Problems and Exercises in General Chemistry

N. L. Glinka
Н. Л. Глинка

ЗАДАЧИ И УПРАЖНЕНИЯ
ПО ОБЩЕЙ ХИМИИ

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Preface

Professor N. Glinka's book *Problems and Exercises in General Chemistry* requires no special recommendation. For many years, it has won merited popularity both among secondary school pupils and higher school students and among lecturers in chemistry. This popularity is explained not only by the appropriate selection of the exercises and the clarity of the introductory passages preceding the problems, but also, which is of equal importance, by the congruity of the present book to the well-known textbook *General Chemistry* by the same author.

The late author last revised the book in 1964 when he was preparing its 13th edition; the succeeding Russian editions were published without any revision or alteration. During this period, however, Glinka's *General Chemistry* was revised quite appreciably, which was due both to the intensive development of the chemical science and to the changes in the secondary and higher school syllabuses in chemistry. This required the relevant revision of the problem book, carried out for the 21st Russian edition by a group of authors. The following chapters were completely or almost completely rewritten: Chapter 2, by T. E. Alekseeva, Cand. Sc. (Chem.), Chapters 3, 4, and 9, by Associate Professor N. B. Platunova, Cand.Sc. (Chem.), Chapter 5, by Associate Professors Kh. M. Rubina, Cand.Sc. (Chem.) and V. A. Rabinovich, Cand.Sc. (Chem.), and Chapter 8, by T. E. Khripunova, Cand.Sc. (Chem.) and V. A. Rabinovich. Chapters 1 and 10 were revised and supplemented by T. E. Alekseeva, Chapters 6 and 7—by Kh. M. Rubina, Chapter 11—by N. B. Platunova and T. E. Alekseeva.

This first English edition has been translated from the 21st Russian edition.
In addition to problems and exercises of a traditional form, many sections of the present book contain review questions that will permit the student to see how well he or she has mastered the relevant material. Each question is followed by a set of answers, from among which one or more correct ones must be chosen; sometimes it is also necessary to substantiate the answer by selecting the correct explanation from among a number of choices following the question. Should the chosen answer fail to coincide completely or partly with those given at the end of the book, this will indicate that the student must again study the introductory text to the given section, or the relevant material in the textbook.

In preparing this edition, the authors and editors tried to retain the style and merits of Glinka’s original problem book, and at the same time to bring it closer to the content and nature of the latest editions of Glinka’s General Chemistry. We shall be grateful to our readers—both students and lecturers—for all their remarks aimed at a further improvement of this book.

The authors express their gratitude to Prof. G. P. Luchinsky and Associate Professor Z. E. Golbraikh whose remarks and advice facilitated the improvement of the book.

V. A. Rabinovich, Kh. M. Rubina
Contents

Preface 5

Chapter 1. Simple Stoichiometric Calculations 11
1. Equivalent. Law of Equivalents 11
2. Fundamental Gas Laws 15
3. Partial Pressure of a Gas 18
5. Determining the Molecular Masses of Gaseous Substances 26
6. Derivation of Chemical Formulas. Calculations Involving Chemical Formulas and Equations 29

Chapter 2. Basic Classes of Inorganic Compounds 35

Chapter 3. Structure of the Atom. Radioactivity 45
1. Electronic Structure of Atoms. Dependence of Element Properties on the Structure of Their Atoms 45

Chapter 4. The Chemical Bond 59
1. Kinds of Chemical Bond. Ways of Forming a Covalent Bond 59
2. Molecular Polarities. Geometrical Structure of Molecules 68
3. Ionic Bond. Polarization of Ions 74
4. Hydrogen Bond. Intermolecular Interaction 77

Chapter 5. Fundamental Laws of Chemical Reactions 80
1. Energy Conversions in Reactions. Thermochemical Calculations 80
2. Rate of a Chemical Reaction. Chemical Equilibrium 95
Chapter 6. Solutions

1. Concentration of Solutions. Solubility 114
2. Energy Effects in the Formation of Solutions 123
3. Physicochemical Properties of Dilute Solutions of Non-Electrolytes 125

Chapter 7. Solutions of Electrolytes 132

1. Weak Electrolytes. Dissociation Constant and Degree of Dissociation 132
2. Strong Electrolytes. Activity of Ions 141
3. Ion Product of Water. pH 143
4. Solubility Product 148
5. Exchange Reactions in Electrolyte Solutions. Hydrolysis of Salts 154

Chapter 8. Oxidation-Reduction Reactions. Fundamentals of Electrochemistry 165

1. Oxidation Number. Oxidation and Reduction 165
2. Oxidizing and Reducing Agents 169
3. Balancing Oxidation-Reduction Equations 175
4. Chemical Sources of Electrical Energy. Electrode Potentials 182
5. Direction of Oxidation-Reduction Reactions 191
6. Electrolysis 195

Chapter 9. Complex Compounds 203

1. Determining the Composition of a Complex Ion 203
2. Nomenclature of Complex Compounds 205
3. Equilibria in Solutions of Complex Compounds 207

Chapter 10. General Properties of Metals. Alloys 212

Chapter 11. The Periodic System of Elements. Properties of Elements and Their Compounds 219

1. General 219
2. Hydrogen 220
3. The Halogens 222
4. Oxygen Subgroup Elements 225
5. Nitrogen Subgroup Elements 229
6. Carbon and Silicon 236
7. Group I Metals 238
8. Group II Metals. Water Hardness 241
9. Group III Elements 245
10. Metals of Groups IV, V, VI, and VII 247
11. The Noble Gases. Group VIII Metals 251
Appendix

Table 1. Selected SI Units 255
Table 2. Conversion of Selected Non-System Units to SI Units 256
Table 3. Values of Selected Fundamental Physical Constants 256
Table 4. Names of Most Important Acids and Their Salts 256
Table 5. Standard Enthalpies of Formation \( \Delta H^\circ_{\text{fus}} \), Entropies \( S^\circ_{\text{fus}} \), and Gibbs Energies of Formation \( \Delta G^\circ_{\text{fus}} \) of Selected Substances at 298 K (25 °C) 258
Table 6. Dissociation Constants of Selected Weak Electrolytes in Aqueous Solutions at 25 °C 260
Table 7. Activity Coefficients of Ions at Different Ionic Strengths of Solution 262
Table 8. Solubility Product \( K_{sp} \) of Selected Sparingly Soluble Electrolytes at 25 °C 263
Table 9. Standard Electrode Potentials \( \varphi^\circ \) in Aqueous Solutions at 25 °C 264
Table 10. Instability Constants of Selected Complex Ions in Aqueous Solutions at 25 °C 266
Table 11. Atomic Masses to Four Significant Figures 268

Mendeleev's Periodic Table of the Elements 270
Four-Place Logarithms 272
Answers to Problems 276
Index 284
1. Equivalent. Law of Equivalents

An equivalent of a substance is defined to be an amount of it such that combines with one mole of hydrogen atoms or replaces the same number of hydrogen atoms in chemical reactions.

The mass of one equivalent of an element is called its equivalent mass.

Example 1. Find the equivalent and the equivalent masses of the elements in the compounds HBr, H₂O, and NH₃.

Solution. In the compounds named, 1 mole of bromine atoms, 1/2 mole of oxygen atoms, and 1/3 mole of nitrogen atoms combine with one mole of hydrogen atoms. Consequently, by definition, the equivalents of bromine, oxygen, and nitrogen are 1 mole, 1/2 mole, and 1/3 mole, respectively. Proceeding from the molar masses of atoms of these elements, we find that the equivalent mass of bromine is 79.9 g/mol, of oxygen 16 × 1/2 = 8 g/mol, and of nitrogen 14 × 1/3 = 4.67 g/mol.

To determine the equivalent (or equivalent mass) of an element, we do not necessarily have to proceed from its hydrogen compound. The equivalent (equivalent mass) can be calculated using the composition of a compound of the given element with any other one whose equivalent is known.

Example 2. When 5.6 g of iron combined with sulphur, 8.8 g of iron sulphide were formed. Find the equivalent mass of iron and its equivalent if the equivalent mass of sulphur is 16 g/mol.

Solution. It follows from the data of the example that iron sulphide contains 8.8 - 5.6 = 3.2 g of sulphur per 5.6 g of iron. According to the law of equivalents, the masses of reacting substances are proportional to their equivalent masses. Hence,

5.6 g of iron are equivalent to 3.2 g of sulphur

\[ E_{Fe} \text{ g/mol of iron are equivalent to } 16 \text{ g/mol of sulphur whence } \]

\[ E_{Fe} = \frac{5.6 \times 16}{3.2} = 28 \text{ g/mol} \]
The molar mass of iron numerically coinciding with its relative molecular mass is 56 g/mol. Since the equivalent mass of iron (28 g/mol) is half the molar mass of its atoms, one mole of iron contains two equivalents. Consequently, the equivalent of iron is \( \frac{1}{2} \) mole.

The law of equivalents allows us to derive the following formulas for calculating the equivalent masses of compounds:

\[
E_{\text{oxide}} = \frac{M_{\text{oxide}}}{\text{Number of element atoms} \times \text{Valence of element}}
\]

\[
E_{\text{acid}} = \frac{M_{\text{acid}}}{\text{Basicity of acid}}
\]

\[
E_{\text{base}} = \frac{M_{\text{base}}}{\text{Acidity of base}}
\]

\[
E_{\text{salt}} = \frac{M_{\text{salt}}}{\text{Number of metal atoms} \times \text{Valence of metal}}
\]

where \( M \) is the molar mass of the relevant compound.

Example 3. Determine the mass of the sodium hydrogen sulphate formed when a solution containing 8 g of NaOH is neutralized with sulphuric acid.

Solution. We find the equivalent mass of sodium hydroxide:

\[ E(\text{NaOH}) = \frac{M(\text{NaOH})}{1} = 40 \text{ g/mol}. \]

Consequently, 8 g of NaOH form \( \frac{8}{40} = 0.2 \) of the equivalent mass of NaOH. According to the law of equivalents, the mass of the salt formed is also 0.2 of its equivalent mass.

We find the equivalent mass of the salt:

\[ E(\text{NaHSO}_4) = \frac{M(\text{NaHSO}_4)}{1} = 120 \text{ g/mol}. \]

The mass of the sodium hydrogen sulphate formed is \( 120 \times 0.2 = 24 \text{ g} \).

In solving problems containing information on the volumes of gaseous reactants, it is good practice to use the value of the equivalent volume.

The equivalent volume is defined as the volume occupied in the given conditions by one equivalent of a substance. The value of the equivalent volume of a gaseous substance can be found if we remember that the molar volume of any gas consisting of monatomic molecules contains one mole of atoms, that of a gas consisting of diatomic molecules—two moles of atoms, and so on. For instance, 22.4 litres of H\(_2\) in standard conditions (standard temperature and pressure)
contain two moles of hydrogen atoms. Since the equivalent of hydrogen is one mole, 22.4 litres of \( \text{H}_2 \) contain two hydrogen equivalents; hence, the equivalent volume of hydrogen is \( 22.4/2 = 11.2 \text{ l/mol} \).

**Example 4.** A certain amount of a metal whose equivalent mass is 28 g/mol displaces 0.7 litre of hydrogen measured in standard conditions from an acid. Find the mass of the metal.

**Solution.** Knowing that the equivalent volume of hydrogen is 11.2 l/mol, we form a proportion:

\[
\frac{28 \text{ g metal}}{x \text{ g metal}} = \frac{11.2 \text{ litres} \text{ hydrogen}}{0.7 \text{ litre} \text{ hydrogen}}
\]

Solving for \( x \):

\[
x = \frac{0.7 \times 28}{11.2} = 1.75 \text{ g}
\]

**PROBLEMS**

1. In the combustion of 5.00 g of a metal, 9.44 g of the metal oxide are formed. Find the equivalent mass of the metal.

2. The same amount of a metal combines with 0.200 g of oxygen and with 3.17 g of a halogen. Calculate the equivalent mass of the halogen.

3. The mass of one litre of oxygen is 1.4 g. How many litres of oxygen are needed for the combustion of 21 g of magnesium whose equivalent is \( 1/2 \) mole?

4. Find the equivalent masses of a metal and sulphur if 3.24 g of the metal form 3.48 g of its oxide and 3.72 g of its sulphide.

5. Calculate the atomic mass of a divalent metal and determine the metal if 8.34 g of it are oxidized by 0.680 litre of oxygen (in standard conditions).

6. Arsenic forms two oxides one of which contains 65.2% and the other 75.7% of the element. Determine the equivalent masses of arsenic in both cases.

7. 1.00 g of a metal combines with 8.89 g of bromine and with 1.78 g of sulphur. Find the equivalent masses of bromine and the metal if the equivalent mass of sulphur is 16.0 g/mol.

8. The equivalent mass of chlorine is 35.5 g/mol, and the molar mass of copper atoms is 63.5 g/mol. The equivalent mass of copper chloride is 99.5 g/mol. What is the formula of copper chloride?
9. 14.7 g of sulphuric acid were needed to dissolve 16.8 g of a metal. Calculate the equivalent mass of the metal and the volume of the hydrogen liberated (in standard conditions).

10. The reduction of 1.80 g of a metal oxide required 833 ml of hydrogen measured in standard conditions. Calculate the equivalent masses of the oxide and the metal.

11. A certain amount of a metal whose equivalent mass is 27.9 g/mol displaces 700 ml of hydrogen measured in standard conditions from an acid. Find the mass of the metal.

12. Identical amounts of hydrogen are displaced from an acid by 1.60 g of calcium and 2.16 g of zinc. Determine the equivalent mass of zinc knowing that the equivalent mass of calcium is 20.0 g/mol.

13. Sulphuric and orthophosphoric acids have the same molecular mass. What is the ratio of the masses of these acids needed to neutralize the same amount of an alkali if the sulphate and dihydrogen orthophosphate were formed, respectively?

14. Copper forms two oxides. For the same amount of copper, twice as much oxygen was used to form the first oxide than to form the second one. What is the ratio of the valences of the copper in the first and second oxides?

15. The salt Na₂HPO₄ formed when orthophosphoric acid was reacted with an alkali. Find the equivalent mass of orthophosphoric acid for this case.

16. The neutralization of 2.45 g of an acid requires 2.00 g of sodium hydroxide. Calculate the equivalent mass of the acid.

17. The reaction of 5.95 g of a substance with 2.75 g of hydrogen chloride yielded 4.40 g of a salt. Calculate the equivalent masses of the substance and the salt formed.

18. 0.376 g of aluminium reacted with an acid to displace 0.468 litre of hydrogen measured in standard conditions. Find the equivalent volume of the hydrogen knowing that the equivalent mass of aluminium is 8.99 g/mol.

REVIEW QUESTIONS

19. What does the equivalent of a chemical element depend on? (a) On the valence of the element; (b) it is always a constant quantity.
20. Which of the following two formulas expresses the law of equivalents correctly?

(a) \( \frac{m_1}{m_2} = \frac{E_2}{E_1} \); (b) \( m_1E_2 = E_1m_2 \)

21. Phosphorus forms two chlorides differing in composition. The equivalent of which element remains constant in these compounds? (a) Chlorine; (b) phosphorus.

22. Choose the correct values of the equivalent volumes of oxygen and hydrogen in standard conditions: (a) 11.2 litres of \( O_2 \) and 22.4 litres of \( H_2 \); (b) 11.2 litres of \( O_2 \) and 11.2 litres of \( H_2 \); (c) 5.6 litres of \( O_2 \) and 11.2 litres of \( H_2 \).

23. The equivalent mass of a metal is 12 g/mol. What is the equivalent mass of its oxide? (a) 24 g/mol; (b) it cannot be determined; (c) 20 g/mol.

24. The equivalent mass of a metal is double that of oxygen. How many times is the mass of its oxide greater than the mass of the metal? (a) 1.5 times; (b) 2 times; (c) 3 times.

25. Sulphur forms the chlorides \( S_2Cl_2 \) and \( SCl_3 \); the equivalent mass of the sulphur in \( SCl_3 \) is 16 g/mol. Choose the correct value of the equivalent mass of the sulphur in \( S_2Cl_2 \): (a) 8 g/mol; (b) 16 g/mol; (c) 32 g/mol.

26. Is the equivalent of chromium in the compounds \( CrCl_3 \) and \( Cr_2(SO_4)_3 \) the same? (a) Yes; (b) no.

27. Is the equivalent mass of iron in the compounds \( FeCl_2 \) and \( FeCl_3 \) the same? (a) Yes; (b) no.

2. Fundamental Gas Laws

The state of a gas is characterized by its temperature, pressure, and volume. If the temperature of a gas is 0 °C, and its pressure equals standard atmospheric pressure (101.325 kPa or 760 mmHg), the conditions in which the gas is are called standard. The volume occupied by a gas in these conditions is denoted by \( V_0 \), and the pressure by \( p_0 \).

According to Boyle’s law, at constant temperature, the pressure of a gas is inversely proportional to its volume:

\[ \frac{p_2}{p_1} = \frac{V_1}{V_2} \quad \text{or} \quad pV = \text{const} \]
Example 1. At a certain temperature, the pressure of a gas occupying a volume of 3 litres is 93.3 kPa (700 mmHg). What will the pressure be if the volume of the gas is diminished to 2.8 litres without changing the temperature?

Solution. Denoting the required pressure by \( p_2 \), we can write:

\[
\frac{p_2}{93.3} = \frac{3}{2.8}
\]

whence

\[
p_2 = \frac{93.3 \times 3}{2.8} = 100 \text{ kPa (750 mmHg)}
\]

Gay-Lussac's law states that at constant pressure, the volume of a gas is directly proportional to the absolute temperature (\( T \)):

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad \frac{V}{T} = \text{const}
\]

Example 2. At 27 °C, the volume of a gas is 600 ml. What volume will the gas occupy at 57 °C if the pressure remains constant?

Solution. Let us denote the required volume by \( V_2 \), and the temperature corresponding to it by \( T_2 \). According to the data of the example, \( V_1 = 600 \text{ ml} \), \( T_1 = 273 + 27 = 300 \text{ K} \), and \( T_2 = 273 + 57 = 330 \text{ K} \). Using these values in the expression of Gay-Lussac's law, we get:

\[
\frac{600}{300} = \frac{V_2}{330}
\]

whence

\[
V_2 = \frac{600 \times 330}{300} = 660 \text{ ml}
\]

At constant volume, the pressure of a gas is directly proportional to the absolute temperature:

\[
\frac{p_1}{T_1} = \frac{p_2}{T_2}
\]

Example 3. At 15 °C, the pressure in a cylinder with oxygen is \( 91.2 \times 10^3 \) kPa. At what temperature will it become equal to \( 101.33 \times 10^3 \) kPa?

Solution. Let the required temperature be \( T_2 \). According to the data of the example, \( T_1 = 273 + 15 = 288 \text{ K} \), \( p_1 = 91.2 \times 10^3 \text{ kPa} \), and \( p_2 = 101.33 \times 10^3 \text{ kPa} \). Introducing these values into the last equation, we find

\[
T_2 = \frac{101.33 \times 10^3 \times 288}{91.2 \times 10^3} = 320 \text{ K or } 47 \text{ °C}
\]
The relationship between the volume of a gas, its pressure, and temperature can be expressed with the aid of an equation combining Boyle’s and Gay-Lussac’s laws and expressing the combined gas law:

\[ \frac{pV}{T} = \frac{p_0V_0}{T_0} \]

where \( p \) and \( V \) are the pressure and volume of a gas at the given temperature \( T \), and \( p_0 \) and \( V_0 \) are the volume and pressure of the gas in standard conditions.

This equation allows us to find any of the quantities indicated if the others are known.

Example 4. At 25 °C and a pressure of 99.3 kPa (745 mmHg), a certain amount of a gas occupies a volume of 152 ml. Calculate the volume that the same amount of the gas will occupy at 0 °C and a pressure of 101.33 kPa.

Solution. Using the data of the example in the last equation, we obtain:

\[ V_0 = \frac{pVT_0}{p_0T} = \frac{99.3 \times 152 \times 273}{101.33 \times 298} = 136.5 \text{ ml} \]

PROBLEMS

28. At 17 °C, a certain amount of a gas occupies a volume of 580 ml. What volume will the same amount of the gas occupy at 100 °C if its pressure remains constant?

29. The pressure of a gas occupying a volume of 2.5 litres is 121.6 kPa (912 mmHg). What will its pressure be if the gas is compressed to a volume of one litre without changing its temperature?

30. By how many kelvins must a gas confined in a closed vessel at 0 °C be heated for its pressure to increase twofold?

31. At 27 °C and a pressure of 720 mmHg, the volume of a gas is 5 litres. What volume will the same amount of gas occupy at 39 °C and a pressure of 104 kPa?

32. The pressure of a gas in a closed vessel is 96.0 kPa at 7 °C. What will the pressure be if the vessel is cooled to −33 °C?

33. In standard conditions, 1 g of air occupies a volume of 773 ml. What volume will the same mass of air occupy at 0 °C and a pressure of 93.3 kPa (700 mmHg)?
34. The pressure of a gas in a closed vessel at 12 °C is 100 kPa (750 mmHg). What will the pressure of the gas be if the vessel is heated to 30 °C?
35. A steel cylinder with a capacity of 12 litres contains oxygen under a pressure of 15.2 MPa at 0 °C. What volume of oxygen in standard conditions can be obtained from the cylinder?
36. The temperature of nitrogen in a steel cylinder at a pressure of 15.2 MPa is 17 °C. The maximum pressure tolerated for the cylinder is 20.3 MPa. At what temperature will the pressure of the nitrogen reach the maximum permissible value?
37. A certain amount of a gas occupies a volume of 608 ml at a pressure of 98.7 kPa and a temperature of 91 °C. Find the volume of the gas in standard conditions.
38. The reaction of 1.28 g of a metal with water liberated 380 ml of hydrogen measured at 21 °C and 104.5 kPa (784 mmHg). Determine the equivalent mass of the metal.

REVIEW QUESTIONS

39. How should the conditions be changed to prevent the volume of a given gas from growing when its mass is increased? (a) The temperature must be lowered; (b) the pressure must be increased; (c) no conditions can be found.
40. What values of the temperature and pressure correspond to standard conditions for gases? (a) \( t = 25 ^\circ C, \ p = 760 \ \text{mmHg} \); (b) \( t = 0 ^\circ C, \ p = 1.013 \times 10^5 \ \text{Pa} \); (c) \( t = 0 ^\circ C, \ p = 760 \ \text{mmHg} \).

3. Partial Pressure of a Gas

The partial pressure of a gas in a mixture is the pressure which the gas would exert if it alone occupied the entire volume that the mixture occupied in the same physical conditions.

Example 1. Two litres of \( O_2 \) and four litres of \( SO_2 \) taken at the same pressure equal to 100 kPa (750 mmHg) are mixed; the volume of the mixture is six litres. Calculate the partial pressures of the gases in the mixture.
Solution. According to the data of the example, the volume of the oxygen increased after being mixed by $6/2 = 3$ times, and that of the sulphur dioxide by $6/4 = 1.5$ times. The partial pressures of the gases diminished by the same number of times. Hence, $p(O_2) = 100/3 = 33.3$ kPa, and $p(SO_2) = 100/1.5 = 66.7$ kPa.

The law of partial pressures states that the total pressure of a mixture of gases that do not react chemically with one another equals the sum of the partial pressures of each gas in the mixture.

Example 2. Three litres of CO$_2$ are mixed with four litres of O$_2$ and six litres of N$_2$. Prior to mixing, the pressures of the CO$_2$, O$_2$, and N$_2$ were 96, 108, and 90.6 kPa, respectively. The total volume of the mixture is 10 litres. Find the pressure of the mixture.

Solution. Similar to the solution of the preceding example, we determine the partial pressures of the individual gases:

\[
p(CO_2) = \frac{96 \times 3}{10} = 28.8 \text{ kPa}
\]
\[
p(O_2) = \frac{108 \times 4}{10} = 43.2 \text{ kPa}
\]
\[
p(N_2) = \frac{90.6 \times 6}{10} = 54.4 \text{ kPa}
\]

The total pressure of the gas mixture equals the sum of the partial pressures:

\[
p = 28.8 + 43.2 + 54.4 = 126.4 \text{ kPa}
\]

If a gas is collected over a liquid, it must be borne in mind in calculations that its pressure is partial and equals the difference between the total pressure of the gas mixture and the partial pressure of the vapour of the liquid.

Example 3. What volume is occupied in standard conditions by 120 ml of nitrogen collected over water at 20 °C and a pressure of 100 kPa (750 mmHg)? The pressure of saturated water vapour at 20 °C is 2.3 kPa.

Solution. The partial pressure of the nitrogen equals the difference between the total pressure and the partial pressure of the water vapour:

\[
p(N_2) = p - p(H_2O) = 100 - 2.3 = 97.7 \text{ kPa}
\]

Denoting the required volume by $V_0$ and using the equation of the combined gas law, we get:

\[
V_0 = \frac{pVT_0}{TP_0} = \frac{97.7 \times 120 \times 273}{293 \times 101.3} = 108 \text{ ml}
\]
PROBLEMS

41. Nitrogen under a pressure of 96 kPa (720 mmHg) in an amount of 0.04 m³ is mixed with 0.02 m³ of oxygen. The total volume of the mixture is 0.06 m³, and its total pressure is 97.6 kPa (732 mmHg). What was the pressure of the oxygen taken?

42. A gas mixture is prepared from 2 litres of H₂ (p = 93.3 kPa) and 5 litres of CH₄ (p = 112 kPa). The total volume of the mixture is 7 litres. Find the partial pressures of the gases and the total pressure of the mixture.

43. A gas mixture consists of NO and CO₂. Calculate the content of the gases in the mixture in % (vol.) if their partial pressures are 36.3 and 70.4 kPa (272 and 528 mmHg).

44. A closed vessel with a capacity of 0.6 m³ contains a mixture consisting of 0.2 kg of CO₂, 0.4 kg of O₂, and 0.15 kg of CH₄ at 0 °C. Calculate (a) the total pressure of the mixture; (b) the partial pressure of each gas; and (c) the composition of the mixture in per cent (volume).

45. A gas mixture has been prepared from 0.03 m³ of CH₄, 0.04 m³ of H₂, and 0.01 m³ of CO. The initial pressures of the CH₄, H₂, and CO were 96, 84, and 108.8 kPa (720, 630, and 816 mmHg), respectively. The volume of the mixture is 0.08 m³. Determine the partial pressures of the gases and the total pressure of the mixture.

46. A gas meter over water contains 7.4 litres of oxygen at 23 °C and 104.1 kPa (781 mmHg). The pressure of saturated water vapour at 23 °C is 2.8 kPa (21 mmHg). What volume will be occupied by the oxygen in the gas meter in standard conditions?

47. 0.350 g of a metal displaced from an acid 209 ml of hydrogen collected over water at 20 °C and 104.3 kPa. The pressure of saturated water vapour at this temperature is 2.3 kPa. Find the equivalent mass of the metal.

48. 250 ml of hydrogen are collected over water at 26 °C and 98.7 kPa. The pressure of saturated water vapour at 26 °C is 3.4 kPa. Calculate the volume of the hydrogen in standard conditions and its mass.

49. 0.604 g of a divalent metal displaced from an acid 581 ml of hydrogen collected over water at 18 °C and 105.6 kPa. The pressure of saturated water vapour at 18 °C is 2.1 kPa. Find the relative atomic mass of the metal.
REVIEW QUESTIONS

50. A vessel is filled with a mixture of oxygen and nitrogen. At what ratio of the partial pressures will the masses of the gases be identical? (a) \( p(O_2) = p(N_2) \); (b) \( p(O_2) = 0.875 \ p(N_2) \); (c) \( p(O_2) = 1.14 \ p(N_2) \).

51. The partial pressure of oxygen in the air is 22 kPa. What is the oxygen content in per cent (volume)? (a) 42%; (b) 21%; (c) 10.5%.

52. Hydrogen was collected in one case over water, and in another over mercury in the same conditions. In both cases, the volume of the gas was the same. Were identical amounts of hydrogen collected over both liquids? (a) Yes; (b) the amount of hydrogen collected over the mercury was greater; (c) the amount of hydrogen collected over the water was greater.

Molar Volume of a Gas

In addition to the mass and volume, the amount of substance proportional to the number of elementary entities contained in a substance is often used in chemical calculations. In each case, the elementary entity (molecule, atom, ion, etc.) must be specified exactly. The unit of the amount of substance is the mole.

The mole is the amount of a substance containing as many molecules, atoms, ions, electrons, or other elementary entities as there are carbon atoms in 0.012 kilogram of the carbon isotope \(^{12}\text{C}\).

The number of elementary entities contained in one mole of a substance (Avogadro’s number) has been determined with a high accuracy. In practical calculations, it is taken equal to \(6.02 \times 10^{23}\) mol\(^{-1}\).

It is not difficult to show that the mass of one mole of a substance (its molar mass) expressed in grams numerically equals the relative molecular mass of the substance expressed in atomic mass units.*

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* The atomic mass unit (amu) is defined as \(1/12\)th of the mass of an atom of the carbon isotope \(^{12}\text{C}\). \(1\ \text{amu} = 1.66 \times 10^{-27}\) kg.
For instance, the relative molecular mass (or simply the molecular mass) of free chlorine Cl$_2$ is 70.90 amu. Consequently, the molar mass of molecular chlorine is 70.90 g/mol. But the molar mass of chlorine atoms is half this value (35.45 g/mol) because one mole of chlorine molecules Cl$_2$ contains two moles of chlorine atoms.

Example 1. Express the mass of one molecule of CO$_2$ in grams.

Solution. The molecular mass of CO$_2$ is 44.0 amu. Consequently, the molar mass of CO$_2$ is 44.0 g/mol. One mole of CO$_2$ contains $6.02 \times 10^{23}$ molecules. Hence we find the mass of one molecule:

$$m = \frac{44.0}{6.02 \times 10^{23}} = 7.31 \times 10^{-23} \text{ g}$$

Avogadro's law states that \textit{equal volumes of all gases at the same temperature and pressure contain the same number of molecules.}

In other words, the same number of molecules of any gas occupies the same volume in identical conditions. But one mole of any gas contains the same number of molecules. Therefore, one mole of any gas occupies the same volume in identical conditions. This volume is known as the \textit{molar volume} of a gas and in standard conditions (0 °C, a pressure of 101.325 kPa) it is 22.4 litres.

Example 2. A mixture of equivalent amounts of hydrogen and oxygen is in a closed vessel at a temperature above 100 °C. How will the pressure in the vessel change if the mixture is exploded and the contents of the vessel are then returned to their initial temperature?

Solution. When hydrogen and oxygen react, every two molecules of H$_2$ and one molecule of O$_2$ yield two molecules of H$_2$O. Consequently, as a result of the reaction, the total number of molecules diminishes to two-thirds of the original one. Since the reaction proceeds at constant volume, and upon completion of the reaction the contents of the vessel are returned to their initial temperature, a decrease in the number of molecules to two-thirds of the original one leads to a similar decrease in the pressure.

Example 3. Calculate the volume occupied by 5.25 g of nitrogen at 26 °C and 98.9 kPa (742 mmHg).

Solution. Knowing the molar volume and molar mass (28.0 g/mol) of nitrogen, we calculate the volume that will be occupied by 5.25 g of nitrogen in standard conditions:

28.0 g of nitrogen occupy a volume of 22.4 litres
5.25 g of nitrogen occupy a volume of $V_0$

whence

$$V_0 = \frac{5.25 \times 22.4}{28.0} = 4.20 \text{ litres}$$
We next reduce the volume obtained to the conditions indicated in the example:

\[ V = \frac{p_0 V_0 T}{pT_0} = \frac{101.3 \times 4.20 \times 299}{98.9 \times 273} = 4.71 \text{ litres} \]

The volume content of a gas in a gas mixture is defined as the part of the volume of the gas mixture that would be occupied by the amount of the given gas contained in it at the same temperature and at a partial pressure equal to the total pressure of the gas mixture; this quantity can be expressed as a fraction of the total volume (a volume fraction) or as a percentage of the total volume (a per cent by volume).

For instance, the statement that "the content of carbon dioxide in air is 0.03% (vol.)" signifies that at a partial pressure of CO₂ equal to the total pressure of the air, and at the same temperature, the carbon dioxide contained in the air occupies 0.03% of the total volume occupied by the air.

Example 4. How many moles of oxygen are contained in one litre of air if its volume content is 21% (in standard conditions)?

Solution. In standard conditions, the oxygen contained in one litre of air occupies a volume of 0.21 litre. Knowing the molar volume of oxygen, we find the number of its moles in 0.21 litre of O₂:

1 mole occupies a volume of 22.4 litres
\[ x \text{ moles occupy a volume of } 0.21 \text{ litre} \]

\[ x = \frac{0.21}{22.4} = 0.093 \text{ mole of O}_2 \]

PROBLEMS

53. Compare the numbers of molecules contained in 1 g of NH₃ and in 1 g of N₂. In what case and how many times is the number of molecules greater?

54. Express the mass of one molecule of sulphur dioxide in grams.

55. Is the number of molecules in 0.001 kg of H₂ and in 0.001 kg of O₂ the same? In one mole of H₂ and in one mole of O₂? In one litre of H₂ and in one litre of O₂ in identical conditions?

56. How many molecules are there in 1.00 ml of hydrogen in standard conditions?

57. What volume is occupied by $27 \times 10^{21}$ molecules of a gas in standard conditions?
58. What is the ratio of the volumes occupied by one mole of O₂ and one mole of O₃ (in identical conditions)?
59. Equal masses of oxygen, hydrogen, and methane are taken in identical conditions. Find the ratio of the volumes of the gases.
60. The answer received to the question as to what volume will be occupied by one mole of water in standard conditions was 22.4 litres. Is this answer correct?
61. How many molecules of carbon dioxide are contained in one litre of air if the volume content of the CO₂ is 0.03% (in standard conditions)?
62. Calculate the mass of (a) 2 litres of H₂ at 15 °C and 100.7 kPa (755 mmHg); (b) 1 m³ of N₂ at 10 °C and 102.9 kPa (772 mmHg); and (c) 0.5 m³ of Cl₂ at 20 °C and 99.9 kPa (749.3 mmHg).
63. Determine the volume occupied by 0.07 kg of N₂ at 21 °C and 142 kPa (1065 mmHg).
64. Potassium chlorate when heated decomposes with the formation of KCl and O₂. How many litres of oxygen at 0 °C and 101.3 kPa can be produced from one mole of KClO₃?
65. How many moles are there in 1 m³ of any gas in standard conditions?
66. What is the atmospheric pressure at the peak of a mountain if at 0 °C the mass of one litre of air taken there is 700 mg?
67. The reaction of one volume of CO and one volume of Cl₂ yields one volume of phosgene. Find its formula.
68. What volume of CO₂ is obtained in the combustion of two litres of butane? The volumes of both gases have been measured in identical conditions.
69. A closed vessel contains a mixture consisting of three volumes of O₂ and one volume of CH₄ at 120 °C and 600 kPa. What will the pressure in the vessel be if the mixture is exploded and the contents of the vessel are returned to their initial temperature?
70. After the explosion of 0.020 litre of a mixture of hydrogen and oxygen, 0.0032 litre of the latter remained. Find the initial composition of the mixture in per cent by volume.
71. When a mixture of equal volumes of SO₂ and O₂ passes through a contact apparatus, 90% of the SO₂ mole-
cules transform into SO₃. Calculate the composition (in percent by volume) of the gas mixture leaving the contact apparatus.

72. A mixture consisting of three volumes of Cl₂ and one volume of H₂ was left standing in a closed vessel in diffused light at a constant temperature. After some time, the chlorine content in the mixture diminished by 20%. Did the pressure in the vessel change? What did the composition of the mixture become (in percent by volume)?

73. The reaction of NH₃ with Cl₂ yields hydrogen chloride and nitrogen. In what volume proportions do the NH₃ and Cl₂ react and what is the ratio of the volumes of the gases produced?

74. What volume of H₂ (at 17 °C and 102.4 kPa) is liberated when 1.5 kg of zinc are dissolved in hydrochloric acid?

75. The explosion of a mixture consisting of one volume of a gas being studied and one volume of H₂ yielded one volume of water vapour and one volume of nitrogen. All the measurements were made in identical conditions. Find the formula of the gas being studied.

REVIEW QUESTIONS

76. Equal volumes of N₂ and O₂ are taken in identical conditions. What is the relationship between the masses of the two gases? (a) \( m(O₂) > m(N₂) \); (b) \( m(N₂) > m(O₂) \); (c) \( m(O₂) = m(N₂) \).

77. Equal volumes of H₂ and Cl₂ were mixed. How will the volume of the mixture change after the reaction? (a) It will not change; (b) it will increase twofold; (c) it will be halved.

78. What is the relationship between the volumes occupied by one mole of HCl and one mole of Cl₂ (\( T \) and \( p \) are the same)? (a) \( V(HCl) > V(Cl₂) \); (b) \( V(HCl) = V(Cl₂) \); (c) \( V(HCl) < V(Cl₂) \).

79. When heated, HBr decomposes to the end. The volume of the gas does not change. What are the products of the decomposition reaction? (a) H and Br atoms; (b) H₂ and Br₂ molecules; (c) H₂ molecules and Br atoms.
5. Determining the Molecular Masses of Gaseous Substances

To find the molecular mass of a substance in amu, the molar mass of the substance in g/mol numerically equal to it is usually determined.

A. Determination of the Molecular Mass from the Density of a Gas.

Example 1. The density of a gas relative to air is 1.17. Find the molecular mass of the gas.

Solution. It follows from Avogadro’s law that at the same pressure and the same temperature the masses (m) of equal volumes of gases relate to each other like their molar masses (M):

\[ \frac{m_1}{m_2} = \frac{M_1}{M_2} \]

where \( m_1/m_2 \) is the relative density of the first gas with respect to the second, denoted by the symbol \( d \).

Hence, according to the data of the example:

\[ d = \frac{M_1}{M_2} = 1.17 \]

The average molar mass of air \( M_2 \) is 29.0 g/mol. Consequently, \( M_1 = 1.17 \times 29.0 = 33.9 \) g/mol, which corresponds to a molecular mass of 33.9 amu.

B. Determination of the Molecular Mass of a Gas from Its Molar Volume.

Example 2. Determine the molecular mass of a gas if in standard conditions 0.824 g of it occupies a volume of 0.260 litre.

Solution. In standard conditions, one mole of any gas occupies a volume of 22.4 litres. By calculating the mass of 22.4 litres of the given gas, we shall find its molar mass.

0.824 g of the gas occupies a volume of 0.260 litre

\[ x \text{ g of the gas occupy a volume of 22.4 litres} \]

\[ x = \frac{22.4 \times 0.824}{0.260} = 71.0 \text{ g} \]

Consequently, the molar mass of the gas is 71.0 g/mol, and its molecular mass is 71 amu.

C. Determination of the Molecular Mass from the Clapeyron-Mendeleev Equation.

The Clapeyron-Mendeleev equation (equation of state of an ideal gas) relates the mass \( (m, \text{ kg}) \), temperature \( (T, \text{ K}) \), pressure \( (p, \text{ Pa}) \), and volume \( (V, \text{ m}^3) \) of a gas to its molar
mass \( (M, \, \text{kg/mol}) \):

\[
pV = \frac{m}{M} RT
\]

Here \( R \) is the molar gas constant equal to 8.314 J (mol \cdot K)^{-1}. Using this equation, we can calculate the value of any of the quantities in it if we know the other ones.

Example 3. Calculate the molar mass of benzene if the mass of 600 ml of its vapour at a temperature of 87 °C and a pressure of 83.2 kPa is 1.30 g.

Solution. We convert the data of the example to SI units \( (p = 8.32 \times 10^4 \, \text{Pa}, \, V = 6 \times 10^{-4} \, \text{m}^3, \, m = 1.30 \times 10^{-3} \, \text{kg}, \, \text{and} \, T = 360 \, \text{K}) \) and introduce the results obtained into the Clapeyron-Mendeleev equation. We get:

\[
M = \frac{1.30 \times 10^{-3} \times 8.31 \times 360}{8.32 \times 10^4 \times 6 \times 10^{-4}} = 78.0 \times 10^{-3} \, \text{kg/mol} = 78.0 \, \text{g/mol}
\]

The molecular mass of benzene is 78.0 amu.

PROBLEMS

80. The mass of 200 ml of acetylene in standard conditions is 0.232 g. Find the molar mass of acetylene.

81. Calculate the molar mass of a gas if the mass of 600 ml of it in standard conditions is 1.714 g.

82. The mass of 0.001 m^3 of a gas (0 °C, 101.33 kPa) is 1.25 g. Calculate (a) the molar mass of the gas; (b) the mass of one molecule of the gas.

83. The mass of 0.001 m^3 of a gas in standard conditions is 0.0021 kg. Determine the molar mass of the gas and its density relative to air.

84. The density of ethylene relative to oxygen is 0.875. Find the molecular mass of the gas.

85. The mass of 0.001 m^3 of a gas in standard conditions is 0.004 52 kg, while the mass of 0.001 m^3 of nitrogen is 0.004 25 kg. Calculate the molecular mass of the gas proceeding from (a) its density relative to nitrogen; (b) the molar volume.

* In other units, \( R \) has the following values: 62.36 l \cdot \text{mmHg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}; 1.987 \, \text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.
86. How many atoms do mercury vapour molecules consist of if the density of mercury vapour relative to air is 6.92?

87. At a certain temperature, the density of sulphur vapour relative to nitrogen is 9.14. How many atoms does a sulphur molecule consist of at this temperature?

88. Calculate the molar mass of acetone if the mass of 500 ml of its vapour at a temperature of 87 °C and a pressure of 96 kPa (720 mmHg) is 0.93 g.

89. The mass of 624 ml of a gas is 1.56 g at 17 °C and 104 kPa (780 mmHg). Calculate the molecular mass of the gas.

90. What volume is occupied by 1 kg of air at 17 °C and 101.33 kPa?

91. A 20-litre gas meter is filled with a gas. The density of the gas relative to air is 0.40, its pressure is 103.3 kPa (774.8 mmHg), and its temperature is 17 °C. Calculate the mass of the gas.

92. The mass of a 750-ml flask filled with oxygen at 27 °C is 83.3 g. The mass of the empty flask is 82.1 g. Find the pressure of the oxygen.

93. Calculate the mass of 1 m³ of air at 17 °C and 83.2 kPa (624 mmHg).

**REVIEW QUESTIONS**

94. Which of the facts listed below can be a proof of the fact that gaseous neon is monatomic? (a) Neon forms no compounds with other elements; (b) the density of neon is half that of the noble gas argon following it in the periodic table; (c) the density of neon is almost half that of fluorine, the preceding element in the periodic table.

95. What is the density of chlorine relative to air? (a) 2.44; (b) 3.0; (c) it can be found only experimentally.

96. A gaseous oxide contains 30.4% of nitrogen. An oxide molecule contains one nitrogen atom. What is the density of the gas relative to oxygen? (a) 0.94; (b) 1.44; (c) 1.50.

97. The mass of 2.24 litres of a gas (in standard conditions) is 2.8 g. What is the molecular mass of the gas (in amu)? (a) 14; (b) 28; (c) 42.
98. The mass of a sulphur atom is double that of an oxygen atom. Can we decide on this basis that the density of sulphur vapour relative to oxygen is two? (a) Yes; (b) no.

6. Derivation of Chemical Formulas.
Calculations Involving Chemical Formulas and Equations

The formulas of substances show what elements and in what amounts the substances consist of. There are distinguished simplest or empirical and molecular formulas. An empirical formula indicates the simplest possible atomic composition of the molecules of a substance corresponding to the relationship between the masses of the elements forming the given substance. A molecular formula shows the actual number of atoms of each element in a molecule (for substances having a molecular structure).

To derive the empirical formula of a substance, it is sufficient to know its composition and the atomic masses of the elements forming the given substance.

Example 1. Find the empirical formula of chromium oxide containing 68.4% of chromium.

Solution. Let \( x \) and \( y \) be the number of chromium and oxygen atoms in the empirical formula of the oxide, respectively. The atomic masses of these elements are 52 and 16 amu. Consequently, the masses of the chromium and oxygen in the oxide are in the ratio of \( 52x : 16y \). According to the data of the example, this ratio is \( 68.4 : (100 - 68.4) \) = \( 68.4 : 31.6 \). Therefore,

\[
52x : 16y = 68.4 : 31.6
\]

whence

\[
x : y = \frac{68.4}{52} : \frac{31.6}{16} = 1.32 : 1.98
\]

To express the ratio obtained in integers, we divide both terms by the smaller of them:

\[
x : y = \frac{1.32}{1.32} : \frac{1.98}{1.32} = 1 : 1.5
\]

and then multiply both terms of the last ratio by two:

\[
x : y = 2 : 3
\]
Hence, the empirical formula of chromium oxide is \( \text{Cr}_2\text{O}_3 \).

Example 2. The complete combustion of 2.66 g of a substance yields 1.54 g of \( \text{CO}_2 \) and 4.48 g of \( \text{SO}_2 \). Find the empirical formula of the substance.

**Solution.** The composition of the combustion products shows that the substance contained carbon and sulphur. In addition to these two elements, it could include oxygen.

We find the mass of the carbon in the substance from the mass of the \( \text{CO}_2 \) formed. The molar mass of \( \text{CO}_2 \) is 44 g/mol, one mole of it containing 12 g of carbon. We determine the mass \( m \) of the carbon in 1.54 g of \( \text{CO}_2 \):

\[
\frac{44}{12} = \frac{1.54}{m} \implies m = \frac{12 \times 1.54}{44} = 0.42 \text{ g}
\]

Similar calculations show that the mass of the sulphur contained in 4.48 g of \( \text{SO}_2 \) is 2.24 g.

Hence, the burnt substance contained 2.24 g of sulphur per 0.42 g of carbon. Since the sum of these two masses equals the total mass of the burnt substance (2.66 g), it contained no oxygen.

We compute the ratio of the number of carbon (\( x \)) and sulphur (\( y \)) atoms in a molecule of the burnt substance:

\[
x : y = \frac{0.42}{12} : \frac{2.24}{32} = 0.035 : 0.070 = 1 : 2
\]

Consequently, the empirical formula of the substance is \( \text{CS}_2 \).

To find the molecular formula of a substance, we must know its molecular mass in addition to its composition.

Example 3. A gaseous compound of nitrogen and hydrogen contains 12.5\% (mass) of hydrogen. The density of the compound relative to hydrogen is 16. Find the molecular formula of the compound.

**Solution.** We find the ratio of the number of nitrogen atoms (\( x \)) to that of hydrogen atoms (\( y \)) in a molecule of the compound:

\[
x : y = \frac{87.5}{14} : \frac{12.5}{1} = 6.25 : 12.5 = 1 : 2
\]

The empirical formula of the compound is \( \text{NH}_2 \). A molecular mass of 16 corresponds to this formula. We find the true molecular mass of the substance from its density relative to hydrogen:

\[
M = 2 \times 16 = 32
\]

Thus, the true molecular mass of the substance is double that calculated from its empirical formula. Hence, the molecular formula of the compound is \( \text{N}_2\text{H}_4 \).

In an equation of a chemical reaction, each formula stands for one mole of the relevant substance. Therefore, knowing the molar masses of the substances participating in a reac-
tion, we can use the equation of the reaction to find the relationship between the masses of the substances entering into the reaction and formed as a result of its proceeding. If gaseous substances take part in a reaction, its equation allows us to find their volume relationships.

Example 4. Find the mass of sulphuric acid needed for the complete neutralization of 20 g of sodium hydroxide.

Solution. The equation of the reaction is:

\[ \text{H}_2\text{SO}_4 + 2\text{NaOH} = \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \]

The molecular masses of \( \text{H}_2\text{SO}_4 \) and \( \text{NaOH} \) are 98 and 40 amu, respectively; consequently, their molar masses are 98 and 40 g/mol. According to the reaction equation, one mole of \( \text{H}_2\text{SO}_4 \) reacts with two moles of \( \text{NaOH} \), i.e.

98 g of \( \text{H}_2\text{SO}_4 \) neutralize 80 g of \( \text{NaOH} \)

\[ x \text{ g of } \text{H}_2\text{SO}_4 \text{ neutralize } 20 \text{ g of } \text{NaOH} \]

Hence,

\[ x = \frac{98 \times 20}{80} = 24.5 \text{ g} \]

Example 5. Chlorine can be produced by reacting sulphuric acid with a mixture of \( \text{MnO}_2 \) and \( \text{NaCl} \). The reaction follows the equation:

\[ 2\text{NaCl} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 = 2\text{NaHSO}_4 + \text{MnSO}_4 + \text{Cl}_2 + 2\text{H}_2\text{O} \]

What volume of chlorine (in standard conditions) can be produced from 100 g of sodium chloride?

Solution. According to the reaction equation, one mole of \( \text{Cl}_2 \) is obtained from two moles of \( \text{NaCl} \). Having calculated the mass of two moles of \( \text{NaCl} \) (117 g), we form a proportion:

117 g of \( \text{NaCl} \) yield 22.4 litres of \( \text{Cl}_2 \)

100 g of \( \text{NaCl} \) yield \( x \) litres of \( \text{Cl}_2 \)

Hence:

\[ x = \frac{22.4 \times 100}{117} = 19.15 \text{ litres} \]

PROBLEMS

99. Find the empirical formula of a substance containing 43.4\% of sodium, 11.3\% of carbon, and 45.3\% of oxygen.

100. Find the empirical formula of a substance whose composition includes hydrogen, carbon, oxygen, and nitrogen in the mass ratio 1:3:4:7.

101. Find the empirical formula of vanadium oxide if 2.73 g of the oxide contain 1.53 g of the metal.
102. A substance contains 26.53% of potassium, 35.37% of chromium, and 38.10% of oxygen. Find its empirical formula.

103. Find the formula of the crystal hydrate of barium chloride knowing that 36.6 g of the salt when roasted lose 5.4 g in mass.

104. Find the molecular formula of butyric acid containing 54.5% of carbon, 36.4% of oxygen, and 9.1% of hydrogen, if the density of its vapour relative to hydrogen is 44.

105. Find the molecular formula of a substance containing 93.75% of carbon and 6.25% of hydrogen if the density of the substance relative to air is 4.41.

106. The combustion of 4.3 g of a hydrocarbon yields 13.2 g of CO₂. The density of the hydrocarbon vapour relative to hydrogen is 43. Derive the molecular formula of the substance.

107. Two volumes of CO₂ and one volume of N₂ form upon the explosion of a mixture obtained from one volume of a gas and two volumes of oxygen. Find the formula of the gas.

108. Find the molecular formula of a compound of boron with hydrogen if the mass of one litre of this gas equals the mass of one litre of nitrogen, and the boron content in the substance is 78.2%.

109. Calculate the mass of the nitrogen contained in one kilogram of (a) potassium nitrate KNO₃; (b) ammonium nitrate NH₄NO₃; (c) Ammophos (NH₄)₂HPO₄.

110. Calculate the per cent composition of the following compounds: (a) Mg(OH)₂; (b) Fe(NO₃)₂; (c) H₂SO₄; (d) (NH₄)₂SO₄.

111. What mass of iron can be produced from 2 tonnes of iron ore containing 94% of Fe₂O₃?

112. Sodium hydroxide NaOH in an amount of 9 g was added to a solution containing 10 g of H₂SO₄. What is the reaction of the solution obtained?

113. A solution containing 34.0 g of AgNO₃ is mixed with a solution containing the same mass of NaCl. Will all of the silver enter into the reaction? How many grams of AgCl were obtained as a result of the reaction?

114. The combustion of 3.00 g of anthracite yielded 5.30 litres of CO₂ measured in standard conditions. What is the carbon content of the anthracite in per cent?
115. A solution containing 0.20 mole of FeCl₃ was reacted with 0.24 mole of NaOH. How many moles of Fe(OH)₃ formed, and how many moles of the FeCl₃ remained in the solution?

116. How many litres of detonating gas (in standard conditions) are produced in the decomposition of one mole of water by an electric current?

117. What volume of acetylene (in standard conditions) can be produced by reacting water with 0.80 kg of CaC₂?

118. How many grams of NaCl can be obtained from 265 g of Na₂CO₃?

119. When a mixture consisting of 10 moles of SO₂ and 15 moles of O₂ was passed over a catalyst, 8 moles of SO₃ were formed. How many moles of SO₂ and O₂ did not enter into the reaction?

120. How many grams of NH₄Cl form when 7.3 g of HCl are mixed with 4.0 g of NH₃? Find the mass of the gas remaining after the reaction.

121. What volume of air is needed for the combustion of 1 m³ of a gas having the following composition in % (vol.): 50% of H₂, 35% of CH₄, 8% of CO, 2% of C₂H₆, and 5% of noncombustible admixtures? The air contains 21% (vol.) of oxygen.

122. Water gas consisting of equal volumes of CO and H₂ is produced when water vapour is passed over red hot coal. What volume of water gas (in standard conditions) can be obtained from 3.0 kg of coal?

123. Calcium carbonate decomposes into CaO and CO₂ when heated. What mass of natural limestone containing 90% of CaCO₃ is needed to produce 7.0 tonnes of unslaked lime?

124. A solution containing 5.0 g of KOH was poured into a solution containing 6.8 g of AlCl₃. Find the mass of the precipitate formed.

125. Calculate the mass of the crystal hydrate Cu(NO₃)₂·3H₂O obtained by dissolving 10 g of copper in nitric acid and then evaporating the solution.

126. When 3.90 g of a mixture of aluminium and its oxide were reacted with a solution of sodium hydroxide, 840 ml of a gas evolved measured in standard conditions. Find the per cent composition of the initial mixture.
127. Hydrochloric acid was reacted with 5.10 g of a powder of partly oxidized magnesium, and 3.74 litres of \( \text{H}_2 \) measured in standard conditions were liberated. What was the percentage of the magnesium in the powder?

128. A sample of iron shavings with a mass of 3.4260 g yielded 0.0998 g of SiO\(_2\) after the relevant treatment. Calculate the silicon content in the iron being analysed.

129. What volume of hydrogen (in standard conditions) is needed to reduce 125 g of MoO\(_3\) to the metal?

130. When hydrochloric acid was reacted with 1.20 g of an alloy of magnesium with aluminium, 1.42 litres of hydrogen measured at 23 °C and 100.7 kPa were liberated. Calculate the per cent composition of the alloy.

131. To determine the NaCl content in commercial NaOH, 2.00 g of the latter were dissolved in water and an excess amount of an AgNO\(_3\) solution was added to this solution. The precipitate formed was washed and dried. Its mass was 0.287 g. Find the mass of the NaCl in the initial sample.

**REVIEW QUESTIONS**

132. The empirical formula of hydrazine is \( \text{NH}_2 \). What is its true formula if the density of hydrazine vapour relative to air is 1.1? (a) \( \text{NH}_2 \); (b) \( \text{N}_3\text{H}_4 \); (c) \( \text{N}_2\text{H}_6 \).

133. The empirical formula of a compound of carbon with hydrogen is \( \text{CH}_2 \). What is the molecular formula of the compound if the mass of one litre of the gas equals that of one litre of nitrogen? (a) \( \text{C}_3\text{H}_6 \); (b) \( \text{C}_2\text{H}_4 \); (c) \( \text{C}_4\text{H}_8 \).

134. What is the molecular formula of a compound of nitrogen with oxygen if the density of this gas relative to hydrogen is 15? (a) \( \text{NO} \); (b) \( \text{N}_2\text{O} \); (c) \( \text{NO}_2 \).

135. A metal displaced 16.8 ml of \( \text{H}_2 \) (in standard conditions) from an acid. What volume of \( \text{N}_2 \) is needed to combine with this amount of hydrogen into \( \text{NH}_3 \)? (a) 11.2 ml; (b) 5.6 ml; (c) 8.4 ml.

136. The decomposition of \( \text{CaCO}_3 \) yielded 11.2 litres of \( \text{CO}_2 \). What is the mass of KO\(_2\) required to combine with the \( \text{CO}_2 \) to form the carbonate? (a) 56 g; (b) 112 g; (c) 28 g.

137. Determine the reaction of a solution into which 90 g of NaOH and 73 g of HCl have been introduced. (a) Neutral; (b) acid; (c) alkaline.
Inorganic compounds can be classified with respect to either their composition or their properties (the functional features). With respect to composition, they are subdivided first of all into binary compounds (containing two elements) and compounds containing three and more elements (ternary and higher compounds).

Binary compounds include, for example, compounds of elements with oxygen (oxides), halogens (halides—fluorides, chlorides, bromides, iodides), sulphur (sulphides), nitrogen (nitrides), phosphorus (phosphides), carbon (carbides), and compounds of metals with hydrogen (hydrides). Binary compounds are named by first specifying the ordinary English name of the less electronegative (more metallic) element. The name of the second element (the more electronegative one, almost always a non-metal) is obtained by adding the suffix -ide to its stem. For example, \( \text{Al}_2\text{O}_3 \) is aluminium oxide (but \( \text{OF}_2 \) is oxygen fluoride because fluorine is a more electronegative element than oxygen), \( \text{NaCl} \) is sodium chloride, \( \text{CaC}_2 \) is calcium carbide. If the less electronegative element is a metal and can be in different oxidation states, a Roman numeral equal to the oxidation number of the element follows its name in parentheses. Examples are copper(I) oxide \( \text{Cu}_2\text{O} \), copper(II) oxide \( \text{CuO} \), and iron(III) chloride \( \text{FeCl}_3 \).

When naming binary compounds formed between non-metals, a system is preferred in which the number of atoms of each element in a molecule is specified by a Greek prefix: mono-, di-, tri-, tetra-, penta-, hexa-, and so on. The monoprefix is omitted when superfluous. Examples are carbon monoxide \( \text{CO} \), carbon dioxide \( \text{CO}_2 \), sulphur hexafluoride \( \text{SF}_6 \), nitrogen dioxide \( \text{NO}_2 \), and dinitrogen tetroxide \( \text{N}_2\text{O}_4 \).
Hydrogen compounds of non-metals exhibiting acid properties until lately were an exception from the above rules, and their names were formed according to the rules adopted for acids (see below). According to the recommendations of the IUPAC, these compounds are to be named following the above rules as binary compounds of hydrogen, for instance, hydrogen chloride HCl and hydrogen sulphide H₂S.

An important group among ternary and higher compounds is formed by hydroxides, i.e. substances that include hydroxyl groups OH and that can be considered as compounds of oxides with water. Among them are both bases (basic hydroxides) such as NaOH and Ca(OH)₂, and acids (acid hydroxides) such as HNO₃ and H₂SO₄, as well as substances capable of displaying both acidic and basic properties (amphoteric hydroxides). The names of hydroxides exhibiting acidic properties are formed according to the rules established for acids (see below). The names of basic hydroxides are formed by using the word “hydroxide” after the name of the relevant element followed, when required, by its oxidation number in Roman numerals in parentheses. For example, lithium hydroxide LiOH, and iron(II) hydroxide Fe(OH)₂.

With respect to their functional features, inorganic compounds are subdivided into classes depending on the characteristic functions they perform in chemical reactions. For instance, oxides are grouped into non-salt-forming (indifferent) and salt-forming. The latter, in turn, are divided into basic, acidic, and amphoteric oxides.

The name basic is applied to oxides that form salts when they react with acids or acid oxides. Bases correspond to basic oxides. For example, the base calcium hydroxide Ca(OH)₂ corresponds to calcium oxide CaO, and cadmium hydroxide Cd(OH)₂ to cadmium oxide CdO.

The name acidic (acid) is applied to oxides that form salts when they react with bases or basic oxides. By attaching water directly or indirectly, acidic oxides form acids. For instance, silicon dioxide SiO₂ forms silicic acid H₄SiO₄, and dinitrogen pentoxide N₂O₅ forms nitric acid HNO₃.

Acidic oxides can be obtained by removing water from the relevant acids, which is why they are also known as acid anhydrides.
Oxides that form salts when they react either with acids or bases are called amphoteric. These oxides include ZnO, Al₂O₃, SnO, SnO₂, PbO, and Cr₂O₃.

Non-salt-forming oxides react neither with acids nor with bases. They include, for example, dinitrogen monoxide N₂O and nitrogen monoxide NO.

Oxygen compounds of elements exist that relate to the class of oxides as regards their composition, but actually belong to the class of salts as regards their structure and properties. These are the compounds named peroxides.

Peroxides are salts of hydrogen peroxide H₂O₂ such as Na₂O₂ and CaO₂. A feature of the structure of these compounds is the presence of two bonded oxygen atoms —O—O— (an "oxygen bridge").

An important class of inorganic compounds with a view to functional features is formed by acids. From the standpoint of the theory of electrolytic dissociation, acids include substances capable of dissociating in a solution with the formation of hydrogen ions. From the viewpoint of the protolytic (proton) theory of acids and bases, acids are defined as substances that can be donors of protons, i.e. that can give up a hydrogen ion.

A feature of acids is their ability to react with bases, and with basic and amphoteric oxides to form salts, for example:

\[
\begin{align*}
2\text{HNO}_3 + \text{Cu(OH)}_2 & = \text{Cu(NO}_3)_2 + 2\text{H}_2\text{O} \\
2\text{HCl} + \text{CaO} & = \text{CaCl}_2 + \text{H}_2\text{O} \\
\text{H}_2\text{SO}_4 + \text{ZnO} & = \text{ZnSO}_4 + \text{H}_2\text{O}
\end{align*}
\]

With respect to the presence of oxygen in their composition, acids are grouped into oxyacids (for example, H₂SO₄ and HNO₃) and hydriacids containing no oxygen (for example, HBr and H₂S). According to the number of hydrogen atoms in a molecule of an acid capable of being replaced by metal atoms, there are distinguished monobasic (for instance, hydrogen chloride HCl and nitric acid HNO₃), dibasic (sulphurous H₃SO₃ and carbonic H₂CO₃), tribasic (orthophosphoric H₃PO₄) acids, etc.

The names of acids come from the element forming the acid. Hydriacids are named like binary compounds of non-metals, including acids containing a group of elements such as hydrogen cyanide HCN. According to the classical system
still found in many books, and also used when speaking of aqueous solutions of hydracids, the root of the name of the element (or group of elements) forming the acid is sandwiched between the prefix hydro- (or hydr-) and the suffix -ic followed by the word acid. Examples are hydrochloric acid HCl and hydrocyanic acid HCN.

The names of oxyacids are also formed from the name of the relevant element. The latter, however, may exist in different oxidation states, and there may be an acid corresponding to each state. The prefixes per- and hypo- and the suffixes -ic and -ous are used to denote these conditions. Examples of the names of oxyacids for an element with four oxidation states in descending order of the latter are perchloric acid HClO₄, chloric acid HClO₃, chlorous acid HClO₂, and hypochlorous acid HClO (usually written HOCl). When there are two oxidation states, the suffix -ic denotes the higher one and the suffix -ous the lower one (sulphuric acid H₂SO₄ and sulphurous acid H₂SO₃).

When an element in the same oxidation state forms several acids each containing one atom of the given element in a molecule (for example, HPO₃ and H₃PO₄), the prefix meta-is used with the name of the acid containing the smallest number of oxygen atoms, and the prefix ortho- with the name of the one containing the greatest number of oxygen atoms (metaphosphoric acid HPO₃ and orthophosphoric acid H₃PO₄).

If an acid molecule contains two atoms of the acid-forming element, its name is preceded by the prefix di- (diphosphoric acid H₄P₂O and disulphuric acid H₂S₂O₇).

Acids containing the group of atoms —O—O— can be treated as derivatives of hydrogen peroxide. They are named peracids. If necessary, the name of such an acid includes a prefix indicating the number of atoms of the acid-forming element in a molecule, and following the prefix per-, for example

- \( H₂SO₅ \) peroxysulphuric acid
- \( H₂S₂O₈ \) persulphuric acid
Still another important class of inorganic compounds characterized by common properties is formed by bases. According to the theory of electrolytic dissociation, they include substances capable of dissociating in solution to form hydroxide ions, i.e. basic hydroxides.

A feature of bases is their ability to react with acids, acidic or amphoteric oxides and form salts, for example:

$$\text{KOH} + \text{HCl} = \text{KCl} + \text{H}_2\text{O}$$
$$\text{Ba(OH)}_2 + \text{CO}_2 = \text{BaCO}_3 + \text{H}_2\text{O}$$
$$2\text{NaOH} + \text{Al}_2\text{O}_3 = 2\text{NaAlO}_2 + \text{H}_2\text{O}$$

From the angle of view of the protolytic (proton) theory, bases are substances that can be acceptors of protons, i.e. can attach a hydrogen ion. From this standpoint, not only basic hydroxides should be related to bases, but also some other substances such as ammonia whose molecule can pick up a proton and form an ammonium ion:

$$\text{NH}_3 + \text{H}^+ = \text{NH}_4^+$$

Indeed, ammonia, like basic hydroxides, can react with acids to form salts:

$$\text{NH}_3 + \text{HCl} = \text{NH}_4\text{Cl}$$

Depending on the number of protons that can be attached to a base, there are distinguished monoacid bases (for example, LiOH, KOH, NH₃), diacid bases [Ca(OH)₂, Fe(OH)₂], etc.

Amphoteric hydroxides can dissociate in aqueous solutions both like acids (with the formation of hydrogen cations) and like bases (with the formation of hydroxyl anions); they can be both donors and acceptors of protons. This is why amphoteric hydroxides form salts when they react with acids and with bases. When they react with acids, amphoteric hydroxides exhibit properties of bases, and when they react with bases—properties of acids:

$$\text{Zn(OH)}_2 + 2\text{HCl} = \text{ZnCl}_2 + 2\text{H}_2\text{O}$$
$$\text{Zn(OH)}_2 + 2\text{NaOH} = \text{Na}_2\text{ZnO}_2 + 2\text{H}_2\text{O}$$

Examples of amphoteric hydroxides are Zn(OH)₂, Al(OH)₃, Pb(OH)₂, Sn(OH)₂, and Cr(OH)₃.
Salts can be considered as the products of the complete or partial replacement of the hydrogen atoms in an acid molecule by metal atoms or as the products of the complete or partial replacement of the hydroxyl groups in a basic hydroxide molecule by acid residues. Upon complete replacement of the hydrogen atoms in an acid molecule, neutral (normal) salts are obtained, and upon incomplete replacement, acid salts. Acid salts are formed by polybasic acids.

Upon the partial replacement of the hydroxyl groups in a molecule of a basic hydroxide by acid residues, basic salts (hydroxosalts) are formed. Basic salts can be formed only by polyacid hydroxides.

Acid salts are produced in the reaction of acids with bases when the amount of base used is insufficient for the formation of a neutral salt, for instance:

\[ \text{H}_2\text{SO}_4 + \text{NaOH} = \text{NaHSO}_4 + \text{H}_2\text{O} \]

Basic salts are produced when the amount of acid used is insufficient for the formation of a neutral salt, for instance:

\[ \text{Fe(OH)}_3 + \text{H}_2\text{SO}_4 = \text{FeOHSO}_4 + 2\text{H}_2\text{O} \]

The names of salts are formed from the name of the cation and that of the acid anion (sodium chloride, copper sulphate). The name of the anion is derived from the root of the Latin name of the acid-forming element (for example, calcium plumbate CaPbO\(_3\)). The oxidation number of the metal forming the cation is indicated when required in Roman numerals in parentheses.

The anion of a hydracid salt is given the suffix -ide. Examples are sodium bromide NaBr, iron(II) sulphide FeS, and potassium cyanide KCN.

The names of oxyacid anions are given the suffix -ate for the higher oxidation state of the acid-forming element and the suffix -ite for the lower oxidation state. When the prefixes per- and hypo- are used for acids, they are retained in the names of the relevant salts. For example, salts of sulphuric acid are called sulphates, of sulphurous acid—sulphites, of perchloric acids—perchlorates, and of hypochlorous acid—hypochlorites.
If a molecule of an acid contains two atoms of the acid-forming element, the numerical prefix \textit{di-} is added to the name of the anion. For example, the salts of disulphuric acid $\text{H}_2\text{S}_2\text{O}_7$ are called disulphates, and those of diphosphoric acid $\text{H}_4\text{P}_2\text{O}_7$—diphosphates.

Anions of peracids are named by adding the prefix \textit{per-}. For instance, salts of persulphuric acid $\text{H}_2\text{SO}_5$ are called persulphates, and of perdisulphuric acid $\text{H}_2\text{S}_2\text{O}_8$—perdisulphates.

The names of the most important acids and their salts are given in the Appendix (Table 4).

Acid salts are named in the same way as neutral ones, except that the word hydrogen is added before the name of the anion with a Greek prefix (\textit{di-}, \textit{tri-}, etc.) indicating the number of hydrogen atoms remaining unreplaced. Examples are barium hydrogen carbonate $\text{Ba(HCO}_3\text{)}_2$, sodium dihydrogen arsenate $\text{NaH}_2\text{AsO}_4$, and lithium hydrogen sulphide $\text{LiH}_2\text{S}$.

The names of basic salts are also formed like those of neutral ones, except that the word hydroxide is added indicating the presence of unreplaced hydroxide groups. Examples are iron(II) chloride hydroxide $\text{FeOHC}_\text{I}$, nickel sulphate hydroxide $(\text{NiOH})_2\text{SO}_4$, and aluminium nitrate dihydroxide $\text{Al(OH)}_2\text{NO}_3$.

Sometimes, the formation of a basic salt is attended by the detachment of water, for instance:

$$\text{Bi(OH)}_2\text{Cl} = \text{BiOCl} + \text{H}_2\text{O}$$

The salts formed (oxosalts) in such cases contain no hydroxide groups, but retain the properties of basic salts, particularly the ability of reacting with acids to form neutral salts:

$$\text{BiOCl} + 2\text{HCl} = \text{BiCl}_3 + \text{H}_2\text{O}$$

The names of the oxygen-containing cations in oxosalts ($\text{BiO}^+$, $\text{SbO}^+$, $\text{UO}_2^+$, etc.) are derived from the stem of the Latin name of the metal with the addition of the suffix \textit{-yl}: bismuthyl $\text{BiO}^+$, stibyl (antimonyl) $\text{SbO}^+$, uranyl $\text{UO}_2^+$. Accordingly, $\text{BiOCl}$ is called bismuthyl chloride, $\text{UO}_2(\text{NO}_3)_2$—uranyl nitrate, etc.
PROBLEMS

138. Write the formulas of the anhydrides of the following acids: \( H_2SO_4, H_3BO_3, H_4P_2O_7, HClO, HMnO_4 \).

139. Write the formulas of the oxides corresponding to the following hydroxides: \( H_2SiO_3, Cu(OH)_2, H_3AsO_4, H_2WO_4, Fe(OH)_3 \).

140. Compile the equations of the reactions that can be used to carry out the following transformations:

\[
\begin{align*}
Ba & \rightarrow BaO \rightarrow BaCl_2 \rightarrow Ba(NO_3)_2 \rightarrow BaSO_4 \\
Mg & \rightarrow MgSO_4 \rightarrow Mg(OH)_2 \rightarrow MgO \rightarrow MgCl_2
\end{align*}
\]

141. Write the equations of the reactions that can be used to carry out the following transformations:

\[
\begin{align*}
Zn & \rightarrow K_2ZnO_2 \\
S & \rightarrow H_2SO_3 \\
NH_3 & \rightarrow HNO_3 \\
Cu & \rightarrow CuS
\end{align*}
\]

142. Which of the indicated gases enter into a chemical reaction with an alkali solution: \( HCl, H_2S, NO_2, N_2, Cl_2, CH_4, SO_2, NH_3 \)? Write the equations of the relevant reactions.

143. What salts can be obtained having at one's disposal \( CuSO_4, AgNO_3, K_3PO_4, BaCl_2 \)? Write the equations of the reactions and name the salts obtained.

144. Name the following compounds: \( K_2O_2, MnO_2, BaO_2, MnO, CrO_3, V_2O_5 \).

145. How can we prove the amphoteric nature of \( ZnO, Al_2O_3, Sn(OH)_2, \) and \( Cr(OH)_3 \)?

146. Is it possible to prepare a solution containing simultaneously (a) \( Ba(OH)_2 \) and \( HCl \); (b) \( CaCl_2 \) and \( Na_2CO_3 \); (c) \( NaCl \) and \( AgNO_3 \); (d) \( KCl \) and \( NaNO_3 \)? Indicate what combinations are impossible and why.

147. Which of the acids listed below form acid salts: \( HI, H_2Se, H_2SeO_3, H_2C_2O_4, CH_3COOH \)?

148. What acids can be obtained by the direct reaction with water of the oxides: \( P_2O_5, CO_2, N_2O_5, NO_2, SO_2 \)?

149. With which of the substances listed below will hydrochloric acid react: \( N_2O_5, Zn(OH)_2, CaO, AgNO_3, H_3PO_4, H_2SO_4 \)? Write the equations of the reactions.
150. Which of the following substances react with sodium hydroxide: HNO₃, CaO, CO₂, CuSO₄, Cd(OH)₂, P₂O₅? Write the equations of the reactions.

151. Write the equations of reactions illustrating the basic properties of FeO, Cs₂O, HgO, and Bi₂O₃.

152. Write the equations of reactions proving the acid nature of SeO₂, SO₃, Mn₂O₇, P₂O₅, and CrO₃.

153. Write the equations of the reactions used to prepare magnesium chloride (a) by reacting an acid with the metal; (b) by reacting an acid with a base; (c) by reacting a salt with a salt.

154. Write the equations of the reactions between acids and bases leading to the formation of the salts: NaNO₃, NaHSO₄, Na₃H₂PO₄, K₂S, and Fe₂(SO₄)₃.

155. What substances can be obtained upon the reaction of an acid with a salt? An acid with a base? A salt with a salt? Give examples of the relevant reactions.

156. Write the formulas of the neutral and acid salts of potassium and calcium formed by (a) carbonic acid; (b) arsenous acid.

157. Name the following salts: SbONO₃, [Fe(OH)₂]₂CrO₄, (AlOH)SO₄, Cd(HS)₂, Ca(H₂PO₄)₂.

158. What substances must be reacted to produce sodium dihydrogen orthoantimonate, sodium metachromite, potassium hydrogen arsenate, and aluminium sulphate hydroxide? Write the equations of the reactions.

159. Write the equations of the reactions of formation of Mg₂P₂O₇, Ca₃(PO₄)₂, Mg(ClO₄)₂, and Ba(NO₃)₂ as a result of the reaction (a) of a basic and an acidic oxide; (b) of a base and an acidic oxide; (c) of a basic oxide and an acid; (d) of a base and an acid.

160. Write the equations of reactions that can be used to prepare the following substances in a laboratory: (a) hydrogen chloride; (b) lead sulphide; (c) barium sulphate; (d) silver orthophosphate; (e) iron(III) hydroxide; (f) copper(II) nitrate.

161. Give the names of the following salts: (a) Zn(NO₃)₂; (b) NaH₂SbO₄; (c) K₂H₂P₂O₇; (d) Al(OH)₂NO₃; (e) CaCrO₄; (f) K₃AsO₄; (g) Na₃Cr₂O₇; (h) Ba(HSO₄)₂; (i) CrOHSO₄; (j) (CuOH)₂CO₃; and (k) NaHS.
REVIEW QUESTIONS

162. Which of the hydroxides indicated below can form basic salts? (a) Cu(OH)$_2$; (b) Ca(OH)$_2$; (c) LiOH; (d) Al(OH)$_3$; (e) KOH.

163. What acid is P$_2$O$_5$ the anhydride of? (a) Phosphorous; (b) diphosphoric; (c) orthophosphoric.

164. What acid can Cl$_2$O$_7$ be considered the anhydride of? (a) Perchloric; (b) chloric; (c) hypochlorous.

165. Which of the following compounds is a peroxide? (a) NO$_2$; (b) K$_2$O$_2$; (c) BaO$_2$; (d) MnO$_2$.

166. In the reaction of neutralization of potassium hydroxide with orthoarsenic acid, the equivalent mass of the latter was found to equal 142 g/mol. What salt was formed in the reaction? (a) Potassium orthoarsenate; (b) potassium hydrogen orthoarsenate; (c) potassium dihydrogen orthoarsenate.

167. What formula corresponds to manganic acid? (a) HMnO$_4$; (b) H$_4$MnO$_4$; (c) H$_2$MnO$_4$.

168. Which of the following formulas does barium chlorate correspond to? (a) BaCl$_2$; (b) Ba(OCl)$_2$; (c) Ba(ClO$_3$)$_2$; (d) Ba(ClO$_4$)$_2$.

169. What name corresponds to the salt (CuOH)$_2$CO$_3$? (a) Copper carbonate hydroxide; (b) copper(II) carbonate hydroxide; (c) copper(II) carbonate dihydroxide.

170. What salt is formed in the reaction of one mole of zinc hydroxide and two moles of orthophosphoric acid? (a) Zinc orthophosphate; (b) zinc dihydrogen orthophosphate; (c) zinc orthophosphate hydroxide; (d) zinc hydrogen orthophosphate.

171. What reaction leads to the preparation of a neutral salt from magnesium chloride hydroxide? (a) MgOHCl + NaOH; (b) MgOHClO$_3$ + NaOH; (c) MgOHClO$_3$ + HCl; (d) MgOHCl + HCl.
1. Electronic Structure of Atoms.
Dependence of Element Properties on the Structure of Their Atoms

In solving problems associated with the electronic structure of atoms, we must proceed from the fact that any stable state of an electron in an atom is characterized by definite values of the quantum numbers \( n, l, m, \) and \( s \). The state of an electron in an atom corresponding to definite values of the quantum numbers \( n, l, m \) is known as an atomic electron orbital.

Every atomic orbital (AO) is characterized by a definite distribution in space of the wave function \( \psi \) whose square determines the probability of finding an electron in the corresponding region of space. Atomic orbitals corresponding to values of \( l \) equal to 0, 1, 2, and 3 are called \( s, p, d, \) and \( f \) orbitals, respectively. In graphical diagrams of the electronic structure of atoms, each orbital is represented by the symbol □.

According to the Pauli exclusion principle, an atom cannot contain two electrons characterized by an identical set of quantum numbers. It follows that any atomic orbital can be occupied by not more than two electrons, and these must have different spin quantum numbers. This is depicted by the symbol ⚪️

An arrangement of the electrons in the AO's in which the energy of the atom is minimum corresponds to the stable (unexcited) state of a many-electron atom. This is why the AO's are filled in the order of a consecutive growth in their
energies (without any violation of the Pauli exclusion principle!). The order in which electrons fill the AO's is determined by Klechkovsky's rules, which take into account the dependence of the energy of an orbital on the values of both the principal \(n\) and the orbital \(l\) quantum numbers. According to these rules, the AO's are filled by electrons in the order of a consecutive increase in the sum \(n + l\) (Klechkovsky's first rule), and with identical values of this sum—in the order of a consecutive increase in the principal quantum number \(n\) (Klechkovsky's second rule).

Example 1. What sublevel is filled in an atom by electrons after filling of the sublevel \(4p\)?

Solution. The sum of \(n + l\) equal to \(4 + 1 = 5\) corresponds to the sublevel \(4p\). The sublevels \(3d\) \((3 + 2 = 5)\) and \(5s\) \((5 + 0 = 5)\) are characterized by the same sum of \(n + l\). But a smaller value of \(n\) (i.e. \(n = 3\)) corresponds to the state \(3d\) than to the state \(4p\); consequently, the sublevel \(3d\) will be filled before the sublevel \(4p\). Therefore, filling of the sublevel \(4p\) will be followed by filling of the sublevel \(5s\), which a value of \(n\) greater by unity \((n = 5)\) corresponds to.

Example 2. What sublevel will be filled after the sublevel \(4s\)?

Solution. The sum of \(n + l = 4 + 0 = 4\) corresponds to the sublevel \(4s\). The sublevel \(3p\) is characterized by the same sum of \(n + l\), but the filling of this sublevel precedes that of the sublevel \(4s\) because a higher value of the principal quantum number corresponds to the latter. Hence, after the sublevel \(4s\), a sublevel with the sum of \(n + l = 5\) will be filled; of all the possible combinations of \(n + l\) corresponding to this sum \((n = 3, l = 2; n = 4, l = 1; \text{and } n = 5, l = 0)\), the first to be realized will be the one with the smallest value of the principal quantum number, i.e. filling of the sublevel \(4s\) will be followed by filling of the sublevel \(3d\).

The arrangement of the electrons in the AO's within the limits of one energy sublevel is determined by Hund's rule, according to which the arrangement of the electrons in the AO's of an energy sublevel at which the absolute value of the total spin of the atom is maximum corresponds to the minimum energy of an atom. With any other arrangement of the electrons, the atom will be in an excited state, i.e. will have a higher energy.

Example 3. Draw up the electron configuration of the silicon atom and the graphical representation of the filling of this atom's valence orbitals with electrons in the ground and in the excited states.

Solution. We draw up the electron configuration of the silicon atom: \(1s^22s^22p^63s^23p^2\). The orbitals of the outer (third) electron layer, i.e. the \(3s\), \(3p\), and unfilled \(3d\) orbitals, are the valence orbitals in this
atom. The graphical representation of how the electrons fill these orbitals is as follows:

\[
\begin{array}{c}
3s \\
3p \\
3d \\
\end{array}
\]

The arrangement of the electrons in the 3p sublevel is shown here in accordance with Hund’s rule: the total spin of the atom has a maximum value (1). The other possible arrangements of the electrons in the 3p sublevel, for instance

\[
\begin{array}{c}
3p \\
\ \ \ \ |
\end{array}
\text{ or } \begin{array}{c}
3p \\
\ \ \ \ |
\end{array}
\]

correspond to a zero value of the total spin of the atom and, therefore, to an excited state of the atom.

When a certain amount of energy is spent, one of the 3s electrons of the silicon atom can be transferred to the vacant 3p orbital; this causes the energy of the atom to increase, so that the new electron configuration \(1s^22s^22p^63s^23p^8\) also corresponds to one of the possible excited states of silicon:

\[
\begin{array}{c}
3s \\
3p \\
3d \\
\end{array}
\]

**Electron analogues** are defined as elements whose valence electrons are in orbitals having the same configuration for all these elements. Electron analogues are arranged in one subgroup in the periodic table of elements.

**Example 4.** On what grounds are chlorine and manganese placed in the same group of the periodic table? Why are they in different subgroups?

**Solution.** The electron configurations of the atoms are:

Cl \(1s^22s^22p^63s^23p^5\)

Mn \(1s^22s^22p^63s^23p^63d^{10}4s^2\)

The valence electrons of chlorine are \(3s^23p^5\), and of manganese—\(3d^{10}4s^2\); hence, these elements are not electron analogues and must not be arranged in the same subgroup. But the valence orbitals of the atoms of these elements accommodate the same number of electrons—7. On these grounds, both elements are placed in the same seventh group of the periodic table, but in different subgroups.
By the ionization energy is meant the energy that must be spent to detach an electron from an atom with the transformation of the latter into a positively charged ion. The ionization energy is customarily expressed in electron volts (eV); 1 eV corresponds to an ionization energy of 96.48 kJ/mol.

The ionization energy can be determined by bombarding atoms with electrons accelerated in an electric field. The lowest potential difference at which the velocity of an electron becomes sufficient for ionization of the atoms is known as the ionization potential of the atoms of a given element. The ionization potential \( (I) \) expressed in volts (V) numerically equals the ionization energy \( (E) \) expressed in electron volts.

When sufficient energy is spent, two, three, and more electrons can be detached from an atom. The first ionization potential corresponds to the energy of removing the first electron, the second—to the energy of removing the second electron, and so on.

As electrons are consecutively detached from an atom, the positive charge of the ion formed grows. Hence, more energy is needed to remove each consecutive electron, so that the consecutive ionization potentials of an atom \( (I_1, I_2, I_3, \ldots) \) grow. This can be seen using the beryllium, boron, and carbon atoms as examples:

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<th>C</th>
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<td>( I_1 )</td>
<td>9.3</td>
<td>8.3</td>
<td>11.3</td>
</tr>
<tr>
<td>( I_2 )</td>
<td>18.2</td>
<td>25.2</td>
<td>24.4</td>
</tr>
<tr>
<td>( I_3 )</td>
<td>253.9</td>
<td>37.9</td>
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</tbody>
</table>

The ionization potential grows especially sharply when an electron is detached having a principal quantum number smaller than that of the preceding electron. For instance for Be \( (1s^22s^2) \), the difference between \( I_1 \) and \( I_2 \) is much smaller than that between \( I_2 \) and \( I_3 \). This is associated with the greater energy needed to remove the third electron, which unlike the two preceding ones is closer to the nucleus.

The ionization potential grows with an increase in the charge of the nucleus and a decrease in the atomic or ionic radius, other conditions being equal. From this angle of view, a tendency of an increase in the ionization potential should
be observed in a period with a growth in the charge of a nucleus (when an electron is removed having the same principal quantum number). Indeed, the values of $I_1$ and $I_2$ for Be are lower than the corresponding values for C.

But besides this, the ionization potential depends on the electron configuration of an atom or ion. Particularly, completely or half filled sublevels have an increased stability. It follows from a comparison of the electron configurations of the atoms being considered

\[
\begin{align*}
\text{Be} & : 1s^2 2s^2 \\
\text{B} & : 1s^2 2s^2 2p^1 \\
\text{C} & : 1s^2 2s^2 2p^2
\end{align*}
\]

that the electron configuration of the Be atom is most stable (the 2s sublevel is completely filled); this is why more energy goes to ionize it. In boron, notwithstanding the growth in the charge of its nucleus, the detachment of $p$ electrons requires less energy.

**PROBLEMS**

172. How many values of the magnetic quantum number $m$ are possible for the electrons of an energy sublevel whose orbital quantum number is $l = 2$? $l = 3$?

173. What maximum number of electrons can an atom contain in an electron layer with the principal quantum number $n = 4$?

174. Use Klechkovsky's rule to determine the order of filling electron orbitals for which the sum of $n$ and $l$ is (a) 5, (b) 6, and (c) 7.

175. Indicate the atomic number of the element in which (a) filling of the $4d$ orbitals by electrons is completed, and (b) filling of the $4p$ sublevel begins.

176. What sublevel is filled in atoms after the sublevel $5s$?
177. In what element does filling of the sublevel 4f begin? 
In what element is the filling of this sublevel completed? 
178. What sublevel is filled in atoms after filling of the 
sublevel 5p? After filling of the sublevel 5d? 
179. Write the electron configurations of atoms of ele­
ments with a nuclear charge of (a) 8, (b) 15, (c) 18, (d) 23, 
(e) 53, (f) 63, and (g) 83. Show the filling of the valence orbitals 
of these atoms by electrons graphically. 
180. Indicate which of the following electron configura­
tions are impossible and explain why they cannot be real­
ized: (a) 1p^6, (b) 3p^6, (c) 3s^2, (d) 2s^2, (e) 2d^1, (f) 5d^2, (g) 3f^12, 
(h) 2p^4, and (i) 3p^7. 
181. How many vacant 3d orbitals do the excited atoms 
of the following elements have? (a) Cl, (b) V, and (c) Mn. 
182. How many unpaired electrons are there in the unex­
cited atoms of (a) B, (b) S, (c) As, (d) Cr, (e) Hg, and 
(f) Eu? 
183. Represent the electron configurations of the Fe^{3+} and 
Fe^{2+} ions graphically. How can the high stability of the 
electron configuration of the Fe^{2+} ion be explained? 
184. Indicate the features of the electron configurations of 
copper and chromium atoms. How many 4s electrons do un­
excited atoms of these elements contain? 
185. The configuration of the valence electron layer of 
an atom of an element is (a) 5s^25p^4, and (b) 3d^54s^2. Determine 
the atomic number and name of the element. 
186. The electron configuration of a certain atom is 
1s^22s^22p^63s^23p^63d^84s^2. What is the element? 
187. Write the electron configurations of the ions 
(a) Sn^{2+}, (b) Sn^{4+}, (c) Mn^{2+}, (d) Cu^{2+}, (e) Cr^{3+}, and (f) S^{2−}. 
188. In elements of what periods are the outer layer 
electrons characterized by a value of n + l = 5? 
189. List the electron analogues among the elements of 
Group VI of the periodic table. Write in a general form the 
electron configurations of the valence electron sublevels in 
atoms of these elements.
190. On what grounds are chromium and sulphur, phos­
phorus and vanadium placed in one group of the periodic 
table? Why are they in different subgroups? 
191. Why does copper have a smaller atomic volume than 
potassium placed in the same group and the same period?
192. The values of the consecutive ionization potentials for a carbon atom (in V) are: \( I_1 = 11.3, I_2 = 24.4, I_3 = 47.9, I_4 = 64, \) and \( I_5 = 392. \) Explain (a) the behaviour of the change in the ionization potentials, and (b) the reason of the sharp jump from \( I_4 \) to \( I_5 \).

193. The ionization energies of the noble gas atoms (in eV) are: He—24.6, Ne—21.6, Ar—15.8, Kr—14.0, Xe—12.1, and Rn—10.8. Explain the behaviour of the change in the ionization energy in this subgroup.

194. The values of the first ionization potentials of Group I elements are (in V): Li—5.4, Cs—3.9, Cu—7.7, and Ag—9.2. Indicate (a) in the elements of what subgroup of Group I the metallic properties are more pronounced, and (b) how the different behaviour of the change in the values of the ionization potentials in the subgroups can be explained.

195. Is the ionization energy of a cesium atom and a lithium atom in which the valence electron was preliminarily excited to the 6s sublevel the same? Substantiate the answer.

196. How does the value of the first ionization potential of second period elements change with a growth in their atomic number? How can the fact be explained that the first ionization potential of the Be atom is higher than that of the Li and B atoms?

197. Explain the behaviour of the change in the ionization energy (in eV) in the row Mg-Al-Si:

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_1 )</td>
<td>7.6</td>
<td>6.0</td>
<td>8.2</td>
</tr>
<tr>
<td>( I_2 )</td>
<td>15.0</td>
<td>18.8</td>
<td>16.3</td>
</tr>
<tr>
<td>( I_3 )</td>
<td>80.1</td>
<td>28.4</td>
<td>33.5</td>
</tr>
</tbody>
</table>

**REVIEW QUESTIONS**

198. What is the physical meaning of the atomic orbitals generally depicted as follows?

\[ \begin{array}{c}
\text{s} \quad \text{o} \\
\text{p} \quad \text{∞}
\end{array} \]

(a) A surface of equal electron density confining an arbitrary part of the electron cloud; (b) the trajectory of an electron;
(c) a surface confining the electron cloud; (d) a surface of equal electron density confining a definite part of the electron cloud.

199. How does the energy of an electron in a many-electron atom depend on the orbital quantum number at a constant value of the principal quantum number? (a) It increases with a growth in \( l \); (b) it diminishes with a growth in \( l \); (c) it remains constant.

Because (1) the dimensions of the electron cloud are determined only by the value of the principal quantum number \( n \); (2) at the same value of \( n \) electrons with a greater value of \( l \) are screened to a greater extent by the inner electrons; (3) with an increase in \( l \) the degree of degeneration of a sublevel grows.

200. How do the values of the first ionization potentials change in the row of elements Li, Be, B, C, N, O, F, and Ne? (a) They grow; (b) they diminish; (c) they change irregularly, but have a tendency of growing.

201. In atoms of what element is the first ionization potential higher—of beryllium or boron? (a) Of Be; (b) of B.

Because (1) in passing from Be to B the charge of the nucleus grows; (2) electron configurations with a completely filled sublevel have an increased stability; (3) when passing from Be to B the dimensions of an atom decrease.

202. Which of the following electron configurations of the ground state of an atom is correct?

(a)

```
     s
  \   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
```

(b)

```
     s
  \   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
```

(c)

```
     s
  \   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
\   \   \   \   \   \   \   \   \\
```
Because (1) in cases... Hund's rule is violated; (2) in cases... the Pauli exclusion principle is violated; (3) in cases... the energy of the atom is not minimum.


Radioactivity. Nuclear Reactions

The chemical symbols in this section stand not for atoms of the relevant elements, but for their nuclei. The subscript indicates the charge of the nucleus numerically coinciding with the atomic number of the element in the periodic table, and the superscript indicates the mass number $A = Z + N$, where $Z$ is the number of protons ($p$) in the nucleus determining the charge of the latter, and $N$ is the number of neutrons ($n$) in the nucleus. The nuclei of all the atoms of a given element have the same charge, i.e. contain the same number of protons; the number of neutrons may differ.

Atoms having an identical charge of their nuclei, but different mass numbers, are called isotopes (for instance, $^{35}_{17}$Cl and $^{37}_{17}$Cl).

Atoms having the same mass numbers, but a different number of protons in their nuclei, are called isobars (for instance, $^{40}_{19}$K and $^{40}_{20}$Ca).

Example 1. The symbol of an isotope of an element is $^{m}_{z}$E. Indicate (a) the name of the element; (b) the number of neutrons and protons in its nucleus; and (c) the number of electrons in the electron shell of the atom.

Solution. The charge of the nucleus in an atom of the required element, i.e. 92, numerically coincides with the number of the element in the periodic table. Element No. 92 is uranium, its symbol is U.

The number of neutrons in the given nucleus is $N = A - Z = 238 - 92 = 146$.

The number of electrons in an atom equals the charge of its nucleus; in our case the number of electrons is 92.

By radioactivity is meant the spontaneous transformation of an unstable isotope of one chemical element into an iso-
Problems and Exercises in General Chemistry

The half-life $T_{1/2}$ is the time needed for half of the original amount of a radioactive isotope to decay. During the first half-life, one-half of the initial number of isotope nuclei $N_0$ decays, and there remain $\frac{1}{2}N_0 = 2^{-1}N_0$ nuclei. During the second half-life, one-half of $2^{-1}N_0$ nuclei decays, and there remain $\frac{1}{2} \times 2^{-1}N_0 = 2^{-2}N_0$ nuclei, and so on. At the end of the $n$th half-life, $2^{-n}N_0$ nuclei of the initial isotope remain. A similar expression holds for the mass $(m)$ of the undecayed isotope: $m = 2^{-n}m_0$, where $m_0$ is the initial mass of the isotope.

Example 2. The half-life of a radioactive isotope is three hours. What mass of it remains undecayed in 18 hours if the initial mass of the isotope was 200 g?

Solution. The number of half-lives that elapsed during the storage time of the radioactive isotope was $18/3 = 6$. Hence, the mass of the undecayed isotope remaining after 18 hours of storage is:

$$m = 2^{-n}m_0 = 2^{-6} \times 200 = \frac{200}{64} = 3.125 \text{ g}$$

The main kinds of radioactive decay include $\alpha$ decay, $\beta^-$ and $\beta^+$ decay, electron capture, and spontaneous fission. These kinds of radioactive decay are often attended by the emission of gamma rays, i.e. of hard (with a small wavelength) electromagnetic radiation.

**Alpha Decay.** An alpha particle is a nucleus of the helium atom $^4\text{He}$. A nucleus emitting an alpha particle loses two protons and two neutrons, consequently, the charge of the nucleus diminishes by 2, and its mass number by 4. The daughter nucleus belongs to an element having an atomic number two less than the parent element: $^{4}_2\text{He} \rightarrow \rightarrow ^2_2\text{He} + ^4_2\text{He}$.

**Electron ($\beta^-$) Decay.** A $\beta^-$ particle is an electron. Electron decay is preceded by the process $^0_0\text{n} \rightarrow ^0_1\text{e}^- + ^1_1\text{p}$ occurring in the nucleus. Hence, upon the emission of an electron, the charge of the nucleus grows by one, while the mass number does not change. The daughter nucleus is an isobar of the parent and belongs to an element whose atomic
number is one greater than that of the parent element: \( z' E \rightarrow z e^- + z+1E' \).

**Positron (\(\beta^+\)) Decay.** A \(\beta^+\) particle, a positron (\(e^+\)), has the mass of an electron and a charge equal to that of an electron, but of the opposite sign. Positron decay is preceded by the nuclear process \( 1\, ^p_p \rightarrow 1\, ^n_n + e^+ \). The number of protons in a nucleus in positron decay diminishes by one, while the mass number does not change. The daughter nucleus is an isobar of the parent and belongs to an element whose atomic number is one less than that of the parent element: \( z' E \rightarrow z e^+ + z^-1E' \).

**Electron Capture.** When a nucleus captures an electron from the \(K\) layer that is the closest to the nucleus, the number of protons in the nucleus decreases because of the process \( 1\, ^p_p + e^- \rightarrow 1n_n \). The charge of the nucleus diminishes by one, while the mass number remains unchanged. The daughter nucleus belongs to an element (an isobar of the parent one) whose atomic number is one less than that of the parent element: \( z' E + e^- \rightarrow z^-1E' + h\nu \).

When a periphery electron passes over to the vacant place in the \(K\) layer, energy is evolved in the form of a quantum of X-ray radiation.

**Example 3.** Complete the following equations of radioactive decay:

(a) \(^{232}\text{Th}\) \(\alpha\) \(\rightarrow\); (b) \(^{239}\text{Np}\) \(\beta^-\) \(\rightarrow\); (c) \(^{57}\text{Co}\) \(\beta^+\);

(d) \(^{39}\text{K}\) \(K\) capture \(\rightarrow\)

**Solution.**

(a) \(^{232}\text{Th} \rightarrow ^{228}\text{He} + ^{228}\text{Ra}\); (b) \(^{239}\text{Np} \rightarrow ^{239}\text{Pu}\);

(c) \(^{57}\text{Co} \rightarrow ^{57}\text{Fe} + ^{55}\text{Fe}\); (d) \(^{39}\text{K} + e^- \rightarrow ^{39}\text{Ar} + h\nu\)

Equations of nuclear reactions (including those of radioactive decay) must obey the rule that the sum of the mass numbers of the reactants should equal that of the products (the equality of the superscripts), no account being taken of the masses of electrons, positrons, and photons, and the rule that the sum of the charges of the reactants must equal that of the products (the equality of the subscripts).
Example 4. Complete the equations of the following nuclear reactions:

(a) $^{53}\text{Cr}+\alpha\rightarrow n+\ldots$;  
(b) $^{19}\text{F}+{\dot{p}}\rightarrow \ldots+\gamma$

Solution. 
(a) We write the equation of the reaction in the form:

$$^{53}\text{Cr}+\alpha\rightarrow n+\text{A}_{2}\text{E}$$

For the superscripts, we have $53 + 2 = 1 + A$, whence $A = 53 + 2 - 1 = 54$. For the subscripts, we have $24 + 1 = 0 + Z$, whence $Z = 25$.

The nucleus $^{54}\text{E}$ formed is a manganese isotope. The completed equation of the reaction is:

$$^{53}\text{Cr}+\alpha\rightarrow n+^{54}\text{Mn}$$

A concise form of writing an equation of a nuclear reaction is: parent nucleus [bombarding particle, emitting particle] daughter nucleus. Consequently, the above equation becomes

$$^{53}\text{Cr}[\alpha, n]^{54}\text{Mn}$$

(b) $^{19}\text{F}+{\dot{p}}\rightarrow \text{A}_{2}\text{E}+\gamma$

For the superscripts: $19 + 1 = A + 0$; $A = 20$.

For the subscripts: $9 + 1 = Z + 0$; $Z = 10$.

The daughter nucleus $^{20}\text{E}$ is a neon isotope.

The complete equation of the nuclear reaction is

$$^{19}\text{F}+{\dot{p}}\rightarrow ^{20}\text{Ne}+\gamma$$

The concise form of the equation is $^{19}\text{F}[p, \gamma]^{20}\text{Ne}$.

PROBLEMS

203. The symbol of an isotope of an element is $^{24}\text{E}$. Indicate (a) the name of the element, (b) the number of protons and neutrons in the nucleus, and (c) the number of electrons in the electron shell of the atom.

204. The nucleus of an atom of an element contains 16 neutrons, and the electron shell of the atom—15 electrons. Name the element whose isotope the given atom is. Write its symbol indicating the charge of the nucleus and the mass number.

205. The mass number of an atom of an element is 181, and the electron shell of the atom contains 73 electrons. Indicate the number of protons and neutrons in the nucleus of the atom and name the element.

206. Natural chlorine compounds contain chlorine in the form of the isotopes $^{35}\text{Cl} [75.5\% \text{ (mass)}]$ and $^{37}\text{Cl} [24.5\%$
(mass)]. Calculate the average atomic mass of natural chlorine.

207. Natural magnesium consists of the isotopes $^{24}\text{Mg}$, $^{25}\text{Mg}$, and $^{26}\text{Mg}$. Calculate the average atomic mass of natural magnesium if the content of the individual isotopes in atomic per cent is 78.6, 10.1, and 11.3, respectively.

208. Natural gallium consists of the isotopes $^{71}\text{Ga}$ and $^{69}\text{Ga}$. In what quantitative ratio are the numbers of atoms of these isotopes if the average atomic mass of gallium is 69.72 amu?

209. Find the mass of the isotope $^{81}\text{Sr}$ ($T_{1/2} = 8.5 \text{ h}$) remaining after 25.5 hours of storage if its initial mass was 200 mg.

210. Find the percentage of the atoms of the isotope $^{129}\text{I}$ ($T_{1/2} = 25 \text{ min}$) remaining after its storage for 2.5 hours.

211. The half-life of the $\beta^+$ radioactive isotope $^{24}\text{Na}$ is 14.8 hours. Write the equation of the decay reaction and calculate how many grams of the daughter product are formed from 24 g of $^{24}\text{Na}$ during 29.6 hours.

212. Complete the following equations of radioactive decay reactions:

(a) $^{238}\text{U} \rightarrow ^{\alpha} \rightarrow$; (b) $^{232}\text{U} \rightarrow ^{\alpha} \rightarrow$; (c) $^{238}\text{Pu} \rightarrow ^{\alpha} \rightarrow$;

(d) $^{87}\text{Rb} \rightarrow ^{\beta^-} \rightarrow$; (e) $^{234}\text{Th} \rightarrow ^{\beta^-} \rightarrow$; (f) $^{57}\text{Mn} \rightarrow ^{\beta^+} \rightarrow$;

(g) $^{18}\text{F} \rightarrow ^{\beta^+} \rightarrow$; (h) $^{14}\text{C} \rightarrow ^{\beta^+} \rightarrow$; (i) $^{44}\text{Ti} \rightarrow ^{\beta^+} \rightarrow$.

In what cases is the daughter atom an isobar of the parent atom?

213. What kind of radioactive decay is observed in the following transformations? (a) $^{226}\text{Ra} \rightarrow ^{226}\text{Rn}$; (b) $^{237}\text{Np} \rightarrow ^{237}\text{Pu}$; (c) $^{152}\text{Sm} \rightarrow ^{152}\text{Nd}$; (d) $^{111}\text{Pd} \rightarrow ^{111}\text{Ag}$.

214. Write the equations of the nuclear reactions: (a) $^{28}\text{Ni} + ^1\text{H} \rightarrow ? \rightarrow ? + ^4\text{He}$; (b) $^{10}\text{B} + ^4\text{He} \rightarrow ? + ^4\text{He}$; (c) $^{37}\text{Al} + ^1\text{H} \rightarrow ? + ^4\text{He}$; (d) $? + ^1\text{H} \rightarrow ^{55}\text{Br} \rightarrow ? + ^4\text{He}$.

215. Write the complete equations of the following nuclear reactions: (a) $^{64}\text{Zn} [p, n]$; (b) $^{61}\text{V} [\alpha, n]$; (c) $^{66}\text{Fe} [D, ?]$; (d) $? [\alpha, D]$; (e) $^{58}\text{Mn} [? , \alpha]$.

216. How will the mass number and the charge of an isotope atom change (a) in the consecutive emission of an $\alpha$ particle and two $\beta^-$ particles, (b) upon the absorption of two
protons by the nucleus and the emission of two neutrons, and (c) upon the absorption of one alpha particle and the emission of two deuterons?

217. How many α and β− particles must a 226Ra nucleus lose to obtain a daughter element with a mass number of 206 belonging to Group IV of the periodic table? Name this element.

218. An atomic nucleus of the isotope 235U transformed into a 226Ra nucleus as a result of radioactive decay. How many α and β− particles did the parent nucleus emit?

REVIEW QUESTIONS

219. The isotope 40K transforms into the isotope 40Ca. What kind of radioactive decay occurs in this case? (a) Alpha decay; (b) β− decay; (c) β+ decay; (d) electron capture; (e) spontaneous fission.

220. What kind of radioactive decay leads to the formation of a daughter nucleus that is an isobar with respect to the parent nucleus? (a) Alpha decay; (b) β− decay; (c) β+ decay; (d) electron capture; (e) none of these processes.

221. How do the mass number and charge of an atom change upon the emission of one α particle and two β− particles? (a) The charge diminishes by 2, and the mass number by 4; (b) the charge grows by 2, while the mass number diminishes by 4; (c) the charge does not change, while the mass number diminishes by 4; (d) neither the charge nor the mass number changes.

222. A photon of hard gamma radiation knocks a proton out of a 25Mg nucleus. What is formed is (a) the isotope nucleus 25Mg; (b) the isobar nucleus 12Mg; (c) the isotope nucleus 25Na; (d) the isobar nucleus 25Na.

223. What radioactive family does the isotope 207Pb belong to? (a) 232Th; (b) 237Np; (c) 237Ac; (d) 238U.

224. Can the isotope 222Rn with a half-life of 3.2 days be found in nature? (a) Yes; (b) no.

Because (1) the half-life of this isotope is much less than the age of the Earth; (2) this isotope is a member of a radioactive family; (3) radon has longer-living isotopes.
1. Kinds of Chemical Bond. Ways of Forming a Covalent Bond

The description of the chemical bond in any molecule is in essence a description of the distribution of the electron density in it. According to the nature of this distribution, covalent, ionic, and metallic* bonds are traditionally distinguished.

A covalent bond is a chemical bond between two atoms formed by a pair of electrons shared by these atoms (H₂, Cl₂, etc.).

An ionic bond is the result of electrostatic interaction of oppositely charged ions having separate electron shells (Cs⁺F⁻, Na⁺Cl⁻, etc.).

A purely ionic bond is only an extreme case. In the overwhelming majority of molecules, the chemical bonds have a nature that is intermediate between purely covalent and purely ionic bonds. They are polar covalent bonds formed by a pair of electrons shared by two atoms and displaced towards the nucleus of one of the participating atoms. If this displacement is not great, the bond approaches a purely covalent one in its nature. The greater this displacement, the closer is a bond to a purely ionic one.

To assess the ability of an atom of a given element to attract electrons towards itself that are responsible for bond formation, the value of the relative electronegativity (χ) is used. The higher the electronegativity of an atom, the stronger does it attract the shared electrons. In other words, when a covalent bond is formed between two atoms of different elements, the shared electron cloud shifts towards the atom with the higher electronegativity, and to a greater

* A metallic bond is realized in metals. This kind of bond is treated in studying metals.
extent when the difference between the electronegativities ($\Delta\chi$) of the two atoms is higher. Consequently, a growth in $\Delta\chi$ is attended by an increase in the ionic nature of a bond. The values of the electronegativities for atoms of selected elements relative to that of fluorine taken equal to 4.0 are given in Table 1.

**Table 1**

Relative Electronegativities of Selected Atoms

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.98</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
<td>3.07</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Na</td>
<td>0.93</td>
<td>1.2</td>
<td>1.6</td>
<td>1.9</td>
<td>2.2</td>
<td>2.6</td>
<td>3.0</td>
</tr>
<tr>
<td>K</td>
<td>0.91</td>
<td>1.04</td>
<td>1.8</td>
<td>2.0</td>
<td>2.1</td>
<td>2.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Rb</td>
<td>0.89</td>
<td>0.99</td>
<td>1.5</td>
<td>1.7</td>
<td>1.8</td>
<td>2.1</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Example 1. Calculate the difference between the relative electronegativities of the atoms for the bonds H—O and O—E in the compounds $E(OH)_2$, where E is Mg, Ca, or Sr, and determine (a) which of the bonds H—O or O—E is closer to an ionic one in each molecule, and (b) what is the nature of the ionization of these molecules in an aqueous solution.

**Solution.** We use Table 1 to calculate the difference between the relative electronegativities for the bonds O—E: $\Delta\chi(Mg-O) = 3.5 - 1.2 = 2.3$, $\Delta\chi(Ca-O) = 3.5 - 1.04 = 2.46$, and $\Delta\chi(Sr-O) = 3.5 - 0.99 = 2.51$. The value of $\Delta\chi$ for the bond O—H is 3.5 — 2.1 = 1.4.

Thus (a) in all the molecules considered, the bond E—O is more polar, i.e. is closer to an ionic one, and (b) ionization in aqueous solutions will occur along the most ionic bond in accordance with the equation $E(OH)_2 = E^{2+} + 2OH^{-}$; consequently, all the compounds will ionize like bases.

Two approaches can be used for a quantum-mechanical description of a covalent bond and the structure of molecules: the method of valence bonds and the method of molecular orbitals.
The method of valence bonds (the VB method) is based on the following propositions:

1. A covalent chemical bond is formed by two electrons with antiparallel (opposite) spins and belonging to two atoms. Such a shared electron pair can be formed either as the result of the pairing of two unpaired electrons belonging to different atoms (the usual mechanism of bond formation), or at the expense of a pair of electrons of one atom—the donor—and a vacant orbital of a second atom—the acceptor (the donor-acceptor mechanism of bond formation).

2. The strength of a covalent bond grows with an increasing degree of overlapping of the interacting electron clouds. Hence, a covalent bond is formed in the direction in which this overlapping is the greatest.

Example 2. Explain the mechanism of formation of the SiF₄ molecule and the SiF³⁻ ion. Can the CF₃⁻ ion exist?

Solution. The electron configuration of a silicon atom is 1s²2s²2p⁶3s²3p⁴. The electron structure of its valence orbitals in the unexcited state can be represented as follows:

When excited, a silicon atom passes over to the state 1s²2s²2p⁶3s¹3p⁴, and the electron structure of its valence orbitals can be represented as follows:

The four unpaired electrons of the excited atom can participate in the formation of four covalent bonds according to the usual mechanism with fluorine atoms (1s²2s²2p⁶) each having one unpaired electron, with the production of the SiF₄ molecule.

To form the SiF³⁻ ion, two F⁻ ions (1s²2s²2p⁶), all of whose valence electrons are paired, must be attached to the SiF₄ molecule. The bond is a donor-acceptor one at the expense of a pair of electrons of each of the fluoride ions and two vacant 3d orbitals of the silicon atom.
Carbon \((1s^2\ 2s^2\ 2p^2)\) can form the compound \(\text{CF}_4\) similar to \(\text{SiF}_4\), but the valence possibilities of carbon will be exhausted (there are no unpaired electrons, unshared electron pairs, and no vacant orbitals at the valence level). The \(\text{CF}_4^+\) ion cannot be formed.

Example 3. How will the strength of the bond \(H—E\) change in the series \(\text{H}_2\text{O—H}_2\text{S—H}_2\text{Se—H}_2\text{Te}\)?

Solution. In this series, the dimensions of the valence electron clouds of the elements (O, S, Se, and Te) grow, which diminishes the degree of their overlapping with the electron cloud of a hydrogen atom and leads to an increasing remoteness of the region of overlapping from the nucleus of the atom of the relevant element. This weakens the attraction of the nuclei of the interacting atoms to the region of overlapping of the electron clouds, i.e. to weakening of the bond. The increasing screening of the nuclei of the elements being considered in the series \(\text{O—S—Se—Te}\) owing to an increase in the number of intermediate electron layers leads to the same result. Consequently, the strength of the bond \(H—E\) diminishes when going from oxygen to tellurium.

The method of molecular orbitals is based on the assumption that the state of the electrons in a molecule can be described as a collection of molecular electron orbitals (molecular electron clouds), with a definite set of molecular quantum numbers corresponding to each molecular orbital (MO). As in any other many-electron system, the Pauli exclusion principle remains in force for a molecule. Therefore, each MO can accommodate not over two electrons that must have opposite spins. Hund’s rule also holds, according to which a distribution of the electrons between energy-equivalent orbitals such that the absolute value of the total spin of the molecule is maximum corresponds to the minimum energy of a molecule. If an MO has unpaired electrons, the molecule is paramagnetic, and if all the electrons are paired, it is diamagnetic.

In a particular case, the molecular electron cloud can be concentrated near one of the atomic nuclei in the molecule; such an electron virtually belongs to one atom and does not participate in the formation of a bond. These MO’s are called antibonding; they correspond to the AO’s of isolated atoms in their energy.

If the predominating part of an electron cloud belongs to two or several nuclei, this corresponds to the formation of two- or multiple-centre bonds, respectively. In such cases, the molecular wave function can be represented as a linear combination of the atomic wave functions of the interacting
electrons (the method of linear combination of atomic orbitals—the MO LCAO method).

If two AO's combine (for instance, the 1s AO's of two hydrogen atoms), two MO's form that differ in their energy from the original AO's; one of them corresponds to a lower energy of the electrons (a bonding MO), and the other to a higher energy of the electrons (an antibonding MO) in comparison with their energy in the AO's.

In the general case, \( n \) initial AO's form \( n \) MO's. A chemical bond appears between atoms when the number of electrons in the bonding MO's exceeds their number in the antibonding MO's. By the multiplicity (order) of a bond in the MO method is meant the half-difference of the number of bonding and the number of antibonding electrons. A single bond corresponds to two bonding electrons not compensated by antibonding electrons.

The higher the multiplicity of a bond, the smaller is its length and the higher is the bond dissociation energy.

Example 4. Explain from the standpoints of the MO method the possibility of the existence of the molecular ion \( \text{He}^+ \) and the impossibility of the existence of the molecule \( \text{He}^2 \).

Solution. The molecular ion \( \text{He}^+ \) has three electrons. The energy-level diagram showing the formation of this ion, with account taken of the Pauli exclusion principle, is as follows:

\[
\begin{array}{ccc}
\text{AO} & \text{MO} & \text{AO} \\
\text{He} & \text{He}^+ & \text{He}^+ \\
1s & \sigma^b 1s & 1s \\
\end{array}
\]

The bonding orbital accommodates two electrons, and the antibonding orbital, one. Hence, the bond multiplicity in this ion is 0.5, and it must be stable with respect to its energy.

Conversely, the \( \text{He}^2 \) molecule must be unstable as regards its energy because of the four electrons that have to be accommodated on the MO's, two will occupy a bonding MO and two, an antibonding one. Consequently, the formation of an \( \text{He}^2 \) molecule will not be attended by the liberation of energy. The multiplicity of a bond in this case is zero—no molecule forms.
A diagram showing the formation of MO’s with the participation of the $2p$ orbitals of two identical atoms is given in Fig. 1. A glance at the figure shows that the six $p$ orbitals produce six MO’s: three bonding and three antibonding. One bonding and one antibonding MO’s belong to the sigma type: they are formed by the interaction of $p$ orbitals whose electron clouds are oriented along the bond axis (MO’s produced from $s$ AO’s also belong to this type). Two bonding and two antibonding MO’s are formed by the interaction of $p$ orbitals whose electron clouds are oriented at right angles to the bond axis; these orbitals belong to the pi type.

Example 5. Which of the molecules $\text{Ba}$ and $\text{Cs}$ has a higher energy of dissociation into atoms? Compare the magnetic properties of these molecules.

Solution. We draw energy-level diagrams showing the formation of $\text{B}_2$ and $\text{C}_2$ molecules (Fig. 2). The difference between the number of bonding and the number of antibonding electrons in the $\text{B}_2$ molecule can be seen to be two, and in the $\text{C}_2$ molecule, four. This corresponds to a bond multiplicity of 1 and 2, respectively. Consequently, the $\text{C}_2$ molecule having a higher multiplicity of the bond between the atoms must be more stable. This conclusion corresponds to the experimentally established values of the energy of dissociation into atoms of the molecules $\text{B}_2$ (278 kJ/mol) and $\text{C}_2$ (605 kJ/mol).
In the \( B_2 \) molecule, two electrons are arranged, according to Hund's rule, in two \( \pi^b_{2p} \) orbitals. The presence of two unpaired electrons imparts paramagnetic properties to this molecule. In the \( C_2 \) molecule, all the electrons are paired, consequently, this molecule is diamagnetic.

\[
\begin{align*}
\text{AO's} & \quad \text{MO's} & \quad \text{AO's} \\
B & \quad B_2 & \quad C & \quad C_2
\end{align*}
\]

\[
\begin{align*}
\sigma^b_{2s} & \quad \sigma^b_{2p} & \quad \pi^b_{2p} & \quad \sigma^b_{2p} \\
\pi^b_{2p} & \quad \sigma^b_{2p} & \quad \pi^b_{2p} & \quad \sigma^b_{2p} \\
\sigma^b_{2s} & \quad \sigma^b_{2s} & \quad \sigma^b_{2s} & \quad \sigma^b_{2s}
\end{align*}
\]

\( \text{Fig. 2. Energy-level diagrams showing the formation of } B_2 \text{ and } C_2 \text{ molecules} \)

In heteronuclear (formed of different elements) diatomic molecules, the bonding MO's in their energy are close to the orbitals of the more electronegative atom, and the antibonding MO's are close to the AO's of the less electronegative atom.

Example 6. How are the electrons distributed between the MO's in the \( \text{CN} \) molecule and in the \( \text{CN}^- \) molecular ion formed according to the equation \( \text{C}^- + \text{N} \rightarrow \text{CN}^- \)? In which of these particles is the bond length smaller?

Solution. After drawing energy-level diagrams showing the formation of the particles being considered (Fig. 3), we arrive at the conclusion that the multiplicity of the bond in \( \text{CN} \) and \( \text{CN}^- \) is 2.5 and 3, respectively. The \( \text{CN}^- \) ion in which the multiplicity of the bond between the atoms is greater has the smaller bond length.
225. The ionization energy of fluorine and chlorine atoms is 17.4 and 13.0 eV, respectively, while their energy of affinity to an electron is 3.45 and 3.61 eV. For which of these elements is the formation of ionic compounds more characteristic? Indicate the sign of the charge on the halide ions in these compounds.

226. Indicate the type of chemical bond in the molecules H₂, Cl₂, and HCl. Draw a diagram of electron cloud overlapping.

227. Using the table of relative electronegativities, calculate their difference for the bonds K—Cl, Ca—Cl, Fe—Cl, and Ge—Cl. Which of the bonds is most ionic?

228. What is the nature of the bond in the molecules NCl₃, CS₂, ICl₅, NF₃, OF₂, ClF, and CO₂? Indicate for each of them the direction of displacement of the shared electron pair.

229. Write the electron dot formula of the chloroform molecule CHCl₃ and indicate (a) which bond is the most polar, and (b) in what direction the electron cloud of this bond is displaced.

230. Calculate the difference between the relative electronegativities of atoms for the bonds H—O and O—Hal (where
Hal is Cl, Br, or I) in the compounds HOHal and determine (a) which of the bonds in each molecule is more ionic, and (b) the nature of the dissociation of the molecules in an aqueous solution.

231. Calculate the difference between the relative electronegativities of the atoms for the bonds H—O and O—As. Which of the bonds is more polar? What class of hydroxides does As(OH)$_3$ belong to?

232. How does the bond strength change in the series HF-HCl-HBr-HI? Indicate the reasons for these changes.

233. Describe the electron configuration of the BF$_3$ molecule and the BF$_4^-$ ion from the standpoint of the VB method.

234. Compare the methods of covalent bond formation in the molecules CH$_4$, NH$_3$, and in the ion NH$_4^+$. Can the ions CH$_5^+$ and NH$_3^{2+}$ exist?

235. What atom or ion is the donor of an electron pair in the formation of the BH$_4^-$ ion?

236. Explain from the standpoint of the VB method the ability of the oxides NO and NO$_2$ to form dimeric molecules.

237. Explain from the standpoint of the VB method the possibility of the formation of the C$_2$N$_3$ molecule.

238. Describe the electron configuration of the CO and CN molecules from the standpoints of the VB and MO methods. Which of these molecules is characterized by a greater bond multiplicity?

239. Consider from the standpoint of the MO method the possibility of formation of the B$_2$, F$_2$, and BF molecules. Which of them is the most stable?

240. Why can no stable molecules Be$_2$ and Ne$_2$ exist?

241. How do the bond length, the dissociation energy, and the magnetic properties change in the series O$_2^-$.O$_2^-$.O$_2^-$.O$_2^-$? Motivate your answer.

242. Which of the particles NO+, NO, or NO$^-$ has the smallest bond length?

243. Explain from the standpoint of the VB and MO methods the change in the dissociation energy (kJ/mol) of the molecules in the series F$_2$ (155)-O$_2$ (493)-N$_2$ (945).

244. The dissociation energy of the N$_2$ and CO molecules is 945 and 1071 kJ/mol, respectively. Explain the closeness of these values from the angles of view of the VB and MO methods.
REVIEW QUESTIONS

245. What is the covalence of carbon in the CO molecule? (a) Two; (b) three; (c) four.
Because (1) an unexcited carbon atom has two unpaired electrons; (2) the carbon atom can be an acceptor of an electron pair; (3) the carbon atom has four valence electrons.

246. Can a reaction occur between HF and SiF₄? (a) Yes; (b) no.
Because (1) the HF molecule is polar, and the SiF₄ molecule is not polar; (2) both molecules have no unpaired electrons; (3) the number of valence orbitals of silicon is greater than four, and part of them are not occupied by valence electrons; (4) the number of valence electrons of silicon is four; (5) the HF molecule can play the role of an electron pair donor.

247. What magnetic properties does the O₂ molecule have? (a) Diamagnetic; (b) paramagnetic.
Because (1) the O₂ molecule contains an even number of electrons; (2) the total spin of the O₂ molecule differs from zero.

248. What is the bond multiplicity in an NO molecule? (a) Two; (b) two and a half; (c) three.
Because (1) the number of bonding electrons in the pi orbitals is four; (2) the number of bonding electrons is five greater than that of antibonding electrons; (3) the nitrogen atom has three unpaired electrons.

249. Which of the particles listed below is paramagnetic? (a) N₂; (b) O₂; (c) NO; (d) CO; (e) CN.

250. Which of the particles listed below cannot exist in a stable state from the standpoint of the MO theory? (a) H₂⁺; (b) H⁺; (c) H₂; (d) He₂; (e) HHe.

2. Molecular Polarities.
Geometrical Structure of Molecules

In the formation of a polar covalent bond, the shifting of the shared electron cloud leads to the density of the negative electrical charge being higher near the more electronegative atom and lower near the less electronegative one. As a result, the first atom acquires a surplus negative
charge, and the second one—a surplus positive charge of the same magnitude. Such a system of two charges equal in magnitude, opposite in sign, and at a definite distance from each other is called an electric dipole.

The strength of the field set up by a dipole is proportional to the dipole moment of a molecule, which is the product of the magnitude of the charge of an electron $q$ ($1.60 \times 10^{-19}$ C) and the distance $l$ between the centres of the positive and negative charges in the dipole:

$$\mu = ql.$$ 

The dipole moment of a molecule is a quantitative measure of its polarity. The dipole moments of molecules are usually measured in debyes (D). $1 \text{ D} = 3.33 \times 10^{-30}$ C·m.

Example 1. The length of the dipole of an HCl molecule is $0.22 \times 10^{-8}$ cm. Calculate the dipole moment of the molecule.

Solution. $q = 1.60 \times 10^{-19}$ C, $l = 0.22 \times 10^{-8}$ cm or $2.2 \times 10^{-11}$ m.

$$\mu = ql = 1.60 \times 10^{-19} \times 2.2 \times 10^{-11} = 3.52 \times 10^{-30} \text{ C} \cdot \text{m} =$$

$$= \frac{3.52 \times 10^{-30}}{3.33 \times 10^{-30}} \text{ D} = 1.06 \text{ D}$$

The dipole moment is a vector quantity directed from the positive end of a dipole to its negative one. For this reason, the dipole moment of a polyatomic molecule should be considered as the vector sum of the dipole moments of the bonds: it depends not only on the polarity of each bond, but also on the mutual arrangement of the bonds.

For instance, the molecule $\text{AB}_2$ can have either a linear (a) or a V-shaped (b) structure:

![Diagram](a)

The molecule $\text{AB}_3$ can be constructed in the form of an equilateral plane triangle (a), a triangular pyramid (b), or the letter T (c):

![Diagram](b)
In linear $AB_2$, triangular $AB_3$, tetrahedral and square $AB_4$ molecules, the dipole moments of the $A-B$ bonds compensate one another so that the net dipole moments of these molecules are zero. Such molecules are not polar, notwithstanding the polarity of the individual bonds.

In V-shaped $AB_2$ molecules, pyramidal and T-shaped $AB_3$ molecules, the dipole moments of the individual bonds are not compensated; the dipole moments of such molecules do not equal zero.

Example 2. The dipole moment of the ammonia molecule is 1.48 D. Calculate the length of the dipole. Can the molecule be assumed to have the shape of a regular triangle?

**Solution.**

\[
\mu = 1.48 \text{ D} = 1.48 \times 3.33 \times 10^{-30} \text{ C.m} = 4.93 \times 10^{-30} \text{ C.m}, \quad q = 1.60 \times 10^{-19} \text{ C.}
\]

Hence,

\[
l = \frac{\mu}{q} = \frac{4.93 \times 10^{-30}}{1.60 \times 10^{-19}} = 3.08 \times 10^{-11} \text{ m} = 0.0308 \text{ nm}
\]

The $NH_3$ molecule cannot have the shape of an equilateral triangle because in this case its dipole moment would equal zero. It is actually constructed in the form of a triangular pyramid with the nitrogen atom at its vertex and the hydrogen atoms at the corners of its base.

To explain the geometrical structure of molecules, in other words to explain the directional nature of covalent bonds, the notion of hybridization of the AO's in the central atom is used. According to this notion, the formation of chemical bonds may be preceded by a change in the valence orbitals of an atom: the original non-equivalent atomic orbitals, as it were, intermix and form orbitals identical in energy. Redistribution of the electron density occurs that requires the expenditure of energy and is not realized in isolated atoms. As a result of hybridization, however, the
electron cloud stretches out in a direction towards the interacting atom, owing to which its overlapping with the electron clouds of the latter grows. This leads to the formation of a stronger chemical bond and, consequently, to the evolution of extra energy, which compensates the expenditure of energy for hybridization.

The number of hybrid AO's equals the number of original AO's of an atom participating in hybridization. If one $s$ and one $p$ orbitals participate in hybridization ($sp$ hybridization), two equivalent $sp$ orbitals are formed; one $s$ and two $p$ orbitals produce three $sp^2$ orbitals ($sp^2$ hybridization), and so on.

The hybrid clouds corresponding to a given kind of hybridization are arranged in an atom so that the interaction between electrons is minimum, i.e. as far as possible from one another. Therefore, in $sp$ hybridization, the electron clouds are oriented in opposite directions, in $sp^2$ hybridization—in directions lying in one plane and making angles of 120 degrees with one another (i.e. in directions towards the corners of an equilateral triangle), in $sp^3$ hybridization—towards the corners of a tetrahedron (the angle between these directions is 109°28'), and in $sp^3d^2$ hybridization—towards the corners of an octahedron (i.e. in mutually perpendicular directions). The hybrid orbital directional characteristics for selected kinds of hybridization are shown in Table 2. Each arrow depicts the direction of the axis of one of the clouds.

**Table 2**

<table>
<thead>
<tr>
<th>Kind of hybridization</th>
<th>$sp$</th>
<th>$sp^2$</th>
<th>$sp^3$</th>
<th>$sp^3d^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of hybrid clouds</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

Directions of orientation of hybrid clouds

[Diagram of hybrid orbital directional characteristics]
The spatial structure of a molecule is determined by the kind of hybridization of the valence orbitals in the central atom and by the number of unshared electron pairs in its valence electron layer.

Example 3. By what kind of hybridization of the AO's of nitrogen is the formation of the NH₄⁺ ion and the NH₃ molecule explained? What is the spatial structure of these particles?

Solution. Both in the ammonium ion and in the ammonia molecule, the valence electron layer of the nitrogen atom contains four electron pairs:

\[
\begin{array}{c}
\text{H} \\
\vdots \\
\vdots \\
\vdots \\
\text{H} \\
\text{H} \\
\end{array} 
\]

Consequently, in both cases, the electron clouds of the nitrogen atom will be the greatest distance apart in \( sp^3 \) hybridization, when their axes are directed towards the corners of a tetrahedron. In the NH₄⁺ ion, all the corners of the tetrahedron are occupied by hydrogen atoms, so that this ion has a tetrahedral configuration with the nitrogen atom at the centre of the tetrahedron.

When an ammonia molecule forms, the hydrogen atoms occupy only three corners of a tetrahedron, while the electron cloud of the unshared electron pair of the nitrogen atom is directed towards the fourth corner. This can be depicted as follows:

The figure thus formed is a triangular pyramid with the nitrogen atom at its vertex and the hydrogen atoms at the corners of its base.

PROBLEMS

251. The dipole moment of the HCN molecule is 2.9 D. Calculate the length of the dipole.
252. The length of the dipole of the hydrogen fluoride molecule is \( 4 \times 10^{-11} \) m. Calculate its dipole moment in coulomb-metres and in debyes.
253. The dipole moments of H₂O and H₂S molecules are 1.84 and 0.94 D, respectively. Calculate the lengths of the dipoles. In which molecule is the bond more polar? Indicate
254. Describe the spatial structure of the non-polar BeCl₂ molecule. What AO’s of beryllium participate in the formation of the Be—Cl bonds?

255. The dipole moment of the SO₂ molecule is 1.61 D, and that of the CO₂ molecule is zero. Are the valence angles OSO and OCO the same? Motivate your answer.

256. The dipole moment of the CS₂ molecule is zero. By what type of hybridization of carbon’s atomic orbitals is the formation of this molecule described?

257. The dipole moments of BF₃ and NF₃ molecules equal 0 and 0.2 D, respectively. By what types of hybridization of the AO’s of boron and nitrogen is the formation of these molecules described?

258. What types of hybridization of carbon AO’s correspond to the formation of the molecules CH₄, C₂H₆, C₂H₄, C₃H₈?

259. Indicate the type of hybridization of silicon’s AO’s in SiH₄ and SiF₄ molecules. Are these molecules polar?

260. In SO₂ and SO₃ molecules, the sulphur atom’s is in the state of sp² hybridization. Are these molecules polar? What is their spatial structure?

261. When SiF₄ reacts with HF, the strong acid H₄SiF₆ is formed that dissociates into H⁺ and SiF₆²⁻ ions. Can the reaction between CF₄ and HF proceed in a similar way? Indicate the type of hybridization of silicon’s AO’s in the SiF₆²⁻ ion.

REVIEW QUESTIONS

262. Is the geometrical configuration of BF₃ and NF₃ molecules the same? (a) Yes; (b) no.
Because (1) the covalence of the central atom in both molecules is the same; (2) one of the molecules is polar, and the other is not.

263. In what molecule—BF₃ or NH₃—is the value of the dipole moment greater? (a) The dipole moments are equal; (b) in BF₃; (c) in NH₃.
Because (1) the difference between the electronegativities of the atoms in the BF₃ molecule is greater than in the NH₃ molecule; (2) the BF₃ molecule has a planar structure, while...
the \( \text{NH}_3 \) molecule is pyramidal; (3) the nitrogen atom has an unshared pair of electrons, while the boron atom has a free (vacant) valence orbital.

264. Indicate the type of hybridization of carbon’s AO’s in the carbon dioxide molecule. (a) \( sp \); (b) \( sp^2 \); (c) \( sp^3 \); (d) there is no hybridization.

Because (1) all the valence electrons of the carbon atom participate in bond formation; (2) the carbon atom has two unpaired electrons in the \( 2p \) orbitals; (3) the \( \text{CO}_2 \) molecule has a linear structure.

3. Ionic Bond. Polarization of Ions

An ionic bond is non-directional and does not have saturation. In this connection, ionic compounds tend to associate. All ionic compounds in the solid state form ionic crystal lattices in which each ion is surrounded by several ions of the opposite sign. All the bonds of a given ion with its neighbouring ions are equivalent so that the entire crystal can be considered as a single molecule.

The properties of ionic compounds are determined in many respects by the mutual polarization of ions in them. The polarization of an ion manifests itself in the relative displacement of the nucleus and the electrons of the outer electron shell surrounding it under the action of the electric field of the adjacent ion; the valence electrons are displaced towards the cations. Such a deformation of the electron shell leads to diminishing of the ionic nature of a bond and to its transformation into a polar covalent bond.

The polarizability of ions (i.e. their ability to deform under the action of an external electric field) is characterized by the following features:

1. With an identical magnitude of the charge and equal ionic radii, the polarizability of anions is greater than that of cations.

2. The polarizability of ions having a similar electron configuration grows with an increase in the ionic radius (i.e. with an increasing number of electron layers). For instance, the polarizability of halide and alkali metal ions grows in the following order:

\[ \text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-; \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ \]
3. With an identical charge and identical ionic radius, the polarizability of ions with an 18-electron shell (for example, Cu\(^+\) and Cd\(^{2+}\)) is higher than that of ions with a noble-gas electron configuration (Na\(^+\), Ca\(^{2+}\), etc.).

The polarizing power of an ion (i.e. its ability to deform, or polarize, another ion) grows with an increasing charge and diminishing ionic radius and depends greatly on its electron structure. Ions with a noble-gas electron configuration (for example, Ca\(^{2+}\) and Ba\(^{2+}\)) have a weaker polarizing power than ions with an unfilled electron layer (Ti\(^{2+}\), Fe\(^{2+}\), Pb\(^{2+}\), etc.). The strongest polarizing power (with the same charge of an ion) is exhibited by ions with an 18-electron structure of their outer layer (Cu\(^+\), Ag\(^+\), Zn\(^{2+}\), Cd\(^{2+}\), Hg\(^{2+}\)).

Since the dimensions of anions, as a rule, are greater than those of cations, anions have a higher polarizability and a lower polarizing power than cations. Consequently, when a cation reacts with an anion, the anion is mainly subjected to polarization; the polarization of the cation may be ignored in the majority of cases.

**Example 1.** The ionic radii of Na\(^+\) and Cu\(^+\) are the same (0.098 nm). Explain the difference between the melting points of sodium chloride (801 °C) and copper(I) chloride (430 °C).

**Solution.** Since the Na\(^+\) and Cu\(^+\) ions have identical charges and dimensions, the difference in their polarizing power is explained by the features of their electron structure. The Cu\(^+\) ion has an 18-electron outer shell and polarizes the Cl\(^-\) anion more strongly than the Na\(^+\) ion having a noble-gas electron configuration. Consequently, in copper(I) chloride, polarization results in the transfer of a greater part of the electron charge from the anion to the cation than in sodium chloride. The effective charges of the ions in a CuCl crystal are smaller than in an NaCl one, while the electrostatic interaction between them is weaker. This is what explains the lower melting point of CuCl in comparison with NaCl whose crystal lattice is close to the purely ionic type.

**Example 2.** Calcium fluoride does not dissociate into atoms even at 1000 °C, while copper(II) iodide is unstable even at ordinary temperatures. How can the different stability of these compounds be explained?

**Solution.** The Cu\(^{2+}\) ion with a 17-electron outer shell and a comparatively small radius (0.08 nm) has a strong polarizing power, while the I\(^-\) ion with greater dimensions (r = 0.22 nm) has a high polarizability. Hence, the polarization of the I\(^-\) anion by the Cu\(^{2+}\) cation leads to the complete transition of an electron from the anion to the cation: the Cu\(^{2+}\) ion is reduced to Cu\(^+\), and the I\(^-\) ion is oxidized to free iodine, The compound CuI\(_2\) does not exist.
The Ca\(^{2+}\) ion has a noble-gas electron configuration, and its radius is 0.104 nm; this is why its polarizing action on an anion is weaker than that of the Cu\(^{2+}\) ion. On the other hand, the polarizability of the F\(^{-}\) ion having comparatively small dimensions \((r = 0.133 \text{ nm})\) is considerably lower than that of the I\(^{-}\) ion. When a weakly polarizing Ca\(^{2+}\) cation reacts with a weakly polarizable anion F\(^{-}\), the electron shells of the ions do not virtually deform; the compound CaF\(_2\) is very stable.

**PROBLEMS**

265. Proceeding from the notions on the nature of an ionic bond, explain why ionic compounds exist as ionic crystals, and not as separate molecules in ordinary conditions.

266. The melting point of CaCl\(_2\) is 780 °C, and that of CdCl\(_2\) is 560 °C; the radii of the Ca\(^{2+}\) and Cd\(^{2+}\) ions are 0.104 and 0.099 nm, respectively. Explain the difference between the melting points.

267. In going from CsF to CsI, the melting point of the crystals lowers. Explain the observed course of the change in the melting points.

268. Explain the instability of copper(I) and silver(I) hydroxides.

269. Explain the lower stability of AuCl\(_3\) in comparison with AuCl and that of PbCl\(_4\) in comparison with PbCl\(_2\) from the standpoints of the notions of ion polarization.

270. K\(_2\)CO\(_3\) melts at 890 °C without decomposing, while Ag\(_2\)CO\(_3\) decomposes already at 220 °C. Explain this difference.

271. BaCl\(_2\) dissociates to the end in aqueous solutions, while HgCl\(_2\) does not virtually dissociate. Explain this difference between the properties of the salts.

**REVIEW QUESTIONS**

272. Which of the following ions has a higher polarizing power? (a) Na\(^+\); (b) Ca\(^{2+}\); (c) Mg\(^{2+}\); (d) Al\(^{3+}\).

273. Which of the compounds SrF\(_2\) and PbF\(_2\) has a higher melting point? (a) SrF\(_2\); (b) PbF\(_2\); (c) they have approximately the same melting points.

Because (1) the radii of the Sr\(^{2+}\) and Pb\(^{2+}\) ions have close values; (2) the Sr—F bond is more ionic than the Pb—F one.

274. Which of the compounds MgCO\(_3\) and ZnCO\(_3\) is thermally more stable? (a) MgCO\(_3\); (b) ZnCO\(_3\).
Because (1) magnesium hydroxide exhibits only basic properties while zinc hydroxide is amphoteric; (2) a cation with a noble-gas electron configuration has a smaller polarizing action on an anion than a cation of the same size and charge with an 18-electron configuration of its outer layer.

275. Which of the ions Ca$^{2+}$ and Cd$^{2+}$ has a stronger polarizing action on anions? (a) Ca$^{2+}$; (b) Cd$^{2+}$; (c) the polarizing action of these ions is identical.

Because (1) the charges of the ions are the same, and their radii are close [$r$(Ca$^{2+}$) = 0.104 nm, and $r$(Cd$^{2+}$) = 0.099 nm]; (2) calcium is in the fourth, and cadmium in the fifth period of the periodic table of elements; (3) the Ca$^{2+}$ ion has a noble-gas electron configuration, and the Cd$^{2+}$ ion, an 18-electron configuration of its outer layer.

4. Hydrogen Bond. Intermolecular Interaction

A hydrogen atom, when bonded to an atom of a highly electronegative element, can form a second chemical bond. The latter is known as a hydrogen bond. The presence of hydrogen bonds leads to the appreciable polymerization of water, hydrogen fluoride, and many organic compounds. For example, at moderate temperatures, hydrogen fluoride is a polymer (HF)$_n$, where $n$ may reach six, and formic acid is a dimer even in the gaseous phase.

The energy of hydrogen bonds usually ranges from 8 to 40 kJ/mol. The presence of hydrogen bonds is the cause of anomalously high melting and boiling points of some substances because the breaking of these bonds requires an extra expenditure of energy.

Example 1. Hydrogen sulphide at room temperature is a gas, and water is a liquid. How can this difference in their properties be explained?

Solution. Oxygen is a more electronegative element than sulphur. Consequently, stronger hydrogen bonds appear between water molecules than between those of hydrogen sulphide*. The breaking of these

* The energy of the hydrogen bonds between H$_2$S molecules is very small—it is less than the average energy of thermal motion of the molecules at room temperature. Consequently, the formation of hydrogen bonds does not virtually affect the properties of hydrogen sulphide.
bonds needed for water to pass over to the gaseous state requires a considerable outlay of energy, and this is what leads to the anomalous rise in the boiling point of water.

The forces retaining the particles of a liquid or solid near one another are of an electrical nature. But these forces differ quite appreciably depending on what the particles are—whether they are atoms of a metal or non-metal element, ions, or molecules.

Intermolecular interaction occurs in substances with a molecular structure. The forces of intermolecular interaction, also called van-der-Waals forces, are weaker than the forces resulting in the formation of a covalent bond, but they manifest themselves at greater distances. They are based on the electrostatic interaction of molecular dipoles.

Three kinds of intermolecular interaction are distinguished: orientational or dipole-dipole, induction, and dispersion interaction.

Example 2. The boiling points (in K) of the noble gases are:

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>Ne</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
<th>Rn</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>4.3</td>
<td>27.2</td>
<td>87.3</td>
<td>119.9</td>
<td>165.0</td>
<td>211.2</td>
</tr>
</tbody>
</table>

How can the elevation of the boiling point with a growth in the atomic number of a noble gas be explained?

Solution. The growth in the atomic number of the noble gases is attended by an increase in the dimensions of their atoms while retaining a similar configuration of the outer electron layer of an atom. Consequently, the polarizability of the atoms grows, and the result is an increase in the forces of dispersion interaction between them; the detachment of the atoms from one another occurring when a substance passes from the liquid into the gaseous state requires a constantly growing expenditure of energy. This is what leads to elevation of the boiling point.

**PROBLEMS**

276. What is the nature of van-der-Waals forces? What kind of interaction between particles leads to the transition of Ne, N₂, HI, Cl₂, BF₃, and H₂O to the condensed state?

277. The boiling points of BF₃, BCl₃, BBr₃, and BI₃ are 172, 286, 364, and 483 K, respectively. Explain this regularity.

278. The boiling points of NF₅, PF₅, and AsF₅ are 144, 178, and 336 K, respectively. Explain the regularity observed.
279. The boiling points $T_b$, heats of vaporization $\Delta H_{vap}$, and the dipole moments $\mu$ are given below for three series of similar compounds:

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_b$, K</th>
<th>$\Delta H_{vap}$, kJ/mol</th>
<th>$\mu$, D</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>292.7</td>
<td>32.6</td>
<td>1.91</td>
</tr>
<tr>
<td>HCl</td>
<td>188.1</td>
<td>16.2</td>
<td>1.03</td>
</tr>
<tr>
<td>HBr</td>
<td>206.4</td>
<td>17.6</td>
<td>0.79</td>
</tr>
<tr>
<td>HI</td>
<td>237.8</td>
<td>19.8</td>
<td>0.42</td>
</tr>
<tr>
<td>H₂O</td>
<td>373.0</td>
<td>40.7</td>
<td>1.84</td>
</tr>
<tr>
<td>H₂S</td>
<td>212.8</td>
<td>18.7</td>
<td>0.93</td>
</tr>
<tr>
<td>H₂Se</td>
<td>231.7</td>
<td>19.9</td>
<td>0.24</td>
</tr>
<tr>
<td>H₂Te</td>
<td>271</td>
<td>23.4</td>
<td>—</td>
</tr>
<tr>
<td>NH₃</td>
<td>239.7</td>
<td>23.3</td>
<td>1.48</td>
</tr>
<tr>
<td>PH₃</td>
<td>185.7</td>
<td>14.7</td>
<td>0.55</td>
</tr>
<tr>
<td>AsH₃</td>
<td>210.7</td>
<td>16.7</td>
<td>0.03</td>
</tr>
<tr>
<td>SbH₃</td>
<td>255</td>
<td>21.1</td>
<td>—</td>
</tr>
</tbody>
</table>

Explain why $T_b$ and $\Delta H_{vap}$ do not change monotonously in each series of compounds with a monotonous change in the polarity of the molecules.
1. Energy Conversions in Reactions. Thermochemical Calculations

The most important quantities characterizing chemical systems include the internal energy $U$, the enthalpy $H$, the entropy $S$, and the Gibbs energy (isobaric-isothermal potential) $G$. All these quantities are functions of state, i.e. depend only on the state of a system, but not on how this state has been reached.

A chemical reaction is attended by a change in the internal energy of the reacting systems. If the internal energy of a system diminishes ($\Delta U < 0$), the reaction proceeds with the evolution of energy (an exothermic reaction). If the internal energy of the system grows ($\Delta U > 0$), the process is attended by the absorption of energy from the surrounding medium (an endothermic reaction).

If as a result of a chemical reaction a system absorbed the amount of heat $Q$ and performed the work $W$, the change in the internal energy $\Delta U$ is determined by the equation

$$\Delta U = Q - W$$

According to the law of energy conservation, $\Delta U$ depends only on the initial and final states of a system, but does not depend on how the process (reaction) was conducted. Conversely, $Q$ and $W$ will differ when a process is conducted in different ways: only the difference between these quantities (i.e. $Q - W$), but not each of them separately, is a function of state. The functions $U$, $Q$, and $W$ are usually expressed in joules or kilojoules.

If a reaction proceeds at constant volume ($\Delta V = 0$, an isochoric process), the work of expansion of the system ($W = p\Delta V$) is zero. If no other kinds of work (for instance, electrical) are performed, $\Delta U = Q_V$, where $Q_V$ is the
heat effect of the reaction (i.e. the amount of heat absorbed by the system) proceeding at constant volume. For an exothermic reaction, \( Q_V < 0 \), for an endothermic reaction, \( Q_V > 0 \).*

Chemical reactions proceed more frequently not at constant volume, but at constant pressure \( p \) (\( \Delta p = 0 \), an isobaric process). In such cases, it is more convenient to use not the internal energy \( U \), but the enthalpy \( H \), determined by the equation

\[
H = U + pV
\]

The enthalpy can be seen to have the same dimension as the internal energy, and it is therefore usually expressed in joules or kilojoules.

At constant pressure

\[
\Delta H = \Delta U + p \Delta V
\]

i.e. the change in the enthalpy equals the sum of the change in the internal energy (\( \Delta U \)) and the work of expansion (\( p \Delta V \)) done by the system. If no other kinds of work are performed, \( \Delta H = Q_p \), where \( Q_p \) is the heat effect of a reaction proceeding at constant pressure. For an exothermic reaction, \( Q_p < 0 \), for an endothermic one, \( Q_p > 0 \).

The change in the internal energy or enthalpy is customarily related to the case when all the reactants and all the products are in standard states. A standard state of a substance at a given temperature is defined as its state in the form of a pure substance at a pressure (for gases—at a partial pressure of the given gas) equal to standard atmospheric pressure (101.325 kPa or 760 mmHg). The changes in the relevant quantities related to the standard states are called standard changes, and the superscript \(^0\) is used with their symbols. For instance, \( \Delta U^0 \) is the standard change in the internal energy in a chemical reaction, and \( \Delta H^0 \)

* These signs of the heat effects have been adopted in chemical thermodynamics. In thermochemistry, the opposite system of signs is often used, i.e. the heat liberated by a system is considered to be positive. But no matter what signs are used for the heat effects, reactions proceeding with the liberation of heat into the surrounding medium are called exothermic, and those proceeding with the absorption of heat by the system are called endothermic.
is the standard change in the enthalpy in a reaction (or, more briefly, the standard enthalpy of a reaction).

The standard enthalpy of a reaction involving the formation of one mole of a given substance from elementary substances is known as the standard enthalpy of formation of this substance*. This quantity is usually expressed in kilojoules per mole.

The enthalpy and the internal energy of formation of elementary substances, according to the above definition, equal zero. If an element forms several elementary substances (graphite and diamond, white and red phosphorus, etc.), the state of the element in the form of the most stable modification in the given conditions is considered to be the standard one (graphite for carbon, O₂ for oxygen, etc.) whose enthalpy and internal energy of formation are adopted equal to zero.

Chemical equations in which the changes in the enthalpy (the heat effects of reactions) are indicated are called thermochemical equations. For example, the equation

\[ \text{PbO}(c) + \text{CO}(g) = \text{Pb}(c) + \text{CO}_2(g); \quad \Delta H^\circ = -64 \text{ kJ} \]

signifies that when one mole of PbO is reduced with carbon monoxide, an amount of heat equal to 64 kJ is liberated**.

The symbols (c), (lq), and (g) stand for the crystalline, liquid, and gaseous state of a substance, respectively.

A corollary to the law of energy conservation is the law experimentally established by G. Hess in 1840 (Hess’s law) that is the cornerstone of thermochemical calculations.

The heat effect of a chemical reaction (i.e. the change in the enthalpy or internal energy of a system as a result of a reaction) depends only on the initial and the final state of the substances participating in the reaction and does not depend on the intermediate stages of the process.

* The abbreviated terms “enthalpy of formation”, “heat of formation”, and so on are often used, the standard quantities being understood, however. If when speaking of the heat of formation no mention is made of the conditions in which the reaction is conducted, what is usually meant is the heat of formation at constant pressure (\(Q_p\)).

** In thermochemistry, such equations are frequently written in a different form (see the footnote on page 81):

\[ \text{PbO}(c) + \text{CO}(g) = \text{Pb}(c) + \text{CO}_2(g) + 64 \text{ kJ} \]
It follows from Hess's law, particularly, that thermochemical equations can be summated, subtracted, and multiplied by numerical factors.

Example 1. Proceeding from the heat of formation of gaseous carbon dioxide ($\Delta H^o = -393.5$ kJ/mol) and the thermochemical equation

$$
C \text{(graphite)} + 2N_2O(g) = CO_2(g) + 2N_2(g); \quad \Delta H^o = -557.5 \text{ kJ (1)}
$$
calculate the heat of formation of $N_2O(g)$.

**Solution.** Denoting the required quantity by $x$, we write the thermochemical equation of formation of $N_2O$ from elementary substances:

$$
N_2(g) + \frac{1}{2}O_2(g) = N_2O(g); \quad \Delta H^o_1 = x \text{ kJ (2)}
$$

We also write the thermochemical equation of the reaction of formation of $CO_2(g)$ from elementary substances:

$$
C \text{(graphite)} + O_2(g) = CO_2(g); \quad \Delta H^o_2 = -393.5 \text{ kJ (3)}
$$

Equations (2) and (3) can give us Eq. (1). To obtain the latter, we multiply Eq. (2) by two and subtract the resulting equation from (3). We get:

$$
C \text{(graphite)} + 2N_2O(g) = CO_2(g) + 2N_2(g);
\Delta H^o = (-393.5 - 2x) \text{ kJ (4)}
$$

Comparing Eqs. (1) and (4), we find $-393.5 - 2x = -557.5$, whence $x = 82.0$ kJ/mol.

Example 2. Find the standard change in the enthalpy $\Delta H^o$ for the reaction of methane combustion

$$
\text{CH}_4(g) + 2\text{O}_2(g) = \text{CO}_2(g) + 2\text{H}_2\text{O}(g)
$$

knowing that the enthalpies of formation of $\text{CO}_2(g)$, $\text{H}_2\text{O}(g)$, and $\text{CH}_4(g)$ are $-393.5$, $-241.8$, and $-74.9$ kJ/mol, respectively.

**Solution.** We write the thermochemical equations of the reactions of formation of $\text{CO}_2$, $\text{H}_2\text{O}$, and $\text{CH}_4$:

$$
\text{C (graphite)} + O_2(g) = \text{CO}_2(g); \quad \Delta H^o(\text{CO}_2) = -393.5 \text{ kJ (1)}
$$

$$
\text{H}_2(g) + \frac{1}{2}O_2(g) = \text{H}_2\text{O}(g); \quad \Delta H^o(\text{H}_2\text{O}) = -241.8 \text{ kJ (2)}
$$

$$
\text{C (graphite)} + 2\text{H}_2(g) = \text{CH}_4(g); \quad \Delta H^o(\text{CH}_4) = -74.9 \text{ kJ (3)}
$$

By adding Eq. (1) to the doubled Eq. (2) and subtracting Eq. (3) from the sum obtained, we get the thermochemical equation of the reaction we are interested in:

$$
\text{CH}_4(g) + 2\text{O}_2(g) = \text{CO}_2(g) + 2\text{H}_2\text{O}(g); \quad \Delta H^o = \\
= \Delta H^o(\text{CO}_2) + 2\Delta H^o(\text{H}_2\text{O}) - \Delta H^o(\text{CH}_4)
$$

Using the data of the example, we find the required quantity:

$$
\Delta H^o = -393.5 - 241.8 \times 2 + 74.9 = -802.2 \text{ kJ}
$$
The last example illustrates an important corollary to Hess’s law whose use simplifies many thermochemical calculations:

The standard change in the enthalpy of a chemical reaction equals the sum of the standard enthalpies of formation of the products less the sum of the standard enthalpies of formation of the reactants.

Both sums are determined with account taken of the number of moles of the substances participating in the reaction in accordance with its equation.

Example 3. Using Table 5 of the Appendix, calculate \( \Delta H^\circ \) for the reaction:

\[ 2\text{Mg}(c) + \text{CO}_2(g) = 2\text{MgO}(c) + \text{C}(\text{graphite}) \]

**Solution.** From Table 5, the standard enthalpies of formation of \( \text{CO}_2 \) and \( \text{MgO} \) are \(-393.5\) and \(-601.8\) kJ/mol, respectively (we remind our reader that the standard enthalpies of formation of elementary substances equal zero!). Hence, for the standard enthalpy of the reaction, we find:

\[
\Delta H^\circ = 2\Delta H^\circ(\text{MgO}) - \Delta H^\circ(\text{CO}_2) = -601.8 \times 2 + 393.5 = -810.1 \text{ kJ}
\]

Example 4. Proceeding from the values of \( \Delta H^\circ \) for the reactions:

\[ \text{MgO}(c) + 2\text{H}^+(\text{aq}) = \text{Mg}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{lq}); \quad \Delta H_1^\circ = -145.6 \text{ kJ} \]
\[ \text{H}_2\text{O}(\text{lq}) = \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}); \quad \Delta H_2^\circ = 57.5 \text{ kJ} \]

calculate the value of \( \Delta H_3^\circ \) for the reaction of dissolution of magnesium oxide in water:

\[ \text{MgO}(c) + \text{H}_2\text{O}(\text{lq}) = \text{Mg}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}); \quad \Delta H_3^\circ \]

The symbol (aq) stands for a dilute aqueous solution.

**Solution.** According to Hess’s law, we can write:

\[
\Delta H_3^\circ = \Delta H_1^\circ + 2\Delta H_2^\circ \quad \text{whence}
\]

\[
\Delta H_3^\circ = -145.6 + 57.5 \times 2 = 30.6 \text{ kJ}
\]

The direction in which a chemical reaction proceeds spontaneously is determined by the joint action of two factors: (1) the tendency of a system to pass into a state with the lowest internal energy (for isobaric processes—with the lowest enthalpy), and (2) the tendency of achieving the most probable state, i.e. a state that can be realized in the greatest number of equally probable ways (microstates).

The measure of the first of these tendencies for isobaric processes is the change in the enthalpy in a chemical reaction:
the negative sign of $\Delta H$ indicates a decrease, and the positive sign, an increase in the enthalpy of the system.

The measure of the probability of the state of a system in thermodynamics is the entropy $S$—a quantity proportional to the logarithm of the number of equally probable microstates by means of which the given macrostate* can be achieved. The entropy has the dimension of energy divided by temperature; it is usually related to one mole of a substance (the molar entropy) and is expressed in J/(mol·K).

It is clear from the above that the entropy grows when a substance transforms from the crystalline state to the liquid one and from the liquid state to the gaseous one, when crystals dissolve, gases expand, and in chemical reactions leading to an increase in the number of particles, especially of particles in the gaseous state. Conversely, all processes as a result of which the order of a system grows (condensation, polymerization, compression, diminishing of the number of particles) are attended by a decrease in the entropy.

Example 5. Without performing calculations, determine the sign of the entropy change in the following reactions:

\[ \text{NH}_4\text{NO}_3(c) = N_2\text{O}(g) + 2\text{H}_2\text{O}(g) \] (1)
\[ 2\text{H}_2(g) + \text{O}_2(g) = 2\text{H}_2\text{O}(g) \] (2)
\[ 2\text{H}_2(g) + \text{O}_2(g) = 2\text{H}_2\text{O}(lq) \] (3)

Solution. In reaction (1), one mole of a substance in the crystalline state forms three moles of gases, hence $\Delta S_1 > 0$. In reactions (2) and (3), both the total number of moles and the number of moles of the gaseous substances diminish so that $\Delta S_2 < 0$ and $\Delta S_3 < 0$. The quantity $\Delta S_3$ has a more negative value than $\Delta S_2$ because $S[H_2O(lq)] < < S[H_2O(g)]$.

A statement similar to that considered above for $\Delta H$ holds for the entropy: the change in the entropy of a system ($\Delta S$) as a result of a chemical reaction equals the sum of the entropies of the products less the sum of the entropies of the reactants. As in calculation of the enthalpy, summation is performed with account taken of the number of moles of the substances participating in the reaction.

* We remind our reader that a macrostate is characterized by definite values of the macroscopic properties of a system (temperature, pressure, volume, etc.): a microstate is characterized by a definite state of each particle in a system. A large number of various microstates can correspond to the same macrostate of a system.
It must be borne in mind that unlike the enthalpy of formation, the entropy of an elementary substance even in the crystalline state does not equal zero because at a temperature other than absolute zero the macrostate of a crystal can be achieved not by a single microstate, but by a large number of equally probable microstates.

A function of state simultaneously reflecting the influence of both tendencies mentioned above on the direction of chemical processes is the Gibbs energy, which is related to the enthalpy and entropy by the equation

\[ G = H - TS \]

where \( T \) is the absolute temperature.

The Gibbs energy can be seen to have the same dimension as the enthalpy, and it is therefore generally expressed in joules or kilojoules.

For isobaric-isothermal processes (i.e. processes occurring at constant temperature and pressure), the change in the Gibbs energy is

\[ \Delta G = \Delta H - T \Delta S \]

As for \( \Delta H \) and \( \Delta S \), the change in the Gibbs energy \( \Delta G \) as a result of a chemical reaction (or, more briefly, the Gibbs energy of a reaction) equals the sum of the Gibbs energies of formation of the products less the sum of the Gibbs energies of formation of the reactants; summation is performed with a view to the number of moles of the substances participating in the reaction.

The Gibbs energy of formation is related to one mole of a substance and is usually expressed in kJ/mol; \( \Delta G^0 \) of formation of the most stable modification of an elementary substance is taken equal to zero.

In conditions of a constant temperature and pressure, chemical reactions proceed spontaneously in the direction of diminishing of the Gibbs energy (\( \Delta G < 0 \)).

Table 3 shows the possibility (or impossibility) of the spontaneous proceeding of a reaction with different combinations of the signs of \( \Delta H \) and \( \Delta S \).

For instance, if \( \Delta H < 0 \) for a reaction (an exothermic reaction), and \( \Delta S > 0 \), it follows from the last equation that at all temperatures \( \Delta G < 0 \). This signifies that the reaction
Table 3
Directions of Reactions with Different Signs of $\Delta H$ and $\Delta S$

<table>
<thead>
<tr>
<th>Sign of change in function</th>
<th>Possibility (impossibility) of spontaneous proceeding of reaction</th>
<th>Example of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ $\Delta S$ $\Delta G$</td>
<td>Possible at any temperature</td>
<td>$C_9H_6(lq) + 7.5O_2(g) = 6CO_2(g) + 3H_2O(g)$</td>
</tr>
<tr>
<td>$+$ $-$ $+$</td>
<td>Impossible at any temperature</td>
<td>$N_2(g) + 2O_2(g) = 2NO_2(g)$</td>
</tr>
<tr>
<td>$-$ $-$ $\pm$</td>
<td>Possible at sufficiently low temperature</td>
<td>$3H_2(g) + N_2(g) = 2NH_3(g)$</td>
</tr>
<tr>
<td>$+$ $+$ $\pm$</td>
<td>Possible at sufficiently high temperature</td>
<td>$N_2O_4(g) = 2NO_2(g)$</td>
</tr>
</tbody>
</table>

can proceed spontaneously at any temperatures. If $\Delta H < 0$ and $\Delta S < 0$, the reaction is possible ($\Delta G < 0$) provided that the term $\Delta H$ in the equation for the Gibbs energy is greater in magnitude than the term $T\Delta S$; since the magnitude of the term $T\Delta S$ increases with a growth in the factor $T$, this condition will be observed at sufficiently low temperatures. In other words, at low temperatures, the spontaneous proceeding of exothermic reactions is most probable even if the entropy of the system diminishes.

At high temperatures, as can be seen from the table, reactions attended by a growth in the entropy are most probable, including endothermic reactions.

Example 6. At a certain temperature $T$, the endothermic reaction $A \rightarrow B$ proceeds virtually to the end. Determine: (a) the sign of $\Delta S$ of the reaction; (b) the sign of $\Delta G$ for the reaction $B \rightarrow A$ at the temperature $T$; and (c) the possibility of the reaction $B \rightarrow A$ proceeding at low temperatures.

Solution. (a) Spontaneous proceeding of the reaction $A \rightarrow B$ indicates that $\Delta G < 0$. Since $\Delta H > 0$, it follows from the equation $\Delta G = \Delta H - T\Delta S$ that $\Delta S > 0$. For the reverse reaction $B \rightarrow A$, we have $\Delta S < 0$.

(b) For the reaction $A \rightarrow B$, we have $\Delta G < 0$. Hence, for the reverse reaction at the same temperature, $\Delta G > 0$.

(c) The reaction $B \rightarrow A$, which is the reverse reaction of $A \rightarrow B$, is exothermic ($\Delta H < 0$). The magnitude of the term $T\Delta S$ is small for
low temperatures, so that the sign of $\Delta G$ is determined by that of $\Delta H$. Hence, at sufficiently low temperatures, the reaction $B \rightarrow A$ can proceed.

The values of $\Delta H$, $\Delta S$, and $\Delta G$ of a reaction depend not only on the nature of the reactants, but also on their state of aggregation and concentrations. To obtain comparable data characterizing various reactions, the standard changes in the enthalpy $\Delta H^\circ_T$, the entropy $\Delta S^\circ_T$, and the Gibbs energy $\Delta G^\circ_T$ are compared, i.e. changes that occur when all the substances participating in a reaction (both the reactants and the products) are in their standard states; the subscript in the above symbols indicates the absolute temperature at which the process is conducted.

Table 5 of the Appendix gives the values of $S^\circ_298$, and also of $\Delta H^\circ_298$ and $\Delta G^\circ_298$ of formation of selected substances at 298 K (25 °C). These data allow us to perform a variety of thermodynamical calculations.

Example 7. Will the reactions

$$\text{Cl}_2(g) + 2\text{HI}(g) = \text{I}_2(c) + 2\text{HCl}(g) \quad (1)$$
$$\text{I}_2(c) + \text{H}_2\text{S}(g) = 2\text{HI}(g) + \text{S}(c) \quad (2)$$

proceed spontaneously in the forward direction at 298 K? How will elevation of the temperature affect the direction of these reactions?

Solution. To answer the first question, we must find the values of $\Delta G^\circ$ for the reactions being considered. In Table 5 of the Appendix, we find $\Delta G^\circ_{\text{form(HI)}} = 1.8 \text{ kJ/mol}$, $\Delta G^\circ_{\text{form(HCl)}} = -95.2 \text{ kJ/mol}$, and $\Delta G^\circ_{\text{form(H}_2\text{S)}} = -33.8 \text{ kJ/mol}$. Hence for reactions (1) and (2), we find, respectively,

$$\Delta G^\circ_1 = -95.2 \times 2 - 1.8 \times 2 = -194.0 \text{ kJ}$$
$$\Delta G^\circ_2 = 1.8 \times 2 - (-33.8) = 37.4 \text{ kJ}$$

The negative sign of $\Delta G^\circ$ indicates the possibility of reaction (1) proceeding spontaneously; the positive sign of $\Delta G^\circ_2$ signifies that reaction (2) cannot proceed in the conditions indicated.

The answer to the second question of the example is determined by the sign of $\Delta S^\circ$ for the reactions being considered. In reaction (1), the number of moles of the substances in the gaseous state diminishes, and in reaction (2) it grows. It thus follows that $\Delta S^\circ_1 < 0$, and $\Delta S^\circ_2 > 0$, i.e. in the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ the term $-T\Delta S^\circ$ is positive for reaction (1) and negative for reaction (2). Hence, when the factor $T$ grows (elevation of the temperature), the value of $\Delta G^\circ_1$ will increase (i.e. become less negative), and that of $\Delta G^\circ_2$ will decrease (become less positive). This means that elevation of the temperature will hinder the proceeding of reaction (1) and favour the proceeding of reaction (2) in the forward direction.
Example 8. Using reference data, establish whether the reduction of titanium dioxide to the free metal following the reaction

\[ \text{TiO}_2(c) + 2\text{C(graphite)} = \text{Ti(c)} + 2\text{CO(g)} \]

is possible at temperatures of 298 and 2500 K. Disregard the temperature dependence of \( \Delta H^\circ \) and \( \Delta S^\circ \).

**Solution.** In Table 5 of the Appendix, we find for 298 K:

\[ \Delta G^\circ_{\text{form(TiO}_2)} = -888.6 \text{ kJ/mol}, \quad \Delta G^\circ_{\text{form(CO)}} = -137.1 \text{ kJ/mol}. \]

Hence for the reaction being considered:

\[ \Delta G^\circ_{298} = 2\Delta G^\circ_{\text{form(CO)}} - \Delta G^\circ_{\text{form(TiO}_2)} = \]

\[ = -137.1 \times 2 - (-888.6) = 614.4 \text{ kJ} \]

Since \( \Delta G^\circ_{298} > 0 \), reduction of TiO\(_2\) at 298 K is impossible.

To calculate \( \Delta G^\circ_{2500} \), we use the equation \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \). In accordance with the indication in the data of the example, we take the values of \( \Delta H^\circ \) and \( \Delta S^\circ \) for 298 K. To calculate \( \Delta H^\circ \) and \( \Delta S^\circ \) of the reaction, we have to find the values of \( \Delta H^\circ_{\text{form}} \) and \( S^\circ \) for the reactants in Table 5. They are \( \Delta H^\circ_{\text{form(TiO}_2)} = -943.9 \text{ kJ/mol}, \Delta H^\circ_{\text{form(CO)}} = -110.5 \text{ kJ/mol}, S^\circ(\text{TiO}_2) = 50.3 \text{ J/(mol·K)}, S^\circ(\text{C}) = 5.7 \text{ J/(mol·K)}, S^\circ(\text{Ti}) = 30.6 \text{ J/(mol·K)}, \) and \( S^\circ(\text{CO}) = 197.5 \text{ J/(mol·K)}. \)

We determine \( \Delta H^\circ \) of the reaction:

\[ \Delta H^\circ = 2\Delta H^\circ_{\text{form(CO)}} - \Delta H^\circ_{\text{form(TiO}_2)} = \]

\[ = -110.5 \times 2 - (-943.9) = 722.9 \text{ kJ} \]

Similarly, we calculate \( \Delta S^\circ \) of the reaction:

\[ \Delta S^\circ = S^\circ(\text{Ti}) + 2S^\circ(\text{CO}) - S^\circ(\text{TiO}_2) - 2S^\circ(\text{C}) = \]

\[ = 30.6 + 197.5 \times 2 - 50.3 - 5.7 \times 2 = 425.6 - \]

\[ - 61.7 = 363.9 \text{ J/K} \]

We now find \( \Delta G^\circ_{2500} \) of the reaction, expressing \( \Delta S^\circ \) in kJ/K:

\[ \Delta G^\circ_{2500} = \Delta H^\circ_{2500} - T\Delta S^\circ_{2500} = 722.9 - 2500 \times \frac{363.9}{1000} = \]

\[ = 722.9 - 909.8 = -186.9 \text{ kJ} \]

Hence, \( \Delta G^\circ_{2500} < 0 \), so that reduction of TiO\(_2\) with graphite at 2500 K is possible.

**Problems**

280. When 2.1 g of iron combine with sulphur, 3.77 kJ are evolved. Calculate the heat of formation of iron sulphide.

* When solving the problems of this section, use Table 5 in the Appendix if necessary.
281. Find the amount of heat liberated in the explosion of 8.4 litres of detonating gas taken in standard conditions.

282. Determine the standard enthalpy ($\Delta H^\circ_{298}$) of formation of PH$_3$ proceeding from the equation:

$$2\text{PH}_3(g) + 4\text{O}_2(g) = \text{P}_2\text{O}_5(c) + 3\text{H}_2\text{O}(lq); \Delta H^\circ = -2360 \text{ kJ}$$

283. Proceeding from the heat effect of the reaction

$$3\text{CaO}(c) + \text{P}_2\text{O}_5(c) = \text{Ca}_3(\text{PO}_4)_2(c); \Delta H^\circ = -739 \text{ kJ}$$
determine $\Delta H^\circ_{298}$ of formation of calcium orthophosphate.

284. Proceeding from the equation of the reaction

$$\text{CH}_3\text{OH}(lq) + \frac{3}{2} \text{O}_2(g) = \text{CO}_2(g) + 2\text{H}_2\text{O}(lq); \Delta H^\circ = -726.5 \text{ kJ}$$
calculate $\Delta H^\circ_{298}$ of formation of methyl alcohol.

285. In the reduction of 12.7 g of copper(II) oxide with coal (with the formation of CO), 8.24 kJ are absorbed. Determine $\Delta H^\circ_{298}$ of formation of CuO.

286. Upon the complete combustion of ethylene (with the formation of liquid water), 6226 kJ were evolved. Find the volume of the oxygen that entered into the reaction in standard conditions.

287. Water gas is a mixture of equal volumes of hydrogen and carbon monoxide. Find the amount of heat evolved in the combustion of 112 litres of water gas taken in standard conditions.

288. Equal volumes of hydrogen and acetylene taken in identical conditions are burned with the formation of H$_2$O(g). In which case is more heat liberated, and how many times more?

289. Determine $\Delta H^\circ_{298}$ for the reaction $3\text{C}_2\text{H}_2(g) = 3\text{H}_2\text{O}(lq)$ if $\Delta H^\circ_{298}$ for the reaction of combustion of acetylene with the formation of CO$_2$(g) and H$_2$O(lq) is $-1300 \text{ kJ/mol}$, and $\Delta H^\circ_{298}$ of formation of benzene(lq) is 82.9 kJ/mol.

290. Find $\Delta H^\circ_{298}$ of formation of ethylene using the following data:

$$\text{C}_2\text{H}_4(g) + 3\text{O}_2(g) = 2\text{CO}_2(g) + 2\text{H}_2\text{O}(g); \Delta H^\circ = -1323 \text{ kJ}$$

$$\text{C (graphite)} + \frac{1}{2} \text{O}_2(g) = \text{CO}_2(g); \Delta H^\circ = -393.5 \text{ kJ}$$

$$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{H}_2\text{O}(g); \Delta H^\circ = -241.8 \text{ kJ}$$
291. Compare $\Delta H^*_{298}$ for the reaction of reduction of iron(III) oxide using various reducing agents at 298 K:

(a) $\text{Fe}_3\text{O}_3(c) + 3\text{H}_2(g) = 2\text{Fe}(c) + 3\text{H}_2\text{O}(g)$
(b) $\text{Fe}_3\text{O}_3(c) + 3\text{C(graphite)} = 2\text{Fe}(c) + 3\text{CO}(g)$
(c) $\text{Fe}_3\text{O}_3(c) + 3\text{CO}(g) = 2\text{Fe}(c) + 3\text{CO}_2(g)$

292. Find the mass of methane upon the complete combustion of which (with the formation of liquid water) heat is evolved that is sufficient for heating 100 g of water from 20 to 30 °C. Assume that the molar heat capacity of water is 75.3 J/(mol·K).

293. Calculate $\Delta H^*_{298}$ of formation of MgCO$_3$(c) at 298 K using the following data:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH$^\circ$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C(graphite)} + \text{O}_2(g) = \text{CO}_2(g)$</td>
<td>$-393.5$</td>
</tr>
<tr>
<td>$2\text{Mg}(c) + \text{O}_2 = 2\text{MgO}(c)$</td>
<td>$-1203.6$</td>
</tr>
<tr>
<td>$\text{MgO}(c) + \text{CO}_2(g) = \text{MgCO}_3(c)$</td>
<td>$-117.7$</td>
</tr>
</tbody>
</table>

294. Proceeding from $\Delta H^*_{298}$ of formation of H$_2$O(g) and the following data:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH$^\circ$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{FeO}(c) + \text{CO}(g) = \text{Fe}(c) + \text{CO}_2(g)$</td>
<td>$-18.2$</td>
</tr>
<tr>
<td>$2\text{CO}(g) + \text{O}_2 = 2\text{CO}_2(g)$</td>
<td>$-566.0$</td>
</tr>
</tbody>
</table>

calculate $\Delta H^*_{298}$ for the reaction

$\text{FeO}(c) + \text{H}_2(g) = \text{Fe}(c) + \text{H}_2\text{O}(g)$

295. Calculate $\Delta H^*_{298}$ for the reactions:

(a) $\text{C}_2\text{H}_6(g) + \frac{7}{2} \text{O}_2(g) = 2\text{CO}_2(g) + 3\text{H}_2\text{O}(g)$

(b) $\text{C}_6\text{H}_6(1q) + \frac{15}{2} \text{O}_2(g) = 6\text{CO}_2(g) + 3\text{H}_2\text{O}(1q)$

296. Calculate $\Delta H^*_{298}$ for the reactions:

(a) $2\text{Li}(c) + 2\text{H}_2\text{O}(1q) = 2\text{Li}^+(aq) + 2\text{OH}^-(aq) + \text{H}_2(g)$
(b) $2\text{Na}(c) + 2\text{H}_2\text{O}(1q) = 2\text{Na}^+(aq) + 2\text{OH}^-(aq) + \text{H}_2(g)$

Take the standard enthalpies of formation of Li$^+$ (aq), Na$^+$ (aq), and OH$^-$ (aq) equal to $-278.5$, $-239.7$, and $-228.9$ kJ/mol, respectively.

297. Calculate the value of $\Delta H^*_{298}$ for the reactions of transformation of glucose proceeding in an organism:

(a) $\text{C}_6\text{H}_{12}\text{O}_6(c) = 2\text{C}_2\text{H}_5\text{OH}(1q) + 2\text{CO}_2(g)$
(b) $\text{C}_6\text{H}_{12}\text{O}_6(c) + 6\text{O}_2(g) = 6\text{CO}_2(g) + 6\text{H}_2\text{O}(1q)$
Which of these reactions supplies more energy to the organism?

298. Does the value of \( \Delta H^\circ \) for a reaction depend on the presence of catalysts in a system? Substantiate your answer.

299. Explain why processes of dissolving substances in water can proceed spontaneously not only with an exothermic (\( \Delta H < 0 \)), but also with an endothermic (\( \Delta H > 0 \)) effect.

300. Without performing calculations, find the sign of \( \Delta S^\circ \) for the following processes:

   (a) \( 2\text{NH}_3(g) = \text{N}_2(g) + 3\text{H}_2(g) \)
   (b) \( \text{CO}_2(c) = \text{CO}_2(g) \)
   (c) \( 2\text{NO}(g) + \text{O}_2(g) = 2\text{NO}_2(g) \)
   (d) \( 2\text{H}_2\text{S}(g) + 3\text{O}_2(g) = 2\text{H}_2\text{O}(lq) + 2\text{SO}_2(g) \)
   (e) \( 2\text{CH}_3\text{OH}(g) + 3\text{O}_2(g) = 4\text{H}_2\text{O}(g) + 2\text{CO}_2(g) \)

301. Determine the sign of the change in the entropy for the reaction

\[ 2\text{A}_2(g) + \text{B}_2(g) = 2\text{A}_2\text{B}(lq) \]

Can this reaction proceed in standard conditions? Substantiate your answer.

302. Indicate the signs of \( \Delta H \), \( \Delta S \), and \( \Delta G \) for the following processes: (a) expansion of an ideal gas in a vacuum; (b) evaporation of water at 100 °C and a partial pressure of the water vapour of 101.325 kPa (760 mmHg); and (c) crystallization of supercooled water.

303. Determine the signs of \( \Delta H^\circ \), \( \Delta S^\circ \), and \( \Delta G^\circ \) for the reaction

\[ \text{AB}(c) + \text{B}_2(g) = \text{AB}_3(c) \]

proceeding at 298 K in the forward direction. Will \( \Delta G^\circ \) grow or diminish with elevation of the temperature?

304. Why can the sign of \( \Delta H \) be the criterion determining the direction of the spontaneous proceeding of a reaction at low temperatures, and the sign of \( \Delta S \) be such a criterion at sufficiently high temperatures?

305. Calculate the values of \( \Delta G^\circ_{298} \) for the following reactions and establish the direction in which they can proceed spontaneously in standard conditions at 25 °C:

   (a) \( \text{NiO}(c) + \text{Pb}(c) = \text{Ni}(c) + \text{PbO}(c) \)
   (b) \( \text{Pb}(c) + \text{CuO}(c) = \text{PbO}(c) + \text{Cu}(c) \)
   (c) \( 8\text{Al}(c) + 3\text{Fe}_2\text{O}_4(c) = 9\text{Fe}(c) + 4\text{Al}_2\text{O}_3(c) \)
306. Using reference data, show that the reaction
\[ \text{Cu}(c) + \text{ZnO}(c) = \text{CuO}(c) + \text{Zn}(c) \]
is impossible.

307. Determine which of the following reactions is possible in standard conditions at 25 °C:

(a) \[ \text{N}_2(g) + \frac{1}{2} \text{O}_2(g) = \text{N}_2\text{O}(g) \]
(b) \[ 4\text{HCl}(g) + \text{O}_2(g) = 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(l) \]
(c) \[ \text{Fe}_3\text{O}_4(c) + 3\text{CO}(g) = 2\text{Fe}(c) + 3\text{CO}_2(g) \]

308. Calculate \( \Delta G^\circ \) for the reaction
\[ \text{CaCO}_3(c) = \text{CaO}(c) + \text{CO}_2(g) \]
at 25, 500, and 1500 °C. Disregard the temperature dependence of \( \Delta H^\circ \) and \( \Delta S^\circ \).

Plot a graph of the temperature dependence of \( \Delta G^\circ \) and use it to find the temperature above which the reaction in standard conditions can proceed spontaneously.

309. Calculate the values of \( \Delta G^\circ_{298} \) for the following reactions of reduction of iron(II) oxide:

(a) \[ \text{FeO}(c) + \frac{1}{2} \text{C(graphite)} = \text{Fe}(c) + \frac{1}{2} \text{CO}_2(g) \]
(b) \[ \text{FeO}(c) + \text{C(graphite)} = \text{Fe}(c) + \text{CO}(g) \]
(c) \[ \text{FeO}(c) + \text{CO}(g) = \text{Fe}(c) + \text{CO}_2(g) \]

The proceeding of which of these reactions is most probable?

310. Which of the following oxides can be reduced by aluminium at 298 K: CaO, FeO, CuO, PbO, Fe_2O_3, Cr_2O_3?

311. Which of the following oxides can be reduced by hydrogen to the free metal at 298 K: CaO, ZnO, SnO_2, NiO, Al_2O_3?

312. Indicate which of the reactions of formation of nitrogen oxides can proceed spontaneously and at what temperatures (high or low):

(a) \[ 2\text{N}_2(g) + \text{O}_2(g) = 2\text{N}_2\text{O}(g); \quad \Delta H^\circ_{298} > 0 \]
(b) \[ \text{N}_2(g) + \text{O}_2(g) = 2\text{NO}(g); \quad \Delta H^\circ_{298} > 0 \]
(c) \[ 2\text{NO}(g) + \text{O}_2(g) = 2\text{NO}_2(c); \quad \Delta H^\circ_{298} < 0 \]
(d) \[ \text{NO}(g) + \text{NO}_2(g) = \text{N}_2\text{O}_3(c); \quad \Delta H^\circ_{298} < 0 \]
(e) \[ \text{N}_2(g) + 2\text{O}_2(g) = 2\text{NO}_2(g); \quad \Delta H^\circ_{298} > 0 \]
REVIEW QUESTIONS

313. Indicate the correct relationship of the standard changes in the enthalpy for the following reactions:

\[
\begin{align*}
H_2(g) + O(g) &= H_2O(g) \\
\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) &= H_2O(g) \\
2H(g) + O(g) &= H_2O(g)
\end{align*}
\]

(a) \(\Delta H^\circ_1 < \Delta H^\circ_2 < \Delta H^\circ_3\); (b) \(\Delta H^\circ_1 > \Delta H^\circ_2 > \Delta H^\circ_3\).

314. Indicate which of the following statements are correct: 
(a) endothermic reactions cannot proceed spontaneously; 
(b) endothermic reactions can proceed at sufficiently low temperatures; 
(c) endothermic reactions can proceed at sufficiently high temperatures if the change in the entropy of the reaction is positive.

315. Without performing calculations, indicate for which of the processes listed below the change in the entropy is positive:

(a) \(MgO(c) + H_2(g) = Mg(c) + H_2O(lq)\)
(b) \(C(graphite) + CO_2(g) = 2CO(g)\)
(c) \(CH_3COOH(aq) = CH_3COO^-(aq) + H^+(aq)\)
(d) \(4HCl(g) + O_2(g) = 2Cl_2(g) + 2H_2O(g)\)
(e) \(NH_4NO_3(c) = NaO(g) + 2H_2O(g)\)

316. In which of the following cases is a reaction possible at any temperatures? (a) \(\Delta H^\circ < 0, \Delta S^\circ > 0\); (b) \(\Delta H^\circ < 0, \Delta S^\circ < 0\); (c) \(\Delta H^\circ > 0, \Delta S^\circ > 0\).

317. In which of the following cases is a reaction impossible at any temperatures? (a) \(\Delta H^\circ > 0, \Delta S^\circ > 0\); (b) \(\Delta H^\circ > 0, \Delta S^\circ < 0\); (c) \(\Delta H^\circ < 0, \Delta S^\circ < 0\).

318. If \(\Delta H^\circ < 0\) and \(\Delta S^\circ < 0\), in which of the following cases can a reaction proceed spontaneously? (a) \(|\Delta H^\circ| > |T\Delta S^\circ|\); (b) \(|\Delta H^\circ| < |T\Delta S^\circ|\).

319. With a view to the sign of \(\Delta G^\circ_{298}\) for the following reactions

\[
\begin{align*}
PbO_2(c) + Pb(c) &= 2PbO(c); \quad \Delta G^\circ_{298} < 0 \\
SnO_2(c) + Sn(c) &= 2SnO(c); \quad \Delta G^\circ_{298} > 0
\end{align*}
\]
determine which oxidation states are more characteristic for lead and tin. (a) For lead +2, for tin +2; (b) for lead +2, for tin +4; (c) for lead +4, for tin +2; (d) for lead +4, for tin +4.

320. What is the sign of $\Delta G$ for the process of ice melting at 263 K? (a) $\Delta G > 0$; (b) $\Delta G = 0$; (c) $\Delta G < 0$.

321. Taking into account that $\text{NO}_2(g)$ is coloured, and $\text{N}_2\text{O}_4$ is colourless, and proceeding from the sign of the change in the entropy in the reaction $2\text{NO}_2(g) = \text{N}_2\text{O}_4(g)$, predict how the colour will change in the system $\text{NO}_2$-$\text{N}_2\text{O}_4$ with elevation of the temperature. (a) It will increase; (b) it will fade out.

2. Rate of a Chemical Reaction.
Chemical Equilibrium

The rate of a chemical reaction is measured by the amount of substance entering into a reaction or formed in the reaction in unit time and in unit volume of the system (for a homogeneous reaction) or on unit surface area of a phase interface (for a heterogeneous reaction)*.

For a homogeneous process occurring at constant volume, the rate of a reaction can also be determined through the changes in the concentrations of the reactants or products:

The rate of a homogeneous chemical reaction is measured by the change in the concentration of one of the reactants or products occurring in unit time.

For a reactant, this definition can be expressed by the equation

$$J = -\frac{\Delta c}{\Delta t}$$

and for a product

$$J = \frac{\Delta c}{\Delta t}$$

where $\Delta c$ is the change in the concentration of the relevant substance during the time $\Delta t$.

* In view of the difficulties often encountered in determining the area of a phase interface, the rate of a heterogeneous reaction is frequently related to a unit mass or volume of the solid phase.
The signs in the right-hand sides of these equations are different because in the course of a reaction the concentrations of the reactants diminish ($\Delta c < 0$), and those of the products grow ($\Delta c > 0$).

The rate of a reaction depends on the nature of the reactants and products, their concentration, temperature, and on the presence of catalysts in the system. When the collision of two reacting particles (molecules, atoms) is needed for a reaction to occur, the dependence of the reaction rate on the concentrations is determined by the law of mass action: at a constant temperature, the rate of a chemical reaction is directly proportional to the product of the concentrations of the reactants.

For instance, for a reaction of the type

$$A + B \rightarrow AB$$

the law of mass action is expressed as follows:

$$J = k [A][B]$$

Here $[A]$ and $[B]$ are the concentrations of the reactants, and the constant of proportionality $k$ is the rate constant of the reaction whose value depends on the nature of the reactants.

A reaction occurs much less often through the collision of three reacting particles. For example, a reaction of the type

$$A + 2B \rightarrow AB$$

can proceed according to the mechanism of triple collisions:

$$A + B + B \rightarrow AB$$

In this case, in accordance with the law of mass action, we can write:

$$J = k [A][B][B]$$

i.e.

$$J = k [A][B]^2$$

The simultaneous collision of more than three particles is extremely improbable. Consequently, reactions whose equations include a great number of particles (for instance, $4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O$) proceed in several steps, each
of which occurs because of the collision of two (less frequently, three) particles. In such cases, the law of mass action can be applied to the individual steps of a process, but not to a reaction as a whole.

In heterogeneous reactions, the concentrations of the substances in the solid phase do not usually change in the course of a reaction, and for this reason they are not included in the equation of the law of mass action.

Example 1. Write the expressions of the law of mass action for the reactions

(a) \(2\text{NO}(g) + \text{Cl}_2(g) \rightarrow 2\text{NOCl}(g)\)

(b) \(\text{CaCO}_3(c) \rightarrow \text{CaO}(c) + \text{CO}_2(g)\)

Solution. (a) \(J = k[\text{NO}]^2[\text{Cl}_2]\).

(b) Since calcium carbonate is a solid whose concentration does not change in the course of the reaction, the required expression will be \(J = k\), i.e. in the given case the rate of the reaction at a definite temperature is constant.

Example 2. How will the rate of the reaction

\(2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)\)

change if the volume of the reaction vessel is diminished to one-third of its initial value?

Solution. Before the volume is changed, the rate of the reaction is expressed by the equation:

\[J = k[\text{NO}]^2[\text{O}_2]\]

Owing to the decrease in the volume, the concentration of each of the reactants grows three times. Hence, we now have

\[J' = k(3[\text{NO}])^2(3[\text{O}_2]) = 27k[\text{NO}]^2[\text{O}_2]\]

Comparing the expressions for \(J\) and \(J'\), we see that the rate of the reaction will grow 27 times.

The temperature dependence of the rate of a reaction (or the rate constant of a reaction) can be expressed by the equation:

\[
\frac{J_{t+10}}{J_t} = \frac{k_{t+10}}{k_t} = \gamma
\]

Here \(J_t\) and \(k_t\) are the rate and rate constant of a reaction at a temperature of \(t\) °C, \(J_{t+10}\) and \(k_{t+10}\) are the same quantities at a temperature of \((t + 10)\) °C, and \(\gamma\) is the temperature coefficient of the reaction rate whose value for most reactions ranges from two to four (van't Hoff's rule). In the general
case, if the temperature changed by \( \Delta t \) °C, the last equation becomes:

\[
\frac{J_{t+\Delta t}}{J_t} = \frac{k_{t+\Delta t}}{k_t} = e^{\Delta t / 10}
\]

Example 3. The temperature coefficient of the reaction rate is 2.8. How many times will the reaction rate increase when the temperature is raised from 20 to 75 °C?

Solution. Since \( \Delta t = 55 \) °C, denoting the reaction rates at 20 and 75 °C by \( J \) and \( J' \), respectively, we can write:

\[
\frac{J'}{J} = 2.8^{55/10} = 2.8^{5.5} \quad \text{or} \quad \log \frac{J'}{J} = 5.5 \log 2.8 = 5.5 \times 0.447 = 2.458
\]

Hence, \( J'/J = 287 \). The reaction rate will increase 287 times.

The last example shows that the rate of a chemical reaction grows very greatly upon elevation of the temperature. This is associated with the fact that an elementary act of a chemical reaction does not occur each time reacting molecules collide: only those molecules react (active molecules) that have sufficient energy to break or weaken the bonds in the initial particles and thus create the possibility of the formation of new molecules. Consequently, every reaction is characterized by a definite energy barrier; to surmount it, activation energy is needed—a certain excess energy (in comparison with the average energy of the molecules at a given temperature) that molecules must have for their collision to be effective, i.e. to result in the formation of a new substance. Elevation of the temperature is attended by a rapid increase in the number of active molecules, and this is what leads to a sharp growth in the rate of a reaction.

The dependence of the rate constant \( k \) of a reaction on the activation energy (\( E_a, \) J/mol) is expressed by the Arrhenius equation

\[
k = ZP e^{-E_a/RT} \quad \text{or} \quad k = ZP \exp \left( -\frac{E_a}{RT} \right)
\]

where \( Z \) is the number of collisions of the molecules per second in unit volume; \( e \) is the base of natural logarithms (\( e = 2.718+ \)), \( R \) is the molar gas constant (\( R = 8.314 \) J·mol\(^{-1}\)·K\(^{-1}\)); \( T \) is the temperature, K; and \( P \) is the steric factor.
The necessity of introducing the factor \( P \) in the Arrhenius equation is explained by the fact that collisions even between active molecules do not always result in a reaction, but only when the molecules have a definite orientation. The factor \( P \) is proportional to the ratio of the number of ways of the mutual orientation of the molecules favourable for proceeding of a reaction to the total number of possible ways of orientation: the greater this ratio, the more rapidly will a reaction proceed. The steric factor \( P \) is usually much smaller than unity; it has an especially great influence on the rate of reactions proceeding with the participation of complex molecules (for example proteins), when the total number of various possible orientations is very great, and the number of orientations favourable for proceeding of a reaction is very limited.

The Arrhenius equation shows that the rate constant of a reaction grows with a decreasing activation energy.

Example 4. Substance A transforms into substance C according to the reaction

\[
A \xrightarrow{k_1} B \xrightarrow{k_2} \rightarrow C
\]

the second step of the reaction being attended by the absorption of heat; \( k_1 < k_2 \) and \( k_2 > k_3 \). Depict the energy diagram of the process schematically and determine the sign of \( \Delta H \) of the reaction as a whole.

Fig. 4. Energy diagram of the reaction \( A \rightleftharpoons B \rightarrow C \)

Solution. Let us consider the part of the energy diagram relating to the first step of the reaction—transformation of reactant A into intermediate B (section AB in Fig. 4). Since the rate constant of the reverse reaction (B \( \rightarrow \) A) \( k_2 \) is greater than that of the forward reaction \( k_1 \), the activation energy of the reverse reaction must be smaller than the activation energy of the forward reaction (\( E'_a < E''_a \)). This means that as a result of the transformation of substance A into substance B the energy of the system grows (see Fig. 4).
As regards the second step of the reaction—the transformation of substance B into product C (section BC in Fig. 4), for similar reasons \((k_2 > k_1)\) the energy barrier for the process \(B \rightarrow C\) must be greater than for the process \(B \rightarrow A\) \((E_{2a} > E_{1a})\). Accordingly, the maximum on section BC must be higher than that on section BA.

Finally, since according to the data of the example the second step of the reaction is endothermic, a higher energy level must correspond to the final state of the system (substance C) than to the intermediate state (substance B), and this is what is reflected in the diagram. It can be seen that the reaction as a whole is attended by the absorption of heat, i.e. \(\Delta H > 0\).

The rate of a chemical reaction grows in the presence of a catalyst. The latter causes unstable intermediates (activated complexes) to appear whose decomposition leads to the formation of the products. The activation energy of the reaction is lowered, and now some molecules become active whose energy was insufficient for conducting the reaction in the absence of the catalyst. As a result, the total number of active molecules grows, and the rate of the reaction increases.

It follows from the Arrhenius equation, in which \(E_a\) is an exponent, that even a small decrease in the activation energy results in a considerable growth in the reaction rate. For instance, biological catalysts—enzymes—sharply lower the activation energy of chemical reactions proceeding in living organisms, and these reactions proceed sufficiently rapidly at comparatively low temperatures.

Example 5. The activation energy of a reaction is 75.24 kJ/mol in the absence of a catalyst, and 50.14 kJ/mol with a catalyst. How many times will the rate of the reaction grow in the presence of a catalyst if the reaction proceeds at 25 °C?

Solution. Let the activation energy of the reaction without a catalyst be \(E_a\), and with one, \(E_a'\), let \(k\) and \(k'\) be the respective rate constants of the reaction. Using the Arrhenius equation, we find:

\[
\frac{k'}{k} = \frac{\exp\left(-\frac{E_a'}{RT}\right)}{\exp\left(-\frac{E_a}{RT}\right)} = \exp\left(\frac{E_a - E_a'}{RT}\right)
\]

whence

\[
\ln\frac{k'}{k} = 2.30 \log\frac{k'}{k} = \frac{E_a - E_a'}{RT}, \quad \text{and} \quad \log\frac{k'}{k} = \frac{E_a - E_a'}{2.30RT}
\]

Introducing the data of the example into the last equation, expressing the activation energy in joules, and taking into account that
When a chemical reaction proceeds, the concentrations of the reactants diminish. In accordance with the law of mass action, this lowers the reaction rate. If a reaction is reversible, i.e. can proceed both in the forward and the reverse direction, with time the rate of the reverse reaction will grow because the concentrations of the products increase. When the rates of the forward and reverse reactions become the same, a state of chemical equilibrium sets in, and no further change in the concentrations of the reactants and products occurs.

For the reversible chemical reaction

\[ A + B \rightleftharpoons C + D \]

the dependence of the rates of the forward \((J_f)\) and reverse \((J_r)\) reactions on the concentrations of the reactants and products is expressed by the relations

\[ J_f = k_f[A][B] \quad \text{and} \quad J_r = k_r[C][D] \]

In the state of chemical equilibrium, \(J_f = J_r\), i.e.

\[ k_f[A][B] = k_r[C][D] \]

whence

\[ \frac{k_f}{k_r} = \frac{[C][D]}{[A][B]} = K \]

where \(K\) is the equilibrium constant of the reaction.

The concentrations in the expression for the equilibrium constant are called the equilibrium concentrations. The equilibrium constant is a quantity, constant at a given temperature, expressing the relationship between the equilibrium concentrations of the products (numerator) and reactants (denominator). The greater the equilibrium constant, the further does a reaction proceed, i.e. the greater is the yield of its products.
It is proved in chemical thermodynamics that for the general case of the chemical reaction
\[ aA + bB + \ldots \rightleftharpoons cC + dD + \ldots \]
a similar expression holds for the equilibrium constant \( K \) of the reaction:
\[ K = \frac{[C]^c[B]^d \ldots}{[A]^a[B]^b \ldots} \]

The expression for the equilibrium constant of a heterogeneous reaction, like that for the law of mass action, includes only the concentrations of the substances in the liquid or gaseous phase because the concentrations of solid substances remain constant as a rule.

A catalyst does not affect the value of the equilibrium constant because it lowers the activation energy of the forward and reverse reactions by the same amount and therefore changes the rates of the forward and reverse reactions by the same magnitude. A catalyst only accelerates the attaining of equilibrium, but does not affect the quantitative yield of the products.

Example 6. In the system \( A(g) + 2B(g) \rightleftharpoons C(g) \), the equilibrium concentrations are \([A] = 0.06 \text{ mol/l}, [B] = 0.12 \text{ mol/l}, \) and \([C] = 0.216 \text{ mol/l}\). Find the equilibrium constant of the reaction and the initial concentrations of substances \( A \) and \( B \).

Solution. The equilibrium constant of the given reaction is expressed by the equation
\[ K = \frac{[C]}{[A][B]^2} \]
Introducing the data of the example into it, we get
\[ K = \frac{0.216}{0.06 \times (0.12)^2} = 250 \]

To find the initial concentrations of substances \( A \) and \( B \), we shall take into account that, in accordance with the equation of the reaction, one mole of \( A \) and 2 moles of \( B \) yield one mole of \( C \). Since according to the data of the example, 0.216 mole of substance \( C \) was formed in each litre of the system, 0.216 mole of \( A \) and \( 0.216 \times 2 = 0.432 \) mole of \( B \) were consumed. Thus, the required initial concentrations are:
\[ [A]_0 = 0.06 + 0.216 = 0.276 \text{ mol/l} \]
\[ [B]_0 = 0.12 + 0.432 = 0.552 \text{ mol/l} \]

Example 7. Eight moles of \( \text{SO}_2 \) and four moles of \( \text{O}_2 \) are mixed in a closed vessel. The reaction proceeds at constant temperature. By
the moment when equilibrium sets in, 80% of the initial amount of $SO_2$ enters into the reaction. Determine the pressure of the gas mixture in equilibrium if the initial pressure was 300 kPa.

**Solution.** The equation of the proceeding reaction is

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

According to the data of the example, 80%, i.e. 6.4 moles, of $SO_2$ entered into the reaction. Hence, 1.6 moles of $SO_2$ remained unconsumed. By the reaction equation, one mole of $O_2$ is consumed for each two moles of $SO_2$ with the formation of two moles of $SO_3$. Hence, 3.2 moles of $O_2$ reacted with 6.4 moles of $SO_2$ to form 6.4 moles of $SO_3$; $4 - 3.2 = 0.8$ mole of $O_2$ remained unused.

Therefore, the total number of moles of the gases was $8 + 4 = 12$ before the reaction, and $1.6 + 0.8 + 6.4 = 8.8$ moles after equilibrium was reached. In a closed vessel at constant temperature, the pressure of a gas mixture is proportional to the total amount of the gas forming it. Consequently, the pressure in equilibrium ($p$) can be found from the proportion $12 : 8.8 = 300 : p$, whence

$$p = \frac{8.8 \times 300}{12} = 220 \text{ kPa}$$

**Example 8.** At a certain temperature, the constant of dissociation of hydrogen iodide into the elementary substances is $6.25 \times 10^{-3}$. What per cent of HI dissociates at this temperature?

**Solution.** The equation of the reaction of HI dissociation is:

$$2HI \rightleftharpoons H_2 + I_2$$

Let us denote the initial concentration of HI by $c$ (mol/l). If by the moment when equilibrium sets in, $x$ moles of each $c$ moles of hydrogen iodide dissociate, according to the equation of the reaction $0.5x$ moles of $H_2$ and $0.5x$ moles of $I_2$ are formed. Consequently, the equilibrium concentrations are:

$$[HI] = (c - x) \text{ mol/l}; \quad [H_2] = [I_2] = 0.5x \text{ mol/l}$$

We introduce these values into the expression for the equilibrium constant of the reaction:

$$K = \frac{[H_2][I_2]}{[HI]^2}; \quad 6.25 \times 10^{-3} = \frac{0.5x \cdot 0.5x}{(c - x)^2}$$

Extracting a square root from both sides of the equation, we obtain:

$$0.25 = \frac{0.5x}{c - x}$$

whence $x = 0.333c$.

Thus, by the moment when equilibrium sets in, 33.3% of the initial amount of hydrogen iodide dissociates.

When the conditions (temperature, pressure, concentration of one of the reactants or products) in which a reaction proceeds change, the rates of the forward and reverse processes change differently and chemical equilibrium is violat-
As a result of the reaction proceeding more rapidly in one of the possible directions, a state of new chemical equilibrium sets in that differs from the initial one. The process of transition from one equilibrium state to a new equilibrium is called the displacement or shifting of chemical equilibrium. Its direction obeys Le Chatelier's principle:

*If any change of conditions is imposed on a system in equilibrium, the equilibrium will shift in such a way as to counteract the imposed change.*

For instance, elevation of the temperature leads to the shifting of equilibrium in the direction of the reaction attended by the absorption of heat, i.e. by cooling of the system; an increase in the pressure causes equilibrium to shift in the direction of a decrease in the total number of moles of gaseous substances, i.e. in the direction leading to lowering of the pressure; the removal from a system of one of the products results in equilibrium being displaced in the direction of the forward reaction; diminishing of the concentration of one of the reactants leads to shifting of equilibrium in the direction of the reverse reaction.

**Example 9.** In what direction will equilibrium shift in the systems

(a) \( \text{CO}(g) + \text{Cl}_2(g) \rightleftharpoons \text{COCl}_2(g) \)

(b) \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g) \)

if at a constant temperature the pressure is increased by diminishing the volume of the gas mixture?

**Solution.** (a) Proceeding of the reaction in the forward direction leads to diminishing of the total number of moles of the gases, i.e. to lowering of the pressure in the system. Consequently, according to Le Chatelier's principle, an increase in the pressure causes equilibrium to shift in the direction of the forward reaction.

(b) The reaction is not attended by a change in the number of moles of the gases and thus does not result in a change in pressure. In this case, this change will not cause equilibrium to shift.

The equilibrium constant \( K_T \) of a chemical reaction is related to the standard change in the Gibbs energy of this reaction \( \Delta G^* \) by the equation:

\[
\Delta G^*_T = -2.3RT \log K_T
\]

For 298 K (25 °C), this equation becomes:

\[
\Delta G^*_{298} = -5.69 \log K_{298}
\]

where \( \Delta G^*_{298} \) is expressed in kJ/mol.
The last equations show that \( \Delta G^o \) can have a negative sign only when \( \log K > 0 \), i.e. \( K > 1 \), and a positive one when \( \log K < 0 \), i.e. \( K < 1 \). This means that at negative values of \( \Delta G^o \) equilibrium is shifted in the direction of the forward reaction, and the yield of the products is comparatively great. When \( \Delta G^o \) is positive, equilibrium is shifted in the direction of the reverse reaction, and the yield of the products of the forward reaction is comparatively small. It must be stressed in this connection that the sign of \( \Delta G^o \) indicates the possibility or impossibility of a reaction proceeding only in standard conditions, when all the reactants and products are in standard states. In the general case, however, the possibility (or impossibility) of a reaction is determined by the sign of \( \Delta G \), and not of \( \Delta G^o \).

Example 10. Using reference data, find the approximate value of the temperature at which the equilibrium constant of the reaction of formation of water gas

\[
\text{C(graphite) + H}_2\text{O(g) } \rightleftharpoons \text{CO(g) + H}_2\text{(g)}
\]

is unity. Disregard the temperature dependence of \( \Delta H^o \) and \( \Delta S^o \).

Solution. It follows from the equation

\[
\Delta G^o_T = -2.3RT \log K_T
\]

that when \( K_T = 1 \), the standard Gibbs energy of a chemical reaction is zero. It thus follows from the equation

\[
\Delta G^o_T = \Delta H^o_T - T \Delta S^o_T
\]

that at the corresponding temperature \( \Delta H^o_T = T \Delta S^o_T \), whence

\[
T = \frac{\Delta H^o_T}{\Delta S^o_T}
\]

According to the data of the example, we may use the values of \( \Delta H^o_{298} \) and \( \Delta S^o_{298} \) of the reaction, which we find in Table 5 of the Appendix, for our calculations:

\[
\Delta H^o_{298} = \Delta H^o_{\text{form(CO)}} - \Delta H^o_{\text{form(H}_2\text{O)}} = -110.5 - (-241.8) = 131.3 \text{ kJ}
\]

\[
\Delta S^o_{298} = S^o_{298}(\text{CO}) + S^o_{298}(\text{H}_2) - S^o_{298}(\text{C}) - S^o_{298}(\text{H}_2\text{O}) = 197.5 + 130.5 - 5.7 - 188.7 = 133.6 \text{ J/K} = 0.1336 \text{ kJ/K}
\]

Hence,

\[
T = \frac{131.3}{0.1336} = 983 \text{ K}
\]
PROBLEMS

322. Find the value of the rate constant for the reaction \( A + B \rightarrow AB \) if at concentrations of substances A and B equal to 0.05 and 0.01 mol/l, respectively, the rate of the reaction is \( 5 \times 10^{-6} \) mol/(l·min).

323. How many times will the rate of the reaction \( 2A + B \rightarrow A_2B \) change if the concentration of substance A is doubled, and that of substance B is halved?

324. How many times must the concentration of substance \( B_2 \) in the system \( 2A_2(g) + B_2(g) = 2A_2B(g) \) be increased for the rate of the forward reaction to remain unchanged when the concentration of substance A is lowered to one-fourth of its initial value?

325. One mole of gas A and two moles of gas B are introduced into one vessel, and two moles of gas A and one mole of gas B into a second vessel having the same capacity. The temperature is the same in both vessels. Will the rate of the reaction between gases A and B in these vessels differ if it is expressed by the equation (a) \( J_1 = k_1[A][B] \); (b) \( J_2 = k_2[A]^2[B] \)?

326. In a certain time after the beginning of the reaction \( 3A + B \rightarrow 2C + D \), the concentrations of the substances were \( [A] = 0.03 \) mol/l, \( [B] = 0.01 \) mol/l, and \( [C] = 0.008 \) mol/l. What were the initial concentrations of reactants A and B?

327. In the system \( CO + Cl_2 = COCl_2 \), the \( CO \) concentration was increased from 0.03 to 0.12 mol/l, and that of the chlorine from 0.02 to 0.06 mol/l. How many times did the rate of the forward reaction increase?

328. The reaction between substances A and B is expressed by the equation \( A + 2B \rightarrow C \). The initial concentrations of the reactants are \( [A]_0 = 0.03 \) mol/l and \( [B]_0 = 0.05 \) mol/l. The rate constant of the reaction is 0.4. Find the initial rate of the reaction and the rate after a certain time when the concentration of substance A diminishes by 0.01 mol/l.

329. How will the rate of the reaction \( 2NO(g) + O_2(g) \rightarrow 2NO_2(g) \) change if (a) the pressure in the system is increased three times; (b) the volume of the system is diminished to one-third of its initial value; and (c) the concentration of the NO is increased three times?
330. Two reactions proceed at 25 °C at the same rate. The temperature coefficient of the rate of the first reaction is 2.0, and of the second, 2.5. Find the ratio of the rates of these reactions at 95 °C.

331. What is the temperature coefficient of the reaction rate if the rate grows 15.6 times when the temperature is increased by 30 kelvins?

332. The temperature coefficient of the rate of a reaction is 2.3. How many times will the rate of the reaction increase if the temperature is raised by 25 kelvins?

333. At 150 °C, a reaction terminates in 16 minutes. Assuming the temperature coefficient of the reaction rate to be 2.5, calculate how long it will take this reaction to terminate if it is conducted (a) at 200 °C, and (b) at 80 °C.

334. Will the value of the rate constant of a reaction change (a) when one catalyst is replaced with another one, and (b) when the concentrations of the reactants and products are changed?

335. Does the heat effect of a reaction depend on its activation energy? Substantiate your answer.

336. For which reaction—the forward or the reverse one—is the activation energy greater if the forward reaction proceeds with the liberation of heat?

337. How many times will the rate of a reaction proceeding at 298 K grow if its activation energy is lowered by 4 kJ/mol?

338. What is the activation energy of a reaction if its rate doubles when the temperature is raised from 290 to 300 K?

339. What is the value of the activation energy for a reaction whose rate at 300 K is ten times greater than at 280 K?

340. The activation energy of the reaction \( \text{O}_3(g) + \text{NO}(g) \rightarrow \text{O}_2(g) + \text{NO}_2(g) \) is 10 kJ/mol. How many times will the rate of the reaction change when the temperature is raised from 27 to 37 °C?

341. Does the temperature coefficient of the reaction rate depend on the value of the activation energy? Substantiate your answer.

342. Does the value of the activation energy of a reaction in heterogeneous catalysis depend on the surface area of the catalyst and on its structure?
343. The reaction \( 2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) \) proceeds with the liberation of heat. For the reaction to begin, however, the initial mixture of gases has to be heated. How can this be explained?

344. Depict schematically the energy diagram of the exothermic reaction \( A + B \rightleftharpoons AB \). Which reaction—the forward or the reverse one—is characterized by a greater rate constant?

345. Depict schematically the energy diagram of the reaction \( A \rightleftharpoons B \rightleftharpoons C \) if \( k_1 > k_2 > k_3 \), and for the reaction as a whole \( \Delta H > 0 \).

346. Why does the initiation of the chain in the chain reaction \( \text{H}_2 + \text{Cl}_2 = 2\text{HCl} \) begin with the radical \( \text{Cl}^- \), and not with the radical \( \text{H}^- \)?

347. The reaction \( \text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2 \) proceeds in a closed vessel at a constant temperature; the reactants are taken in equivalent amounts. When equilibrium sets in, 50% of the initial amount of CO remains. Determine the pressure of the equilibrium gas mixture if the initial pressure was 100 kPa (750 mmHg).

348. The equilibrium \( \text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g) \) has set in in a closed vessel; the equilibrium constant is unity. Determine (a) what per cent of the \( \text{CO}_2 \) is transformed into \( \text{CO} \) at the given temperature if one mole of \( \text{CO}_2 \) and five moles of \( \text{H}_2 \) are mixed, and (b) the volume proportions in which the \( \text{CO}_2 \) and \( \text{H}_2 \) were mixed if by the moment when equilibrium was established, 90% of the original amount of hydrogen entered into the reaction.

349. When the system

\[
\text{Na}(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g); \quad \Delta H^\circ = -92.4 \text{ kJ}
\]

is in equilibrium, the concentrations of the reactants and product are \([\text{N}_2]\) = 3 mol/l; \([\text{H}_2]\) = 9 mol/l, and \([\text{NH}_3]\) = 4 mol/l. Determine (a) the initial concentrations of \( \text{H}_2 \) and \( \text{N}_2 \), (b) the direction in which equilibrium will be displaced with elevation of the temperature, and (c) the direction in which equilibrium will be displaced if the volume of the reaction vessel is diminished.

350. The equilibrium constant of the reaction \( \text{FeO}(c) + \text{CO}(g) \rightleftharpoons \text{Fe}(c) + \text{CO}_2(g) \) at a certain temperature is 0.5.
Find the equilibrium concentrations of the CO and CO₂ if the initial concentrations of these substances were [CO]₀ = 0.05 mol/l and [CO₂]₀ = 0.01 mol/l.

351. Equilibrium in the system H₂(g) + I₂(g) ⇌ 2HI(g) set in at the following concentrations: [H₂] = 0.025 mol/l, [I₂] = 0.005 mol/l, and [HI] = 0.09 mol/l. Determine the initial concentrations of the iodine and hydrogen.

352. At a certain temperature, equilibrium in the system 2NO₂ ⇌ 2NO + O₂ was established at the following concentrations: [NO₂] = 0.006 mol/l, [NO] = 0.024 mol/l, and [O₂] = 0.012 mol/l. Find the equilibrium constant of the reaction and the initial concentration of the NO₂.

353. For the reaction H₂(g) + Br₂(g) ⇌ 2HBr(g) at a certain temperature, K = 1. Determine the composition (in per cent by volume) of the equilibrium reaction mixture if the initial mixture consisted of 3 moles of H₂ and 2 moles of Br₂.

354. The equilibrium constant of the reaction A(g) + B(g) ⇌ C(g) + D(g) is unity. What per cent of substance A will be transformed if three moles of substance A are mixed with five moles of substance B?

355. After the mixing of gases A and B, equilibrium sets in in the system A(g) + B(g) ⇌ C(g) + D(g) at the following concentrations: [B] = 0.05 mol/l and [C] = 0.02 mol/l. The equilibrium constant of the reaction is 4 × 10⁻². Find the initial concentrations of substances A and B.

356. Find the equilibrium constant of the reaction N₂O₄ ⇌ 2NO₂ if the initial concentration of the N₂O₄ was 0.08 mol/l, and by the moment when equilibrium was established 50% of the N₂O₄ had dissociated.

357. The reaction AB(g) ⇌ A(g) + B(g) proceeds in a closed vessel. The equilibrium constant of the reaction is 0.04, and the equilibrium concentration of substance B is 0.02 mol/l. Find the initial concentration of substance AB. What per cent of substance AB decomposed?

358. The equilibrium constant of the reaction A + B ⇌ C + D is unity. The initial concentration [A]₀ = 0.02 mol/l. What per cent of substance A transforms if the initial concentrations [B]₀ equal 0.02, 0.1, and 0.2 mol/l?

359. The system

\[ \text{C(graphite)} + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g); \quad \Delta H^\circ = 172.5 \text{ kJ} \]
is in a state of equilibrium. Indicate (a) how the content of the CO in the equilibrium mixture will change with elevation of the temperature at a constant pressure, and with an increase in the total pressure at a constant temperature, and (b) whether the equilibrium constant will change with an increase in the total pressure and at a constant temperature, when the temperature is raised, and when a catalyst is introduced into the system.

360. In what direction will the following equilibria shift:

\[ 2\text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g); \quad \Delta H^\circ = -566 \text{ kJ} \]
\[ \text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g); \quad \Delta H^\circ = 180 \text{ kJ} \]

(a) when the temperature is lowered? (b) when the pressure is increased?

361. How is the equilibrium of the following reactions:

\[ 2\text{H}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g); \quad \Delta H^\circ = -483.6 \text{ kJ} \]
\[ \text{CaCO}_3(c) \rightleftharpoons \text{CaO}(c) + \text{CO}_2(g); \quad \Delta H^\circ = 179 \text{ kJ} \]

affected by (a) an increase in the pressure, and (b) elevation of the temperature?

362. Indicate by what changes in the concentrations of the reactants and product the equilibrium of the reaction \( \text{CO}_2(g) + \text{C(graphite)} \rightleftharpoons 2\text{CO}(g) \) can be shifted to the right.

363. In what direction does equilibrium of the reaction \( \text{A}_2(g) + \text{B}_2(g) \rightleftharpoons 2\text{AB}(g) \) shift if the pressure is doubled and the temperature is simultaneously increased by 10 kelvins? The temperature coefficients of the rates of the forward and reverse reactions equal 2 and 3, respectively. What is the sign of \( \Delta H^\circ \) for this reaction?

364. Using tabulated data, calculate the equilibrium constants for the following reactions at 298 and at 1000 K:

(a) \( \text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \)
(b) \( \text{CO}_2(g) + \text{C(graphite)} \rightleftharpoons 2\text{CO}(g) \)
(c) \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \)

Disregard the changes in \( \Delta H^\circ \) and \( \Delta S^\circ \) with the temperature.

365. Calculate the temperature at which the equilibrium constant of the reaction \( 2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \) equals unity. Disregard the changes in \( \Delta H^\circ \) and \( \Delta S^\circ \) with the temperature.
In what direction will equilibrium shift at a lower temperature?

366. Assuming that $\Delta H^\circ$ and $\Delta S^\circ$ for the reaction $4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{H}_2\text{O}(g) + 2\text{Cl}_2(g)$ do not depend on the temperature, find the temperature at which the equilibrium constant of this reaction is unity.

367. The standard change in the Gibbs energy for the reaction $\text{A} + \text{B} \rightleftharpoons \text{AB}$ at 298 K is $-8$ kJ/mol. The initial concentrations are $[\text{A}]_0 = [\text{B}]_0 = 1$ mol/l. Find the equilibrium constant of the reaction and the equilibrium concentrations of substances $\text{A}$, $\text{B}$, and $\text{AB}$.

368. Why does a reaction virtually fail to proceed in many cases although $\Delta G^\circ$ for the reaction is negative? In what ways can a reaction be made to occur in such cases?

369. The value of $\Delta G^\circ$ within a certain temperature interval is positive for the reaction $\text{A}_2(g) + \text{B}_2(g) \rightleftharpoons 2\text{AB}(g)$. Does this mean that substance $\text{AB}$ cannot be obtained in this temperature interval by the direct reaction of $\text{A}_2$ and $\text{B}_2$? Substantiate your answer.

REVIEW QUESTIONS

370. How will the rate of the reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ change if the volume of the reaction vessel is doubled? (a) It will diminish to one-fourth of its initial value; (b) it will diminish to one-eighth of its initial value; (c) it will grow four times; (d) it will grow eight times.

371. How can one explain the growth in the reaction rate when a catalyst is introduced into a system? (a) By a decrease in the activation energy; (b) by an increase in the average kinetic energy of the molecules; (c) by a growth in the number of collisions; (d) by a growth in the number of active molecules.

372. Which of the following procedures will lead to a change in the rate constant of a reaction? (a) A change in the pressure; (b) a change in the temperature; (c) a change in the volume of the reaction vessel; (d) the introduction of a catalyst into the system; (e) a change in the concentration of the reactants and products.

373. How does agitation affect the rate of a heterogeneous chemical reaction? (a) In all cases it increases the rate of the
reaction; (b) in some cases it increases the rate of the reaction; (c) it does not affect the rate of the reaction.

374. The increase in a reaction rate with temperature is due chiefly to: (a) an increase in the average kinetic energy of the molecules; (b) a growth in the number of active molecules; (c) a growth in the number of collisions.

375. The rate of which reactions increases with temperature? (a) Of any; (b) of reactions proceeding with the evolution of energy; (c) of reactions proceeding with the absorption of energy.

376. If the rate constant of one reaction \( (k') \) is greater than that of a second reaction \( (k'') \), what relationship between the activation energies of these reactions is correct? (a) \( E_a' > > E_a'' \); (b) \( E_a' < E_a'' \); (c) it cannot be determined.

377. Which of the following procedures lead to a change in the value of the equilibrium constant of a chemical reaction? (a) A change in the pressure; (b) a change in the temperature; (c) replacement of the catalyst; (d) a change in the concentrations of the reactants and products.

378. If the volume of a closed reaction vessel in which the equilibrium \( 2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \) set in is halved, (a) the rates of the forward and reverse reactions will remain the same; (b) the rate of the forward reaction will become double that of the reverse one; (c) equilibrium will not shift; (d) equilibrium will shift to the right; (e) equilibrium will shift to the left.

379. What changes will cause equilibrium to shift to the left in the system \( 4\text{HCl}(g) + \text{O}_2(g) \rightleftharpoons 2\text{Cl}_2(g) + 2\text{H}_2\text{O}(g) \)? (a) An increase in the concentration of the \( \text{O}_2 \); (b) an increase in the concentration of the \( \text{Cl}_2 \); (c) an increase in the pressure; (d) an increase in the volume of the reaction vessel.

380. In what direction will equilibrium shift in the system \( 4\text{Fe}(c) + 3\text{O}_2(g) \rightleftharpoons 2\text{Fe}_2\text{O}_3(c) \) when the pressure grows? (a) In the direction of the forward reaction; (b) in the direction of the reverse reaction; (c) in no direction.

381. What changes will increase the equilibrium concentration of product \( \text{AB} \) in the system \( \text{A}(g) + \text{B}(g) \rightleftharpoons \text{AB}(g) \) if \( \Delta H^\circ \) of the reaction is negative? (a) The introduction of a catalyst into the system; (b) elevation of the temperature; (c) lowering of the temperature; (d) the introduction of an extra amount of substance \( \text{B} \) into the reaction vessel.
382. For a spontaneously proceeding reaction, \( \Delta S^\circ < 0 \). How will the equilibrium constant change with elevation of the temperature? (a) It will increase; (b) it will diminish; (c) the data of the problem do not allow the change to be determined.

383. The value of the equilibrium constant of the reaction \( H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g) \) grows with the temperature. What is the sign of \( \Delta H^\circ_{298} \) for this reaction? (a) \( \Delta H^\circ > 0 \); (b) \( \Delta H^\circ < 0 \); (c) the data of the problem do not allow it to be determined.

384. We have \( \Delta G^\circ > 0 \) for a reaction. Which of the following statements are correct? (a) \( K > 1 \); (b) \( K < 1 \); (c) the products predominate in the equilibrium mixture; (d) the reactants predominate in the equilibrium mixture.

385. The equilibrium constant of a reaction at 293 K is \( 5 \times 10^{-3} \), and at 1000 K it is \( 2 \times 10^{-6} \). What is the sign of \( \Delta H^\circ \) for this reaction? (a) \( \Delta H^\circ > 0 \); (b) \( \Delta H^\circ < 0 \).
1. Concentration of Solutions. Solubility

The concentration of a solution is defined as the content of the solute in a definite mass or a definite volume of the solution or solvent.

The ways of expressing the concentration used in chemistry are given below:

<table>
<thead>
<tr>
<th>Ways of expressing concentration</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Per cent concentration by mass (c)</td>
<td>The number of mass units of solute contained in 100 units of mass of solution; for example, c = 32.5% (mass)</td>
</tr>
<tr>
<td>Molar-volume concentration or molarity (cm)</td>
<td>The number of moles of solute dissolved in one litre of solution; for example, cm = 1.5 M or cm = 1.5 mol/l</td>
</tr>
<tr>
<td>Molal concentration or molality (m)</td>
<td>The number of moles of solute dissolved in 1000 g of solvent; for example, m = 1.5 moles per 1000 g of H₂O</td>
</tr>
<tr>
<td>Equivalent concentration or normality (cn)</td>
<td>The number of solute equivalents in one litre of solution; for example, cn = 0.75 N</td>
</tr>
<tr>
<td>Mole fraction: of solute (x₂)</td>
<td>The ratio of the number of moles of solute (n₂) to the sum of the numbers of moles of the solvent (n₁) and the solute: ( x₂ = n₂/(n₁ + n₂) )</td>
</tr>
<tr>
<td>of solvent (x₁)</td>
<td>The ratio of the number of moles of solvent (n₁) to the sum of the number of moles of the solvent and solute: ( x₁ = n₁/(n₁ + n₂) )</td>
</tr>
</tbody>
</table>
Example 1. 50 g of the crystal hydrate FeSO₄·7H₂O were dissolved in 250 g of water. Calculate the per cent concentration of the crystal hydrate and the anhydrous iron(II) sulphate in the solution.

Solution. The mass of the solution obtained is 300 g. We find the per cent concentration of the crystal hydrate from the proportion:

\[
\frac{300 \text{ g of solution}}{50 \text{ g of crystal hydrate}} = \frac{100\%}{z}\%
\]

\[
z = \frac{50 \times 100}{300} = 16.7\%
\]

Now we calculate the content of the anhydrous salt in 50 g of the crystal hydrate. The molar mass of FeSO₄·7H₂O is 278 g/mol, and that of FeSO₄ is 152 g/mol. We find the content of FeSO₄ in 50 g of FeSO₄·7H₂O from the proportion:

\[
\frac{278}{152} = \frac{50}{z}\% \Rightarrow z = \frac{50 \times 152}{278} = 27.4\text{ g}
\]

Hence, the per cent concentration of the anhydrous salt in 300 g of the solution is

\[
c = \frac{27.4 \times 100}{300} = 9.1\%
\]

Example 2. Find the masses of water and of blue vitriol CuSO₄·5H₂O needed to prepare one litre of a solution containing 8% of the anhydrous salt. The density of an 8% solution of CuSO₄ is \(\rho = 1.084\text{ g/ml}\).

Solution. The mass of one litre of the solution obtained will be \(1.084 \times 1000 = 1084\text{ g}\). This solution must contain 8% of the anhydrous salt, i.e. \(1084 \times 0.08 = 86.7\text{ g}\). We find the mass of CuSO₄·5H₂O (its molar mass is 249.7 g/mol) containing 86.7 g of the anhydrous salt (molar mass 159.6 g/mol) from the proportion:

\[
249.7 : 159.6 = z : 86.7
\]

\[
z = \frac{249.7 \times 86.7}{159.6} = 135.6\text{ g}
\]

The mass of the water needed to prepare the solution is \(1084 - 135.6 = 948.4\text{ g}\).

Example 3. What volume of 96% sulphuric acid (with a density of 1.84 g/ml) and what mass of water must be taken to prepare 100 ml of a 15% solution of H₂SO₄ (\(\rho = 1.10\text{ g/ml}\))? 

Solution. We find the mass of 100 ml of a 15% solution of H₂SO₄. It is \(100 \times 1.10 = 110\text{ g}\). The mass of H₂SO₄ in 110 g of this solution is \(15 \times 110/100 = 16.5\text{ g}\).

We now find the volume of a 96% solution containing 16.5 g of H₂SO₄. One millilitre of the solution with a mass of 1.84 g contains \(1.84 \times 0.96 = 1.77\text{ g}\) of H₂SO₄. Consequently, the required volume of the initial solution of H₂SO₄ is \(16.5/1.77 = 9.32\text{ ml}\).

Hence, to prepare 100 ml of a 15% solution of H₂SO₄, we need 9.32 ml of a 96% solution of the acid and \(110 - 16.5 = 93.5\text{ g}\) of H₂O.
Example 4. What volume of water must be added to 200 ml of a 30\% solution of NaOH (\( \rho = 1.33 \text{ g/ml} \)) to obtain a 10\% solution of the alkali?

Solution. The mass of 200 ml of the initial solution of NaOH is 200 \times 1.33 = 266 g. This solution contains 30\% of NaOH, i.e. 266 \times 0.3 = 79.8 g. According to the data of the example, this mass is 10\% of the total mass of the dilute solution. Consequently, the mass of the solution obtained will be (79.8/10) \times 100 = 798 g. Hence, 798 - 266 = 532 g of water must be added to the initial solution.

Example 5. Find the molality and the mole fraction of the solute in a 67\% solution of saccharose \( C_{12}H_{22}O_{11} \).

Solution. We calculate the mass of the saccharose per 1000 g of water from the proportion:

\[
1000 : 33 = z : 67; \quad z = \frac{67 \times 1000}{33} = 2030 \text{ g}
\]

Since the molar mass of saccharose is 342 g/mol, the molality is \( m = \frac{2030}{342} = 5.96 \) moles per 1000 g of \( H_2O \).

The mole fraction of the solute is \( x = \frac{n_1}{n_1 + n_2} \). 100 g of the solution contain 67 g of saccharose and 33 g of water, whence \( n_1 = \frac{67}{18} = 3.73 \) and \( n_2 = \frac{33}{342} = 0.097 \). Hence:

\[
x = \frac{0.196}{1.83 + 0.196} = 0.097
\]

Example 6. Find the molality, normality, and molarity of a 15\% solution of \( H_2SO_4 \) (\( \rho = 1.10 \text{ g/ml} \)).

Solution. To calculate the molality, let us first find the mass of the sulphuric acid per 1000 g of water:

\[
1000 : 85 = z : 15; \quad z = \frac{15 \times 1000}{85} = 176.5 \text{ g}
\]

The molar mass of \( H_2SO_4 \) is 98 g/mol; hence, \( m = \frac{176.5}{98} = 1.80 \) moles per 1000 g of \( H_2O \).

To calculate the normality and the molarity of the solution, we shall find the mass of the sulphuric acid contained in 1000 ml (i.e. in \( 1000 \times 1.1 = 1100 \) g) of the solution:

\[
1100 : 100 = y : 15; \quad y = \frac{1100 \times 15}{100} = 165 \text{ g}
\]

The equivalent mass of sulphuric acid is 49 g/mol. Consequently, \( c_n = \frac{165}{49} = 3.37 \text{ \text{N}} \) and \( c_m = \frac{165}{98} = 1.68 \text{ \text{mol/l}} \).

Example 7. What volumes of 2 and 6 \( M \) solutions of HCl have to be mixed to prepare 500 ml of a 3 \( M \) solution? Disregard the change in the volume in mixing.

Solution. 500 ml of a 3 \( M \) solution contain 0.5 \times 3 = 1.5 moles of HCl. Let us denote the required volume of the 6 \( M \) solution by \( z \); hence, the required volume of the 2 \( M \) solution will be \( 0.5 - z \) litres. \( z \) Litres of a 6 \( M \) solution contain 6z moles of HCl, while \( (0.5 - z) \) litres of a 2 \( M \) solution contain 2 \( (0.5 - z) \) moles of HCl. Since the total number of moles must equal 1.5, we can write:

\[
6z + 2 (0.5 - z) = 1.5; \quad z = 0.125 \text{ l}
\]
Consequently, to prepare the required solution, we must take 125 ml of the 6 M and 375 ml of the 2 M solution of HCl.

Example 8. To neutralize 42 ml of H$\text{}_2$SO$_4$, it was necessary to add 14 ml of a 0.3 N alkali solution. Determine the molarity of the H$\text{}_2$SO$_4$ solution.

Solution. Since the substances react in equivalent amounts, we can write

\[ c_{n, ac}V_{ac} = c_{n, alk}V_{alk} \]

where \( c_{n, ac} \) and \( c_{n, alk} \) are the normalities of the acid and alkali, and \( V_{ac} \) and \( V_{alk} \) are the relevant volumes.

Consequently,

\[ c_{n, ac} \times 42 = 14 \times 0.3; \quad c_{n, ac} = \frac{14 \times 0.3}{42} = 0.1 \]

i.e. the concentration of the acid is 0.1 N. The equivalent of sulphuric acid is 0.5 mole. Hence, the molarity of the acid is 0.1 \times 0.5 = 0.05 mol/l.

The solubility of a substance is measured by the concentration of its saturated solution. The solubility of solids and liquids is usually expressed by the value of the solubility coefficient, i.e. the mass of a substance dissolving in given conditions in 100 g of the solvent with the formation of a saturated solution.

The solubility of gases is often characterized by the absorption coefficient, which expresses the volume of a gas dissolving in one volume of the solvent with the formation of a saturated solution. According to Henry's law, the mass of a gas that dissolves at a constant temperature in a given volume of a liquid is directly proportional to the partial pressure of the gas. It follows from Henry's law that the volume of a dissolving gas (and, consequently, the absorption coefficient) does not depend on its partial pressure at a given temperature.

Example 9. A saturated solution of KNO$_3$ contains 52.4% of the salt at 60 °C. Find the solubility coefficient of the salt at this temperature.

Solution. We find the solubility coefficient from the proportion:

\[ \frac{52.4 \text{ g of KNO}_3}{100 \text{ g of } H_2O} = \frac{z \text{ g of KNO}_3}{100 \text{ g of } H_2O} \]

\[ z = \frac{100 \times 52.4}{47.6} = 110 \text{ g} \]
Hence, the solubility of KNO₃ at 60 °C is 110 g in 100 g of H₂O.

Example 10. When 300 g of a 15% solution were cooled, part of the solute precipitated, and the concentration of the solution became equal to 8%. What is the mass of the precipitated substance?

Solution. 300 g of a 15% solution contain 45 g of the solute and 255 g of the solvent. Upon cooling, the amount of the solvent did not change. We find the content of the solute in 255 g of the solvent from the proportion:

\[ \frac{8 \times 255}{92} = 22.2 \text{ g} \]

Therefore, when the solution was cooled, 45 — 22.2 = 22.8 g of the solute precipitated.

Example 11. The absorption coefficients of oxygen and nitrogen at 0 °C are 0.049 and 0.023, respectively. A gas mixture containing 20% (vol.) O₂ and 80% (vol.) N₂ was agitated with water at 0 °C until a saturated solution was obtained. Find the per cent content (by volume) of the gases dissolved in the water.

Solution. According to the data of the example, 49 ml of O₂ and 23 ml of N₂ dissolve in one litre of water. These volumes cannot be compared directly, however, because the partial pressures of the dissolved gases are different and are 0.2 and 0.8 of the total pressure of the gas mixture, respectively. If we take the latter as unity, the volumes of the dissolved oxygen and nitrogen reduced to this pressure will be 49 \times 0.2 = 9.8 ml of O₂ and 23 \times 0.8 = 18.4 ml of N₂; the total volume of the dissolved gases, consequently, will be 9.8 + 18.4 = 28.2 ml.

We find the per cent content of each gas:

\[ \frac{9.8 \times 100}{28.2} = 35\% \text{ (vol.) O₂} \quad \text{and} \quad \frac{18.4 \times 100}{28.2} = 65\% \text{ (vol.) N₂} \]

PROBLEMS

386. Express in per cent the concentration of a solution containing 40 g of glucose in 280 g of water.

387. How many grams of Na₂SO₃ are needed to prepare five litres of an 8% solution (\( \rho = 1.075 \text{ g/ml} \))?

388. One millilitre of a 25% solution contains 0.458 g of the solute. What is the density of the solution?

389. One hundred grams of water were evaporated from 400 g of a 50% solution of H₂SO₄. What is the per cent concentration of the remaining solution?
390. At 25 °C, the solubility of NaCl is 36.0 g in 100 g of water. Express the concentration of the saturated solution in per cent.

391. How many grams of a 30% solution of NaCl must be added to 300 g of water to obtain a 10% solution of the salt?

392. In what mass of water must 67.2 litres of HCl be dissolved (the volume is measured in standard conditions) to obtain a 9% solution of HCl?

393. What mass of a 20% solution of KOH must be added to 1 kg of a 50% solution to obtain a 25% solution?

394. Determine the per cent concentration of a solution obtained by mixing 300 g of a 25% and 400 g of a 40% solution.

395. When 400 g of a 20% solution were cooled, 50 g of the solute precipitated. What is the per cent concentration of the remaining solution?

396. What volume of water has to be added to 100 ml of a 20% solution of H₂SO₄ (ρ = 1.14 g/ml) to obtain a 5% solution?

397. One litre of water was added to 500 ml of 32% HNO₃ (ρ = 1.20 g/ml). What is the per cent concentration of the HNO₃ in the solution obtained?

398. To what volume must 500 ml of a 20% solution of NaCl (ρ = 1.152 g/ml) be diluted to obtain a 4.5% solution (ρ = 1.029 g/ml)?

399. Find the per cent concentration of a nitric acid solution, one litre of which contains 224 g of HNO₃ (ρ = 1.24 g/ml).

400. The density of a 26% solution of KOH is 1.24 g/ml. How many moles of KOH are contained in five litres of the solution?

401. To prepare a 5% solution of MgSO₄, 400 g of MgSO₄·7H₂O were taken. Find the mass of the solution obtained.

402. How many moles of MgSO₄·7H₂O must be added to 100 moles of water to obtain a 10% solution of MgSO₄?

403. Determine the per cent concentration of CuSO₄ in the solution obtained when 50 g of blue vitriol CuSO₄·5H₂O were dissolved in 450 g of water.

404. In what mass of water must 25 g of CuSO₄·5H₂O be dissolved to obtain an 8% solution of CuSO₄?
405. How many grams of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ have to be dissolved in 800 g of water to obtain 10% $\text{Na}_2\text{SO}_4$?

406. How many grams of a 2% solution of $\text{AgNO}_3$ will produce 14.35 g of an $\text{AgCl}$ precipitate when reacted with an excess amount of $\text{NaCl}$?

407. How many litres of $\text{NH}_3$ (the volume is measured in standard conditions) must be dissolved in 200 g of a 10% solution of $\text{NH}_4\text{OH}$ to obtain a 15% solution of the ammonium hydroxide?

408. How many grams of $\text{SO}_3$ have to be dissolved in 400 g of $\text{H}_2\text{O}$ to produce a 15% solution of $\text{H}_2\text{SO}_4$?

409. Find the mass of $\text{NaNO}_3$ needed to prepare 300 ml of a 0.2 $\text{M}$ solution.

410. How many grams of $\text{Na}_2\text{CO}_3$ are contained in 500 ml of a 0.25 $\text{N}$ solution?

411. What volume of a 0.1 $\text{N}$ solution contains 8 g of $\text{CuSO}_4$?

412. To neutralize 30 ml of a 0.1 $\text{N}$ solution of an alkali, 12 ml of an acid solution were needed. Determine the normality of the acid.

413. Find the molarity of a 36.2% solution of $\text{HCl}$ whose density is 1.18 g/ml.

414. What volume of a 1 $\text{M}$ solution and what volume of a 1 $\text{N}$ solution contain 114 g of $\text{Al}_2(\text{SO}_4)_3$?

415. The solubility of cadmium chloride at 20 °C is 114.1 g in 100 g of water. Calculate the per cent concentration and the molality of a saturated solution of $\text{CdCl}_2$.

416. How many millilitres of a 96% solution of $\text{H}_2\text{SO}_4$ ($\rho = 1.84$ g/ml) must be taken to prepare 1 litre of a 0.25 $\text{N}$ solution?

417. How many millilitres of a 0.5 $\text{M}$ solution of $\text{H}_2\text{SO}_4$ can be prepared from 15 ml of a 2.5 $\text{M}$ solution?

418. What volume of a 0.1 $\text{M}$ solution of $\text{H}_3\text{PO}_4$ can be prepared from 75 ml of a 0.75 $\text{N}$ solution?

419. What volume of a 6.0 $\text{M}$ solution of $\text{HCl}$ must be taken to prepare 25 ml of a 2.5 $\text{M}$ solution of $\text{HCl}$?

420. The density of a 40% solution of $\text{HNO}_3$ is 1.25 g/ml. Calculate the molarity and the molality of this solution.

421. Calculate the per cent concentration of a 9.28 $\text{N}$ $\text{NaOH}$ solution ($\rho = 1.310$ g/ml).
422. Calculate the mole fractions of alcohol and water in a 96% solution of ethyl alcohol.

423. 666 g of KOH are dissolved in 1 kg of water; the density of the solution is 1.395 g/ml. Find (a) the per cent concentration, (b) the molarity, (c) the molality, and (d) the mole fractions of the alkali and the water.

424. The density of a 15% solution of H₂SO₄ is 1.105 g/ml. Calculate (a) the normality, (b) the molarity, and (c) the molality of the solution.

425. The density of a 9% solution of saccharose C₁₂H₂₂O₁₁ is 1.035 g/ml. Calculate (a) the concentration of the saccharose in g/l, (b) the molarity, and (c) the molality of the solution.

426. How many grams of water must be taken to prepare a solution of sodium chloride containing 1.50 moles of NaCl per 1000 g of H₂O if 10 g of NaCl are at hand?

427. How many millilitres of a 2 N solution of H₂SO₄ are needed to prepare 500 ml of a 0.5 N solution?

428. What volume of a 0.05 N solution can be obtained from 100 ml of a 1 N solution?

429. What volume of a 2 M solution of Na₂CO₃ must be taken to prepare one litre of a 0.25 N solution?

430. How many millilitres of concentrated hydrochloric acid (ρ = 1.19 g/ml) containing 38% HCl must be taken to prepare one litre of a 2 N solution?

431. 400 ml of water were added to 100 ml of 96% H₂SO₄ (density 1.84 g/ml) to obtain a solution having a density of 1.220 g/ml. Calculate its per cent and equivalent concentrations.

432. Calculate the normality of concentrated hydrochloric acid (density 1.18 g/ml) containing 36.5% HCl.

433. How many millilitres of 10% sulphuric acid (ρ = 1.07 g/ml) are needed for neutralizing a solution containing 16.0 g of NaOH?

434. One litre of a solution contains 18.9 g of HNO₃, and one litre of another solution contains 3.2 g of NaOH. In what volume ratio must these solutions be mixed to obtain a solution having a neutral reaction?

435. What volume of a 0.2 N alkali solution is needed to precipitate all the iron contained in 100 ml of a 0.5 N solution of FeCl₃ in the form of Fe(OH)₃?
436. How many grams of CaCO₃ will precipitate if an excess of a soda solution is added to 400 ml of a 0.5 N solution of CaCl₂?

437. Eight millilitres of an NaOH solution were needed to neutralize 20 ml of a 0.1 N acid solution. How many grams of NaOH does one litre of the NaOH solution contain?

438. The neutralization of 40 ml of an alkali solution required 24 ml of a 0.5 N H₂SO₄ solution. What is the normality of the alkali solution? What volume of a 0.5 N solution of HCl would be needed for the same purpose?

439. To neutralize a solution containing 2.25 g of an acid, 25 ml of a 2 N alkali solution were needed. Determine the equivalent mass of the acid.

440. The neutralization of 20 ml of a solution containing 12 g of an alkali per litre required 24 ml of a 0.25 N acid solution. Calculate the equivalent mass of the alkali.

441. What volume of a 15% solution of H₂SO₄ (ρ = = 1.10 g/ml) is needed for the complete dissolving of 24.3 g of Mg? of 27.0 g of Al?

442. For the complete precipitation of BaSO₄ from 100 g of a 15% solution of BaCl₂, 14.4 ml of H₂SO₄ were needed. Find the normality of the H₂SO₄ solution.

443. 300 g of NH₄Cl were dissolved with heating in 500 g of water. What mass of NH₄Cl will precipitate from the solution when it is cooled to 50 °C if the solubility of NH₄Cl at this temperature is 50 g in 100 g of water?

444. The solubility of potassium chlorate at 70 °C is 30.2 g, and at 30 °C, 10.1 g in 100 g of water. How many grams of potassium chlorate will precipitate from 70 g of a solution saturated at 70 °C if it is cooled to 30 °C?

445. The solubility coefficient of copper sulphate at 30 °C is 25 g per 100 g of H₂O. Will an 18% solution of the salt be saturated at this temperature?

446. How many grams of potassium nitrate will crystallize from 105 g of a solution saturated at 60 °C if it is cooled to 0 °C? The solubility coefficients of the salt at these temperatures are 110 g and 13 g in 100 g of H₂O, respectively.

447. One litre of water is saturated with CO₂ at 0 °C under a pressure of 506.6 kPa (3800 mmHg). What volume will the dissolved gas occupy if it is separated from the water and
Solutions

reduced to standard conditions? The solubility of CO₂ at 0 °C is 171 ml in 100 ml of H₂O.

448. The solubility of ammonia at 20 °C is 702 ml in 1 ml of water. Express the concentration of a saturated ammonia solution in per cent by mass. Assume that the partial pressure of the NH₃ equals standard atmospheric pressure.

449. One litre of water at 0 °C dissolves 4.62 litres of H₂S. At what pressure must the H₂S be dissolved to obtain a 5% solution?

450. Assuming that the atmospheric air contains 21% (vol.) O₂ and 79% (vol.) N₂, calculate the per cent composition (by volume) of the air liberated from water having a temperature of 20 °C. The coefficient of absorption of oxygen at this temperature is 0.031, and that of nitrogen 0.0154.

451. A gas mixture containing 40% (vol.) N₂O and 60% (vol.) NO was dissolved at 17 °C and constant pressure in water up to complete saturation of the latter. Calculate the per cent composition (by volume) of the gas mixture after it is liberated from the water if at 17 °C the coefficients of absorption of N₂O and NO are 0.690 and 0.050, respectively.

452. The coefficient of absorption of CO₂ at 0 °C is 1.71. At what pressure will be the solubility of CO₂ in water at the same temperature 16 g/l?

2. Energy Effects in the Formation of Solutions

The enthalpy of solution of a substance is defined as the change in the enthalpy when one mole of the substance dissolves in the given solvent.

It must be remembered that the enthalpy of solution depends on the temperature and the amount of solvent taken. The values cited in the given section relate, unless otherwise indicated, to room temperature (18-20 °C) and dilute solutions (400-800 moles of water per mole of solute).

Example 1. When 10 g of ammonium chloride were dissolved in 233 g of water, the temperature lowered by 2.80 K. Determine the enthalpy of solution of NH₄Cl.

Solution. When the above amount of salt is dissolved, a quite dilute solution is formed whose specific heat capacity (c) can be taken equal to that of water, i.e. 4.18 J/(g·K). The total mass of the solu-
tion \((m)\) is 243 g. We use the drop in the temperature \((\Delta t)\) to find the amount of heat absorbed:

\[
Q = cm \Delta t = 4.18 \times 243 \times (-2.80) = -2844 \text{ J} \approx -2.84 \text{ kJ}
\]

Consequently, the change in the enthalpy when 10 g of the salt are dissolved is 2.84 kJ. The molar mass of \(\text{NH}_4\text{Cl}\) is 53.5 g/mol. Hence, the enthalpy of solution of the salt is:

\[
\Delta H = \frac{2.84 \times 53.5}{10} = 15.2 \text{ kJ/mol}
\]

**Example 2.** When 10 g of anhydrous calcium chloride were dissolved in water, 6.82 kJ were evolved, while when 10 g of the crystal hydrate \(\text{CaCl}_2 \cdot 6\text{H}_2\text{O}\) were dissolved in water, 0.87 kJ was absorbed. Calculate the enthalpy of formation of the crystal hydrate from the anhydrous salt and water.

**Solution.** The process of dissolving the anhydrous salt can be represented as proceeding in two steps:

\[
\text{CaCl}_2(c) + 6\text{H}_2\text{O}(lq) = \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(c) \quad (\Delta H_1)
\]

\[
\text{CaCl}_2 \cdot 6\text{H}_2\text{O}(c) + n\text{H}_2\text{O}(lq) = \quad \text{CaCl}_2(\text{sol}) + (n + 6)\text{H}_2\text{O}(\text{sol}) \quad (\Delta H_2)
\]

where "sol" stands for solution; \(\Delta H_1\) is the enthalpy of formation of the crystal hydrate, and \(\Delta H_2\) is the enthalpy of its solution.

The net equation is:

\[
\text{CaCl}_2(c) + (n + 6)\text{H}_2\text{O}(lq) = \text{CaCl}_2(\text{sol}) + \quad + (n + 6)\text{H}_2\text{O}(\text{sol}) \quad (\Delta H_3)
\]

where \(\Delta H_3\) is the enthalpy of solution of the anhydrous salt.

According to Hess’s law, \(\Delta H_3 = \Delta H_1 + \Delta H_2\), whence \(\Delta H_1 = = \Delta H_3 - \Delta H_2\).

To find the required quantity \((\Delta H_1)\), we must consequently calculate the enthalpy of solution of the anhydrous salt \((\Delta H_3)\) and of the crystal hydrate \((\Delta H_2)\).

The molar mass of \(\text{CaCl}_2\) is 111 g/mol. Since the change in the enthalpy when dissolving 10 g of \(\text{CaCl}_2\) is 6.82 kJ, we have:

\[
\Delta H_3 = \frac{(-6.82) \times 111}{10} = -75.7 \text{ kJ/mol}
\]

The molar mass of \(\text{CaCl}_2 \cdot 6\text{H}_2\text{O}\) is 219 g/mol, whence

\[
\Delta H_2 = \frac{0.87 \times 219}{10} = 19.1 \text{ kJ/mol}
\]

For the enthalpy of formation of the crystal hydrate, we finally get:

\[
\Delta H_1 = \Delta H_3 - \Delta H_2 = -75.7 - 19.1 = -94.8 \text{ kJ/mol}
\]
PROBLEMS

453. When 10 g of NaOH were dissolved in 250 g of water, the temperature rose by 9.70 K. Determine the enthalpy of solution of NaOH adopting the specific heat capacity of the solution equal to 4.18 J/(g·K).

454. When one mole of H₂SO₄ was dissolved in 800 g of water, the temperature rose by 22.4 K. Determine the enthalpy of solution of H₂SO₄ assuming the specific heat capacity of the solution to equal 3.76 J/(g·K).

455. The enthalpy of solution of NH₄NO₃ in water is 26.7 kJ/mol. By how many kelvins will the temperature lower when 20 g of NH₄NO₃ are dissolved in 180 g of H₂O if the specific heat capacity of the solution obtained is taken equal to 3.76 J/(g·K)?

456. When 8 g of CuSO₄ were dissolved in 192 g of water, the temperature rose by 3.95 kelvins. Determine the enthalpy of formation of CuSO₄·5H₂O from the anhydrous salt and water if the enthalpy of solution of the crystal hydrate is known to be 11.7 kJ/mol, and the specific heat capacity of the solution is 4.18 J/(g·K).

457. The enthalpy of solution of Na₂SO₄·10H₂O in water is 78.6 kJ/mol. Calculate by how many kelvins the temperature will drop when 0.5 mole of this salt is dissolved in 1000 g of water, taking the specific heat capacity of the solution equal to 4.18 J/(g·K).

3. Physicochemical Properties of Dilute Solutions of Non-Electrolytes

Dilute solutions of non-electrolytes have a number of properties (colligative properties) whose quantitative expression depends only on the number of solute particles in solution and on the amount of solvent. Some colligative properties of solutions are used to determine the molecular mass of the solute.

The dependence of these properties on the concentration is expressed by the following equations:

1. Depression of the vapour pressure of a solvent over a solution, \( \Delta p \) (Raoult's law):

\[
p_1 = x_1 p_0; \quad \Delta p = p_0 - p_1 = x_2 p_0 = p_0 \frac{n_2}{n_1 + n_2}
\]
where $p_1$ is the partial pressure of the saturated vapour of the solvent over the solution; $p_0$ is the saturated vapour pressure over the pure solvent; $x_1$ is the mole fraction of the solvent; $x_2$ is the mole fraction of the solute; $n_1$ is the number of moles of the solvent; and $n_2$ is the number of moles of the solute.

2. Depression of the freezing point of a solution $\Delta t_f$ (or, which is the same, $\Delta T_f$):

$$\Delta t_f = K m$$

where $K$ is the cryoscopic constant of the solvent, and $m$ is the molality of the solute.

3. Elevation of the boiling point of a solution, $\Delta t_b$ (or $\Delta T_b$):

$$\Delta t_b = E m$$

where $E$ is the ebullioscopic constant of the solvent.

4. The osmotic pressure, $p$, kPa:

$$p = c R T$$

where $c$ is the molar concentration; $R$ is the molar gas constant [8.31 J/(mol·K)]; and $T$ is the temperature, K.

The values of the cryoscopic and ebullioscopic constants for selected solvents are given below:

<table>
<thead>
<tr>
<th></th>
<th>$K$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.86</td>
<td>0.52</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.1</td>
<td>2.57</td>
</tr>
<tr>
<td>Ethyl alcohol</td>
<td>—</td>
<td>1.16</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>1.73</td>
<td>2.02</td>
</tr>
</tbody>
</table>

Let us consider examples of solving problems with the use of the above equations.

**Example 1.** At 25 °C, the saturated vapour pressure of water is 3.166 kPa (23.75 mmHg). Find the saturated vapour pressure at the same temperature over a 5% aqueous solution of carbamide (urea) CO(NH$_2$)$_2$.

**Solution.** For calculations using the formula $p_1 = x_1 p_0$, we must find the mole fraction of the solvent $x_1$. One hundred grams of the solution contain 5 g of carbamide (with a molar mass of 60.05 g/mol) and 95 g of water (with a molar mass of 18.02 g/mol). The number of moles of carbamide and water are, respectively,

$$n_2 = \frac{5}{60.05} = 0.083 \quad \text{and} \quad n_1 = \frac{95}{18.02} = 5.272$$
We find the mole fraction of the water:

\[ x_1 = \frac{n_1}{n_1 + n_2} = \frac{5.272}{5.272 + 0.083} = \frac{5.272}{5.355} = 0.985 \]

Consequently,

\[ p_1 = 0.985 \times 3.166 = 3.119 \text{ kPa (or 23.31 mmHg)} \]

Example 2. Calculate the temperature at which a solution containing 54 g of glucose \( \text{C}_6\text{H}_{12}\text{O}_6 \) in 250 g of water will freeze.

Solution. When calculated for 1000 g of \( \text{H}_2\text{O} \), the glucose content in the solution is 216 g. Since the molar mass of the glucose is 180 g/mol, the molality of the solution is \( m = 216/180 = 1.20 \text{ mol per 1000 g of } \text{H}_2\text{O} \).

By the formula \( \Delta T_f = K \cdot m \), we find \( \Delta T_f = 1.86 \times 1.20 = 2.23 \text{ K} \).

Consequently, the solution will freeze at \( 0 - 2.23 = -2.23^\circ \text{C} \).

Example 3. A solution containing 8 g of a substance in 100 g of diethyl ether boils at 36.86 °C, whereas the pure ether boils at 35.60 °C. Determine the molecular mass of the solute.

Solution. From the data of the example, we find \( \Delta T_b = 36.86 - 35.60 = 1.26 \text{ K} \). From the equation \( \Delta T_b = E \cdot m \), we find \( m = \Delta T_b / E \), whence \( m = 1.26/2.02 = 0.624 \text{ mol per 1000 g of ether.} \)

It follows from the initial data that 1000 g of the solvent contain 80 g of the solute. Since this mass corresponds to 0.624 mol, we find the molar mass of the substance from the expression:

\[ M = \frac{80}{0.624} = 128.2 \text{ g/mol} \]

The molecular mass of the solute is 128.2 amu.

Example 4. At 20 °C, the osmotic pressure of a solution 100 ml of which contain 6.33 g of the colouring substance of blood—hematin, is 243.4 kPa. Determine the molecular formula if the elementary composition of hematin is known (in per cent by mass): C—64.6, H—5.2, N—8.8, O—12.6, and Fe—8.8.

Solution. From the equation \( p = cRT \), we find the molarity of the solution:

\[ c = \frac{p}{RT} = \frac{243.4}{8.31 \times 293} = 0.1 \text{ mol/l} \]

Now, we calculate the molecular mass of hematin. It can be seen from the initial data of the example that one litre of the solution contains 63.3 g of hematin, which forms 0.1 mol. Thus, the molar mass of hematin is 63.3/0.1 = 633 g/mol, and its molecular mass is 633 amu.

We find the simplest formula of hematin. Denoting the numbers of atoms of C, H, N, O and Fe in a hematin molecule by \( x \), \( y \), \( z \), \( m \), and \( n \), respectively, we can write:

\[ x : y : z : m : n = \frac{64.6}{12} : \frac{5.2}{4} : \frac{8.8}{14} : \frac{12.6}{16} : \frac{8.8}{56} = \]

\[ = 5.38 : 5.2 : 0.629 : 0.788 : 0.157 = \]

\[ = 34.3 : 33.1 : 4.0 : 5.0 : 1 \approx 34 : 33 : 4 : 5 : 1 \]
Therefore, the simplest formula of hematin is $\text{C}_{84}\text{H}_{33}\text{N}_4\text{O}_5\text{Fe}$. A molecular mass of 633 corresponds to this formula (because $34 \times 12 + 33 \times 1 + 4 \times 14 + 5 \times 16 + 56 \times 1 = 633$), which coincides with the value found above. Hence, the molecular formula is the same as the simplest one, i.e. $\text{C}_{84}\text{H}_{33}\text{N}_4\text{O}_5\text{Fe}$.

PROBLEMS

458. What is the osmotic pressure of a 0.5 $M$ solution of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ at 25 °C?

459. Calculate the osmotic pressure of a solution containing 16 g of saccharose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 350 g of $\text{H}_2\text{O}$ at 293 K. Assume the density of the solution to be unity.

460. How many grams of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ must be contained in 0.5 litre of a solution for its osmotic pressure (at the same temperature) to be the same as that of the solution one litre of which contains 9.2 g of glycerin $\text{C}_3\text{H}_5(\text{OH})_3$?

461. At 25 °C, the osmotic pressure of an aqueous solution is 1.24 MPa. Calculate the osmotic pressure of the solution at 0 °C.

462. At 25 °C, the osmotic pressure of a solution containing 2.80 g of a high-molecular compound in 200 ml of the solution is 0.70 kPa. Find the molecular mass of the solute.

463. One litre of a solution of a non-electrolyte whose osmotic pressure is 243.4 kPa is mixed at 20 °C with three litres of a solution of a non-electrolyte whose osmotic pressure is 486.8 kPa. Find the osmotic pressure of the new solution.

464. A solution, 100 g of which contain 2.30 g of a substance, has an osmotic pressure of 618.5 kPa at 298 K. Find the molecular mass of the substance.

465. How many moles of a non-electrolyte must one litre of a solution contain for its osmotic pressure at 25 °C to be 2.47 kPa?

466. One millilitre of a solution contains $10^{18}$ molecules of a dissolved non-electrolyte. Calculate the osmotic pressure of the solution at 298 K.

467. Find the vapour pressure over a solution containing 13.68 g of saccharose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 90 g of $\text{H}_2\text{O}$ at 65 °C if the saturated vapour pressure over water at the same temperature is 25.0 kPa (187.5 mmHg).
468. What is the saturated vapour pressure over a 10% solution of carbamide \( \text{CO(NH}_2\text{)}_2 \) at 100 °C?

469. At 315 K, the saturated vapour pressure over water is 8.2 kPa (61.5 mmHg). How will the vapour pressure lower at this temperature if 36 g of glucose \( \text{C}_6\text{H}_{12}\text{O}_6 \) are dissolved in 540 g of water?

470. At 293 K, the saturated vapour pressure over water is 2.34 kPa (17.53 mmHg). How many grams of glycerin \( \text{C}_3\text{H}_5(\text{OH})_3 \) have to be dissolved in 180 g of water to lower the vapour pressure by 133.3 Pa (1 mmHg)?

471. By how many kelvins will the boiling point of water grow if 9 g of glucose \( \text{C}_6\text{H}_{12}\text{O}_6 \) are dissolved in 100 g of water?

472. At approximately what temperature will a 50% solution of saccharose \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \) boil?

473. At approximately what temperature will a 40% solution of ethyl alcohol \( \text{C}_2\text{H}_5\text{OH} \) freeze?

474. How many grams of saccharose \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \) have to be dissolved in 100 g of water to (a) lower the freezing point by one kelvin? (b) raise the boiling point by one kelvin?

475. In what proportion must the masses of water and ethyl alcohol be for a solution freezing at -20 °C to be obtained when they are mixed?

476. A motor vehicle radiator was filled with 9 litres of water to which 2 litres of methyl alcohol (\( \rho = 0.8 \text{ g/ml} \)) were added. After this, what is the lowest temperature at which the vehicle can be parked outdoors without a danger that the water in the radiator will freeze?

477. When 5.0 g of a substance are dissolved in 200 g of water, a non-conducting solution is obtained that freezes at -1.45 °C. Find the molecular mass of the solute.

478. When 13.0 g of a non-electrolyte were dissolved in 400 g of diethyl ether \( (\text{C}_2\text{H}_5)_2\text{O} \), the boiling point rose by 0.453 K. Find the molecular mass of the solute.

479. When 3.24 g of sulphur were dissolved in 40 g of benzene, the boiling point of the latter rose by 0.81 K. How many atoms does a molecule of sulphur in the solution consist of?

480. 2.09 g of a substance whose elementary composition in per cent by mass is C—50.69, H—4.23, and O—45.08 were dissolved in 60 g of benzene. The solution freezes at
4.25 °C. Establish the molecular formula of the substance. Pure benzene freezes at 5.5 °C.

481. A water-alcohol solution containing 15% of alcohol \( (\rho = 0.97 \text{ g/ml}) \) freezes at \(-10.26 \text{ °C} \). Find the molecular mass of the alcohol and the osmotic pressure of the solution at 293 K.

482. 100 g of \( \text{H}_2\text{O} \) contain 4.57 g of saccharose \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \). Find (a) the osmotic pressure at 293 K, (b) the freezing point of the solution, (c) the boiling point of the solution, and (d) the saturated vapour pressure over the solution at 293 K. The saturated vapour pressure over water at 293 K is 2.337 kPa (17.53 mmHg). Assume the density of the solution to equal that of water.

**REVIEW QUESTIONS**

483. What is the osmotic pressure of a solution containing one mole of glycerin in 22.4 litres of \( \text{H}_2\text{O} \) at 0 °C? (a) \( 1.01 \times 10^2 \) kPa; (b) \( 1.01 \times 10^6 \) kPa; (c) 760 mmHg.

484. What is the osmotic pressure of a solution containing simultaneously 0.25 mol of alcohol and 0.25 mol of glucose in two litres of water at 273 K? (a) 760 mmHg; (b) 380 mmHg; (c) 4256 mmHg.

485. What will be the relationship between the osmotic pressures at 273 K if 5 g of alcohol \( \text{C}_2\text{H}_5\text{OH} \) \( (p_1) \), 5 g of glucose \( \text{C}_6\text{H}_{12}\text{O}_6 \) \( (p_2) \), and 5 g of saccharose \( \text{C}_{12}\text{H}_{22}\text{O}_{11} \) \( (p_3) \) are dissolved in 250 ml of water? (a) \( p_3 > p_2 > p_1 \); (b) \( p_1 > p_2 > p_3 \).

486. What will be the ratio of the masses of formalin \( \text{HCHO} \) and glucose \( \text{C}_6\text{H}_{12}\text{O}_6 \) contained in equal volumes of solutions having the same osmotic pressure at the given temperature? (a) 1 : 1; (b) \( M(\text{HCHO}) : M(\text{C}_6\text{H}_{12}\text{O}_6) \).

487. How many moles of a non-electrolyte must one litre of a solution contain for its osmotic pressure at 0 °C to be 2.27 kPa (17 mmHg)? (a) 0.001 mol; (b) 0.01 mol; (c) 0.1 mol.

488. What is the molarity of a non-electrolyte solution if its osmotic pressure at 0 °C is 2.27 kPa? (a) 0.1 mol/l; (b) 0.01 mol/l; (c) 0.001 mol/l.

489. At what temperature does an aqueous solution containing \( 3 \times 10^{23} \) molecules of a non-electrolyte in 250 g of \( \text{H}_2\text{O} \) freeze? (a) 273 K; (b) 269.28 K; (c) 271.14 K.
490. What is the relationship between the freezing points of 0.1% solutions of glucose ($t_1; M = 180$ amu) and albumin ($t_2; M = 68000$ amu)? (a) $t_1 > t_2$; (b) $t_1 = t_2$; (c) $t_1 < t_2$.

491. What is the relationship between the boiling points of 10% solutions of CH$_3$OH ($t_1$) and C$_2$H$_6$OH ($t_2$)? (a) $t_1 > t_2$; (b) $t_1 < t_2$; (c) $t_1 = t_2$.

492. Dissolved in 200 g of water are (1) 31 g of carbamide CO(NH$_2$)$_2$, and (2) 90 g of glucose C$_6$H$_{12}$O$_6$. Will the boiling points of these solutions be the same? (a) Yes; (b) no.

493. 250 g of an organic solvent contain $x$ g of a dissolved non-electrolyte with the molecular mass $M$. The cryoscopic constant of the solvent is $K$. Which expression for $\Delta t_{fr}$ is correct? (a) $Kx/M$; (b) $4Kx/M$; (c) $Kx/4M$.

494. An aqueous solution of a non-electrolyte boils at 373.52 K. What is the molal concentration of this solution? (a) $m = 1$; (b) $m = 0.1$; (c) $m = 0.01$ mol per 1000 g of H$_2$O.
1. Weak Electrolytes. Dissociation Constant and Degree of Dissociation

When electrolytes are dissolved in water or other solvents consisting of polar molecules, they experience electrolytic dissociation, i.e. break up to a greater or smaller extent into positively and negatively charged ions—cations and anions. Electrolytes dissociating only partly in solutions are known as weak electrolytes. Equilibrium sets in in such solutions between the undissociated molecules and their dissociation products—ions. The following equilibrium sets in, for example, in an aqueous solution of acetic acid:

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-
\]

whose constant (the dissociation or ionization constant) is related to the concentrations of the relevant particles by the equation:

\[
K = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}
\]

By the degree of dissociation \( \alpha \) of an electrolyte is meant the fraction of its molecules that have experienced dissociation, i.e. the ratio of the number of its molecules that have broken up into ions in the given solution to the total number of its molecules in the solution.

For the electrolyte MX dissociating into the ions M\(^+\) and X\(^-\), the dissociation constant and the degree of dissociation are related by the equation (Ostwald's dilution law):

\[
K = \frac{\alpha^2}{1-\alpha} c
\]

where \( c \) is the molar concentration of the electrolyte, mol/l.
If the degree of dissociation is considerably smaller than
unity, it may be assumed in approximate calculations that
$1 - \alpha \approx 1$. The equation of the dilution law is thus simpli-
fied:

$$K = \alpha^2 c$$

whence

$$\alpha = \sqrt{\frac{K}{c}}$$

The latter equation shows that dilution of a solution
(i.e. diminishing of the concentration $c$ of an electrolyte)
is attended by an increase in the degree of dissociation of
the electrolyte.

If the degree of dissociation of the electrolyte MX in its
solution is $\alpha$, the concentrations of the $M^+$ and $X^-$ ions in
the solution are the same and are:

$$[M^+] = [X^-] = \alpha c$$

Introducing into this equation the value of $\alpha$ from the
preceding one, we obtain:

$$[M^+] = [X^-] = c \sqrt{\frac{K}{c}} = \sqrt{Kc}$$

For calculations connected with the dissociation of acids,
it is often convenient to use not the constant $K$, but the
dissociation constant index $pK$, which is determined by the
equation

$$pK = - \log K$$

It is evident that when $K$ grows, i.e. when an acid is
stronger, the value of $pK$ diminishes; hence, the weaker an
acid, the greater is the value of $pK$ for it.

Example 1. The degree of dissociation of acetic acid in a 0.1 $M$
solution is $1.32 \times 10^{-2}$. Find the dissociation constant of the acid and
the value of $pK$.

Solution. We insert the data of the example into the dilution law
equation:

$$K = \frac{\alpha^2}{1 - \alpha} \varepsilon = \frac{(1.32 \times 10^{-2})^2}{1 - 0.0132} \times 0.1 = 1.77 \times 10^{-5}$$

whence $pK = - \log (1.77 \times 10^{-5}) = 5 - \log 1.77 = 5 - 0.25 = 4.75$. 
Calculations using the approximate formula \( K = \alpha^2c \) give a close value of \( K \):

\[
K = (1.32 \times 10^{-2})^2 \times 0.1 = 1.74 \times 10^{-5}
\]

whence \( pk = 4.76 \).

Example 2. The dissociation constant of hydrogen cyanide (hydrocyanic acid) is \( 7.9 \times 10^{-10} \). Find the degree of dissociation of HCN in a 0.001 \( M \) solution.

**Solution.** Since the dissociation constant of HCN is very small, we may use the approximate formula for calculations:

\[
\alpha = \sqrt{\frac{K}{c}} = \sqrt{\frac{7.9 \times 10^{-10}}{10^{-3}}} = 8.9 \times 10^{-4}
\]

Example 3. Calculate the concentration of hydrogen ions in a 0.1 \( M \) solution of hypochlorous acid HOCl (\( K = 5 \times 10^{-8} \)).

**Solution.** We find the degree of dissociation of HOCl:

\[
\alpha = \sqrt{\frac{K}{c}} = \sqrt{\frac{5 \times 10^{-8}}{0.1}} = 7 \times 10^{-4}
\]

whence \([H^+] = \alpha c = 7 \times 10^{-4} \times 0.1 = 7 \times 10^{-5}\) mol/l.

The example can be solved in a different way, using the equation \([H^+] = \sqrt{\frac{K}{c}}\):

\[
[H^+] = \sqrt{5 \times 10^{-8} \times 0.4} = 7 \times 10^{-5}\) mol/l

If an ion common to one of the ions formed in the dissociation of a weak electrolyte is introduced into its solution, equilibrium of dissociation is violated and shifts in the direction of formation of the undisassociated molecules so that the degree of dissociation of the electrolyte diminishes. For instance, the addition of an acetate (for example, sodium acetate) to an acetic acid solution leads to an increase in the concentration of the CH\(_3\)COO\(^-\) ions, and, in accordance with Le Chatelier’s principle, the equilibrium of the dissociation

\[
CH_3COOH \rightarrow H^+ + CH_3COO^-
\]

shifts to the left.

Example 4. How will the concentration of the hydrogen ions in a 0.2 \( M \) solution of formic acid HCOOH (\( K = 1.8 \times 10^{-4} \)) diminish if 0.1 mol of the salt HCOONa is added to one litre of this solution? Assume the salt to be completely dissociated.

**Solution.** We find the initial concentration of the \( H^+ \) ions in the solution (before the addition of the salt) by the equation:

\[
[H^+] = \sqrt{\frac{K \cdot c}{c}} = \sqrt{1.8 \times 10^{-4} \times 0.2} = 6 \times 10^{-3}\) mol/l
Solutions of Electrolytes

Let the concentration of the hydrogen ions in the solution after the addition of the salt be \( x \). Hence, the concentration of undissociated acid molecules will be \( 0.2 - x \). The concentration of the \( \text{HCOO}^- \) ions will be composed of two quantities: of the concentration produced by dissociation of the acid molecules, and of the concentration due to the presence of the salt in the solution. The first of these quantities is \( x \), and the second is 0.1 mol/l. Consequently, the total concentration of the \( \text{HCOO}^- \) ions is \( 0.1 + x \). Using the values of the concentrations in the expression for the dissociation constant of formic acid, we get:

\[
K = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x(0.1 + x)}{0.2 - x} = 1.8 \times 10^{-4}
\]

Since in the presence of the common \( \text{HCOO}^- \) ions the dissociation of the formic acid is suppressed, its degree of dissociation will be small, and the quantity \( x \) in comparison with 0.1 and 0.2 may be ignored. Hence, the last equation is simplified:

\[
K = \frac{0.1x}{0.2} = 1.8 \times 10^{-4}
\]

whence \( x = 3.6 \times 10^{-4} \) mol/l. Comparing the initial concentration of the hydrogen ions with that found, we see that the addition of the salt \( \text{HCOONa} \) caused the hydrogen ion concentration to diminish to \( 3.6 \times 10^{-5} \), i.e. to \( 1/16.6 \) of its original value.

Stepwise equilibria corresponding to the consecutive dissociation steps set in in solutions of polybasic acids and of bases containing several hydroxyl groups. For instance, orthophosphoric acid dissociates in three steps:

\[
\begin{align*}
\text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- \quad (K_1 = 7.5 \times 10^{-3}) \\
\text{H}_2\text{PO}_4^- & \rightleftharpoons \text{H}^+ + \text{HPO}_3^- \quad (K_2 = 6.3 \times 10^{-8}) \\
\text{HPO}_3^- & \rightleftharpoons \text{H}^+ + \text{PO}_4^- \quad (K_3 = 1.3 \times 10^{-12})
\end{align*}
\]

with a definite value of the dissociation constant corresponding to each step. Since \( K_1 \gg K_2 \gg K_3 \), dissociation in the first step is the highest, and it sharply diminishes in each following step, as a rule.

Example 5. The dissociation constants for the two steps of hydrogen sulphide dissociation \( K_1 \) and \( K_2 \) are \( 6 \times 10^{-8} \) and \( 1 \times 10^{-14} \), respectively. Calculate the concentrations of the \( \text{H}^+ \), \( \text{HS}^- \), and \( \text{S}^2- \) ions in a 0.1 M solution of \( \text{H}_2\text{S} \).

Solution. Since the dissociation of \( \text{H}_2\text{S} \) proceeds chiefly in the first step, we may disregard the concentration of the \( \text{H}^+ \) ions formed in second-step dissociation and assume that \( [\text{H}^+] \approx [\text{HS}^-] \). Hence,

\[
[\text{H}^+] \approx \sqrt{K_1c} = \sqrt{6 \times 10^{-8} \times 0.1} = 7.7 \times 10^{-5} \text{ mol/l}
\]
We find the value of \([S^2^-]\) from the expression for the second dissociation constant:

\[ K_2 = \frac{[H^+][S^2^-]}{[HS^-]} \]

Since \([H^+] \approx [HS^-]\), then \(K_2 \approx [S^2^-]\), i.e. \([S^2^-] = 1 \times 10^{-14} \text{ mol/l}\).

Dissociation (ionization) of an electrolyte leads to the fact that the total number of solute particles (molecules and ions) in its solution grows in comparison with a solution of a non-electrolyte having the same molar concentration. Consequently, the properties depending on the total number of solute particles in a solution (the colligative properties) such as the osmotic pressure, depression of the vapour pressure, elevation of the boiling point, and depression of the freezing point manifest themselves in electrolyte solutions to a greater extent than in ones of non-electrolytes having an equal concentration. If dissociation results in the total number of particles in an electrolyte solution growing \(i\) times in comparison with the number of molecules of the electrolyte, this must be taken into consideration when calculating the osmotic pressure and other colligative properties. The formula for calculating the depression of the solvent vapour pressure \(\Delta p\) acquires the following form in this case:

\[ \Delta p = p_0 \frac{in_2}{n_1 + in_2} \]

where \(p_0\) is the saturated vapour pressure over the pure solvent; \(n_2\) is the number of moles of the solute; \(n_1\) is the number of moles of the solvent; and \(i\) is the isotonic coefficient or van't Hoff's coefficient.

Similarly, the depression of the freezing point \(\Delta t_f\) and the elevation of the boiling point \(\Delta t_b\) of an electrolyte solution are found by the formulas:

\[ \Delta t_f = iKm \]
\[ \Delta t_b = iEm \]

where \(m\) is the molal concentration of the electrolyte, and \(K\) and \(E\) are the cryoscopic constant and the ebullioscopic constant of the solvent, respectively.
Finally, the osmotic pressure \( p, \) kPa of an electrolyte solution is calculated by the formula
\[
p = \text{i}cRT
\]
where \( c \) is the molar concentration of the electrolyte, mol/l; \( R \) is the molar gas constant (8.31 J·mol\(^{-1}\)·K\(^{-1}\)); and \( T \) is the absolute temperature, K.

It is not difficult to see that the isotonic coefficient \( i \) can be calculated as the ratio of \( \Delta p, \Delta t_{fr}, \Delta t_{b}, \) and \( p \) found experimentally to the same quantities calculated without account taken of dissociation of an electrolyte (\( \Delta p_{\text{calc}}, \Delta t_{fr, \text{calc}}, \Delta t_{b, \text{calc}}, p_{\text{calc}} \)):
\[
i = \frac{\Delta p}{\Delta p_{\text{calc}}} = \frac{\Delta t_{fr}}{\Delta t_{fr, \text{calc}}} = \frac{\Delta t_{b}}{\Delta t_{b, \text{calc}}} = \frac{p}{p_{\text{calc}}}
\]

The isotonic coefficient \( i \) is related to the degree of dissociation of an electrolyte \( \alpha \) by the expression:
\[
i = 1 + \alpha (k - 1) \quad \text{or} \quad \alpha = \frac{i - 1}{k - 1}
\]
where \( k \) is the number of ions into which an electrolyte molecule breaks up in dissociation (for KCl, \( k = 2 \); for BaCl\(_2\) and Na\(_2\)SO\(_4\), \( k = 3 \); etc.).

Hence, having found the value of \( i \) from experimental values of \( \Delta p, \Delta t_{fr}, \) etc., we can calculate the degree of dissociation of an electrolyte in a given solution. It must be borne in mind that for strong electrolytes the value of \( \alpha \) found in this way expresses only the "apparent" degree of dissociation because in solutions strong electrolytes dissociate completely. The observed deviation of the apparent degree of dissociation from unity is associated with interionic interactions in a solution (see the following section).

**Example 6.** A solution containing 0.85 g of zinc chloride in 125 g of water freezes at \(-0.23^\circ\)C. Determine the apparent degree of dissociation of the ZnCl\(_2\).

**Solution.** First of all, we find the molal concentration \((m)\) of the salt in the solution. Since the molar mass of ZnCl\(_2\) is 136.3 g/mol, we have:
\[
m = \frac{0.85 \times 1000}{136.3 \times 125} = 0.050 \quad \text{mol per 1000 g of H}_2\text{O}
\]

We now find the depression of the freezing point without account taken of the electrolyte dissociation (the cryoscopic constant of water
Comparing the value thus found with the experimentally established depression of the freezing point, we calculate the isotonic coefficient $i$:

$$i = \frac{\Delta t_{fr, \text{calc}}}{\Delta t_{fr, \text{calc}}} = \frac{0.23}{0.093} = 2.47$$

We now find the apparent degree of dissociation of the salt:

$$\alpha = \frac{i-1}{k-1} = \frac{2.47-1}{3-1} = 0.735$$

**Example 7.** Calculate the saturated vapour pressure of water over a solution at a temperature of 100 °C containing 5 g of sodium hydroxide in 180 g of water. The apparent degree of dissociation of NaOH is 0.8.

**Solution.** We find the isotonic coefficient $i$:

$$i = 1 + \alpha (k - 1) = 1 + 0.8 (2 - 1) = 1.8$$

We calculate the depression of the vapour pressure over the solution by the equation

$$\Delta p = p_0 \frac{i n_2}{n_1 + i n_2}$$

The saturated vapour pressure over water at 100 °C is 101.31 kPa (760 mmHg). The molar mass of sodium hydroxide is 40 g/mol, and that of water is 18 g/mol. Hence, $n_1 = 180 : 18 = 10$ mol, and $n_2 = 5 : 40 = 0.125$ mol. Therefore:

$$\Delta p = 101.31 \times \frac{1.8 \times 0.125}{10 + 1.8 \times 0.125} = 101.31 \times \frac{0.225}{10.2} = 2.23 \text{ kPa (or 16.7 mmHg)}$$

We find the required saturated vapour pressure over the solution:

$$p = p_0 - \Delta p = 101.31 - 2.23 = 99.08 \text{ kPa (or 743.1 mmHg)}$$

**Example 8.** Find the isotonic coefficient for a 0.2 $M$ solution of an electrolyte if one litre of the solution is known to contain $2.18 \times 10^{28}$ particles (molecules and ions) of the solute.

**Solution.** The number of electrolyte molecules taken to prepare one litre of the solution is $6.02 \times 10^{23} \times 0.2 = 1.20 \times 10^{23}$. The number of solute particles formed in the solution was $2.18 \times 10^{28}$. The isotonic coefficient shows how many times the latter number is greater than the number of molecules taken, i.e.:

$$i = \frac{2.18 \times 10^{28}}{1.20 \times 10^{23}} = 1.82$$
PROBLEMS *

495. A solution containing 0.5 mol of NaCl, 0.16 mol of KCl, and 0.24 mol of K₂SO₄ in one litre must be prepared. How can this be done if we have at our disposal only NaCl, KCl, and Na₂SO₄?

496. The dissociation constant of butyric acid C₃H₇COOH is \(1.5 \times 10^{-5}\). Calculate the degree of its dissociation in a 0.005 \(M\) solution.

497. Find the degree of dissociation of hypochlorous acid HOCl in a 0.2 \(N\) solution.

498. The degree of dissociation of formic acid HCOOH in a 0.2 \(N\) solution is 0.03. Determine the dissociation constant of the acid and the value of \(pK\).

499. The degree of dissociation of carbonic acid H₂CO₃ in the first step in a 0.1 \(N\) solution is \(2.11 \times 10^{-3}\). Calculate \(K_1\).

500. At what concentration of the solution will the degree of dissociation of nitrous acid HNO₂ be 0.2?

501. The degree of dissociation of acetic acid in a 0.1 \(N\) solution is \(1.32 \times 10^{-2}\). At what concentration of nitrous acid HNO₂ will its degree of dissociation be the same?

502. How much water must be added to 300 ml of a 0.2 \(M\) solution of acetic acid for the degree of dissociation of the acid to double?

503. What is the hydrogen ion concentration \([H^+]\) in an aqueous solution of formic acid if \(\alpha = 0.03\)?

504. Calculate the value of \([H^+]\) in a 0.02 \(M\) solution of sulphurous acid. Ignore the second-step dissociation of the acid.

505. Calculate the values of \([H^+]\), \([HSe^-]\) and \([Se^{2-}]\) in a 0.05 \(M\) solution of H₂Se.

506. How will the hydrogen ion concentration lower if 0.05 mole of sodium acetate is added to one litre of a 0.005 \(M\) acetic acid solution?

507. Calculate the concentration of CH₃COO⁻ ions in a solution, one litre of which contains one mole of CH₃COOH and 0.1 mole of HCl, assuming the dissociation of the latter to be complete.

* In solving the problems of this section, use Table 6 of the Appendix giving the dissociation constants of electrolytes when necessary.
508. Proceeding from the values of the consecutive dissociation constants of orthophosphoric acid, determine the sign of the change in the Gibbs energy $\Delta G^\circ$ for each of the three dissociation steps. For which of them does $\Delta G^\circ$ have the greatest magnitude?

509. A solution containing 2.1 g of KOH in 250 g of water freezes at $-0.519 \, ^\circ C$. Find the isotonic coefficient for this solution.

510. At $0 \, ^\circ C$, the osmotic pressure of a 0.1 $N$ solution of potassium carbonate is 272.6 kPa. Determine the apparent degree of dissociation of the $K_2CO_3$ in the solution.

511. A solution containing 0.53 g of sodium carbonate in 200 g of water freezes at $-0.13 \, ^\circ C$. Calculate the apparent degree of dissociation of the salt.

512. In one case 0.5 mol of sugar and in another 0.2 mol of CaCl$_2$ are dissolved in equal amounts of water. The freezing points of both solutions are the same. Find the apparent degree of dissociation of the CaCl$_2$.

513. At 100 $^\circ C$, the vapour pressure of a solution containing 0.05 mol of sodium sulphate in 450 g of water is 100.8 kPa (756.2 mmHg). Determine the apparent degree of dissociation of the Na$_2$SO$_4$.

514. One litre of a 0.01 $M$ solution of acetic acid contains $6.26 \times 10^{21}$ of its molecules and ions. Determine the degree of dissociation of the acid.

515. The apparent degree of dissociation of potassium chloride in a 0.1 $N$ solution is 0.80. What is the osmotic pressure of this solution at 17 $^\circ C$?

**REVIEW QUESTIONS**

516. What is the relationship between the values of the osmotic pressure in 0.1 $M$ solutions of KNO$_3$ ($p_1$) and CH$_3$COOH ($p_2$)? (a) $p_1 > p_2$; (b) $p_1 = p_2$; (c) $p_1 < p_2$.

517. The freezing points of monomolal solutions of hydrogen cyanide HCN and glucose C$_6$H$_{12}$O$_6$ are close. What conclusion can be reached about the degree of dissociation of HCN? (a) The degree of dissociation of HCN is close to unity; (b) the degree of dissociation is close to zero.

518. Indicate the correct relationship between the boiling points of very dilute solutions of AlCl$_3$ ($t_1$) and CaCl$_2$
(t₂) having the same molal concentrations. (a) t₁ = t₂; (b) t₁ < t₂; (c) t₁ > t₂.

519. What arrangement of 0.01 M solutions of the four substances indicated corresponds to diminishing of the osmotic pressure?

(a) CH₄COOH-NaCl-C₆H₁₂O₆-CaCl₂
(b) C₆H₁₂O₆-CH₃COOH-NaCl-CaCl₂
(c) CaCl₂-NaCl-CH₃COOH-C₆H₁₂O₆
(d) CaCl₂-CH₃COOH-C₆H₁₂O₆-NaCl

520. Indicate the proper relationship between the freezing points of solutions of ammonium cyanide NH₄CN (t₁) and acetic aldehyde CH₃CHO (t₂) each of which contains 5 g of the solute in 100 g of water. (a) t₁ = t₂; (b) t₁ > t₂; (c) t₁ < t₂.

521. Indicate the correct relationship between the values of the standard change in the Gibbs energy for the processes of dissociation of water (ΔG₁°) and acetic acid (ΔG₂°). (a) ΔG₁° > ΔG₂°; (b) ΔG₁° = ΔG₂°; (c) ΔG₁° < ΔG₂°.

2. Strong Electrolytes. Activity of Ions

Electrolytes that virtually completely dissociate in aqueous solutions are known as strong electrolytes. The latter include most salts, which already in the crystalline state are built up of ions, the hydroxides of the alkali and alkaline-earth metals, and some acids (HCl, HBr, HI, HClO₄, HNO₃).

The concentration of the ions is quite great in solutions of strong electrolytes so that the forces of interionic interaction manifest themselves appreciably even at a low concentration of an electrolyte. As a result, the ions are not completely free in their motion, and all the properties of the electrolyte depending on the number of ions manifest themselves more weakly than should be expected upon the complete dissociation of the electrolyte into ions not interacting with one another. This is why the state of ions in a solution is described, in addition to their concentration, by their activity, i.e. the conditional (effective) concentration of the ions in accordance with which they act in
chemical processes. The activity of an ion \( a \) (mol/l) is related to its molar concentration in a solution \( c \) by the equation
\[
a = fc
\]
where \( f \) is the activity coefficient of the ion (a dimensionless quantity).

The activity coefficients of ions depend on the composition and concentration of the solution, on the charge and nature of the ion, and on other conditions. In dilute solutions (\( c \leq 0.5 \text{ mol/l} \)), however, the nature of the ion only slightly affects the value of its activity coefficient. It can be considered approximately that in dilute solutions the activity coefficient of an ion in the given solvent depends only on the charge of the ion and the ionic strength of the solution \( I \), which equals the half-sum of the products of the concentration \( c \) of each ion and the square of its charge \( z \):
\[
I = 0.5 \left( c_1 z_1^2 + c_2 z_2^2 + \ldots + c_n z_n^2 \right) = 0.5 \sum_{i=1}^{n} c_i z_i^2
\]

Table 7 of the Appendix gives values of the activity coefficients of ions in dilute solutions depending on their charge and the ionic strength of the solution. The activity coefficient of an ion in a dilute solution can be calculated approximately by the formula
\[
\log f = -0.5 z^2 \sqrt{I}
\]

Example 1. Calculate the ionic strength and activity of the ions in a solution containing 0.01 mol/l of MgSO\(_4\) and 0.01 mol/l of MgCl\(_2\).

Solution. The ionic strength of the solution is:
\[
I = 0.5 \left[ c(\text{Mg}^{2+}) z_1^2 + c(\text{SO}_4^{2-}) z_2^2 + c(\text{Cl}^-) z_3^2 \right] =
= 0.5 \left( 0.02 \times 4 + 0.01 \times 4 + 0.02 \right) = 0.07
\]

We find the activity coefficient of the Mg\(^{2+}\) ion (and the activity coefficient of the SO\(_4^{2-}\) ion equal to it) by the formula
\[
\log f = -0.5 z^2 \sqrt{I} = -0.5 \times 4 \sqrt{0.07} = -0.53 = 1.47
\]
whence \( f = 0.30 \).

We find the activity coefficient of the chloride ion in a similar way:
\[
\log f = -0.5 \times 1 \times \sqrt{0.07} = -0.13 = 1.87
\]
whence \( f = 0.74 \).

We now find the activity of each ion, using the equation \( a = fc \):
\[
a(\text{Mg}^{2+}) = 0.02 \times 0.30 = 0.006 \text{ mol/l};
\]
\[
a(\text{SO}_4^{2-}) = 0.01 \times 0.30 = 0.003 \text{ mol/l};
\]
\[
a(\text{Cl}^-) = 0.02 \times 0.74 = 0.0148 \text{ mol/l}
\]
PROBLEMS *

522. Calculate the approximate values of the activity of the K⁺ and SO₄²⁻ ions in a 0.01 M solution of K₂SO₄.

523. Calculate the approximate values of the activity of the Ba²⁺ and Cl⁻ ions in a 0.002 N solution of BaCl₂.

524. Find the approximate value of the activity coefficient of the hydrogen ion in a 0.0005 M solution of H₂SO₄ containing also 0.0005 mol/l of HCl. Assume that the sulphuric acid dissociates completely in both steps.

525. Calculate the ionic strength and the activity of the ions in a solution containing 0.01 mol/l of Ca(NO₃)₂ and 0.01 mol/l of CaCl₂.

526. Calculate the ionic strength and the activity of the ions in a 0.1% solution of BaCl₂. Assume the density of the solution to be unity.

527. Calculate the activity of the hydrogen ion in a 0.005 N solution of HCl containing, in addition, 0.15 mol/l of NaCl.

528. Find the approximate values of the activity coefficients of the ions Cl⁻, SO₄²⁻, PO₄³⁻, and [Fe(CN)₆]⁴⁻ in a solution with an ionic strength of 0.0001.

3. Ion Product of Water. pH

Water is a very weak electrolyte and dissociates to a very small extent, forming hydrogen ions** and hydroxide ions:

\[ \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \]

The following dissociation constant corresponds to this process:

\[ K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \]

Since the degree of dissociation of water is very small, the equilibrium concentration of undissociated water molecules [H₂O] with sufficient accuracy equals the total con-

* When solving the problems of this section, use the values of the activity coefficients of the ions from Table 7 of the Appendix if necessary.

** Hydrogen ions do not exist in a solution in the free state, but form hydroxonium ions H₃O⁺. Hence, it would be proper to write the process of water dissociation as follows: \( 2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \).
centration of water, i.e. \( 1000 : 18 = 55.55 \) mol/l. In dilute aqueous solutions, the concentration of water changes only slightly, and it can be considered to be constant. Hence, the expression for the dissociation constant of water can be transformed as follows:

\[
[H^+][OH^-] = K[H_2O] = K_w
\]

where the constant \( K_w \), equal to the product of the concentrations of the \( H^+ \) and \( OH^- \) ions, is a constant quantity at a given temperature and is known as the ion product of water*.

In pure water, the concentrations of the hydrogen ions and hydroxide ions are the same, and at \( 25^\circC \) they are \( 10^{-7} \) mol/l. It thus follows that at this temperature \( K_w = \approx 10^{-14} \). Since the dissociation of water is an endothermic process, it intensifies with elevation of the temperature, and the value of \( K_w \) increases. Below are given the values of \( K_w \) at different temperatures, and also the values of \( pK_w \)—the negative logarithms of the ion product of water frequently used in calculations:

<table>
<thead>
<tr>
<th>( r, ^\circC )</th>
<th>10</th>
<th>18</th>
<th>25</th>
<th>37</th>
<th>50</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_w \times 10^{14} )</td>
<td>0.29</td>
<td>0.57</td>
<td>1.00</td>
<td>2.47</td>
<td>5.47</td>
<td>9.61</td>
<td>25.1</td>
<td>55.0</td>
</tr>
<tr>
<td>( pK_w )</td>
<td>14.54</td>
<td>14.24</td>
<td>14.00</td>
<td>13.61</td>
<td>13.26</td>
<td>13.02</td>
<td>12.60</td>
<td>12.26</td>
</tr>
</tbody>
</table>

Solutions in which the hydrogen ion and hydroxide ion concentrations are the same are called neutral solutions. For instance, at \( 25^\circC \) in a neutral solution, \([H^+] = [OH^-] = \approx 10^{-7} \) mol/l. In acid solutions, \([H^+] > [OH^-] \), in alkaline solutions \([H^+] < [OH^-] \).

Instead of the concentrations of the \( H^+ \) and \( OH^- \) ions, it is more convenient to use their common logarithms taken with the reverse sign; these quantities are denoted by the symbols \( pH \) and \( pOH \), which are also customarily used as their names:

\[
pH = - \log [H^+]; \quad pOH = - \log [OH^-]
\]

* Strictly speaking, what is constant is the product of the activities of the \( H^+ \) and \( OH^- \) ions: \( K_w = a(H^+) \times a(OH^-) \), and not the product of their concentrations. For dilute solutions, however, for which the activity coefficients are close to unity, this difference may be disregarded in not very accurate calculations.
Taking logarithms of the expression \([H^+] \cdot [OH^-] = K_w\)
and reversing the signs, we get:

\[pH + pOH = pK_w\]

Particularly, at 25°C

\[pH + pOH = 14\]

At this temperature, in neutral solutions, \(pH = 7\), in acid ones, \(pH < 7\), and in alkaline ones, \(pH > 7\).

**Example 1.** The hydrogen ion concentration in a solution is \(4 \times 10^{-3}\) mol/l. Determine the pH of the solution.

*Solution.* Rounding off the value of the logarithm to 0.01, we get:

\[pH = -\log (4 \times 10^{-3}) = -3.60 = -(3 - 0.60) = 2.40\]

**Example 2.** Determine the hydrogen ion concentration in a solution whose pH is 4.60.

*Solution.* According to the data of the example, \(-\log [H^+] = 4.60\). Consequently, \(\log [H^+] = -4.60 = 5.40\).

Hence, using the table of logarithms at the end of the book, we find \([H^+] \approx 2.5 \times 10^{-5}\) mol/l.

**Example 3.** What is the hydroxide ion concentration in a solution whose pH is 10.80?

*Solution.* From the relationship \(pH + pOH = 14\), we find:

\[pOH = 14 - pH = 14 - 10.80 = 3.20\]

Hence, \(-\log [OH^-] = 3.20\) or \(\log [OH^-] = -3.20 = 6.80\).

For this value of the logarithm, we get \([OH^-] = 6.31 \times 10^{-4}\) mol/l.

**Example 4.** Determine the concentrations of \(H_2CO_3\), \(HCO_3^-\), and \(CO_3^{2-}\) in a 0.01 \(M\) solution of carbonic acid if the pH of this solution is 4.18.

*Solution.* We find the hydrogen ion concentration in the solution:

\[-\log [H^+] = 4.18; \log [H^+] = -4.18 = 5.82\]

whence \([H^+] = 6.61 \times 10^{-5}\) mol/l.

Now, using the data of Table 6 of the Appendix, we shall write the expression for the first-step dissociation constant of carbonic acid:

\[K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.45 \times 10^{-7}\]

Introducing the values of \([H^+]\) and \([H_2CO_3]\), we find

\([HCO_3^-] = \frac{4.45 \times 10^{-7} \times 10^{-5}}{6.61 \times 10^{-5}} = 6.73 \times 10^{-6}\) mol/l
Similarly, we write the expression for the second-step dissociation constant of $\text{H}_2\text{CO}_3$:

$$K_2 = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.69 \times 10^{-11}$$

and find the value of $[\text{CO}_3^{2-}]$:

$$[\text{CO}_3^{2-}] = \frac{4.69 \times 10^{-11} \times 6.73 \times 10^{-5}}{6.61 \times 10^{-8}} = 4.8 \times 10^{-11} \text{ mol/l}$$

When more accurate calculations are needed to characterize the state of $\text{H}^+$ ions in a solution, one must calculate the quantity $\text{p}a(\text{H}^+)$ equal to the negative logarithm of the activity of the hydrogen ions in the solution:

$$\text{p}a(\text{H}^+) = -\log a(\text{H}^+) = -\log [f(\text{H}^+)c(\text{H}^+)]$$

instead of the pH.

Example 5. Determine the activity of the hydrogen ions and the value of $\text{p}a(\text{H}^+)$ for a $2.5 \times 10^{-3}$ mol/l solution of $\text{HCl}$ containing also $2.5 \times 10^{-3}$ mol/l of KCl.

Solution. For electrolytes consisting of singly charged ions, the value of the ionic strength is numerically equal to the total concentration of the solution; in the given case, $I = 2.5 \times 10^{-3} + 2.5 \times 10^{-3} = 5 \times 10^{-3}$. At this ionic strength, the activity coefficient of a singly charged ion is 0.95 (see Table 7 of the Appendix). Consequently,

$$a(\text{H}^+) = 0.95 \times 2.5 \times 10^{-3} = 2.38 \times 10^{-3}$$

We now find the value of $\text{p}a(\text{H}^+)$:

$$\text{p}a(\text{H}^+) = -\log a(\text{H}^+) = -\log (2.38 \times 10^{-3}) = -3.38 = 2.62$$

**PROBLEMS**

529. Find the hydrogen ion concentration in solutions in which the hydroxide ion concentration (in mol/l) is (a) $10^{-4}$, (b) $3.2 \times 10^{-6}$, and (c) $7.4 \times 10^{-11}$.

530. Find the hydroxide ion concentration in solutions in which the hydrogen ion concentration (in mol/l) is (a) $10^{-3}$, (b) $6.5 \times 10^{-8}$, and (c) $1.4 \times 10^{-12}$.

* In solving the problems of this section, use Tables 6 and 7 of the Appendix when needed. Unless otherwise indicated, it is assumed that the solutions are at 20-25 °C, so that $K_w$ can be taken equal to $10^{-14}$. 
531. Calculate the pH of solutions in which the hydrogen ion concentration (in mol/l) is (a) $2 \times 10^{-7}$, (b) $8.1 \times 10^{-3}$, and (c) $2.7 \times 10^{-10}$.

532. Calculate the pH of solutions in which the hydroxide ion concentration (in mol/l) is (a) $4.6 \times 10^{-4}$, (b) $5 \times 10^{-6}$, and (c) $9.3 \times 10^{-9}$.

533. Calculate the pH of a 0.01 N solution of acetic acid in which the degree of dissociation of the acid is 0.042.

534. Determine the pH of a solution, one litre of which contains 0.1 g of NaOH. Assume the dissociation of the alkali to be complete.

535. How many times is the hydrogen ion concentration in the blood (pH = 7.36) greater than in the spinal fluid (pH = 7.53)?

536. Determine [$H^+$] and [$OH^-$] for a solution whose pH is 6.2.

537. Calculate the pH of the following solutions of weak electrolytes: (a) 0.02 M NH$_4$OH, (b) 0.1 M HCN, (c) 0.05 N HCOOH, and (d) 0.01 M CH$_3$COOH.

538. What is the concentration of an acetic acid solution whose pH is 5.2?

539. Calculate the values of $a(OH^-)$ and $p_a(OH^-)$ for a 0.2 N solution of NaOH, assuming that $f(OH^-) = 0.8$.

540. Using the data of Table 7 of the Appendix, find $p_a(H^+)$ for a 0.005 N solution of HCl containing, in addition, 0.015 mol/l of NaCl.

541. The degree of dissociation of a weak monobasic acid in a 0.2 N solution is 0.03. Calculate the values of [$H^+$], [$OH^-$], and pOH for this solution.

542. Calculate the pH of a solution prepared by mixing 25 ml of a 0.5 M solution of HCl, 10 ml of a 0.5 M solution of NaOH, and 15 ml of water. Assume that the activity coefficients of the ions equal unity.

543. Calculate the pH of a 0.1 N solution of acetic acid containing, in addition, 0.1 mol/l of CH$_3$COONa. Assume that the activity coefficients of the ions equal unity.

544. How will the pH change if we double the amount of water in (a) a 0.2 M solution of HCl, (b) a 0.2 M solution of CH$_3$COOH, (c) a solution containing 0.1 mol/l of CH$_3$COOH and 0.1 mol/l of CH$_3$COONa?
REVIEW QUESTIONS

545. Indicate which of the series of acids listed below correspond to a growth in the pH in solutions having the same molar concentration. (a) HCN, HF, HOCl, HCOOH, CH₂ClCOOH; (b) HNO₃, HNO₂, CH₃COOH, HCN; (c) HCl, CH₂ClCOOH, HF, H₃BO₃.

546. The pH of a 0.01 N solution of a monobasic acid is four. Which statement about the strength of this acid is correct? (a) The acid is weak; (b) the acid is strong.

547. How will the acidity of a 0.2 N solution of HCN change when 0.5 mol/l of potassium cyanide KCN is added to it? (a) It will grow; (b) it will diminish; (c) it will not change.

548. How must the hydrogen ion concentration in a solution be changed for the pH of the solution to grow by unity? (a) It must be increased 10 times; (b) it must be increased by 1 mol/l; (c) it must be diminished to one-tenth of its original value; (d) it must be diminished by 1 mol/l.

549. How many hydrogen ions are contained in 1 ml of a solution whose pH is 13? (a) 10¹³; (b) 6.02 × 10¹³; (c) 6.02 × 10⁷; (d) 6.02 × 10¹⁰.

550. How will the pH of water change if 10⁻² mol of NaOH is added to 10 litres of it? (a) It will grow by 2; (b) it will grow by 3; (c) it will grow by 4; (d) it will diminish by 4.

551. What is the pH of a neutral solution at 50°C? (a) 5.5; (b) 6.6; (c) 7.0.

4. Solubility Product

In a saturated solution of a sparingly soluble strong electrolyte, equilibrium sets in between the precipitate (solid phase) of the electrolyte and its ions in the solution, for example:

\[ \text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-} \]

in precipitate \hspace{1cm} in solution

Since the state of ions in electrolyte solutions is determined by their activities, the equilibrium constant of the latter process is expressed by the following equation:

\[ K = \frac{a(\text{Ba}^{2+})a(\text{SO}_4^{2-})}{a(\text{BaSO}_4)} \]
The denominator of this fraction, i.e. the activity of the solid barium sulphate, is a constant quantity, so that the product $K_a(BaSO_4)$ is also constant at a given temperature. It follows that the product of the activities of the $Ba^{2+}$ and $SO_4^{2-}$ ions is also a constant quantity. The latter is known as the solubility product and is designated by $K_{sp}$:

$$a(Ba^{2+})a(SO_4^{2-})=K_{sp}(BaSO_4)$$

**The product of the activities of the ions of a sparingly soluble electrolyte contained in its saturated solution (the solubility product) is a constant quantity at a given temperature.**

If an electrolyte is very poorly soluble, the ionic strength of its saturated solution is close to zero, and the activity coefficients of its ions differ only slightly from unity. In such cases, the product of the activities of the ions in the expression for $K_{sp}$ can be replaced by the product of their concentrations. For instance, the ionic strength of a saturated solution of $BaSO_4$ is of the order of $10^{-5}$, and the solubility product of this compound can be written as follows:

$$K_{sp}(BaSO_4) = [Ba^{2+}][SO_4^{2-}]$$

In the examples and problems given below, unless specially indicated, the possible difference of the activity coefficients of the ions from unity will be disregarded, and the solubility product will be expressed through the concentrations of the relevant ions.

If a molecule of an electrolyte forms two or more identical ions upon dissociation, the concentrations (activities) of these ions must be raised to the relevant powers in the expression for $K_{sp}$, for example:

$$K_{sp}(CaF_2) = [Ca^{2+}][F^-]^2; \quad K_{sp}[Ca_3(PO_4)_2] = [Ca^{2+}]^3[PO_4^{3-}]^2$$

When the concentration of one of the ions of an electrolyte in its saturated solution is increased (for instance, by introducing another electrolyte containing the same ion), the product of the concentrations of the electrolyte ions becomes greater than $K_{sp}$. Equilibrium between the solid phase and the solution shifts in the direction of precipitate formation. Consequently, the condition for the formation of a precipitate is the greater value of the product of the concentrations of the ions belonging to a sparingly soluble electrolyte in
comparison with its solubility product. As a result of precipitate formation, the concentration of the other ion in the composition of the electrolyte also changes. New equilibrium sets in at which the product of the concentrations of the electrolyte ions again becomes equal to \( K_{sp} \).

Conversely, if the concentration of one of the ions in a saturated electrolyte solution is diminished (for instance, by combining it with another ion), the product of the ion concentrations will be lower than the value of \( K_{sp} \), the solution will become unsaturated, and equilibrium between the liquid phase and the precipitate will shift in the direction of dissolving the precipitate. Hence, the precipitate of a sparingly soluble electrolyte dissolves provided that the product of the concentrations of its ions is lower than the value of \( K_{sp} \).

We can use the values of \( K_{sp} \) to calculate the solubility of sparingly soluble electrolytes in water and in solutions containing other electrolytes. The values of \( K_{sp} \) for a number of electrolytes are given in Table 8 of the Appendix.

Example 1. The solubility of magnesium hydroxide \( \text{Mg(OH)}_2 \) at 18 °C is \( 1.7 \times 10^{-4} \) mol/l. Find the solubility product of \( \text{Mg(OH)}_2 \) at this temperature.

Solution. When each mole of \( \text{Mg(OH)}_2 \) dissolves, one mole of \( \text{Mg}^{2+} \) ions and twice this number of \( \text{OH}^- \) ions pass into the solution. Hence, in a saturated solution of \( \text{Mg(OH)}_2 \)

\[
[Mg^{2+}] = 1.7 \times 10^{-4} \text{ mol/l}; [OH^-] = 3.4 \times 10^{-4} \text{ mol/l}
\]

whence

\[
K_{sp}[\text{Mg(OH)}_2] = [Mg^{2+}][OH^-]^2 = 1.7 \times 10^{-4} (3.4 \times 10^{-4})^2 = 1.96 \times 10^{-11}
\]

Example 2. The solubility product of lead iodide at 20 °C is \( 8 \times 10^{-9} \). Calculate the solubility of the salt (in mol/l and in g/l) at this temperature.

Solution. Let us denote the required solubility by \( s \) (mol/l). Therefore, a saturated solution of \( \text{PbI}_2 \) contains \( s \) mol/l of \( \text{Pb}^{2+} \) ions and \( 2s \) mol/l of \( \text{I}^- \) ions. Hence:

\[
K_{sp}(\text{PbI}_2) = [\text{Pb}^{2+}][\text{I}^-]^2 = s (2s)^2 = 4s^3
\]

whence

\[
s = \sqrt[3]{\frac{K_{sp}(\text{PbI}_2)}{4}} = \sqrt[3]{\frac{8 \times 10^{-9}}{4}} = 1.3 \times 10^{-3} \text{ mol/l}
\]

Since the molar mass of \( \text{PbI}_2 \) is 461 g/mol, the solubility of \( \text{PbI}_2 \) expressed in g/l is \( 1.3 \times 10^{-3} \times 461 = 0.6 \) g/l.
Example 3. How does the solubility of calcium oxalate $\text{CaC}_2\text{O}_4$ in a $0.1\; M$ solution of ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$ decrease in comparison with its solubility in water? Assume that the ionization of the ammonium oxalate is complete.

Solution. We first calculate the solubility of calcium oxalate in water. Denoting the concentration of the salt in a saturated solution by $s$ (mol/l), we can write:

$$K_{sp}(\text{CaC}_2\text{O}_4) = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{-}] = s^2$$

Using the value of $K_{sp}(\text{CaC}_2\text{O}_4)$ from Table 8 of the Appendix, we obtain:

$$s = \sqrt{K_{sp}(\text{CaC}_2\text{O}_4)} = \sqrt{2 \times 10^{-8}} = 4.5 \times 10^{-4}\;\text{mol/l}$$

Now we find the solubility of the same salt in a $0.1\; M$ solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$; we denote it by $s'$. The concentration of the $\text{Ca}^{2+}$ ions in a saturated solution will also be $s'$, while the concentration of the $\text{C}_2\text{O}_4^{-}$ ions will be $(0.1 + s')$. Since $s' \ll 0.1$, the quantity $s'$ may be disregarded in comparison with $0.1$, and we may consider that $[\text{C}_2\text{O}_4^{-}] = 0.1\;\text{mol/l}$. We can therefore write:

$$K_{sp}(\text{CaC}_2\text{O}_4) = 2 \times 10^{-9} = s' \times 0.1$$

and

$$s' = \frac{2 \times 10^{-9}}{0.1} = 2 \times 10^{-8}\;\text{mol/l}$$

Consequently, in the presence of ammonium oxalate, the solubility of $\text{CaC}_2\text{O}_4$ drops to $2 \times 10^{-8}/4.5 \times 10^{-4}$, i.e. to about $1/2200$ of its original value in water.

Example 4. Equal volumes of $0.02\; N$ solutions of calcium chloride and sodium sulphate are mixed. Will a calcium sulphate precipitate form?

Solution. We find the product of the concentrations of the $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ ions and compare it with the solubility product of calcium sulphate. The initial molar concentrations of the $\text{CaCl}_2$ and $\text{Na}_2\text{SO}_4$ solutions are the same and equal $0.01\;\text{mol/l}$. When the initial solutions are mixed, the total volume of the solution will be doubled. The ion concentrations $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ will thus be halved in comparison with the initial ones. Hence,

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = 0.005 = 5 \times 10^{-3}\;\text{mol/l}$$

We find the product of the ion concentrations:

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = (5 \times 10^{-3})^2 = 2.5 \times 10^{-5}$$

In Table 8 of the Appendix, we find $K_{sp}(\text{CaSO}_4) = 1.3 \times 10^{-4}$.

The found value of the product of the ion concentrations is less than this value. Consequently, the solution will not be saturated with respect to the calcium sulphate, and no precipitate forms.

If a saturated solution of a sparingly soluble electrolyte also contains other electrolytes, the ionic strength of the
solution may be quite considerable. In such cases, the activity coefficients must be taken into account in calculations involving the solubility product.

Example 5. The solubility product of calcium oxalate \( \text{CaC}_2\text{O}_4 \) is \( 2 \times 10^{-9} \). Find the solubility of this salt in a \( 0.1 \text{ M} \) solution of ammonium oxalate \( (\text{NH}_4)_2\text{C}_2\text{O}_4 \).

Solution. We express the solubility product of \( \text{CaC}_2\text{O}_4 \) through the activity of its ions:

\[
K_{sp}(\text{CaC}_2\text{O}_4) = a(\text{Ca}^{2+})a(\text{C}_2\text{O}_4^{2-}) = \frac{[\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]}{[\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]} f(\text{Ca}^{2+})f(\text{C}_2\text{O}_4^{2-})
\]

Denoting the required solubility of the salt by \( s \), we find that \( [\text{Ca}^{2+}] = s \text{ mol/1} \), and \( [\text{C}_2\text{O}_4^{2-}] = 0.1 \text{ mol/1} \). Hence,

\[
2 \times 10^{-9} = 0.1s/(\text{Ca}^{2+})/(\text{C}_2\text{O}_4^{2-}); \quad s = \frac{2 \times 10^{-8}}{f(\text{Ca}^{2+})f(\text{C}_2\text{O}_4^{2-})}
\]

To find the values of the activity coefficients, we must calculate the ionic strength of a \( 0.1 \text{ M} \) solution of \( (\text{NH}_4)_2\text{C}_2\text{O}_4 \):

\[
I = 0.5 (0.2 \times 1^2 + 0.1 \times 2^2) = 0.3
\]

According to Table 7 of the Appendix, at this ionic strength, the activity coefficients of doubly charged ions are 0.42. Consequently,

\[
s = \frac{2 \times 10^{-8}}{0.42 \times 0.42} = 1.1 \times 10^{-7} \text{ mol/1}
\]

Comparing the value thus found with the results of an approximate calculation disregarding the activity coefficients (see Example 3) we see that this resulted in an appreciable error.

PROBLEMS*

552. The solubility of \( \text{CaCO}_3 \) at \( 35^\circ \text{C} \) is \( 6.9 \times 10^{-5} \text{ mol/1} \). Calculate the solubility product of this salt.

553. Calculate the solubility product of \( \text{PbBr}_2 \) at \( 25^\circ \text{C} \) if the solubility of the salt at this temperature is \( 1.32 \times 10^{-2} \text{ mol/1} \).

554. What is the solubility product of \( \text{Ag}_2\text{CrO}_4 \) if 0.0166 g of the salt dissolves in 500 ml of water at \( 18^\circ \text{C} \)?

555. Two litres of water were needed to dissolve 1.16 g of \( \text{PbI}_2 \). Find the solubility product of the salt.

* In solving the problems of this section, use Tables 7 and 8 of the Appendix when needed.
556. Proceeding from the solubility product of calcium carbonate, find the mass of CaCO₃ contained in 100 ml of its saturated solution.

557. Determine the mass of silver present in the form of ions in one litre of a saturated AgBr solution.

558. What volume of water is needed to dissolve 1 g of BaSO₄ at 25 °C?

559. What volume of a saturated solution of Ag₂S contains 1 ml of the dissolved salt?

560. How many times is the solubility (in mol/l) of Fe(OH)₂ in water greater than that of Fe(OH)₃ at 25 °C?

561. Will a precipitate of silver sulphate form if a 1 N solution of H₂SO₄ is added to an equal volume of a 0.02 M solution of AgNO₃?

562. Will a silver chloride precipitate form if 450 ml of a 0.0001 N solution of AgNO₃ are added to 50 ml of a 0.001 N solution of HCl?

563. Will a precipitate of lead chloride form if a 0.4 N solution of NaCl is added to an equal volume of a 0.1 N solution of Pb(NO₃)₂?

564. How will the concentration of silver ions in a saturated solution of AgCl diminish if such an amount of hydrochloric acid is added to it that the concentration of the Cl⁻ ions in the solution becomes equal to 0.03 mol/l?

565. Calculate the solubility of CaF₂ in water and in a 0.05 M solution of CaCl₂. How many times is the solubility in the first case greater than in the second?

566. What fraction does the solubility of AgCl in a 0.001 N solution form of its solubility in water? Perform the calculations taking into account the activity coefficients and using Table of the Appendix.

**REVIEW QUESTIONS**

567. In which of the following cases is the solution of the electrolyte MX unsaturated? (a) [M⁺⁺] [X⁻⁻] < Ksp; (b) [M⁺⁺] [X⁻⁻] = Ksp; (c) [M⁺⁺] [X⁻⁻] > Ksp.

568. Let the solubility of AgCl in water, in 0.01 M CaCl₂, in 0.01 M NaCl, and 0.05 M AgNO₃ be s₁, s₂, s₃ and s₄, respectively. What relationship between these quantities is
correct? (a) \( s_0 > s_1 > s_2 > s_3 \); (b) \( s_0 > s_2 > s_1 > s_3 \); (c) \( s_0 > s_1 = s_2 > s_3 \); (d) \( s_0 > s_2 > s_3 > s_1 \).

569. A solution containing 0.01 mol/l of \( \text{CaCl}_2 \) and 0.01 mol/l of \( \text{SrCl}_2 \) is slowly added to a 0.01 \( N \) solution of \( \text{H}_2\text{SO}_4 \). What substance begins to precipitate earlier? (a) \( \text{SrSO}_4 \); (b) \( \text{CaSO}_4 \).

570. The solubility products of \( \text{NiC}_2\text{O}_4 \) and \( \text{Na}_3\text{AlF}_6 \) are the same \( (4 \times 10^{-10}) \). What relationship between the solubilities (mol/l) of these salts is correct? (a) \( s(\text{NiC}_2\text{O}_4) > s(\text{Na}_3\text{AlF}_6) \); (b) \( s(\text{NiC}_2\text{O}_4) = s(\text{Na}_3\text{AlF}_6) \); (c) \( s(\text{NiC}_2\text{O}_4) < s(\text{Na}_3\text{AlF}_6) \).

571. The solubility products of \( \text{AgBrO}_3 \) and \( \text{Ag}_2\text{SO}_4 \) are \( 5.5 \times 10^{-5} \) and \( 2 \times 10^{-8} \), respectively. Indicate the correct relationship between the solubilities \( (s, \text{mol/l}) \) of these salts. (a) \( s(\text{AgBrO}_3) < s(\text{Ag}_2\text{SO}_4) \); (b) \( s(\text{AgBrO}_3) \approx s(\text{Ag}_2\text{SO}_4) \); (c) \( s(\text{AgBrO}_3) > s(\text{Ag}_2\text{SO}_4) \).

572. How will the solubility of \( \text{CaF}_2 \) in a 0.1 \( M \) solution of \( \text{KNO}_3 \) change in comparison with its solubility in water? (a) It will grow; (b) it will diminish; (c) it will remain unchanged.

5. Exchange Reactions in Electrolyte Solutions. Hydrolysis of Salts

The exchange reactions occurring in electrolyte solutions are participated in by the ions in the solutions in addition to the undissociated molecules of weak electrolytes, solids, and gases. For this reason, the essence of these processes is expressed most completely when they are written in the form of net ionic equations. In these equations, the weak electrolytes, sparingly soluble compounds, and gases are written in the molecular form, and the strong electrolytes in the solution, in the form of their constituent ions. For example, the equations of the neutralization of strong acids by strong bases

\[
\text{HClO}_4 + \text{NaOH} = \text{NaClO}_4 + \text{H}_2\text{O}
\]

\[
2\text{HNO}_3 + \text{Ca(OH)}_2 = \text{Ca(NO}_3)_2 + 2\text{H}_2\text{O}
\]

are expressed by the same net ionic equation

\[
\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}
\]
from which it follows that the essence of these processes consists in the formation of a weakly dissociating electrolyte—water—from hydrogen ions and hydroxide ions.

Similarly, the equations of the reactions

\[
\begin{align*}
\text{BaCl}_2 + \text{H}_2\text{SO}_4 & = \text{BaSO}_4 + 2\text{HCl} \\
\text{Ba(NO}_3\text{)}_2 + \text{Na}_2\text{SO}_4 & = \text{BaSO}_4 + 2\text{NaNO}_3
\end{align*}
\]

express the same process of formation of a precipitate of a sparingly soluble electrolyte—barium sulphate—from \(\text{Ba}^{2+}\) and \(\text{SO}_4^{2-}\) ions:

\[
\text{Ba}^{2+} + \text{SO}_4^{2-} = \text{BaSO}_4
\]

The above examples show that exchange reactions in solutions of electrolytes proceed in the direction of combination of the ions leading to the formation of sparingly soluble substances (precipitates or gases) or of molecules of weak electrolytes.

Example 1. Write the equations of the reactions between the following substances in the net ionic form: \(\text{CH}_3\text{COONa}\) and \(\text{H}_2\text{SO}_4\); \(\text{Na}_2\text{CO}_3\) and \(\text{HNO}_3\); \(\text{HCN}\) and \(\text{Ca(OH)}_2\); \(\text{Pb(NO}_3\text{)}_2\) and \(\text{K}_2\text{CrO}_4\).

Solution. Since \(\text{CH}_3\text{COOH}\), \(\text{HCN}\), and \(\text{H}_2\text{O}\) are weak electrolytes, and \(\text{CO}_3^2-\) and \(\text{PbCrO}_4\) are substances sparingly soluble in water, the required equations will have the following form:

\[
\begin{align*}
\text{CH}_3\text{COO}^- + \text{H}^+ & = \text{CH}_3\text{COOH} \\
\text{CO}_3^{2-} + 2\text{H}^+ & = \text{CO}_2^{\uparrow} + \text{H}_2\text{O} \\
\text{HCN} + \text{OH}^- & = \text{CN}^- + \text{H}_2\text{O} \\
\text{Pb}^{2+} + \text{CrO}_4^{2-} & = \text{PbCrO}_4^{\downarrow}
\end{align*}
\]

When both the reactants and the products contain sparingly soluble substances (or weak electrolytes), equilibrium shifts in the direction of formation of the least soluble or least dissociated substances. For example, in the neutralization of a weak acid with a strong base

\[
\text{CH}_3\text{COOH} + \text{KOH} = \text{CH}_3\text{COOK} + \text{H}_2\text{O}
\]

or

\[
\text{CH}_3\text{COOH} + \text{OH}^- = \text{CH}_3\text{COO}^- + \text{H}_2\text{O}
\]

two weak electrolytes participate in the reaction—a weak acid (\(\text{CH}_3\text{COOH}\)) and water. Equilibrium is greatly shifted in the direction of formation of the weaker electrolyte—water, whose dissociation constant \((1.8 \times 10^{-16})\) is much
smaller than that of acetic acid \((1.8 \times 10^{-5})\). Such a reaction will not go to the end, however: a small amount of undissociated molecules \(\text{CH}_3\text{COOH}\) and ions \(\text{OH}^-\) remain in the solution, so that the latter will be not neutral (as in the neutralization of a strong acid with a strong base), but weakly basic.

Similarly, in the neutralization of a weak base with a strong acid:

\[
\text{Zn(OH)}_2 + 2\text{HNO}_3 = \text{Zn(NO}_3)_2 + 2\text{H}_2\text{O}
\]

or

\[
\text{Zn(OH)}_2 + 2\text{H}^+ = \text{Zn}^{2+} + 2\text{H}_2\text{O}
\]

equilibrium will be greatly shifted to the right—in the direction of formation of the weaker electrolyte (water), but when equilibrium is reached, the solution will contain a small amount of undissociated molecules of the base and \(\text{H}^+\) ions, and will be weakly acidic.

Thus, neutralization reactions in which weak acids or bases participate are reversible, i.e. can proceed not only in the forward, but also in the reverse direction. This signifies that when we dissolve in water a salt comprising an anion of a weak acid or a cation of a weak base, a hydrolysis process occurs, i.e. an exchange reaction between a salt and water, the result of which is the formation of a weak acid or a weak base.

If a salt is formed by a weak acid and a strong base, hydrolysis causes hydroxide ions to form in the solution, which becomes basic, for instance:

\[
\text{KCN} + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{KOH}
\]

\[
\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-
\]

It can be seen that in such cases the anion of the salt undergoes hydrolysis.

In the hydrolysis of a salt formed by a strong acid and a weak base, the cation of the salt becomes hydrolyzed; the hydrogen ion concentration in the solution grows, and it becomes acidic, for example:

\[
\text{ZnCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)Cl} + \text{HCl}
\]

\[
\text{Zn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{ZnOH}^+ + \text{H}^+
\]
When a salt formed by a weak acid and a weak base reacts with water, both its cation and its anion become hydrolyzed; for example, in the hydrolysis of lead acetate

\[ \text{Pb(CH}_3\text{COO)}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Pb(OH)CH}_3\text{COO} + \text{CH}_3\text{COOH} \]

two processes occur simultaneously:

\[ \text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PbOH}^+ + \text{H}^+ \]
\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \]

In this case, the reaction of the solution depends on the relative strength of the acid and base forming the salt. If \( K_{\text{acid}} \approx K_{\text{base}} \), the cation and the anion become hydrolyzed to an equal extent, and the solution will be neutral; if \( K_{\text{acid}} > K_{\text{base}} \), the cation of the salt becomes hydrolyzed to a greater extent than the anion so that the concentration of the \( \text{H}^+ \) ions in the solution will be greater than that of the hydroxide ions, and the solution will be slightly acidic; finally, if \( K_{\text{acid}} < K_{\text{base}} \), the anion of the salt mainly becomes hydrolyzed, and the solution will be slightly basic.

Salts formed by a strong acid and a strong base do not become hydrolyzed because in this case the neutralization reaction, which is the opposite of hydrolysis, is virtually irreversible, i.e. goes to completion.

The hydrolysis of a salt formed by a weak acid \( \text{HA} \) and a strong base is characterized by the hydrolysis constant \( K_h \):

\[ K_h = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = \frac{K_w}{K_{\text{acid}}} \]

where \( K_w \) is the ion product of water.

The last expression shows that the weaker an acid, i.e. the lower its dissociation constant, the greater is the hydrolysis constant of its salts.

Similarly, for a salt of a weak base \( \text{MOH} \) and a strong acid:

\[ K_h = \frac{[\text{H}^+][\text{MOH}]}{[\text{M}^+]} = \frac{K_w}{K_{\text{base}}} \]

Therefore, \( K_h \) is the greater, the smaller is \( K_{\text{base}} \), i.e. the weaker is the base \( \text{MOH} \).

The degree of hydrolysis \( h \) is defined as the fraction of an electrolyte that has become hydrolyzed. It is related to the hydrolysis constant \( K_h \) by an equation similar to the
Ostwald dilution law for the dissociation of a weak electrolyte:

\[ K_h = \frac{h^2c}{1-h} \]

Most often, the hydrolyzed part of a salt is very small, and the concentration of the hydrolysis products is insignificant. In such cases, \( h \ll 1 \), and this quantity may be disregarded in the denominator of the last formula. Hence, the relationship between \( K_h \) and \( h \) becomes simpler:

\[ K_h = h^2c \text{ or } h = \sqrt[2]{\frac{K_h}{c}} \]

The last equation shows that the degree of hydrolysis of a given salt increases when its concentration diminishes; in other words, when a solution of a hydrolyzing salt is diluted, the degree of its hydrolysis grows.

**Example 2.** Calculate the degree of hydrolysis of potassium acetate in a 0.1 M solution and the pH of the solution.

**Solution.** The equation of the hydrolysis reaction is:

\[ \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^- \]

To calculate the degree of hydrolysis, we first find the hydrolysis constant. For this purpose, we use the value of the dissociation constant of acetic acid (1.8 \( \times \) 10\(^{-5} \)) given in Table 6 of the Appendix:

\[ K_h = \frac{K_w}{K_{\text{acid}}} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} \]

We now find the degree of hydrolysis:

\[ h = \sqrt[2]{\frac{K_h}{c}} = \sqrt{\frac{5.56 \times 10^{-10}}{0.1}} = 7.5 \times 10^{-5} \]

To calculate the pH, we must take into account that as a result of the hydrolysis of each CH₃COO\(^-\) anion, one hydroxide ion forms. If the initial concentration of the hydrolyzing anions is c mol/l, and the fraction \( h \) of these anions becomes hydrolyzed, \( hc \) mol/l of OH\(^-\) ions will be produced. Hence,

\[ [\text{OH}^-] = hc = 7.5 \times 10^{-5} \times 0.1 = 7.5 \times 10^{-6} \text{ mol/l} \]

and

\[ \text{pOH} = -\log [\text{OH}^-] = -\log (7.5 \times 10^{-6}) = -(6.88) = \]

\[ = -(6.92) = 5.12 \]

whence

\[ \text{pH} = 14 - \text{pOH} = 14 - 5.12 = 8.88 \]
The hydrolysis of salts formed by weak polybasic acids proceeds in steps, the products of the first hydrolysis steps being acid salts. For instance, in the hydrolysis of potassium carbonate, the \( \text{CO}_3^{2-} \) ion attaches one hydrogen ion to form the hydrogen carbonate ion \( \text{HCO}_3^- \):

\[
\text{CO}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{OH}^{-}
\]

or in the molecular form

\[
\text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{KHCO}_3 + \text{KOH}
\]

This is the first hydrolysis step. The relevant hydrolysis constant is determined by the value of the dissociation constant of the acid (\( \text{HCO}_3^- \)) formed in hydrolysis, i.e. by the second dissociation constant of carbonic acid \( \text{H}_2\text{CO}_3 \) \((4.7 \times 10^{-11})\). Hence

\[
K_{h1} = \frac{K_w}{K_{\text{acid},2}} = \frac{4 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4}
\]

The accumulation of \( \text{OH}^- \) ions in the solution prevents the further proceeding of hydrolysis. If the hydroxide ions produced are combined, however (for example, by adding an acid to the solution), the \( \text{HCO}_3^- \) anion, in turn, becomes hydrolyzed (the second step of hydrolysis):

\[
\text{HCO}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^{-}
\]

or in the molecular form:

\[
\text{KHCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 + \text{KOH}
\]

The second-step hydrolysis constant is determined by the value of the first dissociation constant of carbonic acid \((4.5 \times 10^{-7})\):

\[
K_{h2} = \frac{K_w}{K_{\text{acid},1}} = \frac{4 \times 10^{-14}}{4.5 \times 10^{-7}} = 2.2 \times 10^{-8}
\]

We can see that \( K_{h2} \ll K_{h1} \). This is associated with the fact that the first-step dissociation constant, as a rule, is considerably greater than the second-step one. Consequently, in approximate calculations connected with the hydrolysis of salts of weak polybasic acids, only first-step hydrolysis may be taken into consideration.

The hydrolysis of salts formed by weak bases of polyvalent metals also proceeds in steps. First-step hydrolysis yields
a basic salt, for instance:

\[ \text{ZnCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{ZnOHCl} + \text{HCl} \]
\[ \text{Zn}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{ZnOH}^+ + \text{H}^+ \]

The second step of hydrolysis is the reaction with water of the basic salt formed (or, more exactly, of the hydroxocation formed):

\[ \text{ZnOHCl} + \text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_2 + \text{HCl} \]
\[ \text{ZnOH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Zn(OH)}_2 + \text{H}^+ \]

In such cases, \( K_{h,1} \) is considerably greater than \( K_{h,2} \) and if the \( \text{H}^+ \) ions formed are not combined, second-step hydrolysis will virtually not proceed.

Example 3. Determine the pH of a 0.1 \( M \) solution of potassium orthophosphate.

Solution. We shall assume that hydrolysis proceeds virtually only in the first step:

\[ \text{K}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{HPO}_4 + \text{KOH} \]
\[ \text{PO}^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HPO}^{2-} + \text{OH}^- \]

The hydrolysis constant for this step is determined by the dissociation constant of the formed weak acid \( \text{HPO}^{2-} \), i.e. by the third dissociation constant of orthophosphoric acid \( (1.3 \times 10^{-12}) \):

\[ K_{h,1} = \frac{K_w}{K_3} = \frac{10^{-14}}{1.3 \times 10^{-12}} = 7.7 \times 10^{-3} \]

We find the degree of hydrolysis:

\[ h = \sqrt{\frac{K_{h,1}}{c}} = \sqrt{\frac{7.7 \times 10^{-3}}{0.1}} = 2.8 \times 10^{-2} \]

The concentration of the hydroxide ions produced is \( h \cdot c \), i.e.

\[ [\text{OH}^-] = 2.8 \times 10^{-2} \times 0.1 = 2.8 \times 10^{-3} \]

whence

\[ \text{pOH} = -\log (2.8 \times 10^{-3}) = 2.55 \]

We finally obtain:

\[ \text{pH} = 14 - \text{pOH} = 11.45 \]

If we introduce a reagent combining with the \( \text{H}^+ \) or \( \text{OH}^- \) ions formed in hydrolysis into a solution of a hydrolyzing salt, in accordance with Le Chatelier's principle equilibrium
will shift in the direction of an intensification of hydrolysis; as a result, hydrolysis may go to the end, to the formation of its products. The H+ (or OH-) ions can be combined into water molecules by introducing into the solution not only an alkali (or acid), but also another salt whose hydrolysis leads to the accumulation of OH- (or H+) ions in the solution; the H+ and OH- ions will neutralize one another, this causing the mutual intensification of the hydrolysis of both salts and the formation of the hydrolysis products. For instance, when solutions of Na₂CO₃ and AlCl₃ containing excess OH- and H+ ions, respectively, are mixed, the mutual intensification of hydrolysis leads to the liberation of CO₂ and the formation of an Al(OH)₃ precipitate:

\[
2\text{AlCl}_3 + 3\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{CO}_2 + 6\text{NaCl}
\]

\[
2\text{Al}^{3+} + 3\text{CO}_3^{2-} + 3\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{CO}_2
\]

The least soluble of the hydrolysis products precipitates in such cases. For example, the solubility of copper hydroxide carbonate (CuOH)₂CO₃ is lower than that of copper hydroxide Cu(OH)₂. Therefore, when solutions of CuSO₄ and Na₂CO₃ are mixed, it is (CuOH)₂CO₃ that is the hydrolysis product:

\[
2\text{CuSO}_4 + 2\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} = (\text{CuOH})_2\text{CO}_3 + \text{CO}_2 + 2\text{Na}_2\text{SO}_4
\]

\[
2\text{Cu}^{2+} + 2\text{CO}_3^{2-} + \text{H}_2\text{O} = (\text{CuOH})_2\text{CO}_3 + \text{CO}_2
\]

The equilibrium of hydrolysis can also be shifted by a change in the temperature. Since the reverse process of hydrolysis—neutralization—proceeds with the liberation of heat, a hydrolysis reaction is an endothermic process. Consequently, elevation of the temperature leads to the intensification of hydrolysis, whereas lowering of the temperature, to its diminishing.

**PROBLEMS**

573. Write the net ionic equations of the reactions leading to the formation of sparingly soluble precipitates or gases: (a) Pb(NO₃)₂ + KI; (b) NiCl₂ + H₂S; (c) K₂CO₃ +

* In solving the problems of this section use Table 6 of the Appendix to calculate the hydrolysis constants when needed.
Problems and Exercises In General Chemistry

$+ \text{HCl};$ (d) $\text{CuSO}_4 + \text{NaOH};$ (e) $\text{CaCO}_3 + \text{HCl};$ (f) $\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4;$ and (g) $\text{AlBr}_3 + \text{AgNO}_3.$

574. Write the net ionic equations of the reactions leading to the formation of poorly dissociating compounds: (a) $\text{Na}_2\text{S} + \text{H}_2\text{SO}_4;$ (b) $\text{FeS} + \text{HCl};$ (c) $\text{HCOOK} + \text{HNO}_3;$ (d) $\text{NH}_4\text{Cl} + \text{Ca(OH)}_2;$ and (e) $\text{NaOCl} + \text{HNO}_3.$

575. Write the net ionic equations of the following neutralization reactions: (a) $\text{HCl} + \text{Ba(OH)}_2;$ (b) $\text{HF} + \text{KOH};$ (c) $\text{Fe(OH)}_3 + \text{HNO}_3;$ (d) $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH};$ (e) $\text{HNO}_2 + \text{NH}_4\text{OH};$ (f) $\text{H}_2\text{S} + \text{NH}_4\text{OH}.$

Indicate which of these reactions are reversible and which irreversible.

576. Write the net ionic equations of the reactions between aqueous solutions of the following substances: (a) $\text{NaHCO}_3$ and $\text{HCl};$ (b) $\text{FeCl}_3$ and $\text{KOH};$ (c) $\text{Pb(CH}_3\text{COO)}_2$ and $\text{Na}_2\text{S};$ (d) $\text{KHS}$ and $\text{H}_2\text{SO}_4;$ (e) $\text{Zn(NO}_3)_2 + \text{KOH(excess)};$ (f) $\text{Ca(OH)}_2 + \text{CO}_2;$ and (g) $\text{Ca(OH)}_2 + \text{CO}_2\text{(excess)}.$

Indicate for each case the reason why equilibrium shifts in the direction of the forward reaction.

577. Which of the salts listed below become hydrolyzed? $\text{NaCN}, \text{KNO}_3, \text{KOC}_1, \text{NaN}_2\text{O}_2, \text{NH}_4\text{CH}_3\text{COO}, \text{CaCl}_2, \text{NaClO}_4, \text{KHCOO},$ and $\text{KBr}.$ Write the net ionic equation of hydrolysis for each of the hydrolyzing salts and indicate whether its aqueous solution is neutral, acidic, or basic.

578. Indicate which of the salts listed below become hydrolyzed: $\text{ZnBr}_2, \text{K}_2\text{S}, \text{Fe}_2\text{(SO}_4)_3, \text{MgSO}_4, \text{Cr(NO}_3)_3, \text{K}_2\text{CO}_3, \text{Na}_2\text{PO}_4,$ and $\text{CuCl}_2.$ For each of the hydrolyzing salts write the molecular and net ionic equations of hydrolysis for each step and indicate whether an aqueous solution of the salt is neutral, acidic, or basic.

579. What colour will litmus acquire in aqueous solutions of $\text{KCN}, \text{NH}_4\text{Cl}, \text{K}_2\text{SO}_3, \text{NaNO}_3, \text{FeCl}_3, \text{Na}_2\text{CO}_3,$ and $\text{Na}_2\text{SO}_4?$ Substantiate your answer.

580. Calculate the hydrolysis constant of potassium fluoride; determine the degree of hydrolysis of this salt in a 0.01 $M$ solution and the pH of the solution.

581. Calculate the hydrolysis constant of ammonium chloride, determine the degree of hydrolysis of this salt in a 0.01 $M$ solution and the pH of the solution.

582. Determine the pH of a 0.02 $N$ solution of soda $\text{Na}_2\text{CO}_3,$ taking only first-step hydrolysis into account.
583. Compare the degree of hydrolysis of the salt and the pH of the solution in 0.1 M and 0.001 M solutions of potassium cyanide.

584. At 60 °C, the ion product of water is $K_w = 10^{-13}$. Assuming that the dissociation constant of hypochlorous acid does not change with the temperature, find the pH of a 0.001 N solution of KOCl at 25 and 60 °C.

585. The pH of a 0.1 M solution of the sodium salt of a monobasic organic acid is 10. Calculate the dissociation constant of the acid.

586. Proceeding from the values of the dissociation constants for the relevant acids and bases, indicate the reaction of aqueous solutions of the following salts: NH$_4$CN, NH$_4$F, (NH$_4$)$_2$S.

587. At pH < 3.1, the indicator methyl red is coloured red, at pH > 6.3 it is yellow, and at intermediate values of the pH it is orange. What will the colour of the indicator be in a 0.1 M solution of NH$_4$Br?

588. A solution of NaH$_2$PO$_4$ is weakly acidic, and that of Na$_3$PO$_4$ strongly basic. Explain these facts and motivate them by the relevant net ionic equations.

589. Why is a solution of NaHCO$_3$ weakly basic, and a solution of NaHSO$_3$ weakly acidic?

590. When aqueous solutions of Cr(NO$_3$)$_3$ and Na$_2$S are poured into the same vessel, a precipitate of chromium(III) hydroxide is formed and a gas is liberated. Write the molecular and net ionic equations of the reaction.

**REVIEW QUESTIONS**

591. In what direction will the equilibrium of the reaction AgI(c) + NaCl(aq) ⇌ AgCl(c) + NaI(aq) shift? (a) In the direction of the forward reaction; (b) in the direction of the reverse reaction.

592. In what direction will the equilibrium of the reaction CH$_3$COONa + CH$_3$CICOOH ⇌ CH$_3$COOH + + CH$_3$CICOONa shift in an aqueous solution? (a) In the direction of the forward reaction; (b) in the direction of the reverse reaction.

593. Indicate which order of arrangement of solutions having an equal molecular concentration corresponds to a
growth in the pH. (a) NH₄Cl-NaNO₃-CH₂ClC00Na-NaF-CH₃COONa-NaCN; (b) NaCN-CH₃COONa-NaF-CH₂ClC00Na-NaNO₃-NH₄Cl.

594. Litmus changes its colour within a pH range from 5 to 8.3. What will be the colour of a 0.001 M solution of sodium acetate CH₃COONa (Kₐ = 5.6 × 10⁻⁹) containing litmus? (a) Red; (b) violet; (c) blue.

595. The indicator methyl orange changes its colour from red to yellow within a pH range from 3.2 to 4.4. What will be the colour of a 0.1 M aqueous solution of ammonium acetate CH₃COONH₄ containing methyl orange? (a) Red; (b) orange; (c) yellow.

596. The dissociation constants of hydrazoic acid HN₃ and ammonium hydroxide NH₄OH are approximately the same. What will be the relationship between the values of the pH in solutions of NaN₃ (pH₁) and NH₄NO₃ (pH₂) having the same molar concentration? (a) pH₁ > pH₂; (b) pH₁ ≈ pH₂; (c) pH₁ < pH₂.

Because (1) both salts become hydrolyzed to an equal degree; (2) the cation becomes hydrolyzed in one salt, and the anion in the other.

597. Which of the following reagents will intensify the hydrolysis of FeCl₃ when added to its solution? (a) HCl; (b) NaOH; (c) ZnCl₂; (d) Na₂CO₃; (e) NH₄Cl; (f) Zn; (g) H₂O.
1. Oxidation Number. Oxidation and Reduction

The oxidation number (or oxidation state) of an element in a compound is determined as the number of electrons that have passed from one atom of a given element to other atoms (positive oxidation), or to one atom of a given element from other atoms (negative oxidation).

The following rules should be adhered to in determining the oxidation number of an element in a compound: (1) the oxidation number of an element in an elementary substance is taken equal to zero; (2) the algebraic sum of the oxidation numbers of all the atoms in a molecule is zero; (3) elements having a constant oxidation number in compounds are the alkali metals (+1), the metals of the main subgroup of Group II, zinc, and cadmium (+2); (4) hydrogen exhibits an oxidation number of +1 in all its compounds except metal hydrides (NaH, CaH₂, etc.), where its oxidation number is -1; (5) the oxidation number of oxygen in its compounds is -2 except peroxides (-1) and oxygen fluoride OF₂ (+2).

Proceeding from the above, it is a simple matter, for example, to establish that in the compounds NH₃, N₂H₄, NH₂OH, N₂O, NO, HNO₂, NO₂, and HNO₃, the oxidation number of nitrogen is -3, -2, -1, +1, +2, +3, +4, and +5, respectively.

In oxidation-reduction (redox) reactions, the oxidation number of one or more elements in the reacting substances changes. The losing of electrons by an atom attended by an increase in its oxidation number is called oxidation; the gaining of electrons by an atom attended by a decrease in its oxidation number is called reduction.
A substance containing an element that undergoes oxidation is called a reducing agent. A substance containing an element that undergoes reduction is called an oxidizing agent. For instance, in the reaction

\[ 4\text{Al} + 3\text{O}_2 = 2\text{Al}_2\text{O}_3 \]

aluminium raises its oxidation number from 0 to +3 and is a reducing agent. As a result of the reaction, the reduced form of aluminium (free aluminium) is oxidized and transforms into its conjugate oxidized form (aluminium in the +3 oxidation state). The oxygen in this reaction lowers its oxidation number from 0 to —2 and is an oxidizing agent; as a result of the reaction the oxidized form of oxygen (free oxygen) is reduced and transforms into its conjugate reduced form (oxygen in the —2 oxidation state). Both processes—oxidation and reduction—proceed simultaneously. The total number of electrons lost by the reducing agent equals the total number of electrons gained by the oxidizing agent.

In the above reaction, two substances react; one of them is an oxidizing agent (oxygen), and the other, a reducing agent (aluminium). Such reactions relate to intermolecular oxidation-reduction ones. The reaction

\[ 4\text{H}_3\text{PO}_3 = 3\text{H}_3\text{PO}_4 + \text{PH}_3 \]

is an example of autoxidation-autoreduction (disproportionation) reactions in which compounds are simultaneously formed that contain a given element in a more oxidized and a more reduced state than the initial one. The initial substance displays functions of both an oxidizing and a reducing agent. In the last reaction, phosphorous acid \( \text{H}_3\text{PO}_3 \) (the oxidation number of phosphorus is +3) simultaneously plays the role of an oxidizing agent, the phosphorus being reduced to the —3 oxidation state (\( \text{PH}_3 \)), and of a reducing agent, the phosphorus being oxidized to the +5 oxidation state (\( \text{H}_3\text{PO}_4 \)). Such reactions are possible if the relevant element is in an intermediate oxidation state in the initial compound. For instance, in the example considered, the oxidation number of the phosphorus in the initial compound (+3) is intermediate between the possible maximum (+5) and minimum (—3) oxidation numbers of this element,
In the reaction

$$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 = \text{Na}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$$

the chromium, whose oxidation number decreases from $+6$ to $+3$, is reduced, and the nitrogen, whose oxidation number rises from $-3$ to $0$, is oxidized. Both these elements are in the same initial substance. Reactions of this kind are known as **intramolecular oxidation-reduction reactions**. They include, for example, many reactions of thermal decomposition of complex substances.

**PROBLEMS**

598. Determine the oxidation number of sulphur in the following compounds: $\text{SO}_2$, $\text{H}_2\text{S}$, $\text{Na}_2\text{SO}_3$, $\text{CS}_2$, $\text{H}_2\text{SO}_4$, $\text{As}_2\text{S}_3$.

599. Determine the oxidation number of chromium in the following compounds: $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cr}_2\text{O}_3$, $\text{Fe(CrO}_2)_3$, $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Cr}_2(\text{SO}_4)_3$, $\text{K}_2[\text{Cr(OH)}_6]$.

600. Indicate which of the following processes are oxidation and which are reduction: $\text{S} \rightarrow \text{SO}_4^{2-}$; $\text{S} \rightarrow \text{S}^{2-}$; $\text{Sn} \rightarrow \text{Sn}^{4+}$; $\text{K} \rightarrow \text{K}^+$; $\text{Br}_2 \rightarrow 2\text{Br}^-$; $2\text{H}^+ \rightarrow \text{H}_2$; $\text{H}_2 \rightarrow 2\text{H}^-$; $\text{V}^{2+} \rightarrow \text{VO}_2^-$; $\text{Cl}^- \rightarrow \text{ClO}_3^-$; $\text{IO}_3^- \rightarrow \text{I}_2$; $\text{MnO}_4^- \rightarrow \text{MnO}_2^-$.

601. Indicate in which of the following processes the nitrogen is oxidized and in which of them it is reduced, and how the oxidation number of the nitrogen changes in each case: $\text{NH}_4^+ \rightarrow \text{N}_2$; $\text{NO}_2^- \rightarrow \text{NO}$; $\text{NO}_2^- \rightarrow \text{NO}_3^-$; $\text{NO}_2 \rightarrow \text{NO}_3^-$.

602. Which of the following reactions are oxidation-reduction ones?

(a) $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$
(b) $\text{NH}_4\text{Cl} = \text{NH}_3 + \text{HCl}$
(c) $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$
(d) $2\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 = \text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$
(e) $\text{H}_2\text{BO}_3 + 4\text{HF} = \text{HBF}_4 + 3\text{H}_2\text{O}$
(f) $\text{Fe} + \text{S} = \text{FeS}$

603. Indicate for the following reactions which substances and which elements in them are oxidizing agents and which are reducing agents:

(a) $\text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O} = 2\text{HBr} + \text{H}_2\text{SO}_4$
(b) $\text{Mg} + \text{H}_2\text{SO}_4 = \text{MgSO}_4 + \text{H}_2$
(c) $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
(d) $3\text{I}_2 + 6\text{KOH} = \text{KIO}_3 + 5\text{KI} + 3\text{H}_2\text{O}$
604. Which of the following reactions are intermolecular oxidation-reduction ones, intramolecular oxidation-reduction ones, and disproportionation ones?

(a) \(4\text{KMnO}_4 + 4\text{KOH} = 4\text{K}_2\text{MnO}_4 + \text{O}_2 + 2\text{H}_2\text{O}\)
(b) \(\text{H}_2\text{SO}_4 + 2\text{H}_2\text{S} = 3\text{S} + 3\text{H}_2\text{O}\)
(c) \(\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O}\)
(d) \(4\text{P} + 3\text{KOH} + 3\text{H}_2\text{O} = \text{PH}_3 + 3\text{K}_2\text{HPO}_4\)
(e) \(2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2\)
(f) \(2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} = 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4\)

REVIEW QUESTIONS

605. Indicate which of the reactions listed below are oxidation-reduction ones:

(a) \(\text{Cr}_2(\text{SO}_4)_3 + 6\text{RbOH} = 2\text{Cr(OH)}_3 + 3\text{Rb}_2\text{SO}_4\)
(b) \(2\text{Rb} + 2\text{H}_2\text{O} = 2\text{RbOH} + \text{H}_2\)
(c) \(2\text{CuI}_2 = 2\text{CuI} + \text{I}_2\)
(d) \(\text{NH}_4\text{Cl} + \text{NaOH} = \text{NaCl} + \text{NH}_3 + \text{H}_2\text{O}\)
(e) \(2\text{K}_4[\text{Fe(CN)}_6] + \text{Br}_2 = 2\text{K}_3[\text{Fe(CN)}_6] + 2\text{KBr}\)

606. Indicate the disproportionation reactions among the following transformations:

(a) \(\text{S} + \text{KOH} \rightarrow \text{K}_2\text{SO}_3 + \text{K}_2\text{S} + \text{H}_2\text{O}\)
(b) \(\text{Au}_2\text{O}_3 \rightarrow \text{Au} + \text{O}_2\)
(c) \(\text{HCl} + \text{CrO}_3 \rightarrow \text{CrCl}_3 + \text{Cl}_2 + \text{H}_2\text{O}\)
(d) \(\text{HClO}_3 \rightarrow \text{ClO}_2 + \text{HClO}_4\)
(e) \(\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + \text{NH}_3\)
(f) \(\text{AgNO}_3 \rightarrow \text{Ag} + \text{NO}_2 + \text{O}_2\)

607. Up to what products can water be oxidized? (a) to \(\text{O}_2\) and \(\text{H}^+\); (b) to \(\text{OH}^-\) and \(\text{H}_2\); (c) to \(2\text{OH}^-\).

608. In which of the following transformations does oxygen perform the functions of a reducing agent?

(a) \(\text{Ag}_2\text{O} \rightarrow \text{Ag} + \text{O}_2\)
(b) \(\text{F}_2 + \text{H}_2\text{O} \rightarrow \text{HF} + \text{O}_2\)
(c) \(\text{NH}_3 + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O}\)
(d) \(\text{AgNO}_3 + \text{KOH} + \text{H}_2\text{O}_2 \rightarrow \text{Ag} + \text{KNO}_3 + \text{O}_2\)
2. Oxidizing and Reducing Agents

Elements in their maximum oxidation state can only be reduced because all their atoms can do is gain electrons. Examples are sulphur in the +6 oxidation state (H₂SO₄), nitrogen in the +5 state (HNO₃ and nitrates), manganese in the +7 state (permanganates), chromium in the +6 state (chromates and dichromates), and lead in the +4 state (PbO₂).

Conversely, elements in the minimum oxidation state can only be oxidized because all their atoms can do is lose electrons. Examples are sulphur in the —2 oxidation state (H₂S and sulphides), nitrogen in the —3 state (NH₃ and its derivatives), and iodine in the —1 state (HI and iodides).

Substances containing elements in intermediate oxidation states have oxidation-reduction duality. They are capable of either gaining electrons or losing them depending on the partner they are reacting with and the conditions of conducting the reaction.

Some of the most important oxidizing and reducing agents are characterized below.

Oxidizing Agents

1. Oxidizing properties are characteristic of typical non-metals (F₂, Cl₂, Br₂, I₂, O₂) in the elementary (free) state. Halogens playing the part of oxidizing agents acquire the —1 oxidation state, the oxidizing properties weakening from fluorine to iodine:

   \[
   2F₂ + 2H₂O = 4HF + 0₂
   \]

   \[
   4Cl₂ + H₂S + 4H₂O = 8HCl + H₂SO₄
   \]

   \[
   I₂ + H₂S = 2HI + S
   \]

   Oxygen when reduced transforms into the —2 oxidation state (H₂O or OH⁻):

   \[
   4NH₃ + 5O₂ = 4NO + 6H₂O.
   \]

   \[
   4FeSO₄ + O₂ + 2H₂O = 4(FeOH)SO₄
   \]

2. Among the oxyacids and their salts, the most important oxidizing agents include KMnO₄, K₂CrO₄, K₂Cr₂O₇, concentrated sulphuric acid, nitric acid and nitrates, the oxyacids of the halogens and their salts,
Potassium permanganate, displaying oxidizing properties at the expense of Mn(VII), is reduced to various products depending on the acidity of the solution: in an acid solution—to Mn²⁺ (the oxidation number of the manganese is +2), in a neutral and weakly basic solution—to MnO₂ (oxidation number +4), and in a strongly basic solution—to the manganate ion MnO₄⁻ (oxidation number +6):

\[
5K_2SO_3 + 2KMnO_4 + 3H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 3H_2O
\]

\[
3K_2SO_3 + 2KMnO_4 + H_2O = 3K_2SO_4 + 2MnO_2 + 2KOH
\]

Potassium chromate and dichromate (K₂CrO₄ and K₂Cr₂O₇) are oxidizing agents in an acid solution, being reduced to the Cr³⁺ ion. Since in an acid solution the equilibrium

\[
2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O
\]

shifts to the right, the Cr₂O₇⁻ ion is the oxidizing agent:

\[
K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = Cr_2(SO_4)_3 + 3S + K_2SO_4 + 7H_2O
\]

Concentrated sulphuric acid exhibits oxidizing properties at the expense of the sulphur in the +6 oxidation state, which can be reduced to the +4 state (SO₂), 0 (free sulphur), or −2 (H₂S). The composition of the reduction products is determined mainly by the activity of the reducing agent, and also by the proportion of the reducing agent and sulphuric acid, the acid concentration, and the temperature of the system. Reduction proceeds further when the reducing agent is more active and the concentration of the acid is higher. For instance, metals with a low activity (Cu, Sb, etc.), hydrogen bromide, and some non-metals reduce concentrated sulphuric acid to SO₂:

\[
Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O
\]

\[
2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O
\]

\[
C(\text{coal}) + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O
\]

Active metals (Mg, Zn, etc.) reduce concentrated sulphuric acid to free sulphur or hydrogen sulphide*:

\[
3Mg + 4H_2SO_4 = 3MgSO_4 + S + 4H_2O
\]

\[
4Zn + 5H_2SO_4 = 4ZnSO_4 + H_2S + 4H_2O
\]

* The reduction of sulphuric acid is sometimes attended by the formation of H₂S, S and SO₂ in various proportions.
Nitric acid exhibits oxidizing properties at the expense of its nitrogen in the +5 oxidation state, the oxidizing power of HNO₃ increasing with its concentration. Concentrated nitric acid oxidizes most elements to their maximum oxidation number. The composition of the products of HNO₃ reduction depends on the activity of the reducing agent and the concentration of the acid; reduction of the nitrogen proceeds further when the reducing agent is more active and the dilution of the acid is greater:

\[
\begin{array}{cccccc}
\text{NO}_2 & \text{NO} & \text{N}_2\text{O} & \text{N}_2 & \text{NH}_4^+ \\
\text{concentration of acid} & < & \text{activity of reducing agent}
\end{array}
\]

Consequently, when concentrated nitric acid reacts with non-metals or with metals having a low activity, nitrogen dioxide is formed

\[
P + 5\text{HNO}_3 = \text{H}_3\text{PO}_4 + 5\text{NO}_2 + \text{H}_2\text{O}
\]

\[
\text{Ag} + 2\text{HNO}_3 = \text{AgNO}_3 + \text{NO}_2 + \text{H}_2\text{O}
\]

When more dilute nitric acid reacts with metals having a low activity, nitrogen monoxide may be liberated:

\[
3\text{Cu} + 8\text{HNO}_3(35\%) = 3\text{Cu(NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}
\]

while when active metals are involved, the products include dinitrogen oxide or free nitrogen*

\[
4\text{Zn} + 10\text{HNO}_3(\text{dil}) = 4\text{Zn(NO}_3)_2 + \text{N}_2\text{O} + 5\text{H}_2\text{O}
\]

\[
5\text{Zn} + 12\text{HNO}_3(\text{dil}) = 5\text{Zn(NO}_3)_2 + \text{N}_2 + 6\text{H}_2\text{O}
\]

(the symbol "dil" stands for dilute).

Greatly diluted nitric acid when reacted with active metals may be reduced to the ammonium ion, which forms ammonium nitrate with the acid:

\[
4\text{Mg} + 10\text{HNO}_3(\text{very dil}) = 4\text{Mg(NO}_3)_2 + \text{NH}_4\text{NO}_3 + 3\text{H}_2\text{O}
\]

Unlike the \(\text{SO}_4^{2-}\) ion, the \(\text{NO}_3^-\) ion exhibits oxidizing properties not only in an acid, but also in a basic solution. In solutions, the \(\text{NO}_3^-\) ion is reduced by active metals to \(\text{NH}_3\):

\[
4\text{Zn} + \text{NaNO}_3 + 7\text{NaOH} + 6\text{H}_2\text{O} = 4\text{Na}_2[\text{Zn(OH)}_4] + \text{NH}_3
\]

* A mixture of the products of HNO₃ reduction is formed in such cases, as a rule.
and in melts, to the relevant nitrites:

$$Zn + KNO_3 + 2KOH = K_2ZnO_4 + KNO_2 + H_2O$$

The oxyacids of the halogens (for example, $HOC_1$, $HClO_3$, $HBrO_3$, $HIO_3$) and their salts when acting as oxidizing agents are usually reduced to a halogen oxidation state of $-1$ (for chlorine and bromine) or $0$ (for iodine):

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 = KCl + 3Fe_2(SO_4)_3 + 3H_2O$$
$$KBrO + MnCl_2 + 2KOH = KBr + MnO_2 + 2KCl + H_2O$$
$$HIO_3 + 5HI = 3I_2 + 3H_2O$$

3. **Hydrogen** in the $+1$ oxidation state is an oxidizing agent chiefly in solutions of acids (as a rule, when they react with metals preceding hydrogen in the electromotive series):

$$Mg + H_2SO_4(dil) = MgSO_4 + H_2$$

The hydrogen in water, however, can be an oxidizing agent when the water reacts with strong reducing agents:

$$2K + 2H_2O = 2KOH + H_2$$

4. **Metal ions** in their maximum oxidation state (for instance, $Fe^{3+}$, $Cu^{2+}$, and $Hg^{2+}$) when performing the function of oxidizing agents transform into ions with a lower oxidation number:

$$2FeCl_3 + H_2S = 2FeCl_2 + S + 2HCl$$
$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

**Reducing Agents**

1. Among elementary substances, typical reducing agents include active metals (alkali and alkaline-earth metals, zinc, aluminium, iron, etc.), and also some non-metals such as hydrogen, carbon (in the form of graphite or coal), phosphorus, and silicon. In an acid solution, metals become oxidized to positively charged ions, while in a basic solution the metals that form amphoteric hydroxides (for example zinc, aluminium, and tin) enter the composition of negatively charged anions or hydroxocomplexes. Carbon is most often oxidized to CO or $CO_2$, and phosphorus, when reacted with strong oxidizing agents, to $H_3PO_4$. 

2. In *hydracids* (HCl, HBr, HI, H_2S) and their salts, the carriers of the reducing function are the anions which upon being oxidized generally form elementary substances. In the series of halide ions, the reducing properties increase when going from Cl\(^-\) to I\(^-\).

3. The *hydrides* of the alkali and alkaline-earth metals containing the H\(^-\) ion exhibit reducing properties, readily becoming oxidized to free hydrogen:

\[
\text{CaH}_2 + 2\text{H}_2\text{O} = \text{Ca(OH)}_2 + 2\text{H}_2
\]

4. Metals in their minimum oxidation state (the ions Sn\(^{2+}\), Fe\(^{2+}\), Cu\(^+\), Hg\(^{2+}\), etc.), when they react with oxidizing agents, can increase their oxidation number:

\[
\begin{align*}
\text{SnCl}_2 + \text{Cl}_2 &= \text{SnCl}_4 \\
5\text{FeCl}_2 + \text{KMnO}_4 + 8\text{HCl} &= 5\text{FeCl}_3 + \text{MnCl}_2 + \text{KCl} + 4\text{H}_2\text{O}
\end{align*}
\]

**Oxidation-Reduction Duality**

Below are given typical examples of compounds that can display both oxidizing and reducing properties.

1. *Iodine* in the free state, notwithstanding its more strongly expressed oxidizing function, can play the role of a reducing agent when reacted with strong oxidizing agents, for instance:

\[
\text{I}_2 + 5\text{Cl}_2 + 6\text{H}_2\text{O} = 2\text{HIO}_3 + 10\text{HCl}
\]

In addition, disproportionation reactions are characteristic of all the halogens, except fluorine, in an alkaline medium:

\[
\begin{align*}
\text{Cl}_2 + 2\text{KOH} &= \text{KOC}_\text{I} + \text{KCl} + \text{H}_2\text{O} \quad \text{(in the cold)} \\
3\text{Cl}_2 + 6\text{KOH} &= \text{KClO}_3 + 5\text{KCl} + 3\text{H}_2\text{O} \quad \text{(when heated)}
\end{align*}
\]

2. *Hydrogen peroxide* H\(_2\)O\(_2\) contains oxygen in the \(-1\) oxidation state. In the presence of reducing agents, it can lower its oxidation number to \(-2\), while when reacted with oxidizing agents it can increase its oxidation number and transform into free oxygen:

\[
\begin{align*}
5\text{H}_2\text{O}_2 + \text{I}_2 &= 2\text{HIO}_3 + 4\text{H}_2\text{O} \quad \text{(H}_2\text{O}_2\text{— oxidizing agent)} \\
3\text{H}_2\text{O}_2 + 2\text{KMnO}_4 &= 2\text{MnO}_3 + 2\text{KOH} + 3\text{O}_2 + 2\text{H}_2\text{O} \\
&\quad \quad \text{(H}_2\text{O}_2\text{— reducing agent)}
\end{align*}
\]
3. Nitrous acid and nitrites, playing the role of reducing agents at the expense of the NO$_2^-$ ion, are oxidized to nitric acid or its salts:

$$5\text{HNO}_3 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 =$$

$$= 5\text{HNO}_3 + 2\text{MnSO}_4 + \text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$$

When acting as an oxidizing agent, the NO$_3^-$ ion is usually reduced to NO, and in reactions with strong reducing agents—to lower oxidation states of nitrogen:

$$2\text{NaNO}_3 + 2\text{NaI} + 2\text{H}_2\text{SO}_4 = 2\text{NO} + \text{I}_2 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$$

**PROBLEMS**

609. Proceeding from the electron configuration of the atoms, indicate whether the following can be oxidizing agents: sodium atoms, sodium cations, oxygen in the $-2$ oxidation state, iodine in the 0 oxidation state, fluoride ions, hydrogen cations, nitrite ions, and hydride ions.

610. Which of the following ions can be reducing agents, and which cannot and why? $\text{Cu}^{2+}$, $\text{Sn}^{2+}$, $\text{Cl}^-$, $\text{VO}_3^-$, $\text{S}^{2-}$, $\text{Fe}^{2+}$, $\text{WO}_4^{2-}$, $\text{IO}_3^-$, $\text{Al}^{3+}$, $\text{Hg}^{2+}$, and $\text{Hg}^{2+}$.

611. Which of the substances listed below and at the expense of what elements usually exhibit oxidizing properties, and which exhibit reducing properties? Indicate those of them that possess oxidation-reduction duality: $\text{H}_2\text{S}$, $\text{SO}_2$, CO, Zn, $\text{F}_2$, $\text{NaNO}_2$, $\text{KMnO}_4$, $\text{HOCIO}$, and $\text{H}_3\text{SbO}_3$.

612. Indicate in which of the following skeleton reactions hydrogen peroxide is an oxidizing agent and in which it is a reducing agent:

(a) $\text{I}_2 + \text{H}_2\text{O}_2 \rightarrow \text{HIO}_3 + \text{H}_2\text{O}$
(b) $\text{PbO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{Pb(OH)}_2 + \text{O}_2$
(c) $\text{KClO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{KCl} + \text{O}_2 + \text{H}_2\text{O}$
(d) $\text{KMnO}_4 + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2 + \text{KOH} + \text{O}_2 + \text{H}_2\text{O}$

613. Indicate in which of the following reactions hydrazine $\text{N}_2\text{H}_4$ is an oxidizing agent and in which it is a reducing
agent:

\[ \text{NaH}_4 + 4\text{AgNO}_3 + 4\text{KOH} = \text{N}_2 + 4\text{Ag} + 4\text{KNO}_3 + 4\text{H}_2\text{O} \]

\[ \text{N}_2\text{H}_4 + \text{Zn} + 2\text{KOH} + 2\text{H}_2\text{O} = 2\text{NH}_3 + \text{K}_2[\text{Zn(OH)}_4] \]

How does the oxidation number of nitrogen change in each case?

3. Balancing Oxidation-Reduction Equations

It is good practice to adhere to the following procedure in balancing oxidation-reduction equations.

1. Write a skeleton equation indicating the reactants and products, identify the elements whose oxidation numbers change in the reaction, and find the oxidizing and reducing agents.

2. Write skeleton equations of the oxidation and reduction half-reactions indicating the reactant and product ions or molecules actually existing in the conditions of the reaction.

3. Equate the number of atoms of each element in the left-hand and right-hand sides of the half-reaction equations. Remember that in aqueous solutions, \( \text{H}_2\text{O} \) molecules and \( \text{H}^+ \) or \( \text{OH}^- \) ions may participate in the reactions.

4. Equate the total number of charges in both sides of each half-reaction; to do this, add the required number of electrons to the left-hand or right-hand side of a half-reaction.

5. Choose the factors (basic coefficients) for the half-reactions so that the number of electrons lost in oxidation will equal their number gained in reduction.

6. Add the two half-reaction equations together with a view to the basic coefficients found.

7. Put the coefficients in the equation of the reaction. All electrons should cancel. It must be borne in mind that in aqueous solutions, combining of the excess oxygen and attachment of oxygen by the reducing agent occur differently in acidic, neutral, and basic solutions. In acidic solutions, the excess oxygen combines with hydrogen ions to form water molecules, while in neutral and basic solutions it combines with water molecules to form hydroxide ions,
for instance:
\[
\text{MnO}_4^- + 8\text{H}^+ + 5e^- = \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad \text{(acidic solution)}
\]
\[
\text{NO}_3^- + 6\text{H}_2\text{O} + 8e^- = \text{NH}_3 + 9\text{OH}^- \quad \text{(neutral or basic solution)}
\]

Oxygen is attached by the reducing agent in acidic and neutral solutions at the expense of water molecules with the formation of hydrogen ions, and in basic solutions at the expense of hydroxide ions with the formation of water molecules, for example:
\[
\text{I}_2 + 6\text{H}_2\text{O} = 2\text{IO}_3^- + 12\text{H}^+ + 10e^- \quad \text{(acidic or neutral solution)}
\]
\[
\text{CrO}_4^{2-} + 4\text{OH}^- = \text{CrO}_2^- + 2\text{H}_2\text{O} + 3e^- \quad \text{(basic solution)}
\]

Example 1. Balance the reaction equation of oxidation of hydrogen sulphide with chlorine water proceeding according to the skeleton equation

\[
\text{H}_2\text{S} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{HCl}
\]

*Solution.* In the course of the reaction, the oxidation number of chlorine lowers from 0 to $-1$ (the chlorine is reduced), and that of the sulphur increases from $-2$ to $+6$ (the sulphur is oxidized).

The half-reaction equation of chlorine reduction is:
\[
\text{Cl}_2 + 2e^- = 2\text{Cl}^-
\]

In balancing the half-reaction equation of sulphur oxidation, we proceed from the process \(\text{H}_2\text{S} \rightarrow \text{SO}_4^{2-}\). In the course of this process, the sulphur atom combines with four oxygen atoms from four water molecules. Eight \(\text{H}^+\) ions are formed, and two more \(\text{H}^+\) ions are released from the \(\text{H}_2\text{S}\) molecule. Consequently, a total of ten hydrogen ions are produced:
\[
\text{H}_2\text{S} + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 10\text{H}^+
\]

The left-hand side of the skeleton equation contains only uncharged particles, while the total charge of the ions in the right-hand side is $+8$. Hence, oxidation results in the release of eight electrons:
\[
\text{H}_2\text{S} + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 10\text{H}^+ + 8e^-
\]

Since the ratio of the number of electrons gained in the reduction of the chlorine and that lost in the oxidation of the sulphur is $1:4$, when adding the reduction and oxidation half-reaction equations we have to multiply the first of them by 4 and the second by 1:
\[
\begin{align*}
\text{Cl}_2 + 2e^- & = 2\text{Cl}^- & (4) \\
\text{H}_2\text{S} + 4\text{H}_2\text{O} & = \text{SO}_4^{2-} + 10\text{H}^+ + 8e^- & (1) \\
4\text{Cl}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O} & = 8\text{Cl}^- + \text{SO}_4^{2-} + 10\text{H}^+
\end{align*}
\]

The molecular form of the equation obtained is:
\[
4\text{Cl}_2 + \text{H}_2\text{S} + 4\text{H}_2\text{O} \rightarrow 8\text{HCl} + \text{H}_2\text{SO}_4
\]
Sometimes, a reducing agent includes two oxidizing elements. This case is dealt with in the following example.

Example 2. Oxidation of arsenic(III) sulphide by concentrated nitric acid follows the skeleton equation

$$\text{As}_2\text{S}_3 + \text{HNO}_3 \rightarrow \text{H}_2\text{AsO}_4 + \text{H}_2\text{SO}_4 + \text{NO}$$

Balance the equation.

**Solution.** In the course of the reaction, both the arsenic and the sulphur are oxidized: the oxidation number of the arsenic increases from $+3$ to $+5$ and that of the sulphur from $-2$ to $-6$. One $\text{As}_2\text{S}_3$ molecule transforms into two $\text{AsO}_4^{2-}$ and three $\text{SO}_4^{2-}$ ions:

$$\text{As}_2\text{S}_3 \rightarrow 2\text{AsO}_4^{2-} + 3\text{SO}_4^{2-}$$

The oxygen needed for this process to occur in an acidic solution is supplied by water molecules. Eight water molecules form two $\text{AsO}_4^{2-}$ ions, and twelve more form three $\text{SO}_4^{2-}$ ions. Altogether, consequently, twenty water molecules will take part in the oxidation half-reaction with the release of forty hydrogen ions:

$$\text{As}_2\text{S}_3 + 20\text{H}_2\text{O} \rightarrow 2\text{AsO}_4^{2-} + 3\text{SO}_4^{2-} + 40\text{H}^+$$

There are no charged particles in the left-hand side of the skeleton equation, while the total charge of the particles in the right-hand side is $+28$; hence, $28$ electrons are given up when one molecule of $\text{As}_2\text{S}_3$ is oxidized. We finally get the equation of the oxidation half-reaction in the following form:

$$\text{As}_2\text{S}_3 + 20\text{H}_2\text{O} = 2\text{AsO}_4^{2-} + 3\text{SO}_4^{2-} + 40\text{H}^+ + 28\text{e}^-$$

In balancing the half-reaction equation of nitrogen reduction, we proceed from the process $\text{NO}_3^- \rightarrow \text{NO}$. In the course of this process, two oxygen atoms are liberated which in an acidic solution combine with four hydrogen ions to form two water molecules:

$$\text{NO}_3^- + 4\text{H}^+ \rightarrow \text{NO} + 2\text{H}_2\text{O}$$

The total charge of the ions in the left-hand side of the skeleton equation is $+3$, while the right-hand side contains no charged particles. Consequently, three electrons participate in the reduction process:

$$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- = \text{NO} + 2\text{H}_2\text{O}$$

The ratio of the number of electrons participating in oxidation to that in reduction is $28 : 3$. Consequently, in adding the half-reaction equations, we multiply the first of them by $3$ and the second by $28$:

$$3\text{As}_2\text{S}_3 + 28\text{NO}_3^- + 112\text{H}^+ + 60\text{H}_2\text{O} = 6\text{AsO}_4^{2-} + 9\text{SO}_4^{2-} +$$

$$+ 28\text{NO} + 120\text{H}^+ + 56\text{H}_2\text{O}$$
After combining like terms in both sides of the equation, we get:

\[ 3\text{As}_2\text{S}_3 + 28\text{NO}_3^- + 4\text{H}_2\text{O} = 6\text{AsO}_4^{3-} + 9\text{SO}_4^{2-} + 28\text{NO} + 8\text{H}^+ \]

or in the molecular form:

\[ 3\text{As}_2\text{S}_3 + 28\text{HNO}_3 + 4\text{H}_2\text{O} = 6\text{H}_2\text{AsO}_4 + 9\text{H}_2\text{SO}_4 + 28\text{NO} \]

When an oxidation-reduction reaction proceeds outside an aqueous solution, it is recommended not to balance half-reaction equations, but only to calculate the number of electrons participating in oxidation and reduction.

Example 3. Balance the equation of the reaction of iron(III) oxide reduction by coal. The reaction follows the skeleton equation:

\[ \text{Fe}_3\text{O}_8 + \text{C} \rightarrow \text{Fe} + \text{CO} \]

**Solution.** The iron reduces, lowering its oxidation number from +3 to 0; the carbon oxidizes, and its oxidation number grows from 0 to +2. We compile skeleton equations of these processes, indicating the oxidation states of the elements by Roman numerals (in contrast to the charges of the ions):

\[
\begin{align*}
\text{Fe}^{+\text{III}} + 3\text{e}^- &= \text{Fe}^0 & | & 2 \\
\text{C}^{0} &= \text{C}^{+\text{II}} + 2\text{e}^- & | & 3
\end{align*}
\]

The ratio of the number of electrons participating in reduction to that in oxidation is 3 : 2. Consequently, each two iron atoms in the reaction are reduced by three carbon atoms. We finally get:

\[ \text{Fe}_3\text{O}_8 + 3\text{C} = 2\text{Fe} + 3\text{CO} \]

**PROBLEMS**

614. Draw up the equations of the oxidation and reduction half reactions for the following reactions and determine in which cases hydrogen is an oxidizing agent and in which cases it is a reducing agent:

(a) \( 2\text{Al} + 6\text{HCl} = 2\text{AlCl}_3 + 3\text{H}_2 \)

(b) \( 2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O} \)

(c) \( 2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2 \)

(d) \( \text{BaH}_2 + 2\text{H}_2\text{O} = \text{Ba(OH)}_2 + 2\text{H}_2 \)

615. Balance the equations of the oxidation or reduction half reactions with account taken of the acidity of the solution:
Oxidation-Reduction Reactions. Electrochemistry

(a) acidic solution (b) neutral solution (c) basic solution

\[ \text{NO}_3^- \rightarrow \text{NO}_2^- \quad \text{NO}_2^- \rightarrow \text{NO}_3^- \quad \text{CrO}_4^{2-} \rightarrow \text{CrO}_4^{3-} \]
\[ \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \quad \text{MnO}_4^- \rightarrow \text{MnO}_2 \quad \text{Al} \rightarrow \text{AlO}_2^- \]
\[ \text{Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-} \quad \text{SO}_4^{2-} \rightarrow \text{SO}_3^{2-} \quad \text{NO}_3^- \rightarrow \text{NH}_3 \]

616. Complete the equations of the reactions:

(a) \( \text{Mn(OH)}_2 + \text{Cl}_2 + \text{KOH} = \text{MnO}_2 + \)
(b) \( \text{MnO}_4^- + \text{O}_2 + \text{KOH} = \text{K}_2\text{MnO}_4 + \)
(c) \( \text{FeSO}_4 + \text{Br}_2 + \text{H}_2\text{SO}_4 = \)
(d) \( \text{NaAsO}_3 + \text{I}_2 + \text{NaOH} = \text{NaAsO}_4 + \)

617. Complete the equations of the following reactions in which concentrated nitric acid is the oxidizing agent:

(a) \( \text{C} + \text{HNO}_3 \rightarrow \text{CO}_2 + \)
(b) \( \text{Sb} + \text{HNO}_3 \rightarrow \text{HSbO}_3 + \)
(c) \( \text{Bi} + \text{HNO}_3 \rightarrow \text{Bi(NO}_3)_3 + \)
(d) \( \text{PbS} + \text{HNO}_3 \rightarrow \text{PbSO}_4 + \text{NO}_2 + \)

618. Complete the equations of the following reactions in which concentrated sulphuric acid is the oxidizing agent:

(a) \( \text{HBr} + \text{H}_2\text{SO}_4 \rightarrow \text{Br}_2 + \)
(b) \( \text{S} + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \)
(c) \( \text{Mg} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \)

619. Complete the equations of the reactions:

(a) \( \text{KI} + \text{Fe}_3\text{(SO}_4)_3 \rightarrow \text{I}_2 + \)
(b) \( \text{KI} + \text{CuCl}_2 \rightarrow \text{CuCl} + \)
(c) \( \text{SnCl}_2 + \text{HgCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + \)

620. Complete the equations of the following reactions in which the oxidizing (or reducing) agent is additionally used to bind the products:

(a) \( \text{HBr} + \text{KMnO}_4 \rightarrow \text{MnBr}_2 + \)
(b) \( \text{HCl} + \text{CrO}_3 \rightarrow \text{Cl}_2 + \)
(c) \( \text{NH}_3(\text{excess}) + \text{Br}_2 \rightarrow \text{N}_2 + \)
(d) \( \text{Cu}_2\text{O} + \text{HNO}_3 \rightarrow \text{NO} + \)
621. Complete the equations of the following reactions and write them in the net ionic form:

(a) \( K_2S + K_2MnO_4 + H_2O \rightarrow S + \)
(b) \( NO_2 + KMnO_4 + H_2O \rightarrow KNO_3 + \)
(c) \( KI + K_2Cr_2O_7 + H_2SO_4 \rightarrow I_2 + \)
(d) \( Ni(OH)_2 + NaClO + H_2O \rightarrow Ni(OH)_3 + \)
(e) \( Zn + H_2AsO_3 + H_2SO_4 \rightarrow AsH_3 + \)

622. Complete the equations of the following reactions and indicate the part played in each case by the hydrogen peroxide:

(a) \( PbS + H_2O_2 \rightarrow \)
(b) \( HClO + H_2O_2 \rightarrow HCl + \)
(c) \( KI + H_2O_2 \rightarrow \)
(d) \( KMnO_4 + H_2O_2 \rightarrow MnO_2 + \)
(e) \( I_2 + H_2O_2 \rightarrow HIO_3 + \)
(f) \( PbO_2 + H_2O_2 \rightarrow O_2 + \)

623. Complete the equations of the following reactions. Pay attention to the oxidation-reduction duality of the elements in an intermediate oxidation state:

(a) \( KI + KNO_2 + CH_3COOH \rightarrow NO + K MnO_4 + KNO_2 + H_2SO_4 \rightarrow KNO_3 + \)
(b) \( H_2SO_3 + Cl_2 + H_2O \rightarrow H_2SO_4 + H_2SO_3 + H_2S \rightarrow S + \)
(c) \( Na_2S_4O_6 + I_2 \rightarrow Na_2S_4O_6 + Cl_2 + I_2 + H_2O \rightarrow HIO_3 + \)

624. Complete the equations of the following autoxidation-autoreduction (disproportionation) reactions:

(a) \( I_2 + Ba(OH)_2 \rightarrow Ba(IO_3)_2 + \)
(b) \( K_2SO_3 \rightarrow K_2S + \)
(c) \( HClO_3 \rightarrow ClO_2 + \)
(d) \( P_2O_5 + H_2O \rightarrow PH_3 + \)
(e) \( P + KOH + H_2O \rightarrow KH_2PO_2 + PH_3 \)
(f) \( Te + KOH \rightarrow K_2TeO_3 + \)
625. Complete the equations of the following intramolecular oxidation-reduction reactions. Indicate in each case what atom or ion is oxidized and what atom or ion is reduced:

(a) CuI₂ → CuI + I₂
(b) Pb(NO₃)₂ → PbO + NO₃ +
(c) KClO₃ → KCl +
(d) NH₄NO₃ → N₂ +
(e) KMnO₄ → K₂MnO₄ + MnO₂ +

626. Complete the equations of the following reactions, taking into account that the reducing agent contains two oxidizing elements:

(a) Cu₃S + HNO₃(conc) → H₂SO₄ +
(b) FeS₂ + O₂ →
(c) FeO₂Cr₂O₃ + K₂CO₃ + O₂ → K₂CrO₄ + Fe₂O₃ +
(d) FeSO₄ + KMnO₄ + H₂SO₄ → Fe₃(SO₄)₂ +

627. Complete the equations of the following reactions and write them in the molecular form:

(a) C₆O₃⁻⁻ + I₂ → CO₂ +
(b) BiO₅⁻ + Cr³⁺ + H⁺ → Bi³⁺ + CrO₄²⁻ +
(c) SeO₃⁻ + I⁻ + H₂O → Se +
(d) IO₃⁻ + SO₂ + H₂O →

628. Complete the equations of the following reactions and write them in the molecular form:

(a) MnO₄⁻ + I⁻ + H₂O →
(b) HPO₄⁻ + Hg²⁺ + H₂O → Hg +
(c) P + IO₅⁻ + OH⁻ →
(d) PCl₅ + ClO₅⁻ + H₂O →
(e) AsO₃⁻⁻ + I₂ + H₂O → AsO₄⁻⁻ +
(f) Bi³⁺ + Br²⁻ + OH⁻ → BiO₃⁻ +
(g) Sb³⁺ + Zn + H⁺ → SbH₃ +
Complete the equations of the following reactions and write them in the net ionic form:

(a) $\text{FeSO}_4 + \text{O}_2 + \text{H}_2\text{O} \rightarrow$
(b) $\text{P} + \text{K MnO}_4 + \text{H}_2\text{O} \rightarrow \text{KH}_2\text{PO}_4 + \text{K}_2\text{HPO}_4 +$
(c) $\text{Mn(NO}_3)_2 + \text{NaBiO}_3 + \text{HNO}_3 \rightarrow \text{HMnO}_4 +$
(d) $\text{FeS}_3 + \text{HNO}_3(\text{conc}) \rightarrow \text{H}_2\text{SO}_4 +$
(e) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \rightarrow \text{N}_2 +$

Complete the equations of the following reactions and write them in the net ionic form:

(a) $\text{BiCl}_3 + \text{SnCl}_2 + \text{KOH} \rightarrow \text{Bi} +$
(b) $\text{NaClO}_3 + \text{H}_2\text{S} \rightarrow \text{H}_2\text{SO}_4 +$
(c) $\text{KCrO}_4 + \text{Br}_2 + \text{KOH} \rightarrow$
(d) $\text{MnSO}_4 + (\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{H}_2\text{SO}_4 \rightarrow \text{HMnO}_4 +$


Electrode Potentials

If an oxidation-reduction reaction is conducted so that the oxidation and reduction processes are separated in space and the possibility is provided for the electrons to pass from the reducing to the oxidizing agent via a conductor (an external circuit), a directed flow of electrons—an electric current—will appear in the external circuit. The energy of a chemical oxidation-reduction reaction is converted into electrical energy. Devices in which such a conversion occurs are called chemical sources of electrical energy or galvanic cells.

A galvanic cell consists of two electrodes—metals immersed in solution of electrolytes; the latter communicate with each other, usually via a porous partition. The electrode at which oxidation occurs is called the anode; the one at which reduction occurs is called the cathode.

When a galvanic cell is represented schematically, the interface between a metal and a solution is designated by a vertical line, and the interface between solutions of electrolytes by a double vertical line. For example, a galvanic cell whose operation is based on the reaction

$$\text{Zn} + 2\text{AgNO}_3 = \text{Zn(NO}_3)_2 + 2\text{Ag}$$
is represented as follows:

\[ \text{Zn} | \text{Zn(NO}_3)_2 \parallel \text{AgNO}_3 | \text{Ag} \]

This cell can also be written in the net ionic form:

\[ \text{Zn} | \text{Zn}^{2+} \parallel \text{Ag}^+ | \text{Ag} \]

In the given case, the metal electrodes participate directly in the reaction. At the anode, the zinc is oxidized:

\[ \text{Zn} = \text{Zn}^{2+} + 2e^- \]

and passes into solution as ions; at the cathode, the silver is reduced:

\[ \text{Ag}^+ + e^- = \text{Ag} \]

and is deposited on the electrode as the metal. By adding the equations of the electrode processes (with account taken of the number of gained and lost electrons), we get the net equation of the reaction:

\[ \text{Zn} + 2\text{Ag}^+ = \text{Zn}^{2+} + 2\text{Ag} \]

Sometimes, the metal of an electrode does not change in an electrode process, but participates only in transferring electrons from the reduced form of a substance to its oxidized form. For example, in the galvanic cell

\[ \text{Pt} | \text{Fe}^{3+}, \text{Fe}^{2+} \parallel \text{MnO}_4^-, \text{Mn}^{2+}, \text{H}^+ | \text{Pt} \]

the role of the inert electrodes is played by the platinum. Iron(II) is oxidized at the platinum anode:

\[ \text{Fe}^{2+} = \text{Fe}^{3+} + e^- \]

and manganese(VII) is reduced at the platinum cathode:

\[ \text{MnO}_4^- + 8\text{H}^+ + 5e^- = \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

By multiplying the first of these equations by five and adding it to the second one, we get the net equation of the reaction:

\[ 5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ = 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

The maximum voltage of a galvanic cell corresponding to the reversible proceeding of a reaction in it is called the electromotive force (e.m.f.) \( E \) of the cell. If a reaction occurs in standard conditions, i.e. if all the substances participating in it are in their standard states, the observed e.m.f.
is called the standard electromotive force $E^\circ$ of the given cell.

The e.m.f. of a galvanic cell can be represented as the difference between two electrode potentials $\varphi$, each of which corresponds to a half-reaction occurring at one of the electrodes. For instance, for the silver-zinc cell considered above, the e.m.f. is equal to the difference

$$E = \varphi_{Ag} - \varphi_{Zn}$$

where $\varphi_{Ag}$ and $\varphi_{Zn}$ are the potentials corresponding to the electrode processes occurring at the silver and the zinc electrode, respectively.

In calculating the e.m.f., the lower (from the algebraic viewpoint) electrode potential is subtracted from the higher one.

The dependence of an electrode potential on the concentrations of the substances participating in the electrode processes and on temperature is expressed by the Nernst equation:

$$\varphi = \varphi^\circ + \frac{2.3RT}{zF} \log \frac{[Ox]}{[Red]}$$

where $\varphi^\circ$ is the standard electrode potential; $R$ is the molar gas constant; $T$ is the absolute temperature; $F$ is Faraday's constant (96,500 C/mol); $z$ is the number of electrons participating in the electrode process; $[Ox]$ and $[Red]$ are the products of the concentrations (activities) of the substances taking part in the relevant half-reaction in the oxidized (Ox) and reduced (Red) forms.

For example, for the electrode process $Fe^{3+} + e^- = Fe^{2+}$, we have $z = 1$, $[Ox] = [Fe^{3+}]$, and $[Red] = [Fe^{2+}]$.

For the half-reaction $MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$, we have $z = 5$, $[Ox] = [MnO_4^-]$ $[H^+]^5$, $[Red] = [Mn^{2+}]^5$.

When a process is conducted in standard conditions, the concentration (activity) of each substance participating in the reaction equals unity so that the logarithmic term in the Nernst equation vanishes and, consequently, $\varphi = \varphi^\circ$.

Thus, the standard electrode potential is defined as the potential of a given electrode at concentrations (activities) of all

* For dilute solutions, the concentration of the water $[H_2O]$ may be considered constant and included in $\varphi^\circ$. 
the substances participating in the electrode process equal to unity.

As applied to the examples of electrode processes considered above, the Nernst equation, after the values of \( R \), \( F \) and \( T \) are introduced into it, acquires the following form for 25 °C (298 K):

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Electrode process*</th>
<th>Nernst equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>Zn** + 2e^- = Zn</td>
<td>( \varphi = \varphi^0 + \frac{0.059}{2} \log [\text{Zn}^{2+}] )</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag* + e^- = Ag</td>
<td>( \varphi = \varphi^0 + 0.059 \log [\text{Ag}^+] )</td>
</tr>
<tr>
<td>Pt</td>
<td>Fe^3+, Fe^3+</td>
<td>( \varphi = \varphi^0 + 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} )</td>
</tr>
<tr>
<td>Pt</td>
<td>MnO_2, Mn^2+, H^+</td>
<td>MnO_2 + 8H^+ + 5e^- = Mn^{2+} + 4H_2O</td>
</tr>
</tbody>
</table>

* It is customary practice to write the equations of electrode processes in the direction of reduction (except when an oxidation process is being considered specially).

In the last of the examples considered, as in other cases when water participates in an electrode process, the electrode potential depends on the concentration of the H^+ (or OH^-) ions, i.e. on the pH of the solution.

The standard hydrogen electrode at which the process

\[ 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2 \]

occurs at an activity (concentration) of the hydrogen ions equal to unity (pH = 0), and a partial pressure of the gaseous hydrogen equal to standard atmospheric pressure conditionally taken as unity, is adopted as the reference electrode whose standard potential is assumed to be zero.

If, while keeping the partial pressure of the H\(_2\) constant, we change the concentration (activity) of the H\(^+\) ions in the solution, the potential of the hydrogen electrode will change and will no longer be zero; at 25 °C its value, as follows from the Nernst equation, is determined by the expression

\[ \varphi = -0.059pa(\text{H}^+) \]
or, without account taken of the activity coefficient:

\[ \varphi = -0.059pH \]

Particularly, in neutral solutions (pH = 7), \( \varphi = -0.059 \times 7 \approx -0.41 \text{ V} \).

Table 9 of the Appendix gives the values of the standard electrode potentials \( \varphi^o \) measured relative to the standard hydrogen electrode for a number of electrochemical systems*. The lower the algebraic value of \( \varphi^o \), the stronger are the reducing properties of the relevant electrochemical system; conversely, the higher the value of \( \varphi^o \), the stronger are the oxidizing properties of a system.

Assume that a galvanic cell consists of two electrodes (1 and 2) whose potentials are \( \varphi_1 \) and \( \varphi_2 \), and \( \varphi_1 > \varphi_2 \). This signifies that electrode 1 will be the positive and electrode 2 the negative pole of the cell whose e.m.f. equals the difference \( \varphi_1 - \varphi_2 \). A reduction half-reaction will proceed at electrode 1 (the cathode), and an oxidation half-reaction at electrode 2 (the anode).

**Example 1.** A galvanic cell consists of metallic zinc immersed in a 0.1 M zinc nitrate solution, and metallic lead immersed in a 0.02 M lead nitrate solution. Calculate the e.m.f. of the cell, write the equations of the electrode processes, and represent the cell schematically.

**Solution.** To find the e.m.f. of the cell, we must calculate the electrode potentials. For this purpose, in Table 9 of the Appendix, we find the values of the standard electrode potentials of the systems \( \text{Zn}^{2+}/\text{Zn} \) (–0.76 V) and \( \text{Pb}^{2+}/\text{Pb} \) (–0.13 V), and then calculate the values of \( \varphi \) by the Nernst equation:

\[
\begin{align*}
\varphi_{\text{Zn}} &= -0.76 + \frac{0.059}{2} \log 0.1 = -0.76 + 0.030(-1) = -0.79 \text{ V} \\
\varphi_{\text{Pb}} &= -0.13 + \frac{0.059}{2} \log 0.02 = -0.13 + 0.030(-1.7) = -0.18 \text{ V}
\end{align*}
\]

We find the e.m.f. of the cell:

\[ E = \varphi_{\text{Pb}} - \varphi_{\text{Zn}} = -0.18 - (-0.79) = 0.61 \text{ V} \]

Since \( \varphi_{\text{Pb}} > \varphi_{\text{Zn}} \), reduction will occur at the lead electrode, i.e. it will be the cathode:

\[ \text{Pb}^{2+} + 2e^- = \text{Pb} \]

* By an electrochemical system is meant a collection of substances participating in the relevant electrode process,
The oxidation process
\[ \text{Zn} = \text{Zn}^{2+} + 2e^- \]
will occur at the zinc electrode, i.e. it will be the anode.

This galvanic cell can be represented schematically as follows:
\[ \text{Zn} | \text{Zn(NO}_3\text{)}_2(0.1M) \parallel \text{Pb(NO}_3\text{)}_2(0.02M) | \text{Pb}^+ \]

Example 2. Calculate the potential of a silver electrode in a saturated solution of AgBr \((K_{\text{sp}} = 6 \times 10^{-13})\) containing, in addition, 0.1 mol/l of potassium bromide.

**Solution.** We write the Nernst equation for the system Ag\(^+\)/Ag:
\[ \varphi = \varphi^0 + 0.059 \log [\text{Ag}^+] \]

The value of \(\varphi^0\) for this system is (Table 9 of the Appendix) 0.8 V. Since the potassium bromide can be considered as completely dissociated, we have \([\text{Br}^-] = 0.1 \text{ mol/l}\). Hence we find the concentration of the silver ions:
\[ [\text{Ag}^+] = \frac{K_{\text{sp}}(\text{AgBr})}{[\text{Br}^-]} = \frac{6 \times 10^{-13}}{0.1} = 6 \times 10^{-12} \text{ mol/l} \]

We now introduce the values of \(\varphi^0\) and \([\text{Ag}^+]\) into the equation for the electrode potential:
\[ \varphi = 0.80 + 0.059 \log (6 \times 10^{-12}) = 0.80 + 0.059 (-12 + 0.78) = 0.80 - 0.66 = 0.14 \text{ V} \]

Example 3. Calculate the activity of the H\(^+\) ions in a solution in which the hydrogen electrode potential is −82 mV.

**Solution.** From the equation
\[ \varphi = -0.059 \ln a(\text{H}^+) \]
we find
\[ \ln a(\text{H}^+) = \frac{\varphi}{-0.059} = \frac{0.082}{0.059} = 1.39 \]
Consequently,
\[ -\log a(\text{H}^+) = 1.39; \log a(\text{H}^+) = -1.39 = 2.61 \]
whence
\[ a(\text{H}^+) = 0.041 \text{ mol/l} \]

A galvanic cell can be formed not only from different electrodes, but also from identical ones immersed in solutions of the same electrolyte that differ only in their concentration (concentration galvanic cells). As in the cases considered above, the e.m.f. of such a cell equals the difference between the potentials of the electrodes forming it.
Example 4. Determine the e.m.f. of the galvanic cell

\[ \text{Ag} \mid \text{AgNO}_3(0.001M) \parallel \text{AgNO}_3(0.1M) \mid \text{Ag} \]

In what direction will the electrons travel in the external circuit when this cell operates?

**Solution.** The standard electrode potential of the system Ag\(^+\)/Ag is 0.80 V. Denoting the potential of the left-hand electrode by \( \varphi_1 \), and of the right-hand one by \( \varphi_2 \), we obtain:

\[
\varphi_1 = 0.80 + 0.059 \log 0.001 = 0.80 + 0.059 (-3) = 0.62 \text{ V}
\]

\[
\varphi_2 = 0.80 + 0.059 \log 0.1 = 0.80 - 0.059 = 0.74 \text{ V}
\]

We calculate the e.m.f. of the cell:

\[
E = \varphi_2 - \varphi_1 = 0.74 - 0.62 = 0.12 \text{ V}
\]

Since \( \varphi_1 < \varphi_2 \), the left-hand electrode will be the negative pole of the cell, and the electrons will travel in the external circuit from the left-hand to the right-hand electrode.

**PROBLEMS**

631. Represent schematically two galvanic cells in one of which copper is the cathode and in the other, the anode. Write the equations of the reactions proceeding in the operation of these cells, and calculate the values of the standard e.m.f.’s.

632. In what direction will the electrons travel in the external circuit of the following galvanic cells:
   (a) Mg | Mg\(^2+\) || Pb\(^2+\) | Pb;
   (b) Pb | Pb\(^2+\) || Cu\(^2+\) | Cu;
   (c) Cu | Cu\(^2+\) || Ag\(^+\) | Ag if all the electrolyte solutions are monomolar? What metal will dissolve in each of these cases?

633. A galvanic cell consists of a silver electrode immersed in a 1 M AgNO\(_3\) solution and a standard hydrogen electrode. Write the equations of the electrode processes and the net reaction occurring in operation of the cell. What is its e.m.f.?

634. The e.m.f. of a galvanic cell consisting of a standard hydrogen electrode and a lead electrode immersed in a 1 M solution of a lead salt is 126 mV. When the circuit of the cell is closed, the electrons in the external circuit travel from the lead to the hydrogen electrode. What is the poten-

---

* In solving the problems of this section, use the table of standard electrode potentials (Table 9 of the Appendix) when needed.
tial of the lead electrode? Write the cell notation. What processes occur at its electrodes?

635. Calculate the electrode potentials of magnesium in a solution of its salt at Mg\(^{2+}\) ion concentrations of 0.1, 0.01, and 0.001 mol/l.

636. Calculate the potential of a hydrogen electrode immersed in pure water, in a solution with a pH of 3.5, and in a solution with a pH of 10.7.

637. The potential of a hydrogen electrode in an aqueous solution is -118 mV. Calculate the activity of the H\(^+\) ions in this solution.

638. Calculate the potential of a lead electrode in a saturated PbBr\(_2\) solution if [Br\(^-\)] = 1 mol/l and \(K_{sp}(PbBr_2) = 9.1 \times 10^{-8}\).

639. The e.m.f. of a cell consisting of a copper and a lead electrode immersed in 1 M solutions of salts of these metals is 0.47 V. Will the e.m.f. change if 0.001 M solutions are taken? Substantiate your answer.

640. Is it possible to form a galvanic cell in whose external circuit the electrons would travel from the electrode with a more positive standard potential to the electrode with a more negative standard potential? Explain your answer.

641. A galvanic cell is composed of a standard zinc electrode and a chromium electrode immersed in a solution containing Cr\(^{3+}\) ions. At what concentration of the Cr\(^{3+}\) ions will the e.m.f. of the cell be zero?

642. What processes occur at the electrodes of the galvanic cell Zn | Zn\(^{2+}\) (c\(_1\)) || Zn\(^{2+}\) (c\(_2\)) | Zn if c\(_1\) < c\(_2\)? In what direction do the electrons travel in the external circuit?

643. A galvanic cell consists of a standard hydrogen electrode and a hydrogen electrode immersed in a solution with a pH of 12. At which electrode will the hydrogen be oxidized during operation of the cell and at which one will it be reduced? Calculate the e.m.f. of the cell.

644. The e.m.f. of a galvanic cell composed of two hydrogen electrodes is 272 mV. What is the pH of the solution in which the anode is immersed if the cathode is in a solution with a pH of 3?

645. We have an oxidation-reduction system [Fe(CN)\(_6\)]\(^3-\) + + e\(^-\) ⇌ [Fe(CN)\(_6\)]\(^4-\). At what ratio of the concentrations
of the oxidized and reduced forms will the potential of the system be 0.28 V?

646. In what cases does the electrode potential depend on the pH of the solution? How will the electrode potentials of the following electrochemical systems change with a growth in the pH: (a) \( \text{CrO}_4^{2-} + 2\text{H}_2\text{O} + 3e^- \rightleftharpoons \text{CrO}_2^2 + 4\text{OH}^-; \) (b) \( \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}; \) (c) \( \text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}. \) Substantiate your answer.

**REVIEW QUESTIONS**

647. What is the potential of a hydrogen electrode at pH = 10? (a) -0.59 V; (b) -0.30 V; (c) 0.30 V; (d) 0.59 V.

648. By how much will the potential of a zinc electrode change if the solution of the zinc salt in which it is immersed is diluted 10 times? (a) It will grow by 59 mV; (b) it will diminish by 59 mV; (c) it will grow by 30 mV; (d) it will diminish by 30 mV.

649. A hydrogen electrode is immersed in a solution with pH = 0. By how much will the potential of the electrode change if the solution is neutralized to pH = 7? (a) It will grow by 0.41 V; (b) it will grow by 59 mV; (c) it will diminish by 0.41 V; (d) it will diminish by 59 mV.

650. How will the e.m.f. of the galvanic cell \( \text{Pb} | \text{Pb}^{2+} || \text{Ag}^+ | \text{Ag} \) change if hydrogen sulphide is added to the solution containing the lead ions? (a) It will grow; (b) it will diminish; (c) it will remain unchanged.

651. Which of the proposed ways can be used to increase the e.m.f. of the galvanic cell \( \text{Pt}, \text{H}_2 | \text{HCl} (c_1) || \text{HCl} (c_2) | \text{H}_2, \text{Pt}? \) (a) Diminish the concentration of the HCl at the cathode; (b) diminish the concentration of the HCl at the anode; (c) increase the concentration of the HCl at the cathode; (d) increase the concentration of the HCl at the anode.

652. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to obtain the maximum e.m.f.? (a) 0.1 \( M \) HCl; (b) 0.1 \( M \) CH\(_3\)COOH; (c) 0.1 \( M \) H\(_3\)PO\(_4\).
5. Direction of Oxidation-Reduction Reactions

In the operation of a galvanic cell, the electrochemical system with the higher value of the electrode potential is the oxidizing agent, and that with the lower value, the reducing agent.

As in any other spontaneous processes, a reaction in a galvanic cell is attended by diminishing of the Gibbs energy. But this means that upon the direct interaction of the reacting substances the reaction will proceed in the same direction. Hence, by comparing the electrode potentials of the relevant systems, we can determine the direction of an oxidation-reduction reaction beforehand.

Example 1. In what direction can the reaction

$$2\text{NaCl} + \text{Fe}_2(\text{SO}_4)_3 = 2\text{FeSO}_4 + \text{Cl}_2 + \text{Na}_2\text{SO}_4$$

proceed spontaneously?

*Solution*. The equation of the reaction in the net ionic form is

$$2\text{Cl}^- + 2\text{Fe}^{3+} = 2\text{Fe}^{2+} + \text{Cl}_2$$

We write the standard electrode potentials of the electrochemical systems participating in the reaction (Table 9 of the Appendix):

$$\text{Cl}_2 + 2e^- = 2\text{Cl}^- \quad \varphi_1^0 = 1.36 \text{ V}$$
$$\text{Fe}^{3+} + e^- = \text{Fe}^{2+} \quad \varphi_2^0 = 0.77 \text{ V}$$

Since $\varphi_1^0 > \varphi_2^0$, the chlorine will be the oxidizing agent, and the $\text{Fe}^{3+}$ ion, the reducing agent; the reaction will proceed from right to left.

In the last example, the standard electrode potentials of the reacting electrochemical systems differed quite appreciably so that the direction of the process was determined unambiguously by the values of $\varphi^0$ at any practically achievable concentrations of the reacting substances. When the values of $\varphi^0$ being compared are close, however, the direction of a process may change depending on the concentrations of the reaction participants.

Example 2. In what direction can the reaction

$$2\text{Hg} + 2\text{Ag}^+ = 2\text{Ag} + \text{Hg}_2^{2+}$$

proceed spontaneously at the following concentrations of the ions participating in the reaction: (a) $[\text{Ag}^+] = 10^{-4} \text{ mol/l}$ and $[\text{Hg}_2^{2+}] = 10^{-1} \text{ mol/l}$, and (b) $[\text{Ag}^+] = 10^{-1} \text{ mol/l}$ and $[\text{Hg}_2^{2+}] = 10^{-4} \text{ mol/l}$?
Solution. We write the values of the standard electrode potentials for the reacting electrochemical systems:

\[
\begin{align*}
\text{Hg}_2^+ + 2e^- &= 2\text{Hg} \quad \varphi_i^* = 0.79 \text{ V} \\
\text{Ag}^+ + e^- &= \text{Ag} \quad \varphi_i^* = 0.80 \text{ V}
\end{align*}
\]

We now calculate the values of the electrode potentials for the concentrations indicated in the data of the example:

(a) \(\varphi_1 = \varphi_i^* + \frac{0.059}{2} \log [\text{Hg}_2^+] = 0.79 + 0.030 \log 10^{-1} = 0.79 - 0.03 = 0.76 \text{ V}\)

\(\varphi_2 = \varphi_i^* + 0.059 \log [\text{Ag}^+] = 0.80 + 0.059 \log 10^{-4} = 0.80 - 0.24 = 0.56 \text{ V}\)

In the given case, \(\varphi_1 > \varphi_2\), and the reaction will proceed from right to left.

(b) \(\varphi_1 = 0.79 - 0.030 \log 10^{-4} = 0.79 - 0.12 = 0.67 \text{ V}\)

\(\varphi_2 = 0.80 + 0.059 \log 10^{-1} = 0.80 - 0.06 = 0.74 \text{ V}\)

Now \(\varphi_1 < \varphi_2\), and the reaction will proceed from left to right.

The standard e.m.f. \(E^0\) of a galvanic cell is related to the standard Gibbs energy \(\Delta G^0\) of the reaction proceeding in the cell by the expression

\[zFE^0 = -\Delta G^0\]

where \(z\) is the number of electrons participating in the reaction, and \(F\) is Faraday’s constant.

On the other hand, \(\Delta G^0\) is related to the equilibrium constant \(K\) of a reaction by the equation (see p. 104):

\[\Delta G^0 = - 2.3RT \log K\]

It follows from the last two equations that

\[zFE^0 = 2.3RT \log K\]

This equation allows us to calculate the equilibrium constant of an oxidation-reduction reaction according to the experimentally determined value of the standard e.m.f.

For 25 °C (298 K), the last equation after introducing the values of \(R\) [8.31 J/(mol·K)] and \(F\) (96 500 C/mol) into it acquires the form

\[
\log K = \frac{zE^0}{0.059}
\]
Example 3. Find the equilibrium constant at 25 °C for the reaction
\[ \text{Hg}^2+ (\text{NOS}_2) + 2\text{Fe(NOS}_2)_2 = 2\text{Hg} + 2\text{Fe(NOS}_2)_2 \]

**Solution.** The net ionic equation of the reaction is
\[ \text{Hg}^2+ + 2\text{Fe}^2+ = 2\text{Hg} + 2\text{Fe}^3+ \]

Two electrochemical systems participate in the reaction:
\[ \text{Hg}^2++2\text{e}^- = 2\text{Hg} \quad \varphi^o_1 = 0.79 \text{ V} \]
\[ \text{Fe}^3++\text{e}^- = \text{Fe}^2+ \quad \varphi^o_2 = 0.77 \text{ V} \]

We find the value of the standard e.m.f. for the cell being considered:
\[ E^o = \varphi^o_1 - \varphi^o_2 = 0.79 - 0.77 = 0.02 \text{ V} \]

We now calculate the equilibrium constant of the reaction:
\[ \log K = \frac{2E^o}{0.059} = \frac{2 \times 0.02}{0.059} = 0.678; \quad K = 4.76 \]

**PROBLEMS** *

653. Indicate the direction in which the following reactions can proceed spontaneously:
(a) \[ \text{H}_2\text{O}_2 + \text{HClO} = \text{HCl} + \text{O}_2 + \text{H}_2\text{O} \]
(b) \[ 2\text{HIO}_3 + 5\text{H}_2\text{O}_2 = \text{I}_2 + 5\text{O}_2 + 6\text{H}_2\text{O} \]
(c) \[ \text{I}_2 + 5\text{H}_2\text{O}_2 = 2\text{HIO}_3 + 4\text{H}_2\text{O} \]

654. Which of the following reactions can proceed spontaneously:
(a) \[ \text{H}_3\text{PO}_4 + 2\text{HI} = \text{H}_3\text{PO}_3 + \text{I}_2 + \text{H}_2\text{O} \]
(b) \[ \text{H}_3\text{PO}_3 + \text{SnCl}_4 + \text{H}_2\text{O} = 2\text{HCl} + \text{Sn} + \text{H}_3\text{PO}_4 \]
(c) \[ \text{H}_3\text{PO}_3 + \text{Pb(NO}_3)_2 + \text{H}_2\text{O} = \text{Pb} + 2\text{HNO}_3 + \text{H}_3\text{PO}_4 \]
(d) \[ \text{H}_3\text{PO}_3 + 2\text{AgNO}_3 + \text{H}_2\text{O} = 2\text{Ag} + 2\text{HNO}_3 + \text{H}_3\text{PO}_4 \]

655. Can a salt of iron(III) be reduced to a salt of iron(II) in an aqueous solution by (a) potassium bromide, (b) potassium iodide?

656. Using the table of standard electrode potentials, calculate the equilibrium constants for the following reactions:
(a) \[ \text{Zn} + \text{CuSO}_4 = \text{Cu} + \text{ZnSO}_4 \]
(b) \[ \text{Sn} + \text{Pb(CH}_3\text{COO})_2 = \text{Sn(CH}_3\text{COO})_2 + \text{Pb} \]

* In solving the problems of this section, use the values of the standard electrode potentials (Table 9 of the Appendix).
657. Calculate the equilibrium constants for the reactions proceeding (a) in a cadmium-zinc galvanic cell, and (b) in a copper-lead cell.

658. Can tin(IV) be reduced to tin(II) with the aid of the following reactions?

(a) \( \text{SnCl}_4 + 2\text{KI} = \text{SnCl}_2 + \text{I}_2 + 2\text{KCl} \)

(b) \( \text{SnCl}_4 + \text{H}_2\text{S} = \text{SnCl}_2 + \text{S} + 2\text{HCl} \)

Substantiate your answer by calculating the equilibrium constants for the reactions.

REVIEW QUESTIONS

659. Nickel plates are lowered into aqueous solutions of the salts listed below. With which salts will the nickel react? (a) MgSO₄; (b) NaCl; (c) CuSO₄; (d) AlCl₃; (e) ZnCl₂; (f) Pb(NO₃)₂.

660. Between which of the pairs of substances (metal + aqueous electrolyte solution) listed below will a displacement reaction proceed? (a) Fe + HCl; (b) Ag + Cu(NO₃)₂; (c) Cu + HCl; (d) Zn + MgSO₄; (e) Mg + NiCl₂.

661. An aqueous solution of H₂S has reducing properties. Which of the ions listed below can be reduced by this solution? (a) Fe³⁺ to Fe²⁺; (b) Cu²⁺ to Cu⁺; (c) Sn⁴⁺ to Sn²⁺.

662. Bromine water (a solution of bromine in water) is an oxidizing agent often used in the laboratory. Which of the following ions can be oxidized with bromine water? (a) Fe³⁺ to Fe⁴⁺; (b) Cu⁺ to Cu²⁺; (c) Mn³⁺ to MnO₄⁻; (d) Sn⁴⁺ to Sn²⁺.

663. A solution of copper(II) sulphate is reacted with potassium chloride or potassium iodide. In which cases will the copper(II) be reduced to copper(I)? (a) In both cases; (b) when reacted with KCl; (c) when reacted with KI; (d) in none of the cases.

664. Which of the following reactions can proceed spontaneously when an aqueous solution of potassium permanganate is reacted with silver?

(a) \( \text{MnO}_4^- + \text{Ag} = \text{MnO}_2^- + \text{Ag}^+ \)

(b) \( \text{MnO}_4^- + 3\text{Ag}^+ + 2\text{H}_2\text{O} = \text{MnO}_2^- + 3\text{Ag} + 4\text{OH}^- \)

(c) \( \text{MnO}_4^- + 8\text{H}^+ + 5\text{Ag} = \text{Mn}^{2+} + 5\text{Ag}^+ + 4\text{H}_2\text{O} \)
665. Which of the following reactions can proceed spontaneously in a neutral aqueous solution?

(a) $\text{MnO}_4^- + \text{Cl}^- \rightarrow \text{MnO}_2 + \text{Cl}_2$
(b) $\text{MnO}_4^- + \text{Br}^- \rightarrow \text{MnO}_2 + \text{Br}_2$
(c) $\text{MnO}_4^- + \text{I}^- \rightarrow \text{MnO}_2 + \text{I}_2$

666. In an aqueous solution, $[\text{Hg}^{2+}] = 0.01 \text{ mol/l}$, $[\text{Fe}^{3+}] = 0.01 \text{ mol/l}$, $[\text{Fe}^{2+}] = 0.001 \text{ mol/l}$. Which of the following reactions will proceed?

(a) $2\text{FeCl}_3 + \text{Hg} = 2\text{FeCl}_2 + \text{HgCl}_2$
(b) $\text{HgCl}_2 + 2\text{FeCl}_2 = \text{Hg} + 2\text{FeCl}_3$

6. Electrolysis

By electrolysis is meant the collection of processes occurring when a direct current passes through a system consisting of two electrodes and a melt or solution of an electrolyte.

As in a galvanic cell, the electrode at which reduction occurs in electrolysis is called the cathode, and the one at which oxidation occurs is called the anode.

If a system in which electrolysis is being conducted contains various oxidizing agents, the most active of them will be reduced at the cathode, i.e. the oxidized form of the electrochemical system which the maximum value of the electrode potential corresponds to. For example, in the electrolysis of an acidic aqueous solution of a nickel salt at standard concentrations (or, more exactly, activities) of the $\text{H}^+$ and $\text{Ni}^{2+}$ ions ($[\text{H}^+] = [\text{Ni}^{2+}] = 1 \text{ mol/l}$), reduction of both the nickel ion

$$\text{Ni}^{2+} + 2e^- = \text{Ni} \quad \varphi_1 = -0.25 \text{ V}$$

and the hydrogen ion:

$$2\text{H}^+ + 2e^- = \text{H}_2 \quad \varphi_2 = 0$$

is possible.

But since $\varphi_1 < \varphi_2$, hydrogen will be liberated at the cathode in these conditions.

The cathode process will be different in the electrolysis of a neutral aqueous solution ($[\text{H}^+] = 10^{-7} \text{ mol/l}$) of a nickel salt. Here the potential of the hydrogen electrode is $\varphi_3 =$
= \(-0.41\) V (see p. 186). In this case at the previous concentration of the nickel ion (1 mol/l), we have \(\varphi_1 > \varphi_2\), and nickel will be deposited at the cathode.

The above example shows that in the electrolysis of aqueous solutions of salts that are close to neutral, metals whose electrode potentials are appreciably more positive than \(-0.41\) V are reduced at the cathode. If the potential of a metal is considerably more negative than \(-0.41\) V, hydrogen will be liberated at the cathode*. At values of the electrode potential of a metal close to \(-0.41\) V, both reduction of the metal and liberation of hydrogen (or the joint occurrence of both processes) are possible depending on the concentration of the metal salt and the electrolysis conditions.

Similarly, when a system undergoing electrolysis contains several reducing agents, the more active of them will be oxidized at the anode, i.e. the reduced form of the electrochemical system that is characterized by the smallest value of the electrode potential. For instance, in the electrolysis of an aqueous solution of copper sulphate with inert electrodes (for instance, of carbon), both the sulphate ion may be oxidized at the anode:

\[
2\text{SO}_4^{2-} = \text{S}_2\text{O}_3^{-} + 2\text{e}^- \quad \varphi_1^* = 2.01 \text{ V}
\]

and water**:

\[
2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad \varphi_2^* = 1.23 \text{ V}
\]

Since \(\varphi_2^* \ll \varphi_1^*\), the second of the possible processes will occur in the given case, and oxygen will be liberated at the anode. If the inert electrode is replaced with a copper one, however, another oxidizing process—the anode dissolving of copper—becomes possible, namely:

\[
\text{Cu} = \text{Cu}^{2+} + 2\text{e}^- \quad \varphi_3^* = 0.34 \text{ V}
\]

* It must be borne in mind that in the electrolysis of neutral or basic solutions, the liberation of hydrogen at the cathode is a result of the electrochemical reduction of water:

\[
2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_2 + 2\text{OH}^{-}
\]

** In basic solutions, the liberation of oxygen at the anode is a result of the process:

\[
4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-
\]
This process is characterized by a lower value of the electrode potential than for the other possible anode processes ($\varphi_2^* \ll \varphi_1^*$ and $\varphi_2^* \ll \varphi_3^*$). Consequently, in these conditions, copper will be oxidized at the anode.

In the electrolysis of aqueous solutions of nitrates, perchlorates, and phosphates, like sulphates, the water is usually oxidized at an inert anode with the formation of free oxygen. But other oxygen-containing anions in the electrolysis of aqueous solutions of their salts may undergo anode oxidation. The processes occurring at an inert anode in the electrolysis of the salts of certain chlorine acids in a basic solution are an example:

$$\text{ClO}_3^- + 4\text{OH}^- = \text{ClO}_4^- + 2\text{H}_2\text{O} + 4e^- \quad \varphi^0 = 0.50 \text{ V}$$

$$\text{ClO}_4^- + 2\text{OH}^- = \text{ClO}_4^- + \text{H}_2\text{O} + 2e^- \quad \varphi^0 = 1.19 \text{ V}$$

In the electrolysis of aqueous solutions of chlorides, two processes are possible at an inert anode:

$$2\text{Cl}^- = \text{Cl}_2 + 2e^- \quad \varphi_1^* = 1.36 \text{ V}$$

$$2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4e^- \quad \varphi_2^* = 1.23 \text{ V}$$

Although here $\varphi_1^* > \varphi_2^*$, it is the first process that occurs (oxidation of the chloride ion). This is associated with the considerable overvoltage of the second process: the material of the anode inhibits its proceeding.

**Example 1.** Write the equations of the processes occurring in the electrolysis of an aqueous solution of sodium sulphate with an inert anode.

**Solution.** The standard electrode potential of the system $\text{Na}^+ + e^- = \text{Na}^- (-2.71 \text{ V})$ is considerably more negative than the potential of a hydrogen electrode in a neutral aqueous medium ($-0.41 \text{ V}$). Therefore, the electrochemical reduction of water attended by the liberation of hydrogen will occur at the cathode:

$$2\text{H}_2\text{O} + 2e^- = \text{H}_2\uparrow + 2\text{OH}^-$$

while the $\text{Na}^+$ ions migrating to the cathode will accumulate in the part of the solution adjoining it (the cathode space).

The electrochemical oxidation of water leading to the liberation of oxygen will occur at the anode:

$$2\text{H}_2\text{O} = \text{O}_2\uparrow + 4\text{H}^+ + 4e^-$$

because the standard electrode potential corresponding to this system ($1.23 \text{ V}$) is considerably lower than the standard electrode potential ($2.01 \text{ V}$) characterizing the system $2\text{SO}_4^2- = \text{S}_2\text{O}_7^{2-} + 2e^-$. The $\text{SO}_4^{2-}$ ions migrating in electrolysis to the anode will accumulate in the anode space.
Multiplying the equation of the cathode process by two and adding it to the equation of the anode process, we get the net equation of the electrolysis process:

\[
6\text{H}_2\text{O} = 2\text{H}_2 \uparrow + 4\text{OH}^- + \text{O}_2 \uparrow + 4\text{H}^+
\]

(at cathode) (at anode)

Taking into account that electrolysis is attended by the accumulation of Na\(^+\) ions in the cathode space and SO\(_4\)\(^-\) ions in the anode space, the net equation of the process can be written as follows:

\[
6\text{H}_2\text{O} + 2\text{Na}_2\text{SO}_4 = 2\text{H}_2 \uparrow + 4\text{Na}^+ + 4\text{OH}^- + \text{O}_2 \uparrow + 4\text{H}^+ + 2\text{SO}_4^-
\]

(at cathode) (at anode)

Consequently, sodium hydroxide (in the cathode space) and sulphuric acid (in the anode space) will be formed simultaneously with the liberation of hydrogen and oxygen.

Electrolysis processes are characterized quantitatively by laws established by Michael Faraday. They can be given the following general formulation (Faraday’s law): the mass of an electrolyte transformed in electrolysis and also the mass of the substances formed at the electrodes are directly proportional to the amount of electricity that has passed through the electrolyte solution or melt, and to the equivalent masses of the relevant substances.

Faraday’s law is expressed by the following equation:

\[
m = \frac{m_{\text{eq}}It}{F}
\]

where \(m\) is the mass of the substance that has been formed or transformed; \(m_{\text{eq}}\) is its equivalent mass; \(I\) is the current; \(t\) is the time; and \(F\) is Faraday’s constant (96 500 C/mol), i.e. the amount of electricity needed for the electrochemical transformation of one equivalent of a substance.

**Example 2.** A current of 2.5 A passing through an electrolyte solution deposits 2.77 g of a metal in 30 min. Find the equivalent mass of the metal.

**Solution.** We solve the equation of Faraday’s law relative to the equivalent mass of the metal and introduce the data of the example into it (\(m = 2.77\) g, \(I = 2.5\) A, and \(t = 30\) min = 1800 s):

\[
m_{\text{eq}} = \frac{mF}{It} = \frac{2.77 \times 96 500}{2.5 \times 1800} = 59.4 \text{ g/mol}
\]
Example 3. A current of 6 A was passed through an aqueous solution of sulphuric acid during 1.5 h. Calculate the mass of the decomposed water and the volume of the liberated oxygen and hydrogen (in standard conditions).

Solution. We find the mass of the decomposed water from the equation of Faraday’s law, bearing in mind that 1.5 h = 5400 s and $m_{eq}(H_2O) = 9$ g/mol:

$$m(H_2O) = \frac{m_{eq}It}{F} = \frac{9 \times 6 \times 5400}{96 500} = 3.02 \text{ g}$$

In calculating the volumes of liberated gases, we can write the equation of Faraday’s law as follows:

$$V = \frac{V_{eq}It}{F}$$

where $V$ is the volume of the gas, litres, and $V_{eq}$ is its equivalent volume, l/mol.

Since in standard conditions the equivalent volume of hydrogen is 11.2 l/mol, and that of oxygen is 5.6 l/mol, we get:

$$V(H_2) = \frac{11.2 \times 6 \times 5400}{96 500} = 3.76 \text{ litres;}$$

$$V(O_2) = \frac{5.6 \times 6 \times 5400}{96 500} = 1.88 \text{ litres}$$

PROBLEMS*

667. Compile the equations of the processes occurring in the electrolysis of NaOH and NiCl₂ melts using inert electrodes.

668. Represent schematically the electrolysis of aqueous solutions of H₂SO₄, CuCl₂, and Pb(NO₃)₂ with platinum electrodes.

669. Write the equations of the electrode processes occurring in the electrolysis of aqueous solutions of BaCl₂ and Pb(NO₃)₂ with carbon electrodes.

670. Write the equations of the electrode processes occurring in the electrolysis of aqueous solutions of FeCl₃ and Ca(NO₃)₂ with an inert electrode.

671. Represent schematically the electrolysis of an aqueous zinc chloride solution if (a) the anode is of zinc, and (b) the anode is of carbon.

* In solving the problems of this section, use the values of the standard electrode potentials (Table 9 of the Appendix) when needed.
672. Represent schematically the electrolysis of an aqueous copper sulphate solution if (a) the anode is of copper, and (b) the anode is of carbon.

673. In what sequence will the metals be deposited in the electrolysis of a solution containing nickel, silver, and copper sulphates in the same concentration?

674. A solution contains $\text{Fe}^{2+}$, $\text{Ag}^+$, $\text{Bi}^{3+}$, and $\text{Pb}^{2+}$ ions in the same concentration. In what sequence will these ions be deposited in electrolysis if the voltage is sufficient for the deposition of any metal?

675. Represent schematically the processes occurring at copper electrodes in the electrolysis of an aqueous $\text{KNO}_3$ solution.

676. We have a solution containing $\text{KCl}$ and $\text{Cu(NO}_3\text{)}_2$. Propose the simplest way of obtaining virtually pure $\text{KNO}_3$.

677. Nickel precedes hydrogen in the electromotive series. Explain why the electrolytic separation of nickel from aqueous solutions of its salts is possible.

678. Unrefined copper contains admixtures of silver and zinc. What will happen to these admixtures in the electrolytic refining of copper?

679. In the electrolysis of a $\text{CuCl}_2$ solution, 560 ml of a gas were liberated at the anode (in standard conditions). Find the mass of the copper deposited at the cathode.

680. What mass of silver will be deposited when a current of 6 A is passed through a silver nitrate solution for 30 min?

681. How much time is needed for the complete decomposition of two moles of water using a current of 2 A?

682. How can $\text{LiOH}$ be prepared electrolytically from a lithium salt? What amount of electricity is needed to produce one tonne of $\text{LiOH}$? Represent the electrode processes schematically.

683. What volume of oxygen (in standard conditions) is liberated when a current of 6 A is passed through an aqueous $\text{KOH}$ solution for 30 min?

684. What volume of hydrogen (in standard conditions) is liberated when a current of 3 A is passed through an aqueous $\text{H}_2\text{SO}_4$ solution for one hour?

685. What amount of electricity is needed to liberate from a solution (a) 2 g of hydrogen, and (b) 2 g of oxygen?
686. In the electrolysis of an aqueous \( \text{Cr}_2(\text{SO}_4)_3 \) solution using a current of 2 A, the mass of the cathode increased by 8 g. How long was electrolysis conducted?

687. In the electrolysis of an aqueous \( \text{SnCl}_2 \) solution, 4.48 litres of chlorine (in standard conditions) were liberated at the anode. Find the mass of the tin deposited at the cathode.

688. A current of 5 A deposited 1.517 g of Pt in 10 min from a solution of a platinum salt. Find the equivalent mass of the platinum.

689. What is the equivalent mass of cadmium if 1717 C of electricity have to be passed through a solution of its salt to deposit 1 g of cadmium?

690. When a current of 1.5 A was passed for 30 min through a solution of a salt of a trivalent metal, 1.071 g of the metal were deposited at the cathode. Calculate the atomic mass of the metal.

**REVIEW QUESTIONS**

691. Which process occurs in the electrolysis of an aqueous tin(II) chloride solution at a tin anode? (a) \( \text{Sn} \rightarrow \text{Sn}^{2+} + + 2e^- \); (b) \( 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^- \); (c) \( 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \).

692. In the electrolysis of an aqueous nickel(II) sulphate solution, the process \( 2\text{H}_2\text{O} = 2\text{O}_2 + 4\text{H}^+ + 4e^- \) occurs at the anode. What material is the anode made from? (a) Nickel; (b) copper; (c) gold.

693. In the electrolysis of an aqueous potassium sulphate solution, the pH of the solution in the space near an electrode increased. Which pole of the current source is the electrode connected to? (a) The positive pole; (b) the negative pole.

694. In the electrolysis of an aqueous solution of a salt, the pH in the space near one of the electrodes increased. A solution of which salt was being electrolyzed? (a) KCl; (b) CuCl_2; (c) Cu(NO_3)_2.

695. In the electrolysis of an aqueous solution of NaOH, 2.8 litres of oxygen were liberated at the anode (in standard conditions). How much hydrogen was liberated at the cathode? (a) 2.8 litres; (b) 5.6 litres; (c) 11.2 litres; (d) 22.4 litres.
696. In the electrolysis of a copper(II) chloride solution, the mass of the cathode increased by 3.2 g. What occurred at the copper anode?
(a) 0.112 litre of \( \text{Cl}_2 \) was liberated;
(b) 0.56 litre of \( \text{O}_2 \) was liberated;
(c) 0.1 mol of \( \text{Cu}^{2+} \) passed into the solution;
(d) 0.05 mol of \( \text{Cu}^{2+} \) passed into the solution.
1. Determining the Composition of a Complex Ion

By complex compounds are meant definite chemical compounds formed by a combination of individual components and that are complex ions or molecules capable of existing in both the crystalline and the dissolved state.

In a molecule of a complex compound, one of the atoms, generally with a positive charge, occupies the central site and is called the complexing agent or central atom (ion). Around it in direct proximity are arranged (or, as we say, coordinated) oppositely charged ions or neutral molecules called ligands. The complexing agent and the ligands form the inner sphere of a complex compound. The total number of sigma bonds formed by the complexing agent with the ligands is known as the coordination number of the central ion. In accordance with the number of sigma bonds formed by a ligand with the complexing agent, the ligand may be a monodentate, bidentate, or polydentate.

Outside the limits of the inner sphere of a complex compound is its outer sphere containing positively charged ions (if the inner sphere of the complex compound is charged negatively) or negatively charged ions (if the complex ion is charged positively). When the inner sphere has no charge, the outer sphere is absent.

The ions in the outer sphere are mainly bonded to the complex ion by forces of electrostatic interaction and readily detach themselves in solutions, like the ions of strong electrolytes. The ligands in the inner sphere of a complex have covalent bonds with the complexing agent, and they dissociate in a solution, as a rule, only insignificantly. For this reason, qualitative chemical reactions make it possible to detect only outer sphere ions. When writing
formulas of complex compounds, the inner sphere is separated from the outer one by brackets.

Example 1. Only two-thirds of the chlorine contained in a solution of the complex salt CoCl₃·5NH₃ were precipitated from it by silver nitrate. No cobalt ions or free ammonia were detected in the solution of the salt. The electrical conductivity of the solution shows that the salt dissociates into three ions. What is the coordination structure of this compound? Write the equation of dissociation of the complex salt.

Solution. The absence of Co³⁺ ions and free ammonia in the solution of the above salt signifies that these components are in the inner sphere of the complex compound. Also, the inner sphere includes one chloride ion that is not precipitated by the AgNO₃. Hence, the composition of the inner sphere corresponds to the formula [CoCl₃(NH₃)₅]²⁺. The outer sphere contains two chloride ions compensating the charge of the inner sphere of the complex: [CoCl₃(NH₃)₅]Cl₂. The complex salt dissociates in solution as follows:

\[ [\text{CoCl}_3(\text{NH}_3)_5]\text{Cl}_2 = [\text{CoCl}_3(\text{NH}_3)_5]^{2+} + 2\text{Cl}^- \]

which agrees with the data on the electrical conductivity.

In calculating the charge of a complex ion, one must proceed from the fact that this charge equals the algebraic sum of the charges of the complexing agent and the ligands; the charge of the complexing agent is taken equal to its oxidation state.

Example 2. Calculate the charges of the following complex ions formed by chromium(III): (a) [CrCl(H₂O)₅]; (b) [CrCl₂(H₂O)₄]; and (c) [Cr(C₂O₄)₃(H₂O)]⁻.

Solution. We take the charge of the chromium(III) ion equal to +3, the charge of a water molecule is zero, and the charges of the chloride and oxalate ions are −1 and −2, respectively. We compute the algebraic sum of the charges for each of the above compounds: (a) +3 + (+(-1)) = +2; (b) +3 + 2(-1) = +1; and (c) +3 + 2(-2) = −1.

PROBLEMS

697. Silver nitrate precipitates the entire chlorine as silver chloride from a solution of the complex salt PtCl₄·6NH₃, and only one-fourth of the chlorine from a solution of the salt PtCl₄·3NH₃. Write the coordination formulas of these salts, and determine the coordination number of the platinum in each of them.

698. Two complex salts of cobalt are known corresponding to the same empirical formula CoBrSO₄·5NH₃. They differ
in that a solution of one salt gives a precipitate with BaCl₂, but does not form a precipitate with AgNO₃, whereas a solution of the other salt, on the contrary, gives a precipitate with AgNO₃, but does not form a precipitate with BaCl₂. Write the coordination formulas of both salts and the equations of their dissociation into ions.

699. A sufficient amount of an AgNO₃ solution was added to a solution containing 23.35 g of the complex salt CoCl₃·4NH₃. The mass of the precipitated AgCl was 14.35 g. Derive the coordination formula of the salt.

700. The empirical formula of a salt is CrCl₃·5H₂O. If the coordination number of the chromium is six, calculate the volume of a 0.1 N solution of AgNO₃ needed to precipitate the chlorine with an outer sphere bond contained in 200 ml of a 0.01 M solution of the complex salt; assume all the water in the salt to be in the inner sphere.

701. Write the equations of the exchange reactions proceeding between (a) K₄[Fe(CN)₆] and CuSO₄; (b) Na₃[Co(CN)₆] and FeSO₄; and (c) K₃[Fe(CN)₆] and AgNO₃ in the molecular and net ionic forms, bearing in mind that the complex salts formed are insoluble in water.

702. Find the charges of the following complex particles and indicate the cations, anions, and non-electrolytes among them: [Co(NH₃)₆Cl], [Cr(NH₃)₄PO₄], [Ag(NH₃)₃], [Cr(OH)₄], [Co(NH₃)₃(NO₃)₃], [Cu(H₂O)₄].

703. Determine the oxidation state of the complexing agent in the following complex ions:

- [Fe(CN)₆]⁴⁻
- [Ni(NH₃)₆Cl]⁺
- [Co(NH₃)₃(NO₃)₄]⁻
- [Cr(H₂O)₄Br₃]⁺
- [AuCl₄]⁻
- [Hg(CN)₄]²⁻
- [Cd(CN)₄]³⁻

2. Nomenclature of Complex Compounds

The names of complex salts are formed according to the general rule: first the cation is named, and then the anion. The name of a complex cation is formed as follows: first the negatively charged ligands are named, and their Latin names take an -o ending (Cl⁻ is chloro, SO₄²⁻ is sulphato, OH⁻ is hydroxo, etc.). Next the neutral ligands are named,
aqua and amm ine being used for water and ammonia, respectively. The number of identical negatively charged or neutral ligands is indicated by the Greek prefixes mono- for 1 (often omitted), di- (2), tri- (3), tetra- (4), penta- (5), hexa- (6), etc. After this, the central atom is named (using its trivial name) with a Roman numeral in parentheses to indicate the oxidation state. The complex part is written all as a single word with the oxidation state as part of the word.

Example 1. Name the complex salts: \([\text{Pt}(\text{NH}_3)_2\text{Cl}]\text{Cl}\) and \([\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4\).

*Solution.* The name of \([\text{Pt}(\text{NH}_3)_2\text{Cl}]\text{Cl}\) is chlorotriammineplatinum(II) chloride, and that of \([\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4\) is bromopentamminecobalt(III).

The name of a complex anion is formed similar to that of a cation, except that the central atom takes an -ate ending, and the Latin names are used for Fe, Cu, Sn, Pb, and Ag.

Example 2. Name the salts \(\text{Ba}[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]_2\) and \((\text{NH}_4)_2[\text{Pt}(\text{OH})_2\text{Cl}_4]\).

*Solution.* The name of \(\text{Ba}[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]_2\) is barium tetrathiocyanodiamminechromate(III), and that of \((\text{NH}_4)_2[\text{Pt}(\text{OH})_2\text{Cl}_4]\) is ammonium dihydroxotetrachloroplatinate(IV).

The names of neutral complex particles are formed similarly to those of cations, except that the oxidation state is not indicated because it is determined by the electroneutrality of the complex. For example, the name of \([\text{Pt}(\text{NH}_3)_2\text{Cl}_2]\) is dichlorodiammineplatinum.

**PROBLEMS**

704. Name the following complex salts:

- \([\text{Pd}(\text{H}_2\text{O})(\text{NH}_3)_2\text{Cl}]\text{Cl}\)
- \([\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2]\)
- \([\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})\text{CN}]\text{Br}_2\)
- \([\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3\)
- \([\text{Pd}(\text{NH}_3)_2\text{Cl}]\text{Cl}\)
- \(\text{K}_4[\text{Fe}(\text{CN})_6]\)

705. Write the coordination formulas for the following complex compounds: (a) potassium dicyanoargentate; (b) potassium hexanitrocobaltate(III); (c) hexamminenickel(II)
complex compounds:

chloride; (d) sodium hexacyanochromate (III); (e) hexam-
minecobalt(III) bromide; (f) carbonatotetramminechromi-
um (III) sulphate; (g) diaquatetramminenickel (II) nitrate;
(h) magnesium trifluorohydroxoberyllate.

706. Name the following electroneutral complex com-
ounds:

\[ \text{[Cr(H}_2\text{O})_4\text{PO}_4\text{]}_2 \quad \text{[Rh(NH}_3\text{)}_3\text{(NO}_3\text{)}_2\text{]} \]
\[ \text{[Cu(NH}_3\text{)}_2\text{(SCN)}_2\text{]} \quad \text{[Pt(NH}_3\text{)}_2\text{Cl}_4\text{]} \]
\[ \text{[Pd(NH}_3\text{OH})_2\text{Cl}_3\text{]} \]

707. Write the formulas of the following complex non-
electrolytes: (a) phosphatotetramminechromium; (b) di-
chlorodiammineplatinum; (c) trichlorotriamminecobalt; (d)
tetrachlorodiammineplatinum. Indicate the oxidation state
of the complexing agent in each of the complexes.

708. Write the formulas of potassium hexacyanoferrate(II)
and potassium hexacyanoferrate(III).

709. The brick red crystals of roseo-cobaltichloride have
a composition expressed by the formula \[ \text{[Co(NH}_3\text{)}_6\text{(H}_2\text{O})\text{]}\text{Cl}_3 \],
and the crimson red crystals of purpureo-cobaltichloride—
the composition \[ \text{[Co(NH}_3\text{)}_6\text{Cl}][\text{Cl}_2\text{]} \]. Give the formal chemical
names of these salts.

3. Equilibria in Solutions
of Complex Compounds

The outer sphere dissociation of complex salts goes vir-
tually to the end in aqueous solutions, for instance:
\[ \text{[Ag(NH}_3\text{)}_2\text{]}\text{Cl} \rightarrow \text{[Ag(NH}_3\text{)}_2\text{]}^+ + \text{Cl}^- \]. This dissociation is
called primary. The reversible decomposition of the inner
sphere of a complex compound is known as secondary dis-
sociation. For example, the diamminesilver ion dissociates
as follows:
\[ \text{[Ag(NH}_3\text{)}_2\text{]}^+ \rightleftharpoons \text{Ag}^+ + 2\text{NH}_3 \]

Secondary dissociation results in equilibrium being estab-
lished between the complex particle, the central ion, and
the ligands. The dissociation of \[ \text{[Ag (NH}_3\text{)}_2\text{]}^+ \] according
to the above equation is characterized by an equilibrium
constant called the instability constant of the complex ion:

\[ K_{\text{inst}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag(NH}_3\text{)}_2]^+} = 6.8 \times 10^{-8} \]
The values of the instability constants for various complex ions fluctuate within broad limits and are a measure of the stability of a complex. The more stable is a complex ion, the smaller is its instability constant. For instance, among the following compounds of the same type having various values of their instability constants:

\[
\begin{array}{cccc}
[\text{Ag(NO}_2\text{)}_2^-] & [\text{Ag(NH}_3\text{)}_2]^+ & [\text{Ag(S}_2\text{O}_3\text{)}_2]^3- & [\text{Ag(CN)}_2^-] \\
1.3 \times 10^{-3} & 6.8 \times 10^{-6} & 1 \times 10^{-13} & 1 \times 10^{-21}
\end{array}
\]

the complex \([\text{Ag(CN)}_2^-]\) is the most stable, and \([\text{Ag(NO}_2\text{)}_2^-]\) is the least stable.

The values of the instability constants for selected complexes are given in Table 10 of the Appendix.

Instability constants whose expressions include the concentrations of ions and molecules are called concentration ones. Instability constants containing the activities of ions and molecules instead of their concentrations are stricter and do not depend on the composition and ionic strength of a solution. Below, in solving problems, we shall consider the solutions to be sufficiently dilute so as to assume that the activity coefficients of the components of a system equal unity and use the concentration constants for our calculations.

**Example 1.** The instability constant of the \([\text{Ag(CN)}_2^-]\) ion is \(1 \times 10^{-21}\). Calculate the concentration of the silver ions in a 0.05 \(M\) solution of \(K[\text{Ag(CN)}_2]\) also containing 0.01 \(mol/l\) of KCN.

**Solution.** The secondary dissociation of the complex ion follows the equation:

\[
[\text{Ag(CN)}_2^-] \rightleftharpoons \text{Ag}^+ + 2\text{CN}^-
\]

In the presence of an excess of \(\text{CN}^-\) ions due to the dissociation of KCN (which may be considered complete), this equilibrium is shifted to the left so much that the amount of \(\text{CN}^-\) ions formed in secondary dissociation may be disregarded. Hence, \([\text{CN}^-] = c(\text{KCN}) = 0.01 \text{ mol/l}\).

For the same reason, the equilibrium concentration of the \([\text{Ag(CN)}_2^-]\) ions may be equated to the total concentration of the complex salt (0.05 \(mol/l\)).

According to the data of the example:

\[
K_{\text{inst}} = \frac{[\text{Ag}^+] [\text{CN}^-]^2}{[\text{Ag(CN)}_2^-]} = 1 \times 10^{-21}
\]

whence the concentration of the \(\text{Ag}^+\) ions is:

\[
[\text{Ag}^+] = \frac{1 \times 10^{-21} [\text{Ag(CN)}_2^-]}{[\text{CN}^-]^2}
\]
Introducing the values of the concentrations of the CN\(^-\) and [Ag(CN)\(_2\)]\(^-\) ions, we obtain:

\[
[\text{Ag}^+] = \frac{10^{-24} \times 0.05}{(0.01)^2} = 5 \times 10^{-16} \text{ mol/l}
\]

The shifting of dissociation equilibrium in systems containing complex ions follows the same rules as in solutions of simple (non-complex) electrolytes, namely: equilibrium shifts in the direction of the most complete binding of the complexing agent or ligand so that the concentrations of these particles remaining unbound in the solution take on the minimum possible values in these conditions.

To find the direction of the shift in equilibrium, we must assess the values of the equilibrium concentrations of the ions in the system being considered.

**Example 2.** Solutions of simple cadmium salts form a cadmium hydroxide precipitate Cd(OH)\(_2\) with alkalies, and a cadmium sulphide precipitate CdS with hydrogen sulphide. How can we explain that when an alkali is added to a 0.05 M solution of K\(_4\)Cd(CN)\(_4\) containing 0.1 mol/l of KCN, no precipitate is formed, while when hydrogen sulphide is passed through this solution, a precipitate of CdS is formed? Assume that the instability constant of the [Cd(CN)\(_4\)]\(^2-\) ion is 7.8 \times 10\(^{-18}\).

**Solution.** The conditions for the formation of precipitates of Cd(OH)\(_2\) and CdS can be written as follows:

\[
\text{[Cd}^{2+}\text{][OH}^-\text{]} > K_{sp}\text{[Cd(OH)}_2\text{]} = 4.5 \times 10^{-15}
\]

\[
\text{[Cd}^{2+}\text{][S}^2-\text{]} > K_{sp}\text{[CdS]} = 8 \times 10^{-27}
\]

The concentration of the Cd\(^{2+}\) ions in a solution of the complex salt in the given conditions is calculated by the equation (see Example 1):

\[
[\text{Cd}^{2+}] = \frac{K_{\text{inst}}[\text{Cd(CN)}_4]^-}{[\text{CN}^-]^4} = \frac{7.8 \times 10^{-18} \times 0.05}{(0.1)^4} = 3.9 \times 10^{-16} \text{ mol/l}
\]

The concentration of the OH\(^-\) ions sufficient for the precipitation of cadmium hydroxide is found from the inequality:

\[
[\text{OH}^-] > \sqrt{\frac{K_{sp}\text{[Cd(OH)}_2\text{]}}{[\text{Cd}^{2+}]}} = \sqrt{\frac{4.5 \times 10^{-15}}{3.9 \times 10^{-16}}} \approx 1 \text{ mol/l}
\]

Hence, in the system being considered at concentrations of the OH\(^-\) ions below 1 mol/l, the equilibrium [Cd(CN)\(_4\)]\(^2-\) + 2OH\(^-\) ⇌ Cd(OH)\(_2\)\(^+\) + 4CN\(^-\) shifts in the direction of formation of the complex ion.
The condition for the formation of a cadmium sulphide precipitate from the given solution of potassium tetracyanocadmate is found from the inequality:

$$[S^{2-}] > \frac{K_{sp}(CdS)}{[Cd^{2+}]} = \frac{8.0 \times 10^{-27}}{3.9 \times 10^{-19}} \approx 2 \times 10^{-18}$$

Consequently, even at low concentrations of the sulphide ion, the equilibrium $[Cd(CN)_4]^{2-} + S^{2-} \rightleftharpoons CdS + 4CN^-$ virtually completely shifts in the direction of cadmium sulphide formation.

**PROBLEMS**

710. In which cases will a reaction occur between the solutions of the electrolytes indicated below? Write the equations of the reactions in the molecular and the net ionic form:

(a) $K_2[HgI_4] + KBr$
(b) $K_2[HgI_4] + KCN$
(c) $[Ag(NH_3)_2]Cl + K_2S_2O_3$
(d) $K[Ag(CN)_2] + K_2S_2O_3$
(e) $K[Ag(CN)_2] + NH_3$
(f) $K[Ag(NO_3)_2] + NH_3$
(g) $[Ag(NH_3)_2]Cl + NiCl_2$
(h) $K[Ag(CN)_2] + NiCl_2$

711. Calculate the concentration of the Ag$^+$ ions in a 0.1 $M$ solution of $[Ag(NH_3)_2]NO_3$ containing an excess of 1 mol/l of NH$_3$.

712. Calculate the concentration of the cadmium ions in a 0.1 $M$ solution of $K_2[Cd(CN)_4]$ containing, in addition, 6.5 grams of KCN per litre.

713. Calculate the mass of silver in the form of ions in 0.5 litre of a 0.1 $M$ solution of sodium dithiosulphatoargentate Na$_3[Ag(S_2O_3)_2]$ containing in addition 0.1 mol/l of sodium thiosulphate.

714. Will a silver halide precipitate if we add to one litre of a 0.1 $M$ solution of $[Ag(NH_3)_2]NO_3$ containing 1 mol/l of ammonia (a) $1 \times 10^{-5}$ mol of KBr; (b) $1 \times 10^{-5}$ mol of KI? The solubility products are $K_{sp}(AgBr) = 6 \times 10^{-13}$ and $K_{sp}(AgI) = 1.1 \times 10^{-16}$.

715. How many moles of ammonia must be contained in one litre of a 0.1 $M$ solution of $[Ag(NH_3)_2]NO_3$ so that

---

* In solving the problems of this section, use the values of the instability constants of the complex ions (Table 10 of the Appendix) when needed.
the addition of 1.5 g of KCl to one litre of the solution will not precipitate AgCl? $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$.

716. What is the concentration of the silver ions in a 0.08 M solution of $[\text{Ag(NH}_3\text{)}_2]\text{NO}_3$ containing 1 mol/l of ammonia? How many grams of NaCl can be added to one litre of the solution before AgCl begins to precipitate? $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$.

**Review Questions**

717. The instability constants of the complex ions $[\text{Ag(NO}_2\text{)}_2]^-$ and $[\text{Ag(CN)}_2]^-$ are $1.3 \times 10^{-3}$ and $8 \times 10^{-21}$, respectively. What is the relationship between the equilibrium concentrations of the Ag$^+$ ions in solutions of $K[\text{Ag(NO}_2\text{)}_2]$ ($c_1$) and $K[\text{Ag(CN)}_2]$ ($c_2$) having the same molar concentrations? (a) $c_1 > c_2$; (b) $c_1 = c_2$; (c) $c_1 < c_2$.

718. Potassium iodide precipitates silver as AgI from a solution of $[\text{Ag(NH}_3\text{)}_2]\text{NO}_3$, but does not precipitate it from a solution of $K[\text{Ag(CN)}_2]$ of the same molar concentration. What is the relationship between the values of the instability constants of the ions $[\text{Ag(NH}_3\text{)}_2]^+$ ($K_1$) and $[\text{Ag(CN)}_2]^-$ ($K_2$)? (a) $K_1 > K_2$; (b) $K_1 = K_2$; (c) $K_1 < K_2$.

719. The instability constants of the $[\text{Ag(NH}_3\text{)}_2]^+$ and $[\text{Cd(NH}_3\text{)}_4]^{2+}$ ions are close in value ($9.3 \times 10^{-8}$ and $7.6 \times 10^{-8}$, respectively). Indicate the correct relationships between the concentrations of the free metal ion $c(\text{Ag}^+)$ and $c(\text{Cd}^{2+})$ in solutions of $[\text{Ag(NH}_3\text{)}_2]\text{Cl}$ and $[\text{Cd(NH}_3\text{)}_4]\text{Cl}_2$ of the same molar concentration containing, in addition, 0.1 mol/l of NH$_3$. (a) $c(\text{Ag}^+) > c(\text{Cd}^{2+})$; (b) $c(\text{Ag}^+) \approx c(\text{Cd}^{2+})$; (c) $c(\text{Ag}^+) < c(\text{Cd}^{2+})$. 


In the liquid state, most metals dissolve in one another and form a homogeneous liquid alloy. Upon crystallization from the molten state, different metals behave in different ways. The following three cases are the main ones.

1. An alloy is a mechanical mixture of crystals of each of the components forming the alloy.

2. An alloy is a chemical compound formed by the reaction of the metals being alloyed.

3. An alloy is a homogeneous phase of varying composition called a solid solution.

The nature of alloys is most often established by studying their phase diagrams, which show the phases that can exist in given conditions. In these diagrams, the temperature is laid off along the axis of ordinates, and the composition of the alloy along the axis of abscissas.

If two metals M and N do not form a chemical compound when alloyed, the phase diagram in the general case has the form shown in Fig. 5. Point \( a \) shows the melting point of pure metal M. As metal N is added to it, the melting point first lowers, and then, upon a further increase in the content of metal N in the alloy, it grows again until it reaches point \( b \) corresponding to the melting point of pure metal N. Curve \( acb \) shows that of all the alloys formed by metals M and N, the alloy whose composition corresponds to point \( c \) (in the given case it contains 37% of metal N and, therefore, 63% of metal M) has the lowest melting point. The alloy having the lowest melting point is called the eutectic.

When a liquid alloy having a composition differing from that of the eutectic is cooled, the metal whose content in the alloy exceeds its content in the eutectic will separate
from it in the form of the solid phase. For instance, when
an alloy containing 70% of metal N is cooled, first this
metal will separate. This will be attended by lowering of
the solidification point, and the composition of the remain­
ing liquid portion of the alloy will gradually approach that
of the eutectic. When the composition of the liquid part

![Phase diagram of system of two metals forming neither chemical compounds nor solid solutions](image)

Fig. 5. Phase diagram of system of two metals forming neither chemical compounds nor solid solutions

of the alloy reaches that of the eutectic, and its temperature
reaches the eutectic one, the entire liquid part of the alloy
will solidify, forming a mixture of minute crystals of both
metals.

If the metals being alloyed form a chemical compound, the
phase diagram will be of the nature shown in Fig. 6. Here
there are two eutectic points: $c_1$ and $c_2$. The maximum
(point $d$) corresponds to the melting point of the chemical com­
pound formed by metals M and N, while point $e$ on the axis
of abscissas indicates its composition.

Thus, the phase diagram of a system with a chemical com­
pound is composed, as it were, of two diagrams of the first
kind. If the components form two or more chemical com­
pounds with each other, the diagram consists, as it were, of three, four, and more diagrams of the first kind.

Fig. 6. Phase diagram of system of two metals forming one chemical compound

Fig. 7. Phase diagram of system of two metals forming a continuous series of solid solutions

Figure 7 gives an example of a very simple phase diagram for an alloy whose components form solid solutions (the case of unlimited mutual solubility). Points $a$ and $b$ show the
melting points of the pure metals. The shape of the melting (lower) and freezing (upper) curves is due to the fact that the crystals separating when the melt is cooled contain both components. The melt corresponds to region I in the diagram, the coexistence of the melt and the crystals of the solid solution to region II, and the solid solution to region III.

Phase diagrams allow us to solve a number of problems relating to the nature of alloys: establish the structure of alloys, the number and composition of the compounds formed by the metals being alloyed, the composition of the eutectic, etc.

Example 1. We have 400 g of an alloy containing 30% tin and 70% lead. Which of these metals and in what amount is in the alloy in the form of crystals impregnated in the eutectic if the latter contains 64% tin and 36% lead?

Solution. We calculate the mass of each of the metals in 400 g of the alloy: 400 × 0.30 = 120 g of tin and 400 × 0.70 = 280 g of lead.

Since the percentage of the tin in the alloy is lower than that in the eutectic, it is evident that all the tin is in the eutectic. Proceeding from this fact, we find the mass of the eutectic:

\[
\frac{120}{x} = \frac{64}{100}; \quad x = \frac{120 \times 100}{64} = 187.5\text{ g}
\]

The remaining part of the alloy is formed by lead crystals impregnated in the eutectic. Their mass is 400 — 187.5 = 212.5 g.

Example 2. In alloying tin with magnesium, the intermetallic compound Mg2Sn is formed. In what proportion must the metals be taken for the alloy to contain 20% free magnesium?

Solution. We determine the percentage of magnesium and tin in Mg2Sn. We get 28.7% magnesium and 71.3% tin.

According to the data of the example, 100 g of the alloy must contain 20 g of magnesium and 80 g of Mg2Sn. Let us calculate the number of grams of each of the metals in 80 g of Mg2Sn:

\[
80 \times 0.287 = 23\text{ g of Mg}; \quad 80 \times 0.713 = 57\text{ g of Sn}
\]

Consequently, to prepare 100 g of the alloy having the composition indicated in the example, we must take 23 + 20 = 43 g of magnesium per 57 g of tin, i.e. the tin and magnesium must be taken in the ratio 57 : 43.

PROBLEMS

720. How can one explain the common nature of the physical properties of metals? Characterize these properties.
721. On the basis of the method of molecular orbitals (MO), explain the features of the structure of metals in the crystalline state.

722. Indicate the most important ways of extracting metals from their ores.

723. Using Table 5 of the Appendix, determine which of the following reactions can proceed in standard conditions:

\[
\begin{align*}
\text{WO}_3(c) + 3\text{CO}(g) &= \text{W}(c) + 3\text{CO}_2(g) \\
\text{WO}_3(c) + 3\text{C} \text{(graphite)} &= \text{W}(c) + 3\text{CO}(g) \\
\text{WO}_3(c) + 3\text{Ca}(c) &= \text{W}(c) + 3\text{CaO}(c)
\end{align*}
\]

724. Can metallic titanium be produced by the reaction

\[
\text{TiCl}_4(\text{lq}) + 2\text{Mg}(c) = \text{Ti}(c) + 2\text{MgCl}_2(c)
\]

Substantiate your answer by calculating \(\Delta G^\circ_{\text{sys}}\).

725. Using the phase diagram (melting curve) of the system Cd-Bi (Fig. 8), determine which of these metals and at what temperature begins to separate first when cooling liquid melts containing (a) 20\% Bi; (b) 60\% Bi; and (c) 70\% Bi.

726. What metal will separate when a liquid alloy of copper and aluminium containing 25\% copper is cooled if
Fig. 9. Phase diagram of system Mg-Sb

Fig. 10. Phase diagram of system Cu-Mg
the eutectic includes 32.5% copper? How many grams of this metal can be separated from 200 g of the alloy?

727. An alloy of tin and lead contains 73% tin. Find the mass of the eutectic in 1 kg of solid alloy if the eutectic contains 64% tin.

728. Silver coins are usually minted from an alloy consisting of equal masses of copper and silver. How many grams of copper are contained in 200 g of such an alloy in the form of crystals impregnated in the eutectic if the latter contains 28% copper?

729. Using the phase diagram of the system Mg-Sb (Fig. 9), establish the formula of the intermetallic compound formed by these metals. What will be the composition of the solid phase separating first in the cooling of a liquid melt containing 60% antimony? What will the solidified alloy be?

730. Use the phase diagram of the system Cu-Mg (Fig. 10) to find the formulas of the intermetallic compounds formed by these metals.

731. When magnesium and lead are alloyed, an intermetallic compound is formed containing 81% lead. Establish the formula of the compound and calculate how many grams of this compound are contained in 1 kg of the alloy formed by equal masses of magnesium and lead.
1. General

732. According to what principle are the elements combined into groups and subgroups?

733. Why do metallic properties predominate in manganese, a Group VII element, while the halogens in the same group are typical non-metals? In answering, proceed from the structure of the atoms of these elements.

734. How do the valence abilities and coordination numbers of the main subgroup elements change with a growth in the charge of their atomic nuclei? Investigate this matter using the Group VI elements as an example. Write the formulas of sulphuric, selenic, and telluric acids.

735. How does the stability of the higher oxides and hydroxides change in the main and secondary subgroups with a growth in the charge of the atomic nucleus? Support your answer with examples.

736. How can the difference between the properties of the second period elements and those of their electron analogues in the following periods be explained?


738. What are the general regularities in the change of the physical and chemical properties of the elementary substances formed by the elements of the main subgroups of the periodic table (a) in a period, and (b) in a group?

739. How do the acid-basic and oxidation-reduction properties of the higher oxides and hydroxides of elements change with an increasing charge of their atomic nuclei (a) in a period, and (b) in a group?
740. How can the similarity in the chemical properties of the lanthanides be explained?

741. Which element is molybdenum more similar to in its properties—selenium or chromium? How is this explained?

742. Proceeding from the position of the elements in the periodic table, determine (a) in which of the hydroxides—Sn(OH)₂ or Pb(OH)₂—the basic properties are more pronounced; (b) which of the salts hydrolyzes to a greater extent: sodium stannate or sodium plumbate; and (c) which of the oxides is a stronger oxidizing agent: SnO₂ or PbO₂.

743. What are the chemical properties of the artificially prepared element with the atomic number 87? Which of the elements of the periodic system is it most similar to?

2. Hydrogen

744. Describe the atoms of protium, deuterium, and tritium. What is the difference between these atoms? Which hydrogen isotopes are stable?

745. Proceeding from the structure of the hydrogen atom: (a) indicate the possible valence and oxidation states of hydrogen; (b) describe the structure of the H₂ molecule from the angles of view of the valence bond and molecular orbital methods; (c) show why the formation of an H₂ molecule is impossible.

746. Why are no hydrogen bonds formed between hydrogen molecules and oxygen molecules?

747. In the form of what ions can hydrogen enter the composition of chemical compounds?

748. Why is hydrogen related to both Group I and Group VII in the periodic table?

749. How is hydrogen produced commercially and in the laboratory? Give the equations of the reactions.

750. Can aqueous solutions of H₂SO₄, K₂SO₄, KCl, CuSO₄, and NaOH be used as the electrolyte for the electrolytic preparation of hydrogen? Substantiate your answer.

751. The iron-steam method of producing hydrogen is based on the reversible reaction 3Fe + 4H₂O ⇌ Fe₃O₄ + + 4H₂. How must this process be conducted for the reaction to proceed to virtually complete oxidation of the iron?
752. Can hydrogen be dried using concentrated sulphuric acid?
753. How can hydrogen be distinguished from oxygen, carbon dioxide, and nitrogen?
754. How can the purity of hydrogen obtained in the laboratory be checked?
755. Indicate the difference between the properties of atomic and molecular hydrogen. Are the heats of combustion of atomic and molecular hydrogen the same? Substantiate your answer.
757. How are metal hydrides produced? Compile equations of the reactions (a) of preparing calcium hydride, and (b) of its reaction with water.
758. The reaction of calcium hydride with water is sometimes used to fill aerostats in field conditions. How many kilograms of CaH$_2$ have to be used to fill a 500 m$^3$ aerostat (assuming the conditions to be standard)? How much zinc and sulphuric acid would be needed for this purpose?
759. Why do hydrogen and oxygen fail to react at room temperature, while at 700 °C the reaction proceeds virtually instantaneously?
760. Indicate the ways of preparing hydrogen peroxide, give the equations of the reactions.
761. Can H$_2$O$_2$ be prepared by the direct reaction of hydrogen and oxygen? Substantiate your answer.
762. Describe the structure of the H$_2$O$_2$ molecule. Why is this molecule polar?
763. Write the equation of the reaction of hydrogen peroxide decomposition. What kind of oxidation-reduction reactions does it belong to?
764. A small amount of manganese dioxide was added to 150 g of an H$_2$O$_2$ solution. The oxygen liberated in standard conditions occupied a volume of 10$^{-3}$ m$^3$. Calculate the per cent concentration of the initial solution.
765. Write the equation of the reaction of Na$_2$O$_2$ hydrolysis in the net ionic form. Will a solution of Na$_2$O$_2$ retain its bleaching properties if it is boiled?
766. Write balanced equations of the following reactions:

(a) $\text{KMnO}_4 + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow$
(b) $\text{Fe(OH)}_3 + \text{H}_2\text{O} \rightarrow$
(c) $\text{KI} + \text{H}_2\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow$
(d) $\text{H}_2\text{O}_2 + \text{Hg(NO}_3\text{)}_2 + \text{NaOH} \rightarrow \text{Hg} +$
(e) $\text{AgNO}_3 + \text{H}_2\text{O}_2 + \text{NaOH} \rightarrow$

767. Which of the following ions and molecules cannot exist? (a) $\text{H}_2^+$; (b) $\text{H}_3^+$; (c) $\text{H}_4^+$; (d) $\text{H}_2$; (e) $\text{H}_3^-$.
Because (1) the bond multiplicity is zero; (2) the Pauli exclusion principle is violated; (3) the bond multiplicity is less than unity.

768. Which of the following atoms, ions, and molecules are diamagnetic? (a) $\text{H}$; (b) $\text{H}_2$; (c) $\text{H}_3^+$; (d) $\text{H}_4^-$.
Because (1) the particle is not charged; (2) the particle is charged; (3) the total spin of the electrons is zero; 4) the total spin of the electrons is not zero.

769. Detonating gas at room temperature (a) is in a state of chemical equilibrium; (b) is not in a state of chemical equilibrium.
Because (1) the rate of the reaction is zero; (b) the introduction of a catalyst causes the reaction.

770. On the basis of the following values of the electrode potentials:

$$
\begin{align*}
\text{H}_2 + 2e^- & \rightleftharpoons 2\text{H}^- & \varphi^0 &= -2.23 \text{ V} \\
2\text{H}^+ + 2e^- & \rightleftharpoons \text{H}_2 & \varphi &= -0.41 \text{ V (at pH = 7)}
\end{align*}
$$

establish whether the hydride ion can exist in aqueous solutions. (a) Yes; (b) no.

3. The Halogens

771. On the basis of the structure of the halogen atoms, indicate what valence states are characteristic of fluorine, chlorine, bromine, and iodine. What oxidation states do the halogens exhibit in their compounds?

772. Give a comparative characteristic of the halogen atoms, indicating (a) the nature of the change in the first
ionization potentials, and (b) the nature of the change in the energy of affinity to an electron.

773. Give a comparative characteristic of the properties of the elementary substances formed by the halogens, indicating the nature of the change in (a) the standard enthalpies of dissociation of Hal₂ molecules, (b) the state of aggregation of elementary substances at ordinary temperature and pressure, and (c) the oxidation-reduction properties. Name the causes of these changes.

774. Show schematically the chain reaction of chlorine with hydrogen. What role is played by illumination in it? Is the frequency of the light of any significance here?

775. Write equations of the reactions of the halogens with water and alkali solutions (cold and hot).

776. Give examples of possible reactions of halogens with one another. Indicate the oxidation states of the halogens in the products.

777. At 300 °C, the degree of thermal dissociation of HI is 20%. What are the equilibrium concentrations of H₂ and I₂ in the system H₂ + I₂ ⇌ 2HI at this temperature if the equilibrium concentration of HI is 0.96 mol/l?

778. Give a comparative characteristic of the properties of the hydrogen halides, indicating the nature of the change in (a) the boiling and melting points, (b) the thermal stability, and (c) the reducing properties. Explain the regularities observed.

779. Indicate the ways of preparing hydrogen halides. Why is it impossible to prepare HI in the ways used to produce HCl?

780. What materials may be used to manufacture the apparatus employed in the production of hydrogen fluoride?

781. What vessels are used to keep an aqueous solution of hydrogen fluoride?

782. Are the aqueous solutions of sodium fluoride, ammonium fluoride, and silicon fluoride neutral, acidic, or basic?

783. Can hydrogen halides play the role of an oxidizing agent in any reactions? Give a motivated answer.

784. By the action of what halogens can free bromine be liberated from solutions of (a) potassium bromide, (b) potassium bromate? Give a motivated answer using a table of standard electrode potentials.
785. How will (a) the stability, (b) the oxidizing properties, and (c) the acid properties change in the series HClO-HClO₂-HClO₃-HClO₄?

786. How will the acid and oxidation-reduction properties change in the series HClO-HBrO-HIO?

787. Why does only iodine of all the halogens form polybasic oxyacids? Indicate the kind of hybridization of the halogen AO’s in their higher oxyacids.

788. How can we produce HIO₃ from free iodine, manganese dioxide, and hydrochloric acid? Compile the equations of the relevant reactions.

789. What amount of potassium chlorate can be obtained from 168 g of potassium hydroxide?

790. How can chlorinated lime be prepared from calcium carbonate, sodium chloride, and water? Write the equations of the processes. What byproducts are obtained?

791. Explain why it is impossible to produce chlorine oxides by directly reacting chlorine with oxygen.

792. Indicate the laboratory and commercial ways of producing potassium chlorate.

793. Write balanced equations of the following reactions:

(a) F₂ + NaOH →
(b) K₂CO₃ + Cl₂ + H₂O →
(c) KMnO₄ + HCl →
(d) HClO₃ + HCl →
(e) NaCl + KClO₃ + H₂SO₄ →
(f) NaCrO₂ + Br₂ + NaOH →
(g) Ca(OH)₂ + Br₂ + H₂O →
(h) KI + H₂SO₄(conc) →
(i) I₂ + Cl₂ + H₂O →
(j) BrCl₅ + H₂O →
(k) Iₘ + HNO₃(conc) →
(l) KBr + KClO₃ + H₂SO₄ →

REVIEW QUESTIONS

794. Which of the following reactions can be carried out to produce oxygen compounds of halogens?

(a) \( \frac{1}{2} \) Cl₂ + O₂ = ClO₂
(b) F₂ + \( \frac{1}{2} \) O₂ = OF₂
(c) 3Cl₂ + 10HNO₃ = 6HClO₂ + 10NO + 2H₂O
(d) 3I₂ + 10HNO₃ = 6HIO₂ + 10NO + 2H₂O

Use Tables 5 and 9 of the Appendix for your answer.
795. With which of the following substances does HBr react? (a) Ca(OH)$_2$; (b) PCl$_3$; (c) $\text{H}_2\text{SO}_4$ (conc); (d) KI; (e) Mg; (f) KClO$_3$.

Here HBr exhibits the properties of (1) an acid; (2) a base; (3) an oxidizing agent; (4) a reducing agent.

4. Oxygen Subgroup Elements

796. On the basis of the structure of the oxygen atom, indicate its valence abilities. What oxidation states does oxygen exhibit in its compounds?

797. Indicate the laboratory and commercial ways of producing oxygen, and list the most important spheres of its practical use.

798. Characterize molecular oxygen: $\text{O}_2$, indicating (a) its chemical properties; (b) the structure of the molecule according to the MO method; and (c) the magnetic properties of the molecule. What elementary substances does oxygen not react with directly?

799. Describe the electron configuration of the $\text{O}_3$ molecule; compare the chemical activity of ozone $\text{O}_3$ and molecular oxygen $\text{O}_2$. How can ozone be prepared from molecular oxygen?

800. Can oxygen react with (a) hydrogen, and (b) nitrogen at room temperature? Motivate your answer using Table 5 of the Appendix.

801. After the ozonization of a certain volume of oxygen, the volume of the gas was found to diminish by 500 ml. What volume of ozone was formed? What amount of heat was absorbed in its formation if $\Delta H_{\text{form}} = 144.2$ kJ/mol for ozone?

802. On the basis of the structure of sulphur, selenium, and tellurium atoms, indicate the valence and oxidation states that are characteristic of these elements. Write the formulas of their higher hydroxides. Explain your answer.

803. Give a comparative characteristic of the hydrogen compounds of the main subgroup elements of Group VI, indicating and explaining the nature of the change in (a) the thermal stability; (b) the melting and boiling points; (c) the acid-basic and oxidation-reduction properties. Which
of these compounds can be prepared by reacting hydrogen with the relevant elementary substance?

804. What substance is oxidized more readily—sodium sulphide or sodium telluride? Explain your answer.

805. Give a comparative characteristic of sulphurous, selenous, and tellurous acids, indicating the changes in (a) the stability; (b) the acid properties; and (c) the oxidation-reduction properties. Illustrate your answer with reactions.

806. Which Group VI element forms a hexabasic acid? Write its formula. Why do the other elements of this subgroup form no similar acids?

807. How and why do the acid properties in the series sulphuric-selenic-telluric acid change? How do the oxidizing properties change in this series?

808. Explain why hydrogen sulphide does not precipitate manganese sulphide, but does precipitate copper sulphide. Can manganese sulphide be precipitated from an aqueous solution of its salt?

809. Indicate a laboratory method of preparing hydrogen sulphide. How can hydrogen selenide and hydrogen telluride be prepared?

810. What hydrogen compounds does sulphur form? How are they prepared? What is their structure? What oxidation states does sulphur exhibit in these compounds?

811. Compare the reaction of Sb₂S₃ with solutions of (NH₄)₄S and (NH₄)₂S₂.

812. Why does zinc sulphide dissolve in hydrochloric acid, and why does copper sulphide not dissolve in it? In what acid can copper sulphide be dissolved?

813. What are the products of the reaction of iron(III) chloride with (a) hydrogen sulphide, and (b) ammonium sulphide?

814. Explain why ZnS and PbS can be prepared by an exchange reaction in an aqueous solution, while Al₂S₃ and Cr₂S₃ cannot. Indicate a way of preparing Al₂S₃ and Cr₂S₃.

815. Are the solutions of (a) Na₂S, (b) (NH₄)₂S, and (c) NaHS neutral, acidic, or basic?

816. What properties does hydrogen sulphide exhibit when it reacts with aqueous solutions of KMnO₄, H₂O₂, and NaOH?
817. Write balanced equations of the following reactions:

(a) \( S + \text{NaOH} \rightarrow \)  
(b) \( \text{H}_2\text{S} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \)  
(c) \( \text{H}_2\text{S} + \text{KMnO}_4 + \text{H}_2\text{O} \rightarrow \)  
(d) \( \text{FeCl}_3 + \text{H}_2\text{S} \rightarrow \)  
(e) \( \text{FeCl}_3 + \text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow \)  
(f) \( \text{H}_2\text{S} + \text{H}_2\text{SO}_4(\text{conc}) \rightarrow \)

818. Give examples of reactions for preparing \( \text{SO}_2 \) that (a) are attended by a change in the oxidation state of the sulphur, and (b) are not attended by a change in its oxidation state.

819. Are the solutions of \( \text{Na}_2\text{SO}_3 \) and \( \text{NaHSO}_3 \) neutral, acidic, or basic? Calculate the pH of a 0.001 \( M \) solution of \( \text{Na}_2\text{SO}_3 \).

820. Characterize the oxidation-reduction properties of sulphur dioxide and sulphurous acid. Substantiate your answer with examples.

821. Write balanced equations of the following reactions:

(a) \( \text{H}_2\text{S} + \text{SO}_2 \rightarrow \)  
(b) \( \text{H}_2\text{SO}_3 + \text{I}_2 \rightarrow \)  
(c) \( \text{KMnO}_4 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \)  
(d) \( \text{HIO}_3 + \text{H}_2\text{SO}_3 \rightarrow \)

Indicate what properties sulphur dioxide or sulphurous acid displays in each of these reactions.

822. Which of the following desiccants can be used to remove moisture from \( \text{SO}_2 \): \( \text{H}_2\text{SO}_4 \) (conc), \( \text{KOH(c)\text{, P}_2\text{O}_5(c), \text{K}_2\text{CO}_3(c)\)?

823. How many litres of \( \text{SO}_2 \) taken in standard conditions have to be passed through a solution of \( \text{HClO}_3 \) to reduce 16.9 g of it to \( \text{HCl}\)?

824. Does sulphurous acid exhibit oxidizing or reducing properties when it reacts with (a) magnesium; (b) hydrogen sulphide; and (c) iodine? Which of its ions is responsible for these properties in each of the above cases?

825. 448 ml of \( \text{SO}_2 \) (in standard conditions) are passed through 100 ml of a 0.2 \( N \) solution of \( \text{NaOH} \). What salt is formed? Find its mass.

826. Write the equations of the reactions of sodium thiosulphate with (a) chlorine (when its amount is less than or in excess of the stoichiometric amount), and (b) iodine.

827. Write the equation of the reaction of preparing sodium thiosulphate. What is the oxidation state of sulphur in this compound? Does the thiosulphate ion display oxidiz-
ing or reducing properties? Give examples of the relevant reactions.

828. Write balanced equations of the reactions of (a) concentrated \( \text{H}_2\text{SO}_4 \) with magnesium and with silver, and (b) dilute \( \text{H}_2\text{SO}_4 \) with iron.

829. How many grams of sulphuric acid are needed to dissolve 50 g of mercury? How much of the acid will go to oxidize the mercury? Can dilute sulphuric acid be used to dissolve mercury?

830. Is the same amount of sulphuric acid needed to dissolve 40 g of nickel if we take concentrated acid in one case and dilute acid in another? How many grams of sulphuric acid will go to oxidize the nickel in each case?

831. Oleum is transported in iron tank cars. May they be replaced with lead cars? Why does oleum not dissolve iron?

832. What properties can be used to distinguish sodium sulphite from sodium thiosulphate? Give the equations of the reactions.

**REVIEW QUESTIONS**

833. Name the substances whose content in air in considerable amounts is incompatible with the presence of ozone. (a) \( \text{SO}_2 \); (b) \( \text{HF} \); (c) \( \text{H}_2\text{S} \); (d) \( \text{CO}_2 \); (e) \( \text{N}_2 \).

834. What is the relationship between the pH's of isomolar solutions of sodium sulphide (pH₁), selenide (pH₂), and telluride (pH₃)? (a) \( \text{pH}_1 < \text{pH}_2 < \text{pH}_3 \); (b) \( \text{pH}_1 = \text{pH}_2 = \text{pH}_3 \); (c) \( \text{pH}_1 > \text{pH}_2 > \text{pH}_3 \).

835. Which of the following sulphides are not precipitated from aqueous solutions by hydrogen sulphide? (a) \( \text{CuS} \); (b) \( \text{CdS} \); (c) \( \text{FeS} \); (d) \( \text{Fe}_2\text{S}_3 \); (e) \( \text{MnS} \); (f) \( \text{HgS} \); (g) \( \text{PhS} \); (h) \( \text{Cr}_2\text{S}_3 \); (i) \( \text{CaS} \).

Because (1) the solubility product of the sulphide is not reached; (2) the sulphide formed is completely hydrolyzed; and (3) the sulphide ion reduces the cation.

836. Which of the compounds listed below enter into a reaction with sodium thiosulphate: (a) \( \text{HCl} \); (b) \( \text{NaCl} \); (c) \( \text{NaI} \); (d) \( \text{I}_2 \); (e) \( \text{KMnO}_4 \) if (1) the initial substance becomes decolourized; (2) a precipitate forms; (3) a gas evolves?
837. Is an ammonium sulphide solution (a) acidic; (b) neutral; (c) basic?

Because (1) both the cation and the anion of the salt become hydrolyzed; (2) the anion becomes hydrolyzed to a greater extent; (3) the dissociation constant of the ammonium hydroxide is greater than that of the hydrosulphide ion.

838. With which of the following substances does concentrated sulphuric acid react? (a) CO₂; (b) HCl; (c) P; (d) BaCl₂; (e) Ba(OH)₂; (f) Hg; (g) Pt; (h) HI; (i) NH₃.

The sulphuric acid exhibits (1) acid properties; (2) oxidizing properties; (3) neither of these properties.

5. Nitrogen Subgroup Elements

839. Give a comparative characteristic of the atoms of the nitrogen subgroup elements, indicating (a) the electron configurations; (b) the valence abilities; and (c) the most characteristic oxidation states.

840. Describe the electron configuration of NH₃, NH₄⁺, N₂O, NH₂, and HNO₃. What is the oxidation state of the nitrogen in each of these compounds?

841. Give examples of nitrogen compounds whose molecules have donor-acceptor bonds.

842. Describe the electron configuration of the N₂ molecule from the angles of view of the valence bond and molecular orbital methods.

843. Give examples of reactions in which nitrogen is an oxidizing agent, and an example of a reaction in which it is a reducing agent.

844. The solubility of NH₄Cl and NaNO₂ at 20 °C is 37.2 and 82.9 g in 100 g of water, respectively. How many grams of saturated solutions of these salts must be mixed to obtain 24 litres of nitrogen (measured at 20 °C and standard atmospheric pressure) when heated?

845. What nitrogen compounds are obtained by the direct binding (fixation) of atmospheric nitrogen? Give the reactions used to prepare them and indicate the conditions for conducting these reactions.

846. How many tonnes of calcium cyanamide can be produced from 3600 m³ of nitrogen (20 °C, standard atmosphere, standard pressure).
230 Problems and Exercises in General Chemistry

spheric pressure) when it reacts with calcium carbide if the nitrogen losses are 40%?

847. Give examples of combination, hydrogen replacement, and oxidation reactions typical of ammonia.

848. What volume of ammonia (in standard conditions) can be obtained by reacting two litres of a 0.5 \( N \) alkali solution with an ammonium salt?

849. Can \( H_2SO_4 \) or \( P_2O_5 \) be used as desiccants of gaseous ammonia? Motivate your answer.

850. Write the equations of the reactions of thermal decomposition for the following salts: \((NH_4)_2CO_3\), \(NH_4NO_3\), \((NH_4)_2SO_4\), \(NH_4Cl\), \((NH_4)_2HPO_4\), \(NH_4H_2PO_4\), \((NH_4)_2Cr_2O_7\), and \(NH_4NO_2\).

851. Ammonium nitrate can be decomposed in two ways:

\[
\begin{align*}
NH_4NO_3(c) & = N_2O(g) + 2H_2O(g) \\
NH_4NO_3(c) & = N_2(g) + \frac{1}{2} O_2(g) + 2H_2O(g)
\end{align*}
\]

Which of these reactions is more probable and which is more exothermic at 25 °C? Confirm your answer by calculating \( \Delta G_{25^\circ C} \) and \( \Delta H_{25^\circ C} \). How will the probability of these reactions change when the temperature is elevated?

852. What are the properties of hydrazoic acid and its salts? Can \( HN_3 \) be prepared by the direct reaction of nitrogen and hydrogen? Motivate your answer.

853. Write balanced equations of the following reactions and indicate the function of \( HN_3 \) (acidic, oxidizing, reducing) in each of them:

\[
\begin{align*}
(a) \ HN_3 + KMnO_4 + H_2SO_4 & \rightarrow N_2 + MnSO_4 + \\
(b) \ HN_3 + HI & \rightarrow N_2 + NH_4I + I_2 \\
(c) \ HN_3 + Cu & \rightarrow Cu(N_3)_2 + N_2 + NH_3 \\
(d) \ HN_3 + NaOH & \rightarrow \\
\end{align*}
\]

854. Calculate the pH of a 0.1 \( N \) solution of \( NaN_3 \) and the degree of hydrolysis of the salt.

855. Write balanced equations of the reactions:

\[
\begin{align*}
(a) \ N_2H_4 \cdot H_2SO_4 + KMnO_4 + H_2SO_4 & \rightarrow N_2 + \\
(b) \ N_2H_4 + HgCl_2 & \rightarrow N_2 + Hg_2Cl_2 + \\
\end{align*}
\]

What is the function of the hydrazine in these reactions?
856. Characterize the oxidation-reduction properties of hydroxylamine and its salts; give examples of the relevant reactions.

857. Indicate the ways of preparing nitrogen oxides. Why can only nitrogen monoxide be obtained by direct synthesis from N₂ and O₂? Why is an appreciable yield of NO observed only at high temperatures when N₂ and O₂ react?

858. Describe the electron configuration of the NO molecule according to the molecular orbital method.

859. Describe the chemical properties of N₂O and NO. What class of oxides do these compounds belong to?

860. What gas (brown in colour) evolves when concentrated nitric acid reacts with metals? What molecules does it consist of? Why does its colour become more intense when the temperature is elevated and less intense when it is lowered? Will this gas obey Boyle's law if it is compressed at constant temperature? Write the equations of the reactions occurring when this gas is dissolved in water and in an alkali solution.

861. Why does the NO₃ molecule readily dimerize, whereas such a process is not characteristic of SO₃?

862. Are the solutions of NaNO₃, NH₄NO₃, NaNO₂, and NH₄NO₂ neutral, acidic, or basic? Which of the above salts react in a solution acidified with H₂SO₄ (a) with potassium iodide, and (b) with potassium permanganate? Write the equations of the reactions.

863. Write the equations of the reaction of nitric acid with zinc, mercury, magnesium, copper, sulphur, carbon, and iodine. What does the composition of the nitric acid reduction products depend on?

864. Write the equation of the HNO₂ disproportionation reaction.

865. Indicate the chemical reactions as a result of which nitric acid is produced at present from natural substances.

866. In producing nitric acid from a nitrate, why must concentrated sulphuric acid be used and the nitrate taken in the solid form? Why is strong heating of the reaction mixture prohibited?

867. What is the thermal stability of nitrates and nitrites? What happens when the following salts are heated: NaNO₃,
Pb(NO$_2$)$_2$, NH$_4$NO$_2$, NaNO$_3$, Pb(NO$_3$)$_2$, AgNO$_3$, NH$_4$NO$_3$? Write the equations of the reactions.

868. Write balanced equations of the following reactions:

(a) NO$_2$ + Ba(OH)$_2$  \[ \rightarrow \]
(b) NO + KMnO$_4$ + H$_2$O  \[ \rightarrow \]
(c) P + HNO$_3$(conc)  \[ \rightarrow \]
(d) Zn + NaNO$_2$ + NaOH  \[ \rightarrow \] (fusion)
(e) Zn + NaNO$_3$ + NaOH  \[ \rightarrow \] (solution)
(f) Cu$_2$S + HNO$_3$(conc)  \[ \rightarrow \]

869. What is aqua regia? What properties does it have? Write the equation of the reaction between aqua regia and gold.

870. A certain amount of copper has to be dissolved in nitric acid. When will less acid be needed—when a 90% or a 35% solution of HNO$_3$ is used?

871. How can NH$_4$NO$_3$ be obtained by using atmospheric nitrogen and water as the reactants?

872. How is phosphorus produced commercially? Write the equations of the relevant reactions.

873. Indicate the allotrope modifications of phosphorus and the differences in their properties. Do these differences remain after phosphorus passes into the gaseous state? How can we prove that red and white phosphorus are allotrope modifications of the same element?

874. At 800 °C, the density of phosphorus vapour relative to air is 4.27, and at 1500 °C it drops to half of this value. How many atoms does a phosphorus molecule consist of at these temperatures?

875. What amount of heat is liberated in the transformation of one tonne of white phosphorus into the red modification if the heat of transition is 16.73 kJ per mole of atoms?

876. Indicate the names and formulas of the ammonium salts of orthophosphoric acid. Why can ammonia be obtained from them by direct heating, while for preparing ammonia from ammonium chloride, the latter must first be mixed with slaked lime or an alkali?

877. What compounds does phosphorus form with hydrogen? Indicate the ways of preparing them. Compare their properties with those of similar nitrogen compounds,
878. Write balanced equations of the following reactions:

(a) \( \text{P} + \text{Cl}_2 \rightarrow \) 
(b) \( \text{P} + \text{HNO}_3(\text{conc}) \rightarrow \) 
(c) \( \text{P} + \text{Mg} \rightarrow \) 
(d) \( \text{PH}_3 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_3\text{PO}_4 + \) 
(e) \( \text{Mg}_3\text{P}_2 + \text{HCl} \rightarrow \)

879. Characterize the relation of diphosphorus trioxide to water (a) in the cold, and (b) when heated.

880. How can orthophosphoric acid be prepared (a) from free phosphorus, and (b) from calcium orthophosphate? How much phosphorus and how much calcium orthophosphate is needed to prepare 250 g of \( \text{H}_3\text{PO}_4 \)?

881. Why is it impossible to precipitate silver orthophosphate in strongly acidic or strongly basic solutions?

882. Write balanced equations of the following reactions:

(a) \( \text{H}_3\text{PO}_4 + \text{FeCl}_3 + \text{HCl} \rightarrow \text{H}_3\text{PO}_4 + \) 
(b) \( \text{H}_3\text{PO}_2 + \text{I}_2 + \text{H}_2\text{O} \rightarrow \) 
(c) \( \text{H}_3\text{PO}_3 \rightarrow \text{PH}_3 + \) 
(d) \( \text{H}_3\text{PO}_3 + \text{AgNO}_3 + \text{H}_2\text{O} \rightarrow \text{Ag} + \)

883. Indicate a way of preparing arsine and stibine. How are arsenic and antimony mirrors obtained?

884. What arsenic compound is obtained when dilute sulphuric acid and zinc react with \( \text{As}_2\text{O}_3 \)? Write the equation of the reaction.

885. Compare the physical and chemical properties of the hydrogen compounds of the nitrogen subgroup elements, indicating how the following properties change: (a) the boiling and melting points; (b) the thermal stability; (c) the oxidation-reduction properties; and (d) the acidic and basic properties. Name the reasons for these changes.

886. How do the acidic and basic properties change in the series of hydroxides of arsenic(III), antimony(III), and bismuth(III)? How can the sparingly soluble \( \text{Sb(OH)}_3 \) and \( \text{Bi(OH)}_3 \) be separated from each other?

887. Why does an \( \text{SbCl}_3 \) solution become turbid when diluted with water? How can it be made transparent again without filtering it? Write the molecular and net ionic equations of the relevant reactions.
888. What substances form when concentrated HNO₃ is reacted with As₂S₃? Write the equation of the reaction.

889. What substances are known as thioacids? Write the net ionic equations of the reactions for preparing the ammonium salts of thioarsenous and thioantimonic acids.

890. A mixture of the sulphides As₂S₃, Sb₂S₃, and Bi₂S₃ was treated with a sodium sulphide solution. Which sulphide remained undissolved? Write the equations of the sulphide dissolving reactions.

891. Write the equations of the consecutive reactions by means of which it is possible to obtain (a) sodium thioantimonate from SbCl₃, and (b) thioarsenate from Na₃AsO₄.

892. Bismuth dissolves readily in dilute nitric acid, but does not dissolve in hydrochloric and dilute sulphuric acids. What conclusion can be arrived at from these facts with respect to bismuth's place in the electromotive series?

893. How can sodium bismuthate be prepared? What properties does this compound have? Write the equation of the reaction of sodium bismuthate with manganese(II) nitrate in a nitric acid solution.

894. Write balanced equations of the following reactions:

(a) SbCl₃ + HCl + Zn →
(b) AsH₃ + KMnO₄ + H₂SO₄ → H₃AsO₄ +
(c) Sb₂S₃ + HNO₃(conc) →
(d) As₂S₃ + (NH₄)₂S →
(e) Sb₂S₃ + (NH₄)₂S₂ →
(f) BiCl₃ + K₂SnO₃ + KOH → Bi +
(g) Bi(OH)₃ + Br₂ + KOH → KBiO₂ +
(h) NaBiO₂ + Mn(NO₃)₂ + HNO₃ → HMnO₄ +

895. Which of the following molecules are paramagnetic?
(a) NO; (b) NO₂; (c) N₂O₅; (d) N₂O₃; (e) N₂O₅; (f) N₂O.

896. Which of the following compounds can combine with chlorine? (a) NO₂; (b) NH₃; (c) NO; (d) NH₂OH.

Because (1) chlorine is an oxidizing agent; (2) nitrogen has an unshared pair of electrons; (3) the molecule is paramagnetic, while the nitrogen is tetracovalent; (4) the molecule is paramagnetic, while the covalence of nitrogen is
less than four; (5) the molecule is diamagnetic, while the
covalence of nitrogen is less than four.

897. Which of the following compounds are capable of
a dimerization reaction? (a) NO₂; (b) NOCl; (c) N₂H₄;
(d) N₂O.
Because (1) the oxidation state of nitrogen in this com-
pound is not maximum; (2) nitrogen has an unshared pair
of electrons; (3) the molecule is paramagnetic.

898. Which of the following substances are intramolecular
oxidation-reduction reactions characteristic of? (a) KNO₃;
(b) KNO₂; (c) (NH₄)₂Cr₂O₇; (d) (NH₄)₃PO₄.
Because (1) nitrogen in the given substance exhibits
oxidation-reduction duality; (2) gaseous products are liberat-
ed in decomposition; (3) the molecule in addition to the
nitrogen atom that is an oxidizing agent contains an atom
that is a reducing agent; (4) the molecule in addition to the
nitrogen atom that is a reducing agent contains an atom
that is an oxidizing agent.

899. Is a hydroxylamine chloride solution (a) acidic;
(b) neutral; (c) basic?
Because (1) the molecule includes an —OH group; (2) salt
hydrolysis proceeds; (3) the nitrogen in this compound is
tetravalent and does not combine with a hydrogen ion.

900. With which of the following substances does con-
centrated nitric acid react? (a) P₂O₅; (b) HCl; (c) Cl₂; (d) I₂;
(e) CaO; (f) Cu; (g) Al; (h) CO₂, (i) HPO₃.
Here the nitric acid exhibits (1) acid properties; (2) oxidiz-
ing properties; (3) neither acid nor oxidizing properties.

901. Which of the following reactions can be used to
prepare metaphosphoric acid?

\[
\begin{align*}
&\text{(a) } \ce{P2O5 + H2O} \xrightarrow{20 \degree C} \ce{H2PO4} \\
&\text{(b) } \ce{P + HNO3(conc)} \rightarrow \ce{H2PO4} \\
&\text{(c) } \ce{H2PO4} \rightarrow \ce{H3PO4} \\
&\text{(d) } \ce{P2O5 + H2O} \xrightarrow{80 \degree C} \\
\end{align*}
\]

902. Which of the following reactions can be used to
prepare phosphorous acid?

\[
\begin{align*}
&\text{(a) } \ce{P2O5 + H2O} \xrightarrow{20 \degree C} \\
&\text{(b) } \ce{P2O5 + H2O} \xrightarrow{80 \degree C} \\
&\text{(c) } \ce{P + HNO3(conc)} \rightarrow \\
\end{align*}
\]
903. What relationship between the pH's of solutions of the salts SbCl₃ \((pH_1)\) and BiCl₃ \((pH_2)\) having equal molar concentrations is correct? (a) \(pH_1 < pH_2\); (b) \(pH_1 = pH_2\); (c) \(pH_1 > pH_2\).

Because (1) the degree of hydrolysis depends on the concentration of the solution; (2) the salt formed by the weaker base becomes hydrolyzed to a greater degree.

6. Carbon and Silicon

904. Describe the allotropic modifications of carbon and indicate the reason for the difference in their properties.

905. What types of AO hybridization are characteristic of carbon? Describe the structure of the molecules \(\text{CH}_4\), \(\text{C}_2\text{H}_6\), \(\text{C}_2\text{H}_4\), and \(\text{C}_2\text{H}_2\) from the angle of view of the valence bond method.

906. Characterize the physical and chemical properties of carbon dioxide and the fields of its practical use. Write the equations of the reactions of \(\text{CO}_2\) with an alkali solution when the \(\text{CO}_2\) is present in excess and in an insufficient amount.

907. What equilibria set in in an aqueous \(\text{CO}_2\) solution? How does elevation of the temperature of the solution affect the shifting of these equilibria? Can a 1 \(N\) solution of carbonic acid be prepared?

908. Can a neutral solution be prepared by adding a strictly equivalent amount of an alkali to a carbonic acid solution? Motivate your answer.

909. Why is marble reacted with hydrochloric acid instead of sulphuric acid when carbon dioxide is being produced from it? What volume of \(\text{CO}_2\) (in standard conditions) can be obtained from 1 kg of marble containing 96\% \(\text{CaCO}_3\)?

910. Write the molecular and net ionic equations of the hydrolysis of \(\text{Na}_2\text{CO}_3\), \(\text{KHCO}_3\), and \((\text{NH}_4)\text{H}_2\text{CO}_3\). Indicate whether the solution is neutral, acidic, or basic.

911. Calculate the pH of a 0.01 \(M\) potassium carbonate solution.

912. To produce soda, an \(\text{NaOH}\) solution was divided into two equal portions, one of them was saturated with \(\text{CO}_2\) and then mixed with the other portion. What substance was formed after saturation of the first portion? What reaction
occurred when the first portion was mixed with the second one? Write the equations of the reactions.

913. How can CO₂ be freed of an SO₂ admixture by chemical means?

914. How is soda produced by the Solvay process? Does the sequence of saturating the solution (what solution?) with carbon dioxide and ammonia matter? Can potash be produced in a similar way? Substantiate your answer.

915. What volume of CO₂ (in standard conditions) can be prepared from 210 g of NaHCO₃ (a) by roasting, and (b) by reaction with an acid?

916. Describe the properties of carbon monoxide, indicating (a) the electron configuration of the molecule from the angles of view of the valence bond and molecular orbital methods; (b) the relation to water and to aqueous solutions of acids and alkalies; and (c) its oxidation-reduction properties.

917. In what cases is CO formed in the combustion of coal? Why is there a smaller danger of carbon monoxide appearing when a stove is shut with diminishing of the temperature of the coals? To motivate your answer, use Table 5 of the Appendix.

918. Proceeding from ΔH° of formation of CO₂, CO, and steam, prove that the process of generator gas production is exothermic, and that of water gas production endothermic.

919. Calcium carbide is produced by the reaction CaO + C → CaC₂ + CO. Calculate the mass of CaO needed to produce 6.4 tonnes of CaC₂. What volume of CO is produced (in standard conditions)?

920. Indicate the composition and properties of hydrocyanic acid. Why must salts of this acid be stored in tightly closed vessels? Explain your answer with reaction equations.

921. Give a brief description of silicon, indicating (a) the electron configuration of the atom and its valence abilities, and (b) the chemical properties of free silicon.

922. Describe the physical and chemical properties of silicon dioxide, its relation to water, acids, and alkalies.

923. In what direction and why will equilibria shift (a) in the saturation of an aqueous solution of sodium silicate with carbon dioxide, and (b) when a mixture of Na₂CO₃ and SiO₂ is roasted?
924. What acid cannot be stored in an ordinary glass vessel or in one of quartz glass? Why?

925. Write equations of reactions of silicon halide hydrolysis. What is a feature of hydrolysis of SiF₄? Can the hydrolysis of CCl₄ follow this reaction? Motivate your answer.

926. Write the equation of hydrolysis of Na₂SiO₃. How will the degree of hydrolysis of Na₂SiO₃ change when ammonium chloride is added to the solution?

**REVIEW QUESTIONS**

927. What type of hybridization of carbon's atomic orbitals can be used to describe the structure of the CO₂ molecule? (a) sp; (b) sp²; (c) sp³; (d) no hybridization occurs. Because (1) the covalence of carbon in this compound is four; (2) the molecule is not polar; (3) the multiplicity of the carbon-oxygen bond is greater than unity.

928. Which of the following gases when passed through an alkali solution react with it? (a) CO; (b) CO₂; (c) HCN; (d) CF₄.

7. **Group I Metals**

929. How do the radii and ionization potentials of the alkali metal atoms change with an increasing atomic number of the elements? Explain the regularities observed on the basis of the electron configuration of the atoms.

930. How can we explain the different sequence in the arrangement of the alkali metals in the electromotive series and in the periodic table?

931. How and why do the basic properties change in the series LiOH-CsOH?

932. How are the differences in the properties of the main and secondary subgroup elements of Group I explained?

933. Why is the radius of the Cu⁺ ion smaller than that of the K⁺ ion? Which of these ions has a greater polarizing power?

934. In what does the electrolytic method of producing alkali metals differ from that of producing alkali metal
hydroxides? What electrochemical processes occur in both cases?

935. How can potassium hydroxide, hypochlorite, and chlorate be produced by the electrolysis of potassium chloride solutions? Write the equations of the relevant reactions.

936. Commercial sodium hydroxide often contains a considerable admixture of soda. How can this be detected? How can an NaOH solution be freed of this impurity? Compile the equations of the relevant reactions.

937. The reaction of 10 g of sodium amalgam with water produced an alkali solution. To neutralize the latter, 50 ml of a 0.5 N solution of an acid were needed. Determine the per cent content of sodium (by mass) in the amalgam.

938. A precipitate of AgCl with a mass of 0.2850 g was obtained from a mixture of KCl and NaCl with a total mass of 0.1225 g. Calculate the per cent content (by mass) of the KCl and NaCl in the mixture.

939. Write the equations of the reactions for preparing (a) sodium silicate; (b) sodium acetate; (c) sodium nitrate; (d) sodium hydrogen sulphate; and (e) sodium sulphite from sodium carbonate.

940. The decomposition of KClO₃ yielded 3.36 litres of oxygen (in standard conditions). What amount of heat was liberated?

941. What volume of hydrogen measured at 25 °C and 755 mmHg (100.7 kPa) will be liberated when 1 g of an alloy consisting of 30% (mass) potassium and 70% (mass) sodium is reacted with water?

942. Calculate the amount of heat that will be evolved at 25 °C when 8 g of sodium hydride react with water. Take the standard enthalpies of formation of NaH and NaOH equal to —56.4 kJ/mol and —425.9 kJ/mol.

943. Write balanced equations of the following reactions:

(a) Na₂O₃ + KI + H₂SO₄ →
(b) Li₃N + H₂O →
(c) K + O₂(excess) →
(d) KNO₃ →

944. Name the most important alloys of copper and indicate their approximate composition.

945. Write the equations of the reactions of copper with dilute (1:2) and concentrated nitric acid. Why doesn't copper dissolve in hydrochloric acid?
946. How do copper salts react with solutions of alkalies and ammonium hydroxide?

947. What processes occur in the electrolysis of a copper sulphate solution (a) with copper, and (b) with platinum electrodes?

948. Write the equations of the reactions involving the dissolution of copper hydroxide in an acid and in an ammonia solution.

949. Write balanced equations of the following reactions:

(a) \( \text{Ag}_2\text{O} + \text{H}_2\text{O}_2 \rightarrow \)
(b) \( \text{AgBr} + \text{Na}_2\text{S}_2\text{O}_3\text{(excess)} \rightarrow \)
(c) \( \text{Cu} + \text{KCN} + \text{H}_2\text{O} \rightarrow \)

950. Why is silver ammine unstable in acidic solutions?

951. How can you explain the fact that when sodium chloride reacts with a K[Ag(CN)] solution, no silver chloride precipitates, whereas sodium sulphide with the same solution yields a precipitate of Ag\(_2\)S?

952. Explain why AgCl, AgBr, and AgI dissolve well in a KCN solution, while only AgCl and AgBr dissolve in an ammonia solution.

953. Write balanced equations of the following reactions:

(a) \( \text{Au(OH)}_2 + \text{HCl(conc)} \rightarrow \)
(b) \( \text{AuCl}_3 + \text{H}_2\text{O}_2 + \text{KOH} \rightarrow \)
(c) \( \text{AuCl}_3 + \text{SnCl}_2 + \text{H}_2\text{O} \rightarrow \)
(d) \( \text{Au} + \text{NaCN} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \)
(e) \( \text{Au} + \text{HCl} + \text{HNO}_3 \rightarrow \text{HAuCl}_4 + \)

954. In which compound—KCl or AgCl—is the chemical bond of a more covalent nature? How can this be explained?

955. A small piece of a silver coin with a mass of 0.300 g was dissolved in nitric acid and the silver precipitated from the solution obtained as AgCl. The mass of the precipitate after washing and drying was 0.199 g. What was the silver content in per cent (mass) of the coin?

956. A sample of brass with a mass of 1.6645 g yielded 1.3466 g of Cu(SCN)\(_2\) and 0.0840 g of SnO\(_2\) when analysed. Calculate the content of the copper, tin, and zinc in the sample in per cent.
REVIEW QUESTIONS

957. Which of the following compounds react with an ammonia solution? (a) Cu(OH)$_2$; (b) AgCl; (c) AgI.

958. Is a potassium carbonate solution (a) acidic; (b) neutral; (c) basic?

959. With which of the following substances does concentrated HNO$_3$ react? (a) NaOH; (b) CuO; (c) Ag; (d) KCl. Here the nitric acid exhibits (1) acid properties; (2) oxidizing properties.

960. What is the relationship between the pH's of isomolar solutions of NaHSO$_3$ (pH$_1$) and Na$_2$SO$_3$ (pH$_2$)? (a) pH$_1$ > pH$_2$; (b) pH$_1$ = pH$_2$; (c) pH$_1$ < pH$_2$.

961. The addition of which of the following substances intensifies the hydrolysis of sodium carbonate? (a) NaOH; (b) ZnCl$_2$; (c) H$_2$O; (d) K$_2$S.

962. In the electrolysis of an aqueous NaOH solution, 2.8 litres of oxygen were liberated at the anode (in standard conditions). How much hydrogen was liberated at the cathode? (a) 2.8 litres; (b) 5.6 litres; (c) 11.2 litres; (d) 22.4 litres.

963. What are the products of the reaction between potassium iodide and copper(II) chloride if:

\[ \text{Cu}^{2+} + I^- + e^- \rightarrow \text{CuI} \quad \varphi^o = 0.86 \text{ V} \]
\[ I_2 + 2e^- \rightarrow 2I^- \quad \varphi^o = 0.54 \text{ V} \]
\[ \text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- \quad \varphi^o = 1.36 \text{ V} \]

(a) CuI$_2$ and Cl$_2$; (b) CuI$_2$ and KCl; (c) CuI and Cl$_2$; (d) CuI and I$_2$; (e) the reaction is impossible.

8. Group II Metals. Water Hardness

964. Consider the features of the structure of atoms of Group II elements. How does the first ionization potential change with an increasing atomic number of the elements in the main and secondary subgroups?

965. Why is the first ionization potential of the beryllium atom (9.32 eV) higher than that of the lithium atom (5.39 eV), and the second ionization potential (18.21 eV) lower than that of the lithium atom (75.64 eV)?
966. How and why do the basic properties of the hydrox­
ides of the main subgroup metals of Group II change when
go­ing from Be(OH)$_2$ to Ba(OH)$_2$?
967. How does the similarity in the chemical properties
of beryllium and aluminium manifest itself? What causes
this similarity?
968. Give the electron configuration and the geometrical
structure of the BeCl$_2$ molecule. In what hybridization state
is the beryllium atom in the BeCl$_2$ molecule? How will the
type of hybridization change when BeCl$_2$ transforms to the
solid state?
969. Write the formulas of potassium tetrahydroxoberyl­
late and sodium tetrafluoroberyllate. How can these com­
ounds be prepared?
970. Is calcium stable in oxygen, fluorine, nitrogen,
carbon dioxide, and water vapour? Substantiate your answer
by calculating the change in the Gibbs energy in the rele­
vant processes.
971. Can calcium be obtained by reducing its oxide with
aluminium? Substantiate your answer by calculating the
Gibbs energy of the reaction.
972. Write the equations of the reactions of calcium
hydride with (a) oxygen, and (b) water.
973. Calculate $\Delta G^\circ$ for the reaction of combustion of
magnesium in carbon dioxide. Can this reaction proceed
spontaneously?
974. What products form when magnesium burns in air?
Write the equations of their reactions with water.
975. Using Table 5 of the Appendix, calculate the amount
of heat that is liberated in the slaking of 1 kg of lime.
976. Which of the two possible reactions:

(a) $N_2O + 3Mg = Mg_3N_2 + \frac{1}{2}O_2$

(b) $N_2O + Mg = MgO + N_2$

is more probable when magnesium reacts with N$_2$O?
Substantiate your answer with calculations.
977. The roasting of 30 g of a calcium sulphate crystal
hydrate yields 6.28 g of water. What is the formula of the
crystal hydrate?
978. When 5.00 g of CaO containing an admixture of CaCO₃ were dissolved in an acid, 140 ml of gas measured in standard conditions were liberated. What per cent of CaCO₃ (by mass) was contained in the initial sample?

979. Write balanced equations of the following reactions:

(a) \( \text{Ba(OH)}_2 + \text{H}_2\text{O} \rightarrow \)  
(b) \( \text{Be} + \text{NaOH} \rightarrow \)  
(c) \( \text{BaO}_2 + \text{H}_2\text{SO}_4 \rightarrow \)

980. Give equations of reactions pointing to the amphoteric nature of beryllium and zinc hydroxides.

981. Compare the relation of zinc, cadmium, and mercury to dilute and concentrated acids: (a) hydrochloric; (b) sulphuric; and (c) nitric. Write the equations of the relevant reactions.

982. What happens when zinc and cadmium hydroxides are reacted with solutions of (a) an alkali, and (b) ammonia?

983. When 1.56 g of a mixture of zinc carbonate with zinc oxide were roasted, 1.34 g of zinc oxide were obtained. Calculate the composition of the initial mixture (in per cent by mass).

984. Find the amount of heat that will be absorbed in the reduction of 1 kg of zinc oxide with graphite. Disregard the dependence of the enthalpy of the reaction on the temperature.

985. A piece of brass was dissolved in nitric acid. The solution was divided into two parts: an excess of ammonia was added to one of them, and an excess of an alkali to the other. Will the zinc and the copper be in the solution or in a precipitate in these two cases, and in the form of what compounds?

986. Metallic mercury often contains admixtures of "unnoble" metals—zinc, tin, and lead. To remove them, the mercury is treated with an \( \text{Hg(NO}_3\text{)}_2 \) solution. What is this method of purifying mercury based on?

987. How can the only slight dissociation of mercury(II) chloride in a solution be explained?

988. Write balanced equations of the following reactions:

(a) \( \text{Zn} + \text{NaOH} \rightarrow \)  
(b) \( \text{Zn} + \text{NaNO}_3 + \text{NaOH} \rightarrow \text{NH}_3 + \)  
(c) \( \text{Hg} + \text{HNO}_3(\text{excess}) \rightarrow \)
989. The presence of what salts in natural water underlies its hardness? What chemical reactions occur when (a) Na₂CO₃; (b) NaOH; and (c) Ca(OH)₂ are added to hard water? Consider the cases of permanent and temporary hardness.

990. How many grams of Ca(OH)₂ must be added to 1000 litres of water to eliminate a temporary hardness equal to 2.86 meq/l?

991. Calculate the temporary hardness of water knowing that 5 ml of a 0.1 N solution of HCl were needed for the reaction with the hydrogen carbonate contained in 100 ml of this water.

992. What is the temporary hardness of water, one litre of which contains 0.146 g of magnesium hydrogen carbonate?

993. The hardness of water containing only calcium hydrogen carbonate is 1.785 meq/l. Determine the mass of the hydrogen carbonate in one litre of water.

994. How much sodium carbonate must be added to 5 litres of water to eliminate a total hardness of 4.60 meq/l?

995. One litre of water contains 38 mg of Mg²⁺ ions and 108 mg of Ca²⁺ ions. Calculate the total hardness of the water.

996. When 250 ml of water containing calcium hydrogen carbonate were boiled, a precipitate with a mass of 3.5 mg formed. What was the hardness of the water?

997. What is the essence of the ion-exchange method of eliminating water hardness?

REVIEW QUESTIONS

998. With which of the following substances will hydrochloric acid react? (a) Zn; (b) Hg; (c) HgS; (d) Cd(OH)₂; (e) Zn(NO₃)₂; (f) Zn(OH)₂.

999. With which of the following compounds will Zn(OH)₂ react? (a) NaCl; (b) H₂SO₄; (c) NH₄OH; (d) KOH; (e) Fe(OH)₃.
1000. In which solutions are the reducing properties of zinc exhibited more strongly if
\[ \text{Zn}^{2+} + 2e^- = \text{Zn} \quad \varphi^0 = -0.76 \text{ V} \]
\[ \text{ZnO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- = \text{Zn} + 4\text{OH}^- \quad \varphi^0 = -1.26 \text{ V} \]
(a) in acidic solutions; (b) in basic solutions.

1001. The values of the standard electrode potentials for the systems \( \text{Zn}/\text{Zn}^{2+} \) and \( \text{Cd}/\text{Cd}^{2+} \) are \(-0.76 \text{ V}\) and \(-0.40 \text{ V}\), respectively. Which reaction proceeds spontaneously in a cadmium-zinc galvanic cell? (a) \( \text{Zn} + \text{Cd}^{2+} = \text{Cd} + \text{Zn}^{2+} \); (b) \( \text{Cd} + \text{Zn}^{2+} = \text{Zn} + \text{Cd}^{2+} \).

1002. The reaction \( \text{Fe} + \text{Cd}^{2+} \rightarrow \text{Cd} + \text{Fe}^{2+} \) proceeds spontaneously in a galvanic cell. Which electrode is the anode? (a) The iron one; (b) the cadmium one.

1003. Proceeding from the positions of Mg and Be in the periodic table, state which relationship between the hydrolysis constants of the salts \( \text{MgCl}_2 \) and \( \text{BeCl}_2 \) is correct. (a) \( K(\text{MgCl}_2) > K(\text{BeCl}_2) \); (b) \( K(\text{MgCl}_2) = K(\text{BeCl}_2) \); (c) \( K(\text{MgCl}_2) < K(\text{BeCl}_2) \).

9. Group III Elements

1004. Consider the features of the structure of the atoms of the main subgroup elements of Group III. What valence states are characteristic of these elements? How do their metallic properties change with an increasing atomic number of the element?

1005. How does the similarity between the chemical properties of boron and silicon manifest itself? What is this similarity explained by?

1006. Describe the electron configuration of diborane. Are the properties of all the hydrogen atoms in the \( \text{B}_2\text{H}_6 \) molecule the same? Motivate your answer.

1007. What changes does orthoboric acid experience when heated? Write the equations of the relevant reactions.

1008. Write the formulas of sodium metaborate, tetraborate, and boride.

1009. Why does aluminium displace hydrogen from water only when an alkali is added? Write the equations of the relevant reactions.
1010. Write the equations of the reactions of aluminium sulphate with solutions of (a) \((\text{NH}_4)_2\text{S}\), (b) \(\text{Na}_2\text{CO}_3\), and (c) \(\text{KOH}\) (excess).

1011. What mass of aluminium nitride is needed to produce 3 litres of ammonia (in standard conditions)?

1012. What is the difference between the action of excess \(\text{NH}_4\text{OH}\) and aqueous solutions of \(\text{NH}_3\) and \(\text{NaOH}\) on a solution of \(\text{AlCl}_3\)? Write the equations of the relevant reactions.

1013. Using Table 5 of the Appendix, establish whether or not the reaction \(4\text{Al} + 3\text{CO}_2 = 2\text{Al}_2\text{O}_3 + 3\text{C}\) can proceed spontaneously.

1014. In operation of the galvanic cell

\[
\text{Al} | \text{Al}_2(\text{SO}_4)_3 || \text{Cr}_2(\text{SO}_4)_3 | \text{Cr}
\]

31.2 g of chromium were reduced at the cathode. Determine by how much the mass of the aluminium electrode diminished.

1015. Compare the masses of calcium hydride and metallic aluminium needed to prepare 50 litres of hydrogen.

1016. How can (a) aluminium hydroxide, (b) barium sulphate, and (c) potassium aluminate be prepared from ammonium alum? Write the equations of the relevant reactions.

1017. Write balanced equations of the following reactions:

(a) \(\text{B} + \text{HNO}_3(\text{conc}) \rightarrow\)
(b) \(\text{Na}_2\text{B}_4\text{O}_7 + \text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow\)
(c) \(\text{H}_3\text{BO}_3 + \text{NaOH} \rightarrow\)
(d) \(\text{Al}_2(\text{SO}_4)_3 + \text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow\)
(e) \(\text{Al} + \text{NaOH} + \text{H}_2\text{O} \rightarrow\)
(f) \(\text{AlCl}_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow\)

1018. What oxidation states are characteristic of the gallium subgroup elements? In what oxidation state are gallium and indium compounds more stable, and in what state those of thallium?

1019. How can the inclination of aluminium halide molecules to dimerize be explained?

1020. Calculate the solubility of \(\text{Tl}_2\text{CrO}_4\) if the value of \(K_{sp}\) for this salt at 20 °C is \(9.8 \times 10^{-13}\).

1021. How can the similarity of the chemical properties of the lanthanides be explained?

1022. What is lanthanide contraction? How does it affect the properties of the sixth-period \(d\) elements?
REVIEW QUESTIONS

1023. Can a reaction occur between BF₃ and NH₃? (a) Yes; (b) no.
Because (1) in the NH₃ molecule, the outer electron layer of the nitrogen atom is completely filled by electrons; (2) a donor-acceptor bond can be formed between the NH₃ and BF₃ molecules.

1024. With which of the following compounds will KOH react? (a) H₃BO₃; (b) Na₂B₄O₇; (c) Al₂O₃; (d) AlCl₃; (e) Ga(OH)₃.

1025. The addition of which substances will intensify the hydrolysis of AlCl₃? (a) H₂SO₄; (b) ZnCl₂; (c) (NH₄)₂S; (d) Zn.

1026. What products are formed when AlCl₃ and Na₂CO₃ react in an aqueous solution? (a) Al(OH)₃ and CO₂; (b) Al₂(CO₃)₃ and NaCl.

1027. With which of the following substances will concentrated HNO₃ react? (a) B; (b) Al; (c) Al(OH)₃; (d) Na₂B₄O₇.

10. Metals of Groups IV, V, VI and VII

1028. Describe the relation of lead to air, water, and acids. Why doesn't lead dissolve in dilute hydrochloric and sulphuric acids, although it precedes hydrogen in the electromotive series?

1029. Name the oxides of germanium, tin, and lead. How do the acidic and basic properties of the hydroxides change in the series Ge(OH)₂-Pb(OH)₂ and Ge(OH)₄-Pb(OH)₄?

1030. How do the oxidation-reduction properties of compounds change in the series Ge(II)-Pb(II) and Ge(IV)-Pb(IV)?

1031. An alloy of lead and tin was heated with concentrated HNO₃ until the reaction stopped. The undissolved precipitate was filtered off, dried, and roasted. What is the composition of the residue? What is in the solution?

1032. Why are the lead oxides Pb₃O₃ and Pb₂O₄ called mixed? Indicate the oxidation state of lead in these compounds.

1033. Why is the water acidified with hydrochloric acid when preparing an SnCl₂ solution?
1034. How can sodium thiostannate be prepared proceeding from metallic tin?

1035. Using Table 5 of the Appendix and by considering the process \( 2MO + O_2 \rightarrow 2MO_2 \), make a conclusion as to the comparative stability of the different oxidation states of tin and lead.

1036. How can alpha- and beta-stannic acids be prepared? What is the difference between their properties?

1037. Write the formulas of tetrahydroxostannate(II), hexahydroxostannate(IV), hexahydroxoplumbate(IV), hexahydroxoplumbate(II), and sodium thiostannate. How can these compounds be prepared?

1038. Write balanced equations of the following reactions:

(a) \( Ge + HNO_3 \rightarrow \)
(b) \( Sn + HNO_3 \rightarrow \)
(c) \( Sn + KOH \rightarrow \)
(d) \( Pb + KOH \rightarrow \)
(e) \( PbO_2 + HCl \rightarrow \)

1039. Write balanced equations of the following reactions:

(a) \( Pb_2O_4 + KI + H_2SO_4 \rightarrow \)
(b) \( SnCl_2 + FeCl_3 \rightarrow \)
(c) \( SnCl_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow \)
(d) \( Pb_2O_4 + Mn(NO_3)_2 + HNO_3 \rightarrow \)
(e) \( Pb(CH_3COO)_2 + CaOCl_2 + H_2O \rightarrow \)

1040. Write the equations of the reactions proceeding at the electrodes of a lead accumulator when it is being charged and discharged.

1041. Compare the properties of the vanadium subgroup elements with those of the elements of (a) the main subgroup of Group V; (b) the titanium subgroup; and (c) the chromium subgroup.

1042. How can one explain the closeness of the atomic radii of niobium and tantalum, molybdenum and tungsten, and technetium and rhenium?

1043. Substantiate the arrangement of chromium, molybdenum, and tungsten in Group VI. In what are these elements similar to those in the main subgroup?
1044. Describe the properties of chromium, indicating (a) its place in the periodic table and the structure of its atom; (b) the relation of metallic chromium to air, water, and acids; and (c) the composition and nature of chromium oxides and hydroxides.

1045. What chromium compounds are characterized by oxidizing properties? Give examples of reactions in which these properties manifest themselves.

1046. In what solution—acidic or basic—are the oxidizing properties of chromium(VI) more pronounced? The reducing properties of chromium(III)? How can this be explained?

1047. What happens when a sodium sulphide solution is added to a solution of (a) chromium(II) chloride, and (b) chromium(III) chloride? Write the equations of the reactions.

1048. Compile the equations of the reactions of chromium(III) chloride with (a) bromine, and (b) hydrogen peroxide in a basic solution.

1049. How can potassium chrome alum be prepared if potassium dichromate is used as a reactant? Find the mass of the $K_2Cr_2O_7$ needed to prepare 1 kg of the alum.

1050. Why do precipitates having the same composition form when barium salts react with potassium chromate and dichromate solutions?

1051. Are aqueous potassium chromate and dichromate solutions neutral, acidic, or basic? Substantiate your answer.

1052. How can the following transformations be carried out: $Cr_2O_3 \rightarrow K_2CrO_4 \rightarrow K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3 \rightarrow $ $\rightarrow K_2[Cr(OH)_6]$?

1053. How many litres of chlorine (in standard conditions) evolve when one mole of sodium dichromate reacts with excess hydrochloric acid?

1054. Write balanced equations of the following reactions:

(a) $NaCrO_3 + PbO_2 + NaOH \rightarrow$
(b) $CrCl_3 + NaBiO_3 + NaOH \rightarrow$
(c) $Cr_2(SO_4)_3 + Br_2 + NaOH \rightarrow$
(d) $K_2Cr_2O_7 + SO_2 + H_2SO_4 \rightarrow$
(e) $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow$
(f) $FeO \cdot Cr_2O_3 + O_2 + K_2CO_3 \rightarrow Fe_2O_3 + K_2CrO_4 + CO_2$
1055. Indicate the differences in the structure of atoms of the manganese and halogen subgroup elements. In what oxidation states do these elements display the greatest similarity in their properties?

1056. How many grams of potassium permanganate are needed to oxidize 7.60 g of FeSO₄ in a neutral and in an acidic solution?

1057. Write the equations of the reactions in which manganese compounds exhibit (a) oxidizing properties; (b) reducing properties; and (c) oxidizing and reducing properties simultaneously.

1058. How can compounds of manganese(VI) be prepared from compounds with a higher and a lower oxidation state of this element?

1059. Write the equation of the thermal decomposition of potassium permanganate. What kind of oxidation-reduction transformation does this reaction belong to?

1060. Can a solution be prepared that simultaneously contains Sn²⁺ and Hg₂⁺; Sn²⁺ and Fe³⁺; SO₄²⁻ and MnO₄⁻; Cr₂O₇²⁻ and SO₄²⁻? Indicate which combinations of ions are impossible and why.

1061. Write balanced equations of the following reactions:
   (a) KMnO₄ + K₂SO₃ + H₂SO₄ →
   (b) KMnO₄ + K₂SO₃ + H₂O →
   (c) KMnO₄ + K₄SO₄ + KOH →
   (d) KMnO₄ + H₂O₂ + H₂SO₄ →

1062. Write balanced equations of the following reactions:
   (a) KMnO₄ + HCl(conc) →
   (b) KMnO₄ + H₂S + H₂O →
   (c) MnO₂ + HCl(conc) →
   (d) KMnO₄ + KI + H₂SO₄ →
   (e) MnSO₄ + (NH₄)₂S₂O₈ + H₂O →

1063. Write balanced equations of the following reactions:
   (a) KMnO₄ + MnSO₄ + H₂O →
   (b) MnSO₄ + NaBrO₃ + HNO₃ →
   (c) MnSO₄ + Br₂ + NaOH →
   (d) K₂MnO₄ + H₂SO₄ →
   (e) MnSO₄ + PbO₂ + HNO₃ →
   (f) H₂MnO₄ + KNO₃ →
REVIEW QUESTIONS

1064. What is the relationship between the pH's of isomolar solutions of \( \text{Sn(NO}_3\text{)}_2 \) (pH\(_1\)) and \( \text{Pb(NO}_3\text{)}_2 \) (pH\(_2\))? (a) pH\(_1\) > pH\(_2\); (b) pH\(_1\) = pH\(_2\); (c) pH\(_1\) < pH\(_2\).

1065. What is the relationship between the degrees of hydrolysis \( h \) for isomolar solutions of \( \text{CrCl}_2 \) (\( h_1 \)) and \( \text{CrCl}_3 \) (\( h_2 \))? (a) \( h_1 > h_2 \); (b) \( h_1 = h_2 \); (c) \( h_1 < h_2 \).

1066. How can the degree of hydrolysis of \( \text{SnCl}_2 \) be diminished? (a) By heating the solution; (b) by adding acid; (c) by decreasing the pH of the solution.

1067. What reaction can be used to produce lead(II) hydroxide? (a) That of the free metal with water; (b) that of the oxide \( \text{PbO} \) with water; (c) that of a salt of lead(II) with an alkali.

1068. Which of the following processes occurs at the tin electrode in the electrolysis of an aqueous solution of tin(II) chloride?

(a) \( \text{Sn} = \text{Sn}^{2+} + 2e^- \) \( \varphi^0 = -0.14 \text{ V} \)
(b) \( 2\text{Cl}^- = \text{Cl}_2 + 2e^- \) \( \varphi^0 = 1.36 \text{ V} \)
(c) \( 2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 2e^- \) \( \varphi^0 = 1.23 \text{ V} \)

11. The Noble Gases. Group VIII Metals

1069. Can hydrates of the noble gases such as \( \text{Kr} \cdot 6\text{H}_2\text{O} \) be called chemical compounds? Substantiate your answer.

1070. How many atoms does an argon molecule consist of if its density relative to air is 1.38?

1071. Calculate the per cent content (by mass) of xenon in the compound \( \text{Xe}[\text{PtF}_6] \). Name this compound.

1072. What oxidation states are characteristic of the iron family metals?

1073. What is the relation of iron, cobalt, and nickel to acids?

1074. Write the equations of the reactions of iron(III), cobalt(III), and nickel(III) hydroxides with hydrochloric and sulphuric acids.

1075. Write the equations of the reactions of an \( \text{Na}_2\text{CO}_3 \) solution with \( \text{FeCl}_3 \) and \( \text{FeCl}_2 \) solutions.

1076. How can one transform (a) an iron(III) salt into an iron(II) salt, and (b) an iron(II) salt into an iron(III) salt? Give examples of these reactions.
1077. Using Table 5 of the Appendix, establish which of the following reducing agents can reduce the Fe$^{3+}$ ion to the free metal: (a) Zn, (b) Ni, and (c) H$_2$S.

1078. When iron is produced from magnetite, one of the reactions proceeding in the blast furnace is:

$$\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2$$

Using Table 5 of the Appendix, determine the heat effect of the reaction. In what direction will the equilibrium of this reaction shift upon elevation of the temperature?

1079. Which of the following reactions characterizes the dissolving of metallic iron in a solution of hydrochloric acid with pH = 0?

(a) $\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$

(b) $2\text{Fe} + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2$

1080. What iron and carbon alloys are called steels, and what—commercial irons?

1081. Give a diagram of the chemical processes occurring in different parts of a blast furnace. Why is calcium carbonate added to the ore in producing iron?

1082. List the ways you know of converting iron into steel. What chemical processes occur in this conversion?

1083. Can iron(III) sulphide be produced by reacting (a) solutions of FeCl$_3$ and H$_2$S, and (b) solutions of Fe(NO$_3$)$_3$ and (NH$_4$)$_2$S? Substantiate your answer.

1084. In an aqueous solution, iron(II) sulphate is oxidized by the oxygen dissolved in the water to form the basic salt. Write the equation of the relevant reaction.

1085. How is the corrosion of iron affected by its contact with other metals? What metal will be destroyed first on the damaged surface of tin-plated, galvanized, and nickel-plated iron?

1086. What compounds are named ferrites and ferrates? Give examples.

1087. The iron contained in 10 ml of an FeSO$_4$ solution being analysed was oxidized to iron(III) and precipitated in the form of the hydroxide. The mass of the roasted precipitate was found to be 0.4132 g. Calculate the molar concentration of the initial solution.
1088. Describe the electron configuration of the carbonyl compounds of iron and nickel. What are these compounds used for?

1089. How does the stability to oxidation change in the series Fe(II)-Co(II)-Ni(II)? How does the oxidizing power change in the series Fe(III)-Co(III)-Ni(III)?

1090. Write balanced equations of the following reactions:

(a) \( \text{Fe}(\text{OH})_3 + \text{Cl}_2 + \text{NaOH} \text{(conc)} \rightarrow \)
(b) \( \text{FeCl}_3 + \text{KI} \rightarrow \)
(c) \( \text{FeS}_2 + \text{HNO}_3 \text{(conc)} \rightarrow \)
(d) \( \text{CoBr}_3 + \text{O}_2 + \text{KOH} + \text{H}_2\text{O} \rightarrow \)
(e) \( \text{FeSO}_4 + \text{HNO}_3 \text{(conc)} \rightarrow \)
(f) \( \text{Ni}(\text{OH})_3 + \text{HCl} \rightarrow \)

1091. How do platinum and palladium react with hydrogen?

1092. What is obtained when Pt reacts with aqua regia? Write the equation of the reaction.

1093. Name the following complex compounds:

(a) \( [\text{PdCl}_2\text{NH}_3] \)
(b) \( \text{K}_3[\text{RuOHCls}] \)
(c) \( [\text{RhI}_3(\text{NH}_3)_3] \)
(d) \( [\text{PtSO}_4(\text{NH}_3)_4]\text{Br}_2 \)
(e) \( (\text{NH}_4)_2[\text{RhCl}_6] \)
(f) \( \text{Na}_2[\text{PdI}_4] \)
(g) \( [\text{Os}(\text{NH}_3)_6]\text{Br}_3 \)
(h) \( \text{K}_3[\text{IrCl}_2(\text{NO}_3)_4] \)

**REVIEW QUESTIONS**

1094. What is the relationship between the pH's of isomolar solutions of \( \text{FeSO}_4 \) (\( \text{pH}_1 \)) and \( \text{Fe}_3(\text{SO}_4)_3 \) (\( \text{pH}_2 \))? (a) \( \text{pH}_1 > \text{pH}_2 \); (b) \( \text{pH}_1 = \text{pH}_2 \); (c) \( \text{pH}_1 < \text{pH}_2 \).

Because (1) a salt formed by a weaker base hydrolyzes to a greater degree; (a) the degree of hydrolysis depends on the concentration of the solution.

1095. In what direction does equilibrium shift in the system \( 2\text{Fe} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2 \) when the pressure
is lowered? (a) To the left; (b) to the right; (c) equilibrium does not shift.

1096. The addition of which substances will increase the hydrolysis of FeCl$_3$? (a) H$_2$SO$_4$; (b) ZnCl$_2$; (c) (NH$_4$)$_2$CO$_3$; (d) Zn.

1097. What are the products of the reaction of sodium carbonate with an aqueous solution of Fe$_2$(SO$_4$)$_3$? (a) Fe(OH)$_3$ and CO$_2$; (b) Fe$_2$(CO$_3$)$_3$ and Na$_2$SO$_4$.

Because (1) an exchange reaction occurs; (2) mutual amplification of the hydrolysis of the two salts occurs.

1098. With which of the following substances will iron(III) sulphate react in an aqueous solution? (a) NaI; (b) NaBr; (c) with neither of them; (d) with both of them.

Here

\[
\begin{align*}
\text{Fe}^{3+} + e^- &= \text{Fe}^{2+} \quad \varphi^o = 0.77 \text{ V} \\
2e^- + \text{I}_2(c) &= 2\text{I}^- \quad \varphi^o = 0.54 \text{ V} \\
2e^- + \text{Br}_2(\text{lq}) &= 2\text{Br}^- \quad \varphi^o = 1.07 \text{ V}
\end{align*}
\]

1099. What is the formula of cobalt carbonyl? (a) Co(CO)$_4$; (b) CO$_2$(CO)$_8$.

Because (1) the cobalt atom in the ground state has three unpaired $d$ electrons; (2) the cobalt atom in the excited state has four free valence orbitals; (3) the cobalt atom in the excited state has one unpaired electron.
### Appendix

#### Table 1
Selected SI Units

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Unit</th>
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<th>Symbol</th>
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<td>Mass</td>
<td>Kilogram</td>
<td>kg</td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>Second</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>Electric current</td>
<td>Ampere</td>
<td>A</td>
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<td>Temperature</td>
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</tr>
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<td><strong>Derived Units</strong></td>
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<tr>
<td>Density</td>
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</tr>
<tr>
<td>Force, weight</td>
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</tr>
<tr>
<td>Pressure</td>
<td>Pascal</td>
<td>Pa (N/m²)</td>
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</tr>
<tr>
<td>Energy, work, amount of heat</td>
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<td>J (N·m)</td>
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</tr>
<tr>
<td>Power</td>
<td>Watt</td>
<td>W (J/s)</td>
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</tr>
<tr>
<td>Quantity of electricity</td>
<td>Coulomb</td>
<td>C (A·s)</td>
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</tr>
<tr>
<td>Electric voltage, electrical potential, electromotive force (e.m.f.)</td>
<td>Volt</td>
<td>V (W/A)</td>
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Table 2
Conversion of Selected Non-System Units to SI Units

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<tr>
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<th>Unit</th>
<th>Conversion factor to SI</th>
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<td>Length</td>
<td>Micrometre (µm)</td>
<td>1×10^{-6} m</td>
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<tr>
<td></td>
<td>Angstrom (Å)</td>
<td>1×10^{-10} m</td>
</tr>
<tr>
<td>Pressure</td>
<td>Physical atmosphere (atm)</td>
<td>1.01325×10^6 Pa</td>
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<td></td>
<td>Millimetre of mercury (mmHg) or torr</td>
<td>133.322 Pa</td>
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<tr>
<td>Energy, work, amount of</td>
<td>Electron-volt (eV)</td>
<td>1.60219×10^{-19} J</td>
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<td></td>
<td>Calorie (cal)</td>
<td>4.1868 J</td>
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<tr>
<td></td>
<td>Kilocalorie (kcal)</td>
<td>4186.8 J</td>
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<tr>
<td>Dipole moment</td>
<td>Debye (D)</td>
<td>3.33×10^{-30} C·m</td>
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Table 3
Values of Selected Fundamental Physical Constants

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<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Numerical value</th>
</tr>
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<tbody>
<tr>
<td>Speed of light in free space</td>
<td>c</td>
<td>2.997 924 6×10^8 m/s</td>
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<tr>
<td>Planck's constant</td>
<td>h</td>
<td>6.626 18×10^{-34} J·s</td>
</tr>
<tr>
<td>Elementary electric charge</td>
<td>e</td>
<td>1.602 189×10^{-19} C</td>
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<tr>
<td>Avogadro's constant</td>
<td>N_A</td>
<td>6.022 045×10^23 mol⁻¹</td>
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<tr>
<td>Faraday's constant</td>
<td>F</td>
<td>9.648 46×10^4 C/mol</td>
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<tr>
<td>Molar gas constant</td>
<td>R</td>
<td>8.314 4 J/(mol·K)</td>
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Table 4
Names of Most Important Acids and Their Salts

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<tr>
<th>Acid</th>
<th>Name</th>
<th>Name of salt</th>
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<td>HAlO₂</td>
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<td>Meta-aluminate</td>
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<tr>
<td>HASO₃</td>
<td>Meta-arsenic</td>
<td>Meta-arsenate</td>
</tr>
<tr>
<td>H₂AsO₄</td>
<td>Ortho-arsenic</td>
<td>Ortho-arsenate</td>
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<td>HASO₂</td>
<td>Meta-arsenous</td>
<td>Meta-arsenite</td>
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<td>H₃AsO₃</td>
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<tr>
<td>HBO₂</td>
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Table 4 (continued)

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<tr>
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<th>Name of salt</th>
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<td>$\text{H}_3\text{BO}_3$</td>
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<td>Orthoborate</td>
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<td>$\text{H}_3\text{B}_4\text{O}_7$</td>
<td>Tetraboric</td>
<td>Tetraborate</td>
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<tr>
<td>$\text{HBr}$</td>
<td>Hydrogen bromide (hydrobromic)</td>
<td>Bromide</td>
</tr>
<tr>
<td>$\text{HBrO}$</td>
<td>Hypobromous</td>
<td>Hypobromite</td>
</tr>
<tr>
<td>$\text{HBrO}_3$</td>
<td>Bromic</td>
<td>Bromate</td>
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<tr>
<td>$\text{HCOOH}$</td>
<td>Formic</td>
<td>Formate</td>
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<td>$\text{CH}_3\text{COOH}$</td>
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<td>Acetate</td>
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<td>$\text{HCN}$</td>
<td>Hydrogen cyanide (hydrocyanic)</td>
<td>Cyanide</td>
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<td>Carbonate</td>
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<td>Oxalate</td>
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### Table 4 (concluded)

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<td>(pyrosulphate)</td>
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</table>

### Table 5

**Standard Enthalpies of Formation** $\Delta H_{\text{f}298}^\circ$, **Entropies** $S_{\text{f}298}^\circ$, and **Gibbs Energies of Formation** $\Delta G_{\text{f}298}^\circ$ of Selected Substances at 298 K (25 °C)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_{\text{f}298}^\circ$, kJ/mol</th>
<th>$S_{\text{f}298}^\circ$, J/(mol·K)</th>
<th>$\Delta G_{\text{f}298}^\circ$, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ (c)</td>
<td>-1676.0</td>
<td>50.9</td>
<td>-1582.0</td>
</tr>
<tr>
<td>C (graphite)</td>
<td>0</td>
<td>5.7</td>
<td>0</td>
</tr>
<tr>
<td>CCl₄ (lq)</td>
<td>-135.4</td>
<td>214.4</td>
<td>-64.6</td>
</tr>
<tr>
<td>CH₄ (g)</td>
<td>-74.9</td>
<td>186.2</td>
<td>-50.8</td>
</tr>
<tr>
<td>C₂H₂ (g)</td>
<td>226.8</td>
<td>200.8</td>
<td>209.2</td>
</tr>
<tr>
<td>C₂H₄ (g)</td>
<td>52.3</td>
<td>219.4</td>
<td>68.1</td>
</tr>
<tr>
<td>C₂H₆ (g)</td>
<td>-89.7</td>
<td>229.5</td>
<td>-32.9</td>
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<tr>
<td>C₂H₆ (lq)</td>
<td>82.9</td>
<td>269.2</td>
<td>129.7</td>
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<tr>
<td>C₆H₅OH (lq)</td>
<td>-277.6</td>
<td>160.7</td>
<td>-174.8</td>
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<tr>
<td>C₆H₁₂O₆ (glucose)</td>
<td>-1273.0</td>
<td>-</td>
<td>-919.5</td>
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### Table 5 (continued)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H_{298}^\circ$ kJ/mol</th>
<th>$S_{298}^\circ$ J/(mol·K)</th>
<th>$\Delta G_{298}^\circ$ kJ/mol</th>
</tr>
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<tbody>
<tr>
<td>CO (g)</td>
<td>-110.5</td>
<td>197.5</td>
<td>-137.1</td>
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<td>CO$_2$ (g)</td>
<td>-393.5</td>
<td>213.7</td>
<td>-394.4</td>
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<tr>
<td>CaCO$_3$ (c)</td>
<td>-1207.0</td>
<td>88.7</td>
<td>-1127.7</td>
</tr>
<tr>
<td>CaF$_2$ (c)</td>
<td>-1214.6</td>
<td>68.9</td>
<td>-1161.9</td>
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<tr>
<td>Ca$_2$N$_2$ (c)</td>
<td>-431.8</td>
<td>105</td>
<td>-368.6</td>
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<td>CaO (c)</td>
<td>-635.5</td>
<td>39.7</td>
<td>-604.2</td>
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<tr>
<td>Ca(OH)$_2$ (c)</td>
<td>-986.6</td>
<td>76.1</td>
<td>-906.8</td>
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<tr>
<td>Cl$_2$ (g)</td>
<td>0</td>
<td>222.9</td>
<td>0</td>
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<tr>
<td>Cl$_2$O (g)</td>
<td>76.6</td>
<td>286.2</td>
<td>94.2</td>
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<tr>
<td>ClO$_2$ (g)</td>
<td>105.0</td>
<td>257.0</td>
<td>122.3</td>
</tr>
<tr>
<td>Cl$_2$O$_3$ (lq)</td>
<td>251.0</td>
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<td></td>
</tr>
<tr>
<td>Cr$_2$O$_3$ (c)</td>
<td>-1440.6</td>
<td>81.2</td>
<td>-1050.0</td>
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<tr>
<td>CuO (c)</td>
<td>-162.0</td>
<td>42.6</td>
<td>-129.9</td>
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<tr>
<td>FeO (c)</td>
<td>-264.8</td>
<td>60.8</td>
<td>-244.3</td>
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<tr>
<td>Fe$_2$O$_3$ (c)</td>
<td>-822.2</td>
<td>87.4</td>
<td>-740.3</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (c)</td>
<td>-1117.1</td>
<td>146.2</td>
<td>-1014.2</td>
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<tr>
<td>H$_2$ (g)</td>
<td>0</td>
<td>140.5</td>
<td>0</td>
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<tr>
<td>HBr (g)</td>
<td>-36.3</td>
<td>198.6</td>
<td>-53.3</td>
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<tr>
<td>HCN (g)</td>
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<td>113.1</td>
<td>125.5</td>
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<tr>
<td>HCl (g)</td>
<td>-92.3</td>
<td>186.8</td>
<td>-95.2</td>
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<tr>
<td>HF (g)</td>
<td>-270.7</td>
<td>178.7</td>
<td>-272.8</td>
</tr>
<tr>
<td>HI (g)</td>
<td>26.6</td>
<td>206.5</td>
<td>1.8</td>
</tr>
<tr>
<td>HN$_3$ (lq)</td>
<td>294.0</td>
<td>328.0</td>
<td>238.8</td>
</tr>
<tr>
<td>H$_2$O (g)</td>
<td>-241.8</td>
<td>188.7</td>
<td>-223.6</td>
</tr>
<tr>
<td>H$_2$O (lq)</td>
<td>-285.8</td>
<td>70.4</td>
<td>-237.3</td>
</tr>
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<td>H$_2$S (g)</td>
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<td>-33.8</td>
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<tr>
<td>KCl (c)</td>
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<td>-408.0</td>
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<td>KClO$_2$ (c)</td>
<td>-391.2</td>
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<td>-289.9</td>
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<tr>
<td>MgCl$_2$ (c)</td>
<td>-641.1</td>
<td>89.9</td>
<td>-591.6</td>
</tr>
<tr>
<td>Mg$_2$N$_2$ (c)</td>
<td>-461.1</td>
<td>87.9</td>
<td>-400.9</td>
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<tr>
<td>MgO (c)</td>
<td>-601.8</td>
<td>26.9</td>
<td>-569.6</td>
</tr>
<tr>
<td>N$_2$ (g)</td>
<td>0</td>
<td>191.5</td>
<td>0</td>
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<tr>
<td>NH$_3$ (g)</td>
<td>-46.2</td>
<td>192.8</td>
<td>-46.7</td>
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<tr>
<td>NH$_4$NO$_2$ (c)</td>
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<td></td>
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<tr>
<td>NH$_4$NO$_3$ (c)</td>
<td>-365.4</td>
<td>151</td>
<td>-183.8</td>
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</table>
Table 5 (concluded)

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\Delta H^\circ_{298}$</th>
<th>$\Delta S^\circ_{298}$</th>
<th>$\Delta G^\circ_{298}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2O$ (g)</td>
<td>82.0</td>
<td>219.9</td>
<td>104.1</td>
</tr>
<tr>
<td>NO (g)</td>
<td>90.3</td>
<td>210.6</td>
<td>86.6</td>
</tr>
<tr>
<td>$N_2O_3$ (g)</td>
<td>83.3</td>
<td>307.0</td>
<td>140.5</td>
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<tr>
<td>NO$_2$ (g)</td>
<td>33.5</td>
<td>240.2</td>
<td>51.5</td>
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<tr>
<td>$N_2O_4$ (g)</td>
<td>9.6</td>
<td>303.8</td>
<td>98.4</td>
</tr>
<tr>
<td>$N_2O_5$ (c)</td>
<td>-42.7</td>
<td>178.0</td>
<td>114.1</td>
</tr>
<tr>
<td>NiO (c)</td>
<td>-239.7</td>
<td>38.0</td>
<td>-211.6</td>
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<tr>
<td>O$_2$ (g)</td>
<td>0</td>
<td>205.0</td>
<td>0</td>
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<tr>
<td>OF$_2$ (g)</td>
<td>25.1</td>
<td>247.0</td>
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<td>$P_2O_5$ (c)</td>
<td>-820</td>
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<td>-948.8</td>
</tr>
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<td>$P_2O_5$ (c)</td>
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<td>114.5</td>
<td>-1348.8</td>
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<td>PbO (c)</td>
<td>-249.3</td>
<td>66.1</td>
<td>-189.1</td>
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<tr>
<td>PbO$_2$ (c)</td>
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<td>-218.3</td>
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<td>SO$_2$ (g)</td>
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<td>248.1</td>
<td>-300.2</td>
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<td>SO$_3$ (g)</td>
<td>-395.8</td>
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<td>-371.2</td>
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<tr>
<td>SiCl$_4$ (lq)</td>
<td>-687.8</td>
<td>239.7</td>
<td>-</td>
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<td>SiH$_4$ (g)</td>
<td>34.7</td>
<td>204.6</td>
<td>57.2</td>
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<tr>
<td>SiO$_2$ (quartz)</td>
<td>-910.9</td>
<td>41.8</td>
<td>-856.7</td>
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<td>SnO (c)</td>
<td>-266.0</td>
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<td>-256.9</td>
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<td>SnO$_2$ (c)</td>
<td>-580.8</td>
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<td>-519.3</td>
</tr>
<tr>
<td>Ti (c)</td>
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<td>30.6</td>
<td>0</td>
</tr>
<tr>
<td>TiCl$_4$ (lq)</td>
<td>-804.2</td>
<td>252.4</td>
<td>-737.4</td>
</tr>
<tr>
<td>TiO$_2$ (c)</td>
<td>-943.9</td>
<td>50.3</td>
<td>-888.6</td>
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<tr>
<td>WO$_3$ (c)</td>
<td>-342.7</td>
<td>75.9</td>
<td>-763.9</td>
</tr>
<tr>
<td>ZnO (c)</td>
<td>-350.6</td>
<td>43.6</td>
<td>-320.7</td>
</tr>
</tbody>
</table>

Table 6

Dissociation Constants of Selected Weak Electrolytes in Aqueous Solutions at 25 °C

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$K$</th>
<th>$pK = -\log K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid CH$_3$COOH</td>
<td>$1.8\times10^{-5}$</td>
<td>4.75</td>
</tr>
<tr>
<td>Ammonium hydroxide NH$_4$OH</td>
<td>$1.8\times10^{-5}$</td>
<td>4.75</td>
</tr>
<tr>
<td>Boric acid (ertho) H$_3$BO$_3$, $K_1$</td>
<td>$5.8\times10^{-10}$</td>
<td>9.24</td>
</tr>
</tbody>
</table>
### Table 6 (concluded)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$K$</th>
<th>$pK = -\log K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonic acid $\text{H}_2\text{CO}_3$, $K_1$</td>
<td>$4.5 \times 10^{-7}$</td>
<td>6.35</td>
</tr>
<tr>
<td></td>
<td>$K_2$</td>
<td>10.33</td>
</tr>
<tr>
<td>Chloroacetic acid $\text{CH}_2\text{ClCOOH}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>2.85</td>
</tr>
<tr>
<td>Formic acid HCOOH</td>
<td>$1.8 \times 10^{-4}$</td>
<td>3.74</td>
</tr>
<tr>
<td>Hydrazoic acid $\text{HN}_3$</td>
<td>$2.6 \times 10^{-5}$</td>
<td>4.59</td>
</tr>
<tr>
<td>Hydrogen cyanide HCN</td>
<td>$7.9 \times 10^{-10}$</td>
<td>9.10</td>
</tr>
<tr>
<td>Hydrogen fluoride HF</td>
<td>$6.6 \times 10^{-4}$</td>
<td>3.18</td>
</tr>
<tr>
<td>Hydrogen peroxide $\text{H}_2\text{O}_2$, $K_1$</td>
<td>$2.6 \times 10^{-12}$</td>
<td>11.58</td>
</tr>
<tr>
<td>Hydrogen selenide $\text{H}_2\text{Se}$, $K_1$</td>
<td>$1.7 \times 10^{-4}$</td>
<td>3.77</td>
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<td>$K_2$</td>
<td>11.0</td>
</tr>
<tr>
<td>Hydrogen sulphide $\text{H}_2\text{S}$, $K_1$</td>
<td>$6 \times 10^{-8}$</td>
<td>7.22</td>
</tr>
<tr>
<td></td>
<td>$K_2$</td>
<td>14.0</td>
</tr>
<tr>
<td>Hydrogen telluride $\text{H}_2\text{Te}$, $K_1$</td>
<td>$1 \times 10^{-3}$</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>$K_2$</td>
<td>11.0</td>
</tr>
<tr>
<td>Hypobromous acid HOBr</td>
<td>$2.1 \times 10^{-9}$</td>
<td>8.68</td>
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<td>Hypochlorous acid HOCl</td>
<td>$5.0 \times 10^{-8}$</td>
<td>7.30</td>
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<td>Nitrous acid $\text{HNO}_2$</td>
<td>$4 \times 10^{-4}$</td>
<td>3.40</td>
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<td>Oxalic acid $\text{H}_2\text{C}_2\text{O}_4$, $K_1$</td>
<td>$5.4 \times 10^{-2}$</td>
<td>1.27</td>
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<td></td>
<td>$K_2$</td>
<td>4.27</td>
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<td>Phosphoric acid (ortho) $\text{H}_3\text{PO}_4$, $K_1$</td>
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<td>7.20</td>
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<td>$K_3$</td>
<td>11.89</td>
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<td>Selenous acid $\text{H}_2\text{SeO}_3$, $K_1$</td>
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<td>2.46</td>
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<td>$K_2$</td>
<td>7.3</td>
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<td>Silicic acid $\text{H}_2\text{SiO}_3$, $K_1$</td>
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<td>9.66</td>
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<td>$K_2$</td>
<td>11.80</td>
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<td>$1.2 \times 10^{-2}$</td>
<td>1.92</td>
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<td>Sulphurous acid $\text{H}_2\text{SO}_8$, $K_1$</td>
<td>$1.6 \times 10^{-3}$</td>
<td>1.80</td>
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<td>$K_2$</td>
<td>7.24</td>
</tr>
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<td>Tellurous acid $\text{H}_2\text{TeO}_3$, $K_1$</td>
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<td></td>
<td>$K_2$</td>
<td>7.7</td>
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Table 7
Activity Coefficients \( f \) of Ions at Different Ionic Strengths of Solution

<table>
<thead>
<tr>
<th>Ionic strength of solution</th>
<th>( \pm 1 )</th>
<th>( \pm 2 )</th>
<th>( \pm 3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.98</td>
<td>0.78</td>
<td>0.73</td>
</tr>
<tr>
<td>0.002</td>
<td>0.97</td>
<td>0.74</td>
<td>0.66</td>
</tr>
<tr>
<td>0.005</td>
<td>0.95</td>
<td>0.63</td>
<td>0.55</td>
</tr>
<tr>
<td>0.01</td>
<td>0.92</td>
<td>0.60</td>
<td>0.47</td>
</tr>
<tr>
<td>0.02</td>
<td>0.90</td>
<td>0.53</td>
<td>0.37</td>
</tr>
<tr>
<td>0.05</td>
<td>0.84</td>
<td>0.50</td>
<td>0.21</td>
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<td>0.1</td>
<td>0.81</td>
<td>0.44</td>
<td>0.16</td>
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<td>0.2</td>
<td>0.80</td>
<td>0.41</td>
<td>0.14</td>
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<tr>
<td>0.3</td>
<td>0.81</td>
<td>0.42</td>
<td>0.14</td>
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<tr>
<td>0.4</td>
<td>0.82</td>
<td>0.45</td>
<td>0.17</td>
</tr>
<tr>
<td>0.5</td>
<td>0.84</td>
<td>0.50</td>
<td>0.21</td>
</tr>
</tbody>
</table>
### Table 8

Solubility Products $K_{sp}$ of Selected Sparingly Soluble Electrolytes at 25 °C

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$K_{sp}$</th>
<th>Electrolyte</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr</td>
<td>$6 \times 10^{-13}$</td>
<td>Cu(OH)$_2$</td>
<td>$2.2 \times 10^{-20}$</td>
</tr>
<tr>
<td>AgCl</td>
<td>$1.8 \times 10^{-10}$</td>
<td>CuS</td>
<td>$6 \times 10^{-36}$</td>
</tr>
<tr>
<td>Ag$_2$CrO$_4$</td>
<td>$4 \times 10^{-13}$</td>
<td>Fe(OH)$_2$</td>
<td>$1 \times 10^{-18}$</td>
</tr>
<tr>
<td>AgI</td>
<td>$1.1 \times 10^{-18}$</td>
<td>Fe(OH)$_3$</td>
<td>$3.8 \times 10^{-38}$</td>
</tr>
<tr>
<td>Ag$_2$S</td>
<td>$6 \times 10^{-50}$</td>
<td>FeS</td>
<td>$5 \times 10^{-18}$</td>
</tr>
<tr>
<td>Ag$_2$SO$_4$</td>
<td>$2 \times 10^{-5}$</td>
<td>HgS</td>
<td>$1.6 \times 10^{-52}$</td>
</tr>
<tr>
<td>BaCO$_3$</td>
<td>$5 \times 10^{-9}$</td>
<td>MnS</td>
<td>$2.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>BaCrO$_4$</td>
<td>$1.6 \times 10^{-10}$</td>
<td>PbBr$_2$</td>
<td>$9.1 \times 10^{-9}$</td>
</tr>
<tr>
<td>BaSO$_4$</td>
<td>$1.1 \times 10^{-10}$</td>
<td>PbCl$_2$</td>
<td>$2 \times 10^{-5}$</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>$5 \times 10^{-9}$</td>
<td>PbCrO$_4$</td>
<td>$1.8 \times 10^{-14}$</td>
</tr>
<tr>
<td>CaC$_2$O$_4$</td>
<td>$2 \times 10^{-9}$</td>
<td>PbI$_2$</td>
<td>$8.0 \times 10^{-9}$</td>
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<td>CaF$_2$</td>
<td>$4 \times 10^{-11}$</td>
<td>PbS</td>
<td>$1 \times 10^{-27}$</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>$1.3 \times 10^{-4}$</td>
<td>PbSO$_4$</td>
<td>$1.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>Ca$_5$(PO$_4$)$_2$</td>
<td>$1 \times 10^{-29}$</td>
<td>SrSO$_4$</td>
<td>$3.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>Cd(OH)$_2$</td>
<td>$2 \times 10^{-14}$</td>
<td>Zn(OH)$_2$</td>
<td>$1 \times 10^{-17}$</td>
</tr>
<tr>
<td>CdS</td>
<td>$7.9 \times 10^{-27}$</td>
<td>ZnS</td>
<td>$1.8 \times 10^{-24}$</td>
</tr>
</tbody>
</table>
### Table 9

**Standard Electrode Potentials $\varphi^o$ in Aqueous Solutions at 25° C**

<table>
<thead>
<tr>
<th>Element</th>
<th>Electrode process</th>
<th>$\varphi^o$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>$[\text{Ag(CN)}_2]^+$ + $e^-$ = Ag + 2CN$^-$</td>
<td>-0.29</td>
</tr>
<tr>
<td></td>
<td>$\text{Ag}^+ + e^- = \text{Ag}$</td>
<td>0.80</td>
</tr>
<tr>
<td>Al</td>
<td>$\text{AlO}_2^+ + 2\text{H}_2\text{O} + 3e^- = \text{Al} + 4\text{OH}^-$</td>
<td>-2.35</td>
</tr>
<tr>
<td></td>
<td>$\text{Al}^{3+} + 3e^- = \text{Al}$</td>
<td>-1.66</td>
</tr>
<tr>
<td>Au</td>
<td>$[\text{Au(CN)}_2]^+$ + $e^-$ = Au + 2CN$^-$</td>
<td>-0.64</td>
</tr>
<tr>
<td></td>
<td>$\text{Au}^{3+} + 3e^- = \text{Au}$</td>
<td>1.50</td>
</tr>
<tr>
<td></td>
<td>$\text{Au}^+ + e^- = \text{Au}$</td>
<td>1.69</td>
</tr>
<tr>
<td>Ba</td>
<td>$\text{Ba}^{2+} + 2e^- = \text{Ba}$</td>
<td>-2.90</td>
</tr>
<tr>
<td>Bi</td>
<td>$\text{Bi}^{3+} + 3e^- = \text{Bi}$</td>
<td>0.21</td>
</tr>
<tr>
<td>Br</td>
<td>$\text{Br}_2 (\text{ag}) + 2e^- = 2\text{Br}^-$</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>$\text{HBrO} + \text{H}^+ + 2e^- = \text{Br}^- + \text{H}_2\text{O}$</td>
<td>1.34</td>
</tr>
<tr>
<td>Ca</td>
<td>$\text{Ca}^{2+} + 2e^- = \text{Ca}$</td>
<td>-2.87</td>
</tr>
<tr>
<td>Cd</td>
<td>$\text{Cd}^{2+} + 2e^- = \text{Cd}$</td>
<td>-0.40</td>
</tr>
<tr>
<td>Cl</td>
<td>$\text{Cl}_2 + 2e^- = 2\text{Cl}^-$</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td>$\text{HClO} + \text{H}^+ + 2e^- = \text{Cl}^- + \text{H}_2\text{O}$</td>
<td>1.49</td>
</tr>
<tr>
<td>Co</td>
<td>$\text{Co}^{2+} + 2e^- = \text{Co}$</td>
<td>-0.28</td>
</tr>
<tr>
<td></td>
<td>$\text{Co}^{3+} + e^- = \text{Co}^{2+}$</td>
<td>1.81</td>
</tr>
<tr>
<td>Cr</td>
<td>$\text{Cr}^{3+} + 3e^- = \text{Cr}$</td>
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</tr>
<tr>
<td></td>
<td>$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e^- = \text{Cr(OH)}_3 + 5\text{OH}^-$</td>
<td>-0.13</td>
</tr>
<tr>
<td></td>
<td>$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- = 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$</td>
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<tr>
<td>Cu</td>
<td>$[\text{Cu(CN)}_2]^-$ + $e^-$ = Cu + 2CN$^-$</td>
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<tr>
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<td>$\text{Cu}^{2+} + e^- = \text{Cu}^+$</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>$\text{Cu}^{2+} + 2e^- = \text{Cu}$</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>$\text{Cu}^+ + e^- = \text{Cu}$</td>
<td>0.52</td>
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<tr>
<td>F</td>
<td>$\text{F}_2 + 2e^- = 2\text{F}^-$</td>
<td>2.87</td>
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<td>Fe</td>
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<td></td>
<td>$\text{Fe}^{3+} + 3e^- = \text{Fe}$</td>
<td>-0.04</td>
</tr>
<tr>
<td></td>
<td>$[\text{Fe(CN)}_6]^{3-} + e^- = [\text{Fe(CN)}_6]^{4-}$</td>
<td>0.36</td>
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<tr>
<td></td>
<td>$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$</td>
<td>0.77</td>
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<tr>
<td>H</td>
<td>$\text{H}_2 + 2e^- = 2\text{H}^-$</td>
<td>-2.25</td>
</tr>
<tr>
<td></td>
<td>$2\text{H}^+ + 2e^- = \text{H}_2$</td>
<td>0.000</td>
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<tr>
<td>Hg</td>
<td>$\text{Hg}^{2+} + 2e^- = 2\text{Hg}$</td>
<td>0.79</td>
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<tr>
<td></td>
<td>$2\text{Hg}^{2+} + 2e^- = \text{Hg}_2^+$</td>
<td>0.92</td>
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</table>
Table 9 (concluded)

<table>
<thead>
<tr>
<th>Element</th>
<th>Electrode process</th>
<th>$\phi^o$, V</th>
</tr>
</thead>
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<tr>
<td>I</td>
<td>$I_2(c) + 2e^- = 2I^-$</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>$I_2 + 12H^+ + 10e^- = I_2(c) + 6H_2O$</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>$2HIO + 2H^+ + 2e^- = I_2(c) + 2H_2O$</td>
<td>1.45</td>
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<tr>
<td>K</td>
<td>$K^+ + e^- = K$</td>
<td>-2.92</td>
</tr>
<tr>
<td>Li</td>
<td>$Li^+ + e^- = Li$</td>
<td>-3.04</td>
</tr>
<tr>
<td>Mg</td>
<td>$Mg^{2+} + 2e^- = Mg$</td>
<td>-2.36</td>
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<tr>
<td>Mn</td>
<td>$MnO_4^- + e^- = MnO_2^-$</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>$MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4OH^-$</td>
<td>0.60</td>
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<tr>
<td></td>
<td>$MnO_2 + 4H^+ + 2e^- = Mn^{3+} + 2H_2O$</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>$MnO_4^- + 8H^+ + 5e^- = Mn^{3+} + 4H_2O$</td>
<td>1.51</td>
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<tr>
<td>Na</td>
<td>$Na^+ + e^- = Na$</td>
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<tr>
<td>Ni</td>
<td>$Ni^{3+} + 2e^- = Ni$</td>
<td>-0.25</td>
</tr>
<tr>
<td>O</td>
<td>$O_2 + 2H_2O + 4e^- = 4OH^-$</td>
<td>0.40</td>
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<tr>
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<td>$O_2 + 2H^+ + 2e^- = H_2O_2$</td>
<td>0.68</td>
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<tr>
<td></td>
<td>$O_2 + 4H^+ + 4e^- = 2H_2O$</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>$H_2O_2 + 2H^+ + 2e^- = H_2O$</td>
<td>1.78</td>
</tr>
<tr>
<td>P</td>
<td>$H_3PO_4 + 2H^+ + 2e^- = H_3PO_4 + H_2O$</td>
<td>1.02</td>
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<tr>
<td>Pb</td>
<td>$Pb^{3+} + 2e^- = Pb$</td>
<td>-0.13</td>
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<tr>
<td></td>
<td>$Pb^{4+} + 2e^- = Pb^{3+}$</td>
<td>1.69</td>
</tr>
<tr>
<td>Pt</td>
<td>$Pt^{2+} + 2e^- = Pt$</td>
<td>1.19</td>
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<tr>
<td>S</td>
<td>$S + 2H^+ + 2e^- = H_2S$</td>
<td>0.14</td>
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<td></td>
<td>$S_2O_3^{2-} + 2e^- = 2SO_4^{2-}$</td>
<td>2.01</td>
</tr>
<tr>
<td>Se</td>
<td>$Se + 2H^+ + 2e^- = H_2Se$</td>
<td>-0.40</td>
</tr>
<tr>
<td>Sn</td>
<td>$Sn^{2+} + 2e^- = Sn$</td>
<td>-0.14</td>
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<tr>
<td></td>
<td>$Sn^{4+} + 2e^- = Sn^{3+}$</td>
<td>0.15</td>
</tr>
<tr>
<td>Te</td>
<td>$Te + 2H^+ + 2e^- = H_2Te$</td>
<td>-0.72</td>
</tr>
<tr>
<td>Zn</td>
<td>$ZnO_2^{2-} + 2H_2O + 2e^- = Zn + 4OH^-$</td>
<td>-1.22</td>
</tr>
<tr>
<td></td>
<td>$Zn^{2+} + 2e^- = Zn$</td>
<td>-0.76</td>
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</tbody>
</table>
### Table 10

**Instability Constants of Selected Complex Ions**  
**in Aqueous Solutions at 25 °C**

<table>
<thead>
<tr>
<th>Dissociation of complex ion</th>
<th>Instability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ag(NH}_3\text{)}_2]^+ \rightleftharpoons \text{Ag}^{+} + 2\text{NH}_3)</td>
<td>(9.3 \times 10^{-8})</td>
</tr>
<tr>
<td>([\text{Ag(NO}_2\text{)}_2]^– \rightleftharpoons \text{Ag}^{+} + 2\text{NO}_2^-)</td>
<td>(1.8 \times 10^{-3})</td>
</tr>
<tr>
<td>([\text{Ag(S}_2\text{O}_3\text{)}_3]^3– \rightleftharpoons \text{Ag}^{+} + 2\text{S}_2\text{O}_3^2–)</td>
<td>(1.1 \times 10^{-13})</td>
</tr>
<tr>
<td>([\text{Ag(CN)}_2]^– \rightleftharpoons \text{Ag}^{+} + 2\text{CN}^-)</td>
<td>(1.1 \times 10^{-11})</td>
</tr>
<tr>
<td>([\text{HgCl}_4]^{2–} \rightleftharpoons \text{Hg}^{2+} + 4\text{Cl}^-)</td>
<td>(8.5 \times 10^{-16})</td>
</tr>
<tr>
<td>([\text{HgBr}_4]^{2–} \rightleftharpoons \text{Hg}^{2+} + 4\text{Br}^-)</td>
<td>(1.0 \times 10^{-91})</td>
</tr>
<tr>
<td>([\text{HgI}_4]^{2–} \rightleftharpoons \text{Hg}^{2+} + 4\text{I}^-)</td>
<td>(1.5 \times 10^{-89})</td>
</tr>
<tr>
<td>([\text{Hg(CN)}_4]^{2–} \rightleftharpoons \text{Hg}^{2+} + 4\text{CN}^-)</td>
<td>(4.0 \times 10^{-43})</td>
</tr>
<tr>
<td>([\text{Cd(NH}_3\text{)}_4]^3+ \rightleftharpoons \text{Cd}^{3+} + 4\text{NH}_3)</td>
<td>(7.6 \times 10^{-6})</td>
</tr>
<tr>
<td>([\text{Cd(CN)}_4]^2– \rightleftharpoons \text{Cd}^{2+} + 4\text{CN}^-)</td>
<td>(7.8 \times 10^{-18})</td>
</tr>
<tr>
<td>([\text{Cu(NH}_3\text{)}_4]^2+ \rightleftharpoons \text{Cu}^{2+} + 4\text{NH}_3)</td>
<td>(2.4 \times 10^{-12})</td>
</tr>
<tr>
<td>([\text{Cu(CN)}_4]^2– \rightleftharpoons \text{Cu}^{2+} + 4\text{CN}^-)</td>
<td>(5.0 \times 10^{-81})</td>
</tr>
<tr>
<td>([\text{Ni(NH}_3\text{)}_6]^2+ \rightleftharpoons \text{Ni}^{2+} + 6\text{NH}_3)</td>
<td>(1.9 \times 10^{-9})</td>
</tr>
</tbody>
</table>

### Table 11

**Atomic Masses to Four Significant Figures**  
(Scaled to the relative atomic mass \(^{12}\text{C} = 12\) exactly)

The present table is recommended by the IUPAC Committee on Teaching of Chemistry; the data for Lr, Np, No, Pa, Ra, and Tc have been updated in accordance with the 1977 International Table of Atomic Masses.

The values in italics may differ from the atomic masses of the relevant elements in some naturally occurring samples because of a variation in the relative abundance of the isotopes. The numbers in parentheses denote the atomic mass numbers of the isotopes with the longest known half-life.

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Atomic number</th>
<th>Atomic mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Actinium</td>
<td>Ac</td>
<td>89</td>
<td>(227)</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al</td>
<td>13</td>
<td>26.98</td>
</tr>
<tr>
<td>Americium</td>
<td>Am</td>
<td>95</td>
<td>(243)</td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>51</td>
<td>121.8</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>18</td>
<td>39.95</td>
</tr>
<tr>
<td>Element</td>
<td>Symbol</td>
<td>Atomic number</td>
<td>Atomic mass</td>
</tr>
<tr>
<td>------------</td>
<td>--------</td>
<td>---------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>33</td>
<td>74.92</td>
</tr>
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<td>Astatine</td>
<td>At</td>
<td>85</td>
<td>(210)</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>56</td>
<td>137.3</td>
</tr>
<tr>
<td>Berkelium</td>
<td>Bk</td>
<td>97</td>
<td>(247)</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>4</td>
<td>9.012</td>
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<tr>
<td>Bismuth</td>
<td>Bi</td>
<td>83</td>
<td>209.0</td>
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<tr>
<td>Boron</td>
<td>B</td>
<td>5</td>
<td>10.81</td>
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<tr>
<td>Bromine</td>
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<td>35</td>
<td>79.90</td>
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<td>Cd</td>
<td>48</td>
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<tr>
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<td>Cf</td>
<td>98</td>
<td>(251)</td>
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<td>Carbon</td>
<td>C</td>
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<td>12.01</td>
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<td>Ce</td>
<td>58</td>
<td>140.1</td>
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<td>Cs</td>
<td>55</td>
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<td>Element</td>
<td>Symbol</td>
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Four-Place Logarithms
Answers to Problems

Chapter 1

1. 9.01 g/mol.
2. 127 g/mol.
3. 10 litres.
4. 108 g/mol and 16.0 g/mol.
5. 137.4 amu; Ba.
6. 15.0 g/mol; 24.9 g/mol.
7. 79.9 g/mol; 9.0 g/mol.
8. 56.0 g/mol; 3.36 litres.
9. 24.2 g/mol; 16.2 g/mol.
10. 1.74 g.
11. 32.6 g/mol.
12. 1 : 2.
13. 49.0 g/mol.
14. 79.0 g/mol; 58.4 g/mol.
15. 11.2 l/mol.
16. a.
17. b.
18. c.
19. d.
20. e.
21. f.
22. g.
23. h.
24. i.
25. j.
26. k.
27. l.
28. 746 ml.
29. 303.9 kPa.
30. By 273 kelvins.
31. 4.8 litres.
32. 82.3 kPa.
33. 839 ml.
34. 106.3 kPa.
35. 1.8 m$^3$.
36. 114 °C.
37. 444 ml.
38. 39.4 g/mol.
39. a; b.
40. b; c.
41. 100.8 kPa.
42. $p(H_2) = 26.7$ kPa; $p(CH_4) =$
   $= 80.0$ kPa; $p = 106.7$ kPa.
43. 94.0% NO, 6.0% CO.
44. 100 kPa; 17.2% CO$\g$, 47.3% O$\g$, 38.5% CH$\g$.
45. $p(CH_4) = 36$ kPa, $p(H_2) =$
   $= 42$ kPa, $p(CO) = 13.6$ kPa;
   $p = 91.6$ kPa.
46. 6.8 litres.
47. 20.0 g/mol.
48. 215 ml, 0.019 g.
49. 243 amu.
50. b.
51. b.
52. b.
53. 1.06 $\times 10^{-22}$ g.
54. 2.66 $\times 10^{13}$.
55. 1 litre.
56. $1 : 16 : 2$.
57. 8 $\times 10^{18}$.
58. 0.168 g; 1.23 kg; 1.456 kg.
59. 43 litres.
60. 33.6 litres.
61. 44.6 moles.
62. 54.8 kPa (411 mmHg).
63. 8 litres.
64. It will not change.
65. 44% O$\g$, 56% H$\g$.
66. 58% SO$\g$, 35.5% O$\g$, 6.5% SO$\g$.
67. It did not change; 60% Cl$\g$, 30% HCl, 10% H$\g$.
68. 0.54 m$^3$.
69. NaO.
70. a.
77. a. 78. b. 79. b. 80. 26.0 g/mol. 81. 64.0 g/mol. 82. 28 g/mol; 4.65 × 10⁻²³ g. 83. 47 g/mol; 1.62. 84. 28.0 amu. 85. 34.0 amu. 86. One. 87. Eight. 88. 58 g/mol. 89. 28.0 amu. 90. 34.0 amu. 91. 9.94 g. 92. 125 kPa. 93. 1 kg. 94. c. 95. a. 96. b. 97. b. 98. b. 99. Na₂CO₃. 100. COH₄N₂. 101. V₂O₅. 102. K₂Cr₂O₇. 103. BaCl₂·2H₂O. 104. C₆H₁₂O₂. 105. C₁₀H₁₈. 106. C₅H₁₄. 107. C₅N₂. 108. B₂H₆. 109. (a) 138.5 g; (b) 350 g; (c) 212 g. 111. 1315 kg. 112. Alkaline. 113. Yes; 28.7 g of AgCl. 114. 94.6%. 115. 0.08 mole of Fe(OH)₃; 0.12 mole of FeCl₃ remained. 116. 33.6 litres. 117. 0.28 m³. 118. 292.5 g. 119. moles of SO₂ and 11 moles of O₂. 120. 10.7 g of NH₄Cl, 0.6 g of NH₃. 121. 5.0 m³. 122. 11.2 m³. 123. 13.9 tonnes.

Chapter 2
162. a; b; d. 163. b; c. 164. a. 165. b; c. 166. c. 167. c. 168. c. 169. b. 170. b. 171. c; d.

Chapter 3
172. 5; 7. 173. 32. 174. (a) 3d → 4p → 5s; (b) 4d → 5p → 6s; (c) 4f → 5d → 6p → 7s. 175. (a) 47 (Ag); (b) 31 (Ga). 176. 4d. 177. Ce; Yb. 178. 6s; 6p. 181. (a) 5; (b) 2; (c) 0. 182. (a) 1; (b) 2; (c) 3; (d) 6; (e) 0; (f) 7. 185. (a) 52 (Te); (b) 24 (Cr). 186. Fe. 188. IV and V. 198. d. 199. a2. 200. c. 201. a2. 202. c because a1, a3, b3, d2. 203. Cr.
204. \( \text{Pb}\).
205. \( \text{Ta}\).
206. 35.49.
207. 24.32.
208. 1 : 1.78.
209. 25 mg.
210. 1.56%.
211. 18 g.
212. \( \text{Pb} \).
213. b, c, d.
214. c.
215. a2.

Chapter 4

245. b2.
246. a3,5.
247. b2.
248. b2.
249. b, c, e.
250. d.
251. 6.03 \( \times 10^{-11} \) m.
252. \( 6.41 \times 10^{-6} \) C \( \cdot \) m = 1.92 D.
253. 0.038 and 0.020 nm.
262. b2.
263. c2.
264. a3.
272. d.
273. a2.
274. a2.
275. b3.

Chapter 5

280. \( \Delta H^0 = -100.3 \) kJ/mol.
281. 60.5 kJ.
282. 5.3 kJ/mol.
283. \(-4137.5 \) kJ/mol.
284. \(-238.6 \) kJ/mol.
285. \(-162.1 \) kJ/mol.
286. 286.5 litres.
287. 1312 kJ.
288. In the combustion of \( \text{C}_2\text{H}_2 \), 5.2 times more.
289. \(-598.7 \) kJ.
290. 52.4 kJ/mol.
291. (a) 96.8 kJ; (b) 490.7 kJ; (c) \(-26.8 \) kJ.
292. 0.075 g.
293. \(-4143 \) kJ/mol.
294. 23.0 kJ.
295. (a) \(-1423 \) kJ; (b) \(-3301 \) kJ.
296. (a) \(-443.2 \) kJ; (b) \(-365.6 \) kJ.
297. (a) \(-69.2 \) kJ; (b) \(-2803 \) kJ.
305. (a) 22.5 kJ; (b) \(-59.2 \) kJ.
306. \( \Delta S < 0 \), \( \Delta G < 0 \), \( \Delta H < 0 \); \( \Delta G \) will grow with elevation of the temperature.
307. (b) and (c).
308. 129.1 kJ/mol; 50.7 kJ/mol; \(-144.0 \) kJ/mol; about 1080 K.
309. (a) 47.1 kJ; (b) 107.2 kJ; (c) \(-13.0 \) kJ.
310. All except CaO.
311. \( \text{NiO}, \text{SnO}_2 \).
313. b.
314. c.
315. b, c, e.
316. a.
317. b.
318. a.
319. b.
320. a.
321. a.
322. 0.1 l/(mol\cdot min).
323. It will increase twofold.
324. 16 times.
325. (a) No; (b) yes.
326. \( [A]_0 = 0.042 \) mol/l; \( [B]_0 = 0.014 \) mol/l.
327. 12 times.
328. \( J_0 = 3 \times 10^{-5}; J_1 = 7.2 \times 10^{-8}. \)
329. (a) and (b) It will grow 27 times; (c) it will grow 9 times.
330. \( J_2/J_1 = 4.77. \)
331. 2.5.
332. 8 times.
333. (a) 9.3 s; (b) 162 h 46 min.
335. 5 times.
336. 49.9 kJ/mol.
338. 5.9 kJ/mol.
339. 80.3 kJ/mol.
340. 1.44 times.
347. 75 kPa.
Answers to Problems

348. (a) 83.3%; (b) 9 : 1.
349. \([N_2]_0 = 5 \text{ mol/l}; [H_2]_0 = 15 \text{ mol/l}; (b) \text{ to the left}; (c) \text{ to the right.}
350. \([CO] = 0.04 \text{ mol/l}; [CO_2] = 0.02 \text{ mol/l.}
351. \([I_2]_0 = 0.05 \text{ mol/l}; [H_2]_0 = 0.07 \text{ mol/l.}
352. 0.192; \([NO_2]_0 = 0.03 \text{ mol/l.}
353. 49.6% \text{ H}_2, 29.6% \text{ Br}_2, 20.8% \text{ HBr.}
354. \([CO] = 0.04 \text{ mol/l}; [CO_2] = 0.02 \text{ mol/l.}
355. \([A]_0 = 0.22 \text{ mol/l}; [B]_0 = 0.07 \text{ mol/l.}
356. \([AB]_0 = 0.03 \text{ mol/l}; 66.7\%
357. \([NO_2]_0 = 0.03 \text{ mol/l.}
358. 50\%; 83.3\%; 90.9\%.
363. \([AB]_0 = 0.03 \text{ mol/l}; 66.7\%.
364. \(a) 1.1 \times 10^5; 0.91; \ (b) 7.5 \times 10^{-28}; 1.4; \ (c) 2.7 \times 10^8; 1.1 \times 10^{-4}.
365. 319 K.
366. 885 K.
367. \(K = 25.4; [A] = [B] = 0.22 \text{ mol/l}; [AB] = 0.78 \text{ mol/l.}
370. \ a.
371. \ a; d.
372. \ b; d.
373. \ b.
374. \ b.
375. \ a.
376. \ b.
377. \ b.
378. \ b; d.
379. \ b; d.
380. \ a.
381. \ c; d.
382. \ b.
383. \ a.
384. \ b; d.
385. \ b.

Chapter 6

386. 12.5%.
387. 430 g.
388. 1.83 g/ml.
389. 66.7%.
390. 26.5%.
391. 150 g.
280 Answers to Problems

435. 0.25 litre.
436. 10 g.
437. 10 g.
438. 0.3 N; 24 ml.
439. 45 g/mol.
440. 40 g/mol.
441. 594 ml; 891 ml.
442. 10 N.
443. 50 g.
444. 10.8 g.
445. No.
446. 48.5 g.
447. 8.55 litres.
448. 33.2%.
449. 760 kPa.
450. 35% O₂.
451. 90% (vol.) N₂O, 10% (vol.) NO.
452. 483 kPa.
453. —42.2 kJ/mol.
454. —75.6 kJ/mol.
455. By 8.9 K.
456. —77.7 kJ/mol.
457. By 8.1 K.
458. 1.24 MPa.
459. 311 kPa.
460. 9.0 g.
461. 1.14 MPa.
462. 4.95 × 10⁴ amu.
463. 428 kPa.
464. 92 amu.
465. 0.001 mol.
466. 4.1 kPa.
467. 24.8 kPa.
468. 98 kPa.
469. By 54 Pa.
470. 55.7 g.
471. By 0.26 K.
472. At 101 °C.
473. At —27°C.
474. (a) 18.4 g; (b) 65.8 g.
475. 1/167.
476. About —8 °C.
477. Eight.
478. 145 amu.
479. C₈H₄O₄.
480. 32 amu, 13.4 MPa.
481. 311.7 kPa, (b) —0.25 °C, (c) 100.7 °C, (d) 2.33 kPa.
482. a, c.

483. 0.25 litre.
484. c.
485. b.
486. b.
487. a.
488. c.
489. b.
490. c.
491. a.
492. a.
493. b.
494. a.

Chapter 7

495. We must take 0.24 mol of \( \text{Na}_2\text{SO}_4 \), 0.02 mol of \( \text{NaCl} \), and 0.64 mol of \( \text{KCl} \).
496. 0.055.
497. \( 5 \times 10^{-4} \).
498. \( K = 1.8 \times 10^{-4}, pK = 3.75 \).
499. \( 4.5 \times 10^{-7} \).
500. 0.01 mol/l.
501. 2.3 mol/l.
502. 900 ml.
503. \( 6 \times 10^{-3} \) mol/l.
504. 0.014 mol/l.
505. \( [\text{H}^+] = [\text{HSe}^-] = 2.9 \times 10^{-3} \) mol/l; \( [\text{Se}^{2-}] = 10^{-11} \) mol/l.
506. To \( 1/167 \) of its original value.
507. \( 1.3 \times 10^{-4} \) mol/l.
508. For the third step.
509. 1.86.
510. 0.7.
511. 0.9.
512. 0.75.
513. 0.75.
514. 0.04.
515. 434 kPa.
516. a.
517. b.
518. c.
519. c.
520. c.
521. a.
522. \( a(\text{K}^+) = 0.0164 \) mol/l; \( a(\text{SO}_4^{2-}) = 0.0045 \) mol/l.
523. \( a(\text{Ba}^{2+}) = 7.8 \times 10^{-4} \) mol/l; \( a(\text{Cl}^-) = 1.9 \times 10^{-3} \) mol/l.
524. 0.95.
525. \( I = 0.06; a (Ca^{2+}) = 6.4 \times 10^{-3} \text{ mol/l}; \ a(Cl^-) = \ a(NO_3^-) = 1.5 \times 10^{-3} \text{ mol/l}. \)
526. \( I = 0.0144; \ a(Ba^{2+}) = 2.8 \times 10^{-5} \text{ mol/l}; \ a(Cl^-) = 8.4 \times 10^{-5} \text{ mol/l}. \)
527. \( a(H^+) = 3.2 \times 10^{-8} \text{ mol/l}. \)
528. \( f(Cl^-) = 0.99, \ f(SO_4^{2-}) = \ a(NO_3^-) = 1.5 \times 10^{-1} \text{ mol/l}; \ f(PO_4^{3-}) = 0.90; \ f[Fe(CN)_4^{3-}] = 0.83. \)
529. (a) \( 10^{-10} \text{ mol/l}; \) (b) \( 3.12 \times 10^{-9} \text{ mol/l}; \) (c) \( 1.35 \times 10^{-4} \text{ mol/l}. \)
530. (a) \( 10^{-11} \text{ mol/l}; \) (b) \( 1.54 \times 10^{-7} \text{ mol/l}; \) (c) \( 7.14 \times 10^{-3} \text{ mol/l}. \)
531. (a) 6.70; (b) 2.09, (c) 9.57.
532. (a) 10.66; (b) 8.70; (c) 5.97.
533. 3.38.
534. 11.40.
535. 1.5 times.
536. \( [H^+] = 6.3 \times 10^{-7} \text{ mol/l}; \ [OH^-] = 1.6 \times 10^{-8} \text{ mol/l}. \)
537. (a) 10.78; (b) 5.05; (c) 2.52; (d) 3.38.
538. \( 2.2 \times 10^{-8} \text{ mol/l}. \)
539. \( a(OH^-) = 0.16 \text{ mol/l}; \ pa(OH^-) = 0.80. \)
540. 2.35.
541. \( [H^+] = 6.0 \times 10^{-9} \text{ mol/l}; \ [OH^-] = 1.7 \times 10^{-12} \text{ mol/l}; \ pOH = 11.78. \)
542. 0.82.
543. 4.75.
544. It will grow by 0.3; (b) it will grow by 0.15; (c) it will not change.
545. b, c.
546. a.
547. b.
548. c.
549. c.
550. c.
551. b.
552. \( 4.8 \times 10^{-9}. \)
553. \( 9.2 \times 10^{-9}. \)
554. \( 4 \times 10^{-18}. \)
555. \( 8 \times 10^{-9}. \)
556. \( 7.1 \times 10^{-4} \text{ g}. \)
557. \( 8.36 \times 10^{-5} \text{ g}. \)
558. 408 litres.
559. \( 1.6 \times 10^{12} \text{ litres}. \)
560. 32500 times.
561. Yes.
562. Yes.
563. Yes.
564. To 1/2230 of its initial value.
565. (a) \( 2.15 \times 10^{-4} \text{ mol/l}; \) (b) \( 1.4 \times 10^{-4} \text{ mol/l}; \) 15.4 times.
566. 1/72.
567. a.
568. b.
569. a.
570. c.
571. a.
572. a.
580. \( K_H = 1.5 \times 10^{-11}; \ h = 3.9 \times 10^{-4}; \ pH = 7.59. \)
581. \( K_H = 5.6 \times 10^{-10}; \ h = 2.4 \times 10^{-4}; \ pH = 5.63. \)
582. 11.66.
583. In a 0.1 \text{ M} solution, \( h = 1.12 \times 10^{-3}; \ pH = 11.05; \) in a 0.001 \text{ M} solution, \( h = 0.107; \ pH = 10.03. \)
584. 9.15 (25 °C); 9.65 (60 °C).
585. 10^{-7}.
587. Orange.
591. b.
592. a.
593. a.
594. c.
595. c.
596. a2.
597. b; d; f; g.

Chapter 8

605. b, c, e.
606. a, d, e.
607. a.
608. a, b, d.
632. (a) From Mg to Pb; (b) from Pb to Cu; (c) from Cu to Ag.
633. 0.80 V.
634. —0.126 V.
Answers to Problems

635. \(-2.39\) V; \(-2.42\) V; \(-2.45\) V.
636. \(-0.41\) V; \(-0.21\) V; \(-0.63\) V.
637. 0.01 mol/l.
638. \(-0.28\) V.
640. Yes.
641. 0.1 mol/l.
642. 0.71 V
644. 7.8
645. 0.044.
647. a.
648. d.
649. c.
650. a.
651. b, c.
652. b.
653. a, b, c—in the forward direction.
654. b, c, d.
655. (a) No; (b) Yes.
656. (a) \(2 \times 10^9\); (b) 2.2.
657. (a) \(K \approx 1.6 \times 10^{12}\); (b) \(K \approx 8.6 \times 10^{18}\).
658. (a) No, \(K = 6.0 \times 10^{-14}\);
(b) yes, \(K = 2.2\).
659. c, d, f.
660. a, e.
661. a.
662. a, b, d.
663. c.
664. c.
665. c.
666. a.
673. Ag, Cu, Ni.
674. Ag, Bi, Pb, Fe.
679. 1.80 g.
680. 12g.
681. 53.6 h.
682. 4 \(\times 10^9\) C.
683. 627 ml.
684. 1.25 litres.
685. (a) \(1.93 \times 10^5\) C; (b) \(2.41 \times 10^4\) C.
686. 6.19 h.
687. 23.7 g.
688. 48.3 g/mol.
689. 56.2 g/mol.
690. 114.8 amu.
691. a.
692. c.
693. b.
694. a.
695. b.
696. d.

Chapter 9

700. 40 ml.
711. \(9.3 \times 10^{-9}\) mol/l.
712. \(7.8 \times 10^{-15}\) mol/l.
713. 5.9 \(\times 10^{-11}\) g.
714. (a) No; (b) yes.
715. More than 1.0 mole.
716. \([Ag^+] = 7.4 \times 10^{-9}\) mol/l; not more than 1.4 g of NaCl.
717. a.
718. a.
719. c.

Chapter 10

726. 46.2 g.
727. 750 g.
728. 61.4 g.
729. MgSb₂.
730. MgCu₂ and MgCu.
731. 617.3 g.

Chapter 11

758. 470 kg of CaH₂; 1460 kg of Zn and 2190 kg of H₂SO₄.
764. 2.02%.
767. a₁; e₁.
768. b₃.
769. b₂
770. b.
777. 0.12 mol/l.
789. 61.2 g.
794. d.
795. a₁; c₄; e₁, 3; f₄.
801. 1000 ml; 6.44 kJ.
819. 9.1.
823. 13.44 litres.
825. 2.08 g of NaHSO₃.
829. 48.92 g; 24.46 g.
830. 133.6 g and 66.85 g; the same amount of acid is used for oxidation in both cases.
833. a; c.
834. c.
835. c1; d3; e1; h2; i1.
836. a2; 3; d1; e1.
837. c2, 3.
838. c2; d3; e1; f2; h2; i1.
844. 197 g and 152 g.
846. 7.2 tonnes.
848. 67.2 litres.
854. pH = 8.79; \( \rho = 6.2 \times 10^{-5} \).
874. Of 4 and of 2.
875. 5.4 \times 10^6 \text{ kJ}.
909. 215 litres.
911. 28 litres; 56 litres.
919. 5.6 tonnes; 2240 \text{ m}^3.
921. a2.
928. b; c.
937. 5.75\%.
938. 23.6\% KCl; 76.4\% NaCl.
940. 4.69 kJ.
941. 375 ml.
942. 27.8 kJ.
955. 49.9\%.
956. 28.77\% Cu, 3.98\% Sn, 67.25\% Zn.
957. a; b.
958. c.
959. a1; b1; c2.
960. c.
961. b; c.
962. b.
963. d.
973. -744.8 kJ.
975. 1164 kJ.
977. \text{CaSO}_4 \cdot 2\text{H}_2\text{O}.
978. 12.5\%.
983. 40.2\% \text{ZnCO}_3; 59.8\% \text{ZnO}.
984. 2950 kJ.
990. 106 g.
991. 5 meq/l.
992. 2 meq/l.
993. 144.7 mg.
994. 1.22 g.
995. 8.52 meq/l.
996. 0.28 meq/l.
998. a; d; f.
999. b; c; d.
1000. b.
1001. a.
1002. a.
1003. c.
1011. 5.49 g.
1014. By 16.2 mg.
1020. 6.26 \times 10^{-5} \text{ mol/l}.
1023. a2.
1024. a; c; d.
1025. c; d.
1026. a.
1027. a; c; d.
1049. 294.7 g.
1053. 67.2 litres.
1056. 2.83 g; 1.58 g.
1064. c.
1065. c.
1066. b; c.
1067. c.
1068. a.
1071. 29.8\%.
1078. \Delta H^\circ = 39.7 \text{ kJ}.
1087. 0.5173 \text{ mol/l}.
1094. c1.
1095. c.
1096. c; d.
1097. a2.
1098. a.
1099. b3.
INDEX

Acid(s), 36, 37
- basicity, 12
- dibasic, 37
- monobasic, 37
- names, 256ff
- polybasic,
  - salt hydrolysis, 159
  - stepwise equilibria in dissociation, 135
- tribasic, 37
Activity, ions, 141f
Agent(s),
- complexing, 203
- oxidizing, 166, 169ff
- reducing, 166, 172f
Alloys, 212ff
- phase diagrams, 212ff
Amount of substance, 21
Analogue(s), electron, 47
Anhydrides, acid, 36
Anode, 182, 195
Atom,
- central, 203
- many-electron, atomic orbitals, 45f
Atomic mass unit (amu), 21
Base(s), 36, 39
- acidity, 12
- diaacid, 39
- monoacid, 39
Bidentate, 203
Bond,
- chemical, see Bond
- covalent, 59f, 61
- formation, donor-acceptor
  mechanism, 61
- hydrogen, 77
- ionic, 59, 74
- kinds, 59ff
- multiplicity, 63
- order, 63
Bridge, oxygen, 37
Capture, electron, 55
Cathode, 182, 195
Cells, galvanic, 182f
- concentration, 187
- e.m.f., 183f
  - standard, 184, 192
Charge, elementary electric, 256
Coefficient,
- absorption, 117
- activity, 142, 262
- isotonic, 136, 137
  - and degree of dissociation, 137
- solubility, 117
- temperature, reaction rate, 97f
- van't Hoff's, 136
Complex, activated, 100
Complex compounds, 203ff
- coordination number, 203
- equilibria in solutions, 207ff
- formulas, 204
- inner sphere, 203
- ligands, 203
- nomenclature, 205f
- outer sphere, 203
Compounds,
- complex, see Complex compounds
  - inorganic,
    - binary, 35f
    - classification, 35ff
    - ionic, 74
Concentration,
- equilibrium, 101
- equivalent, 114
- molal, 114
- molar-volume, 114
- per cent by mass, 114
Constant,
- Avogadro's, 256
- cryoscopic, 126
- dissociation, 132, 143f
- weak electrolytes, 260f
- ebullioscopic, 126
- equilibrium, 101f
  - and catalyst, 102
  - heterogeneous reaction, 102
  - oxidation-reduction reaction, 192
- solid electrolyte and ions in solution, 148f
  - and standard Gibbs energy, 104f
Faraday's, 198, 256
- hydrolysis, 157
  - first step, 159
Index

Constant,
  hydrolysis,
    second step, 159
instability,
  complex ion, 207f, 265
  concentration, 208
ionization, 132
molar gas, 27, 256
Planck's, 256

Debye (D), 69, 256
Decay, radioactive, 54f
  alpha, 54
  beta, 54f

Degree,
  dissociation, 132f, 137
  hydrolysis, 157f
  and salt concentration, 158

Diagram,
  energy-level, 64f
  phase, see Phase diagram(s)
  reaction energy, 99

Dipole,
  electric, 69
  moment, molecule, 69

Dissociation,
  degree, 132
  apparent, 137
  electrolytic, 132, 136
  water, 143

Duality, oxidation-reduction,
  169, 173f

Electrodes, 182, 195
  inert, 183
  reference, 183
  standard hydrogen, 185

Electrolysis, 195ff

Electrolytes,
  degree of dissociation, 132f, 137
  strong, 141
  weak, 132

Electronegativity, relative, 59f

Element,
  oxidation number, 165
  oxidation state, 165

Energy,
  activation, 98
  Gibbs, 86
  formation, 86, 258ff
  standard change, 88, 258ff

Enthalpy, 81
  standard, of formation, 82, 258ff
  standard change, 84, 88

Entropy, 85
  change in system, 85
  elementary substance, 86
  molar, 85
  standard, 258ff
  change, 88

Equation(s),
  Arrhenius, 98f
  Clapeyron-Mendeleev, 26f
  Nernst, 184f
  net ionic, 154
  nuclear reactions, 55f
  oxidation-reduction reactions, balancing, 175ff
  of state, ideal gas, 26f
  thermochemical, 82

Equilibrium,
  chemical, see Equilibrium complex compounds, in solutions, 207ff
  displacement, 104
  in electrolyte solutions, 155f
  electrolytic dissociation, 132, 134
  hydrolysis, 160f
  shifting, 104
  in complex ion dissociation, 209
  solid electrolyte and ions in solution, 148ff

Equivalent, substance, 11f

Eutectic, 212

Factor, steric, 98f

Forces,
  intermolecular interaction, 78
  van-der-Waals, 78

Functions, state, 80

Gas(es),
  ideal, equation of state, 26f
  molar volume, 22
  molecular mass, 26f
  partial pressure, 18f
Gas(es),
  pressure, at constant volume, 16
  standard conditions, 15
  volume content in gas mixture, 23

Heat effect, 81f
  sign, 81

Hybridization, atomic orbitals, 70f

Hydracids, 37f

Hydrolysis, 156ff
  degree, 157f
  equilibrium, 160f

Hydroxides, 36
  acid, 26
  amphoteric, 36, 39
  basic, 36, 39

Hydroxosalts, 40

Index, dissociation constant (pK), 133

Ions,
  activity, 141f
  activity coefficient, 142, 262
  complex, 204
  instability constant, 207f
  polarizability, 74f
  polarization, 74
  polarizing power, 75

Isobars, 53

Isotopes, 53
  half-life, 54

Law,
  Avogadro’s, 22
  Boyle’s, 15
  combined gas, 17
  equivalents, 12
  Faraday’s, 198
  Gay-Lussac’s, 16
  Henry’s, 117
  Hess’s, 82f
    corollary, 84
    mass action, 96f
  Ostwald’s dilution, 132f
  partial pressures, 19
  Raoul’ts, 125f

Light, speed, 256

Macrostate, 85

Mass(es),
  atomic, 266ff
  equivalent, 11f
  molar, 21f

Method,
  linear combination of AO’s, 63
  molecular orbitals, 62f
  valence bond, 61

Microstate, 85

Molality, 114

Molarity, 114

Mole, 21

Mole fraction, 114

Molecule(s),
  activation energy, 98
  active, 98
  dipole moment, 69
  polyatomic, dipole moment, 69f
  spatial structure, 72

Monodentate, 203

Number,
  Avogadro’s, 21
  coordination, 203
  oxidation, 165

Orbitals,
  atomic electron, 45
  hybrid, directional characteristic, 71
  molecular, antibonding, 62f
  bonding, 63
  formation, 63f

Overvoltage, electrode process, 197

Oxidation, 165

Oxides,
  acidic, 36
  amphoteric, 37
  basic, 36
  non-salt-forming, 36, 37
  salt-forming, 36

Oxosalts, 41

Oxyacids, 37, 38

Particle,
  alpha, 54
  beta, 54f
Index

Peracids, 38
Peroxides, 37
pH, 144f

Phase diagram(s), 212f
  alloys forming no chemical compounds, 212f
  alloys forming chemical compounds, 213f
  alloys forming solid solutions, 214f
  system Cd-Bi, 216
  system Cu-Mg, 217
  system Mg-Sb, 217
pOH, 144f
Polydentate, 203

Potential, electrode, 184
  standard, 184ff, 263f
  ionization, 48f
  and atom's electron configuration, 49
  and nucleus charge, 49
Pressure, osmotic, 137
Principle, Le Chatelier's, 104
  Pauli exclusion, 45
  for molecule, 62
Process, isobaric, 81
  isobaric-isothermal, 86
  isochoric, 80f
Product, solubility, 149f
  sparingly soluble electrolyte, 252

Radioactivity, 53f
Rate, heterogeneous reaction, 95
  homogeneous reaction, 95f
  reaction, 95f
  and catalyst, 100
  and temperature, 97f
Rate constant, 96
  and activation energy, 98f
  and temperature, 97
Reaction(s),
  autoxidation-autoreduction, 166
  change in internal energy, 80
  chemical, see Reaction(s)
  disproportionation, 166
  endothermic, 80, 81, 87, 161
  energy diagram, 99
  exchange, in electrolyte solutions, 154ff
  exothermic, 80, 81, 87
  heat effect, 81f
  at constant pressure, 81
  at constant volume, 81f
  sign, 81
  heterogeneous, 97
  rate, 95
  homogeneous, rate, 95f
  neutralization, 155f, 161
  nuclear, equations, 55f
  oxidation-reduction, 165
    equilibrium constant, 192
    in galvanic cell, direction, 191
    intermolecular, 166
    intramolecular, 167
    rate, 95f, see also Rate
    and temperature, 97f
    rate constant, 96
    and activation energy, 98f
    and temperature, 97
    redox, 165, see also Reaction(s), oxidation-reduction
    reversible, 101
Reduction, 165
Rule(s),
  Hund's, 46f
  for molecule, 62
  Klechkovsky's, 46
  first, 46
  second, 46
  van't Hoff's, 97

Salts, 40
  acid, 40, 41
  basic, 40, 41
  complex,
    primary dissociation, 207
    secondary dissociation, 207
  hydrolysis, 156ff
  constant, 157
  names, 256ff
  neutral, 40
  normal, 40
Solubility, 117
  product, 149f, 262
Solution(s),
  boiling point elevation, 126, 136
  concentration, 114f
dilute, colligative properties, 125
electrolytes, 132ff
  boiling point elevation, 136
colligative properties, 136
equilibrium, 155f
  freezing point depression, 136
  osmotic pressure, 137
freezing point depression, 126, 136
ionic strength, 142, 151f
neutral, 144
osmotic pressure, 126
Solvent, vapour pressure depression, 125f, 136
State, oxidation, 165
Strength, ionic, 142, 151f

Substance(s),
  amount, 21
  empirical formula, 29f
  entropy, 86
  enthalpy of solution, 123
equivalent, 11f
  molecular formula, 29, 30
  solubility, 117
  standard state, 81, 82
Systems, electrochemical, 186

Unit, atomic mass (amu), 21
Units, SI, 255
  basic, 255
  derived, 255

Volume, equivalent, 12f

Water,
  dissociation, 143
dissociation constant, 143f
  ion product, 144
  and temperature, 144
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