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General and Inorganic Chemistry

A tutorial for foreign students

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Учебное пособие предназначено для иностранных студентов Казанского федерального университета, изучающих общую и неорганическую химию. В пособии даны теоретические основы данных разделов химии, а также задачи и упражнения для самостоятельной работы наряду с примерами их решений.

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The tutorial is intended for foreign students of Kazan Federal University studying general and inorganic chemistry. The textbook provides the theoretical foundations of these divisions of chemistry, as well as tasks and exercises for independent work along with examples of their solutions.

Contents

Theme I
Main Classes of Inorganic Compounds

Oxidation state

All materials are composed of chemical elements or combinations of them. All known elements are presented in periodic table of D.I. Mendeleev, who discovered *Periodic law* in the middle of 19th century. The vast majority of these elements occur naturally, but some, such as technetium or curium, are artificial. Almost all elements can forms bonds with other elements. To explain the number of bonds that atoms can form, it is necessary to introduce the conception of the oxidation state. The oxidation state is a formal value, which is equal to the charge that acquires an atom under the assumption of complete displacement of electrons to it or from it. By the displacement of electrons to the atom it acquires a negative charge (negative oxidation state), and by the displacement of electrons from the atom it acquires a positive charge (positive oxidation state). If the charge does not shift, the oxidation state is zero as in all simple substances. In neutral molecules the total sum of positive and negative oxidation states, as the sum of the charges, must be zero. For example, oxidation state of hydrogen is zero in dihydrogen molecule (H_2^0), plus one in water ($H_2^{+1}O^{-2}$), and minus one in sodium hydride ($Na^{+1}H^{-1}$); oxidation state of oxygen is zero in dioxygen molecule (O_2^0), minus two in sodium oxide ($Na_2^{+1}O^{-2}$), minus one in hydrogen peroxide ($H_2^{+1}O_2^{-1}$), and plus two in oxygen fluoride ($O^{+2}F_2^{-1}$), *etc.* Positive oxidation state is often denoted by a Roman numeral in parentheses without the sign of the charge, for example, copper(II) oxide ($Cu^{II}O$). Particles with positive charge are called cations and particles with negative charge are called anions.

How to determine the oxidation states of other elements? There are several simple rules:

1) As mentioned above, in simple compounds (that contain atoms of only one element) an oxidation state of atoms equals zero.

2) Some elements have a constant oxidation state in compounds:

Elements	Oxidation state in compounds	Exceptions
Li, Na, K, …	+1	
Be, Mg, Ca, …	+2	
H	+1	−1 in hydrides of metals (LiH, CaH_2)
O	−2	−1 in peroxides (H_2O_2, Na_2O_2, CaO_2) +2 in oxygen fluoride OF_2 −½ in super oxides (KO_2) $-^1/_3$ in ozonides
F	−1	

3) The sum of oxidation states of all atoms in a neutral chemical compound equals zero.

For example, to calculate the oxidation state of sulfur in H_2SO_4 we can write such an equation taking into account the number of elements in the molelcule:

$$2\cdot(+1) + x + 4\cdot(-2) = 0$$

where +1, x, and −2 are the oxidation states of H, S, and O respectively.

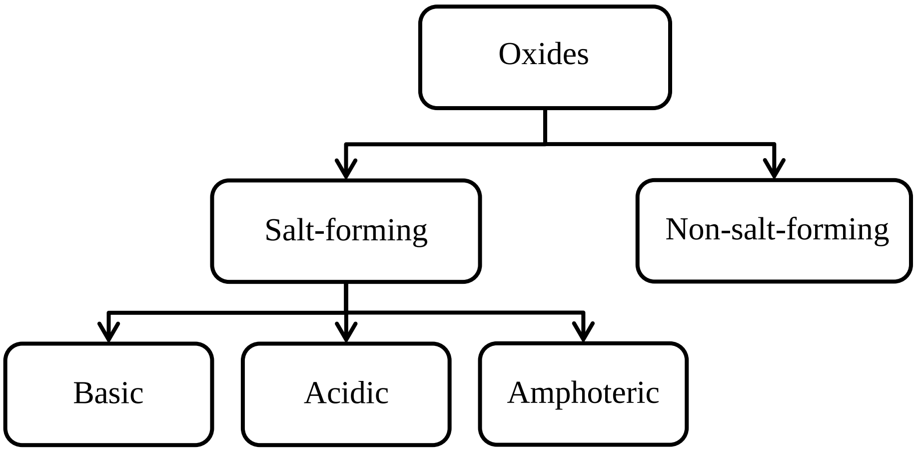
From above written equation it is clear that $x = +6$, so the oxidation state of sulfur in H_2SO_4 is +6.

Let consider now classifications of inorganic compounds. There are two ways of such classifications.

Inorganic compounds are classified according to the composition into binary and multi-element compounds. Binary compounds are called by analogy with sodium chloride ($NaCl$). For example: $CaCl_2$ (calcium chloride), CaO (calcium oxide), CaS (calcium sulfide), Ca_3N_2 (calcium nitride), Ca_3P_2 (calcium phosphide), CaC_2 (calcium carbide), $CaSi_2$ (calcium silicide), CaH_2 (calcium hydride), CO (carbon monoxide or carbon(II) oxide, where II is oxidation state of carbon), CO_2 (carbon dioxide or carbon(IV) oxide), $FeCl_2$ (iron dichloride or iron(II) chloride or ferrous chloride), $FeCl_3$ (iron trichloride or iron(III) chloride or ferric chloride). The OH^-, diatomic anion, is called hydroxide. Therefore, compounds with hydroxide-anion are called as binary compounds, for example: $Fe(OH)_2$ (iron dihydroxide or iron(II) hydroxide or ferrous hydroxide), $Fe(OH)_3$ (iron trihydroxide or iron(III) hydroxide or ferric hydroxide).

There is another classification of inorganic compounds based on the compound properties (a functional classification). It consists of four main classes of compounds: oxides, acids, bases, and salts.

Oxides



The oxides may be salt-forming and non-salt-forming. Salt-forming oxides may be basic, acidic and amphoteric. Basic oxides correspond to bases and they give salts by reaction with acids or acid oxides. For example, CaO (calcium oxide) corresponds to $Ca(OH)_2$ (calcium hydroxide) and it reacts with sulfur(IV) oxide (sulfur dioxide) or with sulfurous acid giving salt, $CaSO_3$ (calcium sulfite). Acidic oxides correspond acids and they give salts by reaction with bases or basic oxides, for example, SO_3 (sulfur(VI) oxide) corresponds H_2SO_4 (sulfuric acid) and it reacts with sodium oxide or with sodium hydroxide giving salt, Na_2SO_4 (sodium sulfate). Amphoteric oxides can react with both acidic and basic oxides as well as with both acids and bases giving salts. The examples of amphoteric oxides are the following: ZnO (zinc oxide), Al_2O_3 (aluminium oxide), Cr_2O_3 (chromium(III) oxide), Mn_2O_3 (manganese(III) oxide), PbO (lead oxide), PbO_2 (lead dioxide) *etc*. However, Na_2O_2 is not an oxide but a salt of a weak acid hydrogen peroxide (H_2O_2) where both protons are replaced by two sodium cations.

Also there are mixed oxides, for example: $Fe^{II}O\cdot Fe^{III}{}_2O_3 = Fe_3O_4$ (ferrous oxide–ferric oxide) and $Mg^{II}O\cdot Cr^{III}{}_2O_3 = MgCr_2O_4$ (magnesium oxide–chromium(III) oxide).

The examples of non-salt-forming oxides: CO, N_2O, and NO. Obviously, they do not react with acidic or basic oxides and do not give salts.

Acids

The following class of inorganic compounds consists of acids. In viewpoint of the *Arrhenius theory of electrolytic dissociation*, acids are the compounds that dissociate in solution with detachment of protons, for example:

$$HCl \rightarrow H^+ + Cl^-$$

But from the viewpoint of *Brønsted-Lowry acid base theory*, acid is the simply proton donor.

Binary oxygen-free acids are called simply as another binary compounds, for example, hydrogen chloride or hydrochloride (HCl), (by analogy) hydrogen cyanide or hydrocyanide (HCN).

The names of oxygen-containing acids are formed by more complex way. If there are only two oxidation states of acid-forming element, then the two suffixes are used, for example:

H_2SO_3 sulfurous acid H_2SO_4 sulfuric acid

In the case of four oxidation states of acid-forming element, then four different names are used. For the chlorine acids the names are the following:

$HClO_4$ perchloric acid

$HClO_3$ chloric acid

$HClO_2$ chlorous acid

HClO hypochlorous acid

Also there are acids with the same oxidation state of acid-forming element:

HPO_3 metaphosphoric acid H_3PO_4 orthophosphoric acid

If an acid contains several acid-forming elements their number should be indicated:

$H_2S_2O_7$ disulfuric (pyrosulfuric) acid

$H_2S_2O_8$ peroxydisulfuric acid

Bases

The third class of inorganic compounds consists of bases. Bases are the compounds that dissociate in solution with detachment of hydroxide-ion (in viewpoint of the *Arrhenius theory of electrolytic dissociation*). From the viewpoint of *Brønsted-Lowry acid base theory* the base is the simply proton acceptor. For example, aqueous ammonia ($NH_3{\cdot}H_2O$) in solution is base because it dissociates with detachment of hydroxide-ion ($NH_3{\cdot}H_2O = NH_4^+ + OH^-$), but ammonia ($NH_3$) in gas is also base because it accepts a proton ($NH_3 + H^+ = NH_4^+$). The usual bases are called just hydroxides, for example, sodium hydroxide (NaOH). However, there are amphoteric hydroxides that react with both acids and bases giving salts or coordination compounds, as can be seen from the following reactions of zinc dihydroxide:

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

$$Zn(OH)_2 + 2NaOH = Na_2[Zn(OH)_4] \xrightarrow{t^\circ} Na_2ZnO_2 + 2H_2O$$

(here t° represents the heating), where Na_2ZnO_2 is a salt of zincous acid (H_2ZnO_2) and sodium tetra-hydroxozincate, $Na_2[Zn(OH)_4]$, relates to coordination compounds.

Analogically, chromium(III) hydroxide ($Cr(OH)_3$) is also amphoteric hydroxide in accordance to the following reactions:

$$Cr(OH)_3 + 3HCl = CrCl_3 + 3H_2O,$$

$$Cr(OH)_3 + 3NaOH = Na_3[Cr(OH)_6]$$

Salts

The fourth class of inorganic compounds consists of salts. Salts are the products of complete or partial substitution of protons in acids or hydroxide-ions in bases as a result of interaction of acids and bases. At the complete substitution of protons or hydroxide-ions the normal salts (neutral salts) are formed, for example, iron(III) sulfate ($Fe_2(SO_4)_3$):

$$2Fe(OH)_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6H_2O$$

At partial substitution of protons in acids the acidic salts (hydrogen salts) are formed, for example, iron(III) hydrogensulfate or hydrosulfate ($Fe(HSO_4)_3$):

$Fe(OH)_3 + 3H_2SO_{4\,(excess)} = Fe(HSO_4)_3 + 3H_2O$

At partial substitution of hydroxide-ions in bases the basic salts (hydroxy salts) are formed, for example, iron(III) hydroxysulfate ($FeOHSO_4$):

$Fe(OH)_{3\,(excess)} + H_2SO_4 = FeOHSO_4 + 2H_2O$

or iron(III) dihydroxysulfate ($\{Fe(OH)_2\}_2SO_4$):

$2Fe(OH)_{3\,(excess)} + H_2SO_4 = \{Fe(OH)_2\}_2SO_4 + 2H_2O$

(note that two basic salts may be in this case). For salts of four mentioned chlorine acids the following names are used:

$KClO_4$ – potassium perchlorate

$KClO_3$ –potassium chlorate

$KClO_2$ – potassium chlorite

$KClO$ – potassium hypochlorite

There are so-called double salts with two different cations and one anion, for example, potassium aluminium sulfate ($KAl(SO_4)_2$) or ammonium chromium(III) sulfate ($NH_4Cr(SO_4)_2$). There are also so-called mixed salts with two different anions and one cation, for example, calcium chloride hypochlorite: $CaCl(OCl)$.

Example of problem solving: Write all possible salts that can be formed by phosphoric acid H_3PO_4 and calcium hydroxide $Ca(OH)_2$. Draw graphical formulas of these salts.

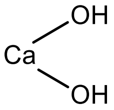
Neutral salt: $Ca_3(PO_4)_2$ calcium phosphate

Basic salt: $(CaOH)_3PO_4$ calcium hydroxy phosphate

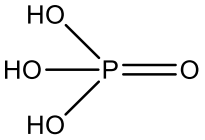
Acid salts: $Ca(HPO_4)$ calcium hydrophosphate

$Ca(H_2PO_4)_2$ calcium dihydrophosphate

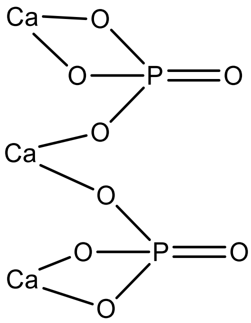
Graphical formulas:



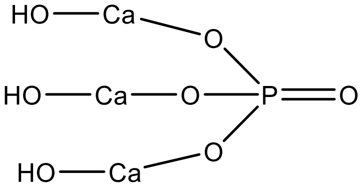
$Ca(OH)_2$



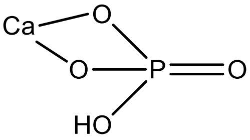
H_3PO_4



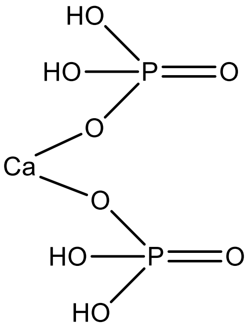
$Ca_3(PO_4)_2$



$(CaOH)_3PO_4$



$Ca(HPO_4)$



$Ca(H_2PO_4)_2$

Problem 1.1: What are the names of all iodic acids? Iodine as the acid-forming element of oxygen-containing acids can take four oxidation states (+7, +5, +3, +1).

Problem 1.2: Write all possible salts that can be formed by sulfurous acid H_2SO_3 and barium hydroxide $Ba(OH)_2$.

Problem 1.3: Write all possible salts that can be formed by nitric acid HNO_3 and aluminum hydroxide $Al(OH)_3$.

Problem 1.4: Write all possible salts that can be formed by iron(III) hydroxide $Fe(OH)_3$ and phosphoric acid H_3PO_4.

Problem 1.5: Draw the graphical formula for iron(III) dihydrogen phosphate ($Fe(H_2PO_4)_3$).

Theme II
Gas Laws

Gas laws have played a large role in establishing stoichiometric laws of chemistry, that is, in determining the composition of gas compounds. The state of a gas is uniquely characterized by three parameters, pressure (*P*), volume (*V*), and temperature (T). For so-called standard conditions (STP, standard temperature and pressure) the temperature is T_o = 273.15 K (Kelvin) and the pressure is P_o = 101.325 kPa (kilopascal) (it should be noted that in Russian literature usually T = 298.15 K for STP and T = 273.15 K for NTP, normal temperature and pressure). For ideal gases (where specific interaction between molecules is absent) the following so-called *Combined Gas Law* is fulfilled:

$$\frac{P_1V_1}{T_1} = const \text{ or } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

where indexes one and two relate to the gas states 1 and 2 respectively.

In a mixture of gases, the total pressure is calculated as the sum of the partial pressures of the component gases. This is *Dalton's Law of Partial Pressures* and can be expressed as following:

$$P = P_A + P_B + P_C + \ldots$$

where P is the total pressure, P_A is the partial pressure of gas A, *etc*.

It is necessary to introduce the important concept of *mole*. The mole is the amount of substance that contains as many of the structural units (or particles) as there are atoms in twelve grams of the isotope ^{12}C. Structural units (particles) might be electrons, atoms, molecules *etc*. In one mole of a substance there are $6.022 \cdot 10^{23}$ particles, and this number is called the *Avogadro constant* or *number*, $N_A = 6.022 \cdot 10^{23}$ mol^{-1}. The mass of one mole of a substance is called the molar mass and is denoted by M, and the volume of one mole is called the molar volume.

Avogadro's Law states that equal volumes of any gases under the same conditions contain equal number of molecules. This implies that one mole of any gas occupies the same volume. Particularly, under standard conditions, this volume is 22.414 liters and is denoted as V_o. Thus, for one mole of gas the *Combined Gas Law* can be written as follows:

$$\frac{PV}{T} = R$$

where R is the molar gas constant and it equals to 8.314 J/(K·mol). And for n moles of gas we can write the relation:

$$\frac{PV}{T} = nR \quad \text{or} \quad PV = nRT$$

where n equals the gas mass m divided by the molar mass M: $n = m/M$.

Now we can write a formula that expresses the so-called *Clapeyron-Mendeleev Law*:

$$PV = \frac{m}{M}RT$$

All the above equations can be used to determine the molar masses.

Problem 2.1: Determine the molar mass of acetone, if the mass of 700 milliliters of its vapor at 77 °C and pressure of 96 kPa is equal to 1.34 grams.

In this task the Clapeyron-Mendeleev Law should be used, but initially it is necessary to convert units of values to the International System of Units (SI).

Solution:

P = 96 kPa = 96000 Pa
V = 700 ml = 0.7 l = $0.7 \cdot 10^{-3}$ m^3
T = 77 °C = 350 K
m = 1.34 g

M – ?

Let's write the Clapeyron-Mendeleev Law:

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{PV} = \frac{1.34 \cdot 8.31 \cdot 350}{96000 \cdot 0.7 \cdot 10^{-3}} = 58\ \text{g/mol}$$

Molar mass can also be determined by the relative density ($D = \rho_1/\rho_2$) of the two gases, where ρ_1 and ρ_2 are densities of the gases 1 and 2 given by relations $\rho_1 = m_1/V$ and $\rho_2 = m_2/V$. The values m_1 and m_2 are masses of the gases 1 and 2 in the same volume V which contains the same number of moles of both gases (n) according to the Avogadro's Law. But the masses m_1 and m_2 are related to the molar masses of gases 1 and 2, M_1 and M_2, by the ratios $m_1 = nM_1$ and $m_2 = nM_2$. From this we obtain the relation:

$$D = \frac{\rho_1}{\rho_2} = \frac{\frac{m_1}{V}}{\frac{m_2}{V}} = \frac{m_1}{m_2} = \frac{nM_1}{nM_2} = \frac{M_1}{M_2}$$

That is, giving the values of the relative density D and the molar mass of the second gas M_2, we can calculate the molar mass of the first gas M_1 by the relation $M_1 = DM_2$.

Problem 2.2: At some temperature the density of the sulfur vapor by oxygen is 7.11. How many atoms does a sulfur molecule consist of at this temperature?

Solution:

$D(S_N)$ = 7.11

N – ?

$$D(S_N) = \frac{M_{S_N}}{M_{O_2}}$$

$$M_{S_N} = DM_{O_2} = 7.11 \cdot 32 = 256 \text{ g/mol}$$

$$N = \frac{M_{S_N}}{M_S} = \frac{256}{32} = 8 \text{ atoms}$$

Finally, the molar mass of the gas M can be determined by the value of the molar volume V_o = 22.4 liter under standard conditions. If under these conditions a gas with mass m occupies a volume V, the molar mass M can be calculated from the following relation:

$n = m/M = \rho V/\rho V_o = V/V_o$ (ρ is density of the gas)

Hence we obtain the equation:

$M = mV_o/V$

Thus, we have considered three ways to determine the molar masses of gases.

Problem 2.3: Mass of 0.002 m^3 of some gas under standard conditions is 0.0042 kg. Determine the molar mass of the gas and its density by air.

Solution:

$V = 0.002 \text{ m}^3 = 2$ liter

$m = 0.0042$ kg = 4.2 g

$M_{air} = 29$ g/mol

M – ?

D – ?

$$M = \frac{mV_0}{V} = \frac{4.2 \cdot 22.4}{2} = 47 \text{ g/mol}$$

$$D = \frac{M}{M_{air}} = \frac{47}{29} = 1.62$$

Problem 2.4: At pressure 96.7 kPa and temperature 71°C the volume of gas equals 800 ml. Find the gas volume at standard conditions.

Problem 2.5: The ethylene density by oxygen is 0.876. What is the molar mass of this gas?

Problem 2.6: Calculate the molar mass of a gas if its mass is 1.8 g and its volume at standard conditions is 630 ml.

Theme III
Chemical Equivalents of Substances and Methods of their Determination

The equivalent is the amount of a substance which is bounded with one mole of hydrogen atoms or replaces the same number of hydrogen atoms in chemical reactions. Let's define equivalents for some elements in the following compounds:

1) HCl (equivalent of chlorine is 1 mole because one chlorine atom is bounded with 1 hydrogen atom);
2) H_2O (equivalent of oxygen is ½ mole because to bind 1 mole of hydrogen atoms only ½ mole of oxygen atoms is needed);
3) NH_3 (equivalent of nitrogen is ⅓ mole because to bind 1 mole of hydrogen atoms only ⅓ mole of nitrogen atoms is needed);
4) CO (equivalent of carbon(II) is ½ mole because one carbon atom is bounded with one oxygen atom and equivalent of oxygen is ½);
5) CO_2 (equivalent of carbon(IV) is ¼ mole because one carbon atom is bounded with two oxygen atoms and equivalent of each oxygen is ½).

As can be seen, the value of an equivalent is the inverse with respect to the valence. The mass of one equivalent of a substance is called the equivalent mass and the volume occupied by one equivalent called the equivalent volume. Therefore, the equivalent mass of hydrogen is equal to its molar mass, about 1 g/mol, and the equivalent mass of oxygen is equal to one half of its molar mass, that is ½·16 = 8 g/mol. The equivalent volume of hydrogen at standard conditions is equal to 22.4/2 = 11.2 l/mol because one dihydrogen molecule consists two hydrogen atoms each of which has the equivalent of 1 mole. In much the same way, the equivalent volume of oxygen at standard conditions is equal to 22.4/4 = 5.6 l/mol because one dioxygen molecule consists two oxygen atoms each of which has the two equivalents of ½ mole, that is, one molecule of dioxygen contains 4 oxygen equivalents.

There is the important stoichiometric law, so-called *Law of Equivalents*. This law states that substances react in amounts that are proportional to their equivalents. For example, for reaction $n\mathrm{A} + m\mathrm{B} = \mathrm{A}_n\mathrm{B}_m$ one can write:

$$\frac{m_A}{M_{eq}(\mathrm{A})} = \frac{m_B}{M_{eq}(\mathrm{B})} = \frac{m_{A_nB_m}}{M_{eq}(\mathrm{A}_n\mathrm{B}_m)}$$

where m_A, m_B and $m_{A_nB_m}$ are the corresponding masses of substances, $M_{eq}(\mathrm{A})$, $M_{eq}(\mathrm{B})$ and $M_{eq}(\mathrm{A}_n\mathrm{B}_m)$ are their equivalent masses.

The equivalent mass of the product should be equal to the sum of the equivalent masses of the reactants. But the equivalent value is inversely proportional to the valence. Thus, the equivalent mass of the compound $\mathrm{A}_n^{m+}\mathrm{B}_m^{n-}$ is given by the following equation:

$$M_{eq}(\mathrm{A}_n^{m+}\mathrm{B}_m^{n-}) = \frac{M_\mathrm{A}}{m} + \frac{M_\mathrm{B}}{n} = \frac{nM_\mathrm{A} + mM_\mathrm{B}}{nm} = \frac{M(\mathrm{A}_n^{m+}\mathrm{B}_m^{n-})}{nm}$$

where the valence or charge of electropositive residue A and electronegative residue B equal *m* and *n* respectively. For example, the equivalent mass of phosphoric acid H_3PO_4 at substitution of all protons with the neutral salt formation equals to $M_\mathrm{eq} = M(H_3PO_4)/3 = 98/3 = 32.66$ g/mol, at substitution of two protons with the acidic monohydrogen salt formation – $M_\mathrm{eq} = M(H_3PO_4)/2 = 98/2 = 49$ g/mol, and at substitution of one proton with the acidic dihydrogen salt formation – $M_\mathrm{eq} = M(H_3PO_4)/1 = 98/1 = 98$ g/mol. As an example, the equivalent mass of the neutral aluminum sulfate equals $M_\mathrm{eq}(\mathrm{Al}_2^{3+}(\mathrm{SO}_4^{2-})_3) = (2\cdot27 + 3\cdot96)/2\cdot3 = 57$ g/mol.

Problem 3.1: 13.22 g of a metal oxide was formed after burning 7 g of some metal. What is the equivalent mass of the metal?

Solution:

$m_\mathrm{oxide} = 13.22$ g
$m_\mathrm{Me} = 7$ g

$M_\mathrm{eq}(\mathrm{Me})$ – ?

The equation of the reaction is

$n\mathrm{Me} + {}^{m}/_{2}\mathrm{O}_2 = \mathrm{Me}_n\mathrm{O}_m$

$m_\mathrm{Me} + m_\mathrm{oxygen} = m_\mathrm{oxide}$ => $m_\mathrm{oxygen} = m_\mathrm{oxide} - m_\mathrm{Me} = 6.22$ g

Let write the Law of Equivalents:

$$\frac{m_{\text{Me}}}{M_{eq}(\text{Me})} = \frac{m_{\text{oxygen}}}{M_{eq}(\text{O})} \Rightarrow \frac{7}{M_{eq}(\text{Me})} = \frac{6.22}{8}$$

Then $M_{\text{eq}}(\text{Me}) = 9$ g/mol.

Problem 3.2: 1.126 g of some metal forms chemical compound with 10 g of bromine. Also 1 g of the metal combines with 1.78 g of sulfur. Find the equivalent masses of bromine and the metal if the equivalent mass of sulfur is 16.0 g/mol.

Problem 3.3: Find the equivalent mass of a metal if 0.85 liters of oxygen oxidize 10.43 g of the metal. What is the name of this metal?

Problem 3.4: Some amount of a metal (its equivalent mass is 12.2 g/mol) replaces 500 ml of hydrogen. What is the mass of the metal?

Theme IV
Atomic Structure

Atoms are composed from nuclei and electrons. Nuclei include protons and neutrons. A proton (p) and a neutron (n) have approximately the same mass, and relative to them, an electron (e) has a negligible mass (1/1836 relative to a proton). A neutron has no charge. A proton has positive charge and an electron has negative charge with the same magnitude as for proton. As a result atom having equal numbers of protons and electrons is uncharged. The recommended IUPAC (International Union of Pure and Applied Chemistry) definition of an element states that "*an element is matter, all of whose atoms are alike in having the same positive charge on the nucleus*". Atoms of the same elements with different numbers of neutrons are called isotopes. Each atom is characterized by its atomic (charge) number (Z), mass number (A), and symbol (E). The atomic number Z is the number of protons in the nucleus, and the mass number A is the number of protons plus number of neutrons. An atom or an isotope is presented through the symbol of element E as follows ${}_{Z}^{A}\text{E}$, for example, one copper isotope ${}_{29}^{63}\text{Cu}$ (an another isotope, ${}_{29}^{65}\text{Cu}$, also exists).

Atom models

There are some models of atomic structure. In 1911, Ernest Rutherford proposed the atom model consisting of a positively charged nucleus around which electrons move in circular orbits. In 1913, Niels Bohr developed a quantized model for an atom. In the Bohr atom, electrons move in planetary-like orbits about the nucleus. The basic assumption that made the Bohr atom different from Rutherford model was that *the energy of an electron in a particular orbit remains constant and that only certain discrete energies are allowed*. This was a very important advance in the development of atomic theory, because by classical theory the orbit would collapse as the electron was attracted towards the nucleus and this is catastrophe. By allowing the electrons to move only in particular orbits, Bohr had quantized his model. There are two Bohr postulates:

1) Electrons in the atom occupy only stationary states with a quantized angular momentum,

$$M = nh/2\pi$$

2) Transitions between the stationary states are accompanied by the absorption or emission of a quantum of electromagnetic energy,

$$h\nu = E_n - E_{n'}$$

where h is the *Planck constant* ($h = 6.626 \cdot 10^{-34}$ J·s), n is the quantum number (integer number), and E_n and $E_{n'}$ are the energies of the stationary states with quantum numbers n and n' respectively. The Bohr model was successful in terms of explanation of the hydrogen atom spectrum but the Bohr atom fails for other reasons.

In 1900, Max Planck states that *electromagnetic radiation is quantized*, that is the radiation is emitted or absorbed only in discrete amounts:

$$E = h\nu$$

In 1905, Albert Einstein considers that *light waves also exhibit particle-like behavior; the particles are called photons and have energies* $E = h\nu$.

In 1924, Louis de Broglie argued that *if radiation could exhibit the properties of both particles and waves, then so too could electrons, and indeed so too could* *every moving particle.* This phenomenon is known as *wave–particle duality* and expressed by the *de Broglie relationship,*

$$\lambda = h/p$$

where $p = mv$ is the linear momentum, m is the mass, v is the velocity of a particle, and λ is the wavelength of wave. This relation shows that a particle (and this includes an electron) with momentum p has an associated wave of wavelength λ. Thus, this equation combines the concepts of classical momentum with idea of wave-like properties. And so, we have begun to move towards quantum (or wave) mechanics and away from classical mechanics.

Indeed, once we give wave-like properties to the electron, it becomes impossible to know exactly both the position and the momentum of the electron at the same instant in time. This is *Heisenberg's uncertainty principle* and it is expressed by the uncertainty relationship:

$$\Delta x \cdot \Delta p_x \approx h$$

where Δx is the uncertainty of the x-coordinate determination (in other words, dispersion), and Δp_x is the uncertainty of the momentum p determination along the x axis. That is, if we know the x-coordinate with high certainty, we can't know the momentum p with high certainty and *vice versa*. Evidently, we must consider only the probability of finding the electron in a given volume of space, rather than trying to define its exact position and momentum. The probability of finding an electron at a given point in space is determined from the function ψ^2 where ψ is the wave function.

This wave function was introduced in 1926 by Erwin Schrödinger in so-called the *Schrödinger wave equation* by the analogy with wave equation in classical mechanics. Let's write the Schrödinger wave equation as follows:

$$\mathbf{H}\psi = E\psi$$

where **H** is called the *Hamiltonian operator*. The meaning of this equation is simple. If we act on the function by the Hamiltonian operator, we obtain as a result the same function multiplied by a scalar, and this scalar is the energy of the system, E. Let's consider the solution of the Schrödinger equation for the hydrogen atom. For this, we introduce a spherical coordinate system with angles θ and φ and a distance from given point to the origin of coordinates (r), where the angle θ is the angle between the *r* vector and the *z* axis and φ is the angle between the projection of the *r* vector on the *xy* plane and the *x* axis. In this case we can obtain the solution of the Schrödinger equation for the hydrogen atom in the following form:

$$\Psi(r,\theta,\varphi) = R_{n,l}(r)\Theta_{l,ml}(\theta)\Phi_{ml}(\varphi),$$

where $R_{n,l}(r)$ is the radial part of the wave function depending only on the *r* vector, and product of the $\Theta_{l,ml}(\theta)$ and $\Phi_{ml}(\varphi)$ functions is angular part of the wave function depending only on the angles θ and φ. The radial component is also dependent upon the integer numbers *n* and *l*, whereas the angular component depends on the integer numbers *l* and m_l. The numbers *n*, *l*, and m_l are called quantum numbers. We consider them in more detail.

Quantum numbers

The principal quantum number *n* determines the energy quantization, that is, the orbital level energy or ‘shell’ energy. The principal quantum number *n* may have any positive integer value between 1 and ∞ (infinity). The following letter designations correspond to these values: 1, 2, 3, 4, 5, *etc.* – K, L, M, N, O, *etc.*

The value of the orbital quantum number *l* determines the quantization of the angular momentum of the electron within the orbital, that is, orbital angular momentum or the orbital shape. For a given value of the principal quantum number *n*, the allowed values of *l* are positive integers lying between 0 and (n–1). The following letter designations correspond to these values: 0, 1, 2, 3, 4, *etc.* – *s*, *p*, *d*, *f*, *g*, *etc.*

The magnetic quantum number m_l determines the quantization of the projection of the orbital angular momentum of the electron on a given direction (which is defined only by the magnetic field). For a given quantum number *l*, the magnetic quantum number m_l has values which are integers between $-l$ and $+l$ (a total of $2l+1$ values), for example, at $l = 2$ we get m_l: –2, –1, 0, 1, 2. In other words the number of m_l values gives the number of orbitals of given type *l*.

When solving the Schrödinger equation, only three considered quantum numbers are obtained and these numbers determine the orbitals of electrons. However, the solution of the *Dirac equation* in relativistic approximation (that is taking into account the finite speed of light) gives fourth quantum number, the spin quantum number, s. In a mechanical picture, an electron may be considered to spin about an axis passing through it and so possesses spin angular momentum in addition to the orbital angular momentum discussed above. The spin quantum number s determines the quantization of the spin angular momentum of an electron and can only have a value of ½. The magnetic spin quantum number m_s determines the quantization of the projection of the spin angular momentum on a given direction (which is defined only by the magnetic field), and this projection has values of +½ or –½ only.

There is a very important *Pauli exclusion principle*: no two electrons in an atom can have exactly the same set of n, l, m_l, and m_s quantum numbers. In accordance with the Pauli exclusion principle this means that each orbital can accommodate a maximum of two electrons with different m_s values.

The principles of the atomic orbitals filling

Let consider the principles of filling atomic orbitals in the ground state, that is, in the state with the lowest energy (in German these rules are called the *Aufbau principle*). There are four such following principles:

1) Orbitals are filled in order of energy with the lowest energy orbitals being filled first.

2) The *Pauli exclusion principle* (considered above).

3) *The Hund's rule* that is as follows: if there is a set of orbitals with the same energy (so-called degenerate orbitals), pairing of electrons in an orbital cannot begin until each orbital in the set contains one electron. Electrons singly occupying orbitals in a degenerate set have the same (parallel) spins.

4) *Klechkovsky rules*, first and second. The *first Klechkovsky rule* is the following: orbitals are filled with increasing values of the sum of two quantum numbers, n and l. The *second Klechkovsky rule* is the following: in the case of the same values of possible sums of two quantum numbers, n and l, state with the lowest value n is filled first.

It should be added that there are extra stable electronic configurations with half or completely filled sublevels with given values of the orbital quantum number l, notably, s^2, p^3, p^6, d^5, d^{10}, f^7, f^{14}. Filling such sublevels leads to violation of the Klechkovsky rules and to the so-called dip of electrons.

Considered principles allow explain the order of filling the electron shells of elements in the *Mendeleev Periodic Table*. Indeed, the order of occupying atomic orbitals in the ground state of an atom usually follows the sequence that corresponds periods from I to VII (see also groups of *s*-, *p*-, *d*- and *f*-elements, lowest energy first):

$1s <$
$2s < 2p <$
$3s < 3p <$
$4s < 3d < 4p <$
$5s < 4d < 5p <$
$6s < 4f \sim 5d < 6p <$
$7s < 5f \sim 6d < 7p$

(However, for example, for the chromium atom the $3d^54s^1$ configuration instead of $3d^44s^2$ configuration is realized and for the copper atom the $3d^{10}4s^1$ configuration instead of $3d^94s^2$ configuration is realized and these are examples of the dip of electrons).

Problem 4.1: How many *p* and *d* orbitals are possible on each energy level?

Solution: The number of orbitals for a given orbital type depends on the quantity of the magnetic quantum numbers m_l. The *p* orbital corresponds to the orbital quantum number $l = 1$. The quantity of m_l can be calculated by formula $2l + 1$. So there are $2\cdot1+1 = 3$ orbitals of *p* type.

For *d* orbitals the orbital quantum number l equals 2. Therefore, there are $2\cdot2+1 = 5$ different m_l numbers for $l = 2$ and 5 orbitals of *d* type.

Problem 4.2: What sublevels are filled after filling 4*p* and 4*d* sublevels?

Solution: According to Klechkovsky rules the sublevels with lower $n + l$ and n are filled first. For 4*p* shell $n + l = 4 + 1 = 5$ and $n = 4$, so for the next fill sublevel $n +$

l = 5 and n = 5. For the 5s sublevel the sum $n + l = 5 + 0 = 5$ and $n = 5$, so this sublevel will be filled after 4p.

For 4d sublevel the sum $n + l = 4 + 2 = 6$ and $n = 4$. So the next fill sublevel should have the same $n + l = 6$ and $n = 5$. For the 5p this is the case.

Wave function

Let's analyze in more detail the properties of the wave function. The square of wave function is proportional to the probability of finding an electron at a point in space. Wave functions are usually normalized to unity. This means that the probability of finding the electron somewhere in space is taken to be unity. Mathematically, the normalization is represented by the integral equation, where the integrating (that is summing) over all space volumes (dV) gives unity. According to above discussion, the $\Psi^2(r,\theta,\varphi)$ function consists of product of the radial part $\{R^2(r)\}$ and the angular part $\{\Theta^2(\theta)\Phi^2(\varphi)\}$:

$$\Psi^2(r,\theta,\varphi) = R^2(r)\Theta^2(\theta)\Phi^2(\varphi)$$

Consider first the radial part and introduce the *radial distribution function* that is given by the expression $4\pi r^2R^2(r)$. It gives the probability of finding an electron in a spherical shell of radius r and thickness dr. The radius r is measured from the nucleus.

Let’s present graphically the dependences of the radial distribution function on radius r for different orbitals (Fig. 4.1).

From the graph we can see maximums and nodes (for 2s, 3p, 4d and 5f orbitals, but not for 1s, 2p, 3d and 4f orbitals). The number of nodes equals $(n – l – 1)$. It is important that electrons may penetrate in inner layers of atom and present with some probability in any point of space (at large distances the radial distribution function is small but finite).

Let now present the angular parts of a wave function, $\Theta^2(\theta)\Phi^2(\varphi)$, that reproduce shapes of orbitals with different quantum numbers (Fig. 4.2).

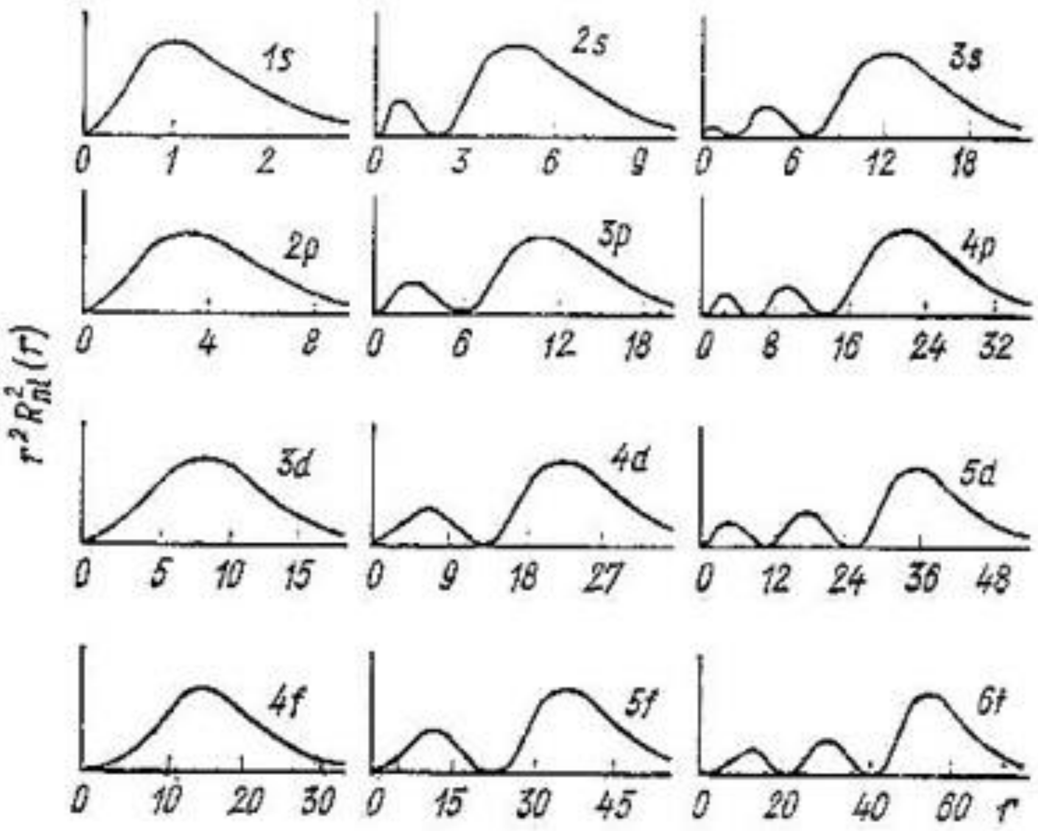


Fig. 4.1. The radial distribution functions for different orbitals.

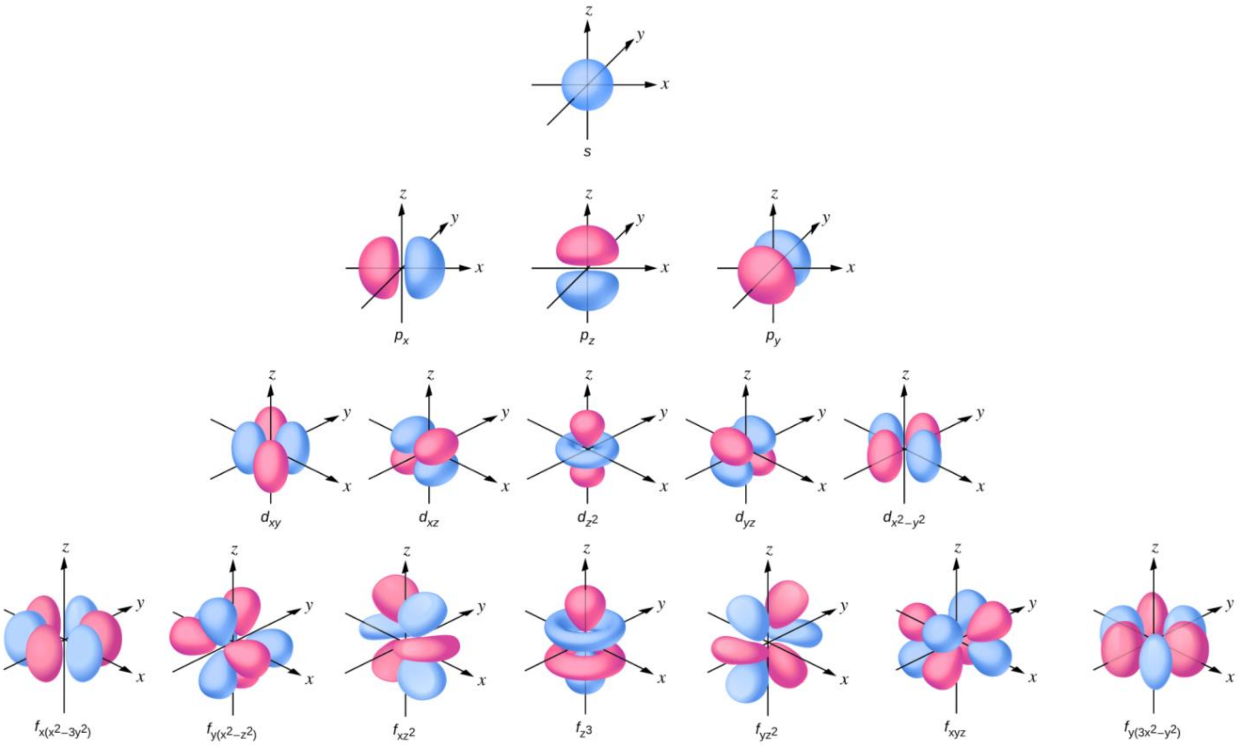


Fig. 4.2. The shapes of different electron orbitals.

Periodic table and properties of atoms

Let’s consider how electrons in atoms influence on one another. Electron-electron interactions appear in two effects, so-called *penetration* and *shielding*. There are two types of electrostatic interaction at work: 1) electrostatic attraction between the nucleus and an electron; 2) electrostatic repulsion between electrons. As can be seen from the above graphics of the radial distribution function, there is a region of space relatively close to the nucleus in which the 2*s* electron is likely to be found, such a region is absent for 2*p* orbital. In effect, an electron in the 2*s* orbital will spend more time nearer to the nucleus than an electron in the 2*p* orbital. This is described as a penetration effect. Thus, the 2*s* orbital penetrates more than the 2*p* orbital. Moreover, in such a way the 2*s* electron screens or shields the 2*p* electron from electrostatic attraction to nucleus, and the 2*p* electron feels the effective nuclear charge Z_{eff}, that is less than actual nuclear charge Z on a constant S: $\text{Z}_{\text{eff}} = Z - S$. This phenomenon is described as a shielding effect. Thus, the 2*s* orbital is more penetrating and more shielding than the 2*p* orbitals. In the whole, the value of penetrating and shielding effects are decreased in the same order for different orbitals: $s > p > d > f$. As a result of week penetrating and shielding effects for *d* and *f* orbitals the so-called *d*- and *f*-contraction are realized. For example, for fourth group, the radius of the Ti atom is less than for the Zr atom, but the radius of the Hf atom is about the same as for the Zr atom, because of filling 4*f* orbitals of the Hf atom (that is *f*-contraction or lanthanoid contraction): Ti < Zr ~ Hf. Analogical tendency appears in the rows Cr < Mo ~ W and V < Nb ~ Ta.

Generally, when moving down a group of the Periodic system, the atom radius increases due to the increase in electron-electron repulsion. When moving to the right along the period of the Periodic system the atom radius decreases due to the increase of the effective charge of the nucleus and the contraction of the electron density to nucleus. As a result, there is periodic dependence of the atom radius on the atomic number.

Consider another characteristic of atoms, notably, the *ionization potential* and the *electron affinity*. The ionization energy or ionization potential is the energy required to remove the electron from atom. Ionization energy (I) is expressed often in the electron-volts, 1 eV = $1.602 \cdot 10^{-19}$C·1V·$6.022 \cdot 10^{23}$ mol^{-1} = 96.49 kJ/mol. For removing the first, second, and third electron, the first, second, and third ionization potentials are introduced respectively, *etc*. At moving down a group of the Periodic system, the ionization potential decreases due to the increase of electron-electron repulsion. At moving to the right along the period of the Periodic system the ionization potential increases due to the increase of the effective charge of the nucleus. That is, the changing the ionization potentials are inversely related to the changing the radii which have been already considered. However, increasing the ionization potentials in the period are non-monotonic, reflecting above mentioned extra-stabilization of electronic configurations with half or completely filled sublevels for given values of the orbital quantum number l, for example, s^2, p^3, and p^6. Note that at ionization of the first and second electrons from the 3*d*-transition metal with electron configuration $3d^n4s^2$, namely *s*-electrons are removed first, because the *s* orbitals are more shielding than the *d* orbitals and removing the *s* electrons greatly increases the effective charge of the nucleus and enhances the attraction to him remaining *d*-electrons.

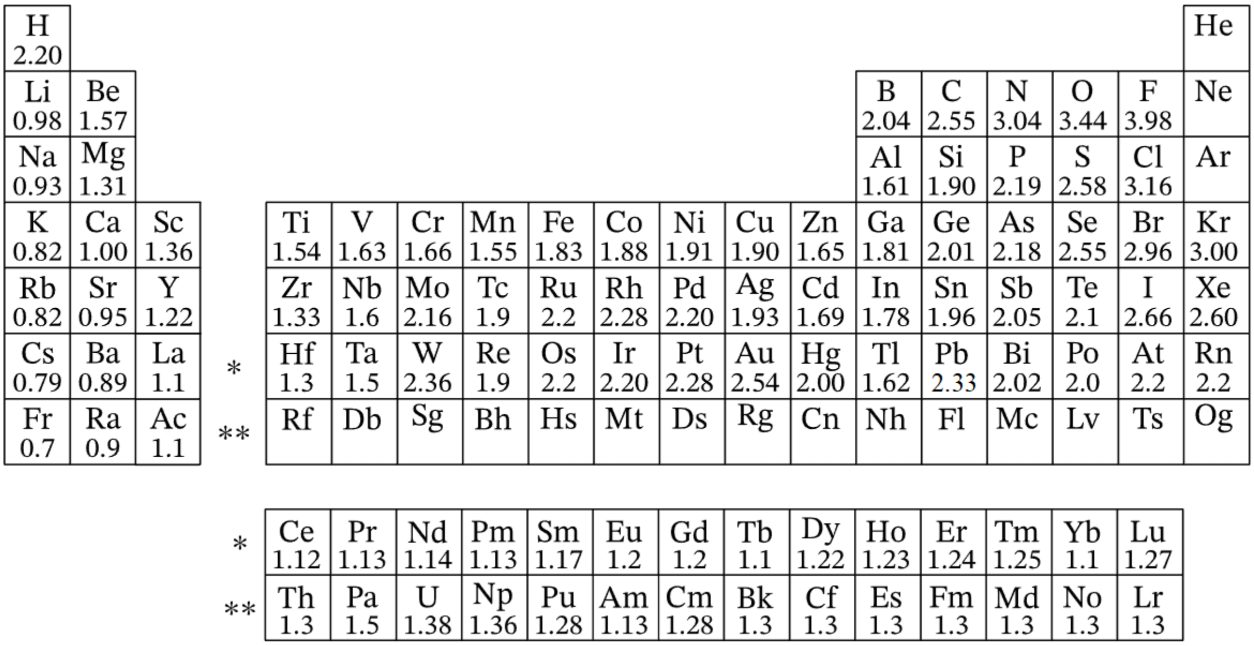
The electron affinity (A) is the energy that accompanies the attachment of an electron to a neutral atom. It is considered to be positive and negative, when the energy is released and absorbed respectively. For metals the electron affinity is negative, but for non-metals it is positive. However, the correlation of electron affinity with an atom radius is absent in view of electrostatic repulsion with entered electron.

Let's introduce the concept of *electronegativity* which was first proposed by Linus Pauling. The electronegativity of an atom is the force with which this atom attracts an electron in a molecule. By Allred-Rochow, this force is proportional to the effective nuclear charge (Z_{eff}) and inversely proportional to its radius (r) squared:

$$\chi = 3590Z_{eff}/r^2 + 0.744$$

Electronegativity values for different atoms (by Pauling) are given in the Table below.

Table 4.1. Electronegativity values of elements by Pauling

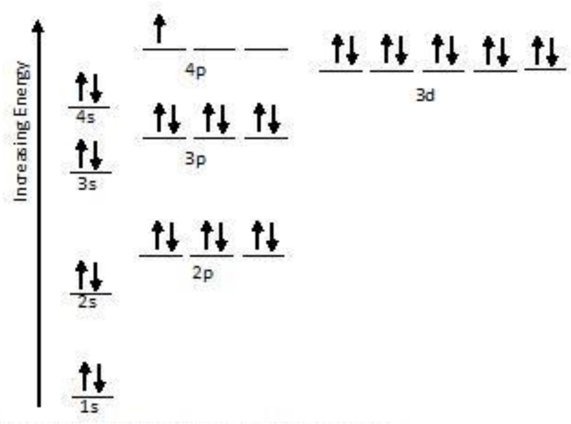


H 2.20																		He
Li 0.98	Be 1.57												B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31												Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36		Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22		Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	La 1.1	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	Ac 1.1	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

*	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
**	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

Problem 4.3: Write electron-graphical scheme of the Ga atom.

Solution:



Electron configuration: $1s^22s^22p^63s^23p^63d^{10}4s^24p^1$.

Problem 4.4: What sublevel is filled after filling 5*p* and 5*d* sublevels?

Problem 4.5: Write electron-graphical scheme of the following atoms in ground state: a) Cr, b) Cu, c) Sm.

Problem 4.6: Write electron-graphical schemes of Fe^{2+} and Fe^{3+} ions. Can you explain higher stability of the electronic configuration of Fe^{3+} ion?

Theme V
Chemical Bond

There are five types of chemical bond: ionic bond (*e.g.*, NaF), covalent bond (*e.g.*, SiC), metallic bond (*e.g.*, metallic Na), van der Waals bond (*e.g.*, between CH_4 in solid state) and hydrogen bond (*e.g.*, HF···HF). We consider only covalent bond. For description of covalent bond two theories may be used, notably, *Valence bond* theory (VB) and *Molecular orbitals* theory (MO).

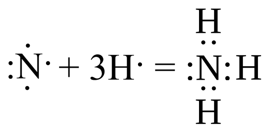
Valence bond theory

VB model considers only electrons at the highest energy levels, such electrons are called external or valence electrons. There are two basic principles of the VB theory.

The first principle: chemical bond between two atoms is formed by the common electron pairs, with two possibilities:

1) Each atom gives on the bond one electron (these electrons must have opposite spins in accordance with the Pauli principle and are called shared pair):

$H\cdot + H\cdot = H:H$ nonpolar covalent bond (the dote means an electron).

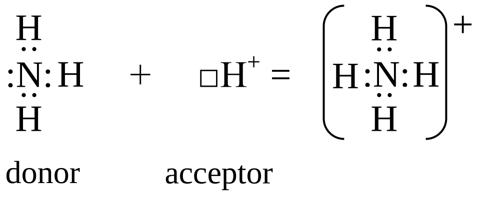


$$:\underset{\cdot}{\dot{N}}\cdot + 3H\cdot = :\overset{H}{\overset{\cdot\cdot}{\underset{\underset{H}{\cdot\cdot}}{N}}}:H$$

polar covalent bonds, because a nitrogen is more electronegative.

A pair of electrons belonging only to nitrogen in NH_3 molecule is called a lone pair.

2) One atom provides the lone electron pair, and the second atom provides a vacant orbital, the first atom is called a donor, and the second is an acceptor, and such a bond is called donor-acceptor bond:

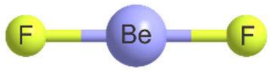


$$:\overset{H}{\overset{\cdot\cdot}{\underset{\underset{H}{\cdot\cdot}}{N}}}:H \quad + \quad \square H^+ = \left(H:\overset{H}{\overset{\cdot\cdot}{\underset{\underset{H}{\cdot\cdot}}{N}}}:H \right)^+$$

The second principle: the most stable bond is formed in the direction of maximum overlapping orbitals. To provide such overlapping the hybridization of orbitals (in other words, mixing orbitals) is introduced. Examples of hybridization leading to various forms of the molecules are the following: *sp* (linear form), sp^2 (trigonal form), sp^3 (tetrahedron), dsp^2 (square-planar form), d^2sp^3 (octahedron), *etc*. Wherein each atom tends to get the more stable electronic shell containing eight electrons with the configuration ns^2np^6 (that is so-called octet rule).

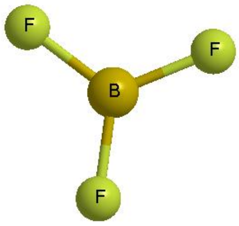
In the dichlorine molecule (Cl_2), the back donation bonds are realized that is each atom is donor by one orbital and acceptor by another orbital (this phenomenon is called as a *back donation*).

1) BeF_2: *sp* hybridization



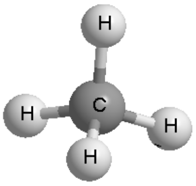
linear structure

2) BF_3: sp^2 hybridization



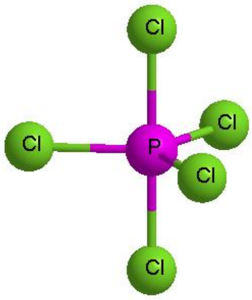
trigonal structure

3) CH_4: sp^3 hybridization



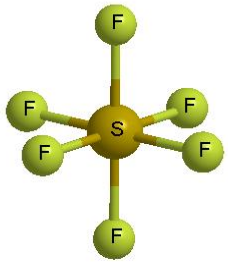
tetrahedral structure

4) PCl_5: dsp^3 hybridization



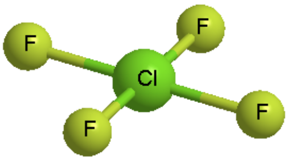
trigonal bipyramidal structure

5) SF_6: d^2sp^3 hybridization



octahedral structure

6) $[ClF_4]^-$: dsp^2 hybridization



square-planar structure

At formation of chemical bonds, the electron density between the atoms is unequal distributed, shifting to a more electronegative atom. Such a shift is quantitatively characterized by the dipole moment. The dipole moment is a vector ($\boldsymbol{\mu}$) whose length is equal to the product of the electron charge on the length from the mass center of the positive charge to the mass center of the negative charge ($\boldsymbol{l}$), and this vector is directed from the mass center of the positive charge to the mass center of the negative charge:

$$\boldsymbol{\mu} = q\boldsymbol{l}$$

The dipole moment of molecule is a vector sum of dipole moments of all bonds.

Problem 5.1: Explain the bond formation by the valence bond theory, write hybridization type and draw the structure of the following molecules:

a) $AlBr_3$, b) AsF_5, c) NH_3, d) SF_4, e) ClF_3, f) H_2O.

Problem 5.2: Which of the molecules in Problem 5.1 have nonzero dipole moment?

Problem 5.3: Explain the bond formation by the valence bond theory, write hybridization type and draw the structure of the following molecules:

a) SOF_4, b) SO_3, c) $[CO_3]^{2-}$, d) NO_2, e) Cl_2O.

Molecular orbitals theory

The Valence bond theory explains well the bonds formation and structures of many molecules. However, there are molecules whose formation cannot be explained by VB theory, for example H_2^+, He_2^+. Also VB theory cannot explain the increasing bond strength with decreasing the number of electrons in some molecules, for example in the row O_2^{2-}, O_2^-, O_2, O_2^+.

Consider the theory of the Molecular orbitals as linear combinations of atomic orbitals (MO LCAO). In this theory assumed that some atomic orbitals are combined in molecular orbitals, so electrons on such orbitals belong to the whole molecule. These combinations result in bonding and anti-bonding orbitals of appropriate symmetry. The electrons of bonding orbitals bind the molecule and those of anti-bonding orbitals break it apart. In the case of the symmetry inconsistency, some of atomic orbitals remain nonbonding orbitals.

Principles of filling molecular orbitals are the same as for atomic orbitals:

1) Orbitals are filled in order of energy with the lowest energy orbitals being filled first.

2) The Pauli exclusion principle.

3) The Hund's rule. If there is a set of orbitals with the same energy (so-called degenerate orbitals), pairing of electrons in an orbital cannot begin until each orbital in the set contains one electron. Electrons singly occupying orbitals in a degenerate set have the same (parallel) spins.

The so-called bond order n is given by the relation:

$$n = (N - N^*)/2$$

where N and N^* are the numbers of electrons on the bonding and anti-bonding orbitals respectively. Division by two in this relation means that the one bond also involves two electrons as in the VB model, but in the general case, the bond order can be fractional. Let's draw the schemes of molecular orbitals for H_2, He_2, He_2^+:

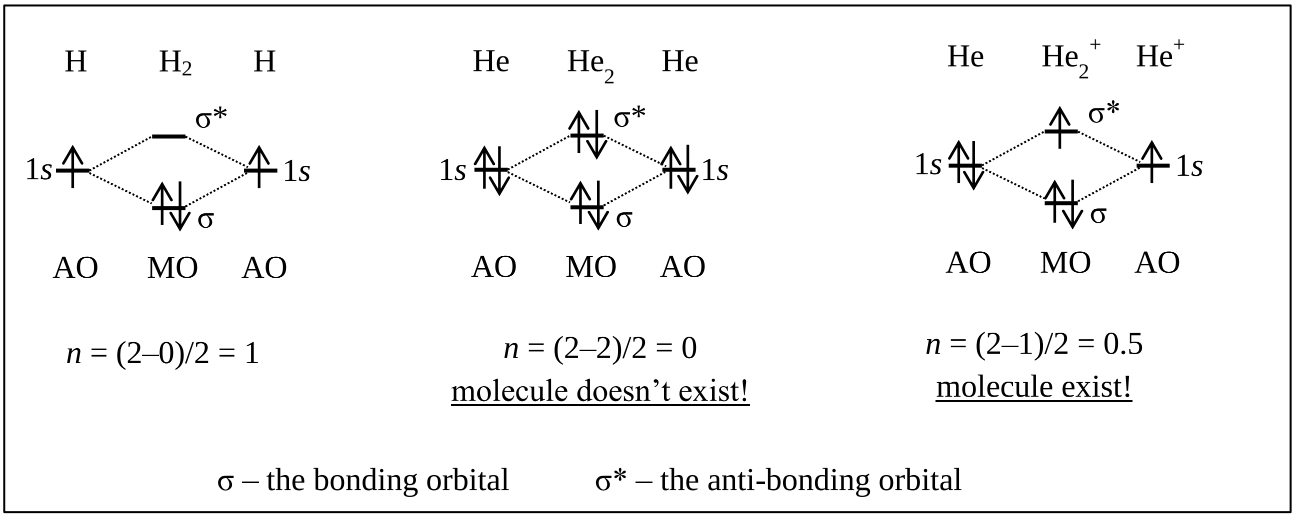


Fig. 5.1. The schemes of molecular orbitals for some molecules (AO – atomic orbital, MO – molecular orbital).

Other examples of application of the MO theory to the diatomic molecules (N_2, NO) are presented on Figure 5.2:

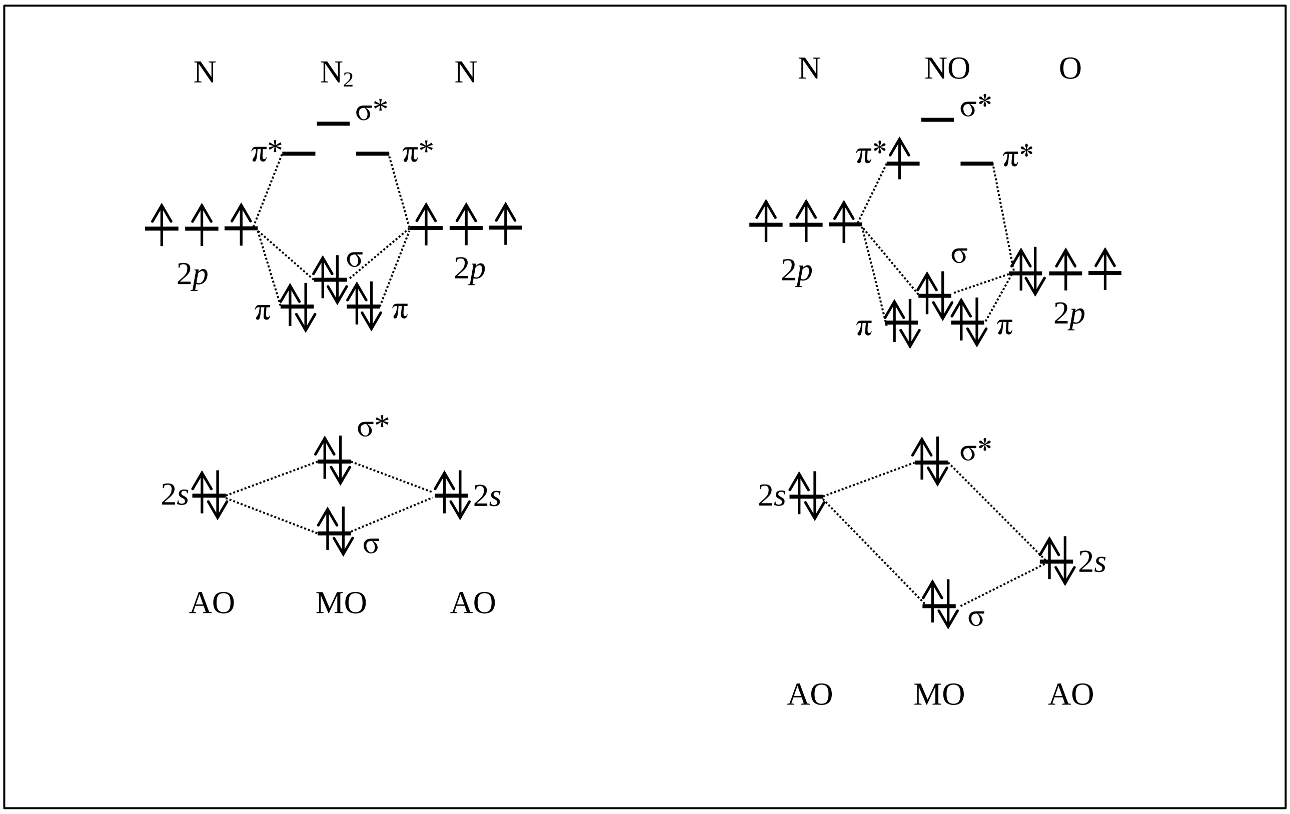


Fig. 5.2. The schemes of molecular orbitals for some molecules (AO – atomic orbital, MO – molecular orbital). Because an oxygen has bigger charge, its AOs have lower energy.

Problem 5.4: Draw MO LCAO diagrams for the following molecules: O_2^+, O_2, O_2^-, O_2^{2-}. Explain the decreasing bond strength in this row of molecules.

Theme VI
Energetics of Chemical Processes

For consideration of energetics of chemical processes, very powerful theory and methods of science called *Thermodynamics* are used. Let's give definition: a thermodynamic system is the region of space that contains a body or several bodies with large number of particles, from 1000 particles (and more but usually about Avogadro number, ~10^{23}). An open system is able to exchange matter and energy with the surroundings. A closed system can exchange energy with the surroundings, but matter cannot be exchanged. An isolated system is completely insulated from the surroundings and cannot exchange both energy and matter.

State parameters are the univocal parameters of state, notably, P, V, and T. This means that just one set of three numbers corresponding P, V, and T characterizes given state. Volume (V) is the external parameter that depends from disposition of external bodies. Pressure (P) is the internal parameter dependent from behavior of particles in the system (of course, an external parameter depends also from an internal parameter). Temperature (T) is the very complex parameter, it is called "driving force" of heat and determines a direction of heat transfer, from system with T_2 to system with T_1, if $T_2 > T_1$. Very important characteristics of a thermodynamic system are *state functions* that depend only on the system state and its state parameters and don't depend on particular ways of the transition from one state to another. The functions of this kind are called the total differentials. State functions are *internal energy* (U), *enthalpy* (H), *entropy* (S), and *Gibbs free energy* (G).

It should be noted that P, V and T are also can be state functions. For example, let's consider ideal gas. It is enough to know only two parameters (e.g. P, V) to calculate the third one (T) by *Clapeyron-Mendeleev Law*. So T is the state function. In generally, we can choose any two values as independent parameters (e.g. P-T, V-T, P-V, S-V, etc.) to calculate other values as state functions.

We consider abovementioned state functions in consecutive order but first define the notions of *phase*, *heat*, and *work.*

Phase is the aggregate of parts of the system that have the same characteristics and are separated from other parts by the phase boundary. As an example, in the system $BaSO_4$–NaCl–H_2O four phases can exist at standard conditions (solid $BaSO_4$, solid NaCl, solution and water vapor).

Heat (Q) and work (A) are the physical values corresponding to energy transfer by the system without changing the external parameter V (heat) and with changing the external parameter V (work) respectively.

First Law of thermodynamics

Consider the *First Law of thermodynamics*. Initially we give the definition of internal energy (U): the internal energy is all the energy of the system with the exception of the energy of its movement as a whole. The change of the internal energy in the transition from state 1 to state 2 is written as follows: $U_2 - U_1 = \Delta U$. The First law of thermodynamics states that the heat (Q) supplied to the system is spent on the internal energy change and on the performance of work against external forces, this Law can be written as the relation:

$$Q = \Delta U + A \text{ or } \Delta U = Q - A$$

The First Law of thermodynamics is a special case of the *Law of the conservation of energy and matter*. Values of ΔU may be negative or positive. In general case, we can't know absolute values of internal energy (U) because all the freedom degrees of the system are unknown and we can determine only the internal energy change (ΔU).

Let's consider three particular cases of the First law of thermodynamics:

1) $Q = 0$ (this process is called as *adiabatic*), then

$$\Delta U = -A$$

2) V = constant (this process is called as *isochoric*), then

$$A = 0 \text{ and } \Delta U = Q$$

3) P = constant (this process is called as *isobaric*), in this case we get

$$Q = \Delta U + A = \Delta U + P\Delta V = (U_2 - PV_2) - (U_1 - PV_1) = H_2 - H_1 = \Delta H$$

where the H_2 and H_1 are the state functions because U_2 and U_1 are the state functions, V_2 and V_1 are the state parameters, and P is the constant state parameter, that is the H

function depends only on the state functions and state parameters. This H state function is called *enthalpy* or heat content, indeed, in this case $\Delta H = Q$. The processes with $\Delta H < 0$ are called *exothermic* and processes with $\Delta H > 0$ are called *endothermic*.

The consequence of the First law of thermodynamics is *Hess's Law of constant heat summation*. This Law states that the thermal effect on going from reactants to products at constant volume (that is the reaction heat, Q) or at constant pressure (that is the enthalpy change, ΔH) is independent of the reaction path taken. But this Law expresses just property of the total differential.

Let's give definition of "*standard state*". A standard state is the state of a system at standard P = 101.325 kPa and fixed temperature (the exact temperature is not specified in this case, but usually T = 298.15 K is taken) for pure substances in condensed or gaseous states and for all components in solution with the concentrations of 1 mol/l. The *standard enthalpy of formation* of a compound, $\Delta_f H^o$, is the enthalpy change at 298 K that accompanies the formation of 1 mole of the compound in its standard state from elementary substances in their standard states. The standard state of an elementary substance at 298 K is the thermodynamically most stable form of the element at standard state. Some examples of the standard states of elements under these conditions are the following: $H_{2(g)}$, $O_{2(g)}$, C (graphite, but not diamond) *etc*. We consider most important consequence of Hess's Law: the value of the standard enthalpy change for a reaction, $\Delta_r H^o$, is the difference between the sum of the standard formation enthalpies of the products ($\Delta_f H_j^o$) and the sum of the standard formation enthalpies of the reactants ($\Delta_f H_j^o$):

$$\Delta_r H^o = \Sigma \nu_j \Delta_f H_j^o - \Sigma \nu_i \Delta_f H_i^o$$

where ν_j and ν_i are the stoichiometric coefficients (or moles) in a reaction for products and reagents respectively. This relation is evident from the graphical representation Fig. 6.1 (from the same elementary substances we obtain both the products and reagents and the difference between their energies is indeed standard enthalpy change for the reaction). It should be emphasize that, by definition, the standard formation enthalpy of elementary substance in its standard state is 0 kJ/mol.

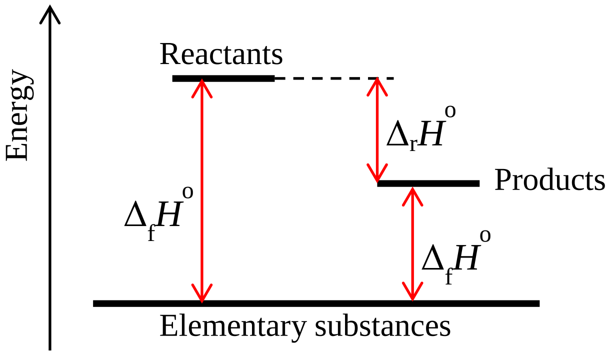


Fig. 6.1. Graphical representation of enthalpy change.

Problem 6.1: Calculate the standard enthalpy change of the reaction:

$$CH_{4\,(g)} + 2O_{2\,(g)} = CO_{2\,(g)} + 2H_2O_{(l)}$$

Solution: Using consequence of Hess's Law we can write:

$$\Delta_r H^o = \Sigma \nu_j \Delta_f H_j^o - \Sigma \nu_i \Delta_f H_i^o = \left(\Delta_f H^o_{CO_2(g)} + 2\Delta_f H^o_{H_2O(l)}\right) - \left(\Delta_f H^o_{CH_4(g)} + 2\Delta_f H^o_{O_2(g)}\right)$$

Then taking into account tabulated values of the standard formation enthalpies of the substances, we get:

$$\Delta_r H^o = (-393.5+2\cdot(-285.8)) - (-74.9+2\cdot 0) = -890.2 \text{ kJ}$$

Second Law of thermodynamics

Consider the *Second Law of thermodynamics*. The First Law of thermodynamics is often stated as "*the perpetual motion machine of the first kind is impossible*". This Law does not constrain the modes of energy transmission. Such constraints introduce the *Second Law of thermodynamics*. There are two equivalent formulations of this Law. The first formulation of Clausius is the following: "*heat can't transfer from a colder to a hotter body without compensation*". The second formulation of Kelvin-Planck states "*impossible to create a machine, the only result of which would be the transformation of the entire amount of heat into work (in other words, "the perpetual motion machine of the second kind is impossible*"). The mathematical expression of the Second Law of thermodynamics requires the introduction of a new state function, *entropy*, *S*. Introduce it through entropy of *isothermic* process (at constant temperature). For example, for the melting process at a constant temperature the following relation can be written:

$\Delta H(\text{melting}) = Q(\text{melting}) = T\Delta S$

Hence we get relation for the new state function, S: $\Delta S = Q/T$ (the dimension of entropy is J/K). Heat Q isn't the state function but heat divided by temperature is the state function. The heat of melting is consumed at increasing disorder. Thus, entropy is a measure of disorder. More precisely, the entropy is interpreted in statistical thermodynamics through the following equation:

$S = k\ln W$

where k is the *Boltzmann's constant* ($k = 1.38\cdot10^{-23}$ J/K) and W is the number of micro-states through which given macro-state is realized. So at the same conditions $S_{(g)} > S_{(l)} > S_{(s)}$.

For a reversible isothermal process we have relation $\Delta S = Q/T$, and for the irreversible isothermal process we get ratio $\Delta S > Q_{irrev}/T$ (because only part of the heat is converted into work according to the Second Law of thermodynamics, $Q_{irrev} < Q$). Then in a reversible adiabatic process (where $Q = 0$) the following relation is fulfilled:

$\Delta S = 0$

and for an irreversible adiabatic process (where $Q_{irrev} = 0$) we have

$\Delta S > 0$

The same relations are valid for the isolated system where also $Q = 0$. Consequently, we get a criterion of irreversibility for the isolated system, $\Delta S > 0$. In such systems entropy increases until it reaches a maximum at which the complete reversibility (that is equilibrium) is achieved.

This is very important result, however, chemists don't work in the isolated systems but work in the isobaric-isothermal conditions, that is at constant pressure and temperature. Is it possible to obtain a condition for the irreversibility in such systems? To do this we need to combine the First and Second Laws of thermodynamics as follows:

$\Delta U = Q - A$

$Q = T\Delta S$

$\Delta U = T\Delta S - A$

Subtracting useless work against external forces, $P\Delta V$, for the rest useful work, A', from the latter equation we obtain the relation

$A' = A - P\Delta V = -\Delta U + T\Delta S - P\Delta V = -(\Delta U + P\Delta V - T\Delta S) = -(\Delta H - T\Delta S) =$

$-\Delta G$

where H and S are the state functions and P and T are the constant state parameters, consequently, G is a new state function. That is, the useful work is done at the decrease of the G function, which is called the *isobaric-isothermal potential* or the *Gibbs free energy* (in honor of J. Willard Gibbs). In the isobaric-isothermal conditions the terms of reversibility and irreversibility of the processes are very simple:

$\Delta G = 0$

for the reversible process (that is in equilibrium) and

$\Delta G < 0$

for the irreversible process. That is process can be spontaneous only if for it the change of the Gibbs free energy is negative:

$\Delta G = \Delta H - T\Delta S < 0$

Upon reaching equilibrium the following relation is fulfilled:

$\Delta G = \Delta H - T\Delta S = 0$

All the possible relationships between the ΔH and ΔS values at which a spontaneously occurring reaction can be realized are presented in the Table:

ΔH	ΔS	ΔG	Spontaneity
–	+	–	Spontaneous
+	–	+	Nonspontaneous
–	–	±	Spontaneous at low enough temperatures
+	+	±	Spontaneous at high enough temperatures

Problem 6.2: Is it possible at standard state conditions and T = 273 K the spontaneous passing reaction with the following thermodynamic parameters, ΔH° = 100 kJ and ΔS° = 200 J/K? At what temperature this reaction will start to proceed?

Solution:

$\Delta H° = 100$ kJ
$\Delta S° = 200$ J/K $= 0.2$ kJ/K

$\Delta G°$ – ?
T – ?

$\Delta G° = \Delta H° - T\Delta S° = 100$ kJ $-$ 273 K·0.2 kJ/K $= 45.4$ kJ > 0

So the reaction is not spontaneous.

To be spontaneous $\Delta G°$ should be negative, therefore:

$$\Delta H° - T\Delta S° < 0$$

$$T > \frac{\Delta H°}{\Delta S°} = \frac{100\ \text{kJ}}{0.2\ \frac{\text{kJ}}{\text{K}}} = 500\ \text{K}$$

Thus at temperature higher 500 K the reaction will be spontaneous.

Third Law of thermodynamics

There is the *Third Law of thermodynamics* which states that a pure, perfect crystal at 0 K has zero entropy, that is, the entropy value tends to zero as the temperature tends to zero,

$S \to 0$ at $T \to 0$ K

In this case we can determine not only change of the entropy, but also the absolute value of entropy at a given temperature, counting its value from zero at temperature of 0 K.

It is important to note that any state function can be considered as a simple member of the algebraic equation of the reaction. Therefore, when we sum, subtract, multiply, or divide the reaction molecules or equations, we have to do the same with the enthalpy, entropy, and Gibbs free energy of the molecule formation or the reaction.

Problem 6.3: Calculate the standard formation enthalpy of methanol if standard enthalpy change of the reaction $\Delta H^0 = -726.5$ kJ:

$CH_3OH_{(l)} + {}^3/_2\, O_{2\,(g)} = CO_{2\,(g)} + 2\, H_2O_{(l)}$

$\Delta H_f^0(CO_{2(g)}) = -393.5$ kJ/mol, $\Delta H_f^0(H_2O_{(l)}) = -285.8$ kJ/mol

Problem 6.4: Is a spontaneous passing of the following reaction possible under standard conditions? At what temperature this reaction will start to proceed?

	$2NO_{2(g)}$	$\rightleftarrows$	$2NO_{(g)}$	+	$O_{2(g)}$	
ΔH^0	34		90		0	kJ/mol
S^0	240		211		205	J/(K·mol)

Problem 6.5: Find ΔG^0 of the reaction at 25, 300 and 900°C neglecting temperature dependence of ΔH^0 and ΔS^0:

$CaCO_{3(s)} = CaO_{(s)} + CO_{2(g)}$

Calculate the temperature at which the reaction starts to proceed spontaneously.

$\Delta H_f^0(CO_{2(g)}) = -393.5$ kJ/mol, $\Delta H_f^0(CaCO_{3(s)}) = -1207$ kJ/mol, $\Delta H_f^0(CaO_{(s)}) = -635.5$ kJ/mol, $S_f^0(CO_{2(g)}) = 213.7$ J/mol·K, $S_f^0(CaCO_{3(s)}) = 88.7$ J/mol·K, $S_f^0(CaO_{(s)}) = 39.7$ J/mol·K.

Theme VII
Chemical Kinetics and Equilibria

Reaction rate

Chemical kinetics has to do with research of the *reaction rates* and *mechanisms*. The reaction rate is the change in concentration of a reactant or a product (Δc) with respect to the time t,

$v = \pm\Delta c/\Delta t,$

and this gives units of the rate as $mol \cdot l^{-1} \cdot s^{-1}$. The reaction rate is always positive, therefore, the plus sign refers to a change in the concentration of the product ($\Delta c > 0$), and the minus sign refers to a change in the concentration of the reactant ($\Delta c < 0$).

Not all molecules take participation in a reaction, but only the most active molecules having energy above a certain value, which is called the activation energy and denoted by E_a. In accordance with the *Maxwell-Boltzmann distribution* the fraction of such molecules increases exponentially with temperature (Fig. 7.1).

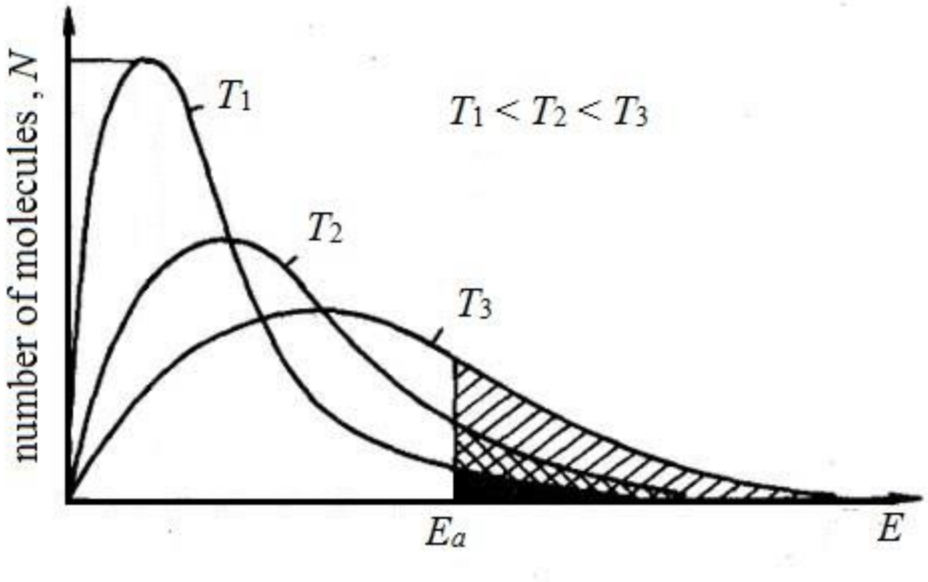


Fig. 7.1. The Maxwell-Boltzmann distribution for different temperatures. An increase in temperature leads to an increase in the number of molecules with an energy higher than the activation energy E_a.

Depict the reaction energy diagram, which shows the energy barriers for the forward and back reaction, that is, the activation energy of these reactions, $E_{\mathrm{a(f)}}$ and $E_{\mathrm{a(b)}}$ respectively.

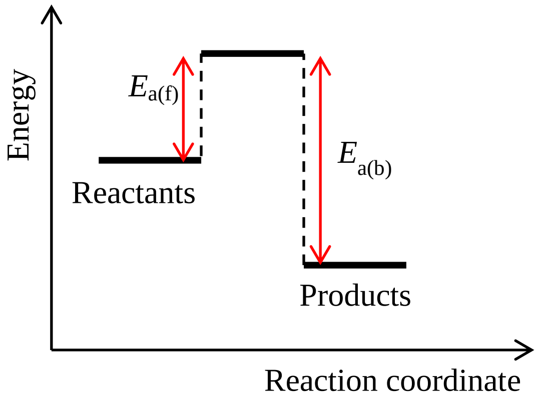


Fig. 7.2. A reaction energy diagram.

It is easy to see that these activation energies are related by a simple equation with the reaction enthalpy:

$$\Delta_r H = E_{\mathrm{a(f)}} - E_{\mathrm{a(b)}}$$

(on the Fig. 7.2 the reaction enthalpy change is negative for the forward reaction and positive for the back reaction).

The reaction rate depends on the nature of the reactants, their concentrations, temperature, and presence of catalysts in the system, and sometimes on the pressure. The concentration dependence of the reaction rate is expressed by the kinetic equation of the following form:

$v = k[A]^a[B]^b[C]^c$

(in the brackets the current concentrations are given). The sum of the concentration powers is called the order of the reaction. This order is determined experimentally and can take any value, including fractional and negative values, because the reaction can proceed in several steps. The k parameter is called the *rate constant* and it is numerically equal to the reaction rate at concentrations of all reagents equal to unity. As can be seen, dimension of the rate constant for the first-order reaction is s^{-1}, for the second-order reaction is $mol^{-1}\cdot l\cdot s^{-1}$, *etc*. If the reaction proceeds in one elementary step, then its order is called the *reaction molecularity* and denotes the number of molecules involved in the reaction. The reaction molecularity may be zero (for solid phase), one, two, and three, but not more.

The kinetic equation for the reactions of the second and third order is called the *Law of mass action* and it reflects the probability of collisions between particles, depending on their concentrations, for example:

$v = k[A][B]$

If the reaction proceeds in several successive steps, the overall reaction rate is limited by the slowest stage.

Let’s solve the kinetic equation for the first-order reaction A → P:

$$-\frac{d[A]}{dt} = k[A].$$

Transform this equation as follows,

$$\frac{d[A]}{[A]} = -kdt$$

after integrating this equation we get the relations for the current concentrations of the reagent A and product P:

$[A] = [A_0]\exp(-kt)$, $[P] = [A_0]\{1 - \exp(-kt)\}$

where $[A_0]$ is the initial concentration of the A reagent at $t = 0$ s. These results can be presented on the graph (Fig. 7.3).

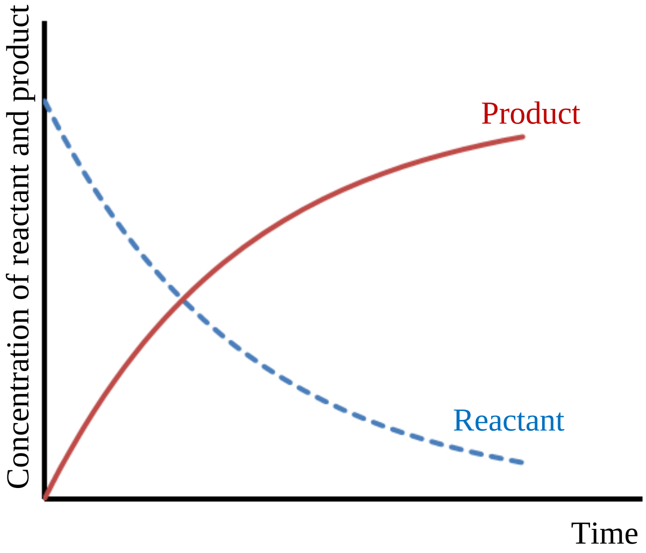


Fig. 7.3. Product and reactant concentration dependences on the reaction time for the first order reaction.

The temperature dependence of the reaction rate may be presented by the *Van't Hoff equation*:

$$v_2 = v_1 \gamma^{\frac{T_2 - T_1}{10}}$$

where temperature coefficient γ = 2-4 for different reactions. In other words, the velocity of chemical reactions is increased in 2-4 times for each rise of 10°C in temperature. However, this experimental rule is not always true.

More accurate description of rate temperature dependence can be given by the *Arrhenius equation* for the temperature dependence of the reaction rate constant:

$$k = Ae^{-\frac{E_a}{RT}}$$

where E_a is the *activation energy*, R is the gas constant, and A is the *pre-exponential factor*.

Problem 7.1: Find the activation energy of a reaction, if after increasing temperature from 290 K until 300 K, the reaction rate becomes twice as much.

Solution:

T_1 = 290 K

T_2 = 300 K

$\frac{v_2}{v_1} = 2$

E_a – ?

Because we consider one reaction the ratio of the reaction rates at different temperatures equals to the ratio of the reaction rate constants:

$$\frac{v_2}{v_1} = \frac{k_2}{k_1} = \frac{Ae^{-\frac{E_a}{RT_2}}}{Ae^{-\frac{E_a}{RT_1}}} = e^{-\frac{E_a}{RT_2}-\left(-\frac{E_a}{RT_1}\right)} = e^{\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} = 2$$

$$\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = ln2$$

$$E_a = \frac{Rln2}{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)} = \frac{RT_1T_2ln2}{T_2 - T_1} = \frac{8.31 \cdot 290 \cdot 300 \cdot 0.693}{300 - 290}$$

$$= 50.1\,\frac{\mathrm{kJ}}{\mathrm{mol}}$$

Chemical equilibria

Let's consider the *chemical equilibria* and start from example of the following reaction:

A + B = C + D

The rate of the forward reaction is decreased in time because decreasing concentrations of A and B, and the rate of the back reaction (C + D) is increased in time because increasing concentrations of C and D. Therefore in some moment the rates of both reactions become equal and equilibrium is established:

$v_\mathrm{f} = v_\mathrm{b}$

$v_\mathrm{f} = k_\mathrm{f}[\mathrm{A}][\mathrm{B}]$

$v_\mathrm{b} = k_\mathrm{b}[\mathrm{C}][\mathrm{D}]$

For this case we have:

$$\frac{k_\mathrm{f}}{k_\mathrm{b}} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} = K$$

where *K* is the *equilibrium constant*. In general case, the following equation can be written:

$$K = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

where *c*, *d*, *a* and *b* are the coefficients of the reaction $aA + bB = cC + dD$. It should be noted that concentrations of solids are not included in the expression for equilibrium constant, only concentrations of gaseous and liquid substances.

The equilibrium constant is related to the change of the *standard Gibbs free energy* ΔG^o by equation:

$$\Delta G^o = -RT\ln K = -2.3RT\log K \text{ (where } \Delta G^o = \Delta H^o - T\Delta S^o\text{)}$$

There is very important *Le Chatelier's principle* for the equilibria. Le Chatelier’s principle states that when an external change is made to a system in an equilibrium, the system will respond so as to oppose the change to achieve a new equilibrium state (Fig. 7.4).

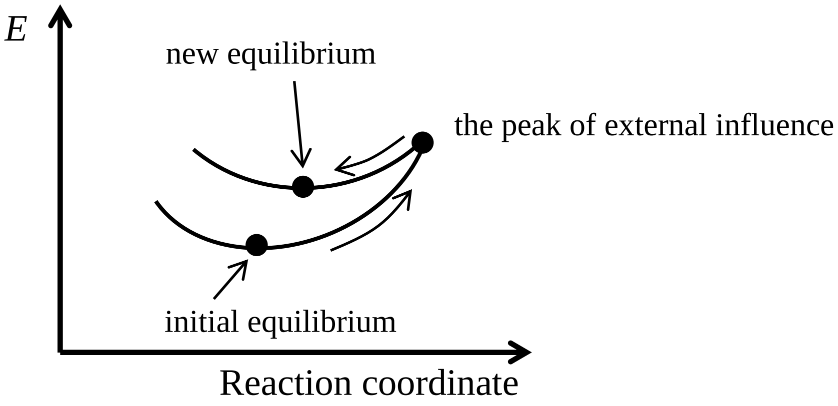


Fig. 7.4. Graphical representation of Le Chatelier's principle.

Consider the consequences of Le Chatelier principle. If the reaction proceeds with release of energy (exothermic process with $\Delta H^o < 0$), then increasing temperature must shift equilibrium toward the energy absorption, that is in the direction of the back reaction. And if the reaction proceeds with absorption of energy (endothermic process with $\Delta H^o > 0$), then increasing temperature must shift equilibrium toward the energy absorption, that is in the direction of the forward reaction. If the number of molecules in the reaction decreases, then increasing their concentrations must shift equilibrium toward the forward reaction, decreasing the reagent concentrations and *vice versa*. Similarly if the number of gaseous particles in the forward reaction decreases, then the pressure increase will shift the equilibrium toward the forward reaction to reduce pressure, because pressure depends on the number of gaseous molecules.

Problem 7.2: The reversible reaction proceeds according to the equation A + B = C + 2D. Initial concentration of each reactant is 6 mol/l. After equilibration we have [C] = 1.2 mol/l. Calculate the equilibrium concentrations of other substances, the equilibrium constant, and the standard Gibbs free energy change.

Solution:

$[A]_0 = [B]_0 = 6$ mol/l
$[C] = 1.2$ mol/l

[A] – ? [B] – ?
K – ? ΔG – ?

Let multiply equation by x:
xA + xB = xC + 2xD
It is seen that x moles of A and B are needed to obtain x moles of C and 2x moles of D. Because [C] = 1.2 mol/l, so $x = 1.2$ mol/l and [D] = 2x = 2.4 mol/l.
Therefore 1.2 mol/l of A and B came in the reaction to form products. So equilibrium concentrations of A and B are the following:
$[A] = [A]_0 - 1.2 = 6 - 1.2 = 4.8$ mol/l
$[B] = [B]_0 - 1.2 = 6 - 1.2 = 4.8$ mol/l

Equilibrium constant:

$$K = \frac{[C][D]^2}{[A][B]} = \frac{1.2 \cdot 2.4^2}{4.8 \cdot 4.8} = 0.3$$

$\Delta G^o = -2.3RT\log K = -2.3 \cdot 8.31 \cdot 273 \cdot \log(0.3) = 2.73$ kJ

Problem 7.3: The increase temperature on 40 °C results in the increase of the reaction rate in 32 times. Calculate the temperature coefficient (γ) of the chemical reaction.

Problem 7.4: Calculate the value of the activation energy, if the reaction rate at 310 K in 25 times higher than the reaction rate at 280 K.

Problem 7.5: Under equilibrium of the reaction

$$N_2\,(g) + 3H_2\,(g) \rightleftarrows 2NH_3\,(g) \qquad \Delta H^0 = -92.4 \text{ kJ}$$

the concentration of substances are the following: $[N_2] = 4$ mol/l, $[H_2] = 12$ mol/l, $[NH_3] = 6$ mol/l.

Find: *a*) the initial concentration of reagents; *b*) in which direction the equilibrium will shift with increasing temperature; *c*) in which direction the equilibrium will shift with increasing pressure; *d*) calculate the equilibrium constant.

Problem 7.6: For the reaction $FeO_{(s)} + CO_{(g)} \rightleftarrows Fe_{(s)} + CO_{2(g)}$ the equilibrium constant is 0.7 at some temperature. Find the equilibrium concentrations of CO and CO_2 if the initial concentrations are the following: $[CO]_0 = 0.07$ mol/l, $[CO_2]_0 = 0.015$ mol/l. Calculate ΔG^o of the reaction.

Theme VIII
Solutions, Solubility, and Modes of Concentrations Expressing. Properties of the Non-electrolyte Solutions

Let's start with a definition of what the solutions are. *Solutions* are homogeneous (that is, single-phase) dispersed systems of variable composition in a state of chemical equilibrium. The solutions differ from suspensions in that the latter are non-homogeneous, that is, containing at least two phases separated by an interface. There are *colloidal systems* that is micro-heterogeneous systems with relatively small dimensions of the dispersed particles. Solutions are stable over time, the suspensions are unstable, and the colloidal solutions are relatively stable. We know that in crystals a short-range order and a long-range order are present, and there is no order in gas. Liquids occupy an intermediate position between crystals and gases, they have a short-range but no long-range order. *Glasses*, that is super-cooled liquids, have properties similar to solutions but in solutions the equilibrium between the associates is labile while it is frozen in the glasses.

Types of concentrations

There are many ways of expressing solution concentrations, let’s consider some of them:

1) The *mass fraction* (denoted as ω)

$$\omega = \frac{m_{solute}}{m_{solution}}$$

The mass fraction of a component is the ratio of the mass of this component to the sum of the masses of all components of the solution. A mass fraction is a dimensionless quantity (it can be expressed as a percentage, but the percentage is not a dimension).

2) The *mole fraction* (denoted as X)

$$X = \frac{n_{solute}}{\sum n_i}$$

The mole fraction of a component of a solution is the ratio of the number of moles of the given component to the sum of the moles of all components. For example, for a two component solution with the n_1 moles of the first component and n_2 moles of the second component we have $X_1 = n_1/(n_1+n_2)$ and $X_2 = n_2/(n_1+n_2)$. Mole fraction is also dimensionless quantity.

3) The *molar concentration or molarity* (denoted as c_{M})

$$c_{\mathrm{M}} = \frac{n_{solute}}{V_{solution}}$$

The molar concentration is the number of moles of a solute per liter of solution (the concentration dimension is mol/l or simple M).

4) The *normal concentration* or equivalent concentration or normality of solution (denoted as c_{N})

$$c_{\mathrm{N}} = \frac{n_{eqv}}{V_{solution}}$$

The normal concentration is the number of equivalents of a solute per liter of solution (the concentration dimension is also mol/l or N). To find n_{eqv} we need to divide the mass of a solute on its equivalent mass ($n_{eqv} = \frac{m}{M_E}$).

5) The *molal concentration or molality* (denoted as c_{m} or m, not to be confused with mass!)

$$c_{\mathrm{m}} = \frac{n_{solute}}{m_{solvent}}$$

The molal concentration is the number of moles of a solute per kilogram of a solvent (the concentration dimension is mol/kg).

Problem 8.1: What the volume of the concentrated hydrochloric acid with density ρ = 1.19 g/ml, containing 38% of hydrogen chloride HCl, need to take for preparation of 1 liter of solution with normality of 2 mol/l?

Solution:

ρ_1 = 1.19 g/ml = 1190 g/l
ω_1 = 0.38
V_2 = 1 liter
c_{N2} = 2 N

V_1 – ?

Solving all such problems should be started with writing the following equation:

$c_{M1}V_1 = c_{M2}V_2$ or $c_{N1}V_1 = c_{N2}V_2$

$$\text{So} \quad V_1 = \frac{c_{N2}}{c_{N1}}V_2$$

To find V_1 it is needed to calculate c_{N1} using known values ρ_1 and ω_1.

Because the basicity of HCl is 1 then $c_{N1} = c_{M1}$.

$$c_M = \frac{n_{\text{solute}}}{V} = \frac{\frac{m_{\text{solute}}}{M_{\text{solute}}}}{\frac{m_{solution}}{\rho}} = \frac{m_{\text{solute}}\rho}{m_{solution}M_{\text{solute}}} = \frac{\omega\rho}{M_{\text{solute}}}$$

$$c_{N1} = c_{M1} = \frac{\omega_1\rho_1}{M_{\text{HCl}}} = \frac{0.38 \cdot 1190}{36.5} = 12.4\ \text{N}$$

Now we can calculate V_1:

$$V_1 = \frac{c_{N2}}{c_{N1}}V_2 = \frac{2}{12.4} \cdot 1 = 0.161\ \text{liter} = 161\ \text{ml}$$

Dissolution

Let’s consider the *dissolution process*. This process involves the destruction of the structure of a solute plus solvation (called hydration in the case of water) to form solvates (called hydrates in the case of water) due to donor-acceptor, dipole-dipole interactions and the formation of hydrogen bonds. Therefore, the enthalpy of the solution of a substance is the sum of the *enthalpy of destroying* the structure of the solute and the *enthalpy of solvation*:

$$\Delta_{\text{sol}}H = \Delta_{\text{destr}}H + \Delta_{\text{solvat}}H$$

(the molar enthalpy of solution refers to complete dissolution of one mole of solute). The enthalpy of a solution may be negative ($\Delta_{\text{sol}}H < 0$ for *exothermic process*) or positive ($\Delta_{\text{sol}}H > 0$ for *endothermic process*). How the solubility of a substance will depend on the temperature at different signs of the enthalpy of solution? The answer to this question can be derived from the Le Chatelier's principle. Remember this principle: when an external action is made to a system in equilibrium, the system will respond so as to oppose the change by this action that is to shift the equilibrium in the direction opposite to the external action, as a result, equilibrium is established at a new level.

The Le Chatelier's principle requires that at increasing temperature, that is, adding heat, equilibrium should be shifted in the direction of the heat absorption partially decreasing the temperature. So, as heat is released during the exothermic dissolution process, the Le Chatelier's principle requires that at increasing temperature the equilibrium should be shifted in the direction of the heat absorption that is in the direction of decreasing solubility. On the other hand, as heat is absorbed during the endothermic dissolution process, the Le Chatelier's principle requires that at increasing temperature equilibrium should be shifted in the direction of increasing solubility.

It should be added that the solubility of gases decreases with increasing temperature, but it increases with increasing pressure. Indeed, according to the Le Chatelier's principle only way to reduce the external pressure is to transfer the gas molecules into a solution that is to increase the gas solubility.

At dissolution the Gibbs free energy change of a system is always negative regardless of the sign of the enthalpy of dissolution, since the dissolution of solids is always accompanied by increasing disorder that is increasing entropy:

$\Delta_{\text{sol}}G = \Delta_{\text{sol}}H - T\Delta_{\text{sol}}S < 0,\ \Delta_{\text{sol}}S > 0.$

Physical-chemical properties of ideal solutions

Let's introduce the definition of an *ideal solution*. Ideal solution is the solution with absence of a specific chemical interaction between the components. Such solutions serve as models for dilute solutions. We consider the physical-chemical properties of ideal solutions of non-electrolytes, they are called colligative properties. The dependence of such properties on concentration is expressed by the following equations:

1) Decreasing the vapor pressure of the solvent over a solution is given by the *first Raoult's law*:

$$P_1 = \frac{n_1}{n_1+n_2}P_0 = N_1P_0 \text{ or } \Delta P = P_0 - P_1 = P_0 - P_0\frac{n_1}{n_1+n_2} = P_0\frac{n_2}{n_1+n_2} = N_2P_0$$

where P_1 is the partial saturated vapor pressure of the solvent over the solution, P_0 is the saturated vapor pressure over the pure solvent, N_1 is the mole fraction of the solvent, N_2 is the mole fraction of solute, n_1 is the number of the solvent moles, n_2 is the number of the solute moles. This relation is easily explained by the Le Chatelier's principle. Indeed, decreasing concentration of the pure solvent due to the introduction of the solute requires an increase in the solvent concentration by the vapor condensation which reduces the vapor pressure.

2) Decreasing the crystallization temperature of a solution (or freezing temperature) is expressed by relation,

$$\Delta t_{\text{cryst}} = Kc_{\text{m}},$$

where K is the *cryoscopic constant* (K = 1.86 for H_2O), and c_m is the *molal concentration* of the solute (in mol/kg).

3) Increasing the boiling temperature of a solution is expressed by relation,

$$\Delta t_{\text{boil}} = Ec_{\text{m}},$$

where E is the *ebullioscopic constant* (E = 0.52 for H_2O), and c_m is the molal concentration of a solute. (The second and third relations together are called the *second Raoult's law* and can be easily explained by the Le Chatelier's principle).

4) The fourth law for colligative properties of solutions relates to *osmotic pressure*. Osmotic pressure (denoted π) is excessive hydrostatic pressure on the solution separated from the pure solvent by a semipermeable membrane which stops the diffusion of the solvent through the membrane (this process is called osmosis). The solvent, for example, water penetrates through the semipermeable membrane spontaneously as this process is accompanied by an increase in entropy ($\Delta S > 0$). Osmotic pressure tends to equalize the concentrations of both solutions due to the counter diffusion of solute and solvent molecules. The osmotic pressure (π) is expressed by the following equation (called the *Van't Hoff law*),

$$\pi = c_{\text{M}}RT$$

where π is given in kPa, c_M is the molar concentration of the solute, $R = 8.314$ J/(K·mol) is the gas constant and T is the temperature (in K).

All four laws for colligative properties allow us to determine the molar mass of solutes. This is their heuristic meaning.

Problem 8.2: What is the concentration of $CuSO_4$ in solution obtained by dissolution of 25 g of $CuSO_4 \cdot 5H_2O$ in 475 g of water?

Problem 8.3: Calculate the molarity and normality of the $CaCl_2$ solution with $\omega = 30\%$ which density $\rho = 1.28$ g/ml.

Problem 8.4: There is 96% H_2SO_4 solution, which density is 1.84 g/ml. How many milliliters of this solution should be taken to prepare 3.6 liters of solution with 2 N concentration?

Problem 8.5: There is 60 ml of H_3PO_4 solution with 0.6 N concentration. What volume of 0.1 M solution can be prepared from initial solution?

Problem 8.6: 200 g of H_2O contains 10 g of sucrose $C_{12}H_{22}O_{11}$. Find: a) osmotic pressure at 293 K; b) crystallization temperature; c) boiling temperature; d) pressure of saturated vapor over solution at 293 K. Saturated vapor pressure under pure water at 293 K is 2.337 kPa. The density of solution is equal to the density of water.

Problem 8.7: After dissolving of 5 g of sulfur in 50 g of benzene the boiling temperature increased by 1.0 K (ebullioscopic constant $E = 2.57$ for benzene). How many atoms does a sulfur molecule consist of in solution?

Theme IX

Electrolytes. Weak Electrolytes: Constant and Degree of Dissociation. Strong Electrolytes. Activity of Ions

Weak electrolytes

Let's consider *electrolytes*, that are substances that can conduct electric current. According to the *Arrhenius theory* the electrolytes dissociate in polar solvents to form a positively and negatively charged ions, namely cations and anions respectively. In particular, acids dissociate with detachment of protons, and bases dissociate with detachment of hydroxide ions. In solution an equilibrium is reached between the un-dissociated molecules and their dissociation products. Dissociation of the so-called *weak electrolytes* characterized by three parameters, namely, the *degree of dissociation* (denoted as α), the *isotonic coefficient* or *Van't Hoff factor* (denoted as i), and the *dissociation constant* (denoted as K). The degree of dissociation is the ratio of the number of moles of the electrolyte dissociated on ions to the total number of moles of the electrolyte introduced into the solution ($\alpha < 1$). Isotonic coefficient is the ratio of the total number of dissolved particles in the electrolyte solution to the number of the electrolyte molecules introduced into the solution ($i > 1$). The equilibrium constant has already been defined in the previous chapter.

Isotonic coefficient relates to the degree of dissociation by the following ratio,

$$ic_M = (c_M - \alpha c_M) + k\alpha c_M$$

where the left side shows the total number of dissolved particles in solution according to the isotonic coefficient definition, the first term on the right side gives the number of particles which remain un-dissociated and the second term on the right side corresponds to the number of particles resultant upon dissociation, and the coefficient k is a number of ions into which one molecule of the electrolyte dissociates (for example, k equals 2 for the NaCl molecule and 3 for the Na_2SO_4 molecule). From this relation after cancellation on c_M we get equation

$$i = (1 - \alpha) + k\alpha$$

and finally

$$\alpha = \frac{i-1}{k-1}$$

For weak electrolytes the degree of dissociation is much less than 1 ($\alpha \ll 1$).

The application of the above laws of ideal solutions to weak electrolytes modifies equations for colligative properties as follows:

1) $P_1 = \frac{n_1}{n_1+in_2}P_0$ or $\Delta P = P_0 - P_1 = P_0 - P_0\frac{n_1}{n_1+in_2} = P_0\frac{in_2}{n_1+in_2}$

2) $\Delta t_{cryst} = iKc_m$

3) $\Delta t_{boil} = iEc_m$

4) $\pi = ic_MRT$

Let’s now obtain an expression for the dissociation constant of weak electrolyte. Consider the equation of dissociation and write the concentration of all particles over their names:

$$\begin{array}{ccccc} c_{\mathrm{M}} - \alpha c_{\mathrm{M}} & K & \alpha c_{\mathrm{M}} & & \alpha c_{\mathrm{M}} \\ \mathrm{MX} & = & \mathrm{M}^{+} & + & \mathrm{X}^{-} \end{array}$$

Expression for an equilibrium (dissociation) constant will be the following:

$$K = \frac{[M^{+}][X^{-}]}{[MX]} = \frac{\alpha c_{\mathrm{M}} \alpha c_{\mathrm{M}}}{c_{\mathrm{M}} - \alpha c_{\mathrm{M}}} = \frac{\alpha^{2} c_{\mathrm{M}}}{1 - \alpha}$$

for very weak electrolytes $\alpha << 1$, so $K = \alpha^{2} c_{\mathrm{M}}$.

From this relation we have

$$\alpha = \sqrt{\frac{K}{c_{\mathrm{M}}}}$$

that is the degree of dissociation of an electrolyte increases with dilution of its solution (this relation is called the *Ostwald’s dilution law*). Then for the concentrations of ions in solution we can get the following expression:

$[\mathrm{M}^{+}] = [\mathrm{X}^{-}] = \alpha c_{\mathrm{M}} = \sqrt{K c_{\mathrm{M}}}$

Let’s derive the corresponding expressions for the special cases of the dissociation of a weak acid and weak base denoting their dissociation constants as K_a and K_b respectively:

$K_a = [\mathrm{H}^{+}][\mathrm{X}^{-}]/[\mathrm{HX}] = \alpha c_{\mathrm{M}} \cdot \alpha c_{\mathrm{M}}/(c_{\mathrm{M}} - \alpha c_{\mathrm{M}}) = \alpha^{2} c_{\mathrm{M}}/(1 - \alpha) \approx \alpha^{2} c_{\mathrm{M}}$, and

$[\mathrm{H}^{+}] = [\mathrm{X}^{-}] = \alpha c_{\mathrm{M}} \cdot = (K_a c_{\mathrm{M}})^{1/2}$

$K_b = [\mathrm{B}^{+}][\mathrm{OH}^{-}]/[\mathrm{BOH}] = \alpha c_{\mathrm{M}} \cdot \alpha c_{\mathrm{M}}/(c_{\mathrm{M}} - \alpha c_{\mathrm{M}}) = \alpha^{2} c_{\mathrm{M}}/(1 - \alpha) \approx \alpha^{2} c_{\mathrm{M}}$, and

$[\mathrm{B}^{+}] = [\mathrm{OH}^{-}] = \alpha c_{\mathrm{M}} \cdot = (K_b c_{\mathrm{M}})^{1/2}$

For calculations instead of the dissociation constant the so-called dissociation constant exponent pK is often used,

$$\mathrm{p}K = -\log K$$

$$\mathrm{p}K_a = -\log K_a,\ \mathrm{p}K_b = -\log K_b$$

The pK values of the water solutions of some weak electrolytes are given in Table 1 of Appendix.

Problem 9.1: The degree of dissociation of formic acid HCOOH in 0.45 M solution is equal to 0.02. Find the dissociation constant K_a and pK_a.

Solution:

$c_{\mathrm{M}} = 0.45$ M	For weak electrolytes
$\alpha = 0.02$	$K_a = \alpha^2 c_{\mathrm{M}} = 0.02^2 \cdot 0.45 = 1.8 \cdot 10^{-4}$
K_a – ? pK_a – ?	Then p$K_a = \log(1.8 \cdot 10^{-4}) = 3.74$

Strong electrolytes

Let’s consider the properties of the solutions of *strong electrolytes*. In solutions of strong electrolytes the values of the degree of dissociation are large, the concentrations *of counter-ions* are also large that provides a significant strength of interaction between the ions, including their association. This restricts the free movement of ions and their participation in chemical reactions. The true degree of the dissociation of strong electrolytes is one, but the apparent degree of dissociation is smaller due to ions interaction and given by the modified equations for colligative properties of weak electrolytes that we have considered above.

Behavior of strong electrolytes in solution is described in terms of the *activity of ions* (a_i) which is introduced instead of concentration into the equations for ideal solutions so as to obtain an adequate description of experimental data. This is not a very good method, but others are absent for the present. The activity is bound with the concentration through the *activity coefficient* (f_i) by the following relation:

$$a_i = f_i \cdot c_{\mathrm{M}}$$

$$f_i \cdot \to 1 \text{ at } c_{\mathrm{M}} \to 0$$

It is obvious that the activity coefficient tends to unity when the ion concentrations tend to zero because the ion-ion interaction in this case becomes negligibly weak.

In the *Debye-Huckel theory* the following approximate expression for the dependence of the activity coefficient on the ion charges and electrolyte concentration was obtained:

$$\log f_i = -0.5 \cdot Z_i^2\, I^{1/2}$$

Here, the symbol I (or μ) denotes the *ionic strength* which is given by the following equation:

$$I = \tfrac{1}{2}\, \Sigma_i Z_i^2 c_i$$

where Z_i is the charge of the i-th ion and c_i is its concentration, and the summation is carried out over all the ions that are present in the solution.

Note that the Debye-Huckel theory assumes that each ion in solution is surrounded by the counter-ions in the form of so-called ionic atmosphere, the size of which depends on the electrolyte concentration.

These relationships allow us to solve problems concerned to solutions of strong electrolytes.

Problem 9.2: Calculate the activities of K^+ and SO_4^{2-} ions in 0.01 M solution of K_2SO_4.

Solution:

$c_M = 0.01$ M

$f_{K^+} - ?\ f_{SO_4^{2-}} - ?$

Let's write the equation of the dissociation of K_2SO_4:

$K_2SO_4 = 2K^+ + SO_4^{2-}$

The concentration of K_2SO_4 is 0.01 M and it is a strong electrolyte, so $[K^+] = 0.02$ M and $[SO_4^{2-}] = 0.01$ M.

Let's calculate the ionic strength of solution:

$I = \tfrac{1}{2}\, \Sigma_i Z_i^2 c_i = \tfrac{1}{2}(Z_{K^+}^2 c_{K^+} + Z_{SO_4^{2-}}^2 c_{SO_4^{2-}}) = \tfrac{1}{2}(1 \cdot 0.02 + 4 \cdot 0.01) = 0.03$

Then $\log f_{K^+} = -0.5 Z_{K^+}^2 \sqrt{I} = -0.5 \cdot 1 \cdot \sqrt{0.03} = -0.087$

$f_{K^+} = 10^{-0.087} = 0.82$ and $a_{K^+} = f c_M = 0.82 \cdot 0.02 = 0.0164$ M

Similarly $f_{SO_4^{2-}} = -0.5 Z_{SO_4^{2-}}^2 \sqrt{I} = -0.5 \cdot 4 \cdot \sqrt{0.03} = -0.346$

$f_{SO_4^{2-}} = 10^{-0.346} = 0.45$

and $a_{SO_4^{2-}} = f c_M = 0.45 \cdot 0.01 = 0.0045$ M

The results mean that the apparent concentration of K^+ ions is 0.0164 M and the apparent concentration of SO_4^{2-} ions is 0.0045 M, but real concentrations are 0.02 M and 0.01 M respectively.

Problem 9.3: How many milliliters of water should be added to 500 ml of 0.4 M acetic acid solution to double the degree of dissociation?

Problem 9.4: How many times will the concentration of hydrogen ions decrease if 0.04 moles of sodium acetate $NaCH_3COO$ is added to 2 liters of 0.02 M solution of acetic acid? The dissociation constant of acetic acid (CH_3COOH) is $1.8 \cdot 10^{-5}$.

Problem 9.5: Calculate the concentration of CH_3COO^- ions in the solution which contains 2 mole of CH_3COOH and 0.4 moles of HCl. The volume of the solution is 1 liter. HCl is fully dissociated in the solution.

Problem 9.6: A solution contains 260 g of water and 0.69 g of sodium carbonate. The crystallization temperature of the solution is –0.13 °C. Calculate the apparent degree of dissociation of sodium carbonate. The cryoscopic constant *K* of water is 1.86.

Problem 9.7: 0.5 moles of sugar and 0.2 moles of $MgCl_2$ were dissolved in equal amounts of water. The crystallization temperatures of both solutions are the same. Calculate the apparent degree of dissociation of $MgCl_2$.

Problem 9.8: Calculate activity H^+ ion in 0.004 M solution of HCl that also contains 0.2 M of NaCl.

Theme X

Ionic Product of Water and Hydrogen Ion Exponent (pH). Buffer Solutions. Solubility Product Constant. Hydrolysis of Salts

Ionic product of water, pH

From the viewpoint of the *Arrhenius theory of electrolytic dissociation*, the equilibrium of acid-base ionization (called also *self-ionization*) of water molecules is written as follows (symbol “w” denotes water):

$$H_2O \overset{K_w}{=} H^+ + OH^-$$

However, from the viewpoint of the *Brønsted-Lowry acid base theory*, this equilibrium may be presented more precisely in the following way:

$$H_2O + H_2O \overset{K_w}{=} H_3O^+ + OH^-$$

Then for the K_w constant we get the relation which includes the activities instead of concentrations (activity of water as any pure solvent is taken to be unity by definition):

$$K_w = a_{H^+}\cdot a_{OH^-} = [H^+][OH^–] = 10^{-14} \text{ (at 298 K)}$$

(from now on, in brackets activity instead of concentrations will be written). Let's find logarithms of both sides of this equation and change signs in the left and right sides:

$$\log K_w = \log[H^+] + \log[OH^–] = –14 \quad \text{or} \quad –\log K_w = –\log[H^+] – \log[OH^–] = 14$$

Defining the negative logarithm (to the base ten) as equilibrium constant exponent $pK_w = –\log K_w$, hydrogen ion exponent $pH = –\log[H^+]$, and hydroxide ion exponent $pOH = –\log[OH^–]$, we have:

$$pK_w = pH + pOH = 14 \text{ (at 298 K)}$$

Thus if we know the pH value, from this equation we can find the pOH value and *vice versa*. The pH value is measured typically by a pH-meter with a glass electrode. In neutral water solution the proton and hydroxide ion concentrations are equal and we get pH + pOH = 2pH = 14 and pH = 7, while the pH value in acidic solutions is less than 7 and in alkaline solution is more than 7.

Problem 10.1: Calculate the pH value in solutions of the following electrolytes: 1) 0.1 M HCN (hydrocyanic acid, $pK_a = 9.10$; 2) 0.02 M NH_4OH (ammonium hydroxide, $pK_b = 4.75$).

Solution:

$c_{HCN} = 0.1$ M
$c_{NH4OH} = 0.02$ M

pH - ?

Let's find the concentrations of corresponding ions:

1) $HCN = H^+ + CN^–$

$[H^+] = (K_a\cdot c_{HCN})^{1/2} = (7.9\cdot10^{–10}\cdot0.1)^{1/2} = 0.9\cdot10^{–5}$ M

$pH = –\log[H^+] = –\log(0.9\cdot10^{–5}) = 5.05$

2) $NH_4OH = NH_4^+ + OH^–$

$[OH^–] = (K_b\cdot c_{HCN})^{1/2} = (1.8\cdot10^{–5}\cdot0.02)^{1/2} = 6\cdot10^{–4}$ M

$pOH = –\log[OH^–] = –\log(6\cdot10^{–4}) = 3.2$

$pH = 14 – pOH = 14 – 3.2 = 10.8$

Let’s consider *buffer solutions*. Buffer solutions consist from weak acid and its salt (HA + MA) or weak base and its salt (BOH + BX). The main feature of the buffer solutions is that they maintain the pH value upon dilution. Why? Write again expression for the equilibrium constant of the dissociation of weak acid HA taking into account the full dissociation of salt MA as a strong electrolyte:

$$\mathrm{HA} \overset{K_a}{=} \mathrm{H^+ + A^-} \qquad \mathrm{MA = M^+ + A^-}$$

$$K_a = [\mathrm{H^+}][\mathrm{A^-}]/[\mathrm{HA}] \approx [\mathrm{H^+}]c_{salt}/c_{acid}$$

This approximate equality is realized because equilibrium of the weak acid dissociation is strongly shifted left and shifted even more at adding anion of the salt (A^-) according to the Le Chatelier’s principle, that is the equilibrium acid concentration equals approximately to the total acid concentration ($[\mathrm{HA}] \approx c_{acid}$) and the equilibrium anion concentration equals approximately to the total salt concentration ($[\mathrm{A^-}] \approx c_{salt}$).

Let’s find the logarithms of both sides of this equation and get the following relation:

$$\log K_a = \log[\mathrm{H^+}] + \log(c_{salt}/c_{acid}),$$

transferring two members of the equation in opposite sides leads to the equation

$$-\log[\mathrm{H^+}] = -\log K_a + \log(c_{salt}/c_{acid}) \text{ or } \mathrm{pH} = \mathrm{p}K_a + \log(c_{salt}/c_{acid}).$$

From the last relation is evident that the pH value in buffer solution does not depend upon the absolute concentrations of the acid and salt, but depends only on their ratio, that is, pH does not change by diluting buffer solution when the ratio of concentrations is unchanged.

Problem 10.2: Calculate the pH value in 0.2 M solution of acetic acid containing in addition also 0.4 M of sodium acetate ($NaCH_3COO$). How to change the pH by the addition of 0.1 M HCl or 0.1 M NaOH? ($\mathrm{p}K_a(CH_3COOH) = 4.75$).

Solution:

$c_{acid} = 0.2$ M
$c_{salt} = 0.4$ M
$c_{HCl} = 0.1$ M
$c_{NaOH} = 0.1$ M

pH - ?

1) $\mathrm{pH} = \mathrm{p}K_a + \log(c_{salt}/c_{acid}) = 4.75 + \log(0.4/0.2) = 5.05$

2) After addition 0.1 M HCl the following reaction will proceed:

$HCl + NaCH_3COO = CH_3COOH + NaCl$,

so concentrations of the acid and salt will be changed:

$c_{salt} = 0.4 - c_{HCl} = 0.4 - 0.1 = 0.3$ M

$c_{acid} = 0.2 + c_{HCl} = 0.2 + 0.1 = 0.3$ M

$\mathrm{pH} = \mathrm{p}K_a + \log(c_{salt}/c_{acid}) = 4.75 + \log(0.3/0.3) = 4.75$

The change of pH is very small!

3) After addition 0.1 M NaOH the following reaction will proceed:

$NaOH + CH_3COOH = NaCH_3COO + H_2O$,

so concentrations of the acid and salt will be changed:

$c_{salt} = 0.4 + c_{NaOH} = 0.4 + 0.1 = 0.5$ M

$c_{acid} = 0.2 – c_{NaOH} = 0.2 – 0.1 = 0.1$ M

$\mathrm{pH} = \mathrm{p}K_a + \log(c_{salt}/c_{acid}) = 4.75 + \log(0.5/0.1) = 5.45$

The pH values are slightly varied by adding rather large amounts of acid or alkali to the buffer solution. But if the amounts of an acid or an alkali be too large the pH will change dramatically. Similar equations hold for buffer solutions prepared from a weak base and its salt.

Solubility product constant

Equilibrium in a saturated solution of a poorly soluble strong electrolyte is characterized by a solubility product constant K_s. For example, in the case of silver sulfide we may write:

$$Ag_2S \overset{K_s}{=} 2Ag^+ + S^{2-}$$

$$K_s = (a_{Ag^+})^2\, a_{S^{2-}}/a_{Ag_2S} = (a_{Ag^+})^2\, a_{S^{2-}} = [Ag^+]^2[S^{2-}]$$

(activity of any solid phase is taken to be unity by definition). In accordance to the Le Chatelier’s principle, if for the compound M_nX_m the product of the ion concentrations exceeds the solubility product constant,

$$[M^{m+}]^n[X^{n-}]^m > K_s$$

this compound must be precipitated because this is the only way to reduce the concentrations and to bring the system into equilibrium with fulfillment of the equation condition,

$$[M^{m+}]^n[X^{n-}]^m = K_s$$

According to the Le Chatelier's principle, in opposite case, if for the compound M_nX_m the product of the ion concentrations doesn't reach the solubility product constant,

$[M^{m+}]^n[X^{n-}]^m < K_s$

solid phase of this compound must be dissolved because this is the only way to increase the concentrations and to bring the system into equilibrium condition $[M^{m+}]^n[X^{n-}]^m = K_s$.

Problem 10.3: Whether is precipitated calcium fluoride, if 42 mg of solid sodium fluoride will be added to one liter of the saturated solution of calcium sulfate? ($K_s(CaSO_4) = 1.4\cdot10^{-3}$, $K_s(CaF_2) = 4\cdot10^{-11}$).

Solution:

$m_{NaF} = 42\cdot10^{-3}$ g
$K_s(CaSO_4) = 1.4\cdot10^{-3}$
$K_s(CaF_2) = 4\cdot10^{-11}$

Sediment - ?

To answer the question we should calculate the ion product $[Ca^{2+}][F^-]^2$ and compare it with $K_s(CaF_2)$.

Let's initially find the concentration of Ca^{2+} ions in the saturated $CaSO_4$ solution.

$CaSO_4 = Ca^{2+} + SO_4^{2-}$

If we denote concentration of $CaSO_4$ by "s" (solubility), then $[Ca^{2+}] = s$ and $[SO_4^{2-}] = s$ in the saturated solution.

So $K_s(CaSO_4) = [Ca^{2+}][SO_4^{2-}] = s^2 = 1.4\cdot10^{-3}$.

$s = \sqrt{1.4\cdot10^{-3}} = \sqrt{14\cdot10^{-4}} = 3.7\cdot10^{-2}$ M

And $[Ca^{2+}] = 3.7\cdot10^{-2}$ M

The concentration of NaF in the solution is:

$$[\mathrm{NaF}] = \frac{m}{MV} = \frac{42\cdot10^{-3}}{42\cdot1} = 10^{-3}\mathrm{M}$$

Also $[F^-] = 10^{-3}$ M because the salt NaF is a strong electrolyte.

Now we can calculate ion product for CaF_2:

$[Ca^{2+}][F^-]^2 = 3.7\cdot10^{-2}\cdot(10^{-3})^2 = 3.7\cdot10^{-8} > K_s(CaF_2) = 4\cdot10^{-11}$

So the sediment of CaF_2 will appear.

Hydrolysis

Turn to consideration of the *hydrolysis* processes. Exchange reactions in solutions may be presented in ion-molecular form. For example, the acid-base neutralization process may be expressed as follows:

$OH^- + H^+ = H_2O$ ($\Delta_r H = -57.4$ kJ/mol, irrespective of the nature of a base and an acid).

The processes reverse to the neutralization reactions are called hydrolysis. If a salt is formed by a weak acid and a strong base, then by reacting it with water the water proton is associated with anion of the weak acid and a hydroxide anion is released into the solution and the medium becomes alkaline, that is, the pH value will be more than 7:

$A^- + H_2O = AH + OH^-$, pH > 7

For example, in solution of salt Na_2MoO_4, formed from the weak molybdic acid H_2MoO_4 and the strong base NaOH, the following two step processes are taken place,

$MoO_4^{2-} + H_2O = HMoO_4^- + OH^-$, pH > 7

$HMoO_4^- + H_2O = H_2MoO_4 + OH^-$

but the hydrolysis by the first step is most strong.

The equilibrium constant for such a hydrolysis reaction (hydrolysis constant) is expressed by the following equation:

$$K_h = \frac{K_\mathrm{w}}{K_\mathrm{a}}$$

The weaker the acid (the higher the pK_a value) the stronger hydrolysis and the higher the pH value.

If the salt is formed by a weak base and a strong acid, then by reacting it with water the water hydroxide ion is associated with cation of the weak base and proton is released into the solution and the medium becomes acidic, that is, the pH value would be less than 7:

$B^+ + H_2O = BOH + H^+$, pH < 7

For example, in solution of salt $Fe_2(SO_4)_3$, formed from the weak base $Fe(OH)_3$ and the strong acid H_2SO_4, the following three step processes may take place:

$Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$, pH < 7

$Fe(OH)^{2+} + H_2O = Fe(OH)_2^+ + H^+$

$Fe(OH)_2^+ + H_2O = Fe(OH)_3 + H^+$

but the hydrolysis by the first step is again most strong.

The equilibrium constant for such hydrolysis reaction is

$$K_h = \frac{K_\mathrm{w}}{K_\mathrm{b}}$$

The weaker the base (the higher the pK_b value), the stronger the hydrolysis and the lower the pH value.

When a salt is formed by a weak base and a weak acid, then the pH value would be dependent on relation between the pK_a and pK_b values. In the case of pK_a > pK_b, hydrolysis will proceed preferably by the anion and medium will be alkaline (pH > 7). In opposite case, pK_b > pK_a, hydrolysis will proceed preferably by the cation and medium will be acidic (pH < 7). In all the considered reactions the hydrolysis equilibrium shifts right only partially. However, if the salt is formed by a weak base and a weak acid and the products of the hydrolysis reaction are released from the reaction medium in the form of gases or precipitates, the hydrolysis proceeds to the end, to the final products. For example, chromium sulfide is immediately hydrolyzed at formation by the following reactions:

$3CrCl_3 + 3Na_2S + 6H_2O = 2Cr(OH)_3 + 3H_2S + 6NaCl$

or in ion-molecular form

$3Cr^{3+} + 3S^{2-} + 6H_2O = 2Cr(OH)_3 + 3H_2S$

In addition we give the interesting hydrolysis reaction with the malachite formation in the solid state:

$2CuSO_4 + 2Na_2CO_3 + H_2O = Cu_2(OH)_2CO_3 + CO_2 + 2Na_2SO_4$

Problem 10.4: Calculate the hydrolysis constant and degree of the hydrolysis of NH_4Cl in solution, if the concentration of NH_4Cl is 0.01 M. What is pH of the solution?

Solution:

c = 0.01 M
$K_\mathrm{b}(NH_4OH) = 1.8\cdot10^{-5}$

K_h - ?
h - ?
pH -?

Hydrolysis equation:
$NH_4^+ + H_2O = NH_4OH + H^+$

$$K_\mathrm{h} = \frac{K_\mathrm{w}}{K_\mathrm{b}} = \frac{10^{-14}}{1.8\cdot10^{-5}} = 5.6\cdot10^{-10}$$

As for dissociation constant for the hydrolysis constant the following equation is true:

$K_h = h^2 c_M$, where h is the degree of hydrolysis.

So $h = \sqrt{\frac{K_h}{c_M}} = \sqrt{\frac{5.6 \cdot 10^{-10}}{0.01}} = 2.4 \cdot 10^{-4}$

$[H^+] = [NH_4^+] = \sqrt{K_h c_M} = \sqrt{5.6 \cdot 10^{-10} \cdot 0.01} = 2.4 \cdot 10^{-6}$ M

$pH = -\log[H^+] = -\log(2.4 \cdot 10^{-6}) = 5.6$

Problem 10.5: What is the concentration of the formic acid in the solution, the pH of which is 5.20? ($pK_a(HCOOH) = 3.74$).

Problem 10.6: Calculate pH of the solutions of the following weak electrolytes:

a) 0.05 M HCOOH; b) 0.08 M NH_4OH; c) 0.2 M HOCl.

Problem 10.7: Calculate the pH of the buffer solution that contains 0.03 M HCOOH and 0.06 M NaHCOO.

Problem 10.8: There are two solutions: 2 liters of 0.01 M $AgNO_3$ solution and 2 liters of 0.5 M H_2SO_4 solution. Will the sediment of Ag_2SO_4 appear after mixing these two solutions? $K_s(Ag_2SO_4) = 2 \cdot 10^{-5}$.

Problem 10.9: 850 ml of 10^{-4} M $AgNO_3$ solution was added to 150 ml of 10^{-3} M HCl solution. Will AgCl precipitate? $K_s(AgCl) = 1.8 \cdot 10^{-10}$.

Problem 10.10: Write the hydrolysis reactions for salts: NaCN, NH_4Cl, $ZnBr_2$, $FeSO_4$.

Problem 10.11: Calculate the hydrolysis constant and degree of the hydrolysis of NaF in water solution if the concentration of NaF is 0.02 M. What is the pH of the solution?

Problem 10.12: Find the pH of 0.02 M solution of Na_2CO_3 taking into account only the first step of the hydrolysis reaction.

Problem 10.13: Compare the degree of the hydrolysis and the pH of KCN solutions that contain 0.1 M and 0.001 M of the salt.

Theme XI
Redox Processes. Searching Coefficients for the Redox Reaction Equations. Electrode Potentials. Direction of the Redox Reactions

Redox reactions are the processes of electron transfer. A substance accepted electrons is called an *oxidant* and a substance donated electrons is called *reductant*. In a redox reaction an oxidant is reduced and a reductant is oxidized. To characterize the redox reactions the concept of the oxidation state was introduced. Remember, that the oxidation state is a formal value equal to the charge that an atom acquires under the assumption of a complete displacement of electrons to it or from it. By the displacement of electrons to an atom it acquires a negative charge (negative oxidation state), and by the displacement of electrons from an atom it acquires a positive charge (positive oxidation state).

Redox reactions may be intermolecular, intramolecular, and disproportionation processes which are accompanied by a simultaneous increase and decrease of the oxidation state of the same element.

$Mg + H_2SO_4 = MgSO_4 + H_2$ intermolecular

$(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3 + 4H_2O$ intramolecular

$4H_3PO_3 = 3H_3PO_4 + PH_3$ disproportionation process

We give some examples of typical oxidants and reductants. Typical oxidants are: O_2, F_2, Cl_2, Br_2, I_2, $K_2Cr^{+6}{}_2O_7$ (reduced to Cr^{3+} in acidic medium), $KMn^{+7}O_4$ (reduced to $Mn^{+6}O_4^{2-}$ in alkaline medium, to $Mn^{+4}O_2$ in neutral medium, and to Mn^{2+} in acidic medium), $KCl^{+5}O_3$, $H_2S^{+6}O_4$ (reduced to $S^{+4}O_2$, S^o, or H_2S^{-2}, with increasing activity of a reductant and acid concentration a deeper reduction is realized), $HN^{+5}O_3$ (reduced to $N^{+4}O_2$, $N^{+2}O$, $N^{+1}{}_2O$, $N^0{}_2$, or $N^{-3}H_4^+$, with increasing activity of a reductant and decreasing acid concentration a deeper reduction is realized), H^+ (reduced to H_2), Fe^{3+} (reduced to Fe^{2+}), Cu^{2+} (reduced to Cu^+), Sn^{4+} (reduced to Sn^{2+}), Pb^{4+} (reduced to Pb^{2+}), Hg^{2+} (reduced to Hg_2^{2+}) *etc*. Typical reductants are: H_2, H^- (CaH_2, $NaBH_4$), C, Si, P, $C^{+2}O$, HCl, HBr, HI, H_2S, Fe^{2+} (oxidized to Fe^{3+}), Cu^+ (oxidized to Cu^{2+}), Sn^{2+} (oxidized to Sn^{4+}), Pb^{2+} (oxidized to Pb^{4+}), Hg_2^{2+} (oxidized to Hg^{2+}). There are compounds which may be both oxidants and reductants in different reactions, for example: I_2 (reduced to I^- and oxidized to $I^{+5}O_3^-$), $H_2O_2^{-1}$ (reduced to H_2O^{-2} and oxidized to $O^0_2 + H_2O^{-2}$), $N^{+4}O_2$ (reduced to $N^{+2}O$ and oxidized to $N^{+5}O_3^-$).

Electron-ion balance method

Problem 11.1: Equilibrate the following redox reaction:

$K_2FeO_4 + HI \rightarrow FeI_2 + I_2 + KI + H_2O$

Solution: Let's consider algorithm of the electron-ion balance method on the example of the reaction:

$K_2FeO_4 + HI \rightarrow FeI_2 + I_2 + KI + H_2O$

1) Indication an oxidant and a reductant and their oxidation states:

   $\underset{\text{oxidant}}{K_2Fe^{+6}O_4} + \underset{\text{reductant}}{HI^{-1}} \rightarrow Fe^{+2}I_2 + I^0_2 + KI + H_2O$,

2) Generating the half-reactions in ionic form separately for the oxidant and the reductant involving real substances in solution, which may be proton, hydroxide ion, or water molecule with attaining material balance (that is, the number of particles of each element should be equal in the left and right parts of both half-reactions):

   $Fe^{+6}O_4^{2-} + 8H^+ \rightarrow Fe^{2+} + 4H_2O$ (half-reaction of reduction),

   $2I^- \rightarrow I^0_2$ (half-reaction of oxidation).

3) Charge balancing both half-reactions by adding or subtracting electrons:

   $Fe^{+6}O_4^{2-} + 8H^+ + 4e^- \rightarrow Fe^{2+} + 4H_2O$

   $2I^- - 2e^- \rightarrow I^0_2$

4) Choosing the least common multiple (LCM) of the numbers of electrons in the two half-reactions and dividing this LCM number by the number of electrons in each half-reaction and multiplying each half-reaction on the result of such dividing (LCM = 4):

   $\times 1 \,\big|\, Fe^{+6}O_4^{2-} + 8H^+ + 4e^- \rightarrow Fe^{2+} + 4H_2O$

   $\times 2 \,\big|\, 2I^- - 2e^- \rightarrow I^0_2$

5) Summing both half-reactions with excluding electrons as a result:

   $Fe^{+6}O_4^{2-} + 8H^+ + 4I^- \rightarrow Fe^{2+} + 2I^0_2 + 4H_2O$

6) Adding counter-ions to represent the reaction equation in molecular form, taking into account the charge and material balance:

$Fe^{+6}O_4^{2-} + 8H^+ + 4I^- \rightarrow Fe^{2+} + 2I^0_2 + 4H_2O$

$+ 2K^+ \quad + 4I^- \qquad\qquad + 2I^- \; + 2I^- + 2K^+$

K_2FeO_4 + $8HI$ → $FeI_2 + 2I_2 + 2KI + 4H_2O$ (final result)

Electrode potentials

Consider conception of *electrode potentials* and the question of the direction of the redox reactions. Electrode potential (another words, reduction potential) is the quantitative characteristic of ability of the system to attach an electron, that is, act as an oxidant. Dependence of reduction potential (φ) on the concentrations of the system components is given by the *Nernst equation*:

$$\varphi = \varphi^0 + \frac{2.303RT}{zF}\log\left(\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}\right) \text{ or}$$

$$\varphi = \varphi^0 + \frac{0.059}{z}\log\left(\frac{[\mathrm{Ox}]}{[\mathrm{Red}]}\right) \text{ (for 298 K)}$$

where φ^0 is the *standard reduction potential* – the potential at the standard activities or concentrations of all components of the half-reaction of reduction that equal to unity, *F* is the *Faraday constant* that equals 96485.3 C/mol (coulomb per mole), and *z* is number of the electrons in the half-reaction, whereas [Ox] and [Red] are the products of the activities or concentrations of the components of the left part of the half-reaction in the oxidized form and the right part of the half-reaction in reduced form respectively. For example, the Nernst equation has the following forms of the half-reactions:

$$Zn^{2+} + 2e \rightarrow Zn, = \varphi^0 + \frac{0.059}{2}\log\left(\frac{a_{\mathrm{Zn}^{2+}}}{a_{\mathrm{Zn}}}\right) = \varphi^0 + \frac{0.059}{2}\log\left(\frac{[\mathrm{Zn}^{2+}]}{1}\right)$$

$$Fe^{3+} + 1e \rightarrow Fe^{2+}, \varphi = \varphi^0 + \frac{0.059}{1}\log\left(\frac{[\mathrm{Fe}^{3+}]}{[\mathrm{Fe}^{2+}]}\right)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O, \varphi = \varphi^0 + \frac{0.059}{6}\log\left(\frac{[\mathrm{Cr_2O_7^{2-}}][\mathrm{H}^+]^{14}}{[\mathrm{Cr}^{3+}]^2 1^7}\right)$$

(remember that activities of solid phase or solvent are assumed equal to unity).

For determination of an electrode potential the *galvanic cell* is composed of two systems, in which the oxidation and reduction half-reactions occur and which are connected by current conductor with the high-resistance voltmeter. For example, we may create the galvanic cell from a zinc electrode (or a plate), immersed into a zinc(II) sulfate solution, and a copper electrode (or a plate), immersed into a copper(II) sulfate solution, which separated by a semipermeable membrane. This galvanic cell is denoted by the following way:

$Zn|ZnSO_4||CuSO_4|Cu$

(lines correspond to boundaries between electrodes and solutions). At anode the oxidation reaction proceeds with dissolving the zinc electrode:

$Zn – 2e^– \rightarrow Zn^{2+}$.

At cathode the reduction reaction proceeds with deposition of copper on the copper electrode:

$Cu^{2+} + 2e^– \rightarrow Cu$

The potential difference measured by the voltmeter, connected to the circuit between the two solutions, is called the electromotive force of this cell, which equals the difference between electrode potentials of these half-reactions,

$E = \varphi_C – \varphi_A$

where φ_C and φ_A are the electrode potentials of cathode and anode respectively. At the cathode the reduction half-reaction and at the anode the oxidation half-reaction occur always, that is, $E > 0$. For the *standard conditions* of both half-reactions we may write

$E^0 = \varphi^0{}_C – \varphi^0{}_A$

The *standard electrode potential* φ^0 of any half-reaction is determined relative to the *standard hydrogen electrode* as a reference electrode for which the cell potential φ^0 has been defined as 0 V. The standard hydrogen electrode consists of a platinum plate immersed into solution of hydrochloric acid with concentration of 1 M through which hydrogen stream is bubbled at a pressure of 1 atmosphere. For the half-reaction in this solution we can write the following relations:

$2H^+ + 2e^– \rightarrow H_{2(g)}$

$\varphi = \varphi^0 + 0.059/(2)\log([H^+]^2/P_{H2}) = 0.059\log[H^+] = 0$

(at $[H^+] = 1$ M, $P_{H2} = 1$ atm, if $\varphi^0 = 0$ V).

The standard electrode potentials of different half-reactions are given in Table 2 of Appendix. It is important that electromotive force of any cells relates to the Gibbs free energy of reaction by the equation

$\Delta G = -zFE$ or $\Delta G^0 = -zFE^0$

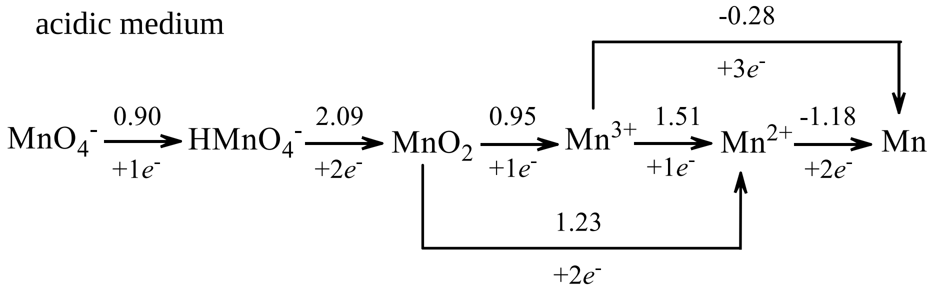
for standard conditions. As we know, spontaneously occurring reaction can be realized only at the condition

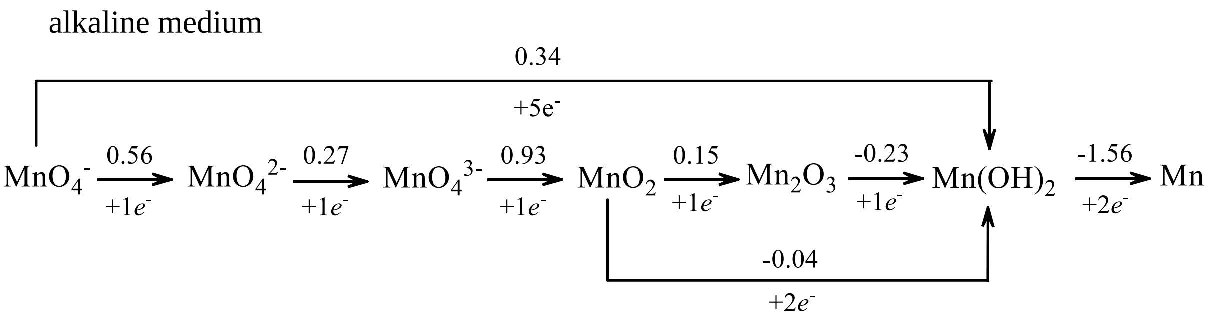
$\Delta G = -zFE < 0$, that is, $E = \varphi_C - \varphi_A > 0$ and $\varphi_C > \varphi_A$

Consequently, from two half-reactions, the reaction with a higher φ value will proceed in forward direction and the reaction with the lower φ value will proceed in back direction.

Latimer diagrams

Some elements may take several oxidation states. Electrode potentials for transitions of such elements from one oxidation state to another are usually present by *Latimer diagram*. Such diagrams for manganese in acidic and alkaline solution are the following:





From Latimer diagram it is seen, that, for example, the electrode potential for $MnO_2 \rightarrow Mn^{3+}$ transition equals 0.95 V in acidic medium and for $MnO_2 \rightarrow Mn_2O_3$

transition φ° = 0.15 V in alkaline medium. To calculate an electrode potential for any transition we should remember law of energy conservation. For example, for the transition:

$$A \rightarrow B \rightarrow C$$

the following equation is true:

$$\Delta G° = \Delta G°_1 + \Delta G°_2,$$

where $\Delta G° = \Delta G°_{A\rightarrow C}$, $\Delta G°_1 = \Delta G°_{A\rightarrow B}$ and $\Delta G°_2 = \Delta G°_{B\rightarrow C}$

In the case of redox reactions the abovementioned relation is fulfilled:

$$\Delta G° = -zFE^0.$$

Using this relation the following equation can be obtained:

$$E° = \frac{z_1 E°_1 + z_2 E°_2}{z}$$

Problem 11.2: Calculate the standard electrode potential for $Mn^{3+} \rightarrow Mn$ transition in acidic medium.

Solution:

Form Latimer diagram it is seen: $E°_1(Mn^{3+} \rightarrow Mn^{2+}) = 1.51$ V and $E°_2(Mn^{2+} \rightarrow Mn) = -1.18$ V. So for $E°(Mn^{3+} \rightarrow Mn)$ we obtain:

$$E° = \frac{z_1 E°_1 + z_2 E°_2}{z} = \frac{1 \cdot 1.51 + 2 \cdot (-1.18)}{3} = -0.28\,V$$

Problem 11.3: Equilibrate the following redox reaction by the electron-ion balance method:

$K_2Cr_2O_7 + FeCl_2 + HCl \rightarrow FeCl_3 + CrCl_3 + KCl + H_2O$

Problem 11.4: Determine in what direction the following reaction will proceed in standard conditions:

$I_{2(s)} + 5H_2O_2 = 2HIO_3 + 4H_2O$

1) $H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$, $\varphi^0 = 1.78$ V

2) $2IO_3^- + 12H^+ + 10e \rightarrow I_{2(s)} + 6H_2O$, $\varphi^0 = 1.19$ V

Problem 11.5: Determine in what direction the following reactions will proceed in standard conditions:

1) $H_3PO_4 + 2HI = H_3PO_3 + I_2 + H_2O$

2) $H_3PO_3 + SnCl_2 + H_2O = 2HCl + Sn + H_3PO_4$

3) $H_3PO_3 + 2AgNO_3 + H_2O = 2Ag + 2HNO_3 + H_3PO_4$

4) $H_3PO_3 + Pb(NO_3)_2 + H_2O = Pb + 2HNO_3 + H_3PO_4$

Problem 11.6: Calculate the potential of nickel electrode inserted in $NiCl_2$ solution with concentration 10^{-2} M? $\varphi^0(Ni^{2+}/Ni^0) = -0.25$ V.

Problem 11.7: The electromotive force of copper-zinc galvanic cell is 1.22 V. A copper electrode is inserted in solution with Cu^2 ions concentration of 0.1 M. Find the concentration of Zn^{2+} ions near zinc electrode. $\varphi^0(Cu^{2+}/Cu^0) = 0.34$ V, $\varphi^0(Zn^{2+}/Zn^0) = –0.76$ V.

Problem 11.8: Calculate the electromotive force of a galvanic cell consisting from two hydrogen electrodes. One electrode is immersed in a solution with pH = 3 and the second is immersed in a solution with pH = 8.

Problem 11.9: Calculate the electrode potential for $MnO_4^- \rightarrow MnO_2$ transition in acidic medium. Use the Latimer diagram from text above.

Problem 11.10: Calculate the electrode potential for $MnO_4^{2-} \rightarrow Mn(OH)_2$ transition in alkaline medium. Use the Latimer diagram from text above.

Theme XII
Coordination Compounds

Coordination compounds are also called *complex compounds*. They are called complex compounds because formed from simpler components coexisting with them in equilibrium in solution. They are called coordination compounds because formed on the principle of co-ordination (in Latin *ordinatio* means “ordering”). That is, coordination compound includes central atom and molecules or ions surrounding the central atom that are called ligands (this term is derived from the Latin verb *ligare* meaning “to bind”). Central atom (called also as complex former) and surrounding ligands compose *first coordination sphere* (Fig. 12.1). Overall number of positions that occupy ligands in the first coordination sphere is called the *coordination number* (CN) of complex former. Number of positions that occupy one ligand in the first coordination sphere is called *denticity* of the ligand. Ligands may be mono-, bi-, tri-, tetra-, penta-, hexa-dentate, *etc.* (every line denotes chain of atoms that connects coordinating atoms of the ligand).

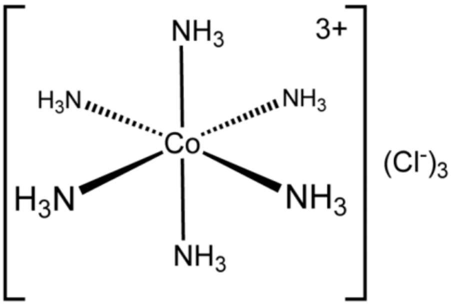


Fig. 12.1. Octahedron structure of $[Co(NH_3)_6]Cl_3$ complex. The coordination number of Co is 6, Cl^- ions are *outersphere* ligands.

Cycle formed by coordination of bidentate ligand to central atom is called chelate ring. First coordination sphere is written within square brackets with charge outside of brackets, for example, $[Pt(NH_3)_2Cl_2]$, $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Fe(CN)_6]^{4-}$, and $[Co(en)_3]^{3+}$ (where symbol en denotes chelating ligand ethylenediamine, $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$). There are some rules used to name such compounds:

- The name of the positive ion is written before the name of the negative ion.
- The name of the ligand is written before the name of the metal to which it is coordinated.
- The Greek prefixes *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, *hexa-*, and so on are used to indicate the number of ligands when these ligands are relatively simple. The Greek prefixes *bis-*, *tris-*, and *tetrakis-* are used with more complicated ligands.
- The names of negative ligands always end in *-o*, as in *fluoro* (F^-), *chloro* (Cl^-), *bromo* (Br^-), *iodo* (I^-), *oxo* (O^{2-}), *hydroxo* (OH^-), and *cyano* (CN^-).
- A handful of neutral ligands are given common names, such as *aquo* (H_2O), *ammine* (NH_3), and *carbonyl* (CO).
- Ligands are listed in the following order: negative ions, neutral molecules, and positive ions. Ligands with the same charge are listed in alphabetical order.
- The oxidation number of the metal atom is indicated by a Roman numeral in parentheses after the name of the metal atom.

- The names of complexes with a net negative charge end in *–ate*. For example, $[Co(SCN)_4]^{2-}$ is the tetrathiocyanatocobaltate(II) ion. When the symbol for the metal is derived from its Latin name, *-ate* is added to the Latin name of the metal. Thus, negatively charged iron complexes are ferrates and negatively charged copper complexes are cuprates.

For example, above written compounds are called respectively dichlorodiammineplatinum, hexaaquanickel(II)-cation, hexaamminenickel(II)-cation, hexacyanoferrate(II)-anion (or ferricyanide-anion), and *tris*-ethylenediamine-cobalt(III)-cation.

As was mentioned, complex compounds coexist in equilibrium with own components in solution. Equilibria of the complex formation are characterized by stepwise and overall stability constants, for example:

$[Ag(H_2O)_2]^+ + NH_3 = [Ag(H_2O)(NH_3)]^+ + H_2O$, K_1 (first stepwise stability constant)

$[Ag(H_2O)(NH_3)]^+ + NH_3 = [Ag(NH_3)_2]^+ + H_2O$, K_2 (second stepwise stability constant)

$[Ag(H_2O)_2]^+ + 2NH_3 = [Ag(NH_3)_2]^+ + 2H_2O$, β (overall stability constant)

It is evident that

$$K_1 = \frac{[\mathrm{Ag(H_2O)(NH_3)^+}]}{[\mathrm{Ag(H_2O)_2}^+][\mathrm{NH_3}]}$$

$$K_2 = \frac{[\mathrm{Ag(NH_3)_2}^+]}{[\mathrm{Ag(H_2O)(NH_3)^+}][\mathrm{NH_3}]}$$

$$\beta = \frac{[\mathrm{Ag(NH_3)_2}^+]}{[\mathrm{Ag(H_2O)_2}^+][\mathrm{NH_3}]^2} = K_1 K_2$$

Problem 12.1: Will silver halide precipitate by adding the following salts to one liter of 0.1 M solution of $[Ag(NH_3)_2]NO_3$, containing also 1 M of ammonia: a) 1.19 mg of KBr, b) 1.66 mg of KI? $\beta([Ag(NH_3)_2]^+) = 1.08\cdot10^7$, solubility products: $K_s(AgBr) = 6\cdot10^{-13}$, $K_s(AgI) = 1.1\cdot10^{-16}$.

Solution:

$c = 0.1$ M
V = 1 liter
$c_{\text{ammonia}} = 1$ M
$m_{\text{KBr}} = 1.19 \cdot 10^{-3}$ g
$m_{\text{KI}} = 1.66 \cdot 10^{-3}$ g
$\beta([\text{Ag(NH}_3)_2]^+) = 1.08 \cdot 10^7$
$K_s(\text{AgBr}) = 6 \cdot 10^{-13}$
$K_s(\text{AgI}) = 1.1 \cdot 10^{-16}$

---

sediment – ?

Let's write an equilibrium equation for $[\text{Ag(NH}_3)_2]^+$ complex compound:

$[\text{Ag(NH}_3)_2]^+ = \text{Ag}^+ + 2\text{NH}_3$

$$\beta = \frac{[\text{Ag(NH}_3)_2{}^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

Due to the presence of ammonia excess in solution the concentration $[\text{NH}_3] = 1$ M (addition from $[\text{Ag(NH}_3)_2]^+$ dissociation is very small). So

$$[\text{Ag}^+] = \frac{[\text{Ag(NH}_3)_2{}^+]}{\beta[\text{NH}_3]^2} = \frac{0.1}{1.08 \cdot 10^7 \cdot 1^2} = 9.3 \cdot 10^{-9}\ \text{M}$$

Also we need to calculate concentrations of salts added in solution:

a) $[\text{KBr}] = \frac{m}{MV} = \frac{1.19 \cdot 10^{-3}}{119 \cdot 1} = 10^{-5}\text{M}$

b) $[\text{KI}] = \frac{m}{MV} = \frac{1.66 \cdot 10^{-3}}{166 \cdot 1} = 10^{-5}\text{M}$

Now let's calculate the ion products and compare them with corresponding K_s values:

a) $[\text{Ag}^+][\text{Br}^-] = 9.3 \cdot 10^{-9} \cdot 10^{-5} = 9.3 \cdot 10^{-14} < K_s(\text{AgBr})$
(no sediment)

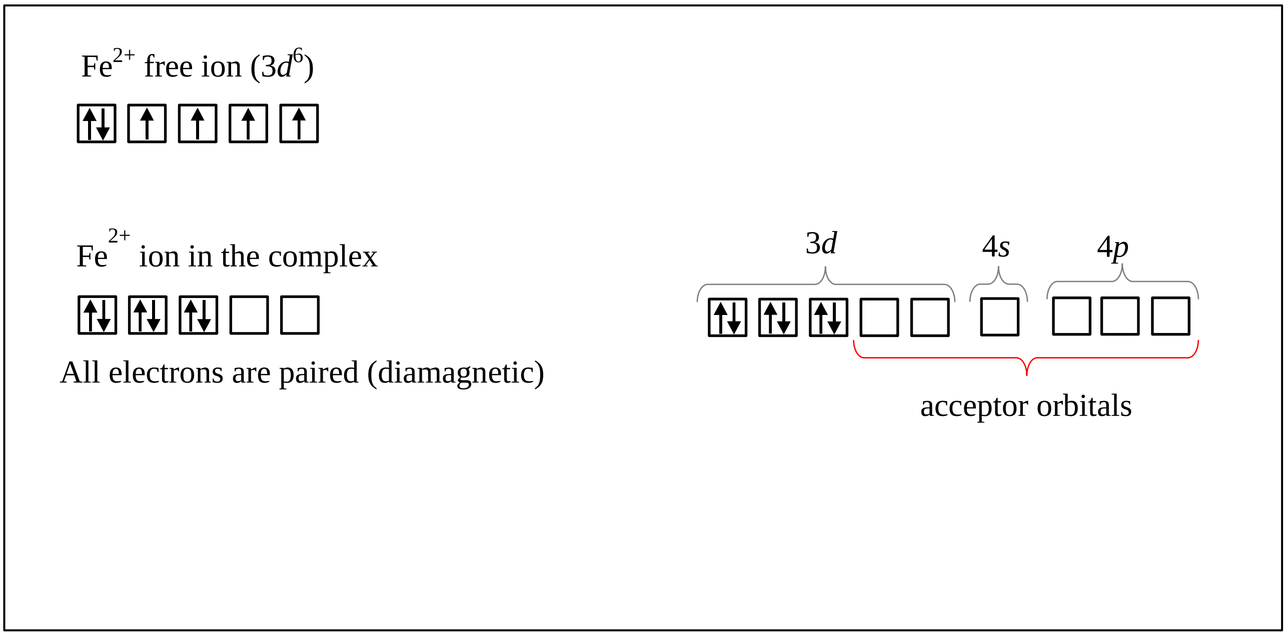
b) $[\text{Ag}^+][\text{I}^-] = 9.3 \cdot 10^{-9} \cdot 10^{-5} = 9.3 \cdot 10^{-14} > K_s(\text{AgI})$
(sediment will appear)

Bonds in coordination compounds

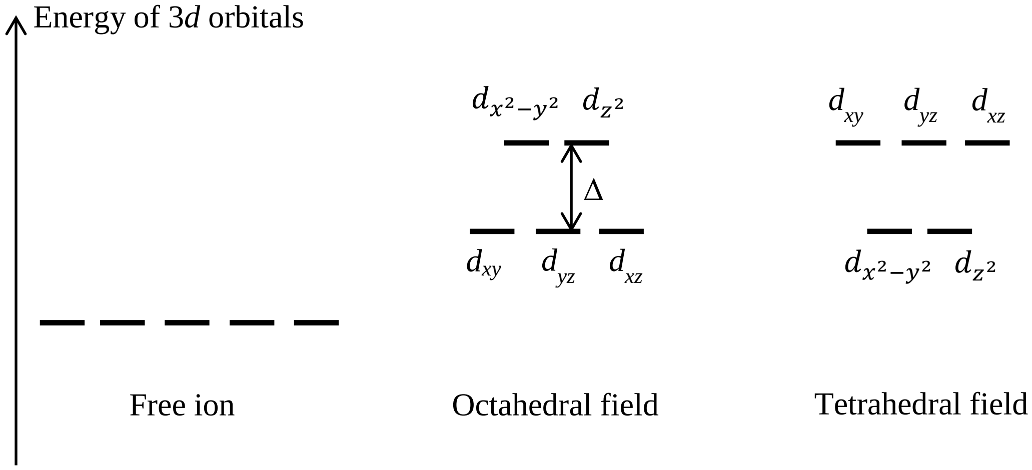
Let's consider two methods for describing the bonds in coordination compounds, namely, *valence bond theory* and *crystal field theory*.

In valence bond theory (VB) the bond formation is interpreted as a result of donor-acceptor interaction where the metal-complex former and ligands are the acceptor and donors respectively. In accordance with the foregoing discussion of the valence bond theory, in the case of complexes the different hybridization types of the central atom orbitals can by realized: sp (linear form, CN = 2), sp^2 (trigonal form, CN = 3), sp^3 (tetrahedron, CN = 4), dsp^2 (plane square, CN = 4), sp^3d (square pyramid or trigonal bipyramid, CN = 5), and sp^3d^2 or d^2sp^3 (octahedron, CN = 6). Hybridization types can be easy determined from the physical-chemical properties of the complexes.

For example, the hexacyanoferrate(II)-ion ($[Fe(CN)_6]^{4-}$) is diamagnetic. Let's prove the hybridization type of the iron(II) ion. It can be seen that Fe^{2+} ion (d^6 configuration) has three *d*-orbitals filled by three electron pairs, and two *d*-orbitals remain free for accepting two electron pairs from the ligands. So, the hybridization type of the Fe^{2+} ion is d^2sp^3.



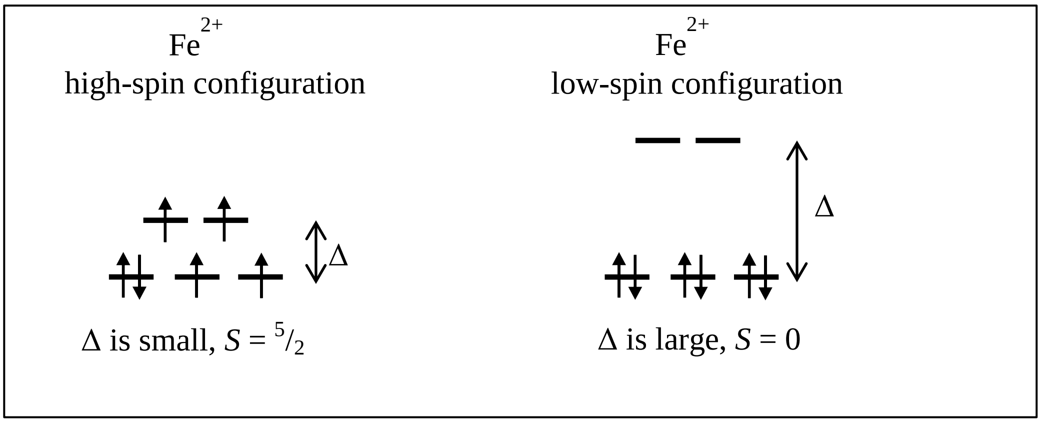
In the crystal field theory the pure electrostatic repulsion between *d*-orbital electrons of central atom and ligand electrons is considered. In an octahedral field the electron densities of the $d_{x^2-y^2}$ and d_{z^2} orbitals are directed toward the ligands and electron densities of the d_{xy}, d_{xz}, and d_{yz} orbitals are directed between the ligand orbitals therefore the $d_{x^2-y^2}$ and d_{z^2} orbitals undergo stronger repulsion compared with the d_{xy}, d_{xz}, and d_{yz} and are destabilized by energy. For a tetrahedral field inverse relationship of energies is realized. That can be represented in the following diagram.



Parameter of the *crystal field splitting* energy is denoted as Δ. The *spectrochemical series* orders ligands according to the crystal field splitting caused by them (increasing Δ parameter):

$I^- < Br^- < Cl^- < OH^- < RCOO^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^- < CO$.
weak field ligands *strong field ligands*

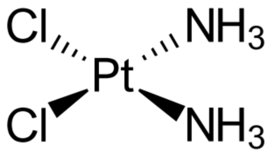
Due to different values of ligand field some metal ion electronic configurations, d^4, d^5, d^6, and d^7, may be high- or low-spin. The adoption of a high- or low-spin configuration will depend upon the relative magnitudes of the Δ parameter and spin-pairing energy, E_p (note that electron pairing is unfavorable process). In the case of *weak field ligands* ($\Delta < E_p$) the high-spin (HS) configuration is realized and for *strong field ligands* ($\Delta > E_p$) the low-spin (LS) configuration is adopted:



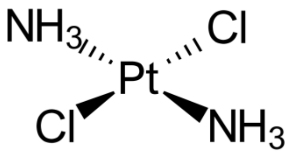
Similarly for Fe^{3+} $3d^5$ configuration $\{S = {}^5/_2$ (HS), $S = ½$ (LS)$\}$.

Isomerism of coordination compounds

Now we consider *isomerism* of coordination compounds. A square planar species of general formula XY_2Z_2 (for example, $[Pt(NH_3)_2Cl_2]$) has two stereoisomers, *cis*-XY_2Z_2 and *trans*-XY_2Z_2 (for example, *cis*-$[Pt(NH_3)_2Cl_2]$ (*cisplatin*) is strong *anticancer* agent and *trans*-$[Pt(NH_3)_2Cl_2]$ is biologically inactive).

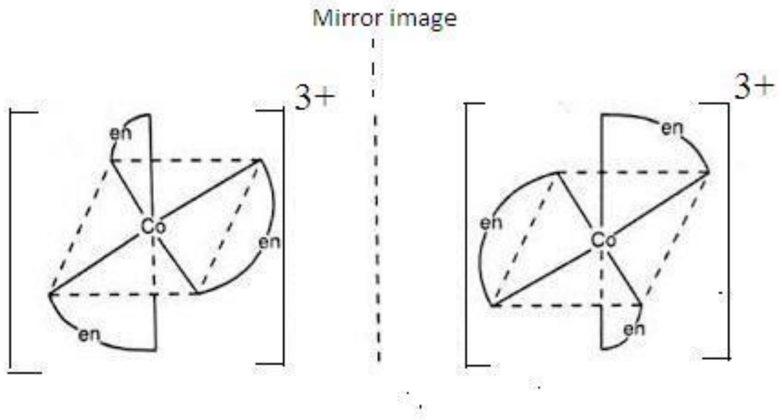


cis



trans

Two molecular species which are mirror images of each other and are non-superposable are called *enantiomers* or *optical isomers*, because they *rotate the polarization plane* of the plane polarized light in different directions, left or right. For example, the compound $[Co(en)_3]^{3+}$ has two enantiomers, Δ-$[Co(en)_3]^{3+}$ (*d*-form) and Λ-$[Co(en)_3]^{3+}$ (*l*-form).

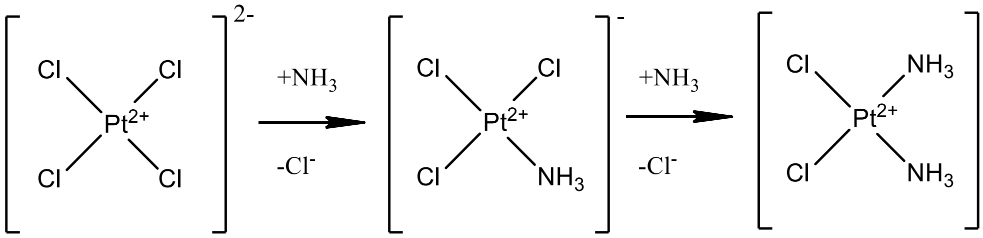


***l*-form** **d*-form**

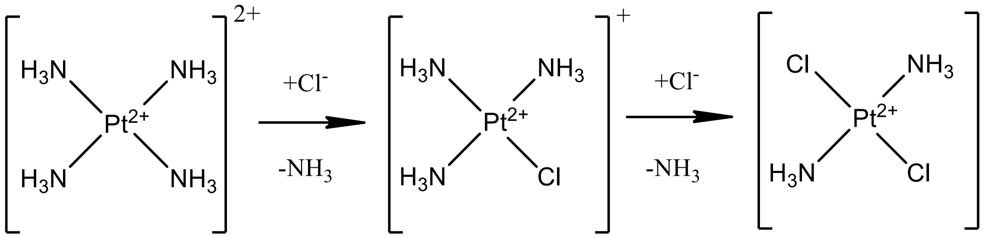
In conclusion, we consider *trans-influence* in coordination compounds which was discovered by the Russian chemist Chernyaev. *Trans-influence* is the ability of given ligand to weaken the bond of metal with the other ligand being in *trans*-position to given ligand. By this ability the ligands are arranged in a *trans-influence series* (related to platinum ion):

$H_2O < OH^- < NH_3 < Cl^- < Br^- < I^- < NO_2^- < NO < CO < CN^-$.

Because chloride-ion is more powerful *trans*-agent than ammonia, when reacting $[PtCl_4]^{2-}$ with NH_3 the *cis*-$[Pt(NH_3)_2Cl_2]$ isomer is obtained whereas when reacting $[Pt(NH_3)_4]^{2+}$ with Cl^- the *trans*-$[Pt(NH_3)_2Cl_2]$ isomer is obtained.



cis isomer



trans isomer

So, *trans-effect* can be used for a directed synthesis of coordination compounds.

Directed synthesis is a dream of all chemists!

Problem 12.2: Name the following neutral complex compounds: $[Cr(H_2O)_4PO_4]$, $[Cu(NH_3)_2(SCN)_2]$, $[Pd(NH_2OH)_2Cl_2]$, $[Rh(NH_3)_3(NO_2)_3]$, $[Pt(NH_3)_2Cl_4]$.

Problem 12.3: Name the following complex salts: $[Pd(H_2O)(NH_3)_2Cl]Cl$, $[Cu(NH_3)_4](NO_3)_2$, $[Co(NH_3)_5SO_4]NO_3$, $K_4[Fe(CN)_6]$, $(NH_4)_3[RhCl_6]$, $K_2[Pt(OH)_5Cl]$, $K_2[Cu(CN)_4]$.

Problem 12.4: Calculate the concentration of Cd^{2+} ions in solution contained 0.1 M of $K_2[Cd(CN)_4]$ and additional 6.5 g/liter of KCN. $\beta([Cd(CN)_4]^{2-}) = 1.3 \cdot 10^{17}$.

Problem 12.5: Will copper sulfide precipitate when 300 ml of 0.001 M potassium sulfide solution is added to 200 ml of 0.01 M $K_2[Cu(CN)_4]$ solution? $\beta([Cu(CN)_4]^{2-}) = 2 \cdot 10^{27}$, $K_s(CuS) = 3.2 \cdot 10^{-38}$.

Problem 12.6: What is the structure of $[CoCl_4]^{2-}$ ion, if the value of its magnetic moment indicates the presence of three unpaired electrons in electronic configuration?

Problem 12.7: The $[AuCl_4]^-$ ion is diamagnetic. What is the structure of this ion?

Appendix

Table 1. Dissociation constants of some weak electrolytes in water solutions at 25°C

Electrolyte	K	$pK = -\log K$
NH_4OH ammonium hydroxide	$1.8\cdot10^{-5}$	4.75
HF hydrogen fluoride	$6.6\cdot10^{-4}$	3.18
HCN hydrogen cyanide	$7.9\cdot10^{-10}$	9.10
H_2S hydrogen sulfide	$K_1 = 6.0\cdot10^{-8}$ $K_2 = 1.0\cdot10^{-14}$	7.22 14.0
H_2Se hydrogen selenide	$K_1 = 1.3\cdot10^{-4}$ $K_2 = 1.0\cdot10^{-11}$	3.89 11.0
H_2Te hydrogen telluride	$K_1 = 1.0\cdot10^{-3}$ $K_2 = 1.0\cdot10^{-11}$	3.0 11.0
HNO_2 nitrous acid	$4\cdot10^{-4}$	3.40
HOCl hypochlorous acid	$5.0\cdot10^{-8}$	7.30
HCOOH formic acid	$1.8\cdot10^{-4}$	3.74
CH_3COOH acetic acid	$1.8\cdot10^{-5}$	4.75
H_2O_2 hydrogen peroxide	$K_1 = 2.6\cdot10^{-12}$	11.58
H_2SO_4 sulfuric acid	$K_2 = 1.2\cdot10^{-2}$	1.92
H_2SO_3 sulfurous acid	$K_1 = 1.6\cdot10^{-2}$ $K_2 = 6.3\cdot10^{-8}$	1.80 7.21
H_2SeO_3 selenous acid	$K_1 = 3.5\cdot10^{-3}$ $K_2 = 5.0\cdot10^{-8}$	2.46 7.3
H_2CO_3 carbonic acid	$K_1 = 4.5\cdot10^{-7}$ $K_2 = 4.7\cdot10^{-11}$	6.35 10.33
H_3BO_3 boric acid	$K_1 = 5.8\cdot10^{-10}$	9.24
H_3PO_4 phosphoric acid	$K_1 = 7.5\cdot10^{-3}$ $K_2 = 6.3\cdot10^{-8}$ $K_3 = 1.3\cdot10^{-12}$	2.12 7.20 11.89

Table 2. Standard electrode potentials in water solutions at 25 °C

Element	Electrode process	φ^0, V
Ag	$Ag^+ + e^- = Ag$	0.80
	$[Ag(CN)_2]^- + e^- = Ag + 2CN^-$	−0.29
Al	$Al^{3+} + 3e^- = Al$	−1.66
Au	$Au^+ + e^- = Au$	1.69
	$Au^{3+} + 3e^- = Au$	1.50
Ca	$Ca^{2+} + 2e^- = Ca$	−2.87
Cl	$Cl_2 + 2e^- = 2Cl^-$	1.36
	$HOCl + H^+ + 2e^- = Cl^- + H_2O$	1.49
Cr	$Cr^{3+} + 3e^- = Cr$	−0.74
	$CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3 + 5OH^-$	−0.13
	$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.33
Cu	$Cu^+ + e^- = Cu$	0.52
	$Cu^{2+} + e^- = Cu^+$	0.15
	$Cu^{2+} + 2e^- = Cu$	0.34
F	$F_2 + 2e^- = 2F^-$	2.87
Fe	$Fe^{2+} + 2e^- = Fe$	−0.44
	$Fe^{3+} + 3e^- = Fe$	−0.04
	$Fe^{3+} + e^- = Fe^{2+}$	0.77
H	$2H^+ + 2e^- = H_2$	0
	$H_2 + 2e^- = 2H^-$	−2.25
I	$I_{2(solid)} + 2e^- = 2I^-$	0.54
	$2IO_3^- + 12H^+ + 10e^- = I_{2(solid)} + 6H_2O$	1.19
	$2HOI + 2H^+ + 2e^- = I_{2(solid)} + 2H_2O$	1.45
Li	$Li^+ + e^- = Li$	−3.04
Ni	$Ni^{2+} + 2e^- = Ni$	−0.25
P	$H_3PO_4 + 2H^+ + 2e^- = H_3PO_3 + H_2O$	−0.28
Pb	$Pb^{2+} + 2e^- = Pb$	−0.13
	$Pb^{4+} + 2e^- = Pb^{2+}$	1.69
Sn	$Sn^{2+} + 2e^- = Sn$	−0.14
	$Sn^{4+} + 2e^- = Sn^{2+}$	0.15
Zn	$Zn^{2+} + 2e^- = Zn$	−0.76

Answers to Problems

2.4 606 ml
2.5 28 g/mol
2.6 64 g/mol

3.2 79.9 g/mol, 9 g/mol
3.3 68.7 g/mol, Ba
3.4 0.54 g

4.4 6s, 6p

5.1 a) sp^2, b) sp^3d, c) sp^3, d) sp^3d, e) sp^3d, f) sp^3
5.2 c, d, e, f
5.3 a) sp^3d, b) sp^2, c) sp^2, d) sp^2, e) sp^3

6.3 –238.6 kJ/mol
6.4 No, 762 K
6.5 129 kJ/mol, 84 kJ/mol, –15 kJ/mol, 1081 K

7.3 2.4
7.4 77.4 kJ/mol
7.5 a) $[N]_0 = 7$ mol/l, $[H_2]_0 = 21$ mol/l
b) to the left, c) to the right, d) $K = 0.005$
7.6 $[CO] = 0.05$ mol/l, $[CO_2] = 0.035$ mol/l,
$\Delta G^0 = 0.88$ kJ

8.2 3.2%
8.3 3.45 M, 6.9 N
8.4 200 ml
8.5 120 ml
8.6 a) 353 kPa, b) –0.27 °C, c) 100.08 °C, d) 2.331 kPa
8.7 eight atoms

9.3 1500 ml
9.4 in 33 times
9.5 $9\cdot10^{-5}$ M
9.6 0.9
9.7 0.75
9.8 0.0024 M

10.5 $2.2 \cdot 10^{-7}$ M

10.6 a) 2.5, b) 11.1, c) 4.0

10.7 4

10.8 no (IP = $6.25 \cdot 10^{-6}$)

10.9 yes (IP = $0.13 \cdot 10^{-7}$)

10.11 $K_h = 1.5 \cdot 10^{-11}$, $h = 2.7 \cdot 10^{-5}$, pH = 7.7

10.12 11.3

10.13 0.1 M: $h = 0.011$, pH = 11
0.001 M: $h = 0.11$, pH = 10

11.6 –0.31 V

11.7 10^{-5} M

11.8 0.3 V

11.9 1.69 V

11.10 0.28 V

12.4 $7.7 \cdot 10^{-15}$ M

12.5 yes

Recommended Literature

1. Glinka N.L. General Chemistry: tutorial. – M.: KnoRus, 2018. – 746 p. (in Russian)
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