of the equilibrium constant.

20. The reaction takes place according to the equation $A_{(g)} + 2B_{(g)} \leftrightarrow 2D_{(g)}$. The initial concentrations of substances A and B were 2 mol/L and 1.8 mol/L, respectively. After some time, the concentration of substance A decreased by 20%.

Calculate: a) the concentration of substance B;

b) how many times the speed of the direct reaction decreased;

c) the equilibrium constant of the reaction.

Chapter 4. Solutions. Theory of electrolytic dissociation

Solutions are extremely important in a variety of chemical processes that determine the vital functions of living organisms and many natural phenomena. All-important physiological fluids are solutions.

Different solutions are used during the processes in technologies. Therefore, technologists need to understand at the molecular level the processes occurring during the dissolution of substances, to know the effects accompanying it, factors that affect the speed and completeness of this process, as well as learn how to operate concepts easily, make calculations and prepare solutions of different compositions and concentrations.

4.1 Basic concepts of the chemistry of solutions

4.1.1 Terminology

The solution is a homogeneous system consisting of two or more components: a solvent, a substance and products of their interaction.

Typically, a solvent is called a component that is in the same state as a resulting solution. For example, in the case of dissolving sugar or salt in water, the solvent is water regardless of the amount of these substances. If both components are in the same aggregate state before dissolution (for example, alcohol and water), then a component, whose volume is larger in value, is taken as a solvent. The homogeneity of the solutions is explained by the fact that, during their formation, as a result of interaction with the solvent, the dissolved substance is disintegrated into molecules or ions that cannot form an independent phase.

Stability of solutions is determined by the size of the distributed particles. As usual, the following solutions are distinguished: true (the size of the formed particles does not exceed 10^{-9} m); colloidal (the size of particles varies from 10^{-9} m to 10^{-7} m); coarse particles (particles are more than 10^{-7} m in diameter). An example of unstable systems is suspensions (solids dissolved in a liquid) and emulsions (liquid substances dissolved in a liquid). These systems are heterogeneous, and they have a particle size of 10^{-7} m to 10^{-5} m. Due to the forces of gravity, distributed particles eventually settle down to the bottom of the dishes or expose to the surface. Colloidal systems are characterised by higher stability.

Solutions are liquid, solid and gaseous. For example, liquids are solutions of salts, sugar, alcohol, vinegar, etc. in water; solid solutions are solutions of one or more metals in another (known as alloys); gaseous are mixtures of gases, air.

Table 4.1 illustrates the differences between solutions and mechanical mixtures.

Table 4.1 Properties of mechanical mixtures, solutions and chemical compounds

System	Composition	Thermal effects during the dissolution	Possibility of separation of components by physical methods
Mechanical mixture	Variable	Not available	Available
Solution	Variable	Available	Available
Chemical compound	Invariable	Available	Not available

As is seen, the solutions have intrinsic properties of both chemical substances and mechanical mixtures. True solutions occupy an intermediate position between chemical compounds and mechanical mixtures. Homogeneity and the presence of thermal effects (exo- and endothermic) during the formation of solutions confirm the chemical interaction between their components. However, the composition of solutions is unstable and can vary in a wide range, as well as the composition of mixtures. The physical constants of solutions are variable: density, boiling point, crystallisation temperature, etc. In this regard, the modern solution theory considers dissolution as a set of the following processes:

solvation — the interaction of the solvent with particles of the dissolved substance;

ionisation — the destruction of the structure of the dissolved substance;

diffusion — the distribution of solvated particles throughout the volume of the solution.

Saturated and unsaturated solutions. Some solutions mix in any ratio, such as, e.g. water and alcohol. Solids, most gases and liquids are soluble in water in certain proportions.

If the substance can no longer dissolve at a given temperature, such a solution is called saturated. A solution, in which the substance can still be dissolved under given conditions, is called unsaturated.

These concepts are not related to the concepts of "concentrated" and "diluted" solution since there is a sufficient amount of low-soluble substances ($Ca(OH)_2$), whose saturated solutions have a low concentration of the dissolved substance.

The saturation of the solution is a measure of the solubility of a substance. The meaning of solubility term is the ability of a substance, when mixed with another substance, to form homogeneous systems. Typically, the solubility of solids and liquids is expressed by the mass of a substance that can dissolve in 100 g of a solvent at a given temperature. The solubility of gases is determined by the volume of gas that can dissolve in 1 litre of solvent at a certain temperature. In this case, a quantitative indicator is used and called the solubility factor. For example, at 18°C in 100 g of water, one can dissolve 35.9 g of sodium chloride. Therefore, the solubility of the named compound would be 35.9 under such conditions.

The solubility depends on the nature of a substance and a solvent. The empirical rule says that similar dissolves in similar. It can be explained from the standpoint of the nature of the chemical bond. As a rule, ionic compounds (salts, alkalis) or substances, whose molecules are polar, are well soluble in polar solvents. The best of polar solvents is water.

Substances with a nonpolar molecular structure are well soluble in nonpolar or low-polar solvents, poorly in water (for example, some colourants of organic nature are well soluble in alcohol and do not dissolve in water; extraction of useful substances from natural raw materials is carried out better in case of infusion in alcohol, etc.).

The solubility of most solids increases with temperature. The mutual solubility of the liquids increases with increasing temperature until a temperature reaches, at which all liquids begin to mix in any proportions.

The solubility of gases decreases with increasing temperature. An example can be a glass of cold water, exposed to heat. After some time, bubbles of gas appear on its walls. Therefore, the solubility of the gas diminished, and it began to stand out.

The solubility of gases increases with increasing pressure and vice versa. For example, to create carbonated beverages, the liquid is filled with carbon dioxide under pressure. When a bottle with a beverage opens, the pressure in it decreases, the solubility of the gas decreases, and it begins to stand out from the solution — foam is formed.

4.1.2 Solution concentration

The composition of the solutions is determined by the content of the dissolved substance, which is characterised by its concentration or fraction.

The amount of dissolved substance contained in a certain amount of solution or solvent is called the concentration of the solution. Solutions with high concentrations of dissolved substances are called concentrated, with small — diluted. The boundaries between them are rather conditional. Quantitative characteristics are used for a complete characterisation of the composition of solutions. The unit of volume of solution or solvent is a cubic meter (m^3) or cubic decimetre (dm^3), which is equal to 1 litre (L).

The most commonly used methods for expressing the contents of the dissolved substance are given in Table 4.2. All methods are interconnected, and the composition of solutions can be presented in any form with the use of mathematical calculations.

The molar concentration (C) is a physical quantity determined by the ratio of the number of moles of the dissolved substance to the volume of solution. This term extends to any kind of conditional particles (atoms, ions, molecules, parts of molecules, etc.). The molar concentration is expressed in moles per cubic decimetre or moles of the dissolved substance in a litre of solution, for example, C(HCl) = 0.1 mol/L. For some values of the molar concentration of solutions, the special terms and designations are used: 1.0000 mol/L (1 *M*) — molar, 0.1000 mol/L (0.1 *M*) — decimolar, 0.0100 mol/L (0.01 *M*) — centimolar.

The equivalent concentration or normality (C_f) is the number of equivalents of a substance contained in 1 litre of solution.

To calculate the equivalent concentration, one must mention the notion of chemical equivalents and their calculation methods. The index f is the equivalence factor. The molar mass of a substance must be multiplied by the equivalence factor to get the equivalent of a substance.

The equivalence factors are:

for acids — a unit divided by the number of hydrogen atoms involved in chemical reactions;

for bases — a unit divided by the number of hydroxyl groups involved in chemical reactions;

for salts — a unit divided by the product of the number of metal ions (cations) and the value of metal ion charge.

Table 4.2 Ways of expressing the composition of solutions

Value		Symbol	Equation	unit of measure	
				main	complementary
Fraction	Mass or percentage concentration	ω (omega)	$\omega = \frac{m_{sub}}{m}$ $\omega = \frac{m_{sub}}{m} \cdot 100$	Dimensionless, %	
	mol	χ (ksi)	$\chi = \frac{\nu_{sub}}{\nu_{sub} + \nu}$	dimensionless	
	bulk	φ (fi)	$\varphi = \frac{V_{sub}}{V}$	dimensionless	
Concentration	molar	C (si)	$C = \frac{\nu_{sub}}{V}$	mol/L	mol/dm^3
	normal (normality, molar concentration of equivalents)	C_f (si–ef)	$C_f = \frac{1}{f} \cdot \frac{\nu_{sub}}{V}$	mol equivalent/L – equiv/L	mol equivalent/dm^3 – equiv/dm^3
	mas	ρ (ro)	$\rho = \frac{m_{sub}}{V}$	kg/L	kg/dm^3
	molal	C_m (si–em)	$C_m = \frac{\nu_{sub}}{m_{solvent}}$	mol/kg	

For oxidation-reduction reactions, the equivalence factor of substances is defined as a unit divided by the number of electrons involved in the oxidation or reduction of particles.

The peculiarity of the equinormal substances (the same in normality) is that they interact with no residue. This is an illustration of the law of equivalents: the substances interact with each other in quantities proportional to their equivalents. The mathematical expression of the law makes it possible to calculate easily both the amount of substance entering into the interaction and the amounts required for the preparation of solutions:

$$C_{f1} \cdot V_1 = C_{f2} \cdot V_2.$$

The values of molar and normal concentrations are calculated to within four decimal places; these methods of expression of concentration are considered accurate and used for chemical analysis. The weight of substances for the preparation of solutions with a concentration expressed in moles per litre is necessarily weighed on the exact analytical scales.

For some values of the equivalent concentration of solutions, special terms and designations are used: 1.0000 mol equivalent/L = 1.000 equiv/L — normal, 0.1000 equiv/L — decinormal, 0.0100 equiv/l – centinormal.

The molal concentration, molality (C_m) is the number of moles of the dissolved substance in 1000 g of solvent. In the general form,

$$C_m = 1000\ \nu_{sub.}/m,$$

where is ν_{sub} is the number of moles of the dissolved substance; m is the amount of solvent in grams (if you express the amount of solvent in kilograms, then the equation transforms into $C_m = \nu_{sub}/m$).

The molar fraction is the ratio of the number of moles of a certain substance to the sum of the moles of all substances contained in the solution.

The mass fraction ω (formerly referred to as a percentage concentration) is often used. It is calculated as the ratio of the mass of the dissolved substance to the mass of the solution, or the number of grams of the dissolved substance contained in 100 g of solution. Thus, a 9% solution of acetic acid corresponds to 100 g solution, which contains 9 grams of glacial acetic acid.

The mass concentration is the ratio of the mass of the dissolved substance to the volume of solution (expressed in kilograms per decimetre cubic or kilograms per litre). Mass concentration, expressed in grams per millilitre, is known as titre. This unit called the classical method of analysis — titrimetry.

The percentage concentration should be calculated to the nearest second decimal point. This way of expressing concentration is considered less accurate than others. It is most often used to calculate the number of ingredients in different production processes.

4.1.3 Colligative properties of solutions. Osmosis

All chemicals are conventionally divided into electrolytes and non-electrolytes. The criterion for such a classification is the electrical conductivity of their solutions and melts.

Substances, aqueous solutions or melts, which conduct an electric current, are called electrolytes (salts, acids, alkalis — substances with ionic and covalent polar bonds).

Substances, aqueous solutions or melts, which do not conduct an electric current, are called non-electrolytes (sugar, alcohol, and acetone — substances with nonpolar covalent bonds).

Physico-chemical properties of dilute solutions of non-electrolytes: the pressure of saturated vapour over the solution, the temperature of boiling, crystallisation and freezing, osmotic pressure — all they vary in proportion to the concentration of solutions.

Such observation is understandable if you take into account the following facts:

1) solutions of non-electrolytes do not conduct electric current because they contain only molecules of solute and solvent;

2) no noticeable interaction occurs between the molecules in the dilute solutions; therefore, the properties of such solutions depend only on the relative number of molecules of matter (mole fraction) and do not depend on its nature.

Colligative properties of solutions are **properties** that depend upon the concentration of solute molecules or ions, but not upon the identity of a solute. **Colligative properties** include vapour pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

Diffusion and osmosis are considered as colligative properties. Diffusion is the process of arbitrarily equalising the concentration of the solution due to the thermal motion of molecules of a dissolved substance and a solvent. Diffusion can be visualised if one pours the concentrated solution of a coloured substance into a glass and add water (trying not to mix the liquids). Due to the two-sided diffusion, the solution will have the same colour throughout the volume after a while.

If a semipermeable membrane (a membrane) is set between a solution and a pure solvent (or solutions with higher and lower concentrations of a dissolved substance), then solvent molecules with a smaller molecule size can penetrate through such a membrane while larger molecules of the dissolved substance cannot pass because of differences in their sizes. Such diffusion will be one-sided. The process of one-sided diffusion of solvent molecules through a semipermeable membrane is called osmosis, and the pressure that causes it is called osmotic.

Solutions having the same osmotic pressure are called isotonic. The same volumes of isotonic solutions contain the same amount of molecules (or particles).

Dutch chemist van't Hoff found that the gas laws are equally applicable to dilute solutions. The solute particles possess kinetic energy and move randomly in the solutions. Thus they have similar behaviour as that of gas molecules. Such observations allowed van't Hoff to formulate the law of osmotic pressure. **When colliding with a semipermeable membrane, the solute molecules exert osmotic pressure equal to the pressure which the solute molecules would exert if it were gas molecule at the same temperature and occupying the same volume as that of solute.** The equation of van't Hoff is as follows:

$$P_{osm} = CRT, \tag{4.1}$$

where P_{osm} is the osmotic pressure; C is the molar concentration of the solute; R is the universal gas constant; T is the absolute temperature.
If we take into account that C = m/M, then you can write

$$P_{osm} = mRT/M, \tag{4.2}$$

where m is the mass of the dissolved substance in grams contained in 1 litre of solution; M is the molecular weight of the substance.

When calculating the osmotic pressure and the molecular mass for these equations, it should be taken in mind that the van't Hoff law can only be applied to dilute solutions.

Osmotic pressure is very important in nature. All biological tissues consist of cells which shells are semipermeable. If a cell is placed in a solution, in which the concentration of dissolved substances is higher than in the cell (in medicine, such a solution is called hypertonic), the water will flow from the cell to the solution, and it will begin to wrinkle (salted vegetables). Such a phenomenon is called plasmolysis. In the case of a cell entering a solution with a lower concentration of dissolved substances (hypotonic), there is a transition of water into the cell and an increase in its volume (swelling of food fibres). This process is called haemolysis. The phenomena of diffusion and osmosis occur during the salting of raw materials of plant or animal origin, used during the technological processes of boiling, soaking, etc.

The pressure of the saturated vapour of the solvent above the solution is lower than the vapour pressure of the solution over the pure solvent (under the same temperature conditions). The dependence of reducing the vapour pressure of solvents above the solution on the solution concentration was quantified by French chemist François-Marie Raoult (1830–1901).

The first Raoult law: The relative lowering of the vapour pressure of a dilute solution of nonvolatile solute is equal to the mole fraction of solute in the solution:

$$\frac{\Delta P}{P_0} = \frac{n_1}{n_1 + n_2}, \qquad (4.3)$$

where $\Delta P = P_0 - P$ is the value of vapour pressure reduction; P_0 is the vapour pressure of solvent; P is the vapour pressure of solution; n_1 and n_2 are the amounts of solute and solvent in moles respectively.

Based on this equation, one can calculate the vapour pressure of the solution or the absolute decrease in vapour pressure. For technologists, it is important to understand such properties of solutions. The presence of a substance dissolved in a solvent increases its boiling temperature and reduces the freezing temperature. The stronger, the more concentrated is the solution. If you dissolve any substance (sugar, kitchen or other mineral salts, glycerol, etc.) in water, then the freezing point of the solution will be lower than 0°C, and the boiling point is higher than 100°C.

The difference in the boiling temperatures or the freezing point between solutions and pure solvents is called an increase of the boiling temperature or a reduction of the freezing point of the solution.

The second Raoult law: For dilute solutions, the rise in boiling temperature and the decrease in freezing temperatures are proportional to the molar concentrations of solutions.

The third Raoult law: Solutions, containing the same amount of dissolved substances in identical amounts of solvent, have the same decrease in freezing temperature and the same rise in boiling temperature.

For each solvent, the changes in the boiling and freezing temperatures are constant.

Cryoscopic constant K_c is a decrease in freezing temperature, corresponding to the dissolution of 1 mol of a substance in 1000 g of solvent (for water, $K_c = 1.86$ deg/mol).

Ebullioscopic constant K_{eb} is an increase in boiling temperature, which occurs when 1 mole of a substance is dissolved in 1000 g of solvent (for water $K_{eb} = 0.52$ deg/mol).

The mathematical expressions of the second and third laws of Raoult, respectively, have the following forms:

$$\Delta t_{boil} = K_{eb}\,C_m; \tag{4.4}$$

$$\Delta t_{freez} = K_c\,C_m, \tag{4.5}$$

where K_{eb} and K_c are ebullioscopic and cryoscopic constants, respectively; C_m is the molality of the solution.

The determination of molecular weights of certain substances is based on the laws of Raoult. The phenomenon of lowering the freezing point of solutions is widely used in the technological processes of refrigerating plants. For example, solutions of salts are used as refrigerants for the production of frozen juices, as well as the preparation of so-called antifreeze — solutions that freeze only at low temperatures. They are used in machines that operate at low temperatures and also for cooling of engines.

In summary

The key concepts, definitions, laws and formulas:

1. Dissolution is a physical-chemical process.

2. The concentration of the solution is the amount of dissolved substance contained in a certain amount of solution or solvent. There are different ways of expressing the concentration of matter, but they all are related mathematical relations and can be translated from one form to another.

3. The criterion for the distribution of substances on electrolytes and non-electrolytes is the electrical conductivity of their solutions and melts.

4. Physico-chemical properties of dilute solutions of non-electrolytes, such as the pressure of saturated vapour over the solution, the temperature of boiling, crystallisation and freezing, and the osmotic pressure, vary in proportion to the concentration of solutions.

5. Formulas:

$\omega = \dfrac{m_{sub}}{m}$ — the mass fraction of the substance in the solution;

$\omega = \frac{m_{sub}}{m} \cdot 100$ — the percentage concentration of the substance in the solution;

$C = \frac{\nu_{sub}}{V}$ — the molar concentration of the substance in the solution;

$C_f = \frac{1}{f} \cdot \frac{\nu_{sub}}{V}$ — the normal concentration of the substance in the solution;

$\rho = \frac{m_{sub}}{V}$ — the mass concentration of the substance in the solution;

$C_m = \frac{\nu_{sub}}{m_{solvent}}$ — the molal concentration of the substance in the solution.

6. Mathematical expressions of osmotic pressure laws:

$P_{osm} = CRT$;

$P_{ocm} = mRT/M$;

7. Mathematical expressions of Raoult's laws:

$$\frac{\Delta P}{P_0} = \frac{n_1}{n_1 + n_2};$$

$\Delta t_{boil} = K_{eb}\ C_m$; $\Delta t_{freez} = K_c\ C_m$.

Necessary practical skills:

1. To calculate the amount of substance needed to prepare a solution in which concentration is expressed in molar, normal, molal, and mass and mole fractions.

2 Based on the law of osmotic pressure and Raoult's laws, to calculate the vapour pressure of a solution, an absolute reduction of vapour pressure, to determine the molecular masses of substances, and to establish the concentration and composition of the solutions according to their physical and chemical characteristics.

4.2 The theory of electrolytic dissociation

The van't Hoff principle and Raoult laws are not valid for solutions of electrolytes (even infinitely diluted). These solutions behave as if they contain more particles of the dissolved substance than it follows from their concentration. Actual figures of boiling point rise, freezing temperature reduction and osmotic pressure in these solutions are always higher than those calculated theoretically. Van't Hoff suggested applying the isotonic coefficient (i) to take into account these deviations:

$$i = \frac{\Delta T_{boil.exp}}{\Delta T_{boil.theor}} = \frac{\Delta T_{fr.exp}}{\Delta T_{fr.theor}} = \frac{P_{osm.exp}}{P_{osm.theor}} . \tag{4.6}$$

Consequently, all experimental values are i times higher than the theoretical ones:

$$P_{osm} = i\ CRT; \quad \Delta t_{boil} = i\ K_e\ C_m; \quad \Delta t_{freez} = i\ K_c\ C_m .$$

For nonelectrolytes, i = 1.

For electrolytes, $NaCl \rightarrow Na^+ + Cl^-$ $i = 2$;

$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$ $i = 3$;

$AlCl_3 \rightarrow Al^{3+} + 3Cl^-$ $i = 4$.

In reality, the experimental value is $1 < i < 2$ for NaCl. The theory of electrolytic dissociation can explain such facts.

4.2.1 Arrhenius theory of electrolytic dissociation

In 1887, Svante Arrhenius made the following assumption:

1. Electrolytes in solutions break down into ions — dissociate; the isotonic coefficient i indicates how many times the total number of particles has increased in the solution as a result of the decomposition of ion molecules.

2. Dissociation is the inverse equilibrium process; the electrolytes during dissolution do not decompose into ions completely; this explains why experimentally, for example, for NaCl, $1 < i < 2$.

3. The forces of interaction of dissolved ions with solvent molecules are weak, that is, solutions are ideal.

Dissociation is the process of decomposition of electrolyte molecules into positively charged ions (cations) and negatively charged ions (anions). Electrolytic dissociation of substances, which occurs with the formation of free ions, explains the electrical conductivity of solutions. The process of electrolytic dissociation can be presented as an equation:

$$KNO_3 \rightarrow K^+ + NO_3^-.$$

One molecule dissociates into two ions.

The dissociation equation of hydrogen chloride under the action of a polar solvent of water is as follows:

$$HCl + H_2O \leftrightarrow H_3O^+ + Cl^-,$$

where H_3O^- is a hydronium ion

To simplify the record, the water molecule is neglected:

$$HCl \leftrightarrow H^+ + Cl^-.$$

Mechanism of electrolytic dissociation of ionic compounds (an ion-dipole mechanism).

Orienting toward the ions of the crystal lattice of sodium chloride (Fig. 4.1), the water molecules form hydrogen bonds with them. A large amount of energy is released, which is called the energy of hydration.

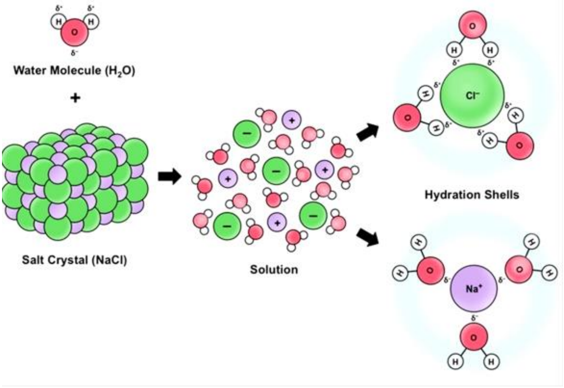


Figure 4.1 Dissociation of NaCl under the influence of a polar solvent of water

Mechanism of electrolytic dissociation of polar compounds (a dipole-dipole mechanism). Under the influence of dipoles of water, the polarised covalent bond is converted into an ionic molecule, and the hydrogen chloride molecule decomposes into two hydrated ions (Fig. 4.2).

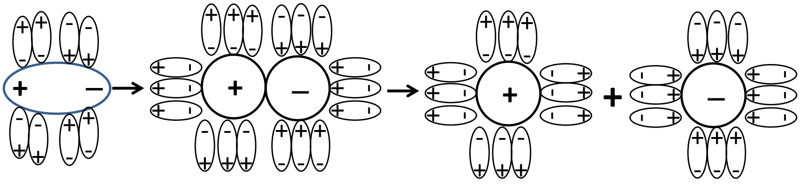


Figure 4.2 Model of dissociation of hydrogen chloride under the influence of a polar solvent of water

Concentrations of ions in solutions of weak electrolytes are qualitatively characterised by the degree and dissociation constant.

Degree of dissociation (α) is the ratio of the number of molecules that split into ions (n) to the total number of dissolved molecules (N):

$$\alpha = n / N.$$

The isotonic coefficient associated with the degree of electrolytic dissociation:

$$i = 1 + \alpha(k - 1) \text{ or } \alpha = \frac{i-1}{k-1}, \qquad (4.7)$$

where k is the number of ions, which result from the decomposition of one molecule of the substance. The degree of electrolytic dissociation is expressed as a percentage or in fractions.

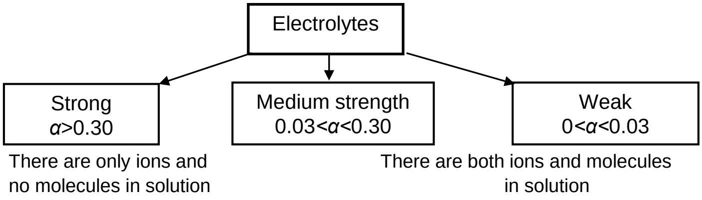
A dynamic equilibrium is being established with the time between non-dissociated molecules and ions of weak electrolytes:

$$NH_4OH \leftrightarrow NH_4^+ + OH^-;$$

$$K_e = \frac{[NH_4^+]\cdot[OH^-]}{[NH_4OH]}, \qquad (4.8)$$

where K_e is the equilibrium constant which corresponds to the dissociation of weak electrolyte. The magnitude of the constant depends on the nature of an electrolyte and a solvent, temperature, but does not depend on the concentration.

Figure 4.3 illustrates the classification and examples of electrolytes.



Acids: *HCl, HBr, HI, H_2SO_4, HNO_3, $HMnO_4$, $HClO_4$, $HClO_3$*	**Acids:** *HF, H_2SO_3, H_3PO_4*	**Acids:** *H_2S, H_2CO_3, H_2SiO_3, H_3BO_3, HAc*
Alkalis: *LiOH, NaOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$*		**Bases**: nonsoluble in water, *NH_4OH*
Salts: - practically all water-soluble		Some **salts**: *$Fe(CNS)_3$, $Hg(CN)_2$, $ZnCl_2$*

Figure 4.3 Classification of electrolytes

Amphoteric bases can dissociate by the following scheme:

$$2H^+ + ZnO_2^{2-} \leftrightarrow Zn(OH)_2 \leftrightarrow Zn^{2+} + 2OH^-.$$

Normal salts are strong electrolytes, which form a metal cation and an anionic acid residue as a result of the dissociation:

$$CuCl_2 \rightarrow Cu^{2+} + 2Cl^{-}.$$

Acidic salts are strong electrolytes. As a result of dissociation, they form a metal cation and a complex anion, which includes hydrogen ions and an acid residue:

$NaHCO_3 \rightarrow Na^{+} + HCO_3^{-}$ $\alpha = 1;$

$HCO_3^{-} \leftrightarrow H^{+} + CO_3^{-}$ $\alpha < 1.$

The basic salts are electrolytes. As a result of dissociation, they form a complex cation containing the metal ion with hydroxyl groups and anions of the acid residue:

$Fe(OH)_2Cl \leftrightarrow Fe(OH)_2^{+} + Cl^{-}$ $\alpha = 1;$

$Fe(OH)_2^{+} \leftrightarrow Fe(OH)^{2+} + OH^{-}$ $\alpha < 1;$

$Fe(OH)^{2+} \leftrightarrow Fe^{3+} + OH^{-}$ $\alpha < 1.$

4.2.2 Reactions in electrolyte solutions. Ionic equations

By the theory of electrolytic dissociation, reactions in electrolyte solutions occur between ions.

Reactions between ions occur only when a slightly soluble or volatile compound or a weak electrolyte is formed as a result of their interaction.

Expressions of the equations of chemical reactions in the ionic form allow us to find out, when the reactions have only one direction, and when they are reversible.

Let us consider several types of chemical reactions from the viewpoint of the theory of electrolytic dissociation and try to determine the patterns of their flow.

Reversible reactions. If you mix the solutions of sodium chloride and potassium nitrate, then no changes will occur. Sodium chloride dissolves in sodium and chloride ions in solution, and potassium nitrate — in potassium ions and nitrate ions. The equation of the reaction occurring between these substances is as follows:

$$NaCl + KNO_3 \rightarrow NaNO_3 + KCl\ .$$

The starting materials are well soluble in water; they are strong electrolytes, and therefore, they exist in the form of ions in the solution. The ionic equation of the reaction can be written as follows:

$$Na^{+} + Cl^{-} + K^{+} + NO_3^{-} \leftrightarrow Na^{+} + NO_3^{-} + K^{+} + Cl^{-}\ .$$

As we see, the same ions are found in the left and right parts of the equation. Thus, the reaction does not actually take place.

Let us consider another reaction:

$$2NaOH + H_2CO_3 \leftrightarrow Na_2CO_3 + 2H_2O.$$

We will record it in the ion-molecular form (all substances, which are strong electrolytes, are written as ions and others — as molecules):

$$2Na^+ + 2OH^- + H_2CO_3 \leftrightarrow 2Na^+ + CO_3^{2-} + H_2O.$$

After reducing the same ions, we obtain:

$$2OH^- + H_2CO_3 \leftrightarrow CO_3^{2-} + H_2O.$$

This reaction is reversible since there are non-dissociated molecules in the left and right parts of the equation. Thus, this reaction does not come to an end.

Irreversible processes. Among practically irreversible reactions, several types can be identified.

Reactions of ion exchange can be considered as accomplished if the following products are formed and detected:

sediment

$CuSO_4 + 2KOH = Cu(OH)_2\downarrow + K_2SO_4$ – molecular form;

$Cu^{2+} + SO_4^{2-} + 2K^+ + 2OH^- = Cu(OH)_2\downarrow + 2K^+ + SO_4^{2-}$ – complete ion form;

$Cu^{2+} + 2OH^- = Cu(OH)_2\downarrow$ – reduced ion form;

gas

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2CO_3;$$

$$2Na^+ + CO_3^{2-} + 2H^+ + 2Cl^- \rightarrow 2Na^+ + 2Cl^- + H_2O + CO_2\uparrow;$$

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2\uparrow;$$

weak electrolyte (H_2O)

$$KOH + HNO_3 \rightarrow KNO_3 + H_2O;$$

$$K^+ + OH^- + H^+ + NO_3^- \rightarrow K^+ + NO_3^- + H_2O;$$

$$OH^- + H^+ \rightarrow H_2O.$$

When writing the equations of ionic reactions in electrolyte solutions, one must bear in mind that:

1) simple substances, oxides, as well as insoluble substances, do not dissociate;

2) if a marginally soluble substance is formed as a result of the reaction, it is considered to be insoluble in the ionic equation;

3) the number of charges of ions in the left and right parts of the equation must be the same;

4) equations should be written in three forms: complete molecular, complete ion and reduced ion.

4.2.3 Dissociation constant

Since the electrolytic dissociation of weak electrolytes is a reversible process, it obeys the action mass law. Thus, the equilibrium constant can be written for the process of dissociation of a weak electrolyte. As an example, consider the dissociation of weak electrolyte KA:

$$\mathrm{KA} \leftrightarrow \mathrm{K}^+ + \mathrm{A}^-.$$

Denote the concentrations of ions as $[K^+]$ and $[A^-]$, and the concentration of non-dissociated molecules through [KA]. Then we write the equilibrium constant as follows:

$$\mathrm{K} = \frac{\left[\mathrm{K}^+\right] \cdot \left[\mathrm{A}^-\right]}{[\mathrm{KA}]}. \tag{4.9}$$

The equilibrium constant of the dissociation process in a weak electrolyte is called the dissociation constant K_d. It, as well as the degree of dissociation, is a quantitative measure of the possibility of substance to dissociate in a solution. The smaller the value of K_d, the weaker the electrolyte and vice versa, the more K_d, the better dissolves the dissolved substance. The dissociation constant does not depend on the concentration of a solution but depends on the temperature. It has the dimension of concentration in moles per litre.

From the equilibrium in a solution of a weak electrolyte, we see that an increase in the concentration of one of the ions $[K^+]$ or $[A^-]$, due to the addition of a substance [KA] to an electrolyte solution containing the same ion, shifts the equilibrium to the left because of the principle of Le Chatelier. Therefore, if a solution of sodium acetate is added to the solution of acetate, the concentration of acid molecules will increase. Dilution of a solution of weak electrolyte contributes to dissociation. The degree of dissociation increases concurrently, and the value of the dissociation constant K_d remains unchanged.

Weak electrolytes, which consist of more than two ions, dissociate stepwise. Each degree of dissociation is characterised by a certain magnitude of the dissociation constant. These dissociation constants are stepped and denoted by K_1, K_2, ... K_n. An example of a multi-ion electrolyte is the orthophosphate acid H_3PO_4. By the sequential splitting of hydrogen ions, three equations of equilibrium can be written, which are characterised by stepped dissociation constants. In this case, almost always $K_1 > K_2 > ... > K_n$, since the energy of the first ion splitting of a neutral molecule is always less:

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-, \quad K_1 = \frac{[H^+]\cdot[H_2PO_4^-]}{[H_3PO_4]} = 7.1\cdot10^{-3};$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}, \quad K_2 = \frac{[H^+]\cdot[HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2\cdot10^{-8};$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}, \; K_3 = \frac{[H^+]\cdot[PO_4^{3-}]}{[HPO_4^{2-}]} = 5\cdot10^{-13}.$$

$$K_1 > K_2 > K_3.$$

The total dissociation constant K_{sum} is defined as

$$H_3PO_4 \leftrightarrow 3H^+ + PO_4^{3-}, \quad K_{sum} = \frac{[H^+]^3\cdot[PO_4^{3-}]}{[H_3PO_4]}.$$

It is equal to the product of stepped dissociation constants:

$$K_{sum} = K_1K_2K_3 = 7.1\cdot10^{-3}\cdot6.2\cdot10^{-8}\cdot5\cdot10^{-13} = 2.2\cdot10^{-22}.$$

Polyacid bases and amphoteric hydroxides dissociate stepwise, for example:

$$Pb(OH)_2 \leftrightarrow PbOH^+ + OH^-;$$

$$PbOH^+ \leftrightarrow Pb^{2+} + OH^-.$$

Dilution law. There is an interconnection between the constant and the degree of electrolytic dissociation, which is called the Ostwald dilution law. We write down the dissociation equation of a weak binary electrolyte of KA type:

$$KA \leftrightarrow K^+ + A^-.$$

Let its concentration $[KA]_0$ is equal to C mol/L, and the degree of dissociation — α. Then the concentration of ions:

$$[KA]_x = [K^+] = [A^-] = C\alpha,$$

and the concentration of non-dissociated molecules equals

$$[KA] = C(1-\alpha).$$

If we substitute the values of the concentrations of all particles of the electrolyte in the expression for its dissociation constant, we obtain:

$$K_d = \frac{[K^+][A^-]}{[KA]} = \frac{C\alpha C\alpha}{C(1-\alpha)}, \text{ or } K_d = \frac{[K^+][A^-]}{[KA]} = \frac{C\alpha^2}{1-\alpha}. \quad (4.10)$$

This equation is a mathematical expression of the Ostwald dilution law.

If the electrolyte is very weak ($\alpha < 0.1$), then the equation is simplified:

$$K_d = \alpha^2 C.$$

Then:

$$\alpha = \sqrt{K_d / C}. \quad (4.11)$$

An important conclusion follows from the latter equation: with a decrease in the concentration of electrolyte, the degree of its dissociation increases.

4.2.4 Properties of strong electrolytes in aqueous solutions

Solutions of strong electrolytes do not obey the dilution law that indicates the irreversibility of the process of dissociation of strong electrolytes. In fact, substances, whose crystals are constructed of ions, completely dissociate in solutions: their actual degree of dissociation is equal to one. The statement that strong electrons are completely dissociated into ions is a basic position in the theory of solutions of strong electrolytes, for which α must be equal to one. However, for concentrated solutions of strong electrolytes $\alpha < 1$. The experimental value of α in strong electrolytes is called the apparent degree of dissociation.

The deviation of α in strong electrolytes from the theoretical value $\alpha = 1$ to lower values can be explained as follows. The electrostatic interaction between ions in the solution is not taken into account in the theory of electrolytic dissociation of Arrhenius, but all effects are explained by the action of Van der Waals forces. It was possible not to take into account the electrostatic interaction between ions in weak electrolytes because of $\alpha \ll 1$. In solutions of strong electrolytes, the contribution of electrostatic interaction cannot be ignored, and therefore, the activity coefficient is introduced.

The coefficient of activity of substances and ions characterises the degree of deviation of the properties of a real solution from the properties of an ideal one, where there is no interaction. The activity coefficient is a function of the concentration of a solution, the nature of an electrolyte, the temperature and the ionic strength of a solution.

It can be said that activity is an imaginary concentration. This value is denoted by the letter a and calculated by the formula:

$$a = f\cdot C, \qquad (4.12)$$

where f is the coefficient of activity, C is the molar concentration of a substance.

The ionic strength of the solution (μ) is half the product of the concentrations of all ions in the solution (C_i) and the square of their charges (z_i):

$$\mu = \frac{1}{2}\left(C_1 z_1{}^2 + C_2 z_2{}^2 + \ldots + C_n z_n{}^2\right). \qquad (4.13)$$

It is believed that, if the ionic strength of a solution is constant, the coefficients of activity of ions also remain constant and do not depend on the ion concentrations.

Since there are no direct methods for determining the coefficients of activity, their values can be found by calculation. In particular, Debye-Hückel's formula can be used to calculate them:

$$\lg f_1 = -\frac{0.5z^2\sqrt{\mu}}{1+\sqrt{\mu}}. \qquad (4.14)$$

If $\mu < 0{,}1$, then $\lg f_i = -0.5z^2\sqrt{\mu}$.

The disadvantage of the theory of strong electrolytes is valid for dilute solutions only. Also, it does not take into account the chemical processes that occur in a solution, in particular, the solvation phenomenon and related possible changes in the activity of a solvent, which is also an active component of the solution.

4.2.5 The solubility product

If the crystals of the low-soluble salt are constructed of ions, then the ions of the salt pass into the solution rather than the molecules. For a low-soluble compound, for example, $BaSO_4$ or AgCl, which is in equilibrium with its saturated solution, the dynamic equilibrium equation has the following form:

$$BaSO_4 \leftrightarrow Ba^{2+} + SO_4^{2-}$$

Solid-phase saturated solution

that is, at constant temperature and per a unit of time, the amount of a salt, which passes into the solution, is equal to the amount of a salt, which falls out of the solution into the precipitate (solid phase). Since the numerical value of the denominator in the expression of the equilibrium constant equals 1 (for a pure solid substance), the following equation is written for the above-mentioned reverse process at constant temperature:

$$[Ba^{2+}]\cdot[SO_4^{2-}] = K,$$

where K is the equilibrium constant between a low-soluble compound and its ions in the solution.

As follows from the equation, the product of the concentrations of ions of a soluble electrolyte in a solution saturated at a certain temperature is a constant value. Such a product is called the product of solubility and denoted by K_{sp}. Then, for a saturated solution $BaSO_4$ (at 25°), we write:

$$K_{sp}(BaSO_4) = [Ba^{2+}]\cdot[SO_4^{2-}] = 1\cdot10^{-10}.$$

In general terms, the expression of the solubility product of a saturated solution of a low-soluble substance K_xA_y, which is decomposed into ions by the equation

$$K_xA_y \leftrightarrow xK^{y+} + yA^{x-},$$

will be written as follows:

$$K_{sp}(K_xA_y) = [K^{y+}]^x\cdot[A^{x-}]^y.$$

For example, for marginally soluble in water salts Ag_2S and $Ba_3(PO_4)_2$:

$$Ag_2S \leftrightarrow 2Ag^+ + S^{2-};$$

$$K_{sp}(Ag_2S) \leftrightarrow [Ag^+]^2[S^{2-}] = 6.3\cdot10^{-50};$$

$$Ba_3(PO_4)_2 \leftrightarrow 3Ba^{2+} + 2PO_4^{3-};$$

$$K_{sp}(Ba_3(PO_4)_2) \leftrightarrow [Ba^{2+}]^3[PO_4^{3-}]^2 = 6\cdot10^{-30}.$$

Based on the values of solubility products (reference data), you can calculate the solubility of various marginally soluble compounds and vice versa. Example:

$$\underset{\text{Solubility(S),mol/L}}{\text{AgCl}} \leftrightarrow \underset{S}{Ag^+} + \underset{S}{Cl^-};$$

$$K_{sp}(AgCl) = [Ag^+][Cl^-] = S \cdot S = S^2 \text{ or } S = \sqrt{K_{sp}}.$$

Since K_{sp} of a compound at a certain temperature is a constant value, an increase in the concentration in solution of one of the ions, on which this compound dissociates, causes a decrease in the concentration of another ion. So, if a solution of a compound containing an ion SO_4^{2-} is added to the saturated solution of $BaSO_4$, then the equilibrium is violated and, according to the principle of Le Chatelier, it shifts to the left, that is, the precipitate of $BaSO_4$ begins to fall out. The same thing happens in the case of the addition of excess barium ions to the saturated solution $BaSO_4$.

Thus, **the addition of the same ions into a solution of a marginally soluble electrolyte decreases its solubility** (this occurs to a specific limit, since an excess of the same name of the ion in the amount exceeding 50%, begins to promote dissolution). This conclusion is of great practical importance, in particular in quantitative analysis, since it allows one to deposit almost entirely one or another ion in the form of a low-soluble compound.

4.2.6 Water dissociation. Ionic product of water. Hydrogen index

Pure water is a weak electrolyte, which conducts insignificantly electric current because dissociation is suppressed by the action of hydrogen bonds typical of water. At 22°C, the degree of electrolytic dissociation equals $1.8 \cdot 10^{-9}$, or only $555 \cdot 10^6$ molecules of water dissociate. The dissociation of water can be written as follows:

$$2H_2O \leftrightarrow H_3O^+ + OH^-.$$

For simplicity and convenience, the equations are written as follows:

$$H_2O \leftrightarrow H^+ + OH^-.$$

Applying the mass action law to this equilibrium, we have:

$$K = \frac{[H^+][OH^-]}{[H_2O]}, \text{ or } [H^+][OH^-] = K[H_2O],$$

where K is the constant of electrolytic dissociation of water equals $1.8 \cdot 10^{-16}$.

Since the degree of water dissociation is very low, practically $[H_2O]$ = const (the number of dissociated molecules is not taken into account) and then

$$\left[H^+\right]\left[OH^-\right] = K_{H_2O}. \qquad (4.15)$$

The constant K_{H_2O} is called the ion product of water.

Since $[H_2O] = 1000 g/18 = 55.56 mol/L$, then $K_{H_2O} = 10^{-14}$ at 22°C.

Therefore, $\left[H^+\right]\left[OH^-\right] = 10^{-14}$.

The value K_{H_2O} is constant at a given temperature.

At room temperature, neutral solutions have the same concentration:

$$\left[H^+\right] = \left[OH^-\right] = 10^{-7}\ mol/L \text{ and } K_{H_2O} = 10^{-14}.$$

Diluted aqueous solutions of acids and bases have the same values of concentrations at the same temperature. Therefore, whatever the concentration of hydrogen ions, the level of hydroxide ions will not have a zero value or vice versa. This allows one to calculate the concentration $[H^+]$ or $[OH^-]$ if one of these values is known:

$$\left[H^+\right] = \frac{10^{-14}}{\left[OH^-\right]} \text{ and } \left[OH^-\right] = \frac{10^{-14}}{\left[H^+\right]}.$$

For example, the concentration of hydrogen ions in the 0.005 *M* solution of sodium hydroxide is

$$\left[H^+\right] = \frac{10^{-14}}{5 \cdot 10^{-3}} = 2 \cdot 10^{-12}\ mol/L.$$

However, it is not very convenient to record the concentrations of ions $[H^+]$ and $[OH^-]$, applying a negative power.

Danish chemist Søren Peter Lauritz Sorensen (1868–1939) introduction of the concept of pH, a scale for measuring acidity and alkalinity. The following ratio determines the value of hydrogen index pH:

$$pH = -\lg\left[H^+\right] \text{ or } pH = -\lg a \qquad (4.16)$$

because the activity of ions in a solution ($a = f\ C$) rather than the concentration of hydrogen ions is determined in experiments. Equation (4.16) can be written in the following form:

$$pH = -\lg \gamma \left[H^+\right], \qquad (4.17)$$

where γ is the activity coefficient of hydrogen ions, whose value verges towards unity in diluted solutions. Then $a \approx \left[H^+\right]$.

Since the concentration of hydrogen ions can vary within the limits of the ionic product, the pH varies in the range of 0 to 14.

In a neutral solution, $\left[H^+\right] = 10^{-7}$ mol/L; $pH = -\lg 10^{-7} = 7$.

In an acidic solution, $[H^+] > 10^{-7}$ mol/L; pH < 7.

For 10^{-3} M solution of HCl, the value of $[H^+] > 10^{-3}$ mol/L; pH = 3.

For the solution KOH of the same concentration:

$$\left[H^+\right] = \frac{K_{H_2O}}{\left[OH^-\right]} = \frac{10^{-14}}{10^{-3}} = 10^{-11}; \text{ pH} = 11.$$

Therefore, for acidic solutions: pH < 7;
for a neutral solution: pH = 7;
for alkali solutions: pH > 7.

Solutions with pH in the range from 0 to 3 are strongly acidic; at pH = 4–6, they are weakly acidic.

Weak alkali solutions have pH = 8–10, and strong alkali — pH = 11–14.

Solutions, which $[H^+] > 1$ mol/L, are characterised by negative pH value. For example, if $[H^+] = 2$ mol/L, pH = –0.3.

If $[H^+] < 10^{-14}$ mol/L, pH > 14. If $[H^+] = 0.5 \cdot 10^{-14}$ mol/L, then pH 14.3.

Study of pH of solutions is of great practical importance in chemistry, biology, medicine, food industry, agriculture, and others.

In summary

The key concepts, definitions, laws and formulas:

1. Ionic reactions can be considered as completed only in those cases when the following substances are formed:

a) insoluble substances that precipitate;

b) gaseous substances;

c) low-dissociated substances.

2. In solutions of weak electrolytes, the electrostatic forces of interaction between ions can be neglected because $\alpha << 1$.

3. In solutions of strong electrolytes, the electrostatic forces of interaction between ions are taken into account by calculating the values of the ionic strength of the solution and the activity coefficients.

4. In a solution saturated at a certain temperature, the product of the concentrations of ions of a soluble electrolyte is a constant value, which is called the solubility product and denoted as K_{sp}. The addition of the same ions (up to 50% of excess) to a solution of a low-soluble electrolyte reduces its solubility.

5. Acidic properties of solutions are characterised by the pH of the medium, which is called the hydrogen index.

6. Simple substances, oxides, as well as insoluble substances, do not dissociate.

7. If a marginally soluble substance is formed as a result of the reaction, it is considered insoluble in the record of the ionic equation.

8. Formula calculation:

the degree of electrolyte dissociation — $\alpha = \sqrt{K_d / C}$;

the solution ionic strength — $\mu = \frac{1}{2}\left(C_1 z_1{}^2 + C_2 z_2{}^2 + \ldots + C_n z_n{}^2\right)$;

the activity — $a = f\,C$;

the solubility product — $K_{sp}(K_x A_y) \leftrightarrow [K^{y+}]^x [A^{x-}]^y$;

the ionic product of water — $[H^+][OH^-] = K_{H_2O}$;

the pH of the medium — $pH = -\lg[H^+]$ or $pH = -\lg a$.

9. The values of pH are

pH < 7 – for acidic solutions;

pH = 7 – for a neutral solution; and

pH > 7 – for alkali solutions.

Necessary practical skills:

1. To work out the equations of ionic reactions in solutions of electrolytes: complete molecular, complete ionic and reduced ionic equations.

2. To calculate the pH of the medium in solutions formed by weak and strong electrolytes.

3. To use constants (K_d, K_{sp}, S) to calculate the equilibrium in solutions of electrolytes; to create conditions for precipitation and to prevent this process.

4.3 Hydrolysis

4.3.1 Hydrolysis equation

The reactions of exchange interactions in solutions are very common and occur not only between electrolytes but also between a dissolved substance and a solvent. The latter type is called a hydrolysis reaction.

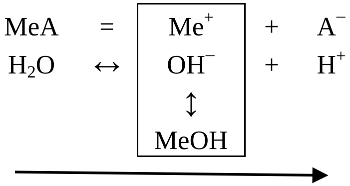
Hydrolysis is an exchange interaction of a substance with water, during which the constituent parts of the substance are combined with the constituent parts of water.

The most striking example of this type of exchange interaction is the hydrolysis of salts. The measurements of pH of aqueous salt solutions have shown that often the values of the hydrogen index are higher (alkaline medium) or smaller (acidic medium) than 7. The reason is the interaction of salt ions with water or the process of hydrolysis.

The essence of the process of hydrolysis of salts is that the salt ions bind the constituents of water (H^+, OH^- or both of these ions) to form a low-dissociated electrolyte. As a result, the equilibrium of the process of electrolytic dissociation of water

$$H_2O \leftrightarrow H^+ + OH^-$$

somewhat shifts to the right. For example, the course of the exchange interaction of the MeA salt with water, which is accompanied by the binding of OH^- water ions with metal cations M^{n+} in a weak electrolyte, can be explained by the following scheme:



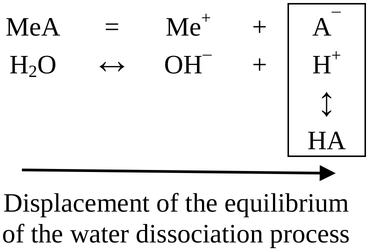
Displacement of the equilibrium of the water dissociation process

The general equation of hydrolysis of such salts is as follows:

$$Me^+ + A^- + H_2O \leftrightarrow MeOH + H^+ + A^-;$$

$$Me^+ + H_2O \leftrightarrow MeOH + H^+.$$

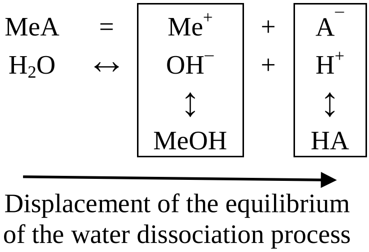
For another group of salts, the process of hydrolysis is provided by the binding of H^+ ions to the anions of the salt to form a weak acid:



In this case, the hydrolysis of the salt can be described by the following ionic equation:

$$A^- + H_2O \leftrightarrow HA + OH^- .$$

The exchange interaction of salt with water occurs to a much greater extent in the case of simultaneous binding of H^+ and OH^- ions with the constituent parts of the salt:



The general equation of hydrolysis has the form

$$Me^+ + A^- + H_2O \leftrightarrow MeOH + HA .$$

When the water ions H^+ and OH^- do not bind, the hydrolysis of salts does not occur, and the equilibrium of the water dissociation process is not shifted.

Consequently, hydrolysis of salts only occurs when water ions bind to salt ions, forming weak acids or weak bases. That is why, only salts, which are formed by weak acids, weak bases or both weak acids and bases, undergo hydrolysis. Salts of strong acids and bases do not yield to hydrolysis.

Hydrolysis of salts is a process that is reversible to neutralisation reactions of weak acids or weak bases which do not occur to the end due to the reverse reaction, namely the hydrolysis of the formed salt:

$$\underset{\text{Acid}}{HA} + \underset{\text{Base}}{MeOH} \leftrightarrow \underset{\text{Salt}}{MeA} + H_2O$$

$$\xrightarrow[\text{Neutralisation reaction}]{\qquad\qquad\qquad}$$

$$\xleftarrow[\text{Hydrolysis reaction}]{\qquad\qquad\qquad}$$

4.3.2 Degree of hydrolysis

Quantitative characteristics of hydrolysis are its degree and constant.

The degree of hydrolysis (h) of salt is the ratio of the concentration of the salt subjected to the hydrolysis to its total concentration. Similar to the degree of dissociation, the degree of hydrolysis can vary from 0 to 1, or from 0 to 100%.

Since hydrolysis is a reverse process, the mass action law can be used for its characterisation and calculation of the equilibrium constant — the constant of hydrolysis (K_h).

Let us consider the equation of hydrolysis of a salt, formed by weak acid and strong base:

$$CN^- + H_2O \leftrightarrow HCN + OH^- .$$

In dilute solutions, the concentration of water is constant; therefore, the hydrolysis equation is written as follows:

$$K_h = \frac{[HCN][OH^-]}{[CN^-]} \tag{4.18}$$

By multiplying the numerator and denominator for the concentration of hydrogen ions [H^+], we obtain:

$$K_h = \frac{[HCN][OH^-]}{[CN^-]} \times \frac{[H^+]}{[H^+]} = \frac{K_{H_2O}}{K_{d(acid)}} . \tag{4.19}$$

Thus, the hydrolysis constant of the salt formed by a strong base and a weak acid is equal to the ratio of the ionic product of water and the dissociation constant of an acid.

The weaker the acid (or, the less value of the dissociation constant), the more it is hydrolysed.

By analogy, we can prove that the constant of hydrolysis of a salt, formed by a weak base and a strong acid, is equal to

$$K_h = \frac{K_{H_2O}}{K_{d(base)}} . \quad (4.20)$$

One can write for a salt formed by a weak base and a weak acid:

$$K_h = \frac{K_{H_2O}}{K_{d(base)} \cdot K_{d(acid)}} . \quad (4.21)$$

To determine the relationship between K_h and h, for example, for a salt of a strong base and a weak acid, the ionic equation of its hydrolysis is written as follows:

$$CN^- + H_2O \leftrightarrow HCN + OH^- .$$

If we denote the initial concentration of the salt in the solution through C (mol/L) and the degree of hydrolysis h, then:

$$[KCN]_0 = \left[CN^-\right]_0 = C ;$$

$$\left[CN^-\right]_0 = C \cdot h = [HCN] = \left[OH^-\right];$$

$$\left[CN^-\right] = C - C \cdot h .$$

The equation for calculating the hydrolysis constant can be written as follows:

$$K_h = \frac{C \cdot h \cdot C \cdot h \cdot}{C(1-h)} , \qquad \text{or} \qquad K_h = \frac{C \cdot h^2}{1-h} . \quad (4.22)$$

The equation is simplified if h <<1:

$$K_h \approx C \cdot h^2 \qquad \text{and} \qquad h \approx \sqrt{\frac{K_h}{C}} . \quad (4.23)$$

Using equation (4.19), one can obtain:

$$h \approx \sqrt{\frac{K_{H_2O}}{C \cdot K_{d(acid)}}} . \quad (4.24)$$

The following conclusions can be drawn from equation (4.24):

1) the degree of hydrolysis will be the greater, the smaller the concentration of the salt solution;

2) salt hydrolysis increases with the rising temperature of the solution, as such a rise increases the concentration of hydrogen ions and hydroxyl (with increasing temperature, the water constant increases);

3) the weaker the acid, whose anion forms a salt (that is, the lower the dissociation acid constant), the more complete is the salt hydrolysis.

4.3.3 Hydrolysis in examples

Example 1. Calculate the pH for an aqueous solution of sodium chloride.

The salts formed by a cation and an anion of strong electrolytes are not subject to hydrolysis.

$$\mathrm{NaCl + HOH \leftrightarrow NaOH + HCl}\ ;$$

$$\mathrm{HOH \rightarrow OH^- + H^+}.$$

The essence of the reaction is the dissociation of water. The equilibrium between the ions of hydrogen and hydroxide is not disturbed. Therefore, the pH of the aqueous solution of sodium chloride has a neutral value.

Example 2. Calculate the pH of the medium in the course of interaction of potassium acetate and sodium carbonate with water.

A strong base and a weak acid form these salts.

a) $\mathrm{KCH_3COOH \rightarrow K^+ + CH_3COOH^-}$.

Hydrolysis proceeds by the anion:

$\mathrm{CH_3COO^- + HOH \leftrightarrow CH_3COOH + OH^-}$ — alkaline environment.

Let us write the complete ion-molecular equation:

$$\mathrm{K^+ + CH_3COO^- + HOH \leftrightarrow CH_3COOH + K^+ + OH^-}$$

and the molecular equation:

$$\mathrm{CH_3COOK + HOH \leftrightarrow CH_3COOH + KOH}\ .$$

b) $\mathrm{Na_2CO_3 \rightarrow 2Na^+ + CO_3^{2-}}$.

Sodium carbonate is formed by a strong base (NaOH) and a weak acid (H_2CO_3). Hydrolysis proceeds by the anion and the reaction of the medium will be determined by a strong component (in this case, it will be alkaline):

$$\mathrm{CO_3^{2-} + HOH \leftrightarrow HCO_3^- + OH^-}\ .$$

From the reduced equation of the first stage of hydrolysis, we obtain the complete ion-molecular equation:

$$2Na^{+} + CO_3{}^{2-} + HOH \rightarrow Na^{+} + HCO_3{}^{-} + Na^{+} + OH^{-}$$

and the molecular equation:

$$Na_2CO_3 + H_2O \rightarrow NaHCO_3 + NaOH.$$

Since an acidic salt has resulted from the hydrolysis, this salt is also subject to further hydrolysis in the second stage:

$$HCO_3{}^{-} + HOH \rightarrow H_2CO_3 + OH^{-};$$

$$Na^{+} + HCO_3{}^{-} + HOH \rightarrow H_2CO_3 + Na^{+} + OH^{-};$$

$$NaHCO_3 + H_2O \rightarrow H_2CO_3 + NaOH.$$

Thus, if the salt is formed by a strong base and weak polybasic acid, then its hydrolysis occurs in several stages; the amount of stages is equal to the basicity of the acid. In our case, the acid is two-base; that is, the hydrolysis has two stages. Moreover, in the first stage, hydrolysis is carried out faster. Hydrolysis is possible in the second stage in case of dilution of the solution and heating.

During the hydrolysis of a carbonate ion, ions of hydroxide are formed as a reaction product. The accumulation of hydroxide ions must prevent hydrolysis by the principle of Le Chatelier. Therefore, in the presence of alkalis, the hydrolysis of sodium carbonate is suppressed. In an acidic medium, the ions of hydroxide are bound, and the hydrolysis is amplified.

Example 3. Calculate the pH of the medium in the course of interaction of a) ammonium chloride, b) aluminium chloride and c) chromium sulfate with water.

These salts are formed by a weak base and strong acid.

a) Ammonium chloride is formed by a weak base (NH_4OH) and a strong acid (HCl). The salt is soluble, that is, it can dissociate in an aqueous solution:

$$NH_4OH \rightarrow NH_4{}^{+} + Cl^{-}.$$

Hydrolysis occurs by the cation; the medium is determined by a strong component so that it will be acidic.

$$NH_4{}^{+} + HOH \leftrightarrow NH_4OH + H^{+};$$

$$NH_4{}^{+} + Cl^{-} + HOH \leftrightarrow NH_4OH + H^{+} + Cl^{-};$$

$$NH_4Cl + HOH \leftrightarrow NH_4OH + HCl.$$

b) Let us record the dissociation of aluminium chloride:

$$AlCl_3 \rightarrow Al^{3+} + 3Cl^- .$$

Hydrolysis occurs by the cation. If the base is weak and polyacid, hydrolysis must proceed gradually. The number of its stages is equal to the acidity of the base. In this case, there are three stages. However, spontaneous hydrolysis is possible only in the first stage; other stages are realised only under certain conditions:

$$Al^{3+} + HOH \leftrightarrow AlOH^{2+} + H^+ ;$$

$$Al^{3+} + 3Cl^- + HOH \leftrightarrow AlOH^{2+} + 2Cl^- + H^+ + Cl^- ;$$

$$AlCl_3 + HOH \leftrightarrow AlOHCl_2 + HCl .$$

The second stage of hydrolysis is possible only in the case of dilution and heating:

$$AlOH^{2+} + HOH \leftrightarrow Al(OH)_2{}^+ + H^+ ;$$

$$AlOH^{2+} + 2Cl^- + HOH \leftrightarrow Al(OH)_2{}^+ + Cl^- + H^+ + Cl^- ;$$

$$AlOHCl_2 + HOH \leftrightarrow Al(OH)_2Cl + HCl .$$

The third stage of hydrolysis is possible only when the aluminium chloride solution is added drop by drop to the boiling water:

$$Al(OH)_2{}^+ + HOH \leftrightarrow Al(OH)_3 + H^+ ;$$

$$Al(OH)_2{}^+ + Cl^- + HOH \leftrightarrow Al(OH)_3{}^+ + H^+ + Cl^- ;$$

$$Al(OH)_2Cl + HOH \leftrightarrow Al(OH)_3 + HCl .$$

c) Let us consider further the hydrolysis of the salt of chromium (III) sulfate:

$$Cr_2(SO_4)_3 \rightarrow 2Cr^{3+} + 3SO_4{}^{2-} .$$

The first stage:

$$Cr^{3+} + HOH \leftrightarrow CrOH^{2+} + H^+ ;$$

$$2Cr^{3+} + 3SO_4{}^{2-} + 2HOH \leftrightarrow 2CrOH^{2+} + 2SO_4{}^{2-} + 2H^+ + SO_4{}^{2-} ;$$

$$Cr_2(SO_4)_3 + 2H_2O \leftrightarrow 2CrOHSO_4 + H_2SO_4 .$$

The second stage:

$$CrOH^{2+} + HOH \leftrightarrow Cr(OH)_2{}^{+} + H^{+};$$

$$2CrOH^{2+} + 2SO_4{}^{2-} + 2HOH \leftrightarrow 2Cr(OH)_2{}^{+} + SO_4{}^{2-} + 2H^{+} + SO_4{}^{2-};$$

$$2(CrOH)SO_4 + 2H_2O \leftrightarrow (Cr(OH)_2)_2SO_4 + H_2SO_4.$$

The third stage:

$$(Cr(OH)_2)^{+} + HOH \leftrightarrow Cr(OH)_3 + H^{+};$$

$$2(Cr(OH)_2)^{+} + SO_4{}^{2-} + 2H_2O \leftrightarrow 2Cr(OH)_3 + 2H^{+} + SO_4{}^{2-};$$

$$(Cr_2(OH)_2)_2SO_4 + 2H_2O \leftrightarrow 2Cr(OH)_3 + H_2SO_4.$$

Example 4. Calculate the pH of the medium when ammonium cyanide interacts water.

This salt is formed by a cation and an anion of weak electrolytes, so the reaction of the medium is determined by the ratio of the strengths of weak electrolytes which are being formed.

$$NH_4CN + H_2O \leftrightarrow NH_4OH + HCN\ ;$$

$$NH_4^{+} + CN^{-} + H_2O \leftrightarrow NH_4OH + HCN\ ;$$

pH > 7 due to $K_d(NH_4OH) = 1.76 \cdot 10^{-5}$, and $K_d(HCN) = 7.2 \cdot 10^{-10}$.

The medium can approach neutral if the dissociation constants of the weak acid and the weak base are close in values.

Another example of a possible reaction in solutions of salts formed by particles of weak electrolytes is the so-called enhancement of hydrolysis. Such a type of hydrolysis complicates the exchange reaction between salts. The salts, which do not belong to marginally soluble and are formed by the anion and cation of very weak polybasic acids and polyacid bases, cannot be obtained by the exchange reaction. The reason is their deep hydrolysis, which often goes to completion.

For example, the salt of aluminium sulfide can be obtained by sintering aluminium with sulfur. This salt is not presented in solubility tables because it is completely hydrolysed during dissolution. Because of complete hydrolysis, aluminium atom bonds ions of hydroxide, and sulfide ions bind hydrogen ions. As a result, no excessive OH^{-} ions nor H^{+} ions are accumulated, and the hydrolysis is not completed at the first stages but goes on to form the end products.

$$2AlCl_3 + 3Na_2S + 6H_2O \rightarrow 2Al(OH)_3 \downarrow + 3H_2S \uparrow + 6NaCl\ ;$$

$$2Al^{3+} + 3S^{2-} + 6H_2O \rightarrow 2Al(OH)_3 \downarrow + 3H_2S \uparrow.$$

Example 5. Determine the pH of the medium during the interaction of sodium hydrogen carbonate with water.

The reaction of hydrolysis of acidic salts of weak polybasic acids may be both acidic and alkalescent. Hydrolysis of sodium hydrogen carbonate:

$$NaHCO_3 + H_2O \leftrightarrow H_2CO_3 + NaOH \ ;$$

$$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^- \ .$$

It is typical for the hydrolysis of salts of such a type that the reaction of dissociation of the anion of acid salt takes place simultaneously with the above-mentioned hydrolysis. It causes the formation of H^+ ions in the solution:

$$HCO_3^- \rightarrow H^+ + CO_3^-$$

and promotes the neutralisation of hydroxide ions.

4.3.4 Reductive-oxidative reactions

Reactions, during which the oxidation state of the elements involved changes, are called reductive-oxidative (redox) reactions. Oxidation is the loss of electrons or an increase in the oxidation state of an atom by a molecule, an ion, or another atom. The reduction is the gain of electrons or a decrease in the oxidation state of an atom by a molecule, an ion, or another atom

Elements, and consequently, substances, which lose electrons, are reductants and which gain electrons, are oxidants.

There are the following types of reductive-oxidative reactions: intermolecular, intramolecular, and disproportionation reactions in which a substance is simultaneously oxidised and reduced, giving two different products (self-oxidation and self-reduction).

4.3.5 Redox reactions in examples

Example 1. Calculate the degree of oxidation:

a) Sulfur in sulfuric acid;

b) Phosphorus in pyrophosphate ion $(P_2O_7)^{4-}$.

The degree of oxidation is the conditional charge of an atom in a compound, which is calculated on the base of the assumption that the compound consists only of ions. The degree of oxidation may have a negative, positive or zero value. The degree of oxidation of monatomic ions is equal to the charge of the ion: for Na^+ — (+1), for Ca^{2+} — (+2), for Cl^- — (−1), etc. In most compounds, hydrogen atoms have an oxidation degree (+1); only in metal hydrides, such as, for example, KH, BaH_2, it is equal to (−1). Oxygen in most compounds has a degree of oxidation (−2); the oxidation degree is (−1) in peroxides, for example, H_2O_2.

The algebraic sum of the degrees of oxidation of atoms in a compound is always zero.

We denote the degree of oxidation of sulfur through x and multiplying the degrees of oxidation of hydrogen (+1) and oxygen (−2) by the numbers of their atoms in the H_2SO_4 molecule, make the equation $(+1)\cdot 2 + x + (-2)\cdot 4 = 0$, therefore $x = +6$

The sum of all degrees of oxidation of atoms in the ion is equal to the charge of the ion. We denote the degree of oxidation of phosphorus in ion $(P_2O_7)^{4-}$ through x and compile the equation: $x\cdot(+2) + (-2)\cdot 7 = (-4)$, then one can calculate $x = 5$.

Example 2. Fit the coefficients in the oxidation-reduction reaction scheme:

$$P + HNO_3 + H_2O \rightarrow H_3PO_4 + NO.$$

The above reaction is an example of an intermolecular oxidation-reduction reaction. Oxidiser and reducing agent are elements of various molecules.

Let us indicate the oxidation of all elements:

0 +1+5−2 +1−2 +1+5−2 +2−2
$P + HNO_3 + H_2O \rightarrow H_3PO_4 + NO$

Phosphorus and nitrogen changed their degrees of oxidation. Phosphorus donates electrons, and its degree of oxidation rises from 0 to (+5). It is a reducing agent.

Nitrogen accepts 3 electrons, changing the degree of oxidation from (+5) to (+2). Nitric acid is an oxidant.

The electron balance scheme is used to find the main coefficients. It is based on the assumption that the amount of electrons given by the reducing agent is equal to the number of electrons attached to the oxidiser. The electron balance sheet is recorded as follows

$$\begin{array}{l|c|c|c} P^0 - 5\bar{e} \rightarrow P^{+5} & 5 & & 3 \\ & & 15 & \\ N^{+5} + 3\,\bar{e} \rightarrow N^{+2} & 3 & & 5 \end{array}$$

It is necessary to find the least common multiple for these two numbers (for 5 and 3) to equilibrate the number of electrons attached to the oxidiser with the number of electrons given by the reducer. The least common multiple is 15, and thus the main coefficients will be 3 for phosphorus and 5 for nitrogen. We substitute the coefficients in the scheme:

$3\overset{0}{P} + 5H\overset{+5}{N}O_3 + H_2O \to 3H_3\overset{+5}{P}O_4 + 5\overset{+2}{N}O$

Now it is necessary to calculate the number of atoms of hydrogen in the left and right parts of the reaction scheme. This amount varies, but it is not possible to change the coefficients before the oxidising or reducing agents because such a change will disrupt the electron balance. Therefore, to preserve the number of hydrogen atoms, one should set the coefficient two before the water formula. Finally, the equation of reaction will have the following form:

$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO.$$

The correctness of the writing of the equation is confirmed by counting the number of oxygen atoms:

in the left part of the equation, they are: $5 \cdot 3 + 2 \cdot 1 = 17$;

in the right part — $3 \cdot 4 + 5 \cdot 1 = 17$.

Therefore, the equation is composed correctly.

Example 3. Fit the coefficients in the oxidation-reduction reaction scheme:

$$KMnO_4 + Na_2SO_3 + H_2SO_4 \to MnSO_4 + Na_2SO_4 + K_2SO_4 + H_2O.$$

Note the degree of oxidation of all elements

$\overset{+1}{K}\overset{+7}{Mn}\overset{-2}{O_4} + \overset{+1}{Na_2}\overset{+4}{S}\overset{-2}{O_3} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \to \overset{+2}{Mn}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{Na_2}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{K_2}\overset{+6}{S}\overset{-2}{O_4} + \overset{+1}{H_2}\overset{-2}{O}$

Manganese and sulfur changed their oxidation degrees. Manganese accepts 5 electrons, changing the degree of oxidation from (+7) to (+2). $KMnO_4$ is an oxidant. Sulfur loses 2 electrons, the degree of its oxidation rises from (+4) to (+6). Na_2SO_3 is a reducing agent.

These changes can be expressed by the following electron equations

$$\begin{array}{l|c|c|c} Mn^{+7} + 5\bar{e} \to Mn^{+2} & 5 & & 2 \\ & & 10 & \\ S^{+4} - 2\bar{e} \to S^{+6} & 2 & & 5 \end{array}$$

We substitute the coefficients in the scheme:

$$2KMnO_4 + 5Na_2SO_3 + 3H_2SO_4 = 2MnSO_4 + 5Na_2SO_4 + K_2SO_4 + 3H_2O.$$

In the left part of the equation $2 \cdot 4 + 5 \cdot 3 + 3 \cdot 4 = 35$ atoms of oxygen; in the right part — $2 \cdot 4 + 5 \cdot 4 + 1 \cdot 4 + 3 \cdot 1 = 35$.

Therefore, the equation is composed correctly.

Example 4. Fit the coefficients in the oxidation-reduction reaction scheme:

$$KMnO_4 + HCl_{(conc)} \rightarrow MnCl_2 + Cl_2 + KCl + H_2O.$$

This equation is an example of an intermolecular oxidation-reduction reaction, where the reducing agent also plays the role of a salt-former in an acid medium.

Manganese is restored to oxidation (+2), forming manganese chloride, and chloride ion of the acid oxidises to free chlorine. HCl is a reducing agent, $KMnO_4$ is an oxidant.

The electron balance of the reaction is recorded as follows

$$\begin{array}{l|c|c|c}
Mn^{+7} + 5\bar{e} \rightarrow Mn^{+2} & 5 & & 2 \\
 & & 10 & \\
2Cl^{-} - 2\bar{e} \rightarrow Cl_2^{0} & 2 & & 5
\end{array}$$

$$2KMnO_4 + HCl \rightarrow 2MnCl_2 + 5Cl_2 + 2KCl + H_2O.$$

After the coefficients are set before the chlorine and hydrogen atoms, the equation has the following form:

$$2KMnO_4 + 16HCl_{(conc)} = 2MnCl_2 + 5Cl_2 + 2KCl + 8H_2O.$$

We have 8 atoms of oxygen in both left and right parts of the equation. Therefore, the equation is composed correctly.

Example 5. Fit the coefficients in the oxidation-reduction reaction scheme:

$$Cu + HNO_{3(dil)} \rightarrow Cu(NO_3)_2 + NO + H_2O.$$

The interaction of metals with acids is also referred to as intermolecular oxidation-reduction reactions.

Nitric acid in dilute solutions differently reacts with metals depending on the concentration of the acid in the solution and the activity of the metal.

The least active metals (silver, mercury) reduce nitric acid only to nitrogen dioxide, whereas more active (copper, iron) to nitrogen monoxide. Some more active metals (zinc, magnesium, cobalt, etc.) in more diluted solutions of a nitric acid reduce it to dinitrogen oxide or ammonium ions.

Various recovery products (N_2O, N_2 or NH_4NO_3) may be formed with active metals, such as magnesium, zinc, etc. if the concentration of the nitric acid is decreasing. The lower the concentration of acid, the lower is the degree of nitrogen reduction.

Let us note the degrees of oxidation of all elements:

$$\overset{0}{Cu} + \overset{+1+5-2}{HNO_{3(dil)}} \rightarrow \overset{+2\ +5-2}{Cu(NO_3)_2} + \overset{+2-2}{NO} + \overset{+1-2}{H_2O}$$

Copper and nitrogen changed the degrees of oxidation. Copper is a reducing agent; nitric acid is an oxidiser and a salt-forming agent.

Let us make an electron balance scheme:

$$\begin{array}{l|c|c|c}
Cu^0 - 2\bar{e} \rightarrow Cu^{+2} & 2 & & 3 \\
 & & 6 & \\
N^{+5} + 3\bar{e} \rightarrow N^{+2} & 3 & & 2
\end{array}$$

$$3Cu + 8HNO_{3(dil)} = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

We have 24 atoms of oxygen in both left and right parts of the equation. Therefore, the equation is composed correctly.

Example 6. Fit the coefficients in the oxidation-reduction reaction scheme:

$$Cu_2S + HNO_3 \rightarrow Cu(NO_3)_2 + H_2SO_4 + NO + H_2O.$$

This equation is an example of an oxidation-reduction reaction, in which the number of elements that change the degree of oxidation is greater than two. Therefore, there are two oxidants or two reducing agents. In this case, it is necessary to determine the total number of electrons that are lost by reducing agents and are gained by oxidants, and then calculate the coefficients in the equation, as shown in the preceding examples.

Indicate the oxidation of all elements:

$$\overset{+1-2}{Cu_2S} + \overset{+1+5-2}{HNO_3} \rightarrow \overset{+2+5-2}{Cu(NO_3)_2} + \overset{+1+6-2}{H_2SO4} + \overset{+2-2}{NO} + \overset{+1-2}{H_2O}$$

Copper, sulfur and nitrogen changed the degree of oxidation. Copper and sulfur are reducing agents. Nitrogen is an oxidiser. In the above-mentioned reductive-oxidative reaction, there are two reducing agents and one oxidiser.

Let us make an electron balance scheme:

$$\begin{array}{l|c|c|c}
\left.\begin{array}{l} 2Cu^{+1} - 2\bar{e} \rightarrow 2Cu^{+2} \\ S^{-2} - 8\bar{e} \rightarrow S^{+6} \end{array}\right\} 10\bar{e} & 10 & 30 & 3 \\
N^{+5} + 3\bar{e} \rightarrow N^{+2} & 3 & & 10
\end{array}$$

Two reducing agents Cu^{+1} and S^{-2} lose 10 electrons, which are gained by one oxidiser HNO_3. The main coefficients are 3 — before Cu_2S and 10 — before NO.

$$3Cu_2S + HNO_3 \rightarrow 6Cu(NO_3)_2 + 3H_2SO_4 + 10NO + H_2O.$$

In the case of this oxidation-reduction reaction, HNO_3 is not only an oxidiser but also a salt-forming compound. After fitting the coefficients in front of the nitrogen and hydrogen atoms, the equation has the following form:

$$3Cu_2S + 22HNO_3 = 6Cu(NO_3)_2 + 3H_2SO_4 + 10NO + 8H_2O.$$

There are 66 atoms of oxygen in both right and left parts of the equation. Consequently, the equation is compiled correctly.

Example 7. Match the coefficients in the oxidation-reduction reaction scheme

$$KClO_3 \rightarrow KCl + O_2.$$

For reactions of intramolecular oxidation-reduction, a change in the oxidation of elements of the same molecule is characteristic. Therefore, both oxidiser and reducing agent are the elements of the same compound.

$+1+5-2$ $+1-1$ 0
$KClO_3 = KCl + O_2$

The degree of oxidation was changed by the atoms of chlorine and oxygen. Chlorine is an oxidiser; oxygen is a reducing agent. The electron balance has the following form:

$$\begin{array}{l|c|c|c} Cl^{+5} + 6\bar{e} \rightarrow Cl & 6 & & 2 \\ & & 12 & \\ O^{-2} - 2\cdot 2\bar{e} \rightarrow O_2 & 4 & & 3 \end{array}$$

We substitute the obtained coefficients in the right-hand side of the equation

$$KClO_3 \rightarrow 2KCl + 3O_2$$

and equalise the number of atoms of chlorine and oxygen in the left and right parts:

$$2KClO_3 = 2KCl + 3O_2.$$

We have six oxygen atoms in both parts of the equation. Consequently, the equation is compiled correctly.

Example 8. Fit the coefficients in the oxidation-reduction reaction scheme:

$$KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2.$$

Let us indicate the oxidation of all elements:

$$\overset{+1+7-2}{\mathrm{KMnO_4}} \to \overset{+1\,+6\,-2}{\mathrm{K_2MnO_4}} + \overset{+4\,-2}{\mathrm{MnO_2}} + \overset{0}{\mathrm{O_2}}$$

The degree of oxidation has changed in the atoms of manganese and oxygen, which are elements of the same compound of potassium permanganate — an oxidant. Oxygen is a reducing agent.

Let us make an electron balance scheme:

$$\begin{array}{l|c|c|c}
\left.\begin{array}{l}\mathrm{Mn}^{+7}+1\bar{e}\to\mathrm{Mn}^{+6}\\ \mathrm{Mn}^{+7}+3\bar{e}\to\mathrm{Mn}^{+4}\end{array}\right\}+4\bar{e} & 4 & & 1\\
 & & 4 & \\
\mathrm{O}^{-2}-2\cdot2\bar{e}\to\mathrm{O}_2 & 4 & & 1
\end{array}$$

As is seen, the coefficients of the oxidiser and the reducing agent on the right side are equal to each other:

$$\mathrm{KMnO_4} \to \mathrm{K_2MnO_4} + \mathrm{MnO_2} + \mathrm{O_2}.$$

We will calculate the number of manganese and oxygen atoms in the right side and set the coefficient 2 in the left part before potassium permanganate.

The equation has the following form:

$$2\mathrm{KMnO_4} = \mathrm{K_2MnO_4} + \mathrm{MnO_2} + \mathrm{O_2}.$$

We have eight oxygen atoms in both parts of the equation. Consequently, the equation is compiled correctly.

Example 9. Fit the coefficients in the oxidation-reduction reaction scheme

$$\mathrm{SnCl_2} + \mathrm{KOH} \to \mathrm{K_2SnO_3} + \mathrm{Sn} + \mathrm{KCl} + \mathrm{H_2O}.$$

In the disproportionation reactions, the same element acts as an oxidiser and a reducing agent. In such cases, a substance with an intermediate oxidation state is as if decomposed into two compounds. In one virtual compound, the oxidation level is higher, and in another, it is lower. Indicate the oxidation of all elements:

$$\overset{+2-1}{\mathrm{SnCl_2}} + \overset{+1-2+1}{\mathrm{KOH}} \to \overset{+1\,+4-2}{\mathrm{K_2SnO_3}} + \overset{0}{\mathrm{Sn}} + \overset{+1-1}{\mathrm{KCl}} + \overset{+1\,-2}{\mathrm{H_2O}}$$

The degree of oxidation has changed for tin. This element, like an oxidiser, gains two electrons, but as a reducing agent, it also loses two electrons. This is a disproportionation reaction.

Let us make an electron balance scheme:

$$\begin{array}{l|c|c|c}
\mathrm{Sn}^{+2}-2\bar{e}\to\mathrm{Sn}^{+4} & 2 & & 1\\
 & & 2 & \\
\mathrm{Sn}^{+2}+2\bar{e}\to\mathrm{Sn}^{0} & 2 & & 1
\end{array}$$

The final form of the reaction is as follows:

$$2SnCl_2 + 6KOH = K_2SnO_3 + Sn + 4KCl + 3H_2O.$$

We have 6 oxygen atoms in both parts of the equation. Consequently, the equation is compiled correctly.

Example 10. Fit the coefficients in the oxidation-reduction reaction scheme

$$K_2SO_3 \rightarrow K_2SO_4 + K_2S.$$

Let us indicate the oxidation of all elements:

$$\overset{+1+4-2}{K_2SO_3} \rightarrow \overset{+1+6-2}{K_2SO_4} + \overset{+1-2}{K_2S}$$

Sulfur changed its degree of oxidation. This element is both an oxidiser and a reducing agent; that is, the equation under consideration is an example of the disproportionation reaction.

Let us make an electron balance scheme:

$$\begin{array}{l|c|c|c} S^{+4} - 2\bar{e} \rightarrow Sn^{+6} & 2 & & 3 \\ & & 6 & \\ S^{+4} + 6\bar{e} \rightarrow S^{-2} & 6 & & 1 \end{array}$$

The equation has the following form:

$$4K_2SO_3 = 3K_2SO_4 + K_2S.$$

We have 12 oxygen atoms in both parts of the equation. Consequently, the equation is compiled correctly.

In summary

The key concepts, definitions, laws, reactions and formulas:

1. Hydrolysis of salts is the exchange interaction of substances with water, during which the constituent parts of the substance are combined with the constituent parts of water:

$$Me^+ + A^- + H_2O \leftrightarrow MeOH + HA.$$

2. Hydrolysis is observed in salts formed by weak acids, weak bases, or weak acids and bases simultaneously. Salts of strong acids and bases cannot be hydrolysed.

3. The degree of hydrolysis of the salt (h) is the ratio of the concentration of the salt that has been hydrolysed to its total concentration. Similarly to the degree of dissociation, the degree of hydrolysis can vary from 0 to 1, or from 0 to 100%.

4. Hydrolysis increases with increasing temperature of the solution, as it increases the concentration of hydrogen ions and hydroxyl ions (with increasing temperature the water constant increases).

5. The degree of hydrolysis will increase with lowering the concentration of the salt solution.

6. The weaker the acid, whose anion forms the salt (i. e., the lower the dissociation constant of the acid), the more complete is the hydrolysis of the salt.

7. Redox reactions are reactions during which the degree of oxidation of the elements that make up the reactants change.

8. The reduction is the process of gaining electrons. Oxidation is the process of electron loss.

9. A reductant is an element or substance that donates electrons. An oxidiser is an element or substance that accepts electrons.

10. The degree of oxidation is the conditional charge of an atom in a compound, calculated on the assumption that the compound consists of ions only. The degree of oxidation can be negative, positive or zero.

11. The hydrolysis constant (K_h) is calculated according to the action mass law.

12. Formulas for calculating the hydrolysis constant for the salt formed by:

a weak acid and strong base — $K_h = \frac{K_{H_2O}}{K_{d(acid)}}$;

a weak base and strong acid — $K_h = \frac{K_{H_2O}}{K_{d(base)}}$;

both weak base and acid — $K_h = \frac{K_{H_2O}}{K_{d(base)} \cdot K_{d(acid)}}$.

13. The degree and constant of hydrolysis are related similarly to the degree and constant of dissociation:

$$K_h = \frac{C \cdot h^2}{1 - h} \approx C \cdot h^2, h = \sqrt{\frac{K_h}{C}}.$$

14. The algebraic sum of the degrees of oxidation of atoms in a compound is always zero.

Necessary practical skills:

1. To work out all types of hydrolysis equations for different types of salts: complete molecular, complete ionic and reduced ionic equations.

2. To calculate the pH of the medium in solutions of salts, taking into account hydrolysis.

3. To use constants (K_d, K_h, S) to calculate the equilibrium in the solutions of salts that are subjected to hydrolysis; to formulate conditions for precipitation and for preventing this process.

4. To calculate the oxidation rates of elements in compounds.

5. To distinguish among the types of redox reactions: intermolecular, intramolecular and disproportionation reactions.

4.4 Problem solving

4.4.1 Examples

Example 4.1 It is necessary to prepare a solution (soln) weighing 500 g with a mass fraction of potassium chloride 14%. Identify the necessary masses of the salt and water.

$$m(KCl) = \frac{m(soln) \cdot \omega(KCl)}{100};\ m(KCl) = \frac{500g \cdot 14}{100} = 70g;$$

$$m(H_2O) = m(soln) - m(KCl);\ m(H_2O) = 500g - 70g = 430g.$$

Answer: 70 g of KCl and 430 g of water should be taken to prepare the required solution.

Example 4.2 Calculate the mass of zinc chloride required to prepare 250 mL of a decinormal solution.

$$M_f\,(ZnCl_2) = \frac{1}{2} M(ZnCl_2) = \frac{65 + 35.5 \cdot 2}{2} = 68\ \text{(g)}$$

$$C_f\,(ZnCl_2) = \frac{\nu_f\,(ZnCl_2)}{V}.$$

Substitute the value of $\nu_f\,(ZnCl_2)$ using the following formula:

$$\nu_f\,(ZnCl_2) = \frac{m(ZnCl_2)}{M_f\,(ZnCl_2)}.$$

Then one can write: $C_f\,(ZnCl_2) = \dfrac{m(ZnCl_2)}{M_f\,(ZnCl_2) \cdot V}$;

therefore, $m(ZnCl_2) = C_f\,(ZnCl_2) \cdot M_f\,(ZnCl_2) \cdot V$.

$$m(ZnCl_2) = 0.1\text{mol} \cdot \text{equiv/L} \cdot 68\text{g}/\text{mol} \cdot \text{equiv} \cdot 0.25\text{L} = 1.7\text{g}.$$

Answer: the mass of zinc chloride 1,7 g.

The mixing of several solutions of the same substance is often considered in tasks. Each solution is characterised by specific masses (m_1 and m_2) and mass fractions (or percentage concentrations) of the dissolved substance (ω_1 and ω_2). After mixing, the mass of the formed solution is equal to the sum of the mass of initial solutions ($m_1 + m_2$).

When solving such tasks, the law of conservation of mass of substances is used in algebraic equations. In particular, it is indicated that the mass of the dissolved substance during the mixing of solutions has not changed. Its mass is written as a product of the mass of the solution and the mass fraction of the dissolved substance, expressed in decimals:

$$m_1\omega_1 + m_2\omega_2 = (m_1 + m_2)\omega .$$

One of the quantities available in the equation is usually unknown, and it needs to be found. Among the components that are mixed, there may be a pure solvent (it is considered as a solution with a concentration equal to zero, i.e. $\omega = 0$) and a dry substance without a solvent (it is considered as a solution with 100% concentration, i.e. $\omega = 1$).

Example 4.3 Determine how much of the solution with a mass fraction of glucose 5% is necessary to dissolve 120 g of glucose and obtain a new solution with a mass fraction of glucose 8%

The value x is the value sought — the mass of the solution with a mass fraction of glucose 5%. In the algebraic equation, we shall write that the mass of glucose in the newly prepared solution is equal to its mass, which is contained in x gram of the solution with $\omega = 5\%$ plus 120 g, dissolved in the latter. The mass of the newly prepared solution is (x + 120) gram, and it contains $(x + 120)\cdot 0.08$ g glucose.

The scheme of changing the quantitative composition of the solution during glucose dissolution is as follows:

$$\boxed{\begin{array}{c} m_1 = x \\ \\ \omega_1 = 0.05 \end{array}} \quad + \quad \boxed{\begin{array}{c} m = 120 \\ \\ \omega = 1 \end{array}} \quad \rightarrow \quad \boxed{\begin{array}{c} m_2 = 120+x \\ \\ \omega_2 = 0.08 \end{array}}$$

Then: $(x + 120)\cdot 0.08 = 0.05x + 120$, and $x = 3680$ g.

Answer: glucose must be dissolved in 3680 g of a solution with a mass fraction of glucose 5%.

Example 4.4 Determine the molar and normal concentration of the solution of sulfuric acid with a mass fraction of H_2SO_4 14% (density 1.57 g/mL).

The molar concentration is determined by

$$C_m = \frac{\nu(\text{subs}) \cdot 100}{V(\text{soln})}.$$

Let us express C_m through the values given in the task, using the following equations:

$$\nu(\text{subs}) = \frac{m(\text{subs})}{M(\text{subs})}; \qquad V(\text{soln}) = \frac{m(\text{soln})}{\rho}.$$

Since $C_m = \frac{m(\text{subs}) \cdot \rho \cdot 1000}{M(\text{subs}) \cdot m(\text{soln})}$ and $\frac{m(\text{subs})}{m(\text{soln})} = \frac{\omega}{100\%}$,

then one can write: $C_m = \frac{\omega \cdot \rho \cdot 1000}{m(\text{soln}) \cdot 100\%} = \frac{\omega \cdot \rho \cdot 10}{m(\text{soln})}$.

Under the condition of the task, $C_m = \frac{14 \cdot 1.57 \cdot 10}{98} = 2.2 \text{mol/L}$.

Similarly, we find the normal concentration

$C_f = \frac{\omega \cdot \rho \cdot 10}{M_f}$, where $M_f = f \cdot M$.

Then $C_f = \frac{C}{f(H_2SO_4)}$; $f(H_2SO_4) = \frac{1}{2}$; $C_f = 2 \cdot 2.2 = 4.4 \text{mol/L}$.

Answer: The molar concentration of H_2SO_4 is 2.2 mol/L; the normal concentration is 4.4 mol/L.

Example 4.5 Water weighing 170 g was added to a solution weighing 80 g with a mass fraction of sodium nitrate 12%. Calculate the mass fraction of sodium nitrate in the resulting solution.

$80\text{g} 12\% \text{NaNO}_3 + 170\text{g} H_2O = x\%$;

1) $m(\text{NaNO}_3) = 80 \cdot 0.12 = 9.6\text{g}$;

2) $m(\text{soln}) = 80 + 170 = 250\text{g}$;

3) $\omega_1(\text{NaNO}_3) = \frac{m(\text{NaNO}_3) \cdot 100\%}{m(\text{soln})} = \frac{9.6 \cdot 100}{250} = 3.84\%$;

Answer: The mass fraction of sodium nitrate is 3.84%.

Example 4.6 Find the masses of solutions of sodium chloride with mass fractions of 10% and 20% necessary for the preparation of 300 g of a solution with a mass fraction of 12%. In the answer, specify a mass of solution with a mass fraction of 10%.

The tasks of mixing solutions with different mass fractions to prepare a solution with a given mass fraction can be solved by applying the mixing rule (or the rule of the cross).

1)
$$\begin{tikzcd}[column sep=small] 10\%\ \mathrm{NaCl} \arrow[dr, dash] & & 8\mathrm{g}\ 10\%\ \mathrm{NaCl} \\ & 12\% \arrow[ur, dash] \arrow[dr, dash] & \\ 20\%\ \mathrm{NaCl} \arrow[ur, dash] & & 2\mathrm{g}\ 20\%\ \mathrm{NaCl} \end{tikzcd} \left.\vphantom{\begin{matrix}a\\b\\c\end{matrix}}\right\} \begin{matrix} 8+2=10\ \mathrm{g} \\ 12\%\ \mathrm{NaCl} \end{matrix}$$

2) 10g 12% NaCl - 8g 10% NaCl

300g - x

$$x = \frac{300 \cdot 8}{10} = 240\ (\mathrm{g})\ 10\%\ \mathrm{NaCl};$$

3) By analogy: $y = \frac{300 \cdot 2}{10} = 60\ (\mathrm{g})\ 20\%\ \mathrm{NaCl}$.

Answer: the weight of the solution with $\omega(NaCl) = 10\%$ is 240 g, the weight of the solution with $\omega(NaCl) = 20\%$ is 60 g.

Example 4.7 An excess of the solution of hydrochloric acid was added to the solution containing sodium chloride and sodium carbonate with a mass of 22.3 g. After the reaction, the solution was evaporated. Mass of solid residue was 23.4 g. Calculate the mass fraction (in per cent) of sodium chloride in the initial mixture.

Let us make a chemical reaction equation:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

$$106\ \mathrm{g/mol} \qquad 2 \cdot 58.5\ \mathrm{g/mol}$$

Indicate the amount of sodium chloride in the starting substance through x, and sodium carbonate — through y mol. According to the task conditions, the mass of the initial mixture can be written as follows: $58.5\,x + 106\,y = 22.3$.

Let us calculate the amount of sodium chloride substance (solid residue), formed after evaporation of the solution:

$$\nu(NaCl) = \frac{m(NaCl)}{M(NaCl)} = \frac{23.4}{58.5} = 0.4\,\mathrm{mol}.$$

By the reaction equation:

$$\frac{\nu(Na_2CO_3)}{\nu(NaCl)} = \frac{K(Na_2CO_3)}{K(NaCl)} = \frac{1}{2},\ \nu(NaCl) = 2\nu(Na_2CO_3) = 2y\,mol.$$

According to the condition of the task, the amount of the solid residue is equal to the sum of the amount of sodium chloride substance, which is a part of the initial mixture, and the amount of sodium chloride substance formed as a result of the reaction:

$$x + 2y = 0.4.$$

We make a system of equations and solve it:

$$\begin{cases} 58.5x + 106y = 22.3, \\ x + 2y = 0.4, \end{cases}$$

$x = 0.2$; $y = 0.1$.

One can calculate the mass fraction of sodium chloride in the initial mixture as follows:

$$\omega(NaCl) = \frac{m(NaCl)\quad 100\%}{m(NaCl + Na_2CO_3)} = \frac{\nu(NaCl)\quad M(NaCl)\quad 100\%}{m(NaCl + Na_2CO_3)} =$$

$$\frac{0.2\quad 58.5\quad 100}{22.3} = 52.5\%.$$

Answer: The mass fraction of sodium chloride in the starting mixture is 52.5%.

Example 4.8 Determine the concentration of ions of a soluble electrolyte in its saturated solution. The solubility product of BaF_2 at 18°C is $1.7\cdot10^{-6}$. Calculate the concentration of Ba^{2+} and F^- ions in a saturated BaF_2 solution at this temperature.

BaF_2 decomposes by the equation $BaF_2 \leftrightarrow Ba^{2+} + 2F^-$.

In the process of BaF_2 dissociation, the amount of ions F^- is twice as much than Ba^{2+} ions. So, $[F^-] = 2[Ba^{2+}]$. The solubility product of salt is $K_{sp(BaF2)} = [Ba^{2+}]\,[F^-]^2$.

If we express the concentration of ions F^- through the concentration of Ba^{2+} ions, then

$$K_{sp(BaF2)} = [Ba^{2+}]\,(2[Ba^{2+}])^2 = 4\,[Ba^{2+}]^3 = 1.7\cdot10^{-6}.$$

The concentration of ions Ba^{2+} is equal to

$$Ba^{2+} = \sqrt[3]{\frac{1.7\cdot10^{-6}}{4}} = 7.5\cdot10^{-3}\ mol/L.$$

The concentration of ions F^- is equal to $F^- = 7.5\cdot10^{-3}\cdot2 = 1.5\cdot10^{-3}$ (mol/L).

Example 4.9 Determine the pH and pOH of the decimolar solution of nitric acid.

Nitric acid is a strong electrolyte. So $[H^+] = C_{HNO3} = 0.1$ mol/L;

$$pH = -\lg 0.1 = 1; \; pOH = 14 - 1 = 13.$$

4.4.2 Problems

To sections 4.1 and 4.2:

1. Determine the molar and normal concentration of 20% calcium chloride solution ($\rho = 1.178$ g/cm^3).

2. Calculate the mass of hydrogen chloride contained in 2 litres of hydrochloric acid ($\rho = 1.108$ g/cm^3) with a mass fraction of a substance of 22%.

3. Calculate the volumes of the solution of sulfuric acid ($\rho = 1.84$ g/cm^3) and the water, which should be mixed to prepare 10 litres of an acid solution with a density of 1.42 g/cm^3.

4. A mixture of 200 mL of a solution of potassium hydroxide with a mass fraction of alkali of 20% ($\rho = 1.173$ g/cm^3) and 500 mL of a solution of the same substance with a mass fraction of 40% ($\rho = 1.408$ g/cm^3) was prepared. Determine the mass fraction (%) of alkali in the resulting solution.

5. Calculate the mass of hydrochloride acid ($\omega = 0.30$), which should be added to 400 g of hydrochloric acid with a mass fraction of 0.15 to obtain a solution with a mass fraction of 0.2.

6. Determine the volume of a 0.5 M potassium hydroxide solution, which should be used to prepare 200 mL of a 0.1 M alkali solution.

7. Determine the volumes of water and a 2 M solution of sulfuric acid necessary for the preparation of 200 mL of a 1.5 M solution of the acid.

8. Calculate the molar and equivalent concentrations of the following solutions:

a) 27.1% solution of ammonium chloride ($\rho = 1.075$ g/cm^3);

b) 6.91% solution of barium hydroxide ($\rho = 1.04$ g/cm^3).

9. Determine the mass fractions of the dissolved substance in the following solutions:

a) nitric acid with a molar concentration of equivalents of 4.8 mol/L ($\rho = 1.16$ g/cm^3);

b) sodium carbonate with a molar concentration of equivalents of 3.07 mol/L ($\rho = 1.15$ g/cm^3).

10. Determine the volume of a 10% sodium carbonate solution ($\rho = 1.105$ g/cm^3) required for the preparation of 5 litres of a 2% solution ($\rho = 1.02$ g/cm^3).

11. Calculate the mass of sodium nitrate, which should be added to 160 g of a solution of this salt with a mass fraction of the solute 10% to get a solution of this salt with a mass fraction of 20%.

12. The solubility of anhydrous sodium carbonate in 100 g of water at 500°C is 47 g, and at 150°C – 16 g. Determine the mass of a salt that crystallises as a result of cooling of 220 g of the solution saturated at 500°C if the formula of the crystalline hydrate is $Na_2CO_3 \cdot 10H_2O$.

13. Complete the equations of exchange reactions in the ion-molecular form:

a) $AgNO_3 + FeCl_3 \rightarrow$
b) $Pb(CH_3COO)_2 + K_2S \rightarrow$
c) $SrSO_4 + BaCl_2 \rightarrow$
d) $CaCl_2 + Na_3PO_4 \rightarrow$
e) $NH_4Cl + NaOH \rightarrow$
f) $Ba(NO_3)_2 + Al_2(SO_4)_3 \rightarrow$
g) $Na_3PO_4 + HCl \rightarrow$
h) $K_2CO_3 + H_2SO_4 \rightarrow$
i) $HClO + NaOH \rightarrow$
j) $NH_4OH + HCN \rightarrow$

14. Write the equations of exchange reactions in the ion-molecular form:

a) $Na_3PO_4 + HClO \rightarrow$
b) $FeCl_2 + NH_4OH \rightarrow$
c) $Cr(OH)_3 + HCl \rightarrow$
d) $NaHS + H_2SO_4 \rightarrow$
e) $AgNO_3 + K_2S \rightarrow$
f) $NaClO + H_2SO_4 \rightarrow$
g) $CrCl_3 + NaOH \rightarrow$
h) $KHSO_3 + KOH \rightarrow$
i) $Fe(OH)_3 + HNO_3 \rightarrow$
j) $CaCO_3 + HCl \rightarrow$

15. Determine the pH of the aqueous solutions in which the concentration of hydrogen cations (mol/L) is: a) 10^{-4}; b) $3.2 \cdot 10^{-6}$; c) $7.4 \cdot 10^{-11}$.

16. Calculate the concentration of H^+ in a 1% solution of acetic acid ($\rho = 1$ g/cm^3).

17. Determine how many times the concentration of cations H^+ in a solution of formic acid is greater than the concentration of these ions in a solution of acetic acid of the same concentration.

18. Determine the concentration of ions $H_2PO_4^-$; HPO_4^{2-} and PO_4^{3-} in a 0.4 M solution of phosphoric acid.

19. Based on the value of K_{sp} for calcium carbonate, calculate the mass of calcium carbonate contained in 100 mL of its saturated solution.

20. Determine whether the precipitate of silver chloride precipitates if a 450 mL solution of silver nitrate with a molar concentration of 0.0001 mol/L equivalents is added to a 50 mL solution of hydrochloric acid with a molar concentration of 0.001 mol/L equivalents.

21. Determine whether the precipitate of lead (II) chloride falls when a solution of sodium chloride with a molar concentration of 0.4 mol/L equivalents is added to a solution of lead (II) nitrate with a molar concentration of 0.1 mol/L equivalents of the same volume.

22. Determine whether the precipitate of silver sulfate falls when sulfuric acid with a molar concentration of 1 mol/L equivalent is added to a 0.02 *M* solution of silver nitrate of the same volume.

23. Determine the solubility of silver chloride: a) in water; b) in a solution of 0.001 *M* hydrochloric acid.

24. Calculate the concentration of ions of Ca^{2+} and PO_4^{3-} in a saturated solution of calcium phosphate if $K_{sp}(Ca_3(PO_4)_2)$ at 250°C is equal to $1{\cdot}10^{-25}$.

25. Calculate the pH of the solution if the concentration of OH^- ions (in mol/L) is:

a) $2.52{\cdot}10^{-5}$; b) $1.78{\cdot}10^{-7}$; c) $4{\cdot}10^{-6}$.

To section 4.3:

In Tasks 1–7, complete the equations in the molecular ionic form for the exchange reactions (a–e) and hydrolysis (f–j).

1. a) $AgNO_3 + FeCl_3 \rightarrow$
   b) $Pb(CH_3COO)_2 + K_2S \rightarrow$
   c) $SrSO_4 + BaCl_2 \rightarrow$
   d) $CaCl_2 + Na_3PO_4 \rightarrow$
   e) $NH_4Cl + NaOH \rightarrow$
   f) $MgCl_2$
   g) Na_2SO_4
   h) K_2CO_3
   i) Al_2S_3
   j) HCOOK

2. a) $Ba(NO_3)_2 + Al_2(SO_4)_3 \rightarrow$
   b) $Na_3PO_4 + HCl \rightarrow$
   c) $K_2CO_3 + H_2SO_4 \rightarrow$
   d) $HClO + NaOH \rightarrow$
   e) $NH_4OH + HCN \rightarrow$
   f) Na_2CO_3
   g) $AlBr_3$
   h) KCl
   i) $(NH_4)_2CO_3$
   j) NaCN

3. a) $Na_3PO_4 + HClO \rightarrow$
   f) $CaCl_2$

b) $FeCl_2 + NH_4OH \rightarrow$
c) $Cr(OH)_3 + HCl \rightarrow$
d) $NaHS + H_2SO_4 \rightarrow$
e) $AgNO_3 + K_2S \rightarrow$
g) K_3PO_4
h) $Cr_2(SO_4)_3$
i) $NaNO_3$
j) CH_3COONH_4

4. a) $NaClO + H_2SO_4 \rightarrow$
b) $CrCl_3 + NaOH \rightarrow$
c) $KHSO_3 + KOH \rightarrow$
d) $Fe(OH)_3 + HNO_3 \rightarrow$
e) $CaCO_3 + HCl \rightarrow$
f) NaI
g) $Cr_2(CO_3)_3$
h) Na_2S;
i) $Fe(NO_3)_3$
j) $KClO$

5. a) $H_2SO_4 + NaOH \rightarrow$
b) $(NH_4)_3PO_4 + H_2SO_4 \rightarrow$
c) $Cu(SO_4)_2 + KOH \rightarrow$
d) $AgNO_3 + NaBr \rightarrow$
e) $ZnSO_4 + Na_2CO_3 \rightarrow$
f) $FeCl_3$
g) $NaBr$
h) $Al_2(SO_4)_3$
i) Na_2SO_3
j) $MgSO_4$

6. a) $Ca(OH)_2 + HCl \rightarrow$
b) $NH_4Cl + Ba(OH)_2 \rightarrow$
c) $Na_2SO_3 + H_2SO_4 \rightarrow$
d) $AlI_3 + AgNO_3 \rightarrow$
e) $KHCO_3 + HNO_3 \rightarrow$
f) $LiNO_2$
g) $NiSO_4$
h) NaI
i) Cr_2S_3
j) K_2CO_3

7. a) $(NH_4)_2SO_4 + KOH \rightarrow$
b) $NiSO_4 + Na_2S \rightarrow$
c) $Pb(NO_3)_2 + MgI_2 \rightarrow$
d) $CdS + HCl \rightarrow$
e) $Zn(NO_3)_2 + NaOH \rightarrow$
f) $Cr_2(SO_3)_3$
g) CH_3COONa
h) $CoBr_2$
i) KNO_3
j) NH_4Cl

8. Determine the constant and the degree of hydrolysis, and the pH for a 0.1 M solution of potassium hydrogen phosphate (K_2HPO_4).

9. Calculate the constant and the degree of hydrolysis, and the pH for a 0.05 M solution of sodium sulfide.

10. Determine the constant and the degree of salt hydrolysis in a solution and the dissociation constant of ammonium hydroxide, if the pH of a 0.1 M ammonium chloride solution is equal to 5.1.

11. Calculate the constant and the degree of salt hydrolysis in a solution and the dissociation constant of formic acid if the pH of a 0.1 M solution of sodium formate is 8.3.

12. Determine the constant and the degree of salt hydrolysis in a solution and the dissociation constant of hypochlorous acid if the pH of a 0.1 *M* solution of sodium hypochlorite is 10.1.

In tasks 13–22, determine the coefficients in oxidation-reduction reactions according to the ion-electron balance method.

13. a) $KMnO_4 + MnSO_4 + H_2O \rightarrow MnO_2 + K_2SO_4 + H_2SO_4$
    b) $C + HNO_3 \rightarrow CO_2 + NO_2 + H_2O$
    c) $K_2Cr_2O_7 + HBr \rightarrow Br_2 + KBr + CrBr_3 + H_2O$
    d) $Cl_2 + KOH \rightarrow KClO_3 + KCl + H_2O$
    e) $KNO_2 + KI + H_2SO_4 \rightarrow NO + I_2 + K_2SO_4 + H_2O$

14. a) $KMnO_4 + NaBr + H_2SO_4 \rightarrow MnSO_4 + Br_2 + K_2SO_4 + Na_2SO_4 + H_2O$
    b) $SO_2 + Br_2 + H_2O \rightarrow H_2SO_4 + HBr$
    c) $CrCl_3 + NaClO + NaOH \rightarrow Na_2CrO_4 + NaCl + H_2O$
    d) $Si + KOH + H_2O \rightarrow K_2SiO_3 + H_2$
    e) $Ca + HNO_3 \rightarrow Ca(NO_3)_2 + N_2O + H_2O$

15. a) $KMnO_4 + K_2SO_3 + KOH \rightarrow K_2MnO_4 + K_2SO_4 + H_2O$
    b) $NO_2 + H_2O \rightarrow HNO_3 + HNO_2$
    c) $Na_2SnO_2 + Cl_2 + NaOH + H_2O \rightarrow Na_2[Sn(OH)_6] + NaCl$
    d) $K_2Cr_2O_7 + CO + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + CO_2 + K_2SO_4 + H_2O$
    e) $Sn + HNO_3 + H_2O \rightarrow H_2SnO_3 + NO$

16. a) $K_2Cr_2O_7 + NaNO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Na_2SO_4 + K_2SO_4 + H_2O$
    b) $MnO_2 + KBr + H_2SO_4 \rightarrow Br_2 + MnSO_4 + K_2SO_4 + H_2O$
    c) $I_2 + Ba(OH)_2 \rightarrow Ba(IO_3)_2 + BaI_2 + H_2O$
    d) $N_2H_4 \rightarrow N_2 + NH_3$
    e) $SnCl_2 + HgCl_2 + HCl \rightarrow Hg + H_2[SnCl_6]$

17. a) $Cr(NO_3)_3 + PbO_2 + HNO_3 \rightarrow H_2Cr_2O_7 + NO_2 + Pb(NO_3)_2 + H_2O$
    b) $S + Cl_2 + H_2O \rightarrow HCl + H_2SO_4$
    c) $KMnO_4 + K_2S + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + S + H_2O$
    d) $MnO_2 + O_2 + KOH \rightarrow K_2MnO_4 + H_2O$
    e) $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$

18. a) $K_2Cr_2O_7 + NaSO_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Na_2SO_4 + K_2SO_4 + H_2O$
    b) $PH_3 + KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + H_3PO_4 + H_2O$
    c) $ClO_2 + Ba(OH)_2 \rightarrow Ba(ClO_2)_2 + Ba(ClO_3)_2 + H_2O$
    d) $K_2[Sn(OH)_4] + Bi(NO_3)_3 + KOH \rightarrow K_2[Sn(OH)_6] + Bi + KNO_3$

e) $K_2Cr_2O_7 + H_2O_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + O_2 + K_2SO_4 + H_2O$

19. a) $KMnO_4 + K_2HPO_3 + KOH \rightarrow K_2MnO_4 + K_3PO_4 + H_2O$
b) $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$
c) $HClO_4 + SO_2 + H_2O \rightarrow H_2SO_4 + HCl$
d) $KBrO \rightarrow KBrO_3 + KBr$
e) $S + NaOH \rightarrow Na_2SO_3 + Na_2S + H_2O$

20. a) $Mn(OH)_2 + Cl_2 + KOH \rightarrow MnO_2 + KCl + H_2O$
b) $CuS + HNO_3 \rightarrow Cu(NO_3)_2 + H_2SO_4 + NO + H_2O$
c) $KMnO_4 + Na_3AsO_3 + H_2O \rightarrow MnO_2 + Na_2AsO_4 + KOH$
d) $HClO_3 \rightarrow HClO_4 + ClO_2 + H_2O$
e) $K_2Cr_2O_7 + (NH_4)_2S + H_2SO_4 \rightarrow S + Cr_2(SO_4)_3 + K_2SO_4 + (NH_4)_2SO_4 + H_2O$

21. a) $SO_2 + H_2AsO_4 + H_2O \rightarrow H_2AsO_3 + H_2SO_4$
b) $MnO_2 + KI + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + I_2 + H_2O$
c) $MnSO_4 + KClO_3 + KOH \rightarrow K_2MnO_4 + KCl + K_2SO_4 + H_2O$
d) $Na_2Cr_2O_7 + NaNO_2 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Na_2SO_4 + NaNO_3 + H_2O$
e) $P + HNO_3 + H_2O \rightarrow H_3PO_4 + NO$

22. a) $Cr_2O_3 + Br_2 + NaOH \rightarrow Na_2CrO_4 + NaBr + H_2O$
b) $HNO_2 \rightarrow HNO_3 + NO + H_2O$
c) $KMnO_4 + HCl \rightarrow MnCl_2 + KCl + Cl_2 + H_2O$
d) $K_2Cr_2O_7 + Al + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Al_2(SO_4)_3 + K_2SO_4 + H_2O$
e) $P + HClO_3 + H_2O \rightarrow H_3PO_4 + HCl$

Chapter 5. Coordination compounds

5.1 Basics of coordination chemistry

5.1.1 Basic notations

In the middle of the last century, it was discovered that there are compounds in which the element exhibits its usual maximum valency (BF_3, NH_3, H_2O, $CrCl_3$, KCl, etc.). Despite the valence saturation, such compounds can interact with each other and form mixed compounds in which the valency no longer obeys the usual explanation, that is, it is much greater than the maximum possible:

$$BF_3 + HF \rightarrow HBF_4\,.$$

The first compounds were called low or first-order compounds, and the second ones were higher, or second-order or complex compounds.

Swiss chemist Alfred Werner (1866–1919) pioneered in the development of coordination chemistry. In 1913, he received the Nobel Prize for his coordination theory of transition metal-amine complexes. Studying the metal-amine complexes such as $[Co(NH_3)_6Cl_3]$, he recognised the existence of several forms of cobalt-ammonia chloride. These compounds have different colour and other characteristics (Table 5.1). The chemical formula has three chloride ions per mole, but the number of chloride ions that precipitate with Ag^+ ions per formula is not always three.

Table 5.1 Structures of cobalt ammonia complexes as a function of the number of ionised chloride

Solid	Colour	Ionised Cl^-	Complex formula
$CoCl_36NH_3$	Yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_35NH_3$	Purple	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_34NH_3$	Green	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_34NH_3$	Violet	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$

He thought only ionised chloride ions would form a precipitate with silver ion. Table 5.1 illustrates the number of ionised chloride ions per formula. To distinguish ionised chloride from the coordinated chloride, Werner formulated the complex formula, explained the structure of the cobalt complexes, and gave the first definition of complex compounds: **They are compounds which, in an aqueous solution, do not decompose at all into their constituents of particles, or decompose in a very small degree.**

At the suggestion of Werner, any element after saturation of its usual valences can also exhibit additional valence — the coordination, through which the formation of bonds takes place.

The complex compound is formed if one or several molecules or negatively charged ions are attached to a central atom or a complexing agent.

Coordination (complex) is called chemical compounds, which crystalline lattices consist of complex groups formed as a result of the interaction of ions or molecules that can exist independently.

Under the action of ammonia, the complex cations $[Cu(NH_3)_4]^{2+}$ are formed in the water solution of copper (II) sulfate, and the coordination compound $[Cu(NH_3)_4]SO_4$ can be isolated from the aqueous solution. In water, the argentum cyanide, AgCN is marginally soluble, but in the presence of potassium, cyanide easily passes into the solution as a result of the formation of a complex anion $[Ag(CN)_2]^-$. It is possible to isolate the coordination salt $K[Ag(CN)_2]$ from this solution.

The main thing in Werner's theory is the definition of the central structure of coordination compounds. According to this theory, all groups forming part of the coordination compound are in some way placed around the atom of a complexing agent which was called by Werner as the central atom (central ion). In the above-mentioned coordinating compounds $[Cu(NH_3)_4]SO_4$ and $K[Ag(CN)_2]$, the central ions are Cu^{2+} and Ag^+ ions, respectively.

Practically all elements of the periodic system can act as central atoms. The most active complexing agents are platinum metals (Pt, Pd), elements of the families of iron (Fe, Co, Ni), copper (Cu, Ag, Au) and zinc (Zn, Cd, Hg). Cations, which are easy to form coordination compounds, have an incomplete or 18-electron (external) energy level. Alkali and alkaline earth metals exhibit the smallest tendency to complexing.

A common metal complex is $Ag(NH)^+$, formed when Ag^+ ions are mixed with neutral ammonia molecules

$$Ag^+ + 2NH_3 \rightarrow Ag(NH_3)^+ . \qquad (5.1)$$

A complex $Ag(S_2O_3)_2^{3-}$ is formed between silver ions and negative thiosulfate ions:

$$Ag + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-} . \qquad (5.2)$$

The central atoms in the coordination compounds may also be nonmetals, for example boron ($K[BF_4]$), silicon ($K_2[SiF_6]$), phosphorus ($K[PF_6]$), etc.

Molecules, or ions, located around the central atom, are called ligands.

In the compounds $K[Ag(CN)_2]$ and $[Cu(NH_3)_4]SO_4$, ligands are the ammonia molecules and cyanide ions, respectively.

Together with the central atom, the ligands form an internal coordinating sphere. It is a convention to write the formula of a complex or complex ion inside of square brackets, while counter ions are written outside of the brackets. Such writing demonstrates that ligands inside the brackets are bound directly to the metal ion, in the metal's first coordination sphere (inner coordination sphere). Ions written outside of the brackets are assumed to be in the second coordination sphere, and they are not directly bound to the metal.

For example, $[PtCl_2(NH_3)_2]$ is the neutral metal complex where the Pt^{+2} metal is bound to two Cl^- ligands and two NH_3 ligands. If a complex is charged, it is called a complex ion (example, $[Pt(NH_3)_4]^{2+}$ is a complex cation). The formation of a coordination compound with ions of opposite charge (example, $[Pt(NH_3)_4]Cl_2$) stabilises a complex ion.

Neutral Complex: $[CoCl_3(NH_3)_3]$.

Complex Cation: $[CO(NH_3)_6]^{3+}$.

Complex Anion: $[CoCl_4(NH_3)_2]^-$.

Coordination Compound: $K_4[Fe(CN)_6]$.

The charge of a complex ion is determined by the algebraic sum of charges of simple ions which form a complex ion. The total charge of the internal sphere should be equal to the total charge of the external sphere.

An important characteristic of the ligands is their capacity, or dentate, which is determined by the number of places that the ligands occupy in the internal coordination area of the complex. There exist monodentate ligands (F^-, Cl^-, Br^-, I^-, CN^-, H_2O), bidentate (CO_3^{2-}, SO_4^{2-}).

The number, indicating how many ligands are coordinated around the central atom, is called the coordination number (c.n.).

The coordinate number is a variable which depends on the nature of the central atom, the ligands, the external sphere of the compound, the nature of the solvent and the external conditions in which the compound is formed. In different compounds, it ranges from 2 to 12. Compounds with c. n. equal to 2, 4, 6 are widespread, whereas compounds with large c. n. (8 or more) are rare.

The coordination number is often twice as much as the oxidation degree of the complexing agent. For example, if the oxidation degree of the complexing agent is +1, then c. n. = 2, etc.

The geometry and arrangement of ligands around the metal centre affect the properties of coordination compounds. Compounds with the same molecular formula can appear as isomers with very different properties. Isomers are molecules that have identical chemical formulas but have different arrangements of atoms in space.

Isomers with different geometric arrangements of ligands are called geometric isomers.

Isomers, whose structures are mirror images of each other, are called optical isomers.

5.1.2 Classification of complex compounds

Complex compounds are classified by charge sign, ligand nature and coordination number.

1. Based on a charge sign of a complex ion, one can distinguish:

- Cationic compounds if the charge of the internal sphere is positive: $[Cr(H_2O)_6]Cl_3$, $[Ag(NH_3)_2]NO_3$.
- Anionic compounds if the charge of the internal sphere is negative: $K_4[Fe(CN)_6]$, $K_2[AgI_4]$.
- Neutral compounds if the internal sphere is uncharged: $[Pt(NH_3)_2Cl_2]$.
- Bicomplexes, where both anion and cation are complexes, are more complicated: $[Co(NH_3)_6][Fe(CN)_6]$.

2. Based on the nature of the ligands, one can distinguish homogeneous and heterogeneous complexes. If the composition of the inner sphere includes the same ligands, then the complex compound is homogeneous. If the composition includes different ligands, such a compound is heterogeneous.

$[Cr(H_2O)_5Cl]Cl_2$ — pentaaquachlorochromium (III) chloride — homogeneous

Homogeneous complexes containing water as a ligand are called aqua complexes, ammonia – ammonia, anions of various acids — acid compounds, hydroxide anions – hydroxocomplexes.

3. By the coordination number of bonds occupied by the ligand, one can distinguish mono-, bi-, tridentate complexes.

5.1.3 Nomenclature of coordination compounds

Structures of coordination compounds can be very complicated, and their names long because the ligands may already have long names.

Coordination complexes have their classes of isomers, different magnetic properties and colours, and various applications (photography, cancer treatment, etc.), so it makes sense that they would have a naming system as well. Since coordination complexes consist of a metal and ligands, their formulas follow the pattern $[\text{Metal Anions Neutrals}]^{\pm\text{Charge}}$, while names are written Prefix Ligands Metal(Oxidation State).

According to the Lewis base theory, ligands are Lewis bases since they can donate electrons to the central metal atom. The metals, in turn, are Lewis acids since they accept electrons. Coordination complexes consist of a ligand and a metal centre cation. The overall charge can be positive, negative, or neutral. Coordination compounds are complex or contain complex ions, for example:

Complex cation: $[CO(NH_3)_6]^{3+}$.

Complex anion: $[CoCl_4(NH_3)_2]^-$.

Neutral complex: $[CoCl_3(NH_3)_3]$.

Coordination compound: $K_4[Fe(CN)_6]$.

A ligand can be an anion or a neutral molecule that donates an electron pair to the complex (NH_3, H_2O, Cl^-). The number of ligands that attach to a metal depends on whether the ligand is monodentate, bidentate, or polydentate. To begin naming coordination complexes, here are some things to keep in mind.

1. Ligands are named first in alphabetical order.
2. The name of the metal comes next.
3. The oxidation state of the metal follows, and it is noted by a Roman numeral in parentheses (II, IV).

The names of complexes start with the ligands, the anionic ones first, followed with neutral ligands and the metal. If the complex is negative, the name ends with "ate". At the very end are located Roman numerals representing the oxidation state of the metal.

$[Co(NH_3)_5Cl]Cl_2$, Chloropentaamminecobalt (III) chloride.
$[Cr(H_2O)_4Cl_2]Cl$, Dichlorotetraaquochromium (III) chloride.
$K[PtCl_3NH_3]$, Potassiumtrichloroammineplatinate (II).
$PtCl_2(NH_3)_2$, Dichlorodiammineplatinum.
$Co(en)_3Cl_3$, tris(ethylenediamine)cobalt (III) chloride.

A bridging ligand is indicated by placing an m- before its name. The m- should be repeated for every bridging ligand. For example, $[(H_3N)_3Co(OH)_3Co(NH_3)](NO_3)_3$, triamminecobalt(III)-m-trihydroxo triamminecobalt(III) nitrate

The following rules are applied to name complex compounds.

Rule 1: anionic ligands

Ligands that act as anions which end in "-ide" are replaced with an ending "-o" (e.g., Chloride → Chloro). Anions ending with "-ite" and "-ate" are replaced with endings "-ito" and "-ato" respectively (e.g., Nitrite → Nitrito, Nitrate → Nitrato).

Table 5.2 Anionic monodentate ligands

Molecular Formula	Ligand Name	Molecular Formula	Ligand Name
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC^-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato
O_2^-	Peroxo	CO_3^{2-}	Carbonato
N_3^-	Axido	S^{2-}	Sulfido
N^{3-}	Nitrido	$-(CH_2-N(CH_2COO^-)_2)_2$	ethylenediaminetetraacetato (EDTA)
NH_2^-	Amido	CH_3COO^-	Acetato

Rule 2: neutral ligands

Most neutral molecules that are ligands carry their standard name.

The few important exceptions are as follows:

H_2O: aqua

NH_3: ammine (not two m's, the amine is for organic compounds; amines are a class of organic nitrogen-containing compounds)

CO: carbonyl

NO: nitrosyl

A few selected examples of normal names that will not change are shown in Table 5.4.

Table 5.3 Select neutral monodentate ligands

The molecular formula of ligand	Ligand name
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine
$NH_2CH_2CH_2NH_2$	Ethylenediamine
$C_5H_4N\text{-}C_5H_4N$	Dipyridyl
$P(C_6H_5)_3$	Triphenylphosphine
$NH_2CH_2CH_2NHCH_2CH_2NH_2$	Diethylenetriamine

Polydentate ligands follow the same rules for anions and neutral molecules.

Table 5.4 Select polydentate ligands

Short name	Extended name
en	Ethylenediamine
ox^{2-}	Oxalato
$EDTA^{4-}$	Ethylenediaminetetraacetato

Rule 3: ligand multiplicity

A Greek prefix indicates the number of ligands present in the complex: mono-, di- (or bis), tri-, tetra-, penta-, hexa, hepta-, octa-, nona-, (ennea-), deca- etc. for 1, 2, 3, ... 10 etc. The exceptions are polydentates that have a prefix already in their name (en and $EDTA^{4-}$ are the most common). When indicating how many of these are present in a coordination complex, put the ligand's name in parentheses and use bis, tris, and tetrakis.

Table 5.5 Prefixes for indicating several ligands in a complex

Number of ligands	Monodentate ligands	Polydentate ligands
1	mono	–
2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	–
6	hexa	–

Prefixes always go before the ligand name; they are not taken into account when putting ligands in alphabetical order. Note that "mono" often is not used. For example, $[FeCl(CO)_2(NH_3)_3]^{2+}$ would be called triamminedicarbonylchloroiron (III) ion.

Remember that ligands are always named first before the metal is.

Rule 4: metals

When naming the metal centre, you must know the formal metal name and the oxidation state. To show the oxidation state, we use Roman numerals inside the parenthesis. For example, chromium has the oxidation state of +3. Therefore, it will have the numeral (III) after its name. Copper, with an oxidation state of +2, is denoted as copper (II). If the overall coordination complex is an anion, the ending "-ate" is attached to the metal centre. Some metals also change to their Latin names in this situation. Copper +2 will change into cuprate (II). The following metals change to their Latin names when they compose a part of an anion complex:

Table 5.6 Latin terms for select metal ion

Transition metal	Latin in complex anions
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

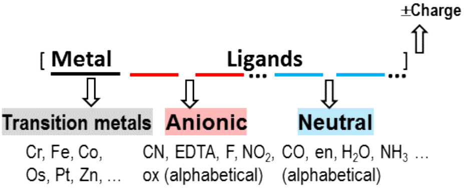
The rest of the metals have -ate added to the end (cobaltate, nickelate, zincate, osmate, cadmate, platinate, mercurate, etc. Note that the -ate tends to replace -um or -ium, if present).

Finally, when a complex has an overall charge, "ion" is written after it. Such writing is not necessary if it is neutral or part of a coordination compound.

Note when naming a coordination compound, it is important that you name the cation first, then the anion. You base this on the charge of the ligand. Think of NaCl. Na, the positive cation, comes first and Cl, the negative anion, follows.

Formulas of coordination complexes

The formula of a coordination complex is written in a different order than its name. The chemical symbol of the metal centre is written first. The ligands are written next, with anion ligands coming before neutral ligands. If there is more than one anion or neutral ligand, they are written in alphabetical order according to the first letter in their chemical formula.



In a coordination compound's name, when one of the ions is just an element, the number of atoms is not indicated with a prefix. Since it still has to be written in the formula, it is determined by balancing the overall charge of the compound. (For example, tetrafluorochromium (VI) chloride becomes $[CrF_4]Cl_2$.

5.1.4 Chemical bonding in complex compounds

In complex compounds, the donor-acceptor interaction and the electrostatic interaction between a complexing agent and ligands are displayed. Very often, both types of forces take part in the formation of complex compounds.

Several theories explain the formation of chemical bonding in complex compounds. We will consider the method of valence bonds. According to this method, the formation of complex compounds occurs due to donor-acceptor interaction.

Ligands are donors and give an indivisible pair of electrons to the formation of a bond. The complexing agent is an acceptor of electrons, receiving them on one of the free valence orbitals.

The orbitals of the central atom, which participate in the formation of the bond, are hybridised. The form of the hybridised orbital depends on two factors, namely the type of orbital of a central atom participating in bonding and the coordination number of a complexing agent.

1) $[Cu(NH_3)_2]Cl$ — sp hybridisation, linear molecule; 4s and 4p orbitals are vacant in Cu.

2) $[Zn(NH_3)_4]Br_2$ — sp^3 hybridisation, tetrahedral molecule.

3) $K_2[Ni(CN)_4]$ — dsp^2 hybridisation, square shape; the electronic configuration of Ni^{2+} is $3d^84s^0$, vacant orbitals are one 3d orbital, 4s and 4p orbitals.

4) $[Co(NH_3)_6](NO_3)_3$ – d^2sp^3 hybridisation, octahedron shape;

5) $Na_3[CoF_6]$ — sp^3d^2 hybridisation, octahedron shape.

The difference in the field that runs around the ligand is essential. There are ligands of strong and weak fields. A so-called spectrochemical series of ligands are known where the ligands are located in the descending order of the value of an induced field:

$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < SCN^- < NH_3 < En < NO_2^- < CN^- < CO$

Being Lewis bases (those who donate electrons), the ligands with less electronegativity will be stronger. Therefore, in general halogen or oxygen donors (H_2O and all others left-of-centre in the spectrochemical series) are usually considered as weak field ligands; the ones in which carbon or nitrogen atom is the donor (SCN^- and others to the right hand) are strong field ligands.

5.1.5 Stability of complex compounds

In aqueous solutions, complex compounds dissociate as strong electrolytes into the inner and outer spheres:

$[Ag(NH_3)_2]Cl \rightarrow [Ag(NH_3)_2]^+ + Cl^-$;

$K_3[Fe(CN)_6] \rightarrow 3K^+ + [Fe(CN)_6]^{3+}$.

The internal sphere behaves as a weak electrolyte and decomposes in a solution to the constituents in a very small degree. The process of dissociation of the internal sphere is written as a reversible process:

$[Ag(NH_3)_2]^+ \leftrightarrow Ag^+ + 2NH_3$;

$[Fe(CN)_6]^{3-} \leftrightarrow Fe^{3+} + 6CN^-$.

Since this process is reversible, then it can be characterised by an equilibrium constant, which in this case is called the constant of instability K_{in}

$$K_{in} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)^+]} = 10^{-8} .$$

The instability constant K_{in} characterises the stability of complex compounds. It does not depend on the concentration of a complex, the concentration of its constituent components, but depends on the nature of the complex and the temperature.

The smaller the value of K_{in}, the more stable the complex is. The values of K_{in} are listed in reference books.

In addition to the instability coefficient, a reciprocal value, the stability coefficient of a complex, K_{st}, can be used. If metal ion (M^{n+}) combines with ligand (L) to form complex ML_n, then

$$M + nL \leftrightarrow ML_n\ ; \tag{5.3}$$

$$K_{st} = \frac{[ML_n]}{[M][L]^n}\ . \tag{5.4}$$

If we know the values of $[M]$, $[L]$ and $[ML_n]$, the value of stability constant K_{st}, (or formation constant) of the complex can be calculated.

In summary

The key concepts, definitions, laws and formulas:

1. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands. A coordination compound contains one or more metal complexes.

2. Ligands (or additives) are molecules or negatively charged ions that attach to the central atom

3. The complexing agent with the ligands forms an inner sphere, which is separated by square brackets when writing the compound formula. Ions not located in the inner sphere compose the outer sphere of the coordination compound.

4. The stability of complex compounds is characterised by a constant of instability (or its reverse value known as a stability constant).

5. By the sign of the charge of a complex ion, complexes are divided into cationic, anionic and neutral for compounds with positively, negatively charged and neutral inner spheres, respectively.

6. The charge of a complex ion is determined by the algebraic sum of charges of simple ions which form a complex ion. The total charge of the internal sphere is equal to the total charge of the external sphere.

7. Coordination number (c.n.) shows how many ligands coordinate around the central atom. The value of c.n. is often twice the degree of oxidation of the central atom.

8. The instability constant of complex compounds, as well as the stability constant, do not depend on the concentration of the complex and its constituent components but depends on the nature of the complex and the temperature. The smaller the K_{in}, the more stable the complex.

9. The stability constant K_{st} is the inverse of the instability constant K_{in}: $K_{in} = 1/K_{st}$. The higher value of stability constant corresponds to the higher concentration of the complexing agent in solution under the equilibrium condition.

10. The dissociation of complex compounds occurs stepwise: each stage is characterised by its K_{in}. The product of the values of K_{in} on all stages gives the total K_{in} of the compound: $K_{in} = K_{in1} \cdot K_{in2} \cdot K_{in3} \cdot K_{ini}$

Necessary practical skills:

1. To write formulas of complex compounds by names and name complex compounds by their formulas.
2. To work out the equations of primary and secondary dissociation of complex compounds, as well as with the use of instability constants.
3. To work out the equations of exchange reactions of complex compounds with solutions of salts.
4. To compile molecular and ionic equations for the formation of complex compounds and their destruction by the addition of appropriate reagents.

5.2 Isomers

There are several types of isomerism frequently encountered in coordination chemistry. Isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another are called structural (or constitutional) isomers. In stereoisomers, molecular bonds are always in the same order, and only spatial arrangement differs.

For inorganic complexes, there are two types of stereoisomers: geometric and optical (see Sections 5.2.1–5.2.5) and three types of structural isomers: ionisation, coordination, and linkage (see 5.2.6, 5.2.7).

Structural isomers, as their name implies, differ in their structure or bonding, which are separate from stereoisomers that differ in the spatial arrangement of the ligands attached, but still, have the same bonding properties.

The different chemical formulas in structural isomers are caused either by a difference in what ligands are bonded to the central atoms or how the individual ligands are bonded to the central atoms.

When determining a structural isomer, you look at: (i) the ligands that are bonded to the central metal, and (ii) which atom of the ligands attached to the central metal.

5.2.1 Optical isomers in inorganic complexes

Optical isomers are related as non-superimposable mirror images and differ in the direction with which they rotate plane-polarised light. These isomers are referred to as enantiomers or enantiomorphs of each other, and their non-superimposable structures are described as being asymmetric.

Optical activity refers to whether or not a compound has optical isomers. A coordinate compound that is optically active has optical isomers, whereas optically inactive compounds do not have optical isomers. Optical isomers have the unique property of rotating light.

A polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarised light through an optically active substance (Fig. 5.1). Some chemical substances are optically active. When light from source #1 is shot through a polarimeter, optical isomers can rotate the light, so it comes out in a different direction on the other end.

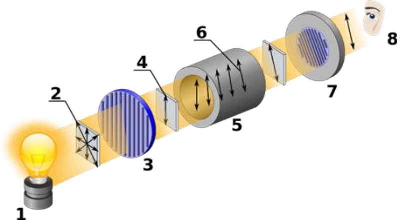


Figure 5.1 Schematic of a polarimeter showing the principles behind its operation

Polarised (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the angle of rotation. The angle of rotation is known as an observed angle.

Unpolarised light (shown as #2 in Fig. 5.1) is passed through a polarising filter (#3 in Fig. 5.1) before travelling through a sample. The polarizer allows only those light waves which move in a single plane, as is shown by #4. Such a change causes the light to become plane polarised.

When the analyser (#7 – in fact, it is a rotatable polarizer) is also placed in a similar position, it allows the light waves coming from the polarizer to pass through it. When it is rotated through the right angle, no waves can pass through the right angle, and the field appears to be dark. The blackest position after polarizer #7 is when the optical axes of both polarizers are perpendicular.

If now a polarimeter glass tube (#5) contains an optically active substance in a solution, this substance causes the plane of polarised light to rotate through a certain angle as is schematically shown by #6. As a result, some light will be detected by the analyser #7.

Then the lens of the analyser #7 is rotated until no light goes through its lens. The rotation angle is then measured to determine the optical rotation caused by the active solution in tube #5.

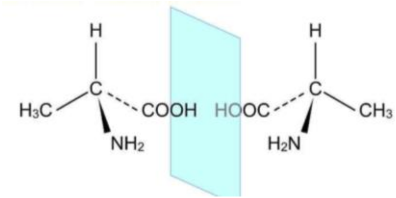
There are two methods for determining optical isomers: using mirror images or using planes of symmetry.

Optical isomers do not exhibit symmetry and do not have identical mirror images. A mirror image of an object is that the object flipped or the way the object would look in front of a mirror. For example, the mirror image of your left hand would be your right hand. Symmetry, on the other hand, refers to when an object looks exactly the same when sliced in a certain direction with a plane. For example, imagine the shape of a square. No matter in what direction it is sliced, the two resulting images will be the same.

Method 1: the mirror image method

The mirror image method uses a mirror image of the molecule to determine whether optical isomers exist or not. If the mirror image can be rotated in such a way that it looks identical to the original molecule, then the molecule is said to be superimposable and has no optical isomers. Otherwise, if the mirror image cannot be rotated in any way such that it looks identical to the original molecule, then the molecule is said to be non-superimposable, and the molecule has optical isomers.

Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another. Therefore, no matter how the structure is rotated, it cannot be placed on top of another with all points matching. An example of this is your hands. Both left and right hands are identical, but they cannot be put on top of each other with all points matching. The examples, which contain bidentate ligands, are ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$.



One more example is alanine, an α-amino acid that is used in the biosynthesis of proteins. Two optical isomers of alanine are mirror images of each other. No matter how you rotate the molecules.

It is impossible to superimpose them on top of each other. In other words, there is no way of rotating the second isomer in space so that it looks exactly the same as the first one.

Method 2: the plane of symmetry method.

The plane of symmetry method uses symmetry to identify optical isomers. In this method, one tries to see if such a plane exists, which, when cutting through the coordinate compound, produces two exact images. In other words, one looks for the existence of a plane of symmetry within the coordinate compound. If a plane of symmetry exists, then no optical isomers exist. On the other hand, if there is no plane of symmetry, the coordinate compound has optical isomers. Furthermore, if a plane of symmetry exists around the central atom, then that molecule is called achiral, but if a plane of symmetry does not exist around the central molecule, then that molecule has a chiral centre.

Nomenclature of optical isomers

Various methods have been used to denote the absolute configuration of optical isomers such as R or S, Λ or Δ, or C and A. The IUPAC rules suggest that for general octahedral complexes C/A scheme is convenient to use. Then, for bis and tris bidentate complexes, the absolute configuration is designated by Lambda Λ (left-handed) and Delta Δ (right-handed).

Priorities are assigned for mononuclear coordination systems based on the standard sequence rules developed for enantiomeric carbon compounds by Cahn, Ingold and Prelog (named for organic chemists Robert Sidney Cahn, Christopher Kelk Ingold, and Vladimir Prelog) or CIP rules. These rules use the coordinating atom to arrange the ligands into a priority order such that the highest atomic number gives the highest priority number (smallest CIP number). Thus, the hypothetical complex $[Co\ Cl\ Br\ I\ NH_3\ NO_2\ SCN]^{2-}$ would assign the I as 1, Br as 2, Cl as 3, SCN as 4, NO_2 as 5 and NH_3 as 6.

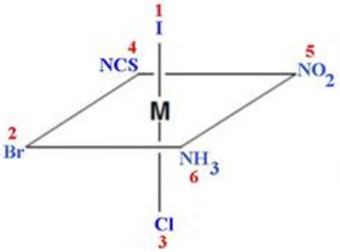
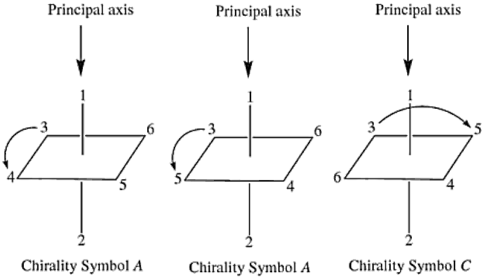


Figure 5.2 One isomer where I and Cl, and Br and NO_2 were found to be *trans*-to each other

The reference axis for an octahedral centre is that axis containing the ligating atom of CIP priority 1 and the *trans* ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared.



The structure is assigned the symbol C or A, according to whether the clockwise (C) or anticlockwise (A) sequence is lower at the first point of difference. In the example shown in Fig. 5.2, this would be C.

The two optical isomers of $[Co(en)_3]^{3+}$ have identical chemical properties and just denoting their absolute configuration does not give any information regarding the direction in which they rotate plane-polarised light (Fig. 5.3). The tris(ethylenediamine)Co(III) complex exists as optical isomers. The Λ- and Δ-forms are non-superimposable mirror images of each other. The difference between isomers can only be determined from measurement, and then the isomers are further distinguished by using the prefixes (–) and (+) depending on whether they rotate left or right. The left-handed (Λ)-$[Co(en)_3]^{3+}$ isomer gives rotation to the right and therefore corresponds to the (+) isomer.

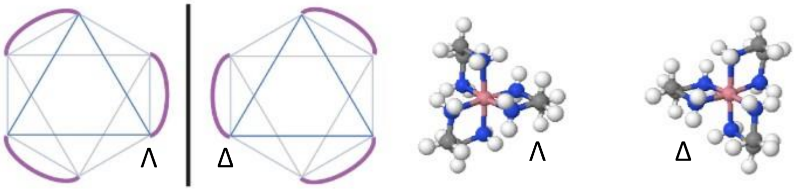


Figure 5.3 Optical isomers (left-handed Λ and right-handed Δ) of $[Co(en)_3]^{3+}$

For tetrahedral complexes, R and S would be used in a similar method to tetrahedral carbon species, and although it is predicted that tetrahedral complexes with four different ligands should be able to give rise to optical isomers, in general, they are too labile and cannot be isolated.

5.2.2 Enantiomers in octahedral complexes with bidentate ligands

Enantiomers are another kind of isomers that occur in octahedral metal complexes. One example of a type of octahedral compounds that can form enantiomers is bidentate complexes. In bidentate complexes (from the Greek two teeth) or chelating complexes (from the Greek crab), a ligand binds very tightly to the metal because it holds onto the metal via more than one atom. Ethylenediamine is one example of a bidentate ligand (Fig. 5.4).

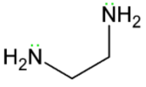


Figure 5.4 Ethylenediamine (sometimes abbreviated en)

In an octahedral complex, the two donor atoms in a bidentate ligand bind *cis* to each other. They cannot reach all the way around the molecule to bind *trans* to each other.

The spatial relationship between the metal and the two atoms connected to it from the same ligand forms a plane. If more than one bidentate ligand is connected to the metal, the relative orientation of one plane to another creates the possibility of mirror images. A complex containing three bidentate ligands can take on the shape of a left-handed propeller or a right-handed propeller.

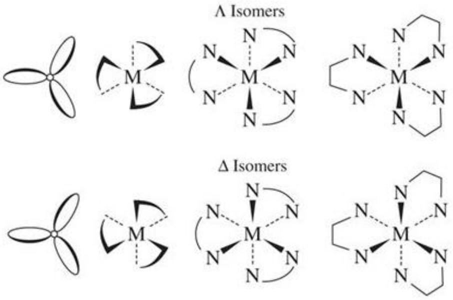


Figure 5.5 A left-handed propeller shape (top – counterclockwise rotation) is seen in Λ isomers. A right-handed propeller (bottom - clockwise) is seen in Δ isomers.

These shapes are alternatively described as a left-handed screw and a right-handed screw. If you can picture turning the shape so that it screws into the page behind it, which direction would you turn the screwdriver? If you would twist the screwdriver clockwise, then you have a right-handed screw. If you would twist the screwdriver counter-clockwise, then you have a left-handed screw.

What do we know about enantiomers?

- Enantiomers usually have identical physical properties,
- enantiomers demonstrate opposite optical rotations.

These kinds of complexes were historically important in demonstrating how small molecules and ions bound to metal cations. By showing that some metal complexes were chiral and displayed optical activity, researchers in the early XX century were able to eliminate some competing ideas about the structures of metal compounds. Today, we know that metal complexes play essential roles in enzymes in biology, and early works of A. Werner on metal complexes laid the background for how we think about these complexes.

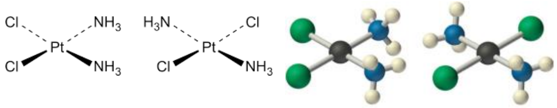
Also, stereochemistry in metal complexes became very important in the late XX century, especially as pharmaceutical companies looked for catalysts that could aid in the production of one enantiomer of a drug, and not the other, to maximise pharmaceutical effectiveness and minimise side effects.

5.2.3 Geometric isomers in cis-platin

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation. The second case occurs when two molecules appear to be connected in the same way on paper but are connected in two different ways in 3D space. These two, different molecules are called stereoisomers.

A straightforward example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $Pt(NH_3)_2Cl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (Fig. 5.6). A ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond. In Fig. 5.6,

The atoms are connected to each other in the same order but differ in their 3D relationships. Left: the *cis*-platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. Right: the *trans*-platin compound is connected in the same way as in *cis*-platin and is still square planar, but there is a different 3D arrangement. Platin is an example of a coordination compound.



Cisplatin

Transplatin

cis-$Pt(NH_3)_2Cl_2$

trans-$Pt(NH_3)_2Cl_2$

Figure 5.6 Two stereoisomers of $Pt(NH_3)_2Cl_2$

For reasons arising from molecular orbital interactions, platin has a square planar geometry at the Pt atom. That arrangement results in two possible ways the ligands could be connected. The two sets of the same ligands could be connected on the same side of the square or opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in 3D space.

The one with the two amines beside each other is called *cis*-platin.

These two ligands are 90 degrees from each other.

The one with the amines across from each other is *trans*-platin.

These two ligands are 180 degrees from each other.

***Cis/ trans* isomers have different physical properties**

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270ºC, but *trans*-platin forms pale yellow crystals and are more soluble than *cis*-platin in water.

***Cis- trans* isomers have different biological properties**

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Inside the cell nucleus, the two ammines in *cis*-platin can be replaced by nitrogen donors from a DNA strand. The DNA molecule must bend slightly to donate to the Lewis acidic platinum. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and cannot be displaced. Thus, it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

5.2.4 Geometric isomers in transition metal complexes

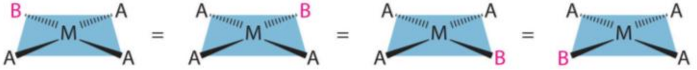
The existence of isomers, coordination compounds with the same formula but different arrangements of the ligands, was crucial in the development of coordination chemistry. Since isomers usually differ in physical and chemical properties, it is important to know which isomer we are dealing with if more than one compound is possible.

Among organic compounds, more than one structure is usually possible for the same molecular formula. Coordination compounds exhibit the same types of isomers as organic compounds, but also several kinds of isomers that are unique.

Planar isomers.

Metal complexes that differ only in which ligands are adjacent to one another (*cis*) or directly across from one another (*trans*) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Since all vertices of a square are equivalent, there is no difference which vertex is occupied by the ligand B in a square planar MA_3B complex. Therefore, only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown below are chemically identical because they can be superimposed simply by rotating the complex in space:



MA_3B square planar complex

There are two isomers for a MA_2B_2 complex: either the A ligands can be adjacent to one another (*cis*), in which case the B ligands must also be *cis*, or the A ligands can be across from one another (*trans*), in which case the B ligands must also be *trans*. As is seen in the scheme below, it is possible to draw the *cis* isomer in four and the *trans* isomer in two different ways. However, all variants are chemically equivalent.

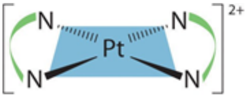
MA_2B_2 square planar complex, *cis* isomer

MA_2B_2 square planar complex, *trans* isomer

Since it is impossible to convert the *trans* structure to the *cis* by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space.

Probably the best-known examples of *cis* and *trans* isomers of a MA_2B_2 square planar complex are anticancer drug *cis*-$Pt(NH_3)_2Cl_2$, also known as *cis*-platin, and *trans*-$Pt(NH_3)_2Cl_2$, which is toxic rather than therapeutic.

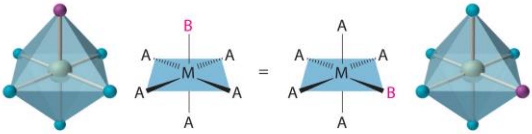
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands.



$[Pt(en)_2]^{2+}$

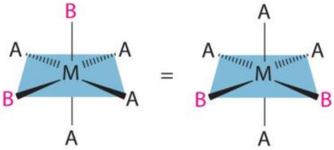
Octahedral isomers.

Octahedral complexes also exhibit *cis* and *trans* isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four “in-plane” ligands are different from the two “axial” ligands, in fact, all six vertices of an octahedron are equivalent. No matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are shown in the scheme on the right side.

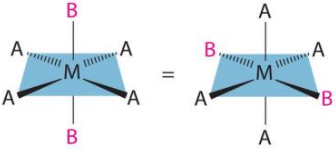


MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving a MA_4B_2 complex, two isomers are possible (see the scheme below). The two B ligands can be *cis* or *trans*. *Cis*- and *trans*-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system

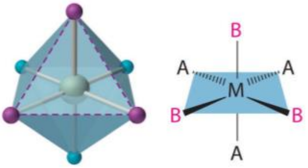


MA_4B_2 octahedral complex, *cis* isomer

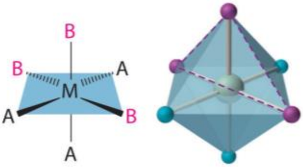


MA_4B_2 octahedral complex, *trans* isomer

Replacing another A ligand by B gives a MA_3B_3 complex for which there are also two possible isomers (see the scheme below).



MA_3B_3 octahedral complex, *fac* isomer



MA_3B_3 octahedral complex, *mer* isomer

In one, called the *fac* isomer (for facial), the three ligands of each kind occupy opposite triangular faces of the octahedron. In the other (the *mer* isomer – for meridional), the three ligands of each type lie on what would be the meridian if the complex were viewed as a sphere.

Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms.

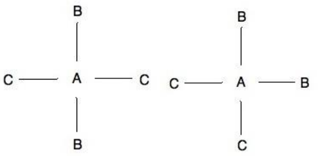
Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion.

Ligands adjacent to one another are *cis*, while ligands across from one another are *trans*.

5.2.5 Stereoisomers of complex metal complexes

Stereoisomers are isomers that have the same molecular formula and ligands but differ in the arrangement of those ligands in 3D space. For example, a molecule with the formula AB_2C_2 has two ways it can be drawn, and it is an example of isomers, specifically *cis-trans* isomers, which will be discussed below.

Isomer 1: Isomer 2:



One thing to remember whenever talking about stereoisomers is that all other options that may come to mind are just rotations of the existing isomers.

For example, a molecule that has both C's on the top right plane and both B's on the bottom left plane is not another isomer. Instead, it is just a 180° rotation of isomer 2.

Stereoisomers are isomers that mainly differ in the way the ligands or atoms are placed relative to the central atom. There are two types of stereoisomers:

i) Geometric isomers that differ in the way the ligand is bound to the metal.

ii) Optical isomers that do not have symmetry and are not superimposable on their mirror images.

In terms of their differences, geometric isomers show much more activity than optical isomers. What this statement means is that optical isomers often display similar properties and do not seem all that different. That is until they react with other optical isomers or when they react with light. One of the main ways optical isomers are detected is their ability to polarise or change the direction of light. Geometric isomers, on the other hand, exhibit different properties from one isomer to another.

Review of molecular geometry

To understand stereoisomers, one must follow all the possible molecular geometries. For stereoisomers, only these geometries will be relevant:

Linear;
Square planar;
Tetrahedral;
Octahedral.

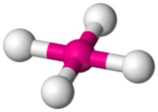
It is also important to remember the coordination number associated with these geometries. Coordination numbers refer to the number of ligands or atoms bound to the central atom. Thus, linear isomer has a coordination number of 2 because it consists of 2 atoms bound to the central atom. Square planar and tetrahedral have a coordination number of 4 while octahedral has a coordination number of 6. These geometries are critical as they dictate whether or not certain isomers exist.

Linear.

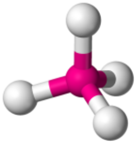
The molecule of xenon difluoride XeF_2 is an example of linear geometry which is shown on the right side.

Square planar.

Square planar is the geometry where the molecule looks like it is a square plane. An example of the molecule xenon tetrafluoride XeF_4 is provided on the right side.



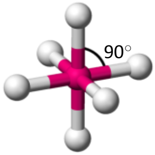
Tetrahedral.



Tetrahedral is the geometry where the molecule looks like a pyramid. An example of the molecule methane CH_4 is provided on the left side.

Octahedral.

Octahedral is the geometry where the bases of two pyramids are stuck together. Otherwise, it can also be thought as to where the centre consists of a square



plane with a ligand sticking out above it and another ligand sticking out below it. An example of the molecule sulfur hexafluoride (SF_6) is provided on the right side.

Sometimes an octahedral molecule may contain polydentate ligands. Polydentate ligands are ligands that "bite" the central atom in several locations. In other words, polydentate ligands can form more than one bond with the central metal, unlike other ligands.

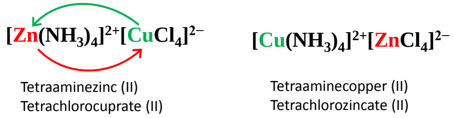
An example of a polydentate ligand is ethylenediamine, a bidentate ligand, which is abbreviated as en.

Applications.

Stereoisomers have many applications in biology. For example, our tongue contains chiral molecules that help us discern the taste of some of the foods we eat. We may eat two of the same leaves, but one may taste bitter, and the other may taste sweet because of chirality. As discussed above, optical isomers also can rotate light in certain directions. In biological terms, chirality is key to the proper functioning of an enzyme because chirality allows the enzyme to function efficiently by being able to bind to only certain substrates.

5.2.6 Coordination isomerism in transition metal complexes

Coordination isomerism occurs in compounds containing complex anionic and cationic parts. It can be considered as occurring by the interchange of some ligands from the cationic part to the anionic one. Hence, there are two complex compounds bound together, one with a negative charge and the other with a positive charge. In coordination isomers, the anion and cation complexes exchange one or more ligands.



5.2.7 Ionisation isomerism in transition metal complexes

Coordination isomerism is a form of structural isomerism in which the composition of the complex ion varies. In a coordination isomer, the total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. Ionisation isomers can be thought of as occurring because of the formation of different ions in solution.

Ionisation isomers are identical except for a ligand has exchanged places with an anion or neutral molecule that was initially outside the coordination complex. The central ion and the other ligands are identical. For example, an octahedral isomer will have five identical ligands, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers are different. As an example, let us consider two isomers, called pentaaquabromocobaltate (II) chloride and pentaaquachlorocobaltate (II) bromide (Fig. 5.7).

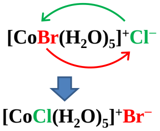


Figure 5.7 Two ionisation isomers. The only difference between isomers consists in which ligands are bound to the centre metal.

The difference between the ionisation isomers can be view within the context of the ions generated when each is dissolved in solution.

For example, when pentaaquabromocobaltate (II) chloride is dissolved in water, Cl^- ions are generated:

$$CoBr(H_2O)_5Cl_{(s)} \rightarrow CoBr(H_2O)^+_{(aq)} + Cl^-_{(aq)}\,, \qquad (5.5)$$

whereas when pentaaquachlorocobaltate (II) bromide is dissolved, Br^- ions are generated:

$$CoCl(H_2O)_5Br_{(s)} \rightarrow CoCl(H_2O)^+_{(aq)} + Br^-_{(aq)}\,. \qquad (5.6)$$

One more example is based on the dissolution of $[PtBr(NH_3)_3]NO_2$ and $[Pt(NO_2)(NH_3)_3]Br$ into an aqueous solution. Two different set of ions will be generated.

Dissolving $[PtBr(NH_3)_3]NO_2$ in an aqueous solution would have the following reaction:

$$[PtBr(NH_3)_3]NO_{2(s)} \rightarrow [PtBr(NH_3)_3]^+_{(aq)} + NO_2{}^-_{(aq)}\,. \qquad (5.7)$$

Dissolving $[Pt(NO_2)(NH_3)_3]Br$ in an aqueous solution would be:

$$[Pt(NO_2)(NH_3)_3]Br_{(s)} \rightarrow [Pt(NO_2)(NH_3)_3]^+_{(aq)} + Br^-_{(aq)}\,. \qquad (5.8)$$

Notice that these two ionisation isomers differ in that one ion is directly attached to the central metal, but the other is not.

Equations (5.7) and (5.8) are valid under the assumption that the platinum-ligand bonds of the complexes are stable (i.e., not labile). Otherwise, they may break, and other ligands (e.g., water) may bind.

Solvate or hydrate isomerisation: a special kind of ionisation isomer.

A hydrate isomer is a specific kind of ionisation isomer where a water molecule is one of the molecules that exchange places.

A very similar type of isomerism results from the replacement of a coordinated group by a solvent molecule (solvate isomerism). In the case of water, this is called hydrate isomerism. The best-known example of this occurs for chromium chloride $CrCl_3 \cdot 6H_2O$, which may contain 4, 5, or 6 coordinated water molecules.

$[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$ — bright-green coloured;

$[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ — grey-green coloured;

$[Cr(H_2O)_6]Cl_3$ — violet coloured.

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution respectively.

In summary

The key concepts, definitions, laws and properties:

1. Complex compounds are characterised by isomerism. Two or more compounds with the same formula but different arrangements of the atoms are called isomers.
2. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible.
3. Hydrate isomerism is characterised by the unequal distribution of water molecules between the inner and outer spheres.
4. Ionisation isomerism consists in a different distribution of anions between inner and outer spheres.
5. Coordination isomerism is associated with a different arrangement of ligands between two complexing agents in a molecule.
6. Spatial isomerism is caused by the different spatial arrangement of ligands of a heterogeneous complex in the same inner sphere.

Necessary practical skills:

1. To distinguish the types of isomers of complex compounds;
2. To recognise the type of isomers by the formulas of compounds; and
3. To predict the change in isomer properties.

5.3 Ligands

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron-pair donors), and the central atom acts as a Lewis acid (electron-pair acceptor). Ligands have at least one donor atom with an electron-pair used to form covalent bonds with the central atom.

The term ligand comes from the Latin word ligare, which means to bind. Ligands can be anions, cations, or neutral molecules. Ligands can be further characterised as monodentate, bidentate, tridentate etc. where the concept of teeth (dent) is introduced, hence the idea of bite angle etc. A monodentate ligand has only one donor atom used to bond to the central metal atom or ion.

5.3.1 Monodentate ligands

The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the centre through only one atom. Some examples of monodentate ligands are: chloride ions (referred to as chloro when it is a ligand), water (referred to as aqua when it is a ligand), hydroxide ions (referred to as hydroxo when it is a ligand), and ammonia (referred to as ammine when it is a ligand).

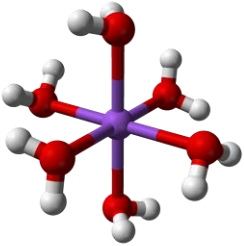


Figure 5.8 Central atom with six monodentate ligands attached

5.3.2 Bidentate ligands

Bidentate ligands have two donor atoms which allow them to bind to a central metal atom or ion at two points. Well-known examples of bidentate ligands are ethylenediamine (en), and the oxalate ion (ox). Shown below is a diagram of ethyle nediamine: the nitrogen (blue) atoms on the edges each have two free electrons that can be used to bond to a central metal atom or ion.

Ethylenediamine (en) is a bidentate ligand that forms a five-membered ring in coordinating to a metal ion M (Fig. 5.9).

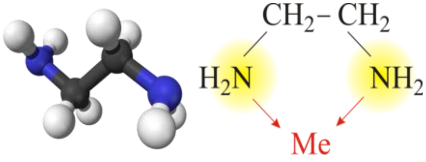


Figure 5.9 Ethylenediamine (en) is an example of a bidentate ligand.

5.3.3 Polydentate ligands

Polydentate ligands range in the number of atoms used to bond to a central metal atom or ion. EDTA, a hexadentate ligand, is an example of a polydentate ligand that has six donor atoms with electron pairs that can be used to bond to a central metal atom or ion.

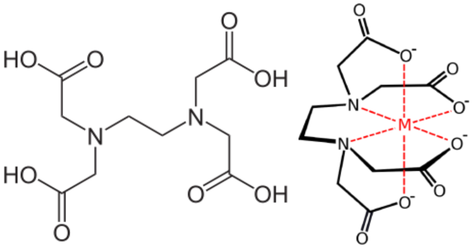


Figure 5.10 Ethylenediamine tetraacetic acid (EDTA) is a hexadentate ligand; it can bind a metal via multiple "teeth": unbound EDTA ion (left) and EDTA bound to a transition metal M (right)

Unlike polydentate ligands, ambidentate ligands can attach to the central atom in two places. A good example of this is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom.

5.3.4 Chelation

Chelation is a process, in which a polydentate ligand is linked to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating (from the Greek chely or chela) agent. The term chelate was first applied in 1920 by English chemists Gilbert T. Morgan (1872–1940) and Harry Dugald Keith Drew (1886–1958). As the name implies, chelating ligands have a high affinity for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands. Both ethylenediamine (Fig. 5.9) and ethylenediaminetetraacetic acid (Fig. 5.10) are examples of chelating agents, but many others are commonly found in the inorganic laboratory.

The chelate effect

The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of similar nonchelating (monodentate) ligands for the same metal.

The macrocyclic effect follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate but because they are covalently constrained to their cyclic form, they allow less conformational freedom.

The ligand is said to be "pre-organised" for binding, and there is little entropy penalty for wrapping it around the metal ion.

For example (Fig. 5.11), heme b is a tetradentate cyclic ligand which strongly attaches transition metal ions, including (in biological systems) Fe^{+2}.

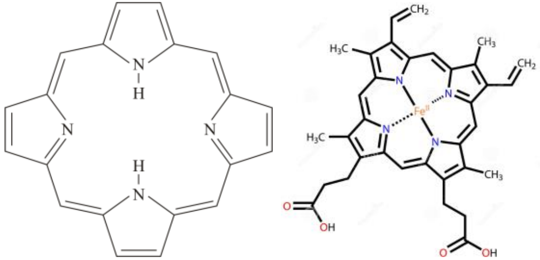
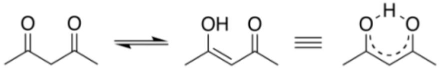


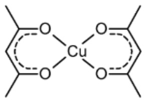
Figure 5.11 A free, unbound porphorin ligand (left) and heme b macrocyclic ligand (right) that binds iron in haemoglobin

Some other common chelating and cyclic ligands are as follows:

Acetylacetonate ($acac^-$, top) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms.

$Acac^-$ is a strong base, so it prefers strong acid cations.





With divalent metal ions, $acac^-$ forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapour deposition (CVD) of thin metal films.

2,2'-Bipyridine (bipy or bpy).

2,2'-Bipyridine and related bidentate ligands such as 1,10-phenanthroline form propeller-shaped complexes with metals such as Ru^{2+} (Fig. 5.12, left). The $[Ru(bpy)_3]^{2+}$ complex is photoluminescent and can also undergo photoredox reactions, making it an attractive compound for both photocatalysis and artificial photosynthesis.

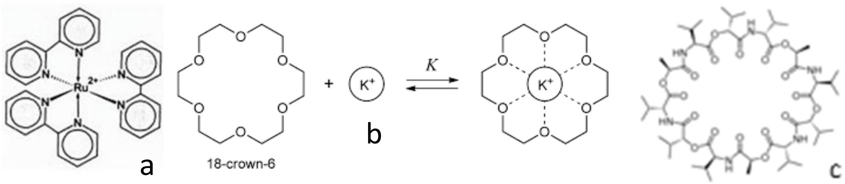


Figure 5.12 Chelate complexing: 2,2'-Bipyridine with Ru (a); 18-crown-6 bpy with K (b); and valinomycin (c)

Crown ethers such as 18-crown-6 2,2'-Bipyridine (Fig. 5.12, centre) are strong cyclic bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.

The chelating properties of crown ethers are mimetic of the natural antibiotic valinomycin (Fig. 5.12, right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a strong cyclic base.

In summary

The key concepts, definitions, laws and formulas:

1. The ligands can be monodentate, bidentate and polydentate.
2. Monodentate ligands connect with the central metal through only one atom
3. Bidentate ligands are those in which two atoms coordinate to the metal centre.
4. Any ligand that binds to a central metal ion by more than one donor atom is a polydentate ligand (or “many teeth”) because it can bite into the metal centre with more than one bond. T
5. When naming a complex ion, the ligands are named before the metal ion.
6. Write the names of the ligands in the following order: neutral, negative, positive. If there are multiple ligands of the same charge type, they are named in alphabetical order. (Numerical prefixes do not affect the order.)
7. Multiple occurring monodentate ligands receive a prefix according to the number of occurrences: di-, tri-, tetra-, penta-, or hexa. Polydentate ligands (e.g., ethylenediamine, oxalate) receive bis-, tris-, tetrakis-, etc.
8. Anions end in -ido. This replaces the final “e” when the anion ends with “-ate” (e.g., sulfate becomes sulfato) and replaces “-ide” (cyanide becomes cyanido).
9. Neutral ligands are given their usual name, with some exceptions: NH_3 becomes ammine; H_2O becomes aqua or aquo; CO becomes carbonyl; NO becomes nitrosyl.

10. Write the name of the central atom/ion. If the complex is an anion, the central atom's name will end in -ate, and its Latin name will be used if available (except for mercury).

11. If the central atom's oxidation state needs to be specified (when it is one of several possible, or zero), write it as a Roman numeral (or 0) in parentheses.

12. End with "cation" or "anion" as separate words (if applicable).

5.4 Problem solving

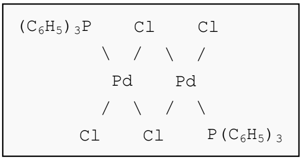
5.4.1 Examples

Example 5.1 Sketch the structures of isomers Co(en)$^{3+}$ complex ion to show that they are mirror images of each other.

If the triangular face of the end-amino group lies on the paper, you can draw lines to represent the en bidentate ligand. These lines will show that the two images are similar to the left-hand and right-hand screws. From the description above, sketch the structures.

Example 5.2 Give the structural formula for chlorotriphenyl phosphinepalladium (II)-m-dichlorochlorotriphenylphosphinepalladium (II).

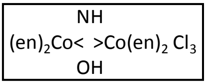
The structure is



Discussion.

How many ionised chloride ions are there per formula?
How many chloride ions act as bridges per formula in this complex?
How many types of chloride ligands are there in this complex?

Example 5.3 Name the complex:



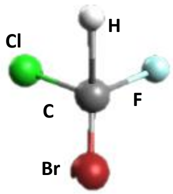
$$\mathrm{(en)_2Co}\begin{matrix}\mathrm{NH}\\ <\quad>\\ \mathrm{OH}\end{matrix}\mathrm{Co(en)_2\,Cl_3}$$

The name is:

Bis(ethylenediamine)cobalt (III)-m-imido-m-hydroxobis(ethylenediamine)cobalt (III) ion.

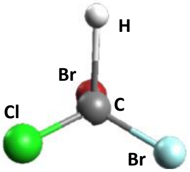
Discussion.

When this compound dissolves in water, is the solution a conductor?
What are the ions present in the solution of this compound?
How many moles of chloride ions are present per mol of the compound?
When potassiumtrichloroammineplatinate (II) dissolves in water, what ions are produced?
What about chloropentaamminecobalt (III) chloride?



Example 5.4 Consider the tetrahedral molecule, CHBrClF (on the left side). Is this molecule optically active? In other words, does this molecule have optical isomers?

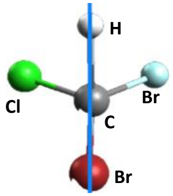
First, take the mirror image method. The mirror image of the molecule is (on the right side):



This mirror image is not superimposable. In other words, the mirror image above cannot be rotated in any such way that it looks identical to the original molecule.

If the mirror image is not superimposable, then optical isomers exist. Thus we know that this molecule has optical isomers.

Let us try approaching this problem using the symmetry method. If we take the original molecule and draw an axis or plane of symmetry down the middle, this is what we get:

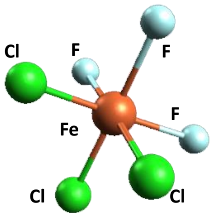


Since the left side is not identical to the right, this molecule does not have a symmetrical centre and thus can be called chiral. Additionally, because it does not have a symmetrical centre, we can conclude that this molecule has optical isomers. In general, when dealing with a tetrahedral molecule that has four different ligands, optical isomers will exist most of the time.

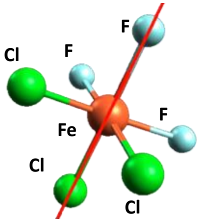
No matter which method you use, the answer will end up being the same.

Optical isomers are because they have no plane of symmetry. In the organic case, for tetrahedral complexes, this is relatively easy to recognise the possibility of this by looking for a centre atom with four different things attached to it. Unfortunately, this is not quite so easy with more complicated geometries.

Example 5.5 Consider the octahedral compound $FeCl_3F_3$ shown on the right side Is this molecule optically active?



Using the mirror image method, we notice that the mirror image is essentially identical to the original molecule. In other words, the mirror image can be placed on top of the original molecule and is thus superimposable. Since the mirror image is superimposable, this molecule does not have any optical isomers.



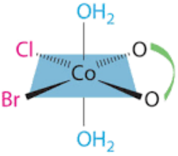
Let us attempt this same problem using the symmetry method. If we draw an axis or plane of symmetry, this is what we get:

Since the left side is identical to the right side, this molecule has a symmetrical centre and is an achiral molecule. Thus, it has no optical isomers

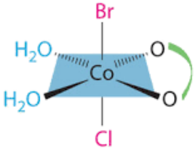
Example 5.6 Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (*cis*) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be *trans*.

Thus either the water ligands can be *trans* to one another, or the two halide ligands can be *trans* to one another, giving the two geometrical isomers shown on the right side:

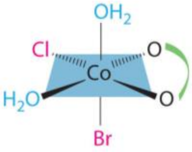


H₂O's *trans*

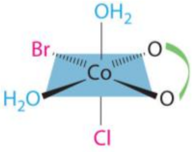


Br, Cl *trans*

Besides, two structures are possible in which one of the halides is *trans* to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and *trans* to one of the oxalate oxygens.



H_2O's *cis*; Br, Cl *cis*;
Cl *trans* to O



H_2O's *cis*; Br, Cl *cis*;
Br *trans* to O

Exchanging the chloride and bromide ligands give the other, in which the bromide ligand is in the same plane as the oxalate ligand and *trans* to one of the oxalate oxygens (see on the left):

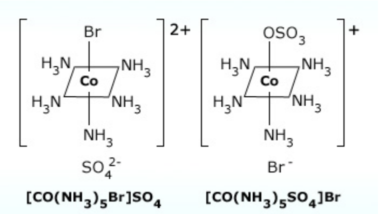
This complex can, therefore, exist as four different geometrical isomers

Example 5.7 Are $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ coordination isomers?

First, we need to confirm that each compound has the same number of atoms of the respective elements (this requires viewing both cations and anions of each compound).

Element	Number of atoms in $[Cr(NH_3)_5(OSO_3)]Br$	Number of atoms in $[Cr(NH_3)_5Br]SO_4$
Cr	1	1
N	5	5
H	15	15
O	4	4
S	1	1
Br	1	1

Now, let us look at what these two compounds look like compounds shown in the picture: $[Co(NH_3)_5(OSO_3)]Br$ (right) and $[Co(NH_3)_5Br]SO_4$ (left) are coordination isomers.



The sulfate group is a ligand with a dative bond to the cobalt atom, and the bromine atom is a counter ion in $[Co(NH_3)_5(OSO_3)]Br$.

For $[Co(NH_3)_5Br]SO_4$, this is the reverse.

$[Co(NH_3)_5(OSO_3)]Br$ and $[Co(NH_3)_5Br]SO_4$ are coordination isomers.

Example 5.8 Are $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$ coordination isomers?

Here, both the cation and anion are complex ions. In the first isomer, NH_3 is attached to Cu and the Cl^- are attached to the platinum. They have swapped in the second case. They are coordination isomers.

Example 5.9 What is one coordination isomer of $[Co(NH_3)_6][Cr(C_2O_4)_3]$?

Coordination isomers involve swapping the species from the inner coordination sphere to one metal (e.g., cation) to the inner coordination sphere of a different metal (e.g., the anion) in the compound. One isomer is completely swapping the ligand sphere, e.g., $[Co(C_2O_4)_3][Cr(NH_3)_6]$.

Alternative coordination isomers are $[Co(NH_3)_4(C_2O_4)][Cr(NH_3)_2(C_2O_4)_2]$ and $[Co(NH_3)_2(C_2O_4)_2][Cr(NH_3)_4(C_2O_4)]$.

Example 5.10 Are $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$ ionisation isomers?

In the first isomer, SO_4 is attached to the cobalt and is a part of the complex ion (the cation), with Br as the anion. In the second isomer, Br is attached to the cobalt as a part of the complex and SO_4 is acting as the anion.

Example 5.11 What is the name of this complex ion: $[CrCl_2(H_2O)_4]^+$?

Let us start by identifying the ligands. The ligands here are Cl and H_2O. Therefore, we will use the monodentate ligand names of "chloro" and "aqua". Alphabetically, aqua comes before chloro, so this will be their order in the complex's name. There are four aqua's and two chloro's, so we will add the number prefixes before the names. Since both are monodentate ligands, we will say "tetra[aqua]di[chloro]".

Now that the ligands are named, we will name the metal itself. The metal is Cr, which is chromium. Therefore, this coordination complex is called tetraaquadichlorochromium (III) ion.

Example 5.12 What is the name of this complex ion: $[CoCl_2(en)_2]^+$?

We take the same approach. There are two chloro and ethylenediamine ligands. The metal is Co, cobalt. We follow the same steps, except that en is a polydentate ligand with a prefix in its name (ethylenediamine), so "bis" is used instead of "bi", and parentheses are added. Therefore, this coordination complex is called dichlorobis(ethylenediamine)cobalt (III) ion

Example 5.13 What is the name of $[Cr(OH)_4]^-$?

Immediately we know that this complex is an anion. There is only one monodentate ligand, hydroxide. There are four hydroxides so that we will use the name "tetrahydroxo". The metal is chromium, but since the complex is an anion, we will have to use the "-ate" ending, yielding "chromate". The oxidation state of the metal is 3 $(x+(-1)4=-1)$. Write this with Roman numerals and parentheses (III) and place it after the metal to get tetrahydroxochromate (III) ion.

Example 5.14 What is the name of $[CuCl_4]^{2-}$?

tetrachlorocuprate (II) ion

Example 5.15 What is the name of $[Pt(NH_3)_4)][Pt(Cl)_4]$?

NH_3 is neutral, making the first complex the positively charged cation. Cl has a -1 charge, making the second complex the anion. Therefore, you will write the complex with NH_3 first, followed by the one with Cl (the same order as the formula). This coordination compound is called tetraammineplatinum (II) tetrachloroplatinate (II).

Example 5.16 What is the name of $[CoCl(NO_2)(NH_3)_4]^+$?

This coordination complex is called tetraamminechloronitrito-N-cobalt (III). N comes before the O in the symbol for the nitrite ligand, so it is called nitrito-N. If an O came first, as in $[CoCl(ONO)(NH_3)_4]^+$, the ligand would be called nitrito-O, yielding the name tetraamminechloronitrito-O-cobalt (III).

Nitro (for NO_2) and nitrito (for ONO) can also be used to describe the nitrite ligand, yielding the names tetraammine chloronitrocobalt (III) and tetraamminechloronitritocobalt (III).

Example 5.17

a. Amminetetraaquachromium (II)
b. Amminesulfatochromium (II)
c. Amminetetraaquachromium (II) sulfate
d. Potassium hexacyanoferrate (III)

Amminetetraaquachromium (II) ion would be written as $[Cr(H_2O)_4(NH_3)]^{2+}$. Both ligands are neutral, so they are ordered alphabetically with H_2O before NH_3. Their order in the formula is the opposite of that in the complex's name since one uses their chemical symbols and the other uses the names of the ligands.

Amminesulfatochromium(II) is written as $[Cr(SO_4)(NH_3)]$. SO_4 is an anion, so it comes before NH_3.

Amminetetraaquachromium(II) sulfate → Try this on your own.

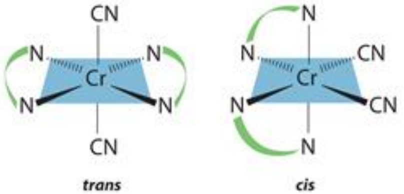
Did you get $[Cr(H_2O)_4(NH_3)]SO_4$? If you did, you are correct.

Potassium hexacyanoferrate (III) → Try this on your own.

Did you get $K_3[Fe(CN)_6]$? Remember to balance the K!

Example 5.18 Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer: Two geometrical isomers are possible: *trans* and *cis*.



5.4.2 Problems

1. How many isomers does the complex $Co(NH_2CH_2CH_2NH_2)_2ClNH_3]^{2+}$ have? Draw the structures of the isomers.

How many isomers does $Co(en)_2Cl_2^+$ have? Sketch the structures of the isomers.

How many isomers does $Co(NH_3)_4Cl_2^+$ have? Sketch the structures of the isomers.

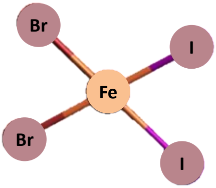
2. Draw the *cis* and *trans* isomers of the following compounds:

a) $(NH_3)_2IrCl(CO)$; b) $(H_3P)_2PtHBr$; c) $(AsH_3)_2PtH(CO)$.

3. Only one isomer of $(tmeda)PtCl_2$ is possible [tmeda = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; both nitrogens connect to the platinum].

Draw this isomer and explain why the other isomer is not possible.

4. Draw all possible geometric isomers for the tetrahedral molecule $MnCl_2F_2$ (with the answer)



5. What type of isomer is the molecule pictured on the right side? Are there any other types of isomers possible for this molecule? (with the answer)

6. Draw all possible stereoisomers for the molecule CrF_3I_3. (with the answer)

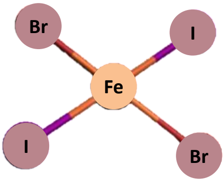
7. What is the difference between a dextrorotatory optical isomer and a laevorotatory optical isomer? (with the answer)

8. Draw the molecule $Fe(en)_3$ and state if it is optically active or not (with the answer)

9. True or false: An octahedral molecule can have *cis-trans* isomers? (with the answer)

Answers

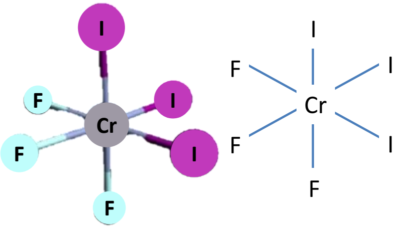
4. $MnCl_2F_2$ has no geometric isomers because tetrahedral molecules do not have geometric isomers.

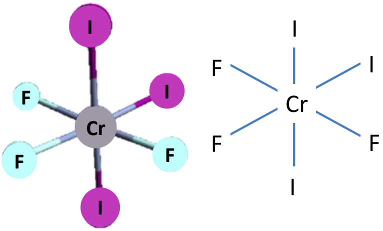


5. The molecule, $FeBr_2I_2$ pictured in problem 5 is a *cis* isomer, or *cis*-$FeBr_2I_2$ because both the Br and I ligands are on the same side. There is one more stereoisomer for this molecule: *trans*-$FeBr_2I_2$, pictured here on the right side:

6. This molecule has two isomers: *mer*-CrF_3I_3 and *fac*-CrF_3I_3, both are pictured below.

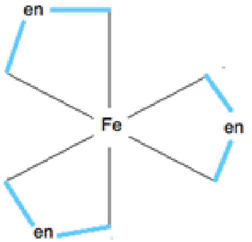
The *mer*-isomer is where the ligands are not on the same plane, and there exists a 90–90–180 degree bond angle between the three identical ligands. The *fac*-isomer is where the ligands are on the same plane, and there exists a 90–90–90 degree bond angle between the three same ligands: *fac*-CrF_3I_3: *mer*-CrF_3I_3:





7. A dextrorotatory optical isomer is an isomer that can rotate light in the right direction. A laevorotatory optical isomer, on the other hand, is an isomer that can rotate light in the left direction.

8. In the molecule $Fe(en)_3$, recall that the en ligand, ethylenediamine is a bidentate ligand.



The 2D structure of this molecule is shown left. Note, the black (thinner) lines represent the bonds, and the blue (wider) lines represent the bonds ethylenediamine binds to.

Using either the symmetry method or the mirror image method, one can observe that this molecule has a chiral centre and that the mirror image is not superimposable on the original molecule. Thus, this molecule is optically active because it has optical isomers.

9. True. Octahedral geometry, as well as square planar geometry, can have *cis-trans* isomers. The only geometry that cannot have cis-trans isomers is tetrahedral.

Chapter 6. Properties of elements

6.1 Overview of periodic trends

The single most important unifying principle in understanding the chemistry of the elements is the systematic increase of the atomic number, which is accompanied by the orderly filling of the atomic orbitals by electrons and leads to the periodicity of such properties as atomic and ionic sizes, ionisation energy, electronegativity, and electron affinity. The same factors also lead to periodic valence electronic configurations, which for each group results in similarities of oxidation states and formation of compounds with common stoichiometry.

The diagonal line, shown in Fig. 6.1, separates metals (to the left of the line) from nonmetals (to the right of the line). Since metals have relatively low electronegativity, they tend to lose electrons in chemical reactions to elements that have relatively high electronegativities, forming compounds in which they have positive oxidation states. Conversely, nonmetals have high electronegativity, and so they seek to obtain electrons in chemical reactions, forming compounds in which they have negative oxidation states. Semimetals (metalloids) lie along a diagonal line separating metals and nonmetals. Not surprisingly, they tend to exhibit properties and reactivity intermediate between the properties of metals and nonmetals. Because the elements of groups 13, 14 and 15 cover a diagonal line separating metals and nonmetals, their chemistry is more complex than expected, based solely on their valence electronic configurations.

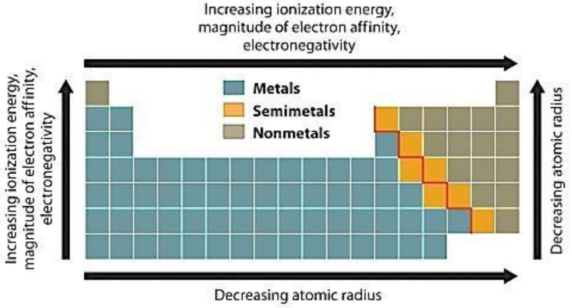


Figure 6.1 Summary of periodic trends in atomic properties

Usually, ionisation energies, electron affinity and electronegativities increase from left to right and from bottom to top. On the contrary, the size of atoms decreases from left to right and from bottom to top. Therefore, the items to the right of the periodic table are the smallest and most electronegative; the elements at the bottom left are the largest and the least electronegative.

Lightest elements

The chemistry of the element of the second period of each group (n = 2: Li, Be, B, C, N, O, and F) differs in many aspects from the chemistry of heaver group members. Therefore, the elements of the third period (n = 3: Na, Mg, Al, Si, P, S, and Cl) are generally more representative of the group to which they belong. The anomalous chemistry of the elements of the second period is the result of three important characteristics: small radii, energetically unavailable d orbitals, and a tendency to form pi (π) bonds with other atoms.

Due to the small radii, the elements of the second period have electronic affinities that are less negative than predicted by general periodic trends. When an electron is added to such a small atom, enhanced electron repulsion tends to destabilise the anion. Moreover, the small size of these elements prevents them from forming compounds in which they have more than four nearest neighbours. Thus, BF_3 forms only a four-coordinate, tetrahedral BF_4^- ion, whereas AlF_3 under the same conditions forms a six-coordinate, octahedral AlF_6^{3-} ion.

Due to the smaller size of the atoms, the simple binary ionic compounds of the second-period elements are also more covalent than the corresponding compounds formed from their heavier congeners. Very small cations derived from the elements of the second period have a high charge-to-radius ratio and can, therefore, polarise the filled valence shell of the anion. The bonding in such compounds has a significant covalent component, providing properties of compounds that can differ significantly from those expected for simple ionic compounds. For example, LiCl, which is partially covalent, is much more soluble than NaCl in solvents with a relatively low dielectric constant, such as ethanol ($\varepsilon = 25.3$ vs 80.1 for H_2O).

Since the d orbitals are never occupied for main quantum numbers less than 3, the valence electrons of the second-period elements occupy only 2s and 2p orbitals. The energy of the 3d orbitals is much higher than the energy of the orbitals 2s and 2p, so their use in bonding is prohibited. Consequently, configurations of electrons with more than four electron pairs around the central element of the second period are not observed. The role of d orbitals in binding in the compounds of elements with coordination numbers 5 and above remains somewhat controversial. Published theoretical descriptions of coupling in molecules such as SF_6 have been published, with no mention of the participation of the d orbitals in sulfur. Arguments based on the availability of the d orbit and the small size of the central atom suggest that coordination numbers above 4 are unusual for the elements of the second period, which is consistent with the experimental results.

One of the biggest differences between the lightest elements and heavier congeners is the tendency of the second-period elements to form species that contain multiple bonds. For example, N is just above P in group 15: N_2 contains an N≡N bond, but each phosphorus atom in a tetrahedral P_4 forms three P–P bonds.

Such a difference in behaviour reflects the fact that within one group of the periodic table, the relative energies of the π bond and the sigma (σ) bond differ. For example, the C=C bond is about 80% stronger than the C–C bond. On the contrary, the Si=Si bond with a smaller p orbital overlap between the valence orbitals due to the larger atomic size is only approximately 40% stronger than the Si–Si bond. Therefore, compounds containing both multiple and single C to C bonds are common for carbon, but compounds containing only Si–Si sigma bonds are more energetically favourable for silicon and other third period elements.

Another important trend that should be noted in the chemistry of group elements is the chemical similarity between the lightest element of one group and the element immediately below and to the right of it in the next group. Such a phenomenon is known as the diagonal effect (Fig. 6.2).

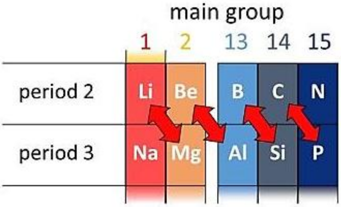


Figure 6.2 The diagonal effect

There are, for example, significant similarities between the chemistry of Li and Mg, Be and Al, and B and Si. Both $BeCl_2$ and $AlCl_3$ are substantially covalent in nature, so they are somewhat soluble in non-polar organic solvents.

In contrast, although Mg and Be are in the same group, $MgCl_2$ behaves as a typical ion halide due to its lower electronegativity and larger magnesium size.

The inert-pair effect

The inert pair effect relates to the empirical observation that the oxidation state of heavier elements of groups 13–17 are often half as much compared to the maximum predicted values for their group. For example, although the +3 oxidation state is common to group 13 elements, the heaviest element of group 13, the thallium (Tl), most likely forms compounds in which it has a +1 oxidation state. Two main factors cause such an effect, namely: an increase in ionisation energies and a decrease in bond strength.

The ionisation energies increase because the filled (n – 1)d or (n – 2)f orbitals are relatively weak when shielding electrons in ns orbitals. Thus, two electrons in the ns orbitals experience an extremely high effective nuclear charge, so they are strongly attracted to the nucleus, reducing their involvement in binding. Therefore, it is much more difficult to remove these ns^2 electrons than expected, as shown in Table 6.1. Since Tl is less likely than Al to lose two ns^2 electrons due to the difference in the first ionisation energies, its most common oxidation state is +1 rather than +3.

Table 6.1 Ionisation energies (I) and average M–Cl bond energies for the group 13 elements

Element	Electron configuration	I_1 (kJ/mol)	$I_1 + I_2 + I_3$ (kJ/mol)	Average M–Cl bond energy (kJ/mol)
B	[He] $2s^2 2p^1$	801	6828	536
Al	[Ne] $3s^2 3p^1$	578	5139	494
Ga	[Ar] $3d^{10} 4s^2 4p^1$	579	5521	481
In	[Kr] $4d^{10} 5s^2 p^1$	558	5083	439
Tl	[Xe] $4f^{14} 5d^{10} 6s^2 p^1$	589	5439	373

The atoms usually increase in size, and the overlap between the valence orbitals of the bonded atoms reduces when going down along a group. Therefore, the bond strength is usually reduced by a column. As shown by the M – Cl bond energies in Table 6.1, the bond strength between the group 3 atom and the chlorine atom decreases by more than 30% from B to Tl. Similar decreases are observed for the atoms of groups 14 and 15.

In summary

The key concepts, definitions and laws:

The chemistry of the third-period element in a group is most representative of the chemistry of the group because the chemistry of the second-period elements is dominated by their small radii, energetically unavailable d orbitals, and tendency to form π bonds with other atoms.

In going down a group in the p block, increasing ionisation energies and decreasing bond strengths result in an inert-pair effect.

The properties of the lightest element in a group are often more similar to those of the element below and on the right of it in the periodic table.

The most important unifying principle in describing the chemistry of the elements is that the systematic increase in atomic number and the orderly filling of atomic orbitals lead to periodic trends in atomic properties. The most fundamental property, leading to periodic variations, is the effective nuclear charge (Z_{eff}).

Because of the position of the diagonal line separating metals and nonmetals in the periodic table, the chemistry of groups 13, 14, and 15 is relatively complex.

The second-period elements ($n = 2$) in each group exhibit unique chemistry compared with their heavier congeners because of their smaller radii, energetically unavailable d orbitals, and greater ability to form π bonds with other atoms.

Increasing ionisation energies and decreasing bond strengths lead to the inert-pair effect, which causes the heaviest elements of groups 13–17 to have a stable oxidation state that is lower by a factor 2 than the maximum predicted for their respective groups.

6.2 Properties of s-block elements

6.2.1 Hydrogen

Most versions of the periodic table place hydrogen in the upper left corner immediately above lithium, implying that hydrogen, with a $1s^1$ electron configuration, is a member of group 1. In fact, the chemistry of hydrogen does not greatly resemble that of the metals of group 1. Indeed, some versions of the periodic table place hydrogen above fluorine in group 17 because the addition of a single electron to a hydrogen atom completes its valence shell.

Isotopes of hydrogen

Hydrogen, the most abundant element in the universe, is the ultimate source of all other elements by the process of nuclear fusion. Table 6.2 compares the three isotopes of hydrogen, all of which contain one proton and one electron per atom.

Table 6.2 Isotopes of hydrogen

	Protium	Deuterium	Tritium
symbol	${}^{1}_{1}\mathrm{H}$	${}^{1}_{2}\mathrm{H}$	${}^{1}_{3}\mathrm{H}$
neutrons	0	1	2
mass (amu)	1.00783	2.0140	3.01605
abundance (%)	99.9885	0.0115	$\sim10^{-17}$
half-life (years)	–	–	12.32
boiling point of X_2 (K)	20.28	23.67	25
melting point/boiling point of X_2O (°C)	0.0/100.0	3.8/101.4	4.5/?

The most common isotope is protium (^{1}H or H), followed by deuterium (^{2}H or D), which has an additional neutron. The rarest isotope of hydrogen is tritium (^{3}H or T), which is produced in the upper atmosphere by a nuclear reaction when cosmic rays strike nitrogen and other atoms. Then it is washed into the oceans by rainfall. Tritium is radioactive, decaying to ^{3}He with a half-life of only 12.32 years. Consequently, the atmosphere and oceans contain only a very low, steady-state level of tritium.

The term hydrogen and the symbol H normally refer to the naturally occurring mixture of the three isotopes.

The different masses of the three isotopes of hydrogen cause them to have different physical properties. Thus H_2, D_2, and T_2 differ in their melting points, boiling points, densities, and heats of fusion and vaporisation.

In 1931, Harold Urey (1893–1981) and co-workers discovered deuterium by slowly evaporating several litres of liquid hydrogen until a volume of about 1 mL remained. When that remaining liquid was vaporised, and its emission spectrum examined, they observed new absorption lines in addition to those previously identified as originating from hydrogen. The natural abundance of tritium, in contrast, is so low that similar experiments could not detect it. Tritium was first prepared in 1934 by a nuclear reaction.

Bonding in hydrogen and hydrogen-containing compounds

The $1s^1$ electron configuration of hydrogen indicates a single valence electron. Because the 1s orbital has a maximum capacity of two electrons, hydrogen can form compounds with other elements in three ways (Fig 6.3).

$$\text{i) Polar covalent bond: } \cdot H \xrightarrow{-1\bar{e}} H^+ \xrightarrow{+Z:} \overset{\delta^-}{Z} - \overset{\delta^+}{H}$$

$$\text{ii) Ionic bond: } \cdot H \xrightarrow{+\cdot M} M^+H^-$$

$$\text{iii) Covalent or polar covalent bond: } \cdot H \xrightarrow{+Z\cdot} Z - H$$

Figure 6.3 Three types of bonding in hydrogen compounds

It is losing its electron to form a proton (H^+) with an empty 1s orbital. The proton is a Lewis acid that can accept a pair of electrons from another atom to form an electron-pair bond. In the acid-base reactions, for example, the proton always binds to a lone pair of electrons on an atom in another molecule to form a polar covalent bond. If the lone pair of electrons belongs to an oxygen atom of a water molecule, the result is the hydronium ion (H_3O^+).

It is accepting an electron to form a hydride ion (H^-) which has a filled $1s^2$ orbital. Hydrogen reacts with relatively electropositive metals, such as the alkali metals (group 1) and alkaline earth metals (group 2), to form ionic hydrides, which contain metal cations and H^- ions.

It is sharing its electron with an electron on another atom to form an electron-pair bond. With a half-filled $1s^1$ orbital, the hydrogen atom can interact with singly occupied orbitals on other atoms to form either a covalent or a polar covalent electron-pair bond, depending on the electronegativity of the other atom.

Summing up, since the 1s orbital can accommodate no more than two electrons, hydrogen can (Fig. 6.3):

(i) bond to other elements by losing an electron to form a proton, which can accept a pair of electrons from a more electronegative atom to form a polar covalent bond;

(ii) gain an electron from an electropositive metal to form a hydride ion, resulting in an ionic hydride; or

(iii) share its half-filled 1s orbital with a half-filled orbital on another atom to form a covalent or a polar covalent electron-pair bond.

Hydrogen can also act as a bridge between two atoms. One well-known example is the hydrogen bond, electrostatic interaction between a hydrogen-bonded to an electronegative atom and an atom that has one or more lone pairs of electrons (Fig. 6.4). Such kind of interaction is represented by the hydrogen-bonding network found in water.

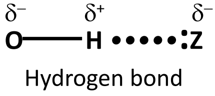


Figure 6.4 The hydrogen bond

Hydrogen can also form a three-centre bond (or electron-deficient bond), in which a hydride bridges two electropositive atoms. Compounds, which contain hydrogen bonded to boron and similar elements, often exhibit this type of bonding. The B–H–B units found in boron hydrides cannot be described in terms of localised electron-pair bonds. Because the H atom in the middle of such a unit can accommodate a maximum of only two electrons in its 1s orbital, the B–H–B unit can be described as containing a hydride that interacts simultaneously with empty sp^3 orbitals on two boron atoms (Fig. 6.5).

In these bonds, only two bonding electrons are used to hold three atoms together, making them electron-deficient bonds. A similar phenomenon takes place in π bonding in ozone and the nitrite ion. In both these cases, the presence of two electrons in a π molecular orbital extending over three atoms is used to explain the fact that the two O–O bond distances in ozone and the two N–O bond distances in nitrite are the same, which otherwise can be explained only by the use of resonance structures.

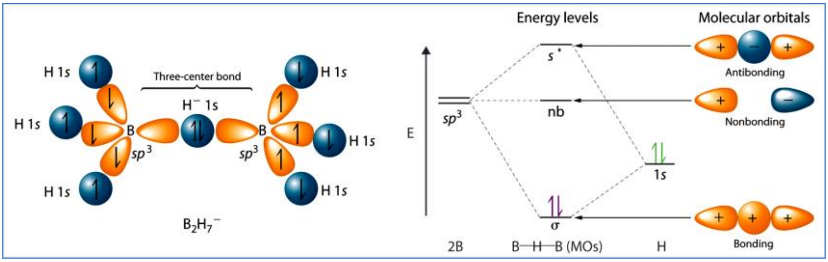


Figure 6.5 Three-centre bond uses two electrons to link three atoms

The covalent bond between hydrogen and a very electronegative element, such as nitrogen, oxygen, or fluorine, is highly polar. The resulting partial positive charge on H allows it to interact with a lone pair of electrons on another atom to form a hydrogen bond, which is typically a linear arrangement of the three atoms, with the hydrogen atom placed asymmetrically between the two heavier atoms.

In the B–H–B unit shown above, a hydride, with a filled 1s orbital, interacts simultaneously with empty sp^3 hybrids on the boron atoms of two BH_3 units to give three molecular orbitals. The two bonding electrons occupy the lowest-energy (σ) bonding orbital, thereby holding all three atoms together.

Synthesis, reactions and compounds

Boyle discovered the most common way to produce small amounts of highly pure hydrogen gas in the laboratory: reacting an active metal (M), such as iron, magnesium, or zinc, with dilute acid:

$$M_{(s)} + 2H^+_{(aq)} \rightarrow H_{2(g)} + M^{2+}_{(aq)} \qquad (6.1)$$

Hydrogen gas can also be generated by reacting metals such as aluminium or zinc with a strong base:

$$Al_{(s)} + OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 3/2H_{2(g)} + [Al(OH)_4]^-_{(aq)} \qquad (6.2)$$

Solid commercial drain cleaners use this reaction to generate gas bubbles that help break up clogs in a drainpipe. Hydrogen gas is also produced by reacting ionic hydrides with water. Because ionic hydrides are expensive, however, this reaction is generally used for only specialised purposes, such as producing HD gas by reacting a hydride with D_2O:

$$MH_{(s)} + D_2O_{(l)} \rightarrow HD_{(g)} + M^+_{(aq)} + OD^-_{(aq)} \qquad (6.3)$$

On an industrial scale, H_2 is produced from methane using catalytic steam reforming, a method used to convert hydrocarbons to a mixture of CO and H_2 known as synthesis gas, or syngas. The process is carried out at elevated temperatures (800°C) in the presence of a nickel catalyst:

$$CH_{4(g)} + H_2O_{(g)} \xrightarrow{Ni} CO_{(g)} + 3H_{2(g)} \qquad (6.4)$$

Most of the elements in the periodic table form binary compounds with hydrogen, which are collectively referred to as hydrides. Binary hydrides, in turn, can be classified in one of three ways, each with its characteristic properties. Covalent hydrides contain hydrogen bonded to another atom via a covalent bond or a polar covalent bond. Covalent hydrides are usually molecular substances that are relatively volatile and have low melting points. Ionic hydrides contain the hydride ion as the anion with cations derived from electropositive metals. Like most ionic compounds, they are typically non-volatile solids that contain 3D lattices of cations and anions. Unlike most ionic compounds, however, they often decompose to $H_2(g)$ and the parent metal after heating.

Metallic hydrides are formed by hydrogen and less electropositive metals such as the transition metals. The properties of metallic hydrides are usually similar to those of the parent metal. Consequently, metallic hydrides are best viewed as metals that contain many hydrogen atoms present as interstitial impurities.

Summary

The three isotopes of hydrogen, protium (^1H or H), deuterium (^2H or D), and tritium (^3H or T), have different physical properties. Deuterium and tritium can be used as tracers, substances that enable biochemists to follow the path of a molecule through an organism or a cell. Hydrogen can form compounds that contain a proton (H^+), a hydride ion (H^-), an electron-pair bond to H, a hydrogen bond, or a three-centre bond (or electron-deficient bond), in which two electrons are shared between three atoms. Hydrogen gas can be generated by reacting an active metal with dilute acid, reacting Al or Zn with a strong base, or industrially by catalytic steam reforming, which produces synthesis gas, or syngas.

6.2.2 Group 1: alkali metals

The alkali metals are so reactive that they are never found in nature in elemental form. Although some of their ores are abundant, isolating them from their ores is somewhat difficult.

Preparation and general properties

Because the alkali metals are among the most potent reductants known, obtaining them in pure form requires a considerable input of energy. Pure lithium and sodium, for example, are typically prepared by the electrolytic reduction of molten chlorides:

$$LiCl_{(l)} \rightarrow Li_{(l)} + 1/2Cl_{2(g)} \qquad (6.5)$$

In practice, $CaCl_2$ is mixed with LiCl to lower the melting point of the lithium salt. The electrolysis is carried out in an argon atmosphere rather than the nitrogen atmosphere typically used for substances that are highly reactive with O_2 and water because Li reacts with nitrogen gas to form lithium nitride (Li_3N). Metallic sodium is produced by the electrolysis of a molten mixture of NaCl and $CaCl_2$. In contrast, potassium is produced commercially from the reduction of KCl by Na, followed by the fractional distillation of $K_{(g)}$. Although rubidium and caesium can also be produced by electrolysis, they are usually obtained by reacting their hydroxide salts with a reductant such as Mg:

$$2RbOH_{(s)} + Mg_{(s)} \rightarrow 2Rb_{(l)} + Mg(OH)_{2(s)} \qquad (6.6)$$

Massive deposits of essentially pure NaCl and KCl are found in nature and are the major sources of sodium and potassium. The other alkali metals are found in low concentrations in a wide variety of minerals, but ores that contain high concentrations of these elements are relatively rare. No concentrated sources of rubidium are known, for example, even though it is the 16th most abundant element on Earth. Rubidium is obtained commercially by isolating the 2%–4% of Rb present as an impurity in micas, minerals that are composed of sheets of complex hydrated potassium–aluminium silicates.

Alkali metals are recovered from silicate ores in a multistep process that takes advantage of the pH-dependent solubility of selected salts of each metal ion. The steps in this process are leaching, which uses sulfuric acid to dissolve the desired alkali metal ion and Al^{3+} from the ore; basic precipitation to remove Al^{3+} from the mixture as $Al(OH)_3$; selective precipitation of the insoluble alkali metal carbonate; dissolution of the salt again in hydrochloric acid; and isolation of the metal by evaporation and electrolysis.

The key steps are acid leaching, basic precipitation of aluminium hydroxide, selective precipitation of insoluble lithium carbonate, conversion to lithium chloride, evaporation, and electrolysis. The other alkali metals and the alkaline earth metals are recovered from their ores by similar processes.

Various properties of the group 1 elements are summarised in Table 6.3. In keeping with overall periodic trends, the atomic and ionic radii increase smoothly from Li to Cs, and the first ionisation energies decrease as the atoms become larger. As a result of their low first ionisation energies, the alkali metals have an overwhelming tendency to form ionic compounds where they have a +1 charge. All the alkali metals have relatively high electron affinities because the addition of an electron produces an anion (M^-) with an ns^2 electron configuration. The densities of the elements generally increase from Li to Cs, reflecting another common trend: because the atomic masses of the elements increase more rapidly than the atomic volumes as you go down a group, the densest elements are near the bottom of the periodic table. An unusual trend in the group 1 elements is the smooth decrease in the melting and boiling points from Li to Cs. As a result, Cs (melting point is 28.5°C) is one of only three metals (the others are Ga and Hg) that are liquids at body temperature (36.6°C).

Table 6.3 Properties of the group 1 elements

	Lithium	Sodium	Potassium	Rubidium	Caesium	Francium
atomic symbol	Li	Na	K	Rb	Cs	Fr
atomic number	3	11	19	37	55	87
atomic mass	6.94	22.99	39.10	85.47	132.91	223
valence electron configuration	$2s^1$	$3s^1$	$4s^1$	$5s^1$	$6s^1$	$7s^1$
melting point/boiling point (°C)	180.5/1342	97.8/883	63.5/759	39.3/688	28.5/671	27/—
density (g/cm^3) at 25°C	0.534	0.97	0.89	1.53	1.93	—
atomic radius (pm)	167	190	243	265	298	—
first ionisation energy (kJ/mol)	520	496	419	403	376	393
most common oxidation state	+1	+1	+1	+1	+1	+1
ionic radius (pm)*	76	102	138	152	167	—
electron affinity (kJ/mol)	−60	−53	−48	−47	−46	—
electronegativity	1.0	0.9	0.8	0.8	0.8	0.7
standard electrode potential (E°, V)	−3.04	−2.71	−2.93	−2.98	−3.03	–
product of reaction with O_2	Li_2O	Na_2O_2	KO_2	RbO_2	CsO_2	–
type of oxide	basic	basic	basic	basic	basic	–
product of reaction with N_2	Li_3N	none	none	none	none	–
product of reaction with X_2	LiX	NaX	KX	RbX	CsX	–
product of reaction with H_2	LiH	NaH	KH	RbH	CsH	–

* The values cited are for four-coordinate ions except for Rb^+ and Cs^+, whose values are given for the six-coordinate ion.

The standard reduction potentials (E°) of the alkali metals do not follow the trend based on ionisation energies. Unexpectedly, lithium is the strongest reductant, and sodium is the weakest (Table 6.3). Because Li^+ is much smaller than the other alkali metal cations, its hydration energy is the highest. The high hydration energy of Li^+ more than compensates for its higher ionisation energy, making lithium metal the strongest reductant in aqueous solution.

Reactions and compounds

All alkali metals are electropositive elements with an ns^1 valence electron configuration, forming the monocation (M^+) by losing the single valence electron. Because removing a second electron would require breaking into the (n – 1) closed shell, which is energetically prohibitive, the chemistry of the alkali metals is largely that of ionic compounds that contain M^+ ions. However, as we discuss later, the lighter group 1 elements also form a series of organometallic compounds that contain polar covalent M–C bonds.

All the alkali metals react vigorously with the halogens (group 17) to form the corresponding ionic halides, where X is a halogen:

$$2M_{(s)} + X_{2(s,\,l,\,g)} \rightarrow 2M^+X^-_{(s)} \qquad (6.7)$$

Similarly, the alkali metals react with the heavier chalcogens (sulfur, selenium, and tellurium in group 16) to produce metal chalcogenides, where Y is S, Se, or Te:

$$2M_{(s)} + Y_{(s)} \rightarrow M_2Y_{(s)} \qquad (6.8)$$

When excess chalcogen is used, however, a variety of products can be obtained that contain chains of chalcogen atoms, such as the sodium polysulfides (Na_2S_n, where n = 2–6). For example, Na_2S_3 contains the S_3^{2-} ion, which is V-shaped with an S–S–S angle of about 103°.

Reacting the alkali metals with oxygen, the lightest element in group 16, is more complex, and the stoichiometry of the product depends on both the metal: oxygen ratio and the size of the metal atom. For instance, when alkali metals burn in air, the observed products are Li_2O (white), Na_2O_2 (pale yellow), KO_2 (orange), RbO_2 (brown), and CsO_2 (orange). Only Li_2O has the stoichiometry expected for a substance that contains two M^+ cations and one O^{2-} ion. In contrast, Na_2O_2 contains the O_2^{2-} (peroxide) anion plus two Na^+ cations. The other three salts, with stoichiometry MO_2, contain the M^+ cation and the O_2^- (superoxide) ion. Because O^{2-} is the smallest of the three oxygen anions, it forms a stable ionic lattice with the smallest alkali metal cation (Li^+).

In contrast, the larger alkali metals (potassium, rubidium, and caesium) react with oxygen in the air to give the metal superoxides. Because the Na^+ cation is intermediate in size, sodium reacts with oxygen to form a compound with an intermediate stoichiometry: sodium peroxide. Under specific reaction conditions, however, it is possible to prepare the oxide, peroxide, and superoxide salts of all five alkali metals, except for lithium superoxide (LiO_2).

The alkali metal peroxides and superoxides are potent oxidants that react, often vigorously, with a wide variety of reducing agents, such as charcoal or aluminium metal. For example, Na_2O_2 is used industrially for bleaching paper, wood pulp, and fabrics such as linen and cotton. In submarines, Na_2O_2 and KO_2 are used to purify and regenerate the air by removing the CO_2 produced by respiration and replacing it with O_2. Both compounds react with CO_2 in a redox reaction in which O_2^{2-} or O_2^{-} is simultaneously oxidised and reduced, producing the metal carbonate and O_2:

$$2Na_2O_{2(s)} + 2CO_{2(g)} \rightarrow 2Na_2CO_{3(s)} + O_{2(g)} \qquad (6.9)$$

$$4KO_{2(s)} + 2CO_{2(g)} \rightarrow 2K_2CO_{3(s)} + 3O_{2(g)} \qquad (6.10)$$

The presence of water vapour, the other product of respiration, makes KO_2 even more effective at removing CO_2 because potassium bicarbonate, rather than potassium carbonate, is formed and removes 4 moles of CO_2 compared to two moles in reaction (6.10):

$$4KO_{2(s)} + 4CO_{2(g)} + 2H_2O_{(g)} \rightarrow 4KHCO_{3(s)} + 3O_{2(g)} \qquad (6.11)$$

Lithium, the lightest alkali metal, is the only one that reacts with atmospheric nitrogen, forming lithium nitride (Li_3N). Lattice energies again explain why the larger alkali metals such as potassium do not form nitrides: packing three large K^+ cations around a single relatively small anion is energetically unfavourable. In contrast, all the alkali metals react with the larger group 15 elements phosphorus and arsenic to form metal phosphides and arsenides (where Z is P or As):

$$12M_{(s)} + Z_{4(s)} \rightarrow 4M_3Z_{(s)} \qquad (6.12)$$

The alkali metals react with all group 14 elements, but the compositions and properties of the products vary significantly. For example, reaction with the heavier group 14 elements gives materials that contain polyatomic anions and three-dimensional cage structures, such as e. g. K_4Si_4. In contrast, lithium and sodium are oxidised by carbon to produce a compound with the stoichiometry M_2C_2 (where M is Li or Na):

$$2M_{(s)} + 2C_{(s)} \rightarrow M_2C_{2(s)} \qquad (6.13)$$

The same compounds can be obtained by reacting the metal with acetylene (C_2H_2). In this reaction, the metal is again oxidised, and hydrogen is reduced:

$$2M_{(s)} + C_2H_{2(g)} \rightarrow M_2C_{2(s)} + H_{2(g)} \qquad (6.14)$$

The acetylide ion (C_2^{2-}), formally derived from acetylene by the loss of both hydrogens as protons, is a very strong base. Reacting acetylide salts with water produces acetylene and $MOH_{(aq)}$.

The heavier alkali metals (K, Rb, and Cs) also react with carbon in the form of graphite. Instead of disrupting the hexagonal sheets of carbon atoms, however, the metals insert themselves between the sheets of carbon atoms to give new substances called graphite intercalation compounds.

The stoichiometries of these compounds include MC_{60} and MC_{48}, which are of black/grey colour; MC_{36} and MC_{24} (blue); and MC_8 (bronze). Reacting graphite with alkali metals such as K, Rb, and Cs results in partial reduction of the graphite and insertion of layers of alkali metal cations between sets of n layers of carbon atoms. The stoichiometry and colour of intercalation compounds depend on the number of layers of carbon atoms (n) between each layer of intercalated metal atoms. This schematic diagram in Fig. 6.6 illustrates the most common structures of intercalation compounds.

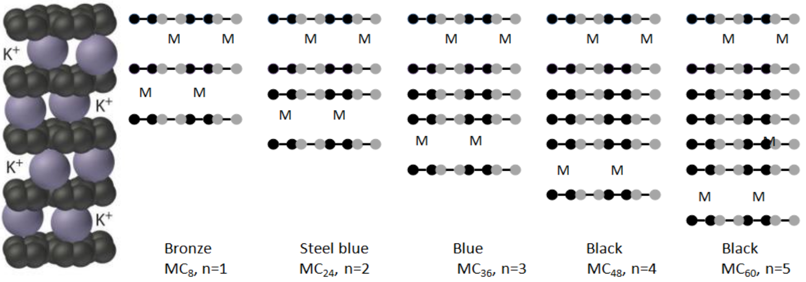


Figure 6.6 Graphite intercalation compounds. Left: in MC_8 (as shown for KC_8) layers of M^+ ions are inserted between every pair of carbon layers, giving n = 1. Right: The stoichiometry and colour of intercalation compounds depend on the number of layers of carbon atoms (n) between each layer of intercalated metal atoms

The high electrical conductivity of these compounds (about 200 times greater than graphite) is attributed to a net transfer of the valence electron of the alkali metal to the graphite layers to produce, for example, $K^+C_8^-$.

All the alkali metals react directly with gaseous hydrogen at elevated temperatures to produce ionic hydrides (M^+H^-):

$$2M_{(s)} + H_{2(g)} \rightarrow 2MH_{(s)} \qquad (6.15)$$

All are also capable of reducing water to produce hydrogen gas:

$$M_{(s)} + H_2O_{(l)} \rightarrow 1/2H_{2(g)} + MOH_{(aq)} \qquad (6.16)$$

Although lithium reacts rather slowly with water, sodium reacts quite vigorously, and the heavier alkali metals (K, Rb, and Cs) react so vigorously that they invariably explode. Although the driving force for the reaction is greatest for lithium, the heavier metals have lower melting points. The heat liberated by the reaction causes them to melt, and the larger surface area of the liquid metal in contact with water greatly accelerates the reaction rate.

Like most elements in groups 1 and 2, sodium reacts violently with water. The products are the $Na^+_{(aq)}$ ion and hydrogen gas, which is potentially explosive when mixed with air.

Alkali metal cations are found in a wide variety of ionic compounds. In general, an alkali metal salt can be prepared by reacting the alkali metal hydroxide with an acid and then evaporating the water:

$$2MOH_{(aq)} + H_2SO_{4(aq)} \rightarrow M_2SO_{4(aq)} + 2H_2O_{(l)} \qquad (6.17)$$

$$MOH_{(aq)} + HNO_{3(aq)} \rightarrow MNO_{3(aq)} + H_2O_{(l)} \qquad (6.18)$$

Hydroxides of alkali metals also can react with organic compounds that contain acidic hydrogen to produce a salt. An example is the preparation of sodium acetate (CH_3CO_2Na) by reacting sodium hydroxide and acetic acid:

$$CH_3CO_2H_{(aq)} + NaOH_{(s)} \rightarrow CH_3CO_2Na_{(aq)} + H_2O_{(l)} \qquad (6.19)$$

Soap is a mixture of the sodium and potassium salts of naturally occurring carboxylic acids, such as palmitic acid [$CH_3(CH_2)_{14}CO_2H$] and stearic acid [$CH_3(CH_2)_{16}CO_2H$]. Lithium salts, such as lithium stearate [$CH_3(CH_2)_{14}CO_2Li$], are used as additives in motor oils and greases.

Complexes of the alkali metals

Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to react with simple Lewis bases to form metal complexes. Complex formation is most significant for the smallest cation (Li^+) and decreases with increasing radius. In aqueous solution, for example, Li^+ forms the tetrahedral $[Li(H_2O)_4]^+$ complex (Fig. 6.7). In contrast, the larger alkali metal cations compose octahedral $[M(H_2O)_6]^+$ complexes (Fig. 6.7). The Li^+ ion is so small that it can accommodate only four water molecules around it, but the larger alkali metal cations tend to bind six water molecules.

Complex formation is primarily due to the electrostatic interaction of the metal cation with polar water molecules. Because of their high affinity for water, anhydrous salts that contain Li^+ and Na^+ ions (such as Na_2SO_4) are often used as drying agents. These compounds absorb trace amounts of water from nonaqueous solutions to form hydrated salts, which are then easily removed from the solution by filtration.

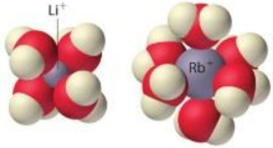


Figure 6.7 The tetrahedral $[Li(H_2O)_4]^+$ and octahedral $[Rb(H_2O)_6]^+$ complexes.

Liquid ammonia solutions

Alkali metals can dissolve reversibly in liquid ammonia. Similar to their reactions with water, reacting alkali metals with liquid ammonia eventually produce hydrogen gas and the metal salt of the conjugate base of the solvent — in this case, the amide ion (NH_2^-) rather than hydroxide:

$$M_{(s)} + NH_{3(l)} \rightarrow 1/2H_{2(g)} + M^+_{(am)} + NH_2^-{}_{(am)} \qquad (6.20)$$

where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction (6.20) tends to be rather slow.

In many cases, the alkali metal amide salt (MNH_2) is not very soluble in liquid ammonia and precipitates, but when dissolved, very concentrated solutions of the alkali metal are produced. One mole of Cs metal, for example, will dissolve in as little as 53 mL (40 g) of liquid ammonia. The pure metal is easily recovered when the ammonia evaporates.

Solutions of alkali metals in liquid ammonia are intensely coloured and good conductors of electricity due to the presence of solvated electrons (e^-, NH_3), which are not attached to single atoms. A solvated electron is loosely associated with a cavity in the ammonia solvent that is stabilised by hydrogen bonds.

Most metals are insoluble in virtually all solvents, but the alkali metals (and the heavier alkaline earth metals) dissolve readily in liquid ammonia to form solvated metal cations and solvated electrons, which give the solution a deep blue colour. The colour can change with increasing concentration of metal.

In addition to solvated electrons, solutions of alkali metals in liquid ammonia contain the metal cation (M^+), the neutral metal atom (M), metal dimers (M_2), and the metal anion (M^-). The anion is formed by adding an electron to the singly occupied ns valence orbital of the metal atom. Even in the absence of a catalyst, these solutions are not very stable and eventually decompose to the thermodynamically favoured products: $M^+NH_2^-$ and hydrogen gas by reaction (6.20). Nonetheless, the solvated electron is a potent reductant that is often used in synthetic chemistry.

Organometallic compounds of the group 1 elements

Compounds that contain a metal covalently bonded to a carbon atom of an organic species are called organometallic compounds. The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components. Because of its small size, lithium, for example, forms an extensive series of covalent organolithium compounds, such as methyllithium ($LiCH_3$), which are by far the most stable and best-known group 1 organometallic compounds. These volatile, low-melting-point solids or liquids can be sublimed or distilled at relatively low temperatures and are soluble in nonpolar solvents. Like organic compounds, the molten solids do not conduct electricity to any significant degree. Organolithium compounds tend to form oligomers with the formula $(RLi)_n$, where R represents the organic component.

Typical applications

Because sodium remains liquid over a wide temperature range (97.8–883°C), it is used as a coolant in specialised high-temperature applications, such as nuclear reactors and the exhaust valves in high-performance sports car engines. Caesium, because of its low ionisation energy, is used in photosensors in automatic doors, toilets, burglar alarms, and other electronic devices. In these devices, caesium is ionised by a beam of visible light, thereby producing a small electric current; blocking the light interrupts the electric current and triggers a response.

Compounds of sodium and potassium are produced on a huge scale in industry and used in many industrial processes: Na_2CO_3 for glass manufacturing; K_2O for porcelain glazes; and Na_4SiO_4 for production of detergents.

Several other alkali metal compounds are also important. For example, Li_2CO_3 is one of the most effective treatments available for manic depression or bipolar disorder. Lithium compounds form a basis for the production of a variety of electrical accumulators.

Summary

The alkali metals are among the most potent reductants known; most can be isolated by electrolysis of their molten salts or, in the case of rubidium and caesium, by reacting their hydroxide salts with a reductant.

Lithium, the strongest reductant, and sodium, the weakest, are examples of the physical and chemical effects of opposing periodic trends. The alkali metals react with halogens (group 17) to form ionic halides; the heavier chalcogens (group 16) to produce metal chalcogenides; and oxygen to form compounds, whose stoichiometry depends on the size of the metal atom. The peroxides and superoxides of alkali metals are potent oxidants.

The only alkali metal to react with atmospheric nitrogen is lithium. Heavier alkali metals react with graphite to form graphite intercalation compounds, substances in which metal atoms are inserted between the sheets of carbon atoms. With heavier group 14 elements, alkali metals react to give polyatomic anions with 3D cage structures. All alkali metals react with hydrogen at high temperatures to produce the corresponding hydrides, and all reduce water to produce hydrogen gas. Alkali metal salts are prepared by reacting a metal hydroxide with an acid, followed by evaporation of the water. Both Li and Na salts are used as drying agents, compounds that are used to absorb water.

Complexing agents can accommodate alkali metal ions of the appropriate size. Alkali metals can also react with liquid ammonia to form solutions that slowly decompose to give hydrogen gas and the metal salt of the amide ion (NH_2^-). These solutions, which contain unstable solvated electrons loosely associated with a cavity in the solvent, are intensely coloured, good conductors of electricity, and excellent reductants.

Alkali metals can react with organic compounds that contain an acidic proton to produce salts. They can also form organometallic compounds, which have properties that differ from those of their metallic and organic components.

6.2.3 Group 2: alkaline earth metals

Like the alkali metals, all six alkaline earth metals are so reactive that they are never found in elemental form in nature. Because they form +2 ions that have very negative reduction potentials, large amounts of energy are needed to isolate them from their ores. Four of the six elements were first isolated in the early XIX century. Beryllium, the lightest alkaline earth metal, was first obtained in 1828 by the following reaction:

$$BeCl_{2(s)} + 2K_{(s)} \xrightarrow{t} Be_{(s)} + 2KCl_{(s)} \qquad (6.21)$$

Radium was discovered in 1898 by processing tons of residue from uranium mines.

Preparation of the alkaline earth metals

Industrial amounts of alkaline earth metals are produced by electrolytic reduction of their molten chlorides, as indicated in this equation for calcium:

$$CaCl_{2(l)} \rightarrow Ca_{(l)} + Cl_{2(g)} \qquad (6.22)$$

Chlorides are obtained from a variety of sources. For example, $BeCl_2$ is produced by reacting HCl with BeO, which is obtained from the stone named $[Be_3Al_2(SiO_3)_6]$.

Chemical reductants can also be used to obtain group 2 metals. For example, large scale production of magnesium is based on the heating of dolomite $CaCO_3 \cdot MgCO_3$ (a form of limestone) with an inexpensive iron/silicon alloy at 1150°C. Initially, CO_2 is released, leaving behind a mixture of CaO and MgO; Mg^{2+} is then reduced:

$$2CaO \cdot MgO_{(s)} + Fe/Si_{(s)} \rightarrow 2Mg_{(l)} + Ca_2SiO_{4(s)} + Fe_{(s)} \qquad (6.23)$$

The alkaline earth metals are somewhat easier to isolate from their ores compared to the alkali metals because their carbonate and some sulfate and hydroxide salts are insoluble.

General properties

Some important properties of the alkaline earth metals are summarised in Table 6.4. Although many of the properties are similar to those of the alkali metals (Table 6.3), some differences are attributed to the differences in the valence electron configurations of the two groups (ns^2 for the alkaline earth metals versus ns^1 for the alkali metals).

As with the alkali metals, the atomic and ionic radii of the alkaline earth metals increase and the ionisation energies decrease from Be to Ba. The first ionisation energy with an ns^2 valence electron configuration is always larger than that of the preceding alkali metal. In contrast to the alkali metals, the heaviest alkaline earth metal (Ba) is the strongest reductant, and the lightest (Be) is the weakest. The standard electrode potentials of Ca and Sr are not very different from that of Ba, indicating that the opposing trends in ionisation energies and hydration energies are of roughly equal importance.

Table 6.4 Properties of the group 2 elements

	Beryllium	Magnesium	Calcium	Strontium	Barium	Radium
atomic symbol	Be	Mg	Ca	Sr	Ba	Ra
atomic number	4	12	20	38	56	88
atomic mass	9.01	24.31	40.08	87.62	137.33	226
valence electron configuration	$2s^2$	$3s^2$	$4s^2$	$5s^2$	$6s^2$	$7s^2$
melting point/boiling point (°C)	1287/2471	650/1090	842/1484	777/1382	727/1897	700/—
density (g/cm^3) at 25°C	1.85	1.74	1.54	2.64	3.62	~5
atomic radius (pm)	112	145	194	219	253	–
first ionisation energy (kJ/mol)	900	738	590	549	503	–
most common oxidation state	+2	+2	+2	+2	+2	+2
ionic radius (pm)*	45	72	100	118	135	–
electron affinity (kJ/mol)	≥ 0	≥ 0	−2	−5	−14	–
electronegativity	1.6	1.3	1.0	1.0	0.9	0.9
standard electrode potential (E°, V)	−1.85	−2.37	−2.87	−2.90	−2.91	–2.8
product of reaction with O_2	BeO	MgO	CaO	SrO	BaO_2	–
type of oxide	amphoteric	weakly basic	basic	basic	Basic	–
product of reaction with N_2	none	Mg_3N_2	Ca_3N_2	Sr_3N_2	Ba_3N_2	–
product of reaction with X_2	BeX_2	MgX_2	CaX_2	SrX_2	BaX_2	–
product of reaction with H_2	none	MgH_2	CaH_2	SrH_2	BaH_2	–

* The values cited are for six-coordinate ions except for Be^{2+}, for which the value for the four-coordinate ion is given.

One major difference between group 1 and group 2 elements is their electron affinities. The alkali metals have a significant affinity for an additional electron because of half-filled ns orbitals. In contrast, the alkaline earth metals generally have little or no tendency to accept an additional electron because their ns valence orbitals are already full. An added electron would have to occupy one of the vacant np orbitals, which are much higher in energy.

Reactions and compounds

Because of low first and second ionisation energies, the group 2 elements almost exclusively form ionic compounds that contain M^{2+} ions. However, the lightest element (Be), with its higher ionisation energy and small size, forms largely covalent compounds. Some compounds of Mg^{2+} also have significant covalent character. Hence organometallic compounds like those discussed for Li in group 1 are also important for Be and Mg in group 2.

All alkaline earth metals react vigorously with the halogens (group 17) to form the corresponding halides (MX_2). Except for the beryllium halides, these compounds are all primarily ionic, containing the M^{2+} cation and two X^- anions. The beryllium halides, with properties more typical of covalent compounds, have a polymeric halide-bridged structure in the solid-state, as shown for $BeCl_2$ (Fig. 6.8). These compounds are volatile, producing vapours that contain the linear X–Be–X molecules. As expected for compounds with only four valence electrons around the central atom, the beryllium halides are potent Lewis acids. They react readily with Lewis bases, such as ethers, to form tetrahedral adducts in which an octet of electrons surrounds the central beryllium:

$$BeCl_{2(s)} + 2(CH_3CH_2)_2O_{(l)} \rightarrow BeCl_2[O(CH_2CH_3)_2]_{2(soln)} \qquad (6.24)$$

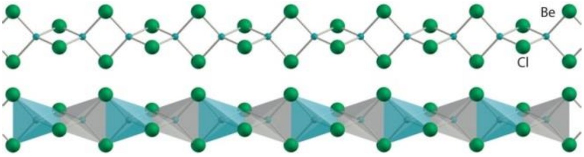


Figure 6.8 Halide-bridged, the polymeric structure of solid beryllium chloride ($BeCl_2$)

The reactions of the alkaline earth metals with oxygen are less complex than those of the alkali metals. All group 2 elements except barium react directly with oxygen to form the simple oxide MO. Barium forms barium peroxide (BaO_2) because the larger O_2^{2-} ion is better able to separate the large Ba^{2+} ions in the crystal lattice. In practice, only BeO is prepared by direct reaction with oxygen, and this reaction requires finely divided Be and high temperatures because Be is relatively inert. The other alkaline earth oxides are usually prepared by the thermal decomposition of carbonate salts:

$$MCO_{3(s)} \xrightarrow{t} MO_{(s)} + CO_{2(g)} \qquad (6.25)$$

The reactions of the alkaline earth metals with the heavier chalcogens (Y) are similar to those of the alkali metals. When the reactants are present in a 1:1 ratio, the binary chalcogenides (MY) are formed; at lower M:Y ratios, salts containing polychalcogenide ions (Y_n^{2-}) are formed.

In the reverse of reaction (6.25), the oxides of Ca, Sr, and Ba react with CO_2 to regenerate the carbonate. Except for BeO, which has significant covalent character and is, therefore, amphoteric, all the alkaline earth oxides are basic. Thus, they react with water to form the hydroxides $M(OH)_2$:

$$MO_{(s)} + H_2O_{(l)} \rightarrow M^{2+}_{(aq)} + 2OH^-_{(aq)} \qquad (6.26)$$

They dissolve in aqueous acid. Hydroxides of the lighter elements are insoluble in water, but their solubility increases with the atomic number of the metal. Because BeO and MgO are much more inert than the other group 2 oxides, they are used as refractory materials in high-temperature applications.

The carbonates of the alkaline earth metals also react with aqueous acid to give CO_2 and H_2O:

$$MCO_{3(s)} + 2H^+_{(aq)} \rightarrow M^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \qquad (6.27)$$

The trend in the reactivities of the alkaline earth metals with nitrogen is the opposite of that observed for the alkali metals. Only the lightest element (Be) does not react readily with N_2 to form the nitride (M_3N_2), although very disperse Be reacts at high temperatures. The higher lattice energy due to the highly charged M^{2+} and N^{3-} ions is sufficient to overcome the chemical inertness of the N_2 molecule, with its N≡N bond. Similarly, all the alkaline earth metals react with the heavier group 15 elements to form binary compounds such as phosphides and arsenides with the general formula M_3Z_2.

When heated, all alkaline earth metals, except for beryllium, react directly with carbon to form ionic carbides with the general formula MC_2. The most important alkaline earth carbide is calcium carbide (CaC_2), which reacts readily with water to produce acetylene. In contrast, beryllium reacts with elemental carbon to form Be_2C, which formally contains the C^{4-} ion (although the compound is covalent).

Consistent with this formulation, the reaction of Be_2C with water or aqueous acid produces methane:

$$Be_2C_{(s)} + 4H_2O_{(l)} \rightarrow 2Be(OH)_{2(s)} + CH_{4(g)} \qquad (6.28)$$

Beryllium does not react with hydrogen except at high temperatures (1500°C), although BeH_2 can be prepared at lower temperatures by an indirect route. All the heavier alkaline earth metals (Mg through Ba) react directly with hydrogen to produce the binary hydrides (MH_2). Such hydrides are ionic compounds, but both BeH_2 and MgH_2 have polymeric structures that reflect partial covalent character. All alkaline earth hydrides are good reducing agents that react rapidly with water or aqueous acid to produce hydrogen gas:

$$CaH_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + 2H_{2(g)} \qquad (6.29)$$

Like the alkali metals, the heavier alkaline earth metals are sufficiently electropositive to dissolve in liquid ammonia. In this case, however, two solvated electrons are formed per metal atom, and no equilibriums involving metal dimers or metal anions are known. Also, like the alkali metals, the alkaline earth metals form a wide variety of simple ionic salts with oxoanions, such as carbonate, sulfate, and nitrate. The nitrate salts tend to be soluble, but the carbonates and sulfates of the heavier alkaline earth metals are quite insoluble due to higher lattice energy and due to the doubly charged cation and anion. The solubility of the carbonates and the sulfates decreases rapidly down the group because hydration energies decrease with increasing cation size.

Complexes of the alkaline earth metals

Because of their higher positive charge (+2) and smaller ionic radii, the alkaline earth metals have a much greater tendency to form complexes with Lewis bases compared to the alkali metals. This tendency is most important for the lightest cation (Be^{2+}) and decreases rapidly with the increasing radius of the metal ion.

The Be^{2+} ion behaves as a Lewis acid, forming complexes with Lewis bases that produce an octet of electrons around beryllium. For example, Be^{2+} salts dissolve in water to form acidic solutions with the tetrahedral $[Be(H_2O)_4]^{2+}$ ion. Due to its high charge-to-radius ratio, the Be^{2+} ion polarises coordinated water molecules and thus enhance their acidity:

$$[Be(H_2O)_4]^{2+}{}_{(aq)} \rightarrow [Be(H_2O)_3(OH)]^{+}{}_{(aq)} + H^{+}{}_{(aq)} \qquad (6.30)$$

In the presence of a strong base, beryllium and its salts compose the tetrahedral hydroxo complex: $[Be(OH)_4]^{2-}$. Hence beryllium oxide is amphoteric. Beryllium also forms a very stable tetrahedral fluoride complex: $[BeF_4]^{2-}$. As was shown in (6.24), beryllium halides behave like Lewis acids by forming adducts with Lewis bases.

The heavier alkaline earth metals also form complexes, but usually with a coordination number of 6 or higher. Complex formation is most important for the smaller cations (Mg^{2+} and Ca^{2+}). Thus aqueous solutions of Mg^{2+} contain the octahedral $[Mg(H_2O)_6]^{2+}$ ion. Like the alkali metals, the alkaline earth metals form complexes with neutral cyclic ligands.

Organometallic compounds with group 2 elements

Like the alkali metals, the lightest alkaline earth metals (Be and Mg) form the most covalent-like bonds with carbon, and they form the most stable organometallic compounds. Organometallic compounds of magnesium with the formula RMgX, where R is an alkyl or aryl group and X is a halogen, known as Grignard reagents, after Frenchman Victor Grignard (1871–1935), are widely used to synthesise various organic compounds, such as alcohols, aldehydes, ketones, carboxylic acids, esters, thiols, and amines.

Typical applications

Elemental magnesium is the only alkaline earth metal that is produced on a large scale. Its low density makes it an important component of the lightweight metal alloys used in aircraft and automobile industries. Most commercial aluminium actually contains about 5% magnesium to improve its corrosion resistance and mechanical properties. Elemental magnesium also serves as an inexpensive and powerful reductant for the production of several metals, including titanium, zirconium, uranium, and even beryllium by the following equation:

$$TiCl_{4(l)} + 2Mg_{(s)} \rightarrow Ti_{(s)} + 2MgCl_{2(s)} \qquad (6.31)$$

The only other alkaline earth that is widely used as the metal is beryllium, which is extremely toxic. A small percentage of beryllium dramatically increases the strength of copper or nickel alloys. The low atomic number of beryllium gives it a very low tendency to absorb x-rays and makes it uniquely suited for applications involving radioactivity, such as nuclear reactors, x-ray tubes, etc.

Millions of tons of calcium are used every year in the form of different compounds, first of all, salts ($CaCl_2$, $CaCO_3$) and oxides (CaO) in metallurgy, building material production, chemical industry, etc.

In summary

The key concepts, definitions and laws:

Hydrogen can lose an electron to form a proton, gain an electron to form a hydride ion or form a covalent bond or polar covalent electron-pair bond.

Although hydrogen has an ns^1 electron configuration, its chemistry does not resemble that of the metals of group 1.

Covalent hydrides are relatively volatile and have low melting points; ionic hydrides are generally non-volatile solids.

The chemistry of the alkali metals is largely that of ionic compounds containing the M^+ ions.

Because of lattice energies, only lithium forms a stable oxide and nitride.

Because of their low positive charge (+1) and relatively large ionic radii, alkali metal cations have only a weak tendency to form complexes with simple Lewis bases.

The properties and reactivities of organometallic compounds differ greatly from those of either the metallic or organic components.

The group 2 elements almost exclusively form ionic compounds containing M^{2+} ions.

Because of their higher ionisation energy and small size, both Be and Mg form organometallic compounds.

Higher lattice energies cause the alkaline earth metals to be more reactive than the alkali metals toward group 15 elements.

The solubility of alkaline earth carbonate and sulfates decrease down the group because the hydration energies decrease.

The alkaline earth metals have a substantially greater tendency to form complexes with Lewis bases than do the alkali metals.

6.3 Properties of p-block elements

The line that divides metals from nonmetals in the periodic table crosses the p block diagonally. As a result, the differences between metallic and nonmetallic properties are evident within each group, even though all members of each group have the same valence electron configuration.

The p block is the only portion of the periodic table where one may encounter the inert-pair effect. Moreover, as with the s-block elements, the chemistry of the lightest member of each group in the p block differs sharply from that of its heavier congeners but is similar to that of the element immediately below and to the right of it in the next group. Thus diagonal similarities in chemistry are observed across the p block.

6.3.1 Group 13

Except for the lightest element (boron), the group 13 elements are all relatively electropositive. Therefore, they tend to lose electrons in chemical reactions rather than gain them. Although group 13 includes aluminium, the most abundant metal on Earth, none of these elements was known until the early XIX century because they are never found in nature in their free state.

Preparation and general properties

As reductants, the group 13 elements are less powerful than the alkali elements and alkaline earth metals. Nevertheless, their compounds with oxygen are thermodynamically stable, and large amounts of energy are needed to isolate them from oxide ores.

Boron is produced on a large scale by reacting borax with acid to produce boric acid ($B(OH)_3$), which is then dehydrated to the oxide (B_2O_3). Reduction of the oxide with magnesium or sodium gives amorphous boron that is only about 95% pure:

$$Na_2B_4O_5(OH)_4{\cdot}8H_2O_{(s)} \xrightarrow{acid} B(OH)_{3(s)} \xrightarrow{t} B_2O_{3(s)} \quad (6.32)$$

$$B_2O_{3(s)} + 3Mg_{(s)} \xrightarrow{t} 2B_{(s)} + 3MgO_{(s)} \quad (6.33)$$

Pure, crystalline boron, however, is extremely difficult to obtain because of its high melting point (2300°C) and the highly corrosive nature of liquid boron. It is usually prepared by reducing pure BCl_3 with hydrogen gas at high temperatures or by the thermal decomposition of boron hydrides such as diborane (B_2H_6):

$$BCl_{3(g)} + 3/2H_{2(g)} \rightarrow B_{(s)} + 3HCl_{(g)} \quad (6.34)$$

$$B_2H_{6(g)} \rightarrow 2B_{(s)} + 3H_{2(g)} \quad (6.35)$$

The reaction shown in (6.34) is used to prepare stiff boron fibres. Hence they are used as structural reinforcing. Boron is also an important component of many ceramics and heat-resistant borosilicate glasses.

In contrast to boron, deposits of aluminium ores such as bauxite, a hydrated form of Al_2O_3, are abundant. However, because aluminium–oxygen compounds are stable, obtaining aluminium metal from bauxite is an expensive process. Aluminium is extracted from oxide ores by treatment with a strong base, which produces the soluble hydroxide complex $[Al(OH)_4]^-$. Neutralisation of the resulting solution with gaseous CO_2 results in the precipitation of $Al(OH)_3$:

$$2[Al(OH)_4]^-_{(aq)} + CO_{2(g)} \rightarrow 2Al(OH)_{3(s)} + CO_3{}^{2-}{}_{(aq)} + H_2O_{(l)} \quad (6.36)$$

Thermal dehydration of $Al(OH)_3$ produces Al_2O_3, and metallic aluminium is obtained by the electrolytic reduction of Al_2O_3 using the Hall–Heroult process. Only aluminium is used on a large scale among all the group 13 elements.

The other members of group 13 are rather rare. They are usually obtained as by-products in the processing of other metals. The extremely low melting point of gallium (29.6°C), however, makes it easy to separate from aluminium. Due to its low melting point and high boiling point, gallium is used as a liquid in thermometers that have a temperature range of almost 2200°C.

Indium and thallium, the heavier group 13 elements, are found as trace impurities in sulfide ores of zinc and lead. Indium is used as a crushable seal for high-vacuum cryogenic devices, and its alloys are used as low-melting solders in electronic circuit boards. Thallium is very toxic, and the toxicity limits its application. Both In and Tl oxides are released in flue dust when sulfide ores are converted to metal oxides and SO_2. The flue dust is now trapped and serve as a relatively rich source of elements such as In and Tl (as well as Ge, Cd, Te, and As).

Table 6.5 summarises some important properties of the group 13 elements. The large differences exist between boron and aluminium in size, ionisation energy, electronegativity, and standard reduction potential. As a result, boron behaves chemically like a nonmetal and aluminium like a metal.

All group 13 elements have ns^2np^1 valence electron configurations, and all tend to lose their three valence electrons to form compounds in the +3 oxidation state. The heavier elements in the group can also form compounds in the +1 oxidation state formed by the formal loss of the single np valence electron. Because the group 13 elements generally contain only six valence electrons in their neutral compounds, these compounds are all moderately strong Lewis acids.

In contrast to groups 1 and 2, the group 13 elements show no consistent trends in ionisation energies, electron affinities, and reduction potentials, whereas electronegativities actually increase from aluminium to thallium. Some of these anomalies, especially for the series Ga, In, Tl, can be explained by the increase in the effective nuclear charge (Z_{eff}) that results from poor shielding of the nuclear charge by the filled (n − 1)d^{10} and (n − 2)f^{14} subshells.

Table 6.5 Properties of the group 13 elements

Property	Boron	Aluminium	Gallium	Indium	Thallium
atomic symbol	B	Al	Ga	In	Tl
atomic number	5	13	31	49	81
atomic mass (amu)	10.81	26.98	69.72	114.82	204.38
valence electron configuration *	$2s^2 2p^1$	$3s^2 3p^1$	$4s^2 4p^1$	$5s^2 5p^1$	$6s^2 6p^1$
melting point/boiling point (°C)	2075/4000	660/2519	29.7/2204	156.6/2072	304/1473
density (g/cm^3) at 25°C	2.34	2.70	5.91	7.31	11.8
atomic radius (pm)	87	118	136	156	156
first ionisation energy (kJ/mol)	801	578	579	558	589
most common oxidation state	+3	+3	+3	+3	+1
ionic radius (pm) **	≈25	54	62	80	162
electron affinity (kJ/mol)	−27	−42	−40	−39	−37
electronegativity	2.0	1.6	1.8	1.8	1.8
standard reduction potential (E°, V)	−0.87	−1.66	−0.55	−0.34	+0.741 of $M^{3+}_{(aq)}$
product of reaction with O_2	B_2O_3	Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O
type of oxide	acidic	amphoteric	amphoteric	amphoteric	basic
product of reaction with N_2	BN	AlN	GaN	InN	none
product of reaction with X_2 ***	BX_3	Al_2X_6	Ga_2X_6	In_2X_6	TlX

* The configuration shown does not include filled d and f subshells.

** The values cited are for six-coordinate ions in the most common oxidation state, except for Al^{3+}, for which the value for the four-coordinate ion is given. The B^{3+} ion is not a known species; the radius cited is an estimated four-coordinate value.

*** X is Cl, Br, or I. Reaction with F_2 gives the trifluorides (MF_3) for all group 13 elements.

Consequently, although the actual nuclear charge increases from 49 to 81 when going from indium to thallium, screening by the filled 5d and 4f subshells is so poor that Z_{eff} increases significantly. Thus the first ionisation energy of thallium is actually greater than that of indium.

Reactions and compounds of boron

Elemental boron is a semimetal that is remarkably unreactive; in contrast, the other group 13 elements all exhibit metallic properties and reactivity. That is why the reactions and compounds of boron are considered separately from those of other elements in the group.

All group 13 elements have fewer valence electrons than valence orbitals, which generally results in delocalised, metallic bonding. With its high ionisation energy, low electron affinity, low electronegativity, and small size, however, boron does not form a metallic lattice with delocalised valence electrons. Instead, boron forms unique and intricate structures that contain multicentre bonds, in which a pair of electrons holds together three or more atoms.

The basic building block of elemental boron is not the individual boron atom. Unlike metallic solids, elemental boron consists of a regular array of B_{12} icosahedra (Fig. 6.9). Each boron atom is connected to five other boron atoms within the B_{12} unit. The allotrope of boron with the simplest structure is α-rhombohedral boron, which consists of B_{12} octahedra in an almost cubic close-packed lattice (Fig. 6.9a). A side view of the structure (Fig. 6.9b) illustrates that icosahedra do not pack together very well that results in the availability of voids in the structure and thus its low density.

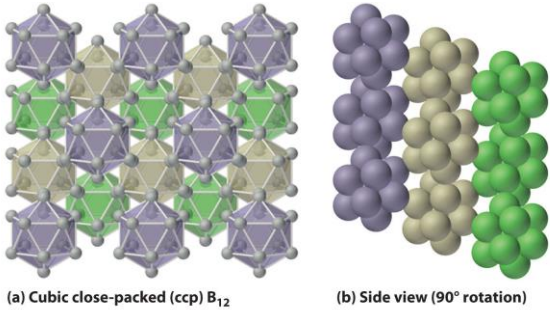


Figure 6.9 Solid boron contains B_{12} icosahedra

Elemental boron can react with many nonmetallic elements to give binary compounds that have a variety of applications. For example, boron nitride (BN) is produced by heating boron with excess nitrogen (6.37); boron oxide (B_2O_3) is produced by heating boron with excess oxygen (6.38), and boron trihalides (BX_3) are formed by heating boron with excess halogen (6.39).

$$2B_{(s)} + N_{2(g)} \xrightarrow{t} 2BN_{(s)} \quad (6.37)$$

$$4B_{(s)} + 3O_{2(g)} \xrightarrow{t} 2B_2O_{3(s)} \quad (6.38)$$

$$2B_{(s)} + 3X_{2(g)} \xrightarrow{t} 2BX_{3(g)} \qquad (6.39)$$

As is typical of elements lying near the dividing line between metals and nonmetals, many compounds of boron are amphoteric, dissolving in either acid or base.

Boron nitride is similar to elemental carbon. With eight electrons, the B–N unit is isoelectronic with the C–C unit and B and N have the same average size and electronegativity as C. The most stable form of BN is similar to graphite, containing six-membered B_3N_3 rings arranged in layers. At high temperature and pressure, hexagonal BN converts to a cubic structure similar to diamond, which is one of the hardest substances known. Boron oxide (B_2O_3) contains layers of trigonal planar BO_3 groups (analogous to BX_3) in which the oxygen atoms bridge two boron atoms. It dissolves many metal and nonmetal oxides, including SiO_2, to give a wide range of commercially important borosilicate glasses.

At high temperatures, boron also reacts with virtually all metals to give metal borides that contain regular 3D networks, or clusters, of boron atoms. Some metal-rich borides such as ZrB_2 and TiB_2 are hard and corrosion-resistant at high temperatures and used in high-temperature applications.

The simplest example of boron hydrides is diborane (B_2H_6), which contains two bridging hydrogen atoms, as shown in Fig. 6.10. The structure of boron-hydrogen compounds cannot be explained with the concepts of simple bonding because all these compounds contain multicentre bonds. In particular, a hydrogen atom, with a filled 1s orbital, interacts simultaneously with empty sp^3 hybrids on the boron atoms of two BH_3 units. The two bonding electrons occupy the lowest-energy (σ) bonding orbital, thereby holding all three atoms (B–H–B) together. Thus, a three-centre bond uses two electrons to link three atoms in the hydrogen-bridged dimer B_2H_6.

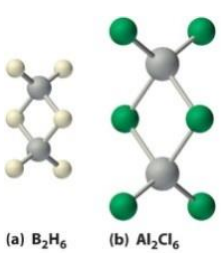


Figure 6.10 Structures of (a) – diborane (B_2H_6) and (b) – aluminium chloride (Al_2Cl_6)

In contrast, the bonding in the halogen-bridged dimer Al_2Cl_6 can be described in terms of electron-pair bonds (Fig. 6.10), in which a chlorine atom bonded to one aluminium atom acts as a Lewis base by donating a lone pair of electrons to another aluminium atom, which acts as a Lewis acid.

The enthalpy of combustion of diborane (B_2H_6) is −2165 kJ/mol, one of the highest values known:

$$B_2H_{6(g)} + 3O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O_{(l)};\quad \Delta H_{comb} = -2165\ \text{kJ/mol} \qquad (6.40)$$

Because boron and hydrogen have almost identical electronegativities, the reactions of boron hydrides are dictated by minor differences in the distribution of electron density in a given compound. In general, two distinct types of reaction are observed: electron-rich species such as the BH_4^- ion are reductants, whereas electron-deficient species such as B_2H_6 act as oxidants.

Reactions and compounds of the heavier group 13 elements

All four of the heavier group 13 elements (Al, Ga, In, and Tl) react readily with the halogens to form compounds with a 1:3 stoichiometry:

$$2M_{(s)} + 3X_{2(s,l,g)} \rightarrow 2MX_{3(s)} \text{ or } M_2X_6 \qquad (6.41)$$

The reaction of Tl with iodine is an exception. Even if the product has the stoichiometry TlI_3, it is not thallium (III) iodide. It is the Tl^+ salt of the triiodide ion (I_3^-) or a thallium (I) compound. This compound forms because the oxidation potential of iodine is not high enough to oxidise thallium to the +3 oxidation state.

Among halides, only the fluorides exhibit behaviour typical of an ionic compound. In contrast, the trichorides, tribromides, and triiodides of aluminium, gallium, and indium, as well as $TlCl_3$ and $TlBr_3$, are more covalent in character and form halogen-bridged dimers represented in Fig. 6.10b. Although the structure of these dimers is similar to that of diborane (B_2H_6), the bonding can be described in terms of electron-pair bonds rather than the delocalised electron-deficient bonding found in diborane. The group 13 trihalides are potent Lewis acids being poor electron-pair donors that react readily with Lewis bases, such as amines, to form a Lewis acid-base adduct:

$$Al_2Cl_{6(soln)} + 2(CH_3)_3N_{(soln)} \rightarrow 2(CH_3)_3N{:}AlCl_{3(soln)} \qquad (6.42)$$

In water, the halides of the group 13 metals hydrolyse to produce the metal hydroxide $M(OH)_3$:

$$MX_{3(s)} + 3H_2O_{(l)} \rightarrow M(OH)_{3(s)} + 3HX_{(aq)} \qquad (6.43)$$

Like boron (6.38), all the heavier group 13 elements react with excess oxygen at elevated temperatures to give the trivalent oxide (M_2O_3), although Tl_2O_3 is unstable:

$$4M_{(s)} + 3O_{2(g)} \xrightarrow{t} 2M_2O_{3(s)} \qquad (6.44)$$

Aluminium, gallium, and indium also react with other chalcogens to form chalcogenides with the stoichiometry M_2Y_3. However, because Tl (III) is too strong an oxidant to form a stable compound with electron-rich anions such as S^{2-}, Se^{2-}, and Te^{2-}, thallium forms only the thallium (I) chalcogenides with the stoichiometry Tl_2Y.

Only aluminium, like boron, reacts directly with N_2 (at very high temperatures) to give AlN, which is used in transistors and microwave devices; GaN and InN can be prepared using other methods. All the metals, again except Tl, also react with the heavier group 15 elements (pnicogens) to form the so-called III–V compounds, such as GaAs, used as semiconductors in microelectronics.

Unlike boron, the heavier group 13 elements do not react directly with hydrogen. Only the aluminium and gallium hydrides are known, but they must be prepared indirectly; AlH_3 is an insoluble, polymeric solid that is rapidly decomposed by water, whereas GaH_3 is unstable at room temperature.

Complexes of group 13 elements

Boron has a relatively limited tendency to form complexes, but aluminium, gallium, indium, and, to some extent, thallium form many complexes. Some of the simplest complexes are the hydrated metal ions $[M(H_2O)_6{}^{3+}]$, which are relatively strong Broensted–Lowry acids that can lose a proton to form the $M(H_2O)_5(OH)^{2+}$ ion:

$$[M(H_2O)_6]^{3+}{}_{(aq)} \rightarrow M(H_2O)_5(OH)^{2+}{}_{(aq)} + H^+{}_{(aq)} \qquad (6.45)$$

Group 13 metal ions also form stable complexes with species that contain two or more negatively charged groups, such as the oxalate ion.

Summary

Boron behaves chemically like a nonmetal, whereas its heavier congeners exhibit metallic behaviour. Many of the inconsistencies observed in the properties of the group 13 elements can be explained by the increase in Z_{eff} that arises from poor shielding of the nuclear charge by the filled $(n-1)d^{10}$ and $(n-2)f^{14}$ subshells. Instead of forming a metallic lattice with delocalised valence electrons, boron forms unique aggregates that contain multicentre bonds, including metal borides, in which boron is bonded to other boron atoms to form three-dimensional networks or clusters with regular geometric structures.

All neutral compounds of the group 13 elements are electron-deficient and behave like Lewis acids. The trivalent halides of the heavier elements form halogen-bridged dimers that contain electron-pair bonds, rather than the delocalised electron-deficient bonds characteristic of diborane. Their oxides dissolve in dilute acid, although the oxides of aluminium and gallium are amphoteric. None of the group 13 elements reacts directly with hydrogen, and the stability of the hydrides prepared by other routes decreases when going down the group. In contrast to boron, the heavier group 13 elements form a large number of complexes in the +3 oxidation state.

6.3.2 Group 14

The elements of group 14 are characterised by a greater range of chemical behaviour than any other family in the periodic table.

Preparation and general properties

The natural abundance of the group 14 elements varies tremendously. Elemental carbon, for example, ranks only 17th on the list of constituents of Earth's crust. Pure graphite is obtained by reacting coke, an amorphous form of carbon used as a reductant in the production of steel, with silica to give silicon carbide (SiC). The carbide is then thermally decomposed at very high temperatures (2700°C) to give graphite:

$$SiO_{2(s)} + 3C_{(s)} \xrightarrow{t} SiC_{(s)} + 2CO_{(g)} \quad (6.46)$$

$$SiC_{(s)} \xrightarrow{t} Si_{(s)} + C_{(graph)} \quad (6.47)$$

One allotrope of carbon, diamond, is metastable under normal conditions. At pressures higher than 50000 atm, however, the diamond structure is favoured and is the most stable form of carbon.

Silicon is the next most abundant on Earth after oxygen. Pure silicon is obtained by reacting impure silicon with Cl_2 to give $SiCl_4$, followed by the fractional distillation of the impure $SiCl_4$ and reduction with H_2:

$$SiCl_{4(l)} + 2H_{2(g)} \xrightarrow{t} Si_{(s)} + 4HCl_{(g)} \quad (6.48)$$

Several million tons of silicon are annually produced with this method. Ultrapure silicon and germanium form the basis of the modern electronics industry.

In contrast to silicon, the concentrations of germanium, lead and tin are much lower. No concentrated ores of germanium are known; like indium, germanium is generally recovered from flue dust obtained by processing the ores of metals such as zinc. Because germanium is essentially transparent to infrared radiation, it is used in optical devices.

Tin and lead are soft metals that are too weak for structural applications, but because tin is flexible, corrosion-resistant, and nontoxic, it is used as a coating in food packaging. Tin is also used in superconducting magnets and low-melting-point alloys such as solder and pewter. By far the single largest use of lead is in lead storage batteries. Pure lead is obtained by heating galena (PbS) in air and reducing the oxide (PbO) to the metal with carbon, followed by electrolytic deposition to increase the purity:

$$PbS_{(s)} + 3/2O_{2(g)} \xrightarrow{t} PbO_{(s)} + SO_{2(g)} \quad (6.49)$$

$$PbO_{(s)} + C_{(s)} \xrightarrow{t} Pb_{(l)} + CO_{(g)} \quad (6.50)$$

$$\text{or } PbO_{(s)} + CO_{(g)} \xrightarrow{t} Pb_{(l)} + CO_{2(g)} \quad (6.51)$$

The group 14 elements have ns^2np^2 valence electron configurations. All form compounds in which they formally lose either the two np and the two ns valence electrons or just the two np valence electrons, giving a +4 or +2 oxidation state, respectively. The relative stability of the +2 oxidation state increases smoothly from carbon to Pb. Table 6.6 illustrates some properties of the group 14 elements.

Many carbon compounds contain multiple bonds formed by π overlap of singly occupied 2p orbitals on adjacent atoms. Compounds of silicon, germanium, tin, and lead with the same stoichiometry as those of carbon, however, tend to have different structures and properties.

For example, CO_2 is a gas that contains discrete O=C=O molecules, whereas the most common form of SiO_2 is the high-melting solid known as quartz, the major component of sand. Instead of discrete SiO_2 molecules, quartz contains a 3D network of Si atoms that is similar to the structure of diamond but with an oxygen atom inserted between each pair of silicon atoms. Thus each silicon atom is linked to four other silicon atoms by bridging oxygen atoms. The tendency to catenate (to form chains of like atoms) reduces rapidly from top to down of group 14 because bond energies for both the E–E and E–H bonds decrease with increasing atomic number (where E is any group 14 element).

Table 6.6 Properties of the group 14 elements

Property	Carbon	Silicon	Germanium	Tin	Lead
atomic symbol	C	Si	Ge	Sn	Pb
atomic number	6	14	32	50	82
atomic mass (amu)	12.01	28.09	72.64	118.71	207.2
valence electron configuration *	$2s^22p^2$	$3s^23p^2$	$4s^24p^2$	$5s^25p^2$	$6s^26p^2$
melting point/boiling point (°C)	4489 (at 10.3 MPa)/3825	1414/3265	939/2833	232/2602	327/1749
density (g/cm^3) at 25°C	2.2 (graphite), 3.51 (diamond)	2.33	5.32	7.27(white)	11.30
atomic radius (pm)	77 (diamond)	111	125	145	154
first ionisation energy (kJ/mol)	1087	787	762	709	716
most common oxidation state	+4	+4	+4	+4	+4
ionic radius (pm)**	≈29	≈40	53	69	77.5
electron affinity (kJ/mol)	−122	−134	−119	−107	−35
electronegativity	2.6	1.9	2.0	2.0	1.8
standard reduction potential (E°, V) (for $EO_2 \rightarrow E$ in acidic solution)	0.21	−0.86	−0.18	−0.12	0.79
product of reaction with O_2	CO_2, CO	SiO_2	GeO_2	SnO_2	PbO
type of oxide	acidic (CO_2)	acidic neutral (CO)	amphoteric	amphoteric	amphoteric
product of reaction with N_2	none	Si_3N_4	none	Sn_3N_4	none
product of reaction with X_2***	CX_4	SiX_4	GeX_4	SnX_4	PbX_2
product of reaction with H_2	CH_4	none	none	none	none

* The configuration shown does not include filled d and f subshells.

** The values cited are for six-coordinate +4 ions in the most common oxidation state, except for C^{4+} and Si^{4+}, for which values for the four-coordinate ion are estimated.

*** X is Cl, Br, or I. Reaction with F_2 gives the tetrafluorides (EF_4) for all group 14 elements, where E represents any group 14 element.

Consequently, inserting a CH_2 group into a linear hydrocarbon such as n-hexane is exergonic ($\Delta G° = -45$ kJ/mol), whereas inserting a

SiH_2 group into the silicon analogue of n-hexane (Si_6H_{14}) costs energy ($\Delta G° \approx +25$ kJ/mol). As a result of this trend, the thermal stability of catenated compounds decreases rapidly from carbon to lead.

There is a large difference between the lightest element (C) and the others in size, ionisation energy, and electronegativity. As in group 13, the second and third elements (Si and Ge) are similar, and there is a reversal in the trends for some properties, such as ionisation energy, between the fourth and fifth elements (Sn and Pb). As for group 13, these effects can be explained by the presence of filled (n – 1)d and (n – 2)f subshells, whose electrons are relatively poor at screening the outermost electrons from the higher nuclear charge.

Reactions and compounds of carbon

Carbon is the building block of all organic compounds, whereas inorganic compounds of carbon include metal carbonates, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners.

The structures of the allotropes of carbon — diamond, graphite, fullerenes, and nanotubes — are distinct, but they all contain simple electron-pair bonds.

All the carbon tetrahalides (CX_4) are known and characterised by the tetrahedral geometry. They are generally not obtained by the direct reaction of carbon with the elemental halogens (X_2) but by indirect methods such as the following reaction, where X is Cl or Br:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)} \qquad (6.52)$$

The stability of carbon tetrahalides decreases rapidly when the halogen increases in size due to poor orbital overlap and enlarged crowding. Since the C–F bond is about 25% stronger than a C–H bond, fluorocarbons are thermally and chemically more stable than the corresponding hydrocarbons, while having a similar hydrophobic character. A polymer of tetrafluoroethylene ($F_2C{=}CF_2$), analogous to polyethylene and known as Teflon, is widely used as a non-stick lining.

Carbon reacts with oxygen to form either CO or CO_2, depending on the stoichiometry. Carbon monoxide is a colourless, odourless, and poisonous gas that reacts with the iron in haemoglobin to form a Fe–CO unit, which prevents haemoglobin from binding, transporting, and releasing oxygen in the blood. In the laboratory, carbon monoxide can be prepared on a small scale by dehydrating formic acid with concentrated sulfuric acid:

$$HCO_2H_{(l)} \xrightarrow{H_2SO_4(l)} CO_{(g)} + H_3O^+_{(aq)} + HSO_4^- \qquad (6.53)$$

Carbon monoxide also reacts with the halogens to form the oxohalides (COX_2). Probably the best known of these is phosgene ($Cl_2C{=}O$), which is used for polyurethanes production in the chemical industry. Since phosgene is highly poisonous, it was used as a chemical weapon in the World War I (1914–1918):

$$CO_{(g)} + Cl_{2(g)} \xrightarrow{t} Cl_2C{=}O_{(g)} \qquad (6.54)$$

Carbon dioxide can be prepared on a small scale by reacting almost any metal carbonate or bicarbonate salt with a strong acid. As is typical of a nonmetal oxide, CO_2 reacts with water to form acidic solutions containing carbonic acid (H_2CO_3). In contrast to its reactions with oxygen, reacting carbon with sulfur at high temperatures produces only carbon disulfide (CS_2):

$$C_{(s)} + 2S_{(g)} \xrightarrow{t} CS_{2(g)} \qquad (6.55)$$

The selenium analogue CSe_2 is also known. Both have the linear structure, and both are vile-smelling (and in the case of CSe_2, highly toxic), volatile liquids. The sulfur and selenium analogues of carbon monoxide, CS and CSe, are unstable because the C≡Y bonds (Y is S or Se) are much weaker than the C≡O bond due to poorer π orbital overlap.

Binary compounds of carbon with less electronegative elements are called carbides. The chemical and physical properties of carbides depend strongly on the identity of the second element, resulting in three general classes: ionic carbides, interstitial carbides, and covalent carbides. The reaction of carbon at high temperatures with electropositive metals such as those of groups 1 and 2 and aluminium produces ionic carbides, which contain discrete metal cations and carbon anions.

The reaction of carbon with most transition metals at high temperatures produces interstitial carbides. Due to the less electropositive nature of the transition metals, these carbides contain covalent metal-carbon interactions, which result in different properties: most interstitial carbides are good conductors of electricity, have high melting points, and are among the hardest substances known. Interstitial carbides exhibit a variety of nominal compositions, and they are often nonstoichiometric compounds whose carbon content can vary over a wide range.

Elements, which demonstrate electronegativity similar to that of carbon, compose covalent carbides, such as silicon carbide (SiC) and boron carbide (B_4C). These substances are extremely hard, have high melting points, and are chemically inert.

Reactions and compounds of the heavier group 14 elements

The structures and properties of compounds of silicon, germanium, tin, and lead are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas grey (α) tin has a diamond-like structure and is a semiconductor. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.

Based on its position in the periodic table, silicon is expected to be amphoteric. In reality, it dissolves in the strong aqueous base to produce hydrogen gas and solutions of silicates, but hydrofluoric acid is the only aqueous acid which reacts with silicon, presumably due to the formation of the stable SiF_6^{2-} ion. Germanium is more metallic in its behaviour than silicon. For example, it dissolves in hot oxidising acids, such as HNO_3 and H_2SO_4, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a Pb^{2+} salt, such as $PbSO_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus CCl_2 is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques. In contrast, $SnCl_2$ is a stable at room temperature polymeric solid and $PbCl_2$ is an insoluble crystalline solid with a structure similar to that of $SnCl_2$.

Although the first four elements of group 14 form tetrahalides (MX_4) with all the halogens, only fluorine can oxidise lead to the +4 oxidation state, giving PbF_4. The tetrahalides of silicon and germanium react rapidly with water to give amphoteric oxides (where M is Si or Ge):

$$MX_{4(s,l)} + 2H_2O_{(l)} \rightarrow MO_{2(s)} + 4HX_{(aq)} \qquad (6.56)$$

In contrast, the tetrahalides of tin and lead react with water to give hydrated metal ions.

Because of the stability of its +2 oxidation state, lead reacts with oxygen or sulfur to form PbO or PbS, respectively, whereas heating the other group 14 elements with excess O_2 or S_8 gives the corresponding dioxides or disulfides, respectively. The dioxides of the group 14 elements become increasingly basic as we go down the group.

Because the Si–O bond is even stronger than the C–O bond (~452 kJ/mol versus ~358 kJ/mol), silicon has a strong affinity for oxygen. In the case of Si–O bonds, the presence of relatively low-energy, empty d orbitals on Si and nonbonding electron pairs in the p or sp^n hybrid orbitals of O results in a partial π bond (Fig. 6.11).

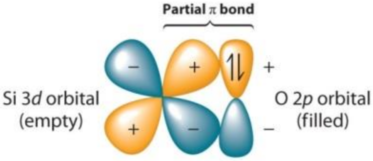


Figure 6.11 Pi bonding between silicon and oxygen

As is seen, both electrons are supplied by oxygen in a partial π bond. Since the newly formed Si–O bond is double, it is significantly stronger and shorter than would otherwise be expected. Compounds with anions that contain only silicon and oxygen are called silicates. Both the number of oxygen atoms shared between silicon atoms and the type of linkage of units vary considerably in different silicates In a large and important class of materials called aluminosilicates, some of the Si atoms are replaced by Al atoms.

Silicon and germanium react with nitrogen at high temperature to form nitrides (M_3N_4):

$$3Si_{(l)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} \qquad (6.57)$$

Silicon nitride has attractive properties for high-temperature applications.

Because of the diagonal relationship between boron and silicon, metal silicides and metal borides exhibit many similarities. Silicides of active metals, such as Mg_2Si, are ionic compounds that contain the Si^{4-} ion. They react with aqueous acid to form silicon hydrides such as SiH_4:

$$Mg_2Si_{(s)} + 4H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + SiH_{4(g)} \qquad (6.58)$$

Unlike carbon, catenated silicon hydrides become thermodynamically less stable as the chain lengthens. Thus straight-chain and branched silanes (analogous to alkanes) are known up to only n = 10. Because E=E and E≡E bonds become weaker with increasing atomic number (where E is any group 14 element), simple silicon, germanium, and tin analogues of alkenes, alkynes, and aromatic hydrocarbons are either unstable (Si=Si and Ge=Ge) or unknown.

The only important organic derivatives of lead are compounds such as tetraethyllead [$(CH_3CH_2)_4Pb$]. Because the Pb–C bond is weak, these compounds decompose at relatively low temperatures to produce alkyl radicals (R·).

Compounds that contain Si–C and Si–O bonds are stable and important. High-molecular-mass polymers called silicones contain a $(Si–O–)_n$ backbone with organic groups attached to Si. The properties of silicones are determined by the chain length, the type of organic group, and the extent of cross-linking between the chains. Without cross-linking, silicones are waxes or oils, but cross-linking can produce flexible materials used in sealants, gaskets, car polishes, lubricants, and even elastic materials.

Summary

The group 14 elements show the greatest range of chemical behaviour of any group in the periodic table. Because the covalent bond strength decreases with increasing atomic size and greater-than-expected ionisation energies due to an increase in Z_{eff}, the stability of the +2 oxidation state increases from carbon to lead. The tendency to form multiple bonds and to catenate decreases as the atomic number increases. The stability of the carbon tetrahalides decreases as the halogen increases in size because of poor orbital overlap.

Carbon forms three kinds of carbides with less electronegative elements: ionic carbides, which contain metal cations and C^{4-} (methide) or C_2^{2-} (acetylide) anions; interstitial carbides, which are characterised by covalent metal-carbon interactions; and covalent carbides, which have three-dimensional covalent network structures. Consistent with periodic trends, metallic behaviour increases down the group. Silicon has a tremendous affinity for oxygen because of partial Si–O π bonding. Dioxides of the group 14 elements become increasingly basic down the group and their metallic character increases. Silicates contain anions that consist of only silicon and oxygen. Aluminosilicates are formed by replacing some of the Si atoms in silicates by Al atoms. Nitrides formed by reacting silicon or germanium with nitrogen are strong, hard, and chemically inert. The hydrides lose their thermodynamic stability when going down the group. Moreover, as atomic size increases, multiple bonds between or to the group 14 elements become weaker. Silicones, which contain a Si–O backbone and Si–C bonds, are high-molecular-mass polymers whose properties depend on their compositions.

6.3.3 Group 15: nitrogen family (pnicogens)

Like the group 14 elements, the lightest member of group 15, nitrogen, is found in nature as the free element, and the heaviest elements (antimony and arsenic) have been known for centuries because they are easily isolated from their ores.

Preparation and general properties

The atmosphere is a huge source of nitrogen gas, whereas Earth's crust is relatively poor in nitrogen. The only important nitrogen ores are large deposits of KNO_3 and $NaNO_3$. Consequently, virtually all nitrogen compounds produced on an industrial scale use atmospheric nitrogen as the starting material. Distillation of liquefied air yields nitrogen gas that is more than 99.99% pure, but small amounts of very pure nitrogen gas can be obtained from the thermal decomposition of sodium azide:

$$2NaN_{3(s)} \xrightarrow{t} 2Na_{(l)} + 3N_{2(g)} \qquad (6.59)$$

Phosphorus is much more abundant in ores than nitrogen. Like aluminium and silicon, phosphorus is always found in combination with oxygen, and large inputs of energy are required to isolate it.

The other three elements of the group are much less abundant. They have a high affinity for the chalcogens. They are usually found as the sulfide ores (M_2S_3), often in combination with sulfides of other heavy elements, such as copper, silver, and lead.

In group 15, as elsewhere in the p block, one can see large differences in size, ionisation energy, electron affinity, and electronegativity between the lightest element (N) and its congeners (Table 6.7). The chemical behaviour of the elements can be summarised rather simply: nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. With their ns^2np^3 valence electron configurations, all form compounds by losing either the three np valence electrons to form the +3 oxidation state or the three np and the two ns valence electrons to give the +5 oxidation state. The stability of higher oxide decreases smoothly from phosphorus to bismuth.

Table 6.7 Properties of the group 15 elements

Property	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
atomic symbol	N	P	As	Sb	Bi
atomic number	7	15	33	51	83
atomic mass (amu)	14.01	30.97	74.92	121.76	209.98
valence electron configuration *	$2s^2 2p^3$	$3s^2 3p^3$	$4s^2 4p^3$	$5s^2 5p^3$	$6s^2 6p^3$
melting point/boiling point (°C)	–210/–196	44.15/281^c	817 (at 3.70 MPa)/603 (sublimes) ***	631/1587	271/1564
density (g/cm^3) at 25°C	1.15 (g/L)	1.82 **	5.75 ***	6.68	9.79
atomic radius (pm)	56	98	114	133	143
first ionisation energy (kJ/mol)	1402	1012	945	831	703
common oxidation state(s)	−3 to +5	+5, +3, −3	+5, +3	+5, +3	+3
ionic radius (pm) §	146 (–3), 16 (+3)	212 (–3), 44 (+3)	58 (+3)	76 (+3), 60 (+5)	103 (+3)
electron affinity (kJ/mol)	0	–72	–78	–101	–91
electronegativity	3.0	2.2	2.2	2.1	1.9
standard reduction potential (E°, V) ($E^V \rightarrow E^{III}$ in acidic solution) §§	+0.93	−0.28	+0.56	+0.65	—
product of reaction with O_2	NO_2, NO	P_4O_6, P_4O_{10}	As_4O_6	Sb_2O_5	Bi_2O_3
type of oxide	acidic (NO_2), neutral (NO, N_2O)	acidic	acidic	amphoteric	basic
product of reaction with N_2	—	none	none	none	none
product of reaction with X_2	none	PX_3, PX_5	AsF_5, AsX_3	SbF_5, $SbCl_5$, $SbBr_3$, SbI_3	BiF_5, BiX_3
product of reaction with H_2	none	none	none	none	none

* The configuration shown does not include filled d and f subshells.

** For white phosphorus.

*** For grey arsenic.

§ The values cited are for six-coordinate ions in the indicated oxidation states. The N^{5+}, P^{5+}, and As^{5+} ions are not known species.

§§ The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O$; for P and As, it is $H_3EO_4 + 2H^+ + 2e^- \rightarrow H_3EO_3 + H_2O$; and for Sb, it is $Sb_2O_5 + 4e^- + 10H^+ \rightarrow 2Sb^{3+} + 5H_2O$.

Besides, the relatively large magnitude of the electron affinity of the lighter group 5 elements enables them to form compounds in the –3 oxidation state (such as NH_3 and PH_3).

In such compounds, three electrons are formally added to the neutral atom to give a filled np subshell. Nitrogen has the unusual ability to form compounds in nine different oxidation states, including –3, +3, and +5. Because neutral covalent compounds of the trivalent group 5 elements contain a lone pair of electrons on the central atom, they tend to behave as Lewis bases.

Reactions and compounds of nitrogen

Like carbon, nitrogen has four valence orbitals (one 2s and three 2p), so it can participate in at most four electron-pair bonds by using sp^3 hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because repulsive interactions occur between lone pairs of electrons on adjacent atoms. These interactions become important at the shorter internuclear distances encountered with second-period elements of groups 15, 16, and 17. Stable compounds with N–N bonds are limited to chains of no more than three N atoms, such as the azide ion (N_3^-).

Nitrogen is the only element of the considered group that normally forms multiple bonds with itself and other second-period elements, using π overlap of adjacent np orbitals. Thus the stable form of elemental nitrogen is N_2, which N≡N bond is much stronger ($D_{N\equiv N}$ = 942 kJ/mol) than the N–N and N=N bonds ($D_{N–N}$ = 167 kJ/mol; $D_{N=N}$ = 418 kJ/mol). Therefore, all compounds with N–N and N=N bonds are thermodynamically unstable concerning the formation of N_2.

In contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: it reacts with metallic lithium to form lithium nitride, and it is reduced to ammonia by certain microorganisms. At higher temperatures, however, N_2 reacts with more electropositive group 13 elements to form binary nitrides, which range from covalent to ionic.

Binary compounds of nitrogen with oxygen, hydrogen, or other nonmetals are usually covalent molecular substances. At elevated temperatures, N_2 reacts with H_2 to form ammonia, with O_2 to form a mixture of NO and NO_2, and with carbon to form cyanogen (N≡C–C≡N). Elemental nitrogen does not react with the halogens or the other chalcogens. Nonetheless, all the binary nitrogen halides (NX_3) are known and prepared by reacting the halogen with NH_3. Except for NF_3, all are toxic, thermodynamically unstable, and potentially explosive.

Both nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are thermodynamically unstable, with positive free energies of formation. Unlike NO, NO_2 reacts readily with excess water, forming a 1:1 mixture of nitrous acid (HNO_2) and nitric acid (HNO_3):

$$2NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{2(aq)} + HNO_{3(aq)} \qquad (6.60)$$

Nitrogen also forms N_2O (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with CO_2 and can be represented as $^{-}N{=}N^{+}{=}O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows (Fig. 6.12):

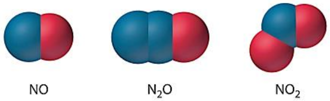


Figure 6.12 Structure of nitrogen oxides

At elevated temperatures, nitrogen reacts with highly electropositive metals to form ionic nitrides, such as Li_3N and Ca_3N_2. These compounds consist of ionic lattices formed by M^{n+} and N^{3-} ions. Just as boron forms interstitial borides and carbon forms interstitial carbides, nitrogen with less electropositive metals forms a range of very hard interstitial nitrides, in which nitrogen occupies holes in a close-packed metallic structure.

Nitrogen also reacts with semimetals at very high temperatures to produce covalent nitrides, such as Si_3N_4 and BN, which are solids with extended covalent network structures similar to those of graphite or diamond. Consequently, they are usually high melting and chemically inert materials.

Ammonia (NH_3) is one of the few thermodynamically stable binary compounds of nitrogen with a nonmetal. It is not flammable in air, but it burns in an O_2 atmosphere:

$$4NH_{3(g)} + 3O_{2(g)} \rightarrow 2N_{2(g)} + 6H_2O_{(g)} \qquad (6.61)$$

About 10% of the ammonia produced annually is used to make fibres and plastics that contain amide bonds, such as nylons and polyurethanes, while 5% is used in explosives. Large amounts of anhydrous liquid ammonia are used as fertiliser.

Nitrogen forms two other important compounds with hydrogen. Hydrazoic acid (HN_3), also called hydrogen azide, is a colourless, highly toxic, and explosive substance. Hydrazine (N_2H_4) is also potentially explosive; it is used as a rocket propellant and to inhibit corrosion in boilers.

Reactions and compounds of the heavier group 15 elements

The heavier group 15 elements form catenated compounds that contain only single bonds, whose stability decreases rapidly in going down the group. For example, phosphorus exists as multiple allotropes, the most common of which is white phosphorus, which consists of P_4 tetrahedra and behaves like a typical nonmetal. White phosphorus is volatile; it has a low melting point and is soluble in nonpolar solvents. Why is it so reactive and so easily converted to more stable allotropes? Heating white phosphorus for several days converts it to red phosphorus, a polymer that is air-stable and virtually insoluble. The third allotrope of phosphorus, black phosphorus, is prepared by heating the other allotropes under high pressure. This allotrope is even less reactive, denser and higher melting than red phosphorus. White phosphorus is an electrical insulator, and red and black phosphorus are semiconductors. The three heaviest group 15 elements, arsenic, antimony, and bismuth, all have a metallic lustre, but they are very brittle and have limited conductivity.

The reactivity of elements decreases as we go down the column. Phosphorus is by far the most reactive of them, forming binary compounds with every element in the periodic table except antimony, bismuth, and the noble gases. Phosphorus reacts rapidly with O_2, whereas arsenic burns in pure O_2 if ignited, and antimony and bismuth react with O_2 only when heated. None of the group 15 elements reacts with nonoxidising acids such as aqueous HCl, but all dissolve in oxidising acids such as HNO_3. Only bismuth behaves like a metal, dissolving in HNO_3 to give the hydrated Bi^{3+} cation.

The heavier elements can use energetically accessible 3d, 4d, or 5d orbitals to form dsp^3 or d^2sp^3 hybrid orbitals for bonding. Consequently, these elements often have coordination numbers of 5 or higher. Phosphorus and arsenic form halides (e.g., $AsCl_5$) that are generally covalent molecular species and behave like typical nonmetallic halides, reacting with water to form the corresponding oxoacids (in this case, H_3AsO_4). All the pentahalides are potent Lewis acids that can expand their coordination to accommodate the lone pair of a Lewis base:

$$AsF_{5(soln)} + F^-_{(soln)} \rightarrow AsF_6{}^-_{(soln)} \qquad (6.62)$$

In contrast, bismuth halides have extended lattice structures and dissolve in water to produce hydrated ions, consistent with the stronger metallic character of bismuth.

Except for BiF_3, which is essentially an ionic compound, the trihalides are volatile covalent molecules with a lone pair of electrons on the central atom. Like the pentahalides, the trihalides react rapidly with water. In the cases of phosphorus and arsenic, the products are the corresponding acids, H_3PO_3 and H_3AsO_3, where E is P or As:

$$EX_{3(l)} + 3H_2O_{(l)} \rightarrow H_3EO_{3(aq)} + 3HX_{(aq)} \qquad (6.63)$$

Phosphorus halides are also used to produce insecticides, flame retardants, and plasticisers.

With energetically accessible d orbitals, phosphorus and, to a lesser extent, arsenic can form π bonds with second-period atoms such as N and O. The first four elements in group 15 also react with oxygen to produce the corresponding oxide in the +3 oxidation state.

The heavier elements form sulfides that range from molecular species with three-dimensional cage structures, such as P_4S_3, to layered or ribbon structures, such as Sb_2S_3 and Bi_2S_3, which are semiconductors.

Reacting the heavier group 15 elements with metals produces substances which properties are susceptible to the metal content. Metal-rich phosphides (such as M_4P) are hard, high-melting, electrically conductive solids with a metallic lustre, whereas phosphorus-rich phosphides (such as MP_{15}) are lower melting and less thermally stable because they contain catenated P_n units. Many organic or organometallic compounds of the heavier elements containing one to five alkyl or aryl groups are also known. Their thermal stability decreases from phosphorus to bismuth.

Summary

In group 15, nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. Nitrogen forms compounds in nine different oxidation states. The stability of the +5 oxidation state decreases from phosphorus to bismuth because of the inert-pair effect. Due to their higher electronegativity, the lighter elements form compounds in the –3 oxidation state. Because of the presence of a lone pair of electrons on the element, neutral covalent compounds of the trivalent elements are Lewis bases. Nitrogen does not form stable catenated compounds because of repulsions between lone pairs of electrons on adjacent atoms, but it forms multiple bonds with other second-period atoms. Nitrogen reacts with electropositive elements to produce solids that range from covalent to ionic. Reaction with electropositive metals produces ionic nitrides, reaction with less electropositive metals produces interstitial nitrides, and reaction with semimetals produces covalent nitrides. The reactivity of the group 15 elements decreases with increasing atomic number. Compounds of the heavier atoms often have coordination numbers of 5 or higher and use dsp^3 or d^2sp^3 hybrid orbitals for bonding. Because phosphorus and arsenic have energetically accessible d orbitals, these elements form π bonds with second-period atoms such as O and N. Phosphorus reacts with metals to produce phosphides. Metal-rich phosphides are hard, high-melting, electrically conductive solids with a metallic lustre, whereas phosphorus-rich phosphides, which contain catenated phosphorus units, are lower melting and less thermally stable.

6.3.4 Group 16: chalcogens

The chalcogens are the first group in the p block to have no stable metallic elements. All isotopes of polonium (Po), the only metal in group 16, are radioactive, and only one element in the group, tellurium (Te), can be described as a semimetal. The lightest element of group 16, oxygen, is found in nature as the free element.

Preparation and general properties

Oxygen is by far the most abundant element in Earth's crust and the hydrosphere (about 44% and 86% by mass, respectively). The same process that is used to obtain nitrogen from the atmosphere produces pure oxygen. Oxygen can also be obtained by the electrolysis of water, the decomposition of alkali metal or alkaline earth peroxides or superoxides, or the thermal decomposition of simple inorganic salts, such as potassium chlorate in the presence of a catalytic amount of MnO_2:

$$2KClO_{3(s)} \xleftrightarrow{t,\ MnO_{2(s)}} 2KCl_{(s)} + 3O_{2(g)} \tag{6.64}$$

Sulfur is not very abundant, but it is found as elemental sulfur in rock formations overlying salt domes, which often accompany petroleum deposits. Sulfur is also recovered from H_2S and organosulfur compounds in crude oil and coal and metal sulfide ores such as pyrite (FeS_2). Because selenium and tellurium are chemically similar to sulfur, they are usually found as minor contaminants in metal sulfide ores and are typically recovered as by-products.

With their ns^2np^4 electron configurations, the chalcogens are two electrons short of a filled valence shell. Thus in reactions with metals, they tend to acquire two additional electrons to form compounds in the –2 oxidation state. This tendency is greatest for oxygen, the chalcogen with the highest electronegativity. The heavier, less electronegative chalcogens can lose either four np electrons or four np and two ns electrons to form compounds in the +4 and +6 oxidation state, respectively, as shown in Table 6.8.

Table 6.8 Properties of the group 16 elements

Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
atomic symbol	O	S	Se	Te	Po
atomic number	8	16	34	52	84
atomic mass (amu)	16.00	32.07	78.96	127.60	209
valence electron configuration*	$2s^22p^4$	$3s^23p^4$	$4s^24p^4$	$5s^25p^4$	$6s^26p^4$
melting point/boiling point (°C)	−219/−183	115/445	221/685	450/988	254/962
density (g/cm^3) at 25°C	1.31 (g/L)	2.07	4.81	6.24	9.20
atomic radius (pm)	48	88	103	123	135
first ionisation energy (kJ/mol)	1314	1000	941	869	812
normal oxidation state(s)	−2	+6, +4, −2	+6, +4, −2	+6, +4, −2	+2 (+4)
ionic radius (pm) **	140 (−2)	184 (−2), 29 (+6)	198 (−2), 42 (+6)	221 (−2), 56 (+6)	230 (−2), 97 (+4)
electron affinity (kJ/mol)	−141	−200	−195	−190	−180
electronegativity	3.4	2.6	2.6	2.1	2.0
standard reduction potential (E°, V) ($E^0 \rightarrow H_2E$ in acidic solution)	+1.23	+0.14	−0.40	−0.79	−1.00
product of reaction with O_2	–	SO_2	SeO_2	TeO_2	PoO_2
type of oxide	–	acidic	acidic	amphoteric	basic
product of reaction with N_2	NO, NO_2	none	none	none	none
product of reaction with X_2	O_2F_2	SF_6, S_2Cl_2, S_2Br_2	SeF_6, SeX_4	TeF_6, TeX_4	PoF_4, $PoCl_2$, $PoBr_2$
product of reaction with H_2	H_2O	H_2S	H_2Se	none	none

* The configuration shown does not include filled d and f subshells.

** The values cited for the hexacations are estimated values for six-coordinate ions.

Also, as in the other groups, the second and third members (sulfur and selenium) have similar properties because of shielding effects. Only polonium is metallic, forming either the hydrated Po^{2+} or Po^{4+} ion in aqueous solution, depending on conditions.

Reactions and compounds of oxygen

The lightest group 16 member has the greatest tendency to form multiple bonds. Thus elemental oxygen is found in nature as a diatomic gas that contains a net double bond: O=O. Electrostatic repulsion between lone pairs of electrons on adjacent atoms prevents oxygen from forming stable catenated compounds. In fact, except for O_2, all compounds that contain O–O bonds are potentially explosive. Ozone, peroxides, and superoxides are all potentially dangerous in pure form. Ozone (O_3), one of the most powerful oxidants known, is used to purify drinking water because it does not produce the characteristic taste associated with chlorinated water. Hydrogen peroxide (H_2O_2) is so thermodynamically unstable that it tends to undergo explosive decomposition when impure:

$$2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)} \ \Delta G^\circ = -119 \text{ kJ/mol} \qquad (6.65)$$

Despite the strength of the O=O bond, O_2 is extremely reactive, reacting directly with nearly all other elements except the noble gases. Some properties of O_2 and related species, such as the peroxide and superoxide ions, are in Table 6.9.

Table 6.9 Properties of oxygen and related diatomic species

Species	Bond order	Number of unpaired ē	O–O distance (pm)*
O_2^+	2.5	1	112
O_2	2	2	121
O^{2-}	1.5	1	133
O_2^{2-}	1	0	149

Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Oxygen is second only to fluorine in its ability to stabilise high oxidation states of metals in both ionic and covalent compounds. For example, AgO is a stable solid that contains silver in the unusual Ag(II) state, whereas OsO_4 is a volatile solid that contains Os(VIII). Because oxygen is so electronegative, the O–H bond is highly polar, creating a large bond dipole moment that makes hydrogen bonding much more important for compounds of oxygen than for similar compounds of the other chalcogens.

Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements that lie on or near the diagonal band of semimetals are generally amphoteric. A few oxides, such as CO and PbO_2, are neutral and do not react with water, aqueous acid, or aqueous base. Nonmetal oxides are typically covalent compounds in which the bonds between oxygen and the nonmetal are polarised ($E^{\delta+}$–$O^{\delta-}$). Consequently, a lone pair of electrons on a water molecule can attack the partially positively charged E atom to form an oxoacid eventually. An example is reacting sulfur trioxide with water to form sulfuric acid:

$$H_2O_{(l)} + SO_{3(g)} \rightarrow H_2SO_{4(aq)} \text{ `} \qquad (6.66)$$

The oxides of the semimetals and of elements such as Al that lie near the metal/nonmetal dividing line are amphoteric, as we expect:

$$Al_2O_{3(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O_{(l)} \qquad (6.67)$$

$$Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Al(OH)_4{}^-{}_{(aq)} \qquad (6.68)$$

Reactions and compounds of the heavier chalcogens

Because most of the heavier elements of groups 16 and 15 are nonmetals, they often form similar compounds. For example, both third-period elements of these groups (phosphorus and sulfur) form catenated compounds and form multiple allotropes. Consistent with periodic trends, the tendency to catenate decreases as we go down the column.

Sulfur and selenium both form a fairly extensive series of catenated species. For example, elemental sulfur forms S_8 rings packed together in a complex "crankshaft" arrangement, and molten sulfur contains long chains of sulfur atoms connected by S–S bonds. Moreover, both sulfur and selenium form polysulfides (S_n^{2-}) and polyselenides (Se_n^{2-}), with $n \leq 6$.

The only stable allotrope of tellurium is a silvery-white substance whose properties and structure are similar to those of one of the selenium allotropes. Polonium, in contrast, shows no tendency to form catenated compounds. The striking decrease in structural complexity from sulfur to polonium is consistent with the decrease in the strength of single bonds and the increase in metallic character as we go down the group.

The reactivity of elements in group 16 decreases from lightest to heaviest. For example, selenium and tellurium react with most elements but not as readily as sulfur does. As expected for nonmetals, sulfur, selenium, and tellurium do not react with water, aqueous acid, or aqueous base, but all dissolve in strongly oxidising acids such as HNO_3 to form oxoacids such as H_2SO_4. In contrast to the other chalcogens, polonium behaves like a metal, dissolving in dilute HCl to form solutions that contain the Po^{2+} ion.

Fluorine reacts directly with all chalcogens except oxygen to produce the hexafluorides (YF_6), which are extraordinarily stable and unreactive compounds. Four additional stable fluorides of sulfur are known; thus, sulfur oxidation states ranging from +1 to +6 (Fig. 6.13). In contrast, only four fluorides of selenium (SeF_6, SeF_4, FSeSeF, and $SeSeF_2$) and only three of tellurium (TeF_4, TeF_6, and Te_2F_{10}) are known.

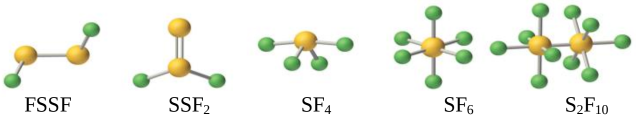

FSSF SSF_2 SF_4 SF_6 S_2F_{10}

Figure 6.13 Structures of fluorides of sulfur

Direct reaction of the heavier chalcogens with oxygen at elevated temperatures gives the dioxides (YO_2), which exhibit a dramatic range of structures and properties. The dioxides become increasingly metallic down the group, as expected, and the coordination number of the chalcogen steadily increases.

The dioxides of sulfur, selenium, and tellurium react with water to produce the weak, diprotic oxoacids (H_2YO_3 — sulfurous, selenous, and tellurous acid, respectively). Both sulfuric acid and selenic acid (H_2SeO_4) are strong acids, but telluric acid [$Te(OH)_6$] is quite different. Because tellurium is larger than either sulfur or selenium, it forms weaker π bonds to oxygen. As a result, the most stable structure for telluric acid is $Te(OH)_6$, with six Te–OH bonds rather than Te=O bonds.

Telluric acid, therefore, behaves like a weak triprotic acid in aqueous solution, successively losing the hydrogen atoms bound to three of the oxygen atoms. As is typical for compounds with elements in their highest accessible oxidation state (+6 in this case), sulfuric, selenic, and telluric acids are oxidants. Because the stability of the highest oxidation state decreases with increasing atomic number, telluric acid is a stronger oxidant than sulfuric acid.

Sulfur and, to a lesser extent, selenium reacts with carbon to form an extensive series of compounds that are structurally similar to their oxygen analogues. For example, CS_2 and CSe_2 are both volatile liquids that contain C=S or C=Se bonds and have the same linear structure as CO_2. Because these double bonds are significantly weaker than the C=O bond, however, CS_2, CSe_2, and related compounds are less stable and more reactive than their oxygen analogues. The chalcogens also react directly with nearly all metals to form compounds with a wide range of stoichiometries and a variety of structures.

Ionic chalcogenides like Na_2S react with aqueous acid to produce binary hydrides such as hydrogen sulfide (H_2S). Because the strength of the Y–H bond decreases with increasing atomic radius, the stability of the binary hydrides reduces rapidly down the group.

Summary

The electronegativity of the chalcogens decreases down the group. The lightest member, oxygen, has the greatest tendency to form multiple bonds with other elements. Nevertheless, it does not form stable catenated compounds due to repulsions between lone pairs of electrons on adjacent atoms. Due to its high electronegativity, reactive behaviour of oxygen is restricted to compounds in which it has a negative oxidation state, and its bonds to other elements tend to be highly polar.

Metal oxides are usually basic, and nonmetal oxides are acidic, whereas oxides of elements along the dividing line between metals and nonmetals are amphoteric.

The reactivity, the strength of multiple bonds to oxygen, and the tendency to form catenated compounds all decrease down the group, whereas the maximum coordination numbers increase. The stability of the highest oxidation state (+6) decreases down the group. Double bonds between S or Se and second-row atoms are weaker than the analogous C=O bonds because of reduced orbital overlap. The stability of the binary hydrides decreases down the group.

6.3.5 Group 17: halogens

Because the halogens are highly reactive, none is found in nature as the free element.

Preparation and general properties

All the halogens except iodine are found in nature as salts of the halide ions (X^-), so the methods used for preparing F_2, Cl_2, and Br_2 all involve oxidising the halide. Reacting CaF_2 with concentrated sulfuric acid produces gaseous hydrogen fluoride:

$$CaF_{2(s)} + H_2SO_{4(l)} \rightarrow CaSO_{4(s)} + 2HF_{(g)} \qquad (6.69)$$

Fluorine is produced by the electrolysis of a 1:1 mixture of HF and $K^+HF_2^-$ at 60–300°C:

$$KHF_2{\cdot}HF_{(l)} \xleftrightarrow{\text{electrolysis}} F_{2(g)} + H_{2(g)} \qquad (6.70)$$

Fluorine is one of the most powerful oxidants known, and both F_2 and HF are highly corrosive.

Although chlorine is significantly less abundant than fluorine, elemental chlorine is produced on an enormous scale. Fortunately, large subterranean deposits of rock salt (NaCl) are found around the world, and seawater consists of about 2% NaCl by mass, providing an almost inexhaustible reserve. Chlorine is prepared industrially by the chloralkali process, which uses the following reaction:

$$2NaCl_{(aq)} + 2H_2O_{(l)} \xleftrightarrow{\text{electrolysis}} 2NaOH_{(aq)} + Cl_{2(g)} + H_{2(g)} \qquad (6.71)$$

Bromine is much less abundant than fluorine or chlorine, but it is easily recovered from seawater.

Because of its low electronegativity, iodine tends to occur in nature in an oxidised form. Hence most commercially important deposits of iodine are iodate salts such as $Ca(IO_3)_2$. The production of iodine from such deposits, therefore, requires reduction rather than oxidation. The process is typically carried out in two steps: reduction of iodate to iodide with sodium hydrogen sulfite, followed by reaction of iodide with additional iodate:

$$2IO_3^-{}_{(aq)} + 6HSO_3^-{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + 6SO_4^{2-}{}_{(aq)} + 6H^+{}_{(aq)} \qquad (6.72)$$

$$5I^-{}_{(aq)} + IO_3^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3I_{2(s)} + 3H_2O_{(l)} \qquad (6.73)$$

Because the halogens all have ns^2np^5 electron configurations, their chemistry is dominated by a tendency to accept an additional electron to form the closed-shell ion (X^-). Electron-electron repulsion is important in fluorine because of its small atomic volume, making the electron affinity of fluorine less than that of chlorine (Table 6.10). Similarly, repulsions between electron pairs on adjacent atoms are responsible for the unexpectedly low F–F bond dissociation energy.

Because it is the most electronegative element in the periodic table, fluorine forms compounds in only the −1 oxidation state.

The halogens all have relatively high ionisation energies, but the energy required to remove electrons decreases as we go down the column. Hence the heavier halogens also form compounds in positive oxidation states (+1, +3, +5, and +7), derived by the formal loss of ns and np electrons.

Table 6.10 Properties of the group 17 elements

Property	Fluorine	Chlorine	Bromine	Iodine	Astatine
atomic symbol	F	Cl	Br	I	At
atomic number	9	17	35	53	85
atomic mass (amu)	19.00	35.45	79.90	126.90	210
valence electron configuration *	$2s^2 2p^5$	$3s^2 3p^5$	$4s^2 4p^5$	$5s^2 5p^5$	$6s^2 6p^5$
melting point/boiling point (°C)	−220/−188	−102/−34.0	−7.2/58.8	114/184	302/—
density (g/cm^3) at 25°C	1.55 (g/L)	2.90 (g/L)	3.10	4.93	—
atomic radius (pm)	42	79	94	115	127
first ionisation energy (kJ/mol)	1681	1251	1140	1008	926
normal oxidation state(s)	−1	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1 (+1, +3, +5, +7)	−1, +1
ionic radius (pm) **	133	181	196	220	—
electron affinity (kJ/mol)	−328	−349	−325	−295	−270
electronegativity	4.0	3.2	3.0	2.7	2.2
standard reduction potential (E°, V) ($X_2 \rightarrow X^-$ in basic solution)	+2.87	+1.36	+1.07	+0.54	+0.30
dissociation energy of $X_2(g)$ (kJ/mol)	158.8	243.6	192.8	151.1	~80
product of reaction with O_2	O_2F_2	none	none	none	none
type of oxide	acidic	acidic	acidic	acidic	acidic
product of reaction with N_2	none	none	none	none	none
product of reaction with H_2	HF	HCl	HBr	HI	HAt

* The configuration shown does not include filled d and f subshells.

** The values cited are for the six-coordinate anion (X^-).

Reactions and compounds

Fluorine is the most reactive element in the periodic table, forming compounds with every other element except helium, neon, and argon. The reactions of fluorine with most other elements range from vigorous to explosive; only O_2, N_2, and Kr react slowly.

There are three reasons for the high reactivity of fluorine:

i) Fluorine is extremely electronegative, and it can remove or at least share the valence electrons of virtually any other element.

ii) Fluorine is characterised by small size, and it tends to form very strong bonds with other elements, making its compounds thermodynamically stable.

iii) The F–F bond is weak due to repulsion between lone pairs of electrons on adjacent atoms, reducing both the thermodynamic and kinetic barriers to a reaction.

With highly electropositive elements, fluorine forms ionic compounds that contain the closed-shell F^{-} ion. In contrast, with less electropositive elements (or with metals in very high oxidation states), fluorine forms covalent compounds that contain terminal F atoms, such as SF_6. Because of its high electronegativity and $2s^2 2p^5$ valence electron configuration, fluorine normally participates in only one electron-pair bond. Only a very strong Lewis acid, such as AlF_3, can share a lone pair of electrons with a fluoride ion, forming AlF_6^{3-}.

The halogens (X_2) react with metals (M) by the following way:

$$M_{(s,l)} + nX_{2(s,l,g)} \rightarrow MX_{n(s,l)} \tag{6.74}$$

For elements that exhibit multiple oxidation states, fluorine tends to produce the highest possible oxidation state and iodine the lowest.

Metal halides in the +1 or +2 oxidation state, such as CaF_2, are typically ionic halides, which have high melting points and are often soluble in water. If the oxidation state of the metal increases, the covalent character of the halide partly appears due to the polarisation of the M–X bond. With its high electronegativity, fluoride is the least polarisable, and iodide, with the lowest electronegativity, is the most polarisable of the halogens. Halides of small trivalent metal ions such as Al^{3+} tend to be relatively covalent. For example, $AlBr_3$ is a volatile solid that contains bromide-bridged Al_2Br_6 molecules. In contrast, the halides of larger trivalent metals, such as the lanthanides, are essentially ionic. For example, indium tribromide ($InBr_3$) and lanthanide tribromide ($LnBr_3$) are all high-melting-point solids that are quite soluble in water.

All halogens react vigorously with hydrogen to give the hydrogen halides (HX). Because the H–F bond in HF is highly polarised ($H^{\delta+}$–$F^{\delta-}$), liquid HF has extensive hydrogen bonds, giving it an unusually high boiling point and a high dielectric constant. Because fluoride has a high affinity for silicon, aqueous hydrofluoric acid is used to etch glass, dissolving SiO_2 to give solutions to the stable SiF_6^{2-} ion.

Except for fluorine, all the halogens react with water in a disproportionation reaction, where X is Cl, Br, or I:

$$X_{2(g,l,s)} + H_2O_{(l)} \rightarrow H^+_{(aq)} + X^-_{(aq)} + HOX_{(aq)} \qquad (6.75)$$

The most stable oxoacids are the perhalic acids, which contain the halogens in their highest oxidation state (+7). The acid strengths of the oxoacids of the halogens increase with increasing oxidation state, whereas their stability and acid strength decreases down the group. Thus perchloric acid ($HOClO_3$, usually written as $HClO_4$) is a more potent acid and stronger oxidant than perbromic acid. Although all the oxoacids are strong oxidants, some, such as $HClO_4$, react rather slowly at low temperatures. Consequently, mixtures of the halogen oxoacids or oxoanions with organic compounds are potentially explosive if they are heated or even agitated mechanically to initiate the reaction.

The halogens react with one another to produce interhalogen compounds, such as ICl_3, BrF_5, and IF_7. In all cases, the heavier halogen, which has the lower electronegativity, occupies the position of the central atom. The maximum oxidation state and the number of terminal halogens increase smoothly as the ionisation energy of the central halogen decreases and the electronegativity of the terminal halogen increases. For example, iodine reacts with the other halogens to form IF_n (n = 1–7), ICl or ICl_3, or IBr, whereas bromine reacts with fluorine to form only BrF, BrF_3, and BrF_5 but not BrF_7. The interhalogen compounds are among the most powerful Lewis acids known, with a strong tendency to react with halide ions to give complexes with higher coordination numbers, such as the IF_8^- ion:

$$IF_{7(l)} + KF_{(s)} \rightarrow KIF_{8(s)} \qquad (6.76)$$

All group 17 elements form compounds in odd oxidation states (–1, +1, +3, +5, +7). The interhalogen compounds are also potent oxidants and strong fluorinating agents; contact with organic materials or water can result in an explosion.

Summary

The halogens are so reactive that none is found in nature as the free element; instead, all but iodine are found as halide salts with the X^- ion. They behave exclusively as of nonmetals. Ionisation energies decrease down the group. Fluorine, the most reactive element in the periodic table, has a low F–F bond dissociation energy due to repulsions between lone pairs of electrons on adjacent atoms. Fluorine forms ionic compounds with electropositive elements and covalent compounds with less electropositive elements and metals in high oxidation states. All the halogens react with hydrogen to produce hydrogen halides. Except for F_2, all react with water to form oxoacids, including the perhalic acids, which contain the halogens in their highest oxidation state. Halogens also form interhalogen compounds; the heavier halogen, with the lower electronegativity, is the central atom.

6.3.6 Group 18: noble gases

The noble gases were all isolated for the first time within only five years at the end of the XIX century.

Preparation and general properties

Fractional distillation of liquid air is the only source of all the noble gases except helium. Although helium is the second most abundant element in the universe (after hydrogen), the helium originally present in Earth's atmosphere was lost into space long ago because of its low molecular mass and resulting high mean velocity. Natural gas often contains relatively high concentrations of helium (up to 7%), and it is the only practical terrestrial source.

The elements of group 18 all have closed-shell valence electron configurations, either ns^2np^6 or $1s^2$ for He. Consistent with periodic trends in atomic properties, these elements have high ionisation energies that decrease smoothly down the group. From their electron affinities, the data in Table 6.11 indicate that the noble gases are unlikely to form compounds in negative oxidation states. A potent oxidant is needed to oxidise noble gases and form compounds in positive oxidation states. Like the heavier halogens, xenon and perhaps krypton should form covalent compounds with F, O, and possibly Cl, in which they have even formal oxidation states (+2, +4, +6, and possibly +8).

Reactions and compounds

For many years, it was thought that the only compounds the noble gases could form were clathrates. Clathrates are solid compounds in which small atoms of a gas, the guest, occupy holes in a lattice formed by a less volatile, chemically dissimilar substance, the host (Fig. 6.14). Because clathrate formation does not involve the formation of chemical bonds between the guest (Xe) and the host molecules (H_2O, in the case of xenon hydrate), the guest molecules are immediately released when the clathrate is melted or dissolved. In addition to the noble gases, many other species form stable clathrates. One of the most interesting is methane hydrate, large deposits of which occur naturally at the bottom of the oceans.

Table 6.11 Properties of the group 18 elements

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
atomic symbol	He	Ne	Ar	Kr	Xe	Rn
atomic number	2	10	18	36	54	86
atomic mass (amu)	4.00	20.18	39.95	83.80	131.29	222
valence electron configuration *	$1s^2$	$2s^2 2p^6$	$3s^2 3p^6$	$4s^2 4p^6$	$5s^2 5p^6$	$6s^2 6p^6$
triple point/boiling point (°C)	– / −269 **	−249 (at 43 kPa) /−246	−189 (at 69 kPa) / −189	−157/−153	−112 (at 81.6 kPa) / −108	−71/−62
density (g/L) at 25°C	0.16	0.83	1.63	3.43	5.37	9.07
atomic radius (pm)	31	38	71	88	108	120
first ionisation energy (kJ/mol)	2372	2081	1521	1351	1170	1037
normal oxidation state(s)	0	0	0	0 (+2)	0 (+2, +4, +6, +8)	0 (+2)
electron affinity (kJ/mol)	> 0	> 0	> 0	> 0	> 0	> 0
electronegativity	—	—	—	—	2.6	—
product of reaction with O_2	none	none	none	none	none	none
type of oxide	—	—	—	—	acidic	—
product of reaction with N_2	none	none	none	none	none	none
product of reaction with X_2	none	none	none	KrF_2	XeF_2, XeF_4, XeF_6	RnF_2
product of reaction with H_2	none	none	none	none	none	none

* The configuration shown does not include filled d and f subshells.

** This is the normal boiling point of He. Solid He does not exist at 1 atm pressure so that no melting point can be given.

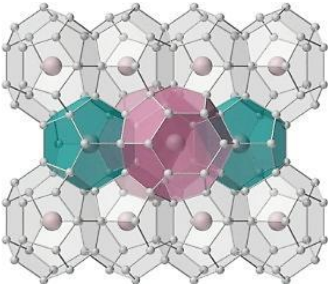


Figure 6.14 Structure of xenon hydrate, a clathrate. The small balls represent the oxygen atoms of the host water molecules and the large balls mark the centres of the guest (Xe)

Among the first reactions of noble gases, oxidation of Xe by PtF_6 was observed experimentally. The reaction involves the transfer of a fluorine atom to xenon to give the XeF^+ ion: $Xe_{(g)} + PtF_{6(g)} \rightarrow [XeF^+][PtF_5^-]_{(s)}$ (6.77)

Subsequent work showed that xenon reacts directly with fluorine under relatively mild conditions to give XeF_2, XeF_4, or XeF_6, depending on conditions; one such reaction is as follows:

$$Xe_{(g)} + 2F_{2(g)} \rightarrow XeF_{4(s)} \qquad (6.78)$$

The ionisation energies of helium, neon, and argon are so high (Table 6.11) that no stable compounds of these elements are known. The ionisation energies of krypton and xenon are lower but still very high; consequently only highly electronegative elements (F, O, and Cl) can form stable compounds with xenon and krypton without being oxidised themselves. Xenon reacts directly with only two elements: F_2 and Cl_2. Although $XeCl_2$ and KrF_2 can be prepared directly from the elements, they are substantially less stable than the xenon fluorides.

Because halides of the noble gases are powerful oxidants and fluorinating agents, they decompose rapidly after contact with trace amounts of water, and they react violently with organic compounds or other reductants. The xenon fluorides are also Lewis acids; they react with the fluoride ion, the only Lewis base that is not oxidised immediately on contact, to form anionic complexes. For example, reacting caesium fluoride with XeF_6 produces $CsXeF_7$, which gives Cs_2XeF_8 when heated:

$$XeF_{6(s)} + CsF_{(s)} \rightarrow CsXeF_{7(s)} \qquad (6.79)$$

$$2CsXeF_{7(s)} \overset{t}{\longleftrightarrow} Cs_2XeF_{8(s)} + XeF_{6(g)} \qquad (6.80)$$

The XeF_8^{2-} ion contains eight-coordinate xenon and has the square antiprismatic structure (Fig. 6.15), which is essentially identical to that of the IF_8^{-} ion. Cs_2XeF_8 is surprisingly stable for a polyatomic ion that contains xenon in the +6 oxidation state, decomposing only at temperatures greater than 300°C. Major factors in the stability of Cs_2XeF_8 are almost certainly the formation of a stable ionic lattice and the high coordination number of xenon, which protects the central atom from attack by other species.

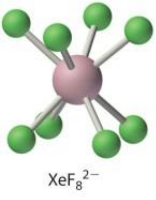


Figure 6.15 Structure of XeF_8^{2-} ion

For a previously "inert" gas, xenon has a surprisingly high affinity for oxygen, presumably because of π bonding between O and Xe. Consequently, xenon forms an extensive series of oxides and oxoanion salts. For example, hydrolysis of either XeF_4 or XeF_6 produces XeO_3, an explosive white solid:

$$XeF_{6(aq)} + 3H_2O_{(l)} \rightarrow XeO_{3(aq)} + 6HF_{(aq)} \qquad (6.81)$$

Treating a solution of XeO_3 with ozone, a strong oxidant, results in further oxidation of xenon to give either XeO_4, a colourless, explosive gas, or the surprisingly stable perxenate ion (XeO_6^{4-}), both of which contain xenon in its highest possible oxidation state (+8).

Because the ionisation energy of radon is less than that of xenon, in principle radon should be able to form an even greater variety of chemical compounds than xenon. Unfortunately, however, radon is so radioactive that its chemistry has not been extensively explored.

Summary

The noble gases have a closed-shell valence electron configuration. The ionisation energies of the noble gases decrease with increasing atomic number. Only highly electronegative elements can form stable compounds with the noble gases in positive oxidation states without being oxidised themselves. Xenon has a high affinity for both fluorine and oxygen, which form stable compounds that contain xenon in even oxidation states up to +8.

Potent oxidants are needed to oxidise the noble gases to form compounds in positive oxidation states.

In summary

The key concepts and laws:

1. Compounds of the group 13 elements with oxygen are thermodynamically stable.
2. Many of the anomalous properties of the group 13 elements can be explained by the increase in Z_{eff} moving down the group.
3. The group 14 elements show the greatest diversity in chemical behaviour of any group; covalent bond strengths decrease with increasing atomic size, and ionisation energies are greater than expected, increasing from C to Pb.
4. The reactivity of the heavier group 15 elements decreases down the group, as does the stability of their catenated compounds.
5. The chalcogens have no stable metallic elements.
6. The tendency to catenate, the strength of single bonds, and the reactivity all decrease moving down the group chalcogens.
7. The halogens are highly reactive.

8. All halogens have relatively high ionisation energies, and the acid strength and oxidising power of their oxoacids decrease down the group.

9. The noble gases are characterised by their high ionisation energies and low electron affinities.

Important definitions, properties and reactions:

1. Group 13 elements are never found in nature in their free state.
2. Neutral compounds of the group 13 elements are electron deficient, so they are generally moderately strong Lewis acids.
3. Elemental boron forms multicentre bonds, whereas the other group 13 elements exhibit metallic bonding.
4. Of the group 13 halides, only the fluorides behave as typical ionic compounds.
5. All group 13 oxides dissolve in dilute acid, but Al_2O_3 and Ga_2O_3 are amphoteric.
6. The relative stability of the +2 oxidation state increases and the tendency to form catenated compounds decreases from carbon to lead in group 14.
7. The group 14 elements follow the same pattern as the group 13 elements in their periodic properties.
8. Pi bonds between carbon and the heavier chalcogenides are weak due to poor orbital overlap.
9. Carbides formed from group 1 and 2 elements are ionic. Transition metals form interstitial carbides with covalent metal-carbon interactions, and covalent carbides are chemically inert.
10. The stability of the group 14 dichlorides increases dramatically from carbon to lead.
11. The dioxides of the group 14 elements become increasingly basic down the group.
12. Because silicon-oxygen bonds are unusually strong, silicon-oxygen compounds dominate the chemistry of silicon.
13. The stability of group 14 hydrides decreases down the group, and $E=E$ and $E\equiv E$ bonds weaken.
14. In group 15, the stability of the +5 oxidation state decreases from P to Bi.
15. Because neutral covalent compounds of the trivalent group 15 elements have a lone pair of electrons on the central atom, they tend to be Lewis bases.

16. B, C, and N all react with transition metals to form interstitial compounds that are hard, high-melting materials.
17. As in group 14, the heavier group 15 elements form catenated compounds that contain only single bonds, whose stability decreases as we go down the group.
18. The reactivity of the heavier group 15 elements decreases as we go down the column.
19. Phosphorus has the greatest ability to form π bonds with elements such as O, N, and C.
19. Group 16 is the first group in the p block with no stable metallic elements.
20. As in groups 14 and 15, the lightest element in group 16 has the greatest tendency to form multiple bonds.
21. Oxides of metals tend to be basic, oxides of nonmetals tend to be acidic, and oxides of elements in or near the diagonal band of semimetals are generally amphoteric.
22. Just as with the other groups, the tendency to catenate, the strength of single bonds, and reactivity decrease down the group.
23. The stability of the highest oxidation state of the chalcogens decreases down the column.
24. The dioxides of the group 16 elements become increasingly basic, and the coordination number of the chalcogen steadily increases down the group.
25. Because the halogens are highly reactive, none is found in nature as the free element.
26. Oxidative strength decreases down group 17.
27. Electrostatic repulsions between lone pairs of electrons on adjacent atoms cause single bonds between N, O, and F to be weaker than expected.
28. As the oxidation state of the metal increases, the covalent character of the corresponding metal halides also increases due to the polarisation of the M–X bond.
29. Both the acid strength and the oxidising power of the halogen oxoacids decrease down the group.
30. All group 17 elements form compounds in odd oxidation states (−1, +1, +3, +5, +7), but the importance of the higher oxidation states generally decreases down the group.

32. The ionisation energies of helium, neon, and argon are so high that no stable compounds of these elements are known.
33. Xenon has a high affinity for both fluorine and oxygen.

6.4 Properties of d-block elements

In this section, the chemistry of the d-block elements, which are also called the transition metals, will be surveyed. Because all the d-block elements are metals, they do not have the extreme variability in chemistry. Instead, these elements exhibit significant horizontal and vertical similarities in chemistry, and all have a common set of characteristic properties due to partially filled d subshells.

Alloys and compounds of the d-block elements are important components of the materials the modern world depends on for its continuing technological development, while most of the first-row transition metals are essential for life.

6.4.1 Trends for transition metals

The transition metals, groups 3–12 in the periodic table, are generally characterised by partially filled d subshells in the free elements or their cations. Although the metals of group 12 do not have partially filled d shells, their chemistry is similar in many ways to that of the preceding groups. Unlike the s-block and p-block elements, the transition metals exhibit significant horizontal similarities in chemistry in addition to their vertical similarities.

Electronic structure and reactivity of the transition metals

The valence electron configurations of the first-row transition metals are given in Table 6.12. As we go across the row (period) from left to right, electrons are added to the 3d subshell to neutralise the increase in the positive charge of the nucleus as the atomic number increases.

Table 6.12 Valence electron configurations of the first-row transition metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$	$4s^2 3d^{10}$

With two important exceptions, the 3d subshell is filled as expected based on the Aufbau principle and Hund’s rule. Unexpectedly, chromium has a $4s^1 3d^5$ electron configuration rather than the $4s^2 3d^4$ configuration as follows from the Aufbau principle, and copper is $4s^1 3d^{10}$

rather than $4s^2 3d^9$. These anomalies were attributed to the extra stability associated with half-filled subshells. Because the ns and (n – 1)d subshells in these elements are similar in energy, even relatively small effects are enough to produce anomalous electron configurations.

In the second-row transition metals, electron-electron repulsions within the 4d subshell cause additional irregularities in electron configurations. For example, Nb and Tc, with atomic numbers 41 and 43, both have a half-filled 5s subshell, with $5s^1 4d^4$ and $5s^1 4d^6$ valence electron configurations, respectively. Further complications occur among the third-row transition metals, in which the 4f, 5d, and 6s orbitals are extremely close in energy. Although La has a $6s^2 5d^1$ valence electron configuration, the valence electron configuration of the next element (Ce) is $6s^2 5d^0 4f^2$. From this point in the table through element 71, all added electrons enter the 4f subshell, giving rise to the 14 elements known as the lanthanides. After the 4f subshell is filled, the 5d subshell is populated, producing the third row of the transition metals. Next comes the seventh period, where the actinides have three subshells (7s, 6d, and 5f) that are so similar in energy that their electron configurations are even more unpredictable.

The size of neutral atoms of the d-block elements gradually decreases from left to right across a row, due to an increase in the effective nuclear charge (Z_{eff}) with increasing atomic number. Also, the atomic radius increases down a group. Because of the lanthanide contraction, however, the increase in size between the 3d and 4d metals is much greater than between the 4d and 5d metals (Fig. 6.16). The effects of the lanthanide contraction are also observed in ionic radii and explain an abnormally slight increase in radius from Mo^{3+} to W^{3+}.

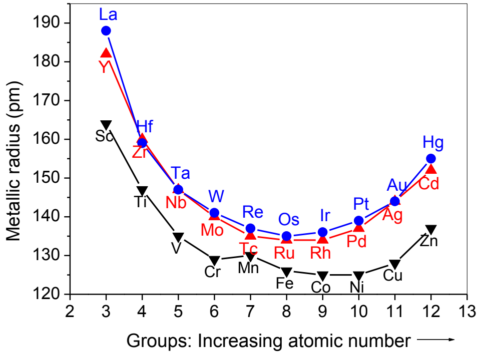
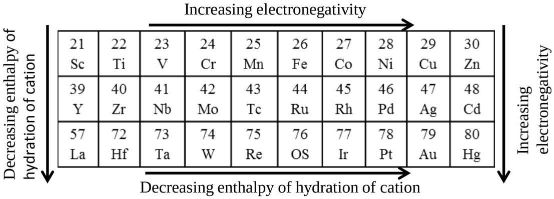


Figure 6.16 The metallic radii of the first-, second-, and third-row transition metals

The second- and third-row transition metals are very similar in size due to the effect of lanthanide contraction.

Electrons in (n – 1)d and (n – 2)f subshells are only moderately effective at shielding the nuclear charge. That is why the effective nuclear charge experienced by valence electrons in the d-block and f-block elements does not change greatly as the nuclear charge increases across a row. The ionisation energies of these elements increase very slowly across a given row. Also, electronegativities, densities and electrical and thermal conductivities increase, and enthalpies of hydration of the metal cations decrease in magnitude in going from the top left to the bottom right corner of the d block (Fig. 6.17). Consistent with this trend, the transition metals become steadily less reactive and more "noble" in character from left to right across a row. The relatively high ionisation energies and electronegativities and relatively low enthalpies of hydration are all major factors in the noble character of metals such as Pt and Au.



21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57 La	72 Hf	73 Ta	74 W	75 Re	76 OS	77 Ir	78 Pt	79 Au	80 Hg

Figure 6.17 Some trends in properties of the transition metals

Trends in transition metal oxidation states.

The similarity in ionisation energies and the relatively small increase in successive ionisation energies lead to the formation of metal ions with the same charge for many of the transition metals. This, in turn, results in extensive horizontal similarities in chemistry, which are most noticeable for the first-row transition metals and the lanthanides and actinides. Thus all the first-row transition metals except Sc form stable compounds that contain the 2+ ion, and, due to the small difference between the second and third ionisation energies for these elements, all except Zn also form stable compounds that contain the 3+ ion. The relatively small increase in successive ionisation energies causes most of the transition metals to exhibit multiple oxidation states separated by a single electron. Manganese, for example, forms compounds in every oxidation state. Because of the slow but steady increase in ionisation potentials across a row, high oxidation states become progressively less stable for the elements on the right side of the d block. The occurrence of multiple oxidation states separated by a single electron causes many, if not most, compounds of the transition metals to be paramagnetic, with one to five unpaired electrons.

The electronegativities of the first-row transition metals increase smoothly from Sc ($\chi = 1.4$) to Cu ($\chi = 1.9$). Thus Sc is a rather active metal, whereas Cu is much less reactive. The steady increase in electronegativity is also reflected in the standard reduction potentials: thus E° for the reaction $M^{2+}_{(aq)} + 2e^- \rightarrow M^0_{(s)}$ becomes progressively less negative from Ti (E° = –1.63 V) to Cu (E° = +0.34 V).

The transition metals form cations by the initial loss of the ns electrons of the metal, even though the ns orbital is lower in energy than the (n – 1)d subshell in the neutral atoms. This apparent contradiction is due to the small difference in energy between the ns and (n – 1)d orbitals, together with screening effects. The loss of one or more electrons reverses the relative energies of the ns and (n – 1)d subshells, making the latter lower in energy. Consequently, all transition-metal cations possess d^n valence electron configurations, as shown in Table 6.13 for the 2+ ions of the first-row transition metals.

Table 6.13 Configurations of d electron of the dications of the first-row transition metals

Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}

The most common oxidation states of the first-row transition metals are shown in Table 6.14. The second- and third-row transition metals behave similarly but with three important differences.

Table 6.14 Common oxidation states of the first-row transition metals *

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
electronic structure	s^2d^1	s^2d^2	s^2d^3	s^1d^5	s^2d^5	s^2d^6	s^2d^7	s^2d^8	s^1d^{10}	s^2d^{10}
oxidation states				I					I	
		II	II	II	II	II	II	II	II	II
	III	III	III	III	III	III	III	III	III	
		IV	IV	IV	IV	IV	IV	IV		
			V	V	V	V	V			
				VI	VI	VI				
					VII					

* Roman numerals are used to indicate the oxidation states of metals

The maximum oxidation states observed for the second- and third-row transition metals in groups 3–8 increase from +3 for Y and La to +8 for Ru and Os, corresponding to the formal loss of all ns and (n – 1)d valence electrons. Farther to the right, the maximum oxidation state decreases steadily, reaching +2 for the elements of group 12 (Zn, Cd, and Hg), which corresponds to a filled (n – 1)d subshell.

Within a group, higher oxidation states become more stable down the group.

Cations of the second- and third-row transition metals in lower oxidation states (+2 and +3) are much more easily oxidised than the corresponding ions of the first-row transition metals. As a result, the heavier elements in each group form stable compounds in higher oxidation states that have no analogues with the lightest member of the group.

Binary transition-metal compounds, such as the oxides and sulfides, are usually written with idealised stoichiometries, such as FeO or FeS, but these compounds are usually cation deficient and rarely contain a 1:1 cation:anion ratio. Thus a substance such as ferrous oxide is a nonstoichiometric compound with a range of compositions.

The acid-base character of transition-metal oxides depends strongly on the oxidation state of the metal and its ionic radius. Oxides of metals in lower oxidation states (less than or equal to +3) have significant ionic character and tend to be basic. Conversely, oxides of metals in higher oxidation states are more covalent and tend to be acidic, often dissolving in the strong base to form oxoanions.

Summary

Partially filled d subshells characterise the transition metals in the free elements and cations. The ns and (n – 1)d subshells have similar energies, so small influences can produce electron configurations that do not conform to the general order in which the subshells are filled. In the second- and third-row transition metals, such irregularities can be difficult to predict, particularly for the third row, which has 4f, 5d, and 6s orbitals that are very close in energy. The increase in atomic radius is greater between the 3d and 4d metals than between the 4d and 5d metals because of the lanthanide contraction. Ionisation energies and electronegativities increase slowly across a row, as do densities and electrical and thermal conductivities. Enthalpies of hydration decrease. Anomalies can be explained by the increased stabilisation of half-filled and filled subshells. Transition-metal cations are formed by the initial loss of ns electrons, and many metals can form cations in several oxidation states. Higher oxidation states become progressively less stable across a row and more stable down a column. Oxides of small, highly charged metal ions tend to be acidic, whereas oxides of metals with a low charge-to-radius ratio are basic.

6.4.2 Groups 3, 4, and 5

Group 3 (Sc, Y, La, and Ac)

As shown in Table 6.15, the observed trends in the properties of the group 3 elements are similar to those of groups 1 and 2. Due to their $ns^2(n - 1)d^1$ valence electron configurations, the chemistry of all four elements is dominated by the +3 oxidation state formed by losing all three valence electrons. These elements are highly electropositive metals and powerful reductants, with La (and Ac) being the most reactive. In keeping with their highly electropositive character, the group 3 metals react with water to produce the metal hydroxide and hydrogen gas:

$$2M_{(s)} + 6H_2O_{(l)} \rightarrow 2M(OH)_{3(s)} + 3H_{2(g)} \tag{6.82}$$

Table 6.15 Properties of the elements of groups 3, 4, and 5

Group	Element	Z	Valence Electron Configuration	Electronegativity	Metallic Radius (pm)	Melting Point (°C)	Density (g/cm^3)
3	Sc	21	$4s^23d^1$	1.36	162	1541	2.99
	Y	39	$5s^24d^1$	1.22	180	1522	4.47
	La	57	$6s^25d^1$	1.10	183	918	6.15
	Ac	89	$7s^26d^1$	1.10	188	1051	10.07
4	Ti	22	$4s^23d^2$	1.54	147	1668	4.51
	Zr	40	$5s^24d^2$	1.33	160	1855	6.52
	Hf	72	$6s^25d^24f^{14}$	1.30	159	2233	13.31
5	V	23	$4s^23d^3$	1.63	134	1910	6.00
	Nb	41	$5s^24d^3$	1.60	146	2477	8.57
	Ta	73	$6s^25d^34f^{14}$	1.50	146	3017	16.65

Group 3 metals react with nonmetals to form primarily ionic compounds. For example, reacting group 3 metals with the halogens produce the corresponding trihalides: MX_3. All group 3 elements react with air to form an oxide coating, and all burn in oxygen to form the so-called sesquioxides (M_2O_3), which react with H_2O or CO_2 to form the corresponding hydroxides or carbonates, respectively. Commercial uses of the group 3 metals are limited, but "mischmetal," a mixture of lanthanides (~40% La), is used as an additive to improve the properties of steel.

Group 4 (Ti, Zr, and Hf)

Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four $ns^2(n-1)d^2$ valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

$$2FeTiO_{3(s)} + 6C_{(s)} + 7Cl_{2(g)} \rightarrow 2TiCl_{4(g)} + 2FeCl_{3(g)} + 6CO_{(g)} \quad (6.83)$$

followed by reduction of the tetrachlorides with an active metal such as Mg.

Group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminium (melting point = 660°C) in applications that require high-temperature or corrosion resistance. Metallic zirconium is used in UO_2-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

Consistent with the periodic trends shown in Fig. 6.1, the group 4 metals become denser, higher melting, and more electropositive down the column (Table 6.15). However, the atomic radius of Hf is slightly smaller than that of Zr due to the lanthanide contraction. Because of their $ns^2(n-1)d^2$ valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits significant chemistry in the +2 and +3 oxidation states, although compounds of Ti^{2+} are usually powerful reductants. The $Ti^{2+}_{(aq)}$ ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

The reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX_4), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of the increasing polarisation of the anions by the cation as its charge-to-radius ratio increases. Thus $TiCl_2$ is an ionic salt, whereas $TiCl_4$ is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO_2) and dichalcogenides (MY_2). Industrially, TiO_2, which is used as a white pigment in paints, is prepared by reacting $TiCl_4$ with oxygen at high temperatures:

$$TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(s)} + 2Cl_{2(g)} \qquad (6.84)$$

The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite. The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH_2), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB_2), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

Group 5 (V, Nb, and Ta)

All group 5 metals are normally found in nature as oxide ores that contain the metals in their highest oxidation state (+5). Because of the lanthanide contraction, the chemistry of Nb and Ta is very similar.

Three-fourths of the vanadium produced annually is used in the production of steel alloys. The other major use of vanadium is as V_2O_5, an important catalyst for the industrial conversion of SO_2 to SO_3 in the contact process for the production of sulfuric acid. In contrast, Nb and Ta have only limited applications, and they are therefore produced in relatively small amounts. The primary application of niobium compound, such as Nb_3Zr and Nb_3Ge, is the manufacturing of superconducting wires, which are used in superconducting magnets. Highly corrosion-resistant tantalum is used as a liner for chemical reactors, in missile parts, and as a biologically compatible material in screws and pins for repairing fractured bones.

Only vanadium, the lightest element, has any tendency to form compounds in oxidation states lower than +5. For example, it forms stable halides in the lowest oxidation state (+2). All three metals react with excess oxygen to produce corresponding oxides in the +5 oxidation state (M_2O_5). Consistent with its covalent character, V_2O_5 is acidic, dissolving in the base to give the vanadate ion ($[VO_4]^{3-}$), whereas both Nb_2O_5 and Ta_2O_5 are comparatively inert. Oxides of these metals in lower oxidation states tend to be nonstoichiometric.

Although group 5 metals react with the heavier chalcogens to form a complex set of binary chalcogenides, the most important is the dichalcogenides (MY_2), whose layered structures are similar to those of the group 4 dichalcogenides. The elements of group 5 also form binary nitrides, carbides, borides, and hydrides, whose stoichiometries and properties are similar to those of the corresponding group 4 compounds. One such compound, tantalum carbide (TiC), has the highest melting point of any compound known (3738°C); it is used for the cutting edges of high-speed machine tools.

6.4.3 Groups 6 and 7

Group 6 (Cr, Mo, and W)

All group 6 metals are normally found in nature as sulfide (molybdenite — MoS_2) or oxide (for example, chromite — $FeCr_2O_4$) ores. The group 6 metals are slightly less electropositive than those of the three preceding groups, and the two heaviest metals are essentially the same size because of the lanthanide contraction (Table 6.16). All three elements have a total of six valence electrons, resulting in a maximum oxidation state of +6. Due to an extensive polarisation of the anions, compounds in the +6 oxidation state are highly covalent. As in groups 4 and 5, the lightest element exhibits variable oxidation states, ranging from Cr^{2+} (a powerful reductant) to CrO_3 (a powerful oxidant). For Mo and W, the highest oxidation state (+6) is by far the most important, although compounds in the +4 and +5 oxidation states are known.

Table 6.16 Properties of the elements of groups 6 and 7

Group	Element	Z	Valence electron configuration	Electronegativity	Metallic radius (pm)	Melting point (°C)	Density (g/cm^3)
6	Cr	24	$4s^1 3d^5$	1.66	128	1907	7.15
	Mo	42	$5s^1 4d^5$	2.16	139	2623	10.20
	W	74	$6s^2 5d^4 4f^{14}$	1.70	139	3422	19.30
7	Mn	25	$4s^2 3d^5$	1.55	127	1246	7.30
	Tc	43	$5s^2 4d^5$	2.10	136	2157	11.50
	Re	75	$6s^2 5d^5 4f^{14}$	1.90	137	3186	20.80

The group 6 halides become more covalent as the oxidation state of the metal increases: their volatility increases and their melting points decrease. Since the electronegativity of the halogens decreases from F to I, they are less able to stabilise high oxidation states; consequently, the maximum oxidation state of the corresponding metal halides decreases. Thus all three metals form hexafluorides, but CrF_6 is unstable at temperatures above −100°C, whereas MoF_6 and WF_6 are stable. Consistent with the trend toward increased stability of the highest oxidation state for the second- and third-row elements, the other halogens can oxidise chromium to only the trihalides, CrX_3 (X is Cl, Br, or I), while molybdenum forms $MoCl_5$, $MoBr_4$, and MoI_3, and tungsten gives WCl_6, WBr_5, and WI_4.

Both Mo and W react with oxygen to form the covalent trioxides (MoO_3 and WO_3), but Cr reacts to form only the so-called sesquioxide (Cr_2O_3). Chromium will form CrO_3, which is a highly toxic compound that can react explosively with organic materials. All the trioxides are acidic, dissolving in the base to form the corresponding oxoanions ($[MO_4]^{2-}$). The sesquioxide of the lightest element in the group (Cr_2O_3) is amphoteric. The aqueous chemistry of molybdate and tungstate is complex, and at low pH, they form a series of polymeric anions called isopolymetallates, such as the $[Mo_8O_{26}]^{4-}$ ions.

Reacting molybdenum or tungsten with heavier chalcogens gives binary chalcogenide phases, most of which are nonstoichiometric and electrically conducting. One of the most stable is MoS_2; it has a layered structure, in which the layers are held together by only weak van der Waals forces, which allows them to slide past one another rather easily. Consequently, both MoS_2 and WS_2 are used as lubricants in a variety of applications, including automobile engines.

The elements of group 6 form binary nitrides, carbides, and borides whose stoichiometries and properties are similar to those of the preceding groups 4 and 5. Tungsten carbide (WC), one of the hardest compounds known, is used to make the tips of drill bits.

Group 7 (Mn, Tc, and Re)

All three group 7 elements have seven valence electrons and can form compounds in the +7 oxidation state. Once again, the lightest element exhibits multiple oxidation states. Compounds of Mn in oxidation states ranging from –3 to +7 are known, with the most common being +2 and +4. In contrast, compounds of Tc and Re in the +2 oxidation state are quite rare. Because the electronegativity of Mn is anomalously low, elemental manganese is unusually reactive.

In contrast, the chemistry of Tc is similar to that of Re because of their similar size and electronegativity, again a result of the lanthanide contraction. Due to the stability of the half-filled $3d^5$ electron configurations, the aqueous Mn^{3+} ion, with a $3d^4$ valence electron configurations, is a potent oxidant that can oxidise water. It is difficult to generalise about other oxidation states for Tc and Re because their stability depends dramatically on the nature of the compound.

Like vanadium, compounds of manganese in different oxidation states have different numbers of d electrons, which leads to compounds with different colours.

Consistent with higher oxidation states being more stable for the heavier transition metals, reacting Mn with F_2 gives only MnF_3, a high-melting, red-purple solid, whereas Re reacts with F_2 to give ReF_7, a volatile, low-melting, yellow solid. Again, reaction with the less oxidising, heavier halogens produces halides in lower oxidation states. In particular, reaction with Cl_2, a weaker oxidant than F_2, gives $MnCl_2$ and $ReCl_6$. The reaction of Mn with oxygen forms only Mn_3O_4, a mixed-valent compound that contains two Mn(II) and one Mn(III) per formula unit and is similar in both stoichiometry and structure to magnetite (Fe_3O_4). In contrast, Tc and Re form high-valent oxides, the so-called heptoxides (M_2O_7), consistent with the increased stability of higher oxidation states for the second and third rows of transition metals. Also consistent with this trend, the permanganate ion $[MnO_4]^{2-}$ is a potent oxidant, whereas $[TcO_4]^-$ and $[ReO_4]^-$ are much more stable. Both Tc and Re form disulfides and diselenides with layered structures analogous to that of MoS_2, as well as more complex heptasulfides (M_2S_7). As is typical of the transition metals, the group 7 metals form binary nitrides, carbides, and borides that are generally stable at high temperatures and exhibit metallic properties.

6.4.4 Groups 8, 9, and 10

Sometimes, especially in older versions of the periodic table, groups 8, 9, and 10 are combined in a single group (group VIII) because the elements of these three groups exhibit many horizontal similarities in their chemistry. In part, these horizontal similarities are due to the fact that the ionisation potentials of the elements, which increase slowly but steadily across the d block, have now become so large that the oxidation state corresponding to the formal loss of all valence electrons is encountered only rarely (group 8) or not at all (groups 9 and 10).

As a result, the chemistry of all three groups is dominated by intermediate oxidation states, especially +2 and +3, for the first-row metals (Fe, Co, and Ni). The heavier elements of these three groups are called precious metals because they are rather rare in nature and mostly chemically inert.

Some properties of the elements in groups 8–10 are summarised in Table 6.17. As in earlier groups, similarities in size and electronegativity between the two heaviest members of each group result in similarities in chemistry. At this point in the d block, there is no longer a clear correlation between the valence electron configuration and the preferred oxidation state. For example, all the elements of group 8 have eight valence electrons, but only Ru and Os have any tendency to form compounds in the +8 oxidation state, and those compounds are powerful oxidants. The predominant oxidation states for all three group 8 metals are +2 and +3. Although the elements of group 9 possess a total of nine valence electrons, the +9 oxidation state is unknown for these elements, and the most common oxidation states in the group are +3 and +1. Finally, the elements of group 10 all have 10 valence electrons, but all three elements are normally found in the +2 oxidation state formed by losing the ns^2 valence electrons. Besides, Pd and Pt form numerous compounds and complexes in the +4 oxidation state.

Table 6.17 Properties of the elements of groups 8, 9, and 10

Group	Element	Z	Valence electron configuration	Electronegativity	Metallic radius (pm)	Melting point (°C)	Density (g/cm^3)
8	Fe	26	$4s^2 3d^6$	1.83	126	1538	7.87
	Ru	44	$5s^1 4d^7$	2.20	134	2334	12.10
	Os	76	$6s^2 5d^6 4f^{14}$	2.20	135	3033	22.59
9	Co	27	$4s^2 3d^7$	1.88	125	1495	8.86
	Rh	45	$5s^1 4d^8$	2.28	134	1964	12.40
	Ir	77	$6s^2 5d^7 4f^{14}$	2.20	136	2446	22.50
10	Ni	28	$4s^2 3d^8$	1.91	124	1455	8.90
	Pd	46	$4d^{10}$	2.20	137	1555	12.00
	Pt	78	$6s^2 5d^8 4f^{14}$	2.20	139	1768	21.50

As one goes across the d-block elements, higher oxidation states become less stable, and they are more stable if we go down a group. Thus Fe and Co form trifluorides, but Ni forms only the difluoride NiF_2. In contrast to Fe, Ru and Os form a series of fluorides up to RuF_6 and OsF_7. The hexafluorides of Rh and Ir are extraordinarily powerful oxidants, and Pt is the only element in group 10 that forms a hexafluoride. Similar trends are observed among the oxides. For example, Fe forms only FeO, Fe_2O_3, and the mixed-valent Fe_3O_4 (magnetite), all of which are nonstoichiometric.

In contrast, Ru and Os form the dioxides (MO_2) and the highly toxic, volatile, yellow tetroxides, which contain formal M=O bonds. As expected for compounds of metals in such high oxidation states, the latter are potent oxidants. The tendency of the metals to form the higher oxides decreases as we go farther across the d block.

Reactivity with the heavier chalcogens is rather complex. Thus the oxidation state of Fe, Ru, Os, Co, and Ni in their disulfides is +2 because of the presence of the disulfide ion (S_2^{2-}), but the disulfides of Rh, Ir, Pd, and Pt contain the metal in the +4 oxidation state together with sulfide ions (S^{2-}). This combination of highly charged cations and easily polarised anions results in substances that are not simple ionic compounds and have significant covalent character.

The groups 8–10 metals form a range of binary nitrides, carbides, and borides. By far, the most important of these is cementite (Fe_3C), which is used to strengthen steel. Palladium is unusual in that it forms a binary hydride with the approximate composition $PdH_{0.5}$. Because the H atoms in the metal lattice are highly mobile, thin sheets of Pd are highly permeable to H_2 but essentially impermeable to all other gases, including He. Consequently, diffusion of H_2 through Pd is an effective method for separating hydrogen from other gases.

6.4.5 Groups 11 and 12

Group 11 (Cu, Ag, and Au)

The coinage metals—copper, silver, and gold—occur naturally; consequently, these were probably the first metals used by ancient humans.

Some properties of the coinage metals are listed in Table 6.18.

Table 6.18 Properties of the elements of groups 11 and 12

Group	Element	Z	Valence electron configuration	Electronegativity	Metallic radius (pm)	Melting point (°C)	Density (g/cm^3)
11	Cu	29	$4s^1 3d^{10}$	1.90	128	1085	8.96
	Ag	47	$5s^1 4d^{10}$	1.93	144	962	10.50
	Au	79	$6s^1 5d^{10} 4f^{14}$	2.40	144	1064	19.30
12	Zn	30	$4s^2 3d^{10}$	1.65	134	420	7.13
	Cd	48	$5s^2 4d^{10}$	1.69	149	321	8.69
	Hg	80	$6s^2 5d^{10} 4f^{14}$	1.90	151	−38.8	13.53

The electronegativity of gold is close to that of the nonmetals sulfur and iodine, which suggests that the chemistry of gold should be somewhat unusual for a metal. The coinage metals have the highest electrical and thermal conductivities of all the metals, and they are also the most ductile and malleable. With an $ns^1(n-1)d^{10}$ valence electron configuration, the chemistry of these three elements is dominated by the +1 oxidation state due to losing the single ns electron. Higher oxidation states are also known, however: +2 is common for Cu and, to a lesser extent, Ag, and +3 for Au due to the relatively low values of the second and third (for Au) ionisation energies. All three elements have significant electron affinities due to the half-filled ns orbital in the neutral atoms. As a result, gold reacts with powerful reductants like Cs and solutions of the alkali metals in liquid ammonia to produce the gold anion Au^- with a $6s^25d^{10}$ valence electron configuration.

All group 11 elements are relatively unreactive, and their reactivity decreases from Cu to Au. They are noble metals that are particularly well suited for use in coins and jewellery. Copper reacts with O_2 at high temperatures to produce Cu_2O and with sulfur to form Cu_2S. Neither silver nor gold react directly with oxygen, although oxides of these elements can be prepared by other routes. Silver reacts with sulfur compounds to form the black Ag_2S coating known as tarnish. Gold is the only metal that does not react with sulfur; it also does not react with nitrogen, carbon, or boron. All the coinage metals do, however, react with oxidising acids. Thus both Cu and Ag dissolve in HNO_3 and hot concentrated H_2SO_4, while Au dissolves in the 3:1 $HCl:HNO_3$ mixture known as aqua regia. Furthermore, all three metals dissolve in basic cyanide solutions in the presence of oxygen to form very stabile $[M(CN)_2]^-$ ions, a reaction that is used to separate gold from its ores.

All the monohalides except CuF and AuF are known (including AgF). Once again, iodine is unable to stabilise the higher oxidation states (Au^{3+} and Cu^{2+}). Thus all the copper (II) halides except the iodide are known, but the only dihalide of silver is AgF_2. In contrast, all the gold trihalides (AuX_3) are known, again except the triiodide. No binary nitrides, borides, or carbides are known for the group 11 elements.

Group 12 (Zn, Cd, and Hg)

Since none of the elements in group 12 has a partially filled $(n-1)d$ subshell, they are not, strictly speaking, transition metals. However, much of their chemistry is similar to that of the elements that immediately precede them in the d block. The group 12 metals are similar in abundance to those of group 11, and they are almost always found in combination with sulfur. Because zinc and cadmium are chemically similar, virtually all zinc ores contain significant amounts of cadmium. All three metals are commercially important, although the use of Cd is restricted because of its toxicity. Zinc is used for corrosion protection, in batteries, to make brass, and, in the form of ZnO, in the production of rubber and paints. Cadmium is used as the cathode in rechargeable NiCd batteries. Large amounts of mercury are used in the production of chlorine and NaOH by the chloralkali process.

As shown in Table 6.18, the group 12 metals are significantly more electropositive than the elements of group 11, and they, therefore, have less noble character. They also have much lower melting and boiling points than the preceding transition metals. In contrast to trends in the preceding groups, Zn and Cd are similar to each other but very different from the heaviest element (Hg). In particular, Zn and Cd are rather active metals, whereas mercury is not.

All three elements in group 12 have $ns^2(n-1)d^{10}$ valence electron configurations; consequently, the +2 oxidation state, corresponding to losing the two ns electrons, dominates their chemistry. Also, mercury forms a series of compounds in the +1 oxidation state that contain the diatomic mercurous ion Hg_2^{2+}.

All the possible group 12 dihalides (MX_2) are known, and they range from ionic (the fluorides) to highly covalent (such as $HgCl_2$). The highly covalent character of many mercuric and mercurous halides is surprising given the large size of the cations, and this has been attributed to the existence of an easily distorted $5d^{10}$ subshell. Zinc and cadmium react with oxygen to form amphoteric MO, whereas mercury forms HgO only within a narrow temperature range (350–400°C). Whereas zinc and cadmium dissolve in mineral acids such as HCl with the evolution of hydrogen, mercury dissolves only in oxidising acids such as HNO_3 and H_2SO_4. All three metals react with sulfur and the other chalcogens to form the binary chalcogenides; mercury also has an extraordinarily high affinity for sulfur.

Summary

The group 3 transition metals are highly electropositive metals and powerful reductants. They react with nonmetals to form largely ionic compounds and with oxygen to form sesquioxides (M_2O_3).

Group 4 metals have a high affinity for oxygen. In their reactions with halogens, the covalent character of the halides increases as the oxidation state of the metal increases because the high charge-to-radius ratio causes extensive polarisation of the anions. The dichalcogenides have layered structures similar to graphite, and the hydrides, nitrides, carbides, and borides are all hard, high-melting-point solids with metallic conductivity.

Group 5 metals also have a high affinity for oxygen. Consistent with periodic trends, only the lightest (vanadium) has any tendency to form compounds in oxidation states lower than +5. These elements also form layered chalcogenides, as well as nitrides, carbides, borides, and hydrides that are similar to those of the group 4 elements. As the metals become more polarisable across the row, their affinity for oxygen decreases.

The group 6 metals are less electropositive and have a maximum oxidation state of +6, making their compounds in high oxidation states largely covalent in character. As the oxidising strength of the halogen decreases, the maximum oxidation state of the metal also decreases. All three trioxides are acidic, but Cr_2O_3 is amphoteric. The chalcogenides of the group 6 metals are generally nonstoichiometric and electrically conducting, and these elements also form nitrides, carbides, and borides that are similar to those in the preceding groups.

The metals of group 7 have a maximum oxidation state of +7, but the lightest element, manganese, exhibits extensive chemistry in lower oxidation states. As with the group 6 metals, reaction with less oxidising halogens produces metals in lower oxidation states, and disulfides and diselenides of Tc and Re have layered structures. Group 7 metals also form nitrides, carbides, and borides that are stable at high temperatures and have metallic properties.

In groups 8, 9, and 10, the ionisation potentials of the elements are so high that the oxidation state corresponding to the formal loss of all valence electrons is encountered rarely (group 8) or not at all (groups 9 and 10). Compounds of group 8 metals in their highest oxidation state are powerful oxidants. The reactions of metals in groups 8, 9, and 10 with the chalcogens are complex, and these elements form a range of binary nitrides, carbides, and borides.

The coinage metals (group 11) have the highest electrical and thermal conductivities and are the most ductile and malleable of the metals. Although they are relatively unreactive, they form halides but not nitrides, borides, or carbides.

The group 12 elements, whose chemistry is dominated by the +2 oxidation state, are almost always found in nature combined with sulfur. Mercury is the only metal that is a liquid at room temperature, and it dissolves many metals to form amalgams. The group 12 halides range from ionic to covalent. These elements form chalcogenides and have a high affinity for soft ligands.

In summary

The key concepts, definitions, laws, properties and reactions:

1. The elements tend to become more polarisable going across the d block, and higher oxidation states become less stable; higher oxidation states become more stable going down a group.
2. Due to a small increase in successive ionisation energies, most of the transition metals have multiple oxidation states separated by a single electron.
3. Most compounds of transition metals are paramagnetic, whereas virtually all compounds of the p-block elements are diamagnetic.
4. All transition-metal cations have d^n electron configurations; the ns electrons are always lost before the (n – 1)d electrons.
5. The highest possible oxidation state, corresponding to the formal loss of all valence electrons, becomes increasingly less stable as we go from group 3 to group 8, and it is never observed in later groups.
6. In the transition metals, the stability of higher oxidation states increases down a column.
7. The chemistry of the group 3 metals is almost exclusively that of the M^{3+} ion; the elements are powerful reductants.
8. The +4 oxidation state dominates the chemistry of the group 4 metals. Only Ti has extensive chemistry in lower oxidation states.
9. The +5 oxidation state dominates the chemistry of the two heaviest group 5 metals (Nb and Ta). The chemistry of the lightest element (V) is dominated by lower oxidation states, especially +4.
10. The +6 oxidation state dominates the chemistry of the two heaviest group 6 metals (Mo and W). Lower oxidation states dominate the chemistry of the lightest element (Cr).
11. Lower oxidation states dominate the chemistry of the group 7 metals (Mn, Tc, and Re). Compounds in the maximum possible oxidation state (+7) are readily reduced.

12. The chemistry of groups 8, 9, and 10 is dominated by intermediate oxidation states such as +2 and +3.

13. Higher oxidation states become less stable across the d-block, but more stable down a group.

14. Although the most important oxidation state for group 11 is +1, the elements are relatively unreactive, with reactivity decreasing from Cu to Au.

15. The most important oxidation state for group 12 is +2; the metals are significantly more electropositive than the group 11 elements, so they are less noble.

6.5 Problem solving

6.5.1 Examples

Example 6.1 Based on the positions of the group 13 elements in the periodic table and the general trends outlined in this section:

a) classify these elements as metals, semimetals, or nonmetals;

b) predict which element forms the most stable compounds in the +1 oxidation state;

c) predict which element differs the most from the others in its chemistry;

d) predict which element of another group will exhibit chemistry most similar to that of Al.

Strategy:

From the position of the diagonal line in the periodic table separating metals and nonmetals, classify the group 13 elements. Then use the trends discussed above to compare their relative stabilities and chemical reactivities.

Solution:

a) Group 13 spans the diagonal line separating the metals from the nonmetals. Although Al and B both lie on the diagonal line, only B is a semimetal; the heavier elements are metals.

b) All five elements in group 13 have an ns^2np^1 valence electron configuration, so they are expected to form ions with a +3 charge from the loss of all valence electrons. The inert-pair effect should be most important for the heaviest element (Tl), so it is most likely to form compounds in an oxidation state that is lower by 2. Thus the +1 oxidation state is predicted to be most important for thallium.

c) Among s and p elements, the lightest member of each group exhibits unique chemistry because of its small size resulting in a high concentration of charge, energetically unavailable d orbitals, and a tendency to form multiple bonds. In group 13, we predict that the chemistry of boron will be quite different from that of its heavier congeners.

d) Within the s and p blocks, similarities between elements in different groups are most marked between the lightest member of one group and the element of the next group immediately below and to the right of it. These elements exhibit similar electronegativities and charge-to-radius ratios. Because Al is the second member of group 13, we predict that its chemistry will be most similar to that of Be, the lightest member of group 2.

Example 6.2 For each application, choose the more appropriate substance based on the properties and reactivities of the alkali metals and their compounds. Explain your choice in each case:

a) For a reaction that requires a strong base in a solution of tetrahydrofuran (THF), would you use LiOH or CsOH?

b) To extinguish a fire caused by burning lithium metal, would you use water, CO_2, N_2 gas, or sand (SiO_2)?

c) Both $LiNO_3$ and $CsNO_3$ are highly soluble in acetone (2-propanone). Which of these alkali metal salts would you use to precipitate I– from an acetone solution?

Strategy:

Use the properties and reactivities discussed above to determine which alkali metal is most suitable for the indicated application.

Solution:

a) Both LiOH and CsOH are ionic compounds that contain the hydroxide anion. The ion Li^+, however, is much smaller than Cs^+ so that the Li^+ cation will be more effectively solvated by the oxygen of THF with its lone pairs of electrons. This difference will have two effects: (1) LiOH is likely to be much more soluble than CsOH in the nonpolar solvent, which could be a significant advantage, and (2) the solvated Li^+ ions are less likely to form tight ion pairs with the OH^- ions in the relatively nonpolar solution, making the OH^- more basic and thus more reactive. Thus LiOH is the better choice.

b) Lithium is a potent reductant that reacts with water to form LiOH and H_2 gas, so adding a source of hydrogen such as water to a lithium fire is likely to produce an explosion. Lithium also reacts with oxygen and nitrogen in the air to form Li_2O and Li_3N, respectively, so we would not expect nitrogen to extinguish a lithium fire. Because CO_2 is a gaseous molecule that contains carbon in its highest accessible oxidation state (+4), adding CO_2 to a strong reductant such as Li should result in a vigorous redox reaction. Thus water, N_2, and CO_2 are all unsuitable choices for extinguishing a lithium fire. In contrast, sand is primarily SiO_2, which is a network solid that is not readily reduced. Smothering a lithium fire with sand is, therefore, the best choice.

c) The salt with the smaller cation has higher lattice energy, and high lattice energies tend to decrease the solubility of a salt. However, the solvation energy of the cation is also important in determining solubility, and small cations tend to have higher solvation energies. High solvation energies tend to increase the solubility of ionic substances. Thus CsI should be the least soluble of the alkali metal iodides, and LiI the most soluble. Consequently, $CsNO_3$ is the better choice.

Example 6.3 Predict the products of each reaction and then balance each chemical equation.

a) $Na_{(s)} + O_{2(g)} \rightarrow$

b) $Li_2O_{(s)} + H_2O_{(l)} \rightarrow$

c) $Li_{(s)} + CH_3Cl_{(l)} \rightarrow$

d) $Li_3N_{(s)} + KCl_{(s)} \rightarrow$

Strategy:

Determine whether one of the reactants is an oxidant or a reductant or a strong acid or a strong base. If so, a redox reaction or an acid-base reaction is likely to occur. Identify the products of the reaction. If a reaction is predicted to occur, balance the chemical equation.

Solution:

a) Sodium is a reductant, and oxygen is an oxidant, so a redox reaction is most likely. We expect an electron to be transferred from Na (thus forming Na^+) to O_2. We now need to determine whether the reduced product is superoxide (O^{2-}), peroxide (O_2^{2-}), or oxide (O^{2-}). Under normal reaction conditions, the product of the reaction of an alkali metal with oxygen depends on the identity of the metal. Because of differences in lattice energy, Li produces the oxide (Li_2O), the heavier metals (K, Rb, Cs) produce the superoxide (MO_2), and Na produces the peroxide (Na_2O_2).

The balanced chemical equation is $2Na_{(s)} + O_{2(g)} \rightarrow Na_2O_{2(s)}$.

b) Li_2O is an ionic salt that contains the oxide ion (O^{2-}), which is the completely deprotonated form of water and thus is expected to be a strong base. The other reactant, water, is both a weak acid and a weak base, so we can predict that an acid-base reaction will occur.

The balanced chemical equation is $Li_2O_{(s)} + H_2O_{(l)} \rightarrow 2LiOH_{(aq)}$.

c) One of the reactants is an alkali metal, a potent reductant, and the other is an alkyl halide. Any compound that contains a carbon–halogen bond can, in principle, be reduced, releasing a halide ion and forming an organometallic compound. That outcome seems likely in this case because organolithium compounds are among the most stable organometallic compounds known. Two moles of lithium are required to balance the equation: $2Li_{(s)} + CH_3Cl_{(l)} \rightarrow LiCl_{(s)} + CH_3Li_{(soln)}$.

d) Lithium nitride and potassium chloride are largely ionic compounds. The nitride ion (N^{3-}) is a very strong base because it is the fully deprotonated form of ammonia, a weak acid. An acid-base reaction requires an acid as well as a base, however, and KCl is not acidic. What about a redox reaction? Both substances contain ions that have closed-shell valence electron configurations. The nitride ion could act as a reductant by donating electrons to an oxidant and forming N_2. KCl is not an oxidant, however, and a redox reaction requires an oxidant as well as a reductant. We conclude that the two substances will not react with each other.

Example 6.4 For each application, choose the most appropriate substance based on the properties and reactivities of the alkaline earth metals and their compounds. Explain your choice in each case. Use any tables you need in making your decision, such as K_{sp} values, lattice energies and band-gap energies.

To neutralise excess stomach acid that causes indigestion, would you use $BeCO_3$, $CaCO_3$, or $BaCO_3$?

Strategy:

Based on the discussion in this section and any relevant information elsewhere in this book, determine which substance is most appropriate for the indicated use.

Solution:

All the alkaline earth carbonates will neutralise an acidic solution by the following equation:

$MCO_{3(s)} + 2H^+_{(aq)} \rightarrow M^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$

Because beryllium and its salts are toxic, however, $BeCO_3$ cannot be used as an antacid.

Of the remaining choices, $CaCO_3$ is somewhat more soluble than $BaCO_3$ (according to the K_{sp} values, see Appendix E), suggesting that it will act more rapidly. Moreover, the formula mass of $CaCO_3$ is 100.1 amu, whereas that of $BaCO_3$ is almost twice as large. Therefore, neutralising a given amount of acid would require twice the mass of $BaCO_3$ compared with $CaCO_3$. Furthermore, the reaction of $BaCO_3$ with acid produces a solution containing Ba^{2+} ions, which are toxic. (Ba^{2+} is a stimulant that can cause ventricular fibrillation of the heart.) Finally, $CaCO_3$ is produced on a vast scale, so $CaCO_3$ is likely to be significantly less expensive than any barium compound. Consequently, $CaCO_3$ is the best choice for an antacid.

Example 6.5 Predict the products of each reaction and then balance each chemical equation.

a) $CaO_{(s)} + HCl_{(g)} \rightarrow$

b) $MgO_{(s)} + \text{excess } OH^-_{(aq)} \rightarrow$

Solution:

a) Gaseous HCl is an acid, and CaO is a basic oxide that contains the O^{2-} ion. This is, therefore, an acid-base reaction that produces $CaCl_2$ and H_2O.

The balanced chemical equation is

$CaO_{(s)} + 2HCl_{(g)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)}$.

b) Magnesium oxide is a basic oxide, so it can either react with water to give a basic solution or dissolve in an acidic solution. Hydroxide ion is also a base. Because we have two bases but no acid, an acid-base reaction is impossible.

A redox reaction is not likely because MgO is neither a good oxidant nor a good reductant.

We conclude that no reaction occurs.

Example 6.6 For each reaction, explain why the given products form.

a) $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(l)$

b) $BCl_{3(l)} + 3H_2O_{(l)} \rightarrow B(OH)_{3(aq)} + 3HCl_{(aq)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution:

a) Molecular oxygen is an oxidant. If the other reactant is a potential reductant, we expect that a redox reaction will occur. Although B_2H_6 contains boron in its highest oxidation state (+3), it also contains hydrogen in the –1 oxidation state (the hydride ion). Because hydride is a strong reductant, a redox reaction will probably occur. We expect that H^- will be oxidised to H^+ and O_2 will be reduced to O^{2-}, but what are the actual products? A reasonable guess is B_2O_3 and H_2O, both stable compounds.

b) Neither BCl_3 nor water is a powerful oxidant or reductant, so a redox reaction is unlikely; a hydrolysis reaction is more probable than that. Nonmetal halides are acidic and react with water to form a solution of the hydrohalic acid and a nonmetal oxide or hydroxide. In this case, the most probable boron-containing product is boric acid $[B(OH)_3]$.

Example 6.7 For each reaction, explain why the given products form.

a) $2Al_{(s)} + Fe_2O_{3(s)} \xrightarrow{t} 2Fe_{(l)} + Al_2O_{3(s)}$

b) $2Ga_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \xrightarrow{t} 3H_{2(g)} + 2Ga(OH)_4{}^-_{(aq)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution:

a) Aluminium is an active metal and a powerful reductant, and Fe_2O_3 contains Fe(III), a potential oxidant. Hence a redox reaction is probable, producing metallic Fe and Al_2O_3. Because Al is an element of group 13 and lies above Fe, which is a transition element, it should be a more active metal than Fe. Thus the reaction should proceed to the right. In fact, this is the thermite reaction, which is so vigorous that it produces molten Fe and can be used for welding.

b) Gallium lies immediately below aluminium in the periodic table and is amphoteric, so it will dissolve in either acid or base to produce hydrogen gas. Because gallium is similar to aluminium in many of its properties, we predict that gallium will dissolve in the strong base.

Example 6.8 For each reaction, explain why the given product forms.

a) $CO_{(g)} + Cl_{2(g)} \rightarrow Cl_2C{=}O_{(g)}$

b) $CO_{(g)} + BF_{3(g)} \rightarrow F_3B{:}C{\equiv}O_{(g)}$

c) $Sr_{(s)} + 2C_{(s)} \xrightarrow{t} SrC_{2(s)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a) Because the carbon in CO is in an intermediate oxidation state (+2), CO can be either a reductant or an oxidant; it is also a Lewis base. The other reactant (Cl_2) is an oxidant, so we expect a redox reaction to occur in which the carbon of CO is further oxidised. Because Cl_2 is a two-electron oxidant, and the carbon atom of CO can be oxidised by two electrons to the +4 oxidation state, the product is phosgene ($Cl_2C{=}O$).

b) Unlike Cl_2, BF_3 is not a good oxidant, even though it contains boron in its highest oxidation state (+3). Nor can BF_3 behave like a reductant. Like any other species with only six valence electrons, however, it is certainly a Lewis acid. Hence an acid-base reaction is the most likely alternative, especially because we know that CO can use the lone pair of electrons on carbon to act as a Lewis base. The most probable reaction is, therefore, the formation of a Lewis acid-base adduct.

c) Typically, both reactants behave like reductants. Unless one of them can also behave like an oxidant, no reaction will occur. We know that Sr is an active metal because it lies far to the left in the periodic table and that it is more electropositive than carbon. Carbon is a nonmetal with a significantly higher electronegativity; it is, therefore, more likely to accept electrons in a redox reaction. We conclude, therefore, that Sr will be oxidised, and C will be reduced. Carbon forms ionic carbides with active metals so that the reaction will produce a species formally containing either C^{4-} or C_2^{2-}. Those that contain C^{4-}

involve small, highly charged metal ions as a rule so that Sr^{2+} will produce the acetylide (SrC_2) instead.

Example 6.9 For each reaction, explain why the given products form.

a) $Pb_{(s)} + Cl_{2(g)} \rightarrow PbCl_{2(s)}$

b) $Mg_2Si_{(s)} + 4H_2O_{(l)} \rightarrow SiH_{4(g)} + 2Mg(OH)_{2(s)}$

c) $GeO_{2(s)} + 4OH^-_{(aq)} \rightarrow GeO_4{}^{4-}{}_{(aq)} + 2H_2O_{(l)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a) Lead is a metal, and chlorine is a nonmetal that is a strong oxidant. Thus we can expect a redox reaction to occur in which the metal acts as a reductant. Although lead can form compounds in the +2 and +4 oxidation states, Pb^{4+} is a potent oxidant (the inert-pair effect). Because lead prefers the +2 oxidation state and chlorine is a weaker oxidant than fluorine, we expect $PbCl_2$ to be the product.

b) This is the reaction of water with a metal silicide, which formally contains the Si^{4-} ion. Water can act as either an acid or a base. Because the other compound is a base, we expect an acid-base reaction to occur in which water acts as an acid. Because Mg_2Si contains Si in its lowest possible oxidation state, however, an oxidation-reduction reaction is also a possibility. However, water is a relatively weak oxidant, so an acid-base reaction is more likely than the redox reaction. The acid (H_2O) transfers a proton to the base (Si^{4-}), which can accept four protons to form SiH_4. Proton transfer from water produces the OH^- ion, which will combine with Mg^{2+} to give magnesium hydroxide.

c) We expect germanium dioxide (GeO_2) to be amphoteric because of the position of germanium in the periodic table. It should dissolve in the strong aqueous base to give an anionic species analogous to silicate.

Example 6.10 For each reaction, explain why the given products form when the reactants are heated.

a) $Sr_{(s)} + N_2O_{(g)} \rightarrow SrO_{(s)} + N_{2(g)}$

b) $NH_4NO_{2(s)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$

c) $Pb(NO_3)_{2(s)} \rightarrow PbO_{2(s)} + 2NO_{2(g)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a) As an alkali metal, strontium is a strong reductant. If the other reactant can act as an oxidant, then a redox reaction will occur. Nitrous oxide contains nitrogen in a low oxidation state (+1), so we would not normally consider it an oxidant. Nitrous oxide is, however, thermodynamically unstable ($\Delta H°_f > 0$ and $\Delta G°_f > 0$), and it can be reduced to N_2, which is a stable species. Consequently, we predict that a redox reaction will occur.

b) When a substance is heated, a decomposition reaction probably will occur, which often involves the release of stable gases. In this case, ammonium nitrite contains nitrogen in two different oxidation states (–3 and +3), so an internal redox reaction is a possibility. Due to its thermodynamic stability, N_2 is the probable nitrogen-containing product, whereas we predict that H and O will combine to form H_2O.

c) Again, this is probably a thermal decomposition reaction. If one element is in a usually high oxidation state and another in a low oxidation state, a redox reaction will probably occur. Lead nitrate contains the Pb^{2+} cation and the nitrate anion, which contains nitrogen in its highest possible oxidation state (+5). Hence nitrogen can be reduced, and we know that lead can be oxidised to the +4 oxidation state. Consequently, it is likely that lead (II) nitrate will decompose to lead (IV) oxide and nitrogen dioxide when heated. Even though PbO_2 is a powerful oxidant, the release of a gas such as NO_2 can often drive an otherwise unfavourable reaction to completion (Le Chatelier's principle). Note, however, that PbO_2 will probably decompose to PbO at high temperatures.

Example 6.11 For each reaction, explain why the given products form.

a) $Bi_{(s)} + 3/2Br_{(l)} \rightarrow BiBr_{3(s)}$

b) $PBr_{3(l)} + 3H_2O_{(l)} \rightarrow H_3PO_{3(aq)} + 3HBr_{(aq)}$

c) $As_{(s)} + Ga_{(s)} \xrightarrow{t} GaAs_{(s)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

Solution:

a) Bromine is an oxidant, and bismuth is a metal that can be oxidised. Hence a redox reaction is likely to occur. To identify the product, recall that bismuth can form compounds in either the +3 or +5 oxidation state. The bismuth is rather difficult to oxidise to the +5 oxidation state because of the inert-pair effect. Hence the product will probably be bismuth (III) bromide.

b) Phosphorus tribromide is a typical nonmetal halide. We expect it to react with water to produce an oxoacid of P(III) and the corresponding hydrohalic acid. Because of the strength of the P=O bond, phosphorous acid (H_3PO_3) is actually $HP(O)(OH)_2$, which contains a P=O bond and a P–H bond.

c) Gallium is a metal with a strong tendency to act as a reductant and form compounds in the +3 oxidation state. In contrast, arsenic is a semimetal. It can act as a reductant to form compounds in the +3 or +5 oxidation state, or it can act as an oxidant, accepting electrons to form compounds in the –3 oxidation state. If a reaction occurs, then a binary compound will probably form with a 1:1 ratio of the elements. GaAs is an example of a III–V compound, many of which are used in the electronics industry.

Example 6.12 For each reaction, explain why the given products form.

a) $Ga_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Ga(OH)_4{}^-_{(aq)}$

b) $3H_2O_{2(aq)} + 2MnO_4{}^-_{(aq)} + 2H^+_{(aq)} \rightarrow 3O_{2(g)} + 2MnO_{2(s)} + 4H_2O_{(l)}$

c) $2KNO_{3(s)} \xrightarrow{t} KNO_{2(s)} + O_{2(g)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a) Gallium is a metal. We expect the oxides of metallic elements to be basic and therefore not to react with aqueous base. A close look at the periodic table, however, shows that gallium is close to the diagonal line of semimetals. Moreover, aluminium, the element immediately above gallium in group 13, is amphoteric.

Consequently, we predict that gallium will behave like aluminium: ($Al_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2Al(OH)_4{}^-_{(aq)}$).

b) Hydrogen peroxide is an oxidant that can accept two electrons per molecule to give two molecules of water. With a strong oxidant, however, H_2O_2 can also act as a reductant, losing two electrons (and two protons) to produce O_2. Because the other reactant is permanganate, which is a potent oxidant, the only possible reaction is a redox reaction in which permanganate is the oxidant and hydrogen peroxide is the reductant. Recall that reducing permanganate often gives MnO_2, an insoluble brown solid. Reducing MnO_4^- to MnO_2 is a three-electron reduction, whereas the oxidation of H_2O_2 to O_2 is two-electron oxidation.

c) This is a thermal decomposition reaction. Because KNO_3 contains nitrogen in its highest oxidation state (+5) and oxygen in its lowest oxidation state (–2), a redox reaction is likely. Oxidation of the oxygen in nitrate to atomic oxygen is a two-electron process per oxygen atom. Nitrogen is likely to accept two electrons because oxoanions of nitrogen are known only in the +5 (NO_3^-) and +3 (NO_2^-) oxidation states.

Example 6.13 For each reaction, explain why the given product forms or no reaction occurs.

a) $SO_{2(g)} + Cl_{2(g)} \rightarrow SO_2Cl_{2(l)}$

$SF_{6(g)} + H_2O_{(l)} \rightarrow$ no reaction

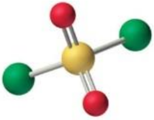
$2Se_{(s)} + Cl_{2(g)} \rightarrow Se_2Cl_{2(l)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form or why no reaction occurs.

Solution:

a) One of the reactants (Cl_2) is an oxidant. If the other reactant can be oxidised, then a redox reaction is likely. Sulfur dioxide contains sulfur in the +4 oxidation state, which is two units less than its maximum oxidation state. Sulfur dioxide is also known to be a mild reducing agent in aqueous solution, producing sulfuric acid as the oxidation product. Hence a redox reaction is probable. The simplest reaction is the formation of



SO_2Cl_2

SO_2Cl_2 (sulfuryl chloride), which is a tetrahedral species with two S–Cl and two S=O bonds.

b) Sulfur hexafluoride is a nonmetallic halide. Such compounds normally react vigorously with water to produce an oxoacid of the nonmetal and the corresponding hydrohalic acid. In this case, however, we have a highly stable species, presumably because all of the sulfur's available orbitals are bonding orbitals. Thus SF_6 is not likely to react with water.

c) Here we have the reaction of a chalcogen with a halogen. The halogen is a good oxidant, so we can anticipate that a redox reaction will occur. Only fluorine is capable of oxidising the chalcogens to a +6 oxidation state, so we must decide between $SeCl_4$ and Se_2Cl_2 as the product. The stoichiometry of the reaction determines which of the two is obtained: $SeCl_4$ or Se_2Cl_2.

Example 6.14 For each reaction, explain why the given products form.

a) $ClF_{3(g)} + Cl_{2(g)} \rightarrow 3ClF_{(g)}$

b) $2KI_{(s)} + 3H_2SO_{4(aq)} \rightarrow I_{2(aq)} + SO_{2(g)} + 2KHSO_{4(aq)} + 2H_2O_{(l)}$

c) $Pb_{(s)} + 2BrF_{3(l)} \rightarrow PbF_{4(s)} + 2BrF_{(g)}$

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution:

a) When the reactants have the same element in two different oxidation states, we expect the product to have that element in an intermediate oxidation state. We have Cl^{3+} and Cl^0 as reactants, so a possible product would have Cl in either the +1 or +2 oxidation state. From our discussion, we know that +1 is much more likely. In this case, Cl_2 is behaving like a reductant rather than an oxidant.

b) At first glance, this appears to be a simple acid-base reaction, in which sulfuric acid transfers a proton to I^- to form HI. Recall, however, that I^- can be oxidised to I_2. Sulfuric acid contains sulfur in its highest oxidation state (+6), so it is a good oxidant. In this case, the redox reaction predominates.

c) This is the reaction of a metallic element with a very strong oxidant. Consequently, a redox reaction will occur. The only question is whether Pb will be oxidised to Pb(II) or Pb(IV). Because BrF_3 is a powerful oxidant and fluorine is able to stabilise high oxidation states of other elements, it is likely that PbF_4 will be the product. The two possible reduction products for BrF_3 are BrF and Br_2. The actual product will likely depend on the ratio of the reactants used. With excess BrF_3, we expect a more oxidised product (BrF). With lower ratios of oxidant to lead, we would probably obtain Br_2 as the product.

Example 6.15 On a virtual planet similar to Earth, at least one isotope of radon is not radioactive. A scientist explored its chemistry and presented his major conclusions in a trailblazing paper on radon compounds, focusing on the kinds of compounds formed and their stoichiometries. Based on periodic trends, how did he summarise the chemistry of radon?

Strategy:

Based on the position of radon in the periodic table and periodic trends in atomic properties, thermodynamics and kinetics, predict the most likely reactions and compounds of radon.

Solution:

We expect radon to be significantly easier to oxidise than xenon. Based on its position in the periodic table, however, we also expect its bonds to other atoms to be weaker than those formed by xenon. Radon should be more difficult to oxidise to its highest possible oxidation state (+8) than xenon because of the inert-pair effect. Consequently, radon should form an extensive series of fluorides, including RnF_2, RnF_4, RnF_6, and possibly RnF_8 (due to its large radius). The ion RnF_8^{2-} should also exist. We expect radon to form a series of oxides similar to those of xenon, including RnO_3 and possibly RnO_4. The biggest surprise in radon chemistry is likely to be the existence of stable chlorides, such as $RnCl_2$ and possibly even $RnCl_4$.

Example 6.16 Two of the group 8 metals (Fe, Ru, and Os) form stable oxides in the +8 oxidation state. Identify these metals; predict the stoichiometry of the oxides; describe the general physical and chemical properties, type of bonding, and physical state of the oxides; and decide whether they are acidic or basic oxides.

Strategy:

Refer to the texts about metallic radii of the first-, second-, and third-row transition metals, trends in properties of the transition metals, valence electron configurations of the first-row transition metals, common oxidation states of the first-row transition metals to identify the metals. Decide whether their oxides are covalent or ionic in character, and, based on this consideration, predict the general physical and chemical properties of the oxides.

Solution:

The +8 oxidation state corresponds to a stoichiometry of MO_4. Because the heavier transition metals tend to be stable in higher oxidation states, we expect Ru and Os to form the most stable tetroxides. Because oxides of metals in high oxidation states are generally covalent compounds, RuO_4 and OsO_4 should be volatile solids or liquids that consist of discrete MO_4 molecules, which the valence-shell electron-pair repulsion model predicts to be tetrahedral. Finally, because oxides of transition metals in high oxidation states are usually acidic, RuO_4 and OsO_4 should dissolve in the strong aqueous base to form oxoanions

Example 6.17 For each reaction, explain why the indicated products form.

a) $TiCl_{4(l)} + 2H_2O_{(l)} \rightarrow TiO_{2(s)} + 4HCl_{(aq)}$

b) $WO_{3(s)} + 3C_{(s)} + 3Cl_{2(g)} \xrightarrow{t} WCl_{6(s)} + 3CO_{(g)}$

c) $Sc_2O_{3(s)} + 2OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow 2[Sc(OH)_4]^-_{(aq)}$

d) $2KMnO_{4(aq)} + 2H_2SO_{4(l)} \rightarrow Mn_2O_{7(l)} + 2KHSO_{4(soln)} + H_2O_{(soln)}$

e) $4CrCl_{2(aq)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 4Cr^{3+}_{(aq)} + 8Cl^-_{(aq)} + 2H_2O_{(l)}$

Strategy:

Refer to the texts about metallic radii of the first-, second-, and third-row transition metals, trends in properties of the transition metals, valence electron configurations of the first-row transition metals, common oxidation states of the first-row transition metals to explain why these products form.

Solution:

a) The most stable oxidation state for Ti is +4, and neither reactant is a particularly strong oxidant or reductant; hence, a redox reaction is unlikely. Similarly, neither reactant is a particularly strong acid or base, so an acid-base reaction is unlikely. Because $TiCl_4$ contains Ti in a relatively high oxidation state (+4), however, it is likely to be rather covalent in character, with reactivity similar to that of a semimetal halide such as $SiCl_4$. Covalent halides tend to hydrolyse in water to produce the hydrohalic acid and either the oxide of the other element or a species analogous to an oxoacid.

b) This reaction involves the oxide of a group 6 metal in its highest oxidation state (WO_3) and two elements, one of which is a reductant (C) and the other an oxidant (Cl_2). Consequently, some sort of redox reaction will occur. Carbon can certainly react with chlorine to form CCl_4, and WO_3 is a potential source of oxygen atoms that can react with carbon to produce CO, which is very stable. If CO is one of the products, then it seems likely that the other product will contain the metal and chlorine. The most likely combination is WCl_6 (leaving the oxidation state of the metal unchanged).

c) One of the reactants is a strong base (OH^-), so an acid-base reaction is likely if the other reactant is acidic. Because oxides like Sc_2O_3, in which the metal is in an intermediate oxidation state, are often amphoteric, we expect Sc_2O_3 to dissolve in the base to form a soluble hydroxide complex.

d) Concentrated sulfuric acid is both an oxidant and a strong acid that tends to protonate and dehydrate other substances. The permanganate ion already contains manganese in its highest possible oxidation state (+7), so it cannot be oxidised further. A redox reaction is impossible, which leaves an acid-base reaction as the most likely alternative. Sulfuric acid is likely to protonate the terminal oxygen atoms of permanganate, allowing them to be lost as water.

e) Molecular oxygen is an oxidant, so a redox reaction is likely if the other reactant can be oxidised. Because chromous chloride contains chromium in its lowest accessible oxidation state, a redox reaction will occur in which Cr^{2+} ions are oxidised, and O_2 is reduced.

In the presence of protons, the reduction product of O_2 is water, so we need to determine only the identity of the oxidation product of Cr^{2+}. Chromium forms compounds in two common higher oxidation states: they are the Cr^{3+} ion, which is the most stable, and the $[Cr_2O_7]^{2-}$ ion, which is a more powerful oxidant than O_2. We, therefore, predict that the reaction will form Cr^{3+}(aq) and water.

6.5.2 Problems

1. Based on the positions of the group 14 elements C, Si, Ge, Sn, and Pb in the periodic table and the general trends outlined in this chapter,

a) classify these elements as metals, semimetals, or nonmetals;

b) predict which element forms the most stable compounds in the +2 oxidation state;

c) predict which element differs the most from the others in its chemistry;

d) predict which element of group 14 will be chemically most similar to a group 15 element.

2. Arrange Rb, H, Be, Na, Cs, and Ca in order of:

a) decreasing atomic size;

b) decreasing the magnitude of electron affinity.

3. Arrange As, O, Ca, Sn, Be, and Sb in order of decreasing metallic character.

4. Two elements are effective additives to solid rocket propellant: beryllium and one other element that has similar chemistry. Based on the position of beryllium in the periodic table, identify the second element.

5. The following table lists the valences, coordination numbers, and ionic radii for a series of cations. Which would you substitute for K^+ in a crystalline lattice? Explain your answer.

Metal	Charge	Coordination number	Ionic radius (pm)
Li	+1	4	76
Na	+1	6	102
K	+1	6	138
Mg	+2	6	72
Ca	+2	6	100
Sr	+2	6	118

6. Some periodic tables include hydrogen as a group 1 element, whereas other periodic tables include it as a group 17 element. Refer to the properties of hydrogen to propose an explanation for its placement in each group. In each case, give one property of hydrogen that would exclude it from groups 1 and 17.

7. Indicate which elements are likely to form ionic, covalent, or metallic hydrides and explain your reasoning:

a) Sr; b) Si;
c) O; d) Li;
e) B; f) Be;
g) Pd; h) Al.

8. In addition to ion-dipole attractions, hydrogen bonding is important in solid crystalline hydrates, such as $Na_4XeO_6 \cdot 8H_2O$. Based on this statement, explain why anhydrous Na_4XeO_6 does not exist.

9. Predict the products of each reaction and balance each chemical equation.

$K_{(s)} + N_{2(g)} \rightarrow$

$Li_3N_{(s)} + H_2O_{(l)} \rightarrow$

$CH_3CH_2Cl_{(soln)} + 2Li \rightarrow$

10. A key step in the isolation of the alkali metals from their ores is selective precipitation. For example, lithium is separated from sodium and potassium by precipitation of Li_2CO_3 ($K_{sp} = 8.15\times10^{-4}$).

If 500.0 mL of a 0.275 *M* solution of Na_2CO_3 is added to 500.0 mL of a 0.536 *M* lithium hydroxide solution, what mass of Li_2CO_3 will precipitate (assuming no further reactions occur)?

What mass of lithium will remain in solution?

11. Which of the indicated alkaline earth metals or their compounds is most appropriate for each application?

a) drying agent for removing water from the atmosphere – $CaCl_2$, $MgSO_4$, or BaF_2;

b) removal of scale deposits (largely $CaCO_3$) in water pipes – HCl(aq) or H_2SO_4(aq);

c) removal of traces of N_2 from purified argon gas – Be, Ca, or Ba.

12. Predict the products of each reaction and then balance each chemical equation.

a) $BaCl_{2(aq)} + Na_2SO_{4(aq)} \rightarrow$

b) $BeO_{(s)} + OH^{-}_{(aq)} + H_2O_{(l)} \rightarrow$

13. Predict the products of each reaction and then balance each chemical equation.

a) $Sr_{(s)} + O_{2(g)} \rightarrow$

b) the thermal decomposition of $CaCO_{3(s)}$

c) $CaC_{2(s)} + H_2O_{(l)} \rightarrow$

d) $RbHCO_{3(s)} + H_2SO_{4(aq)} \rightarrow$

14. The solubility products of $BaSO_4$ and $CaSO_4$ are 1.08×10^{-10} and 4.93×10^{-5}, respectively. What accounts for this difference?

When 500.0 mL of a solution that contains 1.00 *M* $Ba(NO_3)_2$ and 3.00 *M* $Ca(NO_3)_2$ is mixed with a 2.00 *M* solution of Na_2SO_4, a precipitate forms.

What is the identity of the precipitate? How much of it will form before the second salt precipitates?

15. A sample consisting of 20.35 g of finely divided calcium metal is allowed to react completely with nitrogen. What is the mass of the product?

16. For each application, which of the indicated substances would you select and why? Base your selections on the properties and reactivities of the alkaline earth metals and their compounds.

a) source of CO_2 at low temperature – $BeCO_3$ or $CaCO_3$;

b) window material for x-ray tubes – beryllium or strontium;

c) source of iodide ions in aqueous solution – BaI_2 or BeI_2;

d) formation of a stable organometallic compound by reacting a metal with an alkyl halide – calcium or magnesium;

e) synthesis of refractory materials – magnesium oxide or barium oxide.

17. Propose an effective compound for purifying and regenerating air for breathing in a submarine and justify your choice.

18. Calcium magnesium carbonate [$CaMg(CO_3)_2$], also known as dolomite, is a primary constituent of soils. It is formed when water containing magnesium ions comes in contact with calcium carbonate. Do you expect dolomite to be more or less resistant to acid rain than calcium carbonate? Why?

19. Predict the products of the reactions and write a balanced chemical equation and, if necessary, the reaction conditions (heating, pressure, catalyst, etc.) for each reaction.

a) $B_2H_{6(g)} + H_2O_{(l)} \rightarrow$

b) $BBr_{3(l)} + O_{2(g)} \rightarrow$

c) $B_2O_{3(s)} + Ca_{(s)} \rightarrow$

20. Predict the products of the reactions and write a balanced chemical equation for each reaction.

a) $LiH_{(s)} + Al_2Cl_{6(soln)} \rightarrow$

b) $Al_2O_{3(s)} + OH^-_{(aq)} \rightarrow$

c) $Al_{(s)} + N_{2(g)} \rightarrow$

21. Predict the products of the reactions and write a balanced chemical equation for each reaction.

a) $C_{(s)} + \text{excess } O_{2(g)} \rightarrow$

b) $C_{(s)} + H_2O_{(l)} \rightarrow$

c) $NaHCO_{3(s)} + H_2SO_{4(aq)} \rightarrow$

22. Predict the products of the reactions and write a balanced chemical equation and, if necessary, the reaction conditions (heating, pressure, catalyst, etc.) for each reaction.

a) $PbO_{2(s)} \rightarrow$

b) $GeCl_{4(s)} + H_2O_{(l)} \rightarrow$

c) $Sn_{(s)} + HCl_{(aq)} \rightarrow$

d) $CaC_{2(s)} + HCl_{(g)} \rightarrow$

e) $Pb_{(s)} + Br_{2(l)} \rightarrow$

f) $(CH_3)_3N_{(l)} + H_2O_{2(aq)} \rightarrow$

g) $Pb(N_3)_{2(s)} \rightarrow$

23. Write a balanced chemical equation to indicate how you would prepare each compound.

a) CO_2 from CuO;

b) methane from Be_2C;

c) $Si(OH)_4$ from Si;

d) Si_3N_4 from Si.

24. Predict the products of the reactions and write a balanced chemical equation and, if necessary, the reaction conditions (heating, pressure, catalyst, etc.) for each reaction.

a) $NO_{(g)} + H_2O_{(l)} \rightarrow$

b) $NH_4NO_{3(s)} \rightarrow$

c) $Sr_{(s)} + N_{2(g)} \rightarrow$

25. Predict the products of the reactions and write a balanced chemical equation and, if necessary, the reaction conditions (heating, pressure, catalyst, etc.) for each reaction.

a) $PCl_{5(s)} + H_2O_{(l)} \rightarrow$

b) $Bi_2O_{5(s)} \rightarrow$

c) $Ca_3P_{2(s)} + H^+_{(aq)} \rightarrow$

d) $NaNH_{2(s)} + PH_{3(soln)} \rightarrow$

e) $P_4O_{10(s)} + H_2O_{(l)} \rightarrow$

f) $AsCl_{3(l)} + H_2O_{(l)} \rightarrow$

g) $Bi_2O_{3(s)} + H_2O_{(l)} \rightarrow$

h) $Sb_4O_{6(s)} + OH^-_{(aq)} \rightarrow$

26. Predict the products of the reactions and write a balanced chemical equation and, if necessary, the reaction conditions (heating, pressure, catalyst, etc.) for each reaction.

a) $SiO_{2(s)} + H^+_{(aq)} \rightarrow$

b) $NO_{(g)} + O_{2(g)} \rightarrow$

c) $SO_{3(g)} + H_2O_{(l)} \rightarrow$

d) $H_2O_{2(aq)} + I^-_{(aq)} \rightarrow$

27. Unlike the other chalcogens, oxygen does not form compounds in the +4 or +6 oxidation state. Why?

28. Classify each oxide as basic, acidic, amphoteric, or neutral:

a) CaO;

b) SO_2;

c) NO;

d) Rb_2O;

e) PbO_2.

29. Arrange CrO_3, Al_2O_3, Sc_2O_3, and BaO in order of increasing basicity.

30. Of CO_2, NO_2, O_2, SO_2, Cl_2O, H_2O, NH_3, and CH_4, which do you expect to have the

a) most polar covalent bond(s)?

b) least polar covalent bond(s)?

31. Write a balanced chemical equation for the reaction of sulfur with:

a) $O_{2(g)}$;

b) $S^{2-}_{(aq)}$;

c) $F_{2(g)}$;

d) $HNO_{3(aq)}$.

32. Predict the products of the reactions and write a balanced chemical equation and, if necessary, the reaction conditions (heating, pressure, catalyst, etc.) for each reaction.

a) $CaCl_{2(s)} + H_3PO_{4(l)} \rightarrow$

b) $GeO_{2(s)} + HF_{(aq)} \rightarrow$

c) $Fe_2O_3(s) + HCl_{(g)} \rightarrow$

d) $NaClO_{2(aq)} + Cl_{2(g)} \rightarrow$

33. SiF_4 reacts easily with NaF to form SiF_6^{2-}. In contrast, CF_4 is totally inert and shows no tendency to form CF_6^{2-} under even extreme conditions. Explain this difference.

34. Write a balanced chemical equation for the reaction of aqueous HF with:

a) SiO_2;
b) Na_2CO_3;
c) CaO.

35. Write a balanced chemical equation describing each reaction.

a) the burning of sulfur in a chlorine atmosphere;
b) the dissolution of iodine in a potassium iodide solution;
c) the hydrolysis of PCl_3;
d) the preparation of HF from calcium fluoride and sulfuric acid;
e) the thermal decomposition of $KClO_3$;
f) the oxidation of sulfide ion by elemental iodine.

36. Write a balanced chemical equation showing how you would prepare each compound from its elements and other common compounds:

a) XeF_2;
b) XeF_4;
c) XeF_6;
d) $XeOF_4$;
e) XeO_3.

37. Arrange Pt^{4+}, Hg^{2+}, Fe^{2+}, Zr^{4+}, and Fe^{3+} in order of decreasing radius.

38. Give the highest oxidation state observed for Ag, Co, Os, Au, W, and Mn.

39. What do you predict to be the coordination number of Pt^{2+}, Au^+, Fe^{3+}, and Os^{2+}?

40. Predict the products of the reactions and write a balanced chemical equation for each reaction.

a) $AgBr + h\nu$
b) W + excess Cl_2, heated
c) $CuO + H_2$, heated
d) Fe_2O_3 in aqueous acid
e) $RhCl_3 + NH_3$, in water
f) $Fe^{2+} + [MnO_4]^-$, in water

Appendices

A. The periodic table of elements

List of elements (alphabetically)

Name	Symbol	Atomic number	Atomic mass
Actinium	Ac	89	[227]*
Aluminium	Al	13	26.9815386(8)
Americium	Am	95	[243]*
Antimony	Sb	51	121.760(1)
Argon	Ar	18	39.948(1)
Arsenic	As	33	74.92160(2)
Astatine	At	85	[210]*
Barium	Ba	56	137.327(7)
Berkelium	Bk	97	[247]*
Beryllium	Be	4	9.012182(3)
Bismuth	Bi	83	208.98040(1)
Bohrium	Bh	107	[267]*
Boron	B	5	10.811(7)
Bromine	Br	35	79.904(1)
Cadmium	Cd	48	112.411(8)
Caesium	Cs	55	132.9054519(2)
Calcium	Ca	20	40.078(4)
Californium	Cf	98	[251]*
Carbon	C	6	12.0107(8)
Cerium	Ce	58	140.116(1)
Chlorine	Cl	17	35.453(2)
Chromium	Cr	24	51.9961(6)
Cobalt	Co	27	58.933195(5)
Copernicium	Cn	112	[285]*
Copper	Cu	29	63.546(3)
Curium	Cm	96	[247]*
Darmstadtium	Ds	110	[281]*
Dubnium	Db	105	[268]*
Dysprosium	Dy	66	162.500(1)
Einsteinium	Es	99	[252]*
Erbium	Er	68	167.259(3)
Europium	Eu	63	151.964(1)
Fermium	Fm	100	[257]*
Flerovium	Fl	114	[289]*
Fluorine	F	9	18.9984032(5)
Francium	Fr	87	[223]*
Gadolinium	Gd	64	157.25(3)
Gallium	Ga	31	69.723(1)
Germanium	Ge	32	72.64(1)

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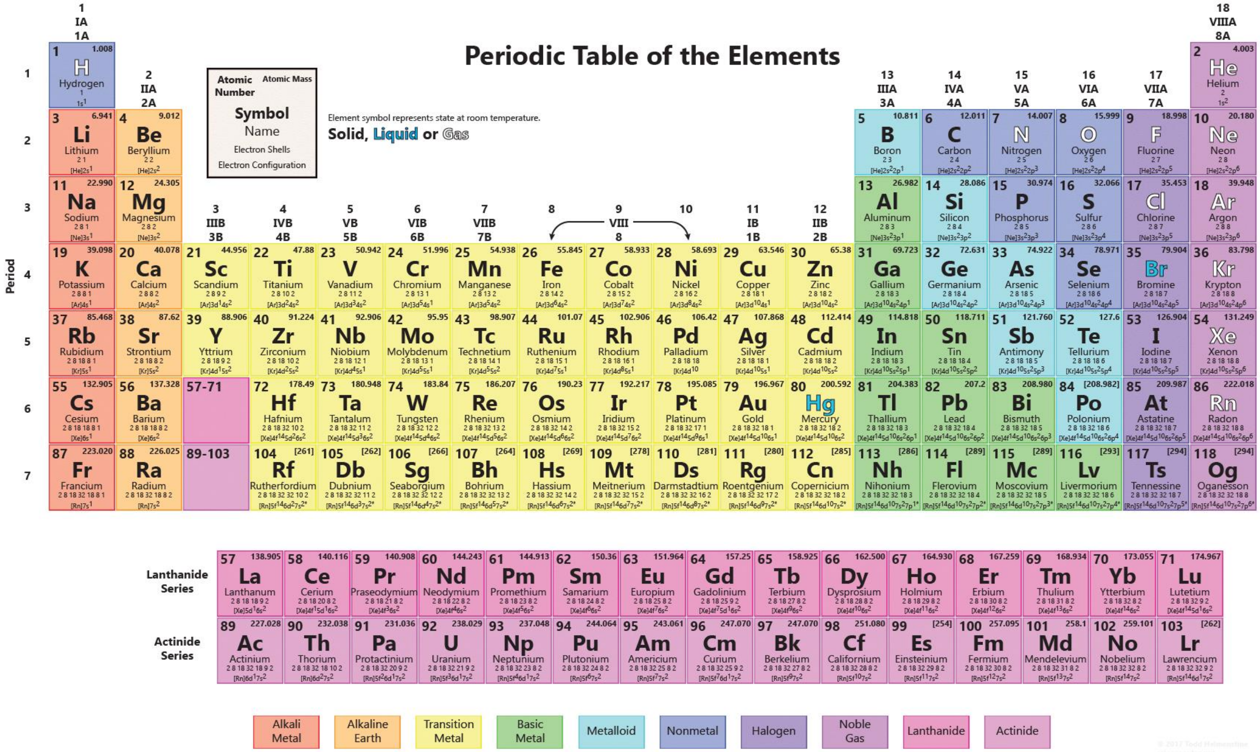
Name	Symbol	Atomic number	Atomic mass
Gold	Au	79	196.966569(4)
Hafnium	Hf	72	178.49(2)
Hassium	Hs	108	[269]*
Helium	He	2	4.002602(2)
Holmium	Ho	67	164.93032(2)
Hydrogen	H	1	1.00794(7)
Indium	In	49	114.818(3)
Iodine	I	53	126.90447(3)
Iridium	Ir	77	192.217(3)
Iron	Fe	26	55.845(2)
Krypton	Kr	36	83.798(2)
Lanthanum	La	57	138.90547(7)
Lawrencium	Lr	103	[262]*
Lead	Pb	82	207.2(1)
Lithium	Li	3	6.941(2)
Livermorium	Lv	116	[293]*
Lutetium	Lu	71	174.967(1)
Magnesium	Mg	12	24.3050(6)
Manganese	Mn	25	54.938045(5)
Meitnerium	Mt	109	[276]*
Mendelevium	Md	101	[258]*
Mercury	Hg	80	200.59(2)
Molybdenum	Mo	42	95.94(2)
Moscovium	Mc	115	[289]*
Neodymium	Nd	60	144.242(3)
Neon	Ne	10	20.1797(6)
Neptunium	Np	93	[237]*
Nickel	Ni	28	58.6934(2)
Nihonium	Nh	113	[286]*
Niobium	Nb	41	92.90638(2)
Nitrogen	N	7	14.0067(2)
Nobelium	No	102	[259]*
Oganesson	Og	118	[294]*
Osmium	Os	76	190.23(3)
Oxygen	O	8	15.9994(3)
Palladium	Pd	46	106.42(1)
Phosphorus	P	15	30.973762(2)
Platinum	Pt	78	195.084(9)
Plutonium	Pu	94	[244]*
Polonium	Po	84	[209]*
Potassium	K	19	39.0983(1)
Praseodymium	Pr	59	140.90765(2)
Promethium	Pm	61	[145]*
Protactinium	Pa	91	231.03588(2)*

Name	Symbol	Atomic number	Atomic mass
Radium	Ra	88	[226]*
Radon	Rn	86	[222]*
Rhenium	Re	75	186.207(1)
Rhodium	Rh	45	102.90550(2)
Roentgenium	Rg	111	[280]*
Rubidium	Rb	37	85.4678(3)
Ruthenium	Ru	44	101.07(2)
Rutherfordium	Rf	104	[267]*
Samarium	Sm	62	150.36(2)
Scandium	Sc	21	44.955912(6)
Seaborgium	Sg	106	[271]*
Selenium	Se	34	78.96(3)
Silicon	Si	14	28.0855(3)
Silver	Ag	47	107.8682(2)
Sodium	Na	11	22.98976928(2)
Strontium	Sr	38	87.62(1)
Sulfur	S	16	32.065(5)
Tantalum	Ta	73	180.94788(2)
Technetium	Tc	43	[98]*
Tellurium	Te	52	127.60(3)
Tennessine	Ts	117	[293]*
Terbium	Tb	65	158.92535(2)
Thallium	Tl	81	204.3833(2)
Thorium	Th	90	232.03806(2)*
Thulium	Tm	69	168.93421(2)
Tin	Sn	50	118.710(7)
Titanium	Ti	22	47.867(1)
Tungsten	W	74	183.84(1)
Uranium	U	92	238.02891(3)*
Vanadium	V	23	50.9415(1)
Xenon	Xe	54	131.293(6)
Ytterbium	Yb	70	173.04(3)
Yttrium	Y	39	88.90585(2)
Zinc	Zn	30	65.409(4)
Zirconium	Zr	40	91.224(2)

* Element has no stable isotope. A value enclosed in brackets, e.g. [209], indicates the mass number of the longest-lived isotope of the element. Three such elements (Th, Pa, and U), however, do have a characteristic terrestrial isotopic composition, and an atomic mass is given for them.

Uncertainty in the last digit in the atomic mass column is shown by the number in parentheses; e.g., 1.00794(7) indicates ±0.00007.

Periodic Table of the Elements



Atomic Number	Atomic Mass
Symbol	
Name	
Electron Shells	
Electron Configuration	

Element symbol represents state at room temperature.

Solid, Liquid or Gas

Period	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1	1 1.008 H Hydrogen 1 $1s^{1}$																	2 4.003 He Helium 2 $1s^{2}$
2	3 6.941 Li Lithium 2 1 [He]$2s^{1}$	4 9.012 Be Beryllium 2 2 [He]$2s^{2}$											5 10.811 B Boron 2 3 [He]$2s^{2}2p^{1}$	6 12.011 C Carbon 2 4 [He]$2s^{2}2p^{2}$	7 14.007 N Nitrogen 2 5 [He]$2s^{2}2p^{3}$	8 15.999 O Oxygen 2 6 [He]$2s^{2}2p^{4}$	9 18.998 F Fluorine 2 7 [He]$2s^{2}2p^{5}$	10 20.180 Ne Neon 2 8 [He]$2s^{2}2p^{6}$
3	11 22.990 Na Sodium 2 8 1 [Ne]$3s^{1}$	12 24.305 Mg Magnesium 2 8 2 [Ne]$3s^{2}$											13 26.982 Al Aluminum 2 8 3 [Ne]$3s^{2}3p^{1}$	14 28.086 Si Silicon 2 8 4 [Ne]$3s^{2}3p^{2}$	15 30.974 P Phosphorus 2 8 5 [Ne]$3s^{2}3p^{3}$	16 32.066 S Sulfur 2 8 6 [Ne]$3s^{2}3p^{4}$	17 35.453 Cl Chlorine 2 8 7 [Ne]$3s^{2}3p^{5}$	18 39.948 Ar Argon 2 8 8 [Ne]$3s^{2}3p^{6}$
4	19 39.098 K Potassium 2 8 8 1 [Ar]$4s^{1}$	20 40.078 Ca Calcium 2 8 8 2 [Ar]$4s^{2}$	21 44.956 Sc Scandium 2 8 9 2 [Ar]$3d^{1}4s^{2}$	22 47.88 Ti Titanium 2 8 10 2 [Ar]$3d^{2}4s^{2}$	23 50.942 V Vanadium 2 8 11 2 [Ar]$3d^{3}4s^{2}$	24 51.996 Cr Chromium 2 8 13 1 [Ar]$3d^{5}4s^{1}$	25 54.938 Mn Manganese 2 8 13 2 [Ar]$3d^{5}4s^{2}$	26 55.845 Fe Iron 2 8 14 2 [Ar]$3d^{6}4s^{2}$	27 58.933 Co Cobalt 2 8 15 2 [Ar]$3d^{7}4s^{2}$	28 58.693 Ni Nickel 2 8 16 2 [Ar]$3d^{8}4s^{2}$	29 63.546 Cu Copper 2 8 18 1 [Ar]$3d^{10}4s^{1}$	30 65.38 Zn Zinc 2 8 18 2 [Ar]$3d^{10}4s^{2}$	31 69.723 Ga Gallium 2 8 18 3 [Ar]$3d^{10}4s^{2}4p^{1}$	32 72.631 Ge Germanium 2 8 18 4 [Ar]$3d^{10}4s^{2}4p^{2}$	33 74.922 As Arsenic 2 8 18 5 [Ar]$3d^{10}4s^{2}4p^{3}$	34 78.971 Se Selenium 2 8 18 6 [Ar]$3d^{10}4s^{2}4p^{4}$	35 79.904 Br Bromine 2 8 18 7 [Ar]$3d^{10}4s^{2}4p^{5}$	36 83.798 Kr Krypton 2 8 18 8 [Ar]$3d^{10}4s^{2}4p^{6}$
5	37 85.468 Rb Rubidium 2 8 18 8 1 [Kr]$5s^{1}$	38 87.62 Sr Strontium 2 8 18 8 2 [Kr]$5s^{2}$	39 88.906 Y Yttrium 2 8 18 9 2 [Kr]$4d^{1}5s^{2}$	40 91.224 Zr Zirconium 2 8 18 10 2 [Kr]$4d^{2}5s^{2}$	41 92.906 Nb Niobium 2 8 18 12 1 [Kr]$4d^{4}5s^{1}$	42 95.95 Mo Molybdenum 2 8 18 13 1 [Kr]$4d^{5}5s^{1}$	43 98.907 Tc Technetium 2 8 18 14 1 [Kr]$4d^{5}5s^{2}$	44 101.07 Ru Ruthenium 2 8 18 15 1 [Kr]$4d^{7}5s^{1}$	45 102.906 Rh Rhodium 2 8 18 16 1 [Kr]$4d^{8}5s^{1}$	46 106.42 Pd Palladium 2 8 18 18 [Kr]$4d^{10}$	47 107.868 Ag Silver 2 8 18 18 1 [Kr]$4d^{10}5s^{1}$	48 112.414 Cd Cadmium 2 8 18 18 2 [Kr]$4d^{10}5s^{2}$	49 114.818 In Indium 2 8 18 18 3 [Kr]$4d^{10}5s^{2}5p^{1}$	50 118.711 Sn Tin 2 8 18 18 4 [Kr]$4d^{10}5s^{2}5p^{2}$	51 121.760 Sb Antimony 2 8 18 18 5 [Kr]$4d^{10}5s^{2}5p^{3}$	52 127.6 Te Tellurium 2 8 18 18 6 [Kr]$4d^{10}5s^{2}5p^{4}$	53 126.904 I Iodine 2 8 18 18 7 [Kr]$4d^{10}5s^{2}5p^{5}$	54 131.249 Xe Xenon 2 8 18 18 8 [Kr]$4d^{10}5s^{2}5p^{6}$
6	55 132.905 Cs Cesium 2 8 18 18 8 1 [Xe]$6s^{1}$	56 137.328 Ba Barium 2 8 18 18 8 2 [Xe]$6s^{2}$	57-71	72 178.49 Hf Hafnium 2 8 18 32 10 2 [Xe]$4f^{14}5d^{2}6s^{2}$	73 180.948 Ta Tantalum 2 8 18 32 11 2 [Xe]$4f^{14}5d^{3}6s^{2}$	74 183.84 W Tungsten 2 8 18 32 12 2 [Xe]$4f^{14}5d^{4}6s^{2}$	75 186.207 Re Rhenium 2 8 18 32 13 2 [Xe]$4f^{14}5d^{5}6s^{2}$	76 190.23 Os Osmium 2 8 18 32 14 2 [Xe]$4f^{14}5d^{6}6s^{2}$	77 192.217 Ir Iridium 2 8 18 32 15 2 [Xe]$4f^{14}5d^{7}6s^{2}$	78 195.085 Pt Platinum 2 8 18 32 17 1 [Xe]$4f^{14}5d^{9}6s^{1}$	79 196.967 Au Gold 2 8 18 32 18 1 [Xe]$4f^{14}5d^{10}6s^{1}$	80 200.592 Hg Mercury 2 8 18 32 18 2 [Xe]$4f^{14}5d^{10}6s^{2}$	81 204.383 Tl Thallium 2 8 18 32 18 3 [Xe]$4f^{14}5d^{10}6s^{2}6p^{1}$	82 207.2 Pb Lead 2 8 18 32 18 4 [Xe]$4f^{14}5d^{10}6s^{2}6p^{2}$	83 208.980 Bi Bismuth 2 8 18 32 18 5 [Xe]$4f^{14}5d^{10}6s^{2}6p^{3}$	84 [208.982] Po Polonium 2 8 18 32 18 6 [Xe]$4f^{14}5d^{10}6s^{2}6p^{4}$	85 209.987 At Astatine 2 8 18 32 18 7 [Xe]$4f^{14}5d^{10}6s^{2}6p^{5}$	86 222.018 Rn Radon 2 8 18 32 18 8 [Xe]$4f^{14}5d^{10}6s^{2}6p^{6}$
7	87 223.020 Fr Francium 2 8 18 32 18 8 1 [Rn]$7s^{1}$	88 226.025 Ra Radium 2 8 18 32 18 8 2 [Rn]$7s^{2}$	89-103	104 [261] Rf Rutherfordium 2 8 18 32 32 10 2 [Rn]$5f^{14}6d^{2}7s^{2*}$	105 [262] Db Dubnium 2 8 18 32 32 11 2 [Rn]$5f^{14}6d^{3}7s^{2*}$	106 [266] Sg Seaborgium 2 8 18 32 32 12 2 [Rn]$5f^{14}6d^{4}7s^{2*}$	107 [264] Bh Bohrium 2 8 18 32 32 13 2 [Rn]$5f^{14}6d^{5}7s^{2*}$	108 [269] Hs Hassium 2 8 18 32 32 14 2 [Rn]$5f^{14}6d^{6}7s^{2*}$	109 [278] Mt Meitnerium 2 8 18 32 32 15 2 [Rn]$5f^{14}6d^{7}7s^{2*}$	110 [281] Ds Darmstadtium 2 8 18 32 32 16 2 [Rn]$5f^{14}6d^{8}7s^{2*}$	111 [280] Rg Roentgenium 2 8 18 32 32 17 2 [Rn]$5f^{14}6d^{9}7s^{2*}$	112 [285] Cn Copernicium 2 8 18 32 32 18 2 [Rn]$5f^{14}6d^{10}7s^{2*}$	113 [286] Nh Nihonium 2 8 18 32 32 18 3 [Rn]$5f^{14}6d^{10}7s^{2}7p^{1*}$	114 [289] Fl Flerovium 2 8 18 32 32 18 4 [Rn]$5f^{14}6d^{10}7s^{2}7p^{2*}$	115 [289] Mc Moscovium 2 8 18 32 32 18 5 [Rn]$5f^{14}6d^{10}7s^{2}7p^{3*}$	116 [293] Lv Livermorium 2 8 18 32 32 18 6 [Rn]$5f^{14}6d^{10}7s^{2}7p^{4*}$	117 [294] Ts Tennessine 2 8 18 32 32 18 7 [Rn]$5f^{14}6d^{10}7s^{2}7p^{5*}$	118 [294] Og Oganesson 2 8 18 32 32 18 8 [Rn]$5f^{14}6d^{10}7s^{2}7p^{6*}$

Lanthanide Series	57 138.905 La Lanthanum 2 8 18 18 9 2 [Xe]$5d^{1}6s^{2}$	58 140.116 Ce Cerium 2 8 18 20 8 2 [Xe]$4f^{1}5d^{1}6s^{2}$	59 140.908 Pr Praseodymium 2 8 18 21 8 2 [Xe]$4f^{3}6s^{2}$	60 144.243 Nd Neodymium 2 8 18 22 8 2 [Xe]$4f^{4}6s^{2}$	61 144.913 Pm Promethium 2 8 18 23 8 2 [Xe]$4f^{5}6s^{2}$	62 150.36 Sm Samarium 2 8 18 24 8 2 [Xe]$4f^{6}6s^{2}$	63 151.964 Eu Europium 2 8 18 25 8 2 [Xe]$4f^{7}6s^{2}$	64 157.25 Gd Gadolinium 2 8 18 25 9 2 [Xe]$4f^{7}5d^{1}6s^{2}$	65 158.925 Tb Terbium 2 8 18 27 8 2 [Xe]$4f^{9}6s^{2}$	66 162.500 Dy Dysprosium 2 8 18 28 8 2 [Xe]$4f^{10}6s^{2}$	67 164.930 Ho Holmium 2 8 18 29 8 2 [Xe]$4f^{11}6s^{2}$	68 167.259 Er Erbium 2 8 18 30 8 2 [Xe]$4f^{12}6s^{2}$	69 168.934 Tm Thulium 2 8 18 31 8 2 [Xe]$4f^{13}6s^{2}$	70 173.055 Yb Ytterbium 2 8 18 32 8 2 [Xe]$4f^{14}6s^{2}$	71 174.967 Lu Lutetium 2 8 18 32 9 2 [Xe]$4f^{14}5d^{1}6s^{2}$
Actinide Series	89 227.028 Ac Actinium 2 8 18 32 18 9 2 [Rn]$6d^{1}7s^{2}$	90 232.038 Th Thorium 2 8 18 32 18 10 2 [Rn]$6d^{2}7s^{2}$	91 231.036 Pa Protactinium 2 8 18 32 20 9 2 [Rn]$5f^{2}6d^{1}7s^{2}$	92 238.029 U Uranium 2 8 18 32 21 9 2 [Rn]$5f^{3}6d^{1}7s^{2}$	93 237.048 Np Neptunium 2 8 18 32 23 8 2 [Rn]$5f^{4}6d^{1}7s^{2}$	94 244.064 Pu Plutonium 2 8 18 32 24 8 2 [Rn]$5f^{6}7s^{2}$	95 243.061 Am Americium 2 8 18 32 25 8 2 [Rn]$5f^{7}7s^{2}$	96 247.070 Cm Curium 2 8 18 32 25 9 2 [Rn]$5f^{7}6d^{1}7s^{2}$	97 247.070 Bk Berkelium 2 8 18 32 27 8 2 [Rn]$5f^{9}7s^{2}$	98 251.080 Cf Californium 2 8 18 32 28 8 2 [Rn]$5f^{10}7s^{2}$	99 [254] Es Einsteinium 2 8 18 32 29 8 2 [Rn]$5f^{11}7s^{2}$	100 257.095 Fm Fermium 2 8 18 32 30 8 2 [Rn]$5f^{12}7s^{2}$	101 258.1 Md Mendelevium 2 8 18 32 31 8 2 [Rn]$5f^{13}7s^{2}$	102 259.101 No Nobelium 2 8 18 32 32 8 2 [Rn]$5f^{14}7s^{2}$	103 [262] Lr Lawrencium 2 8 18 32 32 9 2 [Rn]$5f^{14}6d^{1}7s^{2}$

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Metalloid	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide

B. Standard thermodynamic quantities at 25^{o}C

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
Aluminium:			
Al(s)	0.0	0.0	28.3
Al(g)	330.0	289.4	164.6
$AlCl_3$(s)	−704.2	−628.8	109.3
Al_2O_3(s)	−1675.7	−1582.3	50.9
Barium:			
Ba(s)	0.0	0.0	62.5
Ba(g)	180.0	146.0	170.2
BaO(s)	−548.0	−520.3	72.1
$BaCO_3$(s)	−1213.0	−1134.4	112.1
$BaSO_4$(s)	−1473.2	−1362.2	132.2
Beryllium:			
Be(s)	0.0	0.0	9.5
Be(g)	324.0	286.6	136.3
$Be(OH)_2$(s)	−902.5	−815.0	45.5
BeO(s)	−609.4	−580.1	13.8
Bismuth:			
Bi(s)	0.0	0.0	56.7
Bi(g)	207.1	168.2	187.0
Bromine:			
Br(g)	111.9	82.4	175.0
Br_2(l)	0.0	0.0	152.2
Br^-(aq)	−121.6	−104.0	82.4
Br_2(g)	30.9	3.1	245.5
HBr(g)	−36.3	−53.4	198.7
HBr(aq)	−121.6	−104.0	82.4
Cadmium:			
Cd(s)	0.0	0.0	51.8
Cd(g)	111.8	—	167.7
$CdCl_2$(s)	−391.5	−343.9	115.3
CdS(s)	−161.9	−156.5	64.9
Calcium:			
Ca(s)	0.0	0.0	41.6
Ca(g)	177.8	144.0	154.9
$CaCl_2$(s)	−795.4	−748.8	108.4
CaF_2(s)	−1228.0	−1175.6	68.5
$Ca(OH)_2$(s)	−985.2	−897.5	83.4
CaO(s)	−634.9	−603.3	38.1
$CaSO_4$(s)	−1434.5	−1322.0	106.5
$CaCO_3$(s, calcite)	−1207.6	−1129.1	91.7
$CaCO_3$(s, aragonite)	−1207.8	−1128.2	88.0
Carbon:			
C(s, graphite)	0.0	0.0	5.7
C(s, diamond)	1.9	2.9	2.4
C(s, fullerene—C_{60})	2327.0	2302.0	426.0
C(s, fullerene—C_{70})	2555.0	2537.0	464.0

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Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
C(g)	716.7	671.3	158.1
C(g, fullerene—C_{60})	2502.0	2442.0	544.0
C(g, fullerene—C_{70})	2755.0	2692.0	614.0
CBr_4(s)	29.4	47.7	212.5
CBr_4(g)	83.9	67.0	358.1
CCl_2F_2(g)	−477.4	−439.4	300.8
CCl_2O(g)	−219.1	−204.9	283.5
CCl_4(l)	−128.2	−62.6	216.2
CCl_4(g)	−95.7	−53.6	309.9
CF_4(g)	−933.6	−888.3	261.6
$CHCl_3$(l)	−134.1	−73.7	201.7
$CHCl_3$(g)	−102.7	6.0	295.7
CH_2Cl_2(l)	−124.2	—	177.8
CH_2Cl_2(g)	−95.4	−68.9	270.2
CH_3Cl(g)	−81.9	−58.5	234.6
CH_4(g)	−74.6	−50.5	186.3
CH_3COOH(l)	−484.3	−389.9	159.8
CH_3OH(l)	−239.2	−166.6	126.8
CH_3OH(g)	−201.0	−162.3	239.9
CH_3NH_2(l)	−47.3	35.7	150.2
CH_3NH_2(g)	−22.5	32.7	242.9
CH_3CN(l)	40.6	86.5	149.6
CH_3CN(g)	74.0	91.9	243.4
CO(g)	−110.5	−137.2	197.7
CO_2(g)	−393.5	−394.4	213.8
CS_2(l)	89.0	64.6	151.3
CS_2(g)	116.7	67.1	237.8
C_2H_2(g)	227.4	209.9	200.9
C_2H_4(g)	52.4	68.4	219.3
C_2H_6(g)	−84.0	−32.0	229.2
C_3H_8(g)	−103.8	−23.4	270.3
$C_3H_6O_3$(s) (lactic acid)	−694.1	−522.9	142.3
C_6H_6(l)	49.1	124.5	173.4
C_6H_6(g)	82.9	129.7	269.2
$C_6H_{12}O_6$(s) (glucose)	−1273.3	−910.4	212.1
C_2H_5OH(l)	−277.6	−174.8	160.7
C_2H_5OH(g)	−234.8	−167.9	281.6
$(CH_3)_2O$(l)	−203.3	—	—
$(CH_3)_2O$(g)	−184.1	−112.6	266.4
$CH_3CO_2^-$(aq)	−486.0	−369.3	86.6
n-$C_{12}H_{26}$(l) (dodecane)	−350.9	28.1	490.6
Caesium:			
Cs(s)	0.0	0.0	85.2
Cs(g)	76.5	49.6	175.6
CsCl(s)	−443.0	−414.5	101.2
Chlorine:			
Cl(g)	121.3	105.3	165.2
Cl_2(g)	0.0	0.0	223.1

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	S° (J/mol K)
Cl^-(aq)	−167.2	−131.2	56.5
HCl(g)	−92.3	−95.3	186.9
HCl(aq)	−167.2	−131.2	56.5
ClF_3(g)	−163.2	−123.0	281.6
Chromium:			
Cr(s)	0.0	0.0	23.8
Cr(g)	396.6	351.8	174.5
$CrCl_3$(s)	−556.5	−486.1	123.0
CrO_3(g)	−292.9	—	266.2
Cr_2O_3(s)	−1139.7	−1058.1	81.2
Cobalt:			
Co(s)	0.0	0.0	30.0
Co(g)	424.7	380.3	179.5
$CoCl_2$(s)	−312.5	−269.8	109.2
Copper:			
Cu(s)	0.0	0.0	33.2
Cu(g)	337.4	297.7	166.4
CuCl(s)	−137.2	−119.9	86.2
$CuCl_2$(s)	−220.1	−175.7	108.1
CuO(s)	−157.3	−129.7	42.6
Cu_2O(s)	−168.6	−146.0	93.1
CuS(s)	−53.1	−53.6	66.5
Cu_2S(s)	−79.5	−86.2	120.9
CuCN(s)	96.2	111.3	84.5
Fluorine:			
F(g)	79.4	62.3	158.8
F^-(aq)	−332.6	−278.8	−13.8
F_2(g)	0.0	0.0	202.8
HF(g)	−273.3	−275.4	173.8
HF(aq)	−332.6	−278.8	−13.8
Hydrogen:			
H(g)	218.0	203.3	114.7
H_2(g)	0.0	0.0	130.7
H^+(aq)	0.0	0.0	0.0
Iodine:			
I(g)	106.8	70.2	180.8
I^-(aq)	−55.2	−51.6	111.3
I_2(s)	0.0	0.0	116.1
I_2(g)	62.4	19.3	260.7
HI(g)	26.5	1.7	206.6
HI(aq)	−55.2	−51.6	111.3
Iron:			
Fe(s)	0.0	0.0	27.3
Fe(g)	416.3	370.7	180.5
Fe^{2+}(aq)	−89.1	−78.9	−137.7
Fe^{3+}(aq)	−48.5	−4.7	−315.9
$FeCl_2$(s)	−341.8	−302.3	118.0
$FeCl_3$(s)	−399.5	−334.0	142.3

Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
FeO(s)	−272.0	−251.4	60.7
Fe_2O_3(s)	−824.2	−742.2	87.4
Fe_3O_4(s)	−1118.4	−1015.4	146.4
FeS_2(s)	−178.2	−166.9	52.9
$FeCO_3$(s)	−740.6	−666.7	92.9
Lead:			
Pb(s)	0.0	0.0	64.8
Pb(g)	195.2	162.2	175.4
PbO(s, red or litharge)	−219.0	−188.9	66.5
PbO(s, yellow or massicot)	−217.3	−187.9	68.7
PbO_2(s)	−277.4	−217.3	68.6
$PbCl_2$(s)	−359.4	−314.1	136.0
PbS(s)	−100.4	−98.7	91.2
$PbSO_4$(s)	−920.0	−813.0	148.5
$PbCO_3$(s)	−699.1	−625.5	131.0
$Pb(NO_3)_2$(s)	−451.9	—	—
$Pb(NO_3)_2$(aq)	−416.3	−246.9	303.3
Lithium:			
Li(s)	0.0	0.0	29.1
Li(g)	159.3	126.6	138.8
Li^+(aq)	−278.5	−293.3	13.4
$LiCl$(s)	−408.6	−384.4	59.3
Li_2O(s)	−597.9	−561.2	37.6
Magnesium:			
Mg(s)	0.0	0.0	32.7
Mg(g)	147.1	112.5	148.6
$MgCl_2$(s)	−641.3	−591.8	89.6
MgO(s)	−601.6	−569.3	27.0
$Mg(OH)_2$(s)	−924.5	−833.5	63.2
$MgSO_4$(s)	−1284.9	−1170.6	91.6
MgS(s)	−346.0	−341.8	50.3
Manganese:			
Mn(s)	0.0	0.0	32.0
Mn(g)	280.7	238.5	173.7
$MnCl_2$(s)	−481.3	−440.5	118.2
MnO(s)	−385.2	−362.9	59.7
MnO_2(s)	−520.0	−465.1	53.1
$KMnO_4$(s)	−837.2	−737.6	171.7
MnO_4^-(aq)	−541.4	−447.2	191.2
Mercury:			
Hg(l)	0.0	0.0	75.9
Hg(g)	61.4	31.8	175.0
$HgCl_2$(s)	−224.3	−178.6	146.0
Hg_2Cl_2(s)	−265.4	−210.7	191.6
HgO(s)	−90.8	−58.5	70.3
HgS(s, red)	−58.2	−50.6	82.4
Hg_2(g)	108.8	68.2	288.1
Molybdenum:			

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	S° (J/mol K)
Mo(s)	0.0	0.0	28.7
Mo(g)	658.1	612.5	182.0
MoO_2(s)	−588.9	−533.0	46.3
MoO_3(s)	−745.1	−668.0	77.7
Nickel:			
Ni(s)	0.0	0.0	29.9
Ni(g)	429.7	384.5	182.2
$NiCl_2$(s)	−305.3	−259.0	97.7
$Ni(OH)_2$(s)	−529.7	−447.2	88.0
Nitrogen:			
N(g)	472.7	455.5	153.3
N_2(g)	0.0	0.0	191.6
NH_3(g)	−45.9	−16.4	192.8
NH_4^+(aq)	−132.5	−79.3	113.4
N_2H_4(l)	50.6	149.3	121.2
N_2H_4(g)	95.4	159.4	238.5
NH_4Cl(s)	−314.4	−202.9	94.6
NH_4OH(l)	−361.2	−254.0	165.6
NH_4NO_3(s)	−365.6	−183.9	151.1
$(NH_4)_2SO_4$(s)	−1180.9	−901.7	220.1
NO(g)	91.3	87.6	210.8
NO_2(g)	33.2	51.3	240.1
N_2O(g)	81.6	103.7	220.0
N_2O_4(l)	−19.5	97.5	209.2
N_2O_4(g)	11.1	99.8	304.4
HNO_2(g)	−79.5	−46.0	254.1
HNO_3(l)	−174.1	−80.7	155.6
HNO_3(g)	−133.9	−73.5	266.9
HNO_3(aq)	−207.4	−111.3	146.4
NF_3(g)	−132.1	−90.6	260.8
HCN(l)	108.9	125.0	112.8
HCN(g)	135.1	124.7	201.8
Osmium:			
Os(s)	0.0	0.0	32.6
Os(g)	791.0	745.0	192.6
OsO_4(s)	−394.1	−304.9	143.9
OsO_4(g)	−337.2	−292.8	293.8
Oxygen:			
O(g)	249.2	231.7	161.1
O_2(g)	0.0	0.0	205.2
O_3(g)	142.7	163.2	238.9
OH^-(aq)	−230.0	−157.2	−10.8
H_2O(l)	−285.8	−237.1	70.0
H_2O(g)	−241.8	−228.6	188.8
H_2O_2(l)	−187.8	−120.4	109.6
H_2O_2(g)	−136.3	−105.6	232.7
Phosphorus:			
P(s, white)	0.0	0.0	41.1

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Substance	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/mol K)
P(s, red) −17.6	−17.6	−12.5	22.8
P(s, black)	−39.3	—	—
P(g, white)	316.5	280.1	163.2
P_2(g)	144.0	103.5	218.1
P_4(g)	58.9	24.4	280.0
PCl_3(l)	−319.7	−272.3	217.1
PCl_3(g)	−287.0	−267.8	311.8
$POCl_3$(l)	−597.1	−520.8	222.5
$POCl_3$(g)	−558.5	−512.9	325.5
PCl_5(g)	−374.9	−305.0	364.6
PH_3(g)	5.4	13.5	210.2
H_3PO_4(s)	−1284.4	−1124.3	110.5
H_3PO_4(l)	−1271.7	−1123.6	150.8
Potassium:			
K(s)	0.0	0.0	64.7
K(g)	89.0	60.5	160.3
KBr(s)	−393.8	−380.7	95.9
KCl(s)	−436.5	−408.5	82.6
$KClO_3$(s)	−397.7	−296.3	143.1
K_2O(s)	−361.5	−322.1	94.1
K_2O_2(s)	−494.1	−425.1	102.1
KNO_2(s)	−369.8	−306.6	152.1
KNO_3(s)	−494.6	−394.9	133.1
KSCN(s)	−200.2	−178.3	124.3
K_2CO_3(s)	−1151.0	−1063.5	155.5
K_2SO_4(s)	−1437.8	−1321.4	175.6
Rubidium:			
Rb(s)	0.0	0.0	76.8
Rb(g)	80.9	53.1	170.1
RbCl(s)	−435.4	−407.8	95.9
Selenium:			
Se(s, grey)	0.0	0.0	42.4
Se(g, grey)	227.1	187.0	176.7
H_2Se(g)	29.7	15.9	219.0
Silicon:			
Si(s)	0.0	0.0	18.8
Si(g)	450.0	405.5	168.0
$SiCl_4$(l)	−687.0	−619.8	239.7
$SiCl_4$(g)	−657.0	−617.0	330.7
SiH_4(g)	34.3	56.9	204.6
SiC(s, cubic)	−65.3	−62.8	16.6
SiC(s, hexagonal)	−62.8	−60.2	16.5
Silver:			
Ag(s)	0.0	0.0	42.6
Ag(g)	284.9	246.0	173.0
Ag^+(aq)	105.6	77.1	72.7
AgBr(s)	−100.4	−96.9	107.1
AgCl(s)	−127.0	−109.8	96.3

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Substance	ΔH$_f$° (kJ/mol)	ΔG$_f$° (kJ/mol)	S° (J/mol K)
$AgNO_3$(s)	−124.4	−33.4	140.9
Ag_2O(s)	−31.1	−11.2	121.3
Ag_2S(s)	−32.6	−40.7	144.0
Sodium:			
Na(s)	0.0	0.0	51.3
Na(g)	107.5	77.0	153.7
Na^+(aq)	−240.1	−261.9	59.0
NaF(s)	−576.6	−546.3	51.1
NaF(aq)	−572.8	−540.7	45.2
NaCl(s)	−411.2	−384.1	72.1
NaCl(aq)	−407.3	−393.1	115.5
NaBr(s)	−361.1	−349.0	86.8
NaBr(g)	−143.1	−177.1	241.2
NaBr(aq)	−361.7	−365.8	141.4
NaO_2(s)	−260.2	−218.4	115.9
Na_2O(s)	−414.2	−375.5	75.1
Na_2O_2(s)	−510.9	−447.7	95.0
NaCN(s)	−87.5	−76.4	115.6
$NaNO_3$(aq)	−447.5	−373.2	205.4
$NaNO_3$(s)	−467.9	−367.0	116.5
NaN_3(s)	21.7	93.8	96.9
Na_2CO_3(s)	−1130.7	−1044.4	135.0
Na_2SO_4(s)	−1387.1	−1270.2	149.6
Sulfur:			
S(s, rhombic)	0.0	0.0	32.1
S(g, rhombic)	277.2	236.7	167.8
SO_2(g)	−296.8	−300.1	248.2
SO_3(g)	−395.7	−371.1	256.8
SO_4^{2-}(aq)	−909.3	−744.5	20.1
$SOCl_2$(g)	−212.5	−198.3	309.8
H_2S(g)	−20.6	−33.4	205.8
H_2SO_4(aq)	−909.3	−744.5	20.1
Tin:			
Sn(s, white)	0.0	0.0	51.2
Sn(s, grey)	−2.1	0.1	44.1
Sn(g, white)	301.2	266.2	168.5
$SnCl_4$(l)	−511.3	−440.1	258.6
$SnCl_4$(g)	−471.5	−432.2	365.8
SnO_2(s)	−557.6	−515.8	49.0
Titanium:			
Ti(s)	0.0	0.0	30.7
Ti(g)	473.0	428.4	180.3
$TiCl_2$(s)	−513.8	−464.4	87.4
$TiCl_3$(s)	−720.9	−653.5	139.7
$TiCl_4$(l)	−804.2	−737.2	252.3
$TiCl_4$(g)	−763.2	−726.3	353.2
TiO_2(s)	−944.0	−888.8	50.6
Uranium:			

Substance	$\Delta H_f°$ (kJ/mol)	$\Delta G_f°$ (kJ/mol)	S° (J/mol K)
U(s)	0.0	0.0	50.2
U(g)	533.0	488.4	199.8
UO_2(s)	−1085.0	−1031.8	77.0
UO_2(g)	−465.7	−471.5	274.6
UF_4(s)	−1914.2	−1823.3	151.7
UF_4(g)	−1598.7	−1572.7	368.0
UF_6(s)	−2197.0	−2068.5	227.6
UF_6(g)	−2147.4	−2063.7	377.9
Vanadium:			
V(s)	0.0	0.0	28.9
V(g)	514.2	754.4	182.3
VCl_3(s)	−580.7	−511.2	131.0
VCl_4(l)	−569.4	−503.7	255.0
VCl_4(g)	−525.5	−492.0	362.4
V_2O_5(s)	−1550.6	−1419.5	131.0
Zinc:			
Zn(s)	0.0	0.0	41.6
Zn(g)	130.4	94.8	161.0
$ZnCl_2$(s)	−415.1	−369.4	111.5
$Zn(NO_3)_2$(s)	−483.7	—	—
ZnS(s, sphalerite)	−206.0	−201.3	57.7
$ZnSO_4$(s)	−982.8	−871.5	110.5
Zirconium:			
Zr(s)	0.0	0.0	39.0
Zr(g)	608.8	566.5	181.4
$ZrCl_2$(s)	−502.0	−386	110
$ZrCl_4$(s)	−980.5	−889.9	181.6

C. Dissociation constants and pK_a values for acids at 25°C

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Acetic acid	CH_3CO_2H	$1.75\cdot10^{-5}$	4.756						
Arsenic acid	H_3AsO_4	$5.5\cdot10^{-3}$	2.26	$1.7\cdot10^{-7}$	6.76	$5.1\cdot10^{-12}$	11.29		
Benzoic acid	$C_6H_5CO_2H$	$6.25\cdot10^{-5}$	4.204						
Boric acid	H_3BO_3	$5.4\cdot10^{-10}$*	9.27*	>$1\cdot10^{-14}$*	>14*				
Bromoacetic acid	CH_2BrCO_2H	$1.3\cdot10^{-3}$	2.90						
Carbonic acid	H_2CO_3	$4.5\cdot10^{-7}$	6.35	$4.7\cdot10^{-11}$	10.33				
Chloroacetic acid	CH_2ClCO_2H	$1.3\cdot10^{-3}$	2.87						
Chlorous acid	$HClO_2$	$1.1\cdot10^{-2}$	1.94						
Chromic acid	H_2CrO_4	$1.8\cdot10^{-1}$	0.74	$3.2\cdot10^{-7}$	6.49				
Citric acid	$C_6H_8O_7$	$7.4\cdot10^{-4}$	3.13	$1.7\cdot10^{-5}$	4.76	$4.0\cdot10^{-7}$	6.40		
Cyanic acid	HCNO	$3.5\cdot10^{-4}$	3.46						
Dichloroacetic acid	$CHCl_2CO_2H$	$4.5\cdot10^{-2}$	1.35						
Fluoroacetic acid	CH_2FCO_2H	$2.6\cdot10^{-3}$	2.59						

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Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Formic acid	CH_2O_2	$1.8\cdot10^{-4}$	3.75						
Hydrazoic acid	HN_3	$2.5\cdot10^{-5}$	4.6						
Hydrocyanic acid	HCN	$6.2\cdot10^{-10}$	9.21						
Hydrofluoric acid	HF	$6.3\cdot10^{-4}$	3.20						
Hydrogen selenide	H_2Se	$1.3\cdot10^{-4}$	3.89	$1.0\cdot10^{-11}$	11.0				
Hydrogen sulfide	H_2S	$8.9\cdot10^{-8}$	7.05	$1\cdot10^{-19}$	19				
Hydrogen telluride	H_2Te	$2.5\cdot10^{-3‡}$	2.6‡	$1\cdot10^{-11}$	11				
Hypobromous acid	HBrO	$2.8\cdot10^{-9}$	8.55						
Hypochlorous acid	HClO	$4.0\cdot10^{-8}$	7.40						
Hypoiodous acid	HIO	$3.2\cdot10^{-11}$	10.5						
Iodic acid	HIO_3	$1.7\cdot10^{-1}$	0.78						
Iodoacetic acid	CH_2ICO_2H	$6.6\cdot10^{-4}$	3.18						
Nitrous acid	HNO_2	$5.6\cdot10^{-4}$	3.25						
Oxalic acid	$C_2H_2O_4$	$5.6\cdot10^{-2}$	1.25	$1.5\cdot10^{-4}$	3.81				
Periodic acid	HIO_4	$2.3\cdot10^{-2}$	1.64						
Phenol	C_6H_5OH	$1.0\cdot10^{-10}$	9.99						
Phosphoric acid	H_3PO_4	$6.9\cdot10^{-3}$	2.16	$6.2\cdot10^{-8}$	7.21	$4.8\cdot10^{-13}$	12.32		
Phosphorous acid	H_3PO_3	$5.0\cdot10^{-2}$*	1.3*	$2.0\cdot10^{-7}$*	6.70*				
Pyrophosphoric acid	$H_4P_2O_7$	$1.2\cdot10^{-1}$	0.91	$7.9\cdot10^{-3}$	2.10	$2.0\cdot10^{-7}$	6.70	$4.8\cdot10^{-10}$	9.32
Resorcinol	$C_6H_4(OH)_2$	$4.8\cdot10^{-10}$	9.32	$7.9\cdot10^{-12}$	11.1				
Selenic acid	H_2SeO_4	Strong	Strong	$2.0\cdot10^{-2}$	1.7				
Selenious acid	H_2SeO_3	$2.4\cdot10^{-3}$	2.62	$4.8\cdot10^{-9}$	8.32				
Sulfuric acid	H_2SO_4	Strong	Strong	$1.0\cdot10^{-2}$	1.99				
Sulfurous acid	H_2SO_3	$1.4\cdot10^{-2}$	1.85	$6.3\cdot10^{-8}$	7.2				
meso-Tartaric acid	$C_4H_6O_6$	$6.8\cdot10^{-4}$	3.17	$1.2\cdot10^{-5}$	4.91				
Telluric acid	H_2TeO_4	$2.1\cdot10^{-8‡}$	7.68‡	$1.0\cdot10^{-11‡}$	11.0‡				
Tellurous acid	H_2TeO_3	$5.4\cdot10^{-7}$	6.27	$3.7\cdot10^{-9}$	8.43				
Trichloroacetic acid	CCl_3CO_2H	$2.2\cdot10^{-1}$	0.66						
Trifluoroacetic acid	CF_3CO_2H	$3.0\cdot10^{-1}$	0.52						

* Measured at 20°C, not 25°C.
‡ Measured at 18°C, not 25°C.

D. Dissociation constants and pK_b values for bases at 25°C

Name	Formula	K_b	pK_b
Ammonia	NH_3	1.8×10^{-5}	4.75
Aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13
n-Butylamine	$C_4H_9NH_2$	4.0×10^{-4}	3.40
sec-Butylamine	$(CH_3)_2CHCH_2NH_2$	3.6×10^{-4}	3.44
tert-Butylamine	$(CH_3)_3CNH_2$	4.8×10^{-4}	3.32
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27

Name	Formula	K_b	pK_b
Ethylamine	$C_2H_5NH_2$	4.5×10^{-4}	3.35
Hydrazine	N_2H_4	1.3×10^{-6}	5.9
Hydroxylamine	NH_2OH	8.7×10^{-9}	8.06
Methylamine	CH_3NH_2	4.6×10^{-4}	3.34
Propylamine	$C_3H_7NH_2$	3.5×10^{-4}	3.46
Pyridine	C_5H_5N	1.7×10^{-9}	8.77
Trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20

E. Solubility-product constants (K_{sp}) for compounds at 25°C

Compound Name	Compound Formula	K_{sp}
Aluminium phosphate	$AlPO_4$	9.84×10^{-21}
Barium bromate	$Ba(BrO_3)_2$	2.43×10^{-4}
Barium carbonate	$BaCO_3$	2.58×10^{-9}
Barium chromate	$BaCrO_4$	1.17×10^{-10}
Barium fluoride	BaF_2	1.84×10^{-7}
Barium iodate	$Ba(IO_3)_2$	4.01×10^{-9}
Barium nitrate	$Ba(NO_3)_2$	4.64×10^{-3}
Barium sulfate	$BaSO_4$	1.08×10^{-10}
Barium sulfite	$BaSO_3$	5.0×10^{-10}
Beryllium hydroxide	$Be(OH)_2$	6.92×10^{-22}
Bismuth arsenate	$BiAsO_4$	4.43×10^{-10}
Bismuth iodide	BiI_3	7.71×10^{-19}
Cadmium carbonate	$CdCO_3$	1.0×10^{-12}
Cadmium fluoride	CdF_2	6.44×10^{-3}
Cadmium hydroxide	$Cd(OH)_2$	7.2×10^{-15}
Cadmium iodate	$Cd(IO_3)_2$	2.5×10^{-8}
Cadmium phosphate	$Cd_3(PO_4)_2$	2.53×10^{-33}
Cadmium sulfide	CdS	8.0×10^{-27}
Calcium carbonate	$CaCO_3$	3.36×10^{-9}
Calcium fluoride	CaF_2	3.45×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}
Calcium iodate	$Ca(IO_3)_2$	6.47×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.07×10^{-33}
Calcium sulfate	$CaSO_4$	4.93×10^{-5}
Caesium perchlorate	$CsClO_4$	3.95×10^{-3}
Caesium periodate	$CsIO_4$	5.16×10^{-6}
Cobalt(II) arsenate	$Co_3(AsO_4)_2$	6.80×10^{-29}
Cobalt(II) hydroxide	$Co(OH)_2$	5.92×10^{-15}
Cobalt(II) phosphate	$Co_3(PO_4)_2$	2.05×10^{-35}
Copper(I) bromide	$CuBr$	6.27×10^{-9}
Copper(I) chloride	$CuCl$	1.72×10^{-7}
Copper(I) cyanide	$CuCN$	3.47×10^{-20}

Compound Name	Compound Formula	K_{sp}
Copper(I) iodide	CuI	1.27×10^{-12}
Copper(I) thiocyanate	CuSCN	1.77×10^{-13}
Copper(II) arsenate	$Cu_3(AsO_4)_2$	7.95×10^{-36}
Copper(II) oxalate	CuC_2O_4	4.43×10^{-10}
Copper(II) phosphate	$Cu_3(PO_4)_2$	1.40×10^{-37}
Copper(II) sulfide	CuS	6.3×10^{-36}
Europium(III) hydroxide	$Eu(OH)_3$	9.38×10^{-27}
Gallium(III) hydroxide	$Ga(OH)_3$	7.28×10^{-36}
Iron(II) carbonate	$FeCO_3$	3.13×10^{-11}
Iron(II) fluoride	FeF_2	2.36×10^{-6}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}
Iron(III) hydroxide	$Fe(OH)_3$	2.79×10^{-39}
Iron(III) sulfide	FeS	6.3×10^{-18}
Lanthanum iodate	$La(IO_3)_3$	7.50×10^{-12}
Lead(II) bromide	$PbBr_2$	6.60×10^{-6}
Lead(II) carbonate	$PbCO_3$	7.40×10^{-14}
Lead(II) chloride	$PbCl_2$	1.70×10^{-5}
Lead(II) fluoride	PbF_2	3.3×10^{-8}
Lead(II) hydroxide	$Pb(OH)_2$	1.43×10^{-20}
Lead(II) iodate	$Pb(IO_3)_2$	3.69×10^{-13}
Lead(II) iodide	PbI_2	9.8×10^{-9}
Lead(II)selenite	$PbSeO_4$	1.37×10^{-7}
Lead(II) sulfate	$PbSO_4$	2.53×10^{-8}
Lead(II) sulfide	PbS	8.0×10^{-28}
Lithium carbonate	Li_2CO_3	8.15×10^{-4}
Lithium fluoride	LiF	1.84×10^{-3}
Lithium phosphate	Li_3PO_4	2.37×10^{-11}
Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Magnesium fluoride	MgF_2	5.16×10^{-11}
Magnesium hydroxide	$Mg(OH)_2$	5.61×10^{-12}
Magnesium phosphate	$Mg_3(PO_4)_2$	1.04×10^{-24}
Manganese(II) carbonate	$MnCO_3$	2.24×10^{-11}
Manganese(II) iodate	$Mn(IO_3)_2$	4.37×10^{-7}
Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}
Mercury(I) fluoride	Hg_2F_2	3.10×10^{-6}
Mercury(I) iodide	Hg_2I_2	5.2×10^{-29}
Mercury(I) oxalate	$Hg_2C_2O_4$	1.75×10^{-13}
Mercury(I) sulfate	Hg_2SO_4	6.5×10^{-7}
Mercury(I) thiocyanate	$Hg_2(SCN)_2$	3.2×10^{-20}
Mercury(II) bromide	$HgBr_2$	6.2×10^{-20}
Mercury (II) iodide	HgI_2	2.9×10^{-29}

Compound Name	Compound Formula	K_{sp}
Mercury(II) sulfide (red)	HgS	4×10^{-53}
Mercury(II) sulfide (black)	HgS	1.6×10^{-52}
Neodymium carbonate	$Nd_2(CO_3)_3$	1.08×10^{-33}
Nickel(II) carbonate	$NiCO_3$	1.42×10^{-7}
Nickel(II) hydroxide	$Ni(OH)_2$	5.48×10^{-16}
Nickel(II) iodate	$Ni(IO_3)_2$	4.71×10^{-5}
Nickel(II) phosphate	$Ni_3(PO_4)_2$	4.74×10^{-32}
Palladium(II) thiocyanate	$Pd(SCN)_2$	4.39×10^{-23}
Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}
Potassium perchlorate	$KClO_4$	1.05×10^{-2}
Potassium periodate	KIO_4	3.71×10^{-4}
Praseodymium hydroxide	$Pr(OH)_3$	3.39×10^{-24}
Rubidium perchlorate	$RbClO_4$	3.00×10^{-3}
Scandium fluoride	ScF_3	5.81×10^{-24}
Scandium hydroxide	$Sc(OH)_3$	2.22×10^{-31}
Silver(I) acetate	$AgCH_3CO_2$	1.94×10^{-3}
Silver(I) arsenate	Ag_3AsO_4	1.03×10^{-22}
Silver(I) bromate	$AgBrO_3$	5.38×10^{-5}
Silver(I) bromide	$AgBr$	5.35×10^{-13}
Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Silver(I) chloride	$AgCl$	1.77×10^{-10}
Silver(I) chromate	Ag_2CrO_4	1.12×10^{-12}
Silver(I) cyanide	$AgCN$	5.97×10^{-17}
Silver(I) iodate	$AgIO_3$	3.17×10^{-8}
Silver(I) iodide	AgI	8.52×10^{-17}
Silver(I) oxalate	$Ag_2C_2O_4$	5.40×10^{-12}
Silver(I) phosphate	Ag_3PO_4	8.89×10^{-17}
Silver(I) sulfate	Ag_2SO_4	1.20×10^{-5}
Silver(I) sulfide	Ag_2S	6.3×10^{-50}
Silver(I) sulfite	Ag_2SO_3	1.50×10^{-14}
Silver(I) thiocyanate	$AgSCN$	1.03×10^{-12}
Strontium arsenate	$Sr_3(AsO_4)_2$	4.29×10^{-19}
Strontium carbonate	$SrCO_3$	5.60×10^{-10}
Strontium fluoride	SrF_2	4.33×10^{-9}
Strontium iodate	$Sr(IO_3)_2$	1.14×10^{-7}
Strontium sulfate	$SrSO_4$	3.44×10^{-7}
Thallium(I) bromate	$TlBrO_3$	1.10×10^{-4}
Thallium(I) bromide	$TlBr$	3.71×10^{-6}
Thallium(I) chloride	$TlCl$	1.86×10^{-4}
Thallium(I) chromate	Tl_2CrO_4	8.67×10^{-13}
Thallium(I) iodate	$TlIO_3$	3.12×10^{-6}
Thallium(I) iodide	TlI	5.54×10^{-8}
Thallium(I) thiocyanate	$TlSCN$	1.57×10^{-4}

Compound Name	Compound Formula	K_{sp}
Thallium(III) hydroxide	$Tl(OH)_3$	1.68×10^{-44}
Tin(II) hydroxide	$Sn(OH)_2$	5.45×10^{-27}
Tin(II) sulfide	SnS	1.0×10^{-25}
Yttrium carbonate	$Y_2(CO_3)_3$	1.03×10^{-31}
Yttrium fluoride	YF_3	8.62×10^{-21}
Yttrium hydroxide	$Y(OH)_3$	1.00×10^{-22}
Yttrium iodate	$Y(IO_3)_3$	1.12×10^{-10}
Zinc arsenate	$Zn_3(AsO_4)_2$	2.8×10^{-28}
Zinc carbonate	$ZnCO_3$	1.46×10^{-10}
Zinc fluoride	ZnF_2	3.04×10^{-2}
Zinc hydroxide	$Zn(OH)_2$	3×10^{-17}
Zinc selenide	$ZnSe$	3.6×10^{-26}
Zinc sulfide (wurtzite)	ZnS	1.6×10^{-24}
Zinc sulfide (sphalerite)	ZnS	2.5×10^{-22}

F. Standard reduction potentials at 25°C

Half-reaction	E° (V)
$Ac^{3+} + 3e^- \rightarrow Ac$	−2.20
$Ag^+ + e^- \rightarrow Ag$	0.7996
$AgBr + e^- \rightarrow Ag + Br^-$	0.07133
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22233
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	0.4470
$AgI + e^- \rightarrow Ag + I^-$	−0.15224
$Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$	−0.691
$Ag_2S + 2H^+ + 2e^- \rightarrow 2Ag + H_2S$	−0.0366
$AgSCN + e^- \rightarrow Ag + SCN^-$	0.08951
$Al^{3+} + 3e^- \rightarrow Al$	−1.662
$Al(OH)_4^- + 3e^- \rightarrow Al + 4OH^-$	−2.328
$Am^{3+} + 3e^- \rightarrow Am$	−2.048
$As + 3H^+ + 3e^- \rightarrow AsH_3$	−0.608
$H_3AsO_4 + 2H^+ + 2e^- \rightarrow HAsO_2 + 2H_2O$	0.560
$Au^+ + e^- \rightarrow Au$	1.692
$Au^{3+} + 3e^- \rightarrow Au$	1.498
$H_3BO_3 + 3H^+ + 3e^- \rightarrow B + 3H_2O$	−0.8698
$Ba^{2+} + 2e^- \rightarrow Ba$	−2.912
$Be^{2+} + 2e^- \rightarrow Be$	−1.847
$Bi^{3+} + 3e^- \rightarrow Bi$	0.308
$BiO^+ + 2H^+ + 3e^- \rightarrow Bi + H_2O$	0.320
$Br_2(aq) + 2e^- \rightarrow 2Br^-$	1.0873
$Br_2(l) + 2e^- \rightarrow 2Br^-$	1.066
$BrO_3^- + 6H^+ + 5e^- \rightarrow 1/2Br_2 + 3H_2O$	1.482
$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$	1.423

Half-reaction	E° (V)
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	−0.199
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868
$Ca(OH)_2 + 2e^- \rightarrow Ca + 2OH^-$	−3.02
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.4030
$CdSO_4 + 2e^- \rightarrow Cd + SO_4^{2-}$	−0.246
$Cd(OH)_4^{2-} + 2e^- \rightarrow Cd + 4OH^-$	−0.658
$Ce^{3+} + 3e^- \rightarrow Ce$	−2.336
$Ce^{4-} + e^- \rightarrow Ce^{3+}$	1.72
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.35827
$HClO + H^+ + e^- \rightarrow 1/2Cl_2 + H_2O$	1.611
$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.482
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.81
$ClO_3^- + 6H^+ + 5e^- \rightarrow 1/2Cl_2 + 3H_2O$	1.47
$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	1.451
$ClO_4^- + 8H^+ + 7e^- \rightarrow 1/2Cl_2 + 4H_2O$	1.39
$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$	1.389
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.92
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.913
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.407
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744
$Cr_2O_7^- + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.232
$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$	−0.13
$Cs^+ + e^- \rightarrow Cs$	−3.026
$Cu^+ + e^- \rightarrow Cu$	0.521
$Cu^{2+} + e^- \rightarrow Cu^+$	0.153
$Cu^{2+} + 2e^- \rightarrow Cu$	0.3419
$CuI_2^- + e^- \rightarrow Cu + 2I^-$	0.00
$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^-$	−0.360
$Dy^{3+} + 3e^- \rightarrow Dy$	−2.295
$Er^{3+} + 3e^- \rightarrow Er$	−2.331
$Es^{3+} + 3e^- \rightarrow Es$	−1.91
$Eu^{2+} + 2e^- \rightarrow Eu$	−2.812
$Eu^{3+} + 3e^- \rightarrow Eu$	−1.991
$F_2 + 2e^- \rightarrow 2F^-$	2.866
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.447
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.037
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	0.358
$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$	−0.56
$Fm^{3+} + 3e^- \rightarrow Fm$	−1.89
$Fm^{2+} + 2e^- \rightarrow Fm$	−2.30
$Ga^{3+} + 3e^- \rightarrow Ga$	−0.549

Half-reaction	E° (V)
$Gd^{3+} + 3e^- \rightarrow Gd$	−2.279
$Ge^{2+} + 2e^- \rightarrow Ge$	0.24
$Ge^{4+} + 4e^- \rightarrow Ge$	0.124
$2H^+ + 2e^- \rightarrow H_2$	0.00000
$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.8277
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.776
$Hf^{4+} + 4e^- \rightarrow Hf$	−1.55
$Hg^{2+} + 2e^- \rightarrow Hg$	0.851
$2Hg^{2+} + 2e^- \rightarrow Hg_2{}^{2+}$	0.920
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.26808
$Ho^{2+} + 2e^- \rightarrow Ho$	−2.1
$Ho^{3+} + 3e^- \rightarrow Ho$	−2.33
$I_2 + 2e^- \rightarrow 2I^-$	0.5355
$I_3{}^- + 2e^- \rightarrow 3I^-$	0.536
$2IO_3{}^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$	1.195
$IO_3{}^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$	1.085
$In^+ + e^- \rightarrow In$	−0.14
$In^{3+} + 2e^- \rightarrow In^+$	−0.443
$In^{3+} + 3e^- \rightarrow In$	−0.3382
$Ir^{3+} + 3e^- \rightarrow Ir$	1.156
$K^+ + e^- \rightarrow K$	−2.931
$La^{3+} + 3e^- \rightarrow La$	−2.379
$Li^+ + e^- \rightarrow Li$	−3.0401
$Lr^{3+} + 3e^- \rightarrow Lr$	−1.96
$Lu^{3+} + 3e^- \rightarrow Lu$	−2.28
$Md^{3+} + 3e^- \rightarrow Md$	−1.65
$Md^{2+} + 2e^- \rightarrow Md$	−2.40
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.185
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.224
$MnO_4{}^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.507
$MnO_4{}^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	0.595
$Mo^{3+} + 3e^- \rightarrow Mo$	−0.200
$N_2 + 2H_2O + 6H^+ + 6e^- \rightarrow 2NH_4OH$	0.092
$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$	0.983
$NO_3{}^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.957
$Na^+ + e^- \rightarrow Na$	−2.71
$Nb^{3+} + 3e^- \rightarrow Nb$	−1.099
$Nd^{3+} + 3e^- \rightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.257
$No^{3+} + 3e^- \rightarrow No$	−1.20
$No^{2+} + 2e^- \rightarrow No$	−2.50

Half-reaction	E° (V)
$Np^{3+} + 3e^- \rightarrow Np$	−1.856
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$	−0.146
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.076
$OsO_4 + 8H^+ + 8e^- \rightarrow Os + 4H_2O$	0.838
$P + 3H_2O + 3e^- \rightarrow PH_3(g) + 3OH^-$	−0.87
$PO_4^{3-} + 2H_2O + 2e^- \rightarrow HPO_3^{2-} + 3OH^-$	−1.05
$Pa^{3+} + 3e^- \rightarrow Pa$	−1.34
$Pa^{4+} + 4e^- \rightarrow Pa$	−1.49
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.1262
$PbO + H_2O + 2e^- \rightarrow Pb + 2OH^-$	−0.580
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.6913
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.3588
$Pd^{2+} + 2e^- \rightarrow Pd$	0.951
$Pm^{3+} + 3e^- \rightarrow Pm$	−2.30
$Po^{4+} + 4e^- \rightarrow Po$	0.76
$Pr^{3+} + 3e^- \rightarrow Pr$	−2.353
$Pt^{2+} + 2e^- \rightarrow Pt$	1.18
$[PtCl_4]^{2-} + 2e^- \rightarrow Pt + 4Cl^-$	0.755
$Pu^{3+} + 3e^- \rightarrow Pu$	−2.031
$Ra^{2+} + 2e^- \rightarrow Ra$	−2.8
$Rb^+ + e^- \rightarrow Rb$	−2.98
$Re^{3+} + 3e^- \rightarrow Re$	0.300
$Rh^{3+} + 3e^- \rightarrow Rh$	0.758
$Ru^{3+} + e^- \rightarrow Ru^{2+}$	0.2487
$S + 2e^- \rightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \rightarrow H_2S(aq)$	0.142
$2S + 2e^- \rightarrow S_2^{2-}$	−0.42836
$H_2SO_3 + 4H^+ + 4e^- \rightarrow S + 3H_2O$	0.449
$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	−0.93
$Sb + 3H^+ + 3e^- \rightarrow SbH_3$	−0.510
$Sc^{3+} + 3e^- \rightarrow Sc$	−2.077
$Se + 2e^- \rightarrow Se^{2-}$	−0.924
$Se + 2H^+ + 2e^- \rightarrow H_2Se$	−0.082
$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^-$	−1.24
$Sm^{3+} + 3e^- \rightarrow Sm$	−2.304
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.1375
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.151
$Sr^{2+} + 2e^- \rightarrow Sr$	−2.899
$Ta^{3+} + 3e^- \rightarrow Ta$	−0.6
$TcO_4^- + 4H^+ + 3e^- \rightarrow TcO_2 + 2H_2O$	0.782

Half-reaction	E° (V)
$TcO_4^- + 8H^+ + 7e^- \rightarrow Tc + 4H_2O$	0.472
$Tb^{3+} + 3e^- \rightarrow Tb$	−2.28
$Te + 2e^- \rightarrow Te^{2-}$	−1.143
$Te^{4+} + 4e^- \rightarrow Te$	0.568
$Th^{4+} + 4e^- \rightarrow Th$	−1.899
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.630
$Tl^+ + e^- \rightarrow Tl$	−0.336
$Tl^{3+} + 2e^- \rightarrow Tl^+$	1.252
$Tl^{3+} + 3e^- \rightarrow Tl$	0.741
$U^{3+} + 3e^- \rightarrow U$	−1.798
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	0.991
$V_2O_5 + 6H^+ + 2e^- \rightarrow 2VO^{2+} + 3H_2O$	0.957
$W_2O_5 + 2H^+ + 2e^- \rightarrow 2WO_2 + H_2O$	−0.031
$XeO_3 + 6H^+ + 6e^- \rightarrow Xe + 3H_2O$	2.10
$Y^{3+} + 3e^- \rightarrow Y$	−2.372
$Yb^{3+} + 3e^- \rightarrow Yb$	−2.19
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7618
$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$	−1.199
$Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^-$	−1.249
$ZrO_2 + 4H^+ + 4e^- \rightarrow Zr + 2H_2O$	−1.553
$Zr^{4+} + 4e^- \rightarrow Zr$	−1.45

G. Properties of water

Density: 0.99984 g/cm^3 at 0°C
0.99970 g/cm^3 at 10°C
0.99821 g/cm^3 at 20°C
0.98803 g/cm^3 at 50°C
0.95840 g/cm^3 at 100°C
Enthalpy (heat) of vaporisation: 45.054 kJ/mol at 0°C
43.990 kJ/mol at 25°C
42.482 kJ/mol at 60°C
40.657 kJ/mol at 100°C
Surface tension: 74.23 J/m^2 at 10°C
71.99 J/m^2 at 25°C
67.94 J/m^2 at 50°C
58.91 J/m^2 at 100°C
Viscosity: 1.793 mPa·s at 0°C
0.890 mPa·s at 25°C
0.547 mPa·s at 50°C
0.282 mPa·s at 100°C
Ion-product constant, K_w (or K_{H2O}): 1.15×10^{-15} at 0°C
1.01×10^{-14} at 25°C
5.31×10^{-14} at 50°C

5.43×10^{-13} at 100°C
Specific heat (C_s): 4.2176 J/(g·°C) at 0°C
4.1818 J/(g·°C) at 20°C
4.1806 J/(g·°C) at 50°C
4.2159 J/(g·°C) at 100°C

Vapour pressure of water

T(°C)	P(kPa)	P(mm Hg)	T(°C)	P(kPa)	P(mm Hg)
0	0.61129	4.585	60	19.932	149.50
5	0.87260	6.545	65	25.022	187.68
10	1.2281	9.211	70	31.176	233.84
15	1.7056	12.793	75	38.563	289.24
20	2.3388	17.542	80	47.373	355.32
25	3.1690	23.769	85	57.815	433.64
30	4.2455	31.844	90	70.117	525.91
35	5.6267	42.203	95	84.529	634.01
40	7.3814	55.364	100	101.32	759.95
45	9.5898	71.929	105	120.79	905.99
50	12.344	92.59	110	143.24	1074.38
55	15.752	118.15	115	169.02	1267.74

H. Physical constants

Selected Physical Constants	
Atomic mass unit	1 amu = $1.6605389 \times 10^{-24}$ g
	1 g = 6.022142×10^{23} amu
Avogadro's number	N = 6.022142×10^{23}/mol
Boltzmann's constant	k = 1.380651×10^{-23} J/K
Charge on electron	e = $1.6021765 \times 10^{-19}$ C
Faraday's constant	F = 9.6485338×10^{4} C/mol
Gas constant	R = 0.0820575 (L atm)/(mol K)
	= 8.31447 J/(mol K)
Mass of electron	$m_e = 5.485799 \times 10^{-4}$ amu
	= 9.109383×10^{-28} g
Mass of neutron	m_n = 1.0086649 amu
	= $1.6749273 \times 10^{-24}$ g
Mass of proton	m_p = 1.0072765 amu
	= $1.6726217 \times 10^{-24}$ g
Pi	$\pi = 3.1415927$
Planck's constant	h = 6.626069×10^{-34} J s
Speed of light (in vacuum)	c = 2.99792458×10^{8} m/s (exact)

I. Formation constants (or stability constants) for complex ions in aqueous solutions

	Complex ion	Equilibrium equation	K_{st} *
Ammonia complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \leftrightarrow [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \leftrightarrow [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \leftrightarrow [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \leftrightarrow [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \leftrightarrow [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \leftrightarrow [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \leftrightarrow [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \leftrightarrow [Cr(OH)_4]^-$	8.0×10^{29}
Halide complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \leftrightarrow [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \leftrightarrow [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \leftrightarrow [AlF_6]^{3-}$	6.9×10^{19}
Other complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \leftrightarrow [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \leftrightarrow [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants

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Книга знайомить з основними поняттями неорганічної хімії, такими як атомно-молекулярна теорія, класи неорганічних сполук, структура атома, періодичний закон, хімічні зв'язки, рівновага та кінетика хімічних реакцій, властивості розчинів, структура комплексних сполук, а також основні хімічні властивості елементів. Наводяться приклади розв'язання задач, а також завдання та вправи для самостійної роботи.

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