Ministry of Education and Science of Ukraine
Lutsk National Technical University

ANALYTICAL CHEMISTRY

Methodological instructions for independent work
for applicants for the first (bachelor's) level of higher education
of the educational and professional programme "Food Technologies"
areas of expertise 18 Production and technology
speciality 181 Food technology
full-time and part-time forms of study

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A-46 **Analytical chemistry [**Text]: methodical instructions for independent work for applicants for the first (bachelor's) level of higher education of the educational and professional programme "Food Technologies" of the field of knowledge 18 Production and Technologies, specialty 181 Food Technologies full-time and part-time forms of study / compiled by. I. A. Moroz - Lutsk: Lutsk NTU, 2023. 44 p.

The publication contains tasks for independent work and recommended literature. The main theoretical provisions and examples of problem solving are presented. It is intended for students of specialty 181 Food Technologies of full-time and part-time forms of study.

CONTENTS

INTRODUCTION

Analytical chemistry is the fundamental chemical science of methods for determining the chemical composition of compounds and their mixtures. It occupies a leading position in the system of theoretical and practical training of a specialist in food technology. According to its application, analytical chemistry is divided into qualitative, quantitative chemical analyses and instrumental methods of analysis. In the course of qualitative analysis, students must master the methods of detecting ions, elements and chemical compounds that are part of the substances under study and their mixtures. In the course of quantitative analysis, students must master the methods by which chemical compounds and their mixtures can be quantified.

Methodical instructions for performing independent work in chemistry are compiled for first-year students of the educational programme 181 Food Technologies, full-time and part-time. The topics of the tasks are selected in accordance with the thematic planning of independent work given in the working curriculum in chemistry.

During the semester, students perform independent work in extracurricular time. The student completes the work during the semester and defends it in the week of the KIPT (complex individual tasks). The variant of the work corresponds to the student's serial number in the academic group journal. The work is done in a separate notebook, each new task starting on a new page. The numbers and conditions of the tasks are rewritten in the order indicated in the work.

Independent work constitutes a separate credit module that is mandatory for each student. Each task is assessed 10 points, with a maximum score of 100 points with a weighting factor of 10% to the total score.

1. TABLE OF OPTIONS FOR CONTROL TASKS

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01	1; 21; 41; 61; 81; 101; 121; 141; 161; 181.
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28	8;29; 50; 71; 92; 113; 134 ; 155; 176; 187.
29	9; 30; 51; 72; 93; 114; 135; 156; 177; 188.
30	10; 31; 52; 73; 94; 115; 136; 157; 178; 189.

2. RECOMMENDED LITERATURE

1. Alemasova A.S., Zaitsev V.M., Yenaleva L.Y., Shchepina N.D., Gozhdzinsky S.M. Analytical chemistry: "Knowledge, 2010. 417 p.
2. Gab A.I., Shakhnin D.B., Malyshev V.V. Analytical chemistry and instrumental methods of analysis. - Kyiv: University of Ukraine, 2018. 396 p.
3. Gab A.I., Shakhnin D.B., Malyshev V.V. Analytical chemistry. Qualitative and quantitative analysis. Study guide. - K.: University of Ukraine, 2018. - 212 p.
4. Nabyvanets B.Y., Sukhan V.V., Kalabina L.V. Analytical chemistry of the natural environment. K.: Lybid, 1996. 304 p.
5. Gozhdzinskyi S.M., Zaitsev V.M., Kalibabchuk V.O., Rudkovska L.M. Fundamentals of Analytical Chemistry. - Kyiv: Vyshytsia Shkola, 2002. 141 p.
6. Chemistry. A basic textbook for students of higher educational institutions / Collective of authors - Kharkiv: Folio, 2014. 958 p. (Zaporozhets O.A., Zinko L.S., Part 4, Chapters 1, 2, 6, 9, pp. 580-586, 643-676, 700-704).
7. Sukhan V.V., Trokhymenko O.M., Trokhymenko A.Y. Analytical reagents and technique for preparing their solutions / Edited by Tananaiko O.Y. - Kyiv: Kyiv University Press, 2022. 592 p.
8. Bugayevsky O.A., Drozd A.V., Loginova L.P., Reshetnyak O.O., Yurchenko O.I. Theoretical foundations and methods of solving problems in analytical chemistry. Textbook / Edited by O.A. Bugayevsky. Kharkiv, KNU, 2003. 320 p.
9. Slobodniuk R., Horaychuk A. Analytical chemistry and analysis of food products. - K. : Condor, 2018. 336 p.
10. Dubinina AA, Malyuk LP, Selyutina GA, Letuta TM, Shcherbakova VT. Toxic substances in food products and methods of their determination: a textbook in structural and logical diagrams. Kh.: KhDUHT, 2016. 106 p.
11. Buzhanska M.V., Vasylechko V.O., Lomnytska Y.F., Skorobohatyi Y.P. Food chemistry: analysis and chemical composition of food products: a textbook: Lviv: LTEU Publishing House, 2020. 308 p.

3. TASKS OF THE CALCULATION WORK

Topic 1: WAYS OF EXPRESSION OF CONCENTRATION (mass fraction, molarity).

The most common way of expressing the concentration of a substance in solution used in analytical chemistry is molarity (or molar concentration). The molarity (C) is the number of moles of a substance contained in 1 litre of solution. The polarity is indicated by the capital letter "C", followed by the formula of the substance in the lower index (sometimes in parentheses). For example, the following entry "C_{NaOH} = 0.1 mol/l" refers to a solution containing 0.1 mol of sodium hydroxide in 1 litre. Often, molarity units "mol/l" are denoted in a simplified way - with a capital letter "M". For example, the entry "To 0.5 M NaOH solution ..." refers to a sodium hydroxide solution with a concentration of 0.5 mol/L. By definition, molarity is the ratio of the amount of a substance (mol) to the volume of a solution (l):

$$\mathrm{C_x} = \frac{n_X}{V_{\text{р−ну}}}.$$

Numerical values of molarity can be expressed in mol/l or mmol/l.

Example 1: Calculate the molarity of a solution of potassium sulfate containing 0.01 mol K_2SO_4 in 50 ml.

The volume of the solution in litres is 50/1000 = 0.05 litres. Find the molar concentration of potassium sulfate:

$$\mathrm{C}_{K_2SO_4} = \frac{n_{K_2SO_4}}{V_{\text{р−ну}}} = \frac{0{,}01}{0{,}05} = 0{,}2\ \text{моль/л}.$$

If the mass of a substance is known instead of its quantity, the polarity is calculated using the following formula:

$$C_X = \frac{m_X}{M_X \cdot V_{\text{р−ну}}},$$

where m_X is the mass of the dissolved substance (g), M_X is its molar mass (g/mol).

Molar mass is calculated from the exact atomic masses of the elements that make up a substance. The molecular weights of some substances are given in Appendix 1.

Example 2: A mass of 0.584 g of sodium chloride was dissolved in water and the volume of the solution was brought to 100 ml. What is the molar concentration of NaCl in the resulting solution?

The calculation is performed using the above formula:

$$\mathrm{C}_{NaCl} = \frac{m_{NaCl}}{M_{NaCl} \cdot V_{\text{р−ну}}} = \frac{0{,}584}{58{,}4 \cdot 0{,}1} = 0{,}1\ mol/l$$

The concentration of a substance is often expressed as its *mass fraction* (*ω)* in a solution. The mass fraction shows how much of the mass of a solution is accounted for by the dissolved substance. Most of the time, *ω is expressed as a* percentage. The mass fraction is calculated using the following formula:

$$\omega_X = \frac{m_X}{m_{р-ну}} \cdot 100 .$$

Knowing the density of the solution and its molarity, you can easily calculate the mass fraction:

$$C_X = \frac{10 \cdot \omega_X \cdot \rho_{р-ну}}{M_X} ,$$

where ω_X is the mass fraction of the substance (%),

$\rho_{р-ну}$ is the density of the solution (g/ml or g/cm^3),

M_X is the molar mass of a substance (g/mol),

C_X - molar concentration (mol/l).

Example 3: Calculate the molarity of a 4.88% solution of HNO_3 with a density of 1.025 g/ml.

The molar mass of HNO_3 is 63.01 g/mol. Calculate the molar concentration:

$$C_{HNO_3} = \frac{10 \cdot \omega_{HNO_3} \cdot \rho_{sol}}{M_{HNO_3}} = \frac{10 \cdot 4{,}88 \cdot 1{,}025}{63{,}01} = 0{,}794 \ \text{mol/l}$$

If the density of the solution is not specified in the problem, it is assumed to be 1 g/ml.

Control questions

1. A 0.5611 g mass of potassium hydroxide was dissolved in water and the volume of the solution was made up to 200 ml. Calculate the molar concentration of KOH in the resulting solution.

2. Calculate the molarity of a 9.26% solution of nitric acid with a density of 1.05 g/ml.

3. Pass 224 ml of hydrogen chloride (n.c.) through 200 ml of water and bring the volume of the solution to 500 ml. Calculate the molarity of the resulting hydrochloric acid if the gas was absorbed quantitatively.

4. A 0.4000 g mass of sodium hydroxide was dissolved in water and the volume of the solution was made up to 500 ml. Calculate the molar concentration of NaOH in the resulting solution.

5. Calculate the molarity of a 7.70% solution of sulfuric acid with a density of 1.05 g/ml.

6. How much mass of sodium hydroxide (g) is contained in 200 ml of 0.1 M solution?

7. Dissolve a 0.1420 g mass of sodium sulfate in water and bring the volume of the solution to 100 ml. Calculate the molar concentration of Na_2SO_4 in the resulting solution.

8. Calculate the molarity of a 10.5% solution of hydrochloric acid with a density of 1.05 g/ml.

9. What is the mass of KCl (g) in 100 ml of 0.15 M solution?

10. Dissolve a 0.2861 g mass of $Na_2CO_3 \cdot 10H_2O$ in water and bring the volume of the solution to 400 ml. Calculate the molar concentration of sodium carbonate in the resulting solution.

11. Calculate the molarity of a 13.5% solution of nitric acid with a density of 1.075 g/ml.

12. Pass 112 ml of hydrogen sulphide (n.c.) through 250 ml of water and bring the volume of the solution to 1 litre. Calculate the molarity of the resulting sulfuric acid if the gas was absorbed quantitatively.

13. A 2.082 g mass of barium chloride was dissolved in water and the volume of the solution was made up to 500 ml. Calculate the molar concentration of $BaCl_2$ in the resulting solution.

14. Calculate the molarity of an 11.3% solution of sulfuric acid with a density of 1.075 g/ml.

15. How much volume (ml) of 0.1 M NaOH solution contains 0.200 g of sodium hydroxide?

16. 56 ml of carbon dioxide (n.c.) was passed through 500 mL of water. Calculate the molarity of the resulting solution H_2CO_3, if the gas was absorbed quantitatively.

17. Dissolve a 2.497 g mass of $CuSO_4 \cdot 5H_2O$ in water and bring the volume of the solution to 250 ml. Calculate the molar concentration of copper (II) sulfate in the resulting solution.

18. What is the mass of copper (II) nitrate (g) in 250 ml of 0.05 M solution?

19. What volume of water (ml) should be added to 200 ml of a 0.1 M solution of sodium sulfate to reduce its concentration to 0.02 mol/l?

20. Calculate the molarity of a 5.41% solution of hydrochloric acid with a density of 1.025 g/ml.

Topic 2. WAYS OF EXPRESSION OF CONCENTRATION (normality, titer).

In addition to molar concentration and mass fraction, analytical chemistry also uses normality, titre and titre per substance. These methods of expressing concentration are very relevant when considering titrimetric analysis.

The normal concentration C_{eq} (B) or normality N (B) of a solution with a molar concentration of equivalents of substance B is the ratio of the number of moles of equivalents of a dissolved substance n_{eq} (B) to the volume *Vp of* its solution, the dimension mol-eq/l.

$$C_{eq}(B) = n_{eq}(B) / Vp = m(B) / (M_{eq}(B) - Vp).$$

where, n_{eq} (B) is the number of equivalents of substance B, mol-eq;

M_{eq} (B) or E (B) is the molar mass of equivalents of substance B, g/mol-eq.

The relationship between C(B) and C_{eq} (B): C(B) = C_{eq} (B) - z, where z is the equivalence factor

For example, 1M H_2SO_4 = 2 N H_2SO_4 , i.e. z = 1/ 2.

For example, the entry "$C_{eq\ NaOH}$ = 0.1 mol eq/l" refers to a solution containing 0.1 mol eq of sodium hydroxide in 1 litre. For example, the entry "To 0.5 N NaOH solution ..." refers to a solution of sodium hydroxide with a concentration of 0.5 mol eq/l.

A working solution or titrant is a solution of a substance with a precisely known concentration that interacts with the substance whose concentration is being determined.

Working substance (B) - the substance from which the working solution is prepared.

Working substance titre or simply titre T(B) is the ratio of the mass m(B) of the dissolved substance B to the volume of its solution *Vp, in* g/ml.

$$T(B) = m(B) / Vp,$$

$$T(B) = C_{eq}(B) \cdot M_{eq}(B) / 1000.$$

The titre of a solution T(B) is related to its molarity by the ratio:

$$T(B) = C_M(B) \cdot M(B) / 1000.$$

where *M is the* molar mass of the dissolved substance

C_M is the molar concentration of the solution.

The titer of the working solution B for the test substance A - T(B/A) - is the ratio of the mass m (A) of the test substance A to the equivalent volume *Vsol* of the working solution of the substance B - titrant, dimension g/ml

$$T(B/A) = m(A) / \mathrm{Vp} = C_{eq}(B) \cdot M_{eq}(A) / 1000.$$

T(B/A) - shows how much mass of substance A to be determined reacts with 1 ml of working solution of substance B - titrant.

The mass m(A) of the test substance A is calculated from the volume of the solution of substance B - titrant used for titration

a) for T (B/A), m (A) = T (B/A)$\cdot Vp$(B)

b) by T (B) m (A) = T (B) $\cdot M_{eq}$ (A) / M_{eq} (B)

For example, the titre of a solution of hydrochloric acid with sodium hydroxide T(HCl/NaOH) = 0.002453 g/ml shows that 0.002453 g of sodium hydroxide reacts with 1 ml of hydrochloric acid solution.

Example 1: Determine the volume of a solution of sulfuric acid with a mass fraction of 9.3 % and a density of 1.05 g/ml required to prepare 40 ml of a 0.35 N solution.

Calculate the mass of sulfuric acid in 40 ml of 0.35 N solution:

m (H_2SO_4) = C_{eq} (H_2SO_4) $\cdot$ M_{eq} (H_2SO_4) $\cdot$ $Vsol$ = 0.35 $\cdot$ 98 / (2 $\cdot$ 0.04) = 0.686 g.

Find the volume of a 9.3 % solution of sulfuric acid containing 0.686 g of H_2SO_4

$Vsol$ (H_2SO_4) = 0.686 $\cdot$ 100 /(9.3 $\cdot$1.05) = 7.02 ml.

Example 2: A solution of sodium carbonate is titrated with a solution of hydrochloric acid with a titre of 0.00365 g/ml. Determine the titre of the acid from sodium carbonate.

According to the reaction equation: Na_2CO_3 + 2 HCl = NaCl + CO_2 + H O_2

we find the equivalence factor z (Na_2CO_3) = 1/2 and

M_{eq} (Na_2CO_3) = M (Na_2 CO_3) $\cdot$ z = 106 $\cdot$ 1/2 = 53 g/mol

The molar concentration of the acid will be equal to :

C (HCl) = T (HCl) - 1000 / M (HCl) = 0.00365 $\cdot$ 1000 / 36.5 = 0.1 mol/l

Determining the titre of hydrochloric acid from sodium carbonate

T(HCl/ Na_2 CO_3) = C_{eq} (HCl) $\cdot$ M_{eq} (Na_2CO_3) / 1000 = 0.1$\cdot$53 / 1000 = 0.0053 g/ml.

Example 3: Calculate the mass of sodium chloride in a sample if 19.56 ml of a working solution of argentium nitrate with T($AgNO_3$ /NaCl) = 0.00568 g/ml was used to titrate it. Determine the concentration of the titrant.

The entry T($AgNO_3$ /NaCl) means that 0.00568 g of sodium chloride reacts with 1 ml of argentium nitrate solution, and the mass of sodium chloride reacted with 19.56 ml of argentium nitrate solution is equal:

m(NaCl) = T($AgNO_3$ /NaCl) $\cdot$ Vp = 0.00568 $\cdot$ 19.56 = 0.1112 g.

Calculate the titrant concentration

C($AgNO_3$)= T($AgNO_3$ /NaCl) $\cdot$*1000/M*(NaCl) = 0.00568$\cdot$1000/58.5 = 0.0972 mol/l.

Control questions

21. A 250.0 ml solution of NaOH contains 10.0 g of this substance. Determine the titer and normality of this solution.

22. Determine the T and Cn of the HCl solution if 18.2 ml of HCl were used to titrate 20 ml of borax solution (T_{borax} = 0.09721 g/ml).

23. How many grams of H_2SO_4 are contained in 5 litres of solution if 15 ml of 0.1200 N NaOH solution was used to titrate 20.00 ml?

24. To titrate 0.0340 g of $AgNO_3$, 20.00 ml of HCl was used. Find $T_{HCl/Ag}$.

25. Calculate the normality of the HCl solution and $T_{HCl/NaOH}$ if T_{HCl} = 0.003646g/cm^3 .

26. How much volume of HCl solution (ρ = 1.179g/cm^3) should be taken to prepare 2 litres of HCl solution with a titre of T = 0.003646g/cm^3 .

27. How much volume of 0.1000 N $AgNO_3$ will be used to titrate 12.00 ml of a solution containing 6.50 g/l KCl?

28. How much NaOH should be used to titrate 20.00 cm^3 with 0.1 N HCl?

29. Determine the normality and titre of the HCl solution if 10.00 cm^3 of HCl solution was used to titrate 0.1907 g of sodium tetraborate.

30. To what volume should a solution containing 1.53 g of NaOH be diluted so that 14.70 ml of HCl is used to titrate 20.00 ml of the resulting solution? T_{HCl} = 0.003800g/ml.

31. 250.0 ml of HCl solution contains 20.0 g of this substance. Determine the titer and normality of this solution.

32. Determine the T and Cn of the HCl solution if 9.8 ml of HCl were used to titrate 10 ml of borax solution (T_{borax} = 0.09721 g/ml).

33. How many grams of H_2 SO_4 are contained in 5 litres of solution if 15 ml of 0.1200 N NaOH solution was used to titrate 20.00 ml?

34. To titrate 0.0680 g of $AgNO_3$, 30.00 ml of HCl was used. Find $T_{HCl/Ag}$.

35. Calculate the normality of the HCl solution and $T_{HCl/NaOH}$ if T_{HCl} = 0.00456 g/cm^3 .

36. How much volume of HCl solution (ρ = 1.179g/cm^3) should be taken to prepare 2 litres of HCl solution with a titre of T = 0.003646g/cm^3 .

37. How much volume of 0.1000 n $AgNO_3$ will be used to titrate 12.00 ml of a solution containing 3.25 g/l KCl?

38. How much NaOH should be used to titrate 15.00 cm^3 with 0.1 N HCl?

39. Determine the normality and titre of the HCl solution if 10.00 cm^3 of HCl solution was used to titrate 0.1907 g of sodium tetraborate.

40. To what volume should a solution containing 1.21 g of NaOH be diluted so that 14.70 ml of HCl is used to titrate 15.00 ml of the resulting solution? T_{HCl} = 0.003800g/ml.

Topic 3. EQUATION OF ELECTRONEUTRALITY OF AQUEOUS SOLUTIONS OF PROTOLITHS.

In aqueous solutions, charged particles - ions - are always present. However, despite this, the solution is an electroneutral (uncharged) system, since the total charge of the cations in it is equal in value (but opposite in sign) to the total charge of the anions. Indeed, ions resulting from dissociation or protolysis are always formed in pairs: cation + anion, and the total charge of the solution remains unchanged:

$$NaCl = Na^+ + Cl^- ,$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- ,$$

$$Al_2(SO_4)_3 = 2Al^{3+} + 3SO_4^{2-} ,$$

$$CH_3COOH + H_2O \leftrightarrow H_3O^+ + CH_3COO^- .$$

The equation of electronegativity of an aqueous solution is the equality of the total positive and negative charges expressed in terms of equilibrium molar concentrations of ions. It has the following general form:

$$\sum(n_i \cdot [K^{n_i+}]) = \sum(m_i \cdot [A^{m_i-}]),$$

where $[K^{ni+}]$ is the equilibrium molar concentration of the *i-th* cation with charge ni^+ ,$[A^{mi-}]$ is the equilibrium molar concentration of the *i-th* anion with charge mi^- .

Even in the absence of dissolved substances, water always contains a certain amount of hydroxonium and hydroxyl ions. In this case, the equation of electroneutrality is as follows: $[H_3O^+] = [OH^-]$.

If there are dissolved substances, other cations and anions are also taken into account.

Example 1: Write the equation of electroneutrality for an aqueous solution containing hydrochloric acid. In addition to the ions H_3O^+ and OH^- , this solution also contains Cl^- ions, which are formed due to the dissociation of HCl. The equation of electroneutrality: $[H_3O^+] = [OH^-] + [Cl^-]$.

Example 2: Write an equation of electronegativity for an aqueous solution of sodium sulfate.

As a result of the dissociation of sodium sulphate, the corresponding ions are present in the solution: $Na_2SO_4 = 2Na^+ + SO_4^{2-}$.

As can be seen from this equation, the number of sulphate ions in the solution is half the number of sodium ions, but their charge is twice as high, respectively. This necessitates the multiplier 2 before the concentration of SO_4^{2-} ions in the electroneutrality equation:

$$[Na^+] + [H_3O^+] = [OH^-] + 2 \cdot [SO_4^{2-}] .$$

Example 3: Write the equation of electroneutrality for an aqueous solution of aluminium nitrate acidified with nitric acid.

This solution contains the ions Al^{3+} , H_3O^+ , NO_3^- and OH^- . The presence of HNO_3 in the solution is very important. If the aluminium nitrate solution is not acidified with a strong acid, the Al^{3+} ions will undergo hydrolysis:

$$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^{+} + H_3O^{+} ,$$
$$Al(OH)_2^{+} + 2H_2O \leftrightarrow Al(OH)_2^{+} + H_3O^{+} .$$

In the presence of acid, hydrolysis does not occur, so we can limit ourselves to the above list of ions: $3\cdot[Al^{3+}] + [H_3O^{+}] = [NO_3^{-}] + [OH^{-}]$.

Example 4. Write the equation of electroneutrality for an aqueous solution of sodium carbonate.

In addition to the ions H_3O^{+}, OH^{-}, Na^{+} and CO_3^{2-} , this solution also contains hydrogen carbonate ions formed as a result of the protolysis of CO_3^{2-} :

$$CO_3^{2-} + H_2O \leftrightarrow HCO_3^{-} + OH^{-} .$$

Therefore, the equation of electroneutrality for this solution is as follows:

$$[H_3O^{+}] + [Na^{+}] = [OH^{-}] + [HCO_3^{-}] + 2\cdot[CO_3^{2-}] .$$

Example 5. Write the equation of electroneutrality for an aqueous solution containing hydrochloric acid, sodium chloride, and potassium sulfate.

To make a complete list of the ions present in a given solution, you need to take into account the dissociation of each of these substances. The equation of electronegativity is as follows:

$$[H_3O^{+}] + [Na^{+}] + [K^{+}] = [OH^{-}] + [Cl^{-}] + 2\cdot[SO_4^{2-}] .$$

Control questions

Write the equation of electronegativity for an aqueous solution containing:

41. Ammonia and sodium sulphate.
42. Calcium nitrate and sodium chloride.
43. Barium hydroxide.
44. Orthophosphoric acid.
45. Ammonia.
46. Ammonium sulphate.
47. Ferric(III) nitrate acidified with nitric acid.
48. Potassium chloride and potassium sulphate.
49. Aluminium chloride acidified with hydrochloric acid.
50. Potassium sulphate.
51. Zinc nitrate acidified with hydrochloric acid.
52. Ferric(II) sulphate acidified with sulphuric acid.
53. Sodium bromide and sodium sulphate.
54. Calcium hydroxide.
55. Aluminium nitrate acidified with nitric acid.
56. Potassium carbonate.
57. Sulfuric acid.
58. Potassium sulphate and sodium sulphate.
59. Acetic acid.
60. Zinc chloride acidified with hydrochloric acid.

Topic 4. CALCULATION OF ACIDITY AND BASICITY CONSTANTS.

When solving problems involving the calculation of the pH of solutions, it is often necessary to calculate the value of the acidity or basicity constant of a weak protolith. The point is that the reference book contains values of acidity constants for weak acids and basicity constants for bases, respectively. If the required constant is not listed in the reference book, its value can be easily calculated from the relations for K_a and K_b for the conjugated acid-base pair:

$$K_{a,\,HA} \cdot K_{b,\,A^-} = K_{H_2O} = 10^{-14},$$

$$pK_{a,\,HA} + pK_{b,\,A^-} = pK_{H_2O} = 14,$$

where $K_{,aHA}$ is the acidity constant of a weak acid,

$K_{,bA^-}$ is the basis constant of the conjugate base,

$pK_{,aHA}$ and $pK_{,b\,A^-}$ are the negative decimal logarithms of these constants,

K_{H_2O} and pK_{H_2O} are the autoprotonation constant of water and its negative decimal logarithm (under normal conditions, their values are 10^{-14} and 14, respectively).

Example 1: Find the value of K_a for NH_4^+ .

In the reference book, we find that K_b , $NH_3 = 1.76 \cdot 10^{-5}$ (Appendix 2). Ammonia is a conjugate base to NH_4^+ . Calculate the value of the desired constant:

$$K_{a,NH_4^+} = \frac{10^{-14}}{K_{b \cdot NH_3}} = \frac{10^{-14}}{1{,}76 \cdot 10^{-5}} = 5{,}68 \cdot 10^{-10}.$$

When performing such calculations, one should be careful to remember that the above relationships between K_a and K_b (pK_a and pK_b) are only valid for a conjugated acid-base pair. Let us consider this for the example of HCO_3^- .

Example 2: Find the value of K_b for HCO_3^- .

To calculate the required value of K_b , we will use its relationship with K_a :

$K_b \cdot K_a = 10^{-14}$.

Look up the value of the constant K_a in the reference book for a particle that is a conjugate acid to HCO_3^- . This particle is H_2CO_3 . Sometimes the value K_a for HCO_3^- is mistakenly used instead of H_2CO_3.

That's right:
$$K_{b,HCO_3^-} = \frac{10^{-14}}{K_{a,H_2CO_3}} = \frac{10^{-14}}{4{,}5 \cdot 10^{-7}} = 2{,}22 \cdot 10^{-8},$$

$$K_{b,HCO_3^-} = \frac{10^{-14}}{K_{a,HCO_3^-}} = \frac{10^{-14}}{4{,}8 \cdot 10^{-11}} = 2{,}08 \cdot 10^{-4}.$$

is incorrect:

Control questions

Enter the value:

61. K_a, HS^- , pK_a,HS^- , K_b,HS^- , pK_b,HS^- .

62. K_a, HSO_3^- , pK_a, HSO_3^- , K_b, HSO_3^- , pK_b, HSO_3^- .

63. K_a, HCO_3^- , pK_a, HCO_3^- , K_b, HCO_3^- , pK_b, HCO_3^- .

64. K_a, $HC_2O_4^-$, pK_a, $HC_2O_4^-$, K_b, $HC_2O_4^-$, pK_b, $HC_2O_4^-$.

65. K_a, $H_2PO_4^-$, pK_a, $H_2PO_4^-$, K_b, $H_2PO_4^-$, pK_b, $H_2PO_4^-$.

66. K_a, HPO_4^{2-} , pK_a, HPO_4^{2-}, K_b, HPO_4^{2-}, pK_b, HPO_4^{2-} .

67. K_a, $H_2PO_3^-$, pK_a, $H_2PO_3^-$, K_b, $H_2PO_3^-$, pK_b, $H_2PO_3^-$.

68. K_a, $HCrO_4^-$, pK_a, $HCrO_4^-$, K_b, $HCrO_4^-$, pK_b, $HCrO_4^-$.

69. K_a, $H_3P_2O_7^-$, pK_a, $H_3P_2O_7^-$, K_b, $H_3P_2O_7^-$, pK_b, $H_3P_2O_7^-$.

70. K_a, $H_2P_2O_7^{2-}$, pK_a, $H_2P_2O_7^{2-}$, K_b, $H_2P_2O_7^{2-}$, pK_b, $H_2P_2O_7^{2-}$.

71. K_a, NH_4^+ , pK_a, NH_4^+ , K_b, NH_3 , pK_b, NH_3 .

72. K_a, HCN , pK_a, HCN , K_b, CN^- , p K_b, CN^- .

73. K_a, CH_3COOH , pK_a, CH_3COOH , K_b, CH_3COO^- , pK_b, CH_3COO^- .

74. K_a, C_6H_5COOH , pK_a, C_6H_5COOH , K_b, $C_6H_5COO^-$, pK_b, $C_6H_5COO^-$.

75. K_a, HF , pK_a, HF , K_b, F^- , p K_b, F^- .

76. K_a, HCOOH , pK_a, HCOOH , K_b, $HCOO^-$, pK_b, $HCOO^-$.

77. K_a, $H_2AsO_4^-$, pK_a, $H_2AsO_4^-$, K_b, $H_2AsO_4^-$, pK_b, $H_2AsO_4^-$.

78. K_a, $HAsO_4^{2-}$, pK_a, $HAsO_4^{2-}$, K_b, $HAsO_4^{2-}$, pK_b, $HAsO_4^{2-}$.

79. K_a, $HMoO_4^-$, pK_a, $HMoO_4^-$, K_b, $HMoO_4^-$, pK_b, $HMoO_4^-$.

80. K_a, H_3AsO_3 , pK_a, H_3AsO_3 , K_b, $H_2AsO_3^-$, pK_b, $H_2AsO_3^-$.

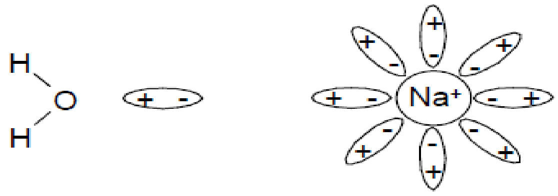
Topic 5. CALCULATION OF THE IONIC STRENGTH OF A SOLUTION AND IONIC ACTIVITY COEFFICIENTS.

Electrolytes in aqueous solutions are in the form of ions formed as a result of dissociation:

$$NaCl = Na^+ + Cl^-, \quad K_2SO_4 = 2K^+ + SO_4^{2-}.$$

Ions form hydrates with polar water molecules:

water molecule *hydrated ion*



Hydrated ions also interact with each other to form ionic pairs or more complex associations. As a result of interionic interaction, the effective concentration of ions is somewhat lower than their actual concentration in solution. In other words, not all ions in an aqueous solution are "active" (free, unassociated). The concentration of such "active" ions is called activity (*a*). The activity of an ion is less than its equilibrium concentration and is related to it by the following relationship:

$$a_{Na^+} = \gamma_{Na^+} \cdot [Na^+],$$

where γ_{Na^+} is the activity coefficient of the Na^+ ion .

The state of each ion is affected by all other ions in the solution. This influence is quantitatively characterised by the *ionic* strength (μ) *of the* solution and is calculated using the following formula:

$$\mu = \frac{1}{2} \cdot \sum [A_i] \cdot z_i^2,$$

where $[A_i]$ is the equilibrium concentration of the *i-th* ion, z_i - its charge.

The ion activity coefficient is related to the ionic strength by the following relationship:

$$\lg\gamma = \frac{-0{,}512z^2\sqrt{\mu}}{1+\sqrt{\mu}} + 0{,}1z^2\mu.$$

If the ionic strength of the solution is low, simpler formulas are used:

$$0{,}01 < \mu \le 0{,}1, \text{ то } \lg\gamma = \frac{-0{,}512z^2\sqrt{\mu}}{1+\sqrt{\mu}},$$

$$\mu \le 0{,}01, \text{ то } \lg\gamma = -0{,}512z^2\sqrt{\mu}.$$

Appendix 3 shows the ion activity coefficients at different values of the ionic strength of the solution.

Example 1: Calculate the ionic strength of a solution of the following composition: 0.1 M NaCl, 0.2 M Na_2SO_4 .

This solution contains the following ions: Na^+ , Cl^- and SO_4^{2-} . In this case, the ions H_3O^+ and OH^- , which are formed as a result of the autoprotolysis of water, are not taken into account, since their concentration is negligible. Let us calculate the equilibrium concentrations of ions:

$[Na^+] = 0.1 + 2\cdot0.2 = 0.5$ M (due to the dissociation of NaCl and Na_2SO_4),
$[Cl^-] = 0.1$ M (due to the dissociation of NaCl),
$[SO_4^{2-}] = 0.2$ M (due to the dissociation of Na_2SO_4).
Now let's calculate the ionic strength of the solution:

$$\mu = \frac{1}{2}\cdot([Na^+]\cdot1^2 + [Cl^-]\cdot(-1)^2 + [SO_4^{2-}]\cdot(-2)^2) = \frac{1}{2}\cdot(0{,}5 + 0{,}1 + 0{,}2\cdot4) = 0{,}7\ .$$

Example 2: Calculate the activity coefficient of the ion SO_4^{2-} in a 0.05 M solution of K_2SO_4 .

First, we calculate the ionic strength of the solution:
$\mu = 0.5\cdot(0.1\cdot1^2 + 0.05\cdot2^2) = 0.15$.
Then the activity coefficient of the sulfate ion:

$$\lg\gamma_{SO_4^{2-}} = \frac{-0{,}512\cdot(-2)^2\sqrt{0{,}15}}{1+\sqrt{0{,}15}} + 0{,}1\cdot(-2)^2\cdot0{,}15 = -0{,}511\ ,$$

$$\gamma_{SO_4^{2-}} = 10^{-0{,}512} = 0{,}31\ .$$

If $\mu < 10^{-3}$, then the influence of the ionic strength of the solution is neglected and it is assumed that $\gamma = 1$ and $a_X = [X]$.

Control questions

Calculate the activity coefficient of ion X and the ionic strength of a solution of this composition:

№	Ion X.	Solution composition
81.	SO_4^{2-}	0.01 M Na_2SO_4 , 0.005 M NaCl
82.	Na^+	0.003 M CH_3COONa, 0.01 M NaOH
83.	K^+	0.02 M KNO_3 , 0.006 M $BaCl_2$
84.	NO_3^-	0.5% $NaNO_3$
85.	Ca^{2+}	0.3% $Ca(NO\ )_{32}$
86.	Cl^-	0.15% NaCl
87.	SO_4^{2-}	0.02 M Na_2SO_4 , 0.003 M NaCl
88.	Na^+	0.005 M CH_3COONa, 0.02 M NaOH
89.	K^+	0.01 M KNO_3 , 0.05 M $BaCl_2$
90.	NO_3^-	0.8% $NaNO_3$
91.	Ca^{2+}	0.5% $Ca(NO_3)_2$
92.	Cl^-	0.3% NaCl
93.	SO_4^{2-}	0.003 M Na_2SO_4 , 0.005 M NaCl
94.	Na^+	0.01 M CH_3COONa, 0.05 M NaOH
95.	K^+	0.02 M KNO_3 , 0.05 M $BaCl_2$
96.	NO_3^-	0.5% HNO_3
97.	Ca^{2+}	1 % $CaCl_2$
98.	Cl^-	0.5% KCl
99.	SO_4^{2-}	0.1 M Na_2SO_4 , 0.05 M NaCl
100.	K^+	0.004 M CH_3COOK, 0.01 M KOH

Topic 6. CALCULATION pH OF AQUEOUS SOLUTIONS

The pH value of the solution is equal to the negative decimal logarithm of the hydroxonium ion activity:

$$pH = -\lg a[H_3O^+].$$

If the ionic strength of the solution is small ($<10^{-3}$), the activity is almost equal to the equilibrium concentration, so you can use this equality:

$$pH = -\lg[H_3O^+] .$$

To calculate the pH of a solution, you need to be able to calculate the equilibrium concentration of hydroxonium ions. To do this, a system of equations is drawn up that includes the equations of material balance, electronegativity, and expressions for the equilibrium constants present in the solution. The solution to this system of equations is the concentration of H_3O^+.

The final form and conditions of application of the formulas for determining the pH of a protolith solution are shown in the table.

Formulas for calculating pH and $[H_3O^+]$ of aqueous solutions of protoliths

Protoliths	Terms	Formulas
Strong acids: HCl, HNO_3 , $HClO_4$, H_2SO_4	$C_{HA} \geq 10^{-6}$ M	$[H_3O^+] = C_{HA}$ $pH = -\lg a_{H_3O^+}$ $\mu < 10^{-3}$, $pH = -\lg C_{HA}$
	$C_{HA} < 10^{-6}$ M	$[H_3O^+] = \frac{C_{HA} + \sqrt{C_{HA}^2 + 4K_{H_2O}}}{2}$
Strong basics (meadows): NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$	$C_B \geq 10^{-6}$ M	$[OH^-] = C_B$ $pOH = -\lg a_{OH^-}$ *for basics* $M(OH)_2$: $[OH^-]= 2C_B$ $\mu < 10^{-3}$, $pH = 14 + \lg C_B$
	$C_B < 10^{-6}$ M	$[OH^-] = \frac{C_B + \sqrt{C_B^2 + 4K_{H_2O}}}{2}$
Weak acids: HNO_2 , NH_4^+ , HF, CH_3COOH, HCN, H_2CO_3 , H_3PO_4	$K_{a,HA} = 10^{-6}$-10 $C_{HA} > 10^{-6}$	$[H_3O^+] = \sqrt{K_{a,HA} \cdot C_{HA}}$, $pH = \frac{1}{2} pK_{a,HA} - \frac{1}{2} \lg C_{HA}$
	$K_{a,HA} > 10^{-4}$ $C_{HA} > 10^{-6}$	$[H_3O^+] = \frac{-K_{a,HA} + \sqrt{K_{a,HA}^2 + 4 \cdot K_{a,HA} \cdot C_{HA}}}{2}$
	$K_{a,HA} \cdot C_{HA} \leq 1$	$[H_3O^+] = \sqrt{K_{H_2O} + K_{a,HA} \cdot C_{HA}}$

Protoliths	Terms	Formulas
Weak basics: NH_3 , CH_3NH_2 , CO_3^{2-} , N_2H_4 , CH_3COO^-	$K_{b,B} = 10^{-6}$-10^{-4} $C_B > 10^{-6}$	$[OH^-] = \sqrt{K_{b,B} \cdot C_B}$ $pOH = \frac{1}{2}pK_{b,B} - \frac{1}{2}\lg C_B$ $pH = 14 - \frac{1}{2}pK_{b,B} + \frac{1}{2}\lg C_B$
	$K_{b,B} > 10^{-4}$ $C_B > 10^{-6}$	$[OH^-] = \frac{-K_{b,B} + \sqrt{K_{b,B}^2 + 4 \cdot K_{b,B} \cdot C_B}}{2}$
	$K_{b,B} \cdot C_B \leq 10^{-14}$	$[OH^-] = \sqrt{K_{H_2O} + K_{b,B} \cdot C_B}$
Ampholites: HCO_3^- , $H_2PO_4^-$, HPO_4^{2-} , HSO_3^-	$K_{a,HA^-} \gg K_{H_2O}$ $C_{HA^-} > K_{a,HA^-}$	$[H_3O^+] = \sqrt{K_{a,H_2A} \cdot K_{a,HA^-}}$ $pH = \frac{pK_{a,H_2A} + pK_{a,HA^-}}{2}$
Buffer mixtures: NH_3 and NH_4^+, CO_3^{2-} and HCO_3^- , HCO_3^- and H_2CO_3		$pH = pK_{a,HA} - \lg\frac{C_{HA}}{C_{A^-}}$ або $pH = pK_{a,HA} - \lg\frac{n_{HA}}{n_{A^-}}$ $\pi = 2{,}30\frac{C_{HA} \cdot C_{A^-}}{C_{HA} + C_{A^-}}$

Example 1: Calculate the pH of a 0.01 M HCl solution.

Chloric acid is a strong protolith, so equality is fair:

$$[H_3O^+] = C_{HCl} = 0.01 \text{ mol/l} .$$

Calculate the ionic strength of the solution and the activity of the H ions$_3$ O$^+$:

$$\mu = 0{,}01; \quad \lg\gamma_{H_3O^+} = -0{,}512z^2\sqrt{\mu} = -0{,}0512; \quad \gamma_{H_3O^+} = 0{,}89 ;$$

$$a_{H_3O^+} = 0{,}89 \cdot 0{,}01 = 0{,}0089 \text{ моль/л} ; \quad pH = -\lg 0{,}0089 = 2{,}05 .$$

Example 2: Calculate the pH of a solution of the following composition: 0.01 M NNO_3 , 0.02 M CH_3 COOH.

If a solution contains both strong and weak acids, the pH is calculated using only the strong acid. The calculation is the same as in the previous example: pH = 2.05.

The same rule applies to a mixture of bases. If a strong and a weak base are present in a solution (e.g. NaOH and NH_3), the pH calculation is performed using only the strong base (NaOH).

Example 3: Calculate the pH of a $2 \cdot 10^{-3}$ M solution of Na_2CO_3 .

Sodium carbonate is a weak base. To calculate pH, you first need to calculate the basicity constant of the carbonate ion:

$$K_{b \cdot CO_3^{2-}} = \frac{10^{-14}}{K_{a,HCO_3^-}} = \frac{10^{-14}}{4{,}8 \cdot 10^{-11}} = 2{,}08 \cdot 10^{-4} .$$

Given the value of K_b and the concentration of the base, select the appropriate formula and calculate the pH of the solution:

$$pH = 14 - \frac{1}{2}pK_{b,CO_3^-} + \frac{1}{2}\lg C_{CO_3^{2-}} = 14 - \frac{1}{2}(3{,}68) + \frac{1}{2}\lg 2\cdot 10^{-3} = 10{,}81 \ .$$

Example 4. Calculate the pH of $2\cdot 10^{-8}$ M NaOH solution.

Sodium hydroxide is a strong base. Its concentration is too low, so we use a formula that takes into account the autoprotolysis of water:

$$[OH^-] = \frac{C_{NaOH} + \sqrt{C^2_{NaOH} + 4K_{H_2O}}}{2} = \frac{2\cdot 10^{-8} + \sqrt{(2\cdot 10^{-8})^2 + 4\cdot 10^{-14}}}{2} = 1.1\cdot 10^{-7}\,\text{M} ,$$

$$pH = 14 + lgC_{OH^-} = 14 + lg1{,}10\cdot 10^{-7} = 7{,}04 \ .$$

Example 5. Calculate the pH of a $5\cdot 10^{-3}$ M solution of $KHCO_3$.

Potassium bicarbonate is an ampholyte because the HCO_3^- ion can both donate and attach a proton. Calculate the pH of the solution using the following formula:

$$pH = \frac{pK_{a,H_2CO_3} + pK_{a,HCO_3^-}}{2} = \frac{6.35 + 10.32}{2} = 8.34 .$$

Example 6. Calculate the pH of a $5\cdot 10^{-5}$ M solution of CH_3COOH.

Sodium acetate is a weak base. Calculate the basicity constant of the acetate ion:

$$K_{b,CH_3COO^-} = \frac{10^{-14}}{K_{a,CH_3COOH}} = \frac{10^{-14}}{1{,}74\cdot 10^{-5}} = 5{,}75\cdot 10^{-10} .$$

Since $K_{,bCH3COO^-} \cdot C_{CH3COO^-} \leq 10^{-14}$, the pH of the solution is calculated as follows:

$$[OH^-] = \sqrt{K_{H_2O} + K_{b,CH_3COO^-}\cdot C_{CH_3COO^-}} = \sqrt{10^{-14} + 5{,}75\cdot 10^{-10}\cdot 5\cdot 10^{-5}} = 1{,}97\cdot 10^{-7}\,\text{M} ,$$

$$pH = 14 + lgC_{OH^-} = 14 + lg1{,}97\cdot 10^{-7} = 7{,}29 \ .$$

Example 7. Calculate the pH of a solution of the following composition: 0.01 M NH_4 Cl, 0.02 M NH_3 .

Ammonium ion and ammonia are a conjugated acid-base pair. Therefore, a solution of this composition is buffered. Let's calculate its pH:

$$pH = pK_{a,NH_4^+} - \lg\frac{C_{NH_4^+}}{C_{NH_3}} = 9{,}25 - \lg\frac{0{,}01}{0{,}02} = 9{,}55 .$$

Example 8. Calculate the pH of a solution of the following composition: 10^{-4} M KOH i $3\cdot 10^{-5}$ M $Ba(OH)_2$.

Both substances are strong bases and completely dissociate in aqueous solution:

$$NaOH = Na^+ + OH^- , \ Ba(OH)_2 = Ba^{2+} + 2OH^- .$$

Find the total concentration of hydroxyl ions:

$$[OH^-] = C_{KOH} + 2\cdot C_{Ba(OH)_2} = 10^{-4} + 2\cdot 3\cdot 10^{-5} = 1{,}6\cdot 10^{-4} \ \text{mol/l}$$

Knowing the concentration of OH ions$^-$, you can easily calculate the pH of a solution:

$$pH = 14 + lgC_{OH^-} = 14 + lg1{,}6\cdot 10^{-4} = 10{,}2 \ .$$

Example 9. Calculate the pH of the solution obtained by passing 22.4 mL of CO_2 (n.o.) through 1 L of water (gas absorbed quantitatively).

As you know, 1 mole of gas under normal conditions occupies a volume of 22.4 litres. Therefore, 22.4 ml of CO_2 corresponds to 10^{-3} moles of this gas, and the concentration of the resulting carbonic acid solution is 1 M. Calculate the pH of the solution:

$$pH = \frac{1}{2}pK_{a,H_2CO_3} - \frac{1}{2}\lg C_{H_2CO_3} = \frac{1}{2}6{,}35 - \frac{1}{2}\lg 10^{-3} = 4{,}68 .$$

Control questions

Calculate the pH of a solution of the following composition (without taking into account the ionic strength of the solution):

101. 10^{-3} M HCl.

102. $5 \cdot 10^{-4}$ M NaOH.

103. 0.01 M CH_3COOH.

104. 0.02 M Na_2CO_3 .

105. 0.1 M $KHCO_3$.

106. 0.05M NH_3 , 0.03 M NH_4Cl.

107. 0.1% HNO_3 .

108. 0.05% KOH.

109. 2.5 g of NH_4Cl dissolved in 500 ml of water.

110. 1 g of CH_3COONa dissolved in 250 ml of water.

111. 0.5 g of KH_2PO4 dissolved in 150 ml of water.

112. 49 mg of CH_3COOK dissolved in 100 ml of 0.01 M CH_3COOH.

113. 10^{-3} M HCl, $2 \cdot 10^{-3}$ M C_6H_5COOH.

114. $2 \cdot 10^{-3}$ M $NaNO_2$, 0.01 M KOH.

115. 0.01 M HCl, through 100 ml of which 11.2 ml of NH_3 was passed (n.c., gas absorbed quantitatively).

116. 0.1 M NaH_2PO_4.

117. 0.2 M K_2 HPO_4.

118. 0.01 M NaOH, through 100 ml of which 22.4 ml of CO_2 (n.c.) was passed.

119. 10^{-7} M HCl.

120. $3 \cdot 10^{-3}$ M KOH, $7 \cdot 10^{-3}$ M NaOH.

Topic 7. SOLUBILITY PRODUCT.

The solubility product is the product of the molar concentrations of ions in a saturated solution raised to the power of their stoichiometric coefficients. In general, the solubility product for compound A B_{nm} can be represented as follows:

$$K_{sp}\,(A_nB_m) = [A]^n[B]^m$$

The ion concentration is determined from the dissociation equation of salt A B_{nm}

$$A_nB_m = nA + mB$$

[A] = nS and [B] = mS, where S is the molar solubility (mol/l).

Substituting into the expression for the solubility product, we obtain:

$$K_{sp}\,(A_nB_m) = (nS)^n(mS)^m/$$

General formula for determining the solubility of S AnBm:

$$K\text{sp}\ (AnBm) = \frac{\sqrt[n+m]{K\text{sp}\ (AnBm)}}{n^n m^m}$$

Example 1: Determine the solubility product of $Pb_3(PO_4)_2$, if 850 ml of saturated solution contains 1.0-10^{-6} g of dissolved salt?

Determine the molar concentration of $Pb_3(PO_4)_2$ if $M(Pb_3(PO_4)_2)$ = 811 (g/mol):

$$C(Pb_3(PO_4)_2) = \frac{m}{MV} = \frac{1{,}0\cdot 10^{-6}}{811\cdot 0{,}85} = 1.45\cdot 10^{-9}\ \text{(mol/l)}.$$

The salt dissociates according to the reaction equation:

$$Pb_3(PO_4)_2 \leftrightarrow 3Pb^{2+} + 2\ PO_4^{3-}$$

Hence: $K_{sp}\,(Pb_3(PO_4)_2) = [Pb^{2+}]^3 \cdot [PO_4^{3-}]^2$.

The molar concentration of a saturated solution of $Pb_3(PO_4)_2$ is $1.45\cdot 10^{-9}$ mol/l, then the concentration of Plumbum ions is three times higher than $Pb_3(PO_4)_2$, so

$$[Pb^{2+}] = 3\cdot 1.45\cdot 10^{-9} = 4.5\cdot 10^{-9}\ \text{mol/l};$$

the concentration of phosphate ions is twice as high as $Pb_3(PO_4)_2$, so

$$[PO_4^{3-}] = 2\cdot 1.45\cdot 10^{-9} = 3.0\cdot 10^{-9}\ \text{mol/l}.$$

$$K_{sp}\,(Pb_3(PO_4)_2) = [Pb^{2+}]^3 \times [PO_4^{3-}]^2 = (4.5\cdot 10^{-9})^3 \times (3.0\cdot 10^{-9})^2 =$$
$$= (9.1\cdot 10^{-26})\cdot(9.0\cdot 10^{-18}) = 8.2\cdot 10^{-43}.$$

Example 2: Calculate the solubility of CaF_2, if it is known that $K_{sp} = 4.0\cdot 10^{-11}$.

The solubility product of CaF_2 is equal:

$K_{sp}\,(CaF_2) = [Ca^{2+}][F^-]^2$; since $CaF_2 \leftrightarrow Ca^{2+} + 2F^-$.

The solubility of CaF_2 is calculated using the formula:

$$K\text{sp}\ (AnBm) = \frac{\sqrt[n+m]{K\text{sp}\ (AnBm)}}{n^n m^m}$$

$$S_{CaF_2} = \frac{\sqrt[3]{\text{ДР}(CaF_2)}}{4} = \frac{\sqrt[3]{4{,}0\cdot 10^{-11}}}{4} = 8{,}55\cdot 10^{-5}\text{mol/l}.$$

Example 3: Determine the solubility product of strontium carbonate if its solubility at 25° C is 0.001554 g/l. $M(SrCO_3)$ = 148 g/mol.

Determine the solubility of $SrCO_3$ in mol/l

$S_{SrCO_3} = \frac{0,001554г/л}{148г/моль} = 1,05 \cdot 10^{-5}$mol/l.

Strontium carbonate dissociates according to the scheme $SrCO_3 \leftrightarrow Sr^{2+} + CO_3^{2-}$.

Based on the dissociation equation, we obtain the formula for the solubility product

$K\text{sp} = [Sr^{2+}] \cdot [CO_3^{2-}] = (1,05 \cdot 10^{-5})^2 = 1,1 \cdot 10^{-10}$.

Example 4. Will $BaSO_4$ precipitate when 2 mL of $BaCl_2$ (C = $1 \cdot 10^{-5}$ mol/l) and 2 ml of H_2SO_4 (C = $1 \cdot 10^{-5}$ mol/l) are poured together?

When two solutions are mixed, the concentration of ions will change. Since the concentration of solutions is inversely proportional to their volume, i.e., $C_1/C_2 = V_2/V_1$, then $C_1 = C_2 \times V_2 / V_1$, from which we calculate the concentration of Ba^{2+} and SO_4^{2-} ions taking into account dilution:

$[Ba^{2+}]=[SO_4^{2-}]=1 \cdot 10^{-5} \times 2/(4) = 5 \cdot 10^{-6}$ mol/l

Calculate the ionic product:

$[Ba^{2+}] \times [SO_4^{2-}]=5 \cdot 10^{-6} \times 5 \cdot 10^{-6} = 2.5 \cdot 10^{-11}$.

In the reference tables (Appendix 4), we find the value of the solubility product of $BaSO_4$ (K_{sp} ($BaSO_4$) = 1.1 10^{-10}). Compare these two values

$[Ba^{2+}] \times [SO_4^{2-}]=(2.5 \cdot 10^{-11}) < K_{sp}$ ($BaSO_4$) (1.1 10).$^{-10}$

Since the ionic product is less than the K_{sp} ($BaSO_4$), the $BaSO_4$ precipitate will not precipitate.

Control questions

121. Calculate the solubility of CaF_2 , if it is known that $K_{sp} = 4.0 \cdot 10^{-11}$.

122. The water solubility of $BaSO_4$ at room temperature is $1.05 \cdot 10^{-5}$ mol/dm^3 . Calculate the K_{sp} ($BaSO_4$) and compare the data with the table.

123. K_{sp} (AgJ) = $1.5 \cdot 10^{-16}$. Calculate the solubility of AgJ in mol/dm^3 and g/dm^3.

124. How many grams of barium are contained in 200 cm^3 of saturated aqueous solution of $BaCO_3$?

125. Determine the solubility product of calcium carbonate if its solubility is 0.00069 g/l at a temperature of 25^o C.

126. Determine the solubility of ferric (III) hydroxide and the concentration of Fe^{3+} ions (g/l) in saturated solution. K_{sp} ($Fe(OH)_3$) = $3.2 \cdot 10^{-38}$.

127. Calculate whether strontium sulphate precipitate will form when equal volumes of 0.001M solutions of $SrCl_2$ and K_2SO_4 are mixed. K_{sp} ($SrSO_4$) = $3.2 \cdot 10^{-7}$.

128. Determine whether barium sulphate precipitates when equal volumes of 0.001M solutions of $BaCl_2$ and K_2SO_4 are mixed? K_{sp} ($BaSO_4$) = $1.1 \cdot 10^{-10}$.

129. Calculate the solubility product of barium pyrophosphate if 100 ml of solution contains $88.47 \cdot 10^{-4}$ g.

130. Calculate the number of grams of Ca^{2+} ions in a saturated solution of calcium orthoarsenate. (K_{sp} ($Ca_3(AsO_4)_2$) = $6.8 \cdot 10^{-19}$).

131. Calculate the solubility of $BaSO_4$, if it is known that $K_{sp} = 1.1 \cdot 10^{-10}$.

132. Determine whether calcium sulphate precipitates when equal volumes of 0.01M solutions of $CaCl_2$ and Na_2SO_4 are mixed? K_{sp} ($CaSO_4$) = $6.26 \cdot 10^{-5}$.

133. Determine the solubility of calcium sulphate and the concentration of Ca^{2+} ions (g/l) in saturated solution. K_{sp} ($CaSO_4$) = $6.26 \cdot 10^{-5}$.

134. K_{sp} (AgCl) = $1.56 \cdot 10^{-10}$. Calculate the solubility of AgCl in mol/dm^3 and g/dm^3.

135. How many grams of calcium are contained in 400 cm^3 of a saturated aqueous solution of $CaCO_3$?

136. Will $BaSO_4$ precipitate when 3 ml of $BaCl_2$ (C = $2 \cdot 10^{-5}$ mol/l) and 3 ml of H_2SO_4 (C = $2 \cdot 10^{-5}$ mol/l) are poured together?

137. Calculate the solubility of $CaCO_3$, if it is known that $K_{sp} = 4.8 \cdot 10^{-9}$.

138. The product of the solubilities of Ag_3PO_4 is $1.3 \cdot 10^{-20}$. Determine: a) the molar concentrations of ions Ag^+ and PO_4^{3-} ; b) the solubility S (mol/l; g/l).

139. Will a precipitate form if 30 ml of a 0.003 M solution of K_2CrO_4 and 20 ml of a 0.0002 M solution of $AgNO_3$ are mixed, if the solubility product of Ag_2CrO_4 is $8.8 \cdot 10^{-12}$?

140. Determine the solubility product of argentium bromate if 0.35 g of $AgBrO_3$ is dissolved in 200 ml of water .

Topic 8. CALCULATIONS IN GRAVIMETRIC ANALYSIS

The task of gravimetric analysis is usually to determine the content of an element (substance), which is calculated based on the mass of the sample and the gravimetric shape of the sediment.

The gravimetric (weighed) form is the compound that is weighed to obtain the final result of the analysis. For example, a precipitate of ferric hydroxide $Fe(OH)_3$ is completely converted to ferric oxide Fe_2O_3 as a result of ignit. The latter is called the gravimetric form, and it is this form that is weighed at the end of the analysis.

$$|Fe| \rightarrow Fe^{3+} \rightarrow \underset{\text{precipitated form}}{Fe(OH)_3} \rightarrow \underset{\text{gravimetric form}}{Fe_2O_3}$$

In practice, chemical laboratories usually use methods that provide ready-made formulas for calculating the results of analysis. These formulas include a constant factor called the *conversion factor F,* which is used to determine the content of an element or component in the sample under analysis if the mass of the gravimetric form of that component is known.

In general, the conversion factor (or analytical gravimetric factor) *F is* calculated by the formula:

$$F = \frac{x \cdot M(A)}{y \cdot M(B)},$$

where, *M(A)* and *M(B)* are the molar masses of component *A* and its gravimetric form *B*;

x and *y* are the integers by which the molar masses are multiplied so that the total number of moles of the element in the numerator and denominator is the same.

For example, to determine the Fe content in the mass of Fe_2O_3 , the conversion factor is determined as follows:

$$F = \frac{2M(\mathrm{Fe})}{M(\mathrm{Fe_2O_3})} = \frac{2 \cdot 55{,}847}{159{,}6922} = 0{,}6995.$$

In this case, x=2, y=1, because one molecule contains two Ferrous atoms. Thus, the number of molecules of Fe in the numerator and denominator is the same and equals 2. Calculate the value of *F* or look it up in a reference table.

To determine the mass of a sample of the substance to be analysed, it is necessary to know the approximate composition of the substance in the sample, as well as the form of the precipitate (crystalline or amorphous) and the expected mass of the gravimetric form.

The minimum weight of the dry matter sample, which is determined (m_{determ}), is calculated using the following formulas:

$$m_{determ} = 0.5 \cdot F; \; m_{determ} = 0.1 \cdot F;$$

where, 0.5 g is the expected mass of gravimetric form (g.f.) for crystalline,

0.1 g – for amorphous sediments;

F is the conversion factor.

If the substance to be analysed contains some impurities, the mass of the sample is calculated using the appropriate formulas:

$$V_{determ} = \frac{0.5\,F100\%}{\rho C,\%}, \; V_{determ} = \frac{0.1\,F100\%}{\rho C,\%},$$

where, ρ *is the* density of the liquid under study.

The content of the substance to be determined is calculated using the following formulas:

$$m_{determ} = m_{g.f.}F,\ w_{determ}(\%) = \frac{m_{g.f.}F100\%}{m_{weight}}.$$

Example 1: Calculate the mass fraction of calcium and magnesium carbonates in limestone if the weight of their mixture is 0.9866g. The analysis yielded 0.3755g of CaO and 0.4105g of $Mg_2P_2O_7$.

The conversion factor of $CaCO_3$, which is determined, to the gravimetric form of CaO is equal:

$$F = \frac{M(CaCO_3)}{M(CaO)} = \frac{100{,}09}{56{,}08} = 1{,}78.$$

Find the mass of $CaCO_3$ in a limestone sample using the formula:

m($CaCO_3$) = F · m(CaO) = 1.78·0.3755 = 0.67g.

Determine the mass fraction of $CaCO_3$ in the suspension:

w($CaCO_3$) = 0.67-100%/ 0.9866 = 67.91%.

The mass fraction of $MgCO_3$ is similarly determined .

The conversion factor of $MgCO_3$, which is determined, to the gravimetric form $Mg_2P_2O_7$ is equal:

$$F = \frac{2M(MgCO_3)}{M(Mg_2P_2O_7)} = \frac{2 \cdot 84{,}03}{222{,}57} = 0{,}75.$$

Mass of $MgCO_3$ in limestone by weight:

m($MgCO_3$) = *F*·*m*($Mg_2P_2O_7$) = 0.75·0.4105= 0.31g.

The mass fraction of $MgCO_3$ in the carbonate mixture is equal:

w ($MgCO_3$) = 0.31·100%/ 0.9866 = 31.42%.

Example 2: Determine the minimum amount of $KCl{\cdot}MgCl_2{\cdot}6H_2{\cdot}O$ that is required to determine Magnesium as MgO .

The first way

We create the equations according to which deposition and determination take place:

$MgCl_2 + 2OH^- \rightarrow Mg(OH)_2\downarrow + 2Cl^-$; $Mg(OH)_2\downarrow \rightarrow MgO\downarrow + H_2O$

precipitated form gravimetric (weight) form

MgO is a crystalline precipitate, so the gravimetric mould should weigh 0.5 g. Determine the mass of $MgCl_2$ to be taken:

x g 0.5 g

$MgCl_2 \rightarrow Mg(OH)_2\downarrow \rightarrow MgO\downarrow$

M = 95 g/mol M = 40 g/mol

n (MgO) = m / M = 0.5 / 40 = 0.0125 (mol)

n (MgO) = n ($MgCl_2$), so n ($MgCl_2$) = 0.0125 (mol);

m ($MgCl_2$) = M · n = 95 g/mol·0.0125 mol = 1.1875 (g)

Determine the mass of the minimum weight of $KCl{\cdot}MgCl_2{\cdot}6H_2O$ that needs to be taken:

m ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) x g ------------------ 1.1875 g m ($MgCl_2$)

M ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) 277.5 g/mol --------- 95 g/mol M ($MgCl_2$)

m ($KCl \cdot MgCl_2 \cdot 6H_2O$) = M ($KCl \cdot MgCl_2 \cdot 6H_2O$) · m ($MgCl_2$) / M ($MgCl_2$) =
= 277,5·1,1875 / 95 = 3,4700 (г)

The second way

To calculate the minimum weight of $KCl \cdot MgCl_2 \cdot 6H_2O$, we first determine the conversion factor:

$$F(KCl \cdot MgCl_2 \cdot 6H_2O / MgO) = \frac{x \cdot M(KCl \cdot MgCl_2 \cdot 6H_2O)}{y \cdot M(MgO)} = \frac{277{,}5}{40} = 6{,}9375$$

The weight of the sample, given that the gravimetric mould should weigh 0.5 g, will be equal to:

m ($KCl \cdot MgCl_2 \cdot 6H_2O$)= 0.5·F = 0.5·6.9375 = 3.4700 (g).

Example 3: How much dolomite containing approximately 20% MgO should be taken to analyse for Magnesium, which is precipitated as $NH_4MgPO_4 \cdot 6H_2O$?

The first way

x g 0.5 g

MgO → $NH_4MgPO_4 \cdot 6H_2O$

M = 40 g/mol M = 245 g/mol

n ($NH_4MgPO_4 \cdot 6H_2O$) = m / M = 0.5 / 245 = 0.002 (mol);

n (MgO) = n ($NH_4MgPO_4 \cdot 6H_2O$), so n (MgO) = 0.002 (mol);

m (MgO) = M · n = 40 g/mol·0.002 mol = 0.08 (g)

Determine the weight of the minimum dolomite sample to be taken:

m (MgO) 0.08 g --------------- 20%

m dolomite x g --------------- 100 %

m dolomite = m (MgO) · 100% / C% = 0.08 ·100% / 20% = 0.4000 (g).

The second way

The following formula can be used to calculate the mass of the minimum dolomite charge: $m_{dolomite} = 0.5 \cdot F \cdot 100\% / C\%$.

Let's define the conversion factor:

$$FMgO / NH_4MgPO_4 \cdot 6H_2O = \frac{x \cdot M(MgO)}{y \cdot M(NH_4MgPO_4 \cdot H_2O)} = \frac{40}{245} = 0{,}1633,$$

$m_{naturally\ occurring\ dolomite}$ = 0.5·0.1633· 100% / 20% = 0.4000 (g).

Control questions

141. Determine the minimum sample of $CuSO_4 \cdot 5H_2O$ that must be taken for analysis for the content of Cu in the form of CuO if the mass of the gravimetric form is 0.5 g?

142. What weight of coal containing about 4% Sulphur should be taken for analysis for S content if it is determined as $BaSO_4$?

143. Determine the number of moles of water in aluminium chloride crystallohydrate by gravimetric analysis if its weight is 0.7244 g and the resulting aluminium oxide is 0.1528 g.

144. What mass of a substance containing 50% Fe should be taken for analysis so that the mass of the calcined precipitate Fe_2O_3 is 0.1 g?

145. What weight of pyrite with a Sulfur content of 50% should be used for analysis to obtain 0.3 g of $BaSO_4$?

146. How much of a substance containing 20% NaCl and 30% KCl should be taken to determine chlorine as AgCl (mass of precipitate 0.5 g).

147. Technical barium chloride contains about 97% $BaCl_2 \cdot 2H_2O$. What weight should be taken to obtain 0.3 g of $BaSO_4$ precipitate?

148. Aluminium sulphate crystallohydrate contains about 88% $Al_2(SO_4)_3 \cdot 18H_2O$. Determine the weight required to determine aluminium in the form Al_2O_3 , if the mass of Al_2O_3 is 0.1 g.

149. Calculate the weight of phosphorite containing 20% P_2O_5 , required to obtain 0.3 g of $Mg_2P_2O_7$.

150. How much of an alloy containing 65% Pb and 15% Sn should be taken to determine these elements, if Plumbum is determined as $PbSO_4$ (precipitate weight 0.5 g) and Stanum as SnO_2 (precipitate weight 0.2 g)?

151. Calculate the mass of a sample of silicate containing 21.74% SiO_2. After igniting, 0.0724 g of SiO_2 was obtained .

152. After appropriate treatment and igniting, 0.1436 g of SiO_2 and 2.1140 g of Fe_2O_3 were obtained from a 1.5462 g cast iron chip. Determine the mass fraction of Silicon and Fe in the cast iron.

153. A 0.4124g ore sample was dissolved and processed accordingly. After igniting, 0.2514g of Sb_2S_3 was obtained. Calculate the mass fraction of stibium in the ore.

154. An alloy of 1.0000g was dissolved and after appropriate treatment 0.2500g of $Cu(OH)_2$ was obtained . Calculate the mass fraction of CuO in the alloy.

155. The content of Fe in the ore is 49.52%. What weight of ore should be taken to obtain 0.4150 g of Fe_2O_3 after appropriate treatment?

156. A precipitate $KClO_4$ was obtained from a solution of potassium salt, the mass of which after igniting was 0.1528 g. Determine the mass of Potassium contained in the solution.

157. Calculate the mass fraction of Fe_3O_4 in magnetic iron ore if 0.4326g of Fe_2O_3 is obtained from 0.6000g of technical iron ore.

158. After appropriate treatment, Cu was isolated from an alloy sample weighing 0.5783g in the form of Cu_2S, whose mass was 0.1274g. Determine the mass fraction of copper in the alloy.

159. Technical barium chloride contains about 94% $BaCl_2 \cdot 2H_2O$. What weight should be taken to obtain 0.5 g of $BaSO_4$ precipitate?

160. Calculate the mass of a sample of silicate containing 23.54% SiO_2. After igniting, 0.0894g of SiO_2 was obtained .

Topic 9. CALCULATIONS IN REFRACTOMETRY.

Refraction, or refraction (from the Latin refractus - refracted), is a change in the direction of straight-line propagation of light when it passes from one medium to another.

Refraction, as well as absorption, of light is the result of its interaction with the medium.

The relative refractive index n_{rel} . is the ratio of the speeds of light in two media:

$$n_{rel} = V_1 / V_2 .$$

where V_1 and V_2 are the speeds of light propagation in medium I and II, respectively, provided that $V_1 > V_2$.

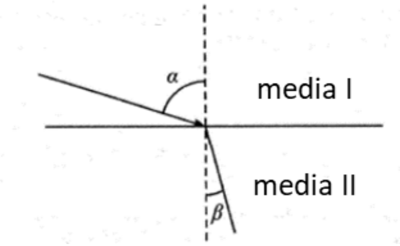
The value of the refractive index depends on the nature of the substance, its density, the wavelength of the incident light, temperature and pressure.

According to the laws of light refraction, when light passes from an optically less dense medium I to a medium with a higher optical density II, the angle of incidence *α is* always greater than the angle of refraction *β* (Figure), and the following equations hold:

$$n_{rel} = sin\alpha \ / \ sin\beta = n_2 / n_1 .$$

where *α is the* angle of incidence of light, *β is the* angle of refraction of light,

n_1 and n_2 are the refractive indices of media I and II (Figure).



Refractometry (from Latin *refractus* - refracted and Greek *metreo* - measure) is a method of studying substances based on the determination of the refractive index and some of its functions. Refractometric analysis is used for the identification of chemical compounds, quantitative and structural analysis, and determination of physical and chemical parameters of substances.

For liquids and solids, the refractive index *n is* most often determined relative to air, and for gases, relative to vacuum.

The value of *n* depends on the wavelength *l of* light and temperature. For example, the refractive index at 20°C for the D-line of the spectrum of the sodium atom (*l* = 589.3 nm) is n_D^{20} . For gases, the pressure dependence of *n* must be taken into account.

The influence of temperature on the refractive index is determined by two factors: changes in the concentration of a substance and the dependence of the polarisability of molecules on temperature. The temperature coefficient of refractive index is proportional to the temperature coefficient of density. Since all liquids expand when heated, their refractive indices decrease with increasing temperature. The temperature coefficient depends on the temperature of the liquid, but can be considered constant over small temperature intervals. Pressure has almost no effect on the refractive index of liquids.

Refractometric analysis is based on the Lorentz-Lorentz formula, which relates the refractive index *n of* an isotropic substance to the number of molecules *N* per unit volume and the polarisability *a of the* substance molecules:

$$\frac{n^2-1}{n^2+2}=\frac{1}{3}N\cdot\alpha.$$

The Lorentz-Lorentz formula allows us to determine the polarisability *a* from the measured refractive indices of a substance *n*.

There is a rule of thumb that states that the refractive index of a complex chemical compound can be calculated by adding the refractive indices of its constituent elements.

The specific refractive index for a particular chemical (at a particular wavelength *l of* light) can be determined by the formula:

$$r=\frac{n^2-1}{n^2+2}\cdot\frac{1}{\rho}.$$

where *ρ is the* density of a substance proportional to the concentration of molecules N.

Atomic refraction is calculated using the formula:

$$R=A\cdot r=\frac{n^2-1}{n^2+2}\cdot\frac{A}{\rho},$$

where *A is the* atomic mass of the element.

The molar refraction is calculated by the formula:

$$R_M=M\cdot r=\frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho}=\frac{1}{3}N_A\cdot\alpha,$$

where *M is the* molecular weight;

N_A – constant Avogadro.

Additivity rule: $R = R_1 + R_2 + ... + R_n$, where R , ,123 ... are the atomic refractions of the elements and the refractions of the chemical bonds in the molecule (given in the reference literature).

Refractometric determination of solutions is based on the relationship between the concentration of a substance in a solution and its refractive index, which is expressed by the formula: $n=n_0+F\cdot C,$

where *n is the* refractive index of the solution;

n_0 - refractive index of the solvent;

C - solution concentration, %;

F is a conversion factor equal to the increase in the refractive index with an increase in concentration by 1% (determined experimentally or calculated from refractive index tables).

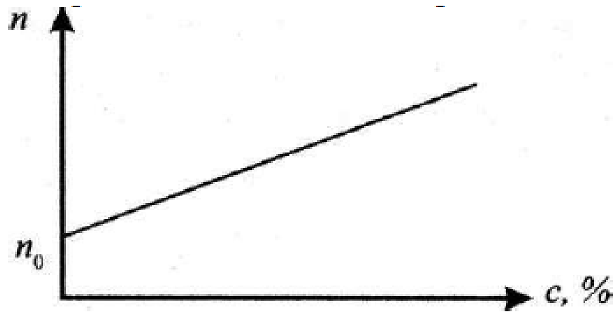
The instruments used to measure n are called refractometers. There are two main types of refractometers: Abbe refractometers and Pulfrich refractometers. Measurements of n are based on determining the value of the refractive index.

For Abbe refractometers, the main and characteristic unit is a prismatic block consisting of measuring and illuminating prisms. The measurement accuracy of the refractive index is ±(1-2-10^{-4}), the measurement limits are 1.3-1.7.

Pulfrich refractometers have a higher measurement accuracy of ±(1-2-10^{-5}), the measurement limit is much higher - 1.9. These instruments do not have a prismatic block.

The dependence of the refractive index *n of* a homogeneous two-component system on its composition is determined experimentally by determining the refractive index for a number of standard systems in which the content of components is known. On the basis of the data obtained, a calibration graph is constructed in the coordinates: refractive index - content

Knowing the refractive index of the system under study, the graph can be used to determine its concentration.



Example 1: Determine the molar refractive index of pentane C_5H_{12} if the refractive index n is 1.3577 and the density is 0.6262. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

The molecular weight of pentane is M(C_5H_{12}) = 72 g/mol. The molar refraction of pentane is calculated by the formula:

$$R_M = \frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho} = \frac{(1{,}3577^2-1)}{(1{,}3577^2+2)}\cdot\frac{72}{0{,}6262} = \frac{0{,}8433\cdot 72}{3{,}8433\cdot 0{,}6262} = 25{,}23.$$

According to the tables of atomic refractions (Appendices 5,6): R_C = 2.418; R_H = 1.100, then

$$R_{C_5H_{12}} = 5\cdot 2{,}418 + 12\cdot 1{,}100 = 12{,}09 + 13{,}20 = 25{,}29$$

Graphical formula of pentane CH_3 -CH_2 -CH_2 -CH_2 -CH_3 , according to the bond refraction tables: $R_{C–C}$ = 1.296; $R_{C–H}$ = 1.676, then by the rule of additivity:

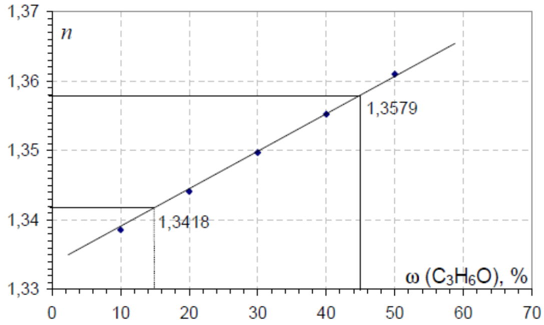
$$R_{C_5H_{12}} = 4\cdot R_{C-C} + 12\cdot R_{C-H} = 4\cdot 1{,}296 + 12\cdot 1{,}676 = 5{,}184 + 20{,}11 = 25{,}29.$$

Example 2: To determine the composition of a water-acetone solution, the refractive indices of standard solutions of this composition were measured:

ω (C_3H_6O), %, %.	10	20	30	40	50
n	1,3386	1,3442	1,3496	1,3552	1,3610

Construct a calibration graph, derive the equation for the refractive index versus concentration, and determine the content (in %) of acetone from the graph and the equation if the refractive index of the solution under study is n_x = 1.3500.

Using the data, we plot a calibration graph of the refractive index versus the concentration of the water-acetone solution:



The equation for the dependence of the refractive index on concentration is determined using the method of selected points: for a concentration of 15%, the refractive index is n = 1.3418, and for a concentration of 45%, n = 1.3579. Write the equation:

$$\begin{cases} 1{,}3418 = n_0 + F\cdot 15; \\ 1{,}3579 = n_0 + F\cdot 45. \end{cases}$$

After solving the system of equations, we find n_0 = 1.3339 and F = 0.00053. Then the dependence equation is as follows: $n = 1.3339 + 0.00053\cdot C$.

From the graph, we find that the refractive index n_x = 1.3500 corresponds to a concentration of 30.4 %, and substituting the refractive index value into the equation, we obtain:

$$C = \frac{n - n_0}{F} = \frac{1{,}3500 - 1{,}3339}{0{,}00053} = \frac{0{,}0161}{0{,}00053} = 30{,}38\,\%.$$

Example 3: The refractive index of a standard 50% aqueous solution of ethylene glycol is $n_{ст.}$ = 1.3831. Assuming that there is a linear relationship between the refractive index and concentration, determine the concentration (in mol/l) of an aqueous solution of ethylene glycol if it is known that the refractive index of the solution under study is n_x = 1.3536, the density is ρ = 1.05 g/cm^3, and the refractive index of the solvent is n_0 = 1.3330.

Using the equation of the relationship between the concentration of a standard solution of a substance and its refractive index, we determine the refractive index increment: $n = n_0 + F\cdot C$, hence

$$F = \frac{n - n_0}{C} = \frac{1{,}3831 - 1{,}3330}{50} = \frac{5{,}01\cdot 10^{-2}}{50} = 1{,}002\cdot 10^{-3}.$$

Determine the mass concentration (in %) of the ethylene glycol solution under test:

$$C = \frac{n - n_0}{F} = \frac{1{,}3536 - 1{,}3330}{1{,}002\cdot 10^{-3}} = \frac{2{,}16\cdot 10^{-2}}{1{,}002\cdot 10^{-3}} = 21{,}56\,\%.$$

Calculate the volume occupied by 100 g of the test solution:

V=m/ρ=100/1.05= 95.24 ml, then

21.56 g - in 95.24 ml

x g - in 1000 ml; x = 226.37 g/l.

Calculate the molar concentration of ethylene glycol: M($C_2H_6O_2$)=62 g/mol, then

$$C_M = \frac{m}{M\cdot V} = \frac{226{,}37}{62\cdot 1} = 3{,}65\,\text{mol/l}$$

Control questions.

161. Determine the molar refraction of carbon tetrachloride CCl_4, if the refractive index n is 1.4603 and the density is 1.604. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

162. Determine the molar refraction of methyl iodide CH_3I if the refractive index n is 1.5257 and the density is 2.2790. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

163. Determine the molar refraction of bromobenzene C_6H_5Br if the refractive index n is 1.5197 and the density is 1.4950. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

164. Determine the molar refraction of acetic acid CH_3COOH if the refractive index n is 1.3698 and the density is 1.0493. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

165. Determine the molar refraction of propyl alcohol C_3H_7OH if the refractive index n is 1.3832 and the density is 0.8035. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

166. Determine the molar refraction of nitrobenzene $C_6H_5NO_2$ if the refractive index n is 1.5455 and the density is 1.2034. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

167. Determine the molar refraction of pyridine C_5H_5N if the refractive index n is 1.5056 and the density is 0.9831. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

168. To determine the composition of aqueous solutions of propyl alcohol, the refractive indices of standard solutions of this composition were measured:

ω (C_3H_8O), %, %.	10	20	30	40	50
n	1,3396	1,3464	1,3532	1,3598	1,3664

Construct a calibration graph, derive the equation for the refractive index versus concentration, and determine the content (in %) of propyl alcohol from the graph and the equation if the refractive index of the solution under study is n_x = 1.3498.

169. To determine the composition of aqueous solutions of ascorbic acid, the refractive indices of standard solutions of this composition:

ω ($C_6H_8O_6$), %	5	10	15	20	25
n	1,3410	1,3490	1,3570	1,3650	1,3730

Construct a calibration graph, derive the equation for the refractive index versus concentration, and determine the content (in %) of ascorbic acid from the graph and the equation if the refractive index of the solution under study is n_x = 1.34598.

170. To determine the composition of aqueous solutions of propyl alcohol, the refractive indices of standard solutions of this composition were measured:

ω (C_3H_8O), %	10	10	15	20	25
n	1,3362	1, 3396	1,3431	1, 3464	1,3502

Construct a calibration graph, derive the equation for the refractive index versus concentration, and determine the content (in %) of propyl alcohol from the graph and the equation if the refractive index of the solution under study is n_x = 1.3424.

171. To determine the composition of aqueous solutions of ascorbic acid, determine the refractive indices of standard solutions of this composition:

ω ($C_6H_8O_6$), %	5	10	15	20	25
n	1,3410	1,3490	1,3570	1,3650	1,3730

Construct a calibration graph, derive the equation for the refractive index dependence on concentration, and determine the content (in %) of ascorbic acid from the graph and the equation if the refractive index of the solution under study n_x =1.3598.

172. The refractive index of a standard 6% aqueous solution of sodium chloride NaCl is n = 1.3433. Assuming that there is a linear relationship between the refractive index and concentration, determine the concentration (in g/ml) of an aqueous solution of sodium chloride if it is known that the refractive index of the solution under study is n_x = 1.3382, the density is ρ = 1.07 g/cm^3 , and the refractive index of the solvent is n_0 = 1.3330.

173. The refractive index of a standard 8.2% aqueous solution of acetone C_3H_6O is n = 1.3473. Assuming that there is a linear relationship between the refractive index and concentration, determine the concentration (in mol/l) of an aqueous solution of acetone if it is known that the refractive index of the solution under study is n_x=1.3524, the density is ρ = 0.96 g/cm^3 , and the refractive index of the solvent is n_0=1.3330.

174. The refractive index of a standard 20% aqueous solution of glycerol $C_3H_8O_3$ is n = 1.3575. Assuming that there is a linear relationship between the refractive index and concentration, determine the concentration (in mol/l) of an aqueous solution of glycerol if it is known that the refractive index of the solution under study is n_x =1.3785, the density is ρ = 1.07 g/cm^3 , and the refractive index of the solvent is n_0 = 1.3330.

175. The refractive index of a standard 19.25% aqueous solution of acetic acid CH_3COOH is n = 1.3468. Assuming that there is a linear relationship between the refractive index and concentration, determine the concentration (in %) of an aqueous solution of acetic acid if it is known that the refractive index of the solution under study is n_x = 1.3385 and the refractive index of the solvent is n_0 = 1.3330.

176. The refractive index of a standard 10% aqueous solution of sodium chloride NaCl is n = 1.3455. Assuming that there is a linear relationship between the refractive index and concentration, determine the concentration (in g/ml) of an aqueous solution of sodium chloride if it is known that the refractive index of the solution under study is n_x = 1.3380, the density is ρ = 1.07 g/cm^3 , and the refractive index of the solvent is n_0 = 1.3328.

177. Determine the molar refraction of bromobenzene C_6H_5Br if the refractive index n is 1.5197 and the density is 1.4950. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

178. Determine the molar refraction of acetic acid CH_3COOH if the refractive index n is 1.3698 and the density is 1.0493. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

179. Determine the molar refraction of nitrobenzene $C_6H_5NO_2$ if the refractive index n is 1.5455 and the density is 1.2034. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

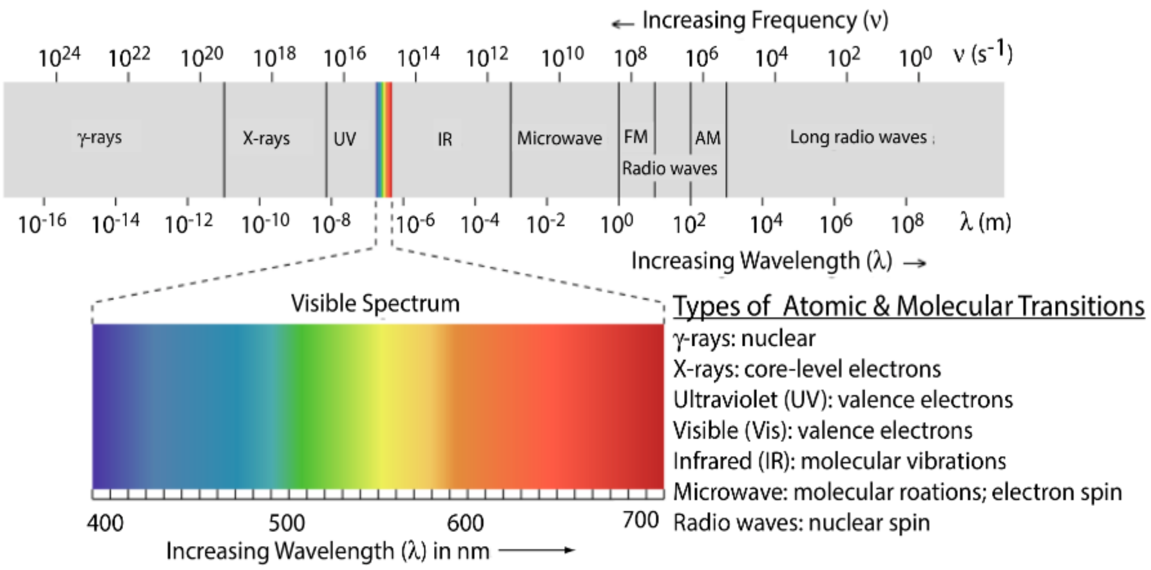
180. Determine the molar refraction of pyridine C_5H_5N if the refractive index n is 1.5056 and the density is 0.9831. Compare the determined refraction with the one calculated from the tables of atomic and bond refractions.

10. CALCULATIONS IN PHOTOMETRY

Photometric analysis is based on the ability of a substance to absorb or reflect electromagnetic radiation in the optical range.

The optical range includes electromagnetic waves with a wavelength (l) between 100 and 10,000 nm. It is divided into three regions:

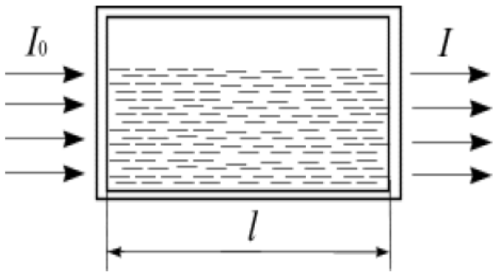
- ultraviolet (UV) – (100-380 nm);
- visible – (380-760 nm);
- infrared (IR) – (760-10000 nm).



An analysis method based on the selective absorption of light radiation by particles, molecules, or ions of a substance in solution is called absorption spectroscopy.

At certain wavelengths, light is absorbed intensively by particles (molecules or ions) of a substance in solution, while at other wavelengths, light is not absorbed. The nature of the absorption depends on the nature of the substance, and this is the basis for qualitative analysis. For quantitative determination of a substance, the dependence of light absorption on its concentration is used. Coloured substances absorb radiation in the visible region of the spectrum - from 380 to 760 nm.

There is a certain relationship between the amount of absorbed electromagnetic radiation, the thickness of the absorbing substance layer and its concentration, which is expressed using the unified law of light absorption - the Bouguer-Lambert-Beer law, whose mathematical expression is:

$D=-\lg T=-\lg\frac{I}{I_0}=\lg\frac{I_0}{I}=\varepsilon\cdot l\cdot C$, D is the optical density of the solution; *T is the* light transmission of the solution; I_0 and I are the initial intensity and the intensity passed through the solution, respectively;	
C is the concentration of the solution, mol/l; l - layer thickness (or cuvette thickness), cm; ε is the molar absorption coefficient (a constant for a certain substance at a certain wavelength of light radiation).	

Example 1: During the photometric determination of titanium with chromotropic acid in a solution containing 0.45 mg of titanium per 1 cm^3 in a cuvette with a layer thickness of 5 cm, a deviation on the galvanometer scale of 90 μA was obtained. For the initial light flux, the deviation on the galvanometer scale is 155 μA. Determine the molar absorption coefficient of the coloured complex.

According to the fundamental law equation, light absorption is Bouguer-Lambert-Beer:

$$I=I_0\cdot 10^{-\varepsilon\cdot l\cdot C} \quad \text{або} \quad \lg I_0-\lg I=\varepsilon\cdot l\cdot C.$$

Calculate the molar concentration of titanium:

$$C=\frac{m}{M\cdot V}=\frac{0{,}45\cdot 10^{-6}}{47{,}9\cdot 0{,}001}=0{,}94\cdot 10^{-5}\ \text{mol/l}$$

From the above equation, we obtain the Bouguer-Lambert-Behr equation:

$$\varepsilon=\frac{\lg I_0-\lg I}{l\cdot C}=\frac{\lg 155-\lg 90}{5\cdot 0{,}94\cdot 10^{-5}}=5023{,}2.$$

Example 2: The molar absorption coefficient of a beryllium complex with acetylacetone in chloroform at 295 nm is 31600. What is the minimum content of Beryllium (in %) in a 1 g suspension dissolved in 50 cm^3 of in a cuvette with a layer thickness of 5 cm, if the minimum optical density recorded by the photometer is 0.025?

Using the Bouguer-Lambert-Behr law, we determine the molar concentration of beryllium:

$$D=\varepsilon\cdot l\cdot C, \qquad C=\frac{D}{\varepsilon\cdot l}=\frac{0{,}025}{31600\cdot 5}=1{,}58\cdot 10^{-7}\ \text{mol/l}$$

Calculate the content of Beryllium in a 50 cm^3 flask:

$$m=\frac{C_M\cdot M\cdot V_к}{1000}=\frac{1{,}58\cdot 10^{-7}\cdot 9{,}01\cdot 50}{1000}=7{,}19\cdot 10^{-8}\ \text{g}$$

Hence, the beryllium content (in %) is equal:

$$\omega(\%)=\frac{m\cdot 100\%}{m_{weight}}=\frac{7{,}19\cdot 10^{-8}\cdot 100}{1}=7{,}91\cdot 10^{-6}\%.$$

Control questions

Using the equation of the combined Bouguer-Lambert-Beer law of light absorption, determine the parameter denoted by "X" in the units given:

N of questions	Test substance	Molar absorption coefficient	Layer thickness, l, cm^{-1}	Concentration of C	Optical density D
181	MnO_4^-	2420	1,0	1.5 g/l	X
182	Al^{3+}	6700	X	2.5-10^{-5} mol/l	0,837
183	Quinoline	4500	2,0	3mg/l	X
184	Azobenzene	1100	5,0	X mol/l	0,356
185	Fe^{3+}	1800	3,0	X mg/l	0,652
186	Al^{3+}	6700	3,0	2.5-10^{-5} mol/l	X
187	Quinoline	4500	3,0	1.5 mg/l	X
188	Azobenzene	1100	3,0	X g/l	0,242
189	MnO_4^-	2420	1,0	1.5 g/l	X
200	Fe^{3+}	1800	2,0	X mol/l	0,852

APPENDICES

Appendix 1. Molecular weights of some substances

Substances	Mr	Substances	Mr	Substances	Mr
HCl	36,46	$Cu(NO_3)_2$	187,56	Na_2SO_4	142,04
H_2SO_4	98,08	$CuCl_2$	134,45	NH_3	17,03
HNO_3	63,01	$CuSO_4$	159,61	NH_4Cl	53,49
H_3PO_4	98,00	$CuSO_4 \cdot 5H_2O$	249,69	KCl	74,55
$BaCl_2$	208,23	$H_2C_2O_4$	90,04	K_2CrO_4	194,19
$Ba(OH)_2$	171,34	$Na_2C_2O_4$	134,00	K_3PO_4	212,27
CH_3COOH	60,05	Na_2CO_3	105,99	K_2HPO_4	174,18
CH_3COOK	98,14	$Na_2CO_3 \cdot 10H_2O$	286,14	KH_2PO_4	136,09
CH_3COONa	82,03	$NaCl$	58,44	KOH	56,11
$Ca(NO_3)_2$	164,09	$NaNO_3$	84,99	KNO_3	101,10
$CaCl_2$	110,98	$NaOH$	40,00	K_2SO_4	174,26

Appendix 2. Proteolysis constants of acids and bases in aqueous solutions

Acids

Formula	K_a	pK_a
H_3AsO_4	$5{,}6 \cdot 10^{-3}$	2,25
$H_2AsO_4^-$	$1{,}7 \cdot 10^{-7}$	6,77
$HAsO_4^{2-}$	$3{,}0 \cdot 10^{-12}$	11,5
H_3AsO_3	$5{,}9 \cdot 10^{-10}$	9,23
$HCOOH$	$1{,}8 \cdot 10^{-4}$	3,75
CH_3COOH	$1{,}74 \cdot 10^{-5}$	4,76
C_6H_5COOH	$6{,}3 \cdot 10^{-5}$	4,20
H_2CO_3	$4{,}5 \cdot 10^{-7}$	6,35
HCO_3^-	$4{,}8 \cdot 10^{-11}$	10,32
$H_2C_2O_4$	$5{,}6 \cdot 10^{-2}$	1,25
$HC_2O_4^-$	$5{,}4 \cdot 10^{-5}$	4,26
HCN	$5{,}0 \cdot 10^{-10}$	9,30
H_2CrO_4	$1{,}6 \cdot 10^{-4}$	3,80
$HCrO_4^-$	$3{,}2 \cdot 10^{-7}$	6,50
H_2MoO_4	$2{,}9 \cdot 10^{-3}$	2,54
$HMoO_4^-$	$1{,}4 \cdot 10^{-4}$	3,86

Formula	K_a	pK_a
HNO_2	$6{,}9 \cdot 10^{-4}$	3,16
H_3PO_4	$7{,}1 \cdot 10^{-3}$	2,15
$H_2PO_4^-$	$6{,}2 \cdot 10^{-8}$	7,21
HPO_4^{2-}	$5{,}0 \cdot 10^{-13}$	12,3
H_3PO_3	$3{,}1 \cdot 10^{-2}$	1,51
$H_2PO_3^-$	$1{,}6 \cdot 10^{-7}$	6,80
$H_4P_2O_7$	$1{,}2 \cdot 10^{-1}$	0,91
$H_3P_2O_7^-$	$7{,}9 \cdot 10^{-3}$	2,10
$H_2P_2O_7^{2-}$	$2{,}0 \cdot 10^{-7}$	6,70
$HP_2O_7^{3-}$	$4{,}8 \cdot 10^{-10}$	9,32
H_2S	$1{,}0 \cdot 10^{-7}$	6,99
HS^-	$2{,}5 \cdot 10^{-13}$	12,6
H_2SO_3	$1{,}4 \cdot 10^{-2}$	1,85
HSO_3^-	$6{,}2 \cdot 10^{-8}$	7,20
HF	$6{,}2 \cdot 10^{-4}$	3,21
H_2O_2	$2{,}0 \cdot 10^{-12}$	11,7

Bases

Formula	K_b	pK_b
NH_3	$1{,}76 \cdot 10^{-5}$	4,75
N_2H_4	$9{,}3 \cdot 10^{-7}$	6,03
NH_2OH	$8{,}9 \cdot 10^{-9}$	8,05
CH_3NH_2	$4{,}6 \cdot 10^{-3}$	3,34
$C_6H_5NH_2$	$4{,}3 \cdot 10^{-10}$	9,37

Appendix 3. Ion activity coefficients at different values of the ionic strength of the solution

μ	γ_{M^+}	$\gamma_{M^{2+}}$	$\gamma_{M^{3+}}$	μ	γ_{M^+}	$\gamma_{M^{2+}}$	$\gamma_{M^{3+}}$
0,001	0,965	0,866	0,724	0,04	0,829	0,473	0,185
0,002	0,951	0,819	0,638	0,05	0,816	0,442	0,160
0,003	0,941	0,785	0,580	0,06	0,804	0,418	0,140
0,004	0,933	0,758	0,536	0,07	0,794	0,398	0,126
0,005	0,926	0,736	0,501	0,08	0,785	0,381	0,114
0,006	0,920	0,716	0,472	0,09	0,778	0,366	0,104
0,007	0,914	0,699	0,447	0,1	0,771	0,353	0,096
0,008	0,909	0,684	0,425	0,2	0,727	0,280	0,057
0,009	0,905	0,670	0,406	0,3	0,706	0,248	0,044
0,01	0,900	0,657	0,389	0,4	0,694	0,233	0,038
0,02	0,868	0,568	0,280	0,5	0,689	0,225	0,035
0,03	0,846	0,512	0,222	0,6	0,686	0,222	0,034

Appendix 4. Solubility products of low-soluble electrolytes at 25°C

Substance	Solubility products	Substance	Solubility products	Substance	Solubility products
$AgBr$	$6{,}3 \cdot 10^{-13}$	$Cd(OH)_2$	$2{,}4 \cdot 10^{-13}$	$NiCO_3$	$1{,}35 \cdot 10^{-7}$
$AgCl$	$1{,}56 \cdot 10^{-10}$	CdS	$3{,}6 \cdot 10^{-29}$	$Ni(OH)_2$	$1{,}6 \cdot 10^{-14}$
$AgCN$	$7 \cdot 10^{-15}$	$Co(OH)_2$	$1{,}6 \cdot 10^{-18}$	NiS (α)	$3 \cdot 10^{-21}$
$AgSCN$	$1{,}16 \cdot 10^{-12}$	CoS (α)	$3{,}1 \cdot 10^{-23}$	$PbCO_3$	$7{,}5 \cdot 10^{-14}$
Ag_2CO_3	$6{,}15 \cdot 10^{-12}$	$Cr(OH)_3$	$6{,}7 \cdot 10^{-31}$	$PbCl_2$	$1{,}7 \cdot 10^{-5}$
Ag_2CrO_4	$4{,}05 \cdot 10^{-12}$	$Cu(OH)_2$	$5{,}6 \cdot 10^{-20}$	$PbCrO_4$	$1{,}77 \cdot 10^{-14}$
$Ag_2Cr_2O_7$	$2 \cdot 10^{-7}$	CuC_2O_4	$2{,}5 \cdot 10^{-22}$	PbI_2	$8{,}7 \cdot 10^{-9}$
AgI	$1{,}5 \cdot 10^{-16}$	Cu_2S	$2 \cdot 10^{-47}$	$Pb(OH)_2$	$\sim 10^{-24}$
$AgOH$	$2 \cdot 10^{-8}$	CuS	$4 \cdot 10^{-38}$	PbS	$1{,}1 \cdot 10^{-29}$
Ag_2S	$5{,}7 \cdot 10^{-51}$	$FeCO_3$	$2{,}11 \cdot 10^{-11}$	$PbSO_4$	$1{,}8 \cdot 10^{-3}$
$Al(OH)_3$	$1{,}9 \cdot 10^{-33}$	$Fe(OH)_2$	$4{,}8 \cdot 10^{-16}$	$Sb(OH)_2$	$5 \cdot 10^{-26}$
$BaCO_3$	$7 \cdot 10^{-9}$	$Fe(OH)_3$	$3{,}8 \cdot 10^{-38}$	$Sb(OH)_3$	$4 \cdot 10^{-42}$
$BaCrO_4$	$2{,}3 \cdot 10^{-10}$	FeS	$3{,}7 \cdot 10^{-19}$	Sb_2S_3	$1 \cdot 10^{-30}$
$BaSO_4$	$1{,}08 \cdot 10^{-10}$	Hg_2Cl_2	$1{,}1 \cdot 10^{-18}$	$SnO(OH)$	$\sim 10^{-11}$
$Bi(OH)_3$	$4{,}3 \cdot 10^{-31}$	Hg_2I_2	$3{,}7 \cdot 10^{-29}$	SnS	$1 \cdot 10^{-28}$
Bi_2S_3	$1{,}6 \cdot 10^{-72}$	HgS	$4{,}0 \cdot 10^{-53}$	$SrCO_3$	$9{,}42 \cdot 10^{-10}$
$CaCO_3$	$4{,}8 \cdot 10^{-9}$	$MgCO_3 \cdot H_2O$	$1 \cdot 10^{-25}$	$SrC_2O_4 \cdot H_2O$	$5{,}6 \cdot 10^{-8}$
$CaC_2O_4 \cdot H_2O$	$7{,}7 \cdot 10^{-7}$	$Mg(OH)_2$	$5{,}5 \cdot 10^{-12}$	$SrCrO_4$	$3{,}6 \cdot 10^{-5}$
$CaCrO_4$	$2{,}3 \cdot 10^{-2}$	MgS	$2 \cdot 10^{-15}$	$SrSO_4$	$2{,}8 \cdot 10^{-7}$
$CaSO_4$	$6{,}26 \cdot 10^{-5}$	$Mn(OH)_2$	$5{,}5 \cdot 10^{-12}$	$Zn(OH)_2$	$1 \cdot 10^{-26}$
$CaSO_4 \cdot H_2O$	$1{,}3 \cdot 10^{-4}$	MnS	$5{,}6 \cdot 10^{-16}$	ZnS (β)	$1{,}1 \cdot 10^{-24}$

Appendix 5. Fötter refractions of chemical bonds

Bond	Bond refraction	Bond	Bond refraction
C–H	1,676	P–C	3,575
C–C	1,296	P–Cl	8,856
C=C	4,17	P–H	4,010
C≡C end	5,87	P–O	3,102
C≡C not end	6,24	P→O	-1,032
C–C cyclopropane circle	1,49	P–S	7,583
C–C cyclobutane circle	1,37	P=S	6,866
C–C cyclopentane circle	1,26	Si–C	2,52
C–C cyclohexane circle	1,27	Si–C_{ap}	2,93
C_{ap}–C_{ap}	2,688	Si–F	1,7
C–F*	1,44	Si–Cl	7,11
C–Cl	6,51	Si–Br	10,24
C–Br	9,39	Si–Si	5,89
C–I	14,61	Si–O	1,80
C–O ethers	1,54	Si–H	3,17
C–O acetals	1,46	Si–S	6,14
C=O	3,32	Si–N	2,16
C=O methylketones	3,49	Ge–C	3,05
C–S	4,61	Ge–Cl	7,6
C=S	11,91	Ge–Br	11,1
C–N**	1,57	Ge–I	16,7
C=N	3,76	Ge–F	1,3
C≡N	4,82	Ge–O	2,47
O–H alcohols	1,66	Ge–S	7,02
O–H acids	1,80	Ge–N	2,33
S–H	4,80	Pb–C	5,26
S–S	8,11	Hg–C	7,21
S–O	4,94	Sn–C	4,16
S→O	-0,20	Sn–C_{ap}	3,78
N–H	1,76	Sn–Cl	8,91
N–O	2,43	Sn–Br	12,00
N→O	1,78	Sn–I	17,92
N=O	4,00	Sn–Sn	10,77
N–N	1,99	Sn–O	3,84
N=N	4,12		

Appendix 5. Atomic refractions

Atoms, groups and features of their structure	Atomic refraction R_D
Carbon (with simple bonds)	2,418
Hydrogen	1,100
Oxygen	
in the hydroxyl group	1,525
on air	1,643
in the carboxyl group	2,211
Nitrogen	
in aliphatic amines	
primary	2,322
secondary	2,499
tertiary	2,840
in nitriles	3,070
in imitations	3,776
Chlorine	5,967
Bromine	8,865
Iodine	13,900

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