Ministry of Education and Science

National Technical University of Ukraine

"Igor Sikorsky Kyiv Polytechnic Institute"

I.V. Kosogina, I.M Astrelin, Yu.M. Fedenko,
S.O. Kyrii

APPLIED INORGANIC CHEMISTRY

Recommended by the Academic Council of the Igor Sikorsky Kyiv Polytechnic Institute

as a textbook for students,

studying on specialty 161 "Chemical technologies and engineering"

Kyiv
Igor Sikorsky Kyiv Polytechnic Institute
2019

Reviewers: Plavan V.P., Doc. Sci., Prof.
Mieskova-Klimenko N.A., Doc. Sci., Prof.
Responsible
editor: Sanginova O.V., PhD., Associate Prof.

The Grief is provided by the Academic Council of Igor Sikorsky Kyiv Polytechnic Institute (protocol № 1 from 20.01.2020p.)

Educational Edition

Authors: Kosogina Iryna Volodymyrivna, PhD.
Astrelin Ihor Mykhaylovych, professor, Doc.Sci.
Fedenko Yurii Mykolayovych, PhD.
Kyrii Svitlana Oleksandrivna, Ph.D.

APPLIED INORGANIC CHEMISTRY

Applied Inorganic Chemistry: textbook / I.V. Kosogina, I.M. Astrelin, Yu.M. Fedenko, S.O. Kyrii – К.: Igor Sikorsky Kyiv Polytechnic Institute, 2019. – 258 p.

General principles of the technique of chemical experiments that are based on the applied application of the basic provisions of theoretical chemistry in processes of inorganic substances technology, in particular, the technologies of production of sulfur-containing products, compounds of bound nitrogen, fertilizers, soda products, alumina, titanium-containing products, processes of applied ecology and water treatment have presented.

Designed for the in-depth study of various aspects of the application in laboratory practice of the basic chemistry principles and the substantiation of the peculiarities of real solutions for future professional activities. It can be used by students in preparation for lecture classes, control works, and can perform laboratory and practical work by students.

CONTENT

INTRODUCTION

Discipline (credit module) "Applied inorganic chemistry" belongs to the cycle of study disciplines of free choice, which initiates the training of students in the specialty "Chemical Technology and engineering", specialization "Chemical technologies of inorganic substances".

The teaching of the academic discipline "Applied inorganic Chemistry" occupies an important place in the initial formation for the future specialist of a strategic view on the deep connection of the inorganic chemistry theoretical provisions with their practical implementation into real technological practice.

The educational material of the discipline is based on the knowledge of inorganic chemistry. The training manual on the credit module "Applied Chemistry" contributes to the mastering and in-depth study of the specified discipline.

The main purpose of the discipline "Applied inorganic Chemistry" is to teach students to use theoretical knowledge gained at lectures and practical classes to solve specific practical tasks and examples from a professional direction, gaining students the ability to identify chemical and technological peculiarities of processes, mainly from chemical technology of inorganic substances. At the same time, the aim is to acquire and deepen theoretical knowledge when students become aware of the basic principles methodology application of chemistry for the practical substantiation of the real (or approaching) decisions on future professional activities.

CHAPTER 1 TECHNIQUE OF LABORATORY EXPERIMENT

1.1 MATERIALS, DEVICES AND METHODS IN APPLIED CHEMISTRY

The chemical glassware produced for the laboratories needs are extremely diverse. One should avoid conducting a specific chemical experiment in glassware not intended for it. The possibility of synthesizing a substance with maximum yield and the required purity largely depends on the proper choice of chemical glassware and the reliable connection of its various types in a laboratory installation using sections, bibbs, tubes, and other connecting elements.

It often has to work with laboratory glassware made of glass and porcelain in the chemical laboratory. Laboratory Glassware can be subdivided into the following types:

1. general purpose laboratory glassware;
2. special purpose laboratory glassware;
3. measuring laboratory glassware;
4. porcelain laboratory glassware.

Conducting any chemical experiment requires the use of standard chemical glassware, as well as auxiliary parts and assemblies - hoses, plugs, sections.

A chemically resistant glass is very important in laboratory practice since it is from it a variety of chemical glassware (flasks, refrigerators, weighing bottles) are made. Adding to the glass B_2O_3, ZnO and increasing the content of Al_2O_3 can achieve resistance to the action of acids and alkalis. A chemically resistant glass is also widely used for the manufacture of various industrial devices - columns, absorbers, cranes, pipes, and the like.

Most of the chemical glassware and accessories are made of glass. The hardness and smoothness of the surface facilitate the washing of glass glassware, and transparency gives experimenters the opportunity to follow the course of chemical reactions and physical processes. The glass well tolerates by the load on compression, worse - by bending, but it does not perceive shock effects. Under the influence of water and aqueous solutions of salts on the glass as a result of the dissolution and hydrolysis of alkali metal silicates, a protective SiO_2 film is formed on the surface of the glass. Such a film is fairly stable in neutral and acid solutions (except for HF), but is destroyed in alkaline solutions by the following reactions:

$$SiO_2 + 4KOH = K_4SiO_4 + 2H_2O;$$

$$H_4SiO_4 + 4KOH = K_4SiO_4 + 4H_2O,$$

which convert into ortho- and polysilicates of alkali and other metals that are part of the glass. To protect the glass from the influence of alkaline medium, it is recommended to create a special film on the surface of a glass vessel, first processing the product with sulfate acid, diluted with water in a ratio of 1: 1, and then, after washing by paraffin or stearin that were melted at a temperature of 200…300 ^{0}C.

The basic requirements for laboratory glassware and glass-ware are thermal and chemical resistance.

Thermal stability is glass ability to withstand sharp fluctuations in temperature without breaking. The maximum temperature difference that the glass can withstand without breaking is the magnitude of its thermal stability. Thermal stability of glassware depends, in particular, on the thickness of the walls. For example, the thermal stability of products made of Czech glass "simax" with a thickness of a wall of a vessel of 1 mm is 312 ^{0}C, at 3 mm – 180 ^{0}C, at 10 mm – 100 ^{0}C [1].

For thermal stability, glass is divided into groups according to their coefficients of linear thermal expansion in the temperature range from 20 to 300 ^{0}C.

The first group is a glass with a coefficient of thermal expansion from $70·10^{-7}$ $К^{-1}$ to $90 ·10^{-7}$ $К^{-1}$**.** The glass of this group is relatively light-melting and prone to bundle, with prolonged heating in the flame of the gas burner, the glass loses its transparency, becomes turbid, and after cooling it is roughened to the touch;

The second group is a glass with high thermal stability, the coefficient of thermal expansion of which is in the range from $50·10^{-7}$ $К^{-1}$ to $65·10^{-7}$ $К^{-1}$. These include molybdenum glass. Molybdenum glass has been named thanks to the ability to form a vacuum-tight junction with metal molybdenum. It is chemically less resistant than any other laboratory glass but is lightweight in glass-blowing treatment.

The third group is a glass with high thermal stability and a coefficient of thermal expansion from $38·10^{-7}$ $К^{-1}$ to $49·10^{-7}$ $К^{-1}$. These include low alkaline borosilicate glass with a high content of silicon oxide "Pirex", TS, "Simax", "Rathoterm";

The fourth group is a particularly high temperature-resistant glass of the quartz type with a coefficient of thermal expansion from $5·10^{-7}$ $К^{-1}$ to $7·10^{-7}$ $К^{-1}$[2].

Chemical resistance is the ability of glass to withstand the destructive effects of water, acids, alkalis, and other chemical reagents. Chemical resistance of glass is determined according to all-Union State Standard 21400-75, which establishes the classes of hydrolytic resistance (water resistance), acid resistance and alkaline resistance of glass due to the loss of the mass of the glass sample after exposure for a certain time in a suitable environment.

According to all-Union State Standard 21400-75, depending on the chemical and thermal stability in Ukraine, for the manufacture of laboratory glassware, glass of the following groups is used:

- chemically resistant class 1
- chemically resistant class 2

- chemically resistant class 3
- thermally and chemically resistant class 1
- thermally and chemically resistant class 2
- thermally stable (borosilicate glass)

1.1.1 GLASS AS A MATERIAL FOR THE MANUFACTURE OF CHEMICAL GLASSWARE

The raw materials for the glass production are: quartz sand SiO_2, soda Na_2CO_3, limestone $CaCO_3$, potash K_2CO_3, sodium sulfate Na_2SO_4, magnesite $MgCO_3$, kaolin $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (Table 1.1).

Table 1.1 – The chemical composition of the glass

Component	Content,% wt
SiO_2	71,0
Na_2O	15,5
CaO	8,5
MgO	3,5
Al_2O_3	1,5

1.1.2 SPECIAL TYPES OF GLASS AND MATERIALS FOR LABORATORY RESEARCH

Three-layer glass - used for the manufacture of windows of cars, trolleybuses, buses, railway cars, metro cars, etc. It consists of two layers of glass, which are glued together by an organic transparent film, so in the case of impact, such glass does not crumble. For the windows of cars is also used special *tempered glass*, which has increased mechanical strength.

Foam glass is a porous building material, from which are made building partitions, thermal insulation, etc. Foam glass is obtained by sintering fine-grinding glass scrap with foaming agents.

Glass fiber is obtained by pulling thin glass fibers from molten glass. From glass fiber is made glass yarn, glass protective fabrics, and it is used in acid-proof filters, and so on. Glass fiber in composition with a plastic gives the opportunity to receive materials from which reactor shells, columns, etc. are made.

Alkaline (predominantly sodium) glass $Na_2O{\cdot}nSiO_2$ is dissolved in water and is used for refractory coating of wood, in the production of soap, to produce silica gel as a binding component in the manufacture of cement, as a glue in everyday life, and the like. It is formed as a result of fusion at a temperature of 1300...1500 °C from quartz sand and soda (or a mixture of sodium sulfate and coal). By treating the resulting glass solid alloy with water in autoclaves at a pressure of 0.4...0.8 MPa, *liquid glass* is obtained, which is estimated by the modulus ratio $SiO_2 : Na_2O$, in the range from 1 to 4.

The addition of lead oxide makes it possible to obtain *crystal glass* with a high light-refractive index. Sometimes lead oxide in crystal glass partially replaced by barium oxide.

Refractory glass (pyrex) contains up to 80% SiO_2 and up to 12% of B_2O_3 and withstands the effect of very high temperatures.

For acid action resistance, fire resistance and the ability to withstand abrupt changes in temperature, the best is *quartz glass*. From it manufactures heaters, quartz apparatus, which, in particular, is used in the production of pure chloride acid with chlorinated water, and so on.

Special silicates *(pyrocerams)* - are silicate materials that have high thermal and corrosion resistance and mechanical strength. They are obtained from glass melt or metallurgical slags and rocks with the addition of catalysts (oxides of titanium, chromium, cerium, vanadium, zirconium, also fluorides and phosphates of alkaline and alkaline earth metals, sulfides of heavy metals), which serve to form the centers of crystallization. As a result of the cooling of the molten mass, glass-like products are re-evaporated (thermosetals) or irradiated (photosilanes). To obtain thermally stable silicate materials, the vitreous mass is cooled abruptly. In the case of their irradiation receive photosensitive silicate materials.

Pyrocerams have a high temperature of softening (from 900 to 1000 ^{0}C), withstand sharp fluctuations in temperature, stable in alkalis, in all acids, except fluoride. By mechanical properties, they are better than steel and inferior to it only by impact strength. Pyrocerams have a coefficient of thermal expansion, close to zero, low dielectric losses and high dielectric constant at high frequencies, and therefore used for the manufacture of insulators. From pyrocerams are made of controlled shells, small diameter pipes, bearings, which operate without lubricant at a temperature of 540 °C, pistons and cylinders of internal combustion engines, carry out the lining of mills, cutters, drillers, and the like. In addition, the pyrocerams are valuable insulation and building material (used for the manufacture of plates, panels, blocks).

Glassy chemical utensils can suddenly break apart for no apparent reason. Often this occurs due to the appearance on its surface of small scratches formed during mechanical cleaning of utensils by sand, coal, metal brush and other solid objects. Scratches can also appear when the utensils put on bricks, ceramic tiles with a rough surface. When fastening glassware in tripods it is often underestimate the pressure of different holders when tightening the screw. Glass objects should be fastened in clamps that are equipped with the lining of elastic materials.

The most widely used for the manufacture of chemical utensils has porcelain. It is a white ceramic material that shines in a thin layer and has a characteristic sound when struck. It differs with water and gas impermeability, mechanical strength. Thermal stability of unglazed porcelain is 1400…1500 ^{0}C. Glazed porcelain is less heat-resistant, therefore it can be used only to 1200 ^{0}C. With prolonged heating of such porcelain already at a temperature of about 1000 ^{0}C, the glaze is expanded and exfoliated.

Porcelain is chemically resistant to the action of most acids and acidic melts, except for HF and H_3PO_4. Hydrogen chloride erodes porcelain at a temperature of 800 ^{0}C, and above 1000 ^{0}C porcelain collapses under the chlorine influence. With the simultaneous presence of carbon-containing substances in these gases, the effect of HCl and Cl_2 is manifested at lower temperatures. Porcelain is also gradually destroyed by contact with molten alkali metal hydroxides, calcium, and barium or their concentrated aqueous solutions.

The composition of porcelain includes SiO_2 (75 %), Al_2O_3 (19…21 %), K_2O (3…4 %). Porcelain is used for the manufacture of crucibles, shuttles, cups, ovens, putty knifes, glasses, and other products. Thin-walled porcelain crucibles can be introduced directly into the flame of a gas burner, and then cooled to room temperature. Thick glassful and cups need to be heated with care, they can`t be heated on an open flame, but need to apply mesh with an asbestos pad.

1.2 THE MAIN TYPES OF CHEMICAL GLASSWARE DEPENDING ON OF ITS USAGE

1.2.1 CHEMICAL GLASSWARE, FLASKS, AND RETORTS[1]

Chemical beakers are low or high cylinders with or without a spout, flat-bottomed or round-bottomed. They are made of different varieties of glass and porcelain, as well as polymeric materials. They can be thin-walled and thick-walled, graduated and simple. Beakers made of fluoroplastic-4 in works with highly aggressive substances are used. Polyethylene or polypropylene beakers for experiments involving fluoride acid are used. If it is necessary to maintain a certain temperature during the reaction or filtering the precipitate,

---

[1] The figures for section 1.2 are borrowed from the sites of firms that are engaged in the purchase and sale of laboratory utensils: Ltd. "MANKOR", Ltd. "Chimlaborreaktiv"

then glasses with a thermostat shirt used. Syntheses of substances with a mass up to 1 kg are carried out in a reactor-beakers with a polished lid, which has several tubes for insertion into the glass of the axis of the mixer, the tubes of the refrigerator and the dividing funnel and other devices. In such wares, it is possible to maintain a vacuum or a little excess pressure.

It is not possible to heat the chemical beakers on the open flame of the gas burner due to their possible cracking. It is necessary to put an asbestos net under beaker or use liquid baths for heating, electric tiles with a ceramic surface.

The flasks can be round-bottomed (Fig.1.1 a), flat-bottomed, conical, with acute-bottom, pear-shaped (Fig.1.1, b), with a different number of necks and branches, with soles and without soles, with a thermostat shirt and a lower descent and other structures. The volume of flasks can vary from 10 ml to 10 l, and the thermal stability reaches 800…1000 ^{0}C. Flasks are intended for conducting preparatory and analytical work. Depending on the complexity, the flasks can have from one to four necks for equipment with their stirrers, refrigerators, dispensers, cocks for connection to the vacuum system or for the supply of gas, etc.

a b

Figure 1.1 – Round-bottomed (a), pear-shaped (b) flasks

Pear-shaped flasks are necessary for case distilling a liquid when the steam must not overheat at the end of the process. The heated surface of such flask does not reduce when the mirror of the liquid is decreased.

The Kjeldahl flask has a long throat and a pear-shaped lower part. It is used for the determination of nitrogen and made from the glass of the brand "Pirex" (Fig. 1.2).

Figure 1.2 – The Kjeldahl flask

Walter and Keller's flasks have a wide throat for inserting inside the receptacles of various gadgets through or without a rubber cork. **Narrow-bottom flasks** can have from one to three throats. They are used in cases when distillation is carried out with a small amount of liquid or to liquid phase removing completely.

The advantage of different types of **flat-bottom flasks** is the steady position on the laboratory table. Conventional conical flasks are called **Erlenmeyer flasks** (Fig. 1.3). The hole usually has slightly rounded edges so the flask can be easily sealed with a rubber stopper or cotton wool. The conical shape allows for easy mixing of the contents during the experiment or by hand, either by a special laboratory shaker or magnetic stirrer. The narrow throat retains the contents from the pouring out, as well as it preserves it better from evaporation than the laboratory beaker. The flat bottom of the conical flask does not allow it to roll over.

The main field of Erlenmeyer flasks application is titrimetric analysis methods.

Figure 1.3 – Erlenmeyer flasks

For the distillation of liquids, the flask with a quite diverse design is used. The simplest of these are the Wurtz flasks. It is round-bottomed flasks with lateral sprout, for which are joined a fridge. For work with liquids with a high boiling point, the sprout should be located closer to the spherical part of the flask. Easy-boiling liquids are distilled in Wurtz flasks with a sprout, located closer to the open end of the throat (Fig. 1.4). In this case, less spatter of liquid falls into the distillate. Available with top, middle, and bottom outlet tubes. Volume from 25 to 1000 ml.

Figure 1.4 – Wurtz flasks

The Kleisen flask is intended for distillation under normal pressure or for vacuum distillation. It is round-bottom or sharp-bottom flask, from the throat of which leaves the second throat with outlet pipe (Fig. 1.5 a).

Favorsky flask is designed for distillation under normal pressure or vacuum distillation. It is a two-throat sharp-bottom flask, the upper throat of which has a tap-tube (Fig. 1.5 b).

Bogdanov flask is intended for the distillation of paraffin (in particular, under vacuum) and the determination of the boiling interval (Fig. 1.5 c).

Bunsen flask[2] —is a flask designed for vacuum filtration. This flask is thick-wall, conical, at the top of it has an aperture for connection with a vacuum pump or with a vacuum line (Fig. 1.5 d). The thickness of flasks walls is 3 ... 8 mm, which allows withstanding the marginal residual pressure (no more than 1400 Pa). The volume of the flask ranges from 100 ml to 5.0 l. When filtering a large amount of liquid, flasks with a bottom tube use to drain the filtrate. In this case, before the drain the water, the water-jet pump turns off and intake air into the flask. Bunsen flasks with a three-way tap are used to remove the filtrate without disconnecting the vacuum.


a b c d

Figure 1.5 – Kleisen flask (a), Favorsky flask (b), Bogdanov flask (c), Bunsen flask (d)

Retorts are an old alchemical ware used in the Middle Ages for sulfate and nitric acids production (Fig. 1.6). The retorts capacity is usually 2 ... 3 l. Now retorts are used for reheating of high-boiling liquids, which are easy to condense even when air cooled.

Figure 1.6 – Retort

---

[2] **Robert Wilhelm Bunsen** (1811-1899) is a German chemist. He was born in Goettingen. His father was a professor, who at the same time served as a university librarian. From ten years, Robert has been engaged in various chemical experiments in his home laboratory and the manufacture of self-made devices for experiments.

Retorts are equipped with special condensate receivers. The upper tube with a stopper in the retort serves for loading, introducing a thermometer or for dispensing liquids or for retorts cleaning.

1.2.2 BELLS, LIDS, GLASSES, AND TEST-TUBES

The bells are ware with thick walls from 3.0 mm to 6.0 mm, ground bottom part and a flange. The ground glass connector attache to thick flat glass and lubricate for tightness. Apply bells for demonstration experiments in large auditoriums, where are possible harmful substances releasing in the form of an aerosol. Researchers use bells for control experiments with flammable substances.

Lids produce of two types: with one or two tubes. Lids allow carried out visual observations for reactions with small portions of substances if they have ability to inflammation, explosion or release of poisonous gases.

Glasses are containers of various purposes from vessels for storing solids and liquids to vessels used for the preparation and purification of gases (Figs 1.7a, b).

Drexel, Munke, Tishchenko, Saluzzo-Wulff bottles, and other are used to clean gases.

In laboratory practice, the most commonly used **Drexel bottle** (Fig. 1.7a). The washing liquid is poured into a glass to 1/2 of its height, and the tube that reaches almost to the glass bottom is connected to the gas source.

а б

Figure 1.7 – Drexel bottle (a), Münke bottle (b)

More efficient washing of the gas is achieved either by creating a septum from the bottom of a glass made of porous glass, or by melting to the lower end of the central tube of a plate or cylinder made of porous glass, which provides a fine crushing of gas bubbles.

For alkaline aqueous solutions use Drexel glass, made of polyethylene and polypropylene. The central tube of such glasses ends with a porous fluoroplastic or polypropylene cartridge. To facilitate the filtration of gas through a porous glass partition makes it wider.

The Münkes bottle has a cylindrical vessel instead of a central tube, and therefore, with a decrease in pressure from the gas supply side, the liquid fills this vessel and does not tip over into that part of the device where the gas comes from. The pressure drops and occurrence of vacuum is particularly often the case in an apparatus in which the gas produced by thermal decomposition of the substance. Münkes Glass thus performs two functions: cleaning of gas and prevent the device from tipping thereto absorbing liquid (figure 1.7b.).

A glass with a spiral central tube contributes to an increase in the contact time of each gas bubble that passes through the liquid with the reagent dissolved in it. Gas bubbles, rising in a spiraling spiral, pass a longer way in this glass than in ordinary Drexel glasses. At the same time, such a glass is also a safety glass, like a Münke glass. Glass with a spiral central tube are used at a flow rate of not more than 60 l/h. At this speed there is a separate motion of the gas bubbles in a spiral.

With small amounts of purified gas and relatively small content in it impurities that are easily removed, are used glass of test-tubes type with a diameter of 20...25 mm and a height up to a section of 100 to 150 mm. Sometimes these glasses are combined with rubber hoses in a battery, consisting of three or more consistently connected vessels.

Tischenko glasses can be used for both liquid and solid reagents (Fig. 1.8). The liquid in Tishchenko glass is poured 1/4 of its height. In such glass the cleared gas passes through a hole in the bottom of the partition, and with the advent of a vacuum from the gas source. The liquid from the right compartment simply flows to the left, and the gas is re-cleaned. In Tishchenko glass for solids, the internal partition does not reach the bottom of a ground-glass stopper, which serves as the bottom of the glass.

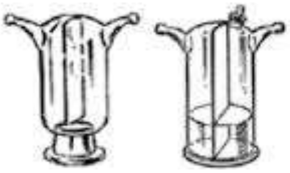


Figure 1.8 – Tischenko glasses

Saluzzo-Wulf glasses are made of thick-walled glass 2.5...3.0 mm with a different number of tubes (Figure 1.9). They are used for receiving and washing gases, as safety vessels before a water jet pump, for the storage of clean water and titrated solutions, liquid dispensers.

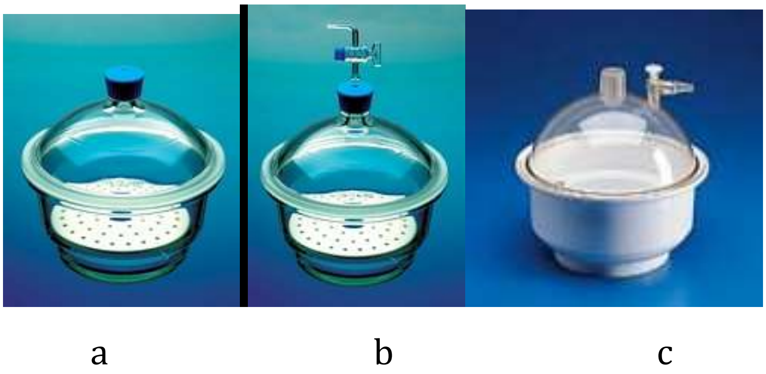
Figure 1.9 – Saluzzo-Wulfa glasses

1.2.3 WASH BOTTLES, DESICCATORS, AND DEWAR'S VESSELS

Wash bottles are vessels that allow sending a thin stream of liquid on precipitate for it washing on a filter, from the walls of glass or from filter (Fig. 1.10). Wash bottles are also used to remove contaminants from the walls of vessels before work.

Desiccators are thick-glass (fig 1.11, a, b) or polymeric materials (Fig. 1.11, c) vessel with a ground-in cover for drying and storing substances that are easy to absorb moisture from the air.

Figure 1.10 – Wash bottles



a b c

Figure 1.11 – Desiccators

All desiccators have a perforated porcelain disc covered with glaze on one side. On the disk contains vessels with drying agents. Desiccators are divided into **Scheibler desiccators** (Fig. 1.11, a) and **vacuum-desiccators** (Fig. 1.11, b, c). Vacuum-desiccators allows faster and more complete removal of moisture from the drying substance. To remove the lid of the vacuum-desiccator, you must first let air into it and carefully open the crane (otherwise, the flow of interrupted air can spread out the dried substance). After that, the lid is removed in the same way as in the Scheibler desiccator.

The vacuum-desiccator, made of polymeric materials, has a polypropylene body and a transparent high polycarbonate lid with two tubes of the top or the side part of the lid, which, like in glass desiccators, is ground-in (Fig. 1.11, c). Side vacuum faucet is made of Teflon. The inner perforated disc is made of polypropylene.

Dewar and Weinhold vessels are double-wall and multi-wall vessels with a vacuumed space between the walls. They are used to store liquid gases. To protect the vessels from heat radiation, their inner walls are silvered or covered with copper. In Dewar and Weinhold vessels, heat transfer is carried out practically due to radiation and heat conduction along the walls. To reduce the evaporation degree of liquid gas, vessels are made of three-wall and multi-wall. They are made of heat-resistant glass or of metal. The space between the walls is evacuated to 0.001 Pa in glass vessels and to 0.01 Pa in metal vessels. To reduce the evaporation of liquid gas, the throat of the vessel makes narrow and high. The upper hole is usually closed to reduce the gas loss by a foam stopper, which does not prevent the flaking of the evaporative gas.

Glass Dewar vessels are installed in a plastic case, between the walls of the vessel and the corps place corrugated cardboard (foam rubber, felt or crust), and the lower part of the vessel is based on a foam or rubber cork with a small opening in the center. Dewar tubes are used for the transfusion of liquid gases at short distances.

1.2.4 CRANES, CLAMPS, VALVES, SHUTTERS AND DRIP TRAPS

Locking devices of various types are important nodes of devices and systems. They provide the ability to regulate gases and liquids, maintain vacuum or excess pressure, and prevent contact with a controlled phase with the environment. Their reliability depends on the correctness of the chemical analysis and the quality of the synthesized substance.

Cranes. Simple one-way and multi-way cranes. Cranes can be glass and fluoroplastic cork. In the ready-to-use cranes, the cork is tied with a strong thread to the camshaft so that it does not disappear during storage.

Clamps are used to regulate the flows of gas and liquid on hoses or to fix the grinding. **Hoffman and Mohr clamps** are traditional**.** The advantage of using Hoffman's clamping device is that it can be installed on the hose of an already assembled device, with no need to leave one of the ends of the hose free. When working with a spring clamp Mohr, the end of the hose should be left free. This clamp is installed on rubber hoses of pure water burettes, when only one arm is free to the experimenter and a simple compression of the clamping device will allow for the desired flow of fluid.

When storing ground joint in the collected form, small pieces of thin paper are placed between them to prevent the possibility of jamming the ground joint. Before work begins, ground joint is lubricated. Lubrications increases the tightness of the connection, protects it from corrosive aggressive environments and seals, facilitates the rotation of the rubbed surfaces. The choice of lubrication depends on the type of work and the composition of the liquid or gas.

In nature there are no universal lubricants resistant to all chemical and temperature effects. Therefore, the choice of lubricants depends largely on the type of work.

Ramsay fatty lubricant[3] used for work with vacuum. It is solution of raw rubber in vaseline and paraffin. To get it, mix crude rubber, vaseline and paraffin in proportions from 7:3:1 to 16:8:1.

Special lubricant is a mixture of high molecular weight semi-liquid hydrocarbons, products of refining oil purified from volatile impurities. Special lubricant is resistant to the action of halogens, but due to considerable fluidity it is easily extruded from the sills.

---

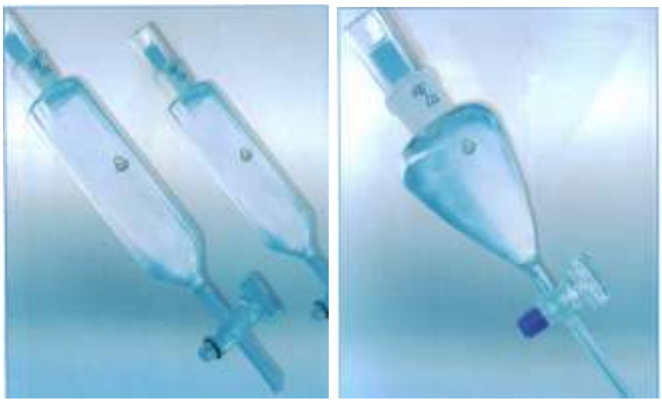
[3] Ramzai William (1852-1916) an English chemist and physicist who discovered several noble gases, the Nobel Prize winner.

Silicone lubricant is a mixture of colorless organosilicon compounds characterized by chemical inertness, hydrophobicity, thermal oxidation stability, relatively small change in viscosity with temperature change. The lubricant can be used at temperatures up to 200 ^{0}C (above 200 ^{0}C it is polymerized with gas release).

Fluoroplastic lubricant is a lubricant on the basis of fluoroplastic-3 with a low degree of polymerization. This lubricant does not work to ozone, sulfur oxide (VI), fuming nitric acid, halogens and other strong oxidizers. Lubricating properties of fluoroplastic lubricant inferior to the properties of silicone.

1.2.5 SEPARATION AND DROP FUNNEL FUNNELS, AMPOULES AND WEIGHING BOTTLES

Separation funnels are an elongated cylindrical or pear-shaped vessel used most often for separating non-mixing liquids (Fig. 1.12, a). The tube in the separation funnel may be short and slightly extended depending on the conditions of usage, but the tube diameter should be such, that the liquid in, it is not delayed. Usually, the crane is not lubricated for prevention entering of lubricant to the liquid. Therefore, separation funnels with fluoroplastic cranes or transparent floating cranes are generally used.



a b

Figure 1.12 – separation (a) and drop (b) funnels

Drop funnels have a long end and a spherical upper part (Fig. 1.12, b). They serve for liquid dosage, which is injected into the reaction vessel by drops or small portions.

Dropping bottles are vessels for liquids that are used drop by drop (Fig. 1.13). In some dropping bottles, a recover of liquid in the pipette is carried out with the help of rubber cartridges, in other liquid come out when inclining vessels, in the third - at the weakening of the finger pressure on the pipette.

Figure 1.13 – Dropping bottles

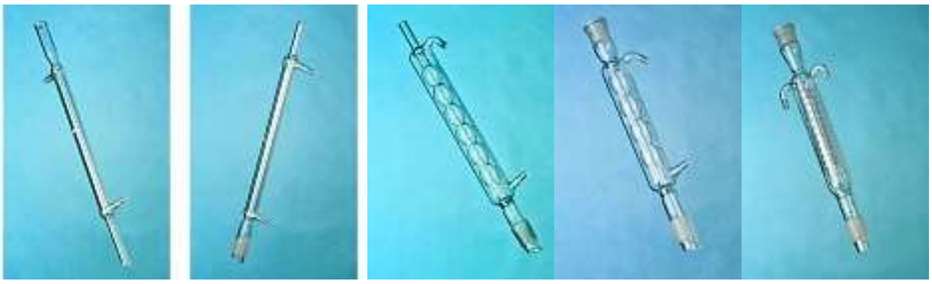
Ampoules are sealed glass containers for the storage of solids, liquids, and gases**.** Thick-walled ampoules are used to store liquefied gases. Also, the ampoules are used for reactions with pressure.

Fixanals are pre-prepared with strictly defined quantities of reagents that are used to obtain solutions of the desired concentration**.**

Weighing bottles are glass container with a polished lid, used for storage and weighing of liquid and solids in small quantities, samples, and test portion. The ground-in surfaces are not lubricated in weighing bottles to avoid lubricant enters into the substance. If high tightness is required, then the weighing bottles with transparent fused ground joint are used.

1.2.6 REFRIGERATORS

The refrigerator is an apparatus for condensing steam using a cooling medium, most often of water (Figure 1.14).



a b c d e

Figure 1.14 – Refrigerators

Refrigerators set either like inclined when it is necessary to collect condensation in the receiver, or vertically to return the condensate to a flask with boiling liquid. In this case, the refrigerator is called *reverse.*

If the temperature of the condensate hardening is higher than the temperature of the cold water, the water in the refrigerator is heated in the thermostat, which prevents the condensation from freezing in the refrigerator inner tube.

Direct-through Weigel-Liebig refrigerator (Fig. 1.14, a, b). This refrigerator is usually used to distill liquids with a boiling point of 100 to 150 °C. The refrigerator has a cool shirt relatively large in diameter. The heat transfer coefficient decreases with the increase in the length of the refrigerator, so it is advisable to use two smaller refrigerators instead of one long refrigerator. The Weigel-Liebig refrigerator can perform the function of an air fridge if it is arranged vertically and steam of high-boiling liquids are sent in a shirt through the upper appendix, and from the bottom select the condensate. As a result of the heating in the central tube, there will be a continuous vertical flow of cold air. In this case, the most efficient refrigerators are refrigerators with a wider central tube and possibly with smaller diameter surrounding shirt.

Allihn ball refrigerator is a typical reverse refrigerator (Fig. 1.14, c, d). Through a larger cooling surface, the Allihn refrigerators are shorter of Weigel - Liebig refrigerators. It is convenient to insert the axis of the mixer through the ball refrigerator, to introduce into the reactor various substances that are well washed into the flask by condensate during heating. The usual number of balls in such refrigerators ranges from 3 to 8. By efficiency, Allihn refrigerator inferior to the Dimroth refrigerator, which can withstand significant temperature differences.

Vest refrigerator has a cool shirt of small diameter, located close to the central slightly curved tube. It is more productive than the Veigel-Liebig refrigerator. Under the same conditions of the liquid distillation, the Vest refrigerator has twice the heat transfer coefficient than direct-flow.

The Dimroth refrigerator is recommended as a reverse refrigerator (Fig. 1.14, e). It has the highest heat transfer coefficient. It is not used for fractional distillation of liquid mixtures due to the large gas volume and the ability to hold a lot of condensation in a sloping position.

1.2.7 MORTAR, CUPS, CRUCIBLES, SHUTTLES AND SPATULAS

Mortar are used for manual grinding of solids. The choice of mortar depends on the hardness of the substance (Fig. 1.15). They can be porcelain, metal, polystyrene, glass and agate. The hardness of the mortar material should always be greater than the hardness of the eraser substance. Grinding a solid, which would not have chosen a mortar, leads to contamination of the mortar by the material. Therefore, grinding of especially pure substances should be carried out in a different way.

For coarse grinding technical products use steel mortar Abikh made of viscous, shock-resistant chromium-nickel steel. Substances are broken by a hammer on pestle on the uterus, turning it after each blow. The final crushing and rubbing of the substance are carried out by rotating the pestle with a light pressure without the use of a hammer. For the convenience of removing crushed material, the cylinder of the mortar makes removable.

Porcelain mortars are the most common in laboratories (Fig. 1.15, a). To grinding the substance, it is poured into a mortar for 1/3 of its volume.

First, with careful punches, by the pestle split large pieces, bringing them to the sizes of wheat grains, and then slowly rub the pestle circularly, without pressing it strongly to the walls of the mortar. During crushing, the substance is periodically cleaned from the walls and the pestle with a porcelain spatula, collecting the substance to the center of the mortar. Hygroscopic and toxic substances are crushed by placing a mortar with a pestle in a plastic bag, the open top of which is tied at the end of the pestle. While crushed, the tied place is being held by the hand.

Agate mortars in appearance are similar to porcelain and used for the same purposes (Figure 1.15, b). Maximum loading of the rubbed substance in such a mortar should not exceed 2 ml. Crystals of quartz SiO_2, corundum Al_2O_3, cassiterite SnO_2 and other substances with a hardness of more than 6 units on the Mohs scale in agate mortars cannot be rubbed due to mechanical destruction of the last.

a b

Figure 1.15 – Porcelain and agate mortar

The mass loss of mortar and pestle (in%) when rubbed corundum and quartz in porcelain mortar is 10,2 and 4,3, and in agate - 2,1 and 1,2 respectively.

For mixing easily erasable substances whose presence is unacceptable impurity metal compounds, use mortar made of *polystyrene* and pestle made of organic glass.

Cups are used for evaporation of different composition of solutions and for work with biological media (Fig. 1.16). They can be porcelain, platinum, silver, quartz, from the glass of the brand "Pirex".

Porcelain cups may be flat-bottomed and round-bottomed. Inside, they are covered with glaze, outside the glaze reaches 1/3-1/2 of the height from the edge of the cup. Rounded cups are easier to clean from residues of evaporated matter. In addition, in such cups, until the end of the solution evaporation, the precipitate is collected in the center, and not smeared throughout the bottom, as in flat-bottomed. The last should be used to evaporate solutions before the crystallization of matter. Such a cup, when cooled down the solution, turns into a crystallizer.

Figure 1.16 – Evaporating cup

Platinum cups are shaped like porcelain. They are used to evaporate solutions containing fluoride acid and its salts. Before work, platinum cups are treated with 6 M HCl until the yellowish-purple spots (iron compounds) disappear on their surface, which should be silvery and unpainted [2].

In porcelain cups, solutions are evaporated either on liquid, air or sand baths. Evaporating solutions in glass and quartz cups on sand saunas is not recommended. When using platinum cups, the sand of the bath should be thoroughly treated with dilute hydrochloric acid to remove impurities of iron compounds from it.

Koch glass and quartz cups are used to store solid non-volatile substances and for biological work, while **Petri cups** made of more thin-walled glass with a low side and used in demonstration experiments, as well as for weighing solids and evaporating air solutions (like crystallizers) (Fig. 1.17).

Figure 1.17 – Petri cups

Crucibles are conical vessels made of refractory materials for incineration or combustion of various substances in analytical operations (Fig. 1.18). The crucibles are made of ceramics, glass and metals. All crucibles, as a rule, have lids (Fig. 1.19).

Figure 1.18 – Porcelain crucible

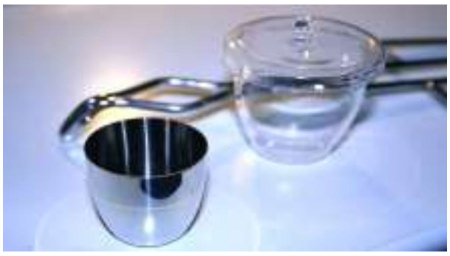


Figure 1.19 – Platinum and Quartz crucible

The crucibles are heated either in crucible and muffle furnaces, or on gas burners without asbestos nets, placing a crucible in a porcelain triangle. Porcelain crucibles withstand heating up to 1200 °C. Heat-resistant crucibles are alund (up to 1500 °C), graphite (in a reducing atmosphere up to 3000 °C). Crucibles are made of other refractory materials. Crucibles of platinum, silver and nickel can withstand heating without deformation to 1400, 700 and

1100 °C. The scope of application of crucibles from these metals is determined by their chemical resistance.

The "shuttle" crucibles are used for the ignition of substances during their analysis and for the synthesis of small amounts of compounds by interaction of solids with gases upon heating (Fig. 1.20). "Shutters" are made from the same materials as ordinary crucibles. Porcelain shutters do not cover the icing; usually they have a ring for which they can be pulled out of a muffle furnace or from a reactor tube.

Figure 1.20 – The "shuttle" crucibles

Spatula spoons or spatulas are porcelain, platinum, stainless steel, polymeric materials. They are necessary for extracting substances from vessels, for mixing solids, removing precipitates from filters (Fig. 1.21).

Figure 1.21 – Spatula spoons

Clock glasses serve as lids of chemical glasses, flasks and miniature cups for weighing small quantities of substances or evaporation.

1.2.8 MEASURING WARE

It is should use only well-washed ware. Pipettes and burettes must be rinsed 2-3 times before use with small portions of the solution that will be measured. After the work, the pipettes are washed with distilled water (in the case of work with aqueous solutions) or ethyl alcohol and rinsed 2-3 times with distilled water, set in a stand for pipettes or in a dry glass cylinder and covered with a paper cap or an inverted test-tube for dust protection.

For accurate measurement of the liquid volume, use measuring ware with labels indicating their nominal volume. Measuring ware includes burettes, graduated (volumetric) flasks, pipettes, measuring (volumetric) cylinders, beakers and graduated test-tubes.

Measured ware manufactured by industry calibrated for a pour or pour out. Burettes, flasks, pipettes used for accurate measurements, are calibrated according to the sample, usually at 20 °C (Fig. 1.22). According to this, burettes, graduated flasks and pipettes are made of 1st or 2nd-grade accuracy. The permissible deviation for burettes and graduated pipettes of the 1st grade corresponds to half the graduating mark of the smallest division of the scale, for the 2nd grade to the smallest division of the scale [3].

Figure 1.22 – Measured ware

The change in the volume of the measuring ware due to the compression or expansion of the glass when the temperature changes are insignificant, which makes it possible to use it at a temperature different from 20 °C to several degrees without correction. For example, the volume of a 1 l flask, calibrated at 20 °C, at 26 °C would be 1,000.15 ml.

Burettes. Burettes are intended for measuring the exact volumes of liquids during titration or for other operations (Fig. 1.23). Direct burettes are manufactured with and without a crane.

Figure 1.23 – Burettes

Burettes without a crane are graduated glass tubes, the upper end of which is open, and the bottom ends by oil. On the oil is put shutter, consisting of a rubber tube of 6...7 cm in length, which previously inserted glass bead, which closes the space of the tube. Instead of a bead, a metallic spring clip can be used. At the free end of the rubber tube, inserts a glass tube with a stretched end in the length of 5 ... 6 cm. Direct burettes with one-way and two-way cranes are also available with a side discharge tube. The discharge tube serves to fill the burette with a titrated solution from the spare capacity. Burettes are issued in normal execution and with automatic zero setting. Micro-burettes are available in 1st and 2nd-grade accuracy. Deviation from the nominal volume of micro-burettes at 20 °C for the entire volume for burettes of grade 1 accuracy is ± 0,006 ml for burettes of grade 2 accuracy ± 0,015 ml [3].

In laboratory practice, the burettes with automatic zero and beaker were widely used. The meniscus of the incoming solution is automatically set to zero. During creating pressure in a glass with the help of a rubber cylinder, the liquid rises through the external feeding tube and fills the burette above the zero mark. As soon as the airflow is stopped, an excess of liquid fuses into a glass through the same tube, the hole of which is at the zero mark. Such burettes issued of class 2 accuracy.

1.3 KEY WORKING METHODS WITH WARE IN THE CHEMICAL LABORATORY

1.3.1 WASHING OF CHEMICAL WARE

The surface of glass, porcelain, metal and polymer materials may contain greasy and resinous contaminants, organic and inorganic compounds, and aerosol particles. Impurities can be absorbed on the surface or rinse out from the walls of chemical ware.

On contaminants that get into chemical ware from the air often don't pay attention because they are visually often imperceptible. Meanwhile, urban air contains the dust that includes SiO_2, Al_2O_3, Fe_2O_3, $CaCO_3$, $MgCO_3$, Pb, compounds of copper, sodium, chlorides, sulfates, and other impurities. Especially in the air of chemical laboratories many impurities of hydrogen chloride, ammonia, and ammonium chloride.

The skill to wash chemical ware is part of the laboratory technique, knowledge of which is obligatory for each laboratory employee. The chemical ware should be clean. Without this condition, it is impossible to work. Therefore, it is necessary to learn wash dishes so well that there was absolute confidence in its purity.

There are several ways to wash chemical ware.

1. Washing with water. In cases where the chemical ware are not contaminated with resin, fatty, and other substances insoluble in water, ware can be washed with warm water. Dishes are considered clean if there are no individual drops on its walls, and the water leaves a uniform thin film on them.

If on the walls of the ware there was a plaque of any salt or precipitate, the ware cleaned (pre-moistened with water) with a special brush and then they are finally washed with water. When working with a brush (wire brush) it is necessary to ensure that its bottom end does not hit the bottom or the walls of the dish, as by this end can knock the bottom or break the wall.

Well-washed in warm water ware necessarily 2-3 times rinsed with distilled water for removal of salts contained in tap water (the presence of salts in tap water is easily detected by a white plaque, evaporated a drop of water on the time-glass).

In large laboratories where there is a separate room for washing dishes, sometimes special appliances for washing dishes with steam are used.

To wash test-tubes with water or steam it is easy to do, in any workshop, a device that consists of a quadrangular solid box with a double bottom. At the top of the bottom 65 tubes with a length of 170 mm and diameter, which adapts to the most used test tubes, are inputted. Each such tube has a spiral spring on top. When attached to the tube test-tube with its bottom is held on this spiral. The box has a drain for water and is provided with two cranes: one for water, the other for steam. Thus, washing the tubes can be carried out both with water and steam.

If the worker has unnecessary solutions containing the salts of mercury, silver, gold, platinum, and iodine, then they cannot be poured into the sink. They should be collected into specially intended banks for this. From the collected solutions, it is possible to regenerate the specified metals.

Also, it is impossible to pour out and throw away in a sink metallic sodium, concentrated solutions of acids and alkalis, a chrome mixture, badly smelling solutions, and toxic substances. Concentrated acids and alkalis must be pre-diluted or, preferably, neutralized to prevent the destruction of the sewage system. Bad smell substances and toxic substances must be neutralize in one way or another, depending on its nature. When pouring them into a sink, it is possible their evaporation and poisoning of air in the laboratory.

2. Washing by steam. Ware cannot always be washed only with water. For example, in such a way it is impossible to remove contamination by fatty substances. Significantly better results can be achieved by ware washing by jet of water vapor. This ware washing method is the best, but it does not use much, because require a long time. If usually, it is necessary from 5 to 10 minutes to wash the flask, by steam it is required at least an hour. In those cases when especially clean ware is required, it is used pre-washing by some conventional method with further steamed.

Washing ware by steam is carried out as follows: into a flask of 3 ... 5 l, up to half is poured the water. Several porous pieces of pumice or glass capillaries put on the bottom (for even and calm boiling). The flask is closed with a stopper, which enters into the flask neck tightly. In the plug is inserted a tube for steaming and a funnel, through which will flow back into the flask condensate from the dishwashing detergent. The end of the funnel is lowered to water by about 2 ... 3 cm for breakthrough of steam prevention. The upper end of the tube is inserted into the washed object, which is fixed in a ring or a paw of a specially mounted tripod. After washing of ware by steam, it is dried either in a drying cabinet, or by purging of clean air, or simply in the air without turning over.

3. Wash with a chromosulfuric acid. Very often in the laboratory for ware washing a chromosulfuric acid is used. Its application is based on the fact that chromic-acid salts in acidic solution are strong oxidants. Usually, for chromosulfuric acid preparation, sulfate acid is used, add about 5% of the crystalline $K_2Cr_2O_7$ powdered in the mortar and carefully heated in a porcelain cup in a water bath until all $K_2Cr_2O_7$ passes into the solution. A mixture that destroys most of the organic substances and converts metal compounds into water-soluble hydrosulphates and hydrochromates is formed because it contains a certain amount of chromium oxide (VI) - a stronger oxidizer than potassium dichromate and concentrated sulfuric acid [1]:

$$K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O.$$

In cases when the ware is not washed with water, it is washed by slightly heated chromosulfuric acid. The last one is poured into contaminated ware, first scalded with water to 1/3 - 1/4 volume and by it carefully and gradually wet the interior walls of the ware. After that, the chrome mixture is poured back into the same ware in which it is stored. After poured the whole mixture, it is not washed off immediately, and give the ware stand for several minutes. Washing the ware with a chromosulfuric acid is carried out initially with ordinary, better with warm water, and then by distilled. Sometimes this procedure with chromosulfuric acid should be carried out more than once.

Once prepared, the chromosulfuric acid serves a very long time. After prolonged usage, its color from the dark orange turns into dark green, which is a sign of its further unsuitability for washing. The laboratory should always have a supply of chromosulfuric acid.

The chromosulfuric acid strongly affects the animal and plant tissues (skin and cloth), and therefore, it is necessary to work with it very carefully. Sometimes you have to wash such a chemical ware, pouring into which of chromosulfuric acid is quite difficult. So, the of chromosulfuric acid is sucked in a pipette with a rubber bulb without a balloon. To the rubber bulb connects the rubber tube, the end of which, is put on the pipette. Griped the rubber bulb by hand to expel air from it, and closed hole by the thumb for receipt of air, the pipette is lowered into a chromosulfuric acid. At the same time, gradually squeeze out the hand, so the inside of the pipette is formed by dilution and the chromosulfuric acid begins to gain in the pipette. After drawing a full pipette and keeping a chromosulfuric acid in it for 1 ... 2 minutes, remove the thumb from the opening of the pear and allow the liquid to drain. After repeating this procedure several times, the pipette is washed as usual.

Pipettes and burettes and similar to them long pipes are convenient to wash by chromosulfuric acid in the following way. It necessary takes a thick cylinder of such height that the tube could be immersed in it, for more than half. In it there are placed tubes, which are should be washed, and fill the cylinder almost to the top by chromosulfuric acid. After standing for some time, the tubes are removed and placed by the back end in the cylinder. The chromosulfuric acid does not apply if the ware are contaminated with such substances as paraffin, kerosene, wax, mineral oils, lubricants, and oil distillation products. In such cases, steam or organic solvents are used.

It should be noted that it is better using easily heated chromosulfuric acid, at least 45 ... 50 ºC. In this case, it is stronger and the result of washing is significantly improved [1].

The treatment of ware is carried out in the draught cupboard because the mixture released a poisonous and volatile oxide CrO_3. The mixture becomes unusable when it becomes green as a result of recovery Cr^{6+} до Cr^{3+}. Store the mixture in a thick-walled porcelain glass, covered with a thick glass plate. The chromosulfuric acid is not suitable for purifying glass porous filters and other porous masses, due to the strong adsorption of chromate by pores (filters become green). Chromium ions are not removed from the pores even during multiple boiling of glass filters in pure water.

4. Washing by potassium permanganate. In addition to the chromosulfuric acid, effective dishwashing detergent is a 5% solution $KMnO_4$.

$KMnO_4$ solution is a strong oxidant, especially heated and acidified with sulfate acid. It is poured into ware that needs to be beforehand washed with hot water and brush. Then, by a thin stream, add a little sulfate acid, which causes warming, which is quite sufficient to remove contamination. Sulfate acid should be taken without significant excess. With such a quantity, the solution temperature will be 50 ... 60 ºC. Usually, up to 100 ml of $KMnO_4$ solution is a sufficient addition of 3 ... 5 ml of sulfate acid [1,3].

It is necessary to take precisely sulfate acid and, in any case, not salt since the last will be oxidized by permanganate to free chlorine, which can lead to poisoning workers.

Sometimes after washing ware with permanganate on its walls, there is a brown bloom that can be removed by ware rinsing with a weak solution of oxalic acid or other organic acid. After that, ware is washed with water. When working with an acid solution of potassium permanganate, it is necessary to follow the same washing techniques and precautions as described above for the chromosulfuric acid. The spent sour solution of potassium permanganate usually pours out and is not reused. If the solution of potassium permanganate is not acidified, it can be used several times. The acidic solution of permanganate is very well cleaned mercury pumps, tubes of barometers.

5. Washing with sulfate acid. When ware is contaminated with resinous substances insoluble in water, as well as in cases where the laboratory does not have a chromosulfuric acid, ware can be washed with concentrated sulfuric acid or concentrated up to 40% solution of alkaline NaOH. Resins are mostly dissolved either in acid or alkali and instead of spending expensive organic solvents to remove them, it is first necessary to use sulfate acid or alkali. For this purpose, an acid or alkali is poured into the ware in an amount such that their volume is equal to the volume of the resin or was slightly larger than the latter, but so that it would be possible to shake the ware without risk. When the resin is too much, the procedure should be repeated several times. The treatment time with acid or alkaline depends on the characteristics of the resin. In some cases, the resin can be removed by shaking the flask for 5-10 minutes, in other cases, it is necessary to handle it for several hours, occasionally shaking the flask.

Use concentrated sulfuric acid and alkali should careful; acid can`t be poured into the sink. Contaminated by resin sulfate acid or alkali must be merged into a special clay or glass jar, which should always be near the water sink. It is impossible to pour the acid and alkali in one jar, as it will be neutralized, which is accompanied by strong heating,

In addition to solutions of sodium hydroxide or potassium, it is advisable to use and less powerful alkalis, for example, lime milk, which is very convenient for washing ware, contaminated with kerosene. For this purpose, in a dish pour a solution of lime milk with a concentration of 5 ...

10% and vigorously shake, repeating the operation 2 ... 3 times. Should not take a lot of lime milk. On a flask of 1 l is enough 100 ... 200 ml [1].

After treatment with lime milk, ware washed with warm water.

6. Washing with organic solutions. Organic solvents include acetone, alcohol, petroleum ether, gasoline, CCl_4, and other solvents.

Organic solvents are used for removing resin and other organic substances from the ware, and which are not dissolved in water, acid or alkali. Most organic solvents are flammable, and therefore the operations with them should be carried out far from the fire necessarily under the exhaust cabinet. It is not worthwhile to throw away contaminated organic solvents, they should be collected individually and regenerated from time to time. Regeneration consists in the distillation of contaminated solvent.

7. Washing with other detergents. Other substances, such as soap, and especially a 10% solution of sodium phosphate, which has good detergent properties, can be used to wash the ware.

During the flasks washing with water, soap and sodium phosphate it is useful to throw a piece of clean filter or other soft paper inside a flask, for mechanically removing from the walls of contaminated stuck.

The Komarovsky mixture consists of equal volumes of 5 ... 6% aqueous solution of hydrogen peroxide and 6 M hydrochloric acid. It is used to remove surface contaminants from glass, quartz and polymeric materials. This mixture leaves the surface purer than chromosulfuric acid or permanganate mixture. Before using, the Komarovsky mixture is heated up to 30 ... 40 °C. After rinsing the vessels with clean water, check for the absence in water the Cl^- ions (with $AgNO_3$) [3].

It is absolutely inadmissible to use sand for mechanical cleaning of ware because it destroys glass with the formation of microcracks. During the ware heating that have the scratches, it is usually crack.

The method of control of the washed glass purity and quartz surface is the observation of the behavior of the water film on it. If the surface is free of impurities of hydrophobic substances (insoluble substances that do not interact with water), then the water film is distributed in a thin uniform layer, wetting the entire surface of the vessel without breaking in the water film. The contaminated surface is wetted with water unevenly, in separate areas.

1.3.2 DRYING OF CHEMICAL WARE

Well-washed ware in some cases should be well-dried. Ware drying are needed when the work should be carried out in the absence of traces of moisture. If the work will be carried out with aqueous solutions, then, as a rule, drying the ware is inefficient. Drying the ware can be done differently:

1. **Drying on the pegs** is the most common method. For this purpose, the laboratory should have a special peg board, which is usually placed above the sink for ware washing. The washed ware are put on pegs and remain on them until they are dry. It is necessary to monitor the cleanness of pegs and wipe them.

In order to avoid possible contamination of the ware by pegs, they must be pre-wrapped with clean filter paper and then placed on them ware. When a funnel is dried on pegs, it is also useful to wrap a piece of filter paper, especially if the ware remains on pegs until the next morning;

2. **Drying on a drying table**. The disadvantage of ware drying on pegs is its possible contamination. Therefore, in the analytical laboratories for which the purity of the ware is extremely important, use drying tables. This is a simple table in which the holes cut through round holes of different diameters. The washed dishes are placed in the nest of the appropriate diameter. Thus, the inner surface of the container avoids contamination. At a distance from the lid of the table, a bowl of thin layer of metal is arranged underneath, to prevent the water flowing on the floor;

3. **Drying by air**. When the washed ware is used immediately, drying

can be carried out with a stream of air. In those laboratories where there is no supply of compressed air, it is necessary to use rubber pipette filler for drying. You can dry both hot and cold air. In both cases, the free end of the rubber pipette filler is planted on a glass with a fused end of a tube of such length that it approached the bottom and from the top it remained at the end of its approximately 10 cm. Through the ware, which are dried, air is blown until the traces of moisture are completely removed. If the pipette is dried, it can be applied directly to the rubber tube of the pipette filler.

When warm drying by air glass tube pots heated over a fire or flame with continuous blowing air. The heating should be carried out with caution, since in cases of uneven heating the ware can crack from a drop of water located on the walls, so the ware needs to be constantly rotated.

Measuring glassware (pipettes, measuring bulbs) can`t be heated above the flame;

4. **Drying with alcohol and ether**. Sometimes it is necessary to dry the ware quickly. In this case, after removing water from the dishes on the top with a filter paper, rinse it first with pure ethyl alcohol, and then with pure sulfuric ether. The steam of ether is removed by blowing cold air.

This method of drying is based on the fact of rinsing by ether, in it dissolves alcohol. This ether, having a low boiling point, easily evaporates when air is blown. The remains of alcohol and ether should not be poured into the sink. They must be collected separately for regeneration.

5. **Drying in a drying cabinet**. Quick drying of the ware can also be done in the drying cabinet. Usually in a drying cabinet ware are placed after some time, when it was standing upside-down, as a result of which all the excess liquid flows out from it. Drying should be carried out at a temperature of 80...100 ºC. On the shelf of the drying cabinet, you need to put a piece of clean filter paper. After drying in the oven, the ware can`t be used immediately, it should cool down.

During washing ware, it is necessary to remember the following:

1. ware should always be washed as purely as possible and rinsed with distilled water;
2. during the work with the washing brush, it is necessary to monitor that the bottom end does not break the bottom and the walls of ware;
3. during the ware drying, it is necessary to ensure that it is not dirty;
4. during ware washing with various organic solvents, it is necessary to economize their;
5. precious precipitate and solutions (iodine, silver, platinum, mercury, etc.) can`t be poured or thrown into the sink, but they must be collected in separate glasses;
6. concentrated solutions of acids and alkalis, bad smells and poisonous substances, chromosulfuric acid, metallic sodium, can`t be thrown/poured into the sink;
7. during the washing with acids, alkalis, and chromosulfuric acid, it should be observed all rules and safety standards.

1.3.3 WEIGHING AND PRINCIPLE OF WORK ON THE BALANCE

Balance are devices for determining body mass. The mass of the body is found by means of the balancing force, which returns the moving part of a balance to the initial position of equilibrium, that is, the balance is the comparing device.

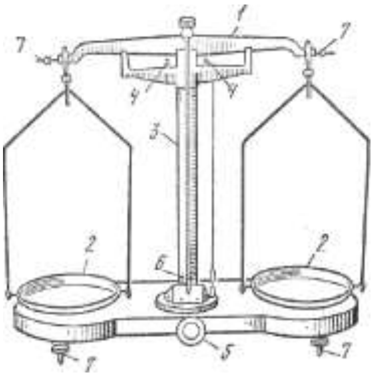
In laboratory practice, the unit of mass m is gram (g) and milligram (mg). Laboratory balance are traditionally divided into **techno-chemical** (usually ruder) and **analytical** ones.

By the way of creating a balancing force, balances are divided into **mechanical weights** (equivalents and unequivocal) and **quadrant** (swing balancing device), **spring** (torsion), **hydrostatic**, and **electronic**.

Methods of weighing are divided into two fundamentally different groups - the method of comparison with the measure, and the method of direct evaluation. By comparison with the measure of mass, a balance is taken as equal to the mass of the balances weighing it (simple weighing) or calculated as the sum of the values of the weight of the weights and the readings of the weights (exact weighing). The method of direct evaluation is to determine the weight of weight gain by the reference device of weights without the use of weights.

In most modern mechanical laboratory balance, a differential weighing method is used, in which most of the measured body mass (over 99%) is balanced by weights or counterweight (zero method), and the small remaining difference between the weight of the weighed body and the weight of the weights is determined by the angle of deviation rocker from the original position of equilibrium (direct method) with reference balance.

Depending on the nature of the experiment being performed, weighing is carried out with varying degrees of accuracy. When weighing on techno-chemical balance (fig 1.24), the accuracy of weighing ± 0,01 g. The main part of them is the equilateral armor 1, to which the hanging cup 2. The crown with a prism rests on column 3.



1 - equine armor, 2 - cup, 3 - column, 4 - arietr, 5 - aretory handle, 6 - arrow, 7 - adjusting screws.

Figure 1.24 - Technochemical balance [3]

A balances are equipped with a special device - an arteri 4, which allows you to slightly raise the spindle over the support, thus protecting from the wear of the prism. In the non-operating condition, as well as at each change in the load on the cups of a balance, should be attached. When the load on the dishes is set, the scales are transferred to the working position by a smooth rotation of the aretri knobs 5 and observe the fluctuations of the rocker on the indicators of the arrow 6. A balances are also provided with adjusting screws 7 for horizontal installation behind the slot and for balancing with unloaded cups.

A box with scales of the following denomination is added to the weights: 100; 50; 20; 20, 10, 5, 2, 2; 0,5; 0,2; 0,2; 0,1; 0,05; 0,02; 0,02; 0,01 g.

Rules of weighing on techno-chemical balance

1. From the weighing, you need to make sure that the scales are installed horizontally and there are no residual objects and stresses, spilled reagents and so on the cups.

2. Check the zero point of a balance. To do this, gently turn the aretre handle and observe the fluctuations of the beam. If the arrow deviates to the right and left to the same number of divisions, then the zero point of a balance coincides with the zero of the scale. In case of need adjustment of weights is carried out by a laboratory assistant.

3. On the left cup of weights place the weighed item, on the right - weigh. It is impossible to weigh contaminated, wet or hot objects and pour the chemicals directly into a cup of scales.

4. To put on weight and to take off objects and attentions it is possible only in an assumed position of weights.

5. Attractions are put on a cup of weights with tweezers. Each time after installing or replacing a swipe, the handle of the aerate returns and check the rejection of the arrow. When weighing the weights to the equilibrium state, the deviation of the arrow becomes smoother.

6. The method of the most rapid achievement of the balance of weights is to consistently select the weight, starting with the large and ending with the smallest.

7. Having determined the set of weightings, in which a balances are in equilibrium, calculate the mass and record in the laboratory journal.

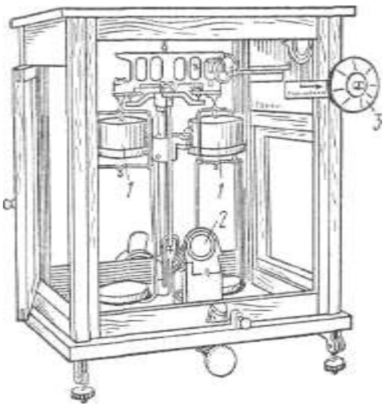
8. Take away swabs with tweezers from a cup of weights in a box and remove the weighed item.

9. If weigh the calculated amount of substance on the scales, after weighing the container, add to the cup of weights the weight of the corresponding mass, and in the packaging pour the substance in the amount necessary for the establishment of equilibrium. Pouring the substance with a spatula or a porcelain spoon, remove the container every time from the cup of scales to avoid contamination.

10. After weighing a balance must remain ready for further work.

In chemical analysis, an increased accuracy of weighing (up to ± 0,0001 g) is required. For this purpose, analytical scales of different design are used. They are equipped with solid prisms, which serve as support pivots of the swing arm and hanging on it cups. The preservation of the prism depends on the accuracy of weighing. A special device (aerate) separates the prisms and supports in the unfinished position of weights. For protection from dust and accidental fluctuations of air weights are placed in glass showcases.

Dempfer analytical balance ADV-200 (Figure 1.25) differ in the presence of dampers 1, which quickly extinguish the fluctuations of the beam. In addition, the arrow of these balance is connected with the optical device, which allows to count on the optical scale 2 mg and a tenth of a milligram. Weight of 0,01 to 0,5 g in this balance is loaded on a special strap of the barbed beam by turning the limb 3.



1 - dampers, 2 - optical scale, 3 - limb

Figure 1.25 - Damping analytical balance [3]

When weighing on analytical balance it is prohibited:

- put on the balance hot or wet items;
- weigh volatile substances in open containers;
- weigh on plain paper (only on calcium);
- to hand over the weight loss;
- take cues from other sets;
- to leave balance after weighing not brought to a state of equilibrium;
- to depart from weights during weighing;
- start weighing without putting a laboratory journal next to the balance.

Weighing rules for analytical damping balance:

1. Turn on the lighting unit with a plug in the electrical grid.
2. Review the scales: the showcase door must be closed, the cups are not loaded and clean, devices for hanging milligrams (limbs) are set to zero.
3. Smoothly turn the lever handle to the left until it stops. The screen should show moving scale. After stopping the balance, the zero division should coincide with the vertical black line on the screen. If a slight deviation from zero is detected, you need to adjust the position of the screen by turning the special knob. After that, attach the balance again and check the zero point again.
4. On the left cup of balance place the weighed item and close the door.

5. On the right of the cup of balance, weighing pockets are placed, starting with the largest in nominal value, estimating the balance of the object approximately. Having put a weight on a cup of balance, the left hand slightly turns the handle of the arietra, not letting it go. If a balance with negative values appears on the screen, this means that the weight of the weight gain is greater than the weight of the subject; this is usually the case at the beginning of the weighing: a scale with positive values appears when the balance of the weight loss is less than the weight of the subject. The handle of the aerate returns to the original position. The balance, which exceeds the weight of the item, is replaced by another smaller and removes scale indicators to obtain a value of attitude that corresponds to the whole number of grams of the subject. After that the door on the right side of the scales is closed.

6. The load from 0,1 to 0,9 g is placed on the right shoulder of the ramp with a smooth turning of the outer disk (large limb) in the upper right of the window. First, it is advisable to install a disk of 0.5 g and check the readings of the balance. The subsequent rotation of the disk in either direction is gradually approaching the mass of the object. Finding the number of tenths of a gram, begin to install a hundredth particle by rotating the inner disk (small limb). The sequence of actions is the same as when you rotate an external drive. As the load is approached to the mass of the object, the deflection of the rocker arm becomes slow, and then you need to move from incomplete turning the handle of the aretre to full turn and to observe the optical scale.

In the laboratory journal, write the weight of the subject, putting in front of the comma the weight of the weight on the cup, the first two digits after the comma - the indicators on the limbs initially large, and then the small, the two following figures - indicators of the optical scale. After recording the result, the scales are transferred to the arreated position.

7. Remove the weighed object, discs carefully creep into a zero position, remove the swabs from the cup and, in the end, check the immutability of the

zero point of the scales. In the analytical balance, the newest types of equilibrium are located near the rocker (built-in weights) and hang on it either by mechanical or automatic adjustment when weighing matter. In this case, the weight gain becomes much lighter and easier, eliminating the need for a thorough centering on the cup of a large mass. Also, the opening of the door of the scales is also excluded, and therefore there are no air vortices inside them that violate the temperature regime of weighing. In modern analytical balance, optical devices are used to count the deviation of the arrow, which allows us to prove the accuracy of the reference to 0.001 ... 0.005 mm. To reduce the number of oscillations of the rocket arm near the equilibrium position, and hence the movement of the arrow with a scale or along the scale, apply oscillator stabilizers - damping.

Damper (Dampfèr - muffler) can have a different structure. The most commonly used clutch damper and plate damper. At the inclination of the scroll wheel, the upper glass damper Curie grips the air in the lower stationary glass and forces it to go out in a long, winding way. The work of the air out is due to the energy of the oscillation of the rocket arm, which leads to rapid inhibition of oscillations.

In the plate damper the role of the upper cup is made by a flat disk piston, rigidly fastened to the end of the scroll wheel. The disk moves in a glass with a small radial clearance. Such a damper is used mainly in double prism scales.

The sensitivity of the balance is the minimum mass change that balance can detect. The sensitivity of cermet balance is determined by the number of divisions of the scale indicated by the rocker arm when loading a cup of 1 mg. The smaller weight of the object, which causes the deviation of the arrow for one division of the scale, is more sensitive. The sensitivity of the balance is the price (in mg) of one scale divider.

1.4 WORK WITH CHEMICAL SUBSTANCES IN APPLIED CHEMISTRY

The work effectiveness of the chemist depends on the degree of substances purity that used. All chemical products are divided into four groups:

1. **raw products** are natural origin and semi-finished products with a high content of impurities;
2. **technical products** manufactured by chemical enterprises, with a relatively small content of impurities;
3. **reagents** intended for analytical, preparatory and other works in laboratories;
4. **Products with special purity,** the quality of which are much higher than chemical reagents.

Reagents and especially pure substances, the quality of which is regulated by standards and technical conditions are used in laboratory practice.

1.4.1 DANGEROUS PROPERTIES OF REACTIVES

Moisture sensitivity. Purely physical character (humidification, dissolution), irreversible chemistry reaction. Sulfides, nitrides, phosphides of alkaline and alkaline-earth metals decompose by water with the formation of the toxic hydride; non-metal halides (PCl_3, PCl_5, S_2Cl_2) and acid halides are hydrolyzed to form the corresponding acids; alkaline, alkaline-earth and pyrophoric metals interact with the release of hydrogen.

Photosensitivity (for example the photochemical reactions). Some substances change colors (aniline, salts of bromo- and iodine-containing acids, mercury preparations, salicylic acid, phenols), others are oxidized (furfural) or reduced (silver compounds).

Heat sensitivity. A significant change in the temperature conditions during storage of a reagent can cause both reversible (transition to another aggregate state) and irreversible changes in properties. Substances subjected to irreversible changes under the influence of heat or cold called thermolabile.

Formalin (aqueous solution of formaldehyde) at a temperature below 9 ^{0}C forms a paraform precipitate that does not pass into the solution when heated. Metal tin (white) at -30 ^{0}C goes into α-modification (gray) in the form of a gray powder.

Fire-hazardous. Fire-hazard substance groups:

1. Reagents that capable of decomposition with an explosion and in the absence of oxygen in the air (ammonium perchlorate, picric acid, many oxides, azides).
2. Compressed, liquefied and dissolved under pressure gases: flammable H_2, methane, acetylene, CO, ammonia, hydrogen sulfide, cyanode; supporting combustion compressed and liquefied air and oxygen.
3. Reagents that released in the interaction with water flammable gases (Na, K, Ca, CaH_2, CaC_2).
4. Flammable liquids capable of dealing with short-term contact with a source of ignition without preheating. **Flashpoint** is the smallest temperature at which a pair of this substance forms above the surface of its mixture with air that flares when the flame approaches.
5. Highly flammable solid reagents capable of flamme with a source of fire and spreading combustion on the surface (red phosphorus, sulfur, selenium, nitrocellulose, naphthalene).
6. Self-flammable reagents, capable of self-heating and self-ignition at contact with air or other substances, when heated to relatively low temperatures (pyrophoric metals, organometallic substances, white phosphorus).

7. Reagents with oxidizing properties that contribute to the development of combustion (non-combustible, but emit oxygen) - peroxides, nitric acid, and some salts, chlorates, bromates, iodates, permanganates.

Toxicity. When working in a chemical laboratory it is necessary to proceed from the fact that **all chemicals are to some extent poisonous**. Absolutely harmless pure water only. By the degree of action on the body, harmful substances are divided into four classes of danger:

1 – extremely dangerous; 2 – highly dangerous; 3 – moderately dangerous; 4 – low dangerous.

Class of Hazardous Substances determined depending on the Indicators given in Table. 1.4. The assignment of a particular substance to one or another class of danger is carried out by an indicator whose value corresponds to the highest class of danger.

Table 1.4 - Class of Hazardous Substances

Indicator	Standards for the hazard class			
	1	2	3	4
The maximum permissible concentration of harmful substances in the air of the working area of the production premises, mg/m^3	<0,1	0,1-1,0	1,0-10,0	> 10,0

A mandatory condition for the safe handling of chemicals is not only the knowledge of the hazard class of all the reagents and solvents that you have to deal with in everyday work, but also the knowledge of the features of their toxic effects, the main measures for the prevention of poisoning, symptoms of poisoning and first aid methods at poisoning. Before starting work with new, unfamiliar substances should not only examine their chemical and physical properties but also be sure to read the guide with their toxic effects and with hygienic standards.

1.4.2 CLASSIFICATION OF SUBSTANCES BY TOXICITY

It is customary to classify all chemical substances by the nature of their actions into the following groups:

1. Substances that cause burns or have an irritant effect on the skin and mucous membranes. This group includes all concentrated mineral acids - sulfate, chloride, nitrate, and others, as well as alkali - potassium hydroxide, sodium hydroxide, lime milk, ammonia, and others.

2. Substances that can irritate the respiratory organs - phosgene, chlorine, chloropicrin, ammonia, sulfur oxides (IV) and (VI), nitrogen oxides, chloride oxides, phosphorus. These substances can cause both acute and chronic poisoning.

3. Substances conventionally referred to as blood poisons, that is, impressive haematogenic organs or are capable of chemical interaction with the components of blood.

4. Substances acting mainly on the nervous system. These include hydrogen sulfide, carbon disulfide, benzene, gasoline, lead, methyl alcohol, aniline, nitrobenzene.

This classification is incomplete because there are many substances that can be attributed to any of the listed groups It can be convenient for assessing the harmful effects of the substance from the toxicological and medical points of view. To consider the same issues related to safety measures with these substances, it is more appropriate to classify substances according to their composition, chemical nature, and structure.

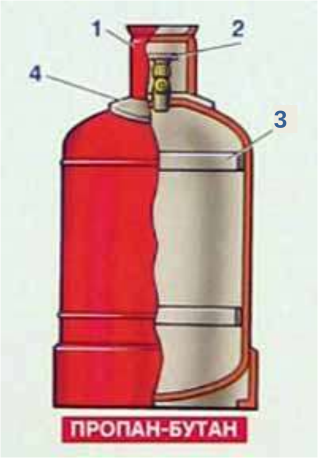
Conditionally all harmful and toxic substances can be divided into two classes:

1) substances of inorganic origin;

2) substances of organic origin.

1.4.3 CYLINDERS (PRESSURE VESSEL) AND THEIR LABELING

Some of the gases used in the laboratory are held in cylinders (steel cylindrical vessels with a spherical bottom and a narrowed upper part, in which the locking valve is screwed in. To prevent the valve damage, on the upper part of the cylinder is put an iron cap. The lower part of the cylinder has a welded stand ("shoe"), which allows the cylinder to be kept upright (Fig. 1.26).



1. Protective cap, 2. Cylinder valve, 3. Underlay rings, 4. Passport data

Figure 1.26 – Cylinder construction

Cylinders intended for gases storing (Cl_2, NH_3, SO_2 etc.), which are liquefy under the pressure. They have an internal tube, which goes from the shut-off valve to the bottom of the cylinder. It is recommended to use such cylinders inverted, in order to the end of the tube is out of the liquid. In this case, the possible release of liquid gas from the valve is eliminated. Locking valves are made of bronze or steel. Their case is screwed into the upper part of the cylinder.

For prevention the false filling of cylinders by other gases, provided the distinctive coloring and marking of cylinders (Table 1.5).

In cylinders that contain liquefied gas, regardless of the amount of fluid in the cylinder, the pressure gage shows the vapor pressure. Cylinders with acetylene are filled with porous mass (pumice, coal), impregnated with acetylene solution in acetone. For cylinders with oxygen used reducer, which do not contain layer of organic material. Lubricate parts of an oxygen reducer with any oil, as well as to put on the output nozzle rubber and other hoses from organic materials, except fluoroplasts, is strictly prohibited. In an oxygen stream, it may become inflamed, causing a cylinder explosion.

Table 1.5 – Recognition of industrial cylinders with compressed gases [2]

Gas	Dyeing of cylinder	Colors of the inscription	Pressure, atm	Possible impurities
N_2	Black	Yellow	150	O_2, Ar, Ne, He
NH_3	Dark yellow	Black	30 (liquid)	H_2O, CO_2, H_2, N_2
H_2C_2	White	Red	15…20(in acetone)	H_2O, O_2, N_2, $(CH_3)_2CO$
H_2	Dark green	Red	150	N_2, O_2, CO, CO_2, CH_4, H_2S
SO_2	Black	White	6 (liquid)	H_2O, O_2, N_2, CO_2
CO_2	Black	Yellow	125 (liquid)	O_2, N_2, H_2O, CO, SO_2, H_2S
O_2	Light blue	Black	150	H_2, N_2, Ar, CO_2, H_2O
CH_4	Red	White	150	N_2, CO_2, H_2O
Cl_2	Green	Blue	30 (liquid)	O_2, N_2, HCl, CCl_2O, CO_2

Valves, reducer and pressure gages for cylinders with acetylene and ammonia are made only with steel. All locking devices containing copper (bronze, brass) should not be used at work with ammonia and acetylene because of their interaction with copper.

The cylinders are kept upright in special racks or attached to the wall or laboratory table with iron clips. The cylinders should be located far away from heating batteries, any heating devices and electric shields. They should also be protected from direct sunlight.

The cylinders are intended for storage, transportation and usage of compressed (nitrogen, air, oxygen, hydrogen sulfide), liquefied (ammonia, sulfur oxide (IV), butane) or dissolved (acetylene) gases at a pressure higher than 0,07 MPa.

Safe operation of cylinders is provided by:

- necessary mechanical strength of cylinders and proper control of their condition;
- preventing false filling of cylinders by other gases (for example, cylinders for noncombustible gases – combustible, gas cylinders – oxygen);
- compliance with the rules of filling, transportation, storage and use of cylinders;
- preventing the false filling of cylinders by other gases (for example, cylinders for noncombustible gases – by combustible, cylinders for combustible gases – by oxygen).

The required mechanical strength of the cylinders is ensured by their high-quality fabrication and periodic inspection. Cylinders for compressed, liquefied and dissolved gases are welded (working pressure in a cylinder up to 3 MPa) or seamless.

During operation, cylinders are tested, which include: an overview of the internal (if possible) and external surfaces of cylinders; weight and strength check; hydraulic test. The inspection of cylinders is carried out in order to detect corrosion, cracks, dents and other damages on their walls to determine the suitability of cylinders for further operation. If the results of the survey are unsatisfactory (cracks, dents, depths of more than 10% of the nominal wall thickness are found), then the cylinders are discarded.

The value of the test pressure and the time of the endurance of the cylinders under such pressure shall be determined by the relevant standards (for standard cylinders) and the technical conditions (for non-standard ones), with the test pressure being not less than one and a half of the working pressure.

Exceptions to the general rules of attestation apply to cylinders with acetylene – a flammable gas widely used in the industry for welding and cutting metal constructions. Due to the high explosive hazard of acetylene, it is stored in dissolved form in cylinders filled with porous mass impregnated with acetone. With periodic verification, the porous mass is not removed, and instead of the hydraulic test, the test with nitrogen is carried out. In this case, the cylinder is lowered to water at a depth of at least 1 m. The state of porous mass in cylinders for acetylene should be checked at least one times every 24 months.

The certification of cylinders is carried out by enterprises, filling-stations and test points, which, in accordance with the established procedure, have received permission for this in the special bodies licensed for verification and certification of cylinders.). After verification, the stamp is placed on the upper spherical part of the cylinder and the date of the next certification is indicated.

In addition, the side valves of gas cylinders filled with combustible gases have a left-hand thread, and cylinders filled with oxygen and other non-combustible gases are right-hand.

The operation, transportation and storage of cylinders at the enterprise must be carried out in accordance with the requirements of the instruction approved in accordance with the established procedure. Workers that serving cylinders must be trained and instructed in accordance with current regulatory documentation. The residual gas pressure in the cylinder must be at least 0,05 MPa.

The main device that provides safety during operation of cylinders is a reducer that reduces the pressure of compressed gas to the working. By design, the reducers can be different (one and two-chamber, direct and indirect), but in all reducer, the low-pressure chamber should have a pressure gage and a spring safety valve, adjusted to the appropriate permissible pressure.

Gas cylinders are stored in special rooms (warehouses) or under eaves that protect them from atmospheric precipitation and sunlight. It is prohibited to keep cylinders with oxygen and flammable gas in one room. Cylinders with poisonous gases are stored in special enclosed spaces. Storage for cylinders with explosive and fire gases must be in the lightning protection zone.

Filled cylinders are kept upright in specially equipped nests, cages or fenced barriers to prevent them from falling. Gas cylinders must be at least 1m away from radiators and other heating appliances and not less than 5m from the sources of open flame. Oxygen cylinders need to be protected from contamination by any lubricant or fat, as they can form an explosive mixture with pure oxygen.

1.4.4 EXAMPLES OF SOME SUBSTANCES CLASSIFICATION IN APPLIED CHEMISTRY

In applied research and experimental preparatory operations in laboratory conditions, specialists in the chemical technology of inorganic substances and water purification technology most often deal with residues of dyes and surfactants in the sewage of industrial waters which need purifying from these pollutants. In order to properly choose the appropriate techniques and technologies, it is necessary to know the composition and properties of substances that should be removed.

TECHNICAL CLASSIFICATION OF DYES

Coloring agents have extremely diverse structure. They have different physic-chemical properties and differently refer to fibrous materials and other objects of the dyeing process. A large variety of dyes caused the need to create their flexible scientific classification. There are two systems of classification of dyes chemical and technical. The chemical classification is based on modern notions about the structure of molecules, the nature of chemical bonds, the theory of substances chromaticity, and involves the separation of dyes into classes on the basis of the commonality of chromophore systems. This classification plays an important role in the development of chemistry and dyes production. However, it does not reflect the technical properties of dyes, their purpose, and methods of application. Therefore, there was a need to develop a technical classification of dyes that would allow to freely orientated in their application. Dyes classified in the same class by chemical classification may have different relations with fibrous or other colored materials. For such dyes usage, it is necessary to use completely different methods.

As a criterion for dyes selection according to the application methods, such properties of dyes as solubility in water or other solvents, the ability to interact with colored polymers, the ability to convert in fibers into compounds with novel properties are taken into account.

The coloring of fibrous and other materials may be based:

1) on the chemical reaction between the dye and the functional groups of the polymer;

2) on the coupling of the dye with the polymer through the adsorption forces;

3) on the ability of dyes to dissolve, to disperse or to mechanically distribute in polymeric and other materials;

4) on the formation of dyes from intermediate products directly in fibers or other materials;

5) on fixing a dye or pigment on a polymeric material with the help of special binders.

Thus, the structure of dyes plays a significant role not only in the chemical but also in the technical classification. However, in the technical classification, the features of the structure of individual groups that are part of the dye, are most important. (NH_2, OH, SO_3H, COOH, Cl, $–CH{=}CH_2$ etc.). They determine the solubility of dyes and their ability to interact with fiber-forming polymers, as well as with other substances, for example, with the salts of certain metals that formed with the dye complex compound in the fiber.

Characteristics of dyes for B.I. Stepanov [4]:

1. Acid dyes. They are water-soluble salts of organic acids, mainly sulfo, less carboxylic acids, sometimes phenolic salts. In aqueous solutions, acid dyes dissociate with the formation of colored anions. The compensating cation is, basically, sodium cation, less often is ammonium. The acid dissociation constant of the sulfonic groups of dyes is 10^{-1} – 10^{-2}, therefore, in dyeing acid dyes exhibit the properties of strong electrolytes.

Acid dyes dyeing protein (wool and silk), as well as synthetic polyamide fibers. Dyeing is usually carried out in an acidic environment in the presence of mineral or organic acids. Sometimes acidic salts are used as an acid reagent. The interaction of acid dyes with fibers is based on the salification between the acid groups of the dye and the amino groups of the fiber. In painted fiber dyes held by ionic bonds. Acid dyes do not paint cellulose fibers.

2. Basic (cationic) dyes. They are water-soluble organic bases. In aqueous solutions dissociate with the formation of painted cations. Compensating anions are usually chloride, hydrosulfate, and oxalate anions. Basic dyes have an affinity for fibers that have amphoteric (protein and synthetic polyamide) and acid (polyacrylonitrile) character. They dye such fabrics by reacting of salification with macromolecules of these fibers due to the acidic groups contained in them (carboxyl, etc.). Basic dyes are kept by ionic bonds in the fiber.

The basic dyes do not have the affinity for cellulose fibers, but can dye them after pre-processing the fiber with phenolic nature substances (synthetic oligomeric phenolic resins, etc.). This gives a weakly acidic character for cellulosic fibers (dyeing using titanium etching). The colors are very clean and bright, but not sufficiently resistant to light and wet windings.

For this reason, the basic dyes are almost not used when dyeing and printing products from cellulose fibers.

Special cationic dyes are well-paint of polyacrylonitrile fibers, forming a color, resistant to any effect.

3. Mordant dyes. The molecules of these dyes contain groups that predetermine their ability to form complexes with metal salts. In the initial form, the mordant dyes are soluble in water. After formation in the fiber of a complex compound with metal, the dye becomes insoluble.

With cellulose fibers, mordant dyes do not have an affinity. They paint cellulose fibers only after the fiber pre-treatment with metal salts due to the formation of an insoluble complex compound with metal in the fiber (mordant cotton dyes). The painting process is characterized by long duration and complexity. For these reasons, mordant dyes for cotton lost their significance. In the presence of acidic (sulfo- or carboxyl) groups, mordant dyes acquire an affinity for protein fibers. With chromium ions (III), these dyes form chrome complexes that are contained in the wool fiber by the forces of ionic and coordination bonds.

Dyes of this type have the properties of both acidic and mordant. They are called acid-mordant or chrome and are widely used for dyeing wool and fur product.

Among the acid-mordant dyes, the special group are metal-containing dyes. They dissolve in water and in the same way as acid dyes, and used for dyeing protein and polyamide fibers. By the structure distinguishes metal-complex dyes are 1: 1 and 1: 2 content. In the first case, one molecule of dye belongs to one metal atom, in the second one there are two. Dyes of the first type paint protein fibers in a strongly-acidic medium, dyes of the second type in neutral or slightly acidic medium.

4. Direct dyes. In molecules of direct dyes, as in acid dyes, there are sulfogroups that give solubility to dyes in water. These dyes have an affinity for cellulose. In aqueous solutions, they dissociate with the formation of colored anions that exhibit a strong ability to associate. Compensative cations usually have sodium cations, less often ammonium or potassium. Direct dyes directly paint natural cellulose and hydrated cellulose fibers, as well as protein (natural silk) and some synthetic fibers. The dyeing is carried out in a weakly or in a neutral medium with the presence of an electrolyte. In cellulose fibers, the dye is kept by hydrogen bonds and by the van der Waals forces, in protein fibers by ionic bonds.

5. Vat dyes. This dyes (pigments) are insoluble in water and can be restored with the formation of derivatives (leuco-compounds), soluble in alkaline media. These dyes have an affinity for cellulose fibers. After dyeing, the reconstituted derivatives oxidize the fiber by air oxygen or other oxidants into the initial insoluble dye. Vat dyes are kept in the fiber due to its insolubility and due to the van der Waals forces action. Vat dyes used primarily for dyeing cellulose fibers. Some vat dyes are able to recover in a light-alkali medium in mild conditions and can be used for dyeing protein fibers.

6. Reactive dyes. These are water-soluble salts of organic acids or bases containing mobile (active) atoms or groups that are torn off at the time of dyeing. They do not have enough affinity for fixing in fiber usually. In the process of dyeing they react with functional groups of fibers and form covalent bonds with it as a result of the splitting of active atoms or groups or disclosure of active bonds. They are used for dyeing of cellulose, protein and some synthetic fibers.

7. Sulphur dyes*.* Such dyes are insoluble in water, containing disulfide groups-S-S-, which can be recovered by sodium sulfide in alkaline medium, while the dye is converted into a soluble form. Sulfur dyes have an affinity for cellulose fibers and are well absorbed by them. Apply sulfur dyes only for dyeing cellulose fibers. Soluble in water, derivatives of sulfur dyes are released under the name of thiols. They paint cellulose fibers in an alkaline medium with the presence of an electrolyte. Upon completion of the dyeing, the thiols are oxidized to the original sulfur dioxide in the fiber.

8. Dyes based on painted materials. They are produced in the intermediate products form. These include components for oxidative coloring of fur (aniline black, its analogs, dyes for fur), etc. They are used mainly in the dyeing of cellulosic materials.

9. Disperse dyes. They represent insoluble or weakly soluble in water dyes that stained hydrophobic fibers (acetate, synthetic) from aqueous dispersions. The process of dyeing consists of the self-moving transition of non-dissociating dye molecules from a dye bath to a dyed fiber. Since the dye is poorly soluble in water, the process is most often carried out at temperatures above 100 °C.

10. Pigments and varnishes. They are insoluble in water and used for dyeing and printing textile materials from any type of fiber due to fixing pigment on fiber with using special astringents. They are also used for the preparation of paint and printing inks, dyeing of rubber and plastic masses, chemical fibers, etc.

11. Dyes soluble in organic media (fat soluble, alcohol-soluble, acetone soluble, etc.). They are water-insoluble and used to color the corresponding organic substances (hydrocarbons, paraffins, fats, alcohols, etc.).

SURFACTANTS

Surfactants (emulsifiers, dispersants, detergents, antistatic agents, softeners) are widely used in the processes of preparation, dyeing, and printing of textile materials, leather, and fur. The surfactants are widely used in the final processing of textile materials, for example, for adding to the tissues hydrophobic, water-repellent, antistatic properties.

The surfactant molecules consist of a hydrophobic hydrocarbon radical (aliphatic chain, sometimes including an aromatic group), and one or more hydrophilic polar groups capable of hydration and which give the solubility for substance. Such a structure, called diphilic, causes the ability of the surfactant adsorbed on the phase-contact surface. Surfactants reduce the surface tension of water by formulating a monomolecular adsorption layer on the surface of the section of water - air and water - solids. Moisturizing, emulsifying, washing and other properties of these compounds are due to a decreasing in the surface tension of water and the affinity of hydrophobic particles of surfactant molecules to insoluble in water fiber-forming polymers.

Since many physicochemical phenomena in the process of staining fibrous materials, leather and fur overlap on the surface of the phase separation between the objects of staining and aqueous solutions of dyes, the introduction of surfactants in the system allows adjust the rate of coloring due to the change (increase) of the wettability of coloring solutions, as well as changes in the color of the dye in solution.

By the nature of electrolytic dissociation are distinguished:

- **anionic** surfactants that dissociate with the formation of anions containing hydrophobic radicals;
- **cationic** surfactants that dissociate with the formation of cations containing hydrophobic radicals;
- **nonionic** surfactants, practically do not dissociate in aqueous solution;
- **ampholytic** surfactants, exhibit the properties of cationic or anionic substances depending on the pH of the medium. The most practical significance has surfactants of the first three groups. They are released in the form of powders, water-based pastes or concentrated aqueous solutions.

Cationic surfactants include soaps, alkyl sulfates, and sulphonates.

Soap is sodium, potassium or ammonium salts of higher fatty acids. In the process of preparing fibrous materials, as well as washing of colored or printed products, use sodium or ammonium oleate $C_{17}H_{33}COOM$ (M = Na or NH_4), as well as soap containing a mixture of sodium stearate $C_{17}H_{35}COONa$ and sodium palmitate $C_{15}H_{31}COONa$. Soaps have a good washing and emulsifying effect. However, they are very sensitive to the action of electrolytes (salts of water hardness), as well as the action of acids.

Alkylsulfates $ROSO_3Na$ are sodium esters of sulfate acid and higher fatty alcohols. They exhibit slightly weaker emulsifying and washing properties than soaps but are more resistant to hardness salts.

1.5 MAIN GENERAL APPROACH OF WORK IN CHEMICAL LABORATORY

1.5.1 SEDIMENTATION

Sedimentation is usually carried out in conical test tubes or graduates (Fig. 1.27). In a test tube, pour the required volume of the test solution and pipette by drops, add the appropriate reagent until complete deposition. The deposition is considered complete if, after short-term settling or centrifugation, there is no turbidity of a clear solution over the precipitate from adding the drop of a reagent. If a colloidal solution is formed as a result of precipitation, then for sediment deposition necessary to add little of the electrolyte and the test tube with the contents heat on the water bath.

Figure 1.27 – Ware for sedimentation (graduates)

1.5.2 MIXING

If the chemical reaction is carried out in an open ware, the solution stirring carried out with a glass rod. If the reaction is carried out in a test tube, mixing is carried out by shaking the test tube. In addition, the mixing of the reaction mixtures can be carried out using mechanical or magnetic stirrers (Fig 1.28 a, b).

a b

Figure 1.28 – Mechanical (a) and magnetic (b) stirrers

1.5.3 FILTERING

Conventional filtration is one of the most used in laboratory practice for the separation of solids from liquid or gaseous (Figure 1.29). Solid particles are separated by filtration of the suspension or aerosol through a porous partition with pore size much smaller than the particle size. The filtration effectiveness depends on the medium, temperature, pressure, a pore size of the filter and the particles retained by it. The larger suspension particles size compared to the filter pore size, the easier it is to filter.

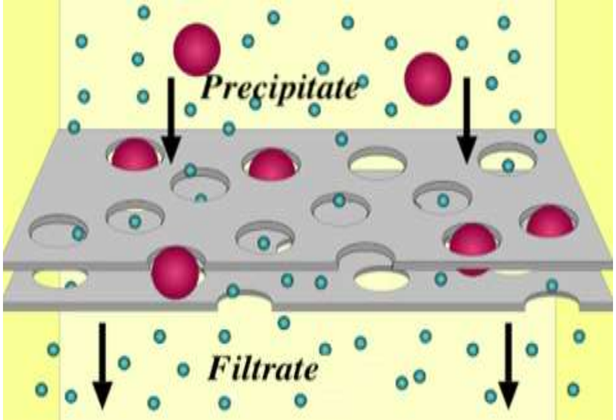


Figure 1.29 – Filtration process mechanism

The essence of the filtering is to liquid with particles of solids passed through the porous partition. The dividing wall that holds solid particles is called a filter. As a filtering material in the laboratory, various organic and inorganic substances are used. Filter materials may be:

1. **fibrous** (cotton, wool, various fabrics, synthetic fibers**)**;
2. **grainy** (quartz sand);
3. **porous** (paper, ceramics, pressed glass).

Often, filtering is carried out using paper filters and smooth glass funnels with a long narrow end (Fig. 1.30 a, b). For the hot concentrated solutions filtration, funnel with a wide, shortened end use for avoiding clogging the narrow tube with obtained crystals by cooling the filtrate

(Fig. 1.30 c). For increasing of filtering surface, a glass funnel with a relief inner surface use (Fig. 1.30, d).

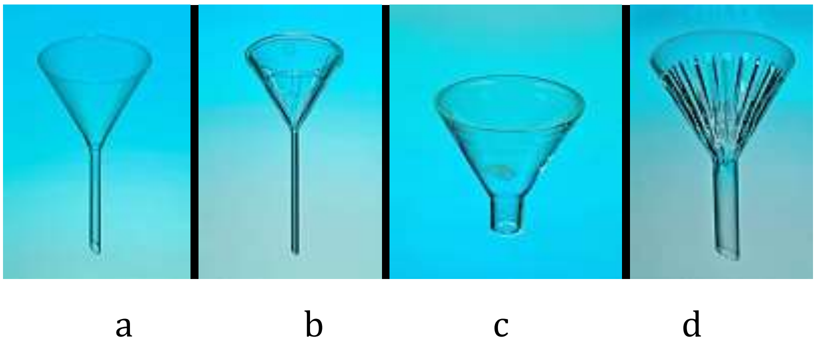


Figure 1.30 – Glass funnels for filtering

During the filtering, the funnel places on a ring tripod. The tip of the funnel should touch the walls of the ware for filtrate. The liquid is drained over a glass stick, pressing it against the wall of the funnel (Fig. 1.31).

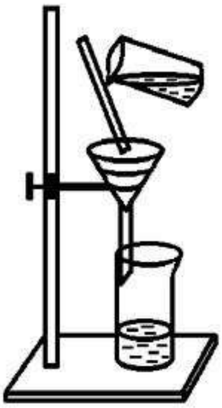


Figure 1.31– Installation for filtering

Before filtration, the precipitate is allowed to settle, then gently, without shaking up the precipitate, drain the liquid on the stick to the filter. To speed up the filtering on the filter, you should maintain a high level of liquid, pouring it in small portions with a glass stick.

Filters can be of different shapes, from various materials, and sizes depending on their purpose.

Cellulose filter papers used for general filtration and exhibiting particle retention levels down to 2.5 μm (Fig. 1.32 a).

Glass and quartz microfibers filter. Glass Fiber Filters are multilayer graded density filters for rapid and efficient filtration of samples with high solids content (Fig. 1.32 b). Quartz Microfiber Filters are used in many air sampling filter applications, including sampling of acidic gases, stacks, flues, and aerosols (Fig. 1.32 c).

Membranes (circles, sheets, and reels) available in different pore sizes and formats including sterile and autoclave packs and colored and gridded forms for specialized application. Anopore inorganic membranes (Anodisc) are well suited for a variety of filtration applications. With a novel aluminum matrix and honeycomb pore structure, Anodisc facilitates controlled filtration. Cellulose acetate membrane filters have very low protein binding, which minimizes sample loss when filtering protein-based aqueous samples. Due to their high chemical resistance, cellulose acetate membrane filters can filter hot liquids and hot gases (Fig. 1.33 a). Non-Sterile Cellulose Nitrate Membrane Filters (0.1 µm pore size) offer narrow sub-micron pore size distribution and low extractable levels. Very fine particles can be retained for recovery or microscopic viewing. Sterile Cellulose Nitrate Membrane Filters recommended for microbiological culturing and sample preparation. It has high strength and flexibility and eliminate the risk of contamination that could impact analysis (Fig.1.33 b). High-quality nylon membranes are suitable for filtering aqueous solutions and most organic solvents. Applications include: filtration of aqueous and organic mobile phases, vacuum degassing, filtration of tissue culture media, microbiological media, buffers, and solutions. Polyethersulfone (PES) membrane filters are hydrophilic and stable in alkaline pH, making them suitable for biological samples and aqueous applications. Polyamide membranes are made from pure polyamide making them the universal filter for clarification. Polyamide membrane filters are mechanically very strong and exhibit excellent wet strength and dry strength. They are hydrophilic making them suitable for aqueous and organic solutions. The membrane filters can be used up to 135°C. Applications include: filtration of aqueous and organic mobile phases, vacuum degassing, filtration of tissue culture media, microbiological media, buffers, and solutions. Mixed Cellulose Ester Membranes (0.2 µm) (Sterile or Non- Sterile) are plain or gridded filters designed to support routine cell counting and particle detection (Fig. 1.33 c).

a b c

Figure 1.32 Cellulose (a), Glass (b) and Quartz (c) filter papers

a b c

Figure 1.33 Anopore inorganic membranes (Anodisc) (a), Sterile Cellulose Nitrate (b), Cellulose Ester Membranes (c)

Speciality cellulose papers offers a range of speciality cellulose papers for specific applications. These filter papers are used for seed germination testing, chromatography blotting, soil testing, and other applications in the sugar industry.

Puradisc Syringe Filters (depending on the material from which they are made) are specifically designed for environmental sample filtration prior to dissolved organic carbon (DOC) and chemical oxygen demand (COD) analysis; cater to a wide variety of sample types and applications, including capillary electrophoresis, biological preparations, protein filtration, and UV spectroscopy sample preparation. Different Puradisc membrane media support diverse chemical solvents and compounds.

The choice of filter material depends on the requirements for the purity of the solution, as well as its properties. It should be remembered that only materials, that do not interact with filtered fluid can be used for filtering. For example, alkalis, especially concentrated, can`t be filtered through a pressed glass filter and other materials containing SiO_2, which dissolves in alkalis.

The filtering can be carried out in different ways: under normal conditions, with heating, in a vacuum.

The temperature has a great influence on the filtration rate. If a hot solution is to be filtered, then special filters or a special funnel for hot filtering with electric or water heating (Fig. 1.35) should be used.

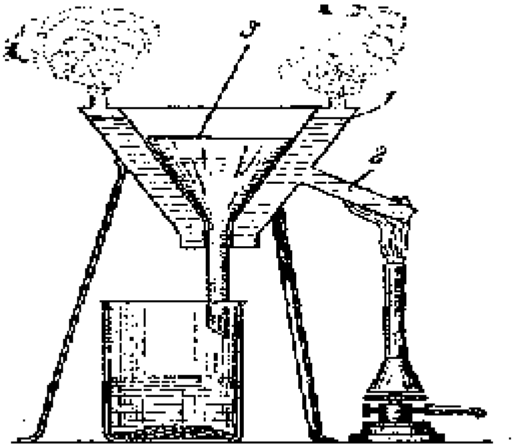
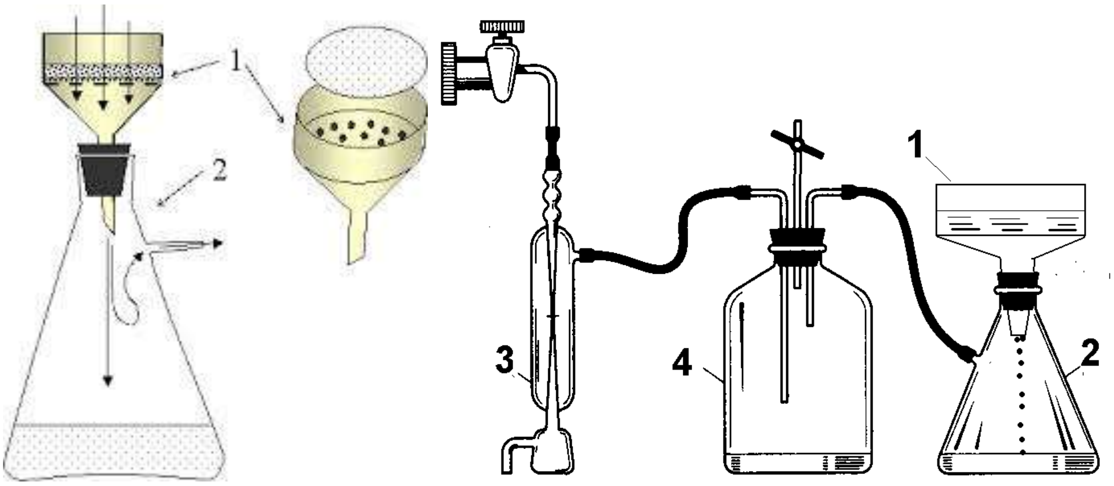


Figure 1.35 – Filtering through the funnel with water heating [3]

Filtering by heating or filtering hot solutions is carried out predominantly with the using of the funnel with shirts. Through a shirt, a heat transfer agent with a certain temperature from the thermostat is passed through. If it is necessary to heat up to 80 ... 90 °C, then the shirt of a funnel is connected to a water steam generator. The vapor is introduced through the upper tube of the shirt.

Another factor influencing the rate of filtering is the pressure under which the liquid passes through the filter. The higher the pressure, the faster the liquid is filtered. Filtering under reduced pressure (under vacuum) allows to achieve a more complete separation of solids from the liquid and increase the process speed. To do this, collect a device consisting of a Buchner funnel, connected with the Bunsen flask, a safety glass, a water jet pump (Fig. 1.36).

The size of the Buchner funnel must correspond to the mass of the precipitate, not the volume of the liquid. On the mesh bottom of the Buchner funnel putting two circles of filter paper, moisten them with distilled water, and attach the device to the pump. Tightly attach the filter to the bottom of the funnel and begin the filtration process. At first, most of the liquid is drained onto the filter, and then part of the liquid is shaken with a precipitate and poured into the funnel.



1 - Buchner funnel; 2 - Bunsen flask; 3 - water jet pump; 4 - safety glass

Figure 1.36 – Filtration under reduced pressure

During the filtering, the precipitate should not overfill the funnel, and the filtrate in the Bunsen flask should not reach the appendix connecting the flask to the safety glass. When the filtering is completed, at first disconnect the Bunsen flask from the safety glass, and then switch off the pump. Funnel with precipitate disconnected from the flask. The filtered precipitate is transferred to a weighing bottle or a sheet of filter paper with a spatula usage.

The large influence on the filtration process has the particles magnitude of the solids, present in the liquid. If the particle size exceeds the pore size of the filter, then the filtering carried out easy. If the particle size of the solid is less than the pore size of the filter, then the solution filtration can`t be achieved and should to change the filter.

Funnels or crucibles with a porous glass bottom are usually used to filter liquids (for example, concentrated acids) that break paper filters. Such filters (filter funnel) are characterized by a different pore size, which is indicated by the corresponding filter numbers (Fig. 1.37). Filter funnel № 1 and № 2 are used for separation of coarse-grained precipitations, № 3 and № 4 for fine-grained. The funnels and crucibles with a glass filtration bottom add instead of the Buchner funnel to the Bunsen flask and connect to the water jet pump.

Figure 1.37 – Filter funnel

Filtration under reduced pressure is carried out with the help of various devices from porcelain and glass. The Buchner and Hirsch porcelain funnels have a perforated porcelain partition, on which is stacked a filter paper (in the larger Buchner funnel, a double layer of filter paper). Put on a perforated partition of filter paper should not find on the walls of the funnel, they are located from the last about 1 mm. The filter is moistened with clean water, after which it adheres tightly to the partition with holes. If necessary, the edge of the filter is pressed by a polymer cylinder or glass stick to the partition. Then, the funnel with the Bunsen flask is connected to the water jet pump by the rubber hose, opening it a bit and making sure in the absence of air bubbles under filter paper. If the precipitate is fluffy, then it is lightly thicken with a glass stick with a flat spatula. The filtering is stopped when the fluid (filtrate) ceases to flow into the Bunsen flask. First, disconnect the

Bunsen flask from the water jet pump. First, disconnect the Bunsen flask from the water jet pump by removing the rubber hose from its tube or by closing the faucet located on the hose. Then switch off the pump. The Bunsen flask is connected to the water jet pump only through safety glass.

If during filtration of fine suspension produces a cloudy filtrate, then it is again passed through the same filter, which allows to clear the filtrate and thickening the precipitate on the filter. Sometimes this operation is repeated 2 to 3 times, until the filtrate becomes transparent.

The level of liquid in the Bunsen flask during filtration should not rise above the lateral appendix.

The disadvantage of Buchner funnels is their nontransparent because they are made from the porcelain. Opacity makes it difficult to control the filtering process and the cleanliness of the funnel surface when they are washed. Therefore, some firms make glass Buchner funnels. The holes in these funnels are often slit-shaped shape.

If, after filtering, the precipitate it is necessary to dry before weighing at a temperature of 130 ... 150 °C and even lightly fry to 300 ... 400 °C, then apply porcelain crucibles Guca. Such crucibles have a porcelain bottom with holes and with the same holes a porcelain insertion round plate. The filter material for crucibles Guca is asbestos fiber or quartz wool.

Glass filters are flow vessels and tubes with fused plates from the porous glass with different pore sizes. The application of the glass filters is diverse.

After work, the glass filters are cleaned by passing through a porous plate a stream of clean water in the direction of return filtering. If the pores of the filter after such an operation remain clogged with particles of the precipitate, they are removed using reagents that convert the particles into soluble compounds. For example, oxides and hydroxides of p- and d-elements are removed from the pores of the filter by hot dilute hydrochloric acid, silver halides by an aqueous solution of ammonia or sodium thiosulfate, and organic substances by a chromium blend.

1.5.4 CENTRIFUGATION

For liquid separation from the precipitate, filtration replaced by centrifugation in case of working with small volumes of solutions. This operation is also used if the fine particles of the precipitate clog filter pores or destroyed at collision with the filtering material. For washing and separation of gelatinous precipitates (for example, hydroxides, sulfides) centrifugation used. For centrifugation, machines called centrifuges are used. Solution with precipitate is placed in special test tubes (conical). Test tubes are located in a centrifuge by pairs and symmetrically against each other. It is necessary that the test tubes have the same mass to prevent vibration of the centrifuge. During the rotation of the centrifugal rotor at high speed, suspended particles under the action of centered forces recline from the center and are collected at the bottom of the test tube (Fig. 1.38).

Figure1.38 – Centrifuge

1.5.5 WASHING OF PRECIPITATE

The precipitate on the filter is washed with cold distilled water, using rinses for these purposes. For precipitate washing, it is possible using of decantation method. Without breaking the precipitate at the bottom of the beaker, the solvent from the beaker is drained with the stick in the funnel.

When the whole solution is fused, 5 ... 10 ml of distilled water added into a beaker with a precipitate, stir and place for some time for precipitation. After 2 ... 3 minutes, carefully transfer the settled water to the same funnel using a stick, leaving a precipitate in the beaker. During the third rinse, shake up precipitate and transfer it to the filter along with the rinsing water.

For precipitate washing obtained as a result of centrifugation, the liquid over the precipitate is drained and then 15 ... 20 drops of distilled water are added to the precipitate. The precipitate is stirred, again centrifuged and drained the liquid over the precipitate. The operation is repeated 2..3 times.

1.5.6 EVAPORATION

Evaporation is the solvent removal from the solution. This process is used to isolate the substance from the solution, as well as to increase the solution concentration. This operation is carried out in porcelain cups and crucibles in water or sand baths (Fig. 1.39).

Figure 1.39 – Cups for evaporation

The solution is poured into a cup no more than 2/3 cup in height. During evaporation, it is necessary to mix the evaporating liquid, to break the crust of crystals on the liquid surface. It is should avoid intense overheating, especially at the end of evaporation, as this may lead to a spattering of the substance and its thermal decomposition. When substance turns into a porridge-like state during evaporation, the evaporation is stopped. Then the substance continues to dry in a drying cabinet.

1.5.7 DRYING

Drying is the release of matter from water or steam**.** During substances drying in a chemical laboratory, it is necessary to take into account their reactivity, resistance to high temperature, to oxidation, hygroscopicity.

Drying of solids in the open air at room temperature is only used if the substance is not hygroscopic. To do this, on a clean sheet of filter paper with a thin layer of put moisture solids. To accelerate drying, the raw material can be pressed several times between sheets of filter paper.

For more completable removal of moisture and for drying hygroscopic substances, use desiccators (Fig. 1.11, p. 1.2). Since the drying process is quite long, vacuum-desiccators are used. At the same time, the rate of evaporation of moisture increases.

If the substance that should be dried is stable in air and decomposes with heating at the temperature range from 100 °C to 130 °C, then for more complete and rapid drying, it is placed in a drying cabinet in which a certain temperature is maintained. When choosing a temperature, should take into account the possibility of sublimation, decomposition or oxidation of matter. During drying, the substance should be stirred from time to time, crushed crust that is formed during the process.

The drying of gases is the release of gases from the vapor contained in them. For drying, the gases are passed through concentrated sulfuric acid or through a layer of the solid dehumidifier, while the dehumidified gas should be inert with respect to the dewatered substances.

1.5.8 CALCINATION

For the complete removal of volatile substances obtained as a result of thermal decomposition, calcining, which is carried out using a flame of a burner, in muffle or crucible furnaces are used (Fig. 1.40). The process of calcination is carried out in the exhaust cabinet. Muffle furnaces are used for calcining with elevated temperatures. Heated crucibles are extracted from a muffle furnace with long crucibles.

Figure 1.40 – Calcination in the flame burner and muffle furnaces

1.6 BASIC METHODS OF CLEANING AND SEPARATION OF CHEMICAL SUBSTANCES

Methods of cleaning substances are different and depend on the substance properties and their usage. In chemical practice, the most common are the following methods: filtration, recrystallization, distillation, sublimation. Gas cleaning is usually carried out by the absorption of gaseous impurities with substances that react with these impurities. Pure substances have the physical and chemical characteristic properties for them. Thus, the degree of substance purity can be checked both by physical and chemical methods. In the first case, determine the density of the substance, the point of melting, boiling, freezing. Chemical testing methods are based on chemical reactions and are methods of qualitative analysis.

1.6.1 RECRYSTALLIZATION

The solids purification by recrystallization is based on the different solubility of the substance in this solvent, depending on the temperature. Under solubility understand the maximum possible content of the dissolved substance in a saturated solution. Solubility is usually expressed in grams of dissolved substance per 100 g of solvent, sometimes at 100 g of solution. The dependence of substance solubility on temperature is expressed by the solubility curves. With a small number of impurities in water, soluble saturation of the main component occurs when the temperature decreases without degradation of quality.

The process of recrystallization consists of several stages:

1. preparation of solution,
2. filtering the hot solution,
3. cooling,
4. crystallization,
5. crystals separation from the mother liquor.

For substance recrystallization, it dissolved in distilled water or in an acceptable organic solvent with a certain temperature. In a hot solvent, by small portions, introduce a crystalline substance until it ceases to dissolve, (i.e., the saturated solution is formed at a given temperature). The hot solution is filtered on a hot water filter. The filtrate is collected into the glass which is placed in a crystallizer with cold water with ice or with a cooling mixture. During the cooling from the filtered saturated solution, small crystals fall out, as the solution at a lower temperature becomes supersaturated. Crystals formed during the crystallization are filtered on a Buchner funnel and then transferred to a folded sheet of filter paper. By glass stick or spatula distribute the crystals evenly, cover with another sheet of filter paper and push the crystals between sheets of filter paper. The operation is repeated several times. Then the crystals are transferred to the weighing bottle. The substance is dried to constant mass in an electric drying cabinet with a temperature of

100…105 °C. The temperature in the oven to this limit should be increased gradually.

For obtain a very pure substance, recrystallization repeated several times.

1.6.2 SUBLIMATION

The process of direct conversion (transition) of a solid to a vapor without the formation of a liquid is called sublimation.

In contrast recrystallization, sublimation is characterized by a higher yield of pure product and occurs at a lower temperature than the melting point of the substance. It is used when it`s not possible to purify the substance by recrystallization since the substance decomposes at a melting point. Distillation of the substance is carried out by heating. When the sublimation temperature is reached, the solid without melting passes into a vapor that condenses into crystals on the surface of the cooled objects (Fig. 1.41). Benzoic acid, naphthalene, ammonium chloride, iodine, and some other substances, can be obtained in pure form using sublimation, in case the impurities are not dislodged. However, this method of purifying substances is limited, because some solids-impurities, are also able to sublimate.

Figure 1.41 – The sublimation process

1.6.3 DISTILLATION

Distillation is the process of separating the liquid from dissolved solids or less volatile liquids in it. Distillation is based on the liquid transformation into steam, followed by vapor condensation into the liquid. By distillation in comparison with the recrystallization, as a rule, is obtained a greater yield of a pure product at a lower cost of time. The distillation is used when the substances that distilled don`t undergo any changes during the heating or liquids that are cleaned has some temperature difference but not too high a boiling point.

There are three ways of liquids distillation [3]:

1. at atmospheric pressure **(simple distillation)**,
2. at reduced pressure **(vacuum distillation)**,
3. **distillation with water vapor**.

Simple distillation is used for separating the target product from practically non-volatile impurities. For example, water purification from non-volatile salts. For this purpose, a traditional installation that consists of a Wurz flask, a direct refrigerator and a receiver is collected (Fig. 1.42).

Figure 1.42 – Simple distillation

When the entire device is assembled, it needs carefully check that the tubes are well-chosen or that the thermometer is correctly installed. Turn on the water to cool the refrigerator. Put a receiver for liquid collecting, which is distilled, and begin to heat the solution to boil. The flask is heated in a water (sandy) bath, less often on a flame burner through an asbestos grid. The temperature of steam of the matter that discharged is measured by a thermometer set at 1 cm below the discharge tube of the Wurtz flask. In order to prevent the sudden boiling of the distilled liquid and entering it into the fridge, put long capillaries or small portions of porcelain (boiling granules) into the flask. Distillation with low pressure (vacuum distillation) is used if the fluid to be distilled under normal conditions can`t withstand heating to its boiling point. The installation for such distillation is more complicated.

For the distillation of insoluble in water substances, distillation with water vapor (for poisonous substances) is used (fig.1.43).

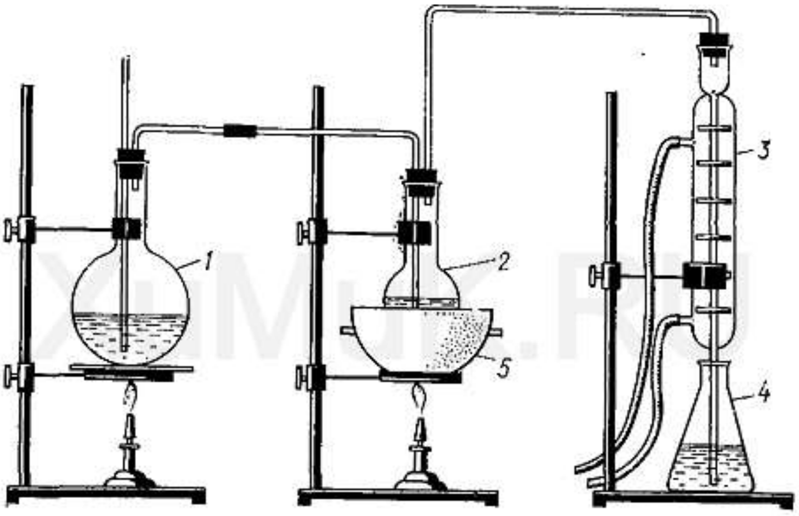


Figure 1.43 – Distillation with water vapor

QUESTIONS FOR SELF-CONTROL TO CHAPTER 1

1. Justify the choice of materials for the manufacture of chemical ware..
2. Describe the basic chemical glass characteristics.
3. Explain the need for the division of chemical ware into general purpose groups, graduated and special.
4. Explain how, based on the design features of the ware, determine its purpose.
5. Explain the difference in the graduated flasks for refluxing and infusion and characterize the areas of their application.
6. Describe the samplers types and the peculiarities of working with them.
7. For what purpose do checking of graduated ware?
8. What is the feature of verifying graduated pipettes?

9. What are the main stages of cleaning a chemical ware?
10. What chemical mixtures for washing dishes, you know??
11. Describe the work with the mixtures using for the washing of chemical ware and their storage rules.
12. Name the ways to control the surface cleanliness of the ware.
13. Give classification of scales with a mechanical type of balancing force creation.
14. Describe the construction of the techno-chemical scales.
15. Describe the construction of analytical scales.
16. Explain the rules of work on electronic and analytical scales and the requirements for the place of installation of the last one.
17. Does the change in the weighing conditions (technical, analytical scales) affect the accuracy of checking the graduated ware?
18. What are the types of moisture of powdered reagents.
19. Describe the main contaminants present in the air of the chemical laboratory.
20. Give reagents qualification.
21. What properties of reagents are considered dangerous? Give examples for each property.
22. Name the group of fire-hazardous substances with examples.
23. To which classes of danger on the degree of action on the body harmful substances are divided?
24. Give the classification of toxic substances on the principle of action on the human body.
25. What are the main safety measures when storing reagents?
26. Give the definition of the types of chemical products.
27. Describe the processes: deposition, stirring, separation of the solution and precipitate.

28. What is filtering? What are the factors influencing the effectiveness of the filtering? What are the main ways of filtering?
29. Describe the processes of calcination and evaporation. What are the main factors that influence the evaporation process?
30. Describe the processes of centrifugation and sediment washing.
31. Name the main filter materials. Specify how by label the filter to determine its destination?
32. Describe the basic methods of purification and separation of substances, namely, processes of recrystallization and sublimation.
33. Describe the basic methods of substances purification and separation, namely the process of distillation. Methods of liquids distillation.

CHAPTER 2 BASIC CONCEPTS IN APPLIED CHEMISTRY

2.1 CLASSIFICATION OF CHEMICAL-TECHNOLOGICAL PROCESSES

Chemical-technological processes (CTPs) can differ significantly in nature of reagents involved in chemical reactions; a number of stages of chemical processes; the number of phases (aggregate states) that form the chemical system; thermal and hydrodynamic regimes.

CTPs are classified according to such basic features: type of chemical reaction, thermodynamic parameters, thermal regime, a phase state of reagents, a character of the process in time, by a stationary process, hydrodynamic regime [5].

1. **By type of chemical reaction**, CTPs are characterized at the molecular level and are divided into **simple** and **complex**.

The simplest are processes that consist only of one, elementary chemical reaction, whose molecular mechanism of flow accurately reflects the initial and final state of the process without the presence of intermediate stages.

Complex processes cover several reactions, which depending on the sequence of their flow can be divided into:

- -- **parallel** (the same source substance simultaneously participates in two or more reactions);
- -- **consistent** (there is a conversion of the initial matter into an intermediate semi-finished product, and it turns into a finite one);
- -- **parallel-consistent** (combined) (in these processes simultaneously occur both parallel and consistent chemical reactions).

2. Depending on the thermodynamic parameters, CTPs are classified according to the thermal effect:

- **exothermic** (with heat release).

$$2SO_2 + O_2 \rightarrow 2SO_3 + Q,$$

- - **endothermic** (with heat absorption).

$$CaCO_3 \leftrightarrow CaO + CO_2 - Q.$$

3. According to the thermal regime, CTPs are characterized at the reactor level and are divided into **adiabatic, isothermal,** and **polythermal.**

Adiabatic processes occur without heat exchange with the environment or heat-exchange equipment. So, in the exothermic reactions, the temperature of the reaction medium increases, and in the endothermic, it decreases.

Isothermal CTPs are carried out at a constant temperature, which is provided by the heat removing if there is an exothermic reaction or heat supply at endothermic reactions.

Polythermal processes are characterized by the fact that CTPs are carried out at several strictly defined temperatures. That is, the temperature regime is created and regulated by specially designed programs.

4. By the process direction:

– **Irreversible** (occurs only in the direction of the products formation). Such reactions are possible if:

there is reagent excess: $CO + 3H_2\ (excess) \rightarrow CH_4 + H_2O,$

a precipitate (low soluble matter) or gas are formed:

$$NO + NO_2 + CO(NH_4)_2 \rightarrow 2N_2 + CO_2 + 2H_2O,$$

$$SO_2 + MgO(suspension) \rightarrow MgSO_3\downarrow,$$

products are removed from the reaction zone.

– **Reversible** (occurs in two directions)

$$CO + H_2O \leftrightarrow CO_2 + H_2.$$

5. According to the phase state of reagents CTPs (flow and reactor level) are divided into:

– **Homogeneous,** if the phase separation surface between the reactants is absent; (g-g, l-l), i.e. all reagents and products are in the same aggregate state):

$$N_2 + 3H_2 \leftrightarrow 2NH_3 + Q.$$

– **Heterogeneous,** if the phase separation surface between the reagents exists, i.e. reagents or products in different aggregate states (g-l, s-l, s-g).

Separately **gas reactions**, where at least one reagent or product is gas are stand out:

- with volume decrease: $2SO_2 + O_2 \leftrightarrow 2SO_3 + Q$;
- with volume increase: $CaCO_3 \leftrightarrow CaO + CO_2 – Q$;
- without changing volume: $CO + H_2O$(steam) $\leftrightarrow CO_2 + H_2$.

6. **By the number of components** in the system:

- one-component;
- two-component;
- three-component.

7. By the process character in time at the level of the reactor and the CTPs, chemical-technological processes are classified into:

periodic (in such processes time from the moment of loading of reagents and raw materials before unloading the product passes for a certain time);

continuous (the loading of raw materials into the reactor and unloading of the product are continuous);

semi-periodic (the process of loading the raw material are carried out continuously, and the unloading of the product are periodically, or vice versa).

8. By the hydrodynamic regime, the CTPs at the flow and reactor levels are divided into **ideal mixing** and **ideal displacement** conventionally.

2.2 THE MAIN INDICATORS OF CTPS

Chemical technology (CT) is based on general chemical principles. The global task of CT is to create non-waste, low-waste and environmentally friendly technologies. It can be achieved by doing the following conditions:

1. Getting the maximum number of products;
2. Getting the minimum amount of waste;
3. Completeness of raw materials bases usage.

The main indicator of the completeness of the process is [5]:

The conversion degree (x_A**)** is the ratio of the number (mass) of the reagent (kg, kmol) that reacts to its initial mass (G_{Ao}):

$$x_A = \frac{(N_{A_0} - N_A)}{N_{A_0}}, \tag{2.1}$$

where N_{A_0} – amount of initial substance, mole;

N_A – the amount of the initial substance that did not enter the chemical reaction, mole.

If the reaction is simple, then the conversion degree becomes the following:

$$x_A = \frac{N_{продукту}}{N_{A_0}}, \tag{2.2}$$

where $N_{продукту}$ – quantity of the product formed, mole;

N_{A_0} – amount of initial substance, mole.

For reversible reactions, an indicator such as the **equilibrium degree of conversion (**$x_A{}^*$**)** is used, which is equal to the ratio of the amount (mass) of the reagent in equilibrium to the initial amount of this reagent:

$$x_A^* = \frac{(N_{A_0} - N^*{}_A)}{N_{A_0}}, \tag{2.3}$$

where N_{A_0} – amount of initial substance, mole;

$N^*{}_A$ – amount of the initial substance in the state of equilibrium, mole.

The degree of conversion can also be expressed through concentration:

$$x_A = \frac{(C_{A_0} - C_A)}{C_{A_0}}, \tag{2.4}$$

where C_{A_0} – concentration of the initial substance, mole/l;

C_A – the initial substance concentration that did not enter the chemical reaction, mole/l.

Or through the mass:

$$x_A = \frac{(G_{A_0} - G_A)}{G_{A_0}}, \tag{2.5}$$

where G_{A_0} – mass of the initial substance, kg;

G_A – mass of the initial substance not entered to the chemical reaction, kg.

x_A **≤ 1, quotient or** x_A **≤ 100 %.**

The degree of conversion characterizes the effectiveness of the process only from the point of view of the raw materials usage. But in the case of parallel or sequential reactions, part of the reagent is converted into by-products. Therefore, one more indicator of the process efficiency is the **product yield.** It characterizes the perfection of production in the transformation of raw materials into the target product terms. There are three types of product yield: **complete, equilibrium and yield from equilibrium**.

The complete product yield ***(***Φ_R***)*** is the ratio of the quantity (mass) of the actually obtained product (G_R) to its maximum (theoretical) amount (mass) (G_{Rmax}). The theoretical product amount is calculated according to the stoichiometric reaction equations:

$$\Phi_R = G_R / G_{R\max}, \tag{2.6}$$

where G_R – mass of the actually obtained product, kg;

G_{Rmax} – maximum (theoretically possible) mass of the obtained product, kg:

$$\Phi_R = N_R / N_{R\max}, \tag{2.7}$$

where N_R the quantity of the actually obtained product, mole;

$N_{R\max}$ – maximum (theoretically possible) quantity of the obtained product, mole.

Equilibrium product yield ***(Φ_R*)*** is the ratio of the product mass formed at the time of reaching the equilibrium state (G_R^*) to the maximum possible (theoretical) mass of the product ($G_{R\max}^*$):

$$\Phi_R^* = G_R^* / G_{R\max}. \tag{2.8}$$

Yield from equilibrium ***(Φ_R^m)*** is the ratio of the actual product mass (G_R) to the product weight (G_R^*) which can be generated at the time of the equilibrium state:

$$\Phi_R^m = G_R / G_R^*. \tag{2.9}$$

Cost factor by raw materials is the amount of raw material needed for the production of a unit of production (1t, 1kg, 1g):

$$\beta_{\text{сировини}} = \frac{G_{\text{сировини}}}{G_{\text{продукту}}}, \tag{2.10}$$

де $G_{\text{сировини}}$ – mass of raw materials, kg;

$G_{\text{продукту}}$ – unit weight of product, kg.

The cost factor by energy is the amount of energy required to produce a unit of product (1t, 1kg, 1g):

$$\beta_{\text{енергії}} = \frac{W}{G_{\text{продукту}}}, \tag{2.11}$$

where W – amount of energy, kWh;

$G_{\text{продукту}}$ – unit weight of product, kg.

2.3 APPLICATION OF EQUILIBRIUM PROCESSES IN APPLIED CHEMISTRY

The equilibrium constant quantitatively characterizes the state of chemical equilibrium. It is the ratio of the product of the equilibrium concentrations of the reaction products to the product of initial substances concentrations in the degrees corresponding to their stoichiometric coefficients in the reaction equation.

By the value of the chemical reaction equilibrium constant and by the composition of the initial reaction mixture, the composition of the mixture after the reaction and the degree of transformation of the starting substances can determine.

According to the law of the mass action, the rate of a chemical reaction is proportional to the product of concentrations of reacting substances. So, for a simple reaction [6]:

$$aA + bB \leftrightarrow rR + sS \pm Q \qquad (2.12)$$

the speed of direct *(u_1)* and reverse reaction *(u_2)* will be written as follows:

$$u_1 = k_1 C_A^a C_B^b, \qquad (2.13)$$

$$u_1 = k_1 C_{\mathrm{R}}^r C_S^s, \qquad (2.14)$$

where k_1 and k_2 are the constants of the velocity of direct and revers reactions; C_A, C_B, C_R, C_S are concentrations of reactants.

Equilibrium constant is calculated as the ratio of the direct reaction rate constant to the reverse at the moment of equilibrium, when $u_1 = u_2$.

$$\mathrm{k}_1 (C_A^*)^a \cdot (C_B^*)^b = \mathrm{k}_2 (C_R^*)^r \cdot (C_S^*)^s, \qquad (2.15)$$

$$k_{рівн} = \frac{k_1}{k_2} = \frac{(C_R^*)^r \cdot (C_S^*)^s}{(C_A^*)^a \cdot (C_B^*)^b}, \tag{2.16}$$

where C_A^*, C_B^*, C_R^*, C_S^* are equilibrium concentrations of reacting substances.

Equation (2.16) is only suitable for reaction under conditions of chemical equilibrium.

The designation and dimension of the equilibrium constant depends on the fact in which units the concentration of the reacting substances is expressed:

K_c - if the concentrations of the reacting substances are expressed in mole/l (C_A, C_B):

$$K_c = \frac{C_R^r \cdot C_S^s}{C_A^a \cdot C_B^b}, \tag{2.17}$$

K_P – if the concentration of the reacting substances is expressed in partial pressures (P_A, P_B):

$$K_P = \frac{P_R^r \cdot P_S^s}{P_A^a \cdot P_B^b}, \tag{2.18}$$

P_i – partial pressure of the i-th component,

$P_i = C_i RT$

where – C_i the concentration of the i-th component, mole/l; R– absolute gas constant, R=8,314 J/(mole·K); T – process temperature, K.

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

$$K_c = \frac{C_{NH_3}^2 \cdot}{C_{N_2}^1 \cdot C_{H_2}^3}$$

$$K_P = \frac{P_{NH_3}^2 \cdot}{P_{N_2}^1 \cdot P_{H_2}^3}$$

where $P_A = \frac{a}{a+b+r+s}P$, $P_B = \frac{b}{a+b+r+s}P$ etc. (P – total pressure in the system);

K_n – if the concentration of the reacting substances is expressed in moles (n_A, n_B etc.):

$$K_n = \frac{n_R^r \cdot n_S^s}{n_A^a \cdot n_B^b}, \tag{2.19}$$

K_N – if the concentration of the reacting substances is expressed in the molar, and in the case of gases in a volumetric fraction (N_A, N_B etc.):

$$K_N = \frac{N_R^r \cdot N_S^s}{N_A^a \cdot N_B^b}, \tag{2.20}$$

Equilibrium constants K_C, K_P, K_n, K_N are linked to each other:

$$K_P = K_C (RT)^{\Delta n} = K_n \left(\frac{RT}{V}\right)^{\Delta n} = K_N P^{\Delta n}, \tag{2.21}$$

where R is absolute gas constant, R=8,314 J/(mole·K); Δn is change in the number of moles of gases.

For the model reaction (2.12) $\Delta n = (r + s) - (a + b)$.

Into expression of K_c of heterogeneous reactions include only the concentrations of gaseous or dissolved substances. The concentration of solids (the number of their mole in the unit volume of each solid), is a constant value and is included to the value of the equilibrium constant K_c:

$$CaCO_3 \leftrightarrow CaO + CO_2$$

$$K_c = \frac{C_{CaO}^1 \cdot C_{CO_2}^1}{C_{CaCO_3}^1}$$

C_{CaCO_3} =const, C_{CaO} = const

$$K_c = C_{CO_2},\ K_p = P_{CO_2}.$$

By the value of K_c it is possible to determine the conversion degree or the degree of completeness of the reaction:

if $K_c \gg 1$, that means that *Спрод >> Свих.реч-н*, i.e. x_A is big.

The most practical usage for calculating the reactions between gases is the equilibrium constant K_P. Since, knowing the total pressure of the gas mixture, the concentrations of components can be expressed through partial pressures. Calculating equilibrium states in the liquid phase, use constants K_c or K_n.

The values of the equilibrium constants for various reactions, which were determined experimentally or calculated analytically, are given in the special reference literature. Using the equilibrium constant to calculate the equilibrium composition of a given chemical reaction, it should take into account what are value K_C, K_P, K_n or K_N. Accordingly, when performing calculations, the appropriate expression of substances concentration should be used. If the reaction occurs without changing in volume, that is, $\Delta n=0$, then:

$$K_C = K_P = K_n. \tag{2.22}$$

At a certain temperature, the equilibrium constant for each reaction is a constant value. Consequently, with the $K_{рівн}$ value, it is possible to calculate the number of reacting substances at the equilibrium moment, and then the equilibrium degree of transformation, which is the maximum for these conditions.

$$2ZnS + 3O_2 \leftrightarrow 2ZnO + 2SO_2,$$

$$K_C = \frac{C^2_{SO_2}}{C^3_{O_2}} \text{ або } K_P = \frac{P^2_{SO_2}}{P^3_{O_2}} \text{ або } K_n = \frac{n^2_{SO_2}}{n^3_{O_2}}.$$

The dependence of the equilibrium constant on the temperature under constant pressure is determined by the van 't Hoff isobar equation:

$$\frac{d \ln K_P}{dT} = -\frac{Q}{RT^2}, \tag{2.23}$$

where Q is thermal effect of the reaction; R is absolute gas constant, R=8,314 J/(mole·K).

From equation (2.23) it follows that in the case of endothermic reactions (Q <0) the derivative $(d \ln K_P/dT)$ always acquires positive values. So, a rise in temperature leads to an increase in the value of K_P (Fig. 2.1, curve 1). For exothermic reactions (Q> 0), the value of the derivative is negative, so, the K_P increases with decreasing temperature (Fig. 2.1, curve 2).

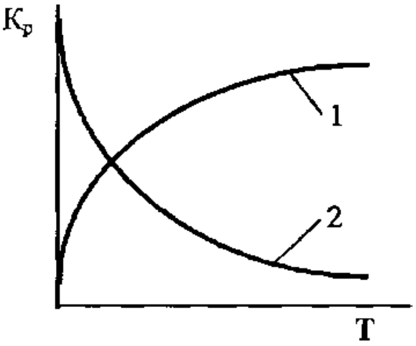


Figure 2.1. – Dependence of the equilibrium constant on the temperature for the endothermic (1) and exothermic (2) reactions [6]

The influence of pressure on the magnitude of the equilibrium constant is determined by the second equation of van 't Hoff:

$$\frac{d\ln K_N}{dP} = -\frac{\Delta V}{RT^2}, \qquad (2.24)$$

where ΔV is change in the molar volume of the reaction mixture; R is absolute gas constant, R=8,314 J/(mole·K).

So, for the reactions that occur with gas volume increasing ($\Delta V>0$), the derivative *($d\ln K_N/dP$)* is negative. That means an increase in pressure will lead to a decrease in the value of K_N (Fig 2.2, curve 2).

Accordingly, for reactions that occur with a decrease in the gas volume ($\Delta V<0$), the derivative is always positive, and the equilibrium constant increases with increasing pressure (Fig. 2.2, curve 1).

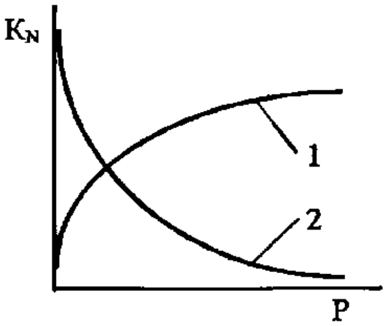


Figure 2.2. – The dependence of the equilibrium constant on the reaction pressure, which occurs with a decrease (1) and an increase (2) of the gas volume [6]

The direction of changing in the course of processes occurring in the equilibrium system with changes in external conditions is determined by **Le Chatelier's Principle**[4]**:** if on the system that is in equilibrium conditions operates an external factor (that leads to a disturbance of the equilibrium), then processes occur in the system (the displacement of the equilibrium), aimed at weakening the action of this factor.

Le Chatelier's Principle is used in order to determine the ways of CTP equilibrium displacement in the direction of target products obtaining. So, the changing of parameters of the technological regime, which will make possible improving the technological parameters of the process: raw materials conversion degree, process selectivity, product output.

The following key factors influence the equilibrium position: **temperature, pressure, and concentration of reacting substances**.

The effect of temperature on equilibrium in the chemical system is given by the example of ammonia synthesis process, which is represented by the equation:

$$3H_2 + N_2 \leftrightarrow 2NH_3.$$

The direct reaction is exothermic. In the equilibrium state, the speed of direct and reverse reactions is the same. So, the amount of heat that is released is equal to the amount of heat that is absorbed. Consequently, for the state of equilibrium, the following record of this reaction is correct:

$$-Q + 3H_2 + N_2 \leftrightarrow 2NH_3 + Q\,.$$

---

[4] Le Chatelier – French scientist, that invented the principle in 1884. In 1897 invented the metallographic microscope, in 1901 developed the conditions for the ammonia synthesis.

$$X_A\uparrow,\ \Phi(NH_3)\uparrow,\ T\downarrow.$$

If in such an equilibrium system, the temperature is increased (by external introduce additional energy in the heat form), then the system tries to counteract this action. It weakens the external influence, that is, reduces the total amount of heat in the system, absorbing its part. At the same time, obviously, an endothermic reaction occurs, which is reversible. In accordance with Le Chatelier's Principle, in this case, the equilibrium will shift towards the source materials, and therefore the conversion degree of raw materials will decrease. Consequently, in order to shift the equilibrium towards the target product (ammonia), it is necessary to reduce the temperature in the system by removing the heat with refrigerant using.

In a system in which the direct reaction is endothermic, for example,

$$CH_4 + H_2O_{(vapor)} \leftrightarrow CO + 3H_2 - Q,$$

$$X_A\uparrow,\ \Phi(H_2)\uparrow,\ T\uparrow,$$

to shift the equilibrium towards the target products, it is necessary to raise the temperature (bring the heat).

The effect of pressure on equilibrium is evaluated only in those cases where at least one of the components of the equilibrium mixture is a gaseous substance. In order to determine how the pressure on equilibrium will affect, the initial and final volumes of the system determined by the stoichiometric equation of the reaction. For this purpose, the number of moles of gaseous substances is determined before and after the reaction. Let the reaction of ammonia synthesis occurred:

$$3H_2 + N_2 \leftrightarrow 2NH_3.$$

$P\uparrow$, if n(initial substances) > n(products) $\Phi(NH_3)\uparrow$.

Since this reaction occurs with a decrease in the gas volume, so if in this system increase the pressure, the system will seek to reduce it. This is possible due to the decrease in the number of moles of gaseous substances. Consequently, in order to shift the equilibrium towards the target product in this system, it is necessary to increase the pressure. Conversely, if as a result of the reaction in the system occurred the number of moles of gaseous substances increasing, for example:

$$CH_4 + H_2O_{(vapor)} \leftrightarrow CO + 3H_2,$$

$$P\uparrow, \text{if } n(\text{initial substances}) < n(\text{products})\ \Phi(H_2)\downarrow,$$

$$\Phi(H_2) \uparrow P\downarrow,$$

then the shift of equilibrium to the right is achieved by decreasing the pressure. If the reaction occurs at a constant volume, for example:

$$CO + H_2O_{(vapor)} \leftrightarrow CO_2 + H_2,$$

$$P\uparrow, n(\text{initial substances}) = n(\text{products})\ \Phi(H_2)=\text{const},$$

that is, the number of moles of gaseous substances before and after the reaction is the same, then the pressure does not affect the equilibrium position.

Consider the influence of the concentrations of the reactive substances on the equilibrium. The introduction of any substances present in the system in an equilibrium state is an external factor whose action the system seeks to reduce. As a result, the equilibrium will shift in one direction or another. If the initial reagent is introduced, the equilibrium shifts to the right, and if the product the equilibrium shifts to the left. For example, to shift the equilibrium towards the formation of a product into the system

$$CH_4 + H_2O_{(vapor)} \leftrightarrow CO + 3H_2$$

introduce an excess of water vapor.

Another way of shifting the equilibrium by changing the concentration towards the product is it removing from the reaction medium. This method is used, for example, for oxidation of SO_2 to SO_3 in the sulfuric acid production by double contacting - double absorption. Oxidation of SO_2 occurs in a five-layer contact apparatus. The gas stream containing SO_3 formed in the first three layers of the catalyst is withdrawn from the contact apparatus, cooled and fed to the absorption of sulfur oxide (VI) into the absorption column. The gas from which the formed SO_3 was removed, is again introduced into the contact apparatus in the fourth, and then the fifth layer of the catalyst, where the oxidation reaction continues. Degree of conversion of SO_2 to SO_3 increase in this case.

The catalyst does not affect the equilibrium position, because in this state it equally accelerates both direct and reverse reactions. Its presence is necessary in order that, due to the acceleration of the reaction at the initial moment of the process, the equilibrium position will be achieved much faster than the non-catalytic process.

However, based on Le Chatelier's Principle it is substantiated only the ways, in which it is possible to shift the equilibrium in a particular system. But in real production processes, when substantiating the values of the technological regime parameters, technological and economic indicators of processes are also taken into account. In particular, it's productivity, transformation degree, product yield, consumption ratios for raw materials and energy, etc. Therefore, it often happens that the recommendations deriving from Le Chatelier's Principle are not respected or applied only for certain conditions of the technological process. Let's look at some specific examples:

To shift the equilibrium in the reaction $2SO_2 + O_2 \leftrightarrow 2SO_3 + Q$, which is characterized by a significant exotherm, in accordance with Le Chatelier's Principle, it should be carried out with the lowest possible temperature. But for industry, this reaction occurs only with a solid catalyst. However, it exhibits a catalytic effect only at a certain temperature, which is called the ignition temperature of the catalyst ($T_{зап}$). Consequently, this reaction is carried out at a temperature not lower than the ignition temperature of the catalyst (for example, for a vanadium catalyst used in said process, $T_{зап}$ = 420...430 °C). To shift the equilibrium to the right, the heat from the reaction medium is diverted, but so that the temperature does not decrease to a value lower than $T_{зап}$ [5].

The same reaction that occurs with a decrease in gas volume, in order to shift the equilibrium towards SO_3, it is necessary carried out at elevated pressure, in accordance with Le Chatelier's Principle. However, in industry in most technological schemes, this process is implemented under atmospheric pressure. In this case, they are guided by economic expediency. On the one hand, at increased pressure, an increase in the degree of conversion of SO_2 is expected, and an increase in the productivity of production by sulfate acid; and on the other hand, the growth of energy costs for excess pressure creation. Since oxidation of SO_2 is usually carried out by air, a significant amount of energy is spent for compressing of inert nitrogen, which in the air is 3.7 times greater than oxygen. It is estimated that the high-pressure air using in this process is economically disadvantageous.

Conversion of carbon (II) oxide with water vapor by reaction: $CO + H_2O_{(vapor)} \leftrightarrow CO_2 + H_2$, the reaction is carried out under increased pressure (in accordance with Le Chatelier's Principle, the pressure in this system does not affect the state of equilibrium). In this case, by an increase in pressure is achieved increasing the speed of the process in its initial stages, because in homogeneous reactions increasing the pressure in the system leads to an increase in concentrations of reacting substances. In addition, high pressure using make it possible to reduce the volume of reactionary equipment.

2.3.1 HOMOGENEOUS CHEMICAL-TECHNOLOGICAL PROCESSES IN APPLIED CHEMISTRY

Homogeneous processes are processes carried out in a homogeneous medium (in a liquid or a gaseous mixture in which the surface of separation of a partition between its separate parts or components is absent). Homogeneous processes in industry are rare. It is difficult to get a homogeneous system, in fact. Any substance contains traces of various impurities in the other phase. So, even in 1 ml of distilled water contains from 20,000 to 30,000 dust particles.

Reactions occur much faster in volume in the homogeneous processes than in heterogeneous. The implementation and management of technological homogeneous processes are much simpler and easier. So many industrial heterogeneous processes are trying to translate into homogeneous.

In industry, for the implementation of homogeneous chemical-technological processes are often carried out operations preceding chemical interaction, namely the absorption of gases by liquids or the condensation of steam, dissolution or melting of solid materials. In both cases, rare-phase systems are obtained. As a result of the liquids evaporation or the separation from them into the gas phase of the useful components, homogeneous gas-phase systems are obtained. An example of a process that is implemented as a liquid phase can be ethanol production. During the process of sulfate acid hydration of ethylene, sulfate acid first absorbs the ethylene, and then formed ethylsulfate acid in the liquid phase homogeneously, which later hydrolyzes with the release of the target product ethanol:

$$CH_2= CH_2 + H_2SO_4 \leftrightarrow C_2H_5OSO_2OH,$$

$$C_2H_5OSO_2OH + HOH \leftrightarrow C_2H_5OH + H_2SO_4.$$

Homogeneous processes in the gas phase are widely used in the technology of inorganic and organic substances, for example, in the production of sulfate, nitrate and chloride acids, chlorination and nitration of organic compounds, etc.

Homogeneous liquid-phase processes are used much more often in the industry. Homogeneous liquid-phase processes include neutralization and exchange-rate reactions in the technology of mineral salts, the preparation of simple and complex esters, polymerization in solutions and meltdowns in the technology of organic substances, alkali heating of benzosulfonic acids in the production of phenol, and separate stages of ethylene sulfate acid hydration in the production of ethyl alcohol.

In a homogeneous medium (gas- and liquid-phase), many processes occur along by the chain mechanism: oxidation, polymerization, hydrocarbon pyrolysis, hydrogen chloride synthesis.

DETERMINATION OF INFLUENCE FOR DIFFERENT FACTORS ON SPEED OF HOMOGENEOUS PROCESSES

For a reasonable choice of optimal conditions for the implementation of the chemical-technological process, it is necessary to have information about the reaction rate depending on a number of factors, (to know the kinetics of the process). Chemical kinetics studies the patterns of the course of thermodynamically possible reactions in time and their mechanism. The rate of a chemical reaction is determined by the changing in the concentration of a specific component in the reaction system per unit time in unit volume.

Much of the chemical processes carried out by stages (except for so-called instant reactions: explosives, etc.).

STAGES OF HOMOGENIC CTP

1. Supply of reagents into the reaction zone;
2. Directly chemical reaction;
3. Discharge of reaction products from the reaction medium zone.

Depending on which stage in the CTP is the limiting, the reaction region is determined.

AREAS OF REACTION BEHAVIOR OF CTP

If the limiting (the slowest) stage of the process is the stage of reagents supply or products removing from the reaction zone, then the process runs in the diffusion region. This means that in order to accelerate the reaction behavior, it is necessary to create conditions for the intensification of these diffusion stages. That is, it is necessary to make mixing.

If the limiting (the slowest) stage of the process is a chemical reaction, then the process runs in the kinetic region. The possible areas of the chemical process are as follows:

1. Diffusion region;
2. Transition region (when the diffusion and chemical interaction velocity is approximately the same);
3. Kinetic region.

FACTORS AFFECTING ON THE SPEED OF CTP

1 the concentration of initial substances C(in. subs.);
2. the concentration of reaction products C(prod.);
3. temperature (T);
4. pressure (P);
5. hydrodynamic mode (mixing) (mixing);
6. catalyst (kat).

The comparison of the effectiveness of each factor's influence, depending on the region of the process, is presented in the table 2.1.

Table 2.1 – Comparison of the effectiveness of each factor's influence, depending on the region of the process.

Diffusion region	Kinetic region
C(in. subs.) –	C(in. subs.) – ↑
C(prod.) – ↓	C(prod.) – ↓
T – ↑	T – ↑
P – ↑	P – ↑
mixing – ↑	mixing – does not affect
Kat – does not affect	Kat – ↑

2.3.2 THE INFLUENCE OF DIFFERENT FACTORS ON THE SPEED OF HOMOGENEOUS PROCESSES

The economic efficiency of any chemical production is determined by productivity and intensity. These indices depend on the speed of a homogeneous chemical reaction that occurs at the molecular level (at the microlevel).

The rate of a chemical homogeneous reaction is the number of elementary acts of chemical conversion in units of volume per unit time.

Consider ways to increase the speed of the chemical reaction A→R, which is described by the equation:

$$u_{\mathrm{A}} = -\frac{dC_A}{d\tau} = kC_A^n, \tag{2.25}$$

where n is order of reaction; k is rate constant; C_A is concentration of the component A.

Substances concentrations in the process of reaction all the time vary, which affects its velocity. Therefore, it should consider the instantaneous speed, namely the reaction rate at the given time.

The rate constant k is determined by the Arrhenius equation:

$$k = k_0 e^{-\frac{E}{RT}}, \tag{2.26}$$

where k_0 – pre-exponential multiplying factor; E –is the activation energy of reacting substances, J/mole; R is absolute gas constant, R=8,314 J/(mole·K).; T is the temperature, *K.*

Substituting equation (2.25) in (2.26), we get [5]:

$$\mathrm{u}_{\mathrm{A}} = k_0 e^{-\frac{E}{RT}} C_A^n. \tag{2.27}$$

From the above equation, it can see that the reaction rate depends, first of all, on the temperature and concentration of reagents. For gas-phase processes, an increase in the concentration of reacting substances is achieved by pressure increasing. The reaction acceleration is also achieved by the activation energy reducing by catalyst using. Consequently, the rate of homogeneous chemical processes is influenced by temperature, concentration of reacting substances, pressure and catalyst:

$$u_A = f(T, C, P, kat).$$

However, the measure of influence by one or another parameter on rate of homogeneous reaction depends on the phase state of the reaction medium. In particular, the rate of liquid-phase and non-catalytic processes depends only on the temperature and concentration of reagents: $u_A = f(T, C)$.

The pressure practically does not affect the speed of the liquid-phase process, since the liquids belong to non-compressive media.

Unlike liquid-phase processes, the rate of homogeneous gas-phase reactions substantially depends, in addition to the temperature and concentration of reagents, but even on the pressure in the system. Therefore, the rate of homogeneous gas-phase and non-catalytic CTP is expressed by such a functional dependence: $u_A = f(T, C, P)$.

The rate of the catalytic homogeneous process depends, obviously, on the catalyst activity, so the functional dependencies for the various processes are follows:

for gas-phase: $u_A = f(T, C, P, kat)$;

for liquid-phase: $u_A = f(T, C, kat)$.

Influence of temperature

From equation (2.26) it can be seen that the increase of temperature uniquely leads to an increase in the reaction rate constant. The rate constant k_2 at a certain temperature T_2 can be determined from the Arrhenius equation if the activation energy (E) and the rate constant k_1 at temperature T_1 are known. To do this, we write the expressions of the Arrhenius equation for two temperatures.

For a simple irreversible reaction, $A \rightarrow R \pm Q$, regardless of its thermal effect, the temperature increase leads to an increase in the speed of the process under the exponential law. In this case, there is a valid Van't Hoff empirical rule. According to it, with a temperature increase of 10 degrees, the reaction rate increases in 2 ... 4 times [6]:

$$\gamma = \frac{k_{T+10}}{k_T} = 2 \ldots 4, \tag{2.28}$$

where γ is temperature coefficient of reaction rate; k_{T+10}, k_T are reaction rate constants at temperatures, respectively (T+10) and T.

But this rule approximately can be used only in the range of average temperatures from 283 to 473 K and with activation energy in the range of 60 ... 120 kJ/mol. The temperature coefficient γ decreases with decreasing activation energy and rising temperature, approaching one at high temperatures.

The activation energy and the pre-exponential multiplying factor are determined exclusively experimentally. For this purpose the Arrhenius equation in a logarithmic form used, which has the form of a straight line equation:

$$\lg k = \lg k_0 - (E/2{,}3RT). \tag{2.29}$$

2.4 THE INFLUENCE OF THE MAIN FACTORS ON THE SPEED OF HETEROGENEOUS PROCESSES IN APPLIED CHEMISTRY

2.4.1 DETECTION OF THE CATALYST INFLUENCE ON THE PROCESS SPEED IN APPLIED CHEMISTRY

Catalysts have a great influence on the chemical processes speed. The catalyst makes possible to accelerate the process due to activation energy reducing, which results to rate constant increasing.

One of the theories, which explains the positive effect of the presence of the catalyst by the process speed, is the theory of the activated complex. one-stage by a multi-stage process. At intermediary stages are formed activated complexes by reagents and catalyst. In this case, as the activation energy of each of the intermediate stages, and the total activation energy of the process is much smaller than the non-catalytic reaction.

Let there be a non-catalytic reaction $A + B \rightarrow R$, whose activation energy is equal to E. In the catalyst presence, on the first stage, there is the interaction of one of the reagents with the catalyst [6]:

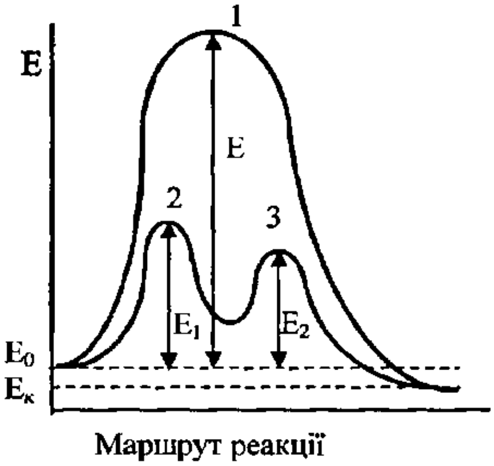
$A + [kat] \rightarrow A[kat]^*$, the activation energy of this reaction E_1.

On the second stage, the interaction of the activated complex A [kat] with another reagent occurs, resulting in the product R:

$A[kat]^* + B \rightarrow AB[kat]^* \rightarrow \rightarrow R[kat]^* \rightarrow R + [kat]$.

The activation energy of this reaction equals E_2.

The energy state of the system for non-catalytic and catalytic processes is shown in Fig. 2.3.



1 – an intermediate compound formation AB in a non-catalytic reaction; 2 – an intermediate activated complex formation A[kat]; 3 – an intermediate activated complex formation AB[kat].

Figure 2.3 – Energy diagram of states for non-catalytic I and catalytic II reactions [6]

If the limiting step is the first stage of the catalytic process ($E_1 > E_2$) then the rate depends on the concentrations of the reagent A and the catalyst. If the limiting step is a second stage ($E_1 < E_2$), then the rate depends on the concentrations of reagents A and B and the catalyst:

$$\mathrm{u} = \mathrm{k}_1 C_A C_{kat},\ \mathrm{u} = \mathrm{k}_2 C_{A[kat]^*} C_B,$$

but

$$K = \frac{C_{A[kat]^*}}{C_A C_{kat}},$$

where

$$C_{A[kat]^*} = K C_A C_{kat}.$$

Then: $\mathrm{u} = \mathrm{k}_2 K C_A C_B C_{kat} = k' C_A C_B C_{kat}.$

The total activation energy of the catalytic process is less than non-catalytic: ($E_1+E_2< E$). The reduction of the activation energy of the catalytic process compared with the non-catalytic $E - (E_1 + E_2) = \Delta E$ actually provides the reaction acceleration.

2.4.2 ESSENCE OF HETEROGENEOUS (NON-CATALYTIC) CHEMICAL-TECHNOLOGICAL PROCESSES IN APPLIED CHEMISTRY

Heterogeneous CTP occurs at the interface of two or more phases, for example, in gas-liquid systems (g-l), gas-solids (g-s), liquid-solids (l-s), liquid-liquid (l-l), if these liquids are not mixed, a solid-solid (s-s), gas-liquid-solid (g-l-s). Compared to homogeneous, heterogeneous processes are much more complicated, due to the substance transferring in the volume of the phase and through their boundary surface. This last sign is common to all heterogeneous processes. To the chemical interaction necessarily precedes the reagent transfer in the volume of one phase to the boundary phase surface followed by diffusion in the volume of another phase.

The reagent (or chemical reaction product) ability to penetrate the volume of one phase through the boundary surface into the volume of another phase depends on the aggregate state and the physical parameters of the phases involved in the heterogeneous CTP. The less density and viscosity of phase, the more intensive diffusion processes will be (it will be "more mobile"). Of the two or more phases, the worst will be those whose density and viscosity will be the smallest. In systems such as g-l, g-g the more mobile phase will be gaseous; in the system l-s is a liquid; l-l is a liquid with lower viscosity and, accordingly, a smaller surface tension. In systems of s-s reactions occur only on the contact surface, the diffusion processes with the participation of reagents are practically absent, and therefore the "mobile" phase is absent in this case.

2.4.3 STAGES OF HETEROGENEOUS PROCESSES

1. supplying the reagent in volume to the phase boundary surface;
2. diffusion of the reagent in the volume of the receiving phase;
3. chemical interaction between the reagentми;
4. diffusion of the reaction product to the phase boundary surface;
5. withdrawal of the reaction product from the volume of the receiving phase.

The given scheme of heterogeneous CTP is called total because it covers all main stages of the process. Such a complete scheme describes, for example, the combustion of coal, which consists of organic (carbon) and non-combustible mineral part, in air. Oxygen diffuses to the surface of the coal particle, adsorbed on its surface, diffuses in the volume of the particle of pores and cracks until it meets chemically active carbon, resulting in a chemical reaction:

$$O_2 + C \rightarrow CO_2.$$

By the reaction produces a gaseous product carbon oxide (IV), which, due to the difference in partial pressures inside the solid and above it in the gas phase, diffuses through the layer of the mineral non-flammable part outside, and then into the volume of air.

But not all heterogeneous processes are total, that is, they don't cover all five stages mentioned above.

2.4.4 SPEED OF HETEROGENEOUS PROCESSES

Since the heterogeneous CTP is complex, multi-stage, then its total speed (u) will depend on the speed of each of the stages and will be expressed by equation [6]:

$$u=kF\Delta C, \qquad (2.30)$$

where k is coefficient the process speed; F is the surface area of contact of phases; ΔC is the driving force of the process.

In essence, this expression is the mass transfer equation. In it, the coefficient of process speed is a complex value that considers the diffusion and kinetic phenomena that exist in the heterogeneous process. The value reversed to the speed coefficient 1/k characterizes the system resistance of the heterogeneous process.

In real heterogeneous CTPs, the speed of individual stages is significantly different. Obviously, the resulting speed of the whole process will be determined by the slowest phase, which is called the controlling step of a process.

Determination of the heterogeneous CTP behavior area is a very important technological task, since it allows choose the means of its intensification and select the appropriate technological equipment. The particular process behavior area is most often determined experimentally by the nature of the influence of various factors on the speed or coefficient of the process speed. These factors include the temperature, the linear velocity of the transfer phase flow, the particles size of the receiving phase. Studies are performed by changing the values of only one parameter for the constant values of others.

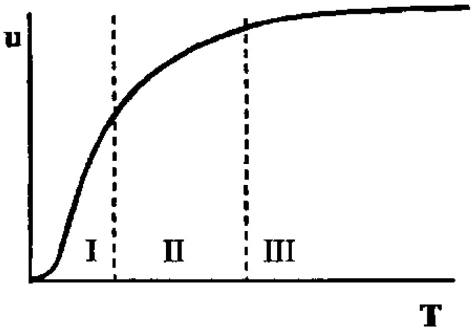
The temperature changing is used to establish the kinetic region of the process. It should be noted that the temperature increase can simultaneously affect the various processes in essence: kinetic (chemical interaction between substances) and diffusion. The temperature influence on the rate of chemical interaction can be estimated from the Arrhenius equation.

In this case, the speed of the process may increase as a result of the rate constant of the chemical reaction increasing. The rate constant can increase as a result of increasing the speed of the diffusion stages of the process, which, in turn, is due to a decrease in the viscosity of the medium.

Using the temperature influence on the intensity of kinetic or diffusion phenomena distinguish the region of the course of the heterogeneous process.

We can highlight three characteristic areas when analyze the temperature influence in a very wide range of its values on the heterogeneous process rate, (Fig. 2.4).

In the first section, there is a sharp increase in the process rate with increasing temperature (the process is limited by chemical interaction). With an increase in temperature by 10 degrees, the rate of the process increases by 2 ... 4 times and corresponds to the constant of chemical reactions rate. The reaction rate increasing is due to intensification of diffusion is relatively small 10 ... 30%, therefore, the first section corresponds to the kinetic region of the process:



Reaction behavior area: I- kinetic; II- intermediate; III – diffusion.

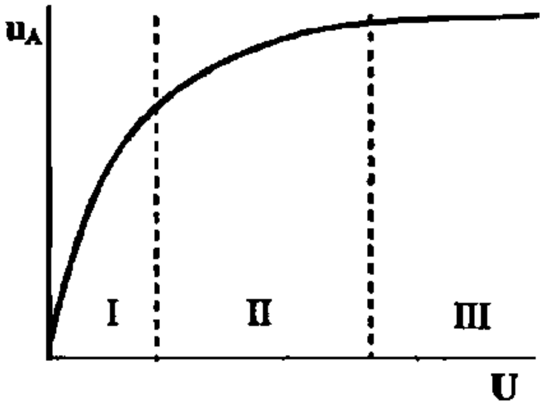
Figure 2.4 – Dependence of heterogeneous CTP rate on temperature [5]

The third section corresponds to a temperature range in which the temperature increase is insignificant or does not affect the speed of the process at all. In this area, the speed of a process depends only on the change in the physical parameters of the medium, especially viscosity. It reducing leads to an increase in the diffusion coefficient of the components of the system. Therefore, this region is called diffusion. The temperature coefficient in the diffusion region is 1.1 ... 1.3, i.e. [6]:

$$\frac{k_{T+10}}{k_T} = 1{,}1 \ldots 1{,}3. \qquad (2.31)$$

In the second (intermediate) section, the effect of temperature on the heterogeneous CTP rate is smaller. An increase in temperature no causes such a significant increase in speed, as in the kinetic region. This is due to the fact, that resistance of all process factors are proportional. The value of the temperature coefficient is 1.3 ... 2 in this area.

Graphic dependence of the heterogeneous CTP rate on the linear flow velocity is shown in Fig. 2.5:

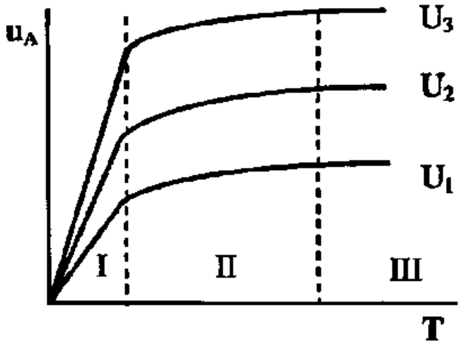


Process behavior area: I – outside-diffusion; II – intermediate; III – kinetic [5]

Figure 2.5 – Dependence of the rate of heterogeneous CTP on the linear velocity (u) of the transmission phase

The plot on the curve, where the greatest influence of the flow velocity on the process rate is observed, belongs to the external diffusion region. It is on it there is a sharp decrease in the thickness of the boundary film. In the second region, the influence of the flow velocity is smaller, because the thickness of the film is decreasing and this area corresponds to the intermediate. Area, where the increase in the value of the argument for constant temperature almost does not affect the flow of heterogeneous CTP (there is practically no change in the thickness of the laminar layer) corresponds to the kinetic. In the third area, the process rate can be increased only by increasing the temperature.

It is possible to specify in what diffusion area (internal or external) occurs heterogeneous CTP with increasing temperature (Fig. 2.5) by increasing the linear velocity of the intermediate phase. If, at its gradual increase in the diffusion region an increase in the total velocity of the process is observed (Fig. 2.6), this is a confirmation of the fact that it occurs in the exterior-diffusion area. At the same time, the temperature intervals of the existence of individual areas do not change.



Process behavior area: I – kinetic; II – intermediate; III – diffusion.

Figure 2.6 – Dependence of the heterogeneous process rate on temperature and linear flow velocity ($U_1 < U_2 < U_3$) [5]

2.4.5 GENERAL PRINCIPLES OF HETEROGENOUS PROCESSES INTENSIFICATION

1. Ways to increase the surface of contacting masses (F)

In all cases, trying to increase the heavier phase surface since the lighter phase (in all types of apparatus) washes the surface of the heavy phase.:

- solid in systems g-s, l-s;
- liquid phase in systems g-l.

In systems g-s, l-s, an increasing of surface is achieved by grinding a solid material. The renewal of the contact surface is achieved by mixing the solid phase with mechanical stirrers. The best mixing is achieved in the apparatus with a fluidized bed. Another surface increasing is obtained by pneumatic or mechanical spraying of the liquid.

If the process occurs in the kinetic region, then the main factor of its intensification is an increase in temperature. Ensuring the optimum temperature value (in addition to purely technological features) also depends on economic factors, that is, on the necessary expenses for a certain temperature regime creation.

If the process occurs in the exterior diffusion region, then for acceleration it is necessary to increase the velocity of the intermediate phase. However, sometimes, for example, when performing the process in the l-s system in a reactor with a stirrer, the speed of the fluid has an optimal value. The relative velocity of the particle movement relative to the liquid can be reduced to zero. Consequently, the thickness of the boundary film from the liquid phase side will increase, and with it, the total diffusion resistance of the system will increase. So, an increase in the velocity of the fluid in the reactor does not always mean an increase in the velocity of the intermedia phase relative to the receiver. However, these considerations provide the basis for choosing the type of reactor for the process, which is limited by external diffusion.

If the heterogeneous CTP is limited by the resistance of the receiving phase, that is, occurs in the pore-diffusion region, then, first of all, it is necessary to reduce the particles size of the receiving phase. In addition, reducing the particle size for the same mass of condensed matter (liquid or solid) will increase their amount and, consequently, increase the total surface area of phase contact in a heterogeneous system. This makes it possible to increase the value of two members of the equation (2.30) the coefficient of speed and surface area. Consequently, the milling (dispersion) of the receiving phase, in any case, should contribute to an increase in the speed of the process.

However, in this case, there are certain reservations regarding the possibility of achieving the minimum particle size:

– First, the grinding of the substance (whether the grinding of solid particles or spraying liquid) requires significant energy consumption.
– Secondly, due to very small sizes, solid particles can form aggregates, result for surface area decrease.
– Thirdly, finely divided particles are easily removed from the reactor with a more mobile phase, which leads to their loss.
– Fourth, fine-particulate solid particles can create a very high hydraulic resistance in reactors that operate in a mode of ideal displacement.

2.4.6 HETEROGENEOUS NON-CATALYTIC PROCESSES

Heterogeneous non-catalytic processes in the "gas-solid" system are typical in the most diverse branches of the chemical industry. These include adsorption and desorption in the processes of purifying gases from harmful or undesirable impurities (hydrogen sulfide absorption by zinc or iron oxides, drying air with synthetic zeolites or silica gel); firing (burning out) of metal ores (oxidizing burning of sulphides of metals, sulfate ores or metal oxides); pyrolysis of solid-phase fuel (coal coking), coal gas and wood gasification; cement clinker obtaining; evaporation and condensation of a pair of substances (sublimation of iodine, zinc waste processing), etc.

2.5 MAIN CONCEPTS OF CATALYSIS

The catalysts usage is the most effective way to increase the speed and selectivity of chemical-technological processes.

2.5.1 ESSENCE AND TYPES OF CATALYSIS

For the industrial usage of any chemical reaction, the required requirement is the high speed of achieving a large yield of the product. But many chemical reactions, which have industrial importance and are thermodynamically possible, practically do not occur due to the enormous activation energy. It is known that overcoming a high energy barrier can be realized by significant increase in temperature. In this case, the reaction is accelerated due to an increase in the kinetic motion of molecules, that is, the increase in the probability of their collision and chemical interaction. However, even if the temperature is economically feasible, which is rare, it is impossible to implement it in practice for most processes. In fact, in reversible exothermic processes, the increasing temperature may shift the equilibrium in the opposite direction to such an extent that the reaction is completely slowed down. Often, the rise in temperature leads to the thermal decomposition of reagents or reaction products, changes in their aggregate state, the acceleration of the formation of adverse or unwanted reaction products. In addition, a significant increase in temperature is limited to the capabilities of modern structural materials. In all these cases it is necessary to apply a catalyst.

For industrial using of any chemical process, the necessary condition is the high speed of achieving a high yield of the product.

Catalysis is an efficient and rational way of accelerating chemical processes. Catalytic processes are widely used in industry, and the scope of their application is progressively increasing: more than 90% of new industries that are introduced into the chemical industry are based on catalytic processes. Catalytic reactions are described by the general laws of thermodynamics and kinetics, but in the presence of the catalyst, these reactions are accelerated in thousands and millions of times and require significantly lower temperatures, which is economically beneficial. A number of technological processes have succeeded only through catalysts using.

Catalysis is used to obtain important inorganic products: hydrogen, ammonia, sulfate and nitric acid. Especially wide and diverse application of catalysis in the organic substance technology, especially in organic synthesis - in the processes of oxidation, hydrogenation, dehydrogenation, hydration, dehydration. The catalysts produce the most important intermediate products for polymers synthesis. The obtaining of macromolecular compounds by polymerization and polycondensation of monomers is also carried out with catalysts participation. The catalysts usage is based on many methods of processing petroleum products: catalytic cracking, reforming, isomerization, aromatization, and alkylation of hydrocarbons. Some important products for the industry would not have been possible to obtain if the chemists did not have the necessary catalysts in their arsenal. A huge role in the appearance of synthetic rubber and bright paints, soap and margarine, plastics and medicines played by accelerators of chemical reactions. With the help of catalysts, natural gases are converted into synthetic fabrics that sparkle in all the colors of the rainbow and are not inferior to the metal for durability.

If several products (target and by-products) are formed in the process, then the maximum yield of the target product can be obtained by applying **selective catalysis**, in which the chemical reaction of the formation of the target product is accelerated, and the catalyst, in this case, does not affect the rate of the adverse reactions.

Catalysis is the change in the rate of chemical reactions under the influence of special substances – catalysts, which, by participating in the reaction, do not change their chemical composition after the end of the reaction. Catalysts can be gases, liquids, and solids. According to the phase composition of reagents and catalysts, catalytic processes are divided into homogeneous, heterogeneous and enzymatic (microheterogeneous).

In **homogeneous** catalysis, the catalyst and reacting substances are in the same phase – gas or solution. In **heterogeneous** catalysis, reagents and catalyst are in different phases. **Enzymatic** (microheterogeneous) catalysis occurs with the participation of biocatalysts of protein nature (enzymes), that form colloidal solutions. The enzymatic catalysis by many indicators differs from conventional catalysis. Enzymatic catalysis occurs much faster. Biochemical catalysis provides the course reaction in a few seconds or even a fraction of a second, whereas it takes days, weeks, or even months for a chemical catalyst to react. As a result of enzymatic reactions, unlike non-enzymatic, no byproducts are formed (almost 100% yield of the final product is achieved). An example of enzymatic catalysis can be called the metabolism and the transformation of energy in cells of a living organism.

If in the catalyst presence, the reaction is accelerated, then such a phenomenon is called positive catalysis. Also, **anti-catalysts** or **inhibitors** used, that is substances that slow down or inhibit chemical reactions. This phenomenon is called negative catalysis.

In general, the accelerating action of the catalyst is fundamentally different from the effect of other factors that intensify the chemical reactions: temperature, pressure, concentration, the surface area of contact of the phases, hydrodynamic conditions. In the case of introduction into the catalyst system, the velocity of the molecules does not change. The catalyst also does not affect the balance of equilibrium, but only accelerates its achievement in the given temperature and pressure. It is a "soft" way of intensifying chemical reactions, which has no restrictions, for example, for the application of high temperatures and pressures.

The influence of the accelerating action of catalysts is to reduce the activation energy that occurs as a result of changing the mechanism of the reaction. The last one may change with the changing in the reaction staging or as a result of the reaction by the chain mechanism. With the mechanism change under the action of the catalyst, the reaction proceeds through a series of elementary stages, each of which requires significantly less activation energy than the reaction without catalyst. The reaction rate is the greater, the lower the activation energy in accordance with the Arrhenius equation.

2.5.2 HOMOGENEOUS CATALYSIS. SPEED OF TRANSFORMATION IN HOMOGENEOUS CATALYSIS

The most common theory explaining the effect of a catalyst in homogeneous catalysis is the so-called "theory of intermediate compounds". According to this theory, the mechanism of catalysis lies in the rapid formation between the reagents and the catalyst of unstable intermediate compounds, after which the reaction products are formed, and the catalyst is released in the unaltered form.

The processes of homogeneous catalysis by the phase state of reactive substances and the catalyst, can be divided into a liquid-phases and gas-phases.

The speed of homogeneous catalytic process depends on a number of factors: concentration of reactive substances, catalyst concentration, temperature, pressure. The main disadvantage of homogeneous catalysis is the difficulty of separating the catalyst from the final production mixture (liquid or gas), as a result of which a part of the catalyst loosing forever, and the product is contaminated by it. In heterogeneous catalysis, the gas or liquid reaction mixture is easily separated from the solid catalyst and this was one of the most important reasons for the widespread heterogeneous catalysis.

2.5.3 HETEROGENOUS CATALYSIS ON SOLID CATALYSTS

In heterogeneous catalysis, the reaction is accelerated as a result of a new reactionary path that requires less activation energy. The changing in the reaction path is due to the intermediate chemical interaction of the reactants with the catalyst that occurs on the catalyst surface, do not form separate phases and are not detected by chemical analysis. These intermediate compounds have less chemical binding energy than molecules in a volume, which causes the low strength of these compounds.

Catalysts in a heterogeneous process are usually metals and their oxides, which good conduct electricity: Cu, Ag, Cr, Mo, W, Fe, Co, Ni, Pt, Pd. All of these metals are transitional elements with an unfinished d-shell, in particular, active catalysts are metals that have unpaired electrons on outer c- and d orbits.

The catalysis process of gaseous reagents on solid catalysts consists of the following stages:

1. supply (diffusion) of reactants from the gas phase to the catalyst surface;
2. diffusion of reagents in catalyst pores;
3. formation of intermediate (activated) complexes "reagents-catalyst";
4. intermediate complexes formation "products-catalyst";
5. products diffusion from the catalyst pores to its surface;
6. withdrawal of reaction products from the catalyst surface to the volume of the gas phase.

If the limiting stages of the process are 1, 6 the process takes place in the external diffusion region and the most effective way of its acceleration is mixing.

If the limiting stages of the process are 2, 5 the process takes place in the intradiffusion region and the most effective means of its acceleration is to reduce the size of the grains and increase the pores of the catalyst.

Stages 3,4 of the process, have a chemical nature and accelerated by an increase in temperature.

Increasing the concentration and pressure of the reactants accelerates all stages of the catalytic process.

2.5.4 REQUIREMENTS TO INDUSTRIAL CATALYSTS

From the development of chemical technology history, it is known that researchers had to test thousands of chemicals before choose one that really has a sufficiently strong catalytic action on a particular reaction. The most striking example of such an empirical, "blind" selection is the search for a catalyst for the synthesis of ammonia when more than two thousand chemical elements and compounds were tested until finally the desired catalyst was found. It turned out to be a specially processed iron with applications of potassium and aluminum oxides. The current state of science and technology of catalysis makes it possible to carry out a targeted catalyst selection for each particular chemical process, which is based on the general laws of catalytic processes and the properties of catalysts. For example, for the oxidation processes, reduction, hydrogenation, dehydrogenation and other, catalysts are metals and their compounds (conductors and semiconductors) that good conduct electrical current, that is, provide an electronic exchange between reagents and a catalyst. As already noted above, it is platinum, palladium, nickel, iron, cobalt, oxides of nickel (II), manganese (IV), chromium (VI), vanadium (V), zinc oxide and zinc sulfide, etc.

Consequently, existing theories of catalysis allow predicting the catalytic action of various compounds. Selected catalyst on the theoretical foundation basis is necessarily tested experimentally. When the catalyst for a given process selected, then before recommend it for implementation, should be figured out if this catalyst complies with some requirements that are imposed by the industry.

Industrial catalysts must possess:

1. Sufficiently high reaction activity.
2. Minimum contact duration.
3. Low temperature ignition.

4. Resistance to contact-poisons.
5. High selectivity.
6. A large specific surface.
7. Respective physical properties (high mechanical strength, heat resistance, thermal conductivity).
8. Affordability and cheapness.

Activity A is defined as the ratio of the rate constants of reactions with catalyst and without catalyst [5]:

$$\mathrm{A} = \frac{\mathrm{k_K}}{\mathrm{k}} = \frac{e^{-(E_K / RT)}}{e^{-(E / RT)}} = e^{\Delta E / RT}, \tag{2.32}$$

where $\Delta E = E - E_K$ is reduction in the activation energy of the catalytic reaction compared to non-catalytic.

The contact time is determined by the ratio [5]:

$$\tau = \frac{V_в}{\mathrm{V_{г.с}}}, \tag{2.33}$$

where $V_в$ is free catalyst volume, m^3; $\mathrm{V_{г.с}}$ is volume of gas mixture passing through the catalyst, m^3/sec.

Since the value of $V_в$ is practically difficult to determine, most often use the fictitious contact time $\tau_ф$ [5]:

$$\tau_ф = \frac{V_{кат}}{\mathrm{V_{г.с}}}, \tag{2.34}$$

where $V_{кат}$ – total catalyst volume, m^3.

The more active catalyst, the lower contact time is required to achieve a given degree of transformation of the $x_{зад}$, illustrating the fig. 2.7.

The ignition temperature is called the minimum temperature of the reaction mixture, in which the process on solid catalyst takes place at a rate sufficient for industrial conditions. The more active catalyst, the lower its ignition temperature.

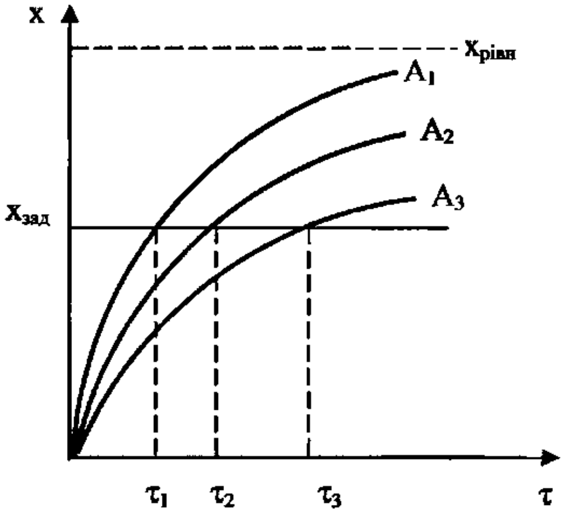


Figure 2.7 – Dependence of transformation degree x from contact time τ for catalysts with different activity A: $A_1 > A_2 > A_3$; $\tau_1 < \tau_2 < \tau_3$; $x_{рівн}$ і $x_{зад}$ – are equilibrium degree and given a degree of conversion respectively [5]

For technology, it is important that this temperature be as low as possible, as it reduces energy costs for the preheating of the reaction mixture and catalysis implementation, facilitates the working conditions of the reactors and simplifies their design. In addition, for reversible exothermic reactions, the flow of catalysis at a lower temperature is thermodynamically advantageous, since the equilibrium moves towards the end products. Therefore, from the few possible catalysts preferably selected that one, that has a lower ignition temperature. For example, catalysts based on iron (III) oxide or vanadium (V) oxide can be used to accelerate the oxidation of SO_2 to SO_3 in the production of sulfate acid. Despite the fact the first one is much cheaper and more affordable, the industry uses a vanadium catalyst precisely because it has a lower ignition temperature than iron.

Catalyst poisoning is a partial or complete loss of activity due to the action of special substances, which are called catalytic poisons and are contained in the form of impurities in the initial reaction mixture. Loss of activity occurs as a result of the chemical interaction of the poison with the catalyst with the formation a catalytically inactive compound or the adsorption of the poison at the active centers of the catalyst, which leads to their blocking.

Poisoning can be reversible and irreversible.

In the case of reversible poisoning, loss of catalyst activity is observed only in the presence of poisons in the mixture fed to catalysis. When a pure mixture comes in, catalytically inactive compounds of the poison decompose with the catalyst or there are poisons desorption from the active centers of the catalyst, resulting in catalyst restores its activity. Often catalysts are blocked due to the deposition of carbon compounds on their surface during various organic reactions, in particular cracking. Such blocking is usually reversible and eliminated at elevated temperatures since, under these conditions, carbonaceous compounds burn out and the catalyst is regenerated.

Irreversible poisoning is persistent; the activity of the catalyst is not restored under any conditions. Therefore, the irreversibly poisoned catalyst is completely replaced by the new one.

For example, the poisons for the platinum catalyst are hydrogen sulfide and other sulfide compounds, Cu^{2+}, Fe^{2+} ions, and others. For vanadium catalyst, Arsenic compounds are poisons. To prevent poisoning, the reaction mixture must be pre-cleaned of catalytic poisons.

Selective catalysis is catalysis, in which from few possible reactions only one target reaction accelerates. Selectivity of the catalyst $S_{кат}$ is determined by the same formula as the selectivity of the total chemical production [5]:

$$S_{кат} = \frac{G_{ц}}{G_{ц} + G_{поб}}, \tag{2.35}$$

where $G_{ц}$ is quantity (weight) of the initial reagent, which has turned into the target product; $G_{поб}$ – is the amount (weight) of the initial reagent that has turned into by-products.

An example of a selective action under conditions of several parallel reactions can be the platinum catalyst used in the catalytic oxidation of ammonia. In this case, three parallel reactions are possible with the formation of nitrogen compounds with varying oxidation degrees: NO, N_2O and N_2 [5]:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O,$$
$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O,$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O.$$

The last two reactions are thermodynamically more probable (especially the latter one), but in the platinum catalyst presence, the first reaction occurs by 98 ... 99%. This is evident the high selectivity of this catalyst.

Mechanical strength is a measure of non-destructive under load, resistance to abrasion under the influence of gas erosion, lack or low degree of catalyst removal from the reaction medium.

Productivity is the quantity of the products obtained per unit of the catalyst surface.

The higher the **specific surface area of the catalyst** (that is, the surface of a unit of its mass or volume), the higher the productivity of this catalyst, that is, the greater the product is formed at the same time per unit mass or catalyst volume loaded into the reactor. The specific surface area of many industrial catalysts is 100 ... 200 m^2/g and more. This ensures catalyst productivity by the target product not lower than 20 $kg/(m^3 \cdot h)$. In order for the catalysts have a large specific surface, they have to be made in the form of finely divided powders or granules with high porosity structure.

2.5.5 COMPOSITION AND PRODUCTION OF SOLID CATALYSTS

Industrial solid catalysts are predominantly non-individual substances, but a complex mixture, which is called a contact mass. In it some substances are actually catalysts, others - carriers, the third – serve as activators (promoters).

Carriers are heat-resistant, inert porous substances that have a large surface and on which are deposited or otherwise put on the catalyst. Application of carriers improves the properties of catalysts, increases the area of contact between reagents and the catalyst and significantly reduces their cost. As carriers use pumice, asbestos, zeolites, silica gel, etc.

Activators (promoters) are substances that increase the activity of the catalyst itself. For example, there are alkali metal oxides and Al_2O_3 for the iron catalyst in the synthesis of ammonia, or alkali oxides, CaO for the vanadium catalyst during the oxidation of SO_2. The mechanism of activator action may be different: it can form with the catalyst more active chemical compounds, may change the electrophysical properties of the catalyst surface, or develop and stabilize its surface. In the last case, the activators are called structural.

For the manufacture of industrial solid catalysts, the following methods are most often used:

1) precipitation of hydroxides or carbonates from solutions of their salts on a carrier (or without it), followed by the formation and calcination of the contact mass;

2) joint compression of all components: catalyst, activator, and carrier with an adhesive substance;

3) a fusion of several substances with subsequent leaching of one of the components or reduction of metals (skeletal catalysts);

4) impregnation of the porous carrier with a solution containing a catalyst and an activator with subsequent mass calcination.

Catalysts are usually made in the grains form, tablets, granules. Sometimes catalysts are used in the form of thin meshes made of metals or their alloys.

QUESTION FOR SELF-CONTROL TO SECTION 2

1. Give the classification of chemical-technological processes.
2. Give the definition and mathematical expression the concept of expense factor for raw materials.
3. Formulate and give a mathematical expression to the concept of expense factor by the energy.
4. Give the definition and mathematical expression to the concept of product output.
5. Formulate and give a mathematical expression to the concept of the conversion degree.
6. Chemical equilibrium in chemical-technological processes. Give the definition of the speed of the direct reaction.
7. What is the effect of the concentration of the substance on the chemical equilibrium displacement?
8. Chemical equilibrium in the chemical-technological process. Formulate the definition of the "speed of the reverse reaction" concept.
9. Indicate and give examples of the total pressure effects on the system with the displacement of chemical equilibrium.

10. Give the definition and mathematical expression to the concept of "rate constant"..
11. Explain what is the effect of temperature by the shift of chemical equilibrium caused.
12. Indicate the main stages of homogeneous chemical-technological processes.
13. Describe the effect of temperature on the homogeneous reactions speed.
14. Give the areas of chemical-technological processes and the method of their determination.
15. Indicate the main stages of heterogeneous chemical-technological processes.
16. What is a transitional state in chemical interaction?
17. Provide an energy diagram for exothermic reactions.
18. Explain the concept of activation energy.
19. Formulate and give a mathematical expression for the kinetic equation of the heterogeneous processes rate.
20. Determine ways to increase the surface of masses contact.
21. Give basic requirements for industrial catalysts.
22. Formulate the concept of catalysis and catalyst.
23. Describe the main types of catalysis.
24. From which the main stages consist process of catalysis of gaseous reactants on solid catalysts?

3 CURRENT STATE AND PERSPECTIVES OF THE DEVELOPMENT OF CHEMICAL BRANCH AND RAW MATERIAL BASE OF UKRAINE

3.1 CLASSIFICATION AND CHARACTERISTICS OF RAW MATERIALS

Despite the enormous variety of types of raw materials, it can be divided by certain features: origin, reserves, chemical composition, aggregate state, genesis [5].

By origin, raw materials are divided into mineral, vegetable and animal, air and water. Briefly describe each of the types of raw materials.

Mineral raw materials are minerals extracted from the earth's interior. In turn, mineral raw materials are divided into ore, nonmetallic, combustible.

Mineral raw materials are rocks, from which it is economically advantageous to produce metals and some nonmetals in a purely pure state. Metal-containing mineral raw materials consist of natural minerals (mainly metal oxides and sulfides ($Fe_{2}0_{3}$, Fe_3O_4, CuS, $FeCuS_2$ and many other or native pure metals (Au)) and related (empty) rock (SiO_2, Al_2O_3, $CaCO_3$, $Al_2O_3 \cdot SiO_2$). Some ores contain compounds of several metals, such ores are called polymetallic, for example: copper-nickel (CuS - NiS - FeS), lead zinc (PbS - ZnS), lead-molybdenum, in fram-molybdenum and so on. By the ore minerals are also some of these species as a main component containing non-metals. For example, sulfuric ore consisting of sulfur-free empty species.

Non-mineral mineral raw materials are rocks used for the production of chemical, construction and other non-metallic materials. It is very diverse in chemical composition and can be used in its original form (silicates (sand, clay), asbestos, mica, etc.) or undergo chemical transformations to obtain the corresponding products (from phosphorites ($Ca_3(PO_4)$) - they are prepared with phosphate acid, from aluminosilicates ($Al_2O_3 \cdot SiO_2$) - aluminum, from carbonates ($CaCO_3$) - lime).

Mineral flammable raw materials (fossil fuels) are brown coal and coal, shale, petroleum, natural gas, which are formed mainly by organic substances, and used as a source of energy (as energy or technological fuels) or raw materials in the chemical industry (mainly in organic synthesis and metallurgy).

Vegetable and animal raw materials are divided into food and technical. Food products include agricultural products such as wheat, sunflower, potatoes, sugar beet, butter, fats, milk, from which margarine, starch, sugar, etc. are obtained. From technical raw materials are products of household and technical purposes: from wood - paper, cellulose, spirits; from cotton - cellulose, explosives; from vegetable oils and animal fats - soaps, paint and varnish materials; from corn, sunflower, rice and cotton scales - feed protein, furfural, xylitol, sorbents; from blood - highly effective sorbents; from whale fat - perfumes.

Air and water are the cheapest, most widespread and affordable types of raw materials and reagents. Air is a powerful source of nitrogen, oxygen, and argon. Practically without pre-preparation, it is used in fuel energy, in the production of nitrate and sulfate acids. Water as a raw material and solvent is used in the production of mineral and organic acids, hydrometallurgy and many other technological processes.

The composition of the air contains mainly nitrogen and oxygen. Oxygen, whose content in the atmosphere reaches 21%, plays an extremely important role in the development of biological processes on Earth. It is a member of many organic compounds and is the driving force behind the oxidative processes underlying the development of the living world of the planet. Under the influence of oxygen, processes are carried out in the human body. Of great importance is oxygen in technological processes, in the synthesis of chemicals, combustion of organic fuels. With taking into account other industries from the earth's atmosphere, not less than 100 billion cubic meters of air is removed. The main source of oxygen reproduction is the ocean.

Nitrogen, whose content in the Earth's atmosphere is almost 78%, is a chemically low-level element. Its role in the organic and biological processes taking place on our planet is still not enough. Nitrogen is a part of proteins and amino acids and is involved in the synthesis of protein substances.

The content of oxygen and nitrogen in the atmosphere practically does not change for many centuries. The most important gases, the content of which in the atmosphere varies both as a result of natural processes and as a result of human production, is water vapor, carbon monoxide (IV), ozone, etc. (Table 3.1).

The water vapor concentrates in the surface layer of the atmosphere up to 10 km, at the height of 25 km there are so-called pearl clouds, and at an altitude of 80 km - silvery.

3.1.1 HYDROSPHERE AS RAW MATERIAL BASE FOR APPLIED CHEMISTRY

The hydrosphere is an essential element of the biosphere and plays a decisive role in many processes that occur in nature and provide human life. The volume of the hydrosphere is 1389 million km^3. It occupies about 3/4 of the land – 449,53 million km^3. Of the total amount of water, 1350 million km^3 or more than 97,2% falls on ocean water.

Table 3.1. – Air composition

Components	Contents	
	%(mass)	%(vol)
Nitrogen	75,52	78,09
Oxygen	23,15	20,94
Argon	1,28	0,93

Carbon oxide	0,046	0,033
Neon	$1{,}2 \cdot 10^{-3}$	$1{,}8 \cdot 10^{-3}$
Helium	$7{,}2 \cdot 10^{-5}$	$5{,}2 \cdot 10^{-4}$
Krypton	$3{,}3 \cdot 10^{-4}$	$1 \cdot 10^{-4}$
Xenon	$3{,}9 \cdot 10^{-5}$	$8 \cdot 10^{-6}$
Nitrogen (II) oxide	$2{,}5 \cdot 10^{-3}$	$2{,}5 \cdot 10^{-4}$
Hydrogen	$3{,}5 \cdot 10^{-6}$	$5 \cdot 10^{-5}$
Methane	$0{,}8 \cdot 10^{-4}$	$1{,}5 \cdot 10^{-4}$
Nitrogen (IV) oxide	$8 \cdot 10^{-5}$	$1 \cdot 10^{-4}$
Ozone	10^{-6}-10^{-5}	$2 \cdot 10^{-6}$
Sulfur (IV) oxide	-	$2 \cdot 10^{-6}$
Carbon (IV) oxide	-	$1 \cdot 10^{-5}$
Ammonia	-	$1 \cdot 10^{-6}$

About 1 g of mineral salts usually contains in 1 dm^3 of fresh water. In seawater, they are much larger. In the Baltic Sea - 5 g / dm^3, the Black Sea - 18 g / dm^3, in the ocean 35 g / dm^3. River water is slightly mineralized - up to 200 mg / dm^3, moderately mineralized 200 ... 500 mg / dm^3 and increased mineralization to 1000 mg / dm^3. At the level with salts water contains a number of natural organic compounds - humus, solid residues, impurities of biological nature (microorganisms, algae, etc.).

The presence in water of oxygen provides the vital functions of its flora and fauna. The content of water soluble in oxygen depends on its temperature and the reactions occurring in the aquatic environment: photosynthesis leads to an increase in the oxygen content, oxidation of organic compounds as a result of aerobic processes reduces the oxygen content in water.

The reserves of water on Earth are enormous. However, mankind in the first place needs fresh water, whose reserves make up about 2% relative to salty water of the ocean.

A significant amount of water, approximately (10 ... 11) · 10^3 km^3, is a component of living organisms living on Earth. The circulation of water on earth and in the atmosphere binds together all parts of the hydrosphere:

oceans, seas, rivers, groundwater, soil and atmospheric moisture. Annual runoff of all rivers of the world with the participation of unstable flood runoff is approximately 37 thousand km^3 (Table 3.2). And this is the resources that are suitable for efficient use at the modern level of technology. However, these resources are very unevenly distributed on the planet, as a result of which many regions of the world do not have their own water for life. In the imported water lives Algeria, a number of cities in Greece, Holland, and others.

Table 3.2 – Annual runoff of rivers in different parts of Earth

Part of the land	Volume, km^3/year
Europe	2900
Asia	12900
Africa	5400
Australia	1600
South America	7500
North America	4700
Greenland	2100
Antarctica	-
Total	37100

Total water consumption for domestic needs in modern cities is about 500 dm^3 per person per day, of which only 2,5 ... 3 dm^3 is used for drinking and cooking. It is difficult to provide reliable data on industrial water consumption, as they are continuously increasing due to the development of the industry of production. The water consumption for the cooling capacitors of the TPP is 120 kg / (kW / h).

Application of NPPs causes an increase in these costs to 220 kg / (kWh). At current rates of energy development, water consumption by power plants should increase further from 250 up to 4500 km^3 / year. The total world water consumption for technological needs will soon increase by 3000 km^3 / year, for irrigation - up to 1500 ... 4500 km^3 / year. The state of water supply is deteriorating due to the dumping of untreated or insufficiently treated water by industrial enterprises, utilities and agro-industry (residues of fertilizers and pesticides) in the water body. One of the consequences of discharging insufficiently treated wastewater is the colored water in the reservoirs, a sharp decrease in the content of oxygen in the water and a violation of the biological regime. It is also contributing to the so-called thermal pollution, resulting from the dumping of a significant amount of more or less heated water.

Lack of fresh water causes the need for artificial desalination plants. Their widespread implementation is hampered mainly by the lack of cheap energy needed to desalinate water.

3.1.2 LITHOSPHERE AS RAW MATERIAL BASE FOR APPLIED CHEMISTRY

Lithosphere - a large covering of the Earth in the thickness of 30 ... 40 km. The upper part of the lithosphere is a soil formed under the influence of living and dead organisms and undergoes physical, chemical and biological processes.

In the lithosphere, the main minerals are concentrated, without which the existence of a modern society is impossible: coal, oil, gas, various ore and nonmetallic minerals. The content of elements in the lithosphere is characterized by the following data, %: oxygen - 49,19; silts - 26,80; ammonium – 7,45; iron - 4,20; calcium - 3,36; sodium – 2,60; potassium – 2,40; magnesium – 1,93.

Particularly important is the efficient, economical use of geological natural fuels, in the first place, oil, gas and coal, metal ores, chemical natural raw materials. The geological resources of our planet are very large. However, it should be borne in mind that, firstly, these resources are practically non-renewable, and secondly, their production is growing at a high pace.

At the current level, the consumption of organic fuels will last for 200 ... 300 years.

A closer deficit can be predicted on other types of raw materials. For example, according to some authors, silver reserves are exhausted within the next 13 ... 40 years, lead is 20 ... 60 years old.

In this regard, the economical extraction of natural resources and, particularly important, the complex use of resources, in which all the useful substances contained in this type of raw material are found to be of great importance.

So, certain results were achieved when processing copper raw materials, which contains 25 valuable elements, of which 21 items are extracted. In the development of mineral deposits large volumes of rocks are sent to dumps that occupy large areas. Meanwhile, dumps of mining productions are valuable raw materials for the production of a number of building materials (crushed stone, sand, clay, etc.).

It is necessary to identify two factors that lead to the reduction of useful economic space. On the one hand, more and more agricultural lands are being allocated to settlements, industrial enterprises, transport communications, under the dumps of breeds, etc. On the other hand, natural factors continue to influence, in the first place, soil erosion. Water erosion causes the blurring and rinsing of the soil, the formation of ravines; wind - dispersal and blasting of the fertile top layer. Every year, through erosion of agricultural turnover, large areas of arable land fall. All this forces us to use serious means to preserve agricultural land.

According to stocks raw materials are divided into:

- non-renewable (ores, minerals, combustibles, the formation of which in the natural environment is a very long geochemical process, and the rate of their formation is many orders of magnitude smaller than production and use);

- reproducible (water, air, vegetable and animal raw materials). By aggregate state the raw materials are divided into:

- solid (mineral ores, carbonates, coal, shale);
- liquid (oil, water, brine);
- gaseous (air, natural gas).

According to the chemical composition of raw materials are classified as follows:

- inorganic (ores, minerals, air, water);
- organic (oil, coal, natural and technological gases).

In addition, the raw material can be classified according to the genesis (formation) to:

- primary (natural), which is formed as a result of natural processes, including biochemical (mineral, vegetable and animal, combustible minerals, water, air);
- artificial, which is obtained by processing of primary (natural) raw materials. For example, kerosene as a raw material for the synthesis of vinyl chloride is a product of the processing of oil as a primary raw material;
- - secondary, it is formed as waste in the process of processing primary (natural) and artificial raw materials into target products, or they are in the form of products of consumption and means of production that have lost their consumer value or functional purpose. These include household wastes (used materials made of polymeric materials, waste paper) and industrial (metal shavings), as well as technically obsolete or non-repairable machines, devices, vehicles, etc.

3.1.3 PRINCIPLES OF SUCTION (CONCENTRATION) AND SEEDS OF RAW

Natural raw materials are usually a multicomponent mixture, which, besides the useful substance, from which the product itself obtains, contains additional components and various impurities. The higher the content of additional components and impurities, and consequently, the lower concentration of the useful component in the raw material, the greater the transport costs (since along with the main component from the place of extraction to the processing plant is carried an empty breed). Energy consumption is also increasing for the movement of raw materials according to the technological scheme, its heating, mixing. The low concentration of the useful component in the raw material leads to a decrease in the speed of the chemical process, the degree of removal or conversion of the main component, leads to over-consumption of reagents and materials, requires the use of the main (reactors) and auxiliary (conveyors, mixing containers, pumps) equipment with considerably larger workers volumes and capacities. In addition, inert components and impurities contained in the raw material may contaminate the resulting product, which will require additional costs for its purification. All this together can dramatically worsen the technical and economic performance of production compared with those using highly concentrated raw materials or pure reagents.

Additional components and impurities may be inert (neutral) or active (reactive). Inert impurities reduce the concentration of valuable components, reduce the speed of physic-chemical processes, but in chemical processes do not take part, that is, by-products in this case are not formed. For example, in air, whose oxygen is a reagent for the oxidation of SO_2 to SO_3 in the production of sulfate acid, nitrogen, argon, carbon dioxide are inert components that do not affect the chemistry of the process.

Active components dramatically impair the quality of the raw material and the course of the technological process of its processing into the product due to the occurrence of adverse (undesirable) reactions. Sometimes they even make it impossible to use raw materials without their preliminary preparation or purification: natural gas containing hydrogen sulfide cannot be used as a fuel in everyday life, as polluting SO_2 is formed; sulfur compounds as components of oil lead to intensive corrosion of equipment and poisoning of catalysts in the processes of its processing.

Consequently, most types of raw materials, especially natural, must be purified from impurities before processing, that is, to concentrate on the main (valuable) component. Such processes are called enrichment. Enrichment is a collection of physical, physic-chemical, chemical and biochemical methods of processing raw materials for the purpose of extracting impurities and obtaining its concentrate with the highest possible content of the main component

The enrichment of raw materials, in particular minerals (ores, coal), is usually complex multi-stage and fairly costly processes, but their application makes it possible to significantly intensify the technological processes of processing of enriched raw materials into products or significantly reduce environmental pollution.

The raw material often contains several useful components. In this case, it is divided into components not only for the purpose of extracting impurities, but also for the separation of valuable components that are contained in multi-component raw materials. At the same time, the technical and economic efficiency of production is increasing sharply, because there is an opportunity to get a wider range of products due to the complex processing of one type of raw material.

Depending on the essence of the processes on which the methods of enrichment and division are based, they can be divided into four groups: physical, physic-chemical, chemical, biochemical [5].

In physical methods of separation occurs only as a result of the course of physical processes under the influence of physical factors that do not lead to chemical transformations. The methods of this group are based on the difference in physical indices or properties (characteristics) of individual components of raw materials (density, hardness, magnetic susceptibility, electrical conductivity, etc.).

Physic-chemical methods consist in separating the mixture into components due to changes in its chemical composition, which occurs under the influence of physical factors (temperature, electromagnetic radiation, etc.).

Chemical methods are based on changing the chemical composition of the mixture due to chemical transformations under the action of specially introduced into the system of reagents. These methods are divided into irreversible and reversible ones.

Biochemical methods are based on the application in enrichment technologies of microorganisms that use a valuable component or, more rarely, impurities as a nutrient.

Very often processes of enrichment or separation of raw materials are carried out as typical chemical and technological processes.

3.2 WATER IN CHEMICAL INDUSTRY

Water is used in virtually all chemical technologies, as well as in the energy, metallurgical, food and many other industries thanks to its unique properties. It is used as raw material (electrochemical production of hydrogen and oxygen), reagent (in the production of nitrogen-hydrogen mixture, alkalis, alcohols, sulfate, nitrate and other acids), solvent (salts, alkalis, acids, organic substances), transporting agent (solid hydrotransport crushed raw material), heat carrier (supply of heat to the reactor or its removal from the apparatus), working fluid (in hydraulic drilling rigs, steam steam in turbines of generators of thermal and nuclear power plants).

The production of each particular product requires a certain amount of water, which, depending on the type of production, can fluctuate very widely. For example, to make 1 ton of steel you need 150 m^3 of water, the production of the same amount of paper - 200 ... 250 m^3, synthetic rubber - 3600 m^3, nickel - 4000 m^3, kapron fiber - 5600 m^3, and to get 1 ton of aluminum - as long as 15,000 m^3. It is obvious that the use of such plants only fresh water is economically disadvantageous. In addition, the discharge of such significant volumes of used water into natural reservoirs would require huge wastewater treatment facilities, and the discharge of untreated wastewater would lead to a sharp deterioration in the quality of natural waters. It is worth noting that today in Ukraine there is a deficit of fresh water, and the quality of available ones often does not meet normative indicators. Moreover, even underground fresh water, which has always belonged to strategic stocks, is increasingly being polluted by industrial, agricultural and domestic waste, which penetrates through soils and breeds. Therefore, in order to save water in the enterprises usually use reversible water, that is, the one that has already been used in the technological process: it is returned to the production cycle after the necessary conditioning. However, it is impossible to completely cycle water flows in production, because there are technological losses - due to the evaporation of water, with damp sludge, etc. The source of industrial water supply is natural water.

Everyone knows that pure water is a colorless liquid without taste and odor, which freezes at a temperature of 0 °C, and boils at 100 °C (at a pressure of 760 mm Hg). Water has a density of 1,00 g / cm^3 (at 4 °C), insignificant thermal conductivity, hardly conducts electric current [7].

The water molecule contains covalent polar bonds O-H, has an angular shape and is polar.

The electrostatic interaction between molecules with the participation of hydrogen atoms is called a hydrogen bond.

3.2.1 TYPES AND CHARACTERISTICS OF NATURAL WATERS

By origin, natural water is divided into atmospheric, surface and underground.

Among all kinds of natural waters on Earth, surface and underground waters are the most important for the industry, in particular, our country. Atmospheric waters are used much less frequently (Table 3.3).

Surface water - is the waters of river, lake and marine reservoirs. Their qualitative and quantitative composition (dissolved salts, gases and organic compounds, dispersed particles, etc.) are very different. River water is characterized by the highest content of dissolved gases, a considerable amount of dispersed particles, relatively small concentrations of organic substances. Lake water is similar to a river in terms of salt content, but the disperse particles in them are usually less, and organic compounds - more. The largest concentrations of dissolved substances (with the exception of gases) among the specified types of water are inherent in sea water.

Table 3.3 – Classification of water by chemical composition

Characteristic	carbonates	hydrocarbonates	sulfates	chlorides
Hydrocarbonates	$NaCO_3$ $MgCO_3$ $CaCO_3$	$Mg(HCO_3)_2$	Na_2SO_4	NaCl
Sulfates Sodium sulfate Sulfate-magnesium	–	$Mg(HCO_3)_2$ $Ca(HCO_3)_2$	Na_2SO_4 $MgSO_4$ $CaSO_4$	–
	–	$Mg(HCO_3)_2$ $Ca(HCO_3)_2$	$MgCl_2$ $MgSO_4$ $CaSO_4$	NaCl
Chloride	–	$Ca(HCO_3)_2$	$CaSO_4$	NaCl, $MgCl_2$ $CaCl_2$

There are 22,5 thousand rivers in length exceeding 4 km, including 117 rivers with length of 100 km and more on the territory of Ukraine. The total length of these rivers is 17 thousand km.

The largest rivers of the country - the Dnipro, Dniester, Seversky Donets, Southern Bug - flow south to the Black Sea. The Western Bug, which flows to the northwest towards Poland and the Baltic Sea, also belongs to major rivers; Tisza is a tributary of the Danube heading towards Hungary, and

Prut is the second largest tributary of the Danube, which forms the border between Moldova and Romania outside Ukraine. The largest influx of the Danube is Kilia, which forms the Danube Delta and is the border between Ukraine and Romania. In addition to these large rivers, the water resources of our country owns more than 63 thousand small rivers.

3.2.2 SANITARY AND TOXICOLOGICAL CHARACTERISTICS OF CHEMICAL IMPURITIES OF WATER

Aluminum. In the event of a violation of the excretory function of the kidneys as a result of various diseases, aluminum can accumulate in the liver and vital parts of the brain. In the latter case, severe disturbances of the function of the central nervous system arise. The content of aluminum in drinking water is mainly due to its receipt from coagulants used in water preparation and its presence in surface waters.

Barium. In natural waters, barium content is 0,001 ... 0,01 mg / dm^3, sometimes – 0,1 mg / dm^3. For the most part, it falls into the sources of water supply to the waste water of the metallurgical, machine-building and pharmaceutical industries and with the waters of paper production. Soluble compounds of barium (chloride and nitrate) are well absorbed and capable of cumulation (accumulation). Barium is a highly toxic substance that, even in small doses, can cause toxic, embryotoxic or mutagenic effects. When it enters the body, it can accumulate in bone tissue, which is dangerous to health. In the case of entering the body in the form of chloride, the lethal dose for adults is 550 ... 600 mg [7].

Beryllium is a toxic and cumulative cellular poison. Penetrating into all organs, cells and organelles and damaging cell membranes, it can cause a wide range of distant effects of adverse effects. Increased concentrations can be observed in underground and surface waters as a result of the receipt of industrial wastewater contaminated by beryllium (aviation and space industry).

Boron. When high levels of boron with drinking water are introduced into the human body, there are significant disorders of the functions of the reproductive system in men and women and the expressed embryotoxic effect. Boron is well absorbed in the digestive canal, but is gradually withdrawn. In high concentrations it is found in highly mineralized groundwater and sea waters.

Molybdenum. The excess of molybdenum in the human body results in metabolic disorders, which are manifested in polyarthralgia and arthrosis. The content of molybdenum in underground and surface waters reaches thirty and one hundredths of a milligram in 1 dm^3. In areas of industrial extraction of molybdenum and industrial waste water contaminated with surface water, its concentration may reach 1 mg / dm^3.

Arsen. Inorganic arsenic is more toxic than organic, and inorganic compounds of Arsen (III) are more dangerous than the compounds of Arsen (V). For prolonged use of water contaminated with arsenic, on the skin there are growths - corns, blood vessels may be affected, tumorous diseases may occur. Constant use of water with an arsenic concentration of 0,2 mg / dm^3 throughout life causes a 5 % risk of developing skin cancer. In the case of acute arsenic poisoning, the central nervous system is affected, which leads to coma, and at doses of 70 ... 80 mg - to death. Possible also is a severe defeat of the digestive canal, nervous system and respiratory tract. Poisoning is also possible at low doses – 3 ... 6 mg / day for a long time. Due to the high activity of the arsenic under conditions of production, manifestations of hyperpigmentation, keratoses and lung cancer are observed. The content of arsenic in fresh ground and surface waters is low, but in places of occurrence of polymetallic ores, it can exceed 1 mg / dm^3. In waste production (hydrometallurgy, ash CHP), there is a high content of arsenic, which is a real source of groundwater pollution [7].

Nitrates and nitrites. Nitrates - products of oxidation of organic nitrogen by bacteria. Nitrites are formed as a result of incomplete oxidation of organic nitrogen by bacteria. Nitrates are the result of fixation in the soil of atmospheric nitrogen (bacterial synthesis). Some nitrates and nitrites accumulate after the rainwashed nitrogen oxides formed as a result of a lightning discharge or come from anthropogenic sources.

The use of fertilizers, the decay of plant and animal waste, domestic wastewater, the entry into the ground of sewage sludge, industrial dumping, washing out of waste disposal sites and washing out of the atmosphere and causes the flow of water from ions NO_2^- and NO_3^-.

The content of nitrate in water, as a rule, is lower than 5 mg / dm^3. However, in small water sources and especially in groundwater, its content may exceed 10 mg / dm^3. Both nitrates and nitrites are very easily absorbed by the body. After receipt of drinking water nitrates and especially nitrites in human blood accumulate methemoglobin, which is not capable of transferring oxygen from the blood into the tissue, resulting in a disease - water-nitrate methemoglobenemia. Methemoglobin is the result of the binding of oxyhemoglobin to nitrites that are formed after the recovery of nitrates in the human stomach. Recovery processes in the stomach are observed in people who have dysbacteriosis, a violation of the enzyme activity of the stomach.

The presence of nitrates and nitrites in water is a carcinogenic danger. Under certain conditions, nitrites can react in the human body with secondary and tertiary amines and amides with the formation of nitrosamines. Some of them are considered carcinogenic. The formation of nitrosamines may increase in people suffering from achlordia (a state of low acidity in the stomach) or an infected bladder.

Lead. Cases of severe poisoning by lead were observed after consumption of water with high content (0,6 ... 2,0 mg / dm^3). Lead comes in the water of lead tubes and reservoirs. Poisoning is accompanied by intestinal colic and exhaustion. This metal has a high cumulative capacity, accumulates in the bones, affects the nervous system, the kidneys and leads to early atherosclerosis. At concentrations in drinking water of 0,1 mg / dm^3, the body cumulates 50 % of absorbed lead, and its content in the blood reaches the limit – 0,025 mg / dm^3. In unpolluted lake and river waters, the lead content does not exceed 0,01 mg / dm^3. However, in the areas of the occurrence of polymetallic ores, its content in groundwater can significantly increase. Calculations made taking into account the use of 2 dm^3 of water per day, prove that the daily intake of lead varies from 10 to 20 micrograms to 1 mg or more. Lead is excreted from the body with urine, feces and sweat. It is contained in the hair and toenails of the hands and feet. In high doses, lead is a cumulative metabolic poison of general action. Symptoms of acute lead poisoning - rapid fatigability and fatigue, a sense of discomfort in the abdomen, irritability, anemia, and in children - a change in behavior [7].

Selenium is contained in water in the form of selenite or selenate, depending on the pH and the presence of salts of some metals, in particular, of the ferrum. Its content in surface waters is much lower - 10 μg / dm^3. In water of some wells the content of selenium exceeds 100 μg / dm^3. In the case of use of groundwater with high levels of selenium, the function of the liver, the formation of enamel and calcium metabolism are disturbed. Typically, in natural waters, selenium content is negligible. From organism it is derived mainly with urine. The consequence of the increased use of selenium by animals is growth retardation, reduced survival, liver damage, and other organs. In some cases, myocardium, kidney and pancreas are present.

Strontium. After prolonged use of groundwater with high levels of strontium in children, there was a violation of the development of bone tissue, such as poor teeth development.

Fluorine. Excess fluoride in drinking water causes the development of a disease - fluorosis, the manifestation of which is the formation of spots on the enamel of teeth. In addition, skeletal osteosynthesis in children can be affected, changes in the muscles of the heart and in the nervous system may occur.

Lack of fluorine in water causes the development of dental caries - the main cause of loss of teeth in adolescence and adulthood. Very important role of fluoride in regulation of mineral exchange of a skeleton. At an early age, it promotes the process of mineralization of bones, and in the sloping - reduces the degree of age demineralization of bone tissue. The necessary amount of it in the human body falls predominantly with drinking water. Significant development of dental caries in the population is observed in the content of fluorine ions in drinking water less than 0,5 mg / dm^3. The caries morbidity decreases after increasing the concentration of fluoro-ions to 1 mg / dm^3. However, an increase in the concentration of fluoride to 1,5 ... 2 mg / dm^3 causes spotty enamel in 15 ... 20 % of the population. When using water with a fluoride concentration of more than 3 ... 6 mg / dm^3 there is a deformation of the skeleton. In high doses, fluoride is very toxic to humans. Pathological changes are hemorrhagic gastroenteritis, acute toxic nephritis and various degrees of damage to the liver and heart muscle. The acute lethal dose is about 5 g of sodium fluoride, that is, about 2 g of fluorine. The first manifestations and symptoms of intoxication are vomiting, abdominal pain, nausea, diarrhea and even seizures [7].

Iron, manganese, copper and zinc belong to low-toxicity elements, the characteristic feature of which is the effect on the organoleptic properties of water.

Iron. In the body, iron engages in oxidative-reduction processes, immunobiological reactions, as part of some enzymes. Blood hemoglobin contains up to 70 % of iron in the human body. The presence in the body of the mechanism of regulation of the balance of iron does not allow to detect its toxic effects. However, its high content in drinking water negatively affects its organoleptic properties. Water with high iron content is unpleasant to taste, has a brown color, forms nodules in the pipes, preventing the flow of water and damaging the tapping fittings.

Mangan belongs to essential micronutrients, because it is a part of many enzymes, hormones and vitamins that affect growth, hematopoiesis, immune formation and reproduction. Absorption of manganese, which enters the body with drinking water, is insignificant as a result of the hydrolysis of its salts to the formation of difficult soluble compounds. According to the WHO, the content of manganese in drinking water up to 0.5 mg / dm^3 does not harm human health. However, the water with such a quantity of manganese has a metallic taste and during washing it paints fabrics.

Copper. Properties of copper in drinking water depend on the pH, concentration of carbonates, chlorides and sulfates in it. In the body, copper is involved in the formation of erythrocytes, the release of tissue iron and the development of the skeleton, the central nervous system and connective tissues. Due to the presence of a homeostatic mechanism of copper content regulation in the human body, it does not accumulate. In low concentrations, copper gives water an unpleasant binder flavor, which limits its content in drinking water.

Zinc. The content of zinc in drinking water usually does not exceed 0,01 mg / dm^3 in surface and 0,05 mg / dm^3 - in groundwater. However, in tap water, its content can increase to 2 mg / dm^3 due to the washing out of galvanized pipes. Zinc is an indispensable trace element, as it is part of vital vitamins and enzymes. Due to its high content in drinking water, it also changes its organoleptic properties. The metallic taste is not felt by its content in water of 5 mg / dm^3 [7].

Chrome. As a result of pollution of natural waters by industrial waste water, in some cases, high content of chromium is observed. The main source of pollution is sewage from galvanic production, textile industry and the smelting of special alloys. In natural conditions, as a rule, there are compounds of chromium (III), in industrial waste - chromium (VI). The compounds of chromium (III) are slightly soluble and poorly absorbed in the digestive canal. Therefore, it is believed that toxic properties are characteristic of chromium compounds (VI). The adverse effects of chromium entering the body are associated with kidney and liver damage. Chromium also causes stomach ulcers and duodenal ulcers. Known allergenic effect of chromium, due to its high ability to complex formation. Chromium also has carcinogenic and mutagenic effects. Chromium compounds (VI) at doses up to 10 mg / kg of body weight cause liver necrosis, nephritis and death in humans. Smaller concentrations lead to irritation of the mucous membrane of the digestive channel.

Nickel. Nickel content in surface water reaches 1 mg / dm3, and in some underground - up to 0,13 mg / dm^3. The receipt of nickel is possible with the waste water of the metallurgical, machine-building and chemical industries. Its concentration in such waters ranges from 0,01 to 274 mg / dm^3. In the case of excessive intake of nickel in the human body biochemical processes on the cellular and subcellular levels are violated. For prolonged contact with aerosols of nickel, workers develop lung and stomach cancer [7].

Mercury. In contaminated water bodies, the concentration of mercury ranges from 0,01 to 0,5 μg / dm^3. In rivers contaminated with sewage, its contents are hundreds and thousands of micrograms in 1 dm^3. Under normal circumstances, no more than 15 % of the mercury absorbed by the body comes from drinking water. It is very toxic and cumulative. The basis of the pathogenesis of chronic mercurial intoxication with small doses is the high affinity of mercury with sulfogidroksidnymi groups of many enzymes and malfunction of cell membranes. Inorganic compounds of mercury accumulate in the kidneys. So, methylmercury rapidly appears in the blood, where 80 ... 90 % of it is associated with red blood cells. The mercury salts are removed from the body by the kidneys, liver, mucous membrane of the stomach, sweat and salivary glands, and also with milk, but the most important route of excretion - with urine and faeces. Poisoning with mercury is mainly manifested in the form of neurological and renal disorders, mostly caused by organic and inorganic compounds of mercury. For inorganic compounds, mercury is characterized by lesions of the kidneys and liver, for organic - neurotoxic and embryotoxic manifestations [7].

Organic matter. It should be noted that organic matter of natural origin - humates, amines and other substances - negatively affect the organoleptic properties of water. Organic substances of anthropogenic origin after entering the water can adversely affect the body. Many of the organic substances have pronounced organoleptic properties (odor, taste, color, ability to foam). So, surfactants in small non-toxic concentrations form a foam, phenols give water a specific odor.

Considerable danger to human health due to the expressed toxicity, cumulative and ability to cause long-term effects (carcinogenic, embryotoxic, gonadotoxic, hereditary structures) are pesticides, polyaromatic carbohydrates, trihalomethanes. Recently, there has been a negative impact of dioxins and dibenzofurans, which are man-made products.

3.2.3 TYPES AND CHARACTERISTICS OF WATER FACILITIES

Underground water - water artesian wells, wells, springs, geysers. These waters, depending on the composition and structure of the rocks and soils, where the aquifer is located, can differ significantly in mineralogical composition. Common to them is the small concentrations of organic substances.

Atmospheric waters are the water of rain and snow precipitation, they differ from all other very low concentrations of mineral and organic substances and the largest (in comparison with other types of waters) content of the dissolved gases.

The quality of water is determined by its physical, chemical and bacteriological parameters, in particular, such as: transparency, color, odor, dry residue, total salt content (mineralization), hardness, oxidation, active water reaction (pH), dissolved gas content, soli-index, salt -caption.

All of these indicators not only characterize water content of certain impurities but are also the basis for choosing the rational technologies for the preparation of natural or circulating water prior to its application in a particular process or wastewater treatment.

Transparency depends on the presence in the water of disperse hollow and colloidal particles that can contaminate the product, gradually clog the pipelines. These particles often adsorb and develop colonies of microorganisms, including pathogens (pathogens).

The color of water is determined by the presence of dissolved organic and mineral substances in water that significantly degrade the quality of water as a reagent or solvent and may adversely affect the quality of the product obtained.

The smell of water can be caused by organic impurities of anthropogenic origin, as well as due to natural biochemical processes (eg, rotting). A noticeable smell shows that there are quite a considerable amount of organic and biologically active compounds, bacteria in water. Such water is unsuitable for direct use as a reagent or solvent in chemical technologies, primarily in pharmaceutical, in public utilities.

5-point scale for water includes the following items [8]:

0 - odorless water;

1 - very weak odor experienced by an experienced specialist;

2 - weak, tangible consumer in the case of his attention;

3 - noticeable, causes a negative reaction of the consumer;

4 - clear, water is not suitable for consumption;

5 - very strong, water is not suitable for consumption.

According to GOST 2874-82 and DSanPiN-10, the odor of drinking water should not exceed 2 points at 20 °C and when heated to 60 °C (Table 3.4).

Dry residue, which is defined as the mass of dry precipitate formed after full evaporation of water, and characterizes the content of dissolved substances.

By degree of mineralization, natural waters are divided into fresh (up to 1 g / dm^3), brackish (1-3 g / dm^3), salted (3 ... 10 g / dm^3), salted (10 ... 50 g / dm^3), rope (over 50 g / dm^3). It is obvious that the higher the mineralization, the more necessary is the purification (desalting) of water before it is used.

Table 3.4 – The indicators, effecting on organoleptic properties of water [7]

Indicators	Norms, not more	
	GOST 2874 – 82	DSanPiN 2.2.4-171-10
pH	6,0 –9,0	6,5 –8,5
Ferrum (Fe), mg / dm^3	0,3	0,3
Total hardness, mg·eq. / dm^3	7,0	7,0
Sulfates, mg / dm^3	500	250
Dry residue, mg / dm^3	1000–1500	1000
Residual polyphosphates, mg / dm^3	3,5	–
Chlorides, mg / dm^3	350	250
Coper (Cu), mg / dm^3	1,0	1,0
Manganese (Mn), mg / dm^3	0,1	0,1
Zinc (Zn), mg / dm^3	5,0	–
Fluoride phenols, mg / dm^3	–	0,0003

The water hardness characterizes the total content (in mg-eq. / dm^3) of dissolved salts of calcium and magnesium. Distinguish between temporary (carbonate), constant (non-carbonate) and total hardness.

Temporary hardness is conditioned by the presence of calcium and magnesium hydrocarbon in water, which can easily be removed from the water by boiling. This produces a dense sediment consisting of $CaCO_3$, $MgSO_3 \cdot Mg(OH)_2$. So, settling on heated surfaces, forms a scale on the walls of reactors, heat exchangers, resulting in a deterioration of heat transfer, decreases the "living" section of the pipelines, contaminated products.

Constant hardness is caused by chlorides, sulfates and other salts of calcium and magnesium. During boiling, it is not eliminated, because no chemical transformations with these salts occur. Consequently, in the presence of these salts, the formation of sediment at elevated temperatures does not occur, but they worsen the quality of the product, contribute to the corrosion of the equipment.

Temporary and constant hardness together form the general hardness of water. According to this indicator water is divided into very soft ones - up to 1,5 mg-eq. / dm^3, softy 1,5 ... 3 mg-ekv / dm^3, moderately hard 3 ... 6 mg-eq. / dm^3, hard 6 ... 9 mg-eq. / dm^3, very hard - more than 9 mg-eq. / dm^3 [5, 8].

The oxidation of water characterizes the water content of substances that can be oxidized. This indicator is defined as the mass (mg) of an oxidant (potassium permanganate or potassium dichromate) spent on the oxidation of reducing substances, which are in units of water. Oxidation is a very important indicator for the characterization of waters, primarily wastewater. The higher this value, the worse the quality of sewage, because for dumping it in natural reservoirs it will lead to the emergence of a deficit of dissolved oxygen.

The active reaction of water is expressed by the pH value. Depending on the value of this parameter, water is divided into acidic pH < 4, weakly acidic 4 < pH < 6.5, neutral 6,5 < pH < 7,5, weakly alkaline 7,5 < pH < 11, alkaline pH > 11.

Dissolved gases, in particular oxygen and carbon dioxide, despite their relatively low concentrations in water, can lead to intense corrosion of steel and concrete structures, especially at elevated temperatures.

By bacteriological indicators belongs to the circle-index (soli-endeah), which characterizes the degree of bacterial contamination of water. According to this indicator water is divided into good up to 3, satisfactory 3 ... 10, poorly contaminated 100 ... 1000, contaminated 1000 ... 10 thousand, highly contaminated more than 10,000. The main requirements for water as a coolant is the lack of salts that determine the carbonaceous hardness , and dissolved oxygen and carbon oxide (IV). The presence of calcium and magnesium hydrocarbons in water will cause the formation of scum, and dissolved in water gases - to corrosion of equipment. In the technology of pure substances and reagents, water should be demineralized, and in the pharmacological - also disinfected, sterilized. Multi-tonnage production (production of mineral fertilizers, salts, acids, etc.) uses lighted water, to which special requirements regarding its chemical composition are not put forward. Water for enrichment processes of solid phase raw materials is usually used without pre-preparation.

Consequently, the technologies of water preparation for different productions will be different from the physico-chemical bases of the purification processes, the number of stages of purification and their combination. The choice of rational technology enables to improve, first of all, the quality of the product, slow down the equipment corrosion, reduce energy costs, create more environmentally friendly production

The constant increase in the level of pollution of natural waters and the reduction of the reserves of clean freshwater, including underground, causes increased attention to the improvement of methods and processes, not only preparation for the use of water in technological processes, but also the treatment of wastewater that is thrown into natural reservoirs. Therefore, various methods that can be used to prepare water for its use in production and for the treatment of wastewater will be considered.

Water Lighting Water illumination is the removal of disperse hollow and colloidal particles. Suspended particles form suspensions, which depending on the size of the particles are divided into coarse (particle size greater than 100 microns), thin (0,5 ... 100 microns) and muddy (0,1 ... 0,5 microns).

Purification of water from suspended particles Physical methods for the removal of suspended particles include: gravity (settling), centrifugal, filtration, non-reagent flotation, membrane.

3.2.4 THE MAIN METHODS OF WATER TREATMENT AND CONDITIONING

The technology of manufacturing any product in general and water preparation in particular is determined by the quality of the raw material and the quality requirements of the finished product. For the preparation of water, use natural water, which is taken from surface or underground sources, and finished products may be drinking or technical water. Therefore, the technology of water preparation is determined by the quality of natural water, its physical, physico-chemical and bacteriological properties and requirements of the consumer.

The technology of preparation of drinking or technical water covers a complex of processes for the purpose of changing its initial composition, improving the natural ingredients and enriching it with those that are lacking. The need to apply this or that process of water preparation occurs if it does not meet the requirements of the consumer. The basis of the choice of the process of water preparation is the comparison of the water quality of the water supply source (data of chemical and technological analyzes) with the data of the state standard on drinking water or the technical conditions of the consumer. The results of the comparison determine the choice of the process of improving the quality of water. At the same time, several processes of water preparation can be competitive. Then the choice of a particular process is carried out in accordance with the data of the environmental-technical-economic analysis, taking into account the minimal costs and achievement of high technological and ecological effects. Processes of water preparation are divided into the following main groups [5]:

- improvement of the organoleptic properties of water (clarification and discoloration, deodorization);
- provision of epidemiological safety (chlorination, ozonation, ultraviolet, radiation and other methods of decontamination);
- conditioning of the mineral composition (fluoridation, de-mineralization, disinfection, demagnetization, softening, desalting).

The main processes for improving the quality of water for economic and drinking purposes are clarification, discoloration and decontamination.

Clarification of water. Water clarification is charged for removing the suspended impurities from the water, make it clearer. Depending on the desired final content of suspended matter in water, clarification is carried out by settling water in sedimentation, hydrocyclones, centrifugation, flotation, filtration, passing through a layer of previously formed suspended sediment in clarifiers and other apparatuses.

To intensify the deposition of suspended substances, their coagulation is used. To do this, water-added chemicals - coagulants. As a result of coagulation, large aggregates are formed, on the surface of which adsorb impurities and suspended particles, which quickly settle under the influence of gravity forces. The process of coagulation is carried out in clarifiers with a layer of frozen flakes or in contact lighteners with a static granular layer.

The extraction from coarse dispersed water is done by centrifugation and in the hydrocyclones followed by clarification on the fast filters, filtration through the grid, on the microfilters or through the tissue. The clarification of water simultaneously with its discoloration occurs in flotters.

Water discoloration - the process of removing colored colloids or dissolved impurities from it, which determine the color of water. It is discolored during coagulation or flotation with the use of oxidants or sorbents. For this purpose, chlorination, filtration through granular activated carbon and pressure flotation with obligatory preliminary coagulation of impurities are used.

Water disinfection - a process for reducing the content of iron salts to the requirements of the state standard for drinking water or consumer specifications. Depending on the forms of the ferrum compounds present in water, use is made of reagent or reagent methods for the removal of ferrum compounds. Widely used water watering followed by filtration on fast filters.

Fluorination of water is usually carried out by introducing into it the composition of fluoride-containing compounds for the prevention of dental disease in tooth decay. A solution of fluoride-containing reagent is added to water before or after filtering on fast filters.

Water disinfection is carried out for the destruction of pathogenic bacteria and viruses in it, by chlorination, ozonation or by introducing potassium permanganate.

In order to prove the quality of water to the requirements of drinking water, in addition to the above measures, the following processes are sometimes used: deodorization (removal of unwanted odors and flavors by the use of aeration, oxidants and sorbents), introduction of alkaline reagents into water and precipitation of hardness salts, desalination (reduction of total water mineralization by electrolysis, reverse osmosis, distillation, ion exchange).

During the preparation of technical water for technological purposes, there is often a need for its clarification, deep softening, complete desalting, demagnetization, demineralization, degassing, and reduction of oxidation. The water used for cooling is usually not cleaned, but it is stabilized to prevent the corrosion of metal pipes of heat exchange devices or their overgrowth with a calcium carbonate precipitate. In some cases, cooling water is chlorinated to prevent bio-cooling of the cooling system.

Neutralization of water. Neutralization of water is carried out in cases where the pH value goes beyond the permissible values specified in the standards for a particular production.

Natural surface waters are predominantly weak-grained as a result of photosynthesis with the participation of the microflora and algae of the reservoir. Neutralization of such waters partially occurs simultaneously with chlorination of water, when as a result of saturation of water chlorine is formed by chlorine. Complete neutralization is carried out by weak solutions of chloride acid. Acid nature usually has industrial recyclable, as well as contaminated natural waters that neutralize lime milk $Ca(OH)_2$.

3.3 CLASSIFICATION OF INDUSTRIAL WASTES AND ENVIRONMENTAL POLLUTION

he influence of human production activity in the last century has sharply increased compared with the activity of other biological organisms. As a result, the mind directed by the person of production activity is creating fundamentally new products and, at the same time, waste products (which in some cases do not occur in nature). Irreversible changes occur, which lead to a sharp violation of the cycle of substances. Industrial pollution of the environment is divided into two groups: material and energy. Material contamination includes: mechanical, physical, chemical and biological waste. Energy contamination includes: thermal emissions, noise, vibration, ultrasound, electromagnetic field, as well as light and ionizing radiation.

Classification of industrial pollution of the environment consists of material contamination:

1) from emissions into the atmosphere: gaseous and vaporous, liquid, solid, mixed;

2) sewage: conditionally clean (reversible), dirty;

3) solid waste: non-toxic, toxic.

energy contamination:

4) thermal emissions; noise, vibration, ultrasound;

5) electromagnetic fields;

6) world infrared and other radiation;

7) ionizing radiation.

Sources of pollution can be industrial enterprises, communal objects, cars, aircraft, river and sea vessels and other objects, where the fuel is burned and various material resources are processed.

If pollution enters the biosphere in insignificant quantities, then under the influence of chemical and biological processes, solar radiation, dissolution in water, scattering on large areas, they can become non-harmful. This is confirmed by the initial period of industrialization, when there were few industrial enterprises and no clean up of harmful emissions was needed.

In our time, the degree of industrialization has become high not only in industrial cities, but also in agricultural areas, so emissions reach a level at which they cause damage to the biosphere and hinder the development of industry and agriculture.

3.3.1. THE MAIN TYPES OF ATMOSPHERIC POLLUTION

About 500 million tons of solid particles (ash, dust, smoke) and about 30-35 billion tons of gaseous pollutants (carbon monoxide, sulfur, nitrogen) are emitted every year in the air. In addition, the fog of acids, compounds of chlorine, fluorine and other compounds contribute significantly to the pollution of the atmosphere (Table 3.5).

Table 3.5 – Receipt of harmful emissions by energy objects

Branches	Emissions, %
Thermal power plants	27,0
Ferrous metallurgy	24,3
Non-ferrous metallurgy	10,5
Oil and petrochemicals	15,5
Road transport	13,3
Building materials industry	8,1
Chemical Industry	1,3

Harmful emissions accompany the work of enterprises in other industries. Thus, metallurgical and coke plants are emitted into the atmosphere, at the level of dust and iron oxides, carbon monoxide, sulfur, nitrogen, ammonia, phenols and fluoride compounds.

Chemical and petrochemical enterprises throw in the air hydrogen sulfide, carbon oxides, acids, aldehydes, ketones. In addition, petrochemical enterprises emit 55 ... 60 % of the total amount of carbohydrates coming from stationary sources.

Many such chemicals are mutagens and carcinogens, that is, they cause genetic changes in humans and animals, as well as oncological diseases.

Cars, airplanes, river and sea vessels are the most powerful sources of carbon dioxide (II) into the atmosphere, hydrocarbons, aldehydes, nitrogen oxides and other toxic substances.

For most developed countries, power plants and the metallurgical industry are sources of more than 70 % of solids and sulfur oxides and more than 50 % of nitrogen oxides in the atmosphere, while emissions from road transport account for the bulk of carbon monoxide, hydrocarbons and a substantial part of 40 ... 50 % nitrogen oxides.

Of the more than 200 atmospheric pollutants, you can distinguish five main:

- solid particles: dust, ash, soot;
- oxides of sulfur, nitrogen, carbon;
- hydrocarbons, which determine 90 ... 98 % of gross emissions of harmful substances in most cities.

For industrial regions, the following mass ratio of intake of substances to the atmosphere is characteristic: about 50 % of carbon oxide (IV), sulfur oxides - about 20 %, solid particles – 20 %, nitrogen oxides - 6 ... 8 %, hydrocarbons - 2 ... 5 % . However, taking into account the higher toxicity of nitrogen oxides, their contribution to atmospheric air pollution can be estimated at 30 ... 35 %, followed by sulfur oxides, carbon monoxide and solids [5].

Air pollutants also include ammonia, hydrogen sulfide, carbon disulfide, ozone, aldehydes, organochlorine compounds.

In Ukraine, stationary sources (mainly energy and metallurgy) dispose of 51 % of carbon oxides, 62 % of nitrogen oxides, and 60 % of hydrocarbons.

The main industrial sources of emissions into the atmosphere of solid particles are power plants, boiler houses, metallurgical and cement plants, ore and coal extraction plants. About 60 % of the total amount of aerosols entering the atmospheric air from industrial sources make up the world's hard particles that come from coal combustion. This is mainly ash and dust, in much lower concentrations - soot, in some cases aerosols containing carcinogens. The ash emissions from combustion of solid fuels depend on the composition of their mineral part, the type of heating device and the efficiency of dust collecting plants.

The harmful effects of dust on the human body depend on a number of factors: air concentration, chemical composition, particle size, dispersion, hardness. For example, particles of less than 5 microns in diameter easily penetrate the lungs when breathing. Dangerous for human health is a dust containing more than 10 % silicon oxide. When burning liquid fuels, a significant amount of fine particulate matter is produced that has a higher toxicity than ordinary dust and badly affects the transparency of the atmosphere.

The mineral content of low-grade coal tends to increase from the usual 15 ... 30 % to 40 ... 50 %. However, due to the continuous increase in the amount of ash trapping and the increase in the proportion of gas and fuel oil in the fuel balance, the overall level of dust in the air is reduced.

Sulfur oxides are one of the largest pollutants of atmospheric air, which is difficult to get rid of. Their annual emissions in the lower atmosphere of the atmosphere exceed 150 million tons, while 60 ... 80 % of this amount is thrown out with combustion products of fuel. The estimated loss from pollution with sulfur oxide (IV) is up to 50 % of the total damage from atmospheric pollution.

Sulfur oxides, as well as acids formed by their combination with water vapor (H_2SO_4, H_2SO_3), have a detrimental effect on human health, cause the destruction of steel structures and building materials, reduce the transparency of the atmosphere, the destruction of forests and garden trees, reduce the yield of agricultural cultures The harmful effect of SO_2 on plants is sharply increased with the presence of nitrogen oxide (IV) in the atmosphere and increased humidity.

Sulfur oxide (IV) - a colorless gas with a sharp characteristic smell of burning sulfur, detrimental effect on the human body, reduces the concentration of hemoglobin in the blood, increases the risk of conjunctivitis.

It is oxidized in the air and interacts with moisture to form an acid that causes burns.

The amount of sulfur oxide (IV), annually polluting the Earth's atmosphere, is estimated at 100-150 million tons, of which not less than 2/3 is emitted from the flue gases of thermal power plants that process sulfur-containing fuels. This means that they annually release 70 ... 80 million tons, which accounts for about half of all its world emissions (Table 3.6).

Table 3.6 – The main sources of sulfur (IV) oxide emissions

Branch	Contents, %
Heat power engineering	50,3
Motor transport	20,0
Non-ferrous metallurgy	7,4
Refining	20,7
Chemical	1,2
Building materials	0,4

Gross emissions of nitrogen oxides into the air make up 6 ... 8 % of the total emissions of harmful substances. By toxicity, nitrogen (IV) oxide is significantly dominated by oxides of sulfur and carbon.

Nitrogen oxides N_2O, NO, NO_2 are gas contaminants of the first class of danger. They cause severe irritation of the mucous membranes, destructively affects the nervous system, affect the brain, cause oxygen starvation and have narcotic properties. When in contact with moisture formed acid, which is an integral part of acid rain. They are chemically aggressive, thus destroying metal structures, roofs of buildings, paints, and fabrics (Table 3.7).

Table 3.7 - The main sources of emissions of nitrogen oxides

Branch	Contents, %
Heat power engineering	72,5

Motor transport	17,3
Ferrous metallurgy	6,1
Building materials	1,8
Chemical	1,7
Refining	0,6

More than 91 % of total nitrogen oxide emissions (51 million tons / year) come to the atmosphere with products of combustion of liquid fuels and gas, only 2,4 million tons of chemicals are emitted.

One of the most toxic substances that enter the atmosphere is incomplete combustion products of fuel: carbon monoxide, aldehydes, organic acids, hydrocarbons. In this group, the most important is carbon monoxide. If the content of dust, sulfur and nitrogen oxides in the air is determined by the level of emissions of toxic substances with products of combustion of fuels, then in cities the content of carbon oxides is bound by 75 ... 97 % with motor vehicles, and in cities with developed metallurgical industry - to the same extent with metallurgy and motor transport.

Reducing CO emissions when using internal combustion engines is one of the most important tasks of modern automotive engineering. Cars with a carburetor drive up to 5 % or more of carbon monoxide from the exhaust gas volume. With the correct adjustment of the engine, this amount can be reduced to 0,2 %. A significant reduction in CO emissions can be achieved by transferring cars to gas or mixed fuels.

Sinter plants, each of which emit 1-7 million cubic meters / year of agglomerate containing up to 1 % CO, should be noted from stationary sources of CO emissions. oxygen converters; electric furnace. Small boilers throw 500 times more CO than bigger power plants.

Along with CO in products of combustion of gas in some cases find formaldehyde, which has high toxicity and a sharp unpleasant smell. In flue gases of boilers operating on fuel oil or natural gas, usually contains up to 70 mg / m^3 of aldehydes. The content of formaldehyde and organic acids is noticeable only with high content of CO in combustion products.

A certain proportion of emissions comes from an atmosphere with precipitation. These include hydrophilic dust, some hydrides and fog acids. In the latter case, the so-called "acid rains" are noted - weak solutions of sulfate, nitrate and nitrite acids, formed as a result of the following reactions:

$$SO_2+H_2O=H_2SO_3;$$

$$SO_3+H_2O=H_2SO_4;$$

$$2NO_2+H_2O=HNO_3+HNO_2.$$

About 40 % of total carbon dioxide accumulates in atmosphere. Accumulation of CO_2 in the atmosphere leads to an imbalance of thermal equilibrium in the atmospheric-terrestrial system. The end result of this process can be global climate change due to the "greenhouse effect".

In addition to carbon dioxide, other gases are involved in the creation of the "greenhouse effect": warming occurred due to an increase in the content in the atmosphere of five gases. The exhaust gas emitted by cars has a lower ozone content, it provides 8 % warming. Chlorine, fluorine, carbon gases, which also cause a decrease in the ozone layer, provide about 20 % warming. Nitrogen (II) oxide released during the decomposition of organic residues, lignite and mineral fertilizers is also the cause of warming. Methane provides about 16 % warming. Two thirds of it is formed in the process of human activity.

The destruction of the ozone layer, which protects the surface, mainly from ultraviolet rays, can cause complex environmental consequences of a global scale. The gases that affect the formation of an ozone hole are the product of human industrial activity. The most dangerous chlorocarbonates, that is, chlorinated and fluorinated hydrocarbon products, are widely used in the production of aerosols, liquefied gases.

3.3.2 POLLUTION OF HYDROSPHERE

The development of industry, agriculture causes the formation of a large amount of wastewater contaminated with various impurities. First of all, it is the waste of refining, chemistry, metallurgy, pulp and paper and food industries. Significantly increasing the volume of pollution coming from the reservoirs of agricultural objects - waste animal breeding, poultry, fertilizers and pesticides.

Sewage, which is diverted from enterprises, in its composition can be divided into three groups [8]:

1) production - used in technological processes of production;

2) household - from sanitary knots, shower and other sources;

3) atmospheric (storm) - rain and snow melting.

Contaminated industrial waste water containing different substances is divided into three groups:

1) contaminated mainly by mineral impurities (thermal power plants, metallurgical enterprises, and machine-building, mining, construction industry);

2) contaminated mainly by organic impurities (enterprises of food, pulp and paper, chemical and microbiological industry);

3) contaminated with organic and mineral impurities (oil refining, petrochemicals, textile and other industries).

Wastewater is extremely damaging to rivers, lakes, seas and even oceans. Relatively harmless are sewage produced after their use as a refrigerant. According to the chemical composition, these waters differ little from the source water and discharge them into the reservoir does not cause particular trouble. The most harmful are sewage resulting from chemical processes (reaction and mother liquors), washing waters formed during the washing of products and products, treatment of technological equipment, waste water coming from mining enterprises, which are formed at ash removed, storm waste water. Many sewage (especially thermal and nuclear power plants) are discharged into the reservoir at elevated temperatures. As a result, so-called thermal pollution of water bodies occurs. In places where hot waste water is released, zones are formed in which the water temperature can exceed 8 ... 12 °C in winter and up to 30 °C in summer, the temperature of water throughout the reservoir. This causes an increase in the accumulation of organic substances in water, which negatively affects the biological life of the reservoirs. The biological contamination of reservoirs is largely contributing to the content of phosphoric and nitrogen compounds in their presence, which creates favorable conditions for the intensive growth of underwater plants, in particular, blue-green algae.

3.3.3 METHODS AND PRINCIPLES OF WASTE WATER CANALIZATION

The vast majority of industrial enterprises and utilities are consumers of a given quantity of water. As a result of its use, it is contaminated with various waste management, loss of production, etc. The concentration and composition of water pollutants is closely related to its application, and for the industrial sector - with the type of production, raw materials, reagents involved in the technological process. As a result, the composition of used water (especially industrial) is very diverse and often fluctuates within a fairly wide range.

Sewage (from the point of sewage) is the water that was used for those or other needs and got additional impurities (contamination) that changed their initial chemical composition or physical properties. Wastewater also refers to water flowing from the territory of settlements, and especially industrial enterprises as a result of rainfall.

Depending on the origin, type and qualitative characteristics of impurities, waste water is divided into household (economic-faecal), industrial (industrial) and atmospheric.

Households include water from kitchens, toilet rooms, showers, baths, laundries, dining rooms, hospitals, and the like. By type of pollution, they can be fecal (contaminated mainly by physiological impurities) and economic (contaminated with different economic wastes).

Industrial wastewater includes water used in technological processes, after which they no longer meet the requirements of these processes to their quality and should be removed from the enterprise. These waters include water discharged to the surface of the earth during extraction of minerals (oil, coal, ore).

By concentration of pollutants, industrial waste water can be divided into three main groups:

1) clean water (after cooling engines of power stations, equipment surfaces). However, these waters often contain a small amount of contaminants, so they are sometimes referred to conditionally clean;

2) contaminated water (conditionally clean, mainly water after washing the finished product);

3) dirty water (the level of pollution is determined by many factors).

Sewage waters of the first and second groups, as a rule, are used as reversible or for dilution of dirty waters in case of unacceptably high concentrations of pollutants in them.

Most industrial enterprises deal with all listed types of industrial waste water. In addition, each of them has one or another amount of household sewage. All waste water that has been formed should be drained (drainage).

Sewerage, or drainage, is a complex of engineering structures, as well as technical and sanitary measures that ensure the organized collection and disposal of waste water from the territory of settlements or industrial enterprises, their cleaning, decontamination and decontamination.

In choosing the principle methods and schemes of the drainage of a particular area, it is necessary first of all to consider the possibility of joint removal and treatment of sewage from settlements and industrial enterprises located within the city or near a city or settlement. The joint drainage of such complex of objects is expedient according to economic indicators and, as a rule, is more reliable in the sanitary sense. Questions regarding the appropriateness of joining the central sewage system of enterprises located far from a populated area or not far from each other, is solved by a technical and economic comparison of options.

In some cases, industrial waste water can not be cleaned directly at the plant due to the specifics of their composition. The cleansing of such waters is greatly simplified in the event of mixing them with domestic waters. However, the discharge of industrial waste water into urban sewage can be carried out only when it meets certain requirements.

If waste water from industrial sewage with significant content of strong acids or alkalis which can cause corrosion of sewage structures or negatively affect the process of the subsequent biochemical purification of a mixture of domestic and industrial sewage is discharged into the sewage system, the latter should be preliminarily neutralized by appropriate reagents to a pH value of 6.5 ... 9 or mutually neutralize sour and alkaline waters by mixing them.

In general, in order to ensure normal conditions of operation of sewage treatment facilities in the case of general biochemical purification of domestic and sewage, the following conditions must be observed, in addition to those specified: the temperature of the mixture to be purified should not exceed 6 ... 30 °C, the total concentration of dissolved the salts in the mixture should not exceed 10 g / dm^3, the biological consumption of oxygen (BSK20) of the mixture should not be greater than 500 mg / dm^3 (for conventional biological filters and aerotanks) and 1000 mg / dm^3 (for aerated sewage water distribution). The content of nutrients should be: at BOD_{20} < 500 mg / dm^3 - at least 15 mg / dm^3 of ammoniacal nitrogen.

3.3.4 CHARACTERISTIC OF POLLUTION AND CLASSIFICATION OF INDUSTRIAL WASTE WATER

Sewage produced at enterprises can be classified into three categories: industrial, domestic and atmospheric.

Industrial waste water, in turn, is divided into three main groups:

1) industrial water produced as a result of direct use of water precisely in technological operations that are contaminated with all substances used in the technological processes of this production. Some of these waters, which are obtained during the final treatment of the finished product, are sometimes poorly contaminated, and such waters are considered practically conditionally clean;

2) water from auxiliary operations and processes, which are formed during surface cooling of technological equipment and power aggregates; the main difference of such waters is, as a rule, elevated temperature;

3) water from auxiliary workshops and maintenance shops (raw materials and finished products storage, transportation of raw materials and fuel, boiler rooms) that are contaminated with various substances.

Industrial waste water, depending on the type and concentration of pollutants, as well as on the amount of wastewater and places of their education, are diverted either by one common stream or by several independent streams.

Yes, independent streams combine:

- Lowly contaminated industrial waste water containing one or more types of pollution;
- industrial waste water containing toxic compounds;

- sour or alkaline sewage;
- industrial waste water with an unpleasant smell;
- very mineralized water;
- industrial waste water containing oils, fats, petroleum products.

In the absence of well-defined types of pollutants, all industrial waste water is combined into one stream. Practically clean water from auxiliary operations, as a rule, is diverted by a separate flow or transported along with storm (rain) waters.

By combining contaminated waste water, it is necessary to take into account the possibility of interaction of different waters with the release of a significant amount of gaseous substances (including explosive products), the formation of sediments, toxic substances.

Domestic wastewaters generated in the enterprise are disposed of and cleaned separately if industrial waste water does not require biochemical purification due to the nature of their pollution. Joint disposal of domestic and industrial waste water is expedient if the latter is contaminated with organic substances subject to biochemical degradation and if the concentration of toxic contaminants in the total flow entering the biological treatment plants does not exceed the maximum permissible concentration (MPC) for biological purification.

By type of pollution, industrial waste water can be divided into three groups:

1) water contaminated mainly by mineral impurities (waste water from enterprises producing mineral fertilizers, acids, construction products and materials, petroleum products, coal-mining enterprises);

2) water contaminated mainly by organic impurities (sewage from chemical and petrochemical enterprises, processing industry, production of polymer films, materials, rubber);

3) waste water contaminated with mineral and organic impurities (oil refining, oil-extracting, petrochemical, light, food industry, organic synthesis).

3.3.5 NEGATIVE IMPACT OF POLLUTANTS ON THE LYTHOSPHERE

The processing and usage of mineral raw materials is accompanied by a large mass of waste and emissions.

Solid waste entering the environment is divided into industrial, agricultural and household.

In turn, industrial solid wastes are divided into several groups: metal, non-metal, combined and complex. Metal wastes include chips, scraps and waste, obtained from the processing of metals, waste from the foundry industry. These wastes are usually recycled, so they are harvested, sorted by stamps and metal types. Nonmetallic wastes include waste dumps, ash, slag, wood waste, plastics.

The largest amount of waste is produced at the enterprises of the following industries:

- mining industry, mining and chemical industry;
- ferrous and nonferrous metallurgy;
- metal processing industries;
- forest and wood industry;
- thermal power plants;
- chemical and related industries;
- cement dust, waste from organic production;
- food industry;
- light and textile industry.

In agriculture there is a large amount of plastic containers, old rubber, out-of-date agricultural machinery, worked parts.

Huge urbanization on our planet has created a serious problem of utilization of urban waste (glass, metal products, plastics, rubber, wood).

Accumulated solid waste clogs large areas of land, and, moreover, can damage plants and living creatures. Thus, some wastes have toxic properties, phosphogypsum wastes, and lack of water poison ground water. The rocks and galitons are occupied by large areas in coal mining and potash fertilizers.

3.3.6 THE IMPACT OF ENERGETIC ON THE ENVIRONMENT

he main part - about 80% of world production of electric energy in our time is produced by burning organic fuel (coal, oil, gas).

For energy production, it is characteristic that expended material resources are completely transformed into waste, and the amount of waste exceeds the amount of spent organic fuel.

Power plants discharge the following types of waste water: cooling water turbine condensers, causing "thermal pollution" of reservoirs: regeneration and washing water from water treatment plants and condensate cleaners; water contaminated with petroleum products; water from external cooling of heating surfaces, working on fuel oil; spent solutions after chemical purification and conservation of equipment; water systems of hydraulic disintegration at the TPP, working on solid fuels.

With cooling water in the reservoir a large amount of heat is dumped. In order to ensure that the influence of heat does not violate normal conditions in the reservoir, discharge of waste water according to sanitary norms should not cause an increase in its own temperature of the reservoir more than 5 °C in the summer, and 3 °C in the winter.

When preparing additional water for steam boilers, a large number of chemical reagents are consumed: alkalis, acids, lime, coagulants, which, after use, form waste water. These waters do not contain toxic impurities, but they make salts of water, change the pH value in water, increase in it the concentration of organic impurities, which form the oxygen deficit in water bodies, increase the flow of anaerobic (without access to oxygen) processes with the removal of harmful products (H_2S, CH_4).

There is a great danger to water bodies that are contaminated by petroleum products. The sources of oil products in the waste water from the TPP are the fuel economy (due to oil drainage from oil coolers of turbines and pump bearings), electrical equipment (transformers, cables) and auxiliary services (depot, garage, compressor). The general expenses of such waters at large TPPs do not exceed 100 m^3 / year at the concentration of oil products not exceeding 50 mg / kg.

During operation of the TPP and NPP it is not possible to completely eliminate the processes of scale formation, which makes it necessary to periodically clean the surfaces of heating from sediments internally. Satisfactorily clean the heating surface only with the use of special reagents for this purpose: alkalis, organic and inorganic acids, detergents, corrosion inhibitors. The total amount of water discharged during chemical washing depends on the type of boiler and the accepted washing technology and can reach 20 thousand tons for one wash. In spent industrial solutions, reagents make up 70 ... 90 % of impurities and their composition is a lot of toxic substances. In the period of stop and simple equipment (boilers, turbines), measures are taken to protect it from corrosion, for example, boilers are filled with special solutions that should be reset before boiler start-up. This event is called conservation of equipment. The "salty" nature of dumping and a sharp change in the concentration of impurities in sewage after chemical purification and conservation of equipment greatly complicate the organization of sewage treatment itself.

3.4 THE CHARACTERISTIC OF WASTES

As known, mineral raw material is a complex mixture consisting of various compounds and inclusions. The concentration of one or another compound or component in the raw material determines its suitability for the production of the target product. To extract one or another component from the mineral raw material it is necessary to make shredding, chemical treatment, crystallization, evaporation, that is, to carry out the technological process. In this case, together with the receipt of the target product, waste or residues are formed which are not end products and due to the volatility of their composition can not be used directly. Thus, waste from production is the residues obtained by the processing of raw materials, materials or semi-finished products into final products and do not meet the requirements for the finished product and which, after pre-treatment (or without it), can be used in another production in quality of raw materials.

In some cases, the resulting waste is highly toxic and dangerous compounds. These are, first and foremost, wastes containing radioactive substances, heavy metals, toxic organic compounds, before the release or disposal of which they require thorough treatment. Obviously, waste should be considered such residues, which are practically impossible to use at this stage of technology development and which must be disposed of and constructed or buried. Another type of waste that can be recycled at this stage of technology development should be called technological residues (or secondary raw materials).

To date, there has been a large accumulation of various waste from production and consumption, which have become so-called secondary material resources (SMR). Wastes that are technologically used as a source of raw materials and energy are categorized as material resources, and those that do not find application and continue to accumulate relate to the potential of SMR.

A general diagram of the process of accumulation and possible ways of using SMR is given in fig. 3.1

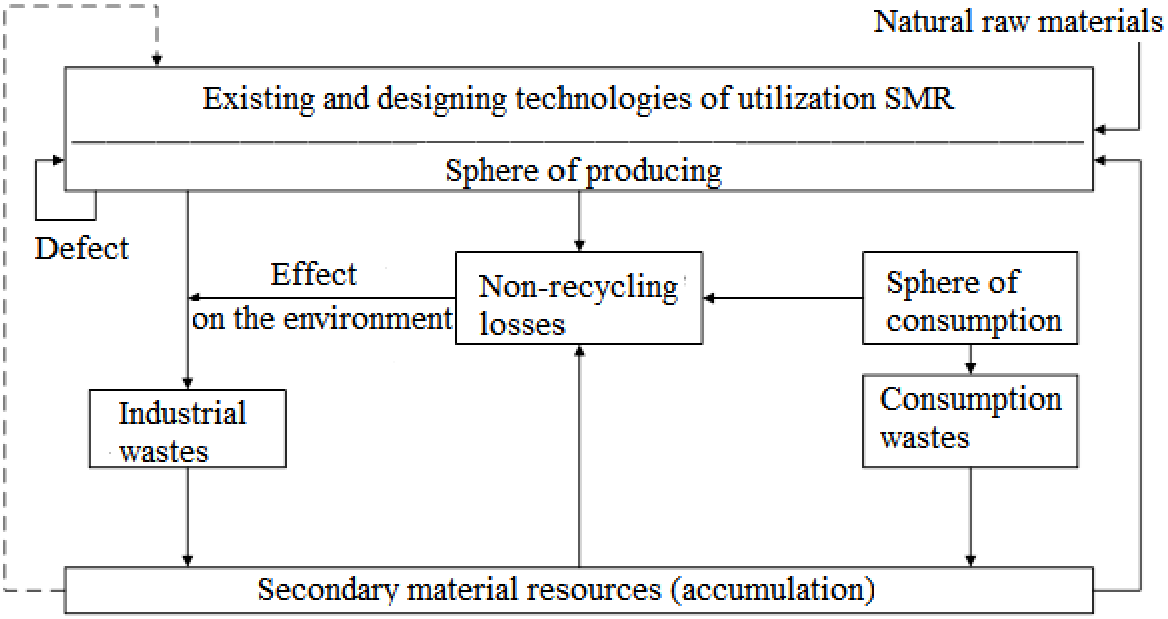


Fig. 3.1 – Scheme of accumulation and possible ways of using SMR [9]

It is evident that from this scheme in principle full waste recycling is possible, except for irreversible losses that arise both in the sphere of production and in the sphere of consumption. Moreover, one of the ways to dispose of HMC is to use them as raw materials for the technologies being created, and the other - in adding them to the original natural raw materials for the purpose of their further processing.

3.4.1 THE CLASSIFICATION OF WASTES

Approaches to the waste classification system are very diverse. Classify waste by two main features: source of formation and direction of use. The classification scheme by the source of education includes several steps that show how secondary material resources (production and consumption wastes) can be converted into end products used in the same enterprise and in related industries or which are subject to storage and disposal.

The classification of waste is based on the method of design study, which is used to select the method of production of any chemical product. It takes into account the main characteristics of the waste, the methods and place of processing, the products of processing and the area of their use.

Waste obtained in the chemical industry can be classified either by aggregate state or by the method of their disposal. The most common and understandable classification is aggregate state.

Solid waste is waste that is obtained in the form of powders, dust, ingots or hardened mass. These include: scum, ash, dust particles and soot, waste plastics and rubber, mineral-based metal-containing residues after ore dressing, organic debris.

Liquid waste is a waste that is almost entirely composed of a liquid phase and contains dissolved in water or other solvents of salt, alkali, acids, as well as impurities of suspended solids. In addition, the amount of suspended particles does not exceed the level at which their deposition occurs. Liquid waste - mobile and easily pumped by pumps used to transport liquids in the chemical industry. The concentration of soluble substances should not exceed the solubility limit at which they crystallize from the solution under normal conditions. To liquid waste, first of all, industrial waste water, which can be discharged into the sewage without pre-treatment at the plant; waste water contaminated with toxic and poisonous compounds requiring special treatment (water containing acids, alkali, chlorides, fluorides, bromides, dissolved metals, toxic organic compounds, etc.); spent organic solvents and organic toxic liquids (production of pesticides).

Gaseous waste is the gas emissions of industrial furnaces, drying equipment, feeders, gas separation of chemical processes, etc. These include various gases with intense smell and containing dispersed solid or liquid particles in the form of fog, as well as containing NO_x, SO_2, HCl, HF, etc., a pair of organic substances, vapor-air mixtures contaminated with toxic impurities.

In a separate category should also include waste that is obtained in the form of slurries, which can not be attributed to either liquid or solid waste. Typically, they are amorphous or fine crystalline masses containing from 20 to 98 % by weight. water and poorly transported without pre-treatment (drying, freezing, etc.). These waste include the remnants of filtration and sedimentation processes, sludges obtained by neutralization or special treatment of liquid waste, sludge or sludge, obtained during the purification of faecal wastewater. To this category, include resins, sour and viscous gum, residual oil products obtained in organic synthesis.

Considering the system of classification of chemical wastes, one can not ignore such an important characteristic as toxicity. On this basis, the chemical waste can be divided into:

- harmless;
- toxic;
- especially toxic.

The notion of "toxicity" includes the degree of exposure of chemical waste to wildlife. First of all, it relates to humans, and then to animals and plants. Almost all chemical wastes are toxic, and their effect depends on the dose of the substance to which the person or the environment is exposed. In addition, many chemicals have the ability to accumulate both in the body and in the environment and thus enhance their toxic effects over time. Waste and disposal of chemical toxic waste leads to the disappearance of toxic components during evaporation and washing into the environment, where their circulation occurs. Obviously, when classifying chemical waste, it is necessary to indicate the degree of their toxicity, for determining which one must know the chemical composition, the available concentration of these substances in the environment, the ability to accumulate and biological degradation. Toxic and especially toxic should be classified as a specific category of "specific" waste that requires special disposal methods before they are disposed of or disposed of.

Figure 3.2 shows the scheme of classification of chemical wastes, taking into account their aggregate state, chemical nature and specificity.

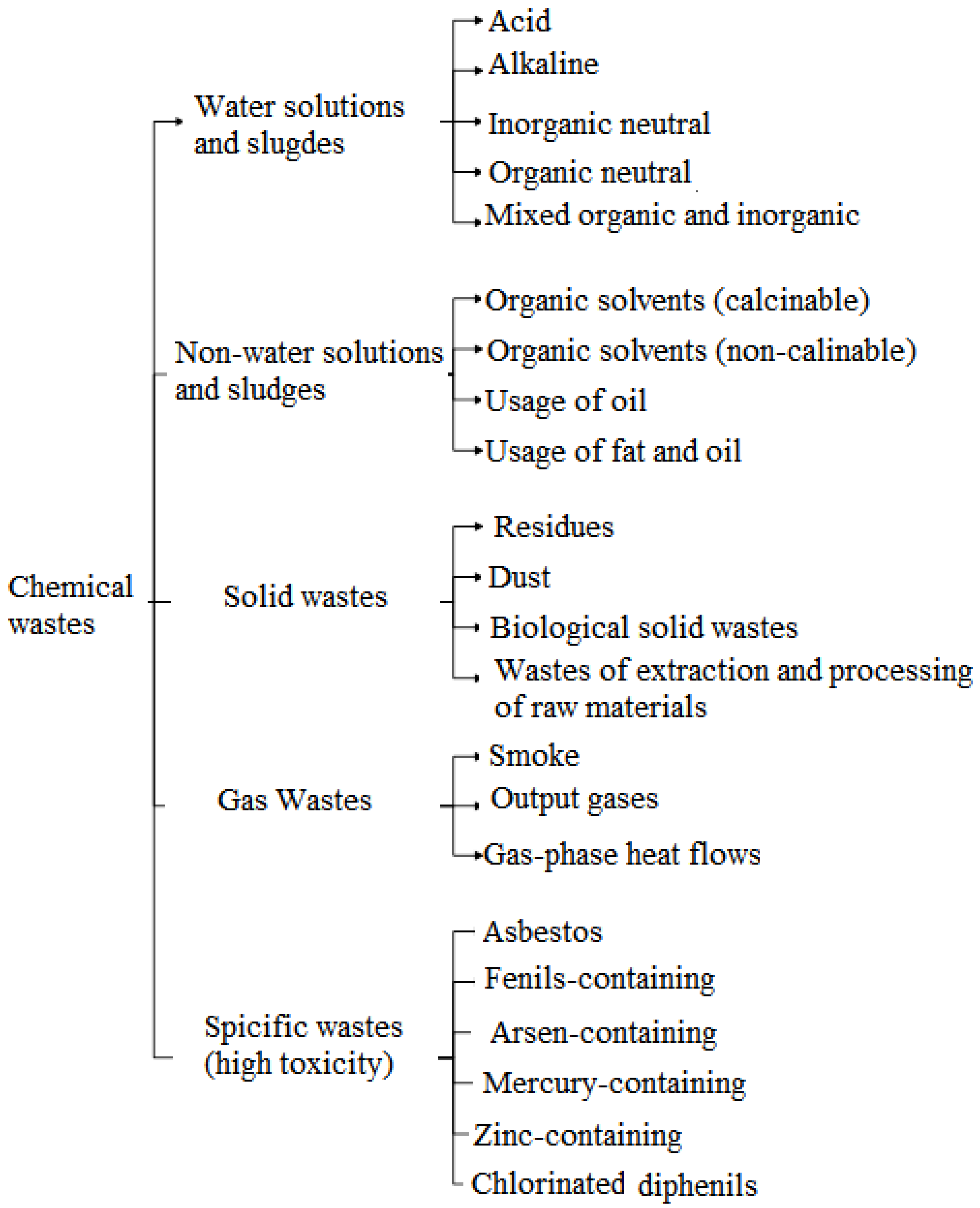


Fig. 3.2 – Scheme of the classification of chemical wastes [9]

3.4.2 METHODS OF CHEMICAL INDUSTRY WASTE DISPOSAL AND LIQUIDATION

In the process of utilization or disposal of waste, various physical, physico-chemical, biochemical and other known methods used in chemical technology are used. Specific features and physical and chemical properties of waste used as raw material require adaptation of known methods and techniques used for their processing.

3.4.2.1 PHYSICO-CHEMICAL METHODS OF WASTE PROCESSING

Figure 3.3 shows the classification of chemical wastes by methods of their utilization and liquidation. At the heart of this classification is the principle that defines the initial and ultimate goal of the processing or disposal of chemical waste.

Depending on the composition of the waste and its physical, chemical and mechanical properties, at the first stage of choosing the rational way of processing, it is necessary to determine:

1) phase separation method;
2) the method of removing individual components;
3) the need for chemical or biochemical treatment;
4) the possibility of their removal without pre-processing.

Usually one particular method of disposal or disposal is not enough, it is necessary to apply them in combination. For example, for primary treatment - deposition, filtration, coagulation, flotation, evaporation, for secondary treatment - deposition with reagents, for tertiary treatment - sorption on activated carbon, biological treatment, ultrafiltration, etc. In some cases, one operation is sufficient, for example, separation of the water-organic solution by distillation or evaporation.

Analyzing Figure 3.3 it can be seen that, if necessary, the phase separation of waste, alternative methods can be: deposition under the influence of gravitational forces, filtering, coagulation - flocculation, flotation, evaporation, centrifugation; for the removal of individual components - ion exchange, sorption, membrane separation methods (reverse osmosis, dialysis and electrodialysis, ultrafiltration), evaporation, steam distillation, solvent extraction; for chemical processing - neutralization, precipitation, oxidation-reduction processes, hydrolysis, electrolysis, combustion, catalysis, photolysis; for biological treatment - aerobic treatment in aerators, biofilters, ponds and fields of irrigation and anaerobic decomposition. In some cases, waste is not subject to any processing, but is removed by injection into the sea, storage in sludge and landfills, laying in underground layers or burned.

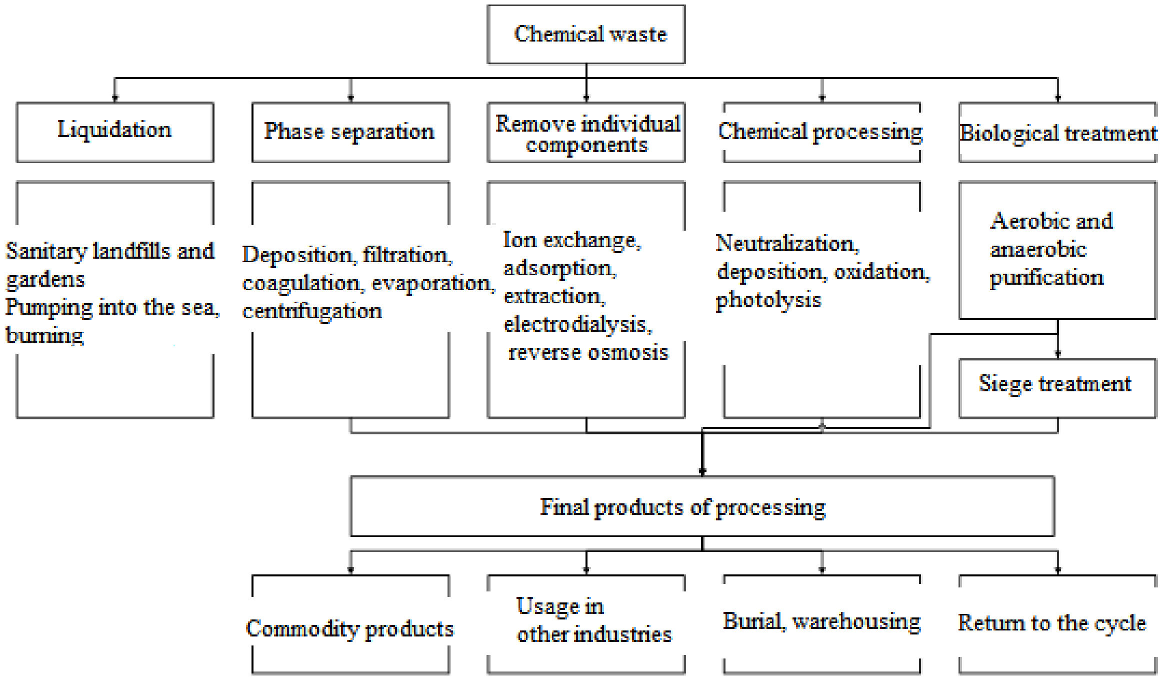


Fig. 3.3 – Scheme of classification chemical wastes by the methods of their utilization and liquidation [9]

3.4.2.2 METHODS OF LIQUIDATION OF INDUSTRIAL WASTES

To this day, many industrial waste was subjected to removal (or liquidation) with the prior disposal or without it. Such an approach to waste management is outdated; only those wastes which can not be practically used or converted to target products by modern methods are subject to elimination. But in many cases, as a result of physico-chemical treatment of waste, that is, the removal of certain useful components from them, new solid or slag-like residues are formed, the further processing of which is inappropriate. Thus, in the technology of waste processing, the final stage of the process can be the elimination of highly toxic waste or final sediment, the removal of which useful elements is practically impossible.

Of the existing waste disposal methods found in Ukraine and abroad, landfills and demining sites, sanitary landfill, dumping or injection into deep underground wells, combustion and pyrolysis can be noted.

Landfills and slag drives

Landfills are land plots outside the city, where industrial and household waste is almost uncontrolled. Often, to reduce the amount of waste stored, they are ignited. Such a method of waste storage has extremely negative consequences and is currently prohibited by law in many countries of the world, since landfills are a serious source of pollution both in the air and in the water environment. When storing chemical waste in open landfills, the interaction of components of waste with moisture and oxygen is formed, resulting in the formation of toxic or harmful compounds that are leaked or absorbed by rain and surface waters, followed by entering the rivers and lakes. However, such landfills of industrial waste still exist: it is a land-based storage of halite waste, phosphogypsum, mines - waste of processing plants for pyrite raw materials; various slags

Shaft storage facilities are specially constructed terrestrial structures that are designed for storing and defending slurries. Typically, slurries are equipped with a special drainage system for drainage of sewage, and their bottom and shore are insulated with a waterproof layer of compacted clay, polymeric materials, bitumen, etc .; sewage flows into the special drainage ditches or drainage system.

This storage method is also not a solution to the problem as a whole. Shroud - open buildings, from the surface of which constantly released gaseous substances into the atmosphere, and in the event of damage to the drainage or insulation layer - the leak of contaminated wastewater. In addition, water in any case requires additional treatment at the treatment facilities before discharging them to the sewage system.

Widespread distribution abroad has received the so-called sanitary land dumping of wastes. This method is commonly used to dispose of solid waste. When designing such sanitary landings it is necessary to take into account the amount of waste, composition and physical and chemical properties; choose the place with a preliminary study of the soil; to control the state (pollution) of ground and groundwater; to provide protection against toxic gases emitted during waste storage; to carry out maintenance of the content of filling (compaction technique, daily or periodic filling with a layer of ground); to conduct the final coverage of landfills with an earth layer of thickness not less than 60 cm.

The sanitary filling of waste can be carried out both in special ditches and prepared pits, as well as by land storage - the formation of drills in height from 2,5 to 14 m. The main condition for the operation of such landfills is the sealing of waste and their daily filling with a layer of land. Thus, the worked out suspensions of scrubber cleaning of gases from SO_2 together with ash power plants can be eliminated; at such storage of waste there is an anaerobic timetable with the release of CH_4 and CO_2.

Solidification of waste

The dumping of toxic chemical wastes, even on controlled sanitary landfills, is impossible without their pre-treatment. Therefore, preliminary disposal of waste is necessary. For this purpose, one can use neutralization, treatment of some waste streams by others to obtain difficult soluble compounds.

The most common way of decontamination of chemical wastes is their solidification (immobilization), that is, the transformation of toxic components into insoluble compounds and the formation of easily transportable blocks (agglomerates), of which toxic impurities can not be washed out. This technique is often used to dispose of particularly harmful and toxic wastes, such as radioactive, mercury-containing waste, which includes heavy metals, as well as industrial sludges and sediments that are poorly transported. Solidification of industrial wastes ensures their safe storage and prevents groundwater contamination.

For the conversion of waste into harmless hardened blocks, technical techniques are used based on the addition of the following astringent components to the waste: cement, lime and its derivatives, bitumen, paraffins, organic polymers, silicate materials, etc. Also used is the method of encapsulation of waste, when toxic waste is enveloped in an inert film. When choosing the necessary method for solidification, the volume of waste and the degree of their toxicity should be taken into account; composition and physical and chemical properties; costs; the presence of a binder; characteristic of end products.

Pumping waste in the deep horizons

Another method of disposal of waste by their disposal is the injection of liquid waste into the deep horizons. Pumping is carried out through absorbing wells below the level of groundwater in the water layers.

When choosing the location and volume of wells, it is necessary to take into account:

- geological characteristics of the absorption horizon (porosity, penetration, tightness, created by the upper layers, seasonal fluctuations of groundwater level, etc.);
- waste composition (content of suspended particles, hydrogen sulphide, SO_2, microflora, etc.);
- pH of the solution (variation range ± 0,5 from pH of soil solutions);
- the need to take measures to protect artesian sources;
- the need to control the operation of wells.
- the need to take measures to protect artesian waters;
- the need to control the operation of wells.

3.4.2.3 THERMAL METHODS OF WASTE UTILIZATION

One of the most acceptable methods of waste utilization is their combustion or pyrolysis. These methods are used for both liquid and solid waste. The use of pyrolysis or high-temperature burning makes it possible to reduce waste by about 85 %.

The main advantages of the combustion method in comparison with other methods of waste utilization are the versatility, the ability to process any waste that can not be destroyed by other ways, the ease of automation, the ability to use the heat of waste gases, that is, to utilize the calorific value of the burned part of the waste, and the remainder or ash after combustion used as fertilizer.

Industrial incinerators are used for burning waste: chamber, shaft, drum, cyclone and fluidized bed furnaces. A promising direction in this area is the use of vortex and cyclone furnaces, as well as combined plants, which include cyclone furnaces and fluidized-bed furnaces. For each particular case, it is possible to improve the flare furnace burners, waste and waste utilization systems, waste gas treatment methods, and subsequent use of combustion products.

Considering different ways of utilization (utilization) of chemical waste, it must be concluded that the choice of one or another method for waste utilization is appropriate only after it has been established that this waste does not represent value as a raw material or energy source. The choice of waste utilization method depends on the following factors:

- volume and composition of waste;
- location of the plant producing the waste (city, countryside, industry concentration, availability of natural or artificial reservoirs, availability of free land and geological characteristics);
- availability of the plant and district energy (proximity to energy sources);
- availability of standard equipment;
- transport capabilities.

Each of the known methods of waste utilization has its advantages and disadvantages. For the preliminary analysis of existing methods in Table 3.6, their main advantages and disadvantages are presented.

3.5 STATE AND MEASURES TO DECREASE WASTE CONTENT IN WASTEWATER

There are powerful non-ferrous metallurgical enterprises in Ukraine, in which the waste from the extraction and processing of raw materials is 1,5 million cubic meters per year, and the total amount produced is 20 million tons. These include: Zaporizhzhya Aluminum Plant, Dneprodzerzhinsky Chemical Plant with waste from uranium production, Dneprovsky Aluminum Plant, Mykolayiv Alumina Plant. The mudslides of these enterprises, which have not been modernized for many years, constitute an extraordinary danger, and waste from their production (in particular, red waste sludge of 1,2 million tons / year) accumulate and accumulate in sludge.

Table 3.8 – Characteristics of methods for liquidation of chemical wastes[9]

Method of liquidation (storage)	Advantages	Disadvantages
Sanitary utilization	Earth can be used if all necessary precautions are taken	Need unoccupied land
Shlamoshova	If preliminary treatment of waste is carried out, then there is no risk of contamination of surface and groundwater. Does not require an insulating layer when the waste is disposed of	There is a potential risk of water contamination in the event of persistent chemical waste or in the event of damage to the insulating layer. It is associated with the use of expensive and not always available insulating materials
shaa	Relatively inexpensive method	Requires large land plots. Earth can not be used. Potential source of water and air pollution. Requires the use of expensive and not always available insulating materials
Burning	Effective to neutralize toxic compounds. Does not require the use of land	Relatively expensive. Requires extra fuel consumption. Residues that require storage are formed. In the process of combustion, secondary pollutants are formed
Underground burial	No need to use the surface of the earth	Requires specific geological conditions. May be a source of uncontrolled groundwater pollution in the future
Descent into the top reservoirs	Relatively inexpensive. Does not require the use of land	Potential source of water pollution. It is economically inexpedient if it is not near the reservoirs

Mykolayiv Alumina Plant is the largest in Ukraine and one of the largest non-ferrous metallurgical enterprises in Europe. The main products: metallurgical alumina, aluminum hydroxide, gallium, foundry products in assortment, alumina cup. The main hazards of the plant are sludge №1 and №2 (Fig. 3.4).

1 – plant; 2 – sludge storage №1; 3 – sludge storage №2

Fig. 3.4 – Scheme of the Mykolayiv Alumina Plant and its sludge storages

Sludge storage №1 is an artificially constructed capacity with a total area of 188 hectares, intended for storage of sludge and illuminated backwater, taking into account atmospheric precipitation. The volume of accumulation of red mud (alumina production), which is formed in the thermal processes of metallurgy of aluminum, as of 01.01.15 exceeds 26 million tons. The shaft holds for hydraulic structures of the filling type and is classified as hydrodynamically dangerous. In the government decision on the construction of the Mykolayiv Alumina Plant it was envisaged that it would be fully processed with the start of operation of the plant, but this was not done. The shaft is already close to filling and the problem of secondary use of sludge is very acute. Today it is operated as a technological water reservoir of circulating water supply.

Sludge storage №2 represents an artificially created capacity with a total area of 112 hectares, intended for «dry» storage of red mud. Capacity of the facility – 27,8 million m^3, service life – 24,9 years. The shaft storage facility since 2008 is operated for its direct purpose and is filled by about 15 %.

Both sludges are environmentally hazardous objects. Factors of danger are:

1) the potential possibility of destruction of the main dam of the reservoir №1 due to over-exploitation as a technological reservoir, climate change, indefinite storage period of accumulated red mud;

2) pollution by the filtration waters of the sludge storage №1 of the Bug estuary due to their incomplete catch;

3) pollution of atmospheric air by alkaline evaporation of sludge pulp from trenchhouses №1 and №2;

4) pollution and deterioration of soil quality;

5) pollution of atmospheric air and soil with dust from red mud from the sludge storages №1 and №2.

The indicated hazards are real and are confirmed by the practice of operating sludge storage devices. Thus, in 2003, the filtration water flow was recorded at the bottom slope of the damming dam of the sludge number 1. In 2011, there was a sawing of red mud from the sludge number 2 due to unfavorable meteorological conditions. On February 11 and 24, 2011, due to adverse weather conditions (low humidity and air temperature, cloudy wind gusts), an event related to the large-scale and long-term pollution of atmospheric air with red mud dust in the zone of location of the sludge storage №2 of the Mykolaiv Alumina Plant occurred. On January 26, 2012, there was recorded the fact that the red mud was dumped at the sludge storage №1 and №2 of the Mykolayiv Alumina Plant (within the sanitary protection zone). Project decisions on the construction of the reservoir №2 in the part of prevention of atmospheric air pollution measures to prevent the occurrence of this extraordinary situation was not foreseen.

To prevent the emergence of such environmentally hazardous situations, the management of the alumina plant, the relevant state authorities, take the necessary measures:

1) pumping and return of filtration water into sludge storage;

2) improvement of the system of dampening of dams and beaches of sludges;

3) reclamation of individual sections of the reservoirs;

4) loosening of beaches of sludges with special equipment;

5) introduction of measures for fixing the surfaces of the beach vegetation.

When carrying out an environmental risk assessment, it is necessary to take into account the mutual influence of preventive measures. Thus, for example, additional humidification of the sludge storage №2 during climatic cataclysms can lead to the destruction of the dam. The landing of the southern cane as a means to prevent peeling can lead to the destruction of the anti-filter screen with the roots of plants. Therefore, the complexity of the assessment of the environmental hazard of such complex objects as the reservoir, come to the fore.

Since the Government's decision to build the Mykolaiv Alumina Plant provided for its complete processing with the start of the operation of the plant, but this was not done, the sludge is already close to filling and the problem of secondary use of sludge is very acute.

The bauxite, which processes the Mykolaiv Alumina Plant, consists of aluminum hydroxides (gibbsite, bemite, amorphous aluminum hydroxides) and ferrum (goethite, alumogite, hematite, disperse hematite) and minerals (kaolinite, quartz, zircon, rutile, anatase, pyrite). Technological scheme of bauxite processing includes milling it in ball mills in the presence of concentrated alkaline solution with the addition of calcium hydroxide in the form of lime milk. The resulting pulp is pumped for further processing. The leaching of aluminum from bauxite is carried out in autoclaves with mechanical mixing. The pulp after separation is directed to condensation and washing machines, where the aluminate solution is separated from the sludge. The last one, after a six-time flushing, gets to the drain.

To the alkaline-aluminate solution aluminum comes in the form of a solution of aluminates, but a part of the metal is combined with the silica dissolved in the meadows and creates insoluble hydroaluminosilicate of sodium in alkalis, which passes to the sludge. The minerals of titanium, ferrum and zirconium are chemically inert under these conditions and, accordingly, also fall into the sludge. Calcite partially changes and passes to an aluminate solution, or to a slime.

In the process of storage in the sludge there are changes under the influence of alkaline technical water pH 11 ... 13, as well as carbon (IV) oxide and oxygen air. Chemical transformations in the slime are significantly activated with the increase in air temperature, which in summer can reach 50 °C. The main active phases of the Bayer slime are hydrosilicides of calcium (nozean and kancherinite), which, under the influence of carbon dioxide in 1 ... 3 years, decompose on calcium hydrocarbamide and amorphous silica. The activity of this process is affected by the amount of silica in hydrosilicates, which it slows down, and the presence of isomorphous impurities of the ferrum and titanium. At elevated temperature calcium hydrocarboaluminate decomposes on calcium carbonate and hydrargylite. Alumogetite and hematite in the lying slime practically do not change.

The key to solving the problem of accumulation of red mud is the development of a comprehensive recycling technology that uses red sludge or transforms it into a secondary resource.

Methods of utilization and use of red mud, according to the unique physical and chemical properties of red mud, can be divided into three categories:

1. recovery of components of useful metals in red mud;
2. reuse of red slurry as raw material;
3. application of red mud to protect the environment, for example, as an adsorbent for water purification.

The global reserves of "red mud" currently stored in terrestrial drives are estimated at more than 2,7 billion tons, with an annual increase of about 120 million tons per year (Figure 3.5). In the future, this will cause more and more tensions with regard to the state of the environment. This large stream of waste during the processing of bauxite is stored in separate places, where it is stored, carefully controlled and regulated by strict regulations. Despite the disadvantages associated with this "red mud" storage, nonetheless, this is the best solution based on the balance of economic, environmental and social aspects. Unfortunately, waste bins of bauxite processing are usually located at a considerable distance from the industrial base, where waste utilization is possible.

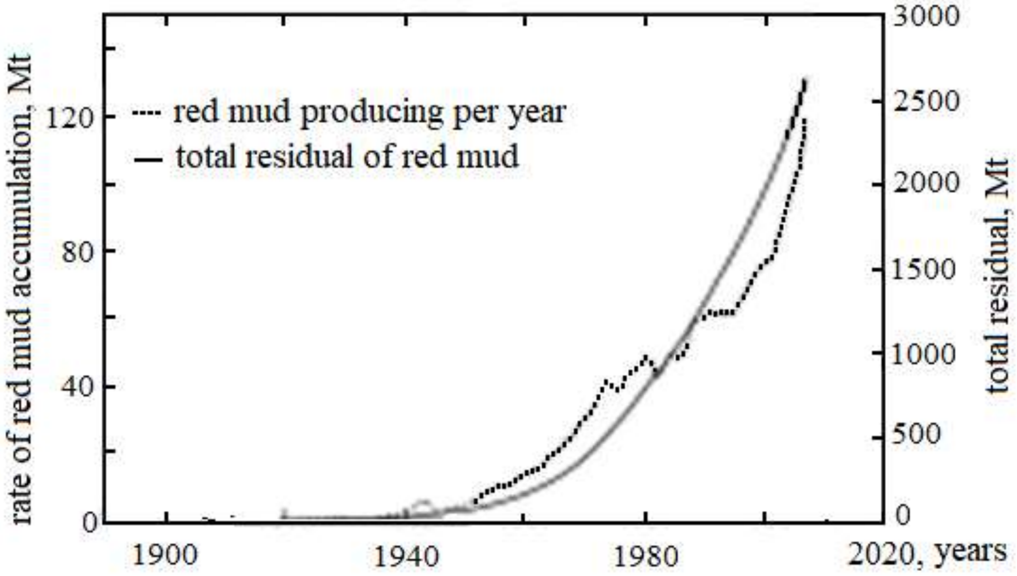


Fig. 3.5 – Annual formation of "red mud" in the world and its aggregate balance[5]

Researchers from Russia, Hungary, America and Japan conducted pilot studies on the production of red sludge. And researchers from China made steel directly from the ferrum removed from the red mud. Increasing the degree of removing red silage from the red mud (up to 86 %) is possible by

---

[5] Li, W.D. New Separation Technology Research of Iron from Bayer Progress Red Mud; Central South University Library: Changsha, China, 2006.

applying the technology of magnetic separation of red mud. Chinese scientists researched the basic laws of magnetic separation of red mud and determined the parameters of the magnetic separation process. One of the ways to use red mud is to restore rare earth elements in red mud. Thus, a method has been developed for the recovery and removal of scandium, uranium and thorium from a clay suspension of red mud by adsorption of rare earth metals with ion exchangers with regeneration of metals from resin (up to 50 % per scandium). A method for the restoration of scandium from red mud, obtained in the Bayer process, by the method of acid dissolution, with the intensity of leaching of scandium by more than 80 % is proposed. The red sludge was bled to remove water and then scrape Sc with a solution of low concentrated sulfate acid, leaving the impurities in the residues. It is possible to obtain ions of metals Ti, Sc, Fe and Al by the method of double leaching with acid from a red mud. It was investigated that extraction of Sc from red slurry can be obtained by obtaining the final product with 95 % purity by means of hydrochloric acid as a healing agent, with a liquid-solid ratio of 5 : 1, a reaction temperature of 60 °C and a reaction time of 1 hour.

Taking into account the peculiarities of the chemical and mineral composition of the red mud, it is advisable to use it in ferrous metallurgy as a ferrum-containing raw material in the blast furnace process, as well as as an additive in the manufacture of gratings from iron ore concentrate. In both cases, preliminary removal of ballast impurities (silica and alumina) from the red mud and the increase of the content of ferrous oxides is necessary. To this end, sludge treatment with concentrated alkali is used at a temperature above 100 °C. To reduce the alkali content in the filtered and washed red mud, its causticification with calcium oxide (hydroxide) in an autoclave at a pressure of 0,3 ... 2,0 MPa is used. To activate the cleaning of sludge from alkalis causticification can be carried out in the presence of humic acid. In this case, the gums of alkali metals are formed, which are easily separated from the sludge. As an additive containing humic acid, coal is used. When preparing sludge for metallurgical processing, it must be dehydrated by mixing sludge with unpolluted lime. The main operation of the metallurgical processing of red mud - a regenerative felling, which can be carried out at a ratio of sludge and reducing agent (gas coke, coal) in a proportion of 3 : 1.

In the construction industry, red mud can be used for the production of cement, building ceramics (brick, ceramic tile), wall materials, in the construction of roads, and as a binder admixture - in cement-clay compositions. There are known studies in the production of cement using red slime, ash, lime and gypsum as raw materials. The use of red sludge not only reduces energy consumption in cement production, but also improves the initial strength of cement and resistance to sulfate attack. The use of red mud as a stabilizer of cement has been studied. The possibility and expediency of production of cement from red slime as a component of Portland cement raw materials was explored. In China, studies have been conducted on the production of cement from red sludge containing aluminum compounds. Studies were conducted on slag and red sludge activated by a solid alkaline activator, resulting in modified red sludge with high compressive strength and excellent corrosion resistance when using up to 30 % red mud in the molding mass. The addition of red slurry to the starting mixture improves the quality of the cement.

At present, the Mykolayiv Alumina Plant ships to cement plants 50 ... 60 thousand tons of red mud per year, the potential volume of deliveries is 400 ... 450 thousand tons per year. But there are additional requirements for the cement producers for the composition of the sludge, which is related to the restriction of the total content of alkali and water-soluble compounds. In addition, Fe_2O_3 content should not exceed 50 %, but there are currently no specific regulations on limiting the chemical composition of red mud for the cement industry.

The production of slag brick has recently been implemented in Germany. Red slurries in the amount of 10 ... 50 % are mixed with clay, press and burn. Similar works have been done in Hungary. The burning temperature is 950 ... 1250 °C. In addition to sludge 51 ... 90 %, additives are used quartz sand, volcanic rocks, silicate slime, as well as plastic clay 7,5 ... 15 %. As an alternative to the traditional raw materials used in the production of bricks, the use of red mud can not only reduce the cost of raw materials, but also has great environmental significance. In world practice it is shown the possibility of producing fire-resistant brick, decorative brick with black granules and ceramic granite on the basis of red mud. Since 70 % and 80 % of the active components of SiO_2 and CaO are recovered in red slurry and ash, these wastes are the ideal raw material for the production of fire-resistant bricks for reasons of cost and performance.

Also, red sludge can be used as a reinforcing additive in the production of iron ore residues instead of scarce alkaline bentonite. An additive of 3 % sludge is approximately identical to the addition of 1 % bentonite. At the same time, the rhizomes are enriched with a ferrum of 0,23 %, which is equivalent to an increase in the productivity of the blast furnace by 0,6 % and a decrease in the specific consumption of coke by 0,2 %. However, it has been shown that using the red sludge the Mykolayiv Alumina Plant deteriorates the physical, chemical and mechanical properties of burned obticides, complicate the conditions of their production.

On the basis of red slurry, quartz sand, fluorite, manganese and chromium-containing wastes, they successfully produce black glass decorative materials that have good mechanical strength, chemical resistance and optical properties.

Concrete is a new trend in the production of porous building materials, which have significant advantages, such as thermal insulation, fire resistance, seismic resistance, and is made of lime and silicon materials. Foam concrete made of red mud, developed using 15 % of cement, 12 ... 15 % lime, 35 ... 40 % of red mud and 33 ... 35 % of quartz sand according to its properties corresponds to the lowest level of intensity of concrete block strength, and the technology of its production does not differ from production of other foam concrete.

For PVC (polyvinyl chloride), red mud is not only a filler that has a reinforcing effect, but is also an effective and cheap thermostable stabilizer, ensuring the filling of PVC products with excellent antimicrobial properties. Its service life is higher in 2 ... 3 times than ordinary PVC products. At the same time, the flow of red mud is better than other fillers, and therefore the technological properties of plastic on its basis are improved. Composite plastics made of red mud are flame retardant and can be used as plastic solar water heaters and building profiles.

When made from slime ceramics, the products form elastic deformation, which leads to the formation of cracks, and the addition of bentonite can prevent this. Water absorption of ceramic products obtained from a mixture of clay and sludge, significantly decreases with increasing content of clay in the mixture and increased temperature of burning. In general, it is much lower compared to the corresponding indicator of clean slurry products. The use of red mud in the composition of ceramic masses by the method of semi-dry pressing was inappropriate. The studying of the possibility of using a slime for the manufacture of wall materials from ceramic masses, carried out on the Mykolayiv Alumina Plant, showed that its maximum content in the mixture should not exceed 5 ... 10 %.

Red mud is also used as an absorber for the removal of sulfur from industrial gases. In this case, it is mixed with sodium aluminate and subjected to the resulting mixture of heat treatment and grinding.

Red mud can be used as a soil reclamation and fertilizer, which contains a wide range of trace elements. The introduction of certain of its doses in sootlot soils positively affects the growth and productivity of buckwheat, barley and corn, the yield of sugar beet and the withdrawal of sugar. Red mud is a more effective ameliorant in saline soils of southern regions of Ukraine compared to phosphogypsum. It also promotes the fixation of calcium in the exchange-soil complex, forming organo-mineral compounds with colloids of soils. The latter prevents the displacement of calcium from the exchange-soil complex with sodium ions when the soil is softened-softening. However, despite the positive effect of red mud on the quality and yield of the soil, its use is not always appropriate, especially on technogenically contaminated soils. The sludge contains an increased amount of heavy metals, some of which has significant migration potential, which can negatively affect the soil microflora, contribute to the contamination of agricultural products. Particularly noteworthy is the presence of moving aluminum forms in the sludge, which is the result of the processing of bauxite by Bayer's method. It is known that the excess of aluminum in the body can cause a complex of disorders of the central nervous system. The absence of red nitrogen, potassium and other biologically important elements in the red mud greatly reduces its value as a mineral fertilizer.

Red slurry has a positive effect on soils of the environment, contaminated with heavy metal elements. One explanation for the mechanism is that red sludge can absorb heavy metal and variable valence metal ions such as Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, Cr^{6+}, Mn^{4+}, Co^{3+} and Hg^{2+} from formed oxide compounds. At the heart of another mechanism of binding of heavy metals is the reaction of precipitation of carbonate in a red slime with heavy metal ions, which causes the deposition of the latter. In turn, the activity and reactivity of heavy metal ions in the soil decreases, microbial activity and plant growth increase.

The possibility of absorption by activated red sludge of about 18% of the gas emissions of SO_2 from the total volume released in production is established. The binding rate of SO_2 initially is 100 %, after 10 cycles decreases to 94 %. The adsorption of SO_2 on the red sludge occurs due to the chemical reaction and physical adsorption and requires small particle sizes (50 % of particles smaller than 45 microns) and a large specific surface area (10 ... 20 m^2 / g) to increase the speed and depth of the chemical reaction. The mechanism of sorption can be represented as follows:

$$SO_2(g) + Na_2O \rightarrow Na_2SO_3;$$

$$4SO_2(g) + 4Na_2O \rightarrow 3Na_2SO_4 + Na_2S;$$

$$4.5SO_2(g) + Al_2O_3 \rightarrow Al_2(SO_4)_3 + 1{,}5S;$$

$$4SO_2(g) + 4CaO \rightarrow 3CaSO_4 + CaS.$$

The adsorption capacity of red mud treated with acid in relation to ions F- and NO3- was studied to reduce the pH of the red mud. The influence of temperature activation and acid treatment on the efficiency of the absorption by red mud from the waste water of methylene blue dye was revealed, and an increase in the absorption rate was achieved approximately 5 times.

A significant disadvantage of red mud, which makes it difficult to use, is high humidity - up to 80 %. Existing sludge dewatering technologies are energy-efficient and ineffective. In addition, when developing standards and technical standards for slurry preparation, transportation and use of sludge, it should be borne in mind that under humidity of 8 ... 12 %, dry sludge undergoes deflation (wind removal).

Thus, analyzing the main ways of utilization of red mud, one can distinguish the main promising directions: the use of waste alumina production as a secondary raw material, namely for binding of heavy metals, dyes and sulfur-containing compounds after acid activation of red mud and their heat treatment. The reactivity of oxide compounds in the red sludge promotes the mobilization and adsorption of heavy metal ions such as Cu^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+} and Cd^{2+} from water and soils, thus reducing the degree of contamination of the research objects.

Since red mud of the Mykolayiv Alumina Plant contains a large amount of ferrum, it is first of all appropriate to use it as a raw material for a coagulation water treatment reagent. This will ensure a significant saving of raw materials, materials, energy resources, reduce the technogenic load on the environment, and provide water treatment technology with efficient and inexpensive coagulant. Appropriate technologies have been developed at Igor Sikorsky Kyiv Polytechnic Institute, the Department of Technology of Inorganic Substances, Water Purification and General Chemical Technology.

SELF-CONTROL QUESTIONS (CHAPTER 3)

1. Give the classification and characteristics of the raw materials.
2. Hardness of water: the concept and types of water hardness.
3. Define the term "Sewerage".
4. Give the classification of material industrial pollution.
5. Describe the concept of "acid rain". Lead the chemistry of their formation.
6. Describe the main types of atmospheric pollution.
7. Oxidation: concepts and types, dimension.
8. Formulate the principle by which natural water is grouped into groups.
9. Indicate the factors on which the harmful influence of dust on the human body depends.
10. List and describe water quality metrics.
11. Give a classification of energy contamination.
12. Describe the classification of industrial solid waste.
13. Give the basic methods of water purification.

CHAPTER 4 CHEMICAL SUBSTANCES AND REACTIONS IN PROCESSES OF INORGANIC MATERIALS MANUFACTURE

4.1 CHEMICAL SUBSTANCES AND REACTIONS IN THE INDUSTRY OF SULFURIC PRODUCTS

4.1.1 GENERAL CHARACTERISTIC OF SULFUR

Sulfur belongs to the p-elements of group VI of the periodic system (together with oxygen, elements of the Selenium subgroup Se, tellurium Te and polonium Ro).

These elements are called chalcogen (from Greek "copper and born"). This is due to the fact that most copper ores consist of compounds that contain sulfur and a small amount of selenium, tellurium (Cu_2S chalcosite, $CuFeS_2$ chalcopyrite).

Sulfur is a relatively common element on Earth: its content is 0,03 % mol. or 0,05 to 0,1 % by weight. It occurs in a free state (native sulfur), but its main mass is concentrated in the form of minerals, which belong to two main groups - sulfide and sulfate:

- Iron pyrites (pyrite) FeS_2, lead gloss (galenite) PbS, zinc blast (sphalerite) ZnS, cinnabar HgS;
- Gypsum $CaSO_4 \cdot 2H_2O$, $CaSO_4$ anhydrite, Glauber salt (Mirabilite) $Na_2SO_4 \cdot 10H_2O$, Barite $BaSO_4$, salt of $MgSO_4 \cdot 7H_2O$.

Sulfur compounds are also found in combustible minerals: oil, natural gas (H_2S), seawater (Na_2SO_4, $MgSO_4$).

Sulfur is also part of the biological tissues of all plants and animals. In plants, sulfur accumulates mainly in seeds and leaves. Cabbage contains 0,8 % S. Animals - preferably in wool to 4 %, claws, horns and ratites.

Sulfur is a part of proteins (amino acids):

- Cysteine $HSCH_2CH(NH_2)COOH$;
- Cystine $(SCH_2CH(NH_2)COOH)_2$;

- Methionine ($CH_3SCH_2CH_2CH_2CH(NH_2)COOH$).

The specific odors of garlic, onion, mustard, and cabbage are due to the presence of organic sulfur compounds.

4.1.2 CHEMICAL PROPERTIES OF SULFUR

Sulfur is a very active nonmetal. Already at room temperature sulfur is able to oxidize most active metals and mercury, while heating - and other simple and complex compounds. These reactions form sulfides - binary sulfur compounds in which it has a degree of oxidation -2:

$Ca + S^0 = CaS^{-2}$; $Hg + S = HgS$;

$Fe + S = FeS$; $Zn + S = ZnS$, $\Delta G^0_{f,\,298} = -201$ kJ/mole.

Compared to oxygen, sulfur is a weaker oxidizer. This is evidenced by the smaller negative values of the standard Gibbs energy of the formation of sulfides in comparison with the corresponding oxides:

$2Zn + O_2 = 2ZnO$, $\Delta G^0_{f,\,298} = -321$ kJ/mole.

Unlike oxygen, sulfur is readily oxidized by various oxidants and acquires the characteristic oxidation states that are characteristic of it. So, it burns in the air:

$$S^0 + O_2 = S^{+4}O_2,\ \Delta G^0_{f,\,298} = -321 \text{ kJ/mole.}$$

It can be oxidized during heating with concentrated sulfate or nitric acid:

$S^0 + 2H_2S^{+6}O_4 \text{ (conc.)} \xrightarrow{T} 3S^{+4}O_2 + 2H_2O$,

$S^0 + 6HN^{+5}O_3 \text{ (conc.)} \xrightarrow{T} H_2S^{+4}O_4 + 6N^{+4}O_2 + 2H_2O$.

In hot solutions of alkalis, sulfur disproportionates:

$3S^0 + 6NaOH = 2Na_2S^{-2} + Na_2S^{+4}O_3 + 3H_2O$.

Sulfur in the form of a simple substance detects oxidation-reducing properties (duality): a typical example is the reaction of self-oxidation-self-healing (disproportionation), where the sulfur atom simultaneously acts as an oxidizer and reducing agent:

-2________0_______________$+4$

Na_2S S Na_2SO_3

In reaction with alkali, sulfur plays the role of both an oxidizer and a reducing agent, and the meadow is the role of the medium in which the reaction runs. Sodium sulfide is a reduced form of oxidant, Na_2SO_3 is an oxidized form of a reducing agent, and water is a metabolic product.

For the distribution of coefficients, an arrow is indicated by the number of oxidant attached and given by the reductant of the electrons, and the corresponding number is set as the coefficients.

The oxidation-reducing duality possesses all the substances in which the element has an intermediate degree of oxidation. In particular, this property is characterized by sulfur and all compounds of sulfur with an oxidation degree of +4.

We also note that all compounds with an extremely low oxidation element (for sulfur is -2) may be in oxidation-reduction reactions only with reducing agents (H_2S, sulfides), and with extremely high oxidant only (SO_3, H_2SO_4 conc.).

In the normal state, two unpaired electrons are in the sulfur atom. As active nonmetallic sulfur, when interacting with metals and hydrogen, two electrons are attached and acquires a negative (negative) oxidation degree -2. Due to the sequential excitation of electrons in interaction with a more electronegative element (O_2, F_2), sulfur forms compounds with positive oxidation steps (+4, +6) [6].

+6 SO_3, H_2SO_4, Na_2SO_4, SO_2Cl_2 (oxohalogenide - chloride sulfuryl), $KHSO_4$, $H_2S_2O_8$, $K_2S_2O_7$ (disulphate, pyrosulphate);

+4 SO_2, H_2SO_3, $SOCl_2$ (chloride thionyl, thionyl chloride), Na_2SO_3, $KHSO_3$;

+2 SCl_2 (unstable, easily decomposed; uncharacteristic degree of oxidation);

+1 S_2Cl_2 (unstable, easily decomposed; uncharacteristic degree of oxidation);

0 S8;

-1 H_2S_2, Na_2S, FeS_2 (polysulphides, iron persulfide);

-2 H_2S, Na_2S.

4.1.3 СІРКА І СІРКОВМІСНІ РЕЧОВИНИ В ПЕРЕРОБЦІ

In the industry, sulfur and sulfur-containing substances are most often, firstly, they either translate themselves (as an unwanted product, "flammable gases") into SO_2:

$$S_2 + 2O_2 = 2SO_2,$$

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

The raw material for SO_2 production is also gypsum (phosphogypsum):

$$2CaSO_4 = 2CaO + 2SO_2 + O_2 \ (1400\ ^0C).$$

SO_2 is formed during pyrometallurgical processing of sulfide ores of non-ferrous metals:

For example: $\underset{\text{chalcosin, "copper shine"}}{2Cu_2S} + 3O_2 = 2Cu_2O + 2SO_2,$

then: $Cu_2S + 2Cu_2O = 6Cu + SO_2.$

From SO_2, which is formed in one way or another, they behave in different ways: more or less concentrated 7 ... 12 % sulfur (IV) oxide goes to processing in SO_3, and then into sulfate acid:

Low-concentration (throwing) SO_2 must be captured, neutralized from environmental factors.

4.1.4 UTILIZATION METHODS OF LOW-CONCENTRATED (SOURCE) SO_2

1. Sulfite-hydrosulfite method (Wellman-Lord process):

$2Na_2CO_3 + SO_2 + H_2O = 2NaHCO_3 + Na_2SO_3;$

$2NaHCO_3 + SO_2 = Na_2SO_3 + 2CO_2 + H_2O;$

$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3$.

2. Ammonia method:

$SO_2 + NH_4OH = NH_4HSO_3$;

$SO_2 + 2\ NH_4OH = (NH_4)_2SO_3 + H_2O$.

3. Acid-cathalytic method:

$MnO_2 + MnSO_4 + 2H_2SO_4 = Mn_2(SO_4)_3 + H_2O$;

$Mn_2(SO_4)_3 + SO_2 + H_2O \rightarrow 2MnSO_4 + 2H_2SO_4$;

$MnSO_4 + SO_2 + O_2 = Mn_2(SO_4)_3$.

4. Claus's method:

$2SO_2 + 4H_2S \xleftrightarrow{Al_2O_3, T=250} 3S_2 + 4H_2O$,

$SO_2 + 2H_2S = 3S + H_2O$.

4.2 CHEMICAL SUBSTANCES AND REACTIONS IN PROCESSES OF MANUFACTURE OF COLD NITROGEN

4.2.1 GENERAL CHARACTERISTICS OF NITROGEN

Nitrogen is one of the few elements that is in a free state, mainly in the air 75,6 %.

Frequently free nitrogen is part of natural gas. Very rarely found in the earth's crust in the form of $NaNO_3$, even less often KNO_3, $Ca(NO)_2$.

Opened nitrogen in 1772, English. scientist Rutherford and almost simultaneously Shele, J. Priestley, Cavendish and Lavoisier, who first saw in this gas an independent element.

In nature, there are two stable isotope Nitrogen N14, N15.

Under normal conditions, nitrogen is chemically inert. Obtained by its rectification of air. Nitrogen is part of the amino acids in the form of proteins.

In the atmosphere of nitrogen, the products are stored for a long time, because gas is not active.

Due to high electronegativity, Nitrogen generates numerous compounds in which the oxidation states are -3, -2, -1, with the lowest of them corresponds to the filling of the electron shell of its atom to a stable configuration of inert gas neon. These compounds include nitrides and hydrogen compounds of nitrogen (ammonia, hydrazine, hydroxylamine and their derivatives). In the case of a combination with more electronegative elements (fluorine, oxygen), the levels of oxidation of Nitrogen are +1, +2, +3, +4, +5. The most important compounds of Nitrogen include its oxygen-containing compounds - oxides, acids, salts.

Under normal circumstances, nitrogen is a colorless gas with low melting temperatures (-210 °C) and boiling (-198,8 °C), odorless, poorly soluble in water (under normal conditions in 100 volumes of water - 2,35 volume of nitrogen).

The atoms in the nitrogen molecule are interconnected by a triple covalent bond, which is completely unique. There are no other diatomic homoatomic molecules, where the bond of this type was realized and was so strong.

Nitrogen compounds accumulate in the soil in the form of ammonia NH_3 or NH_4^+, NO_2^-, NO_3^- ions. They are all soluble in water and can be washed away from the ground by ground waters. These Nitrogen compounds are used by plants in the process of growth, then they pass into the organisms of animals that eat these plants. The excrement of animals, as well as dead plants under the action of certain bacteria, decompose with the release of nitrogen in the atmosphere, which ends the cycle of Nitrogen in nature.

4.2.2 CHEMICAL PROPERTIES OF NITROGEN

Nitrogen in its compounds may have degrees of oxidation -3, -2, -1, 0, +1, +2, +3, +4, +5 [6].

The classification of the main types of inorganic compounds of Nitrogen in terms of its oxidation is given by the following scheme:

+5 – N_2O_5, HNO_3, $NaNO_3$;

+4 – NO_2;

+3 – N_2O_3, HNO_2, $NaNO_2$, NF_3;

+2 – NO;

+1 – N_2O;

0 – N_2;

-1 – NH_2OH;

-2 – N_2H_4;

-3 – NH_3, Li_3N, BN, Si_3N_4, I_3N, NH_4OH.

Under normal conditions, nitrogen directly reacts only with lithium, during heating - with other metals and some less electronegative nonmetals with the formation of nitrides, which have a degree of oxidation -3:

$6Li + N_2 = 2Li_3N$;

$3Mg + N_2 = Mg_3N_2$;

$3Si + 2N_2 = Si_3N_4$;

$2B + N_2 = 2BN$.

Due to the high thermal stability of nitrogen, it does not burn and does not support combustion, but magnesium burns in its environment. This is explained by the fact that in the case of the formation of nitride in the interaction of nitrogen with magnesium energy is allocated more than necessary to break the bond N-N in the molecule N_2.

The artificial extraction of atomic nitrogens is carried out by passing a gaseous N2 under reduced pressure through a field of high-frequency electric discharge. Atomic Nitrogen is much more active than molecular: at room temperature it reacts with sulfur, phosphorus, arsenic, as well as with mercury and many other metals with the formation of nitrides.

Nitrogen is oxidized by fluorine. Due to the exothermic reaction between simple substances, NF_3 nitrogen fluoride is formed in which nitrogen has an oxidation degree of +3. 3 other halogens, nitrogen does not directly interact, but such compounds exist and are extracted by indirect methods. At high temperatures, pressures and the presence of catalysts, nitrogen interacts with hydrogen, oxygen, carbon, and other elements, for example:

$O_2 + N_2 = 2NO$;

$3H_2 + N_2 = 2NH_3$.

4.2.3 NITROGEN AND NITROGEN SUBSTANCES IN PROCESSING

Nitrides Metal nitrides, unlike halides and sulfides, do not belong to salts, because there is no acid that would suit them. Properties of nitrides depend on the nature of the metal.

Nitrides of active metals, primarily s-elements of groups I and II, are easily decomposed with water to form metal hydroxide and ammonia:

$Li_3N + 3H_2O = 3\ LiOH + NH_3$;

$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$.

$NH_4Cl(_{\text{CONC.}}) + 3Cl_2 = 4HCl + Cl_3N$.

Already during relatively weak heating (about 90 °C) or in the case of impact, Cl_3N with an explosion decomposes into simple substances:

$2Cl_3N = 3Cl_2 + N_2$.

In water, Cl_3N almost does not dissolve, but slowly almost completely hydrolyzes the scheme:

$Cl_3N + 3H_2O = 3HClO + NH_3$.

Under the influence of iodine on a concentrated NH_3 solution, a dark brown precipitate of iodine nitride is isolated:

$NH_3 + 3I_2 = I_3N + 3HI$.

This compound is extremely unstable and in dry form explodes at the slightest touch with the formation of simple substances.

Nitrides of other nonmetals (BN, Si_3N_4, Ge_3N_4, etc.) are solid polymeric substances with high melting temperatures (2000 ... 3000 °C). They belong to dielectrics or semiconductors.

The most numerous and diverse are nitride d-elements. In appearance, these nitrides resemble metals and have metallic properties (gloss, electron conductivity). These are crystalline substances of variable composition with a metal bond, for example, TiN, Fe_4N, Fe_3N, Ni_3N, Cr_2N, which are formed as a result of embedding of nitrogen atoms in the cavity of a crystalline metal lattice, which causes its strengthening. That is why nitrides of d-metals are characterized by high hardness and refractoriness, and the refractory nitrides often exceed the refractoriness of the initial metals.

Ammonia. The main source for the industrial production of nitrogen compounds is nitrogen.

$N_2 + 3H_2 = 2NH_3 + Q$

4.2.4 GENERAL CHARACTERIZATION OF HYDROGEN

There are two stable isotopes in nature:

^1H – protium 99,98 %

^2H- deuterium 0,02 %

Artificially obtained radioactive isotopes:

^3H - tritium (persistent)

^4H – unstable.

For the first time, hydrogen was studied by Cavendish and named "flammable air" in 1766.

In 1783 Lavoisier showed that when combustion gas forms water and included it in the list of chemical elements.

And Lavoisier in his writings found that combustion - is the interaction of oxygen with matter. It was the first time that the air analysis was carried out and found that air was a mixture of gases and identified its main components.

June 27, 1783 Lavoisier together with Laplace received water for the first time, joining oxygen and hydrogen. The quantities of gas and the mass of water received were determined. Passing a couple of received water through heated iron, which oxidizes it and as a result hydrogen is released, that is, it was found that the water is - H_2O.

Lavoisier is changing the technology of gunpowder and improves the quality of flames.

The content of hydrogen in the atmospheric air is $3{,}5 \cdot 10^{-6}$ % by weight. In the lithosphere and hydrosphere – 1 %, in water – 11,2 %.

Hydrogen - the most common element in space, in the form of plasma, is more than 70 % of the mass of the sun and stars.

The aggregate state of hydrogen is gas.

$T_{melt.} = -259{,}1\ ^{\circ}C$, $T_{boil.} = -252{,}6\ ^{\circ}C$.

Hydrogen forms compounds with almost all elements (other than noble metals).

4.2.5 SYNTHESIS OF HYDROGEN

In industry, hydrogen is produced by the interaction of hydrocarbons (mainly methane) with water vapor: $CH_4 + H_2O_{vapour} = CO + 3H_2$, and under laboratory conditions in the Kip apparatus (zinc reaction with diluted hydrochloric acid).

Hydrogen is one of the few elements that quickly found an important technical use only two decades after its discovery - France. Chemist Charles used hydrogen to fill the balloon.

Now hydrogen is used in the production of ammonia, methyl alcohol, in the synthesis of liquid fuels, for welding metals with hydrogen-oxygen flame, for the production of tungsten, molybdenum, rhenium from their oxides and fluorides, in the hydrogenation of fats and oils.

Hydrogen and its compounds are promising for the storage and transport of energy, the isotope of hydrogen - as fusion. Hydrogen is a promising fuel for internal combustion engines (no harmful emissions are generated when it is used).

The reaction of ammonia synthesis is exothermic, and its flow is accompanied by a decrease in entropy, so displacement of the equilibrium towards the formation of the final product contributes to increasing the pressure in the system and reducing the temperature.

The largest shift in equilibrium towards NH_3 formation and the most appropriate ratios of substances is achieved at relatively low temperatures and high pressures. Thus, at a temperature of 200 °C and a pressure of 100 MPa, the NH_3 yield is 98,29 %. However, the synthesis of ammonia, even at a relatively high temperature, for example, 700 °C, is extremely slow, which is completely unacceptable for industry. If, however, the temperature can be significantly increased to accelerate the reaction to the required level, then the equilibrium can be reached quickly, but the ammonia content in the system will be very small (the equilibrium will shift toward the source substances). The synthesis of ammonia is carried out in the presence of a catalyst that provides the necessary increase in the reaction speed without the simultaneous displacement of the equilibrium state. In this process, a platinum catalyst, a sponge iron catalyst, which contains promoters (Al_2O_3, K_2O and CaO) is used.

The increase in pressure causes the displacement of the equilibrium towards the formation of ammonia and the growth of the reaction rate due to an increase in the partial pressure of the original reagents.

In the industry, the catalytic process of ammonia synthesis is often carried out at temperatures of 400 ... 500 °C and a pressure of 30 ... 32 MPa. The hydrogen required for the preparation of the nitrogen-water mixture is obtained by converting natural gas into a mixture of water vapor and air [5]:

$CH_4 + 0,5O_2 = CO + 2H_2 + Q$;

$CH_4 + H_2O = CO + 3H_2 – Q$;

$CO + H_2O = CO_2 + H_2 – Q$;

$CH_4 + CO_2 = 2CO + 2H_2 – Q$.

Extremely numerous and diverse are complex compounds of metals in which the ligand is ammonia.

For ammonia, the reactions of substitution of hydrogen atoms to metal atoms are peculiar. They are carried out by heating metals in ammonia, for example: $2Al + 2NH_3 = 2AlN + 3H_2$.

Such reactions are a convenient method for obtaining nitrides of metals. Sometimes, instead of metals, you can use their oxides or halides, for example:

$3Cu_2O + 2NH_3 = 2Cu_3N + 3H_2O$;

$CrCl_3 + NH_3 = CrN + 3HCl$.

The course of these reactions is due to the volatility of water or halogen hydrodes at high temperatures.

Formation of amides is possible when passing dry ammonia over molten sodium, where ammonia plays the role of reducing agent:

$2Na + 2NH_3 = 2NaNH_2 + H_2$.

Amides are completely hydrolyzed in water:

$NaNH_2 + H_2O = NH_3 + NaOH$.

With the interaction of dry ammonia with molten lithium or with cautious heating of amides, imides are formed:

$NH_3 + 2Li = Li_2NH + H_2$;

$2LiNH_2 = Li_2NH + NH_3$.

The degree of oxidation of the nitrogen atom in the ammonia molecule and ammonium salts is -3. It is the lowest possible for this element, therefore ammonia belongs to the restorers. However, his restorative ability is expressed rather weakly. This is due to the fact that NH_3 and NH_4^+ are relatively stable. Thus, ammonia does not burn in the air, does not oxidize in solutions with many oxidants, for example, compounds of chromium (VI), but in the environment of pure oxygen burns with a yellow flame:

$4NH_3 + 3O_2 = 2N_2 + 6H_2O$,

and in the presence of catalysts the process takes place according to the reaction:

$4NH_3 + 5O_2 = 4NO + 6H_2O$.

Strong oxidizers are capable of oxidizing ammonia in its solutions. For example, it reacts quickly with halogens (Cl_2, Br_2):

$2NH_3 + 3Cl_2 = N_2 + 6HCl$.

Ammonia is capable of reducing oxides, for example:

$2NH_3 + 3CuO = 3Cu + N_2 + 3H_2O$.

Ammonium salts are stable under normal conditions, but during heating they decompose. The nature of the products, as well as the peculiarities of the reactions, are determined by the properties of the acid that forms the salt.

If the anion of acid has a strong oxidative ability, then the oxidation of ammonium nitrogen salt occurs, for example:

$NH_4NO_3 \xrightarrow{t} N_2O + 2H_2O$;

$NH_4NO_2 \xrightarrow{t} N_2 + 2H_2O$;

$(NH_4)_2Cr_2O_7 \xrightarrow{t} Cr_2O_3 + N_2 + 4H_2O$.

Hydrazine. Hydrazine N_2H_4 is extracted by cautionary oxidation of ammonia in aqueous solution of sodium hypochlorite:

$2NH_3 + NaOCl = N_2H_4 + NaCl + H_2O$.

Under normal conditions, hydrazine is a colorless, toxic liquid that evaporates easily ($T_{boil.}$ = 113,5 °C), with ammonia resembling a smell, with high dielectric permeability.

The degree of oxidation of the hydrosynium - 2, it can be both a reducing agent and an oxidizer; is a strong reducing agent, especially in an alkaline environment, the main product of its oxidation is free nitrogen. Hydrazine is a stronger reducing agent than ammonia, due to less stability.

Oxidized not only by oxygen, but by ammonia as well as by air:

$N_2H_4 + O_2 = N_2 + 2H_2O$;

$5N_2H_4 + 4\ KMnO_4 + 6\ H_2SO_4 = 5N_2 + 4\ MnSO_4 + 2K_2SO_4 + 16\ H_2O$.

Hydrazine in aqueous solutions can easily restore ions of non-active metals from their salts to the formation of metallic mirrors:

$4AgNO_3 + N_2H_4 = 4Ag + N_2 + 4\ HNO_3$.

Hydrazine disproportionates during heating:

$3N_2H_4 \xrightarrow{t} N_2 + 4NH_3$.

Hydroxylamine NH_2OH. Degree of oxidation -1, characteristic of reducing properties, products of oxidation are free nitrogen or N_2O:

$2NH_2OH + I_2 + 2KOH = N_2 + 2KI + 4H_2O$.

Hydroxylamine disproportionates during heating:

$3NH_2OH \xrightarrow{t} N_2 + NH_3 + 3H_2O$.

Nitrous hydrochloric acid - HN_3 is a strong oxidant, formed by oxidation of hydrazine with nitrous acid. In anhydrous state it is very unstable and easily explodes when heated or struck [6]:

$N_2H_4 + HNO_2 = HN_3 + 2H_2O$.

A mixture of nitrogen-water-borne and concentrated hydrochloric acids during heating can dissolve even gold and platinum, that is behaves like a royal vodka. Extreme oxidation activity of this mixture is caused by the reaction of oxidation of hydrochloric acid with nitrogen-containing water and the release of atomic chlorine due to this:

$3HCl + HN_3 = Cl_2 + NH_4Cl + N_2$.

Lead azide $Pb (N_3)_2$ is used in detonators (substances whose explosion causes an instantaneous decomposition of other explosives).

Nitrogen (I) oxide. Nitrogen (I) oxide N_2O is extracted by thermal decomposition (250 °C) of ammonium nitrate:

$NH_4NO_3 \xrightarrow{t} N_2O + 2H_2O$

or weak heating of sulfamic acid NH_2SO_2OH with nitric acid HNO_3:

$HNO_3 + NH_2SO_2OH = N_2O + H_2SO_4 + H_2O$.

Under normal conditions, nitrogen (I) oxide N_2O is a colorless gas ($T_{melt.}$ = - 91,0 °C, $T_{boil.}$ = - 88,5 °C) with a weak, pleasant odor. He has narcotic properties that can relieve pain. This was based on the use of its mixtures with air for narcosis during surgical operations. Sometimes it is called a merry gas.

Nitrogen (I) oxide in very small quantities is always contained in the air ($5 \cdot 10^{-5}$ % vol.). During cooling of its saturated solutions a crystalline hydrate $N_2O \cdot 6H_2O$ is formed, which in the case of heating decomposes on the starting materials (a method of obtaining pure N_2O). However, stable compounds nitric oxide (I) N_2O does not form with water and therefore belongs to non-soluble oxides. At a temperature of 500 °C it decomposes into simple substances. That is why it supports the burning of carbon-containing materials (the glinting flint flashes in the environment of this oxide, because it decomposes, it gives more oxygen than it contains in the air).

Nitrogen (I) oxide is able to oxidize metals, phosphorus, carbon, sulfur, organic compounds, recovering to free nitrogen:

$Cu + N_2O = CuO + N_2$.

Mixtures of N_2O with hydrogen or ammonia explode during heating:

$H_2 + N_2O = N_2 + H_2O$;

$2NH_3 + 3 N_2O = 4 N_2 + 3 H_2O$.

Nitrogen(II) oxide. Effective reducing agent, non-sulfur oxide.

$N_2 + O_2 = 2NO$ (it is formed during lightning discharges and during catalytic oxidation of ammonia: $4NH_3 + O_2 = 4NO + 6\ H_2O$).

Nitrogen(II) oxide quickly oxidized in the air:

$2NO + O_2 = 2NO_2$;

$2NO + Cl_2 = 2NOCl$.

NO oxidizes to nitric acid with strong oxidants:

$5NO + 3\ KMnO_4 + 6\ H_2SO_4 = 5\ HNO_3 + 3MnSO_4 + 3KHSO_4 + 2H_2O$;

$2NO + HClO_3 + H_2O = 2\ HNO_3 + HCl$.

It can also be an oxidizer (carbon, phosphorus, sulfur, metals can also be oxidized):

$2H_2 + 2\ NO \xrightarrow{t} N_2 + 2\ H_2O$;

$2NO + H_2SO_3 + 3\ H_2O = 2NH_2OH + 3\ H_2SO_4$.

Nitrogen(II) oxide and nitrous acid.

$NO + NO_2 = N_2O_3$;

$N_2O_3 + H_2O = 2\ HNO_2$;

$NO + NO_2 + H_2O = 2\ HNO_2$.

Disproportionation reaction with HNO_2:

$3HNO_2 = HNO_3 + 2NO + H_2O$.

HNO_2 has the characteristic properties of an oxidant:

$2HI + 2HNO_2 = I_2 + 2NO + 2H_2O$;

$H_2S + 2HNO_2 = S + 2NO + 2H_2O$.

Nitrogen (IV) oxide.

$2NO+O_2 = 2NO_2$.

Disproportionation reaction with NO_2:

$2NO_2 + H_2O = HNO_3 + HNO_2$;

$2NO_2 + KOH = KNO_3 + KNO_2 +H_2O$;

$4NO_2 +O_2 +2\ H_2O = 4HNO_3$.

NO is a strong oxidant:

$2S+2NO_2 \xrightarrow{t} 2SO_2 + N_2$;

$8P + 10NO_2 \xrightarrow{t} 4P_2O_5 + 5N_2$;

$2C + 2NO_2 \xrightarrow{t} 2CO_2 + N_2$.

NO_2 can be as a restorer:

$2NO_2 + O_3 = N_2O_5 + O_2$.

Nitrogen (V) oxide.

$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3$.

Nitric acid is a colorless, oily liquid that smoke in the air. Its density is $\rho = 1{,}52$ g / cm^3, the freezing point is -41°C and boiling 86 °C (Table 4.1).

It is a strong oxidizer, most metals oxidize it to oxides, and then to the corresponding salts, dissolving in acid.

The iron oxidizes with dilute nitric acid, and in the concentrated it passes through the formation of a thin oxide film.

Table 4.1 - Sorts of nitric acid

Sort	Dissolved acid, % HNO_3	Concentrated, % HNO_3
I	≥ 55	≥ 98
II	≥ 47	≥ 97
III	≥ 45	–

About 40 % of the production of nitric acid is spent on the production of mineral fertilizers. It is used in technology of explosives, rocket fuels, synthetic dyes, nitrates.

Traditionally, raw materials for nitric acid are ammonia, air and water. Direct synthesis of nitrogen oxide (II) from components of air in electric arc plasma torches is of considerable interest, but very high energy consumption factors (specific energy consumption) are inhibited by the industrial application of this known method of fixing atmospheric nitrogen.

Synthesis of nitric acid:

1. stage - catalytic oxidation of ammonia:

$4NH_3 + O_2 = 4NO + 6 H_2O$;

2. stage - oxidation of nitrogen (II) oxide:

$2NO + O_2 = 2NO_2$;

3. Stage - sorption of nitrogen (II) oxide with water:

$2NO_2 + H_2O = HNO_3 + HNO_2$;

$3HNO_2 = HNO_3 + 2NO + H_2O$.

4.2.6 MAIN METHODS OF UTILIZATION NO

1. Oxidation with ozone

– in gas phase:

$NO + O_3 = NO_2 + O_2$;

– in liquid phase:

$2NO + O_3 + H_2O = 2 HNO_3$.

2. Oxidation with strong oxidants

$3H_2O_2 + 2NO = 2HNO_3 + 2H_2O$;

$KMnO_4 + NO = KNO_3 + MnO_2$;

$K_2Cr_2O_7 + 2NO + 3H_2O = 2KNO_3 + 2Cr(OH)_3$.

3. Utilization (discharging) with ammonia

$4NH_3 + NO = 5N_2 + 6H_2O$.

4.3 CHEMICAL SUBSTANCES AND REACTIONS IN THE PRODUCTION OF PHOSPHORUS PRODUCTS

Phosphorus had discovered in 1669. Phosphorus is the one bearing the light. Content in the earth's crust – 0,093 % by mass.

Most important minerals:

Phosphorite - $Ca_5(PO_4)_3(OH, CO_3)$;

Apatite (fluorapatite) - $Ca_5(PO_4)_3F(Ca_{10}(PO_4)_6F_2)$.

Biological role - is a part of DNA; in the human body about 1,5 kg of phosphorus and it is distributed as follows:

muscles - 0,3 - 0,85 %;

bones – 6,7 -7,1 %;

blood - 345 mg / dm^3.

4.3.1 MODIFICATIONS OF PHOSPHORUS

The white phosphorus α-modification has a cubic lattice, $\rho = 1{,}83$ g / cm^3.

$T_{melt.} = 44{,}14$ °C, $T_{boil.} = 257$ °C.

White phosphorus β-modification has a rhombic grating, $\rho = 1{,}88$ g / cm^3, is formed from α-modification at T = 77,8 °C.

In the air, white phosphorus quickly oxidizes and lights up, forming a white thick smoke of phosphoric anhydride:

$4P + 5O_2 = 2P_2O_5$.

When heated to 270 ... 300 °C, without the access of air, white phosphorus becomes a more stable modification - red phosphorus, which at the normal temperature does not light up.

Chlorine and sulfur compounds of phosphorus are used to produce various organophosphorus compounds. Red phosphorus is used in the production of matches. A mixture of phosphorus with glue crushed glass is applied to the lateral surfaces of the matchboxes. The weight on the head of the match is a mixture of sulfuric antimony, potassium chlorate (chlorophyll salt $KClO_3$), and peroxide plum. When rubbing a match's head on the lateral surface of the matchbox there is a local temperature increase that causes a reaction between phosphorus and the composition deposited on the head in a rich oxygen, so the match is ignited.

In molten form, phosphorus causes strong burns, in combination with strong oxidants, forms flammable and explosive mixtures. To this item are fables about green lights in cemeteries and swamps. In fact, it oxidizes phosphorous hydrogen RN_3, which is formed in the process of decay of tissues without access to oxygen.

Alchemist Zhanjard in 1783, when trying to dissolve phosphorus in the meadow, received a smelter of gas "phosphine", which flares up when in contact with air:

$P + 3KOH + 3H_2O \rightarrow PH_3\uparrow + 3KH_2PO_2$ (hypophosphite);

$3Mg + 2P \rightarrow Mg_3P_2$ (phosphide).

If the test tube from Mg_3P_2 is thrown into water, then gas phosphorus will light above its surface.

PH_3 - phosphine (phosphorus hydride) is a colorless poison gas with a smell of stale fish, 1,2 times heavier than air, soluble in water, benzene, and carbon monoxide CS_2. The purified gas flares only at T = 150 °C, and the technical product ignites due to the presence of diphosphines P_2N_4 [6].

4.3.2 CHEMICAL PROPERTIES OF PHOSPHORUS

Synthesis:

$Ca_3(PO_4)_2 + 5C + 2SiO_2 = 2P + 5CO + 3CaO{\cdot}2SiO_2$ (the reaction is possible at high temperatures)

Interaction:

$4P + 3O_{2(lack)} = 2P_2O_3$;

$4P + 5O_{2(excess)} = 2P_2O_5$;

$2P + 3Cl_{2(lack)} = 2PCl_3$;

$2P + 5Cl_{2(excess)} = 2PCl_5$;

$2P + 3S_{(lack)} = P_2S_3$;

$2P + 5S_{2(excess)} = 2P_2S_5$;

$P + 5HNO_{3(conc.)} = H_3PO_4 + 5NO_2 + H_2O$;

$4P + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2$

4.3.3 OXIDATION GRADES OF PHOSPHORUS

+5 – P_2O_5, H_3PO_4, Na_3PO_4;

+3 – P_2O_3, H_3PO_3, Na_2HPO_3;

+ 1 – H_3PO_2, NaH_2PO_2;

0 – P_4;

-2 – P_2H_4;

-3 – PH_3, Mg_3P_2.

Phosphate forms in acidic environment:

$H_3P^{+5}O_4 \rightarrow H_4P^{+4}{}_2O_6 \rightarrow H_3P^{+3}O_3 \rightarrow H_3P^{+1}O_2 \rightarrow P^0 \rightarrow H^{-2}{}_2P_4 \rightarrow P^{-3}H_3$

Phosphate forms in alkaline environment:

$PO_4^{3-} \rightarrow HPO_3^{2-} \rightarrow H_2PO_2^{1-} \rightarrow P^0 \rightarrow PH_3$

Phosphides, phosphine (oxidation grade -3)

$4P + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2$;

$3Mg + 2P = Mg_3P_2$;

$Mg_3P_2 + 6H_2O = 3Mg(OH)_2 + 2PH_3$;

$3CaO \cdot P_2O_5 + 8Mg = 3CaO + 5MgO + Mg_3P_2$ (The resulting mixture is used to illuminate buoys when marking channels in a storm).

Me_xP (Me - Mn , Re, Cr, Mo).

Interaction:

$2P + 3H_2 = 2PH_3$;

$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$;

$3P_2H_4 = 2PH_3 + P_4H_2 + 2H_2$;

$Ca_3P_2 + 6HCl = 2PH_3 + 3CaCl_2$;

$Ca_3P_2 + 6H_2O = 2PH_3 + 3Ca(OH)_2$.

4.3.4 PHOSPHORUS ACIDS

Phosphate acid - is transparent crystals, strongly hygroscopic, on wet air spill in the form of a syrupy liquid. Concentration is 70 ... 85 %, ρ = 1,7 g / cm^3. At a temperature above 213 °C, it loses water and passes into pyrophosphate acid (Table 4.2).

Table 4.2 - Phosphoric Acids

Acid	Name
H_3PO_2	phosphoric acid
H_3PO_3	phosphorus
HPO_3	metaphosphate
H_3PO_4	phosphate
$H_4P_2O_7$	pyrophosphate

Formation of phosphorus-containing acids:

$P_4O_6 + 6H_2O = 4H_3PO_3$;

$P_4O_{10} + 2H_2O = 4HPO_3$;

$P_4O_{10} + 4H_2O = 2H_4P_2O_7$;

$P_4O_{10} + 6 H_2O = 4H_3PO_4$.

Metaphosphate acid: HPO3 (ice):

Transparent ice bits, which need to be stored in a jar, filled with paraffin; poisonous Metaphosphate acid is slowly dissolved in the solution, and when it is boiled, it rapidly converts to phosphate, joining water (Table 4.3):

$HPO_3 + H_2O = H_3PO_4$.

Pyrophosphate acid of $H_2P_2O_7$ in its pure form is a mild glassy mass. In the solution in the cold slowly, and when boiling the solution quickly decomposes into phosphate. When burned above 700 °C it goes into metaphosphate:

$H_4P_2O_7 = 2HPO_3 + H_2O$.

Phosphoric acid:

$2P_4$+3Ba$(OH)_2$ +6H_2O=2PH_3 +3Ba$(H_2PO_2)_2$;

Ba$(H_2PO_2)_2$ + H_2SO_4 = 2H_3PO_2 + $BaSO_4$.

2NaH_2PO_2 + $NiCl_2$ + 2H_2O= 2H_3PO_3 + Ni + H_2 + 2NaCl.

H_3PO_2 + 2Zn + 4HCl = PH_3 + 2$ZnCl_2$+2H_2O.

Characteristic disproportionation reaction of phosphoric acid:

3H_3PO_2 = PH_3 + 2H_3PO_3.

Table 4.3 - Qualitative analysis for determining the type of phosphoric acid

Acid	Effect on the protein	Qualitative reaction
HPO_3	Destruction	HPO_3+$AgNO_3$ = $AgPO_3$+HNO_3 White precipitate
H_3PO_4	No action	H_3PO_4+ 3$AgNO_3$ = Ag_3PO_4+3HNO_3 Yellow precipitate
$H_4P_2O_7$	No action	$H_4P_2O_7$+ 4$AgNO_3$ = $Ag_4P_2O_7$+4HNO_3 White precipitate

Phosphorus (III) oxide, phosphorus acid

Synthesis:

P_2O_3 + 3H_2O = 2H_3PO_3;

PCl_3 + 3H_2O= H_3PO_3 + 3HCl;

P_2O_3 + 2NaOH + H_2O = 2NaH_2PO_3.

Interaction:

H_3PO_3 + $HgCl_2$ + H_2O=H_3PO_4 + Hg+2HCl;

H_3PO_3+3Zn+ 6HCl=PH_3 + 3$ZnCl_2$ + 3H_2O;

4H_3PO_3 = PH_3 + 3H_3PO_4.

4.3.5 METHODS OF SYNTHESIS PHOSPHORIC ACID

In order to obtain phosphatic acid, which serves as a raw material for the production of double superphosphate, two methods are used in the industry - extraction and thermal (Table 4.4).

1. Thermal method:

$4P + 5O_2 = 2P_2O_5$;

$P_2O_5 + 3H_2O = 2\ H_3PO_4$.

The advantage is possibility to get phosphate acid of any concentration, even 100%.

2. Extraction method:

The extraction method is based on the principle that is widely used in chemical technology - strong acid displaces the less acidic of its salt, which is part of the natural phosphates: apatite or phosphorite, is more economical than the thermal method.

Table 4.4 - Characteristics of commercial phosphate acid

Substance	Mass fraction, %	
	Brand V	**Brand G**
Phosphate acid H_3PO_4, not less	72	72
Sulphates (SO_4^{2-}), not more	2.5	5,5
Ferum (Fe), not more	0,8	not normed
Fluorine compounds in terms of fluorine (F), not more	0,5	not normed
Arsen (As), not more	0,0005	0,004
Lead (Pb), not more	0,01	not normed
Ігізутвув particles, not more	0,1	5

In an extractive way, crushed phosphate (for example, apatite concentrate) is treated with 75 % sulfate acid with excess:

$Ca_5F(PO_4)_3 + 5H_2SO_4 + 5nH_2O \rightarrow 3H_3PO_4 + 5(CaSO_4 \cdot nH_2O) + HF$,

where n = 2; 0,5 or 1.

METHODS OF ORGANIZATION OF THE EXTRACTIVE METHOD FOR THE PRODUCTION OF PHOSPHATIC ACID

- Dihydrate process (to obtain calcium sulfate dihydrate)

C (H_3PO_4) = 30 ... 32 %, $CaSO_4 \cdot 2H_2O$

Disadvantages:

- low concentration of production acid;
- low yield P_2O_5;
- high costs (due to evaporation);
- high amount of waste gypsum $CaSO_4 \cdot 2H_2O$
- Semihydrate process (to obtain calcium sulfate semi-hydrate)

C (H_3PO_4) = 40 ... 50 %, $CaSO_4 \cdot 0,5H_2O$

- Semi-hydrated-dihydrate process

C (H_3PO_4) = 37 ... 45 %, $CaSO_4 \cdot 0.5H_2O$

Advantages:

+ degree of conversion P_2O_5 - 98,5%;

+ obtaining pure semi-finished product - gypsum $CaSO_4 \cdot 2H_2O$

- Dihydrate-semi-grained process

C (H_3PO_4) = 35 %, $CaSO_4 \cdot 2H_2O$.

In the dihydrate method, fluorine is released into the gas phase in the form of SiF_4 and HF, which is 50 % of its content in the raw material. In the solution of H_3PO_4 - fluoride is in the form of H_2SiF_6. In phosphogypsum - as undiluted fluorapatite and insoluble silicium fluoride.

4.3.6 WAYS OF UTILIZATION OF MANUFACTURE WASTE OF PHOSPHORIC ACID

The main waste of phosphate acid production is Phosphogypsum $CaSO_4 \cdot 2H_2O$, which is used in the production of building materials, high strength of gypsum binder, cement clinker, sulfate acid, etc.

The most toxic component of phosphate raw materials are fluorine compounds. In natural phosphates, fluorine is a part of the highly soluble compounds, but when processed, it is converted into readily soluble forms. Fluorine compounds have a toxic effect on flora and fauna, but they serve as valuable raw materials for organic synthesis, in the production of glass and nonferrous metallurgy. The content of fluorine in kg (in terms of 1t P_2O_5) in the extractive phosphatic acid depends on the method of its production.

It is expedient to use the waste gas heat as an energy source for process equipment or for obtaining a water vapor. The disadvantage of this technique is the need for special heat exchange equipment, resistant to aggressive environment of waste gases.

For 1 ton of thermal H_3PO_4 8 ... 11 tons of slag are used, which is used for the manufacture of parts of chemical equipment, tiles, bricks, heat-insulating materials.

The ferritic phosphide alloy FeP, FeP_2 (ferrophosphorus) contains 15 ... 28 % of phosphorus, 63 ... 87 % of the ferrum and a small amount of carbon and silicon. It is used in the metallurgy industry as an additive in foundry production. At present, in the development stage, there is a method for the deposition of ferrophosphorus followed by sintering with Na_2SO_4 to produce phosphorus salts.

In the production of thermal phosphatic acid, slimes with a 30 % moisture content of 0,1-0,15 tons are formed, which is a suspension of dust with a phosphorus content of up to 65 %. To remove valuable phosphorus, this sludge is returned to the electric furnace and evaporated with hot stove gas with subsequent combustion and the production of H_3PO_4.

4.4 MANUFACTURING OF MINERAL FERTILIZERS

Mineral fertilizers are substances that contain chemical elements that are necessary for the normal growth and development of plants. The plant consists of about 60 chemical elements: Carbon, Oxygen, Hydrogen, Nitrogen, Phosphorus, Potassium, Sulfur, Ferum, Calcium, Mangan, Boron, Zinc, Magnesium, Kuprom, Molybdenum, which are involved in the metabolism. Every year, when harvesting and as a result of erosion from the soil, nutrients that are needed for plants are removed. The soil is impoverished, which leads to lower yields. Sources of substances necessary for plant nutrition are the air and the liquid phase of the soil. Carbon in the form of carbon dioxide plants are derived from the air during photosynthesis. Oxygen is also consumed from the air and, in addition, like hydrogen, comes from the soil in the water. Other elements of the plant are obtained from the soil in the form of mineral salts, which are soluble in water or weak organic acids.

Among them, the greatest importance for plant nutrition are Nitrogen, Phosphorus and Potassium. Very important for each plant organism is Nitrogen. Suffice it to say that Nitrogen is a vegetable protein, where its content is 15 ... 19 %. Nitrogen is also required in the synthesis of vitamins, enzymes and other physiologically active substances of the plant. If the plant does not receive enough nitrogens, then its growth is delayed, and the leaves are prematurely yellow.

Phosphorus is part of the enzyme and phosphatide of the protoplasm and plays an important role in the processes of cell division and the transfer of hereditary properties. With a lack of Phosphorus, the fruits slowly ripen, they accumulate less sugar and starch.

Potassium compounds regulate the function of enzymes, stimulate metabolism and plant growth. In addition, Potassium regulates the water regime of plants and contributes to their resistance to drought and frosts. It is this element that blocks the entry into plants of radioactive cesium and heavy metals. When introducing potassium fertilizers the yield of agricultural crops is significantly increased, and at the same time the quality of products improves: sugar content in beet root, starch in potatoes.

Fertilizers containing Nitrogene, Phosphorus, and Potassium compounds are called macrofluids.

Consumption of plants B, S, Mn, Zn, Mo, Co and other elements is relatively small. However, for example, Sulfur, along with Nitrogen, is part of the protein. Mangan promotes photosynthesis and the formation of chlorophyll in green parts of plants. Bohr enhances carbohydrate and protein metabolism, enhances the resistance of plants to diseases. Affect the metabolism of plants in the plants are also Molybdenum and Zinc. The crops of forage crops depend on the presence in the soil of Cobalt. All of these elements are called trace elements, may be part of microfertilizers or are used as additives to macrofuel and to be incorporated into the soil together with them.

The first fertilizers were various organic remains and ashes from plant burning. Subsequently, the nutritional properties of some natural mineral salts were detected. However, not all of these salts were well soluble in water and weak organic acids in the soil. Therefore, there was a need for the chemical processing of natural compounds in order to obtain from them easier to digest plants. So there was an industrial production of mineral fertilizers. Intensive development began in the XIX century. In the second decade of the 20th century, when the problem of fixing (binding) atmospheric nitrogen by the ammonia method was solved, nitrogen fertilizers were added to the range of mineral fertilizers, the raw material for which atmospheric nitrogen is produced.

It should be noted that not all substances that contain chemical elements necessary for plants can be used as fertilizers for agricultural production. This requires that the product be as cheap as possible, made from cheap and affordable raw materials in a relatively simple way, well kept and transported to it was convenient to bring it into the soil and, most importantly, to be well absorbed by plants.

4.4.1 CLASSIFICATION OF FERTILIZERS

1. By origin [5]:
    1.1 Natural;
    1.2 Synthetic.
2. By chemical composition:
    2.1 Inorganic (mineral) - phosphate and bone meal, potassium ores;
    2.2 Organic - manure, peat;
    2.3 Organo-mineral - brown coal, mixtures of fertilizers.
3. For agrochemical values:
    3.1 Direct - are assimilated directly by plants;
    3.2 Indirect - improve the physical, chemical and biological properties of soils.
4. For a nutrient:

Nitric, phosphate, potassium, nitrogen-phosphate, nitric-potassium phosphate, manganese, copper, zinc-containing.

5. By the number of main nutritional elements:
    5.1 Simple - contain one nutrient element;
    5.2 Complex - Containing two or more nutrients;
        5.2.1 Complex (chemical compounds) such as: $NH_4H_2PO_4$, $(NH_4)_2HPO_4$,
        5.2.2 Mixed (mechanical mixture of various substances).
6. By solubility:
    6.1 Water soluble - nitrogen, potassium;
    6.2 Acid soluble;
    6.3 Citrate-soluble;

6.4 Lemon soluble - some phosphate and microfertilizers;

6.5 Conditionally insoluble (prolonged action).

7. By aggregate state:

7.1 Granulated, powdered;

7.2 Liquid fertilizers;

7.3 Suspended fertilizers.

8. By the nature of assimilation by plants:

8.1 Physiologically sour, in which cation is assimilated by plants, ie soil pH at the same time falling ($(NH_4)_2SO_4$, KCl, K_2SO_4);

8.2 Physiologically alkaline, when the anion is absorbed, and the pH of the soil increases ($NaNO_3$);

8.3. Physiologically neutral, which does not change the pH of the soil, ie digested both cation and fertilizer anion (NH_4NO_3).

Quite commonly used simple fertilizers are ammonium sulfate, phosphorous flour and simple superphosphate. Other fertilizers - or more concentrated or complex (Tables 4.5 - 4.7). Issue triple complex fertilizers (nitrogen-phosphoric-potassium) with the ratio of nutrients (N : P_2O_5 : K_2O) 1 : 1 : 1, 1 : 1,5 : 1, 1 : 1,5 : 1,5, etc., and double, for example , nitrogen-phosphorous 1 : 4,1; phosphoric-potassium 1 : 1,1 [5].

Almost all mineral fertilizers (except phosphorous flour) are produced in granular form with a granule diameter of not more than 4 mm, so that when applied to the soil, it was possible to use the agricultural machinery used for sowing seeds.

Table 4.5 - Nutrient content in some nitrogen fertilizers [5]

Fertilizer	Chemical formula	Contents N, % mass.
Ammonium nitrate	NH_4NO_3	34...35
Carbamide	$(NH_2)_2CO$	46...46,3
Ammonium sulfate	$(NH_4)_2SO_4$	21

Table 4.6 - The content of nutrients in some phosphate fertilizers [5]

Fertilizer	Chemical formula	Contents P_2O_5, % mass.
Phosphorous flour	A mixture of minerals	20…29
Simple superphosphate	$Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4 \cdot 0{,}5 H_2O$	20
Double superphosphate	$Ca(H_2PO_4) \cdot 2H_2O$	43…49

Table 4.7 - The content of nutrients in some complex fertilizers [5]

Fertilizer	Chemical formula	Contents of nutrient, % mass.		
		N	P_2O_5	K_2O
Potassium chloride	KCl	–	–	55,2…55,5
Ammofos	$NH_2H_2PO_4+(NH_4)_2HPO_4$	10…12	42…52	–
Nitrofocus	A mixture of substances	11	10	11
Nitroamofosca	A mixture of substances	13…17	17…19	17…19

4.4.2 MANUFACTURE OF NITROGEN FERTILIZERS

Nitrogenous fertilizers are divided into:

Ammonia - contain nitrogen in the form of cation NH_4^+, ($(NH_4)_2SO_4$, liquefied ammonia, 20 ... 25 % aqueous ammonia solution NH_4OH));

Nitrate - contain nitrogen in the form of anion NO_3^- (calcium nitrate $Ca(NO_3)_2$, sodium nitrate $NaNO_3$);

Ammonium nitrate - (ammonium nitrate NH_4NO_3);

Amides - contain nitrogen in the form of groups NH_2- or -CN_2 (carbamide $(NH_2)_2CO$, calcium cyanamide $CaCN_2$).

All nitrogen fertilizers are water soluble. In Ukraine, in the largest volumes, ammonium nitrate and urea are produced.

4.4.3 CHEMISTRY OF THE PROCESS OF SYNTHESIS AMMONIUM SILICA

Ammonium nitrate NH_4NO_3 (ammonium nitrate) contains 34 ... 35 % nitrogen, is well absorbed by plants and is a universal fertilizer suitable for all soils and crops. However, a significant disadvantage of ammonium nitrate is its hygroscopicity (the ability to absorb moisture from the environment). Ammonium nitrate can exist, depending on temperature and humidity, in several crystalline forms. When you switch from one form to another, its volume changes. Due to the hygroscopicity and the ability to change its volume of ammonium nitrate, it quickly clumps to the formation of large lumps that need to be crushed before introduction into the soil. For grinding and sifting of ammonium nitrate, about 60 % of the amount of production costs of this fertilizer is consumed. When heated, the ammonium nitrate is decomposed by the reactions:

$NH_4NO_3 \rightarrow NH_3 + HNO_3 - Q;$

$NH_4NO_3 \rightarrow N_2O + 2H_2O + Q.$

Dry powder salt can explode from friction or detonation by reaction: $NH_4NO_3 \rightarrow N_2 + 0{,}5O_2 + 2H_2O + Q$

Admixture of ammonium nitrate reduces its granulation, powdery low-hygroscopic applications (lime, gypsum, bone meal), fusion with less hygroscopic salts (calcium phosphate).

Ammonium nitrate is used in large quantities for the production of explosives.

Ammonium nitrate is produced from synthetic ammonia and nitric acid, which is also produced from ammonia in all industrialized countries. The essence of the production of ammonium nitrate is the interaction of gaseous ammonia and dilute nitric acid, resulting in the formation of a solution of ammonium nitrate:

$NH_3 + HNO_3 \rightarrow NH_4NO_3 + 144{,}9$ kJ/mole.

The velocity of this virtually irreversible chemical reaction in the gas-liquid system is very high, therefore, in general, the heterogeneous process is limited by the rate of delivery of reagents and occurs in the diffusion region. The reaction produces a large amount of heat, which in a special reactor design is used to evaporate water and concentration of the produced fertilizer.

Nitrogen fertilizers are the most effective among all others. More than 60 % of the total increase in yield is obtained precisely due to the effect of nitrogen fertilizers. The lowest cost of nitrogene from all nitrogen fertilizers is liquid synthetic ammonia. If conditionally accept the cost of 1 t Nitrogen in ammonia for 100, the cost of 1 t Nitrogen in ammonia will be 106, in ammonium nitrate - 150, in carbamide - 160, in ammonium sulphate - 200, in calcium saltpetre - 280, in cyanamide calcium - 350 and in sodium nitrate - 480. Thus, the cost of Nitrogen in liquid nitrogen fertilizers is the lowest. In addition, the introduction of liquid fertilizers is better mechanized. However, for storage of liquid fertilizers, special containers and tanks are required, as well as machines for applying these fertilizers to the soil. In addition, in ammonia water, the concentration of Nitrogen is low, and consequently, the costs of its transportation are significant, so the production of such fertilizers should be organized only in areas of its direct use. In spite of these shortcomings, in recent years more and more attention has been paid to the production and application of liquid nitrogen fertilizers in agriculture [5].

The cost of urea and ammonium nitrate is almost the same. In the production of both of these fertilizers, the cost of raw materials in cost accounts for almost 80 % of all costs. Carbamide production (compared to ammonium nitrate) requires twice as much electricity, although it is almost 3,5 times more steam. Given the availability of cheap water vapor, urea can be manufactured at significantly lower cost than ammonium nitrate. Therefore, the volumes of production of this more concentrated fertilizer, which, in addition, has the best physico-chemical properties compared to ammonium nitrate, increases every year. Comparing ammonium nitrate and urea, it is not enough to take into account only the cost price. It should be borne in mind that the cost of transporting, storing and introducing carbamide into soil is much lower than that of ammonium nitrate. Therefore, the production of urea has undeniable economic advantages over the production of ammonium nitrate.

The main types of nitrogen fertilizers - ammonium nitrate, urea, ammonium sulfate - belong to physiologically acid fertilizers. Therefore, due to their introduction, naturally neutral soils are acidified, and sour - they become even more acidic and lose fertility. The soil reaction can be controlled by liming or physiologically alkaline fertilizers, in particular calcium, sodium nitrate or calcium cyanamide. However, the cost of these fertilizers is high, and the volume of production in Ukraine is insufficient.

4.4.4 CHEMISTRY OF SYNTHESIS OF NITROGEN FERTILIZERS

$Na_2CO_3 + NO_2 + NO \rightarrow 2NaNO_2 + CO_2$;

$Na_2CO_3 + 2NO_2 \rightarrow NaNO_2 + NaNO_3 + CO_2$;

$3NaNO_2 + 2HNO_3 \rightarrow 3NaNO_3 + 2NO + H_2O$;

$NaNO_3 + KCl \rightarrow KNO_3 + NaCl$;

$Ca(OH)_2 + NO + NO_2 \rightarrow Ca(NO_2)_2 + H_2O$;

$2\ Ca(OH)_2 + 4NO_2 \rightarrow Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O$;

$3Ca(NO_2)_2 + 4\ HNO_3 \rightarrow 3Ca(NO_3)_2 + 2H_2O + 4NO$;

$Ca_5(PO_4)_3F + 10HNO_3 \rightarrow 3H_3PO_4 + 5Ca(NO_3)_2 + HF$.

Synthesis of carbamide

1. $2\ NH_3 + CO_2 = NH_4COONH_2 + Q$;

2. $NH_4COONH_2 = (NH_2)_2CO + H_2O$;

$(NH_2)_2CO + 0{,}5\ O_2 + H_2O = (NH_4)_2CO_3$.

4.4.5 MANUFACTURING OF PHOSPHATIC FERTILIZERS

The main raw material for the production of phosphate fertilizers is natural ores: phosphates and apatites.

Apatity - minerals of volcanic origin. In apatites, Phosphorus is contained in the form of minerals with the general formula $Ca_5X(PO_4)_3$, where X is Cl, OH or F.

The most common in nature is fluorapatite $Ca_5F(PO_4)_3$. The chemically pure fluorapatite contains 42,2 % P_2O_5, 55,6 % CaO and 3,8 % F. Natural mineral due to the presence of various impurities contains an average of 40,7 % P_2O_5 and 2,8 ... 3,4 % F In addition to fluorapatite, apatite ore includes other minerals, among which the nepheline $3Na_2O \cdot K_2O \cdot 4Al_2O_3 \cdot 9SiO_2$ predominates.

Phosphorite - ore of sedimentary origin. They were formed as a result of coexistence in the seas and oceans of apatite, silica of oxide, iron and aluminum hydroxides, calcium and magnesium, carbonates and products of destruction of rocks. This explains the difference in structure and mineral composition of apatite and phosphorites. In phosphates Phosphorus is contained in the form of calcium phosphate $Ca_3(PO_4)_2$, which is not soluble in water and poorly soluble in soil acids. Therefore Phosphorus, which is a part of calcium phosphate, is difficult to digest by plants. However, under the influence of mineral acids (H_2SO_4, H_3PO_4, HNO_3), calcium salt is converted into acid, in which one or two atoms of Hydrogen orthophosphoric acid are replaced by Calcium ($Ca(H_2PO_4)_2$ and $CaHPO_4$) atoms. The single-substituted sour calcium salt of phosphatic acid $Ca(H_2PO_4)_2$ is already well soluble in water and in organic acids of the soil, so the sour calcium salts are well and quickly assimilated by plants.

Ukraine possesses numerous deposits of phosphates and apatites. Unfortunately, many deposits are low-power or have low quality ores and therefore they are unsuitable for industrial use. However, some deposits are quite promising (for example, Stremigorodskoe Titanium-Apatity deposit (Zhytomyr oblast, Volodymyr-Volynskyi district, ore deposits - 16 million tons of P_2O_5, whose content in ore is 2,7 %), Osikivka phosphorus deposit (Donetsk oblast , Starobeshivsky area, ore reserves – 7,7 million tons of P_2O_5, content of P_2O_5 in ore – 4,8 %), Novopoltavskaya deposit of apatite rare earth ores

(Zaporizhzhya oblast, reserves of ore - 46 million tons of P_2O_5, P_2O_5 content in ore - 4,5 %), Ratnivsk phosphate (Volyn region, Kamen-Kashirsky district, reserves of ore – 7,3 million tons of P_2O_5, content of P_2O_5 in ore. In Ukraine, 8 large deposits with reserves of 100 ... 120 million tons of P_2O_5 were discovered in Ukraine. Using its own phosphate raw materials will allow Ukraine to produce much cheaper phosphate fertilizers than those made from high-value imported raw materials. It is also planned to buy phosphorus in Algeria, Tunisia, Egypt for the production of mixed fertilizers (Table 4.8).

Table 4.8 - Reserves of phosphate ores

Country	Million tones of P_2O_5	%
Morocco	15810	25,1
USA	15028	23,8
China	9530,4	15,1
Russian Federation	4827,5	7,7
Kazakhstan	4306	6,8
Mexico	1683	2,7
Others	11856,7	18,8
Total	63067,4	100

Basic phosphate fertilizers:

- phosphorous flour;
- simple superphosphate;
- double superphosphate;
- precipitate;
- Zneftoren phosphates;
- thermophosphates;
- phosphate slag.

Phosphorous flour is a finely divided natural phosphorite. It contains 20 ... 25 % P_2O_5 in the form of medium calcium salt of phosphate, which is difficult to digest by plants. To make phosphorous flour can be used for any crops. However, it should be noted that the effectiveness of this fertilizer depends largely on the characteristics of the liquid phase of the soil. When applied to acidic soils, it gives almost the same effect as acidic salts of phosphatic acid. Significant doses of phosphorous flour, feeding the plant Phosphorus, have a positive effect on yields for 15 ... 20 or even more years. The production of phosphorous flour is very simple. It does not require special high-value equipment and consists only in grinding, drying and sifting phosphorite.

Simple superphosphate is a mixture of acidic calcium salt of phosphate acid and gypsum ($Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4 \cdot 2H_2O$), contains 15 ... 20 % P_2O_5 in an easily digestible form. It is manufactured by the chemical industry in the form of powder of gray color or granules. As disadvantages of simple superphosphate it should be noted relatively low content of phosphorus in it, which is explained by the presence of large quantities of ballast - gypsum. Therefore, simple superphosphate does not belong to concentrated fertilizers, and transporting it to long distances is economically unprofitable. A simple superphosphate is obtained from finely crushed phosphorite or apatite, acting on them with 62 ... 68 % sulfate acid.

The total reaction of formation of superphosphate can be expressed by the following equation:

$$2Ca_5F(PO_4)_3 + 7H_2SO_4 + 17H_2O \rightarrow 3[Ca(H_2PO_4)_2 \cdot H_2O] + $$
$$+ 7(CaSO_4 \cdot 2H_2O) + 2HF.$$

At many plants, simple superphosphate is granulated. The physical and agrochemical properties of granular superphosphate are much better than powdered. Granular superphosphate has a lower humidity, does not bite and does not cling. It is more convenient for transportation and storage. It can be introduced into the soil with seed drills together with seeds, which ensures its even distribution and better use.

As a result of the acid decomposition of natural phosphates, HF is released, which, when interacting with silicon (IV) with the oxide contained in the raw material, forms silicon (IV) fluoride and hexafluorosilicate acid by the following reactions:

$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$;

$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O$.

The resulting H_2SiF_6 remains in superphosphate, bind to impurities in insoluble salts - sodium or potassium hexafluorosilicates. From the total content of the fluorine in the starting material in superphosphate remains 55 ... 60 %, and the rest is released into the gas phase in the form of SiF_4. For purification of toxic fluoride gases in the production of superphosphate, water absorption is used to obtain a by-product of production - 8 ... 25% aqueous solution of hexafluorosilicate acid by the reaction:

$3SiF_4 + (n + 2)\ H_2O \rightarrow 2H_2SiF_6 + SiO_2 \cdot nH_2O$.

Double superphosphate contains in plants easily digestible 44 ... 48 % P_2O_5 in the form of $Ca(H_2PO_4)_2 \cdot H_2O$ salt. Obtained double superphosphate, using phosphate for the decomposition of non-sulfate, but phosphatic acid, resulting in natural phosphate being converted into acidic salt without the formation of ballast gypsum. Consequently, double superphosphate is a concentrated phosphate fertilizer. Under industrial conditions, it can be produced using the same technological scheme as a simple superphosphate, that is, by a chamber method, as well as by a tubeless (current) circuit.

Precipitate $CaHPO_4 \cdot 2H_2O$ is also a concentrated phosphorus fertilizer. It contains 32 % P_2O_5, which is easily absorbed by plants on acidic and weakly acid soils. It is obtained by acting phosphatic acid on limestone or lime milk, following the following aggregate reactions:

$CaCO_3 + H_3PO_4 + H_2O \rightarrow CaHPO_4 \cdot 2H_2O + CO_2$;

$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 \cdot 2H_2O$.

The resulting crystalline product is separated on a vacuum filter from the mother liquor, dried and crushed.

Thermal phosphates are called products obtained by sintering or fusion of natural phosphates with various applications: phosphate acid, silica, limestone (znefluorenic phosphates), magnesium silicates (fused magnesium phosphates), alkali compounds (thermophosphates). During the heat treatment, the crystalline lattice of natural phosphates collapses, resulting in the formation of phosphates, soluble in ground acids. Therefore, thermal phosphates can be used as fertilizers on all soils.

Prospective is the production of thermophosphates in the plasma stream in arc or high-frequency plasma torches. The degree of transformation of phosphorite into the lemon-soluble form reaches 96,5 %. As a result of fusion of phosphate with potash K_2CO_3, fertilizers are obtained, which, in addition to phosphorus, contains another nutrient component - Potassium, the content of which in terms of K_2O is 12 %. The obtained thermophosphates obtained in plasma do not clot and are fertilizers of prolonged action.

The group of thermal phosphates is also arbitrarily referred to as phosphate slags, which are formed as by-products in the case of steel smelting from phosphorus-containing pig iron by tomass or open-hearth furnaces. In phosphate slags Phosphorus is contained in the form of tetracalciphosphate $Ca_4P_2O_9$ and calcium silicate phosphates, which are soluble in weak acids. Depending on the method of obtaining and quality of the starting material, the phosphate slag contains from 8 to 16 % of the digestible P_2O_5.

4.4.6 MANUFACTURE OF POTASSIUM FERTILIZERS

The raw material for the production of potassium fertilizers are natural potassium ores containing minerals: silicon (KCl), siliconite (KCl · NaCl), kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$), Langbeinit ($K_2SO_4 \cdot 2MgSO_4$), carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$) . The crushed ores containing water-soluble potassium minerals - kainite or silvinite can be used as fertilizers directly. But they are poor in potassium - in silvinite contains an average of 14 % K_2O, and in kainit only 8 ... 10 %. The disadvantage of these natural potassium fertilizers, in addition to the low content of potassium, is a large number of ballast substances, in particular chlorides, which harm many so-called chlorophobe crops (potatoes, hops, tobacco, grapes, tomatoes). Therefore, natural salts constitute a small proportion in the total amount of potassium fertilizers, which include potassium chloride, potassium sulphate and kalimagnezia [5].

Potassium chloride KCl - concentrated potassium fertilizer. Pure potassium chloride contains 63,2 % K_2O, and the product used as fertilizer is 50 ... 60 % K_2O. Potassium chloride is a little hygroscopic, it can be applied to most crops. The raw materials for the production of potassium chloride are mainly silvinite, which Ukraine has not its own deposits. Therefore, potassium chloride is purchased in Russia, which owns the world's largest silvinite deposit in the Middle Urals, near the city of Solikamsk, and in Belarus, which also has a large Silvinite deposit (Soligorsk Pellet Enterprise).

Ukraine has one of the largest deposits of polymineral potassium ores in the world, located in the Carpathian region (Kalush, Ivano-Frankivsk region and Stebnyk, Lviv region). These ores contain more than 16 minerals, including gallet (NaCl), kainite and langbejnit, which accounts for the largest proportion. For processing of polymineral ore in potassium fertilizers - kalimagnesia and potassium sulfate - two industrial methods are used: branch and flotation. The halter method of processing is based on the different solubility of ore minerals with increasing temperature. The solubility of potassium-magnesium minerals increases with increasing temperature, and halite is almost unchanged. So, if you prepare a solution saturated with these salts at normal temperature, and then heat it and treat it with crushed ore, then easily soluble potassium-magnesium minerals (sylvin, kainite, carnalite) and partially soluble (langebaynit, kserite $MgSO_4 \cdot H_2O$), and sodium chloride almost does not pass into solution.

In the process of dissolution there is a conversion between potassium chloride and magnesium sulfate [5]:

$$2KCl + 2MgSO_4 + 6H_2O \rightarrow K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + MgCl_2.$$

When the solution is cooled, the resulting stenocide $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ will be released in the form of crystalline salt, and the remaining solution is reheated and used for the next ore processing cycle. The excess solution is extracted from the main ore processing cycle and fed into the so-called cycle of regeneration of salts from it. The isolated senite is dried to obtain kalimagnesia ($K_2SO_4 \cdot MgSO_4$), which contains 28 ... 30 % K_2O.

Senite can also be converted into potassium sulphate - a concentrated potassium fertilizer containing 46 ... 50 % K_2O. The cell is decomposed with a solution of potassium chloride or water by the following reactions [5]:

$$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + 2KCl \rightarrow 2K_2SO_4 + MgCl_2 + 6H_2O;$$

$$2\ K_2SO_4 \cdot MgSO_4 \cdot 6H_2O + H_2O \rightarrow K_2SO_4 + \underbrace{K_2SO_4 + 2MgSO_4 + 13H_2O.}_{\text{solution}}$$

The flotation method of ore processing was realized on an industrial scale at the Stebnitsky potash enterprise. In this way, the ore is first crushed to particle size < 0,5 mm and treated with a reversible solution containing flotation reagents - fatty acids C7 ... C9, which manifest themselves as both foaming agents and as collectors; polyacrylamide and liquid glass serve as depressors. To control the pH of the medium for potassium polymineral ore, use NaOH and HCl. Hydrophobic particles of potassium-magnesium minerals are enveloped during flotation with a film of the flotation agent and pop up in the form of foam, leaving mainly gallite below. The flotation mode, in comparison with the branch, has some advantages:

- simplicity, implementation at normal temperatures, which reduces the corrosion of the apparatus and improves working conditions,

- obtaining a product of lower cost,

- lower capital costs.

However, this method ensures the production of a product of only low quality - the content of K_2O in the flotation concentrate does not exceed 18.5 % K_2O, the degree of removal of potassium in the concentrate does not exceed 48 ... 50 %. In addition, the high content of hardly soluble Langbeinit, Keserite and clay impurities in Precarpathian ores resulted in a sharp increase in the cost of flotation reagents, which means that the cost of the flotation concentrate obtained was higher than that of the Kalimagnesia obtained in the branch way. In this regard, the flotation mode of the processing of pre-Carpathian potash ore in the industry is not currently used.

4.5 TYPES OF SODA PRODUCTS, THEIR CHARACTERISTICS AND APPLICATIONS

Under the general name "soda products", the chemical industry produces a variety of chemicals, such as [5]:

1) soda ash (sodium carbonate) - Na_2CO_3;
2) drinking soda (sodium bicarbonate) - $NaHCO_3$;
3) crystalline soda (dehydrated sodium carbonate) - $Na_2CO_3 \cdot 10H_2O$;
4) heavy soda (monohydrate of sodium carbonate) - $Na_2CO_3 \cdot H_2O$;
5) caustic soda (caustic sodium) - NaOH.

The most important among them is soda ash - a white crystalline substance with a density of 2,53 g / cm^3 and a bulk density of 0,5 ... 0,6 g / cm^3, which is well soluble in water. Aqueous solutions of soda ash have an alkaline reaction. Its solubility in water rises sharply with increasing temperature of 3 soda ash, producing potable and crystalline soda, as well as a portion of caustic soda. More than half of all produced soda ash is used in the chemical and light industry. It, in particular, is used in the production of synthetic and artificial fibers, soaps from higher fatty acids and other detergents and washing powders. Significant volumes of soda ash are spent on purification and softening of industrial water. Almost one third of the produced soda ash is used for glass production. In high temperature cooking glass of soda turns into Na_2O, whose content in the glass reaches 15 %.

The consumer of soda ash is also colored and ferrous metallurgy. Soda is used during the flotation of nonferrous metal ores, as well as in the production of aluminum, nickel, tungsten, and the like. For example, for obtaining from bauxite 1 t of alumina (semiproduct aluminum production), about 150 kg of soda ash is required. In ferrous metallurgy, soda is used to remove sulfur and phosphorus from cast iron, which greatly improves the quality of the latter. To this end, up to 50 kg of soda ash is added per ton of cast iron. A large amount of soda ash is used in the petroleum industry for the purification of petroleum products.

The need for various industries in soda ash is continuously increasing. Therefore, its production is constantly expanding.

Potable soda is a white crystalline powder, which is readily soluble in water, but it produces a slightly less alkaline medium than after dissolving the soda ash. Drinking soda is mainly used in the food industry, in particular in the confectionery industry, as well as in the pharmaceutical industry for the manufacture of certain drugs. Widely used drinking soda and in everyday life. It also serves as a charger for fire extinguishers. Due to the interaction with any acid, which is also in the fire extinguisher, an intense carbon dioxide stream is formed, which is used to extinguish the fire.

Crystal soda is widely used in photography and households.

Heavy soda is obtained from nepheline raw materials. It has a bulk density of 0,8 to 1,0 g / cm^3, it is consumed mainly by ferrous metallurgy and glass industry.

Caustic soda is used in the production of aluminum from bauxite, in the oil and refining industry, for the production of chemical fibers, cellulose and many other industries. It is available in solid form and contains 96,0 ... 98,5 % NaOH, as well as in the form of a liquid with a concentration of 43 ... 46 % NaOH.

From ancient times, soda was extracted from a range of soda lakes and ash of marine and saline plants. Such soda ash was used to make soap and glass. Widely used in ancient Egypt in 1370 BC to produce glass. Today, some soda lakes are still industrial (Lake of Lower Egypt, Lake Magad in East Africa, Lake California, Lake Tantar in Siberia). At the end of the eighteenth century, when the lack of natural soda and its high cost began to slow down the development of those industries where it was used, the question arose about the need for synthetic methods of obtaining it.

In 1791, the French physician and chemist Leblanc offered a method for obtaining soda from sodium sulfate, which was produced from the kitchen salt and sulfate acid, its fusion with limestone and coal in rotary kilns at a temperature of 950 ... 1000 °C with the formation of soda float by reaction :

$$\underline{Na_2SO_4 + 2C + CaCO_3} \rightarrow Na_2CO_3 \cdot CaS + 2CO_2.$$

sodium float

Sodium float was chopped and leached with water after cooling. A solution of soda, separated from insoluble CaS residue, was evaporated and a solid product containing 85 ... 90 % Na_2CO_3 was obtained. This method was multistage, it produced a large amount of CaS waste, and the resulting soda had a high cost and low quality.

In 1861, the Belgian chemists of the Solve brothers created the so-called ammonia method of producing soda ash, which is now producing this product as it is much more economical. The ammonia method proved to be much more profitable than the Leblana method, and gave the opportunity to obtain the final product of high purity.

4.5.1 STAGES OF STNTHESIS OF SODIUM BY SOLVE'S METHOD

1. Preparation and purification of NaCl brine from hardness salts

$MgCl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Mg(OH)_2\downarrow$;

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$.

2. Ammonization of purified brine NaCl

$2NH_3 + CO_2 + H_2O \rightarrow (NH_4)_2CO_3$.

3. Carbonization of ammonium saline solution

$(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$;

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$.

4. Ammonia regeneration

$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3\uparrow + H_2O$;

$(NH_4)_2CO_3 \rightarrow 2NH_3\uparrow + CO_2\uparrow + H_2O$;

$NH_4HCO_3 \rightarrow NH_3\uparrow + CO_2\uparrow + H_2O$.

5. Obtaining CO_2 from limestone

$C + CaCO_3 \rightarrow CaO + CO_2$.

6. Calcination of sodium hydrocarbonate

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$.

The essence of the ammonia production method of soda is that the solution NaCl (brine), saturated with ammonia, treated with carbon (IV) oxide. In this case, the solid phase of sodium bicarbonate forms and falls into the solid phase, and the process itself is called carbonization. After separating from the solution and calcining the precipitate $NaHCO_3$, it decomposes with the formation of Na_2CO_3. This stage of the process, accompanied by the removal of water vapor and carbon (IV) oxide, is called calcination.

The carbon (IV) oxide) used in the carbonization stage is obtained from limestone (firing in furnaces at a temperature of 1000 °C), which contains up to 40 % by volume. CO_2 and before carbonization is thoroughly washed off with water from impurities. For carbonization also the carbon (IV) oxide formed during the course of the calcination reaction is used.

The ammonia chloride NH_4Cl is produced by the ammonia production method of soda. However, it is laid out, releasing from it ammonia, which is again used in production. Decomposition of NH_4Cl occurs under the action of lime milk $Ca(OH)_2$, which is produced by quenching the lime obtained from the burning of limestone. Released ammonia returns to the process - to the stage of ammoniation of brine and is used in recycling. The removal of production in the ammonia method of soda production is a solution of calcium chloride. These solutions are usually poured into pits near the soda plants, resulting in the so-called "white seas", near which nothing grows. Partial use of wastes to obtain from them the commodity products (NH_4Cl and $CaCl_2$) as a whole does not solve the problem.

For the production of 1 ton of soda ash, the ammonia consumes up to 1,6 tons of NaCl, 1,4 tons of limestone, 90 kg of coke, 40 kWh of electricity, 120 kg of conventional fuel and 75 m^3 of water. Losses of ammonia in the system are periodically replenished. In this regard, 1 ton of soda ash consumes up to 2,5 kg of ammonia. The cost of soda ash is quite low, which is one of the main advantages of the ammonia production process. However, the low level of use of raw materials (below 50 %) and pollution of the environment with waste, in particular calcium chloride solutions, do not promote its spread. 1 t of soda is formed up to 9 m^3 of waste solutions containing an average of 10 % $CaCl_2$ and 8 % NaCl [5].

The main areas of improvement of soda technology are the combination of the production of nitrogen fertilizers and the creation of non-waste technologies. In the first of these directions, the concentrated CO_2, which is formed during the purification of the nitrogen-hydrogen mixture, is used. In addition, there is no need to import ammonia from other enterprises, since it comes from the production of nitrogen fertilizers, and in the production of soda there is no regeneration of NH_3, that is, no solutions of calcium chloride are formed. Solutions of ammonium chloride in this case are used for the production of mineral fertilizers.

4.5.2 MAIN DIRECTIONS FOR THE ESTABLISHMENT OF DISTINCTIVE TECHNOLOGIES OF SODA PRODUCTS

Replacement of raw materials

The most important is the use of sodium sulfate instead of sodium chloride, while the process of obtaining soda ash is described by the following general equation:

$$Na_2SO_4 + 2H_2O + 2NH_3 + 2SO_2 = 2NaHCO_3 + (NH_4)_2SO_4 + Q.$$

Next, decomposing sodium bicarbonate, get the finished product and ammonium sulfate, which is a mineral fertilizer. It is obtained from a filtrate by evaporation. All processes are similar to the ammonia method of soda production, only there are no processes of dissolution of rock salt, brine purification and ammonia regeneration, which greatly simplifies the technology of soda ash, and waste is not formed - calcium chloride.

Perspective can be considered as obtaining soda from the mineral nepheline $(Na, K)_2O \cdot Al_2O_3 \cdot 2SiO_2$, significant deposits of which are in Ukraine. The essence of the process of producing soda with nepheline is that at first nepheline sintered with limestone, while binding silica to calcium silicate by the following reaction:

$$(Na, K)_2O \cdot Al_2O3 \cdot 2SiO_2 + 4CaCO_3 = (Na, K)_2O \cdot Al_2O_3 + 2(2CaO \cdot SiO_2) + 4CO_2.$$

The formed soluble aluminates of sodium and potassium are removed with water, and the solid residue of insoluble calcium silicate is directed to the production of cement. A solution of sodium and potassium aluminates is carbonized:

$(Na, K)_2O \cdot Al_2O_3 + CO_2 + 3H_2O \rightarrow (Na, K)_2CO_3 + 2Al(OH)_3$.

The precipitate of aluminum hydroxide is separated from the solution of carbonates, fired and alumina Al_2O_3, suitable for the production of metallic aluminum, is obtained. A solution of sodium and potassium carbonate is evaporated to give a mixture of Na_2CO_3 and K_2CO_3, a heavy soda Na_2CO_3, H_2O, soda ash Na_2CO_3 and potash K_2CO_3. For such a complex processing of raw materials for the production of 1 ton of soda, it is necessary to spend more than 4 tons of nepheline and 7,5 tons of limestone. At the same time, one more ton of Al_2O3 and 7,5 tons of cement can be obtained.

One of the trends in the development of soda production is the use of accumulated waste. For example, from the waste solutions you can select pure calcium chloride. It is used for drying gases and other substances, for the production of metallic calcium, chloride barium, and also as an additive to cement (for better hardening in winter), for the enrichment of coal, in medicine, etc. However, all calcium chloride of soda plants has not yet been fully commercially used. It is suggested that part of the solution of ammonium chloride should not be processed with lime milk, but it should be isolated from the NH_4Cl y crystalline form and used as ammonium fertilizer, as well as during soldering, moltenation, zinc plating, in electroplating, and in the textile industry. A solution of ammonium chloride can also be treated with lime but with a mixture of $Ca(OH)_2$ and $Mg(OH)_2$, which is obtained if the limestone is replaced by $CaCO_3 \cdot MgCO_3$ dolomite. Then 1 ton of soda can still produce 1,7 t of bischofite $MgCl_2 \cdot 6H_2O$, which is used as a therapeutic preparation, and in the production of metallic magnesium by electrolysis [5].

Further development of soda production is also provided by the use of more efficient equipment. For example, calcination is carried out in fluidized-bed furnaces, centrifuges are used to separate crystals of sodium bicarbonate from the solution, instead of drum vacuum filters, use more efficient bubble columns, and also seek to fully automate the entire process.

4.6 CHEMICAL SUBSTANCES AND REACTIONS IN PIGMENT PRODUCTION PROCESSES

Pigments are the basis of paints, varnishes of organic and inorganic origin. The main task of the use of pigments - anti-corrosion and decorative purposes.

The pigments perform certain functions:

The function of an inhibitor (aluminum, zinc dust), an inhibitory function is associated with the prevention of aging of the film under the influence of light due to the fact that the pigment can diffuse the incident light or reflect it. Blue pigments absorb the long-wavelength spectrum of light, while the red ones are short-wave, and long reflects. Pigments of bright colors are used as signaling.

There are thermoscopic pigments that change the color depending on the temperature (thermosensitive paint).

Luminophores - after action on them light (UV and visible spectrum glow in the dark.

Phototropy - a property of TiO_2 (with impurities) to restore its color in the dark.

CLASSIFICATION OF PIGMENTS

By color:

Achromatic:

- white - titanium, lead;
- gray - zinc and aluminum dust;
- black - soot.

Chromatic:

1. Red, orange, yellow;

- red - iron (Fe^{2+}, Fe^{3+}),
- orange - sulfur-containing (S^{2-}), selenium-containing (Se^{2-}),
- yellow - cadmium content (Cd^{2+})

- pink - manganese (Mn^{2+}, Mn^{5+}).

2. Blue, green, violet;

- chromium (Cr^{3+}),
- cobalt-containing (Co^{2+})
- ferrocyanates $[Fe\ (CN)_6]^{4-}$.

TITANIUM PIGMENTS

The raw material for the production of TiO_2 is natural minerals of various composition and origin (Table 4.8).

Table 4.8 - Raw material for titanium pigments

Natural minerals	Formula	Contents TiO_2,%
Anatase	TiO_2	90 – 100
Brook	TiO_2	90 – 100
Rutile	TiO_2	90 – 100
Ilmenite	$TiO_2 \cdot Fe_2O_3$	50 – 60
Perovskite	$TiO_2 \cdot CaO$	57 – 59

TiO_2 - chemically inert, resistant to most reagents and aggressive environments. Insoluble in water, hydrogen sulfide, fatty organic and mineral acids, except concentrated sulfuric acid.

$T_{melt.}(TiO_2)$ = 1560 ... 1880 °C.

Table 4.9 - Changing the pigment color of TiO2 depending on the type of impurity

Impurities	Color of TiO_2
Cr_2O_3	Brownish yellow
CoO	Gray-yellow
Fe_2O_3	Yellowish
V_2O_5	Gray-blue
PbO	Gray

The color of TiO_2 varies depending on the impurities (more than 10-4%), which is due to the deformation of the crystalline lattice (Table 4.9).

MAIN MANUFACTURERS AND EXPORTERS OF TITANIUM OXIDE (IV):

- KEMIRA PIGMENTS OY (Finland)
- PJSC "Crimean TITAN" (Ukraine, Autonomous Republic of Crimea)
- OJSC Sumykhimprom (Ukraine, Sumy)
- KRONOS TITAN GmbH & Co. KG OHG (Germany)
- Sachtleben (Germany)
- Kerr-McGee (USA)
- DuPont (USA)

STAGES OF PRODUCING TITANIUM (IV) OXIDE

1. Preparation of solutions of titanium sulfate (by treatment of ilmenite concentrates with sulfate acid).

As a result, a mixture of titanium sulfate and ferrous sulfates (II) and (III) is obtained, the latter is reduced by metallic iron to the degree of iron oxidation +2. After recovery on the drum vacuum filters separates solutions of sulfates from the sludge. The ferrum sulfate (II) is separated in a vacuum crystallizer.

2. Hydrolysis of solution of sulfate salts of titanium.

Hydrolysis is carried out by introducing embryos that are prepared by precipitating $Ti(OH)_4$ from solutions of titanium sulfate with sodium hydroxide. At the hydrolysis step, particles of a hydrolyzate (titanium oxide (IV) hydrates) are formed that have a high adsorption capacity, especially with respect to Fe^{3+} salts, precisely for this reason, at the previous stage, trivalent iron is recovered to a double-valent. By varying the conditions for hydrolysis (concentration, duration of stages, number of nuclei, acidity), the yield of hydrolyzate particles with given properties is reached, depending on the intended application.

3. Heat treatment of titanium (IV) oxide hydrates.

At this stage, by varying the drying temperature and using additives (zinc oxide, titanium chloride) and other methods, it is possible to conduct a rutile (i.e., the transformation of titanium oxide into rutile modification). For heat treatment rotary drum kilns are used in the length of 40 ... 60 m. When heat treatment evaporates water (titanium hydroxide and titanium oxide hydrates are converted into titanium oxide (IV) form), as well as sulfur oxide (IV).

4.7 APPLICATION AND METHODS OF MANUFACTURE OF CHLORIDE ACID

Chloric acid is one of the most important inorganic acids. It is used in the production of various chlorides, dyes, rubber, in the processes of tanning and dyeing of the skin, etching of metals, for the purpose of rubbing fats and oils, the production of sugar, in galvanoplastics.

Liquid and gaseous hydrogen chloride, mainly used for chlorination of various organic compounds.

Earlier, chloride acid was produced by the action of sulfate acid on the cooking salt and the resulting acid was called hydrochloric acid. It had a low concentration of 22 ... 26 % HCl and contained a large amount of impurities. Now for the production of chloride acid is used and synthetic hydrogen chloride, which is a by-product of chlorination of organic substances.

From synthetic hydrogen chloride, obtained from chlorine and hydrogen, produce synthetic technical chloride acid with two grades A and B (mark B - two grades), which differ in concentration and content of impurities (Table 4.10), as well as reactive chloride acid (Table 4.11).

Table 4.10 - Requirements for the quality of synthetic technical hydrochloric acid (TC 6-01-193-80) [5]

Indicator	Norms for brands		
	A	B	
		Brand	
		I	II
Contents, %:			
HCl, no less than	35,0...38,0	31,5	31,0
Fe, no more than	0,003	0,003	0,02
H_2SO_4 in terms of SO_3, not more than	0,005	0,005	0,03
As, no more than	0,0002	0,0002	0,0002
Non-volatile matter during ignition, no more than	0,02	0,02	0,15
Density, ρ, g / cm^3	1,174...1,188	≥1,156	≥1,154

Table 4.11 - Requirements for the quality of reactive chloride acid [5]

Indicator, % mass.	Norms for classification		
	Chemically pure	Pure for the analysis	Clean
Content,% HCl, not less than	35,0...38,0	35,0...38,0	35,0...38,0
Maximum content of impurities,%			
The residue after calcination (in the form of sulfates)	0,001	0,001	0,005
Free chlorine (Cl)	0,00005	0,00005	0,0001
Sulphates SO_4^{2-}	0,0002	0,0005	0,001
Sulfates SO_3^{2-}	0,0005	0,001	0,001
Ammonium salts (NH_4^+)	0,0003	0,0003	0,0003
Fe	0,00005	0,0001	0,0005
As	0,000005	0,00001	0,00002
Heavy metals (Pb)	0,0001	0,0001	0,0002

The acid derived from the waste gases of petrochemicals contains 22 ... 26 % HCl, a significant amount of organic impurities and is very corrosive. To prevent corrosion, such an acid is added by an inhibitor that allows the storage and transport of chloride acid in conventional steel containers and railway tanks. The cost of such an acid is much lower than synthetic, so this method is increasingly used in the industry. Pure concentrated (100 %) hydrogen chloride obtains from this acid after purification, which is used in the production of organochlorine products.

Synthesis of HCl is based on the reaction:

$Cl_2 + H_2 \rightarrow 2HCl + 183,7$ kJ/mole.

At room temperature without illumination chlorine practically does not interact with hydrogen. The reaction is accelerated by heating, by the action of light or in the presence of a catalyst, and proceeding through the radical (chain) mechanism. In this case, chlorine dissociates atoms, which, when interacting with hydrogen molecules, form hydrogen chloride and a hydrogen radical. This radical, in turn, reacts with a molecule of chlorine with the formation of HCl and the formation of a chlorine radical and so on. Under certain conditions, the interaction of chlorine with hydrogen is accompanied by an explosion. In order to prevent the explosion, in the production conditions, thorough mixing of gases in an ejector burner is used, where chlorine and hydrogen are fed each separately, and hydrogen - in a small 5 ... 10 % excess. The gases mix and interact with each other already in the flame of flame from combustion of hydrogen.

Chloric acid is formed as a result of absorption of hydrogen chloride formed by water. This process can be carried out by removing heat of absorption and adiabatically, that is, without removing heat. The last method, named after the author's name in Gasparyan's way, is simpler and more efficient, therefore it is mainly used in industry for the production of acid of various kinds. The method is based on the fact that due to the high amount of absorption heat not removed by heat exchange devices, the acid temperature rises, it boils. As a result of boiling from acid, water evaporates, to carry out this process it is necessary to spend a certain amount of thermal energy which, in the absence of supply of heat from the outside, is removed from the acid, that is, the acid is cooled down. This makes it possible to absorb new portions of gaseous hydrogen chloride. The maximum concentration of acid obtained in such conditions is 35 % HCl.

The production of synthetic HCl and chloride acid consists of four main stages:

1) the synthesis of HCl;

2) the cooling of the resulting gas;

3) absorption of hydrogen chloride with water to produce production of chloride acid of various grades;

4) purification of waste gases from the residues of HCl.

SELF-CONTROL QUESTIONS (CHAPTER 4)

1. What substances are the main products of the chemical technology of inorganic substances?
2. What do you see as the role of the chemical technology of inorganic substances in solving environmental problems of our time?
3. What do you mean by the term "complex use of natural chemical raw materials"?
4. What actions of the Government of Ukraine can be aimed at protecting the domestic commodity producer of chemical products?
5. What are the chemical elements that are most important in the consumption of plants?
6. Identify the chemistry and the stages of obtaining sulfate acid.
7. Provide methods of neutralizing SO_2.
8. List the oxidation states of sulfur and give examples for each case.
9. Give NO removal methods.
10. List the oxidation steps of Nitrogene and give examples for each case.
11. Provide chemistry for the production of nitric acid.
12. Provide chemistry of thermal and extraction methods for the production of phosphate acid.
13. List the levels of phosphorus oxidation and give examples for each case.

14. Give the main phosphorus-containing acids their name and the name of the salts.
15. Give the fertilizer classification.
16. Give the chemical formulas of the main nitrogen fertilizers, their names and the content of them in the nutrient element.
17. Give the chemical formulas of the main phosphate fertilizers, their names and the content of the nutrient element in them.
18. Give the chemical formulas of the main potassium fertilizers, their names and the content of the nutrient in them.
19. Formulate the physical and chemical properties of fertilizers (consumer characteristics).
20. Describe the chemistry of the soda production process by the method of Leblana.
21. Bring the chemistry of the soda process to the Solve method.
22. The main types of soda: give the chemical formulas and areas of their application.
23. Compare the methods of obtaining soda, indicate their disadvantages and advantages.
24. Describe the chemistry of the stage of the formation of soda by the ammonia method.
25. Give the stages and chemistry of obtaining HCl.
26. Basic chlorinated acids, their names and salts names.
27. Specify the composition of the main raw material for the production of titanium pigments.

REFERENCES

1. Воскресенский П. И. Основы техники лабораторных работ / П. И. Воскресенский. – М.: Госхимиздат, 1986. – 272 с.
2. Степин Б. Д. Техника лабораторного эксперимента в химии / Б. Д. Степин. – М.: Химия, 1999. – 600 с.
3. Рачинский Ф. Ю. Техника лабораторных работ / Ф. Ю. Рачинский, М. Ф. Рачинская. – Л.: Химия, 1982. – 432 с.
4. Степанов Б. И. Введение в химию и технологию органических красителей / Б. И. Степанов. – М., Химия, 1984. – 583 с.
5. Загальна хімічна технологія / В. Т. Яворський, Т. В. Перекупко, З. О. Знак, Л. В. Савчук. – Львів: Видавництво Національного університету "Львівська політехніка", 2014. – 540 с.
6. Загальна та неорганічна хімія: Підруч. для студ. вищ. навч. закладів: У 2-х ч. – Ч. І / О. М. Степаненко, Л. Г. Рейтер, В. М. Ледовських, С. В. Іванов. – К.: Пед. преса, 2002. – 520 с.
7. Капранов С. В. Вода та здоров’я / С. В. Капранов, О. М. Тітомир. – Луганськ: Янтар, 2006. – 184 с.
8. Запольський А. К. Водопостачання, водовідведення та якість води / А. К. Запольський. – К.: Вища школа, 2005. – 671 с.
9. Захаров А. Вопросы малоотходных и безотходных технологий [Текст]: у 2 кн. – Кн. 1: Вопросы малоотходных и безотходных технологий / А. Захаров, Р. Каминская. – М.: Изд-во СЭВ, 1979. – 190 с.
10. Стеклянная химическая лабораторная посуда [Електронний ресурс] – Режим доступу до ресурсу: http://mankor.ua/catalog/yams_laboratory_glassware.
11. Каталог продукции компании "ХИМЛАБОРРЕАКТИВ" [Електронний ресурс] – Режим доступу до ресурсу: http://www.hlr.com.ua/upload/iblock/b56/b56cc731654a391cbf70e9ec6ae23687.pdf.