## МИНИСТЕРСТВО ЗДРАВООХРАНЕНИЯ РЕСПУБЛИКИ БЕЛАРУСЬ БЕЛОРУССКИЙ ГОСУДАРСТВЕННЫЙ МЕДИЦИНСКИЙ УНИВЕРСИТЕТ КАФЕДРА ОБЩЕЙ ХИМИИ

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# ВВЕДЕНИЕ В ОБЩУЮ ХИМИЮ INTRODUCTION TO THE GENERAL CHEMISTRY

Учебно-методическое пособие



Минск БГМУ 2014

УДК 54(811.111)-054.6(075.8) ББК 24.1(81.2 Англ-923) Х95

Рекомендовано Научно-методическим советом университета в качестве учебно-методического пособия 26.11.2014 г., протокол № 3

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Х95 Введение в общую химию = Introduction to the General Chemistry : учеб.-метод. пособие / В. В. Хрусталёв, Е. В. Барковский, Т. А. Хрусталёва. – Минск : БГМУ, 2014.-64 с.

ISBN 978-985-567-113-9.

Издание содержит теоретический материал по общей химии, примеры расчетов для проведения 27 занятий.

Предназначено для иностранных студентов подготовительного отделения.

УДК 54(811.111)-054.6(075.8) ББК 24.1(81.2 Англ-923)

ISBN 978-985-567-113-9

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#### **PREFACE**

The book provides an introduction into the General Chemistry. It is necessary for foreign students who are going to pass the Chemistry exam into the Belorussian State Medical University in English.

Actually, this book is a kind of compromise between translation of chemistry text-books from Russian to English and popularizing material from original American sources. Authors hope that they combined the best Belorussian traditions with the best international points of view on Chemistry teaching. Even though entrance exam into University usually requires some knowledge on very specific set of rules mostly based on simplifications and overestimations, this book not just deals with those "rules of thumb" but also provides modern explanations and interpretations.

Authors are looking forward to receive any feedback from readers and colleagues regarding style and content of the book.

#### **LESSON 1**

### 1.1 PHYSICAL AND CHEMICAL PROPERTIES OF SUBSTANCES: WHAT IS THE DIFFERENCE?

The question from the title of this subsection is very important. It can be rephrased in the following ways. What is chemistry? What is the subject of the discipline you are starting (or, hopefully, continuing) to study? What is the difference between chemistry and physics?

Physical properties of a substance are: state of matter (solid, liquid, gas and plasma), density (the ratio between the mass and the volume), color (pink, blue, green, etc.), taste (sour, sweet, bitter, salty), solubility (the mass of substance that can be solved in water or other liquids at a given temperature), boiling temperature (the temperature of vaporization), freezing temperature (the temperature of crystallization).

Chemical properties of a substance are described as its abilities to form other substances in different conditions.

In physical processes a substance changes at least one of its conditions: its volume, its shape, its position in the space, etc., while new substances are not formed. Phase transitions are also physical processes. There are several traditional examples of such physical processes: melting of the ice and crystallization of the water, boiling of the water and condensation of the vapor.

Chemical processes are described by chemical reactions. A chemical reaction is a process that leads to the transformation of one set of chemical substances to another. Substances from the first set are called "reactants". Substances from the second set are called "products". For example, sulfur and oxygen (the reactants) may react with each other and form sulfur dioxide (the product).

Chemical equation for this reaction is as follows:  $S + O_2 = SO_2$ .

The rearrangement of atoms happens in chemical reactions, while atoms themselves stay the same. Nuclear reactions are not chemical reactions, even though new substances are formed in them. In those nuclear reactions atoms of one chemical element turn to atoms of another chemical element. So, nuclear reactions are studied in the course of physics and not chemistry.

There are several signs of chemical reactions: the thermal change (in some cases the heat is produced in chemical reaction, in other cases the heat is adsorbed from surroundings during the chemical reaction); the smell (for example, hydrogen sulfide has a smell of rotten eggs); formation of a gas without any characteristic smell; the change in color; precipitation (formation of insoluble substance).

Finally, chemistry is the science on the interactions of matter with other matter and with energy.

#### **Questions:**

- a. List several physical properties of water, sugar and salt.
- b. A piece of chalk has been dissolved in hydrochloric acid. Was it a physical or chemical process?
  - c. What is the difference between reactants and products?
- d. What are the signs of chemical reactions? How can you know that some chemical reaction happened?
  - e. What is the subject of chemistry?

#### 1.2 ATOMS AND MOLECULES

Atom is the smallest piece of an element that maintains the identity of that element.

There are many substances that exist as two or more atoms connected together. These combinations are called molecules. A molecule is the smallest part of a substance that has the physical and chemical properties of that substance.

Some elements exist in form of molecules. For example, hydrogen and oxygen exist as two-atom molecules. Sulfur may exist as an eight-atom molecule,  $S_8$ , while phosphorus may exist as a four-atom molecule,  $P_4$ . Other elements, such as carbon (C), exist as individual atoms, rather than molecules.

In general, when nonmetal connects with other nonmetal, the compound typically exists as molecule.

A **chemical compound** is a chemical substance consisting of **two or more different chemical elements**. Chemical compounds can be molecular compounds held together by covalent bonds, salts held together by ionic bonds, intermetallic compounds held together by metallic bonds, or complexes held together by coordinate covalent bonds. Pure metals consist of atoms, positively charged ions and free electrons (electron "gas").

Pure chemical elements are not considered chemical compounds, even if they consist of molecules that contain only multiple atoms of a single element (such as  $H_2$ ,  $S_8$  etc.), which are called diatomic molecules or polyatomic molecules.

Substances composed from atoms of the same element are historically called "simple substances". So, the term "pure chemical element" is a synonym of the term "simple substance".

**Allotropy** is the property of some chemical elements to exist in **two or more different forms**, known as allotropes of these elements.

Coming back to carbon, the allotropes of that element include diamond (where the carbon atoms are bonded together in a tetrahedral lattice arrangement) and graphite (where the carbon atoms are bonded together in sheets

of a hexagonal lattice). The term allotropy is used for pure chemical elements

only, and not for chemical compounds. Allotropy refers only to different substances which exist as pure chemical elements within the same phase (i. e. different solid, liquid or gas substances).

#### **Questions:**

- a. What is atom?
- b. What is molecule?
- c. List some substances which consist of molecules.
- d. List some substances of nonmolecular structure.
- e. Give a definition of pure chemical element.
- f. Give a definition of chemical compound.
- g. Give a definition of simple substance.
- h. What is allotropy?
- i. Are oxygen  $(O_2)$  and ozone  $(O_3)$  allotropes?

#### 1.3. SYMBOLS OF CHEMICAL ELEMENTS

 ${\it Table~1.3} \\ {\bf English~names~of~chemical~elements~and~their~symbols}$ 

Element Name	Symbol	Element Name	Symbol
Aluminum Al		Mercury	Hg
Argon	Ar	Molybdenum	Mo
Arsenic	As	Neon	Ne
Barium	Ba	Nickel	Ni
Beryllium	Be	Nitrogen	N
Bismuth	Bi	Oxygen	0
Boron	В	Palladium	Pd
Bromine	Br	Phosphorus	P
Calcium	Ca	Platinum	Pt
Carbon	С	Potassium	K
Chlorine	Cl	Radium	Ra
Chromium	Cr	Radon	Rn
Cobalt	Co	Rubidium	Rb
Copper	Cu	Scandium	Sc
Fluorine	F	Selenium	Se
Gallium	Ga	Silicon	Si
Germanium	Ge	Silver	Ag
Gold	Au	Sodium	Na
Helium	Не	Strontium	Sr
Hydrogen	Н	Sulfur	S
Iodine	I	Tantalum	Ta
Iridium	Ir	Tin	Sn
Iron	Fe	Titanium	Ti
Krypton	Kr	Tungsten	W
Lead	Pb	Uranium	U
Lithium	Li	Xenon	Xe
Magnesium	Mg	Zinc	Zn
Manganese	Mn	Zirconium	Zr

The coefficient always goes before the compound or molecule, not after. Coefficient shows the number of molecules, compounds or moles.

The subscript is written in small numbers by the bottom right corner of the symbol. Subscript shows the number of certain atoms or groups of atoms in a given compound or molecule.

For example, 4H<sub>2</sub>O means four (coefficient) molecules of water. Water consists of two (subscript) hydrogen atoms and a single oxygen atom.

Chemical formula  $2Al_2(SO_4)_3$  means two (coefficient) compounds of aluminum sulfate. Aluminum sulfate consists of two (subscript) aluminum ions and three (subscript behind the brackets) sulfate anions. Each sulfate anion consists of a single sulfur atom and four (subscript inside the brackets) oxygen atoms.

#### **Exercises:**

- a. What does the coefficient show?
- b. What does the subscript show?
- c. Write chemical formulas of compounds made up from i) single iron atom and three chlorine atoms; ii) two aluminum atoms and three oxygen atoms; iii) single calcium atom, single carbon atom and three oxygen atoms.
- d. Read the names of the following salts:  $CuSO_4$ ,  $CuSO_3$ , CuS,  $Mg(NO_3)_2$ ,  $Mn(NO_2)_2$ .
- e. Read the names of the following hydroxides: Fe(OH)<sub>3</sub>, Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, KOH, NaOH.
- f. Read the names of the following acids:  $H_2SO_4$ ,  $H_3PO_4$ ,  $HNO_3$ ,  $HNO_2$ , HCl.

#### **LESSON 2**

#### 2.1 ATOMIC MASS AND MOLECULAR MASS

The atomic mass unit (u) is defined as one-twelfth of the mass of a carbon-12 atom, an isotope of carbon that has six protons and six neutrons in its nucleus. By this scale, the mass of a proton is 1.00728 u, the mass of a neutron is 1.00866 u, and the mass of an electron is 0.000549 u (1835 times lower than the mass of a proton, 1837 times lower than the mass of a neutron, and 1821 times lower than the atomic mass unit). Approximate mass of an atom may be estimated simply — by counting the total number of protons and neutrons in the nucleus (that number is known as mass number).

The molecular mass is the sum of mass numbers of all the atoms in a molecule.

#### 2.2 THE MOLE AND MOLAR MASS

Chemists usually deal with millions, billions, and trillions of atoms and molecules at a time. Mole is a unit of amount that relates quantities of substances on a scale that is easy to interact with.

Chemistry uses a unit of amount called mole. A mole is a *number of things* equal to the number of atoms in exactly 12 g of carbon-12. Experimental measurements have determined that this number is very large:

1 mol = 
$$6.02214179 \times 10^{23}$$
 things ( $N_A = Avogadro's number$ )

In chemical calculations we usually use two digits after the point:  $N_A = 6.02 \cdot 10^{23}$ .

Once again, a mole means a number of things  $(6.02 \cdot 10^{23} - a)$  very big number), just like a dozen means a certain number of things (twelve).

**Molar mass** is the mass of 1 mole of a given substance. Molar mass is measured in grams per mole.

The number of moles (n) is equal to the ratio between mass (m, measured in grams) and molar mass (M, measured in gram/mole).

$$n = m / M$$

The numbers representing molar mass and molecular mass of the given substance are exactly the same, even though molar mass is measured in grams per mole, while molecular mass is measured in relative units.

#### **Ouestions:**

- a. Give the definition of the atomic mass unit.
- b. What is the molecular mass?
- c. How to determine a mass number of an atom?
- d. How to determine molecular mass of a molecule?
- e. What is Avogadro's number?
- f. What is the meaning of mole?
- g. Give a definition of molar mass.
- h. Why numbers representing molecular and molar masses are always the same?

#### **Exercises:**

- a. Calculate molecular masses of the following substances:  $HNO_3$  (Nitric acid); KOH (Potassium hydroxide);  $ZnSO_4$  (Zinc sulfate);  $Fe_2O_3$  (Iron (III) oxide);  $MgCO_3$  (Magnesium carbonate);  $Mg_3(PO_4)_2$  (Magnesium phosphate);  $Al_2(SO_4)_3$  (Aluminum sulfate).
- b. Calculate molar masses of the following substances: MgO (Magnesium oxide); HCl (Hydrochloric acid); FeSO<sub>4</sub> (Iron (II) sulfate); Al(OH)<sub>3</sub> (Aluminum hydroxide); NH<sub>4</sub>NO<sub>3</sub> (Ammonium nitrate); Cu(NO<sub>3</sub>)<sub>2</sub> (Copper (II) nitrate); BaSO<sub>4</sub> (Barium sulfate).

- c. How many molecules (or chemical compounds) are there in 0.5 moles of  $CO_2$  (Carbon dioxide); in 3 moles of  $FeSO_4$  (Iron (II) sulfate); in 0.0005 moles of  $H_2O$  (Water); 0.1 moles of  $Na_2HPO_4$  (Disodium phosphate); 0.15 moles of NaCl (Sodium chloride)?
- d. How many molecules (or chemical compounds) are there in 128 g of O<sub>2</sub> (Oxygen); in 100 g of KCl (Potassium chloride); in 200 g of FeO (Iron (II) oxide); in 0.5 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Potassium dichromate); in 30 g of H<sub>2</sub> (Hydrogen)?
- e. Determine the number of moles for  $18.06 \cdot 10^{23}$  H<sub>2</sub>O (Water) molecules;  $3.01 \cdot 10^{22}$  HNO<sub>3</sub> (Nitric acid) compounds;  $1.8 \cdot 10^{22}$  C (Carbon) atoms;  $1 \cdot 10^{15}$  Na<sup>+</sup> (Sodium cation) ions;  $0.5 \cdot 10^{30}$  SO<sub>4</sub><sup>2-</sup> (Sulfate anion) ions?
- f. What is the mass of 5 mol of  $Al_2O_3$  (Aluminum oxide); 0.2 mol of  $H_2$  (Hydrogen); 2.5 mol of  $Mg^{2+}$  (Magnesium cation); 50 mol of  $H_2SO_4$  (Sulfuric acid); 0.001 mol of NaOH (Sodium hydroxide)?
- g. How many moles are present in 250 g of H<sub>2</sub>O (Water); in 100 g of H<sub>2</sub>SO<sub>4</sub> (Sulfuric acid); 5 g of CaCO<sub>3</sub> (Calcium carbonate); 0.5 g of FeSO<sub>4</sub> (Iron (II) sulfate); 80 g of H<sub>2</sub>S (Hydrogen sulfide)?
- h. Determine the mass (in grams) of a single  $N_2$  (Nitrogen) molecule;  $NH_3$  (Ammonia) molecule;  $SO_4^{2-}$  ion (Sulfate anion);  $PO_4^{3-}$  ion (Phosphate anion);  $HPO_4^{2-}$  ion (Hydrogenphosphate anion)?

#### LESSON 3

#### 3.1 VALENCE

Valence (it also may be written as valency or valence number) is the number of chemical bonds a given atom has formed in a given molecule.

The number of bonds formed by a given element was originally thought to be a fixed chemical property. In fact, in most cases this is not true. For example, phosphorus often has a valence of three, but can also have other valences.

Nowadays the definition of valence has become quite different from the classic one. The current International Union of Pure and Applied Chemistry (IUPAC) version of that term, adopted in 1994: "The maximum number of univalent atoms (originally hydrogen or chlorine atoms) that may combine with an atom of the element under consideration, or with a fragment, or for which an atom of this element can be substituted".

Valence is written in Roman numbers which has no sign (no plus or minus). For example, the valence of hydrogen is always equal to "I". In the most of the substances the valence of oxygen is equal to "II".

Each chemical bond is represented by a line in diagrams. Total number of lines near the given atom is equal to its valence. For example, the valence of sulfur in sulfur trioxide is equal to six. The valence of phosphorus in phosphoric acid is equal to five (figure 3.1).

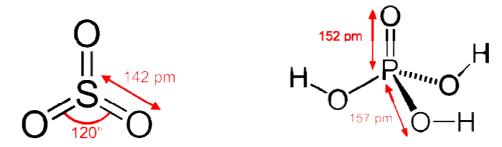


Figure 3.1. Structures of SO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>

#### 3.2 CHEMICAL EQUATIONS AND THEIR BALANCING

The law of conservation of matter says that matter cannot be created or destroyed. In chemical equations, the number of atoms of each element in the reactants must be the same as the number of atoms of each element in the products. The mass of all the products should be the same as the mass of all reactants (if we are not taking into account the famous Einstein's equation  $E = mc^2$  — the change in energy characteristic to every chemical reaction should lead to some little changes in the mass of substances).

Coefficients are used to balance a chemical equation.

Coefficient is a number in a chemical equation indicating the number of molecules (or moles) of the substance.

The sense of the balance is to make the law of conservation of matter obey.

#### **Exercises:**

- 1. Balance the following chemical equations:
- a)  $Na + H_2O \rightarrow NaOH + H_2\uparrow$
- b)  $Al_2O_3 + HCl \rightarrow AlCl_3 + H_2O$
- c)  $P + O_2 \rightarrow P_2O_5$
- d)  $Mg + O_2 \rightarrow MgO$
- e)  $Cr_2O_3 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + H_2O$
- f)  $Fe(OH)_3 + H_3PO_4 \rightarrow FePO_4 + H_2O$
- g)  $Zn(OH)_2 + HNO_3 \rightarrow Zn(NO_3)_2 + H_2O$
- h)  $Fe_2O_3 + Al \rightarrow Fe + Al_2O_3$
- 2. Finish chemical equations and then balance them:
- a)  $Zn + Cl_2 \rightarrow ?$
- b) Fe + ?  $\rightarrow$  FeCl<sub>3</sub>
- c) Ca + HCl  $\rightarrow$  ? + H<sub>2</sub> $\uparrow$
- d)  $Mg + HCl \rightarrow MgCl_2 + ?$
- e) FeO + HCl  $\rightarrow$  ? + H<sub>2</sub>O
- f)  $CuO + HNO_3 \rightarrow ? + H_2O$
- g)  $Al(OH)_3 \rightarrow ? + H_2O$
- h)  $CaCO_3 \rightarrow ? + CO_2 \uparrow$

#### **LESSON 4**

#### 4.1 CALCULATIONS USING CHEMICAL EQUATIONS

Here is the example of simplest chemical calculation. What is the mass of phosphoric acid  $(H_3PO_4)$  required for the complete neutralization of 100 g of calcium hydroxide  $(Ca(OH)_2)$ ?

There are at least two ways to make a calculation using chemical equation.

The first way allows calculations without direct referring to the quantity of matter (number of moles). The given mass of one of the reactants or products may be written just upon that chemical substance. The molar mass may be written under that substance. One should refer to the Periodic table to find atomic masses in case if he or she does not remember them by heart. The molar mass of the substance with unknown mass may also be written under the formula. Remember that molar masses of substances should be multiplied by coefficients from the balanced equation. To find out the unknown mass of the substance A (H<sub>3</sub>PO<sub>4</sub> in our case) one has to multiply the known mass of another substance B (Ca(OH)<sub>2</sub>) by the molar mass of the unknown substance A and by the coefficient before that substance. Then the result of the multiplication has to be divided by the molar mass of the substance B (previously multiplied by the coefficient before the substance B).

The second way to find the same answer is based on the quantity of matter calculation. At first one has to divide the mass of substance A by its molar mass to find out the number of moles. Then one has to multiply the number of moles of substance A by the coefficient before the substance B and divide the result by the coefficient before the substance A. The result of this calculation is the number of moles of substance B. The last step is to multiply the chemical quantity of substance B by its molar mass.

- 1)  $n(Ca(OH)_2) = m(Ca(OH)_2) / M (Ca(OH)_2) = 100 / 74 = 1.35 \text{ mol}$
- 2)  $n(H_3PO_4) = (1.35 \cdot 2) / 3 = 0.9 \text{ mol}$
- 3)  $m(H_3PO_4) = n(H_3PO_4) \cdot M(H_3PO_4) = 0.9 \cdot 98 = 88.2 g$

In some cases it is easier to use the first method (when you just need to calculate the mass). In other cases when you should estimate the quantity of matter the second method should be chosen.

#### 4.2 CASES WITH LIMITING REACTANT

There can be an excess of one of the reactants in the reaction mixture. In this case one should use the mass of the limiting reactant to calculate the mass of the product (or products).

It is easy to recognize the limiting reactant. Once again there are at least two ways to do it. In the first way one should determine an amount of one product (either moles or mass) assuming all of each reactant reacts. Whichever reactant gives the *lesser* amount of product is the limiting reactant. The lowest number is the correct answer.

The second way is to calculate numbers of moles for each reactant and to compare those numbers with coefficients from the chemical equation. To make a comparison numbers of moles should be divided by coefficients. For the limiting reactant that ratio will be the lowest.

Ca	+	$N_2$	+	$3O_2$	$\rightarrow$	$Ca(NO_3)_2$
0.4 mol	:	0.2  mol	:	1.2 mol		numbers of moles
1	:	1	:	3		coefficients
0.4	:	0.2	:	0.4		ratios

In this case the limiting reactant is  $N_2$ . There is an excess of Ca (0.4 - 0.2 = 0.2 moles will be left after the end of the reaction) and  $O_2$   $(1.2 - 0.2 \cdot 3 = 0.6 \text{ moles will not take part in the reaction)}$ , while  $N_2$  will react completely. The quantity of  $Ca(NO_3)_2$  will be equal to 0.2 moles.

#### **Exercises:**

- a) What mass of  $O_2$  is needed to produce 8 g of CuO by the way of Cu oxidation?
- b) Calculate the mass of  $Al_2S_3$  produced in  $Al + S = Al_2S_3$  reaction from 4.5 g of Al.
- c) What mass of  $Fe_2O_3$  must react to generate 324 g of  $Al_2O_3$  in the reaction  $Fe_2O_3 + Al \rightarrow Fe + Al_2O_3$ ?
- d) What mass of  $H_2SO_4$  reacts with 10 g of KOH according to the equation:  $H_2SO_4 + KOH = K_2SO_4 + H_2O$ ?
- e) What mass of NaCl is produced after the mixing of 15 g of NaOH with the concentrated HCl solution?
- f) How many moles of  $O_2$  are needed to prepare 1.00 g of  $Ca(NO_3)_2$  from  $Ca,\ N_2$  and  $O_2$ ?
- g) What mass of Hg is produced due to decomposition of 4.34 g of HgO in case if the mass of  $O_2$  is equal to 0.32 g?
- h) What mass of Hg is produced due to decomposition of 4.34 g of HgO in case if the mass of  $O_2$  is equal to 0.28 g?
- i) What mass of NaHCO<sub>3</sub> is needed to produce 2.659 mol of CO<sub>2</sub> in the reaction NaHCO<sub>3</sub>  $\rightarrow$  Na<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O + CO<sub>2</sub>?
- j) What is the mass of  $H_2O$  which can be produced from the mixture of 0.75 g of  $H_2$  and 4 g of  $O_2$ ?

k) What is the mass of  $P_2O_5$  produced in  $P + O_2 = P_2O_5$  reaction from 1.24 g of P and 3.6 g of  $O_2$ ?

#### LESSON 5

#### 5.1 MOLAR VOLUME OF GASES

Kinetic theory of gases is the fundamental model that describes the physical properties of gases. It is based on the following statements:

- 1. Gases consist of tiny particles of matter that are in constant motion.
- 2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic; that is, there is no net loss of energy from the collisions.
- 3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
- 4. There are no interactive forces (i. e., attraction or repulsion) between the particles of a gas.
- 5. The average speed of gas particles is dependent on the temperature of the gas.

An ideal gas exactly follows the statements of the kinetic theory. However, real gases are not ideal. Many gases deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements so well that the kinetic theory of gases is well accepted by the scientific community.

For ideal gases, the molar volume is given by the ideal gas equation  $(p \cdot V = n \cdot R \cdot T)$ : this is a good approximation for many common gases at standard temperature and pressure.

The molar volume of an ideal gas at 1 atmosphere of pressure and at 0  $^{\circ}$ C (in normal conditions) is equal to 22.4 L/mol. According to the ideal gas equation molar volume (V/n) is equal to (R·T)/p. The higher the temperature, the higher is the molar volume. The higher is the pressure, the lower is the molar volume. One may say that the molar volume of any gas in normal conditions is very close to 22.4 L/mol.

Molar volume is equal to the volume divided by the quantity of matter, just like molar mass is equal to the mass divided by the quantity of matter.

$$Vm = V / n$$

$$M = m / n$$

Molar mass varies greatly for different substances (including gases), while molar volume for gases is always the same (22.4 L/mol in normal conditions).

To calculate a volume of the gas with known mass one may use the following formula:

$$V = (Vm \cdot m) / M$$

To make a calculation using chemical equation one should write molar volume under the gas and multiply it by the coefficient. Here is the example.

360 g 
$$X L$$
?  
 $O_2 + 2H_2 \rightarrow 2H_2O$   
36 g  $2 \cdot 22.4 L/mol = 44.8 L$ 

$$X = V(H_2) = (360 \cdot 44.8) / 36 = 448 L$$

#### **Exercises:**

- a) Calculate the volume of 0.5 mol NH<sub>3</sub>; 0.001 mol H<sub>2</sub>; 50 mol CH<sub>4</sub>?
- b) What is the volume of 40 g of  $N_2$ ; 8 g of  $CH_4$ ; 30 g of  $Cl_2$ ?
- c) Calculate the number of moles for 28 L of O<sub>2</sub>; 150 L of N<sub>2</sub>; 0.2 L of H<sub>2</sub>?
- d) Calculate the mass of 3.36 L of HCl; 27 L of NH<sub>3</sub>; 200 L of H<sub>2</sub>S?
- e) What is the volume of  $CO_2$  produced in  $CaCO_3 = CaO + CO_2$  reaction from 400 g of  $CaCO_3$ ?
- f) What is the volume of  $H_2$  produced in Fe + HCl = FeCl<sub>2</sub> +  $H_2$  reaction from 15.3 g of iron?
- g) What is the volume of  $H_2$  produced in  $Al + HCl = AlCl_3 + H_2$  reaction from 18.2 g of aluminum?
- h) What is the volume of  $H_2$  produced in  $Cr + H_2SO_4 = Cr_2(SO_4)_3 + H_2$  reaction from 11.1 g of chrome and 32 g of sulfuric acid?
- i) Calculate the volume of oxygene  $(O_2)$  required to burn down 3.8 L of acetylene  $(C_2H_2)$ .

#### 5.2 RELATIVE DENSITIES OF GASES

Relative density is the ratio of the density (mass of a unit volume) of a substance to the density of a given reference material. In case of gases, relative density of one gas relatively to another equals to the ratio between the molar masses of those gases. For example, density of oxygen by hydrogen is equal to the ratio between molar mass of oxygen and molar mass of hydrogen.

$$D_{H_2}(O_2) = M(O_2) \, / \, M(H_2) = 32 \, / \, 2 = 16$$

Average molar mass of the dry air is equal to 29 g/mol. So, density of nitrogen per dry air equals to molar mass of nitrogen divided by 29 g/mol.

$$D_{dry air}(N_2) = M(N_2) / M(dry air) = 28 / 29 = 0.97$$

#### **Exercises:**

- a) Calculate relative density of chlorine gas per dry air.
- b) Calculate relative density of phosgene (COCl<sub>2</sub>) per dry air.
- c) What are the molar mass and the number of atoms in the molecule of sulfur which density per oxygen is equal to 8?
- d) Calculate relative molecular mass of a gas which relative density per dry air is 1.52.

#### **LESSON 6**

## Sample ticket for control task #1 on main concepts and laws of chemistry

- 1. How many molecules are there in 1 L of liquid water and in water vapor (in normal conditions)?
- 2. What is the mass of sulfur reacted with oxygen and produced 5.6 L of SO<sub>2</sub> (in normal conditions):

$$S + O_2 \rightarrow SO_2$$

3. Balance the following chemical equations:

$$Ag + O_2 \rightarrow Ag_2O$$

$$Pb(NO_3)_2 + Cr \rightarrow Cr(NO_3)_3 + Pb$$

$$Al_2O_3 + KOH^{334} R KAIO_2 + H_2O$$

$$Ca(OH)_2 + H_3PO_4 \rightarrow Ca_3(PO_4)_2 + H_2O$$

- 4. Calculate the mass of ammonia  $(NH_3)$  which has a volume of 33.6 L (in normal conditions)?
- 5. What is the volume of hydrogen sulfide formed in the reaction between hydrogen and sulfur? The mass of hydrogen is equal to 8.5 g, the mass of sulfur is equal to 3.4 g.
- 6. Calculate the volume of oxygen required to burn down 4.2 L of methane  $(CH_4)$ .

#### **LESSON 7**

#### 7.1 THE PERIODIC TABLE OF ELEMENTS

A periodic table is a tabular display of the chemical elements, organized on the basis of their atomic numbers, electron configurations, and recurring chemical properties. Elements are presented in order of increasing atomic number (number of protons in nucleus). Number of protons in nucleus determines electronic configuration. Electronic configuration determines chemical properties.

Historically, D. I. Mendeleev arranged elements in the order of the increase of their atomic masses. In the most of the cases atomic mass correlates well with the number of protons in nucleus, while several exceptions are known. For example, atomic number of K (19) is higher than atomic number of Ar (18), while the mass number of K (39) is lower than the mass number of Ar (40). One also may be interested in similar situation with Te and I.

A *period* is a horizontal row in the periodic table. Metallic properties of elements are decreasing from left to right of each period, while nonmetallic properties are increasing. In this terminology metallic properties mean the ability to loss electron(s). Nonmetallic properties mean the ability to gain electron(s).

The first, second and third periods are usually referred to as "short periods", while other periods (from fourth to the sevenths one) are called "long periods" because they include d-elements.

A *group* (or family) is a vertical column in the periodic table. Elements within the same group generally have the same electron configuration in their valence shell. Consequently, elements in the same group tend to have a shared chemistry and exhibit a clear trend in properties with increasing atomic number.

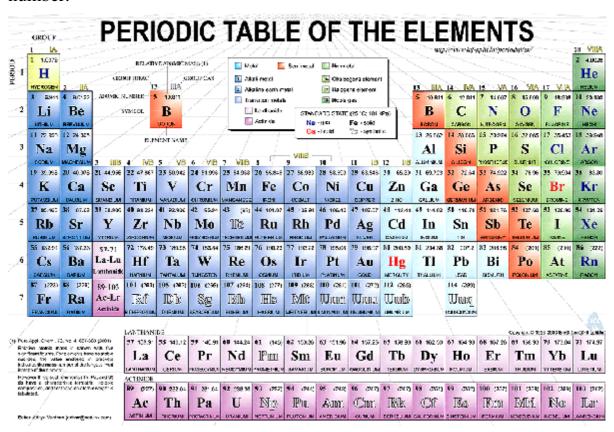


Figure 7.1 The Periodic table of chemical elements

Under an international naming convention, the groups are numbered numerically from 1 to 18 from the leftmost column (the alkali metals) to the rightmost column (the noble gases). Previously, they were known by roman numerals. The roman numerals were followed by either an "A" if the group was in the s- or p-block, or a "B" if the group was in the d-block. The roman numerals used correspond to the last digit of today's naming convention (e. g. the group 4 elements were group IVB, and the group 14 elements was group IVA). In addition, groups 8, 9 and 10 used to be treated as one triple-sized group, known collectively as group VIII. In 1988, the new IUPAC naming system was put into use, and the old group names were deprecated. However, in the most of the periodic tables both classifications are present.

From the top to the bottom in a group, the atomic radii of the elements increase. Since there are more filled energy levels, valence electrons are found farther from the nucleus. It is easier to remove an electron since the atoms are less tightly bound. That is why metallic properties are increasing from the top to the bottom of each group, while nonmetallic properties are decreasing.

The most metallic (those with the strongest metallic properties) elements (such as cesium and francium) are found at the bottom left of the periodic table and the most nonmetallic elements (oxygen, fluorine, chlorine) are found at the top right. The combination of horizontal and vertical trends in metallic character explains the stair-shaped dividing line between metals and nonmetals found on some types of periodic tables, and the practice of sometimes categorizing several elements adjacent to that line as metalloids or semimetals.

#### 7.2 How to use the periodic table?

To determine the number of protons one should find the ATOMIC NUMBER of the element. The atomic number of the element is also equal to the number of electrons.

ATOMIC MASS given in the periodic table is the weighted average mass for all the isotopes with the respect of their abundance in Nature. Isotopes are atoms with equal numbers of protons in their nuclei but with different numbers of neutrons. Since chemical properties are determined by the number of electrons in the valence shells, isotopes demonstrate identical chemical properties and slightly different atomic masses.

For example, boron exists as about 20% boron-10 (five protons and five neutrons in the nuclei) and about 80% boron-11 (five protons and six neutrons in the nuclei). The weighted average atomic mass of boron is calculated as follows:

 $0.20 \times 10 \text{ u} = 2.0 \text{ u}$  $0.80 \times 11 \text{ u} = 8.8 \text{ u}$ 

Sum = 10.8 u = the average weighted atomic mass of Boron

Thus, 10.8 u is the atomic mass of boron in the Periodic table.

#### **Questions:**

- a. Give the definition of the term "period".
- b. Give the definition of the term "group".
- c. How do metallic properties of elements change when you move from the left to the right of the same period?
- d. How do nonmetallic properties of elements change when you move from the top to the bottom of the same group?
  - e. Is calcium a more active metal than strontium?
  - f. Is phosphorus a more active nonmetal than chlorine?
  - g. What elements are known under the name "metalloids"?
  - h. Give the definition of the term "isotopes".

#### **Exercises:**

- a. Find out numbers of period and group for K, Na, Ca, Al, Fe, Cr, Zn, C, P, N, S, O, Cl.
- b. Calculate numbers of neutrons for the following atoms: N-15; Sn-119; U-235; Cs-137; P-31; Na-23; Sb-122; Hg-200.
  - c. What element has 12 protons in its nucleus?
  - d. What element has 25 electrons?
- e. Calculate abundances of C-12 and C-13 in case if there are just those two isotopes of Carbon in Nature.

#### LESSON 8

#### **8.1 QUANTUM NUMBERS**

In the quantum-mechanical model of an atom, the state of an electron is described by four quantum numbers. The first quantum number is called the *principal quantum number* (n). The principal quantum number largely determines the energy of an electron. Electrons in the same atom that have the same principal quantum number are said to occupy the same electron shell of the atom. The principal quantum number can be any nonzero positive integer: 1, 2, 3, 4, 5, 6, 7, ...

Within a shell, there may be multiple possible values of the next quantum number, the *angular momentum quantum number* ( $\ell$ ). The  $\ell$  quantum number has a minor effect on the energy of the electron but also affects the spatial distribution of the electron in three-dimensional space — that is, the shape of an electron's distribution in space. The value of the  $\ell$  quantum number can be any integer between 0 and n-1:

$$\ell = 0, 1, 2, ..., n - 1$$

Thus, for a given value of n, there are different possible values of  $\ell$ :

If <i>n</i> equals to	l can be in numbers	in letters		
1	0	S		
2	0, 1	s, p		
3	0, 1, 2	s, p, d		
4	0, 1, 2, 3	s, p, d, f		

Electrons within a shell that have the same value of  $\ell$  are said to occupy the same subshell in the atom. Commonly, instead of referring to the numerical value of  $\ell$ , a letter represents the value of  $\ell$  (to help distinguish it from the principal quantum number).

Any s orbital is spherically symmetric, and there is only one orbital in any s subshell. Any p orbital has a two-lobed, dumbbell-like shape; because there are three of them, we normally represent them as pointing along the x-, y-, and z-axes. Four of the d orbitals are four-lobed rosettes, while the fifth one

contains two lobes and a torus around the center of an atom. Shapes of seven f-orbitals are even more complicated than those of d-orbitals (figure 8.1).

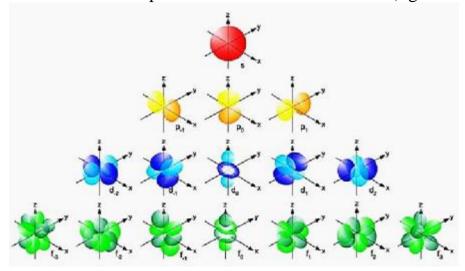


Figure 8.1 Shapes of electron orbitals

The next quantum number is called the *magnetic quantum number*  $(m_{\ell})$ . For any value of  $\ell$ , there are  $2\ell+1$  possible values of  $m_{\ell}$ , ranging from  $-\ell$  to  $\ell$ :  $-\ell \le m_{\ell} \le \ell$ 

The following explicitly lists the possible values of  $m_{\ell}$  for the possible values of  $\ell$ :

If $\ell$ equals	The <i>ml</i> values can be
0	0
1	-1, 0, +1
2	-2, -1, 0, +1, +2
3	-3, -2, -1, 0, +1, +2, +3

The particular value of  $m_{\ell}$  dictates the orientation of an electron's distribution in space. When  $\ell$  is zero,  $m_{\ell}$  can be only zero, so there is only one possible orientation. When  $\ell$  is 1, there are three possible orientations for an electron's distribution. When  $\ell$  is 2, there are five possible orientations of electron distribution. This goes on and on for other values of  $\ell$ , but we need not consider any higher values of  $\ell$  here. Each value of  $m_{\ell}$  designates a certain orbital. Thus, there is only one orbital when  $\ell$  is zero, three orbitals when  $\ell$  is 1, five orbitals when  $\ell$  is 2, and so forth. The  $m_{\ell}$  quantum number has no effect on the energy of an electron.

The final quantum number is the *spin quantum number* ( $m_s$ ). Electrons and other subatomic particles behave as if they are spinning (we cannot tell if they really are, but they behave as if they are). Electrons themselves have two possible spin states, and because of mathematics, they are assigned the quantum numbers +1/2 and -1/2. These are the only two possible choices for the spin quantum number of an electron.

#### 8.2 ELECTRON CONFIGURATIONS OF ATOMS

**Pauli exclusion principle**: no two electrons in an atom can have the same set of four quantum numbers.

If you follow the arrows in order, they pass through the subshells in the order that they are filled with electrons in atoms (figure 8.2). After the 3p subshell is filled, filling the 4s subshell first actually leads to a lesser overall energy than filling the 3d subshell.

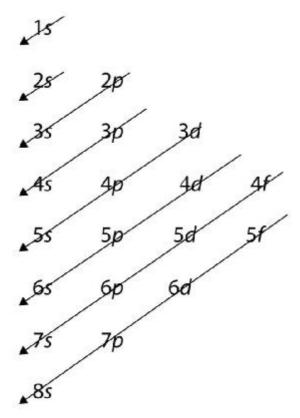


Figure 8.2 The scheme of the filling of electron subshells

Here is an example of complete electron configuration for Sn, which has 50 electrons.

Sn:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$ 

Short electron configuration includes only the valence subshells.

Sn:  $5s^24d^{10}5p^2$ 

The same electron configuration can be written as follows.

Sn: [Kr]  $5s^24d^{10}5p^2$ 

The first part of that form of electron configuration ([Kr]) means that Sn has the same electron configuration as Kr (the first noble gas with atomic number lower than that of the given element), while the second part  $(5 s^2 4d^{10} 5p^2)$  shows electrons which are present in Sn and absent in Kr.

The shape of the periodic table mimics the filling of the subshells with electrons.

The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called valence electrons; the highest-numbered shell is called the valence shell, while the inner electrons are called *core electrons*. The valence electrons largely control the chemistry of an atom.

Elements in each column of the Periodic table have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the s and p blocks. In the d and f blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

**Hund's Rule** of Maximum Multiplicity is an observational rule which states that the atom is more stable when it has the highest number of unpaired electrons. Accordingly, it can be taken that if two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs. For example, electrons occupy three p-orbitals in Nitrogen atom, while they could occupy just two of them. In the last case there would be one pair of electrons. According to the Hund's rule that configuration is unstable, unlike the one represented below.

$$\begin{array}{c|c}
2s^2 & 2p^3 \\
\mathbf{N} & \uparrow \downarrow & \uparrow & \uparrow & \uparrow
\end{array}$$

As one can see, electrons "enjoy their freedom", just like people do when they are choosing their sits in the bus. Interestingly, electron configurations of some d-elements, including Chrome (4s<sup>1</sup>3d<sup>5</sup> and not 4s<sup>2</sup>3d<sup>4</sup>), can be explained in the similar manner. However, shifted electron configuration of Copper (4s<sup>1</sup>3d<sup>10</sup>) is usually explained by the increased stability of completely filled d-block.

#### **Questions:**

- a. What does the principal quantum number characterize?
- b. What are the possible values of the principal quantum number?
- c. What does the angular momentum quantum number characterize?
- d. What are the possible values of the angular momentum quantum number?
  - e. What does the magnetic quantum number characterize?
  - f. What are the possible values of the magnetic quantum number?
  - g. What does the spin quantum number characterize?
  - h. What are the possible values of the spin quantum number?
  - i. Formulate the Pauli exclusion principle.
  - j. Formulate the Hund's rule.

#### **Exercise:**

Write down complete and short electron configurations for the following elements: Ca, Na, Ba, Al, O, S, F, Sn, Br, Fe, Zn, Cu, Ag, Pt, Ce.

#### LESSON 9

#### 9.1 Types of chemical bonds

**Ionic bonding** typically occurs when it is easy for one atom to lose one or more electrons and for another atom to gain one or more electrons.

Electrons can move from one atom to another; when they do, species with overall electric charges are formed. Such species are called *ions*. Species with overall positive charges are termed *cations*, while species with overall negative charges are called *anions*. Metals tend to form cations, while nonmetals tend to form anions.

The magnitude of the charge (the number of lost or gained electrons) is listed as a right superscript next to the symbol of the element. If the charge is a single positive or negative one, the number 1 is not written; if the magnitude of the charge is greater than 1, then the number is written usually *before* the "+" or "-" sign.

When electrons are shared between two atoms, they make a bond called a **covalent bond**. The equal sharing of electrons in a covalent bond is called a **nonpolar covalent bond**. For example, in  $H_2$  molecule the two atoms involved in the covalent bond are both hydrogen atoms, each nucleus attracts the electrons by the same amount. Thus the electron pair is equally shared by the two atoms.

A covalent bond between different atoms that attract the shared electrons by different amounts and cause an imbalance of electron distribution is called a **polar covalent bond**.

Covalent bond may be formed by the pair of electrons from one atom and an empty electron orbital of the second atom. In that case the first atom (with two paired electrons) is called "donor" and the second atom (with an empty orbital) is called acceptor.

Sigma ( $\sigma$ ) bonds are the strongest type of covalent bonds due to the direct overlap of orbitals. They are formed by head-on overlapping between atomic orbitals (figure 9.1).

Pi  $(\pi)$  bonds are usually weaker than sigma bonds. From the perspective of quantum mechanics, this bond's weakness is explained by significantly less overlap between the component p-orbitals due to their parallel orientation.

A typical double bond consists of one sigma bond and one pi bond; for example, the C=C double bond in ethylene (figure 9.2).

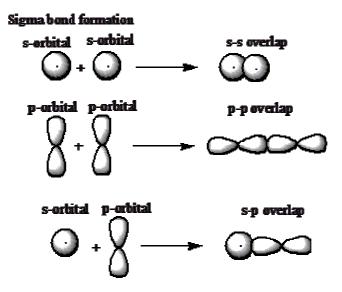


Figure 9.1 Formation of sigma bonds

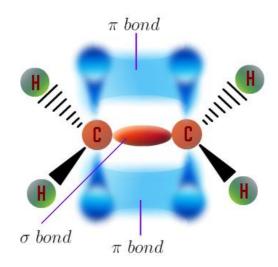


Figure 9.2 Sigma and pi bonds in the molecule of ethylene (H<sub>2</sub>C=CH<sub>2</sub>)

A typical triple bond, for example in acetylene (figure 9.3), consists of one sigma bond and two pi bonds in two mutually perpendicular planes containing the bond axis. Two pi bonds are the maximum that can exist between a given pair of atoms.

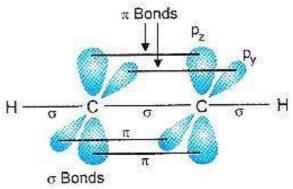


Figure 9.3 Sigma and pi bonds in the molecule of acetylene (HC≡CH).

A pi bond is weaker than a sigma bond, but the combination of pi and sigma bond is stronger than either bond by itself. For bonds that involve the same two elements, a double bond is stronger than a single bond, and a triple bond is stronger than a double bond.

A **hydrogen bond** is the electromagnetic attractive interaction of a polar hydrogen atom in a molecule or chemical group and an electronegative atom, such as nitrogen, oxygen or fluorine, from another molecule or chemical group. It is not a covalent chemical bond. The hydrogen atom has an attraction to another electronegative atom. These attractions can occur between molecules (*intermolecularly*), or within different parts of a single molecule (*intramolecularly*). The hydrogen bond is weaker than covalent or ionic bonds. This type of bond occurs in both inorganic molecules such as water and organic molecules like DNA and proteins.

The electronegative atom attracts the electron cloud from around the hydrogen nucleus and, by decentralizing the cloud, leaves the atom with a positive partial charge. A hydrogen bond results when the positive charge of H<sup>+</sup> attracts a lone pair of electrons on another heteroatom, which becomes the hydrogen-bond *acceptor*. Once again, the same hydrogen atom should make polar covalent bond with fluorine, oxygen or nitrogen, and hydrogen bond with another electronegative atom (fluorine, oxygen or nitrogen).

**Metallic bonding** constitutes the electrostatic attractive forces between the delocalized electrons, called conduction electrons, gathered in an electron cloud, and the positively charged metal ions.

#### **Ouestions:**

- a. Describe the ionic bond
- b. Describe the covalent nonpolar bond
- c. Describe the covalent polar bond
- d. What is the difference between sigma and pi covalent bonds?
- e. Describe covalent double and triple bonds
- f. How does the fourth bond in NH<sub>4</sub><sup>+</sup> ion form?
- g. What is known about the mechanism of hydrogen bond formation?
- h. Describe bonds which are present in metals.

#### 9.2 ELECTRONEGATIVITY

Any covalent bond between two different elements is polar. However, the degree of polarity is different for different bonds. A covalent bond between two different elements may be so slightly imbalanced that the bond is, approximately, nonpolar. A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond.

Electronegativity is a chemical property that describes the tendency of an atom or a functional group to attract electrons (or electron density) towards itself. The higher the electronegativity number, the more an element or compound attracts electrons towards it.

The covalent polar bond between two different atoms (A–B) is stronger than would be expected by taking the average of the strengths of the A–A and B–B bonds. This additional stabilization of the bond between atoms of two different elements is due to the contribution of ionic component to the bonding. There is an additional energy that comes from ionic factors, i. e. from the polar character of the bond.

In general, electronegativity increases from left to right along each period, and decreases from the top to the bottom of every group. Fluorine is the most electronegative of the elements, while cesium and francium are the least electronegative ones.

Н																
2.1																
Li	Be											В	C	N	0	F
1.0	1.5											1.5	2.5	3.0	3.5	4.0
Na	Mg											Al	Si	Ρ	S	CI
0.9	1.2											1.5	1.8	2.1	2,5	3.0
К	Ca	Sc	Ti	٧	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As.	Se	Br
8.0	1.0	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.8	1.9	1.6	1.6	1.8	2.0	2.4	2.8
Rb.	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	1
8.0	1.0	1.2	1.4	1.6	1.8	1.9	2.2	2.2	2.2	1.9	1.7	1.7	1.8	1.9	2.1	2.5
Cs	Ba		Hf	Ta	W	Re	Os	1r	Pt	Au	Hg	TI	Pb	Bi	Po	At
0.7	0.9		1.3	1.5	1.7	1.9	2.2	2.2	2.2	2.4	1.9	1.8	1.9	1.9	2.0	2.2
Fr	Ra	1		3-0							ili -		0.	3 8	0 0	55
0.7	0.9															

Figure 9.1 The table of chemical elements with their electronegativity levels

The polarity of a covalent bond can be judged by determining the difference of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table.

Table 9.1 Thresholds in the difference in electronegativity levels between two atoms

Difference in electronegativity between two atoms	Bond Type
0	nonpolar covalent
0 < 0.4	slightly polar covalent
0.4–1.9	definitely polar covalent
> 1.9	likely ionic

**Exercise.** Determine the type of chemical bond(s) in the following compounds: CO, HI,  $H_2S$ ,  $OF_2$ ,  $CH_4$ ,  $H_2SO_4$ , NaOH,  $SiH_4$ ,  $FeCl_3$ , KCl,  $K_2Cr_2O_7$ ,  $Al_2O_3$ ,  $Cu_{31}Sn_8$ , SbSn.

#### LESSON 10

#### 10.1 OXIDATION STATE

The *oxidation state* is an indicator of the degree of oxidation of an atom in a chemical compound. The formal oxidation state is the *hypothetical charge* that an atom would have if all bonds to atoms of different elements were 100 % ionic. Oxidation states are typically represented by integers, which can be positive, negative, or equal to zero.

Oxidation state of pure chemical element is equal to zero.

Hydrogen has an oxidation state of +1 and oxygen has an oxidation state of -2 when they are present in the most of compounds. Exceptions to this rule are hydrides of active metals (such as LiH, NaH, CaH<sub>2</sub>) and silane (SiH<sub>4</sub>), peroxides (H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>), superoxides (KO<sub>2</sub>) and compounds made from fluorine and oxygen (F<sub>2</sub>O and F<sub>2</sub>O<sub>2</sub>).

Alkali metals (Li, Na, K, Rb, Cs, Fr) have an oxidation state of +1, while metals from the IIA group (Be, Mg, Ca, Sr, Ba) and Zinc (Zn) have an oxidation state of +2 in almost all of their compounds. Aluminum always demonstrates +3 oxidation state.

The main rule to calculate oxidation states of each of the atoms in a molecule is as follows. The algebraic sum of oxidation states of all atoms in a neutral molecule must be equal to zero, since molecule has no charge. In has either positive or negative charge. That is why the algebraic sum of the oxidation states of the atoms from a given ion is equal to the total charge of the ion.

Oxidation state historically was thought to reflect the number of electrons transferred from one atom to the other. The number of electrons is an integer. However, there are many compounds in which oxidation states for some atoms are not integers (for example, in the  $Fe_3O_4$  compound). That compound can really be represented by the formula  $FeO \cdot Fe_2O_3$ .

Most elements have more than one possible oxidation state. Carbon has nine integer oxidation states, and there are also molecules in which the average degree of oxidation of several carbons is fractional. For example, try to calculate oxidation state of carbon in propane molecule ( $C_3H_8$ ).

#### 10.2 OXIDATION STATE, OXIDATION NUMBER AND VALENCE

The term "oxidation number" has a different meaning than the term "oxidation state". The term "oxidation number" is used *in coordination chemistry only*. It reflects the charge that central atom would have if all the ligands were removed along with the electron pairs that were shared with the central atom.

In certain compounds the module of the oxidation state is equal to the valence of an atom. One should realize that valence and oxidation state may be different for a given atom. For example, the valence of nitrogen in its diatomic molecule is equal to three (III), since there is a triple bond between two atoms. The oxidation state for both atoms from  $N_2$  is equal to 0. Strange situation is known for CO molecule in which oxidation state of oxygen is equal to -2, while its valence is equal to III (third bond is formed by donor-acceptor mechanism).

Maximal oxidation state is usually equal to the number of the group (written in Roman numbers) in which the given element is located in the Periodic table.

Minimal oxidation state of the metal is equal to zero. Minimal oxidation state of the nonmetal is equal to the eight minus the number of its group (written in Roman numbers).

#### **Questions:**

- a. Give the definition of the term "oxidation state"
- b. Give the definition of the term "oxidation number"
- c. Give the definition of the term "valence"
- d. How to calculate oxidation state in a compound?
- e. How to calculate oxidation state in an ion?

#### **Exercises:**

- a. Determine oxidation state and valence in each of the compounds: PH<sub>3</sub>, P<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, H<sub>3</sub>PO<sub>4</sub>, Mg<sub>3</sub>P<sub>2</sub>, NaBr, HBrO, KBrO<sub>3</sub>, Br<sub>2</sub>O<sub>5</sub>, Br<sub>2</sub>, NaCl, NaClO, NaClO<sub>2</sub>, NaClO<sub>3</sub>, NaClO<sub>4</sub>, Cl<sub>2</sub>, MnO, MnO<sub>2</sub>, MnCl<sub>2</sub>, KMnO<sub>4</sub>, K<sub>2</sub>MnO<sub>4</sub>, CH<sub>4</sub>, CaC<sub>2</sub>, SiH<sub>4</sub>, C<sub>6</sub>H<sub>6</sub>
- b. Determine oxidation state and valence in each of the ions:  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $HPO_4^{2-}$ ,  $H_2PO_4^{-}$ ,  $ClO_4^{-}$ ,  $MnO_4^{-}$ ,  $NO_2^{-}$ ,  $SiO_3^{2-}$ ,  $[Al(OH)_4]^-$ ,  $[Al(OH)_6]^{3-}$ .

#### **LESSON 11**

#### 11.1 SEVERAL WAYS TO CLASSIFY CHEMICAL REACTIONS

A single-replacement reaction is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products.

2HCl (compound 1) + Zn (element 1)  $\rightarrow$  ZnCl<sub>2</sub> (compound 2) + H<sub>2</sub> (element 2)

A double-replacement reaction occurs when parts of two ionic compounds are exchanged, making two new compounds. A characteristic of a double-replacement equation is that there are two compounds as reactants and two different compounds as products.

$$CuCl_2 + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2AgCl\downarrow$$

A composition reaction (combination reaction or a synthesis reaction) is a chemical reaction in which a single substance is produced from multiple reactants. A single substance as a product is the key characteristic of the composition reaction. There may be a coefficient other than one for the substance, but if the reaction has only a single substance as a product, it can be called a composition reaction.

 $2H_2(reactant 1) + O_2(reactant 2) \rightarrow 2H_2O(a single substance)$ 

A decomposition reaction starts from a single substance and produces more than one substance. One substance as a reactant and more than one substance as the products is the key characteristic of a decomposition reaction.

 $2NaHCO_3(a \text{ single substance}) \rightarrow Na_2CO_3(product 1) + CO_2(product 2) + + H_2O(product 3)$ 

A *combustion reaction* is a chemical reaction in which a reactant combines with oxygen to produce oxides of all other elements from that compound as products.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

An **exothermic reaction** is a chemical reaction that releases energy in the form of heat. It is the opposite of an **endothermic reaction** in which the system absorbs energy from its surroundings in the form of heat.

A **reversible reaction** is a chemical reaction that results in an equilibrium mixture of reactants and products. If the concentrations of the reactants at equilibrium are very small, then such a reaction may be considered to be an **irreversible reaction**, although in reality small amounts of the reactants are still expected to be present in the reacting system. A truly irreversible chemical reaction is usually achieved when one of the products completely exits the reacting system in form of gas or insoluble substance.

#### 11.2 REDOX REACTIONS

If the oxidation state of at least one element changes due to chemical reaction, that reaction is called reduction-oxidation (redox) reaction. In the simplest redox reaction there is a single substance called **oxidizer** which contains atoms gaining electrons, and a single substance called **reducer** which contains atoms losing electrons. We may say that atoms of oxidizer take electrons from atoms of reducer. In the example below sulfur takes electrons from zinc. Oxidation state of sulfur changes from 0 to -2. Oxidation state of zinc changes from 0 to +2.

 $Zn + S \rightarrow ZnS$ 

So, Sulfur is an oxidizer, while Zinc is a reducer.

#### **Questions:**

- a. Describe key characteristic of a single-displacement reaction
- b. Describe key characteristic of a double-displacement reaction
- c. Describe key characteristic of a composition reaction.
- d. Describe key characteristic of a decomposition reaction.
- e. Describe key characteristic of a combustion reaction.
- f. What is the difference between exothermic and endothermic reactions?
- g. What is the difference between reversible and irreversible reactions?

h. How can you understand that a given reaction is redox reaction?

#### **Exercise:**

Finish chemical reactions and classify them  $CuSO_4 + Fe \rightarrow \\ Ca(OH)_2 + H_3PO_4 \rightarrow \\ Fe(OH)_3 \rightarrow \\ Na_2O + N_2O_5 \rightarrow \\ C_6H_6 + O_2 \rightarrow \\$ 

#### LESSON 12

#### 12.1 DEFINITIONS OF REDUCTION AND OXIDATION

The increase in oxidation state of an atom (when it becomes *more positive*) through a chemical reaction is known as an <u>oxidation</u>; a decrease in oxidation state of an atom (when it becomes *more negative*) is known as a <u>reduction</u>.

Oxidation-reduction (*redox*) reactions involve the formal transfer of electrons, a net gain in electrons being a reduction and a net loss of electrons being an oxidation. The process of losing and gaining electrons occurs simultaneously. However, mentally we can separate the two processes. The total number of electrons being lost must equal the total number of electrons being gained for a redox reaction to be balanced.

#### 12.2 BALANCING REDUCTION-OXIDATION REACTIONS

To balance redox reaction one should write each oxidation and reduction reaction separately, listing the number of electrons explicitly in each. Individually, the oxidation and reduction reactions are called half-reactions. Then one should multiply each half-reaction by the certain integer number until the number of electrons on each side cancels completely. Then one should use those two integers as coefficients in the whole reaction.

The example of redox reaction is given below.

 $KMnO_4 + HCl \rightarrow KCl + MnCl_2 + Cl_2 + H_2O$ 

The first thing one should do is to calculate oxidation states:

$$K^{+}Mn^{7+}O^{2-}_{4} + H^{+}Cl^{-} \rightarrow K^{+}Cl^{-} + Mn^{2+}Cl^{-}_{2} + Cl^{0}_{2} + H^{+}_{2}O^{2-}_{3}$$

The second step is to notice those atoms for which the oxidation state has been changed (they are written in bold underlined font).

The third step is to write down two half reactions. The first half reaction is the reaction of reduction (Mn<sup>7+</sup> has gained 5 electrons). The second half reaction is the reaction of oxidation (two Cl<sup>-</sup> have lost 2 electrons). Mn<sup>7+</sup> acted as oxidizer, while Cl<sup>-</sup> acted as reducer. There is a cool mnemonic phrase which

helps not to confuse oxidation and reduction. "LEO the lion says GER" — Loss of Electrons is Oxidation, Gain of Electrons is Reduction.

$$Mn^{7+}$$
 +5e  $\rightarrow$   $Mn^{2+}$  5 2  
 $2Cl^{-}$  -2e  $\rightarrow$   $Cl^{0}_{2}$  2 5

The number of gained electrons should be equal to the number of lost electrons. If we multiply the first half-reaction by 2 then 10 electrons will be gained. If we multiply the second half-reaction by 5 then 10 electrons will be lost. 2 is the coefficient before Mn<sup>7+</sup> (KMnO<sub>4</sub>) and Mn<sup>2+</sup> (MnCl<sub>2</sub>). 5 is the coefficient before Cl<sub>2</sub> and not HCl, since only a part of Cl<sup>-</sup> has been reduced to form Cl<sub>2</sub>.

$$2KMnO_4 + ?HCl \rightarrow ?KCl + 2MnCl_2 + 5Cl_2 + ?H_2O$$

As one can see, electron balance helped to find out 3 from 6 coefficients in the reaction. Other coefficients can be found easily.

$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O$$

Remember that electron balance is *just a mathematical method* to find out coefficients in chemical reactions. It has a little (if any) chemical or physical sense.

**Exercise.** Balance the following reactions and determine coefficients before oxidizer and reducer

$$\begin{split} NO + O_2 &\to NO_2 \\ Fe + S &\to FeS \\ SO_2 + O_2 &\to SO_3 \\ K + MgCl_2 &\to KCl + Mg \\ Cu + HNO_3 &\to Cu(NO_3)_2 + NO_2 + H_2O \\ Cu + H_2SO_4 &\to CuSO_4 + SO_2 + H_2O \\ H_2O_2 + KMnO_4 + H_2SO_4 &\to O_2 + MnSO_4 + K_2SO_4 + H_2O \\ FeSO_4 + KMnO_4 + H_2SO_4 &\to Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + H_2O \\ C_7H_{16} + O_2 &\to CO_2 + H_2O \end{split}$$

#### LESSON 13

#### 13.1 CHEMICAL EQUILIBRIUM

Chemical equilibrium is the state in which both reactants and products are present at concentrations which have no further tendency to change with time. Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction. This process is called *dynamic equilibrium*.

Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$H_2 + I_2 \rightarrow 2HI$$

The way the equation is written, we are led to believe that the reaction goes to completion, that all the  $H_2$  and the  $I_2$  react to make HI. However, this is not the case. The reverse chemical reaction is also taking place:

$$2HI \rightarrow H_2 + I_2$$

It acts to undo what the first reaction does. Eventually, the reverse reaction proceeds so quickly that it matches the speed of the forward reaction. When that happens, any continued overall reaction stops: the reaction has reached chemical equilibrium (sometimes just spoken as *equilibrium*; plural *equilibria*), the point at which the forward and reverse processes balance each other's progress.

Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow:

$$H_2 + I_2 \rightleftarrows 2HI$$

The double arrow implies that the reaction is going in both directions.

#### **Questions:**

- 1. Define *chemical equilibrium*. Give an example.
- 2. Explain what is meant when it is said that chemical equilibrium is dynamic.

#### 13.2 THE LAW OF MASS ACTION

The law of mass action relates the amounts of reactants and products at equilibrium for a chemical reaction.

The equilibrium constant is written as  $K_{eq}$ .

The  $K_{\text{eq}}$  is a characteristic numerical value for a given reaction at a given temperature; that is, each chemical reaction has its own characteristic  $K_{\text{eq}}$ .

Coming back to  $H_2 + I_2 \leftrightarrow 2HI$  reaction, the  $K_{eq}$  is expressed as:

$$K_{\text{eq}} = [\text{HI}]^2 / ([\text{H}_2] \cdot [\text{I}_2])$$

[HI], [H2] and [I2] are concentrations of HI,  $H_2$  and  $I_2$ , respectively.

In other words, the numerator of the expression for  $K_{\rm eq}$  has the concentrations of every product, while the denominator of the expression for  $K_{\rm eq}$  has the concentrations of every reactant, leading to the common **products over** reactants definition for the  $K_{\rm eq}$ .

However, the law of mass action is valid only for concerted one-step reactions that proceed through a single transition state and **is not valid in general** because rate equations do not, in general, follow the stoichiometry of the reaction. It means that there are usually several steps in each reaction. Maximal number of particles which may appear in the same point of space, collide with each other simultaneously and so react is equal to three. So, we can be sure that the maximal number of reacting particles (atoms, molecules or ions) in each step of the reaction is equal to three.

Adding a catalyst will affect both the forward reaction and the reverse reaction in the same way and will not have an effect on the equilibrium

constant. The catalyst will speed up both reactions thereby increasing the speed at which equilibrium is reached.

#### **Exercises:**

- a. Write the equilibrium equation between elemental hydrogen and elemental chlorine as reactants and hydrochloric acid as the product.
- b. Write the equilibrium equation between iron(III) sulfate as the reactant and iron(III) oxide and sulfur trioxide as the products.
  - c. Write the  $K_{eq}$  expression for each reaction.
    - 1.  $NO + NO_2 \rightleftarrows N_2O_3$
    - 2.  $C_2H_5OH + NaI \rightleftharpoons C_2H_5I + NaOH$
    - 3.  $PCl_3 + Cl_2 \rightleftharpoons PCl_5$

#### 13.3 LE CHATELIER'S PRINCIPLE

Chemical equilibrium can be shifted by changing the conditions that the system experiences. When we stress the equilibrium, the chemical reaction is no longer at equilibrium, and the reaction starts to move back toward equilibrium in such a way as to decrease the stress. The formal statement is called Le Chatelier's principle: "If an equilibrium is stressed, then the reaction shifts to reduce the stress".

There are several ways to stress an equilibrium. One way is to add or remove a product or a reactant in a chemical reaction at equilibrium. When additional reactant is added, the equilibrium shifts to reduce this stress: it makes more product. When additional product is added, the equilibrium shifts to reactants to reduce the stress. If reactant or product is removed, the equilibrium shifts to make more reactant or product, respectively, to make up for the loss.

When reactants or products are added or removed, the value of the  $K_{eq}$  does not change. The chemical reaction simply shifts, in a predictable fashion, to reestablish concentrations so that the  $K_{eq}$  expression reverts to the correct value.

Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase. Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas. If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

Because temperature is a measure of the energy of the system, increasing temperature can be thought of as adding energy. The reaction will react as if a reactant or a product is being added and will act accordingly by shifting to the other side. For example, if the temperature is increased for an endothermic reaction, essentially a reactant is being added, so the equilibrium shifts toward

products. Decreasing the temperature is equivalent to decreasing a reactant (for endothermic reactions) or a product (for exothermic reactions), and the equilibrium shifts accordingly.

#### **Exercises:**

a. Given this reaction at equilibrium:

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

In which direction — toward reactants or toward products — does the reaction shift if the equilibrium is stressed by each change?

- 1. H<sub>2</sub> is added.
- 2. NH<sub>3</sub> is added.
- 3. NH<sub>3</sub> is removed.
- b. Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftarrows COBr_2(g)$$

In which direction — toward reactants or toward products — does the reaction shift if the equilibrium is stressed by each change?

- 1. Br<sub>2</sub> is removed.
- 2. COBr<sub>2</sub> is added.
- c. What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

d. What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftarrows 2O_3(g)$$

e. Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftarrows PCl_5 + 60 \text{ kJ}$$

f. Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57 \text{ kJ} \rightleftarrows 2NO_2$$

g. Given this equilibrium, predict the direction of shift for each stress.

$$H_2(g) + F_2(g) \rightleftharpoons 2HF(g) + 546 \text{ kJ}$$

- 1. increased temperature
- 2. addition of H<sub>2</sub>
- 3. decreased pressure
- h. Given this equilibrium, predict the direction of shift for each stress.

$$2SO_2(g) + O_2(g) \rightleftarrows 2SO_3(g) + 196 \text{ kJ}$$

- 1. removal of SO<sub>3</sub>
- 2. addition of  $O_2$
- 3. decreased temperature
- i. Given this equilibrium, predict the direction of shift for each stress listed.

$$CO_2(g) + C(s) + 171 \text{ kJ} \rightleftarrows 2CO(g)$$

- 1. addition of CO
- 2. increased pressure
- 3. addition of a catalyst

#### **LESSON 14**

#### 14.1 THE RATE OF CHEMICAL REACTION

The **reaction rate** (rate of reaction) or **speed of reaction** for a reactant or product in a particular reaction is intuitively defined as how fast or slow a reaction takes place. The rates of chemical reaction may be measured in mol/L·sec or mol/L·min.

In other words the rates of chemical reaction are the difference in concentration of the given reactant (measured in mol/L) during the given time (measured in seconds or minutes).

#### 14.2 FACTORS INFLUENCING RATE OF REACTION

The nature of the reaction. Some reactions are naturally faster than others. The number of reacting species, their physical state (the particles that form solids move much more slowly than those of gases or those in solution), the complexity of the reaction and other factors can greatly influence the rate of a reaction.

*Concentration*. Reaction rate increases with concentration, as described by the rate law and explained by collision theory. As reactant concentration increases, the frequency of collision increases.

*Pressure.* The rate of gaseous reactions increases with pressure, which is, in fact, equivalent to an increase in concentration of the gas. The reaction rate increases in the direction where there are fewer moles of gas and decreases in the reverse direction. For condensed-phase reactions, the pressure dependence is weak.

*Temperature*. With the increase of temperature more of the colliding particles will have the necessary activation energy resulting in more successful collisions (when bonds are formed between reactants).

A catalyst. The presence of a catalyst increases the reaction rate (in both the forward and reverse reactions) by providing an alternative pathway with a lower activation energy.

*Surface Area.* In reactions on surfaces, which take place for example during heterogeneous catalysis, the rate of reaction increases as the surface area does. That is because more particles of the solid are exposed and can be hit by reactant molecules.

In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating *the law of mass action*, which states that

the speed of a chemical reaction is proportional to the quantity of the reacting substances.

$$r = k_f[A]^{n'}[B]^{m'}$$

In this equation  $k_f$  is the *reaction rate coefficient* or *rate constant* of the forward reaction, although it is not really a constant, because it includes all the parameters that affect reaction rate, except for concentration, which is explicitly taken into account. Of all the parameters described before, temperature is normally the most important one.

The exponents n' and m' are called reaction orders and depend on the reaction mechanism. In the original Waage and Guldberg equation those exponents were nothing but the stoichiometric coefficients from the reaction. Original *law of mass action* works well only in case if there is only a single act in the whole chemical reaction.

As one can understand, the rate of the backward reaction is calculated in similar way.

$$r = k_b[C]^{x'}[D]^{y'}$$

Rates of forward and backward reactions are equal to each other in the state of equilibrium.

**Exercise.** Express the equilibrium constant using two equations for the rates of forward and backward reactions calculation (they are given above).

#### 14.3 TEMPERATURE COEFFICIENT OF CHEMICAL REACTION

The  $Q_{10}$  temperature coefficient is a measure of the rate of change of a biological or chemical system as a consequence of increasing the temperature by 10 °C.

The  $Q_{10}$  is calculated as:

$$Q_{10} = \left(\frac{R_2}{R_1}\right)^{10/(T_2 - T_1)}$$

where  $R_1$  is the rate of reaction at the temperature 1  $(T_1)$ ;  $R_2$  is the rate of reaction at the temperature 2  $(T_2)$ .

Temperature in this case may be measured either in Celsius degrees or in Kelvins.

The same equation may be re-written in the following way.

$$R_2 = R_1 \cdot Q_{10}^{(T2-T1)/10}$$

Using this equation one may calculate the rates of reaction at temperature 2 knowing the rates of that reaction at temperature 1 and the  $Q_{10}$  coefficient.

 $Q_{10}$  is a unitless quantity, as it is the factor by which a rate changes, and is a useful way to express the temperature dependence of a process.

For most biological systems, the  $Q_{10}$  value is ~ 2 to 3. However, the "rule of thumb" that the rate of any chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special cases of biological systems.

#### **Exercises:**

- a. Write down the kinetic equations for the following reactions according to the original Waage and Guldberg law of mass action:
  - $-2NO(gas) + Cl_2(gas) = 2NOCl(gas)$
  - $Ca(OH)_2(solid) + CO_2(gas) = CaCO_3(solid) + H_2O(gas)$
  - $Fe_2O_3(solid) + 3CO(gas) = 2Fe(solid) + 3CO_2(gas)$
- b. How the rates of the reaction  $N_2 + 3H_2 = 2NH_3$  will change in case of a) the two times increase of reactants concentration; b) the three times increase of the pressure; c) the four times increase of the volume of gas mixture?
- c. How the rates of the reaction  $2SO_2 + O_2 = 2SO_3$  will change in case of a) the two times decrease of reactants concentration; b) the three times decrease of the pressure; c) the four times decrease of the volume of gas mixture?
- d. How will the rates of chemical reaction change in case of the temperature increase from 40°C to 100°C? The rates of that reaction become two times faster with the increase of temperature equal to 10°C.
- e. The Q10 coefficient is equal to 4. How will the rates of this reaction change in case of a) 20°C temperature increase; b) 30° temperature increase; c) 40°C temperature decrease?
- f. The Q10 coefficient for a certain reaction is equal to 3. At 20°C that reaction lasts for 2 minutes. How long that reaction lasts a) at 40°C; b) at 50°; c) 0°C?

#### **LESSON 15**

## Sample ticket for control task #2 on the periodic table, the structure of atom and elements of chemical kinetics

- 1. Determine oxidation state for each atom in the following compounds: Mn<sub>2</sub>O<sub>7</sub>, H<sub>3</sub>AsO<sub>4</sub>, KAIO<sub>2</sub>, Zn(ClO<sub>4</sub>)<sub>2</sub>, MgHPO<sub>4</sub>.
- 2. Write down electron configurations for Ca, Sb, W, Cr, Cu.
- 3. Balance chemical reactions using electron balance method (with two half-reactions):
  - a)  $HCl + KCIO_3 \rightarrow Cl_2 + KCl + H_2O$
  - b)  $H_2S + KMnO_4 + H_2SO_4 \rightarrow MnSO_4 + S + K_2SO_4 + H_2O$
  - c)  $PH_3 + KMnO_4 + H_2SO_4 \rightarrow H_3PO_4 + MnSO_4 + K_2SO_4 + H_2O_4 + H_2O_5 + H_2O_5 + H_2O_5 + H_2O_5 + H_2O_5 + H_2O_5 + H_2O_5$

- 4. Q10 coefficient for a given chemical reaction is equal to 3. At 20 °C reaction lasts for 7 minutes. Determine how long that reaction lasts at 60 °C.
  - 5. Given this equilibrium, predict the direction of shift for each stress.

$$3Fe(solid) + 4H_2O(gas) \rightleftarrows Fe_3O_4(solid) + 4H_2(gas)$$

- a. removal of H<sub>2</sub>
- b. addition of H<sub>2</sub>O
- c. decrease in pressure

# **LESSON 16**

# **16.1 OXIDES**

An **oxide** is a binary chemical compound that contains oxygen in the oxidation state of -2 and other chemical element. Different oxides of the same element are distinguished by Roman numerals denoting their oxidation number: iron (II) oxide (FeO) versus iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>).

Oxides may be produced either by the way of combustion (of both pure chemical elements and compounds), or by decomposition of certain acids, bases and salts.

$$C + O_2 \rightarrow CO_2$$

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

$$2CuS + 3O_2 \rightarrow 2CuO + 2SO_2$$

$$H_2SiO_3 \rightarrow H_2O + SiO_2$$

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

$$ZnCO_3 \rightarrow ZnO + CO_2$$

Due to its electronegativity, oxygen forms stable chemical bonds with almost all elements to give the corresponding oxides. Noble metals (such as gold or platinum) are prized because they resist direct chemical combination with oxygen, and substances like gold (III) oxide must be generated by indirect routes.

Oxides of most metals adopt polymeric structures with M-O-M crosslinks. Because these crosslinks are strong, the solids tend to be insoluble in solvents, though they are attacked by acids and bases. The formulas are often deceptively simple, while many of them are nonstoichiometric compounds.

$$Fe3O4 = FeO \cdot Fe2O3$$
$$3CrO2 = Cr2O3 \cdot CrO3$$
$$4VO2 = V2O3 \cdot V2O5$$

Metal oxides are substances of ionic crystal structure, while the most of nonmetal oxides are molecules. For example, carbon dioxide ( $CO_2$ ) and carbon monoxide ( $CO_3$ ) are molecular oxides. However, silicon oxide ( $SiO_2$ ) is a substance with atomic crystal structure. Phosphorus pentoxide is a complex molecular oxide with a deceptive name, the formula being  $P_4O_{10}$  ( $P_2O_5 \cdot P_2O_5$ ).

Some polymeric oxides when heated depolymerize to give molecules, examples being selenium dioxide ( $SeO_2$ ) and sulfur trioxide ( $SO_3$ ).

Oxides can be attacked by acids and bases. Those attacked only by acids are *basic oxides*.

$$BaO + 2HCl \rightarrow BaCl_2 + H_2O$$

Those attacked only by bases are acidic oxides.

$$P_2O_5 + 6KOH \rightarrow 2K_3PO_4 + 3H_2O$$

Oxides that react with both acids and bases are amphoteric.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$$

In water solution complex salt is formed.

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$$

Metals tend to form basic oxides, non-metals tend to form acidic oxides, and amphoteric oxides are formed by elements near the boundary between metals and non-metals (metalloids) and by elements from d-block.

Behavior of oxides for d-elements depends on their oxidation state.

Basic oxides:	MnO	and	CrO
Amphoteric oxides:	$MnO_2$	and	$Cr_2O_3$
Acidic oxides:	$Mn_2O_7$	and	$CrO_3$

# 16.2 BASIC AND ACIDIC ANHYDRIDES

Oxides of more electropositive elements are called "basic anhydrides". Exposed to water, oxides of alkali and earth-alkali metals form basic hydroxides. For example, sodium oxide is basic — when hydrated, it forms sodium hydroxide.

$$Na_2O + H_2O \rightarrow 2NaOH$$

Oxides of other metals cannot react with water, though their insoluble hydroxides can be produced in reactions between their soluble salts and alkali.

$$CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 \downarrow + 2NaCl$$

Oxides of more electronegative elements are called "acid anhydrides"; adding water, they form oxoacids (oxygen containing acids).

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$

Basic oxides react with acidic oxides and form salts.

$$3CaO + P_2O_5 \rightarrow Ca_3(PO_4)_2$$

Less volatile acidic oxides react with salts of more volatile oxides. Volatility is the tendency of a substance to vaporize. In other words, the more volatile oxide simply flies away and cannot participate in the reverse reaction anymore.

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \uparrow$$

Some oxides do not show behavior as either acid or basic anhydrides (for example: CO, SiO,  $N_2O$ , NO). They are known under the name "neutral oxides". In other words, those oxides do not form salts.

# **Questions:**

- a. Give examples of basic, acidic and amphoteric oxides.
- b. How do the properties of oxides change if we go from left to right in a period of the Periodic table?
- c. How do the properties of oxides change if we go from top to bottom in a group of the Periodic table?
  - d. What is anhydride?
  - e. What is volatility?

# **Exercises:**

- a. Write down formulas of the following compounds: potassium oxide; sodium oxide; phosphorus oxide (III); phosphorus oxide (V); nitrogen oxide (III); nitrogen oxide (V); iron oxide (III); manganese oxide (III); manganese oxide (IV); manganese oxide (VII).
- b. What are the formulas of oxides corresponding to the following hydroxides: Mg(OH)<sub>2</sub>; LiOH; Fe(OH)<sub>2</sub>; Fe(OH)<sub>3</sub>; Cu(OH)<sub>2</sub>; Cr(OH)<sub>3</sub>?
- c. Write down reactions between i) calcium oxide and sulfur oxide (VI); ii) iron oxide (III) and phosphorus oxide (V); iii) zinc oxide and nitrogen oxide (V); iv) sodium oxide and carbon dioxide.
- d. Write down reactions between i) calcium oxide and sulfuric acid; ii) iron oxide (II) and nitric acid; iii) chrom oxide (III) and sulfuric acid; iv) aluminum oxide and phosphoric acid.
- e. Write down reactions between i) sodium hydroxide and carbon dioxide; ii) potassium hydroxide and nitrogen oxide (III); iii) barium hydroxide and hydrochloric acid; iv) calcium oxide and hydrogen sulfide.
- f. Imagine how can the following oxides be produced: CaO; Al<sub>2</sub>O<sub>3</sub>; CO<sub>2</sub>; SiO<sub>2</sub>?
  - g. Calculate the mass of iron in 500 g of i) FeO; ii) Fe<sub>2</sub>O<sub>3</sub>; iii) Fe<sub>3</sub>O<sub>4</sub>.

# **LESSON 17**

#### **17.1 BASES**

The Brønsted-Lowry theory defines bases as proton (hydrogen ion) acceptors, while the more general Lewis theory defines bases as electron pair donors, allowing other Lewis acids than protons to be included. The oldest Arrhenius theory defines bases as substances which produce hydroxide anions  $(OH^-)$  in water solutions. By altering the autoionization equilibrium  $(H_2O = H^+ OH^-)$ , bases give solutions with a hydrogen ion activity lower than that of pure water (pH > 7.0).

Bases can be thought of as the chemical opposite of acids. A reaction between an acid and base is called neutralization — aqueous solutions of bases react with aqueous solutions of acids to produce water and salts.

A strong base is a basic chemical compound that is able to deprotonate very weak acids in an acid-base reaction. Common examples of strong bases are the hydroxides of alkali metals and alkaline earth metals like NaOH and Ca(OH)<sub>2</sub>. Here is a list of strong bases:

- Lithium hydroxide (LiOH)
- Sodium hydroxide (NaOH)
- Potassium hydroxide (KOH)
- Rubidium hydroxide (RbOH)
- Cesium hydroxide (CsOH)
- Calcium hydroxide (Ca(OH)<sub>2</sub>)
- Strontium hydroxide (Sr(OH)<sub>2</sub>)
- Barium hydroxide (Ba(OH)<sub>2</sub>)

# 17.2 ALKALIS

Alkali is a base that dissolves in water.

The word "alkali" is derived from Arabic *al qalīy* (or *alkali*), meaning *the calcined ashes*, referring to the original source of alkaline substances. A water-extract of burned plant ashes, called *potash* and composed mostly of potassium carbonate ( $K_2CO_3$ ), was mildly basic ( $K_2CO_3 + H_2O = KHCO_3 + KOH$ ). After heating this substance with calcium hydroxide (*slaked lime*), a far more strongly basic substance known as *caustic potash* (potassium hydroxide) was produced ( $K_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + 2KOH$ ). Caustic potash was traditionally used in conjunction with animal fats to produce soft soaps, one of the caustic processes that rendered soaps from fats in the process of saponification, known since antiquity. Plant potash lent the name to the element potassium, which was first derived from caustic potash, and also gave potassium its chemical symbol **K** (Kalium), which ultimately derives from al**k**ali.

There are various definitions for alkali. Alkali is often defined as a subset of base. Two examples of alkali definitions are given below.

- A hydroxide of alkali metal or alkaline earth metal (this includes Mg(OH)<sub>2</sub> but excludes NH<sub>4</sub>OH).
- Any base that is water-soluble and forms hydroxide ions or the solution of a base in water (this excludes Mg(OH)<sub>2</sub> but includes NH<sub>4</sub>OH).

Magnesium hydroxide is an example of an atypical alkali since it has low solubility in water, while the dissolved portion is considered a strong base due to complete dissociation of its ions.

Soluble hydroxides of alkali metals and alkaline earth metals (i. e. alkalis) are often called "alkali salts". There are commonly used names of some alkali salts. "Caustic soda" is sodium hydroxide (NaOH). "Caustic potash" is potassium hydroxide (KOH). "Limewater" is calcium hydroxide (Ca(OH)<sub>2</sub>). Lime

a general term for calcium-containing inorganic materials, in which carbonates, oxides and hydroxides predominate. The word "lime" originates with its earliest use as building mortar and has the sense of "sticking or adhering".

Alkali can be produced in the reaction between active metals (or their oxides) and water. Active metals are: Cs, Rb, K, Na, Li, Ba, Sr, Ca. Magnesium, aluminium and zinc can react with water, but the reaction is usually *very slow* unless the metal samples are specially prepared to remove the surface

layer of oxide which protects the rest of the metal.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

$$Na_2O + H_2O \rightarrow 2NaOH$$

Insoluble bases can be produced in reactions between soluble salts and alkalis.

$$ZnSO_4 + 2KOH \rightarrow Zn(OH)_2 \downarrow + K_2SO_4$$

In case of the excess of alkali complex soluble salts can be formed.

$$ZnSO_4 + 4KOH \rightarrow K_2[Zn(OH)_4] + K_2SO_4$$

**Chemical properties.** Alkalis react with both acids and acidic oxides. The products of those reactions are salts and water.

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

$$2NaOH + SO_3 \rightarrow Na_2SO_4 + H_2O$$

Alkalis react with certain salts (in case if one of the products of the reaction is insoluble or volatile).

$$2KOH + FeCl_2 \rightarrow 2KCl + Fe(OH)_2 \downarrow$$

$$KOH + NH_4Cl \rightarrow KCl + NH_3\uparrow + H_2O$$

All bases, except NaOH and KOH, are decomposed at high temperatures. The products of such decomposition are oxide and water.

$$Ca(OH)_2 \rightarrow CaO + H_2O$$

Amphoteric hydroxides react with both acids and alkalis.

$$Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O$$

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$$

In water solution complex salt is formed.

$$Al(OH)_3 + NaOH \rightarrow Na[Al(OH)_4]$$

# **Questions:**

- a. Give a definition of base.
- b. Give a definition of alkali.
- c. Give a definition of hydroxide.
- d. What metals are active?

# **Exercises:**

- a. Imagine how can the following substances be produced: i) KOH; ii) LiOH; iii) Fe(OH)<sub>3</sub>; iv) Mg(OH)<sub>2</sub>; v) Zn(OH)<sub>2</sub>.
- b. How can Zn(OH)<sub>2</sub> be produced from the set of the following substances: Na; H<sub>2</sub>SO<sub>4</sub>; ZnO; H<sub>2</sub>O?

- c. How can  $Fe(OH)_3$  be produced from the set of the following substances: K; HCl;  $Fe_2O_3$ ;  $H_2O$ ?
- d. What substances react with KOH? Write down equations of possible reactions. Al<sub>2</sub>O<sub>3</sub>; Ca(HCO<sub>3</sub>)<sub>2</sub>; HCl; CO<sub>2</sub>; H<sub>2</sub>SO<sub>4</sub>; KNO<sub>3</sub>; Zn(OH)<sub>2</sub>; NaHCO<sub>3</sub>; K<sub>2</sub>CO<sub>3</sub>; SO<sub>3</sub>; H<sub>3</sub>PO<sub>4</sub>; NH<sub>4</sub>Cl.
- e. What substances react with Zn(OH)<sub>2</sub>? Write down equations of possible reactions. KOH; H<sub>2</sub>O; H<sub>2</sub>SO<sub>4</sub>; CaCl<sub>2</sub>; NaCl; HNO<sub>3</sub>; CO<sub>2</sub>; SO<sub>2</sub>; SO<sub>3</sub>; HCl; NaOH; H<sub>3</sub>PO<sub>4</sub>.
  - f. Finish chemical reactions
    - i. NaOH +  $P_2O_5 \rightarrow$
    - ii. NaOH +  $Cr_2(SO_4)_3 \rightarrow$
    - iii. NaOH +  $CO_2 \rightarrow$
    - iv. NaOH + NH<sub>4</sub>NO<sub>3</sub>  $\rightarrow$
    - v.  $NaOH + Cr(OH)_3 \rightarrow$
    - vi.  $Fe(OH)_3 + H_2SO_4 \rightarrow$
    - vii.  $Fe(OH)_2 + HNO_3 \rightarrow$
    - viii.  $Fe(OH)_3 \rightarrow$
    - ix.  $Ca(OH)_2 + H_3PO_4 \rightarrow$
    - $x. KOH + MgCl_2 \rightarrow$
    - xi.  $KOH + N_2O_5 \rightarrow$
    - xii.  $Al_2(SO_4)_3 + KOH \rightarrow$
    - xiii.  $Sr(OH)_2 + H_2SO_4 \rightarrow$
    - xiv.  $Cr(OH)_3 + HCl \rightarrow$
    - xv.  $Al(OH)_3 + NaOH \rightarrow$

#### LESSON 18

# **18.1 ACIDS**

An Arrhenius acid is a compound that increases the  $H^+$  ion concentration in aqueous solution. The  $H^+$  ion is just a bare proton, and it is rather clear that bare protons are not floating around in an aqueous solution. Instead, chemistry has defined the hydronium ion  $(H_3O^+)$  as the actual chemical species that represents an  $H^+$  ion. Classic Arrhenius acids can be considered ionic compounds in which  $H^+$  is the cation.

If an acid is composed of only hydrogen and one other element, the name is hydro- + the stem of the other element + -ic acid. For example, the compound HCl(aq) is hydrochloric acid, while H<sub>2</sub>S(aq) is hydrosulfuric acid. If these acids were not dissolved in water, the compounds would be called hydrogen chloride and hydrogen sulfide, respectively. Both of these substances are well known as molecular compounds; when dissolved in water, however, they are treated as acids.

If a compound is composed of hydrogen ions and a polyatomic anion, then the name of the acid is derived from the stem of the polyatomic ion's name. Typically, if the anion name ends in -ate, the name of the acid is the stem of the anion name plus -ic acid; if the related anion's name ends in -ite, the name of the corresponding acid is the stem of the anion name plus -ous acid.

Acids may be produced in reactions between acidic oxides and water.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Less volatile acids react with salts of more volatile acids.

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

Table 18.1 Formulas and names of some acids

Formula	Name
CH <sub>3</sub> COOH	acetic acid
HCl	hydrochloric acid
HClO <sub>3</sub>	chloric acid
HClO <sub>4</sub>	perchloric acid
HBr	hydrobromic acid
HI	hydroiodic acid
HF	hydrofluoric acid
$HNO_2$	nitrous acid
HNO <sub>3</sub>	nitric acid
$H_2C_2O_4$	oxalic acid
$H_3PO_4$	phosphoric acid
$H_2SO_4$	sulfuric acid
$H_2SO_3$	sulfurous acid

Chemical properties. Acids have some properties in common. They react with metals situated before hydrogen in the electrochemical series of metals to give off  $H_2$  gas.

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2\uparrow$$

Electrochemical series of metals:

$$Li>K>Sr>Ca>Na>Mg>Al>Zn>Cr>Fe>Cd>Co>Ni>Sn>>Pb>\underline{\boldsymbol{H}}>Cu>Ag>Hg>Pt>Au$$

Acids react with basic and amphoteric oxides.

$$H_2SO_4 + CuO \rightarrow CuSO_4 + H_2O$$

$$6HNO_3 + Al_2O_3 \rightarrow 2Al(NO_3)_3 + 3H_2O$$

Acids react with salts in case if insoluble substances or gases are formed. For example, they react with carbonate and hydrogen carbonate salts to give off CO<sub>2</sub> gas.

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2\uparrow + H_2O$$
  
 $Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + 2CO_2\uparrow + 2H_2O$ 

Acids that are ingested typically have a sour, sharp taste. The name *acid* comes from the Latin word *acidus*, meaning "sour".

# 18.2 NEUTRALIZATION REACTION

Acids and bases react with each other to make water and an ionic compound called a salt. A salt, in chemistry, is any ionic compound made by combining an acid with a base. A reaction between an acid and a base is called a neutralization reaction and can be represented as follows:

acid + base 
$$\rightarrow$$
 H<sub>2</sub>O + salt

The stoichiometry of the balanced chemical equation depends on the number of H<sup>+</sup> ions in the acid and the number of OH<sup>-</sup> ions in the base.

# **Questions:**

- a. Give the formula for each acid.
  - 1. perchloric acid
  - 2. hydriodic acid
  - 3. hydrosulfuric acid
  - 4. phosphorous acid
- b. Name each acid.
  - 1. HF
  - 2. HNO<sub>3</sub>
  - $3. H_2C_2O_4$
  - 4. H<sub>2</sub>SO<sub>4</sub>
  - 5. H<sub>3</sub>PO<sub>4</sub>
  - 6. HCl
- c. Name some properties that acids have in common.

#### **Exercises:**

- a. Imagine how the following acids can be produced: H<sub>3</sub>PO<sub>4</sub>; HNO<sub>3</sub>; HNO<sub>2</sub>; HCl; H<sub>2</sub>SO<sub>4</sub>; H<sub>2</sub>SO<sub>3</sub>; H<sub>2</sub>S.
- b. What metals among the given list react with hydrochloric acid: Li; Ba; Cu; Mg; Al; Au; Ag?
- c. What substances react with sulfuric acid? Write down equations of possible reactions. CuCl<sub>2</sub>; Fe(OH)<sub>3</sub>; ZnO; HCl; Al(OH)<sub>3</sub>; SiO<sub>2</sub>; Pb(NO<sub>3</sub>)<sub>2</sub>; KOH; BaCl<sub>2</sub>; CuO; Mg(OH)<sub>2</sub>; Zn.
- d. What substances react with nitric acid? Write down equations of possible reactions. AgCl; Fe(OH)<sub>2</sub>; CuO; HBr; Zn(OH)<sub>2</sub>; CO<sub>2</sub>; NaNO<sub>3</sub>; KCl; Ba(OH)<sub>2</sub>; H<sub>3</sub>PO<sub>4</sub>; Sr(OH)<sub>2</sub>; Cr.
  - e. Finish chemical reactions:
    - i.  $P_2O_5 + H_2O \rightarrow$
    - ii.  $HCl + Mg(OH)_2 \rightarrow$
    - iii.  $Al(OH)_3 + HCl \rightarrow$
    - iv. Fe + HCl  $\rightarrow$
    - v.  $SO_2 + H_2O \rightarrow$
    - vi.  $Fe_2O_3 + H_2SO_4 \rightarrow$
    - vii. Fe + HI  $\rightarrow$
    - viii.  $N_2O_5 + H_2O \rightarrow$

- ix.  $CaO + H_3PO_4 \rightarrow$
- x. LiCl + H<sub>3</sub>PO<sub>4</sub>  $\rightarrow$
- f. What is the mass of ZnSO<sub>4</sub> which was produced from 9.8 g of sulfuric acid and 8.1 g of ZnO?
- g. What is the mass of K<sub>3</sub>PO<sub>4</sub> which was produced from 49 g of phosphoric acid and 80 g of KOH?

# **LESSON 19**

# **19.1 SALTS**

**Salts** are ionic compounds that result from the neutralization reaction of an acid and a base. They are composed of such numbers of cations (positively charged ions) and anions (negative ions) that the product is electrically neutral (without a net charge). These component ions can be inorganic such as chloride (Cl $^-$ ), as well as organic such as acetate (CH $_3$ COO $^-$ ) and monoatomic ions such as fluoride (F $^-$ ), as well as polyatomic ions such as sulfate (SO $_4^{2-}$ ).

There are several varieties of salts. Salts that dissociate to produce hydroxide ions when dissolved in water are *basic salts* (Fe(OH)<sub>2</sub>Cl) and salts that dissociate to produce hydronium ions in water are *acid salts* (NaHSO<sub>4</sub>). *Neutral salts* are those that are neither acid nor basic salts. Zwitterions contain an anionic center and a cationic center in the same molecule but are not considered to be salts. Examples include amino acids, many metabolites, peptides, and proteins.

Acidic salts can be produced from neutral salts after the addition of acid.

 $CaSO_4 + H_2SO_4 \rightarrow Ca(HSO_4)_2$ 

Basic salts can be produced from neutral salts after the addition of base.

 $CaSO_4 + Ca(OH)_2 \rightarrow (CaOH)_2SO_4$ 

# 19.2 SOLUBILITY CHART OF SALTS

Many ionic compounds can be dissolved in water. The exact combination of ions involved makes each compound have a unique solubility in any solvent. The solubility is dependent upon how well each ion interacts with the solvent, so there are certain patterns.

For example, all salts of sodium, potassium and ammonium are soluble in water, as are all nitrates and many sulfate salts except barium sulfate, calcium sulfate (sparingly soluble) and lead (II) sulfate.

However, ions that bind tightly to each other and form highly stable lattices are less soluble, because it is harder for these structures to break apart for the compounds to dissolve. For example, most carbonate salts are not soluble in water, such as lead carbonate and barium carbonate. Soluble

carbonate salts are: sodium carbonate, potassium carbonate and ammonium carbonate.

Salts are formed by a chemical reaction between:

- A base and an acid, e.g.,  $NH_4OH + HCl → NH_4Cl + H_2O$
- A metal and an acid, e.g.,  $Mg + H_2SO_4$  →  $MgSO_4 + H_2$ ↑
- A metal and a non-metal, e.g.,  $Ca + Cl_2 \rightarrow CaCl_2$
- A base and an acid anhydride, e.g.,  $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$
- An acid and a basic anhydride, e.g.,  $2HNO_3 + Na_2O \rightarrow 2NaNO_3 + H_2O$
- Salts can also be formed if solutions of different salts are mixed with each other or with acid or alkali solutions. Their ions recombine, and in some cases new salt (base or even acid) precipitates (see: the solubility chart below):  $Pb(NO_3)_2 + Na_2SO_4 \rightarrow PbSO_4 \downarrow + 2NaNO_3$ . The same thing can be said about reactions in which gases are formed:  $NH_4Cl + KOH \rightarrow KCl + NH_3 \uparrow + H_2O$
- Metal is able to substitute another metal in a salt in case if it is situated before the second one in the reactivity series:  $CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$ Table 19.1

# Solubility chart

				27.272																		
cation anion	H.	Li'	K.	Na'	NH;	Ba²	Ca²	Mg²	Sr2	Al3º	Cr3.	Fe2"	Fe³'	Ni²'	Co2	Mn²	Zn²ʻ	Ag*	Hg²	Pb²	Sn²	Cu²
OH"		S	S	S	S	S	M	1	M	1	1	1	1			1	1	D	D	1	I	
F	S	S	S	S	S	M	1	1	M	S	L	1	1	S	S	M	S	S	M	1	S	S
CI.	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	1	S	M	S	S
Br	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	T	М	M	S	S
ľ	S	S	S	S	S	S	S	S	S	S	U	S	U	S	S	S	S	I	T	I	M	S
S <sup>2-</sup>	S	S	S	S	S	S	D	D	S	D	D	T	D	T	I	I	T	1	T	1	I	1
HS <sup>-</sup>	S	S	S	S	S	S	S	S	S	U	U	U	U	U	T	U	U	U	U	U	U	U
SO <sub>3</sub> -	S	S	S	S	S	M	M	M	1	U	D	M	U	T	I	U	M	1	1	1	U	U
HSO <sub>3</sub>	S	U	S	S	S	S	S	S	S	U	U	U	U	U	U	U	U	U	U	U	U	U
SO <sub>4</sub> -	S	S	S	S	S	I	M	S	T	S	S	S	S	S	S	S	S	M	D	1	S	S
HSO,	S	S	S	S	S	U	U	U	D	U	U	U	U	U	U	U	U	U	U	1	U	U
NO <sub>3</sub>	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	D	S
NO <sub>2</sub>	S	S	S	S	S	S	S	S	S	U	U	U	U	S	M	U	U	М	U	U	U	U
PO <sub>4</sub> 3-	S	1	S	S	D	1	I	I	I	T	T	1	1	T	1	1	I	1	1	1	I	1
HPO <sub>4</sub>	S	Ü	S	S	S	Ī	Ì	M	Ī	U	U	Ī	Ú	U	U	T	U	U	U	M	Ī	U
H <sub>2</sub> PO <sub>4</sub>	S	S	S	S	S	S	S	S	S	U	U	S	U	U	U	S	S	S	U	D	U	U
CO <sub>3</sub> -	S	S	S	S	S	I	I	T	T	U	U	T	U	I	I	T	T	T	U	1	U	1
HCO,	S	S	S	S	S	S	S	S	S	U	U	S	U	Ü	U	U	U	Ü	U	S	U	U
CH3COO	S	S	S	S	S	S	S	S	S	D	S	S	D	S	S	S	S	S	S	S	D	S
SiO <sub>3</sub> -	ī	S	S	S	U	ī	ī	Ĭ	ī	II	II	ī	ĪĪ	u	u	Ī	ī	Ū	U	ī	Ū	Ū

#### **Reactivity series of metals**

Active metals – those which react with water and acids										
Cs	Rb	K	Na	Li	Ba	Sr	Ca			
Metals	Metals which react with acids and produce salts and $H_2$									
Mg	Al	Mn	Zn	Cr	Fe	Cd	Co	Ni	Sn	Pb
Metals which react with strong oxidizing acids only and don't produce H <sub>2</sub>										
Sb	T	7			A	<b>T</b>				

The reactivity series is sometimes quoted in the strict reverse order of standard electrode potentials, when it is also known as the "electrochemical series":

$$Li > K > Sr > Ca > Na > Mg > Al > Zn > Cr > Fe > Cd > Co > Ni > Sn > Pb >$$
  
 $\geq \underline{\mathbf{H}} > Cu > Ag > Hg > Pt > Au$ 

The positions of lithium and sodium are changed on such a series; gold and platinum are also inverted, although this has little practical significance as both metals are highly unreactive. Hydrogen is included in standard electrode potentials order because the power of a reducing agent is measured relatively to the standard hydrogen electrode.

# **Questions:**

- a. Give a definition of the term "salt".
- b. What is the difference between normal, acidic and basic salts?
- c. How can the reactivity series of metals be used?
- d. How can the solubility chart be used?

# **Exercises:**

- a. Write down the formulas of the following compounds: iron (III) sulfate; sodium sulfate; barium dihydrogen phosphate; magnesium hydrogen carbonate; magnesium hydroxy chloride; potassium sulfide; potassium hydroxy sulfate; iron (III) dihydroxy chloride; calcium hydrogen phosphate.
- b. What substances react with AgNO<sub>3</sub>? Write down equations of possible reactions. HCl; FeSO<sub>4</sub>; CaCl<sub>2</sub>; BaCl<sub>2</sub>; H<sub>2</sub>SO<sub>4</sub>; NaI; KBr; K<sub>3</sub>PO<sub>4</sub>; Na<sub>2</sub>CO<sub>3</sub>; Ba(NO<sub>3</sub>)<sub>2</sub>.
  - c. How can the following salts be produced: KCl;  $Fe_2(SO_4)_3$ ;  $Zn(NO_3)_2$ ?
- d. Which salts react with each other: i)  $CaCO_3 + KCl$ ; ii)  $MgCl_2 + Na_2CO_3$ ; iii)  $NaCl + K_2CO_3$ ; iv)  $BaCl_2 + K_2SO_4$ .
  - e. Finish equations of chemical reactions:
    - i.  $BaCl_2 + Na_3PO_4 \rightarrow$
    - ii.  $Fe_2(SO_4)_3 \rightarrow$
    - iii.  $H_3PO_4 + Mg(OH)_2 \rightarrow$
    - iv.  $HgSO_4 + Zn \rightarrow$
    - v.  $BaCO_3 + HCl \rightarrow$
    - vi.  $AIOHSO_4 + H_2SO_4 \rightarrow$

- vii.  $Al + H_2SO_4 \rightarrow$ viii.  $AlCl_3 + NaOH \rightarrow$ ix.  $Na[Al(OH)_4] + HCl \rightarrow$
- x.  $Ca(OH)_2 + H_3PO_4 \rightarrow$
- f. What is the mass of silver chloride produced in the reaction between 5.85 g of sodium chloride and 33.8 g of silver nitrate?
- g. What is the mass of barium sulfate produced in the reaction between 9.8 g of sulfuric acid and 41.6 g of barium chloride?
- h. What kind of salt is produced in the reaction between 10.5 g of calcium hydroxide and 13.7 g of nitric acid?
- i. What kind of salt is produced in the reaction between 12.3 g of sodium hydroxide and 26 g of copper chloride?

#### LESSON 20

# 20.1 CLASSIC CHAINS OF CHEMICAL REACTIONS

Chain of chemical reactions is one of the most commonly used types of tasks in chemistry. In the classic type of that kind of task student has to write down all the reactions from each chain. Each next substance must be somehow produced from the previous substance. Student has a kind of freedom to choose additional reactants and conditions to make reactions possible. In case if the one-step reaction is impossible (for example, it is impossible to produce insoluble base directly from the metal), two or even more reactions should be written to complete one step in the chain.

# **Exercise:**

- a.  $CaCO_3 \rightarrow CaO \rightarrow Ca(OH)_2 \rightarrow Ca(HCO_3)_2 \rightarrow CaCO_3$
- b.  $Mg \rightarrow MgO \rightarrow Mg(OH)_2 \rightarrow MgCl_2 \rightarrow Mg(NO_3)_2$
- c. Ba  $\rightarrow$ Ba(OH)<sub>2</sub>  $\rightarrow$  BaOHCl  $\rightarrow$  BaCl<sub>2</sub>  $\rightarrow$  BaCO<sub>3</sub>
- d.  $K \rightarrow KOH \rightarrow KHSO_4 \rightarrow K_2SO_4 \rightarrow KCl$
- e. Al  $\rightarrow$  Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>  $\rightarrow$  Na[Al(OH)<sub>4</sub>]  $\rightarrow$  Al(NO<sub>3</sub>)<sub>3</sub>  $\rightarrow$  Al(OH)<sub>3</sub>
- f.  $NaHCO_3 \rightarrow CO_2 \rightarrow CaCO_3 \rightarrow Ca(HCO_3)_2 \rightarrow CaO$
- g.  $Cu \rightarrow CuS \rightarrow CuSO_4 \rightarrow CuCl_2 \rightarrow Cu(NO_3)_2$
- h.  $CuSO_4 \rightarrow SO_3 \rightarrow NaHSO_4 \rightarrow Na_2SO_4 \rightarrow NaHSO_4$
- i.  $Fe \rightarrow FeCl_2 \rightarrow Fe(NO_3)_2 \rightarrow FeSO_4 \rightarrow Fe(OH)_2$
- j.  $K \to K_2O \to KOH \to KCl \to KNO_3$

# 20.2 MODERN CHAINS OF CHEMICAL REACTIONS

Modern type of the chain of chemical reactions includes two tasks in one. At first, student must write down all the reactions. All the reactants, conditions and by-products are given (if they are not clearly obvious), while main products are hidden behind the letters. At second, student must find out molar mass

of the last product, or the sum of molar masses for several substances (for example, for substance hidden behind the letter "B" and substance hidden behind the letter "D").

# **Exercise:**

a. Calculate the sum of molar masses for compounds A, B, C and D from the chain of chemical reactions.

$$\mathrm{H}_2 \xrightarrow{+\mathit{Cl}_2} \mathrm{A} \xrightarrow{+\mathit{Zn}} \mathrm{A} \xrightarrow{-\mathit{ZnCl}_2} \mathrm{B} \xrightarrow{+\mathit{O}_2} \mathrm{C} \xrightarrow{+\mathit{Na}} \mathrm{C} \xrightarrow{-\mathit{NaOH}} \mathrm{D}$$

b. Calculate the sum of molar masses for compounds B and D from the chain of chemical reactions.

$$\operatorname{Na} \xrightarrow{+H_2O} \operatorname{A} \xrightarrow{+CO_2} \operatorname{B} \xrightarrow{+NaOH} \operatorname{C} \xrightarrow{-H_2O} \operatorname{C} \xrightarrow{+HCl} \operatorname{D}$$

c. Calculate the sum of molar masses for compounds B, C and D from the chain of chemical reactions.

$$\mathrm{Fe}(\mathrm{OH})_{3} \xrightarrow{+\ 1HCl} - \mathrm{H}_{2}O \xrightarrow{} \mathrm{A} \xrightarrow{+\ 1HCl} - \mathrm{H}_{2}O \xrightarrow{} \mathrm{B} \xrightarrow{+\ 1HCl} - \mathrm{H}_{2}O \xrightarrow{} \mathrm{C} \xrightarrow{+\ 3KOH} \to \mathrm{D}$$

d. Calculate the molar mass of compound D from the chain of chemical reactions.

$$\mathrm{Al} \xrightarrow[-H_2O,-NO_2]{+HNO_3} \to \mathrm{A} \xrightarrow[-3KNO_3]{+4KOH} \to \mathrm{B} \xrightarrow[-KCl,-H_2O]{+HCl} \to \mathrm{C} \xrightarrow[-3H_2O]{+3KOH} \to \mathrm{D}$$

e. Calculate the sum of molar masses for compounds C and D from the chain of chemical reactions.

$$\operatorname{Ca} \xrightarrow{+O_2} \operatorname{A} \xrightarrow{+CO_2} \operatorname{B} \xrightarrow{t} \operatorname{C} \xrightarrow{+2KOH} \operatorname{D}$$

# **LESSON 21**

# Sample ticket for control task #3 on main types of inorganic chemical compounds

1. Write down equations of chemical reactions between the following substances in case if they are possible

$$CaO + Na2O \rightarrow$$

$$Na2O + NO \rightarrow$$

$$CaO + N2O5 \rightarrow$$

$$K2O + Al2O3 \rightarrow$$

$$BaO + H2O \rightarrow$$

$$N2O5 + H2O \rightarrow$$

$$SiO2 + H2O \rightarrow$$

$$Al2O3 + H2O \rightarrow$$

$$KAlO2 + HCl \rightarrow$$

$$Cu(OH)2 + Na2SO4 \rightarrow$$

$$BaCO3 + KOH \rightarrow$$

- 2. Classic chains of chemical reactions
- a.  $P_2O_5 \rightarrow H_3PO_4 \rightarrow Ca(H_2PO_4)_2 \rightarrow Ca_3(PO_4)_2 \rightarrow H_3PO_4$
- b.  $Ca \rightarrow Ca(OH)_2 \rightarrow CaOHCl \rightarrow CaCl_2 \rightarrow CaCO_3$

# 3. Modern chains of chemical reactions

Calculate the sum of molecular masses for compounds A, B, C and D from chains of chemical reactions:

a. 
$$C \xrightarrow{+10_2} A \xrightarrow{+1NaOH} B \xrightarrow{+1NaOH} C \xrightarrow{+CaCl_2} D$$
  
b.  $Ca_3(PO_4)_2 \xrightarrow{+1H_3PO_4} A \xrightarrow{+1H_3PO_4} B \xrightarrow{+1Ca(OH)_2} C \xrightarrow{+1Ca(OH)_2} D$ 

# **LESSON 22**

# 22.1 QUALITATIVE DESCRIPTION OF SOLUTIONS

The **major component** of a solution is called the **solvent**. The **minor component** of a solution is called the **solute**. By major and minor we mean whichever component has the greater presence by mass or by moles. Sometimes this becomes confusing, especially with substances with very different molar masses. For example, if the mass percentage of ethanol solution in water is equal to 70%, the mole percentage of ethanol is still equal to 47.6 % (because molar mass of water is lower than that for ethanol). Obviously, such expression as "98% ethanol" widely used for a solution in which there are 98 % of ethanol and just 2% of water is not correct, because ethanol is still mistakenly considered to be solute and not solvent.

Salt water is a solution of solid NaCl in liquid water; soda water is a solution of gaseous  $CO_2$  in liquid water, while air is a solution of a gaseous solute  $(O_2)$  in a gaseous solvent  $(N_2)$ . In all cases, however, the overall phase of the solution is the same phase as the solvent.

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. **Dilute** describes a solution that has very little solute, while **concentrated** describes a solution that has a lot of solute. One problem is that these terms are qualitative; they describe more or less but not exactly how much.

# 22.2 SOLUBILITIES OF IONIC COMPOUNDS

In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is called the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature.

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is *saturated* with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is *unsaturated*. A solution of 0.00019 g of AgCl per 100 g of H<sub>2</sub>O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H<sub>2</sub>O is also saturated but rather concentrated.

**Solubilities of Some Ionic Compounds** 

*Table 22.1* 

 Solute
 Solubility (g per 100 g of H<sub>2</sub>O at 25 °C)

 AgCl
 0.00019

 CaCO<sub>3</sub>
 0.0006

 NaCl
 36.1

 KBr
 70.7

 NaNO<sub>3</sub>
 94.6

In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called *supersaturated* solutions and they are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.

It should be obvious that some solutes dissolve in certain solvents but not in others. NaCl, for example, dissolves in water but not in vegetable oil. Beeswax dissolves in liquid hexane but not in water.

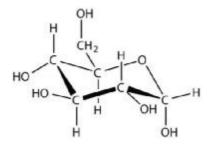
From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl — a very polar substance because it is composed of ions — dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane but not in polar water. This concept leads to the general ancient alchemic rule that "like dissolves like" for predicting whether a solute is soluble in a given solvent. However, this is a general rule, not an absolute statement, so it must be applied with care.

# **Questions:**

- a. Define solute and solvent.
- b. Define *saturated*, *unsaturated*, and *supersaturated* solutions.
- c. Differentiate between polar and nonpolar solvents.
- d. Which solvent is  $Br_2$  more likely soluble in  $CH_3OH$  or  $C_6H_6$ ?

- e. Which solvent is NaOH more likely soluble in  $-CH_3OH$  or  $C_6H_6$ ?
- f. Compounds with the formula  $C_nH_{2n+1}OH$  are soluble in  $H_2O$  when n is small but not when n is large. Suggest an explanation for this phenomenon.
  - g. Glucose has the following structure:

What parts of the molecule indicate that this substance is soluble in water?



# **Exercises:**

- a. A solution is prepared by combining 2.09 g of  $CO_2$  and 35.5 g of  $H_2O$ . Identify the solute and solvent.
- b. A solution is prepared by combining 10.3 g of Hg(liquid) and 45.0 g of Ag(solid). Identify the solute and solvent.
- c. Decide if a solution containing 45.0 g of NaCl per 100 g of  $H_2O$  is unsaturated, saturated, or supersaturated.
- d. Decide if a solution containing 0.000092~g of AgCl per 100~g of  $H_2O$  is unsaturated, saturated, or supersaturated.
- e. Would the solution in Exercise "c" be described as dilute or concentrated? Explain your answer.
- f. Would the solution in Exercise "d" be described as dilute or concentrated? Explain your answer.

#### LESSON 23

# 23.1 MOLARITY AND MOLALITY

Molarity (molar concentration) is defined as the number of moles of solute divided by the number of liters of solution:

molarity = moles of solute / liters of solution C = n(solute) / V(solution)

Molarity is expressed in mol/L which can be simplified as just big letter "M".

A similar in spelling but different in meaning unit of concentration is molality, which is defined as the number of moles of solute per kilogram of solvent, not per liter of solution:

molality = moles of solute / kilograms of solvent  $C_m = n(solute) / m(solvent)$ 

# 23.2 MASS PERCENTAGE

Another way to specify an amount of solute is percentage composition by mass (or *mass percentage*, % m/m). It is defined as follows:

% m/m = (mass of solute / mass of entire sample)  $\times$  100 %  $\omega$  = m(solute) / m(solution)

Mass percentage has a wider sense than just a fraction of solute in a solvent multiplied by 100. The same index is used to describe the mass content of a compound. For example, the mass percentage of potassium (K) in potassium oxide  $(K_2O)$  is equal to the ratio between molar mass of potassium multiplied by 2 (imagine that potassium is a solute) and the molar mass of the whole compound (imagine that oxygen is a solvent). In more complicated compounds "solvent" is everything else except atoms for which the mass percentage has to be calculated.

# **Exercises:**

- a. What is the molarity of a solution made by dissolving 13.4 g of NaNO<sub>3</sub> in water? The final volume of that solution is equal to 345 mL.
- b. What is the molality of a solution made by dissolving 332 g of  $C_6H_{12}O_6$  in 4.66 kg of water?
- c. How many moles of MgCl<sub>2</sub> are present in 0.0331 L of a 2.55 M water solution? Density is 1.2 g/mL. What is the mass percentage of MgCl<sub>2</sub>?
- d. How many moles of NH<sub>4</sub>Br are present in 88.9 mL of a 0.228 M water solution? Density is 1.1 g/mL. What is the mass percentage of NH<sub>4</sub>Br?
- e. What volume of 5.56~M NaCl is needed to obtain 2L of 0.85~% NaCl solution? Density is equal to 1~g/mL.
- f. What mass of 96 %  $C_2H_5OH$  is needed to obtain 3L of 40 %  $C_2H_5OH$  solution? Density is equal to 0.94 g/ml.
  - g. Calculate the mass percentage of nitrogen in  $NH_4NO_3$ .
  - h. Calculate the mass percentage of hydrogen in  $H_2C_2O_4{\cdot}2H_2O.$
  - i. Calculate the mass percentage of oxygen in  $CaSO_4 \cdot \frac{1}{2}H_2O$ .

# **LESSON 24**

# 24.1 THEORY OF ELECTROLYTIC DISSOCIATION

**Dissociation** in chemistry is a general process in which ionic compounds separate or split into smaller charged particles — ions. For example, when a hydrogen chloride is put in water, a covalent bond between an electronegative chlorine atom and a hydrogen atom is broken by heterolytic fission, which gives a proton and a negatively charged ion. Dissociation process is frequently confused with ionization. Although it may seem as a case of ionization, in reality the ions of any salt already exist within the crystal lattice. When salt is dissociated, its constituent ions are simply surrounded by water molecules

(i. e. solvation of ions happens) and their effects become visible (e. g. the solution becomes electrolytic). However, no transfer or displacement of electrons occurs. Actually, the chemical synthesis of salt from metals and nonmetals

involves ionization.

**Solvation**, also sometimes called dissolution, is the process of attraction and association of molecules of a solvent with molecules or ions of a solute. As ions dissolve in a solvent they spread out and become surrounded by solvent molecules.

Polar solvents are those with a molecular structure that contains dipoles. The polar molecules of these solvents can solvate ions because they can orient the appropriate partially charged portion of the molecule towards the ion in response to electrostatic attraction. This stabilizes the system and creates a solvation shell (or hydration shell in the case of water), as it is shown in figure 24.1.

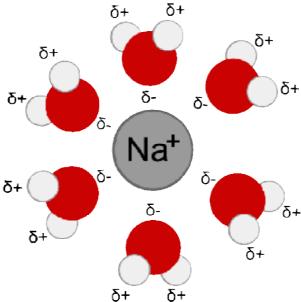


Figure 24.1 A scheme of hydrated sodium cation

Any acid that dissociates 100 % into ions is called a strong acid. If it does not dissociate 100 %, it is a weak acid. CH<sub>3</sub>COOH is an example of a weak acid:

$$CH_3COOH \rightarrow CH_3COO^- + H^+$$

The ratio between the number of dissolved compounds and the number of dissociated compounds is called dissociation degree ( $\alpha$ ). It can be expressed in percent as well. Namely, for 1M acetic acid dissociation degree in water in normal conditions is equal to 0.4 %. The higher is concentration of a weak electrolyte, the lower is the dissociation degree. The lower the concentration, the higher the percent of dissociated compounds.

Because the process of dissociation for weak electrolytes does not go 100 % to completion, it is more appropriate to write it as an equilibrium:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

As it turns out, there are very few strong acids, which are given in the table 24.1 below. If an acid is not listed here, it is a weak acid. It may be 1 % ionized or 99 % ionized, but it is still classified as a weak acid.

The issue is similar with bases: a strong base is a base that is 100 % ionized in solution. If it is less than 100 % ionized in solution, it is a weak base. There are very few strong bases; any base not listed is a weak base.

**Strong Acids and Bases** 

*Table 24.1* 

Acids **Bases** HNO<sub>3</sub> LiOH H<sub>2</sub>SO<sub>4</sub> NaOH HI KOH HBr RbOH **HC1 CsOH** HClO<sub>3</sub> Ca(OH)<sub>2</sub> HClO<sub>4</sub>  $Sr(OH)_2$ Ba(OH)<sub>2</sub>

# 24.2 EQUATIONS OF STEPWISE DISSOCIATION

Weak acids containing several hydrogen atoms which can be dissociated in water solutions dissociate in a stepwise manner, just like phosphoric acid does.

- I.  $H_3PO_4 \rightleftarrows H_2PO_4^- + H^+$
- II.  $H_2PO_4^- \rightleftarrows HPO_4^{2-} + H^+$
- III.  $HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$

Acid salts of weak acids dissociate in a similar stepwise manner.

- I.  $KH_2PO_4 \rightarrow H_2PO_4^- + K^+$
- II.  $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$
- III.  $HPO_4^{2-} \rightleftarrows PO_4^{3-} + H^+$

Weak bases containing several OH<sup>-</sup> groups also dissociate in several steps.

- I.  $Zn(OH)_2 \rightleftarrows ZnOH^+ + OH^-$
- II.  $ZnOH^+ \rightleftarrows Zn^{2+} + OH^-$

Yet another example is for dissociation of basic salt made from weak base.

- I.  $ZnOHCl \rightarrow ZnOH^+ + Cl^-$
- II.  $ZnOH^+ \rightleftarrows Zn^{2+} + OH^-$

Molar mass of any ion can be calculated as a sum of molar masses for all of its atoms. Masses of electrons are usually ignored.

Number of protons in the whole ion equals to the sum of protons in each of its atoms, while the number of electrons is equal to the sum of protons in each of the atoms *minus total charge of the ion*. It means that for negatively charged ions the number of electrons is higher than the number of protons (minus and minus give plus). For positively charged ions the number of electrons is lower than the number of protons.

# **Questions:**

- a. Describe the process of electrolytic dissociation.
- b. What is solvation?
- c. What is dissociation degree?
- d. What is the difference between weak and strong acids, weak and strong bases?
- e. How do acidic compounds containing several hydrogen atoms which can become  $H^+(H_3O^+)$  ions dissociate?
- f. How do basic compounds containing several OH groups which can become OH ions dissociate?

# **Exercise:**

Write down equations of stepwise dissociation for each of the compounds from the list below and calculate molar mass, number of protons and number of electrons for each ion:

```
HCl, HI, HBr, H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>SO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>

KOH, Ca(OH)<sub>2</sub>, Ba(OH)<sub>2</sub>, Cr(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, NH<sub>4</sub>OH

KCl, Fe(NO<sub>3</sub>)<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>3</sub>PO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, Cr(NO<sub>3</sub>)<sub>3</sub>

KHSO<sub>4</sub>, NaHSO<sub>3</sub>, CaHPO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub>, Zn(HSiO<sub>3</sub>)<sub>2</sub>

CaOHNO<sub>3</sub>, BaOHCl, (ZnOH)<sub>2</sub>SO<sub>4</sub>, SrOHNO<sub>3</sub>, Al(OH)<sub>2</sub>Cl, (Cr(OH)<sub>2</sub>)<sub>2</sub>SO<sub>4</sub>
```

#### LESSON 25

# 25.1 IONIC EQUATIONS

Ionic equations are used to display what chemical processes really take place in the water solution. Imagine that two solutions are mixed together. As a result, another solution can be formed in which all the ions from two solutions are present, while those ions don't react with each other. For example, chemical reaction does not take place in the mixture of NaCl and KOH solutions:

$$NaCl + KOH \neq NaOH + KCl$$
  
 $Na^{+} + Cl^{-} + K^{+} + OH^{-} \neq Na^{+} + OH^{-} + K^{+} + Cl^{-}$ 

However, in case if insoluble substance is formed, one may write down the short ionic equation.

$$AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl \downarrow$$
  
 $Ag^+ + NO_3^- + Na^+ + Cl^- \rightarrow Na^+ + NO_3^- + AgCl \downarrow$   
 $Ag^+ + Cl^- \rightarrow AgCl \downarrow$ 

The final so-called "short" ionic equation is common for all the reactions between soluble salts of silver and soluble chlorides. In ionic reactions strong electrolytes are decomposed into ions. All the soluble salts are considered to be strong electrolytes (together with strong acids and alkali).

# 25.2 EXAMPLES OF IONIC EQUATIONS

In case if volatile substance (gas) is formed after the double replacement reaction, then one may also write down a short ionic equation. Remember that NH<sub>4</sub>OH decomposes into NH<sub>3</sub> (gas) and H<sub>2</sub>O, H<sub>2</sub>CO<sub>3</sub> decomposes into CO<sub>2</sub> and H<sub>2</sub>O, H<sub>2</sub>SO<sub>3</sub> decomposes into SO<sub>2</sub> and H<sub>2</sub>O, while H<sub>2</sub>S is volatile itself (without any decomposition).

$$\begin{aligned} Na_2CO_3 + 2HCl &\rightarrow 2NaCl + CO_2\uparrow + H_2O \\ \frac{2Na}{c} + CO_3^{2-} + 2H^+ + \frac{2Cl^-}{c} &\rightarrow \frac{2Na^+}{c} + \frac{2Cl^-}{c} + CO_2\uparrow + H_2O \\ CO_3^{2-} + 2H^+ &\rightarrow CO_2\uparrow + H_2O \end{aligned}$$

That ionic equation is a common one for all the reactions between soluble carbonates and strong acids.

Neutralization reactions between strong acids and strong bases can be described by the common short ionic equation as well.

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$$
  
 $2H^+ + SO_4^{2-} + 2K^+ + 2OH^- \rightarrow 2K^+ + SO_4^{2-} + 2H_2O$   
 $H^+ + OH^- \rightarrow H_2O$ 

All weak electrolytes are not written as ions in ionic equations.

$$HNO_2 + NaOH \rightarrow NaNO_2 + H_2O$$
  
 $HNO_2 + Na^+ + OH^- \rightarrow Na^+ + NO_2^- + H_2O$   
 $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$ 

# **Exercises:**

- a. Continue the following chemical reactions and write down ionic equations for them
  - 1.  $NaHCO_3 + NaOH \rightarrow$
  - 2.  $K_2SiO_3 + HCl \rightarrow$
  - 3.  $BaCl_2 + Na_2SO_4 \rightarrow$
  - 4. KHCO<sub>3</sub> +  $H_2SO_4 \rightarrow$
  - 5.  $Zn(OH)_2 + NaOH \rightarrow$
  - 6.  $CaCl_2 + AgNO_3 \rightarrow$
  - 7.  $CuSO_4 + H_2S \rightarrow$
  - 8. BaCO<sub>3</sub> + HNO<sub>3</sub>  $\rightarrow$
  - 9.  $FeCl_2 + KOH \rightarrow$
  - 10.  $Na_3PO_4 + CaCl_2 \rightarrow$
  - 11.  $FeSO_4 + (NH_4)_2S \rightarrow$
  - 12.  $Cr(OH)_3 + KOH \rightarrow$

b. Imagine what chemical reactions may be expressed by the following ionic equations

- 1.  $Zn^{2+} + H_2S = ZnS + 2H^+$
- 2.  $Mg^{2+} + CO_3^{2-} = MgCO_3$
- 3.  $H^+ + OH^- = H_2O$
- 4.  $HCO_3^- + OH^- = CO_3^{2-} + H_2O$
- 5.  $HCO_3^- + H^+ = CO_2 + H_2O$
- 6.  $CO_3^{2-} + 2H^+ = CO_2 + H_2O$
- 7.  $Ag^{+} + Cl^{-} = AgCl$
- 8.  $Fe(OH)_2 + 2H^+ = Fe^{2+} + 2H_2O$
- 9.  $Cd^{2+} + 2OH^{-} = Cd(OH)_{2}$
- $10. NO_2^- + H^+ = HNO_2$

# **LESSON 26**

# 26.1 WHEN HYDROLYSIS IS IMPOSSIBLE

Certain salts affect the acidity or basicity of aqueous solutions because some of the ions will undergo hydrolysis. The general rule is that salts with ions that are **parts of strong acids or bases will not hydrolyze**, while salts with ions that are **parts of weak acids or bases will hydrolyze**.

Consider NaCl. When it dissolves in an aqueous solution, it separates into Na<sup>+</sup> ions and Cl<sup>-</sup> ions:

$$NaCl \rightarrow Na^{+} + Cl^{-}$$

Will the Na<sup>+</sup> ion hydrolyze? If it does, it will interact with the OH<sup>-</sup> ion to make NaOH:

$$Na^+ + H_2O \rightarrow NaOH + H^+$$

However, NaOH is a strong base, which means that it is 100 % ionized in solution:

$$NaOH \rightarrow Na^{+} + OH^{-}$$

The free OH ion reacts with the H ion to remake a water molecule:

$$H^+ + OH^- \rightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the Na<sup>+</sup> ion. What about the Cl<sup>-</sup> ion? Will it hydrolyze? If it does, it will take an H<sup>+</sup> ion from a water molecule:

$$Cl^- + H_2O \rightarrow HCl + OH^-$$

However, HCl is a strong acid, which means that it is 100 % ionized in solution:

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

The free H<sup>+</sup> ion reacts with the OH<sup>-</sup> ion to remake a water molecule:

$$H^+ + OH^- \rightarrow H_2O$$

The net result? There is no change, so there is no effect on the acidity or basicity of the solution from the Cl<sup>-</sup> ion. Because neither ion in NaCl affects

the acidity or basicity of the solution, NaCl is an example of salt which is not hydrolyzed at all.

# 26.2 WHEN HYDROLYSIS IS POSSIBLE

Things change, however, when we consider a salt like CH<sub>3</sub>COONa. We already know that the Na<sup>+</sup> ion won't affect the acidity of the solution. What about the acetate ion? If it hydrolyzes, it will take an H<sup>+</sup> from a water molecule:

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$$

Does this happen? Yes, it does. Why? *Because* CH<sub>3</sub>COOH *is a weak acid*. Any chance a weak acid has to form, it will (the same with a weak base). As some CH<sub>3</sub>COO<sup>-</sup> ions hydrolyze with H<sub>2</sub>O to make the molecular weak acid, OH<sup>-</sup> ions are produced. OH<sup>-</sup> ions make solutions basic. Thus CH<sub>3</sub>COONa solutions are slightly basic.

There are also salts which aqueous solutions are slightly acidic.  $NH_4Cl$  is an example. When  $NH_4Cl$  is dissolved in  $H_2O$ , it separates into  $NH_4^+$  ions and  $Cl^-$  ions. We have already seen that the  $Cl^-$  ion does not hydrolyze. However, the  $NH_4^+$  ion will:

$$NH_4^+ + H_2O \rightarrow NH_4OH + H^+$$
 (which may be written as  $NH_3 + H_3O^+$ )

 $H_3O^+$  ion is the hydronium ion, the more chemically proper way to represent the  $H^+$  ion. This is the classic acid species in solution, so a solution of  $NH_4^+$  ions is slightly acidic. The molecule  $NH_3$  is a weak base, and it will be formed when it can, just like a weak acid will be formed when it can.

So there are two general rules: 1) if an ion derives from a strong acid or base, it will not affect the acidity of the solution; 2) if an ion derives from a weak acid, it will make the solution basic; if an ion derives from a weak base, it will make the solution acidic.

Hydrolysis is stepwise for compounds consisting from cations of weak bases with charge higher than +1 and anions of weak acids with charge lower than -1.

- I.  $Zn(NO_3)_2 + H_2O \rightleftarrows ZnOHNO_3 + HNO_3$   $Zn^{2+} + 2NO_3^- + H_2O \rightleftarrows ZnOH^+ + NO_3^- + H^+ + NO_3^ Zn^{2+} + H_2O \rightleftarrows ZnOH^+ + H^+$
- II.  $ZnOHNO_3 + H_2O \rightleftarrows Zn(OH)_2 \downarrow + HNO_3$   $ZnOH^+ + NO_3^- + H_2O \rightleftarrows Zn(OH)_2 \downarrow + H^+ + NO_3^ ZnOH^+ + H_2O \rightleftarrows Zn(OH)_2 \downarrow + H^+$

Another example is for salt containing anion with 2– charge.

- I.  $Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH$   $\frac{2Na^+}{4} + CO_3^{2^-} + H_2O \rightleftarrows \frac{Na^+}{4} + HCO_3^{-} + \frac{Na^+}{4} + OH^ CO_3^{2^-} + H_2O \rightleftarrows HCO_3^{-} + OH^-$
- II. NaHCO $_3$  + H $_2$ O  $\rightleftarrows$  H $_2$ CO $_3$  (it decomposes into CO $_2$ ↑ and H $_2$ O) + NaOH

$$Na^+ + HCO_3^- + H_2O \rightleftarrows CO_2 \uparrow + H_2O + Na^+ + OH^-$$

$$HCO_3^- + H_2O \rightleftarrows CO_2\uparrow + H_2O + OH^-$$

**Exercises.** Write down equations of hydrolysis for salts from the list below in case if hydrolysis is possible. Write them in stepwise manner. Indicate whether pH level is higher or lower than 7 in the resulting solutions.

- 1. KCl
- 2. KNO<sub>2</sub>
- 3. NH<sub>4</sub>Br
- 4. CH<sub>3</sub>COOK
- 5. ZnSO<sub>4</sub>
- 6.  $Al(NO_3)_3$
- 7.  $Na_3PO_4$
- 8. K<sub>2</sub>S
- 9. CuSO<sub>4</sub>
- 10. NaBr
- 11. Na<sub>2</sub>S
- 12. K<sub>2</sub>CO<sub>3</sub>
- 13. CoCl<sub>2</sub>
- 14.  $(NH_4)_2CO_3$
- 15. KNO<sub>3</sub>
- 16. CrCl<sub>3</sub>
- 17.  $Cu(NO_3)_2$
- 18. NaI
- 19. K<sub>3</sub>PO<sub>4</sub>
- 20.  $Pb(NO_3)_2$

# LESSON 27

# Sample ticket for control task #4 on electrolytic dissociation

1. Imagine what chemical reactions can be expressed by those short ionic equations:

$$HSiO_{3}^{-} + OH^{-} = SiO_{3}^{2-} + H_{2}O$$
  $S^{-2} + 2H^{+} = H_{2}S$ 

2. Calculate number of protons and number of electrons for the following ions:

3. Finish chemical reactions and write them in short ionic form:

$$Fe_2(SO_4)_3 + NaOH \rightarrow$$

$$CaCO_3 + HCl \rightarrow$$

$$BaCl_2 + AgNO_3 \rightarrow$$

$$K_2CO_3 + MgCl_2 \rightarrow$$

4. Write down hydrolysis reactions (if they are possible). Provide short ionic reactions and identify whether pH is higher or lower than 7.0 in solutions of those salts.

 $\begin{array}{cccc} NH_4NO_3 & KHSO_3 & Na_2SO_4 & CaCl_2 \\ NH_4Cl & Na_2SO_4 & Al(NO_3)_3 & K_2CO_3 \end{array}$ 

# LITERATURE

- 1. *Барковский, Е. В.* Неорганическая химия: пособие-репетитор: теоретические основы. Примеры решения типовых задач. Тесты для самоконтроля / Е. В. Барковский. Минск: Аверсэв, 2008. 416 с.
- 2. *Ткачёв*, *С. В.* Основы общей и неорганической химии : учеб.-метод. пособие / С. В. Ткачёв. 12-е изд. Минск : БГМУ, 2014. 136 с.
- 3. *Ball, D. W.* Introductory Chemistry, v. 1.0. / D. W. Ball. Washington : Flat World Education, Inc., 2014. 352 p.
- 4. *Wilson, D.* Kaplan AP Chemistry 2014–2015 / D. Wilson. New York: Kaplan Publishing, 2014. 396 p.

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# Учебное издание

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# ВВЕДЕНИЕ В ОБЩУЮ ХИМИЮ INTRODUCTION TO THE GENERAL CHEMISTRY

Учебно-методическое пособие

Ответственный за выпуск Е. В. Барковский Переводчик В. В. Хрусталёв Компьютерный набор В. В. Хрусталёва Компьютерная верстка Н. М. Федорцовой

Подписано в печать 27.11.14. Формат 60×84/16. Бумага писчая «Снегурочка». Ризография. Гарнитура «Times». Усл. печ. л. 3,72. Уч.-изд. л. 3,1. Тираж 112 экз. Заказ 650.

Издатель и полиграфическое исполнение: учреждение образования «Белорусский государственный медицинский университет». Свидетельство о государственной регистрации издателя, изготовителя, распространителя печатных изданий № 1/187 от 18.02.2014. Ул. Ленинградская, 6, 220006, Минск.