Ministry of Education and Science of Ukraine
Sumy State University

T. V. Dychenko, G. O. Yanovska

MEDICAL CHEMISTRY

Study guide

Recommended by the Academic Council of Sumy State University

Sumy
Sumy State University
2020

UDC 577.1:61(075.8)
D 98

Reviewers:
M. V. Pogorelov – MD, DMS, Professor, Deputy Director for scientific work of the Medical Institute of Sumy State University;
N. N. Chaichenko – Doctor of Pedagogical Sciences, Professor of the Sumy State Pedagogical University named after A. S. Makarenko

Recommended for publishing
by the Academic Council of Sumy State University
as a study guide
(*minutes № 12 of 21.05.2020)*

Dychenko T. V.
D 98 Medical chemistry : study guide / T. V. Dychenko, G. O. Yanovska. – Sumy : Sumy State University, 2020. – 172 p.
ISBN 978-966-657-841-2

The study guide is intended for English-speaking students of higher education establishments of the 4th accreditation level of medical, pharmaceutical and chemical specialties.

UDC 577.1:61(075.8)

ISBN 978-966-657-841-2

CONTENTS

P.

CHAPTER 1. CHEMISTRY OF BIOGENIC ELEMENTS 7

1.1. General Information about Biogenic Elements 7

1.2. The Biogenic s- and p-Block elements: Biological Role and Application in Medicine 9

1.3. The Biogenic d- Block Elements: Biological Role, Application in Medicine 19

CHAPTER 2. COORDINATION COMPOUNDS 29

2.1. Structure of the Coordination Compounds. A. Werner's Coordination Theory 29

2.2. Classification of Coordination Compounds 33

2.3. Nomenclature of Coordination Compounds 34

2.4. Coordinate Bonds. Shape of the Complex Ion. Isomers 38

2.5. Dissociation of Coordination Compounds 43

2.6. Coordination Compounds in Medicine 44

CHAPTER 3. CHEMICAL THERMODYNAMICS ... 51

3.1. Thermodynamics Terminology 51

3.2. The Laws of Thermodynamics 53

3.3 Internal Energy and Enthalpy 54
3.4. Thermochemical Equations. Hess’s Law 57
3.5. Spontaneity and Disorder. Entropy 61
3.6. Gibbs Free Energy. Process Direction Criteria .. 64
3.7. Application of Thermodynamic Laws for Living Systems 68
CHAPTER 4. CHEMICAL KINETICS 74
4.1. The Main Concepts of Chemical Kinetics 74
4.2. Factors Affecting the Reaction Rate 75
4.3. Chemical Equilibrium 78
4.4. Le Chatelier’s Principle States 79
CHAPTER 5. SOLUTIONS 85
5.1. Theory of Solutions 86
5.2. Methods of Expressing of Solution Concentrations 88
5.3. Colligative Properties of Solutions 104
5.4. Aqueous Solutions of Acids, Bases and Salts .. 113
5.5. The Dissociation of Water. The pH Scale 117
5.6. Hydrolysis 121
5.7. Buffer Solution 125

CHAPTER 6. OXIDATION-REDUCTION REACTIONS 135
6.1. Oxidation States 135
6.2. Oxidation-Reduction: Some Definitions 137
6.3. Balancing Oxidation-Reduction Equations 138
6.4. Galvanic Elements. The Nernst Equation for Single Electrode Potential 145
CHAPTER 7. COLLOIDAL PROPERTIES OF SOLUTIONS 151
7.1. Colloidal Particles. Classifications of Colloid Systems 151
7.2. Electric Properties of Colloids. Micelles 155
7.3. Applications of Colloidal Solutions 158
REFERENCES 163
GLOSSARY 164

To the Students!

Welcome to the course of medical chemistry! You are about to embark on an exciting journey. This study guide has been written for students like you mind – those who are encountering the subject for the first time. The book`s central goal is to make your journey both stimulating and enjoyable by helping you understand the guiding principles of the subject and applying these principles to your field of study. Work all the problems within each chapter. These are drill problems that allow you to check whether you have mastered the material. Some of them are solved for you in the text.

Work as many end-of-chapter problems as you can. The more problems you work, the more comfortable you will be with the subject and the more prepared you will be for the material in subsequent chapters.

The glossary at the end of the book can be a very useful study guide. Take advantage of all of these features.

Good luck in your study!

CHAPTER 1

CHEMISTRY OF BIOGENIC ELEMENTS

Practical skills

After studying the subject, you will be able:

1. To classify the chemical elements.
2. To have the idea about the biological role of the most essential s-, p- and d-block elements.

1.1. General Information About Biogenic Elements

Living organisms contain different quantities of all known chemical elements. Hydrogen, carbon, nitrogen, and oxygen make up 96% of the mass of the human body when calcium, phosphorus, potassium, and sulfur constitute 3% of the weight of the human body. Iodine, iron, sodium, chlorine, magnesium, copper, manganese, cobalt, zinc, and other elements make up 1%. All elements perform a wide variety of functions critical to life. Depriving a living organism of any of these elements results in disease and possibly death.

The **biogenic elements** are the chemical elements required for the construction and vital activity of cells and organisms.

Classifications of biogenic elements

According to the content of elements in the human body, the biogenic elements are divided into such groups:

1. **Macroelement**s (> 10^{-2} %). These are C, H, O, N, P, S, Na, Ca, K, Cl.
2. **Microelements** (< 10^{-2} %). These are Mg, Cu, Zn, Mn, Co, Fe, I, Al, Mo, etc.
3. **Ultramicroelement**s (< 10^{-12} %). These are Ra, Hg, Au, U, ect.

According to the importance of chemical elements for the vital activity of a person, they can be classified as:

1. **Irreplaceable elements**. They are constantly in the human body. These are C**, H, O**, N, K, P, S, Na**, Ca,** Cl, Mg, Cu, Zn, Mn, Co, Fe, I, Mo, V, etc. The deficiency of these elements leads to the infringement of the vital activity of the organism.

2. **Impurity elements**. They are also could be found in the human body, but their biological role is not always known or is little studied yet. These are Ga, Sb, Sr, Br, F, B, Be, Li, Si, Sn, Cs, As, Ba, Ge, Rb, Pb, Ra, Bi, Cd, Cr, Ni, Ti, Ag, Th, Hg, Ce, Se.

3. **Microimpurity elements**. They are found in the human body, but there is no information about their content or biological roles. These are Sc, Tl, In, La, Pr, W, Re, etc.

According to the electronic structure of an atom, the chemical elements can be divided into four blocks, namely, s-, p-, d- and f-blocks.

s-Block Elements of groups IA and IIA form the s-blocks as their outermost shell electrons are located in the s-subshell.

p-Block. Elements of Groups IIIA to O are known as p-block elements. It is because their outermost shell electrons are located in the p-subshell.

d-Block. d-Block elements have their highest energy electrons in the inner d-subshell. They are also called “transition elements”.

The human organs accumulate biogenic elements differently, and they are nonuniformly distributed between organs and tissues. The majority of microelements are concentrated in the liver, bones and muscles. Some chemical elements show a specific affinity to this or that organ. Thus, it is known that iodine concentrates in the thyroid gland, fluorine – in the tooth enamel, aluminum and arsenic – in the hair and nails, molybdenum – in the kidneys and barium – in the retina of the eye.

Chemical elements in the human body carry out various functions.

1.2. The Biogenic s- and p- Block Elements: Biological Role and Application in Medicine

Sodium is a compound of many foodstuffs, for instance, of common salt. It is necessary for humans to maintain the balance of the physical fluid system. Sodium is also required for nerve and muscle functioning. Too much sodium can damage our kidneys and increases the chances of high blood pressure.

The amount of sodium a person consumes each day varies from individual to individual and from culture to culture: some people get as little as 2 g/day, some as much as 20 grams.

Contact of sodium with water, including perspiration, causes the formation of sodium hydroxide fumes, which are highly irritating to the skin, eyes, nose, and throat. This may cause sneezing and coughing. Very severe exposures may result in breathing difficulty, coughing, and chemical bronchitis. Skin contact may cause itching, tingling, thermal and caustic burns, and permanent damage. Eye contact may result in permanent damage and loss of sight.

Potassium can be found in vegetables, fruit, potatoes, meat, bread, milk, and nuts. It plays an important role in the physical fluid system of humans, and assists nerve functions. Potassium, as the ion K^+ is concentrated inside cells, and 95 % of potassium in the body is stored in this way. If kidney function is impaired, potassium accumulates in the body. This can lead to anxious heartbeats. Potassium can affect you when breathed in. Inhalation of dust or mists can irritate the eyes, nose, throat, lungs with sneezing, coughing, and sore throat. Higher exposures may cause accumulation of fluid in the lungs, and this can cause death. Skin and eye contact can cause severe burns leading to permanent damage.

Calcium is the most abundant metal in the human body: it is the main constituent of bones and teeth, and it has vital metabolic functions.

Calcium is the most commonly found in milk and milk products, but also in vegetables, nuts, and beans. It is an essential component for the preservation of human skeleton and teeth. It also assists the functions of nerves and muscles. The use of more than 2.5 grams of calcium per day without medical necessity can lead to the development of kidney stones and sclerosis of kidneys and blood vessels.

A lack of calcium is one of the main causes of osteoporosis. Osteoporosis is a disease in which the bones become extremely porous, subject to fracture, and heal slowly, occurring mainly in women following menopause and often leading to curvature of the spine from vertebral collapse.

Unlike most people think, there is an intense biological activity inside our bones. They are continuously renewed by new tissue replacing the old one. During childhood and adolescence, there’s more production of new tissue than the destruction of the old one, but at some point, somewhere around the 30 or 35 years of age, the process is inverted, and we start to lose more tissue than what we can replace. In women the process accelerates after the menopause (This period is marked by natural and permanent cessation of menstruation, usually occurring between the ages of 45 and 55); this is because the body stops producing the hormone known as estrogen, one of which functions is to preserve the skeletal mass.

Evidence suggests that we need a daily intake of 1.000 milligrams of calcium to preserve the bony mass in normal conditions. It is actual both for men and pre-menopausic women. The recommended daily intake rises to 1.500 for menopausic women.

The main calcium sources are dairy products, but also nuts, some green vegetables like spinach, and cauliflower, beans, lentils.

Calcium works together with magnesium to create new osseous mass. Calcium should be taken with magnesium in a 2:1 rate, that is, if you ingest 1000 mg of calcium, you should also ingest 500 mg of magnesium. Some magnesium sources in the diet are seafood, whole-grains, nuts, beans, wheat oats, seeds, and green vegetables.

Other necessary measures to prevent osteoporosis are:

- Doing regular exercises (at least three times a week)
- Taking adequate amounts of manganese, folic acid, vitamin B_6, vitamin B_{12}, omega-3 (it aids calcium absorption and stimulates new osseous mass production), and vitamin D (it aids calcium absorption in the small intestine).
- Give up of sugar, saturated grease, and animal proteins
- Give up of alcohol, caffeine, gaseous drinks
- Not smoking

Other triggers for osteoporosis are the hereditary factor and stress.

Magnesium. Humans take in between 250 and 350 mg/day of magnesium and need at least 200 mg, but the body deals very effectively with this element, taking it from food when it can, and recycling what we already have when it cannot.

There is no evidence that magnesium produces systemic poisoning, although persistent over-indulgence in taking magnesium supplements and medicines can lead to muscle weakness, lethargy, and confusion.

Aluminum is one of the most widely used metals and also one of the most frequently found compounds in the earth's crust. Due to these facts, aluminum is commonly known as an innocent compound. But still, when one is exposed to high concentrations, it can cause health problems. The water-soluble form of aluminum causes harmful effects, and these particles are called ions. They are usually found in a solution of aluminum in combination with other ions, for instance, as aluminum chlorine.

The uptake of aluminum can occur through food, breathing, and skin contact. Long-lasting uptakes of significant concentrations of aluminum can serious by affect health, such as damage to the central nervous system:

- Dementia
- Loss of memory
- Listlessness
- Severe trembling

Aluminum is a risk in specific working environments, such as mines, where it can be found in water. People that work in factories where aluminum is applied during production processes may endure lung problems when they breathe in aluminum dust. Aluminum can cause problems for kidney patients when it enters the body during kidney dialyzes.

Inhalation of finely divided aluminum and aluminum oxide powder has been reported as a cause of pulmonary fibrosis and lung damage. This effect, known as Shaver's disease, is complicated by the presence of silica and oxides of iron in the inhaled air. Aluminium may also be implicated in Alzheimer's disease.

Iodine. Many medicines and cleansers for skin wounds contain iodine.

Iodine is a building material of thyroid hormones that are essential for growth, the nervous system, and the metabolism. Humans that eat little to no bread can experience iodine shortages. The function of the thyroid gland will then slow down, and the thyroid gland will start swelling up. This phenomenon is called struma. This condition is rare now since a little iodide is added to the table salt. Large quantities of iodine can be dangerous because the thyroid gland will work hard. This affects the entire body: it causes disturbed heartbeats and loss of weight.

Elemental iodine (I_2) is toxic, and its vapor irritates the eyes and lungs. The maximum allowable concentration in the air when working with iodine is just 1 mg/m^3. All iodides are toxic if taken in excess. Iodine 131 is one of the radionuclides involved in atmospheric testing of nuclear weapons. It is a long-lived radionuclide that produced and continue to produce increased cancers risk for decades and centuries to come. Iodine 131 increases the risk of cancer and possibly other diseases of the thyroid and those caused by thyroid gland hormonal deficiency.

Chlorine is a highly reactive gas. It is a natural element. The largest users of chlorine are companies that make chlorinated solvents: ethylene dichloride, polyvinyl chloride (PVC), chlorofluorocarbons, and propylene oxide. Paper companies use chlorine to bleach paper. Water and wastewater treatment plants use chlorine to reduce the levels of microorganisms that can spread the disease to humans (disinfection) in the water.

Exposure to chlorine can occur in the workplace or in the environment following releases to air, water, or land. People who use laundry bleach and swimming pool chemicals containing chlorine products are usually not exposed to chlorine itself. Chlorine is generally found only in industrial settings.

Chlorine enters the body breathed in with contaminated air or when consumed with contaminated food or water. It does not remain in the body due to its reactivity.

The effects of chlorine on human health depend on the amount of chlorine that is present and the length and frequency of the exposure. Chlorine exposure also depends on the health of a person or the state of the environment when exposed.

Breathing small amounts of chlorine for short periods adversely affects the human respiratory system. This effect can range from coughing and chest pain to water retention in the lungs. Chlorine irritates the skin, eyes, and respiratory system. These effects are not likely to occur at levels of chlorine that are normally found in the environment.

Human health effects associated with breathing or otherwise consuming small amounts of chlorine over long periods of time are not known. Some studies show that workers develop adverse effects from repeat inhalation exposure to chlorine, but others do not.

Fluorine. Small amounts of fluorine are naturally present in water, air, plants, and animals. As a result, humans are exposed to fluoride through food and drinking water and breathing air. Fluorine can be found in any kind of food in relatively small quantities. Large quantities of fluorine can be found in tea and shellfish.

Fluorine is essential for the maintenance of bone strength. Fluorine can also protect us from dental decay if it is applied through toothpaste twice a day. If fluorine is absorbed too frequently, it can cause teeth decay, osteoporosis, and harm to kidneys, bones, nerves, and muscles.

Fluorine gas is released in the industries. This gas is hazardous, as it can cause death at very high concentrations. At low concentrations, it causes eye and nose irritations.

Silicon does not concentrate on a particular organ of the body, but is found mainly in the connective tissues and skin. Silicon is a non-toxic element as well as in all its natural forms, namely, silica and silicates, which are the most abundant.

Elemental silicon is an inert material, which appears to lack the property of causing fibrosis in lung tissue. However, slight pulmonary lesions have been reported in laboratory animals from intratracheal injections of silicon dust. Silicon dust has a little adverse effect on the lungs and does not appear to produce significant organic disease or toxic effects when exposures are kept beneath exposure limits. Silicon may cause chronic respiratory effects. Crystalline silica (silicon dioxide) is a potent respiratory hazard. However, the likelihood of crystalline silica generation during standard processing is very low. LD50 (oral) –3160 mg/kg. (LD50: Lethal dose 50, that means single-dose of a substance that causes the death of 50% of animal population from exposure to the substance by any route other than inhalation. They are usually expressed as milligrams or grams of material per kilogram of animal weight).

Silicon crystalline irritates the skin and eyes when coming in contact. Inhalation will cause irritation to the lungs and mucus membrane. Irritation to the eyes will cause watering and redness. Reddening, scaling, and itching are characteristics of skin inflammation. Lung cancer is associated with occupational exposures to crystalline silica, specifically quartz and cristobalite. An exposure-response relationship has been reported in studies of miners, diatomaceous earth workers, granite workers, pottery workers, refractory brick workers, and other workers.

Several epidemiological studies have reported statistically significant numbers of excess deaths or cases of immunologic disorders and autoimmune diseases in silica-exposed workers. These diseases and disorders include scleroderma, rheumatoid arthritis, systemic lupus erythematosus, and sarcoidosis.

Recent epidemiological studies have reported statistically significant associations of occupational exposure to crystalline silica with renal diseases and subclinical renal changes.

Crystalline silica may affect the immune system, leading to mycobacterial (tuberculous and nontuberculous) or fungal infections, especially in workers with silicosis.

Occupational exposure to breathable crystalline silica is associated with bronchitis, chronic obstructive pulmonary disease (COPD), and emphysema. Some epidemiologic studies suggest that these health effects may be less frequent or absent in nonsmokers.

Boron. Humans can be exposed to boron through fruit and vegetables, water, air, and consumer products. We have a regular daily intake of about 2 mg and about 18 mg in our body in total.

When humans consume large amounts of boron-containing food, the boron concentrations in their bodies may rise to levels that can cause health problems. Boron can infect the stomach, liver, kidneys, and brains and can eventually lead to death. When exposure to small amounts of boron takes place, irritation of the nose, throat, or eyes may occur. It takes 5 g of boric acid to make a person ill and 20 grams or more to put its life in danger.

Eating fish or meat will not increase the boron concentrations in our bodies, as boron does not accumulate within the tissues of animals.

Arsenic is one of the most toxic elements that can be found. Despite their toxic effect, inorganic arsenic bonds occur on earth naturally in small amounts. Humans may be exposed to arsenic through food, water, and air, through skin contact with soil or water that contains arsenic.

Levels of arsenic in food are relatively low, as it is not added due to its toxicity. But levels of arsenic in fish and seafood may be high because fish absorb arsenic from the water they live in. Luckily this is mainly the relatively harmless organic form of arsenic, but fish that contain significant amounts of inorganic arsenic may be a danger to human health.

Arsenic exposure may be higher for people that work with arsenic, for people that live in houses that contain conserved wood of any kind, and for those who live on farmlands where arsenic-containing pesticides have been applied in the past.

Exposure to inorganic arsenic can cause various health effects, such as irritation of the stomach and intestines, decreased production of red and white blood cells, skin changes, and lung irritation. It is suggested that the uptake of significant amounts of inorganic arsenic can intensify the chances of cancer development, especially the chances of development of skin cancer, lung cancer, liver cancer, and lymphatic cancer.

Very high exposure to inorganic arsenic can cause infertility and miscarriages with women, and it can cause skin disturbances, declined resistance to infections, heart disruptions, and brain damage with both men and women. Finally, inorganic arsenic can damage DNA. A lethal dose of arsenic oxide is generally regarded as 100 mg.

Organic arsenic can cause neither cancer nor DNA damage. But exposure to high doses may cause certain effects on human health, such as nerve injury and stomachaches.

Selenium. Humans may be exposed to selenium in several different ways. Selenium exposure takes place either through food or water, or when we come in contact with soil or air that contains high concentrations of selenium. This is not very surprising because selenium occurs naturally in the environment extensively, and it is very widespread.

The exposure to selenium mainly takes place through food, because selenium is naturally present in grains, cereals, and meat. Humans need to absorb specific amounts of selenium daily in order to maintain good health. Food usually contains enough selenium to prevent disease caused by shortages. Selenium uptake through food may be higher than normal in many cases because, in the past, many selenium-rich fertilizers have been applied on farmlands.

People who live near hazardous waste-sites will experience a higher exposure through soil and air. Selenium from hazardous waste-sites and farmland ends up in groundwater or surface water through irrigation. This phenomenon causes selenium to end up in local drinking water so that exposure to selenium through water will be temporarily increased.

People who work in metal, selenium-recovery and paint industries also tend to experience higher selenium exposure, mainly through breathing. Selenium is released to the air through coal and oil combustion.

People who eat a lot of foods from grains that grow near industrial sites may experience higher exposure to selenium through food. Exposure to selenium through drinking water may be increased when selenium from hazardous waste disposals ends up in water wells.

Exposure to selenium through the air usually occurs only in the workplace. It can cause dizziness, fatigue, and irritations of the mucous membranes. When the exposure is extremely high, the cumulation of fluid in the lungs and bronchitis may occur.

Selenium uptake through food is usually high enough to meet human needs; shortages are rare. When shortages occur, people may experience heart and muscle problems.

When selenium uptake is too high, health effects will be likely to come about. The seriousness of these effects depends upon the concentrations of selenium in the food and how often this food is eaten.

The health effects of various forms of selenium can vary from brittle hair and deformed nails to rashes, heat, swelling of the skin, and severe pains. When selenium ends up in the eyes, people experience burning, irritation, and tearing.

Selenium poisoning may become so severe in some cases that it can even cause death.

Overexposure of selenium fumes may produce accumulation of fluid in the lungs, garlic breath, bronchitis, pneumonitis, bronchial asthma, nausea, chills, fever, headache, sore throat, shortness of breath, conjunctivitis, vomiting, abdominal pain, diarrhea, and enlarged liver. Selenium is an eye and upper respiratory irritant and sensitizer. Overexposure may result in red staining of the nails, teeth, and hair.

Selenium dioxide reacts with moisture to form selenious acid, which is corrosive to the skin and eyes.

Carcinogenicity. The International Agency for Research on Cancer (IARC) has listed selenium within Group 3 (The agent is not classifiable as to its carcinogenicity to humans).

Phosphorus can be found in the environment most commonly as phosphates. Phosphates are essential substances in the human body, because they are a part of DNA materials and they take part in energy distribution. Phosphates can also be found commonly in plants.

Phosphate is a dietary requirement, and the recommended intake is 800 mg/day. A healthy diet provides between 1000 and 2000 mg/day, depending on the extent to which phosphate-rich foods are consumed.

Humans have changed the natural phosphate supply radically by the addition of phosphate-rich manures to the soil and by the use of phosphate-containing detergents. Phosphates were also added to a number of foodstuffs, such as cheese, sausages, and hams.

Too much phosphate can cause health problems, such as kidney damage and osteoporosis. Phosphate shortages can also lead to health problems due to the extensive use of drugs.

Phosphorus, in its pure form, has a white color. White phosphorus is the most dangerous form of phosphorus that is known to us. When white phosphorus occurs in nature, this can be a serious danger to our health. White phosphorus is extremely poisonous, and in many cases, exposure to it will be fatal.

In most cases, people that died of white phosphorus exposure had been accidentally swallowing rat poison. Before people die from white phosphorus exposure, they often experience nausea, stomach cramps, and drowsiness. White phosphorus can cause skin burns. While burning, white phosphorus may cause damage to the liver, the heart, or the kidneys.

Sulfur. All living organisms need sulfur. It is essential for humans because it is part of the amino acid methionine, which is an absolute dietary requirement for us. The amino acid cysteine also contains sulfur. The average person contains in around 900 mg of sulfur per day, mainly in the form of protein.

Elemental sulfur is not toxic, but many simple sulfur derivates, are, such as sulfur dioxide (SO_2) and hydrogen sulfide, are toxic.

Sulfur can be found, commonly, in nature as sulfides. During several processes, sulfur bonds are added to the environment that is damaging both animals and humans. These damaging sulfur bonds are also shaped in nature during various reactions, mostly when substances, that are not naturally present, have already been added. They are unwanted because of their unpleasant smells and are often highly toxic.

Globally, sulphuric substances can have the following effects on human health:

- Neurological effects and behavioral changes
- Disturbance of blood circulation
- Heart damage
- Effects on eyes and eyesight
- Reproductive failure
- Damage to immune system
- Stomach and gastrointestinal disorders
- Damage to liver and kidney functions
- Hearing defects
- Disturbance of the hormonal metabolism
- Dermatological effects
- Suffocation and lung embolism

1.3. The Biogenic d- Block Elements: Biological Role and Application in Medicine

Zinc is a trace element that is essential for human health. When people absorb too little zinc, they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing, and skin sores. Zinc-shortages can even cause congenital disabilities.

Although humans can handle large concentrations of zinc, too much zinc can still cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea, and anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis. Extensive exposure to zinc chloride can cause respiratory disorders.

In the workplace, environmental contamination with zinc can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity.

Zinc can be a danger to the fetus and newborn. After mothers have absorbed large concentrations of zinc, their babies may be exposed to it through their blood or milk of their mothers.

Iron can be found in meat, wholemeal products, potatoes, and vegetables. The human body absorbs iron from animal products faster than iron from plant products. Iron is an essential part of hemoglobin, a red coloring agent of the blood that transports oxygen through out bodies.

Iron may cause conjunctivitis, choroiditis, and retinitis if it contacts and remains in tissues. Chronic inhalation of excessive concentrations of iron oxide fumes or dust may result in the development of pneumoconiosis (siderosis), which is observed as an x-ray change. No physical impairment of lung function has been associated with siderosis. Inhalation of excessive concentrations of iron oxide may enhance the risk of lung cancer development in workers exposed to pulmonary carcinogens. LD50 (oral, rat) = = 30 gm/kg. (LD50: Lethal dose is 50 mg/kg).

A more common problem for humans is iron deficiency which leads to anemia. A man needs an average daily intake of 7 mg of iron and a woman – 11 mg; a normal diet will generally provide all that is needed.

Vanadium compounds are not regarded as a serious hazard. However, workers exposed to vanadium peroxide dust were found to suffer severe eye, nose, and throat irritations.

The uptake of vanadium by humans takes place mainly through foodstuffs such as buckwheat, soya beans, olive oil, sunflower oil, apples, and eggs.

Vanadium can have a number of health effects when the uptake is too high. When vanadium uptake takes places through air, it can cause bronchitis and pneumonia.

The acute effects of vanadium are the irritations of lungs, throat, eyes, and nasal cavities.

Other health effects of vanadium uptake are:

- Cardiac and vascular disease
- Inflammation of stomach and intestines
- Damage to the nervous system
- Bleeding of the liver and kidneys
- Skin rashes
- Severe trembling and paralyzes
- Nose bleeds and throat pains
- Weakeness
- Sickness and headaches
- Dizziness
- Behavioral changes

The health hazards associated with exposure to vanadium are dependent on its oxidation state. This product contains elemental vanadium. Elemental vanadium could be oxidized to vanadium pentoxide during welding. The pentoxide form is more toxic than the elemental form. Chronic exposure to vanadium pentoxide dust and fumes may cause severe irritation of the eyes, skin, upper respiratory tract, persistent inflammations of the trachea and bronchi, pulmonary edema, and systemic poisoning. Signs and symptoms of overexposure include conjunctivitis, nasopharyngitis, cough, labored breathing, rapid heartbeat, lung changes, chronic bronchitis, skin pallor, greenish-black tongue, and allergic skin rash.

Manganese is a very common compound that can be found everywhere on earth. Manganese is one out of three toxic essential trace elements, which means that it is not only necessary for humans to survive, but it is also toxic when too high concentrations are present in a human body. When people do not live up to the recommended daily allowances, their health will decrease. But when the uptake is too high, health problems will also occur.

The uptake of manganese by humans mainly takes place through food, such as spinach, tea, and herbs. The foodstuffs that contain the highest concentrations are grains, rice, soya beans, eggs, nuts, olive oil, green beans and oysters. After absorption in the human body, manganese will be transported through the blood to the liver, kidneys, pancreas, and endocrine glands.

Manganese affects mainly the respiratory tract and brains. Symptoms of manganese poisoning are: hallucinations, forgetfulness, and nerve damage. Manganese can also cause Parkinson, lung embolism, and bronchitis. When men are exposed to manganese for a longer period of time, they may become impotent. A syndrome that is caused by manganese has symptoms such as schizophrenia, dullness, weak muscles, headaches, and insomnia.

Since manganese is an essential element for human body, its shortage can cause the following health effects:

- Obesity
- Glucose intolerance
- Blood clotting
- Skin problems
- Lowered cholesterol
- Skeleton disorders
- Congenital disabilities
- Changes in hair color
- Neurological symptoms

Chronic Manganese poisoning may result from prolonged inhalation of Manganese dust and fume. The central nervous system is the main site of damage from the disease, which may result in permanent disability. Symptoms include languor, sleepiness, weakness, emotional disturbances, spastic gait, recurring leg cramps, and paralysis. A high incidence of pneumonia and other upper respiratory infections has been found in workers exposed to dust or

Manganese compounds fume. Manganese compounds are experimental equivocal tumorigenic agents.

Copper can be found in many kinds of food, in drinking water and in air. Because of that, we absorb eminent quantities of copper each day by eating, drinking, and breathing. The absorption of copper is necessary because copper is a trace element that is essential for human health. Although humans can handle higher concentrations of copper, too much copper can still cause eminent health problems.

Copper concentrations in air are usually quite low so that exposure to copper through breathing is negligible. But people that live near smelters that melt copper ore into metal do experience this kind of exposure.

People who live in houses that still have copper plumbing are exposed to higher levels of copper than most people because copper is released into their drinking water through corrosion of pipes.

Occupational exposure to copper often occurs. In the working environment, copper contagion can lead to a flu-like condition known as metal fever. This condition is caused by hypersensitivity and will pass in two days.

Cobalt is widely dispersed in the environment, therefore, humans may be exposed to it by breathing air, drinking water, and eating food that contains cobalt. Skin contact with soil or water that contains cobalt may also enhance exposure.

Cobalt is not often freely available in the environment, but when cobalt particles are not bound to soil or sediment particles, its uptake by plants and animals is higher, and its accumulation in plants and animals may occur.

Cobalt is beneficial for humans because it is a part of vitamin B_{12}, which is essential for human health. Cobalt is used to treat anemia with pregnant women because it stimulates the production of red blood cells. The total daily intake of cobalt is variable and may be as much as 1 mg, but almost all will pass through the body unadsorbed, except that in vitamin $B_{12.}$

However, too high concentrations of cobalt may damage human health. When we breathe in excessively high levels of cobalt through the air, we experience lung effects, such as asthma and pneumonia. This mainly occurs with people who work with cobalt. When plants grow on contaminated soils, they will accumulate very small particles of cobalt, especially in the plants we eat, such as fruits and seeds. Soils near mining and melting facilities may contain very high amounts of cobalt so that the uptake by humans through eating plants can cause health effects.

Health effects that are a result of the uptake of high concentrations of cobalt are:

- Vomiting and nausea
- Vision problems
- Heart problems
- Thyroid damage

Health effects may also be caused by radiation of cobalt isotopes. This can cause sterility, hair loss, vomiting, bleeding, diarrhea, coma, and even death. This radiation is sometimes used for cancer patients to destroy tumors. These patients also suffer from hair loss, diarrhea, and vomiting.

Cobalt dust may cause asthma-like diseases with symptoms ranging from cough, shortness of breath and dyspnea to decreased pulmonary function, nodular fibrosis, permanent disability, and death. Exposure to cobalt may cause weight loss, dermatitis, and respiratory hypersensitivity. LD 50 (oral, rat)- 6171 mg/kg. (LD50 = Lethal dose 50 = single dose of a substance that causes the death of 50 % of an animal population from exposure to the substance by any route other than inhalation. LD50 is usually expressed as milligrams or grams of material per kilogram of animal weight (mg/kg or g/kg).)

Carcinogenicity: International Agency for Research on Cancer (IARC) has listed cobalt and cobalt compounds within-group 2B (agents which are possibly carcinogenic to humans). ACGIH has placed cobalt and inorganic compounds in category A3 (Experimental animal carcinogen – the agent is carcinogenic in experimental animals at a relatively high dose, by route(s), histologic type(s), or by mechanism(s) that are not considered relevant to worker exposure).

Cobalt has been classified to be carcinogenic to experimental animals by the Federal Republic of Germany.

Cadmium. The human uptake of cadmium occurs mainly through food. Foodstuffs that are rich in cadmium can significantly increase the cadmium concentration in human bodies. Examples are: liver, mushrooms, shellfish, mussels, cocoa powder, and dried seaweed.

An exposure to significantly higher cadmium levels occurs when people smoke. Tobacco smoke transports cadmium into the lungs. Blood will carry it through the rest of the body, where it can increase effects by potentiating cadmium that is already present from cadmium-rich food.

Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air and people that work in the metal refinery industry. When people breathe in cadmium, it can severely damage their lungs. This may even cause death.

Cadmium is first transported to the liver through the blood. There, it is bound to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the excretion of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is excreted from a human body.

Other health effects that can be caused by cadmium are:

- Diarrhea, stomach pains, and severe vomiting
- Bone fracture
- Reproductive failure and possibly even infertility
- Damage to the central nervous system
- Damage to the immune system
- Psychological disorders
- Perhaps DNA damage or cancer development

Nickel is a compound that occurs in the environment only at very low levels. Humans use nickel for many different applications. The most common application of nickel is the use as an ingredient of steel and other metal products. It can be found in metal products such as jewelry.

Foodstuffs naturally contain small amounts of nickel. Chocolate and fats are known to contain severely high quantities. Nickel uptake will boost when people eat large quantities of vegetables from polluted soils. Plants are known to accumulate nickel, and as a result, the nickel uptake from vegetables will be eminent. Smokers have a higher nickel uptake through their lungs. Finally, nickel can be found in detergents.

Humans may be exposed to nickel by breathing air, drinking water, eating food, or smoking cigarettes. Skin contact with nickel-contaminated soil or water may also result in nickel exposure. In small quantities, nickel is essential, but when the uptake is too high, it can be a danger to human health.

An uptake of too large quantities of nickel has the following consequences:

- Higher chances of development of lung cancer, nose cancer, larynx cancer, and prostate cancer
- Sickness and dizziness after exposure to nickel gas
- Pulmonary embolism
- Respiratory failure
- Birth defects
- Asthma and chronic bronchitis
- Allergic reactions such as skin rashes, mainly from jewelry
- Heart disorders

Nickel fumes are respiratory irritants and may cause pneumonitis. Exposure to nickel and its compounds may result in the development of dermatitis known as “nickel itch” in sensitized individuals. The first symptom is usually itching, which occurs up to 7 days before skin eruption occurs. The primary skin eruption is erythematous, or follicular, which may be followed by skin ulceration. Nickel sensitivity once acquired, appears to persist indefinitely.

Carcinogenicity: Nickel and certain nickel compounds have been listed by the National Toxicology Program (NTP) as being reasonably anticipated to be carcinogens. The International Agency for

Research on Cancer (IARC) has listed nickel compounds within group 1 (there is sufficient evidence for carcinogenicity in humans) and nickel within group 2B (agents which are possibly carcinogenic to humans). OSHA does not regulate nickel as a carcinogen. Nickel is on the ACGIH Notice of Intended Changes as a Category A1, confirmed human carcinogen.

Chromium. People can be exposed to chromium through breathing, eating, or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water, the level of chromium is usually low as well, but contaminated well water may contain the dangerous chromium (IV) and chromium (VI). For most people, eating food that contains chromium (III) is the main route of chromium uptake, as chromium (III) occurs naturally in many vegetables, fruits, meats, yeasts, and grains. Various ways of food preparation and storage may alter the chromium contents in food when food is stored in steel tanks or cans, chromium concentrations may rise.

Chromium (III) is an essential nutrient for humans, and shortages may cause heart conditions, disruptions of metabolisms, and diabetes. But the uptake of too much chromium (III) can cause health effects as well, for instance, skin rashes.

Chromium (VI) is a danger to human health, mainly for people who work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium.

Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in, chromium (VI) can cause nose irritations and nosebleeds.

Other health problems that are caused by chromium (VI) are:

- Skin rashes
- Upset stomachs and ulcers
- Respiratory problems
- Weakened immune systems
- Kidney and liver damage
- Alteration of genetic material

- Lung cancer
- Death

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions. Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms, and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Carcinogenicity: Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (The agent is not classifiable as to its carcinogenicity to humans.) Chromium is not regulated as a carcinogen by OSHA (29 CFR 1910 Subpart Z). ACGIH has classified chromium metal and trivalent chromium compounds as A4, not classifiable as a human carcinogen.

Molybdenum. Based on animal experiments, molybdenum and its compounds are highly toxic. Some evidence of liver dysfunction with hyperbilirubinemia has been reported in workmen chronically exposed in a Soviet Mo-Cu plant. In addition, signs of gout have been found in factory workers and among inhabitants of Mo-rich areas of Armenia. The main features were joint pains in the knees, hands and feet; articular deformities, erythema, and edema of the joint areas.

CHAPTER 2
COORDINATION COMPOUNDS

Practical skills

After studying the subject, you will be able:

1. To determine the type of the complex compound.
2. To name the complex compound.
3. To determine the oxidation state of the central ion (atom), the charge of the complex ion, coordination number.
4. To know the application of coordination compounds in medicine.
5. To write the equation of the complexion dissociation.
6. To write the equation of the constant of the instability of the complex ion.

Coordination compounds are present in minerals and living organisms. Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal ions. The red color of blood is caused by the presence of hemoglobin – a coordination compound containing Fe(II). Chlorophyll, which is found in plants, is a coordination compound similar in structure to hemoglobin, containing Mg(II) instead of Fe(II). Iron enters the composition of myoglobin, oxidases, peroxidases, and cytochromes. More than 60 biologically active substances contain zinc. Cobalt is a part of vitamin B_{12} (cyanocobalamin).

2.1. Structure of the Coordination Compounds. A. Werner's Coordination Theory

Coordination compounds (complex compounds, complexes) are the compounds that contain complex ions that retain their stability when dissolved.

The theory of the complex compound structure was worked out by the Swiss chemist A. Werner (1893).

According to the coordination theory, the central atom (ion) is situated in the center of a molecule of the coordination compound.

Around the central atom (ion), there are oppositely charged ions or neutral molecules, called **ligands**, or **addends**.

The central atom (ion), together with its ligands, is called a **complex ion**.

The coordination number reflects the number of bonds formed between the metal ion and the ligands in the complex ion.

The complex ion makes the **inner sphere** of a coordination compound, denoted by square brackets.

The ions that do not enter the inner sphere form the **outer sphere** (Fig. 2.1).

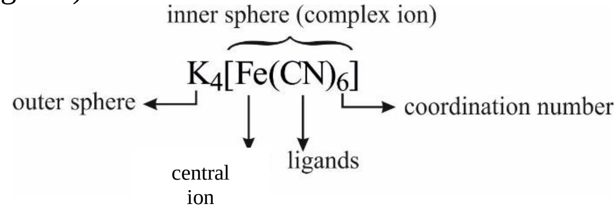


Figure 2.1 – Structure of the coordination compounds

The **charge of the complex ion** is equal to the algebraic sum of the charges of the central atom (ion) and ligands. If the ligands are electrically neutral molecules, the charge of the complex ion is equal to the charge of the central ion. **A molecule of a complex compound is electrically neutral.**

For example, the charge of the $[Fe^{2+}(CN)_6^-]$ is equal to $2 + 6 \cdot (1) = -4$; the charge of $[Cu^{+2}(H_2O)_6^0]$ is equal to $2 + 6 \cdot (0) = = +2$; the charge of $K_4^+[Fe^{+2}(CN)_6^-]$ is equal to $4 \cdot (1) + 2 + 6 \cdot (-1) = = 4 + 2 - 6 = 0$.

Let’s consider the structure of the coordination compound in detail.

Central atom (ion). d-Block elements (transition elements) or ions (Pt, Pd, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg) show the highest complex formation tendency. Most of the transition element complexes have coordination numbers 2, 4, or 6.

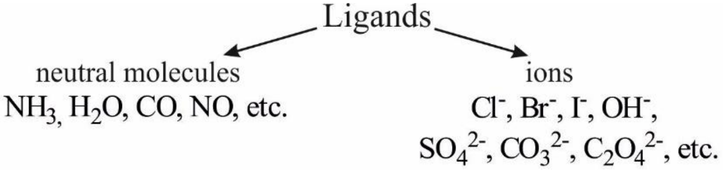
Table 2.1 – Relationship between the oxidation state of the central ion and its coordination number

The oxidation state of the central ion	Coordination number (CN)	Example	
		ion	complex compound
+1	**2**, 3	Cu^+, Ag^+, Au^+	$[Ag(NH_3)_2]Cl$
+2	3, **4**, 6	Cu^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, Fe^{2+}	$[Cu(NH_3)_4]Cl_2$, $K_4[Fe(CN)_6]$
+3	4, 5, **6**	Fe^{3+}, Cr^{3+}, Co^{3+}	$K_3[Co(NO_2)_6]$
+4	**6**, 8	Sn^{+4}, Pt^{+4}	$K_2[PtCl_6]$, $H_2[SnCl_6]$

The central atom (ion) may be presented by nonmetals, for example by boron ($K[BF_4]$), silicon ($K_2[SiF_6]$), and phosphorus ($K[PF_6]$).

The oxidation state of the central atom (ion) may be positive – $K_3[Fe^{+3}(CN)_6]$, $K[\overset{+3}{B}F_4]$; negative – $[\overset{-3}{N}H_4]Cl$; and zero – $[Cl_2(H_2O)_4]$, $[Ni(CO)_4]$. The oxidation state of the central atom is the main factor affecting the coordination number (Tab. 2.1).

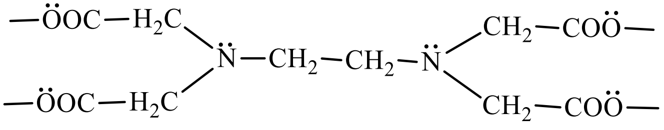
Ligands. The ligands are divided into neutral molecules and ions.



Ligands are the species that donate electron pairs to the central atom (ion). The atom in the ligands which can donate the electron pairs is called a **donor atom**. For example, NH_3 nitrogen is the donor atom.

The ligands may contain one or more donor atoms for coordination with the central atom. Accordingly, the ligands are classified as follows:

1. **Monodentate** (or unidentate) ligands are ligands that donate just one electron pair. For example, NH_3 H_2O, Cl^-, CN^-, OH^-, etc.
2. **Bidentate** ligands are ligands that donate two electron pairs to an atom. For example, SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$, $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ (a classic bidentate chelating ligand is ethylenediamine acts as which is abbreviated as en).
3. **Polydentate** (or multidentate) ligands donate more than two electron pairs. For example, ethylenediaminetetraacetate EDTA (a hexadentate ligand).



The porphyrin ligands in the heme group in hemoglobin are also polydentate.

The polydentate ligands generally form an enhance of a complex, which is called the chelate effect.

Complex ion. The complex ion may be defined as an electrically charged species which consists of a central atom (ion) surrounded by a group of ions or neutral molecules. For example, $[Fe(CN)_6]^{4+}$ is a complex ion in which the central Ferrum ion, Fe^{2+}, is surrounded by six cyanide ions (ligands).

All complex ions are divided into three groups: **complex ion – cation** – $[Cu^{2+}(NH_3)_4]^{2+}$, $[Co^{+3}Br(NH_3)_5]^{2+}$; **complex ion – anion** – $[Fe^{2+}(CN)_6]^{4-}$; **complex neutral molecule** – $[Co^{3+}(NH_3)_3Cl_3^-]^0$, $[Pt^{+2}(NH_3)_4Br_2]^0$.

If the complex ion is a cation, there are anions in the outer sphere complexes: $[Cu(NH_3)_4]SO_4$, $[Ag(NH_3)_2]Cl$.

If the complex ion is an anion, there are cations in the outer sphere complexes. Cations are usually the cations of the alkali and alkaline-earth metals, and the ammonium cation:

$K_4[Fe(CN)_6]$, $Na[Ag(CN)_2]$, $NH_4[AuCl_4]$.

2.2. Classification of Coordination Compounds

According to the charge of the complex ions, coordination compounds are divided into neutral coordination compounds, anionic coordination compounds, and cationic coordination compounds.

For example, a **neutral complex** is a complex ion, which is neutral in charge: $[\mathrm{Cu(NH_3)_2Cl_2}]^0$, $[\mathrm{Pt(NH_3)_4Br_2}]^0$.

An anionic complex is a complex ion which is negative in charge: $\mathrm{K_4[Fe(CN)_6]}^{4-}$, $\mathrm{Na[Ag(CN)_2]}^{-}$.

A cationic complex is a complex ion that is positive in charge: $[\mathrm{Cu(NH_3)_4}]^{2+}\mathrm{Cl_2}$, $[\mathrm{Ag(NH_3)_2}]^{+}\mathrm{Cl}$.

According to **ligands,** coordination compounds are divided into **hydroxo complexes, acido complexes, ammines and aqua complexes**.

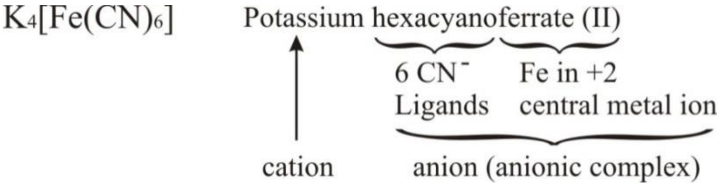
Table 2.2 – Classification of complexes by ligands

Ligand	Name of the coordination compound type	Example
hydroxo ions OH^-	hydroxo complexes	$Na_2[Zn(OH)_4]$
anions of acid residues: CN^-, NO_2^-, Cl^-, I^-, Br^- and others	acido complexes	$K_4[Fe(CN)_6]$, $K_2[HgI_4]$, $Na_3[Co(NO_2)_6]$
neutral molecules: NH_3, H_2O	ammines aqua complexes	$[Ag(NH_3)_2]Cl$, $[Al(H_2O)_6]Cl_3$

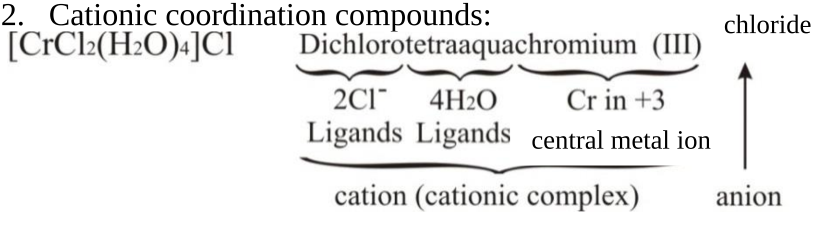
2.3. Nomenclature of Coordination Compounds

Coordination compounds are named according to the nomenclature recommended by the International Union of Pure and Applied Chemistry (IUPAC). The following examples illustrate how the rules are applied:

1. Anionic coordination compounds:



2. Cationic coordination compounds:



3. Neutral coordination compounds:

$[CoCl_3(NH_3)_3]$

$$\underbrace{\underbrace{\text{Trichloro}}_{\substack{3Cl^- \\ \text{Ligands}}}\underbrace{\text{triammine}}_{\substack{3NH_3 \\ \text{Ligands}}}\underbrace{\text{cobalt (III)}}_{\substack{\text{Co in } +3 \\ \text{central metal ion}}}}_{\text{neutral complex}}$$

The nomenclature can be summarized as follows:

1. **The naming of a coordination compound:**

a) if the coordination compound is ionic, then the cation is named before the anion:

$K_3[Fe(CN)_6]$ – potassium hexacyanoferrate (III);

$[CrCl_2(H_2O)_4]Cl$ – dichlorotetraaquachromium (III) chloride.

b) if the coordination compound is neutral, then the name of the complex ion is the name of the compound:

$[CoCl_3(NH_3)_3]$ trichlorotriamminecobalt (III).

2. **The naming of a complex ion in a coordination compound**

All present ligands and the central atom (ion) are named together as one word. The ligands are named before the central atom (ion):

$[CrCl_2(H_2O)_4]^+$– dichlorotetraaquachromium (III).

3. **The naming of the ligands in a complex ion:**

a) the order of the ligands is anionic, neutral, or cationic, $[PtCl_2(NH_3)_4]^{2+}$ dichlorotetraammineplatinum (IV):

- the names of anionic ligands end in – o:

CN^- – cyano;

Cl^- – chloro.

- the names of neutral ligands are the names of the molecules, except NH_3, H_2O, CO and NO:

NH_3 – ammine;

H_2O – aqua.

b) when more than one type of ligands are present, they are named in alphabetical order:

$[Cr(H_2O)_2(NH_3)_3Cl]Br_2$ – chlorotri***am***inodi***aq***uachromium (III) bromide.

Table 2.3 shows the names of some common ligands.

Table 2.3 – Names of some common ligands

Anionic Ligand	Ligand Name	Neutral Ligands	Ligand Name
bromide (Br^-)	bromo	Ammonia (NH_3)	ammine,
chloride (Cl^-)	chloro	water (H_2O)	aqua (aquo),
cyanide (CN^-)	cyano	carbon monoxide (CO)	carbonyl,
fluoride (F^-)	fluoro	H_2N-CH_2-CH_2-NH_2	ethylenediamine
hyroxide (OH^-)	hydroxo		
sulphate (SO_4^{2-})	sulphato		
amide (NH_2)	amido		
nitrite (NO_2^-)	nitro		
nitrate(NO_3^-)	nitrato		

c) within each type of ligand (cationic, anionic or neutral):

- if the number of a particular ligand is more than one, then the number is indicated with the appropriate Greek prefix as shown in Table 2.4;

Table 2.4 – Greek prefix of a number

Number	Greek prefix	Number	Greek prefix
2	Di-	5	Penta-
3	Tri-	6	Hexa-
4	Tetra-		

- the ligands are arranged in alphabetical order, ignoring the numbering prefixes:
  $[Cu(H_2O)_2(NH_3)_4]^{2+}$ – tetraamminediaquacopper (II).

4. The naming of the central atom (ion) in a complex:

a) if the complex is anionic, then the name of the metal ends in -ate:

$[Fe(CN)_6]^{3-}$ hexacyanoferrate (III) (Table 2.5).

Table 2.5 – Names of some common metals in anionic complexes

Metal	Name in Anionic Complex	Metal	Name in Anionic Complex
Titanium (Ti)	Titanate	Nickel (Ni)	Nickelate
Chromium (Cr)	Chromate	Zinc (Zn)	Zincate
Manganese (Mn)	Manganate	Platinum (Pt)	Platinate
Cobalt (Co)	Cobaltate		

For the following metals the English name is replaced by the Latine name, to which the “ate” ending is added:

(Sn) Tin – Stannate; (Pb) Lead – Plumbate;

(Fe) Iron – Ferrate;
(Cu) Copper – Cuprate;
(Ag) Silver – Argentate;
(Au) Gold – Aurate.

If the complex is cationic or neutral, then the name of the metal remains unchanged:
$[CrCl_2(H_2O)_4]^+$ – dichlorotetraaquachromium (III);
$[CoCl_3(NH_3)_3]$ – trichlorotriamminecobalt (III).

Note that the oxidation number of the central metal ion is named immediately after it in Roman numerals, enclosed in brackets.

2.4. *Coordinate Bonds. Shape of the Complex Ion. Isomers*

Ionic bonds are the electrostatic forces of attraction between oppositely charged ions; the ions are the result of electron transfer between atoms. (Fig. 2.2)

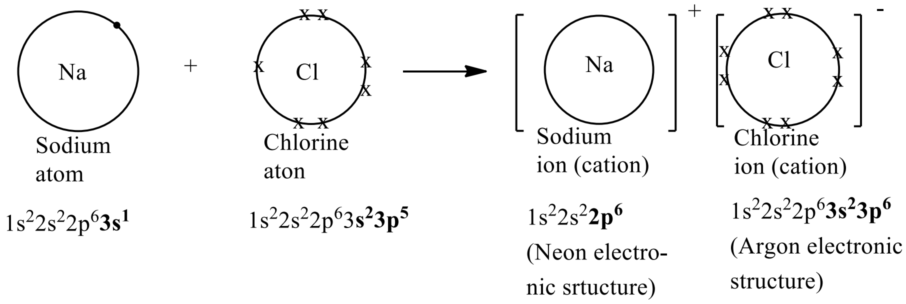


Figure 2.2 – Electron transfer during the reaction between sodium and chlorine

A **covalent bond** is a chemical bond that involves the sharing of electron pairs between two non-metal atoms.

The octet rule states that an atom tries to attain the octet configuration through the bond formation. (Fig. 2.3)

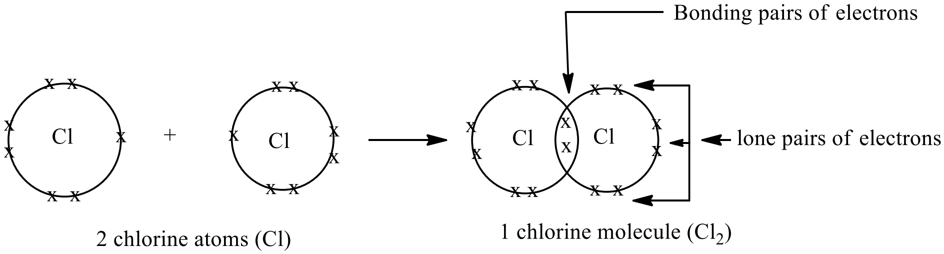


Figure 2.3 – A single covalent bond in a chlorine molecule

In the chlorine molecule, each chlorine atom achieves a stable [Ar] electronic configuration by sharing a pair of electrons. There are electron pairs in the outermost shell of an atom that is not shared or bonded to another atom and are known as the **lone pairs of electrons**.

A dative covalent bond (also known as a **coordinate bond**) is the type of covalent bonding in which the shared pair of electrons is supplied by only one of the bonded atoms.

The atom that supplies the shared pair of electrons is known as the electron donor, while another atom, involved in the dative covalent bond, is known as the electron acceptor. The donor must have an unshared electron pair (i.e., lone pair) in its outer shell, while the acceptor must have at least one empty orbital in its outer shell.

An ammonia molecule will combine with a hydrogen ion by forming a dative covalent bond, as shown below (Fig. 2.4):

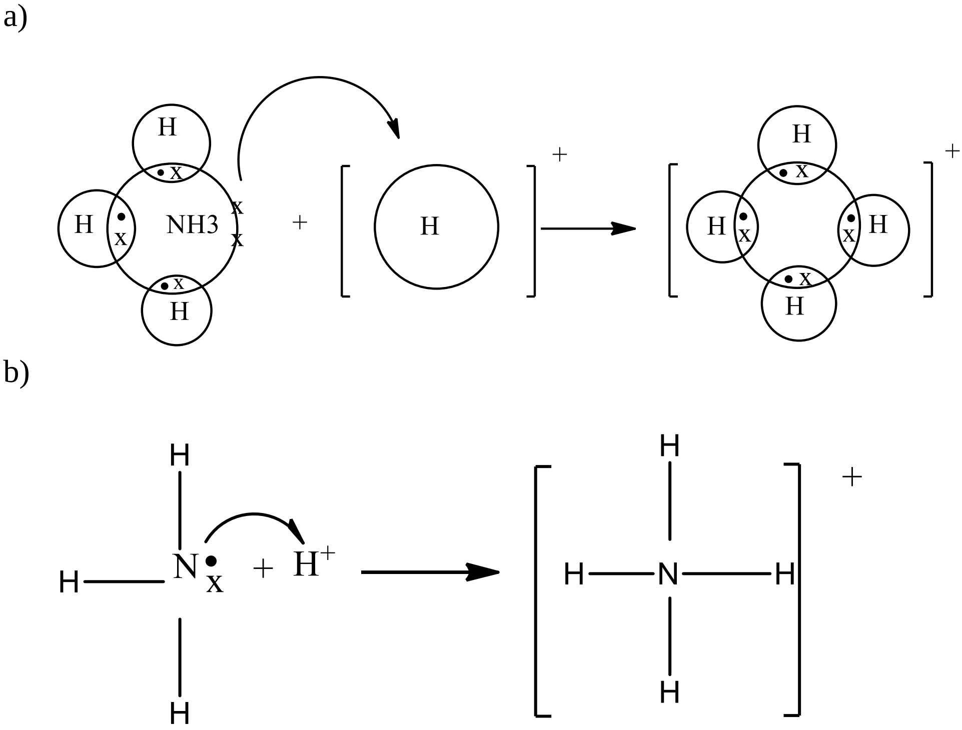


Figure 2.4 – Formation of the dative covalent bond in an NH_4^+ ion:
a) dot and cross diagram; b) single line representation

The central metal ion in the complex makes a number of empty orbitals available for the formation of coordinate bonds with suitable ligands. The number of empty orbitals that are made available for this purpose is equal to the coordination number of the central metal ion. For example, if the coordination number is 4, four empty orbitals are made available in the central metal ion:

$$\underset{acceptor}{Cu^{2+}} + \underset{\text{donor}}{4{:}Cl} \rightarrow [CuCl_4]^{2-}$$

Figure 2.5 shows the schematic view of coordination compound molecule $K_2[CuCl_4]$

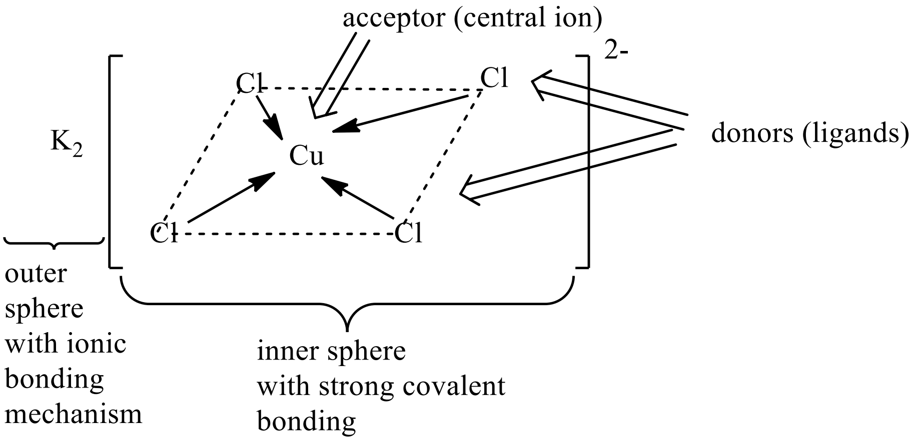
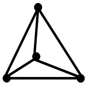
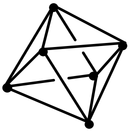


Figure 2.5 – A schematic view of coordination compound molecule $K_2[CuCl_4]$

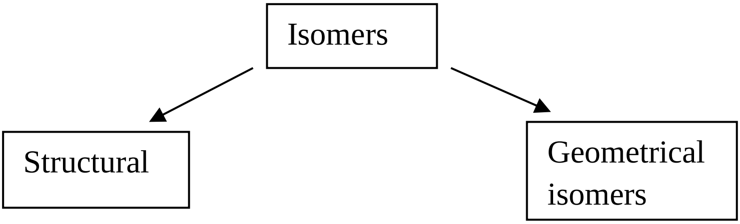
Central ions or atoms with different coordination numbers undergo different hybridizations, giving rise to a number of different empty hybrid orbitals with different shapes (Tab. 2.6).

Table 2.6 – Relationship between coordination numbers, hybridizations and shapes of complexes

Coordination number	Hybrid orbitals involved	Shape of resulting complex	Example
2	sp	linear 	
4	sp^3	tetrahedral 	$[Zn(NH_3)_4]^{2+}$ $[CoCl_4]^{2-}$
4	dsp^2	square planar 	$[Cu(NH_3)_4]^{2+}$ $[CuCl_4]^{2-}$
6	d^2sp^3 or sp^3d^2	octahedral 	$\boldsymbol{[Cr(NH_3)_6]^{3+}}$ $\boldsymbol{[Fe(CN)_6]^{3-}}$

Isomers are compounds, having the same molecular formula but different structural formulas.

There are two kinds of isomers – structural isomers and geometric isomers.



Structural isomers are isomers that has different ligands coordinated with the central metal ion.

For example, $[\boldsymbol{Co}(\boldsymbol{NH_3})_5\boldsymbol{Br}]^{2+}\boldsymbol{SO_4}$ and $[\boldsymbol{Co}(\boldsymbol{NH_3})_5\boldsymbol{SO_4}]^{+}\boldsymbol{Br}^{-}$ complexes are two structural isomers.

The compound $Cr(H_2O)_6Cl_3$ have four structural isomers:

$[Cr(H_2O)_6]Cl_3$ – violet,
$[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ – light green,
$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ – dark green,
$[Cr(H_2O)_3Cl_3] \cdot 3H_2O$ – brown.

Geometric isomers are isomers in which the composition of the first coordination sphere is the same, but the geometric arrangement of the ligands varies.

Geometric isomers are possible for both square planar (4-coordinated) and octahedral (6-coordinated) complexes only. For example, the complex $[Pt(NH_3)_2Cl_2]$ has two isomers differing in color, solubility, reactivity, and the way of preparation. In one of the isomers, the chlorine atoms are diagonally opposite (trans-isomer), and in the other one, they are adjacent to each other (cis-isomer).

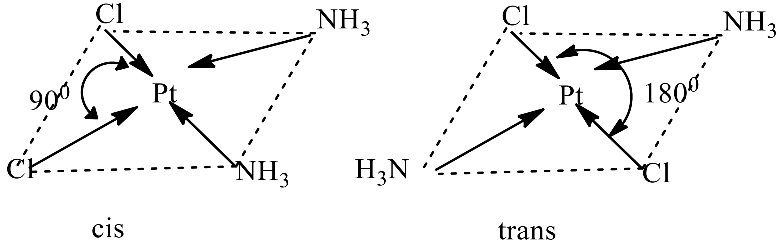


Figure 2.6 – A schematic view of cis- and trans- isomers $[Pt(NH_3)_2Cl_2]$

2.5. Dissociation of Coordination Compounds

The chemical bond between the inner and outer spheres is ionic, so firstly, compound will dissociate as follows:

$$[Cr(H_2O)_2(NH_3)_3Cl]Br_2 \rightarrow [Cr(H_2O)_2(NH_3)_3Cl]^{2+} + 2Br^{-}.$$

It is the first stage of dissociation. At the second stage, coordination compounds dissociate into ligands and central metal ion as follows:

$$[Cr(H_2O)_2(NH_3)_3Cl]^{2+} \rightarrow Cr^{3+} + 2H_2O + 3NH_3 + Cl^-.$$

Constant of instability (dissociation constant (Kd) of a complex ion:

$$Kd[Co^{+3}(NH_3)_4Cl]^{2+} = \frac{[Co^{+3}][NH_3]^4[Cl^-]}{[Co^{+3}(NH_3)_4Cl]^{2+}}.$$

2.6. Coordination Compounds in Medicine

Coordination compounds are present in minerals and living organisms. Many biologically important compounds are coordination compounds in which complicated organic species are bound to metal ions. The red color of blood is caused by the presence of hemoglobin – a coordination compound containing Fe(II). Chlorophyll, which is found in plants, is a coordination compound similar in structure to hemoglobin but containing Mg(II) instead of Fe(II). Iron is a part of the composition of myoglobin, oxidases, peroxidases and cytochromes. More than 60 biologically active substances contain zinc. Cobalt is in the composition of vitamin B_{12} (cyanocobalamin).

Formation and destruction of biological complexes constantly occur in the organism, and metal-ligand homeostasis is maintained on a certain level. Metal-ligand homeostasis can be disturbed due to deficiency or excess of biometal cations, entering of toxic metal cations, entering or formation of alien ligands. The toxicity of d-metals in many cases is explained by the stability of biological complexes, formed by them. Complexing agents are used for the removal of metal poisoning. Antidote therapy of poisonings caused by heavy metal cations is based on the formation of stable complexes (chelation) between these metals and special ligands.

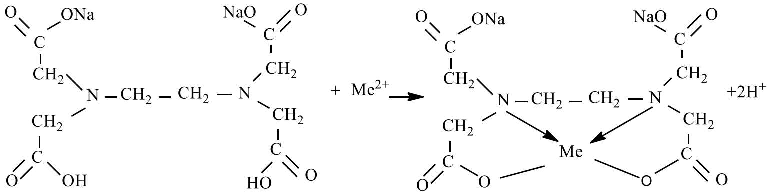
Dimercaprol is an effective antidote against organic arsenic like lewisite but can be used for poisoning due to antimony, gold, and mercury. Penicillamine is an effective antidote for the treatment of poisoning by copper, mercury, and lead. Trilon B (disodium salt of EDTA) is used for the treatment of hypercalcemia and poisoning by calcium compounds.

$CH_2(SH)-CH(SH)-CH_2(SH)$

$CH_3-C(CH_3)(SH)-CH(NH_2)-COOH$

2,3-dimercaptopropan-1-ol
(BAL, dimercaprol)

Penicillamine (dimethylcystein)



B Trilon

Figure 2.7 – Antidote interaction with metal ions

Examples of solving tasks:

Example 2.1. What is the charge on the complex ion in the following:

a) $[Co^{+3}Cl_6]^x$, b) $[Co^{+3}(NH_3)_4Cl_2]^x$, c) $[Cu^{+2}(H_2O)_4]^x$,

d) $[Co^{+3}(NH_3)_3Cl_3]^x$?

Solution:

The charge on the complex ion is always the sum of the charges on the ions or molecules that form the complex:

a) the charge of $[Co^{+3}Cl_6]^x$ is equal to the sum of charges of central ion $Co^{+3}$and six ligands of chloride Cl^- ions.
$[Co^{+3}Cl_6]^x$: charge (x) = +3 + 6·(-1) = -3. $[CoCl_6]^{3-}$;

b) the charge (x) = +3 + 4·(0) + 2·(-1) = +1, $[Co^{+3}(NH_3)_4^0Cl_2^-]^{1+}$;
c) the charge (x) = +2 + 4·(0) = +2, $[Cu^{+2}(H_2O)_4^0]^{+2}$;
d) the charge (x) = +3 + 3·(0) + 3·(-1) = 0, $[Co^{+3}(NH_3)_3^0Cl_3^-]^0$.

Knowing the charge of the complex ion, we can calculate the oxidation state of the central atom (ion), which will be used while writing the names of compounds.

Example 2.2. Calculate the oxidation state (o.s.) of the central ion in the following: a) $[Co(NH_3)_5(H_2O)]^{3+}$;
b) $[Co(H_2O)_4Cl_2]^0$; c) $[Cu^{+2}(CN)_4]^{2-}$.

Solution:

a) $[Co^x(NH_3)_5^0(H_2O)^0]^{3+}$ x + 5·(0) + 0 = +3; x = +3; o.s. of Co = +3;
b) $[Co^x(H_2O)_4^0Cl_2^-]^0$ x + 4·(0) + 2·(-1) = 0; x = +2; o.s. of Co = +2;
c) $[Cu^{+2}(CN)_4^-]^{2-}$ x + 4·(-1) = -2; x = +2; o.s. of Cu = +2.

Example 2.3. Name the following compounds:
a) $K_3[Fe(CN)_6]$; b) $[Cu(NH_3)_4]Cl_2$; (c) $[PtCl_4(NH_3)_2]$.

Solution:

: a) potassium hexacyanoferrate (II); b) tetraamminecopper (II) chloride; c) diamminetetrachloroplatium (III).

Example 2.4. Write the formula of the following compounds: a) pentaammineaquacobalt (III) chloride; b) ammonium hexachloro titanate (IV); c) dihydroxotetraaquairon (II).

Solution:

a) $[Co^{+3}(H_2O)^0(NH_3)_5^0]^{3+}Cl_3^-$; b) $(NH_4)_2[Ti^{+4}Cl_6^-]^{2-}$;
c) $[Fe^{2+}(H_2O)_4(OH)_2^-]$.

Theoretical questions

1. What are the coordination compounds?
2. Give the definitions of ligand, central ion, coordination number, inner sphere, outer sphere, complexion.
3. Give the classification of complexes.
4. Give examples of biologically active complexes.

Exercises for practice

1. What is the charge on the complex ion in the following:

a) $[Ni^{+2}(CN)_6]^x$;
b) $[Co^{+3}Cl_6]^x$;
c) $[Ti^{+3}(H_2O)_6]^x$;
d) $[Fe^{+2}(H_2O)_6]^x$;
e) $[Pd^{+2}Br_4]^x$.

2. Calculated the oxidation state of the central ion in the following:
   a) $[Cu(NH_3)_4]SO_4$;
   b) $Na_2[Cu(OH)_4]$;
   c) $[Co(NH_3)_4Cl_2]NO_3$;
   d) $K_2[PbCl_4]$;
   e) $Na_2[PtBr_6]$.
3. Determine the type of the following compounds:
   a) $K_2[Cu(OH)_4]$;
   b) $[Cu(NH_3)_4]SO_4$;
   c) $Na_2[PbBr_4]$;
   d) $[Fe(H_2O)_6]Cl_2$;
   e) $K[Au(CN)_2]$.
4. Name the following compounds:
   a) $K_4[Ni(CN)_6]$;
   b) $[Cu(NH_3)_4]SO_4$;
   c) $[Pt(NH_3)_2Cl_4]$;
   d) $[Co(NH_3)_4Cl_2]NO_3$;
   e) $[Fe(H_2O)_6]Cl_2$;
   f) $K_2[PtCl_6]$;
   g) $Na[Au(CN)_2]$.
5. Write the formulas of the following compounds:
   a) aquapentaammineferrum (III) bromide;
   b) ammonium hexabromotitanate (IV);
   c) dihydroxotetraaquacobalt (II).

Questions for self-testing

For each of questions 1 through 20, choose one correct, lettered answer.

1. What is the oxidation state of the central metal ion in the compound: $[Fe(H_2O)_6]Cl_2$?
   a) +2 b) +3 c) +4 d) 0
2. What is the oxidation state of the central metal ion in the compound: $K_2[PtCl_6]$?
   a) +2 b) +4 c) +7 d) 0
3. What is the oxidation state of the central metal ion in the compound: $[Cu(NH_3)_4]Cl_2$?
   a) +2 b) +4 c) +9 d) 0

4. What is the oxidation state of the central metal ion in the compound: $Na_2[PdBr_4]$?
a) +2 b) +5 c) 0 d) +6
5. What is the oxidation state of the central metal ion in the compound: $K[Au(CN)_2]$?
a) +2 b) +3 c) 0 d) +5
6. What is the central metal ion in the compound: $[Fe(H_2O)_6]Cl_2$?
a) Fe b) H_2O c) Cl_2 d) O
7. What is the central metal ion in the compound: $K_2[PtCl_6]$?
a) K b) Pt c) Cl d) Na
8. What is the central metal ion in the compound: $[Cu(NH_3)_4]Cl_2$?
a) Cu b) NH_3 c) Cl d) N
9. What is the central metal ion in the compound: $Na_3[CoBr_6]$?
a) Na b) Co c) Br d) K
10. What is the central metal ion in the compound: $K[Au(CN)_2]$?
a) K b) Au c) CN d) C
11. What is the name of the compound: $[Fe(H_2O)_6]Cl_2$?
a) hexaaquaferrum (II) chloride
b) chloropentaamminecobalt (III) chloride
c) ammonium hexachlorotitanate (IV)
d) tribromotriaquacobalt (III)
12. What is the name of the compound: $K_2[PtCl_6]$?
a) hexaamineferrum (II) chloride
b) potassium hexachloroplatinate (IV)
c) tricholorotriaquacobalt (III) bromide
d) hexaqauaferrum (III) hydroxide
13. What is the name of the compound: $[Cu(NH_3)_4]Cl_2$?
a) chloropentaamminecobalt (III) chloride
b) hexaaquaferrum (II) hydroxide
c) tetraamminecopper (II) chloride
d) ammonium hexachlorotitanate (IV)
14. What is the name of the compound: $Na_3[CoBr_6]$?
a) sodium hexabromocobaltate (III)
b) ammonium hexachlorotitanate (IV)

c) chloropentaamminecobalt (III) chloride
d) potassium hexachloroplatinate (IV)

15. What is the name of the compound: $K[Au(CN)_2]$?
a) potassium dicyanoaurate (III)
b) sodium hexabromocobaltate (III)
c) chloropantaamminecobalt (III) chloride
d) potassium hexachloroplatinate (IV)

16. What is the formula of the compound potassium tetracyanonickelate (II)?
a) $Cu_2[Fe(CN)_6]$
b) $K_2[Ni(CN)_4]$
c) $Na_2[PtCl_6]$
d) $[Fe(H_2O)_4Cl_2]Cl$

17. What is the formula of the compound sodium hexachlorocobaltate (III)?
a) $[Fe(H_2O)_6]Cl$
b) $K_2[Ni(CN)_4]$
c) $Na_3[CoCl_6]$
d) $[Cu(NH_3)_4]Cl_2$

18. What is the formula of the compound tetraamminecopper (II) chloride?
a) $[Fe(NH_3)_6]Br_2$
b) $[Cu(NH_3)_4]Cl_2$
c) $Na_2[PtCl_6]$
d) $K[Ag(CN)_2]$

19. What is the formula of the compound potassium hexachloroplatinate (IV)?
a) $Na_2[PtCl_6]$
b) $K_2[PtCl_6]$
c) $[Co(NH_3)_3Cl_3]$
d) $K_3[CoBr_6]$

20. What is the formula of the compound hexaaquaferrum (II) bromide?
a) $K_2[PtCl_6]$
b) $[Co(NH_3)_3Br_3]$
c) $[Fe(H_2O)_6]Br_2$
d) $[Cu(NH_3)_4]Br_2$

21. Write dissociation of constant of $[Cu(NH_3)_4]Cl_2$ by the first and second stages. Write the equation of dissociation constant (Kd) for complex ion.

22. Write dissociation of constant of $K[Au(CN)_2]$ by the first and second stages. Write the equation of dissociation constant (Kd) for complex ions.

23. Write dissociation of constant of $Na_3[CoBr_6]$ by the first and second stages. Write the equation of dissociation constant (Kd) for complex ion.

24. Write dissociation constant of $[Fe(H_2O)_6]Cl_2$ by the first and second stages. Write the equation of dissociation constant (Kd) for complex ion.

CHAPTER 3

CHEMICAL THERMODYNAMICS

Practical skills

After studying the subject, you will be able:

1. To know terms: phase, system, thermodynamic function, enthalpy, entropy, Gibbs free energy, etc.
2. To calculate enthalpy, entropy, Gibbs free energy of the chemical reaction.
3. To predict if the process is spontaneous or not.
4. To determine the influence of criteria (P, T, concentration) on process direction.
7. To know the application of the laws of thermodynamics to living systems.

3.1 Thermodynamics Terminology

Thermodynamics is the study of energy transfer and the effects of energy changes.

Thermochemistry is the study of the heat change of the chemical reaction.

Universe: In the universe, there is no change in the amount of energy.

The Universe = the system + the surroundings.

Surroundings represent that part of the universe with which a system interacts.

The system is any totality of bodies separated from the surroundings by a boundary (real or imaginary) inside which matter and/or energy exchange is possible.

There are several types of system:

Open system: can exchange both matter and energy with the surroundings. A living organism is an open system.

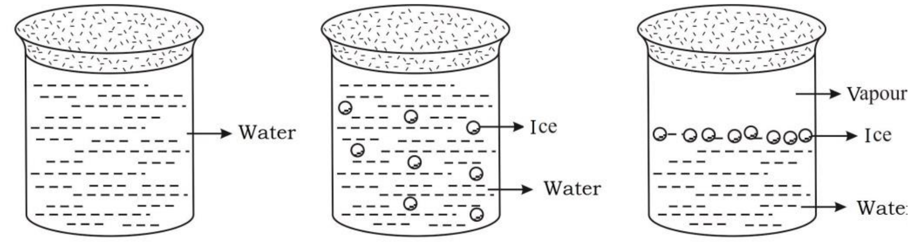
Closed system: can exchange energy but not matter with the surroundings.

An isolated system is a system that exchanges neither matter nor energy with the surroundings.

The homogeneous system is a system that consists of one phase only.

The heterogeneous system is a system with more than one phase.

Phase refers to any part of a system that is physically separated from other parts of the system by a distinct boundary. A phase can be a solid, liquid, vapor (gas) or aqueous solution, which is uniform in both the chemical constitution and physical state (Fig. 3.1).



One-phase system of water

Two-phase system of water

Three-phase system of water

Figure 3.1 – The one-phase, two-phase and three-phase system of water

Thermodynamics distinguishes isochoric, isobaric and isothermal processes.

An isochoric process is a thermodynamic process that takes place at constant volume (V=const).

An isobaric process is a thermodynamic process that takes place at constant pressure (P=const).

An isothermal process is a process that takes place at constant temperature (T=const).

There are exothermic and endothermic processes.

An exothermic process (reaction) is a thermodynamic process that evolves heat to the surroundings.

An endothermic process (reaction) is a process that absorbs heat from the surroundings.
The state of the system is characterized by thermodynamic parameters and state functions.

Thermodynamic parameters are pressure P, temperature T, volume V, and concentration.

A state function is a property that depends only on the state or present condition of the system butnot on how this state is attained.
Some common state functions are internal energy (U), enthalpy (H), entropy (S), and free energy (G).

Examples of solving tasks:

Example 3.1. For each of the following systems, determine whether it is open, closed, or isolated:

– an ice cube and water in a perfect, stoppered thermos;
– the same amount of ice and water in an open flask;
– water in a sealed glass tube.

Solution**:**

1. The ice cube and water form the system and are contained in a stoppered, perfectly insulated thermos. This is an isolated system, that exchanges neither matter nor energy with the surroundings.
2. If ice and water are in an open flask, water may leak out. The flask may be heated or cooled, and the contents will have energy transferred to them or away from them. Because energy and matter may be exchanged with the surrounding, the system is considered an open system.
3. In a sealed glass tube, the matter cannot leave or enter, but energy may be transferred to the system – it is a closed system.

3.2. The Laws of Thermodynamics

The first law of thermodynamics. Energy is conserved; it can be neither created nor destroyed.

The second law of thermodynamics. In an isolated system, natural processes are spontaneous when they lead to an increase in disorder or entropy.

The third law of thermodynamics. The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

3.3. Internal Energy and Enthalpy

Internal energy (U) is the sum of the kinetic and potential energies of the particles that form the system.

A change in the internal energy (ΔU) occurs when a system exchanges energy with its surroundings in the form of heat and/or work. This can be represented by the symbols:

$$\underset{\substack{\text{change}\\ \text{in internal}\\ \text{energy}}}{\Delta U} = \underset{\substack{\text{heat}\\ \text{absorbed by}\\ \text{the system}}}{Q} + \underset{\substack{\text{work done}\\ \text{by the system}}}{W}.$$

If the system is gaseous, work done is given by PΔV, where P – pressure and ΔV – change in volume. The heat absorbed by the system (Q) at constant pressure is equal to the change in **enthalpy** (ΔH).

$$\Delta H = \Delta U + P\Delta V.$$

The above is a mathematical expression of the first law of thermodynamics.

Enthalpy (H) is a term that describes the heat content of a system.

ΔH = heat absorbed by the system at constant pressure.

For a reaction that evolves heat (i.e., heat flows from the system to the surroundings), the sign of ΔH is negative, the sign of Q is positive; Q = – ΔH (exothermic reaction).

For a reaction that absorbs heat (i.e., heat flows from the surroundings to the system), the sign of ΔH is positive, the sign of Q is negative; – Q = ΔH (endothermic reaction).

For example, the burning of carbon to form carbon (IV) oxide evolves heat, thus it is an exothermic reaction and it is represented by the equation:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H^{\circ} = -363.5\ \text{kJ}.$$

In a similar way, endothermic reactions are as follows:

$$C_{(s)} + 2S_{(s)} \rightarrow CS_{2(l)};\ \Delta H^{\circ} = +117\ \text{kJ}.$$

$$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)};\ \Delta H^{\circ} = +90\ \text{kJ}.$$

Standard enthalpy change of formation of a substance is symbolized as (ΔH_f°) and is the enthalpy change when one mole of the compound is formed from its elements under standard conditions. ΔH_f° is measured in kJmol^{-1}.

Standard state conditions are:

- all substances are in their standard states;
- the pressure is 101.3 kPa (101325 Pa = 1 atm = 760 mm Hg);
- the temperature is 298 K (K = ˚C +273).

For example, the standard enthalpy change of formation of sodium chloride is represented as follows:

$$Na_{(s)} + \frac{1}{2}Cl_{2(g)} \rightarrow \underset{\text{1 mole}}{NaCl_{(s)}};\ \Delta H_f^{\circ} = -411\ \text{kJmol}^{-1},$$

$$2Na_{(s)} + Cl_{2(g)} \rightarrow \underset{\text{2 mole}}{2NaCl_{(s)}};\ \Delta H^{\circ} = -822\ \text{kJ}.$$

Table 3.1 – Thermodynamic properties of substances at T = 298.15 K and P = 1 atm.

Substance	**Enthalpy ΔH^0, kJ/mol**	**Entropy ΔS^0, $J/mol \cdot K$**	**Gibbs' energy ΔG^0, kJ/mol**
$HCl_{(g)}$	92.2	186.7	-95.3
$NaCl_{(s)}$	411.0	72.4	-384.1
$O_{2(g)}$	0	205.0	0
$O_{3(g)}$	-142.0	238.8	162.8
$H_2O_{(g)}$	-241.8	188.7	-226.6
$H_2O_{(l)}$	-285.8	69.9	-237.2

$SO_{2(g)}$	296.9	248.5	-300.2
$H_2S_{(g)}$	20.4	205.6	-33.5
$NH_{3(g)}$	-46.2	192.5	-16.5
$NH_{3(l)}$	-80.8	192.6	
$HCN_{(g)}$	132.0	201.7	121.6
$H_3PO_{4(s)}$	-1281.1	110. 5	-1119.2
$C_{(graphite)}$	0	5.7	0
$C_{(diamond)}$	1.8	2.4	2.8
$CO_{(g)}$	-110.5	197.9	-137.1
$CO_{2(g)}$	-393.5	213.6	-393.4
$H_{2(g)}$	0	130.6	0
Methane$_{(g)}$	-74.8	186.2	-50.8
Ethylene$_{(g)}$	52.3	219.4	68.1
Acetylene$_{(g)}$	226.7	200.8	20.2
Benzene$_{(l)}$	49.0	173.2	-124.4
Ethanol$_{(l)}$	-277.8	164.0	-174.1
Glycerin$_{(l)}$	-670.7	20.5	-477.1
Acetaldehyde	-166.0	264.2	-132.9
Acetone$_{(l)}$	-246.8	198.7	-155.4
Acetic acid$_{(l)}$	-487.3	159.8	-398.4
Butyric acid$_{(l)}$	-524.3	255.0	-376.7
Fumaric acid$_{(s)}$	-811.1	166.1	-653.6
Lactic acid$_{(l)}$	-694.0	221.7	
Pyruvic acid$_{(l)}$	-607.5		
Glycine$_{(s)}$	-524.7	109.2	-366.8
Urea$_{(s)}$	-333.2	104.6	-197.1
Urea$_{(l)}$	-319.2	173.8	
Glucose$_{(s)}$	-1274.4		-919.5
Sucrose$_{(s)}$	-2222.0	360.3	-1544.7

ΔH_f° (NaCl) is -411 kJmol^{-1} but not -822 kJ as the definition specifies the formation of 1 mole of the compound.

ΔH° - enthalpy is the heat effect of the reaction.

Table 3.1 lists the standard enthalpy changes of formation ($\mathit{\Delta} H_f^\circ$) of some common substances. It should be noted that the absolute enthalpy of a substance cannot be determined; only the difference in enthalpies between substances can be measured experimentally.

The standard enthalpy change of formation of an element is equal to zero.

$$\mathit{\Delta} H_f^\circ(Na_{(s)}) = 0 \text{ kJmol}^{-1}; \mathit{\Delta} H_f^\circ(Cl_{2(g)}) = 0 \text{ kJmol}^{-1}$$

Standard enthalpy change of combustion ($\Delta \mathrm{H}_\mathrm{c}^\circ$) is the enthalpy change when one mole of the substance is burnt completely in oxygen under standard conditions.

For example,

$$\underset{\text{1 mole}}{C_2H_5OH_{(l)}} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}; \mathit{\Delta} H_c^\circ = -1371 \text{ kJ/mol.}$$

Thermochemistry allows determining standard enthalpy changes of the various reactions, enthalpy of dissolution, melting, neutralization, ionization, atomization, etc.

3.4. Thermochemical Equations. Hess's Law

Thermochemical equations are equations of the reactions in which physical states of substances and the values of any thermodynamic function of the state are indicated. The reaction enthalpy, in this case, is called the **heat effect** of the reaction.

For example,

$$N_{2(g)} + 2O_{2(g)} \rightarrow \underset{\text{2 mole}}{2NO_{2(g)}}; \mathit{\Delta} H^\circ = +67.8 \text{ kJ.}$$

Hess's law: The heat effect of the chemical reaction is independent of the route of the reaction and depends only on the initial and final states of the system.

For example, if there are two routes for reactants A and B to form products C and D, the heat effect of the reaction by route 1 is the same as the heat effect of the reaction by route 2 (Fig. 3.2).

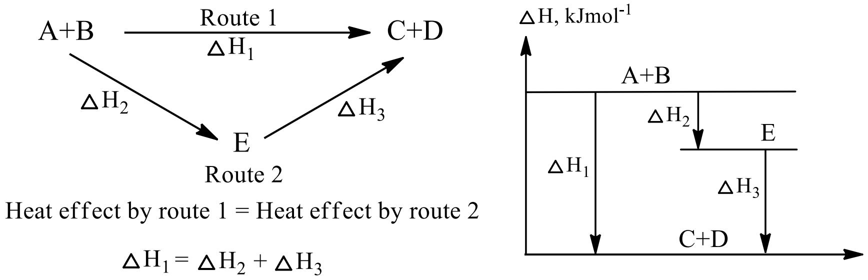
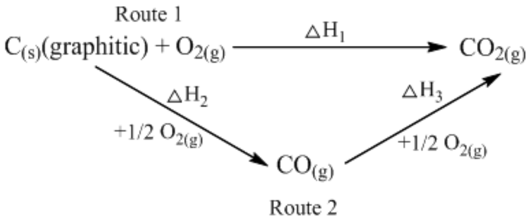


Figure 3.2 – A diagram showing different routes of a chemical reaction

Consider the enthalpy change of $CO_{(g)}$ formation.

It is difficult to measure the heat evolved from the reaction between graphite and O_2 to give CO directly, because it is impossible to prevent the combustion of carbon to form CO_2. However, making use of Hess's law, $\Delta H_f^{\circ}(CO_{2(g)})$ can be determined, as ΔH_1 and ΔH_2 can be obtained directly in a laboratory.



$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H_1$$
$$\Delta H_1 = \Delta H_2 + \Delta H_3$$
$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)};\ \Delta H_2$$
$$\Delta H_2 = \Delta H_1 - \Delta H_3$$
$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_2;\ \Delta H_3$$
$$\Delta H_3 = \Delta H_1 - \Delta H_2$$

According to Hess's law, the enthalpy change of the reaction from $C_{(s)}$ and $O_{2(g)}$ to $CO_{2(g)}$ is a constant, regardless of the route the reaction takes. Hence, enthalpy change in route 1 is the same as the enthalpy change in route 2. i.e.

$$\Delta H_3 + \Delta H_2 = \Delta H_1,$$
$$\Delta H_2 = \Delta H_1 - \Delta H_3,$$

ΔH_1 is the standard enthalpy change of $CO_{2(g)}$ formation.

$$C_{(s)}(graphite) + O_{2(g)} \rightarrow CO_{2(g)};\ \Delta H_1 = -393.5\ \text{kJmol}^{-1}$$

ΔH_3 is the standard enthalpy change of $CO_{(g)}$ combustion.

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_2;\ \Delta H_3 = -283.0\ \text{kJmol}^{-1}$$

ΔH_2 is the standard enthalpy change of $CO_{(g)}$ formation.

$$\Delta H_2 = \Delta H_1 - \Delta H_3 = -393.5 - (-283.0) = -110.5\ \text{kJmol}^{-1}.$$

The standard enthalpy change of carbon monoxide CO formation is $-110.5\ \text{kJmol}^{-1}$.

After calculation, the enthalpy level diagram for the formation of CO and CO_2 can be drawn (Fig. 3.3).

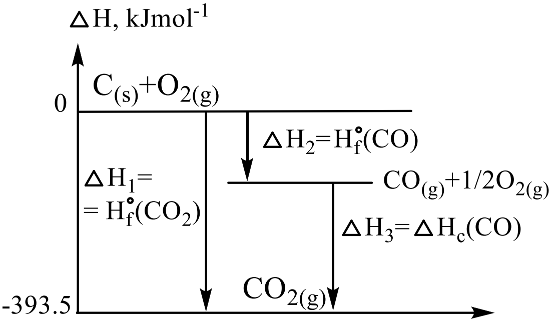


Figure 3.3 – Enthalpy level diagram for determining $\Delta H_f^\circ(CO_{(g)})$

The consequences of Hess's law are:

1. Heat effect of the forward reaction equals the heat effect of the backward reaction taken with the opposite sign: $\Delta H_{forward} = -\Delta H_{backward}$.

For example, $Ca_{(s)} + \frac{1}{2}O_{2(g)} \rightleftarrows CaO_{(s)};\ \Delta H_r^\circ = -635\ \text{kJmol}^{-1}$

$$CaO_{(s)} \rightleftarrows Ca_{(s)} + \frac{1}{2}O_{2(g)};\ \Delta H_r^\circ = +635\ \text{kJmol}^{-1}$$

2. Heat effect, also called enthalpy change of the reaction (ΔH_r°), equals the sum of the enthalpies of the formation of the

products minus the sum of the enthalpies of the reactants formation with the account of stoichiometric coefficients:

$$\Delta H_r^\circ = \sum \Delta H_{f(products)}^\circ - \sum \Delta H_{f(\text{reactants})}^\circ.$$

3. Heat effect enthalpy change of the combustion reaction (ΔH_c°) equals the sum of the heats of the reactant combustion minus the sum of the heats of the combustion of the products:

$$\Delta H_c^\circ = \sum \Delta H_{c(\text{reactants})}^\circ - \sum \Delta H_{c(products)}^\circ.$$

For the reaction $aA + bB = cC + dD$ the heat effects equal:

$$\Delta H_r^\circ = (c\Delta H_f^\circ C + d\Delta H_f^\circ D) - (a\Delta H_f^\circ A + b\Delta H_f^\circ B),$$

$$\Delta H_c^\circ = (a\Delta H_f^\circ A + b\Delta H_f^\circ B) - (c\Delta H_f^\circ C + d\Delta H_f^\circ D).$$

For example, for the reaction $CO_{(g)} + 2H_{2(g)} = CH_3OH_{(g)}$,

$$\Delta H_r^\circ = \Delta H_f^\circ CH_3OH_{(g)} - (\Delta H_f^\circ CO_{(g)} + 2\Delta H_f^\circ H_{2_{(g)}}),$$

$$\Delta H_c^\circ = (\Delta H_c^\circ CO_{(g)} + 2\Delta H_c^\circ H_{2_{(g)}}) - \Delta H_c^\circ CH_3OH_{(g)}.$$

Examples of solving tasks:

Example 3.2. Given the following information, find the heat effect of the reaction (ΔH_r°) and heat effect of the combustion reaction (ΔH_c°) for the reaction

$$CO_{(g)} + 2H_{2(g)} = CH_3OH_{(g)}.$$

	$CO_{(g)}$	$H_{2(g)}$	$CH_3OH_{(g)}$
ΔH_f°, kJmol^{-1}	-110.5	0	-237
ΔH_c°, kJmol^{-1}	-238.0	-285.8	-715.0

Solution:

Use the consequences of Hess's law

$$\Delta H_r^\circ = \sum \Delta H_{f(products)}^\circ - \sum \Delta H_{f(\text{reactants})}^\circ.$$

ΔH_r° = -237-(-110.5+2·0) = -237+110.5 = -126.5 kJ.

$$\Delta H_c^\circ = \sum \Delta H_{c(\text{reactants})}^\circ - \sum \Delta H_{c(products)}^\circ.$$

ΔH°_{c} = (-283.0+2(-285.8))-(-715) = -283.0-571.6+715 = -854.6+715 = -139.6 kJ.

3.5. Spontaneity and Disorder. Entropy

A Spontaneous change is a change that has a natural tendency to occur causes a system to move from a less stable state to a more stable state.

For example, energy always flows from a hot object to a cooler one. The reverse never occurs spontaneously (see the second law of thermodynamics). This concept is illustrated in Figure 3.4.

Figure 3.4 – Heat energy always flows spontaneously from hot to cold and never vice versa.

Another way to look at the second law is in terms of disorder. The quantitative measure of the disorder of a system is entropy, which is symbolized by S (Fig. 3.5).

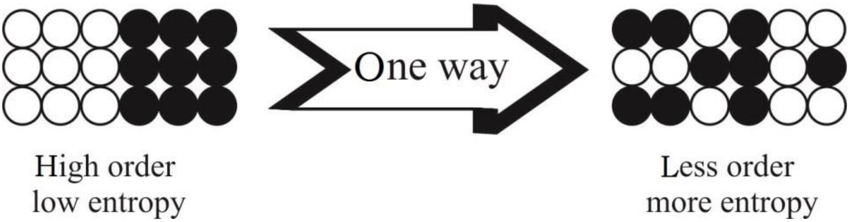


Figure 3.5 – The more mixed the system, the higher its entropy

Entropy (S) is a function of the state, and the changes depend only on the initial and final state of the system. S is measured in $Jmol^{-1}K^{-1}$.

There are two definitions of entropy: one is based on statistics and another – on heat transfer.

The first definition is given by the Boltzmann equation, which describes the relationship between entropy and the amount of disorder in a system:

$$S = K \ln W,$$

where K is Boltzmann's constant ($K = 1.3807 \times 10^{23} J \cdot K^{-1}$), W is a thermodynamic probability, i.e., the number of equally probably microscopic states by means of which the given macroscopic state of a system can be achieved.

It follows from Boltzmann's law that the entropy of a perfect crystal at absolute zero is equal to zero (the third law of thermodynamics). For it $W = 1$, $S = K \ln 1 = 0$. This is the most ordered system. In any other system, the value of W is very large, and S>0. The greater disorder of the system, the greater its entropy.

The other definition of the entropy change is related to the heat absorbed by the equation:

$$\Delta S = \frac{Q}{T}; \text{ units: } J \cdot K^{-1},$$

where Q is the amount of heat absorbed by the system in an isothermal reversible process, and T is the absolute temperature (in Kelvin).

The product TΔS is called «unfree energy».

The entropy depends on:

- phase $S_{(g)} > S_{(L)} > S_{(s)}$ (Figure 3.6);
- temperature (entropy increases with increasing temperature);
- particles mass (the greater the mass, the greater S);
- degree of dispersion (the greater the dispersion, the greater S);
- bond type ($S_{cobalent\text{ b.}} < S_{metalic\text{ b.}}$);
- pressure (entropy decreases with increasing pressure).

S also changes when chemical processes occur. These changes are especially great in reactions leading to a change in the number of molecules of gases: S increases with increasing the number of gas molecules.

In any spontaneous process, the entropy of the universe increases: $\Delta S_{universe} = (\Delta S_{system} + \Delta S_{surroudings})$ >0 (this statement is the second law of thermodynamics).

The total change of entropy of the human body always is positive.

If the entropy change of the universe is less than zero ($\Delta S_{universe}$<0), the process is not spontaneous, but the reverse process is spontaneous.

If the entropy change of the universe is zero ($\Delta S_{universe}$=0), the process described is at equilibrium.

Entropy changes in chemical reactions are calculated by the same method as the enthalpy change, because entropy is a state function:

$$\Delta S_r = \sum S^0_{f(products)} - \sum S^0_{f(reac\,tan\,ts)}.$$

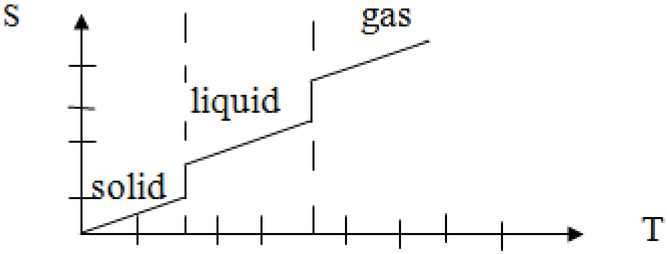


Figure 3.6 – Entropy of substance as a function of temperature

Example 3.3. Given the following information, find the entropy changes in the reaction:

$$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}.$$

Substance	$C_{(s)}$	$H_{2(g)}$	$CH_{4(g)}$
S°, $J \cdot mol^{-1} \cdot K^{-1}$	5.74	130.574	186.16

Solution:

$$\Delta S_r = \sum S^0_{f(products)} - \sum S^0_{f(\text{reactants})},$$

$\Delta S_r = S^\circ(CH_4) - (S^\circ(C) + 2S^\circ(H_2))$,
$\Delta S_r = 186.16-(5.74+2\cdot 130.574) = -80.73\, J \cdot K^{-1}$.

$\Delta S_r < 0$. The entropy change for this process is negative, showing that the entropy of the system decreases as reactants are converted to products.

Example 3.4. Decide which each of the following processes involves an increase or decrease in entropy:

(a) $2NH_4NO_{3(s)} \rightarrow 2N_{2(g)} + 4H_2O_{(g)} + O_{2(g)}$;
(b) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$.

Solution:

(a) entropy increases. A disorder of the system increases because the number of particles increases as 2 moles of solid reactant yield 5 moles of a gas product;

(b) three moles of gaseous reactants produce 2 moles of gaseous product. The number of particles in the system decreases, so the disorder decreases. Entropy decreases.

3.6. Gibbs Free Energy. Process Direction Criteria

Gibbs energy G (or free energy, isobaric potential, isobaric and isothermal potential) was introduced for isothermal reactions proceeding at a constant pressure.

The free energy change of a reaction is a **measure** of the **spontaneity** of the reaction. The more negative the free energy change, the more spontaneous the reaction.

The free energy is related to the enthalpy, entropy, and temperature by the equation

$$G = H - TS.$$

Absolute values of free energy are not determined. Instead, the free energy change, ΔG, is used:

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

The Gibbs free energy is a function of the state. It is measured in $kJ \cdot mol^{-1}$.

The sign of this function change in a reaction can be a criterion of the possibility of the reaction to proceed spontaneously.

$\Delta G<0$ – the process is spontaneous;

$\Delta G>0$ – the process is not spontaneous. The reverse process will be spontaneous;

$\Delta G=0$ – the process is at equilibrium.

The following table summarizes how the ΔG is affected by temperature for the different possibilities of the signs of ΔH and ΔS (Tab. 3.2).

Table 3.2 – Different possibilities of the signs

Sign of			**Conclusion**	**Example**
ΔH°	**ΔS°**	**ΔG°**		
+	–	+	The process is not spontaneous	photosynthesis
+	+	+	The process is not spontaneous at low temperature	melting (s – L); evaporation (L – g)
–	–	–	The process is spontaneous at low temperature	Condensation
–	+	–	The process is spontaneous	combustion of organic compounds
–	–	+	The process is not spontaneous at high temperature	$2H \rightarrow H_2$
+	+	–	The process is spontaneous at high temperature	$Br_2 \rightarrow 2Br$

The free energy change in chemical reactions can be calculated either by using standard free energy of formation (ΔG_f°), or ΔH and ΔS:

$$\Delta G = \sum \Delta G^0_{f(products)} - \sum \Delta G^0_{f(\text{reactants})},$$

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

The standard free energy of formation (ΔG_f°) of a substance is the free energy change when one mole of the compound is formed from the elements under standard conditions. Table 3.1 lists the standard free energy of formation of some common substances.

Example 3.5. Calculate the free energy for the reaction: $CH_2CH_{2(g)} + HCl_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_2CHCl_{(g)} + H_2O_{(g)}$ under standard conditions.

Thermodynamic data for the reactants and products are summarized in the following table.

Substance	$\Delta G_f^{\circ}(KJ \cdot mol^{-1})$	$\Delta H_f^{\circ}(KJ \cdot mol^{-1})$	$S^{\circ}(J \cdot mol^{-1} \cdot K^{-1})$
$CH_2CH_{2(g)}$	81.3	36.36	122.17
$HCl_{(g)}$	-95.3	-92.31	186.80
$O_{2(g)}$	0	0	205.03
$CH_2CHCl_{(g)}$	51.9	35.56	263.88
$H_2O_{(g)}$	-241.8	-228.591	188.71

Solution: The ΔG_r will be calculated by two methods.

1. Using standard free energies of formation: this method is faster if you need ΔG_r at 298 K.

$$\Delta G = \sum \Delta G^0_{f(products)} - \sum \Delta G^0_{f(\text{reactants})}$$

$$\Delta G^\circ = (\Delta G_f^\circ(H_2O) + \Delta G_f^\circ(CH_2CHCl)) - (\Delta G_f^\circ(CH_2CH_2) + \Delta G_f^\circ(HCl) + \frac{1}{2}\Delta G_f^\circ(O_2)) =$$

$= (-241.8 + 51.9) - (81.3 + (-95.3) + 1/2\cdot 0) = -162.7$ kJ.

2. Using ΔH_r and ΔS_r is necessary for estimating ΔG_r at a temperature other than 298 K.

Calculate ΔH_r and ΔS_r

$$\Delta H_r = \sum \Delta H^0_{f(products)} - \sum \Delta H^0_{f(\text{reactants})}.$$

$\Delta H_r = (-228.59 + 35.56) - (36.36 + (-92.31) + 1/2\cdot 0) = -150.3$ kJ.

$$\Delta S_r = \sum \Delta S^\circ_{(products)} - \sum \Delta S^\circ_{(\text{reactants})}.$$

$\Delta S_r = (188.71 + 263.88) - (122.17 + 186.8 + 1/2\cdot 205.03) = 41.1\ J\cdot K^{-1} = 41.1\cdot 10^{-3} kJ\cdot k^{-1}$

$$\Delta G_r = \Delta H_r - T\Delta S_r.$$

At standard temperature (298 K)

$$\Delta G_r = -150.3 - 298\cdot 41.1\cdot 10^{-3} = -162.7 \text{ kJ.}$$

Example 3.6. The equation of reaction for reforming methane is $CH_{4(g)} + H_2O_{(g)}$ ® $CO_{(g)} + 3H_{2(g)}$.

1. Calculate the free energy change for this reaction at standard conditions.
2. Estimate the temperature at which the process becomes spontaneous.

Substance	**$CH_{4(g)}$**	**$H_2O_{(g)}$**	**$CO_{(g)}$**	**$H_{2(g)}$**
$\Delta H_f^\circ(KJ\cdot mol^{-1})$	-75	-241.8	-110.5	0
$S^\circ(J\cdot mol^{-1}\cdot K^{-1})$	186	188.7	197.9	131

Solution:

1. ΔH_r and ΔS_r is calculated by methods already described above using the values of ΔH_f° and ΔS° listed in the table.

$$\Delta H_r = (\Delta H_f^\circ(CO) + 3\Delta H_f^\circ(H_2)) - (\Delta H_f^\circ(H_2O) + \Delta H_f^\circ(CH_4))$$

ΔH_r = (-110.5 + 3·0) - (-241.8 + (-75)) = 206 kJ.

$$\Delta S^\circ = (S^\circ(CO) + 3S^\circ(H_2)) - (S^\circ(H_2O) + S^\circ(CH_4))$$

ΔS° = (1197.9 + 3·131) - (-188.7 + 186) = 216 $J \cdot K^{-1}$ = 0.216 $kJ \cdot K^{-1}$.
At standard conditions (298 K):

$$\Delta G_r = \Delta H_r - T\Delta S_r = 206 - 298 \cdot 0.216 = 142 \text{ kJ}.$$

$$\Delta G = 142 \text{ kJ}, \Delta G > 0.$$

2. Since $\Delta G > 0$, the process is not spontaneous.

When $\Delta G = 0$, $\Delta G^\circ = 0 = \Delta H - T\Delta S$

$$\Delta H = T\Delta S \text{ or } T = \frac{\Delta H}{\Delta S} = \frac{206}{0.216} = 954 \text{ K}.$$

The reaction will become spontaneous at temperature above 954 K.

3.7. Application of Thermodynamic. Law for Living Systems

The reactions that living organisms carry out to obtain the energy they need and to synthesize the compounds they require are commonly known as **metabolism**. Metabolism can be divided into two parts: **catabolism** and **anabolism**. **Catabolism reactions** break down complex nutrient molecules to provide energy and simple precursor molecules for synthesis. **Anabolism reactions** require energy and result in the synthesis of complex biomolecules from simple precursor molecules.

Catabolism: complex molecules → simple molecules + *energy*

Anabolism: simple molecules + *energy* → complex molecules

A living organism is an open system. The total change of entropy of the human body always is positive.

Biochemical reactions accompanied by a decrease in Gibbs energy ($\Delta G < 0$) are called **exergonic** and, respectively, **endergonic** at $\Delta G > 0$.

The energy used by the living body is obtained from the biological combustion of food. The three main classes of foods used by people are carbohydrates, fats, and proteins. For proper nutrition, our diet should consist of balanced proportions of all three types of foods (60–70 g of fats – 20–25% of energy; 100–140 g of proteins – 15–20% of energy; and 55–60% of the energy of carbohydrates per day), plus vitamins, minerals, and water.

The SI unit of heat is kilojoule (kJ). For measuring the energy content of foods, calorie or kilocalorie (kcal) is sometimes used.

$$1\text{kcal}=1000\text{ cal}=4184\text{J}=4.184\text{ kJ}.$$

The accurate determination of heat of combustion of a substance is carried out by using a bomb calorimeter.

Example 3.7. Calculate caloricity of 200 g of nuts containing 16% of proteins, 67% of fats, and 10% of carbohydrates. Caloricity of proteins are 18 kJ/g, fats – 39 kJ/g, carbohydrates – 18 kJ/g.
Solution: Calculate the mass of proteins, fats, and carbohydrates.

$100\ g$ nuts – 16 g proteins $\qquad x=\dfrac{16\cdot 200}{100}=32\ g;$

200 g – x

$100\ g$ nuts – 67 g fats $\qquad x=\dfrac{67\cdot 200}{100}=134\ g;$

200 g – x g

$100\ g$ nuts – 10 g proteins $\qquad x=\dfrac{10\cdot 200}{100}=20\ g.$

200 g – x g

Calculate the caloricity.
32 · 18 kJ/g = 576 kJ,
134 g · 39 kJ/g = 5226 kJ,
20g · 18 kJ/g = 360 kJ,
Caloricity of 200 g of nuts is 576 + 5226 + 360 = 6162 KJ.

Example 3.8. A student requires about 15000 kJ of energy to exercise a normal vital activity. Calculate the amount of bread, butter, and eggs, promoting this amount of energy. The caloric value of wheat bread is 9.91 kJ/g, butter – 30.41 kJ/g, eggs – 6.12 kJ/g.

Solution:

$$1\ g\ \text{bread} - 9.91\ \text{kJ}$$

x g – 15000 kJ $x = \frac{1\cdot 15000}{9.91} = 1513\cdot 62$ g=1.514 kg;

$$1\ g\ \text{butter} - 30.4\ \text{kJ}$$

x g – x g – 15000 kJ $x = \frac{1\cdot 15000}{30.4} = 493.42\ g = 0.493\ k$g;

$$1\ g\ \text{eggs} - 6.12\ \text{kJ}$$

x g – 15000 kJ $x = \frac{1\cdot 15000}{6.12} = 2450.98\ g = 2.451\ k$g.

Exercises for practice

1. Given the reaction $SO_{2(g)} + NO_{2(g)} \leftrightarrow SO_{3(g)} + NO_{(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$SO_{2(g)}$	$NO_{2(g)}$	$SO_{3(g)}$	$NO_{(g)}$
	-296.9	33.5	-396.1	90.2

a) -42.5 b) -636.3 c) 42.1 d) -569.3

2. Given the reaction $2CO_{(g)} + 2H_{2(g)} \rightleftarrows CH_{4(g)} + CO_{2(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$CO_{(g)}$	$2H_{2(g)}$	$CH_{4(g)}$	$CO_{2(g)}$
	-111	0	-75	-393.5

a) 579 b) -357 c) 357 d) -246,5

3. Given the reaction $2CH_{4(g)} \rightleftarrows C_2H_{2(g)} + 3H_{2(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$CH_{4(g)}$	$C_2H_{2(g)}$	$H_{2(g)}$
	-75	227.0	0

a) 77 b) 377 c) -77 d) -377

4. Given the reaction $2Cl_{2(g)} + 2H_2O_{(g)} \leftrightarrow 4HCl_{(g)} + O_{2(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$Cl_{2(g)}$	$H_2O_{(g)}$	$HCl_{(g)}$	$O_{2(g)}$
	0	-241.8	-91.8	0

a) -850.8 b) 850.8 c) 116.6 d) 333.6

5. Given the reaction $2NO_{(g)} + 2H_{2}{}_{(g)} \leftrightarrow 2H_2O_{(g)} + N_{2(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$NO_{(g)}$	$H_{2}{}_{(g)}$	$H_2O_{(g)}$	$N_{2(g)}$
	90.2	0	-241.8	0

a) -850.8 b) 850.8 c) 664 d) -664

6. Given the reaction $NH_{3(g)} + HNO_{2}{}_{(l)} \leftrightarrow N_2 + 2H_2O_{(l)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$NH_{3(g)}$	$HNO_{2}{}_{(l)}$	N_2	$H_2O_{(l)}$
	-46.2	-119.2	0	-285.8

a) -406.2 b) 406.2 c) -120.4 d) -857.4

7. Given the reaction $2PbS_{(s)} + 4O_{2}{}_{(g)} \leftrightarrow 2PbO_{(s)} + 2SO_{3(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$PbS_{(s)}$	$4O_{2}{}_{(g)}$	$PbO_{(s)}$	$SO_{3(g)}$
	-100.4	0	-219.3	-396.1

a) -733.91 b)-1030 c) -120.4 d) -244.3

8. Given the reaction $SO_{2(g)} + 2H_2S_{(g)} \leftrightarrow 2S_{(s)} + 2H_2O_{(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$SO_{2(g)}$	$H_2S_{(g)}$	$S_{(s)}$	$H_2O_{(g)}$
	-296.9	-21	0	-241.8

a) 76.1 b) -144.7 c) 152.2 d) -152.2

9. Given the reaction $CO_{2(g)} + 2SO_{3(g)} \leftrightarrow CS_{2(g)} + 4O_{2(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$CO_{2(g)}$	$SO_{3(g)}$	$CS_{2(g)}$	$O_{2(g)}$
	-393.5	-396.1	88	0

a) 877.6 b) -701.6 c) -1095.1 d) 1273.7

10. Given the reaction $PCl_{3(g)} + 3H_2O_{(g)} \leftrightarrow H_3PO_{3(l)} + 3HCl_{(g)}$, what is ΔH^0 of this reaction?

ΔH_f^0 kj/mol	$PCl_{3(g)}$	$H_2O_{(g)}$	$H_3PO_{3(l)}$	$HCl_{(g)}$
	-287	-241.8	-964.8	-91.8

a) -227.8 b) 227.8 c) 918.2 d) 631.2

11. What is ΔS^0 of this reaction: $CO_{(g)} + H_2O_{(l)} \rightarrow CO_{2(g)} + H_{2(g)}$

	$CO_{(g)}$	$H_2O_{(l)}$	$CO_{2(g)}$	$H_{2(g)}$
S^0, J/mol K	197.54	70.8	213.68	130.58

a) -75.92 b) 75.92 c) 351.44 d) 612.6

12. What is ΔS^0 of this reaction: $Fe_3O_{4(s)} + CO_{(g)} \rightarrow 3FeO_{(s)} + CO_{2(g)}$

	$Fe_3O_{4(s)}$	$CO_{(g)}$	$FeO_{(s)}$	$CO_{2(g)}$
S^0, J/mol K	146,4	197,54	58,79	213,68

a) -46.11 b) -71.47 c) 46.11 d) -13.53

13. What is ΔS^0 of this reaction: $2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(g)}$

	$C_2H_{2(g)}$	$O_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$

S^0, J/mol K	200,8	205,04	213,68	188,7

a) 808.22 b) -3.46 c) 194.68 d) -194.68

14. What is ΔS^0 of this reaction: $C_2H_{4\,(g)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 2H_2O_{(g)}$

	$C_2H_{4(g)}$	$O_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$
S^0, J/mol K	219,4	205,04	213,68	188,7

a) -29.76 b) -22.06 c) 22.06 d) 29.76

15. What is ΔS^0 of this reaction: $2H_2O_{2(l)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

	$H_2O_{2(l)}$	$H_2O_{(g)}$	$O_{2(g)}$
S^0, J/mol K	109,6	188,7	205,04

a) 284.14 b) 363.24 c) -284.14 d) -363.24

16. What is ΔG^0 of this reaction: $CH_{4(g)} + 4CI_{2(g)} \rightarrow CCI_{4\,(g)} + 4HCI_{(g)}$

	$CH_{4(g)}$	$CI_{2\,(g)}$	$CCI_{4(g)}$	$HCI_{(g)}$
ΔG^0, kJ/mol	-50,79	0	-64,6	-95,27

a) -367.27 b) 367.27 c) -394.89 d) -109.08

17. What is ΔG^0 of this reaction: $2H_2S_{(g)} + 3O_{2(g)} \rightarrow 2H_2O_{(g)} + SO_{2(g)}$

	$H_2S_{(g)}$	$O_{2(g)}$	$H_2O_{(g)}$	$SO_{2\,(g)}$
ΔG^0, kJ/mol	-33,01	0	-228,61	-300,4

a) 691.6 b) -562.02 c) -496 d) -691.6

18. What is ΔG^0 of this reaction: $CS_{2\,(g)} + 3O_{2\,(g)} \rightarrow CO_{2\,(g)} + SO_{2\,(g)}$

	$CS_{2(g)}$	$O_{2(g)}$	$CO_{2(g)}$	$SO_{2\,(g)}$
ΔG^0, kJ/mol	67	0	-394,38	-300,4

a) -761.78 b) 761.78 c) -627.78 d) -927.78

19. What is ΔG^0 of this reaction:
$2CH_3OH_{(l)} + 3O_{2\,(g)} \rightarrow 2CO_{2\,(g)} + 4H_2O_{(g)}$

	$CH_3OH_{(l)}$	$O_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$
ΔG^0, kJ/mol	-166,23	0	-394,38	-228,61

a) 456.76 b) -1370.74 c) 1370.74 d) -456.76

20. What is ΔG^0 of this reaction:

$CH_{4\,(g)} + 4CI_{2\,(g)} \rightarrow CCI_{4(g)} + 4HCI_{(g)}$

	$CH_{4(g)}$	$CI_{2\,(g)}$	$CCI_{4(g)}$	$HCI_{(g)}$
ΔG^0, kJ/mol	-50,79	0	-64,6	-95,27

a) -109.08 b) 109.08 c) -394.89 d) 394.89

CHAPTER 4
CHEMICAL KINETICS

Practical Skills

After studying the subject, you will be able:

1. To explain the meaning of terms: reaction rate, rate constant, reaction molecularity.
2. To analyze the dependence of the reaction rate on the concentration and temperature.
3. To calculate the rate of the forward and backward chemical reactions.
4. To calculate equilibrium constant for a chemical reaction
5. To predict chemical reaction shift under the influence of changes in temperature, pressure and concentration.

.

4.1. The Main Concepts of Chemical Kinetics

Chemical kinetics is the study of the rates of chemical reactions, the factors affecting the rates of the reactions, and the mechanisms by which the reactions proceed.

The description of the step-by-step process by which reactants change to products is called the **mechanism** of the reaction.

The rate of a chemical reaction is the change in the concentration of any of the reactants or products per unit time (for homogeneous reaction).

$$Rate\text{ of reaction}=\frac{Decrease\text{ in the concentration of a reactant}}{\text{Time interval}},$$

$$\text{or }=\frac{increase\text{ in the concentration of a product}}{\text{Time interval}}.$$

For any reaction of the type $A+B\rightarrow C+D$,

Reaction rate $=-\frac{\Delta C_A}{\Delta t}=-\frac{\Delta C_B}{\Delta t}=+\frac{\Delta C_C}{\Delta t}=+\frac{\Delta C_D}{\Delta t}$.

The unit for the reaction rate is $mol/L\cdot s\ (mol\cdot L^{-1}s^{-1})$.

We can consider the minus (–) sign as indicating the decrease in reactant concentration, and the plus (+) sings as indicating the increase in the concentration of the product.

For heterogeneous reactions:

$$Rate\text{ of reaction} = \frac{\text{change of amount of a substance}}{\text{Surface area of the reactants} \cdot \text{Time interval}}.$$

Examples of solving tasks:

Example 4.1. In studying the reaction between acetone and bromine, it was found that 0.025 mol of bromine disappeared in 34.5 sec. What was the rate of the reaction?

Solution: The rate of the reaction is defined as moles of bromine disappearing per unit time. Therefore

$$Rate = \frac{0.025\text{ mol}}{1\text{ L} \cdot 34.5\ s} = 7.2 \times 10^{-4}\ mol/L \cdot s.$$

4.2. Factors Affecting the Reaction Rate

The main factors affecting the reaction rate are concentration, temperature, nature of the reacting substances, and catalyst presence.

Concentration of reactants. The greater the concentration of the reactants, the faster the reaction.

The concentration effect is described by the **Law of Mass Action**, formulated in 1867 by Norwegians K. Guldberg and P. Waage: At a constant temperature, the rate of the chemical reaction at each moment is directly proportional to the concentration of the reacting substances.

For reaction $aA + bB \rightarrow dD$ dependence of a homogeneous reaction on the concentration of reacting substances can be represented as:

$$Rate = kC_A^a \cdot C_B^b,$$

where k is a reaction rate constant, which equals the rate of the chemical reaction when the concentrations of all reaction substances equal to 1 mol/L. This equation is called the **kinetic equation**. In kinetic equations, only the concentration of substances in gaseous or liquid form is written because the concentrations of solid substances are constant; thus, as indicated in the reaction rate constant

for reactions $C_{(s)} + O_{2(g)} \rightleftarrows CO_{2(g)}$ and

$2CO_{(g)} + O_{2(g)} \rightleftarrows 2CO_{2(g)}$

kinetic equations are as follows:

$rate = kC_{O_2}$

$rate = kC_{CO}^2 C_{O_2}$

Example 4.2. Given the reaction $H_{2(g)} + I_{2(g)} \rightleftarrows 2HI_{(g)}$. $K = 0.16\ \mathrm{L/mol} \cdot s$, $C_{H_2} = 0.04\ \mathrm{mol/L}$, $C_{I_2} = 0.05\ \mathrm{mol/L}$. What is the chemical reaction rate?

Ans.: Rate = $0.16 \cdot 0.04 \cdot 0.05 = 3.2 \cdot 10^{-4}\ \mathrm{mol/L} \cdot s$.

The above kinetic reactions, being an analytical expression of the law of mass action, are applicable only to ideal systems, in which the stoichiometric equation reflects the reaction mechanism.

In practice, the stoichiometric equation does not reflect the reaction mechanism. Only a few chemical reactions are accomplished in one stage. The majority are accomplished in several elementary stages, in which one, two or three molecules may take place. The number of molecules which react simultaneously at the moment of collision, accomplishing the act of chemical interaction, is called the reaction **molecularity**.

$CaCO_3 \rightarrow CaO + CO_2$ – monomolecular,

$H_2 + I_2 \rightarrow 2HI$ – bimolecular,

$2\mathrm{NO} + \mathrm{O}_2 \rightarrow 2NO_2$ – trimolecular.

The probability of simultaneous collision of three molecules is 1000 times less than the collision of two molecules. The elementary stages of any chemical reaction can be presented as mono- or bimolecular interactions. The rate of multistage reactions is mediated by the rate of its slowest stage.

Thus, the observed rate of the reaction

$$2H_2 + O_2 = 2H_2O$$

does not correspond to the rate predicted by the equation

$$Rate = K[H_2]^2[O_2].$$

Experiments have shown that this reaction is rather complicated. It is accomplished in several stages following the chain mechanism.

The exponents of power in a kinetic equation are determined using special methods. They are called **reaction order** for the respective substance. The general order of the reaction equals the sum of power exponents in the equation of the chemical reaction rate. For a reaction $aA + bB \rightarrow C$, the rate is given by the equation $W = K[A]^x[B]^y$ in which K is the rate constant, [A] and [B] represent concentrations of reactants A and B respectively, and x and y represent orders of reaction with respect to A and B respectively. General order of reaction = x+y.

Temperature. The rate of reaction increases with the increase of temperature. This can be explained by the increased chaotic movement of the molecules, which causes an increase in the collision number. In 1879, J. Van't Hoff formulated an empirical rule:

With temperature elevation by 10 degrees the rate of the chemical reaction increases 2–4 times:

$Rate_{T_2} = Rate_{T_1} \cdot \gamma^{\frac{T_2 - T_1}{10}}$, where $Rate_{T_2}$ and $Rate_{T_1}$ – the reaction rates at temperatures T_2 and T_1, respectively, γ – temperature coefficient showing how many times the rate increases at temperature elevation by 10 degrees.

The nature of the reacting substances. The decisive is the type of chemical bond. For organic substances, the main types of bonds are nonpolar or low-polar covalent σ and π-bonds. The reaction with the substances having σ bonds is slower than with those having π-bonds. Inorganic substances, which have ionic or polar covalent bond, react faster.

The surface area of the reactants. For a reaction involving a solid reactant or catalyst, the smaller is the particle size, the greater is the surface area, and the faster is the reaction.

Pressure. For reactions involving gases, the increasing gas pressure increases its concentration. A given volume contains a greater amount in moles of the gas.

Presence of Catalyst. Catalyst is a substance that increases the rate of a chemical reaction without itself undergoing a permanent change. In the case of reversible reactions, catalyst helps to attain the equilibrium quickly without disturbing the state of equilibrium.

4.3. Chemical Equilibrium

Chemical equilibrium is a state in which the concentrations of reactants and products remain constant over time.

Chemical equilibrium is dynamic in nature in which the forward reaction proceeds at the same rate as the backward reaction.

Reactions that go to completion are **irreversible**:

$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

Reactions that do not proceed to completion are **reversible**:

$$3H_{2(g)} + N_{2(g)} \rightleftarrows 2NH_{3(g)}$$

The sign ⇄ represents the reversibility of a reaction. The reaction from left to right (→) is called the **forward** reaction, while the reaction from right to left (←) is called the **backward** (**reverse**) reaction.

A mathematical relationship derived from the experiment and verified by a theory that describes the equilibrium state is called the **equilibrium constant** expression.

For a reversible reaction at equilibrium:

$$aA + bB \rightleftarrows cC + dD$$

in which A and B are reactants, C and D are products, and a, b, c, d are the stoichiometric coefficients.

The equilibrium constant is written as:

$$K_{eq} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}.$$

For the reaction $3H_2 + N_2 \rightarrow 2NH_3$

$$K_{eq} = \frac{[NH_3]^2}{[H_2]^3[N_2]},$$

$$Rate_f = K_f[H_2]^3[N_2],$$

$Rate_b = K_b[NH_3]^2$,
$Rate_f = Rate_b = K_f[H_2]^3[N_2] = K_b[NH_3]^2$,
$K_{eq} = \frac{K_f}{K_b} = \frac{[NH_3]^2}{[H_2]^3[N_2]}$.

4.4. *Le Chatelier's Principle States*

When a change is introduced into a chemical system at equilibrium, the system will shift in the direction that counteracts that change. The changes in pressure are accompanied by changes in the volume and influence the equilibrium of the reactions. For gas reactions, changes in pressure are equivalent to the changes in concentration. During the process of ammonium synthesis $N_2 + 3H_2 = 2NH_3$ which takes place with volume reduction, a pressure increase will increase the concentration of the initial substances in a greater extent than that of the products. The reaction will shift to the reaction products that are to a smaller volume.

At heating, the system equilibrium will shift to the side of the endothermic process, at cooling – exothermic.

Catalysts do not shift chemical equilibrium as they accelerate both forward and backward (reverse) reactions. In this case, equilibrium will be achieved faster.

Exercises for practice

1. Choose the forward reaction for $2NO_{(g)} + Cl_{2(g)} \rightleftarrows 2NOCl_{(g)}$.

a) $2NOCl_{(g)} \rightarrow 2NO_{(g)} + Cl_{2(g)}$
b) $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$
c) $K_{eq} = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$

2. Choose the forward reaction for $4NH_{3(g)} + 5O_{2(g)} \rightleftarrows 4NO_{(g)} + 6H_2O_{(g)}$.

a) $4NH_{3(g)} + 5O_{2(g)} \to 4NO_{(g)} + 6H_2O_{(g)}$

b) $4NO_{(g)} + 6H_2O_{(g)} \to 4NH_{3(g)} + 5O_{2(g)}$

c) $K_{eq} = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$

3. Choose the forward reaction for $CH_{4(g)} + 2Cl_{2(g)} \rightleftarrows CH_2Cl_{2(g)} + 2HCl_{(g)}$.

a) $K_{eq} = \frac{[CH_2Cl][HCl]^2}{[CH_4][Cl_2]^2}$

b) $CH_2Cl_{2(g)} + 2HCl_{(g)} \to CH_{4(g)} + 2Cl_{2(g)}$

c) $CH_{4(g)} + 2Cl_{2(g)} \to CH_2Cl_{2(g)} + 2HCl_{(g)}$

4. Choose the forward reaction for $4HCl_{(g)} + O_{2(g)} \rightleftarrows 2H_2O_{(g)} + 2Cl_{2(g)}$.

a) $4HCl_{(g)} + O_{2(g)} \to 2H_2O_{(g)} + 2Cl_{2(g)}$

b) $2H_2O_{(g)} + 2Cl_{2(g)} \to 4HCl_{(g)} + O_{2(g)}$

c) $K_{eq} = \frac{[H_2O]^2[Cl_2]^2}{[HCl]^4[O_2]}$

5. Choose the forward reaction for $SO_{2(g)} + 2H_2S_{(g)} \rightleftarrows 2S_{(g)} + 2H_2O_{(g)}$.

a) $2S_{(g)} + 2H_2O_{(g)} \to SO_{2(g)} + 2H_2S_{(g)}$

b) $SO_{2(g)} + 2H_2S_{(g)} \to 2S_{(g)} + 2H_2O_{(g)}$

c) $K_{eq} = \frac{[S]^2[H_2O]}{[SO_2][H_2S]^2}$

6. Choose the rate expression of forward reaction for $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$.

a) $rate = k[N_2][H_2]^3$ b) $rate = k[NH_3]^2$

c) $N_{2(g)} + 3H_{2(g)} \to 2NH_{3(g)}$ d)$2NH_{3(g)} \to N_{2(g)} + 3H_{2(g)}$

7. Choose the rate expression of forward reaction for

$2F_{2(g)} + 2H_2O_{(g)} \rightleftarrows 4HF_{(g)} + O_{2(g)}$.

a) $rate = k[HF]^4[O_2]$ b) $rate = k[F_2]^2[H_2O]^2$

c) $2F_{2(g)} + 2H_2O_{(g)} \rightarrow 4HF_{(g)} + O_{2(g)}$

d) $4HF_{(g)} + O_{2(g)} \rightarrow 2F_{2(g)} + 2H_2O_{(g)}$

8. Choose the rate expression of forward reaction for $4HCl_{(g)} + O_{2(g)} \rightleftarrows 2H_2O_{(g)} + 2Cl_{2(g)}$.

a) $4HCl_{(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} + 2Cl_{2(g)}$

b) $2H_2O_{(g)} + 2Cl_{2(g)} \rightarrow 4HCl_{(g)} + O_{2(g)}$

c) $rate = k[HCl]^4[O_2]$ d) $rate = k[H_2O]^2[Cl_2]^2$

9. Choose the rate expression of forward reaction for $2NO_{(g)} + O_{2(g)} \rightleftarrows 2NO_{2(g)}$.

a) $rate = k[NO_2]^2$ b) $rate = k[NO]^2[O_2]$

c) $2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$ d) $2NO_{2(g)} \rightarrow 2NO_{(g)} + O_{2(g)}$

10. Choose the rate expression of forward reaction for $H_{2(g)} + I_{2(g)} \rightleftarrows HI_{(g)}$.

a) $H_{2(g)} + I_{2(g)} \rightarrow HI_{(g)}$ b) $HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

c) $rate = k[HI]^2$ d) $rate = k[H_2][I_2]$

11. Choose the equilibrium constant expression for the reaction: $2NOCl_{(g)} \rightleftarrows 2NO_{(g)} + Cl_{2(g)}$.

a) $K_{eq} = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$ b) $K_{eq} = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$

c) $K_{eq} = [NO]^2[Cl_2]$ d) $K_{eq} = [NOCl]^2$

12. Choose the equilibrium constant expression for the reaction: ${N_2}_{(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)}$.

a) $K_{eq} = \frac{[N_2][O_2]}{[NO]^2}$ b) $K_{eq} = \frac{[NO]^2}{[N_2][O_2]}$

c) $K_{eq} = [N_2][O_2]$ d) $K_{eq} = [NO]^2$

13. Choose the equilibrium constant expression for the reaction: $2N_2O_{5(g)} \rightleftarrows 4NO_{2(g)} + O_{2(g)}$.

a) $K_{eq} = [N_2O_5]^2$ b) $K_{eq} = [NO_2]^4[O_2]$

c) $K_{eq} = \frac{[N_2O_5]^2}{[NO_2]^4[O_2]}$ d) $K_{eq} = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$

14. Choose the equilibrium constant expression for the reaction: $4H_{2(g)} + 2NO_{2(g)} \rightleftarrows 4H_2O_{(g)} + N_{2(g)}$.

a) $K_{eq} = \frac{[H_2O]^4[N_2]}{[H_2]^4[NO_2]^2}$ b) $K_{eq} = \frac{[H_2]^4[NO_2]^2}{[H_2O]^4[N_2]}$

c) $K_{eq} = [H_2]^4[NO_2]^2$ d) $K_{eq} = [H_2O]^4[N_2]$

15. Choose the equilibrium constant expression for the reaction: $F_{2(g)} + 2ClO_{2(g)} \rightarrow 2FClO_{2(g)}$.

a) $K_{eq} = [F_2][ClO_2]^2$ b) $K_{eq} = [FClO_2]^2$

c) $K_{eq} = \frac{[FClO_2]^2}{[F_2][ClO_2]^2}$ d) $K_{eq} = \frac{[F_2][ClO_2]^2}{[FClO_2]^2}$

16. Determine the direction in which the equilibrium will be shifted by increasing the concentration of CO in the reaction $CO_{(g)} + Cl_{2(g)} \rightleftarrows COCl_{2(g)}$.

a) shifts to left b) shifts to right c) no change

17. Determine the direction in which the equilibrium will be shifted by increasing the pressure in the reaction $N_{2(g)} + O_{2(g)} \rightleftarrows 2NO_{(g)}$.

a) shifts to left b) shifts to right c) no change

18. Determine the direction in which the equilibrium will be shifted by increasing the temperature in the reaction $H_2 + Cl_2 \rightleftarrows 2HCl; \Delta H \prec 0$.

a) shifts to left b) shifts to right c) no change

19. Determine the direction in which the equilibrium will be shifted by increasing the concentration of $CO_{2(g)}$ in the reaction $CO_{2(g)} + C_{(g)} \rightarrow 2CO_{(g)}$.

a) shifts to left b) shifts to right c) no change

20. Determine the direction in which the equilibrium will be shifted by increasing the pressure in the reaction $CO_{2(g)} + H_{2(g)} \rightleftarrows CO_{(g)} + H_2O_{(g)}$.

a) no change b) shifts to right c) shifts to left

21. Write the rate expression of forward and reverse reactions. Write the equilibrium constant expressions for each of the following reactions:

a. $FeO_{(s)} + CO_{(g)} \rightleftarrows Fe_{(s)} + CO_{2(g)}$;

b. $2NO_{(g)} + Cl_{2(g)} \rightleftarrows 2NOCl_{(g)}$.

c. $4NH_{3(g)} + 5O_{2(g)} \rightleftarrows 4NO_{(g)} + 6H_2O_{(g)}$;

d. $C_{(g)} + CO_{2(g)} \rightleftarrows 2CO_{(g)}$.

e. $CH_{4(g)} + 2Cl_{2(g)} \rightleftarrows CH_2Cl_{2(g)} + 2HCl_{(g)}$;

f. $CO_{2(g)} + H_2O_{(l)} \rightleftarrows H_2CO_{3(l)}$.

22. Given the reaction $2NO_{(g)} + 2H_{2(g)} \rightleftarrows 2H_2O_{(g)} + N_{2(g)}$ $\Delta H^o \succ 0$, complete the following table:

Change	Effect on equilibrium
increase $[NO]$	
decrease $[H_2]$	
decrease t^o	

23. Given the reaction $NH_{3(g)} + HNO_{2(g)} \rightleftarrows N_{2(g)} + 2H_2O_{(g)}$ $\Delta H^o \succ 0$, complete the following table:

Change	Effect on equilibrium
increase $[N_2]$	

decrease $[HNO_2]$	
decrease t^o	

24. Given the reaction $2NO_{(g)} + Cl_{2(g)} \rightleftarrows 2NOCl_{(g)}$ $\Delta H^o \succ 0$, complete the following table:

Change	Effect on equilibrium:
increase $[Cl_2]$	
decrease $[NOCl]$	
decrease t^o	

25. Given the reaction $N_2 + 3H_2 = 2NH_3$, the rate constant is 0.24 $[N_2]$ =1.5 mol/L, $[H_2]$ =2.5 mol/L. Calculate the rate of a chemical reaction.

26. Given the reaction $A + B = AB$, the rate of reaction is $4\cdot10^{-5}$ mol/L·s, $[A]$ =0.5 mol/L and $[B]$ =0.2 mol/L. Calculate the rate constant.

27. Given the reaction $2A + B = 2C$, the rate constant is 0.8, $[A]$ =0.3 mol/L and $[B]$ =0.5 mol/L. Calculate the rate reaction.

28. In reaction $2F_2 + 2H_2O \rightleftarrows 4HF + O_2$, the equilibrium concentrations were found to be $[F_2]$ =0.08 mol/L, $[H_2O]$ =0.07 mol/L, $[HF]$ =0.09 mol/L, $[O_2]$ =0.01 mol/L. Calculate the value of the equilibrium constant.

29. In the reaction $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$, the equilibrium concentrations were found to be $[HCl]$ =0.8 mol/L, $[O_2]$ =0.2 mol/L $[H_2O]$ =0.3 mol/L, $[Cl_2]$ =0.4 mol/L. Calculate the value of the equilibrium constant.

30. In the reaction $N_2 + 3H_2 \rightleftarrows 2NH_3$, the equilibrium concentrations were found to be $[N_2]$ =3 mol/L, $[H_2]$ =4 mol/L, $[NH_3]$ =4 mol/L. Calculate the value of the equilibrium constant.

CHAPTER 5

SOLUTIONS

Practical skills

After studying the subject, you will be able:

1. To describe the process of dissolving substances in a solvent.
2. To characterize the influence of different factors on the solubility.
3. To express a solution concentration in mass percent, molarity, molality, normality, and mole fraction.
4. To prepare the solution of a given concentration.
5. To calculate the relative lowering of vapor pressure.
6. To calculate elevation in boiling point and depression in freezing point of the solution.
7. To calculate osmotic pressure.
8. To predict processes that take place in cells placed it in the hypotonic, isotonic, or hypertonic solution.
9. To write the equation for dissociation of acids, bases, and salts.
10. To write the dissociation constant for dissociation of week acids and bases.
11. To calculate pH for the solutions of acids, bases, and salts.
12. To determine the concentration of hydrogen ions according to the pH value.
13. To use the knowledge of this subject for the estimation of the medium acidity of the biological solution (blood, gastric juice, urine, etc.).
14. To write the hydrolysis reactions for salts.
15. To make conclusions about the acidity of biological liquids on the basis of pH.
16. To explain the mechanism of buffer action and ability of buffers to maintain acid-base equilibrium
17. To calculate the pH value of the buffer solution. Henderson – Hasselbalch equation.

18. To determine the change in pH of buffer solution after the addition of strong acids or base.
19. To calculate the buffer capacity.

Good knowledge of the theory of solutions is necessary to explain the physical and chemical essence of such phenomena as diffusion, osmosis, dissolution, hydrolysis, and others, which are the basis of metabolism in nature.

5.1. Theory of Solutions

Solutions are of great importance in the human life and practical activities. All the biological liquids – blood, lymph, intercellular lymph, gastric juice, etc. – are solutions. All biochemical processes in the body occur in aqueous solutions.

Solutions are homogeneous systems consisting of two or more components and the products of their interaction.

Compulsory components of the solution are the **solvent** and the **solute**.

The **solvent** is the solution component that is **present** in the **greatest amounts** or the component that determines the state of matter in which the solution exists.

The **solute** is the solution component, which is **present** in a **lesser amount** than the solvent.

A solution in which **water** is the **solvent** is called an **aqueous solution**.

A solution containing a relatively large amount of a solute is called **concentrated**. If the amount of solute is small, the solution is **diluted**.

Types of solutions

According to their state, solutions can be **liquid**, **solid** and **gaseous**.

In a **liquid solution,** the **solvent** is a **liquid** substance. For example, gasoline is a mixture of a number of liquid hydrocarbons.

Seawater is an aqueous solution of sodium chloride and other ionic solids. Carbonated water is an aqueous solution of CO_2.

All **gaseous mixtures** are **solutions**. The best-known example of a gaseous solution is air, which consists of N_2, O_2, CO_2, and other gases.

In a **solid solution,** the **solvent** is a **solid** substance. The ability to form solid solutions is particularly common to metals, and such solid solutions are called **alloys**—for example, an alloy of nickel and copper, an alloy of gold and silver.

Dissolving substances in a solvent. Solubility

The Russian chemist D.I. Mendeleev, based on his experiments, created the chemical theory of solutions.

The dissolving of substances in a solvent is:

1. the destruction of the crystal lattice
2. the interaction of the solvent with the particles of the solute
3. the uniform distribution of one substance in the total volume of another substance.

The heat can be evolved or absorbed during this process.

Solubility is the ability of the substance to uniformly distribute in the total volume of another substance.

There are **soluble** and **insoluble** substances.

Solubility depends on the nature of substances, temperature, and pressure. For example, the solubility of solid substances increases and the solubility of gases decreases with the raising of temperature. The solubility of gases increases with the raising of pressure.

There are **saturated** and **unsaturated** solutions.

A solution, in which under a certain temperature, the solute cannot be dissolved any more, is called a **saturated** solution.

A solution, in which under a certain temperature, some more solute can be dissolved, is called an **unsaturated** solution.

A supersaturated solution is one that holds in a solution more of the solute than can dissolve in the presence of the solute at that temperature.

5.2. Methods of Expression of Solution Concentration

A solution consists of a mixture of two substances: the solute in a smaller amount dissolved in the solvent, and the component in a larger amount.

Concentration is a measure of the amount of the solute, which is dissolved in a given amount of the solvent.

Mass percent. The percent by mass concentration

The statement “5% aqueous solution of NaCl” has the following meaning: the solution contains 5g of NaCl in 100g of the solution.

The solution contains 5g of NaCl and 100-5=95g of H_2O.

Percent concentration is defined by the equation:

$$W, \% = \frac{\text{mass of solute}}{\text{mass of solution}} \cdot 100\ \%,$$

$$\text{Mass of Solution} = \text{Mass of Solute} + \text{Mass of Solvent}.$$

Mass percent (percent by mass concentration, %) shows how many grams of solute is dissolved in 100 g of solution.

Molar concentration (molarity)

Molar concentration (molarity) is a concentration of a solution expressed as the number of moles of solute per liter of the solution.

Molar concentration is defined by the equation:

$$\text{Molarity}\ \ (C_M)\ = \frac{\text{Number of moles of solute}}{\text{volume of solution}},\ \ \frac{\text{mol}}{\text{L}},$$

$$C_M = \frac{\text{n (solute)}}{\text{V solution}}.$$

A solution in which 1 mol of NaCl is dissolved in 1L (1000 mL) of the solution is described as a 1M solution and is designated by the symbol 1M NaCl.

Molal concentration (molality)

Molality (C_m) is a concentration of a solution that is expressed as a number of moles of solute per kilogram of solvent.

Molal concentration is defined by the equation:

$$\text{Molality } (C_m) = \frac{\text{Number of moles of solute}}{\text{Mass of solvent}}, \text{mol/kg or m},$$

$$C_m = \frac{\text{n (solute)}}{\text{m (solvent)}}.$$

A solution, in which 1 mol of NaCl is dissolved in 1000 g of water, is described as a 1–molal solution and is designated by the symbol 1m NaCl.

Normality (equivalent concentration)

Normality (N) is defined as the number of equivalents of solute per liter of solution.

N is defined by the equation:

$$Normality(N) = \frac{\text{Number of equivalents of solute}}{Volume\ of\ solution}; \frac{Equiv}{L}. \quad mol.eq/L.$$

or

$$Normality(C_N) = \frac{\text{Number of mol of solute}}{f_{eq} \times Volume\ of\ solution}; \frac{mol}{L}.$$

f_{eq} can be calculated for different classes of compounds as follows:

$$f_{eq} = \frac{1}{n},$$

Where, for bases, n is an amount of OH^- groups, for acids – the amount of H^+, and for salts, it is metal valency multiplied by metal index.

Examples:

For NaOH

$$f_{eq} = \frac{1}{1},$$

Amount of OH is 1, so n=1.

For $Al(OH)_3$

$$f_{eq} = \frac{1}{3};$$

Amount of OH is 3, so n=3.

For H_2SO_4

$$f_{eq} = \frac{1}{2};$$

Amount of H is 2, so n=2.

For H_3PO_4

$$f_{eq} = \frac{1}{3};$$

Amount of H is 3, so n=3.

For $ZnSO_4$

$$f_{eq} = \frac{1}{2};$$

For Na_2SO_4

$$f_{eq} = \frac{1}{2};$$

Valency of Na is I, the index is 2, n=2.

For $Al_2(SO_4)_3$

$$f_{eq} = \frac{1}{6};$$

Valency of Al is III, the index is 2, n=6.

This means that 1N solution contains 1 equivalent of solute per liter of solution. Further, we will use the term **equivalent concentration C_E**. These are the same terms because C_E is the number of equivalent moles of a substance per one liter of solution.

1N solution contains 1 equivalent (or 1 mol of equivalent) of solute per liter of solution. This means that C_E = 1 mol/L.

$$\mathrm{C_E} = \frac{\text{Mass of solute}}{\text{Equivalent mass of solute} \cdot \text{Volume of solution}}$$

$$\text{or } \mathrm{C_E} = \frac{\text{Moles of solute equivalent}}{\text{Volume of solution}}.$$

Equivalent mass

The equivalent mass of an **element** is the mass of the element which combines with or displaces 1.008 parts by mass of hydrogen or 8 Parts by mass of oxygen.

$$\text{Eq. mass of an element} = \frac{\text{Atomic mass of the element}}{\text{Valency of the element}}.$$

$$\text{For example, Eq.mass } (O) = \frac{16}{2} = 8,$$

$$Eq.\text{ mass of an acid} = \frac{\text{Molar mass of the acid}}{Basicity \text{ of the acid}}.$$

Basicity is the number of replaceable H^+ ions in a molecule of acid.

$$\text{For example, } Eq.\ mass\,(HNO_3) = \frac{63}{1} = 63\,\frac{g}{mol},$$

$$Eq.mass(H_2SO_4) = \frac{98}{2} = 49\,\frac{g}{mol},$$

$$Eq.mass \text{ of a base} = \frac{\text{Molar mass of the base}}{\text{Acidity of the base}}.$$

Acidity is the number of replaceable OH^- ions in a molecule of a base.

For example,

$$Eq.mass\ (NaOH) = \frac{40}{1} = 40\,\frac{g}{mol},$$

$$Eq.mass\ (Ca(OH)_2) = \frac{74}{2} = 37\,\frac{g}{mol},$$

$$Eq.mass\text{ of a salt} = \frac{\text{Mol. mass of the salt}}{\text{Total valency of the metal atoms}}.$$

$$\text{For example, Eq. mass }(\text{AlCl}_3) = \frac{133.5}{3} = 66.7\ g/mol,$$

$$\text{Eq. mass }(\text{Al}_2(SO_4)_3 = \frac{342}{6} = 57\frac{g}{mol},$$

$$\text{Eq. mass of an oxidizing/reducing agent} = \frac{\text{Mol. mass or At. mass}}{No.\text{ of electrons, lost or gained by one molecule of the substance}}.$$

Mole fraction (χ,%)

Mole fraction is the ratio of the number of moles of a substance to the total number of moles of all substances in the solution.

If, in a solution, n_1 and n_2 are the numbers of moles of solvent and the solute respectively, then

$$\chi\text{ solute, }\% = \frac{n_2}{n_1 + n_2}$$

$$\chi\text{ solvent, }\% = \frac{n_1}{n_1 + n_2}$$

For example, if a solution contains 4 moles of alcohol and 6 moles of water, then mole fraction of alcohol = $\frac{4}{4+6} = 0.4$

and mole fraction of water = $\frac{6}{4+6} = 0.6.$

The sum of the mole fraction of all constituents of a solution is always equal to 1.0. If we multiply it by 100 % we can express mole fraction in %: 40% and 60%, respectively.

Examples of solving tasks

Example 5.1. How would you prepare a 0.5 m aqueous solution of NH_4Cl?

Solution: Weight out 26.75 g of salt (0.5 mol) and dissolve it in 1 kg (1000 g) of solvent (water).

Example 5.2. 50 g of glucose were dissolved in 450 g of water. Calculate the percent by mass concentration of glucose.

Solution:1) Calculate the mass of solution:

$$\text{m (solution)} = \text{m(solvent)} + \text{m (solute)} = 450 \text{ g} + 50 \text{ g} = 500 \text{ g}$$

2) Calculate the percent by mass concentration:

$$\text{mass persent} = \frac{mass\ of\ solute}{mass\ of\ solution} \cdot 100\ \%;$$

$$\text{mass persent} = \frac{50\ g}{500\ g} \cdot 100\ \% = 10\ \%.$$

Example 5.3. How would you prepare 100 g of a 10 % aqueous solution of NH_4Cl?

Solution: $\% = \frac{\text{mass of NH}_4\text{Cl (solute)}}{\text{mass of NH}_4\text{Cl (solute)} + \text{mass of H}_2O\text{ (solvent)}} \cdot 100\%,$

$$10\% = \frac{\text{m (NH}_4\text{Cl)}}{100\text{ g}} \cdot 100\ \%,\ \ \text{m (NH}_4Cl) = \frac{10\ \% \cdot 100\text{ g}}{100\ \%}.$$

The mass of solute $= 10$ g; the mass of $H_2O = 100 - 10 = 90$ g.

Example 5.4. How many grams and moles of NaCl are contained in 220 g of a 25 % NaCl solution?

Solution: 1) $25\ \% = \frac{x}{220} \cdot 100\ \%$,

m (NaCl) $= \frac{25 \cdot 220}{100} = 55\ g$ NaCl..

$$2)\ n(NaCl) = \frac{mass\ of\ (NaCl)}{molar\ mass\ of\ (NaCl)} = \frac{55\ g}{58.5 \frac{g}{mol}} = 0.94\ mol.$$

Example 5.5. Calculate the mass percent (w, %) of NaOH if 500 ml of solution contain 25 g of NaOH; the density of the solution is 1.024 g/ml.

Density is the amount of mass per unit volume.

Solution:

1) $$\text{density} = \frac{\text{mass of solution}}{\text{volume of solution}},$$

$$mass\ (solution) = \text{density} \cdot \text{V (solution)},$$

$$\text{m (solution)} = 1.024\ \text{g/mL} \cdot 500\ \text{mL} = 512\ \text{g}.$$

2)

$$\text{w, \%} = \frac{\text{mass of solute}}{mass\ \text{of solution}} \cdot 100\ \%,$$

$$\text{w, \%} = \frac{25\ g}{512\ g} \cdot 100\ \% = 4.88\ \%.$$

Example 5.6. How would you prepare a 0.5 M aqueous solution of NH_4Cl?

Solution: 0.5 M solution is a 0.5 molar solution and its molarity is 0.5 mol/L. The molar mass of NH_4Cl is 53.5 g/mol.

$$\text{m}\ (NH_4Cl) = \text{M}\ (NH_4Cl) \times 0.5\ \text{mol} = 53.5 \frac{g}{mol} \times 0.5\ mol = $$
$$= 26.75\ g$$

Weigh out 26.75 g (0.5 mol) of salt, and dissolve it in a sufficient amount of water so that the final volume of the solution is one liter. The dilution is done in a calibrated volumetric flask to contain 1000 mL.

Example 5.7. How many moles of solute are contained in 3.0 L of a 1.8 M solution?

Solution: $C_M = \frac{\text{n (solute)}}{\text{V (solution)}}$, $1.8 = \frac{\text{n (solute)}}{3.0}$,

$$\text{n (solute)} = 5.4 \text{ mol.}$$

Example 5.8. What volume of a 2.0 M solution will 0.5 mol of solute contain?

Solution: $2 = \frac{0.5}{\text{V (solution)}}$, $\text{V (solution)} = 0.25 \text{ L.}$

Example 5.9. What will be the molarity of a NaCl solution in which 175.5 g of NaCl is dissolved in 750 mL of solution?

Solution: Since molarity is defined as the number of moles per liter of solution, we must first calculate the number of moles in 175 g of NaCl, then convert 750 mL to liters, and finally calculate C_M:

$$\text{Molar mass of NaCl} = 58.5 \text{ g,}$$
$$\text{n(NaCl)} = 175 \div 58.5 = 3 \text{ mol NaCl,}$$
$$750 \text{ mL} = 0.75 \text{ L,}$$
$$C_M = \frac{3 \text{ mol}}{0.75 \text{ L}} = 4 \frac{\text{mol}}{L} = 4 \text{ M.}$$

Example 5.10. Calculate the molar concentration of a solution where the mass percent of HNO_3 is 25 %, and the density of the solution is 1.151 g/ml.

Solution: Since the volume was not given, you can start with any volume you wish. The molarity will be the same, both for 1 ml and 1000 ml.

1) Calculate the mass of solution:

$$\text{m (solution)} = \text{V (solution)} \cdot \text{density of solution;}$$

$$\text{m (solution)} = \text{V (solution)} \cdot \rho \text{ (solution)};$$

$$\text{m(solution)} = 100 \text{ mL} \cdot 1.151 \text{ g/mL} = 1151 \text{ g}.$$

2) Calculate the mass of solute HNO_3:

$$\text{m(solute)} = \frac{w, \% \cdot \text{m(solution)}}{100\ \%};$$

$$\text{m } (\text{HNO}_3) = \frac{25\ \% \cdot 1151\ g}{100\ \%} = 287.5 \text{ g}.$$

3) Calculate the number of moles of HNO_3 solute:

$$\text{n (solute)} = \frac{\text{m(HNO}_3)}{\text{M (HNO}_3)};$$

$$\text{M (HNO}_3) = 1 + 14 + 16 + 3 = 63 g/mol,$$

$$\text{n (solute)} = \frac{287.5\ g}{63 g/mol} = 4.57\ mol.$$

4) Calculate the molarity (C_M):

$$C_M = \frac{4.57\ mol}{1\ L} = 4.57\ mol/L.$$

Example 5.11. How would you prepare a 0.5 M aqueous solution of NH_4Cl?

Solution: Weigh out 26.75 g of salt (0.5 mol), and dissolve it in 1 kg (1000 g) of solvent (water).

Example 5.12. 500 ml of solution contains 9.8 g of H_2SO_4. Calculate the normality (the equivalent molar concentration). Solution:

$$Eq. mass\ of\ H_2SO_4 = \frac{98}{2} = 49\ g/mol,$$

$$\text{Moles of solute equivalent} = \frac{9.8\ g}{49\ g/mol} = 0.2 mol,$$

$$C_N = \frac{\text{n (solute equivalent)}}{V(solution)} = \frac{0.2\ mol}{0.5\ L} = 0.4\ mol/L.$$

For any neutralization reaction, the following relationship (Law of equivalents) is true:

$$C_N\ (\text{acid}) \times \text{V}(\text{acid}) = C_N\ (\text{base}) \times \text{V}\ (\text{base})$$

Example 5.13. Calculate normality of 21 % H_2SO_4 solution with a density of 1.150 g/mL, and the mass of solution equal 1000 g.
Solution:

$$\text{m (solute)} = \frac{\text{m (solution)} \cdot \text{w,\%}}{100\%};$$

$$\text{m(solute)} = \frac{1000\ g \cdot 21\%}{100\%} = 210\ g.$$

$$Eq.\text{ mass of } \text{H}_2SO_4 = \frac{98}{2} = 49\ g/mol,$$

$$\text{n (solute equivalent)} = \frac{\text{m(H}_2SO_4)}{\text{Eq. mass of H}_2SO_4},$$

$$\text{n (solute equivalent)} = \frac{210\ g}{49\ g/mol} = 4.29\ mol.$$

$$\text{V (solution)} = \frac{\text{m(solution)}}{\rho\ \text{(solution)}} = \frac{1000\ g}{1.150\,\frac{g}{ml}} = 869.6\ ml = 0.869\ L.$$

$$C_N = \frac{n\ (solute\ equivalent)}{\text{V (solution)}} = \frac{4.29\ mol}{0.869\ L} = 4.94\frac{mol}{L}.$$

Or another variant:

$$\text{n (solute)} = \frac{\text{m(H}_2SO_4)}{\text{M(H}_2SO_4)} = \frac{210\ g}{98\ g/mol} = 2.14\ mol,$$

$$\text{n (solute equivalent)} = \frac{210\ g}{49\ g/mol} = 4.29\ mol.$$

$$f_{eq} = \frac{1}{n} = \frac{1}{2},$$

$$C_N = \frac{n\ (solute)}{f_{eq}\times \mathrm{V\ (solution)}} = \frac{2.14\ mol}{\frac{1}{2}\times 0.869\ L} = 4.94\frac{mol}{L}.$$

Theoretical questions

1. What is solution?
2. What components of the solution are compulsory?
3. What are a solvent and a solute? Is water always a solvent for solutions containing water?
4. What is a concentrated solution and a dilute solution?
5. Give examples of liquid, solid, and gaseous solutions?
6. What processes proceed in dissolution?
7. What is the solubility?
8. Name factors that influence the solubility of substances.
9. What solutions are named: saturated, unsaturated, and supersaturated?
10. Give definitions of the following terms: mass percent, molarity, molality, normality, and mole fraction.
11. What formulas are used to calculate the mass percent, molarity, molality, normality, and mole fraction?

Exercises for practice

1. Calculate the concentration of the following solutions in percent by the mass:
    a) 40 g $CaCl_2$ in 160 g H_2O;
    b) 15 g of ethyl alcohol in 175 g H_2O;
    c) 60 g NaCl in 40 g H_2O;
    d) 54 g of glucose in 96 g H_2O.
2. How much of each compound is present in the following solutions:
    a) 25 g of a 4.5 % solution of glucose;
    b) 125 g of a 5 % solution of ammonium sulfate;
    c) 63 g of a 1.2 % solution of insulin?

3. How much of 5 % NaCl solution can be prepared from 5 g of NaCl?
4. Given is 200 g of 5 % solution of NaCl. Add 250 g of 2 % solution of NaCl. Calculate percent by mass concentration of NaCl.
5. How would you prepare the following aqueous solutions:
    a) 50 g of 10 % ethanol solution;
    b) 250 g of 85 % solution?
6. How many grams and moles of KCl are contained in 25 g of 3 % KCl solution?
7. Calculate the number of moles of glucose contained in 55 g of 12 % aqueous solution.
8. Calculate the molarity of the following solutions:
    a) 0.25 mol H_2SO_4 in 1.2 L;
    b) 0.12 mol NaCl in 0.65 L;
    c) 2.3 mol $NaHCO_3$ in 1.8 L;
    d) 0.175 mol HCl in 0.084 L;
    e) 3.5 g $K_2Cr_2O_7$ in 1.2 L of the solution;
    f) 152 g $C_6H_{12}O_6$ in 750 mL;
    g) 48 g $BaCl_2$ in 3 L of the solution.
9. Calculate the number of moles in each of the following solutions:
    a) 35 mL of 1.5 M $CaCl_2$ solution;
    b) 1.2 L of 0.56 M KNO_3 solution;
    c) 0.435 L of 0.45 M LiCl solution;
    d) 74.2 mL of 0.252 M $NaHCO_3$ solution.
10. Calculate the grams of solute, which is present in each of the following solutions:
    a) 2.5 L of 0.5 M NaCl;
    b) 425 mL of 0.65 M $Mg(NO_3)_2$;
    c) 600 mL of 1.6 M K_2CO_3.
11. How would you prepare a 0.5 M aqueous solution of NH_4Cl?
12. What is the mass of 124 ml of a solution with has a density of 1.13 g/ml?

13. The commercial concentrated sulfuric acid is 94 % H_2SO_4 at a density of 1.831 g/mL. What is the molarity of this solution?
14. Calculate the molality of the following solutions:
    a) 0.5 mol glucose in 0.5 kg H_2O;
    b) 9.4 g C_6H_5OH in 200 g H_2O;
    c) 11.5 g C_2H_5OH in 125 g H_2O;
    d) 200 g NaCl in 2.0 kg H_2O.
15. How many grams of iodine, (I_2), must be dissolved in 125 ml of carbon tetrachloride, (CCl_4, density 1.595 g/ml) to produce a 0.158 m I_2 solution?
16. An aqueous solution of hydrofluoric acid, 30 % HF by mass, has a density of 1.101 g/ml. What are the molality and molarity of HF in this solution?
17. A solution contains 1g of naphthaline ($C_{10}H_8$), in 44g of benzene (C_6H_6). What is the mass percent of $C_{10}H_8$ in this solution?
18. Calculate the molarity and normality of a solution containing 9.8 g of H_2SO_4 in 250 mL of the solution.
19. Calculate the mole fraction of ethanol and water in a sample of rectified spirit, which contains 95 % ethanol by mass.
20. Calculate the molality and mole fraction of the solute in an aqueous solution containing 3g of urea (molar mass=60g/mol) per 250 g of water.
21. A solution contains 22 g CH_3COOH and 118 g H_2O; a density is 1.014 g/ml. Calculate the mass percent, molarity, molality, normality and the mole fraction of CH_3COOH.

Questions for self-testing

For each of 1–20 questions, choose one correct, lettered answer.

1. A solution containing 15.0 % by mass of magnesium nitrate $Mg(NO_3)_2$. Calculate how many grams of $Mg(NO_3)_2$ are dissolved in 250 g of the solution.

   a) 37.5 b) 0.06 c) 16.7 d) 15

2. 10 g of magnesium nitrate (Mg $(NO_3)_2$ are dissolved in 200 g of a solution. Calculate mass percent concentration of this solution.

a) 10 b) 5 c) 20 d) 15

3. A solution contains 10.0 % by mass of sodium hydroxide (NaOH). Calculate how many grams of NaOH are dissolved in 150 g of the solution.
   a) 10 b) 20 c) 15 d) 30
4. 100 g of hydrochloric acid (HCl) are dissolved in 500 g of a solution. Calculate mass percent of this solution.
   a) 10 b) 100 c) 0.2 d) 20
5. A solution contains 20.0 % by mass nitric acid (HNO_3). Calculate how many grams of HNO_3 are dissolved in 250 g of the solution.
   a) 50 b) 20 c) 25 d) 10
6. 10 g of sulfuric acid (H_2SO_4) are dissolved in 50 g of a solution. Calculate mass percent of this solution.
   a)10 b) 20 c) 60 d) 0.5
7. A solution contains 38.0 % by mass of hydrochloric acid (HCl). Calculate how many grams of HCl are dissolved in 200 g of the solution.
   a) 38 b) 19 c) 76 d) 7.6
8. 5 g of sodium chloride (NaCl) are dissolved in 100 g of a solution. Calculate mass percent of this solution.
   a) 10 b) 0.5 c) 15 d) 5
9. A solution contains 25.0 % by mass of calcium nitrate ($Ca(NO_3)_2$). Calculate how many grams of $Ca(NO_3)_2$ are dissolved in 200 g of the solution.
   a) 50 b) 25 c) 8 d) 0.125
10. 15 g of potassium hydroxide (KOH) are dissolved in 150 g of a solution. Calculate mass percent of this solution.
    a) 10 b) 20 c) 0.15 d) 15
11. How many moles of solute are in 5 L of a 0.5 M solution?
    a) 2.5 b) 0.5 c) 5 d) 1
12. How many moles of solute are in 3 L of a 0.3 M solution?
    a) 1 b) 0.9 c) 0.3 d) 3

13. 98 g of sulfuric acid (H_2SO_4) are dissolved in 1 L of a solution. Calculate molarity of this solution (molar mass of H_2SO_4 is 98 g/mol)

a) 2 b) 0.5 c) 1 d) 98

14. 40 g of sodium hydroxide (NaOH) are dissolved in 2 L of a solution. Calculate molarity of this solution (molar mass of NaOH is 40 g/mol)

a) 1 b) 40 c) 2 d) 0.5

15. 36.5 g of hydrochloric acid (HCl) are dissolved in 1 litre of a solution. Calculate molarity of this solution (molar mass of HCl is 36.5 g/mol)

a) 1 b) 2 c) 0.5 d) 36.5

16. The molarity of sulfuric acid (H_2SO_4) solution is 1 M. Calculate mass of sulfuric acid (H_2SO_4) in 1 litre of the solution (molar mass of H_2SO_4 is 98 g/mol)

a) 49 b) 98 c) 1 d) 2

17. The molarity of sodium hydroxide (NaOH) solution is 2 M. Calculate the mass of sodium hydroxide (NaOH) in 2 litres of the solution (molar mass of NaOH is 40 g/mol)

a) 40 b) 20 c) 80 d) 10

18. The molarity of nitric acid (HNO_3) solution is 1 M. Calculate the mass of nitric acid (HNO_3) in 0.5 litre of the solution (molar mass of HNO_3 is 63 g/mol)

a) 63 b) 126 c) 6.3 d) 31.5

19. The molarity of potassium hydroxide (KOH) solution is 1 M. Calculate the mass of potassium hydroxide (KOH) in 1 litre of the solution (molar mass of KOH is 56 g/mol)

a) 56 b) 112 c) 28 d) 14

20. 98 g of sulfuric acid H_2SO_4 are diluted to a volume of 2 litres. Determine the molar concentration of the acid in the solution (molar mass of H_2SO_4 is 98 g/mol)

a) 1 b) 2 c) 4 d) 0.5

5.3. Colligative Properties of Solutions

Colligative properties are the properties of solutions that depend only on the number of particles of a solute in a definite amount of the solvent and do not depend on the nature of the solute.

There are four colligative properties:

1. Relative lowering of the saturated vapor pressure of a solvent above a solution (the first Raoult's law).
2. Boiling point elevation of the solution compared with that of the pure solvent (the second Raoult's law).
3. Freezing point depression of the solution compared with that of the pure solvent (the second Raoul's law).
4. Osmotic pressure.

Vapor Pressure of Solutions. Raoult's law

At a certain temperature the pressure of the saturated vapor above any liquid is constant. The saturated vapor pressure of the solvent above the solution is always lower than that above the pure solvent at the same temperature. The difference between these values is called **the vapor pressure lowering over the solution**.

The Raoult's law: The relative depression of the saturated vapor pressure of the solvent above the solution equals the mole fraction of the solute.

The mathematical expression of the first Raoult's law is:

$$\frac{P_o - P_s}{P^o} = \frac{n_2}{n_1 + n_2},$$

Where P^o – vapor pressure of the solvent;

P_s – vapor pressure of the solution;

n_2 – number of moles of the solute;

n_1 – number of moles of the solvent;

$\frac{n_2}{n_1+n_2}$ – mole fraction.

Freezing point depression and boiling point elevation of solutions

Individual substances are characterized by strictly definite temperatures of their transitions from one state to another (the boiling point and the melting or freezing point). For example, water at standard atmospheric pressure (101.3 kPa, 1 atm, 760 mm of Hg) freezes at a temperature of 0^oC and boils at 100 ^oC. The presence of a solute raises the boiling point and lowers the freezing point of the solvent.

The difference between the boiling point of a solution and that one of the pure solvent is called the elevation in the boiling point of the solution (ΔT_b):

$$\Delta T_b = T_{b\ solution} - T_{b\ solvent}.$$

The extent of the boiling point elevation is given by the equation

$$\Delta T_b = E \times C_m,$$

where ΔT_b – the temperature value of the boiling point rise in degrees Kelvin;

E – the ebullioscopic constant characteristic of the solvent, (for water E = 0.52 kg·K/mol; for benzene E = 2.57 kg·K/mol);

C_m – the molal concentration (the molality), mol/kg.

The difference between the freezing point of the pure solvent and that one of the solution is called **the freezing point depression of the solution** (ΔT_f):

$$\Delta T_f = T_{\text{f solvent}} - T_{\text{f solution}}.$$

The extent of freezing point depression is given by the equation

$$\Delta T_f = K \times C_m,$$

where ΔT_f – the freezing point depression of the solution (K);

K – the cryoscopic constant characteristic of the solvent, (for water K = 1.86 kg·K/mol; for benzene K = 5.12 kg·K/mol);

C_m – the molal concentration (the molality), mol/kg.

The second Raoult's law For dilute solutions of non-electrolytes, the elevation of the boiling point and the depression of the freezing point are proportional to the molal concentration of the solution.

Osmosis and osmotic pressure

Osmosis is defined as the physical process of diffusion of a solvent (water) through a ***semi-permeable membrane*** (a membrane which allows the solvent molecules to pass through, but not the solute particles) towards an area of high solute (salt) concentration. This means that solvent (water) follows the osmotic gradient by moving across the semi-permeable membrane from one solution where there is a lower salt concentration towards a second solution with a high salt concentration in order to dilute this and to equalize the concentrations.

This process, known as ***osmosis,*** is shown in Figure 5.1.

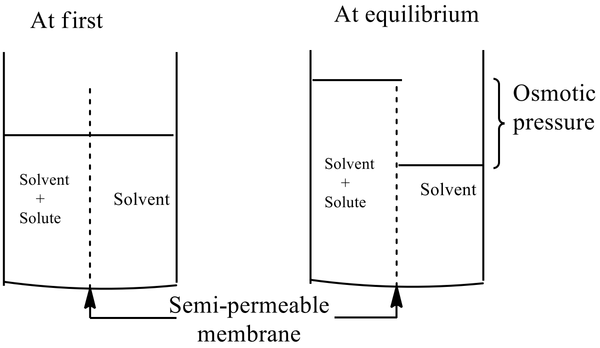


Figure 5.1 – The osmotic pressure of pure solvent snd solution

Osmotic pressure (π) is the pressure that must be applied to a solution when separated from a more dilute solution by a semipermeable membrane, in order to prevent the inflow of a solvent.

In 1886, J. H. Can't Hoff showed that for solutions of nonelectrolytes with moderate concentrations, the dependence of the osmotic pressure on the concentration and temperature of the solution is expressed by the equation.

$$\pi = C_M RT,$$

where π – the osmotic pressure, Pa;

C_M –the molar concentration (molarity), mol/L;

R – the molar gas constant, 8.314×10^3 L·Pa/mol×K ($8.314 J/mol \cdot K$);

T – the temperature, K.

The phenomenon of osmosis plays a very important role in the life of animal and vegetable organisms. The cell envelopes may be defined as the cell membranes that are permeable for water, but almost impermeable for the substances which dissolve in the liquid inside the cells.

The osmotic pressure of human blood is 700–800 kPa. Solutions that have identical osmotic pressure (and equal molar concentrations, of course) are called **isotonic** solutions. 0.9 % solution of NaCl and 5 % solution of glucose are isotonic regarding blood. Solutions with high osmotic pressure are **hypertonic**, and those having a low osmotic pressure are called **hypotonic**.

If placing a living cell to the isotonic solution, it will not change, as the osmotic pressure inside and outside of it will be the same**.** ***Plasmolysis*** will occur if we place a cell to the hypertonic solution as water molecules will pass from the cell to the more concentrated solution, and the cell becomes smaller (shrinks). In a hypotonic solution, ***hemolysis*** of the cells takes place, since water molecules pass from the external solution to the cell as a result of osmosis. The cells grow, swell, and can be destroyed.

Electrolytes have a more pronounced effect on colligative properties than nonelectrolytes do. This is because electrolytes decompose into ions so that the total number of particles in solution grows. And since the colligative properties depend on the number of solute particles per unit volume of the solution, when this number increases, they also grow. For example, Sodium chloride passes into a solution in the form of the ions Na^+ and Cl^-. From one mole of NaCl we get twice the number of 6.02×10^{23} particles. Hence, the depression freezing point or any other colligative property of a NaCl solution must be double, as compared to a solution of a nonelectrolyte having the same concentration. ΔT_b, ΔT_f, P for electrolyte solutions are so many times as much as the number of particles in the electrolyte solution. **Isotonic coefficient (i)** is used for calculation in the electrolyte solution: **i** is equal to the number of ions, which the substance dissociated to. For example, i for NaCl is 2, for $BaCl_2$ is 3, for $AlCl_3$ is 4, for $C_6H_{12}O_6$ is 1, and glucose is non-electrolyte.

So, for the electrolyte solutions:

$$\Delta T_b = i \times E \times C_m,$$
$$\Delta T_f = i \times K \times C_m,$$
$$P = i \times C_m \times R \times T,$$
$$i = \alpha(n-1)+1,$$

where n – number of ions.

Examples of solving tasks:

Example 5.14. An aqueous solution of sucrose is made by dissolving 13.66 g of sucrose ($C_{12}H_{22}O_{11}$) in 90 g of water at 65°C. If the vapor pressure of pure water at 65°C is 25.0 kPa, what would be the vapor pressure of the solution? (Molar mass of $C_{12}H_{22}O_{11}$ =342g/mol).

Solution: $\frac{P_o-P_s}{P_o} = \frac{n_2}{n_1+n_2}$,

P_o = 25 kPa,

$$n_1 = \frac{\text{mass of } H_2O}{\text{molar mass of } H_2O} = \frac{90\ g}{18\ g/mol} = 5\ mol,$$

$$n_2 = \frac{\text{mass of } C_{12}H_{22}O_{11}}{\text{molar mass of } C_{12}H_{22}O_{11}} = \frac{13.66\ g}{342\ g/mol} = 0.0399\ mol,$$

$$\frac{25-P_s}{25}=\frac{0.0399}{5+0.0399}, \quad \frac{25-P_s}{25}=0.0079,$$

$25\text{-}P_s=0.0079 \times 25,$

$P_s=25\text{-}0.1975=24.8$ kPa.

Ans.: The vapor pressure of the solution is 24.8 kPa.

Example 5.15. 54 g of glucose were dissolved in 0.9 L of H_2O. Calculate the boiling point and the freezing point if M(glucose) = 180 g/mol.

Solution: $\Delta T_b = E \times C_m$, $\Delta T_f = K \times C_m$,

$E(H_2O) = 0.52^oC \times kg/mol$, $\mathrm{K}(H_2O) = 1.86^oC \times kg/mol,$

$m(H_2O) = V(H_2O) = 0.9\ kg,$

$$C_m = \frac{v}{m(solvent)} = \frac{m(glu\cos e)}{M \times m(solvent)} = \frac{54\ g/mol}{180\ g/mol \times 0.9kg}$$

$$= 0.33\ mol/kg,$$

$\Delta T_b = 0.52 \times 0.33 = 0.17\ ^0C,$

$\Delta T_f = K \cdot C_m = 1.86 \times 0.33 = 0.62\ ^0C,$

$T_b(H_2O) = 100\ ^0C = 373\ K,$

$T_f(H_2O) = 0\ ^0C = 273\ K,$

$\Delta T_b = T_{b\ \mathrm{solution}} - T_{b\ \mathrm{solvent}},$

$0.17 = T_{b\ \mathrm{solution}} - 373,$

$T_{b\ \mathrm{solution}} = 373 + 0.17 = 373.17\ K = 100.17\ ^oC,$

$\Delta T_f = T_{\mathrm{f\,solvent}} - T_{\mathrm{f\,solution}},$

$0.62 = 273 - T_{\mathrm{f\,solution}},$

$T_{\mathrm{f\,solution}} = 273 - 0.62 = 272.38\ K = -0.62\ ^0C.$

Example 5.16. Calculate the osmotic pressure of 0.01 M solution of cane-sugar at 27°C.

Solution: $C_M = 0.01$ mol/L, T = 273 + 27 = 300 K,

R = 8.314 kPa,

$\Pi = C_M RT = 0.01 \times 8{,}314 \times 300 = 2.49$ kPa

Example 5.17. 18 g of a glucose were contained in 500 ml of solution at 27°C. Calculate the osmotic pressure of $M(C_6H_{12}O_6)$ = 180 g/mol.

Solution:

$$\pi = C_M RT,$$
$$C_M = \frac{\nu}{V} = \frac{m}{M \cdot V},$$
$$C_M = \frac{18\ g}{180\ g/mol \times 0.5\ L} = 0.2\ mol/L,$$
$$\pi = 0.2 \times 8.314 \times (27 + 273) = 498.84\ kPa$$

Example 5.18. A solution containing 63.3 g/L of hemoglobin has an osmotic pressure of 243.4 kPa at 20°C. `Calculate the molar mass of hemoglobin.

Solution:

$$\pi = C_M RT \Rightarrow C_M = \frac{\pi}{RT},$$
$$C_M = \frac{243.4}{8.31 \times 293} = 0.1\ mol/L,$$
$$C_M = \frac{\nu}{V} = \frac{m}{M \cdot V},$$
$$M = \frac{m \cdot V}{C_M} = \frac{63.3 \cdot 1}{0.1} 633\ g/mol.$$

AnsMolar mass of hemoglobin = 633 $\frac{g}{mol}$.

Example 5.19. 4.57 g of $C_{12}H_{22}O_{11}$ were dissolved in 100 g of H_2O. Density of solution = 1 g/mL. Calculate:

a) the osmotic pressure at 293 K;

b) the boiling point, if E_{H_2O} = 0.52, $T_b(H_2O)$ = 100°C;

c) the freezing point, if K_{H_2O} = 1.86, T_f (H_2O) = 0°C;

d) the vapor pressure of the solution at 293 K, if the vapor pressure of pure water at 293 K is 2.337 kPa.

Solution:

a) $\pi = C_M RT;\ \ C_M = \frac{\nu}{V} = \frac{m(C_{12}H_{22}O_{11})}{M(C_{12}H_{22}O_{11}) \times V};$

$$M(C_{12}H_{22}O_{11}) = 342 \frac{g}{mol}.$$

$$V_{solution} = \frac{m}{\rho}, \ \ \mathrm{m}_{solution} = m(H_2O) + m(C_{12}H_{22}O_{11})$$

$$= 100 + 4.57 = 104.57\ g;$$

$$V_{solution} = \frac{104.57\ g}{1g/ml} = 104.57\ ml = 0.105\ L.$$

$$\pi = \frac{m(C_{12}H_{22}O_{11})RT}{M(C_{12}H_{22}O_{11})V},$$

$$\pi = \frac{4.57 \times 8.31 \times 293}{342 \times 0.105} = 309.8\ kPa.$$

b) $\Delta T_b = E \times C_m$;

$$C_m = \frac{v}{m(solvent)} = \frac{m(C_{12}H_{22}O_{11})}{M(C_{12}H_{22}O_{11}) \times m(solvent)},$$

$$C_m = \frac{4.57\ g}{342\ g/mol \times 0.1\ kg} = 0.134\ mol;$$

$\Delta T_b = 0.52 \times 0.134 = 0.069 = 0.07\ ^oC,$
$T_b = 100 + 0.07 = 100.07\ ^oC.$

c) $\Delta T_f = K \times C_m,$
$\Delta T_f = 1.86 \times 0.134 = 0.25\ ^oC,$
$T_f = 0\ ^oC - 0.25 - 0.25\ ^oC$

d) $\frac{\mathrm{P_o - P_s}}{\mathrm{P_o}} = \frac{\mathrm{n_2}}{\mathrm{n_1 + n_2}}$;

$$n_1(H_2O) = \frac{100\ g}{18\ g/mol} = 5.556\ mol;$$

$$n_2(C_{12}H_{22}O_{11}) = \frac{m}{M} = \frac{4.57\ g}{342\ g/mol} = 0.013\ mol,$$

$$\frac{2.337 - P_s}{2.337} = \frac{0.013}{0.013 + 5.556},$$

$$\frac{2.337 - P_s}{2.337} = 0.002,$$

$2.337 - P_s = 0.005,$
$P_s = 2.337 - 0.005 = 2.33\ kPa.$

Theoretical questions

1. What determines the colligative properties? Name them.
2. Define the osmotic pressure.
3. What is Raoult's law? Give its mathematical expression.

Exercises for practice

1. What is the boiling point of 10 % $C_6H_{12}O_6$ solution? $K_b(H_2O) = 0.52°C\ kg/mol$.
2. What is the freezing point of an aqueous solution containing 20 g of $C_{12}H_{22}O_{11}$ in 400 g of water?
3. What mass of CH_3OH must be added to 5.00 kg of water to lower the freezing point to – 3? CH_3OH is a nonelectrolyte; $K_b(H_2O) = 1.86\ {}^0C \cdot kg/mol$.
4. Depression in freezing point of nonelectrolyte solution containing 29.5 g of substance in 100 g of water is 1.6 K. Calculate the molar mass of the substance.
5. Calculate the molar mass of hemoglobin if the osmotic pressure of hemoglobin in water containing 124 g/L of a substance equals 4.4 kPa at 17 ^oC .
6. What is the osmotic pressure of a 0.9 % solution of NaCl at 25^oC ?
7. Calculate the osmotic pressure at 0 ^oC of an aqueous solution containing 18.4 g of $C_3H_8O_3$ in 1 L of water.
8. Calculate the osmotic pressure at 25 of an aqueous solution containing 18 g of glucose ($C_6H_{12}O_6$) in 500 ml of water.
9. What is the expected vapor pressure at 25 ^oC for a solution prepared by dissolving 158 g of sucrose ($C_{12}H_{22}O_{11}$) in 1800 g of water? A vapor pressure of pure water 25 ^oC is at 3168 Pa.
10. What is the boiling point of an aqueous solution containing 468 g of sucrose ($C_{12}H_{22}O_{11}$) in 350 g of water?

$K_b(H_2O) = 0.52\ ^0C\ kg/mol$, normal boiling temperature of water =100 °C.

5.4. Aqueous Solutions of Acids, Bases and Salts

The first theory of acids and bases was proposed by Svante Arrhenius. His idea is that an **acid** is a substance that forms hydrogen ions, H^+, in aqueous solutions. A **bases** is a substance that forms hydroxide ions, OH^-, when dissolved in water.

$$HCl \rightleftarrows H^+ + Cl^-, \qquad NaOH \rightleftarrows Na^+ + OH^-.$$

A Bronsted-Lowry acid is a hydrogen ion donor (proton donor). A Bronsted-Lowry base is a hydrogen ion acceptor (proton acceptor). According to the theory of electrolytic dissociation (S. Arrhenius, 1887), when electrolytes dissolve in water, they decompose (dissociate) into positively charged ions (cations) and negatively charged ions (anions).

For example, $AlCl_3 \rightleftarrows Al^{3+} + 3Cl^-$.

Compounds whose aqueous solutions do not conduct electricity are called **nonelectrolytes**.

Aqueous or molten substances that will conduct an electric current and are decomposed into ions are called **electrolytes**. They include salts, acids, and bases.

S. Arrhenius introduced the concept of the degree of dissociation.

The degree of dissociation (α) of an electrolyte is 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.

The degree of dissociation is designated by the Greek letter α and is customarily expressed either in unit fractions or as a percentage.

Electrolytes are divided into two groups: strong and weak ones. In a strong electrolyte solution $\alpha = 1$. For a weak electrolyte, for example, 0.1 N solution of CH_3COOH, $\alpha = 0.013$ (or 1.3 %).

Salts are strong electrolytes. Salts always completely dissociated in water. For example, $NaCl \rightleftarrows Na^+ + Cl^-$, $Al_2(SO_4)_3 \rightleftarrows$

$2Al^3 + 3SO_4^{2-}$.

Acids and bases that completely dissociate in water are called strong acids or bases (**strong electrolytes**).

For example, $HCl \rightleftarrows H^+ + Cl^-$. HCl is the strong acid, which completely dissociates in aqueous solution to form H^+ and Cl^-.

There are only a few strong acids and bases. The names and formulas of all strong acids and bases are listed below:

$HClO_4$ – Perchloric acid
HNO_3 – Nitric acid
H_2SO_4* – Sulfuric acid
HCl – Hydrochloric acid
HBr – Hydrobromic acid
HI – Hydroiodic acid

LiOH – Lithium hydroxide
NaOH – Sodium hydroxide
KOH – Potassium hydroxide
RbOH – Rubidium hydroxide
CsOH – Cesium hydroxide
$Ca(OH)_2$– Calcium hydroxide
$Sr(OH)_2$–Strontium hydroxide
$Ba(OH)_2$ – Barium hydroxide

*Note: Only the first proton in sulfuric acid is completely dissociable. The first product of the dissociation, HSO_4^-, is a weak acid.

All inorganic acids that are not listed above are weak acids. All organic acids (RCOOH) are weak acids.

Acids and bases that partially dissociate in water are called weak acids or bases (**weak electrolytes**).

For example, $NH_4OH \rightleftarrows NH_4^+ + OH^-$, NH_4OH is a weak base. When dissolved in water, it produces OH^- ions, but the OH^- concentration is considerably lower than the NH_4OH concentration.

For weak acids and bases, dissociation is the reversible process and can be characterized by the **equilibrium constant**.

The constant equilibrium corresponding to the dissociation of a weak electrolyte is known as **the dissociation (or ionization) constant**.

In case of the weak acid, for example, acetic acid, CH_3COOH, the equilibrium constant is called the **acid dissociation constant K_a**, and for the dissociation reaction $CH_3COOH \rightleftarrows H^+ + CH_3COO^-$ the equilibrium constant expression is $K_a = \frac{[H^+]\times[CH_3COO^-]}{[CH_3COOH]}$.

The dissociation process for the weak base NH_4OH is written as $NH_4OH \rightleftarrows NH_4^+ + OH^-$, and the equilibrium constant expression is $K_b = \frac{[NH_4^+]\times[OH^-]}{[NH_4OH]}$. The term **$K_b$** means the **base dissociation constant**.

The K_a and K_b values indicate the extents of dissociation of weak acids and bases. The larger the constants, the stronger the acid or base.

The dissociation constants must be determined experimentally. K_a (CH_3COOH)= $1.8\cdot10^{-5}$, K(CH_3COOH) is higher than K_{HCN}, HCN hydrocyanic K_a = $4\cdot10^{-10}$, (HCN is a weaker acid than CH_3COOH), CH_3COOH is stronger than HCN.

The value of K_a depends on the nature of the electrolyte and the solvent as well as on the temperature, but does not depend on the concentration of the solution.

If we denote the concentration of the electrolyte (NaCl), dissociating into two ions (Na^+ and Cl^-) by C, and the degree of its dissociation in the given solution by α, then the concentration of each of the ions will be Cα, and the concentration of the undissociated molecules will be C(1-α):

$$\begin{array}{ccc} NaCl & \rightleftarrows Na^+ & + Cl^- \\ C(1-\alpha) & C\alpha & C\alpha. \end{array}$$

The equation of the dissociation constant has the form

$$K = \frac{(C\alpha)\times(C\alpha)}{C(1-\alpha)} = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}.$$

This equation expresses **Ostwald's dilution law**.

For solutions, in which the dissociation of an electrolyte is very small, the equation of Ostwald's law is simplified. Since in these cases $\alpha \ll 1$, it has the form:

$$K \approx \alpha^2 C \text{ or } \alpha \approx \sqrt{\frac{K}{C}}.$$

This equation clearly shows the relationship existing between the concentration of a weak electrolyte and the degree of its dissociation: the dissociation degree increases upon the dilution of a solution. The values of the dissociation constant for electrolytes are given in Table 5.1.

The reaction of acids and bases is called a **neutralization reaction**.

Base + Acid = Salt + H_2O

Bases react with acids to form salts and water.

Formula equations for acids-base neutralization reactions can be written in molecular, ionic and net ionic forms:

molecular reaction: $NaOH + HCl = NaCl + H_2O$;

ionic reaction: $Na^+ + OH^- + H^+ + Cl^- = Na^+ + Cl^- + H_2O$;

net ionic reaction: $OH^- + H^+ = H_2O$.

A neutralization reaction simply involves the combination of hydrogen and hydroxide ions to form water.

Table 5.1 – Dissociation constant for selected electrolytes in aqueous solutions at 25 °C

Electrolyte	Dissociation of a compound	Dissociation constant (K)
1	2	3
Acetic acid	$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$	$\mathbf{1.8 \cdot 10^{-5}}$

Continuation of Table 5.1

1	2	3
Benzoic acid	$C_6H_5COOH \rightleftharpoons C_6H_5COO^- + H^+$	$\mathbf{6.4 \cdot 10^{-5}}$
Carbonic acid	$H_2CO_3 \rightleftharpoons HCO_3^- + H^+,$ $HCO_3 \rightleftharpoons CO_3^{2-} + H^+$	$\boldsymbol{K_1 = 4.5 \cdot 10^{-7}}$ $\boldsymbol{K_2 = 4.7 \cdot 10^{-11}}$
Hydrocyanic acid	$HCN \rightleftharpoons CN^- + H^+$	$\mathbf{6.2 \cdot 10^{-10}}$
Lactic acid	$CH_3CH(OH)COOH \rightleftharpoons$ $\rightleftharpoons CH_3CH(OH)COO^- + H^+$	$\mathbf{1.38 \cdot 10^{-4}}$
Citric acid	$HOOCCH_2C(OH)(COOH)CH_2COOH$	$\mathbf{7.5 \cdot 10^{-5}}$
Nitrous acid	$HNO_2 \rightleftharpoons NO_2^- + H^+$	$\mathbf{4 \cdot 10^{-4}}$
H_2O (water)	$H_2O \rightleftharpoons H^+ + OH^-$	$\mathbf{1.8 \cdot 10^{-16}}$
NH_4OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	$\mathbf{1.74 \cdot 10^{-5}}$
Hydro-chloric acid	$HCl \rightleftharpoons Cl^- + H^+$	$\mathbf{10^{7}}$
Nitric acid	$HNO_3 \rightleftharpoons NO_3^- + H^+$	$\mathbf{43.6}$
Sulfuric acid	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-,$ $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	$\boldsymbol{K_1 = 1000}$ $\boldsymbol{K_2 = 10^{-2}}$
Permanaganic acid	$HMnO_4 \rightleftharpoons MnO_4^- + H^+$	$\mathbf{200}$

5.5. Dissociation of Water. The pH Scale

Water is a very poor electrical conductor, yet the fact that it does conduct electric current feebly indicates that some ions are present.

The equation of dissociation of H_2O is $H_2O \rightleftarrows H^+ + OH^-$; in water solution H^+ exists as hydronium ion H_3O^+.

$$H_2O + H_2O \rightleftarrows H_3O^+ + OH^-.$$

In this process, H_2O molecule transfers a proton to another H_2O molecule.

The equilibrium constant expression for this process is

$$K_w = [H_3O^+] \times [OH^-] \text{ or } K_w = [H^+] \times [OH^-].$$

This equilibrium constant also has a special name: the **ion-product of water** K_w.

In pure water at 25^oC: $[H^+] = [OH^-] = 1.0 \times 10^{-7}$,

$$K_w = [H^+] \times [OH^-] = 10^{-7} \times 10^{-7} = 1.0 \times 10^{-14}.$$

The ion-product of water has a value of 1.0×10^{-14} at $25^\circ C$.

Acid solutions have a higher concentration of hydronium ions than 1.0×10^{-7} mol/L; basic solutions have a lower concentration than 1.0×10^{-7} mol/L.

These concentration numbers are extremely small. It is often inconvenient to work with them. In 1909 the chemist Sorensen proposed the pH scale. If a solution has $[H^+] = 10^{-x}$, pH = x. According to this scale, a concentration of 1×10^{-7} mol of H^+ per liter of the solution has expressed a pH of 7. Table 3.2 shows the relationship between the pH and the concentration of H^+.

The pH is the negative of the logarithm of $[H^+]$ $pH = -log[H^+]$

Concentration of H$^+$ (moles per liter)	pH
1×10^{0}	0
1×10^{-1}	1
1×10^{-2}	2
1×10^{-3}	3
1×10^{-4}	4
1×10^{-5}	5
1×10^{-6}	6
1×10^{-7}	7
1×10^{-8}	8
1×10^{-9}	9
1×10^{-10}	10
1×10^{-11}	11
1×10^{-12}	12
1×10^{-13}	13
1×10^{-14}	14

Solution	pH
Gastric juices	1.6 – 1.8
Lemon juice	
Vinegar	2.3
Soft drinks	2.4 – 3.4
Milk	2.0 – 4.0
Urine	6.3 – 6.6
Saliva	5.5 – 7.0
Pure ware	6.2 – 7.4
Blood	7
Fresh egg	7.35 – 7.45
Bile	7.6 – 8.0
	7.8 – 8.6

neutral
↓
1 2 3 4 5 6 7 8 9 10 11 12 13 14
← Acidic → ← Basic →

A pH of 7 is neutral. A pH below 7 is acidic. A pH above than 7 is basic.

The pOH is defined in a similar way to pH:

$$pOH = -log\left[OH^{\mp}\right] \text{ or } [OH^-] = 10^{-pOH}.$$

We can write the equilibrium constant for water in a new way:

$$-log\,K_w = -log[H^+] - log[OH^-] = -log[1 \times 10^{-14}],$$

$$pK_w = pH + pOH = 14,$$

$$pH + pOH = 14.$$

A pH value – is the measure of the active acidity of the medium.

During the biomedical researches, total and active acidities must be well differentiated, as the undissociated molecules of acids and hydrogen ions possess different physiological activity. For example, gastric juice contains many acids of different strength, but its acidity is defined only by hydrogen ions. Therefore, the results of the pH measurements and the titration of gastric juice will be quite different.

The total acidity can be defined by titration. The active acidity is equal to the total acidity for strong electrolytes because strong acid completely (100%) dissociates in solution to form H^+.

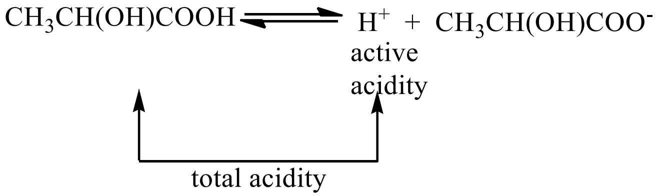
For example, $HCl \rightleftarrows H^+ + Cl^-$.

The concentration of H^+ is equal to the concentration of HCl.

$pH = -\log[H^+] = -\log C$, where C is the molarity.

For the strong base solution: $pOH = -log[\,OH^-] = -log\,C$.

Weak electrolyte partially dissociates in water. For example, acetic acid is a weak acid. After being dissolved in water it produces H^+ ions, but the H^+ concentration is considerably lower than the common concentration of an acid:



$$CH_3CH(OH)COOH \rightleftarrows H^+ + CH_3CH(OH)COO^-$$

To calculate pH of a weak acid solution, it is necessary to know besides the concentrations either the degree of the dissociation (α) or the dissociation constant (Ka):

$$pH = -\log C \cdot \alpha, \text{ or}$$

$$pH = -\log\sqrt{Ka \times C}.$$

For the weak base solution:

$$\text{pOH} = -\log \text{C} \times \alpha, \text{ or}$$

$$pH=-\log\sqrt{K_b \times C},$$

where α is the degree of dissociation (ionization) of the base;

K_b is the base dissociation (ionization) constant;

C is the molarity.

5.6. *Hydrolysis*

In pure water $[H^+] = [OH^-] = 1 \times 10^{-7}$. When NaCl is added to water, the solution remains neutral. When CH_3COONa is added to pure water, the solution becomes basic. When NH_4Cl is added to pure water, the solution becomes acidic:

$$NaCl + H_2O = \text{no reaction},$$
$$CH_3COONa + H_2O \rightleftarrows CH_3COOH + NaOH,$$
$$CH_3COO^- + Na^+ + HOH \rightleftarrows CH_3COOH + Na^+ + OH^-,$$
$$CH_3COO^- + HOH \rightleftarrows CH_3COOH + OH^-,$$
$$Na^+ + HOH = \text{no reaction}.$$

Water reacts with CH_3COO^- to produce OH^-. A solution of CH_3COONa has a pH>7.

A solution of NH_4Cl has a pH<7. The NH_4^+ ion hydrolyzes to produce H^+:

$$NH_4Cl \rightleftarrows NH_4^+ + Cl^-,$$
$$Cl^- + H_2O \rightleftarrows \text{no reaction},$$
$$NH_4^+ + H_2O \rightleftarrows H^+ + NH_4OH,$$
$$NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl.$$

This reaction, in which water reacts with ionic species in solution, is called **hydrolysis.**

Salts of strong acids and strong bases (for example, NaCl) do not hydrolyze pH=7.

Salts of weak acids and strong bases (for example, CH_3COONa) hydrolyze, producing a basic solution: pH>7.

Salts of strong acids and weak bases (for example, NH_4Cl) hydrolyze, producing an acidic solution: pH<7.

Salts of weak acids and weak bases (for example, CH_3COONH_4) will hydrolyze, but the acidity or basicity depends on the equilibrium constants of Ka and Kb. If the Ka value is greater than the Kb value, the resulting solution will be acidic and vice versa.

$$CH_3COONH_4 \rightleftarrows CH_3COO^- + NH_4^+,$$
$$CH_3COO^- + H_2O \rightleftarrows CH_3COOH + OH^-,$$
$$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+,$$
$$CH_3COONH_4 + H_2O \rightleftarrows CH_3COOH + NH_4OH,$$

$Ka(CH_3COOH) = 1.8 \times 10^{-5}$,
$Kb(NH_4OH) = 1.74 \times 10^{-5}$,
$Ka \approx Kb,$ neutral pH=7.

Examples of solving tasks:

Example 5.20. What is the pH of a solution that has H^+ concentration of 1×10^{-5} M?
Solution: $[H^+] = 10^{-5}, pH = -log[10^{-5}] = -(-5) = 5.$

Example 5.21. What is the concentration of H^+ ions in a solution that has a pH of 4?
Solution: The pH value is the negative exponent of 10, so $[H^+] = 1 \cdot 10^{-4}$, $[H^+] = 10^{-4}$ M.

Example 5.22. Calculate the concentration of H^+ ions of Coca-Cola if its pH is 2.5.
Solution:

$$pH = -log[H^+], \qquad 2.5 = -log[H^+],$$
$$[H^+] = 10^{-2.5}, \qquad [H^+] = 3.16 \times 10^{-3} M.$$

Example 5.23. Calculate $[H^+]$ and $[NO_3^-]$ of a 0.175 M solution of nitric acid HNO_3.
Solution: HNO_3 is a strong acid and, therefore, it dissociates in aqueous solution by 100%:

$$HNO_3 \overset{100\%}{\rightleftarrows} H^+ + NO_3^-,$$

Therefore, $[HNO_3] = [H^+] = [NO_3^-] = 0.175\ M.$

Example 5.24. Calculate $[OH^-]$ and $[Ca^{2+}]$ of a 0.01 M solution of $Ca(OH)_2$.

Solution: $Ca(OH)_2$ is a strong base, and therefore, it dissociates in aqueous solution by 100 %. Since, there are two mols of hydroxide ion per mole of $Ca(OH)_2$,

$$[OH^-] = 2 \times [Ca(OH)_2] = 2 \times 0.01 = 0.02\, M \text{ and } [Ca^{2+}] = \\ = [Ca(OH)_2] = 0.01\, M.$$

Example 5.25. What is the pH of 0.001 M solution of HCl?

Solution: HCl is a strong acid, therefore,

$pH = -\,log[\,H^+] = -\,log\,C = log[\,1 \cdot 10^{-3}] = 3.$

Example 5.26. Calculate the pH of a solution, if 500 ml of solution contain 2 g of NaOH.

Solution: NaOH is a strong electrolyte, and it dissociates in aqueous solution by 100 %.

$NaOH \rightleftarrows Na^+ + OH^-$,

therefore $[NaOH] = [Na^+] = [OH^-] = C_M(molarity)$,

$$molarity\ \mathrm{C}_M = \frac{\text{mass of NaOH}}{\text{Molar mass of NaOH} \cdot \text{Volume}},$$

$molar$ mass (NaOH)=23+16+1=40 g/mol,

$$C_M = \frac{2\,g}{40\,g/mol \cdot 0.5\,L} = 0.1\,mol/L,$$

$$[OH^-] = C_M = 0.1\,mol/L,$$

$$pOH = -\,lg[OH^-] = -\,lg\,0\,.\,1 = 1, pH = 14 - pOH = 14 - 1 \\ = 13.$$

Example 5.27. What is the pH of 0.1 M solution of CH_3COOH? Ka $CH_3COOH = 1.8 \times 10^{-5}$.

Ans.: CH_3COOH is a weak electrolyte, therefore,

$pH = -\log\sqrt{Ka \times C}\,,$

$$pH = -\log\sqrt{1.8 \times 10^{-5} \times 0.1} = -\log\sqrt{1.8 \times 10^{-6}} \\ = -\,log(\,1.34 \times 10^{-3}),$$

$pH = 3 - log\,1\,.\,34 = 2.88.$

Theoretical questions

What is acid? Give examples.

What is the base? Give examples.
What is an electrolyte?
What is called “the strong acid or base”? Give examples.
What is called “the weak acid or base”? Give examples.
What is the neutralization reaction?
Give the definition of the degree of dissociation and dissociation constant.
Write the equation that expresses W. Ostwald’s dilution law.
What is pH? Write the formula for pH calculation in acidic and basic solutions.
What is hydrolysis?

Exercises for practice

1. Write the equations for the dissociation of the following substances:
   $HCl, KOH, HNO_3, H_2SO_4, Fe(OH)_2, H_3PO_4, Ba(OH)_2, K_3PO_4, Ca(NO_3)_2, KCN, CH_3COONa, MgSO_3, H_2S.$
2. Write the dissociation constant of the following substances:
3. $HCN, Fe(OH)_2, H_3PO_4, CH_3COOH, H_2S.$
4. Write the molecular, ionic, and net ionic equations of the following reactions:
5. $Ba(OH)_2 + HNO_3 =$

$$Ca(OH)_2 + HCl =$$

6. Calculate [H$^+$] and [Br$^-$] of a 0.05 M solution of HBr acid.
7. Calculate the pH values of the following solutions:

a) 0.001 M HCl; b) 0.05 M NaOH; c) 0.05 M Ba(OH)$_2$; d) 0.002 M H$_2$SO$_4$; e) 0.5 M HCN, $K_a = 4\times10^{-4}$; f) 0.01 M HF, $K_a = 6.7\times10^{-4}$.

8. Calculate the concentration of hydrogen ions in the blood if pH = 7.35.
9. Calculate the [OH$^-$] in the solution of KOH if pH = 12.0.
10. Write the hydrolysis reactions for salts which undergo hydrolysis in the ionic and molecular forms:

$NH_4Cl, Al_2(SO_4)_3, KI, Na_2CO_3, CH_3COOK, Ca(NO_3)_2, NaNO_2, KCN, MgSO_3, MgSO_4, Co(NO_3)_2, NiSO_4, CdSO_4, SnCl_2.$

Predict whether aqueous solutions of these salts are acidic, neutral, or basic.

Questions for self-testing

For each of 10 questions, choose the correct answer and indicate it by the letter.

1. Calculate $[H^+]$ in 0.01 M HNO_3.
   a) 0.01 b) 0.1 c) 0.02 d) 0.005
2. Calculate $[H^+]$ in 0.01 M H_2SO_4.
   a) 0.01 b) 0.02 c) 0.005 d) 0.03
3. Calculate $[OH^-]$ in 0.1 M NaOH.
   a) 0.2 b) 0.3 c) 0.1 d) 0.05
4. Calculate $[OH^-]$ in 0.1 M $Ca(OH)_2$.
   a) 0.1 b) 0.2 c) 0.3 d) 0.4
5. What is the H^+ concentration of a solution that has a pH of 3?
   a) 3 b) 11 c) 10^{-11} d) 10^{-3}
6. What is the H^+ concentration of a solution that has a pH of ?
   a) 10^{-9} b) 10^{-5} c) 9 d) 5
7. What is the H^+ concentration of a solution that has a pH of 4?
   a) 4 b) 10^{-4} c) 10^{-10} d) 10
8. Calculate the pOH of a 0.01 M solution of KOH.
   a) 12 b) 14 c) 2 d) 10^{-2}
9. Calculate the pH of a 0.01 M solution of HCl.
   a) 12 b) 14 c) 2 d) 10^{-2}
10. Calculate pH of a solution that contains 0.00001 M HNO_3.
    a) 9 b) 10^{-9} c) 10^{-4} d) 5

5.7. Buffer Solution

Adding acid or base to a solution, the value of its pH usually changes greatly. If 0.01 mol of NaOH dissolves in 1 L of distilled water, the pH changes from 7 to 12.

The buffer solution is a solution that tends to resist changes in pH when a small amount of acid or base is added to it.

Buffer solution resists the attempts to change the pH by the addition of acid or base. If 0.01 mol of NaOH is added to 1 L of a solution containing 0.1 mol of CH_3COOH and 0,1 mol of CH_3COONa, the pH changes from 4.76 to 4.84.

There are two types of buffers:

Acidic buffer is prepared by mixing a weak acid and a salt of conjugate base, e.g., ethanoic acid and sodium ethanoate. The solution is acidic and is used to resist pH changes in an acidic medium.

Basic buffer is prepared by mixing a weak base and a salt of a conjugate acid, e.g., aqueous ammonia and ammonium chloride. The solution is basic and is used to resist pH changes in a basic medium.

Buffer solutions maintain optimum pH values for the biochemical processes taking place in living systems. The enzymes (biological catalysts) that enable biochemical reactions can function only within a narrow range of pH. Human blood pH is stable in the range of 7.35–7.45, saliva pH – in the range of 6.35–6.85, gastric juice pH – in the range of 1.5–3.0, urine pH – in the range of 4.8–7.5. The pH out of this range is fatal to human life.

How does a buffer act? How does it resist changes in pH when an acid or base is added to it?

Take a buffer solution with an equal concentration of ethanoic acid and sodium ethanoate (acidic buffer) as an example. Sodium ethanoate completely dissociates in water:

$$CH_3COONa \rightleftarrows CH_3COO^- + Na^+.$$

On the other hand, ethanoic acid is only slightly dissociated.

$$CH_3COOH \rightleftarrows CH_3COO^- + H^+,$$
$$Ka(CH_3COOH) = 1.8 \cdot 10^{-5}.$$

If an acid, (e. g. HCl) is added to the system, H^+ ions will react with the CH_3COONa to produce weak acid.

$$CH_3COO^- + Na^+ + H^+ + Cl^- \rightleftarrows Na^+ + Cl^- + CH_3COOH,$$
$$CH_3COO^- + H^+ \rightleftarrows CH_3COOH.$$

A strong acid is substituted by a weak acid, and the pH changes very little.

If a base (NaOH) is added to the buffer, OH^- ions will react with CH_3COOH to produce a salt and H_2O:

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

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

A strong base is substituted by salt, and the pH changes very little.

pH of a buffer solution can be estimated according to the Henderson-Hasselbalch equation.

For acidic buffer: $pH = pK_a + log\frac{[salt]}{[acid]}$ or

$$pH = pK_a + log\frac{\text{molarity of a salt solution}\times volume\ of\ salt\ solution}{\text{molarity of an acid solution}\times volume\ of\ acid\ solution},$$

where $pK_a = -\log K_a$,

where (K_a) is an acid dissociation constant.

For basic buffer: $pOH = pK_b + log\frac{[salt]}{[base]}$ or

$$pOH = pK_b + log\frac{\text{molarity of salt solution} \times \text{volume of salt solution}}{\text{molarity of base solution} \times \text{volume of base solution}},$$

$$\text{where } pK_b = -\log K_b,$$

$$pH = 14 - pOH \quad \text{or}$$

$$\text{pH}=14 - \text{pK}_b + log\frac{[salt]}{[base]}.$$

Buffer solutions are vitally important to living organisms. Buffer systems of the organism:

1. Bicarbonate buffer (H_2CO_3- the acid, $NaHCO_3$ - the salt).
2. Phosphate buffer (NaH_2PO_4 - the acid, Na_2HPO_4 - the salt).
3. Amino acid and protein buffer.
4. Hemoglobin buffer (HHb+KHb).
5. Oxyhemoglobin buffer ($HHbO_2$ + $KHbO_2$).

The major buffers of blood are bicarbonate and hemoglobin.

Examples of solving tasks

Example 5.28. A buffer is prepared by adding 4.1 g of sodium ethanoate to 1 dm^3 of 0.01 M ethanoic acid. What is the pH of the buffer?

($K_a(CH_3COOH)$ = 1.74 x 10^{-5} mol dm^{-3}; molar mass of sodium ethanoate = 82 g mol^{-1}).

Solution: $pH = pK_a + log\frac{[salt]}{[acid]}$,

$$CH_3COONa \rightleftarrows CH_3COO^- + Na^+,$$

$$pH = pK_a + log\frac{[CH_3COO^-]}{[CH_3COOH]}.$$

Number of moles of $CH_3COONa = \frac{4.1}{82} = 0.05\,mol,$

$[CH_3COO^-] = [salt] = \frac{0.05}{1} = 0.05\,mol,$

$[CH_3COOH] = [acid] = 0.01\,M,$

$pH = -log(1.74 \times 10^{-5}) + log\frac{0.05}{0.01} = 4.76 + 0.70 = 5.46.$

Example 5.29

1. Calculate the change in pH when 1 cm^3 of 0.25 M NaOH is added to
   - a) 25 cm^3 of pure water;
   - b) 25 cm^3 of 0.1 M CH_3COOH;
   - c) 25 cm^3 of 0.1 M CH_3COOH containing 0.002 moles of $CH_3COO^-Na^+$.

   ($K_a(CH_3COOH)$ = 1.74 x 10^{-5} mol dm^{-3}).
2. Comment on the obtained results.

Solution:

a) pH of pure water = 7, n is a number of moles,

$$n(NaOH) = 0.25 \times \frac{1}{1000} = 2.5 \times 10^{-4} mol.$$

$C_M(NaOH)$ after dilution $= 2.5 \times 10^{-4} \div \frac{1+25}{1000} = 9.62 \times 10^{-3} M,$

$K_W = [H^+][OH^-],$

$1 \times 10^{-14} = [H^+] \times 9.62 \times 10^{-3},$

$[H^+] = 1.04 \times 10^{-12} M,$

$$pH = -\,log[H^+] = -\,log(1.04 \times 10^{-12}) = 11.98.$$

The change in pH is 11.98 – 7 = 4.98.

b) **Part 1.** Calculation of pH of the 25 cm^3 of 0.1 M CH_3COOH:

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

Number of moles et equilibrium: (0.1-x) mole x mole x mole (in 1 dm^3),

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]},$$

$$1.74 \times 10^{-5} = \frac{x \times x}{0.1 - x},$$

$$x^2 = 1.74 \times 10^{-5}(0.1 - x),$$

$$x^2 + 1.74 \times 10^{-5} - 1.74 \times 10^{-6} = 0,$$

$$x = 1.31 \times 10^{-3} or - 1.33 \times 10^{-3} (rejected),$$

$$pH = -\,log[H^+] = -\,log(\,1.31 \times 10^{-3}) = 2.88.$$

Part 2. Calculation of pH when 1 cm^3 of 0.25 M NaOH is added.

The number of moles of OH$^-$ in 1 cm^3 of 0.25 M NaOH = $= 0.25 \times 1 \times 10^{-3} = 2.5 \times 10^{-4}\,\text{mol}$.

The number of moles of CH_3COOH originally present = $= 0.1 \times 25 \times 10^{-3} = 2.5 \times 10^{-3}\,\text{mol}$.

As the number of moles of OH$^-$ added will react with the same number of moles of CH_3COOH, the number of moles of CH_3COOH left $= 2.5 \times 10^{-3} - 2.5 \times 10^{-4} = 2.25 \times 10^{-3}\,\text{mol}$, the number of moles of sodium ethanoate formed $= 2.5 \times 10^{-4}\,\text{mol}$:

$$pH = pK_a + log\,\frac{[salt]}{[acid]},$$

$$[salt] = [CH_3COO^-] = \frac{2.5 \times 10^{-4}}{(25 + 1) \times 10^{-4}} = 9.62 \times 10^{-3}\ M,$$

$$[acid] = [CH_3COOH] = \frac{2.25 \times 10^{-3}}{(25 + 1) \times 10^{-3}} = 0.0865\ M,$$

$$pH = -\,log(\,1.74 \times 10^{-5}) + log\,\frac{9.62 \times 10^{-3}}{0.0865} = 4.76 - 0.95$$
$$= 3.81.$$

The change in pH=3.81-2.88=0.93.

c) **Part 1**. Calculation of pH of 25 cm^3 of 0.1 M CH_3COOH containing 0.002 moles of $CH_3COO^-Na^+$:

$$pH = pK_a + log\frac{[salt]}{[acid]},$$

$$\text{n (salt) } = 2 \times 10^{-3} mol,$$

$$\text{n (acid) } = 2.5 \times 10^{-3} mol,$$

$$[CH_3COO^-] = \frac{2 \times 10^{-3}}{25 \times 10^{-3}} = 0.08\, M,$$

$$pH = -log(1.74 \times 10^{-5}) + log\frac{0.08}{0.1} = 4.76 - 0.10 = 4.66.$$

Part 2. Calculation of pH when 1cm^3 of 0.25 M NaOH is added to the buffer.

Number of moles of OH$^-$ in 1 cm^3 of 0.25 M NaOH= $0.25 \times 1 \times 10^{-3} = 2.5 \times 10^{-4} mol$

As the number of moles of OH$^-$ added will react with CH_3COOH present in the buffer system,

$\text{n(salt) present} = 2 \times 10^{-3} + 2.5 \times 10^{-4} = 2.25 \times 10^{-3} mol$

$\text{n (acid) present} = 2.5 \times 10^{-3} - 2.5 \times 10^{-4} = 2.25 \times 10^{-3} mol$

$$pH = pK_a + log\frac{[salt]}{[acid]},$$

$$[salt] = [CH_3COO^-] = \frac{2.25 \times 10^{-3}}{(25 + 1) \times 10^{-3}} = 0.0865\, M,$$

$$[acid] = [CH_3COOH] = \frac{2.25 \times 10^{-3}}{(25 + 1) \times 10^{-3}} = 0.0865\, M,$$

$$pH = -log(1.74 \times 10^{-5}) + log\frac{0.0865}{0.0865} = 4.76 + 0 = 4.76.$$

The change in pH $= 4.76 - 4.66 = 0.10$.

A drastic pH change (4.98 units) is shown when 1 cm^3 of 0.25 M NaOH is added to 25 cm^3 of water as there is no buffering effect. There is also a significant change in pH (0.92 unit) for the ethanoic acid solution, which is not a good buffer without the presence of sodium ethanoate. However, the change is insignificant (0.10 unit) when the same amount of NaOH is added to the solution with a buffering effect. It could be seen that a buffer solution can resist the change in pH when a small amount of acid (or base) is added to it.

Example 5.30. To prepare a basic buffer with pH of 9.0, how many grams of ammonium chloride would you add to 100 cm^3 of 0.1M $NH_3 \cdot H_2O$?
$(K_b(NH_3) = 1.74 \times 10^5$ mol /dm^3; M (NH$_4Cl) = 53.5\ g/mol)$
Solution:
$pOH = pK_b + log\frac{[salt]}{[base]}$.
Let x M be the concentration of ammonium chloride in the buffer system. Then:

$$14 - 9 = -log(1.74 \times 10^{-5}) + log\frac{x}{0.1},$$

$$5 = 4.76 + log\frac{x}{0.1},$$

$$x = 0.174.$$

$$\text{n } (NH_4Cl) \text{ used } = 0.174 \times \frac{100}{1000} = 0.0174\ moles.$$

Ans.: The mass of NH_4Cl used $= 0.0174 \times 53.5 = 0.93\ g$.

Example 5.31. The dissociation constant of $H_2PO_4^-$ in water, K$_a$, is 6.2×10^{-8}mol/dm^3 at 298 K, where

$$K_a = \frac{\left[HPO_4^-\right]\left[H^+\right]}{\left[H_2PO_4^-\right]}.$$

Calculate the pH at 298 K:

a) of an aqueous solution of 0.10 M NaH_2PO_4;
b) of an aqueous solution of 0.05 M NaH_2PO_4 and 0.05 M NaH_2PO_4.

(It may be assumed that the concentrations of H_3PO_4 and PO_4^{3-} are negligible in these solutions.)
Solution:
a)

$$NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-,$$
$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+.$$

The number of moles at equilibrium:
(0.1-x) mole x mole x mole (in 1 dm^3).

$$6.2 \times 10^{-8} = \frac{x^2}{0.1 - x},$$

$$x^2 = 6.2 \times 10^{-8}(0.1 - x),$$

$$x^2 + 6.2 \times 10^{-8}x - 6.2 \times 10^{-9} = 0,$$

$x = 7.87 \times 10^{-5}$ or -7.88×10^{-5} (rejected),

pH=-log(7.87×10^{-5}) = 4.10.

b) $[H^+] = \frac{K_a \times [H_2PO_4^-]}{[HPO_4^{2-}]}$.

Taking negative logarithm on both sides,

$$-\log[H^+] = -\log K_a - \log\frac{[H_2PO_4^-]}{[HPO_4^{2-}]},$$

$$pH = pK_a + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = -\log(6.2 \times 10^{-8}) + \log\frac{0.05}{0.05} = 7.2$$

There is a limit to how much a buffer system can resist change. The ability of a buffer solution to keep the assigned pH rate is quantitatively characterized by the buffer capacity.

Buffer capacity is a number of moles of a strong acid or a strong base that is needed to be added to 1 L of buffer solution in order to change its pH for 1 unit. The formula for calculating is:

$$\text{B }(acid) = \frac{C_N \text{ of the adding acid } \times \text{ V of the adding acid}}{\text{V of buffer } \times \Delta \text{ pH}},$$

$$\text{B }(base) = \frac{C_N \text{ of the adding base } \times \text{ V of the adding base}}{\text{V of buffer } \times \Delta \text{ pH}},$$

The higher is the initial concentration of the components of the buffer system. The higher is its buffer capacity.

Example 5.32. 14 mL of sodium hydroxide solution with a molarity of 0.1 mol/L was added to 100 mL of blood, resulting in the

pH change from 7.36 to 9.36. Calculate the buffer capacity of the blood.
Solution:

$$\mathrm{B}\ (base)\ = \frac{C_N \text{ of the adding base } \times \text{ V of the adding base}}{\text{V of buffer } \times \Delta \text{ pH}},$$

Changing of pH = 9.36 – 7.36 = 2

$$\mathrm{B(base)} = \frac{0.1\mathrm{mol/L}\ \times\ 14\cdot 10^{-3}L}{100\cdot 10^{-3}\mathrm{L}\ \times 2} = \frac{14\cdot 10^{-4}}{2\cdot 10^{-1}} = 7\cdot 10^{-3} mol/L$$

Theoretical questions

1. What are buffer solutions?
2. How does a buffer act? How does a buffer regulate pH? When an acid or base is added to buffer solution?
3. What is the Henderson-Hasselbalch equation for the calculation of pH of buffer solutions?
4. What is buffer capacity?
5. Name the most important buffer system of the organism.

Exercises for practice

1. To change the pH value from 7.36 to 7.00 it is necessary to add 35 mL of HCl with normality 0.05 mol/L to 100 mL of blood. Calculate the buffer capacity of the blood.
2. Calculate the volumes of 0.2 mol/L CH_3COOH and 0.2 mol/L CH_3COONa, which ought to be mixed in order to obtain 400 mL of buffer solution, where pH = 5.24 if Ka(CH_3COOH) = $1.8\cdot 10^{-5}$.
3. Calculate the volumes of 0.02 mol/L NaH_2PO_4 and 0.02 mol/L Na_2HPO_4, which ought to be mixed in order to obtain 200 mL of buffer solution where pH = 6.8 if pK($H_2PO_4^-$) = 6.8.
4. Calculate the pH value of a buffer mixture prepared of 150 ml of CH_3COOH solution with a concentration of 0.1 mol/L and

250 ml of 0.2 mol/L CH_3COONa solution if $pK(CH_3COOH)=4.75$.

5. Calculate the pH of a buffer solution prepared by mixing30 cm^3 of 0.1 M ethanoic acid and 20 cm^3 of 0.08 M sodium ethanoate. $(K_a(CH_3COOH) = 1.74 \times 10^{-5} mol/dm^3)$.
6. Calculate the pH value of a buffer solution obtained by mixing 300 ml of 0.1 mol/L NH_4Cl solution with 150 ml of 0.2 mol/L $NH_3 \times H_2O$ solution. $K_b(NH_3 \times H_2O) = 1.8 \cdot 10^{-5}$.
7. What will be the change of the pH value of buffer which consists of 100 mL of 0.3 mol/L CH_3COOH solution and 100 mL of 0.2 mol/L CH_3COONa solution at the addition of 200 mL of 0.05 mol/L HCl solution if $K_a(CH_3COOH)=1.8 \cdot 10^{-5}$?
8. Choose the buffer systems:
   a) HCl; NH_4Cl;
   b) H_2CO_3; $KHCO_3$;
   c) H_2CO_3; $(NH_4)_2CO_3$;
   d) NH_4OH; NH_4Cl.
9. A buffer solution is made by adding 75.0 g of sodium ethanoate to 500.0 cm^3 of 0.64 M solution of ethanoic acid. Assuming there is no volume change during dissolution, calculate the pH of the final solution? $(K_b(NH_3) = 1.7 \times 10^{-5} mol/dm^3)$.
10. A buffer solution is made by adding 50.0 g of ammonium chloride to 1.00 liter of 0.75 M solution of NH_3. Assuming there is no volume change during dissolution, calculate the pH of the final solution.
    $(K_b(NH_3) = 1.7 \times 10^{-5} mol/dm^3)$.
11. Calculate the change in pH after 0.01 mole of gaseous HCl being added to 250.0 cm^3 of a solution containing 0.05 M and 0.15 M NH_4Cl. $(K_b(NH_3) = 1.7 \cdot 10^{-5} mol/dm^3)$.
12. Calculate the change in pH after 2 cm^3 of 0.02 M NaOH being added to 200 cm^3 of a solution containing 0.10 M CH_3COOH and 0.08 M CH_3COONa.
    $(K_a(CH_3COOH) = 1.7 \cdot 10^{-5} mol/dm^3)$

CHAPTER 6
OXIDATION-REDUCTION REACTIONS

Practical skills

After studying the subject, you will be able:

1. To find oxidation states of elements in chemical compounds.
2. To put coefficients in chemical equations (balance).
3. To find oxidant and reductant, processes of oxidation and reduction.
4. To calculate the overall redox potential of a chemical reaction and write a scheme of galvanic elements.

6.1. Oxidation States

The chemical reactions can be divided into two general types: type I reactions, in which the valence shells of the reactants remain unchanged after conversion to products, and type II reactions, in which the valence shells of the reactants are modified by the gain or loss of electrons. Type II reactions are oxidation-reduction or redox reactions.

$H^+Cl^- + Na^+O^{-2}H^+ \longrightarrow Na^+Cl^- + H_2{}^+O^{-2}$ – type I

$4Fe^0 + 2O_2{}^0 \longrightarrow 2Fe^{+3}{}_2O_3{}^{-2}$ – type II

0, +3, –2 are oxidation states (oxidation numbers).

The oxidation state of an atom is the apparent or real charge that an atom has when all bonds between atoms of different elements are assumed to be ionic.

Rules for determining oxidation states:

1. The oxidation state (oxidation number) of an atom in a free (uncombined) element is zero.
2. The total of the oxidation states of all the atoms in a molecule or formula unit is zero. For an ion, this total is equal to the charge on the ion, both in magnitude and sign and regardless of whether the ion consists of a single atom (monatomic) or two or more atoms (polyatomic).

3. In their compounds, the alkali metals (group IA of the periodic table) have an oxidation state of +1; the alkaline earth metals (IIA), +2; and the metals of group III, +3.
4. In its compounds, the oxidation state of hydrogen is +1; that of fluorine is –1.
5. In its compounds, oxygen has an oxidation state of –2. The exception is $H_2^{+1}O_2^{-1}$.
6. In their binary compounds with metals, elements of group VIIA have an oxidation state of –1; those of group VIA, –2; and those of group VA, –3 (binary compounds are comprised of two elements, e.g., KI, $MgBr_2$, BaS).

Examples of solving tasks

Example 6.1. What is the oxidation state of the underlined atom in each of the following (a) $\underline{P}_4$; (b) $\underline{Al}_2O_3$; (c) $\underline{Mn}O_4^-$; (d) $H_2\underline{O}_2$; (e) $K\underline{O}_2$?

Solution:

(a) P_4. This formula represents a molecule of the element phosphorus. For an atom of a free element, the oxidation state is 0 (rule 1). The oxidation state of P in P_4 is 0;

(b) Al_2O_3. The total of the oxidation numbers of all the atoms in a formula unit is 0 (rule 2). The oxidation state of O is –2 (rule 5). The total for three O atoms is –6. The total for two Al atoms is +6. The oxidation state of Al is +3. $3(-2) + 2x = 0$ $x=3$;

(c) MnO_4^-. The total of the oxidation numbers of all the atoms in this ion must be –1 (rule 2). The total of the oxidation numbers of the four O atoms is –8. The oxidation state of Mn is +7;

(d) H_2O_2. Rule 4, stating that H has an oxidation state of +1. The sum of the oxidation number of the two H atoms is +2, and that of the two O atoms is – 2. The oxidation state of O in H_2O_2 is –1;

(e) KO_2. The oxidation state of K = +1. The sum of the oxidation state of the two O atoms is –1. The oxidation state of each O atom in KO_2 is –½.

6.2. Oxidation-Reduction: Some Definitions

When an iron object is exposed to the atmosphere, it rusts. A simplified equations is $4Fe^0 + 3O_2^0 \longrightarrow 2Fe_2^{+3}O_3^{-2}$.
In this reaction, iron combines with oxygen. This is an oxidation-reduction reaction.

The reaction in which electrons lost by one of the reaction components is gained by another component is known as **oxidation-reduction or redox reaction.**

Oxidation is a process in which the oxidation state of some element increases.

$S^{-2} - 2e \longrightarrow S^0$
$Fe^0 - 3e \longrightarrow Fe^{+3}$
$H_2^0 - 2e \longrightarrow 2H^+$ The component loses electrons.

The component supplying the electrons is called the **reducing agent** (reductant) (Figure 6.1).

The reducing agent (reductant) is a substance that causes reduction and is itself oxidized.

The reduction is a process in which the oxidation state of some element decreases.

$S^0 + 2e \longrightarrow S^{-2}$
$Fe^{+3} + 1e \longrightarrow Fe^{+2}$
$O_2^0 + 4e \longrightarrow 2O^{-2}$ The component gains electrons.

The component receiving the electrons is called the **oxidizing agent** (oxidant).

Oxidizing agent (oxidant) is a substance that causes oxidation and is itself reduced.

The two processes – oxidation and reduction – always occur together.

$Fe^0 + 3O_2^0 \longrightarrow 2Fe_2O_3^{-2}$
reductant $Fe - 3e \longrightarrow Fe^{+3}$ oxidation

oxidant $O_2 + 4e \longrightarrow 2O^{-2}$ reduction

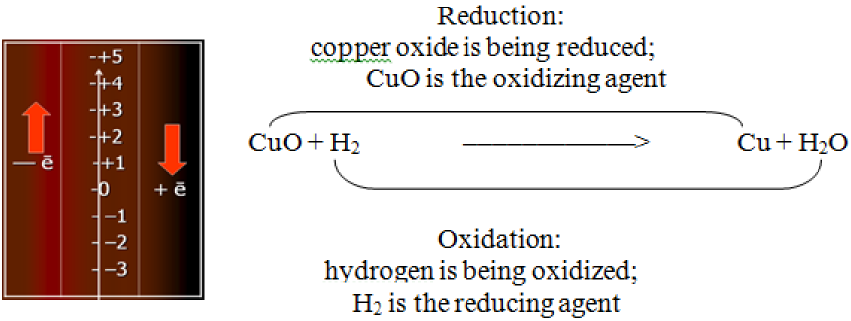


Figure 6.1 – Action of reducing agent

6.3. Balancing Oxidation-Reduction Equations

Balancing redox reactions have all the requirements of balancing other types of chemical reactions: mass must be conserved in the transformation. This requires:

1. Atoms of all elements must be conserved.
2. Electrons must be conserved.
3. The total electric charge must be conserved (follows from electrons being conserved).
4. All coefficients must be integers.

For the charge to be conserved, **the number of electrons lost in the oxidation must equal the number of electrons gained in the reduction.**

Example 6.2. Balance the following equation.

$Al^0 + S^0 \longrightarrow Al_2^{+3}S_3^{-2}$

1. Calculate the oxidation state of all elements in the equation.

2. Identify the oxidation and reduction process and write them separately:

The oxidation state of Al changes from 0 in Al to +3 in Al^{+3}.

$Al^0 - 3e \longrightarrow Al^{+3}$ Al loses electrons. Al is reductant.

This is an oxidation process.

The oxidation state of S changed from S^0 to S^{-2}.
$S^o + 2e \longrightarrow S^{-2}$. S gains electrons. S is the oxidant.
This is a reduction process.
Write the oxidation and reduction processes

reductant	$Al^0 - 3e \longrightarrow Al^{+3}$	6	2	oxidation
oxidant	$S^0 + 2e \longrightarrow S^{-2}$		3	reduction

3. The number of e lost in the oxidation must equal the number of e gained in the reduction.
Al^0 loses 3 electrons.   S gains 2 electrons.
6 is the least common multiple.
2 and 3 are coefficients of Al and S.

$$2Al + 3S = Al_2S_3$$

This method is called the **oxidation state change method**.

Example 6.3. Balance the following oxidation-reduction expression.

$$I_2^0 + Br_2^0 + H_2^+O^{-2} \longrightarrow H^+I^{+5}O_3^{-2} + H^+Br^-,$$

$I_2^o - 10\,e \longrightarrow 2I^{+5}$	10	1
$Br_2^0 + 2e \longrightarrow 2Br^-$		5,

$$I_2^0 - 10e + 5Br_2 + 10e \longrightarrow 2I^{+5} + 10Br,^-$$

$$I_2 + 5Br_2 + H_2O \longrightarrow 2HIO_3 + 10\,HBr.$$

The remaining coefficient (that of H_2O) is determined by inspection.

There are 12 H atoms on the right and only 2 on the left. The coefficient “6” for H_2O produces a balance of H atoms.

$$I_2 + 5Br_2 + 6H_2O \longrightarrow 2HIO_3 + 10HBr.$$

Questions for self-testing

1. What is the oxidation state of N in NH_3?
a) +2 b) -3 c) 0 d) +5

2. What is the oxidation state of P in H_3PO_4?
a) +2 b) -3 c) 0 d) +5

3. What is the oxidation state of S in K_2SO_4?
a) +6 b) -3 c) +5 d) 0

4. What is the oxidation state of Br in $HBrO_3$?
a) -3 b) +5 c) +3 d) 0

5. What is the oxidation state of Mn in $KMnO_4$?
a) -3 b) +7 c) -2 d) 0

6. What is the oxidation state of C in Na_2CO_3?
a) +2 b) +1 c) +4 d) 0

7. Complete the process: $Mn^{+7}+\ldots\rightarrow Mn^{+4}$.
a) $+3\bar{e}$ b) $+7\bar{e}$ c) 0 d) $+5\bar{e}$

8. Complete the process: $Cr^{+2}-\ldots\rightarrow Cr^{+6}$.
a) $-3\bar{e}$ b) $-4\bar{e}$ c) 0 d) $-1\bar{e}$

9. Complete the process: $N^0+\ldots\rightarrow N^{-3}$.
a) $+3\bar{e}$ b) $+7\bar{e}$ c) 0 d) $+2\bar{e}$

10. Complete the process: $Cl^0-\ldots\rightarrow Cl^{+5}$.
a) $-6\bar{e}$ b) $-1\bar{e}$ c) 0 d) $-5\bar{e}$

11. Complete the process: $P^{+5} + \ldots \rightarrow P^{-3}$.
a) $+8\bar{e}$ b) $+1\bar{e}$ c) 0 d) $+10\bar{e}$

12. Complete the process: $Fe^{+3} + \ldots \rightarrow Fe^{0}$.
a) $+2\bar{e}$ b) $+3\bar{e}$ c) 0 d) $+10\bar{e}$

13. Complete the process: $\mathrm{Si}^{-4} - \ldots \rightarrow \mathrm{Si}^{+4}$.
a) $-2\bar{e}$ b) $-3\bar{e}$ c) $-8\bar{e}$ d) 0

14. Choose the oxidation process:
a) $NO_2^- + 1\bar{e} \rightarrow NO$ b) $N_2O_5 + 0\bar{e} \rightarrow KNO_3$
c) $HNO_3 + 8\bar{e} \rightarrow NH_4^+$ d) $NO_2^- - 2\bar{e} \rightarrow NO_3^-$

15. Choose the oxidation process:
a) $\mathrm{IO_3^-} + 6\bar{\mathrm{e}} \rightarrow \mathrm{I^-}$ b) $\mathrm{I_2^0} + 2\bar{\mathrm{e}} \rightarrow 2\mathrm{I^-}$
c) $\mathrm{HIO} + 0\bar{\mathrm{e}} \rightarrow \mathrm{KIO}$ d) $\mathrm{I_2^0} - 5\bar{\mathrm{e}} \rightarrow 2\mathrm{IO_3^-}$

16. Choose the reduction process:
a) $Fe^{3+} - 3\bar{e} \rightarrow FeO_4^{2-}$ b) $Fe(OH)_2 - 1\bar{e} \rightarrow Fe_2(SO_4)_3$
c) $Fe_2O_3 + 1\bar{e} \rightarrow FeSO_4$ d) $FeCl_2 + 0\bar{e} \rightarrow Fe(OH)_2$

17. Choose the reduction process:
a) $P^0 + 3\bar{e} \rightarrow PH_3$ b) $H_3PO_2 - 2\bar{e} \rightarrow H_3PO_3$
c) $H_3PO_4 + 0\bar{e} \rightarrow Ca_3(PO_4)_2$ d) $PH_3 - 8\bar{e} \rightarrow PO_4^{3-}$

18. Choose the reduction process:
a) $MnO_4^{2-} - 1\bar{e} \rightarrow MnO_4^-$ b) $MnO_4^{2-} + 2\bar{e} \rightarrow MnO_2$
c) $MnO_2 + 0\bar{e} \rightarrow MnO_3^{2-}$ d) $Mn^0 - 2\bar{e} \rightarrow Mn^{2+}$

19. Choose the oxidation process:
a) $HCOOH - 2\bar{e} \rightarrow CO_2$ b) $CO + 6\bar{e} \rightarrow CH_4$
c) $Na_2CO_3 + 0\bar{e} \rightarrow CO_2$ d) $H_2C_2O_4 + 1\bar{e} \rightarrow HCOO^-$

20. Choose the reduction process:

a) $SO_3^{2-} + 4\bar{e} \rightarrow S^0$ b) $SO_3 + 0\bar{e} \rightarrow Na_2SO_4$

c) $SO_3^{2-} - 1\bar{e} \rightarrow SO_4^{2-}$ d) $H_2S - 0\bar{e} \rightarrow S^{2-}$

Exercises for practice

1. Balance the following oxidation-reduction equations.

$$K_2MnO_4 + H_2O \rightarrow KMnO_4 + MnO_2 + KOH$$
$$AsH_3 + HNO_3 \rightarrow H_3AsO_4 + NO + H_2O$$
$$Cd + H_2SO_4 \rightarrow CdSO_4 + S + H_2O$$
$$Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$$
$$FeCl_3 + KI \rightarrow FeI_2 + I_2 + KCl$$
$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2S + H_2O$$
$$KClO_3 + KCl + H_2SO_4 \rightarrow Cl_2 + K_2SO_4 + H_2O$$

$$K_2MnO_4 + H_2O \rightarrow KMnO_4 + MnO_2 + KOH$$
$$AsH_3 + HNO_3 \rightarrow H_3AsO_4 + NO + H_2O$$
$$Cd + H_2SO_4 \rightarrow CdSO_4 + S + H_2O$$
$$Cu + H_2SO_4 \rightarrow CuSO_4 + SO_2 + H_2O$$
$$FeCl_3 + KI \rightarrow FeI_2 + I_2 + KCl$$

6.4. Galvanic Elements

Electrochemical cells typically consist of two half-cells. The half-cells separate the oxidation half-reaction from the reduction half-reaction and make it possible for current to flow through an external wire. One half-cell, normally depicted on the left side of the figure, contains the anode. Oxidation occurs at the anode. The anode is connected to the cathode in the other half-cell, often shown on the right side of the figure. Reduction occurs at the cathode. The adding of a salt bridge completes the circuit, allowing current to flow. Anions in the salt bridge flow toward the anode, and cations in the salt bridge flow toward the cathode. The movement of these ions completes the circuit and keeps each half-cell electrically neutral.

The spontaneous reaction of $Zn_{(s)}$ metal with $Cu^{2+}_{(aq)}$ from Cu (II) solution is the prime example for a redox reaction.

$$Zn_{(s)}+Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)}+Cu_{(s)}.$$

The Daniell cell a widely used type of galvanic cell (Fig. 6.2.)

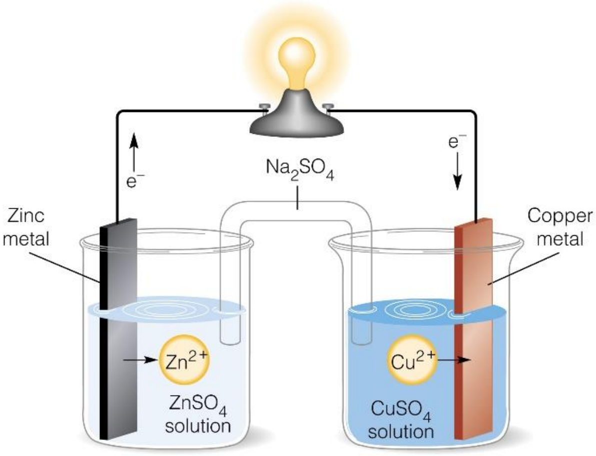


Figure 6.2 – Daniell galvanic cell

When electric current passes through an external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidized to zinc ions which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode, where they are used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:

$$Zn_{(s)} + Cu^{2+} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}.$$

Thus, indirect redox reaction leads to the production of electrical energy. At the zinc rod oxidation occurs. It is the anode of the cell and is negatively charged, while at copper electrode, reduction takes place: it is the cathode of the cell and is positively charged.

In order to calculate the overall redox potential, it is important first, to formulate the individual half-equations as reductions. The standard reduction potential E_{red}^0 for each reaction can be taken from standard tables:

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $\quad E_{red}^0 = + 0.340$ V

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$ $\quad E_{red}^0 = - 0.763$ V

The half-equation with the more positive value is the reduction, whilst another reaction is the oxidation. In this example, Cu^{2+} will be reduced to Cu, whilst $Zn_{(s)}$ metal will be oxidised to Zn^{2+}.

The standard potential E^0 of an oxidation half-equation is the negative value of E_{red}^0.

Reduction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ $\quad E_{red}^0 = + 0.340$ V

Oxidation: $Zn^0(s) - 2e^- \rightarrow Zn^{2+}_{(aq)}$ $\quad E_{ox}^0 = - 0.763$ V

The voltage produced by an electrochemical cell (E_{cell}^0) is calculated as follows:

$$E_{cell}^0 = E_{ox}^0 - E_{red}^0$$

For the example above:

$$E_{cell}^0 = 0.340 \text{ V} - (-0.763 \text{ V}) = 0.340 \text{ V} + 0.763 \text{ V} = + 1.103 \text{ V}$$

Electrochemical cells can be described using cell notation. In this notation, information about the reaction at the anode appears on the left and information about the reaction at the cathode on the right. The salt bridge is represented by a two slashes ||. The solid, liquid, or aqueous phases within a half-cell are separated by a single bar │. The phase and concentration of the various species can be written in the parentheses after the phase notation (s, l, g etc.). Electrodes that participate in the oxidation-reduction reaction are called active electrodes. Electrodes that do not participate in the oxidation-reduction reaction but are there to allow current to flow are inert electrodes. Inert electrodes are often made of platinum or gold because these metals are chemically unreactive. Galvanic cells, also known as voltaic cells, are electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy. When in writing the equations, it is often convenient to separate the oxidation-reduction reactions into half-reactions to facilitate the balancing of the overall equation and to emphasize the actual chemical transformations.

Cell notation for the Daniel cell is as follows:

$$Zn|Zn^{2+}(1M)||Cu^{2+}(1M)|Cu.$$

If you deal with more complicated redox reactions and half-equations have to be multiplied because of the different numbers of electrons in each half-equation, the standard potential E^0 will not be affected by these coefficients. Furthermore, it is important to note that the above calculations can be used only if both reaction partners are present in the same concentration. Concentration can have an effect, and the overall potential is then calculated by using the Nernst equation.

Nernst equation for single electrode potential

$$E_{cell} = E^0 - \frac{RT}{nF} lnQ,$$

where E_{cell} – cell potential of the cell; E^0 – cell potential under standard conditions, R – universal gas constant (8.314 J / mol·K); T – temperature (at standard conditions 298 K); n – number of electrons transferred in the redox reaction, F – Faraday constant (96500 J/mol), Q – reaction quotient.

The calculation of single electrode reduction potential (E_{red}) from the standard single electrode reduction potential ($E°_{red}$) for an atom/ion is given by the Nernst equation.

The Nernst equation for a single electrode reduction potential for a reduction reaction $M^{n+} + ne^- \rightarrow nM$ is

$$E_{red} = E^{Me^{n+}}/_{Me} = E^{Me^{n+}}/_{Me}{}^{0} - \frac{2.303\,RT}{nF} logMe^{n+},$$

where R is the gas constant – 8.314 J/K; Mole; T – absolute temperature; n – number of mole of electron involved; F = 96487 (≈96500) coulomb/mole – the charge carried by one mole of electrons; and $[Me^{n+}]$ – active mass of the ions. For simplicity, it may be taken as equal to the molar concentration of the salt.

The Nernst equation at 25 °C

For measurements carried out at standard temperature 25°C (298 K), the Nernst equation can be expressed as follows if we put everything in the equation where F and T are constants.

$$E_{cell} = E^0 - \frac{0.0592}{n} \log Q.$$

Therefore, as per the Nernst equation, the overall potential of an electrochemic cell is dependent on the reaction quotient.

Cell potential or electromotive force (EMF)

It is the potential difference between electrodes in a galvanic cell, and it is measured in volts. It can be represented as:

$$EMF = E^0\ cathode\ (right\ side) - E^0 anode\ (left\ side),$$

$$E^\circ = E^\circ_{reduction} - E^\circ_{oxidation}.$$

Examples of solving tasks

Example 6.4. Write the half-equations and cell reactions for each of the following cells:

a. $Ag|Ag^+||H^+|H_2|Pt$

b. $Pt|Cr_2O_7^{2-}, Cr^{3+}, H^+ \| Br^-|Br_2(l)|Pt$

Solution:

a) Since the half-equation at the left electrode is taken by convention to be oxidation, we have

$Ag \to Ag^+ + e^-$

Than at the right-hand electrode we must have a reduction

$2H^+ + 2e^- \to H_2$

Multiplying the first half-equation by 2 and summing gives the cell reaction

$2Ag + 2H^+ \to 2Ag^+ + H_{2(g)}$.

b) Following the same procedure as in part (a), we obtain

$2Cr^{3+} + 7H_2O \to Cr_2O_7^{2-} + 14H^+ + 6e^-$;

Left electrode $(Br_2(l) + 2e^- \to 2Br^-) \cdot 3$;

Right electrode $2Cr^{3+} + 7H_2O + 3Br_2(l) \to Cr_2O_7^{2-} + 14H^+ + 6Br^-$.

Example 6.5. Describe in shorthand notation a galvanic cell for which the cell reaction is

$Cu_{(s)} + 2Fe^{3+}_{(aq)} \to Cu^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$.

Solution:

First, divide the cell reaction into half-equations:

Oxidation: $Cu_{(s)} \to Cu^{2+}_{(aq)} + 2e^-$;

Reduction: $Fe^{3+} + e^- \to Fe^{2+}$.

Then write the oxidation as the left-hand electrode and the reduction on the right:

$Cu|Cu^{2+} \| Fe^{2+}, Fe^{3+}|Pt$.

Since both Fe^{2+} and Fe^{3+} are in solution, a Pt electrode is used.

Table 6.1 – Table of standard electrode potentials of metal electrodes

Metal	E^0, V	Metal	E^0, V
Li^+/Li	-3,045	Zn^{2+}/Zn	-0,763
Rb^+/Rb	-2,925	Ga^{3+}/Ga	-0,560
K^+/K	-2,924	Fe^{2+}/Fe	-0,441
Cs^+/Cs	-2,923	Cd^{2+}/Cd	-0,404
Ra^{2+}/Ra	-2,916	Co^{2+}/Co	-0,277

Continuation of Table 6.1

Ba^{2+}/Ba	-2,905	Ni^{2+}/Ni	-0,234
Sr^{2+}/Sr	-2,888	Sn^{2+}/Sn	-0,141
Ca^{2+}/Ca	-2,864	Pb^{2+}/Pb	-0,126
Na^{+}/Na	-2,771	H^{+}/H_2	0,000
Mg^{2+}/Mg	-2,370	Bi^{3+}/Bi	+0,317
Sc^{3+}/Sc	-2,077	Cu^{2+}/Cu	+0,338
Be^{2+}/Be	-1,847	Hg^{2+}/Hg	+0,796
Al^{3+}/Al	-1,700	Ag^{+}/Ag	+0,799
Ti^{3+}/Ti	-1,208	Pd^{2+}/Pd	+0,915
Mn^{2+}/Mn	-1,192	Pt^{2+}/Pt	+0,963
Cr^{2+}/Cr	-0,852	Au^{+}/Au	+1,691

Exercises for practice

1. Calculate E for the following redox pair when Mn^{3+}= 0.5 M and Mn^{2+} = 0.01 M [$E^0(Mn^{3+}/Mn^{2+})$ = 1.51 V, using the Nernst equation.
2. Make scheme of the galvanic element, using meanings of standard electrode potentials of metals (see Tables 6.1–6.2) and concentrations of the solution in which metal plates are dipped into. Write reactions on cathode and anode, the summary reaction for galvanic element, calculate cell potential for this galvanic element.

Table 6.2 – Galvanic elements tasks

Task number	Metal/cation (cation concentration, mol/L)		Task number	Metal/cation (cation concentration, mol/L)	
	first	Second		first	second
1	2	3	4	5	6
1	Zn/Zn^{2+} (0,01)	Ag/Ag^{+} (0,02)	13	$H_2/2H^{+}$ (1)	Cd/Cd^{2+} (0,1)

Continuation of Table 6.2

1	2	3	4	5	6
2	Mg/Mg^{2+} (0,1)	Ag/Ag^{+} (0,01)	14	$H_2/2H^{+}$ (0,01)	Zn/Zn^{2+} (0,01)
3	Zn/Zn^{2+} (0,05)	Cd/Cd^{2+} (0,02)	15	Fe/Fe^{2+} (0,02)	Ag/Ag^{+} (0,2)
4	Cu/Cu^{2+} (0,002)	Cu/Cu^{2+} (0,2)	16	Mg/Mg^{2+} (2)	Mg/Mg^{2+} (0,01)
5	Pb/Pb^{2+} (0,1)	Cu/Cu^{2+} (1)	17	Cu/Cu^{2+} (0,2)	Au/Au^{3+} (1)
6	Ag/Ag^{+} (0,001)	Ag/Ag^{+} (1)	18	$H2/2H^{+}$ (0,02)	Ag/Ag^{+} (0,01)
7	Zn/Zn^{2+} (0,01)	Ni/Ni^{2+} (0,01)	19	$H2/2H^{+}$ (1)	Ni/Ni^{2+} (0,1)
8	Fe/Fe^{2+} (0,1)	Cu/Cu^{2+} (0,01)	20	AI/AI^{3+} (0,01)	Cr/Cr^{3+} (0,5)
9	Mn/Mn^{2+} (0,02)	Ag/Ag^{+} (0,01)	21	AI/AI^{3+} (0,05)	Cd/Cd^{2+} (0,5)
10	Fe/Fe^{2+} (0,1)	Cr/Cr^{3+} (0,1)	22	Cd/Cd^{2+} (0,001)	Co/Co^{2+} (0,01)
11	Ni/Ni^{2+} (0,05)	Cu/Cu^{2+} (0,1)	23	Fe/Fe^{2+} (0,0001)	Ni/Ni^{2+} (0,01)
12	Sn/Sn^{2+} (0,02)	Cu/Cu^{2+} (0,2)	24	$Ag/Ag+$ (0,01)	Ag/Ag^{+} (1)

3. Given the following cell notations, determine the species oxidized, species reduced, and the oxidizing agent and reducing agent, without writing the balanced reactions.

a) $Mg_{(s)}|Mg^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)}|Cu_{(s)}$

b) $Ni_{(s)}|Ni^{2+}_{(aq)} \parallel Ag^{+}_{(aq)}|Ag_{(s)}$

4. One half-cell consists of a silver electrode in a 1 *M* $AgNO_3$ solution, and in the other half-cell, a copper electrode in 1 *M* $Cu(NO_3)_2$ is oxidized.

Questions for self-testing

1. Anode of the Daniell cell is made up of….
a) Zn b) Cu c) Mg d) Al

2. At anode of Daniel cell
    a). oxidation of zinc ions take place
    b). oxidation of copper ions take place
    c). oxidation of zinc take place
    d). oxidation of copper take place
3. The direction of electron flows in the Denial cell is
    a) toward cathode
    b) toward anode
    c) toward zinc electrode
    d) from copper to zinc electrode
4. The EMF of the Daniell cell is
    a) 1.09 V
    b) 0.19 V
    c) 9.01 V
    d) 10.9 V

CHAPTER 7
COLLOIDAL PROPERTIES OF SOLUTIONS

7.1. Colloidal Particles. Classifications of Colloid Systems

Practical skills
After studying the subject, you will be able:

1. To classify the disperse systems according to different criteria.
2. To known the methods of preparation and purification of disperse systems.

Colloids are those (disperse) systems which consist of particles in size of 1 nm –500 nm (1nm = 10^{-9} m). The colloid state is independent of the chemical nature, and every condensed phase can be turned into a colloidal system.

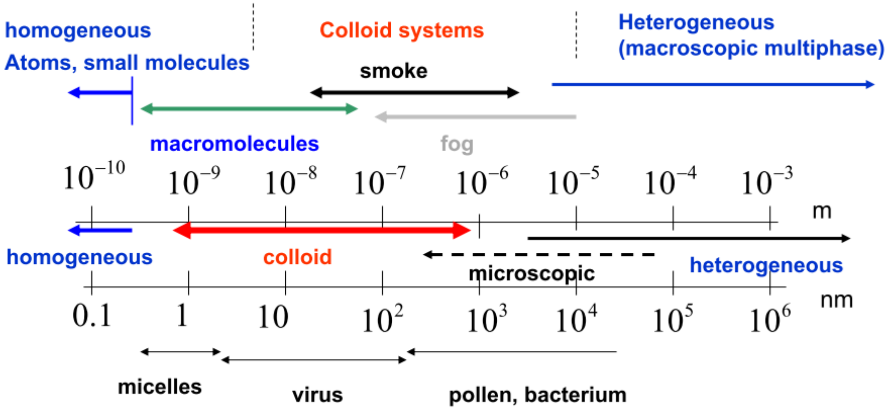


Figure 7.1 – Size of colloidal systems

Dispersed systems (Fig. 7.2, 7.3) consist of particulate matter (dispersed phase), distributed throughout a continuous phase (dispersion medium). They are classified according to the particle diameter of the dispersed material:

Molecular dispersions (less than 1 nm*)*

- Particles invisible in electron microscope.
- Pass through semipermeable membranes and filter paper.
- Particles do not settle down on standing.
- Undergo rapid diffusion (e.g. ordinary ions, glucose solution).

Colloidal dispersions (1 nm – 100 nm)

- Particles not resolved by ordinary microscope, can be detected by electron microscope.
- Particles pass through filter paper but not pass through semipermeable membrane.
- Particles made to settle by centrifugation
- Diffuse very slowly (e.g. colloidal silver, natural and synthetic polymers).

Coarse dispersions (> 100 nm)

- Particles are visible under ordinary microscope
- Do not pass through filter paper or semipermeable membrane.
- Particles settle down under gravity
- Do not diffuse (E.g. emulsions, suspensions, red blood cells).

When a strong beam of light is passes through a colloidal sol, the path of light is illuminated (a visible cone formed). This phenomenon resulting from the scattering of light by the colloidal particles is called the Faraday-Tyndall effect (Fig. 7.4)

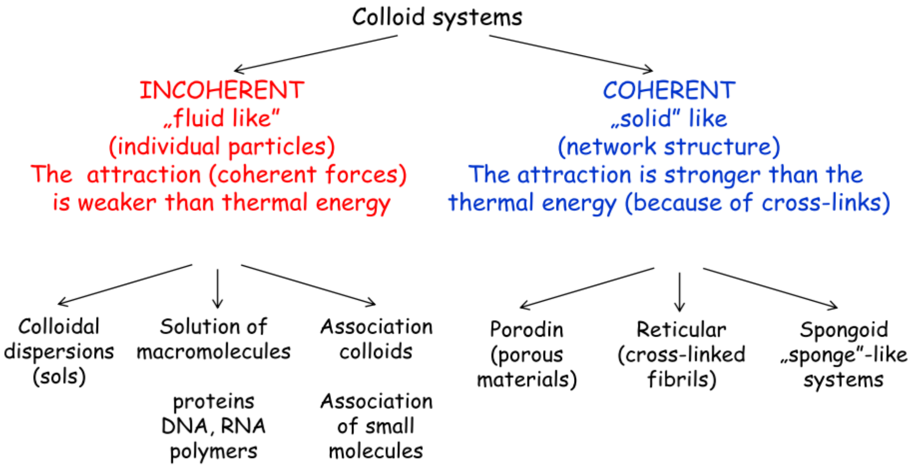


Figure 7.2 – Classification of colloids

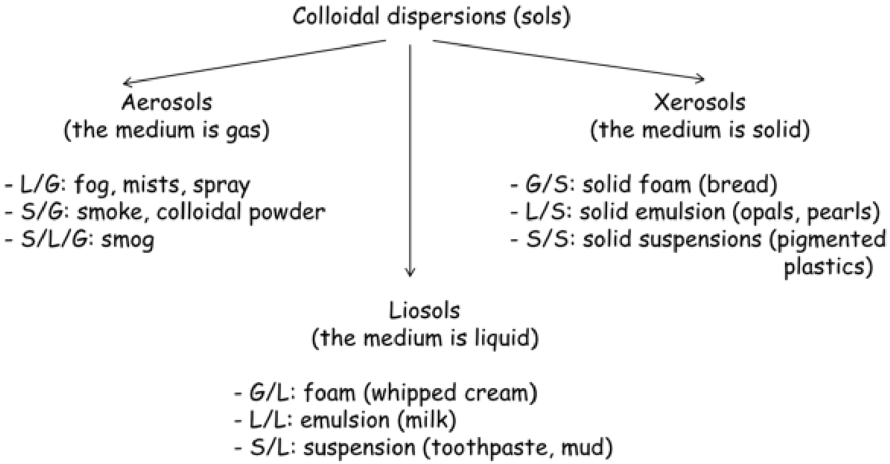


Figure 7.3 – Classification of colloidal dispersions (sols)

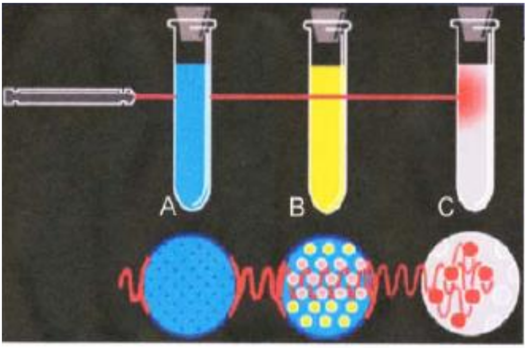


Figure 7.4 – The Faraday-Tyndall effect: A – solution, B – colloidal suspension (transparent), C – colloidal suspension (completely absorbing light)

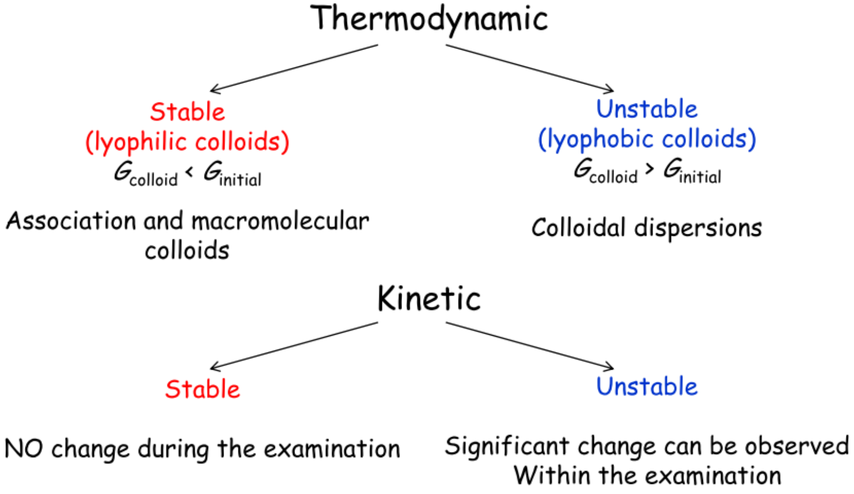


Figure 7.5 – Characterization of colloids by stability

7.2. Electric Properties of Colloids. Micelles

Electric properties of colloids. The particles of a colloidal solution are electrically charged and carry the same type of charge, either negative or positive. The colloidal particles, therefore, repel each other and do not cluster together to settle down. The charge on colloidal particles arises because of the dissociation of the molecular electrolyte on the surface.

Examples of solving tasks

Example 7.1

Following micelle $\{[(Ag_2S)_m\ nAg^+(n - x)NO_3^-]^+ x\ NO_3^-\}$ is formed as a result of interaction of solutions of $AgNO_3$ and Na_2S. If $AgNO_3$ is taken in excess, it dissociates on Ag^+ and NO_3^- ions. Ag_2S is the nucleus of the micelle. Ions of Ag^{+-} are adsorbed on the surface and remain on the surface of colloid. The same kind of ions is adsorbed on the surface of precipitate (Ag^+ potential forming ions). They give charge to the micelle. For this example, it is +1. Counter ions are in less amount (here, it is NO_3^- ions). So, in general, the micelle has a positive charge. It will move to the negatively charged electrode (cathode) under the influence of the electric field. In the diffuse layer, ions are the rest of NO_3^- ions.

If Na_2S is taken in excess, it dissociates on Na^+ and S^{2-} ions. Ag_2S is the nucleus of a micelle. Ions of S^{2-} are adsorbed on the surface and remain on the surface of the colloid. The same kind of ions is adsorbed on the surface of the precipitate (S^{2-} potential forming ions). The formula will be as follows $\{[(Ag_2S)m\ nS^{2-}\ 2(n - x)Na^+]^{2-}\ 2x\ Na^+\}$. They give charge to the micelle; for this example, it is -2. Counter ions are in less amount (here, it is Na^+ ions). So, in general, the micelle has a negative charge. It will move to the positively charged electrode (anode) under the influence of the electric field. In the diffuse layer, ions are the rest of Na^+ ions.

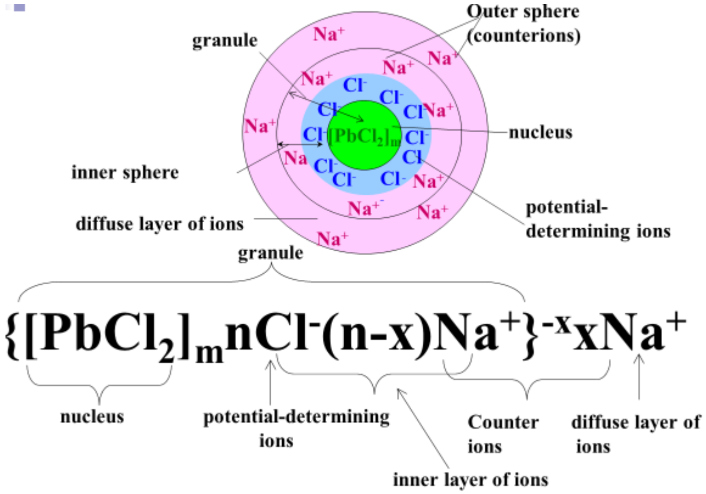


Figure 7.6 – The structure of a micelle obtained by the reaction of an excess of NaCl with $Pb(NO_3)_2$

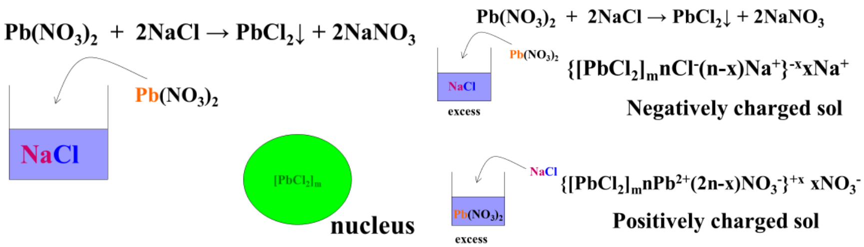


Figure 7.7 – The structure of a colloidal particle (micelle). Micelles with different charge of granules could be obtained depending on the substance which is present in excess

Usually, micelles are had the long nonpolar tail and a polar head. In soap solutions, individual anions of fatty acids dispersed in water can group hydrophilic part of micelles in water, and hydrophobic tails with other hydrophobic tails, which is thermodynamically advantageous.

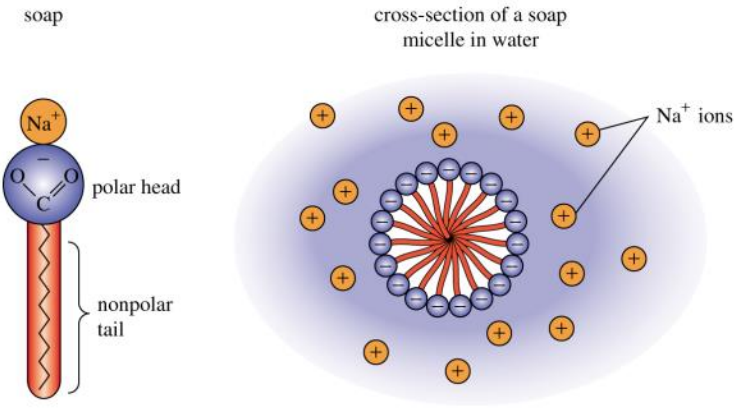


Figure 7.8 – Soap micelle and its cross section

When a colloidal solution is prepared it often containes certain electrolytes that tend to destabilize it. **The following methods are used for purification:**

1. Dialysis: semipermeable cellophane membrane prevent the passage of colloidal particles, yet allows the passage of small molecules or electrolytes.

2. Electrodialysis:

- In the dialysis unit, the movement of ions across the membrane can be speeded up by applying an electric current through the electrodes induced in the solution.

- The dialysis membrane allows small particles (ions) to pass through, but the colloidal size particles (hemoglobin) do not pass through the membrane.
- Electrophoresis is the most known electrokinetic phenomenon. It refers to the motion of charged particles related to the fluid under the influence of an applied electric field.
- If an electric potential is applied to a colloid, the charged colloidal particles move toward the oppositely charged electrode.

7.3. Applications of Colloidal Solutions

1. Therapy. The colloidal system is used as a therapeutic agent in different areas. For example, silver colloid - germicidal action; copper colloid – anticancer; mercury colloid – antisyphilis action.

2. Stability. Lyophobic colloids prevent flocculation in suspensions. For example, colloidal dispersion of gelatin is used in the coating over tablets and granules, which upon drying, leaves a uniform dry film over them and protects them from adverse conditions of the atmosphere.

3. Absorption. As colloidal dimensions are small enough, they have a huge surface area. Hence, the drug constituted colloidal form is released in a large amount. For example, sulfur colloid gives a large quantity of sulfur, and this often leads to sulfur toxicity.

4. Targeted drug delivery. Liposomes are of colloidal dimensions and are prefererably taken up by the liver and spleen.

5. Photography: a colloidal solution of silver bromide in gelatine is applied on glass plates or celluloid films to form sensitive plates in photography.

6. Blood clotting. Blood is a colloidal solution and is negatively charged. When applying a solution of $FeCl_{3,}$ bleeding stops and blood clotting occurs as Fe^{+3} ions neutralize the ion charges on the colloidal particles.

Questions for self-testing

1. Find which electrode (cathode and anode) the micelle granule $\{[(Zn(OH)_2)_m\ nZn^{2+}\ 2(n–x)Cl-]^{2x+}\ 2xCl-\}$ will move to:
   - a) cathode;
   - b) anode;
   - c) both electrodes;
   - d) no correct answer.
2. Choose the granule formula, which was formed by interaction of Na_3PO_4 excess and $MgCl_2$:
   - a) $[(Mg_3(PO_4)_2)_m nMg^{+2} 2(n-x)H^+]^{2x+}$;
   - b) $[(Mg_3(PO_4)_2)_m nMg^{+2} 2(n-x)Cl^-]^{2x+}$;
   - c) $[(Mg_3(PO_4)_2)_m nPO_4^{3-}\ 3(n-x)Na^+]^{3x-}$;
   - d) $[(Mg_3(PO_4)_2)_m\ 2nPO_4^{3-} 8(n-x)Mg^{2+}]^{3x-}$.
3. Choose the granule formula, which was formed by interaction of $MgCl_2$ excess and Na_3PO_4:
   - a) $[(Mg_3(PO_4)_2)_m nMg^{+2} 2(n-x)H^+]^{2x+}$;
   - b) $[(Mg_3(PO_4)_2)_m nMg^{+2} 2(n-x)Cl^-]^{2x+}$;
   - c) $[(Mg_3(PO_4)_2)_m nPO_4^{3-}\ 3(n-x)Na^+]^{3x-}$;
   - d) $[(Mg_3(PO_4)_2)_m\ 2nPO_4^{3-} 8(n-x)Mg^{2+}]^{3x-}$.
4. Chose conditions under which micelle $\{[(FeS)_m\ nS^{-2} 2(n – x)Na^+]^{-2}\ 2xNa^+\}$ is formed by interaction of the solutions of $FeCl_2$ and Na_2S:
   - a) $FeCl_2$ was taken in excess;
   - b) Na_2S was taken in excess;
   - c) equimolar concentrations of both compounds was taken;
   - d) no correct answer.
5. Chose conditions under which the micelle

$\{[(AgI)_m\ nAg_+(n-x)NO_3^-]^+ x\ NO_3^-\}$ is formed by interaction of the solutions of $AgNO_3$ and KI:

a) $AgNO_3$ was taken in excess;
b) KI was taken in excess;
c) equimolar concentrations of both compounds was taken;
d) no correct answer.

6. Find to which electrode (cathode and anode) will move micelle granule $\{[(AgI)_m\ nAg_+(n-x)NO_3^-]^+\ x\ NO_3^-\}$

a) cathode;
b) anode;
c) both electrodes;
d) no correct answer.

7. Find which electrode (cathode and anode) the micelle granule $\{[(FeS)m\ nS^{-2}2(n-x)Na^+]^{-2}\ 2xNa+\}$ will move to:

a) cathode;
b) anode;
c) both electrodes;
d) no correct answer.

8. Find to which electrode (cathode and anode) the micelle granule $[(Cd(OH)2)m\ nCd^{2+}\ 2(n-x)Cl^-]^{2x+}$ will move to:

a) a cathode;
b) anode;
c) both electrodes;
d) no correct answer.

9. Choose the granule formula, which was formed by interaction of AgNO3 excess and KI:

a) $[(AgI)m\ nAg^+(n-x)I^-]$;
b) $[(AgI)m\ nK^+(n-x)NO3^-]$;
c) $[(AgI)m\ nI^-\ (n-x)K^+]$;
d) $[(AgI)m\ nAg^+\ (n-x)NO3^-]$

10. Choose the granule formula, which was formed by the interaction of KI excess and AgNO3:

a) $[(AgI)m\ nAg^{+}(n - x)I^{-}]$;

b) $[(AgI)m\ nK^{+}(n - x)NO3^{-}]$;

c) $[(AgI)m\ nI^{-}\ (n - x)K^{+}]$;

d) $[(AgI)m\ nAg^{+}\ (n - x)NO3^{-}]$

11. Choose the granule formula, which was formed by interaction of H_3PO_4 excess and $Al_2(SO_4)_3$:

a) $[(AlPO4)m\ nSO4^{2-}\ 2(n - x)Na^{+}]^{2-}$;

b) $[(AlPO4)m\ nPO4^{3-}\ 3(n - x)Na^{+}]^{3-}$;

c) $[(Al2(SO4)3)m\ nPO4^{2-}\ 3(n - x)Na^{+}];^{+}$

d) $[(AlPO4)m\ 3nNa^{+}\ (n - x)PO4^{3-}]$.

12. Choose the granule formula, which was formed by interaction of $Al_2(SO_4)_3$ excess and H_3PO_4:

a) $[(AlPO4)m\ nSO4^{2-}\ 2(n - x)Na^{+}]^{2-}$;

b) $[(AlPO4)m\ nPO4^{3-}\ 3(n - x)Na^{+}]^{3-}$;

c) $[(Al2(SO4)3)m\ nPO4^{2-}\ 3(n - x)Na^{+}];^{+}$

d) $[(AlPO4)m\ 3nNa^{+}\ (n - x)PO4^{3-}]$.

13. Chose conditions under which the micelle $\{[(Ag2S)m\ nAg^{+}(n - x)\ NO3^{-}]^{+}\ x\ NO3^{-}\}$ is formed as a result of interaction of the solutions of AgNO3 and Na_2S:

a) AgNO3was taken in excess;

b) Na2S was taken in excess;

c) equimolar concentrations of both compounds were taken;

d) no correct answer.

14. Chose conditions under which the micelle $\{[(Ag2S)m\ nAg^{+}(n - x)NO3^{-}]^{+}\ x\ NO3^{-}\}$ is formed by interaction of the solutions of Na_2S and AgNO3:

a) AgNO3 was taken in excess;

b) Na2S was taken in excess;

c) equimolar concentrations of both compounds were taken;

d) no correct answer.

15. Chose conditions under which the micelle $\{[(MnS)mnMn^{\square+}\ 2(n-x)\ NO3-]^{\square+}\ 2xNO3^{-}\}$is formed by interaction of the following solutions of Na_2S and $Mn(NO_3)_2$:

a) $Mn(NO_3)_2$ was taken in excess;
b) Na2S was taken in excess;
c) equimolar concentrations of both compounds were taken;
d) no correct answer.

16. Chose conditions under which the micelle $\{[(MnS)_m nMn^{2+}\ 2(n-x)NO_3^{-}]^{2+}\ 2xNO_3^{-}\}$is formed by interaction of the solutions of Na_2S and $Mn(NO_3)_2$:

a) equimolar concentrations of both compounds were taken;
b) Na_2S was taken in excess;
c) $Mn(NO_3)_2$ was taken in excess;
d) no correct answer.

17. Chose formula of sol micelle, which was obtained by reaction $BaCl_{2(\text{надл})}+ AgNO_3 \rightarrow$:

a) $[(AgCl)_m\ nAg^{+}2(n-x)Cl^{-}]^{+}2xCl^{-}$;
b) $(AgCl)_m\ n\ Cl^{-}\ \frac{1}{2}(n-x)Ba^{2+}]^{2+}2xCl^{-}$;
c) $[(AgCl)_m\ nBa^{2+}2(n-x)\ Cl^{-}]^{2+}2xCl^{-}$

REFERENCES

1. Zavgorodniy, I. V, Tkachuk, N. M., Grabovetskaya, E. K., Vekshin, V. A. (2007). Acid-bases equilibrium and complex formation in biological liquids: methodical instruction for medical faculty student's self-work in medical chemistry. Module 1. Kharkiv, Ukraine: KSMU.
2. Zavgorodniy, I. V, Tkachuk, N. M., Grabovetskaya, E. K., Vekshin, V. A. (2007). Equilibrium in biological systems at a phase interface : methodical instruction for medical faculty student's self-work in medical chemistry. Module 2. Kharkiv: KSMU.
3. Wong, Y. C., Wong, C. T., Onyirukas, S. O., Akpanisi, L. E. (2002). University General Chemistry: Inorganic and Physical. Africana. – Fep. Publishers Limited. Manhattan Press.
4. Flowers, Paul; Theopold, Klaus; Laugley, Richard; Robinson William R. (2019). Chemistry 2 e. Houston, Texas: OpenStax. Retrieved from https://opentextbc.ca/chemistry/chapter/17-2-galvanic-cells/ and https://opentextbc.ca/chemistry/chapter/17-4-the-nernst-equation/
5. Kalibabchuk, V. I., Halynska, V. I., Hryshchenko, L. I. et al. (2016). Medical chemistry (V.O. Kalibabchuk, Ed). Kyiv: AUS Medicine Publishing.
6. Dychenko, T.V. (2013). Lectures on Medical Chemistry. Sumy. Sumy State University.
7. Dychenko, T. V., Litsman, Y. V., Vorobiyova, I. G. (2013). Methodical instractions for independent student work in Medical Chemistry "Acid-Base Equilibrium and Complex Formation in Biological Liquids". Sumy. Sumy State University.
8. Biogenic elements. Retrieved from http://www.lenntech.com/periodic/elements.htm and http://www.lenntech.com/periodic/elements/s.htm

GLOSSARY

Biogenic elements are the chemical elements required for the construction and vital activity of cells and organisms.

Macroelements (>10^{-2} %). These are C, H, O, N, P, S, Na, Ca, K, Cl.

Microelements (<10^{-2} %). These are Mg, Cu, Zn, Mn, Co, Fe, I, Al, Mo, etc.

Ultramicroelements (<10^{-12} %). These are Ra, Hg, Au, U, etc.

Irreplaceable elements. They are constantly in the human body. These are C, H, O, N, K, P, S, Na, Ca, Cl, Mg, Cu, Zn, Mn, Co, Fe, I, Mo, V, etc. The deficiency of these elements in the body leads to the infringement of the vital activity of the organism.

Impurity elements. They are also constantly present in the human body, but their biological role is not always known or is little studied yet. These are Ga, Sb, Sr, Br, F, B, Be, Li, Si, Sn, Cs, As, Ba, Ge, Rb, Pb, Ra, Bi, Cd, Cr, Ni, Ti, Ag, Th, Hg, Ce, Se.

Microimpurity elements. They are found in the human body, but there is no information about their content or biological roles. These are Sc, Tl, In, La, Pr, W, Re, etc.

s-block, Elements of Groups IA and IIA form the s-blocks as their outermost shell electrons are located in the s-subshell.

p-block. Elements of Groups IIIA to O are known as p-block elements. It is because their outermost shell electrons are located in the p-subshell.

d-block. d-Block elements have their highest energy electrons in the inner d-subshell. They are also called “transition elements”.

Coordination compounds (complex compounds, complexes) are the compounds that contain complex ions that retain their stability when dissolved.

Complex ion is the central atom (ion) together with its ligands.

Ligands or **addends** are oppositely charged ions or neutral molecules, around the central atom (ion)/

Coordination number reflects the number of bonds formed between the metal ion and the ligands in the complex ion**.**

The charge of the complex ion is equal to the algebraic sum of the charges of the central atom (ion) and ligands.

Ionic bonds are the electrostatic forces of attraction between oppositely charged ions; the ions are the result of electron transfer between atoms.

The Covalent bond is a chemical bond that involves the sharing of electron pairs between two non-metallic atoms.

Dative covalent bond (also known as a **coordination bond**) is the type of covalent bonding in which the shared pair of electrons is supplied by only one of the bonded atoms.

Isomers are compounds having the same molecular formulae but different structural formulae.

Structural isomers are isomers that have different ligands coordinated with the central metal ion.

Geometric isomers are isomers in which the composition of the first coordination sphere is the same, but the geometric arrangement of the ligands is different.

Thermodynamics is the study of energy transfer and the effects of energy changes.

Thermochemistry is the study of the heat change of the chemical reaction.

Universe: The Universe = the system + the surroundings. In the universe, there is no change in the amount of energy.

Surroundings represent that part of the universe with which a system interacts.

The System is any totality of bodies separated from the surroundings by a boundary (real or imaginary) inside which matter and/or energy exchange is possible.

There are several types of systems:

Open system can exchange both matter and energy with the surroundings. A living organism is an open system.

Closed system can exchange energy but not matter with the surroundings.

Isolated system is the exchanges neither matter nor energy with the surroundings.

Homogeneous system is a system that consists of one phase only.

Heterogeneous system is a system with more than one phase.

Phase refers to any part of a system that is physically separated from other parts of the system by a distinct boundary. A phase can be a solid, liquid, vapor (gas) or aqueous solution which is uniform in both the chemical constitution and physical state

Isochoric process is a process that takes place at constant volume (V=const).

Isobaric process is the process that takes place at constant pressure (P=const).

Isothermal process is a process that takes place at constant temperature (T=const).

There are exothermic and endothermic processes.

Exothermic process (reaction) is a process that evolves heat to the surroundings.

Endothermic process (reaction) is a process that absorbs heat from the surroundings.

The state of a system is characterized by thermodynamic parameters and state functions.

Thermodynamic parameters are pressure P, temperature T, volume V, and concentration.

State function is a property that depends only on the state or present condition of a system and not on how this state is attained.

Some common state functions are internal energy (U), enthalpy (H), entropy (S) and free energy (G).

The first law of thermodynamics. Energy is conserved; it can be neither created nor destroyed.

The second law of thermodynamics. In an isolated system, natural processes are spontaneous when they lead to an increase in disorder or entropy.

The third law of thermodynamics. The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

Internal energy (U) is the sum of the kinetic and potential energies of the particles that form the system.

Enthalpy (H) is a term that describes the heat content of a system.

ΔH = heat absorbed by the system at constant pressure.

The heat absorbed by the system (Q) at constant pressure is equal to the change in **enthalpy** (ΔH).

$$\Delta H = \Delta U + P\Delta V.$$

Standard enthalpy change of formation of a substance is symbolized as (ΔH_f°) and is the enthalpy change when one mole of the compound is formed from its elements under standard conditions. ΔH_f° is measured in $\mathrm{kJmol^{-1}}$.

Standard state conditions are:

- all substances are in their standard states;
- pressure is 101.3 kPa (101325 Pa = 1 atm = 760 mm Hg);
- temperature is 298 K (K = ˚C +273).

Thermochemical equations are equations of the reactions in which the physical states of the substances and the values of any thermodynamic function of the state are indicated. The reaction enthalpy, in this case, is called the **heat effect** of the reaction.

Hess's law: The heat effect of the chemical reaction is independent of the route of the reaction and depends only on the initial and final state of the system.

Spontaneous change is the change that has a natural tendency to occur, causes a system to move from a less stable state to a more stable state.

Entropy (S) is the quantitative measure of the disorder of a system.

The Free energy change (G) of a reaction is a measure of the spontaneity of the reaction. The more negative the free energy change, the more spontaneous the reaction.

The free energy is related to the enthalpy, entropy, and temperature by the equation

$$G = H - TS.$$

Metabolism is sum of chemical reactions that living organisms carry out to obtain energy they need and to synthesize the compounds they require. Metabolism can be divided into two parts: catabolism and anabolism.

Catabolic reactions break down complex nutrient molecules to provide energy and simple precursor molecules for synthesis.

Catabolism: complex molecules → simple molecules + *energy*

Anabolic reactions require energy and result in the synthesis of complex biomolecules from simple precursor molecules.

Anabolism: simple molecules + *energy* → complex molecules

Chemical kinetics is the study of rates of chemical reaction, the factors affecting the rates of the reactions and mechanism by which the reactions proceed.

Mechanism of the reaction is the description of the step-by-step process by which reactants are changed into products

Chemical reaction rate is the change in the concentration of any of the reactants or products per unit time (for homogeneous reaction).

Law of mass action (C. Guldberg and P. Waage): at a constant temperature, the rate of the chemical reaction at each moment is directly proportional to the concentration of the reacting substances.

Molecularity of reaction is the number of molecules that react simultaneously at the moment of collision, accomplishing the act of chemical interaction.

Chemical equilibrium is a state in which the concentrations of reactants and products remain constant over time. Chemical equilibrium is dynamic in nature in which the forward reaction proceeds at the same rate as the backward reaction.

Irreversible reactions are reactions that go to completion.

Reversible reactions are reactions that do not proceed to completion:

$$3H_{2(g)} + N_{2(g)} \rightleftarrows 2NH_{3(g)}.$$

The sign ⇄ represents the reversibility of a reaction. The reaction from left to right (→) is called the **forward** reaction, while the reaction from right to left (←) is called the **backward** (**reverse**) reaction.

Le Chatelier's Principle states: When a change is introduced into a chemical system at equilibrium, the system will shift in the direction that counteracts that change.

Solutions are homogeneous systems consisting of two or more components and the products of their interaction. Compulsory components of the solution are the solvent and the **solute**.

A Solvent is the solution component that is **present** in the **greatest quantity** or the component that determines the state of matter in which the solution exists.

The Solute is the solution component, which is **present** in a **lesser quantity** than the solvent.

Aqueous solution is a solution in which **water** is the **solvent.**

Concentration is a measure of the amount of the solute, which is dissolved in a given amount of the solvent.

Mass percent (percent by mass concentration, %) shows how many grams of solute is dissolved in 100 g of solution.

Molar concentration (Molarity) (C_M) is a concentration of a solution expressed as the number of moles of solute per liter of solution.

Molality (C_m) is a concentration of a solution that is expressed as a number of moles of solute per kilogram of solvent.

Normality (C_N) is defined as the number of equivalents of solute per liter of solution.

Mole fraction is the ratio of the number of moles of a substance to the total number of moles of all substances in the solution.

Colligative properties are the properties of solutions that depend only on the number of particles of a solute in a definite amount of the solvent and do not depend on the nature of the solute.

The Raoult's law: The relative depression of the saturated vapour pressure of the solvent above the solution equals the mole fraction of the solute.

Elevation in the boiling point of the solution (ΔT_b) is the difference between the boiling point of a solution and that one of the pure solvent.

Freezing point depression of the solution (ΔT_f) is **t**he difference between the freezing point of the pure solvent and that one of the solution.

Second Raoult's law. For dilute solutions of non-electrolytes, the elevation of the boiling point, and the depression of the freezing point are proportional to the molal concentration of the solution.

Osmosis is defined as the physical process of diffusion of a solvent (water) through a ***semi-permeable membrane*** (a membrane which allows the solvent molecules to pass through, but not the solute particles) towards an area of high solute (salt) concentration.

Osmotic pressure (π) is the pressure that must be applied to a solution when separated from a more dilute solution by a semipermeable membrane, in order to prevent the inflow of a solvent.

A Buffer solution is a solution that tends to resist changes in pH when a small amount of acid or base is added to it.

Buffer capacity is a number of moles of a strong acid or a strong base that is needed to be added to 1 L of buffer solution in order to change its pH for 1 unit.

Hydrolysis is a reaction in which water reacts with ionic species in solution.

Acids are substances that produce hydrogen ions, H^+, in aqueous solutions.

Bases are substances that produce hydroxide ions, OH^-, when dissolved in water.

Nonelectrolytes are compounds whose aqueous solutions do not conduct electricity.

Electrolytes are aqueous or molten substances that conduct an electric current and dissociate into ions.

The degree of dissociation (α) of an electrolyte is 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.

Strong electrolytes are substances that completely dissociate in water. Acids and bases that partially dissociate in water are called weak acids or bases (**weak electrolytes**).

Dissociation (or ionization) constant is the constant equilibrium corresponding to the dissociation of a weak electrolyte.

Oxidation state of an atom is the apparent or real charge that an atom has when all bonds between atoms of different elements are assumed to be ionic.

Oxidation-reduction or redox reaction is a reaction in which electrons lost by one of the reaction components are gained by another component.

Oxidation is a process in which the oxidation state of some element increases. The component loses electrons.

The reducing agent (reductant) is the component supplying the electrons.

The reduction is a process in which the oxidation state of some element decreases. The component gains electrons.

Oxidizing agent (oxidant) is the component receiving the electrons.

Galvanic cell consists of two half-cells, such that the electrode of one half-cell is composed of metal A, and the electrode of the other half-cell is composed of metal B; the redox reactions for the two separate half-cells are thus: $A^{n+} + n\ e^{-} \rightleftharpoons A$.

Colloids are those (disperse) systems which consist of particles in size of 1 nm–500 nm (1nm = 10^{-9} m).

Навчальне видання

Диченко Тетяна Василівна,
Яновська Ганна Олександрівна

МЕДИЧНА ХІМІЯ

Навчальний посібник

(Англійською мовою)

Художнє оформлення обкладинки Г. О. Яновської
Редактор С. В. Чечоткіна
Комп’ютерне верстання Г. О. Яновської

Формат 60×84/16. Ум. друк. арк. 10,0. Обл.-вид. арк. 8,82. Тираж 300 пр. Зам. №

Видавець і виготовлювач
Сумський державний університет,
вул. Римського-Корсакова, 2, м. Суми, 40007
Свідоцтво суб’єкта видавничої справи ДК № 3062 від 17.12.2007.