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The book deals with the problems of the world, including Ukraine, provision with power carriers as well as peculiarities of the new developing field of knowledge and industry — hydrogen energetics, which is the only ecologically pure method of power generation of the future. Self-sufficiency conditions of unrenewable and renewable power sources for civilization existence on the Earth are described. The authors' hypotheses concerning oil, natural gas and hard coal origin are discussed. Special attention is paid to ecologic aspects, in particular, greenhouse effect, ozone holes, power generation.

Intended for engineering staff and research scientists engaged in the problems of power prospecting, including prospecting and production of unrenewable and renewable power sources, as well as for postgraduates and students of the secondary and higher educational institutions.

ISBN

PREFACE

The monograph considers the state of the world advanced energetics, and, first of all, highly promising hydrogen energetics (HE) as well as the state ecology, including that in Ukraine. It also deals with the problems in fringing on interests of numerous countries, especially those which do not possess their own energy carriers. The prevailing share of energy is generated by thermoelectric plants (TEP) now, considerably less one-by nuclear power plants (NPP) and only inconsiderable share of energy is generated by ecologically pure plants using renewable energy sources (RES), the energy of the Sun, wind, seas, geothermal power. Hydroelectric stations all over the world (HES) generate 17 % of electric energy.

NPP can generate practically unlimited amounts of electric and thermal energy. Thus NPPs of Ukraine currently generate 39.6–42.2% of the total amount of electric energy consumed in the country. However, NPP are the high-tech enterprises which require high-culture maintenance, observance of technological conditions and do not forgive mistakes in their construction and operation. Besides, the problem of processing of nuclear waste has not been solved and the latter will be stored up to the problem decision.

Power generation by thermoelectric stations, especially by those burning coal, is connected with pollution of the environment by sulphur, nitrogen and metal oxides and even by radioactive elements (radium, thorium, uranium) which deteriorates considerably life conditions on the Earth. Great amounts of ejected CO_2, as the product of organic fuel combustion, supposedly aggravate the greenhouse effects, which is connected with some negative moments. But the ejections do not still threaten the planet life. The latter is determined by the fact that CO_2 takes part in the dynamic circulation for milliards of years: it is assimilated by biota of seas and oceans as well as by plants which, when dying away, are dissociated by anaerobic bacteria with following formation of methane; they are oxidized again to carbon dioxide and its derivatives, i.e. until they are closed by the carbon cycle in nature. At higher CO_2 concentration in the atmosphere, the greater mass of biota is formed and vice versa. In nature CO_2 remains in mobile equilibrium. It cannot go continuously under extended reproduction, since the ejections of other compounds and particles accompanying CO_2 do irreplaceable damage to nature.

Therefore special attention in the monograph is given to analysis of a new branch of energetics — ecologically pure hydrogen energetics (HE) which considers energy generation with the finite product of technological process of oxidation — water which takes part in natural circulation. The authors consider ten basic methods of hydrogen production; and it is shown especially promising to produce hydrogen by thermochemical methods, high-temperature electrolysis, using power-accumulating substances and pyrolysis of bituminous coals by means of NPP waste heat. Since the world reserves of bituminous coals will last 250–300 years, and in Ukraine — 500–600 years, the combination of NPP with HE allow considering the nuclear-hydrogen power plant as a significant alternative of power plants in the future.

One more important problem can be solved when using hydrogen. The known reserves of liquid and gaseous hydrocarbon fossils can be exhausted in the nearest 45–70 years, and this can bring to the crisis situations in a number of the world regions. Elaboration of the processes of synthesis of artificial liquid fuels from bituminous coals with the use of hydrogen and organization of their broad-scale multitonnage production may satisfy the hydrocarbon famine for the period of hundreds of years and even more, if converting some kinds of biota into alcohols and gaseous hydrocarbon fuel on industrial scales.

Two hypotheses advanced by the authors are also discussed in the book: mechanisms of oil origin on the Earth and formation of the «ozone holes». Oil could appear on the Earth because of geoplanetary catastrophe which led to the burying of biota, covering the whole Earth, as a result of its collision with «loose sky wanderer». This could cause the Earth's axis deviation by 23.5° which resulted in the appearance of the seasons on our planet. The «loose sky wanderer's» mass which had fallen on the Earth's surface with its flora and fauna could form a thick surface layer on the Earth, which isolated biota from the air oxygen and created all conditions (temperature, pressure), which lasted for millions of years, to form oil and gas. Proceeding from the above hypothesis, the deposits of oil and natural gas, as well as of bituminous coals can occur at greater depths, even at the depth of 10 km.

The mechanism of emergence and especially healing of «ozone-holes» under the «settling» of the South and North Poles in winter periods has been discussed in detail. Effect of various factors on ozone stability in the troposphere, stratosphere and other layers of the atmosphere has been analyzed.

The proposed monograph consists of nine chapters and a conclusion with analysis of the world energetics problems. These problems determine the engineering progress in numerous branches of industry, the role of hydrogen in solution of energy and ecology problems; the energy balance of energy generation in the world, including Ukraine; energy resources of combustible minerals in the world and in certain countries; peculiarities of nuclear energetics development and its role in power supply in the world countries; evolution of energy generation at NPP, TES and HES of Ukraine and present state of energetics; problems of developing ecologically pure hydrogen energetics. Special attention was given to physico-chemical properties of hydrogen and metal hydrides, production methods for hydrogen as the universal fuel and reagent, problems of ecology and environment, «greenhouse» effect, «ozone holes», acid rains, thermal contamination of the planet. The authors have also analyzed problems of hydrogen energetics and other power sources in the third millennium.

The monograph is not a manual, and so, the authors have chosen a rather free interpretation of certain questions, being their own view.

The authors hope that their purpose to acquaint the reader with the state of modern problems of power engineering all over the world and in Ukraine, hydrogen energetics in particular, was achieved at least in part. We would be greatful for our readers criticism aimed at perfection of the book, and their remarks will be taken into consideration in the future.

Chapter 1

Energy, Engineering Progress, Hydrogen and Ecology

Each century carries the impress of main achievement of humanity. In this respect, one can call the 19th century — the century of metals and chemical elements, generalized in D.I. Mendeleyev's periodical system, the 20th century — that of motors and velocities, exploration of space, depths of seas and oceans, great-scale development of atomic energy, and the 21st century can become the century of new kinds of energy (e. g., thermonuclear), biotechnologies and information systems. Renewable (nontraditional) methods of energy production (hydrogen energetics, methods of conversion of solar radiation energy, energy of the wind, sea waves, geothermal water into electricity; conversion of energy of biological systems) will be developed in the 21st century.

Growth of the Earth population (its number has increased twice in the last 50 years of the 20th century and reached ($6 \cdot 10^9$) and productive forces caused the rise in energy consumption which often led to the crisis situations with energy in the world (military operations on Malvinian Islands and war in the Persian Gulf on Kuwait liberation by multinational forces of the USA, England, France, Germany and other countries under the code name «Storm in Desert», «Shield of the Desert») in the 20th century. The beginning of the 21st century was also marked by war in Iraq started in March, 2003, by the USA, Great Britain and their allies without the approval of UNO. Its aim, as it appeared after the overthrow of Hussein, was the gain of access and control of the richest hydrocarbon deposits all over the world, containing 270 — $280 \cdot 10^9$ t of oil. And it was not the last war in the 21st century, caused by some countries desire to capture power resources of a certain land. That is because the development of economy, functioning of industry, comfortable conditions of life are impossible without energy.

The country economy, based on efficient technologies and continuously assimilated new technical decisions, is connected directly with economical consumption of huge amounts of energy [2–5; 1–4]. The more energy one or another country consumes, the more developed is its economy and, as a result, its science, industry, and agriculture flourish, socionics develops and everyday life of its population improves. So, energy may be considered the basis for progress in science and technology and that of civilization.

People always used organic resources wood, straw, etc., as fuel. According to V.I. Subbotin all the history of humanity is placed between the first fire, made consciously by a primitive man and nuclear reaction fired by our contemporaries in the 20th century. Firewood and dry farm waste served as a basic source of heat both in everyday life and industry up to the mid-19th century. Steam engine invention led to industrial revolution which intensified production, since manual labor was changed by machine production.

On the other hand, man's desire to use energy in concentrated form always led to progress in technology. Cite some instances: a bow — the oldest missile weapon, converting muscular (mechanical) energy into kinetic great power energy; missile machines which use a torque and a lever to obtain great killing and destructive force; the invention of powder, and then of guns (cannons) resulted (because of the use of even higher concentration of energy in small volume) in the following progress in military science. The wish to decrease frictional forces and to use more efficiently (man's, animal's) energy led to the invention of the wheel. A simple horse-drawn cart augmented human force no less than 20 times. The invention of a vertical water wheel raised 6–10 times the labour productivity. Further progress in energy conversion into kinetic energy of motion resulted in the invention of various machines — mechanical «propellers». The invention of steam engine increased human labour productivity hundreds and thousands of times.

The internal combustion engine required high-calorific fuel. Development of industrial technologies led to the use of coal as a source of energy, while increased production of organic mineral resources — oil and oil-based hydrocarbons, and production of natural gas in great amounts led to intensive use of these energy carriers in industry, motor transport and everyday life, since they were considered more technological fuels. This favoured the increase of human mobility and cargo delivery speed. Technological ideas «floated in the air» and, as a result, people developed new kind of energy: hydraulic energy of rivers and sea waves, chemical sources of current, fuel elements, wind energy. But after 50 years of consumption of organic hydrocarbon fuels scientists began to realize finiteness of natural reserves which are also actively used in chemical and light industry to synthesize polymers, artificial fibre, materials, a great number of reagents with preset properties, etc.

There appeared an alternative to organic (chemical) fuel. It was nuclear energetics, which developed intensively all over the world in 1957–1986. As a result, the share of nuclear electric power reached 18 % of the total amount of energy produced in the world; it reached even higher values in a number of countries [6]. Nuclear-powered vessels (ice-breakers, cruisers, torpedo-boats) are ploughing seas, while submarines navigate under water during 6–12 months.

There is a prospect of far space flight outside the solar system in spaceships with polonium-based nuclear power sources [7], with nuclear power plants based of fissure reactors [8], and nuclear electrorocket engines [9]. The blue sky abyss over our planet as well as that of the black space were almost a mystery, which the best intellects of humanity tried to understand. Claudius

Ptolemacus, G. Galilaei, N. Copernicus, K.T. Tsiolkovsky, P.A. Tsandler, Yu.V. Kondratyuk aimed to know the Universe structure and dreamt to conquer space. G. Galilaei was the first to direct the telescope to mysterious Italian sky of stars on January 7, 1610, and to observe a number of celestial bodies that marked the beginning of astronomy. The epoch of Claudius Ptolemacus, G. Galilaei and N. Copernicus was the epoch of hypotheses on the universe structure proceeding from telescopic observations of heavenly stars and bodies. K.E. Tsiolkovsky made the pioneer theoretical investigations of aerodynamics, rocket construction and layed down the foundations of present cosmonautics. K.E. Tsiolkovsky developed the theory of jet propulsion (1896) and theory of multistage rockets (1926–1929), proposed a number of schemes of the long-range rockets and interplanetary rockets. He was the first to mention the necessity of great reserve of energy to overcome terrestrial gravity and resistance of the Earth air shell. He calculated fuel reserves for one or another spaceship in interplanetary flights. The calculations have shown that the overcoming of gravity forces and man's penetration to the space will need high technologies and specific infrastructure which was then called the rocket-space industry. Really, the opening of the terrestrial and interplanetary space and solar system planets, by launching Earth's artificial satellites (the USSR, USA, France, Japan, China, Great Britain, Australia, etc.), piloted flights of spacecrafts, as well as creation of international orbital stations (Mir, Soyuz (USSR), Skylab (USA), etc.) required huge amounts of energy (including the use of liquid hydrogen and oxygen as fuel), development of space science which determined technological progress in numerous new branches of engineering, space instrument engineering and electronics, automatic systems, engine construction, machine building, material science, energetics and all branches of industry.

A valuable contribution to astronautics formation was made by our compatriot Yu.V. Kondratyuk. Being interested in the problem of interplanetary communications, Yu.V. Kondratyuk, independent of K.E. Tsiolkovsky, deduced the basic motion equation for the rocket, made a design and described a four-stage rocket on oxygen-hydrogen fuel, the engine combustion chambers with fuel and oxidizer nozzles arranged in staggered rows (or otherwise), paraboloid nozzles, pumps for fuel supply, regulators, rocket gyroscope control system with the drive to the turret nozzle part and use of floated orientation gyroscopes. He proposed the atmosphere resistance to be used for the rocket deceleration under descent for fuel saving, etc. [10]. In 1929, Yu.V. Kondratyuk published a monograph «The Conquest of Interplanetary Spaces» where he determined the succession of the first stages of space exploration, considered the problems of thermal protection of spacecrafts during their motion in the atmosphere; he suggested using some metals with high combustion heat, metalloids and their hydrogen compounds, e. g., borohydrides as fuels parallel with hydrogen-oxygen fuels. His description of certain parts of interplanetary spacecraft, its control and stabilization system, and other new decisions are also of scientific and practical interest. Numerous theoretical equations and designs proposed in his work are used, and they will be used with astronautics development.

It appears from the above that theoretical foundation for astronautics development in Russia and in the former Soviet Union layed down by enthusiasts became a powerful technological basis for implementing orbital and interplanetary flights of spacecrafts. The above theoretical works could be realized because of well-timed appearance of such genii of cosmonautics as S.P. Korolev, M.V. Keldyah, V.P. Barmin and their followers. Each step forward on the path of exploration of the near space (from October 4, 1957 — date of the launch of the first Earth artificial satellite) and the outer apace — the world of stars and galaxies, was connected with solution of new theoretical and engineering problems: more exact calculations of orbits, flame propagation rates, thrust pulses, search for new more fire-resistant and light materials, thermal protection of spacecrafts, and above all search for the new, more «calorific» fuel.

At the dawn of cosmonautics development chemical fuel (that is hydrocarbon fuel and its derivatives) was the basic one. Concentrated nitric acid and nitrogen tetroxide or such systems as nitric acid-dimethylhydrasin and then liquid oxygen-liquified hydrogen served as oxidizers. Late in the 20th century researchers began to realize that by the mid-21st century organic fuel will be changed by nuclear energy [8, 9]. Nuclear-hydrogen and thermonuclear systems will be used in the nearest future as devices to generate energy [9, 11–13]. Chemical sources of energy will occupy the second place [8, 9, 14], the third place will belong to solar energy conversion by various energy plants [15], and the fourth place will belong to nontraditional sources of energy [l6]. The nuclear-hydrogen power engineering will represent the basic type of energy both in placing spacecrafts on terrestrial orbit and in piloted interplanetary flights. One can distinguish today nuclear rocket engines (NPP), nuclear power plants (NEMP), and nuclear electromotive plants (NBMP) [9, 17]. Nuclear rocket engines have a number of advantages, as compared to other engines, since they allow achieving higher (against liquid-reactive engines (LRE)) specific thrust pulses when using hydrogen — the working medium with minimum molecular mass. It has been established that the increase of specific thrust pulse of the first and second stages of the carrier rocket (CR), e. g. of *Energiya* class, only by 10 m/s, the mass of useful cargo placed into the orbit will increase by 500 and 700 kg. The specific cost of useful cargo orbiting being 10 000 dol./kg the latter allows saving 5–7 million dol. Respectively. The specific thrust pulse does not usually exceed 3000 m/s because of the low working medium exhaust (fuel combustion products) in LRE. Thus the mass of fuel, depending on carrier rocket class, makes about 50–80 % of the start mass of spacecrafts. In this connection the fueled engine weight makes the basic share of the spacecraft mass. That is why that the creation of new engines for CR as well as the perfection of well-known spacecraft engines to raise specific thrust pulse when using ecologically pure fuel (hydrogen-oxygen, methane-oxygen, etc.) become the principal tasks of spacecrafts production in the nearest future. So, hydrogen-oxygen engines, plasma rocket electric engines with the use of electromagnetic energy to accelerate working medium efflux (EMRE) are rather promising engines [17]. When liquid oxygen is combined with liquefied hydrogen, the specific working medium efflux is 4500 m/s. At the same time, plasma EMRE can produce the working medium exhaustion rate about 30 000 m/s and increase dosens of times the specific thrust pulse. The latter determines the low level of energy consumption.

Hydrogen-magnetodynamic rocket engines with variable thrust (MDVT) are rather promising engines for spacecrafts [18]. Such engines can provide a specific thrust pulse equal to 50 000 –300 000 N/s/kg at thrust of 4500-420 kg [19]. Thus spacecrafts with such engines can reach the orbit of Mars for 3 months instead of 12 months, planned before. The volume of fuel for the spacecraft to Mars will be 120 tons at the total takeoff mass of the launched spacecraft — 535 t. The spacecraft with carrier rocket provided with IRE on hydrocarbon fuel cannot be used for piloted interplanetary flights.

Hydrogen which is heated, when passing along heat-releasing elements, and flows out of the nozzle with high velocity serves as the working medium in nuclear-rocket engines of NRE type. The appearing specific thrust pulse, equal to 3000 m/s (950 ts), pushes the spacecraft forward. The outlet temperature of gaseous hydrogen is 3300 K. Rocket engines of NRE type are developed intensively in Russia and USA, since they are of interest for exploration of the Moon and piloted expeditions to the Mars, Europa, Venus and other planets [9]. From the data of [9] Russia is 15–20 years ahead of the USA now in the field of nuclear rocket engines. New technologies providing creation of nuclear power plants are developed in Russia. Their power is more than dozens and hundreds of kW with resource of geostationary operation about 10 years and above under the conditions of nuclear and ecologic safety. Russian scientists also work in the field of creation of bimodal nuclear electromotive plants (NEMP) operating under conditions of NRE on hydrogen, as well as in electrogenerating conditions for airborne energetics of spacecrafts (power of the target and service equipment). Investigations have shown that the nuclear power plants with powers of 50–100 kW are more efficient as compared with traditional solar power plants because of their less mass and overall size and better operational and economic characteristics [9]. Development of the first in the world thermoemissional NPP *Topaz-1* is planned in the future.

It follows from the above that the share of consumed nuclear power will increase in the 21st century, with the decrease of the share of chemical energy. Nuclear and thermonuclear powers will be the basic kinds of energy on our planet in the third millennium. Safety of NPPs in operation will increase considerably in connection with mechanization, automation and creation of the systems of humanless control of technological processes. The humanity will forget about the accident at the nuclear power plant of the USA (Three-Mile-Island, 1979) and Chernobyl catastrophe in Ukraine (1986), about the so-called post-Chernobyl syndrome which impeded nuclear energetics development late in the 20th century all-over the world. It was on April 26, 1986, that the reactor bursted at the 4th unit of the Chernobyl NPP. In the opinion of Academician V.A. Legasov this reactor was imperfect as to its technical and economic characteristics, since it consumed great amounts of nuclear fuel and its construction by non-industrial methods required considerable capital investments. Neither designers nor the operating staff knew about some troubles in the protection systems of the reactor and so did not try to correct them. In the course of experiments which were carried out without the approval of nuclear engineers there occurred the greatest NPP tragedy of the 20th century, which decelerated progress in experimental nuclear physics and practical use of its results. The catastrophe at the Chernobyl NPP was a result of «unreasonable treatment of the atom».

After the accident main attention of nuclear engineers was given to safety of the already constructed NPPs, as well as to elaboration of new-type reactors for NPP, for example, high-temperature reactors with helium heat agent HTGR-1000. Extraordinary measures were taken on the exact following the technological instructions at NPPs all over the world. But in due course some countries, following public opinion, considered the variants of NPPs removal from service and thought about passing to renewable sources of energy (wind energetics, conversion of solar energy, etc.). In Western Europe in the period of stagnation of nuclear energetics there arised a movement of political character for leaving the «nuclear zone» by some states. Thus, German government headed by J. Schrцder, called the «red-green» government, gave a solemn promise to close 19 NPPs in Germany during 4 years, and then they prolonged the term to 30 years.

At the same time, China builds 8 power units and has a plan to construct 45 nuclear units to solve the energy problem in the country. In accordance with Bush-Chainy doctrine it is planned to construct one more (the 104th) power plant in the USA [9] and a nuclear plant at the cost of $2.5\cdot10^9$ Euro in Finland.

Japan gives the leading role to development of nuclear energetics to looser the state energetics dependence on petroleum imports. It is planned to construct l6 to 25 new NPPs in Japan by 2010. In the nearest years Russia supposes to build new NPPs in Chelyabinsk, Khabarovsk, and Primorie lands, to erect additional units at Voronezh, Beloyarsk, Leningrad, Kola and Smolensk NPPs as well as to finish the construction of the units at Kursk, Kalinin, Balakov NPPs. Ukraine continues the construction of two units of the Rovno and Khmelnitsky NPP (despite of the lack of aid promised by EC countries) instead of the closed Chernobyl NPP. Thirty one nuclear power units are constructed now all over the world. The first unit of Rostov NPP was put in operation in 2002. Growth of Russian nuclear production has increased by 30 % for the recent 2 years, which is equivalent to introduction of five large power units. The same number of power units are included annually in national networks all over the world.

Thus, one can consider that the period of stagnation in nuclear power engineering is finished. The USA and Russia have started the active work in development of new nuclear technologies in their power engineering [22]. President V.V. Putin at Summit of Millenium in September 2000 noticed that «Development of large-scale energetics on the basis of new nuclear technologies will permit preserving organic resources of the planet for their non-power use by the present and future generations...». A new energy doctrine of the USA has been elaborated under the leadership of President G. Bush, it is aimed at raising electric power production for the period of 2000–2020 by 45 %. The basic growth of electric power production in the USA will be secured at the expence of the increase of gas component and development of nuclear power sources. Before 1986 there were 444 power units (reactors) of nuclear energetics which produced $2300 \cdot 10^9$ kW/h of electric power a year. After stopping the efficient nuclear power unit «Barsebek-1» in Sweden, conforming to all the safety standards, and several inefficient NPP in the USA, the third unit of the Chernobyl NPP in Ukraine, 438 units with total power of 351 327 MW are in operation all over the world now.

It would be noticed that, as a result of the post-Chernobyl syndrome, the 15-years stagnation took negative effect on development of nuclear energetics. The rates of development of scientific trends, being the basis of the nuclear science — physics of plasma and thermonuclear synthesis, nuclear physics and high-energy physics, physics of accelerators and superpowerful magnetic fields, physics of solids and superconductivity — have been slown down. Financial difficulties in Ukraine and Russia caused disintegration of collective bodies of world-wide known specialists who worked actively in the field of theoretical physics, high-energy physics, nuclear and semiconductor physics, etc.

In connection with the post-Chernobyl syndrome the world industrial energetics (allowing for growing demands for energy) laid special stress on hydrocarbon fuel which began rising in price; the average price of 1 barrel (159) of oil has reached the record level for the last 10 years and sometimes it exceeds 30–35 dol., and, according to states-exporters of oil (OPEC), it can exceed 40 dol. There arised difficulties with gaseous and liquid hydrocarbon fuel because of its limited natural reserves (about 5 % with respect to coal). The increase of amounts of hard combustible fuel even more aggravated the situation with ecology because of the environment pollution. The combustion products (mainly SO_2, NO_x, CO_2 and to less extent CO) got to the atmosphere as well. But the degree of the Earth atmosphere pollution was not so high because of small number of population (1750 — 0.770; 1800 — 0.907; 1900 — 1.617, 1950 — $2.515 \cdot 10^9$) [23]. Our planet population has increased 2.11 times for 40 years (from 1950 ($2.515 \cdot 10^9$ people) to 1990 ($5.328 \cdot 10^9$) people). Today, only China, with population of $1.3 \cdot 10^9$ ejects $23.46 \cdot 10^9$ t of carbon dioxide and occupies the second place in the world as to these wastes [24].

The development of industry and growth of consumption of energy resources (natural gas, oil and coal and their derivatives containing sulphur, nitrogen and other harmful and toxic substances), especially late in the 20th century, as well as the increase of operation temperatures of heat power plant aggregates caused the increase of such environment pollutants as ash, sulphur and nitrogen oxides, benzpyrene and methane taking destructive effect on human habitat. Nitrogen oxide ejections from the supersound aviation take especially dangerous effect on the stratosphere. These ejections can lower twice ozone concentration in the stratosphere. Petroleum refining plants with production of motor fuels and oils eject huge amounts of hydrocarbons into the environment. Fuels and chemical compounds containing harmful ingredients — metal (cadmium, chrome, lead, etc.) oxides, cyanides, tetraethyllead, arsenic and other substances polluting the environment — are more widely used in the motor transport and industry.

As a result, the Earth is threatened not only with power but also ecological crisis since the atmosphere and human habitat ecosystem are polluted with combustion products of natural gas, oil, bituminous and brown coals (hydrogen, nitrogen, sulphur and metal oxides, particles of ash, soot and dust) which cause the «acid rains» and, in the opinion of numerous scientists, can lead to formation of the «ozone» holes and «greenhouse effect». Besides, NPP and TEP are generators of thermal pollution of huge regions of the planet [1–4]. Besides, heat losses in the environment have also considerably increased [3, 4].

In the present only 20 % of the world power resources (nuclear fuel, natural gas) are consumed as electricity, the rest 80 % are consumed as follows: 30 % — in the form of low-potential water steam and water heat are used in municipal and domestic services and in industry, which practically leads to its dissipation in the environment; 30 % — as high-potential heat of overheated vapour and compressed air are used in chemical, petroleum-chemical, metallurgy and other branches of industry, partially, to produce efficient energy carriers, metals, alloys and chemical reagents (ferrous and nonferrous metals, acids, organic and inorganic reagents); 20 % are consumed in transport (oil products, alcohol, hydrogen, synthesis-gas, etc.) [1–4; 25–31].

A cardinal way for the Earth decontamination for the heat «impurities» is to direct low-potential heat to endothermal chemical reactions and metallurgical processes in the volumes which guarantee the conservation of the Earth heat balance. That is why the efforts of researchers and engineering staff would be directed both to utilization of low-potential heat and to the gradual substitution of nonelectric technologies by electro-, plasma-, and laser technologies and creation of autonomous electrotransport (electrocars). On the other hand these efforts would be also directed to the prospects of transformation of chemical energy of hard fuels (bituminous coal, slates, turf) into more ecologically safe heat transfer agents (hydrogen, synthesis gas, liquid synthetic fuel, etc.), to production of energy-accumulating substances (EAS), high-temperature superconductors (HTSC), creation of new technologies capable to revolutionize energetics itself and production, stopping purely extensive path of their development due to the transfer to profitable, maximum «lossless» energetics. Low-potential heat may be also used for hydrogen production by electrolysis of solvatocomplexes of hydrated melts at 573 K [1, 3, 4, 25, 26], as well as for synthesis of various compounds and materials by the methods of high-temperature coordinational chemistry [3, 4, 27]. This is a new scientific trend of inorganic and coordinational chemistry. Most chemical and metallurgical processes are realized at rather high temperatures because of high energies of chemical bonds in simple compounds used in these productions (in metallurgy of metal oxides and sulphides). These simple compounds are transferred into coordinational ones with the big number of ligands in the purposeful high-temperature coordinational chemistry. As a result, because of the great number of bonds formed in the coordination compound, each separate bond energy lowers to the level G°bond = G°compl. (Z, where is coordination number). Such energy level permits thermal, chemical, electro-, photo- and laserochemical transformation of molecules into the finite products or it permits performing the processes of synthesis, redox reactions in considerably milder conditions, i. e., with utilization of low-potential heat for endothermal break of bonds in the coordination compound [3, 27].

The problem of power plants effect on the air basin and surface waters is the most important problem of energy production. Power production is the largest branch of industry, and the volume of its waste in the atmosphere makes 32 %. Such power plants as thermal power stations pollute the air basin by fuel combustion products and thermal ejections, and surface waters — by sewage. But neither of the above negative climate-forming factors, discussed with exaggerations in mass media, is not able to change the planet climate (solar energy is the major climate-forming factor with respect to the Earth), by raising temperature as a result of greenhouse effect or thermal effusions [32]. One would also allow for the fact that metal oxides as well as fine and superfine ash, soot and dust particles interact with the products of nitrogen and sulphur oxides (acids) hydrolysis and hydrocarbon impurities in the atmosphere and form stable aerosol envelopes over great areas of the planet which do not transmit ultra-violet and infra-red solar radiation to the Earth surface.

Hence appears a regional variant of «nuclear winter» realized as a result of «aerosol cold spell». So there exists a possibility of Mutual compensation of two negative factors — the greenhouse effect which can, theoretically, lead to temperature elevation and aerosol effect which can call the cold spell. But at any variant, one would remember the ideas of Academician V. I. Vernadsky, the great scholar of the present and organizer of the Academy of Sciences of Ukraine, on the problems of ionosphere. According to his ideas man's contribution to life development will be commensurable with geochemical contribution to life formation on the planet.

The problems of humanity existence in the vast territories of the Earth have really arised as a result of the environment pollution. In 1990, the USA produced $270 \cdot 10^6$ t of dangerous waste, countries of European Economic Community — almost 28.9, Central and Eastern Europe — 23.3 and all other countries — 15.5 mill.t/yr, which makes only 4.59 % of the total volume. When comparing the population number of the USA (about 285 mill.) and the world ($6 \cdot 10^9$), one can see that 4.7 % of the world population produce 80 % of dangerous waste. China produces $1.6 \cdot 10^9$ t of hard waste, and the amount of waste accumulated in this country reached $6.58 \cdot 10^9$ t [32]. In this respect, Ukraine is far «ahead» of China.

The total mass of waste accumulated in the territory of Ukraine (on the surface) for 1997 exceeded $25 \cdot 10^9$ t [33]. And the waste growth rates in Ukraine are frightening. If in 1980 there were 240 t of waste per one resident of Ukraine, there were 318 t in 1990 and above 400 t in 1996. One can observe a sharp increase in losses of agriculture products from acid rains. About 30 % of agricultured lands are damaged by the acid rains in China. The planet air basin pollutions have gained the transboundary trans-state scale [34]. Gaseous impurities and dispersed particles are distributed in the atmosphere, including its upper layers over their «maternal territories» (USA, Western, Central and Eastern Europe) and then they are dispersed by powerful wind flows over the whole territory of northern hemisphere. Giant amount of gaseous substances (nitrogen, sulphur, carbon oxides benzopyrene, etc.) and hard particles (vanadium, chrome silicon, soot, ash oxides) ejected in the air space by the plants of power complex, by chemical and metallurgy industries of China are distributed in the territory of the Southern hemisphere of our planet. Real costs of civilization are boundless.

The lion's share of dangerous waste is formed from energy generation and coal production. That is the reason of the 100-years long variable investigations on synthesis of more ecologically safe liquid synthetic fuels from bituminous coals and other hard fossils. Numerous countries all over the world possess sufficient reserves of bituminous coals, slates, brown coals which can serve wonderful raw materials for production of artificial liquid fuel in the nearest centuries. In this connection the development of fundamental investigations in the field of synthesis and infrastructure of production of liquid synthetic fuel and various chemical products from coal is an important task for many countries all over the world which have faced the problem of natural oil deficit. Ukraine undergoes the severe energy crisis. It belongs to the states with limited oil and gas resources which do no meet the requirements of industrial, agrarian complex and transport enterprises.

As is evident from the data of geological prospecting Ukraine possesses substantial reserves of natural gas and oil which can last more than 45–70 years. Hydrocarbons production is not well organized in the territory of Ukraine, while the major task of socio-economic development of any country (with temperate climate and all the more with severe climate) is generation of energy using the newest energy-saving and ecologically pure technologies. It is only planned that the home production of natural gas in Ukraine will reach $30 \cdot 10^9$ m^3/yr. in 2002 with demand of $90 \cdot 10^9$ m^3/yr. Though, as it will be shown below, the home researchers predicted forty year ago, that in 1975 Ukraine would produce 22 mill.t of oil (present demand 40 mill.t) and $70 \cdot 10^9$ m^3 of natural gas, in 1980 — 36 and 90, respectively. However it would be born in mind that hydrocarbon energy carriers are exhaustible. Certain optimism is raised by the fact that Ukraine possesses great reserves of bituminous coal and turf which, under development of chemical science, will serve the source of raw material for industrial production of such volumes of liquid synthetic fuel which can meet the state requirements. According to calculations, bituminous coal in Ukraine will last for 500–600 years. Let us hope, that we have time enough for coming not only the era of ecologically pure hydrogen energetics and renewable energy sources but also ecologically pure thermonuclear energy.

It is time to emphasize that hydrogen, which reserves on the Earth are practically boundless [1, 11, 12, 14, 31] has great prospects for production of ecologically pure energy. Hydrogen possesses high-energy intensity, which exceeds 3–5 times thermal energy capacity of gasoline and oil. Hydrogen may be used as the energy source in metallurgy and chemical industry, aviation, spacecrafts and aerospace industry as a whole, in fuel elements, in motor and other types of transport, in municipal and communal services. Hydrogen may be stored in cryogenic vessels, salt mines and underground reservoirs of natural origin; it may be transported for long distances along the developed pipeline network with minimum losses. When producing great volumes of hydrogen (on industrial scales) one can distinguish 10 rather promising methods: electrolysis of alkali water solutions and water vapour at 80–1000 °C; vapour-phase method of methane (natural gas) conversion; hydrogen production from brown and bituminous coals, turf; thermal decomposition of hydrocarbons; thermochemical cycles of hydrogen production; underground coal gasification with hydrogen production; hydrogen production by iron-vapour-phase method as well as under photoelectrolytic transformation of solar radiation energy, use of biocataly-tic systems, etc. Most states in Western Europe (United Kingdom, France, Austria, Germany, Iceland, Italy, Spain, Sweden, Switzerland) perform investigations in the field of hydrogen energetics both following thematic programs «Energy, Environment and Stable Development», «A Single European Hydrogen Project», and national programs, often financed by the country governments [35].

When speaking at the meeting of Royal Society of the United Kingdom of Great Britain on May 23, 2002, Prime-Minister of UK Tony Blair noticed that the climatic variations on the Earth are one of the urgent and most complicated problems. Their decision is not within competence of one certain science. However, the British developments in the field of perfection of solar cells and technologies of hydrogen fuel elements and creation of efficient methods of the use of energy of tides and sea waves give us hope. Think, for example, what if we will succeed in our country to subdue the energy of tidal waves, which exceeds ten times our demand for energy. On their part, the hydrogen utilization technologies can result in creation of vehicles with zero ejections of harmful substances. Scholars and engineers, who develop these technologies, aim at realizing the dream of dangereless cities without harmful effect of ordinary vehicles on the air quality and human health.

Russia and some CIS countries as well as the USA, Canada, Japan and China perform investigations in broad research and development (RdD) works in the field of hydrogen energetics and technology [31]. The state finance of the programs and R&D works in hydrogen themes amounts to hundreds of million dollars a year. The latter is determined by new break-down technologies in the field of hydrogen production, its use as ecologically pure fuel and energy accumulator, by creation of the corresponding hydrogen infrastructure — experimental, pilot-industrial plants and industrial productions. Japan, jointly with foreign partners, realizes the project «World Energy Network with Hydrogen Use» (WE-NET), designed up to 2002. The volume of the project financing is 4 milliard dollars.

It is currently evident that a combination of the principles of hydrogen energetics using energy of renewable sources will further permit substituting liquid hydrogen fuel, which will be exhausted in the nearest 45–70 years. Thus, the renewable sources of energy (energy of the wind and sea waves, solar and geothermal energy) are of special interest for technogenic and social development of the world states. A combination of hydrogen production technologies and pure sources of heat will allow the large regions to become independent of centralized sources of energy and not to contaminate the environments. The South of Ukraine (Odessa, Kherson, Nikolaev, and Donetsk Regions, as well as the Autonomous Republic of the Crimea) can be partially provided with energy from solar power plants, and the whole territory of Ukraine — by energy of wind power stations. The latter are developed intensively in Germany, Austria, Italy, USA. The use of the wind plants and those of solar radiation conversion into the electric and thermal energy is especially promising for the farms of Ukraine. Besides, the chloride-sodium geothermal solutions (15 g of salt per 1 of water) with the temperature of 40–50 °C have been found in the Transcarpathia and Crimea at the depth of 1000 m. They may be used to supply heat to microregions of the cities and villages.

In conclusion, few words about technological progress connected with hydrogen and nuclear energy. Most scientists think that the orbital power plants converting solar energy will be widely used in the Earth infrastructure power supply with further development of cosmonautics. The above plants will supply spatial and on-land objects with power on industrial level. Energy will be transferred from space by solar power plants, spatial reemitters in a form of microwave or optical (superhigh frequency) range of waves. It is supposed [9, 16] that in the future power plants will be created on new physical principles, new energy sources will be found, efficiency of well-known power technologies will be raised and considerable share of electric power production will be transferred into the space.

Progress in astronautics will result in creation of promising purposeful industrial orbital systems for performing new technological processes with the obtaining of alloys and materials with preset properties which cannot be produced under the gravity conditions. There are preconditions for creation of the infrastructure of spatial electronics in special flying spatial technological laboratories or on one of the planets of the solar system. The experiments carried out on spacecrafts in the weightless ness and deepest vacuum permitted obtaining the semiconductor materials (single crystals, epitaxial coatings and articles) of so high quality which is impossible on the Earth [36]. Superthin, 1 molecule thick semiconductor layers possessing quantum-mechanical properties which are not displayed in ordinary «earth» microcircuits can be produced at vacuum epitaxy in space. «Spatial» monomolecular semiconductor materials open prospects for absolutely new microelectronics which will allow creating superhigh-velocity computers of new generations, systems of artificial intelligence, highly efficient solar batteries, etc. Materials obtained at space probe *MIR* permitted the pilot prototypes of unique devices to be manufactured and tested. These are the ultraviolet laser pump for submicrometer photolithography with resolution 0.6–0.8 μm, medical X-ray multicell (cell size 1×1×1 mm) gamma-ray detectors, monocrystals of cadmium telluride and selenide made it possible to manufacture miniindicators of radioactivity, multicell photodetectors, acoustothermometers for measuring temperature of viscera in biologic objects with sensitivity of 0.3 °C, laser TV cells of cadmium sulphide single crystals, transistors on the basis of unilateral epitaxial silicon structures, etc. [36].

The authors of the work [37] suppose that space industrialization will allow the stations accumulating energy and recycling luminous energy to be constructed at the distance of 0.1 A.U. (astronomic unit) from the Sun. These stations will direct the focused flows of SHF energy and laser radiation to special devices arranged in circumterrestrial geostationary orbits, and then, to energy receivers in some region of the Earth surface — for energy consumers. The advantage of such energy-transfer stations consists in their lower specific material consumption and thus, lower dimensions since the solar radiation flux will be incommensurably more intensive at the distance of 0.1 A.U. Besides, it is supposed to deliver small asteroids to circumterrestrial zone and to use their resources for the construction works. Resources of the Moon and then of Mercury will be utilized as building materials.

International Research Centre will be probably created on the Moon in the first half of the 21st century. This will result in obtaining complete data on resources of this celestial body and elaboration of optimal methods of its industrial development. Continuous transport Earth-Moon communication will be organized in that period.

Projects of several expeditions to the Mars will be realized in the 21st century, and the International Research Centre will be created on the Mars proceeding from the expedition results. Russia jointly with NASA (USA) and European Space Agency plan to launch two space vehicles to the Mars in 2014 — one piloted SV with a crew of 6 persons and one cargo SV. It is planned that three astronauts — the expedition participants — will land on the Mars surface and stay there for 30–50 days. Climate of the Mars is not very close to the Earth one: efficient temperature 216 K, temperature variations near the surface (T = 20–30 K; atmosphere composition (vol. %): CO_2 — 95; N_2 — 2.7; Ar — 1.6; O_2 — 0.15); the atmosphere pressure near the surface, depending on the relief, is from 0.18 to 1 kPa (1.35 — 7.5 mm of mercury column under the Earth conditions); soil includes (mass %) the following elements: SiO_2 — 45; Fe_2O — 18, Al_2O_3 — 5, MgO — 8, CaO — 5, SO_2 — 8. The projects of flights to the Mars can be realized owing to the newest achievements in the field of new kinds of fuels (including nuclear fuel), new principles of protection from radioactive radiation, new efficient engines on liquid hydrogen and oxygen, and on nuclear fuel. More powerful information and computer systems will be created. This will result in obtaining complete data on geological resources of rare metals in the ore bodies of the «red» planet and in elaboration of the most rational methods of its industrial development by the Earth dwellers.

The flights of piloted spacecrafts on hydrogen fuel to planet Venus will be probably realized in the 21st century. The USSR launched 16 interplanetary spacecrafts (*Venera-1* — *Venera-2*) for the Venus exploration according to the corresponding program. The first spececraft *Venera-1* (mass 643.5 kg) was launched on 12.02.1961, while *Venera-16* (mass 5300 kg) — on 14.10.1983. Spacecrafts Venera-1 — Venera-16 were supplied with experimental gears, sets of spacecraft-board equipment, including the attitude control systems, systems of power supply from the solar cells, space transport power plants, deep space radiocommunication systems and orbital measurement systems, devices for spectral analysis of composition of the atmosphere, clouds, soil, etc. The investigations in automatic conditions were performed to study the composition and properties of the Venus atmosphere and clouds composition.

First photographs were sent to the Earth from American interplanetary automatic station *Cassini*. The photographs were taken from the distance of 285 mill.km and evidence for normal operation of all the station systems. The flight of interplanetary satellite Cassini lasts for 5 years. The station has already covered a half of the distance between the Saturn and Jupiter orbits. In the near future Cassini will send to the Earth sensational photographs of Saturn's rings and results of analysis of the planet atmosphere. In accordance with calculations the interplanetary satellite *Cassini* will achieve its near-Saturn orbit on July 1, 2004 and will orbit the Saturn during 4 years as its artificial satellite.

The above data about planets Mars, Venus, Mercury, Saturn and Moon could be obtained only owing to the progress in development of new technology, high technologies and energetics which have led to development of space-system engineering and creation of spacecrafts which can fly in automatic mode and find the way to the point of destination in the boundless space and perform efficiently the tasks set by the Man. Cosmonautics has given much the mankind and it promises even more — the unprecedented progress in various fields of science, technology and industry. This is favoured by the completion of the «cold war» which often held the world on the brine of nuclear catastrophe, which could lead to death of every living thing on our planet. Space industrialization to the benefit of people all over the world with the help of cosmonautics can give the mankind a lot of unknown, new material welfare but only provided that UNO will function with the right of legitimate political representative of people from all countries of the world.

REFERENCES

[1] L.P. Kozin, VI Int. Conf. «Hydrogen materials science and chemistry of metal hydrides», Ukraine, Yalta, Sept. 2–8, 1999, pp. 284–285.
[2] L.F. Kozin, D.V. Sokolsky and Yu.P. Balybin, Direct Conversion of Thermal Energy into Electric Energy and Fuel Elements, Vol. 64, No. 2 (1975) 136.
[3] S.V. Volkov, J. Inorg. Chem., No. 11 (1990) 136.
[4] S.V. Volkov, Ukr. Chem. J., No. 7 (1982) 2789.
[5] V.I. Subbotin, Bull. Rus. Acad. Sc., No. 12 (2001).
[6] Yu.P. Yelagin, State of the World Nuclear Energetics. Nucl. Eng. Abroad, No. 1 (1999) 9.
[7] Yu.K. Zavalishin, Object 551, Saransk, Russia, 1996.
[8] A.S. Koroteyev and V.M. Nesterov, Energetics, Bull. Rus. Acad. Sc., No. 5 (2002) 3.
[9] A.I. Kiselev, A.A. Medvedev and V.A. Menshikov, Cosmonautics on the Border of Millenia. Results and Prospects, Mashinostroyenie, Moscow, 2001.
[10] Yu.V. Kondratyuk, Cosmonautics* Encyclopaedia, Sovetskaya Entsiklopedia, Moscow, 1985, 167.
[11] L.P. Kozin and S.V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv, 2002.

[12] E.E. Shpilrain, S.P. Malyshenko and G.G. Kuleshov, Introduction in Hydrogen Energetics. V.A. Legasov (ed.), Energoatomizdat, Moscow, 1984.
[13] V. Belokon, Engineer, No. 9 (2002) 2.
[14] L.P. Kozin and S.V. Volkov, International Conference, Grenoble, 2003.
[15] Yu.V. Pleskov, Photoelectrochemical Conversion of Solar Energy, Khimiya, Moscow, 1990.
[16] E.B. Kuzminsty, G.Ya. Kolbasov, Ya.Yu. Tevtul, and N.B. Golub, Nontraditional Electrochemical Energy Conversion Systems, Akademperiodyka, Kyiv, 2002.
[17] O.A. Gorshkov and A.S. Koroteyeva, Energetics, Proc. Rus. Acad. Sc., No. 5 (2000) 66.
[18] A.N. Arbekov, A.I. Leontyev and V.L. Samsonov, et al., Energetics, Proc. Rus. Acad. Sc., No. 4 (2002) 3.
[19] M.S. El-Genk, Proc. of STAIF-2000. 17th SSNPS, American Institute of Physics, 2000.
[20] V.A. Legasov, Pravda, 1998, May 20.
[21] S.A. Subbotin, V.A. Stukalov and Yu.F. Chernilin, Energy: Economics, Technology, Ecology, No. 3 (2002) 10.
[22] E.P. Velikhov and P. Robinson, Energy: Economics, Technology, Ecology, No. 2 (2003) 33.
[23] S.P. Kapitsa, Bull. Rus. Acad. Sc., 3 (1998) 234.
[24] Great Soviet Encyclopaedia, 3rd ed., USSR, Moscow, 17 (1974) 28.
[25] S.V. Volkov, V.A. Legasov and A.V. Gorodusky, et al., Author's certificate 811 867 of the USSR. MKI^3 C 25 B 1/02 Electrolyte for Hydrogen production, Bull. 23. 1983.
[26] O.G. Zarubitsky, V.A. Legasov, A.V. Gorodysky, et al., Bull. No. 23, 1983.
[27] S.V. Volkov, J. Inorg. Chem., No 25, Vol. 1 (1980) 87.
[28] L.F. Kozin and V.A. Sakharenko, Ukr. Chem. J., Vol. 50, No. 1 (1984) 9.
[29] L.F. Kozin and R.G. Sarmurzina, J. Appl. Chem., Vol. 54, No. 10 (1981) 2176.
[30] L.F. Kozin, Ye.O. Berezhny and B.I. Daniltsev, VI Int. Conf. «Hydrogen Material Science and Chemistry of Metal Hydrides», Ukraine, Yalta, Sept. 2–8, 1999.
[31] S.P. Malyshko, F.N. Pekhota, Energy: Economics, Technology, Ecology, No. 1 (2003) 2.
[32] Lu Yunsian, Proc. Rus. Acad. Sc. Vol. 70, No. 4 (2000) 338.
[33] V.G. Gorshkov, K.Ya. Kondratiev, K.S. Losev, Ecology, No. 3 (1998) 163.
[34] V.I. Vovk, et al., eds, Ukraine in the Context of «Agenda for the 21st Century», Nora Print, Ukraine, Kyiv, 1998.
[35] Tieri Allo, Energy: Economics, Technology, Ecology, No. 12 (2002), 2.
[36] V.Yu. Andropov, V.M. Biryukov and E.V. Markov, Khimiya i zhizn, No. 4 (2000) 14.
[37] V.S. Avdutievsky and L.V. Leskov, Future of Science, Znanie, Moskow, No. 20 (1987) 108.

Chapter 2

Energy Balance

2.1. Energetics on Organic Fuel

The mankind faces three global energy problems in the 21st century:

1) not to let the energy crisis; 2) to decrease the air atmosphere, waters and soil pollution with toxic substances; 3) to lower thermal contamination of the planet as a result of losses from the power and industrial plants in the environment. These three problems can be solved simultaneously by creation of alternative ecologically pure energy systems with hydrogen as heat-transfer agent. Special consideration given to these problems is stimulated by the intensive growth of the planet population which number was $2.5 \cdot 10^9$ in 1950, almost twice increased in 1995, and reached $6.1 \cdot 10^9$ in 2000. From the data of [23] the estimated quantity of the Earth's population will be $7 \cdot 10^9$ by 2007. According to prediction of the International Institute of System Analysis (Austria) the Earth population will be $8.2 \cdot 10^9$ in 2025–2050, and about $12 \cdot 10^9$ by 2100 [2, 3]. According to the optimal estimate of UNO and International Institute of Applied System Analysis (IIASA) the population number of the Earth will reach the constant limit of $11.6 \cdot 10^9$ by 2150, which will not change even by 2200 [1].

Nowadays the mankind uses three kinds of energetics on industrial scale: «organic» energetics; nuclear energetics; energetics based on the use of renewable energy sources (RES). Problems of hydrogen energetics, also related to RES, will be considered as the promising energetics of the future. What are the volumes of organic fuel used by the organic energetics? An analysis of availability of organic fuel resources made in [4] has shown that the world reserves of oil will last for 50 years, those of natural gas for 100, and of coal for 350–500 years. According to prediction of V.I. Subbotin, Member of the Russian Academy of Sciences, oil will remain the basic energy source in Russia during no more than 20 years, and natural gas during 80 years [5].

The Earth population growth is accompanied by the rapid progress in science and technology which has already resulted in the huge jump in development of productive forces in the basic branches of industry consuming the ever increasing quantities of energy. In the period from 1900 to 1925 the annual average increment in the world production of energy was equal to 2.9 % and from 1926 to 1950 it decreased because of wars which embraced great European and Asian territories, and was only 2.2 %. In the period from 1951 to 1975 the energy increment was 4.8 % and from 1976 to 2000 — 5.2 %. The period from 1950 to 2000 was connected with development of power-consuming cosmonautics and realization of the launching of thousands of spacecrafts.

The world energy consumption as a whole doubled every 10–15 years and from 1950 to 2000 it increased five times. The developed industrial countries today concentrate 16 % of the world population, 78 % of the world gross product (WGP) and 55 % of the world energy consumption [6]. Eighty four percent of the world population live in the developing countries, and only 22 % of WGP and 45 % of the world energy consumption fall upon them. It is supposed that the steady tendencies of the 50's being preserved by the beginning of the 21st century, the WGP can double during the next 20 years, the population number will increase by 25 % and power consumption by 50 %. Oil and natural gas being the most technologically effective energy carriers, their role in power supply will surely grow up to certain limit. Oil can cover only 40–42 % of power consumption, natural gas — 28–30 %, and coal 22–25 %. Thus, according to predictions the specific weight of oil and natural gas in the world fuel-power balance will be 68–72 %. It is clear that the share of oil and natural gas as energy carriers will decrease and that of coal will increase.

There are also other interesting reasons. In the 20th century the world energy consumption increased more than 20 times Beginning from the 50's and up to the energy crises of 1973–1974 and 1977–1978 the growth of power resources consumption made 4.5–5.0 % a year. The share of oil and natural gas in electric energy production was 26.9 and 10 % in 1950, and 42.8 and 20.5 % in 1970, respectively. The Earth's population doubled in the 20th century for 40 years, while the power resources consumption doubled for the period of 30 years, and reached the amount of $15 \cdot 10^9$ t of conventional fuel (tc. f)* by 2000 [5]. As it was shown in [7] the world oil production has increased 6.2 times (from 521 mill.t to $3.22 \cdot 10^9$ t) for this period, natural gas — 13 times (from $191 \cdot 10^9$ m^3 to $2.49 \cdot 10^{12}$ m^3), and coal 2.9 times (from $1.55 \cdot 10^9$ t to $4.5 \cdot 10^9$ t) (Fig. 2.1). The world consumption of primary energy carriers reached $8.477 \cdot 10^{12}$ t c. f. in 1998, and 89 % of produced energy fell on the part of «organic» energetics. The share of oil consumption was 39.7 %, coal — 22.0 %, natural gas about 23.0 %, nuclear energetics — 7.64 %, hydroenergetics 5.53 %, and other RES — 2.33 %. It is clear from the above-stated that such hydrocarbon raw materials as oil, natural gas and coal were the basic source of energy in the 90's. The share of oil in the world fuel-energy balance has increased from 27 to 47.9 % for the period from 1950 to 1970, but by the beginning of the 1990's it decreased to 39.2 — 40.8 % (because of resources exhaustion and growth of prices) and in 1996 it was

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* Fuel which releases in combustion 29 288 kJ/kg of fuel (7000 kcal/kg) is taken as conventional fuel.

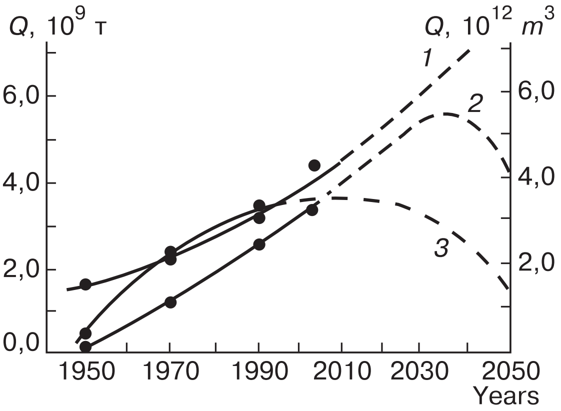

Fig. 1. Production of bituminous coal (*1*), natural gas (*2*) and oil (*3*) in different years

35.6 %. About 39.7 % of produced oil is consumed for the production of electric energy. The share of consumption of natural gas has increased from 9.8 % in 1950 to 18.4 in 1970, and then to 21.9 in 1980, to 22.0 % in 1990; in 1996 it decreased to 20 %, and now it is 23.0 %. The consumption of bituminous coal has decreased from 61.5 % to 30.9 % and to 23 %, respectively, for the period of 1970–1990. It something increased then, an in 1996 it was 34.9 %. In 1998 the consumption of primary energy sources (oil, natural gas, coal, RES and NE) was $402 \cdot 10^{15}$ kJ which was equivalent to $9.58 \cdot 10^9$ t of oil equivalent (t o. eq.). The share of organic fuel was $320 \cdot 10^{15}$ kJ ($7.63 \cdot 10^9$ t o. eq.) [4]. The share of oil, natural gas and coal was $3.39 \cdot 10^9$, $2.02 \cdot 10^9$ and $2.22 \cdot 10^9$ t o. eq., respectively. The consumption of bituminous coal can increase more quietly but it would be remembered that its reserves are exhaustible. Volumes of the world consumption of energy carriers as well as energy consumption in industrial and developing countries in 2000 are shown from the data of Table 1. Characteristics presented do not differ from the data of the work [6]. It is seen that oil was the basic energy carrier in 2000. The consumption of gas and coal relative to that of oil is 57.5 and 50 %, respectively. In 2000 total energy consumption from 5 abovementioned energy carriers in industrial countries was $2.1667 \cdot 10^{15}$ kJ ($6.0191 \cdot 10^{11}$ kWh) and in developing countries — $1.7854 \cdot 10^{11}$ kJ ($4.9781 \cdot 10^{11}$ kWh). The consumption energy generated by nuclear plants (NPP) by developing countries is thrice less than that in industrial countries, and energy from renewable sources 1.6 times less. The question is how the demand for oil, natural gas and other hydrocarbon raw materials will be satisfied in the future? Today, only 5 countries of the Persian Gulf (Saudi Arabia — 26 %, Iraq — 11 %, United Arab Emirates — 10 %, Iran and Kuwait — 9 % each) possess 65 % of proven world reserves of oil (the share of Russia 5 %, Kazakhstan — 7 %, the USA only 2 %). Natural gas, which is most preferable organic fuel from the viewpoint of economy, technology and ecology, is also concentrated in the same Persian Gulf (33 %) and in Russia (33 %). Coal is concentrated in 5 countries of the world

Table 1
World consumption of energy carriers and energy consumption in industrial and developing countries in 2000

Energy carrier	World consumption of energy carriers %	Energy consumption			
		Industrial country		Developing countries	
		$n \cdot 10^{15}$ kJ	$m \cdot 10^{11}$ kWh	$n \cdot 10^{15}$ kJ	$m \cdot 10^{11}$ kWh
Oil	39.5	0.8278	2.2996	0.6086	1.6907
Gas	23.0	0.5680	1.5779	0.4869	1.3553
Coal	22.0	0.3246	0.9017	0.4869	1.3526
RES*	7.86	0.2028	0.5634	0.1273	0.3536
NE**	7.64	0.2435	0.6764	0.0812	0.2256
Total	100.0	$2.1667 \cdot 10^{15}$	$6.0191 \cdot 10^{11}$	$1.7854 \cdot 10^{15}$	$4.9781 \cdot 10^{11}$

Note: RES* — renewable energy sources; NE** — nuclear energetics.

(USA — 25 %, Russia — 15 %, China — 12 %, Ukraine — 9 % and Australia — 9 %), possessing 71 % of the proven world reserves.

The consumption of organic fuel in the world depends on geographic distribution of one or another country and is greatly nonuniform. Fig. 2 demonstrates energy consumption of primary hydrocarbon fuel in some countries and regions of the world (in the units $\Psi \cdot 10^9$ J) per capita. As is evident, the energy consumption per capita in 1998–2000 was in the USA $\Psi = 330 \cdot 10^6$ kJ, $330 \cdot 10^6$ kJ, in the Commonwealth of Independent States — $140 \cdot 10^6$ kJ, in Western Europe — $136.7 \cdot 10^6$ kJ, and in Southern Asia only $21.3 \cdot 10^6$ kJ, which is 15.5 times lower as compared with the USA. The fuel consumption can be also presented in weight units from the data of 5 < It is 11 t c. f. a day per capita in the USA, 8 — in Western Europe, 1.1 — in developing countries which corresponds to 3 kg c. f. a day. A family of 3–6 persons in the middle zone needs 3–4 t c. f/year for comfortable life.

Primary sources of energy are consumed nonuniformly practically in all the countries of the world. Data on commercial primary energy consumption in the world regions for the period of 1970–1998 are given in Table 2. It is evident that the highest quantity of consumed primary energy resources falls to Northern America (the USA and Canada) which consumed $104.3 \cdot 10^{18}$ J (29.4 %) of energy in 1998, while the countries belonging to the Organization for Economic Co-operation and Development (OECD) including Czech Republic, Hungary and Poland consumed $70.1 \cdot 10^{18}$ J (19.7 %), the former USSR (CIS countries) — $37.5 \cdot 10^{18}$ J (10.6 %), and China — $36.0 \cdot 10^{18} \leftarrow$ J (10.1 %). The world countries united into OECD consumed $207.2 \cdot 10^{18} \leftarrow$ J (58.4 %) of primary energy, countries with transition economy — $42.3 \cdot 10^{18}$ J (11.9 %) and developing count-

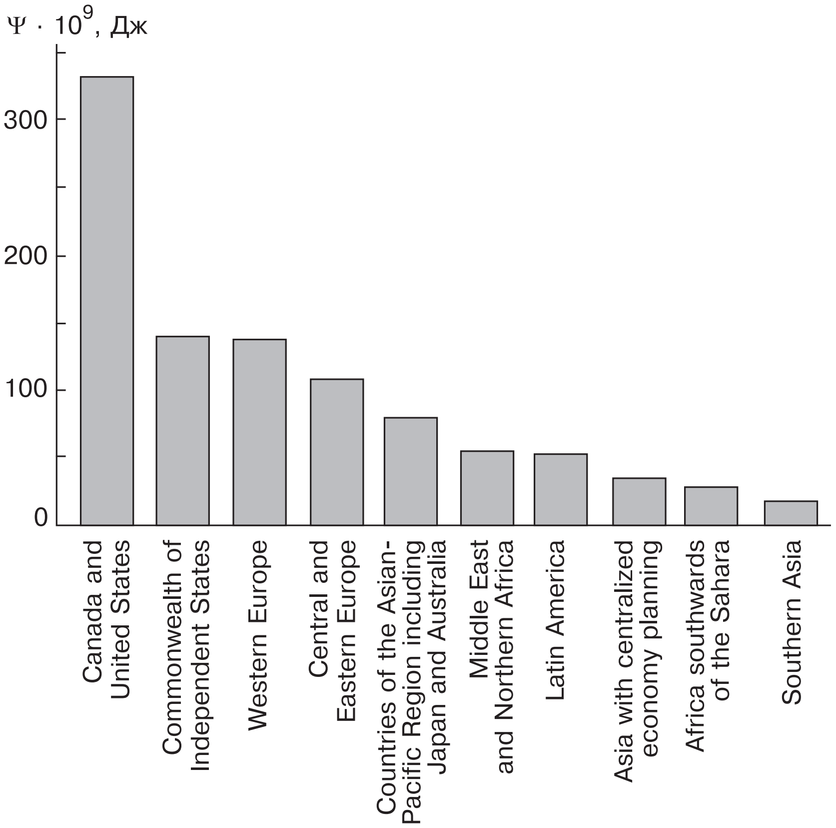

Fig. 2. Primary energy consumption per capita in different regions of the world

ries — $105.5\cdot 10^{18}$ ← J ← (19.7 %). Annual increment of energy for the period of 1970–1998 changed from 0.6 % in CIS countries (the former Soviet Union) to 6.0 % in the Middle East countries.

Instability of the cost policy of exporters with respect to oil is a characteristic peculiarity of «organic» energetics. The latter is conditioned by the fact that industrially developed countries of the world — the USA, Western Europe, Japan, Republic of Korea (Southern) suffered acute deficit of hydrocarbon fuel. Thus, the USA imports 56 % of oil and that is why this country economy reacts immediately to political and economic movements in countries-exporters of oil. Coal is the dominating fossil fuel in energy consumption structure of China (73 %) and only 6 % falls on the share of oil. Hence, sharp changes of prices for oil almost do not affect the China economy.

Change in the cost of oil barrel for the period embracing 150 years in shown in Fig. 3. To plot a function «oil barrel cost-time» we have used the data of [4, 6, 8]. As is evident the world prices for oil depend on time impressed by development of new oil production methods, international economic situations (e. g., the rise of economic activity in 1895–1904, 1920–1925), wars between countries, terroristic actions, etc. The energy crisis of 1937 stopped great flows

Table 2

Global consumption of primary energy (n*10 J) in the world regions in 1970–1998

Regions	Years				Energy shove for 1998, %	Annual energy increment for the petrol 1970–1998, %
	1970	1980	1990	1998		
North. America	74.7	85.6	93.4	104.3	29.4	1.2
South. America	5.7	9.2	11.3	15.1	4.3	3.6
OECD-Europe-I*	51.6	51.9	66.5	70.1	19.7	1.1
OECD-Europe-II[2]*	3.6	6.1	6.5	4.8	1.3	1.0
Former USSR	31.8	47.2	58.5	37.5	10.6	0.6
Middle Est	3.0	5.0	10.6	15.4	4.3	6.0
Africa	2.9	5.6	8.9	11.0	3.1	4.8
China	9.8	17.8	28.5	36.61	10.1	4.8
Asia[3]*	6.0	10.6	18.8	28.1	7.9	5.7
Pacific Countries OECD [4]*	14.1	19.4	26.0	32.8	9.2	3.0
World, total	203.2	269.0	328.9	354.9	100	2.0

* OECD-Europe-I – countries belonging to Organization for Economic Cooperation and development, including Czech Republic, Hungary, Poland.

2* OECD-Europe-II – except for OECD Europe I and CIS Countries (former USSR).

3* Asia – countries of Asia, except China; the Pacific countries OECD.

4* Australia, Japan, Republic of Korea (Southern) and Now Zealand.

of energy carriers to the USA, Western Europe, Japan and United Kingdom, etc. and to other industrially developed countries. As a result, prices for oil increased 4–5 times and most thermoelectric stations in different countries began returning to coal. There were several causes of energy crisis of 1973–1974: out-of-schedule oil production; lack of buffer oil reserves in consumers; defects of geological prospecting in estimating oil reserves in the deposits under development; policy of artificial reduction of prices for oil in the countries of the Near and Middle East, globalization of oil market by several corporations and monopolies. The crisis results proved to be very serious for the economy of the USA, UK, Japan, Denmark and other countries. The industrial countries which had not overcome the energy crises of 1973–1974 faced the crisis of 1977–1978 which decreased energy production by 10–15 % again, called inflation and other economic cataclysms [8–11]. It was expected that the price of 1 barrel of oil will not surpass 64–70 dol. (400 dol./t). But real prices on the peak of energy crisis of 1977–1976 as is seen from Fig. 3 proved to be higher.

Quick reorganization of oil-dependent energetics with the increase of specific weight of bituminous coal, nuclear energetics and nontraditional renewable energy sources — solar, geothermal, wind, biomass energy were necessary to

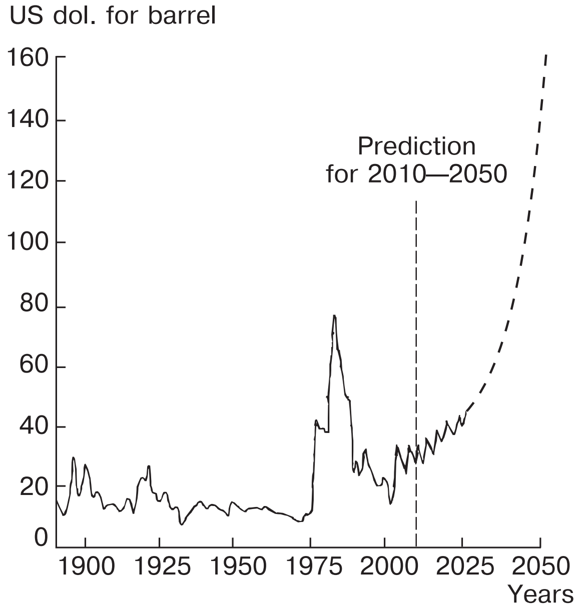

Fig. 3. Dependence of changes in the cost of 1 barrel of oil for the period of 1890–2050 (there is a prediction for 2003–2050)

improve the situation in energetics and to overcome the consequences of energy crisis. Conceptions were proposed to restrict energy consumption and to realize energy-saving potentialities. The surmounted energy crises did harm both to countries-exporters and importers of energy carriers. Oil importers realized that the era of cheap raw materials for energy production was finished and the world entered the epoch of expensive energy. But even in our days energetics of many countries remained and oil-dependent branch.

International market sharply reacted to events of September 11, 2002 in the USA by the increase of one oil barrel price from 31 to 30 US dollars. The maximum increase of prices in the period of 1976–1998, determined by the price policy of OPEC, reached 78 dollars in the 70's. OPEC regulates prices on the world market, controlling the amount of produced oil. If the international price for oil drops below 33 US dollars and holds during 10 days, the countries-members of OPEC reduce oil production by 500 000 barrels a day. In 2001 OFBC used such a technique thrice, and oil production being lowered by 3.5 million barrels it preserved stability of oil market.

It is seen from the data presented in Fig. 3 that the price for one barrel varied in the 20th century, and in the period of three crisis situations it increased twice and above. Thus the average price of one barrel of oil in the period of 1980–2001 it was 19.21 and in the period of 1974–2001 — 34.78 US dollars [6] while the predictions of oil consumption up to 1979 supposed the exponential growth and stable prices for oil up to the end of the 20th century [41]. The unexpected «oil shock» of 1970 disproved the data of predictions. As a result of oil crisis predictions about the future of the world oil market became more careful.

Physical deficit of oil because of the exhaustion of the «black gold» deposits did not affect the oil market in the past historical period. But this deficit will undoubtedly show itself in the future. Since oil reserves are finite, so the prices will grow according to logarithmic law with gradual exhaustion of oil reserves. In Fig.3 the authors give a hypothetical prediction of prices for the barrel of oil for the period of 2010–2050. One can expect that in 2050 the cost of one barrel of oil will reach 160 dollars.

The rise in oil prices will be promoted by the developing countries joining the oil market. The share of energy consumption in these countries will increase to 55 % in 2020, while that of the developed countries will lower to 45 %. The consumption of oil and liquid artificial fuels will grow by 60–70 % to 2020, and by 100–110 % to 2040. Energy consumption in transport will rise by more than 70 % by 2020. In the USA and developed countries there are 777 motor cars per 1000 persons today, and by 2020 this number will increase to 800. The number of cars per 1000 persons will increase from 549 (2000) to 658 (2020) in industrial countries. In CIS countries and Eastern Europe, developing countries and China the above said characteristics will be make 160→220, 40→80, 12→52 cars, respectively, in 2000 and 2020. During two decades the electric energy consumption will increase by 70–80 %.

In accordance with prediction of International Energetic Agency (IEA) as to development of the world energetics in the period from 1997 to 2020 the mankind demand for energy will increase by 57 %. About 90 % of the world demand for electric energy will be satisfied at the expense of oil, gas and coal in 2020. The demand for coal will increase by 45 % owing to China and India. Electric energy production will require 37 % of mined coal, 30 % — of natural gas and 33 % of oil. Coal consumption being increased, the volumes of CO_2 and metal oxides ejection from TES into the environment will increase by 60 % all over the world.

Calculations demonstrate that 3.67 kg of carbon dioxide are formed under complete combustion of 1 kg of carbon in 2.67 kg of oxygen [5]. To burn 1 kg of natural gas (methane) consisting of 0.75 kg of carbon and 0.25 kg of hydrogen one needs 2 kg of oxygen for burning carbon and 2 kg of oxygen to burn hydrogen. As a result one can observe formation of 2.75 kg of carbon dioxide and 2.25 kg of water. Thus, the thermal electric station with total power of 1 GW a year, produces $7 \cdot 10^9$ kWh of electric energy, burns $2.15 \cdot 10^6$ t c. f., and withdraws $5.7 \cdot 10^6$ t of oxygen from the atmosphere, ejecting $7.9 \cdot 10^6$ t of carbon dioxide to the environment. Besides, huge amounts of nitrogen oxides and sulphur oxides are formed in the combustion zone from the air nitrogen, if sulphur is available in organic fuel. When bituminous coal is burnt at TES, as it will be shown in

Chapter 8, huge amounts of sulphur, nitrogen and metals oxides are formed which pollute the environment and affect the health of people in this region.

From the data presented it is seen that only hydrogen, which combustion product is pure water, does not make harm to the environment. But the complete transition of the world energetics to hydrogen fuel will require, as in any other branch, milliards of capital investments. Thus oil and natural gas in the first quarter of the 21st century will continue playing the decisive role in the fuel-energy balance of most countries of the world. In the second quarter of the 21st century there will come a necessity of transition from oil, as the major and most convenient and well-assimilated energy carrier, to less convenient energy sources, such as bituminous coal and nuclear energy. Bituminous coal will be more and more widely used for gasification and production of gaseous and liquid artificial fuels. TES on bituminous coal will be equipped with collectors of sulphur, nitrogen and metal oxides (adsorbers, catalytic systems), thus the power plants equipped with such adsorbers will not affect the environment. Some TES will be transferred to the products of coal gasification and they will work according to the scheme of integrated gasification cycle [4]. This will be caused by the inevitable loss of oil competitiveness (as soon as its reserves will be exhausted) with respect to the coal products (i. e., synthesis gas $CO + H_2$ hydrogen H_2 and artificial liquid fuel) because of the rise in prices for oil.

2.2. Nuclear energetics

The most important part in the mankind fate belongs to nuclear energetics which has no alternatives, the future existence of our civilizations being measured by hundreds and thousands of years. Academician V.I. Vernadsky, an outstanding scholar, thought that the use of nuclear energy in the mankind practice «opens the wider potentialities for the future than the use of steam in the 18th century and electricity in the 19th century, which laid down the foundations of the progress in science and technology» [12, 13]. It was on his initiative, that the works on uranium were started in 1940 in the USSR. Radiochemistry of natural isotopes as well as of uranium and transuranium elements were developed. Investigations on mastering the «intraatomic energy» (according to P.L. Kapitsa) were started on 11.02.1943, and the first nuclear reactor was put in operation in 1948 [14]. The world science history never knew such rates of development in theory and practice as it was with such high-tech branch as nuclear energetics. Theoretical grounds of nuclear physics were created as well as the theory of chain reaction of neutron induced fission (decay) allowing quantitative determination of the charge size and amount of released energy, methods of isotope separation (uranium-235 and uranium-238). Nuclear engineering towns, concentrating plants, plants for industrial isotope separation and the most powerful nuclear industry were created in the country which economy was severely ravaged during the World War II. The considerable progress in development of nuclear energetics was promoted by the fact that the USA and the USSR found themselves in opposition to each other, and this played a positive role in the unprecedented enthusiasm of researchers and engineers in both countries. Nuclear energetics began developing actively in most industrial countries all over the world.

The share of nuclear electric energy in the world which was only 0.6 % in 1970 reached 12 % in 1990 and 17 % in 1996. By the present it has reached 18 % of the total amount of electric energy produced all over the world. From 25 to 78 % of the total amount of all produced energy fall on nuclear plants in the USA, European countries and Japan. For example, 77.21 % of electric energy are produced by NPP in France, 60.1 % in Belgium, 39.0 % in Switzerland, 37 % in the USA, 36 % in Germany 35.2 % in Japan, 26.9 % in UK [5] and about 14 % in other West-European countries [11, 15]. The rates of nuclear energetics powers growth made up 2.7 % a year in the last 10 years of the 20th century. The share of nuclear energy relative to the consumption of all the world primary sources of energy reached 7.64 % [14].

The world countries are divided into three groups as to the development of nuclear energetics and its prospects. The first group includes the developed countries of the world: the USA (103 nuclear power units), Canada, Western Europe (France, Germany, Great Britain, Belgium and others), Japan, Russia and a number of other countries. As to its geostrategic characteristics, Ukraine also belongs to the first group of countries. The major nuclear-energy powers and high-tech nuclear industry of the world are concentrated in the first group of countries. The largest 12 nuclear-energetics companies presented in Table 2 operate in these countries. The first group countries possess the base of knowledge and technological experience that determines the potential for further development of nuclear energy production. The first group countries share in the world experience of NPP operation is 87 %; it reached 10 000 reactor-years in August 2001. But the nuclear energetics development is not so serene. There were tragedies (accidents) which retained further development of nuclear energetics. After the Chernobyl catastrophe the nuclear energetics competes with «organic» energetics, and this energetics resources are extorted by the developed countries from the rest of the world states [48].

The second group includes most developing countries which evolved intensively in the recent decades and can enter the developed world and consolidate there. The second group includes Eastern (North Korea, China) and Southern Asia (India, Pakistan), Latin America (Argentina, Brasilia, Peru), Central (Sweden, Norway, Finland, Austria, Italy, Czechia, Slovakia, Yugoslavia, Greece, and others) and Eastern Europe (Poland, Romania Bulgaria, Hungary, Latvia, Estonia, Lithuania, etc.). In Brasilia, Czechia, Slovakia, Bulgaria, India and China the consumption of nuclear electricity has doubled for the last years. The consumption of nuclear electricity in Russia has increased by 8.8 % with respect to the highest level of 1989. The consumption of nuclear electricity in the Southern and Central America has increased by 5.8 %, in the Asian-Pacific region — by 2.8 %, in Northern America 2.7 %, in Europe by 1.6 %, and in Africa by 1.3 %. The countries belonging to the second group display the most stable adherence to nuclear energetics which is stimulated by the economic reasons — a stable high growth of consumption of the electric and thermal energy as well as the dependence on import of energy resources, including organic resources. Import of energy resources in Japan is 85 %, in the Republic of Korea 97.5 % of 14 nuclear power units connected with the electric and thermal networks in 1998–2000, 13 power units belong to developing countries (India and the Republic of Korea — 4 each, Slovakia — 2, France, Czechia, Brasilia, Pakistan — 1 each).

The third group includes the countries (Equatorial Africa, Central Asia and some other countries) with a decreasing share in the world gross product (WGP). According to [14] these countries cannot be the members of the «nuclear-energy club» in the nearest future. But when proceeding from the demands of the world stability and material progress of all countries over the world with positive growth of the basic gross product, it is necessary to search for the mechanism of these countries transition to the group of developing countries.

It is supposed that the volume of consumable nuclear energy in 2020 in the total amount of the world consumption of energy carriers will make 10 %. We think that the predictions concerning development of renewable energy sources (RES) and nuclear energy (NE) given in the work [6], were pessimistically underestimated (see, Table 1) and the real values of development of the fuel-energy complex will something differ.

It is known that before the Chernobyl accident there existed a conception of the priority development of nuclear energetics in the world countries. It was planned that the power of NPP in European states will increase thrice from 1985 to 2000: from $149.9 \cdot 10^9$ W in 1985 (equal to 16 % of the total power) to $495 \cdot 10^9$ W in 1985 (equal to 38 %); and more than the 4 fold increase was planned in the Asian countries: from $27.5 \cdot 10^9$ W (12 %) to $122 \cdot 10^9$ W (13 %). It was supposed that the energy crisis in hydrocarbon fuel of the 70's being overcome, the world energetics will pass from the use of nonrenewable organic resources to the use of practically inexhaustible nuclear and thermonuclear energy and renewable energy sources. Only in 1983, 301 nuclear reactors with total electric power of $230 \cdot 10^9$ W produced electric energy in 25 countries of the world, and 212 units with total power of $219 \cdot 10^9$ W are at the stage of construction in 29 countries. In the period of 1980 2000 the NPP power would increase by 8.2 — 9.8 % a year. From the data of IAEA the specific weight of NPP in the total production of electric

Table 3

The largest nuclear-energy companies of the world as of the end of 2000 [48]

Companies	Country	Installed power of NPP, MW	Uranium demand in low, t/yr 2000	% of the world electric energy generation in 2000
Electricite de France	France	61 240	9.930	15.8
Rosenergoatom	Russia	19 847	3.960	6.2
Tokyo Electric Power Co.	Japan	15 712	2.715	4.3
Korea Electric Power Co.	South. Korea	12 893	2.360	3.8
Exelon Corp.	USA	12 552	2.440	3.9
National Nuclear Energy Company	Ukraine	11 228	1.895	3.0
British Energy plc.	England	10 685	2.150	3.4
Kansai Electric Power Co. Inc.	Japan	9 270	1.600	2.5
Ontario Power Generation Inc.	Canada	8 982	1.160	1.8
E. on Kemkraft GmbH	Germany	7 657	1.330	2.1
Electrabel S.A.	Belgium	5 583	1.100	1.7
Tennesse Valley Authority	USA	5 517	1.070	1.7
12 companies in total		181 166	31.650	50.3
Other world companies		166 747	31.250	49.7
All over the world		347 913	62.900	100.0

energy all over the world had to be 17 % in 1990 and 23 % in 2000 (and now we have only 7.64 %, see, Table 1).

By the present 438 nuclear reactors have been constructed in different countries of the world which arrangement in our planet is shown in Fig. 4. As is evident, the highest density of arrangement of nuclear reactors falls on Japan, UK, France and the USA. If it were not for the «post-Chernobyl» syndrome, no less than 900–1000 nuclear units with total power of about $700–900 \cdot 10^9$ W would function on the Earth. But in the present, 36 NPP units are constructed by a number of countries. The countries which are constructing NPP are presented in Table 4. Total power of NPP all over the world is $351.327 \cdot 10^9$ W, and power of the constructed NPP will be about $34.756 \cdot 10^9$ W, which equals 9.89 % of the world NPP in operation.

It would be noticed that energy production by NPP constructed in 1970–1985 quickly increased and made up (GWh): 79.0 (1 %) in 1970, 198

Fig. 4. Arrangement of nuclear units of NPP in different regions of the planet

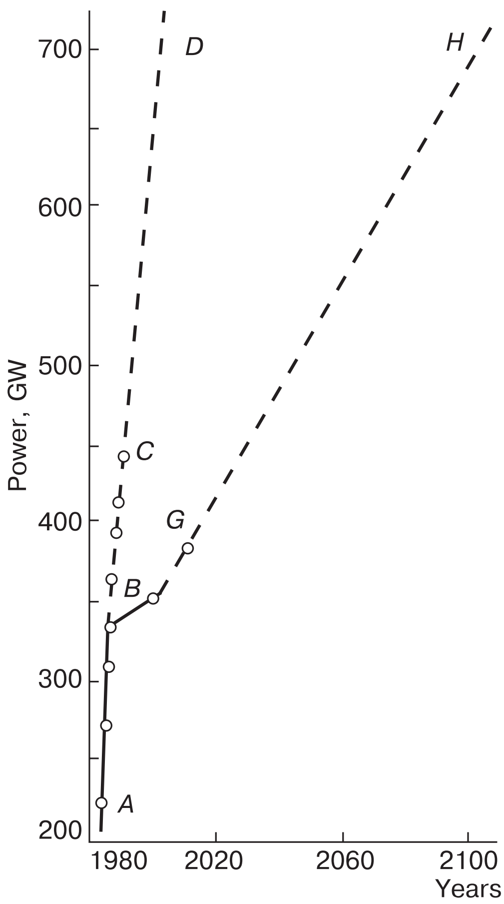

Fig. 5. Growth rates of NPP powers for the period from 1980 to 2100 (at τ > 2000 — prediction)

(3 %) in 1983, 865 (10 %) — in 1982. The power growth rates with time are shown in Fig. 5. It is seen from the Figure (section AB) that in the 80's the NPP power increase by $120 \cdot 10^9$ W (120 GW) for 4 years. If the growth rates of NPP powers of the 80's were preserved (the section BC is the planned increase of NPP powers by 1990), the NPP power in the world would double by 2000 (section CD).

After «Chernobyl» the NPP powers have increased during 14 years of stagnation by 17 GW. The construction of 35 power units given in Table 4 being completed for 10 years (section BG) and these rates being preserved in the future, the NPP power will increase twice (up to 700 GW) only by the end of the century (section GH). The electric energy production by NPP has increase only thrice for the period from 1980 till now as a result of the «post-Chernobyl syndrome». This growth was determined by the improvement of operation indices and by rising the power of the nuclear units [6, 14–18] rather than by the introduction of new NPP. The R&D works on creation of the systems with high resistance of nuclear-energy devices to incorrect decisions in the control of the processes of fission of heavy nuclei and energy

Table 4

Countries constructing nuclear power units and nuclear power plants

Country	In operation		Constructed		Share of nuclear electric energy, %
	Number of units	Power, MW (netto)	Number of units	Power, MW (netto)	
Argentina	2	935	1	692	7.26
USA	103		4*	~ 4000	21.0–37.0
France	58	63 000	2[2]*	~ 3500	77.21–78.0
Japan	53	43 491	3	3190	33.82–35.2
Russia	29	19 843	3	2825	14.95
Rep. of Korea[3]*	16	12 990	4	3820	40.74
Ukraine	13	11 207	4	3800	47.28
Slovakia	6	2408	2	776	53.43
Taiwan	6	4884	2	2560	23.64
Czechia	5	2569	1	912	18.5
China	3	2167	8	6420	1.19
Iran	–	–	2	2111	–
Total:	438	351 327	–	34 756	–

* In the USA 104 NPP are constructed.

[2]* France — 2 nuclear reactors EPR, of 1750 MW (netto) each.

[3]* Republic of Korea (Southern).

transduction were conducted in the period from 1986. The developed safety systems must never execute the instructions being in conflict with the control logic.

According to [5] the system would be capable to arrest the chain reaction under somebody's intrusion to the system of the NPP nuclear unit control. Special attention was given to the determination of optimal time of operation of nuclear units and NPP as a whole. As a result, in accordance with the decisions made by most country governments, leading nuclear institutes, firms, and IAEA the NPP operation term was prolonged to 60 years. The above decision increases the NPP electric generation powers by $14\cdot10^9$ W.

Nuclear energetics is a science-intensive, and first of all, metal-intensive industry. The production and consumption of uranium, nonferrous and especially rare and rare earth metals [19] increased by the end of the 20th century, the consumption of metals being 3–12 times increased during the last decade. It follows that nuclear energetics stimulates the development of other branches of industry (turbine, instrument and rocket production, etc.) and fields of science (material study, high-energy physics, isotope chemistry, kinetics and mechanism of actinides, etc.).

2.3. Renewable Energy Sources

Hydroenergetics. Renewable energy sources (RES) include hydroenergy (with energy of sea waves and tides), energy of wind, geothermal, solar and biomass energy. Contribution of the renewable energy sources (RES of hydroenergetics, biomass energy geothermal, wind energy, etc.) as compared with the total (global) energy consumption of oil, natural gas, coal and nuclear energetics is shown in Fig. 6. It is evident that the contribution of hydroenergetics to the world energy consumption is 5.53 %.

The share of the world hydroenergetics among the renewable energy sources is 70.3 % of generated electric energy. The share of the rest of RES technologies is only 29.7 % of electric energy. In respect of the global energy consumption (in the world) the RES share without hydroenergetics is 2.33 %. With that, the RES energy contribution to the global energetics is (in %): biomass energy — 2.0728 %, geothermal — 0.185, solar energy 0.033, sea energy — 0.0012. Thus, hydroenergetics makes the basic contribution (5.53 %) to energy generation in the world with the help of renewable sources.

According to [4] the renewable energy sources are continuously developing now and provide 7.86 % of the whole world energy consumption. Information on different technologies of RES use for electric energy generation to total data on powers in operation, electric energy production using one or another technology data on tendencies, investments volumes and energy generation methods as well as on electric energy is given in Table 5 cost. As is evident large hydroelectric stations possess the highest powers ($640 \cdot 10^6$ kWh) while small ones generate $23 \cdot 10^6$ kWh. Hydroelectric Q power stations all over the world generate $2600 \cdot 10^9$ kWh/yr of electric energy (large stations 2510 and small ones $90 \cdot 10^9$ kWh/yr).

Table 6 presents the basic total indices of electric energy generation of HEPS in 16 countries of the world 50, generating about $1.699 \cdot 10^9 \leftarrow$ kWh/yr [17]. The estimated economic potential of river discharge (ETRD) on our planet of

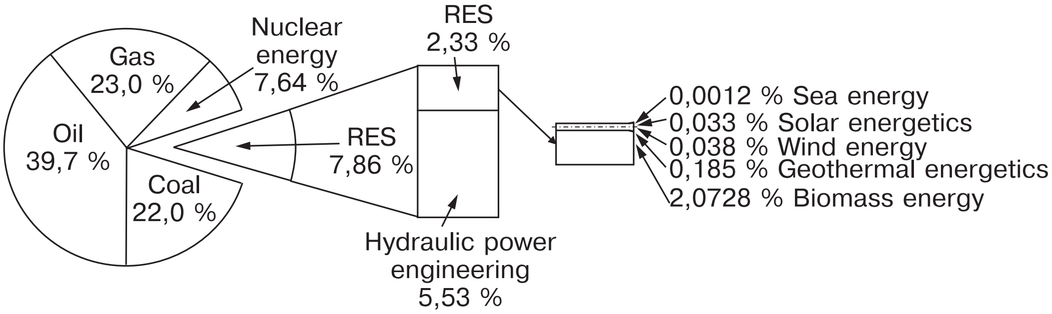

Fig. 6. Share of various kinds of energy in % in the world energy consumption in 1998–2000 (RES-share of renewable energy sources without hydro-energetics)

Table 5

Present state of various technologies of RES use and data concerning tendencies of dynamics of their cost and power [39]

Technologies	Power growth for the last 5 years, % /yr	Operating powers late 1998, 10^9kWh	Power use, %	Electric energy generation, 10^9 kWh	Investment volume, $/kWh	Current energy cost	Potential future energy cost
Wind electric energy	30	$10\cdot10^3$	20–30	$18\cdot10^6$	1100–1700	5–13 c/kWh	3–10 c/kWh
Hydroelectric power stations:							
Large	2	$640\cdot10^3$	35–60	$2510\cdot10^6$	1000–3500	2–8 c/kWh	3–8 c/kWh
Small	3	$23\cdot10^3$	20–70	$90\cdot10^6$	1200–3000	4–10 c/kWh	3–10 c/kWh
Sea energy:							
High tide Low tide	0	$300\cdot10^3$	20–30	$0.6\cdot10^6$	1700–2500	8–15 c/kWh	8–15 c/kWh
Waves	–	exp. phase	20–35	not clear	1500–3000	8–20 c/kWh	not clear
Currents	–	exp. phase	25–35	not clear	2000–3000	8–15 c/kWh	5–7 c/kWh
Thermo	–	exp. phase	70–80	not clear	not clear	not clear	not clear
Biomass energy:							
Electricity	3	$40\cdot10^3$	25–80	$160\cdot10^6$	900–3000	5–15 c/kWh	4–10 c/kWh
Heat	3	$> 200\cdot10^3$	25–80	$> 700\cdot10^6$	250–750	1–5 c/kWh	1–5 c/kWh
Ethanol	3	$18\cdot10^9$		$420\cdot10^9$ J		8–25 $/GJ	6–10 $/GJ
Low temperature	8	$18\cdot10^3$ ($30\cdot10^6$ m^2)	8–20	$14\cdot10^6$	500–1700	3–20 c/kWh	2 or 3–10 c/kWh
Solar photoelectroconverter	30	500	8–20	$0.5\cdot10^6$	5000–10000	25–125 kWh	5 or 6–25 c/kWh
Solar thermal electric energy	5	400	20–35	$1\cdot10^6$	3000–4000	12–18 c/kWh	4–10 c/kWh

$5.5\cdot10$ kW of energy can provide. The generation of $47.520\cdot10^{12}$ ← kWh/yr of electric energy. It is considered now that only 30 % of EPRD are utilized and therefore hydroelectric power stations can generate $14.256\cdot10^{12}$ kWh/yr instead of

Table 6

Basic total technological characteristics of HEPS of 16 world countries

Country	Economically substantiated HEP*, mWh/yr	Total power, mW	Electric energy generation, 10^9 mWh/yr [2*]	Share of hydraulic electric energy, %	Power of constructed HES, MW
USA	3 760 000	75 525	308 800[3*]	8.8	3000
China	1 260 000	72 900	212 900	17.3	35 000
Canada	536 000	65 726	350 000	62.0	882
Brasilia	736 500	56 481	301 198	93.5	12 050
Russia	852 000	43 940	157 500	19.4	8400
Norway	179 600	27 410	116 259	99.4	140
France	71 500	23 100	69 800	15.0	0
India	–	21 963	74 338	25.0	9818
Japan	114 267	21 389	102 587	10.0	1113
Spain	41 600	17 000	39 000	20.0	70
Sweden	90 000	16 204	68 300	47.7	–
Italy	54 000	15 267	51 636	19.4	450
Venezuela	100 000	13 224	57 923	73.0	73
Turkey	123 040	10 215	42 229	38.0	4190
Mexico	32 232	9702	24 616	14.4	900
Ukraine		4700	12 200	7.05	

HEP* – hydraulic energy potential.

[2*] Electric energy generation, 10^9 mWh/yr – miss print in work [50].

[3*] Electric energy generation in the USA by HES is $308\ 800\cdot10^9$ mWh/yr instead 30 880 MW, as is given as work [21].

$2.6\cdot10^{12}$ kWh/yr obtained today as it follows from Table 5. In a number of countries the specific weight of hydraulic power (SWHP) is rather high in the total energy generation. Thus, in Norway, Brazil, Paraguay, Zambia SWHP exceeds 90 %, in Sweden — 47.4 %, USA — 8.8 %, in India, Egypt, Italy, China about 20 %, in Russia — 19.4 % [50], in Ukraine 7.05 % [20]. Hydraulic power generation is (in %); in the USA — 46.6; China — 33.3; Canada — 60.8; Brazil — 60.9; Russia — 40.9; Norway — 48.4, etc. From the data presented it is seen that all the countries have some reserves for increasing the hydraulic power generation.

Both modernization of the operating hydroelectric power stations and the increase of powers by constructing new HEPS takes place now in developing countries, possessing great reserves of hydraulic power. Giant hydroelectric power stations which power will form 3/4 of the world volume of hydroelectric powers are constructed in China, Brazil, India. The greatest HEPS in the world called *Three Canyons* with power of 18 200 MW is erected in China on the Yangtze river; 26 hydraulic turbogenerator units with established power 700 MW each will work at the above HEPS. Annual electric power generation will make $84.7 \cdot 10^9$ kWh. The total cost of the constructed HEPS is $24.6 \cdot 10^9$ US dollars. The China government plans also to build two more HEPS (upwards of *Three Canyons* station on the Yangtze river) with power of 12–15 thou. MW each at total electric energy generation $114–130 \cdot 10^9$ kWh.

Besides, hydroaccumulating electric power stations (HAES), intended to remove electric power deficit during peak-hours, are constructed in industrially developed countries. There are 300 HAES in the world with total establish power of 100 mill. kW. Such HAES may be used in a complex with nuclear power plants to stabilize electric power generation under its low consumption (at night and in the morning), as well as in hydrogen energetics technologies.

About 20 % of EPRD have been assimilated in Russia, 50 % in the European part of Russia, 19 % — in Siberia, and 3 % in the Far East. The total power of HEPS in Russia is 43.9 mill. kW. In 2000, $157.6 \cdot 10^9$ kWh/yr were generated at hydroelectric power plants of Russia, and $12.2 \cdot 10^9$ kWh/yr in Ukraine [20]. It is supposed that the role of hydraulic energy will increase in the nearest decades because of the consumption of hydrocarbon fuel (natural gas, oil) and because of the rise in price for the basic fuel for thermoelectric plants. High reliability of HEPS operation and thus, stability of electric power generation by this renewable energy source is characteristic of hydroenergetics.

High and low tides in the seas and oceans of our planet possess considerable hydroenergetic potential [22, 23]. As it was noticed in Chapter 1, Tony Blair, Prime-Minister of the Great Britain, when he was speaking at the meeting of the UK Royal Society on May 23, 2002, said that the tide waves energy of the coastal strips of the Great Britain being subdued, the country will obtain such amount of energy which will 10 times surpass its demands. The tidal waters of seas and oceans possess especially high energy in narrow straits, when the wave motion velocity can reach 22 km/h. Thus in the Fandy bay in Canada the tidal wave height reaches 18 m, in the Nenzhin bay of the Okhotsk Sea — 13.4 m; in England, France and China the tidal waves height exceeds ten meters. The tidal wave energy was used even in the 11th century, in England, and in the Middle ages in France, Russia, Canada.

The R&D works on the use of the World Ocean energy are carried out all over the world. The best achievements in the field of the sea waves conversion will be assumed as the basis for the future powerful wave electric station (PWE). Two pilot electric power stations are constructed in Norway; each of them will generate about 1.5 mill kWh of electric energy [22, 23]. Great sums are invested in the development of wave energy physics and construction of PWE by the leading companies and governments of Japan, Norway and UK.

Biomass energy. Biomass as the primary source of energy is used on the Earth from time immemorial [24–26]. Even 100 years ago wood, side by side with coals, was the basic energy source in Eurasia. An analysis of the data shows that in different countries up to the second half of the 20th century, from 25 to 34 % of primary energy were obtained from the biomass, and even now 2.0–15.0 % of the total energy in one or another country are obtained from the biomass, depending on the level of the country development [24, 25]. The greatest share of the biomass is used in developing countries, mainly in countryside. Intensive felling with timber use as firewood is observed in these countries. The share of the biomass utilization for energy production is much lower in developed countries. Thus, in the USA the biomass provides only $2.1\cdot10^{12}$ MJ of energy from consumed $82.3\cdot10^{15}$ MJ which corresponds to 2.6 % of the total amount of energy. The USA can produce $(1.5–4.0)\cdot10^{15}$ kJ/yr from phytoremains. According to the data of the First International Conference *Energy from Biomass* Denmark obtains 6 %, Austria 12 %, Sweden 18 %, Finland — 12 % of energy from the biomass. Commercial cultivation of quick-growing trees (poplar, ash, willow, etc.) on inconvenient and nonarable lands for their following use as fuel may be developed in the future. The presented tree varieties have relatively high combustion heat values, equal to 20 730–20 800 kJ/kg of dry wood. Crops of the cultures with great vegetative mass (rape, maize, etc.) in which medium combustion heat of vegetative remains is 16 300 kJ/kg.

Biomass is actively used as a source of energy in the countryside of China for numerous centuries [26]. In 1993 — 70 % of energy for domestic needs were obtained from biomass (timber, plan waste, etc.) in the countryside of China with population of 900 mill. The obtained energy was equivalent to 260 mill. t. c. f. or 40 % of total energy consumption. In 2000 the biomass consumption decreased to 210 mill. t. c. f. which corresponded to 13 % from the total energy consumption. In the European Unit countries biomass is used most efficiently in Portugal, France, Germany, Denmark Italy and Spain [56].

The organic waste value in the world is $7.5–10\cdot10^{9}$ t/yr of dry matter. Besides direct burning of dry biomass (wood, straw, etc.) one can also use other energy technologies for biomass processing to obtain energy: bioconversion (with the use of special strains of microorganisms), thermochemical conversion and gasification with production of electric energy and bio-gas. Energy-generating biostations and plants are rather promising. But it is more promising to use the low temperature heat for biologic processes at nuclear-hydrogen electric power plants (NHEPP) to produce hydrogen by natural gas conversion with utilization of CO_2 at phytotron unit with production of biomass and food products. The use of NHEPP for this purpose will allow decreasing thermal load of NPP on ecology.

From the data of Table 5 one can see the considerable progress in the use of biomass energy when generating electric energy (4.33 % — all the data are presented with respect to RES), heat (18.935 %) and ethanol (3.16 %) which is used as fuel for transport and agricultural vehicles. In developed countries biomass is used in agricultural circulation as it was described in the work [111]. An analysis of biomasses as energy sources is also considered in the works [24–26].

However, biomasses obtained in the agricultural regions of the world are also used as fodder for cattle, for various types of composts for organic fertilizers, and in developed countries of the world — for paper production. That is why that the share of biomass for energy production is small, equal to 2.073 % and there are no reserves for its raising.

It would be also noted that CO_2 is the product of biomass oxidation as well as the product of its conversion (ethanol, methane, biogas, etc.). About 2/3 of population of the former USSR and socialist countries lived in the countryside where biomass (wood, straw and other agriculture wastes) was the main source of energy (heat). After «perestroika» and the USSR disintegration the way of life of rural population has not changed, while the level of industrial production and energy generation have decreased twice in the CIS countries. The amount of CO_2 ejections by industrial plants and TEP has to decrease twice as well. But the amount of CO_2 produced by industry and TEP as compared with the volume of CO_2 in the countryside is so low that total concentration of CO_2 in the air of Eurasian countries has not changed. Thus, biomasses cannot be related to ecologically pure fuels as to CO_2. But in the future the biomass will remain a renewable source of energy. With the increase of the population number and expected exhaustion of oil and gas reserves, it is biomass which will be used in the future in the country-side to produce ethanol, methanol and their mixtures which will prove to be the alternative of liquid fuel, biogas and dry (briquetted) fuel. A considerable share of biomass is used and will be used to produce organic fertilizers, and raise the soil fertility, in virtue of which the use of biomass for production of primary energy will not exceed 6 % of energy in the third millenium.

Geothermal energetics. Geothermal energy was used even in ancient time in both-houses and hot balneological baths. It was the only use of geothermal sources in the course of millenia. «Geothermal vapour», escaping from under the ground was used for the first time for obtaining electric energy in the early 20th century in Italy. There are 4 types of geothermal sources: a) hot water or vapour at moderate depths of 100–4500 m; b) high-pressure water (vapour) containing dissolved methane at the depths of 3–6 km; c) hot dry rocks — anomalously hot geological formations with low amount (or lack) of water; d) magma — melted rocks at 700–1200 °C [8]. Geothermal sources are also divided into the open sources with the temperature of 80–90 °C and closed (underground) with the temperature of 200–300 °C. There are also mountain regions (northern and central regions of Ukraine) with dry mountain rocks with a temperature of 40–60 °C at the depths of 1000 m, and 100–120 °C at the depths of 3000 m (southern and western regions) [27–29]. The share of geothermal energy, with respect to that consumed in the world, makes 0.185 % [23, 25, 26]. A geothermal plant (GTP) of 25 MW is constructed in Germany in the vicinity of Mьnchen.

The GTP is intended for heat supply to the civil and public buildings of the city. They also bore a hole, 1700 m deep, which will supply water with the temperature of 90 °C. Expenditures for the GTP construction are estimated as 14 mill Evro. Geothermal fields (*n* = 270) with the temperature above 150 °C have been prospected in China. Theoretical energy potential of these fields is $6.7 \cdot 10^9$ W. In accordance with the estimates, total geothermal resources of China are $460^* \cdot 10^9$ t c. f. [26]. High reserves of geothermal energy are distributed on the Kuril Islands and Kamchatka peninsula in Russia [23]. The total power of GeoTEP in this region is above 1000 MW. The construction of the Verkhne-Mutnov GeoTEP of 12 MW has been completed on the Kamchatka peninsula. The Mutnov GeoTEP of 25 MW is under construction. The first power unit of 25 MW (4 units of 25 MW each will be built at the GeoTEP) was put in operation in December 2001. Fifty six [26] geothermal fields with hole output above 300 thou. m^3 a day have been prospected in Russia.

Geothermal energy sources occur in the regions of the Earth with active volcanoes. The great number of geothermal sources are known in Central and Southern America, in the Western part of the USA, on the Kamchatka peninsula, in Japan, Taiwan, Indonesia, East Africa, etc. It is considered that 1/3 of the territories of CIS countries possess highly efficient geothermal sources of energy.

Countries utilizing geothermal energy for electric power generation are given in Table 7 [26] . It is seen that the big best quantity of electric energy — $15\,470 \cdot 10^9$ Wh/yr is generated in the USA by the geothermal method. In accordance with the adopted national program of electric power engineering the USA plan to construct geothermoelectric plants (GeoTEP) and to double their power every 5 years during the nearest 20 years. The second place belongs to Philippines, generating electric energy of $9181 \cdot 10^9$ Wh/yr. The total installed power on electric energy generation in 21 countries in 2000 was 7974 MW, while electric power generation on the basis of geothermal energy was $49\,261 \cdot 10^9$ Wh. In 2002 the volume of installed powers of electric power plants (EPE) utilizing geothermal energy was 8256 MW of electric energy [26]. It is expected that by 2005 EPE will exceed 11 000 MW. In the present 58 countries of the world utilize heat of their geothermal georesources not only for electric power generation but also in a form of heat.

It is considered that a geothermal plant of 1 MW is equivalent to 3000 t c. f. Proceeding from the installed powers of electric stations the average coefficient of heat conversion into the electric energy is 70.3 %. Under these conditions the installed thermal power (ITP) is 15 145 MW of thermal powers Quantity of the consumed thermal energy is estimated as $190\,699 \cdot 10^{12}$ J. Total geothermal energy potential in the world is estimated as $140\,000\,000 \cdot 10^{18}$ J or as $38.9 \cdot 10^{18}$ kWh of power (1 kWh is equal to $3.6 \cdot 10^6$ J) [8]. Theoretical geothermal potential accessible for the use in industry is estimated as $600\,000 \cdot 10^{18} \leftarrow$ J or as $1.67 \cdot 10^{17}$ kWh of power.

Table 7

Countries generating geothermal electric energy, their power and generated electric energy

Country	Installed Power MW	Generated electric energy		Country	Installed Power MW	Generated electric energy	
		MW 10^9	%			MW 10^9	%
USA	2228	15 470	79.3	Kenya	45	366	92.8
Philippines	1909	9181	54.9	Guatemala	33	216	74.7
Mexico	755	5681	85.9	Turkey	20	120	68.5
Indonesia	589	4575	88.7	China	29	100	39.4
Italy	785	4403	64.0	Portugal	16	94	67.0
Japan	547	4312	90.0	Russia	23	85	42.2
New Zealand	437	2268	59.2	Ethiopia	8	30	42.8
Iceland	170	1138	76.4	France	4	25	71.4
El Salvador	161	800	56.7	Australia	0.17	1.4	94.6
Costa-Rika	142	592	47.6	Thailand	0.3	1.8	68.5
Nicaragua	70	583	95.1	Total:	7974	49 261	70.5

Table 8 presents a geothermal potential of the Earth continents and Oceania [26]. It is evident that the total high-temperature geothermal potential of the world which can be used for electric energy generation is equal to $33.6\cdot10^{12}$ kWh of power, while low-temperature one exceeds $1400\cdot10^{9}$ kW/yr.

Reserves of geothermal energy in Ukraine are $1\cdot10^{22}$ J which is equivalent to reserves of $3.4\cdot10^{11}$ t c. f. GeoTEP being constructed, the potential installed power of the plants (with account of heat extracted and efficiency of its conversion into electricity) can be $230\cdot10^{9}$ W. From the data of [27] the total geothermal power potential of Ukraine is estimated for thermal powers as $8–9\cdot10^{9}$ W, while for electrogenerating stations or plants — 700–800 MW. Geothermal energy of Ukraine being assimilated, we can save about 15 mill. t c. f. annually [27].

Wind power engineering. Wind energetics share is 0.038 % in the total amount of consumed energy all over the world. Power of operating wind-power stations is 10 mill. kWh, while the quantity of generated electric energy — $18\cdot10^{9}$ kWh. Growth of the wind-driven RES plants in the recent 5 years is 30 % [23, 25, 27, 28]. The use of the wind-driven RES plants in the countries of European continent continuously grows. For example, 8500 wind-driven power plants (WPP) with total power of 5000 MW operate in Germany, which makes a half of all the powers of Europe and 1/3 of WPP power in the world. By 2010 total power of WPP in the world will reach 120 000 MW, i.e. it will increase 5 times as compared to the present level — 25 000 MW [30]. According to predictions the wind power share in the energy balance of the country will reach 5 %

Table 8

Geothermal potential of the world [26]

Continents	High-temperature sources, fit for electric energy generation		Low-temperature sources, fit for direct heat utilization TW/yr (lower boundary)
	Traditional technologies TW/yr*	Traditional and Binary Technologies TW/yr	
Europe	1830	3700	>370
Asia	1970	5900	>320
Africa	1220	2400	>240
Northern America	1330	2700	>120
Latin America	2800	5600	>240
Oceania	1050	2100	>110
World Potential	11 200	22 400	>1400

* TW/yr – terra, equal to 10^{12}.

in 2007, and 18 % by 2020. The installed power of WPP increases by 40 % annually in this country [31].

It would be notices that wind power engineering is the actively developing branch of power engineering especially in Western Europe, China, USA and a number of other countries. Considerable progress in wind power engineering has been achieved in Denmark. The wind power enterprise was put in operation in 2000. It includes 20 wind-driven power plants consisting of 20 *Bonus* company turbines of 2 MW each. In 2003 the Great Britain announced about the supposed increase of wind power plants share in the country to 10 % by 2020, first of all along the coast and even in the sea area. The installed power of wind-driven power plants in China was 262 MW in 1999, 1000 MW in 2000, and in 2005, 2010 and 2015 it will reach 3000, 4900 and 7000 MW, respectively. Utilization coefficient of the installed power in China is 3200–3400 h/yr. Separate wind-driven units in China are grouped into windmill-electric generating plants which installed power reaches 20–25 MW. Such windmill-electric generating plants generate 70–90 GWh of electric energy a year. It is the beginning of wind power engineering development in socium and that is why its contribution to the electric power generation in the world makes only 0.038 % as is seen from Fig. 6.

Solar power engineering. The share of solar power engineering (helios — the Sun) in the total energy consumed in the world is 0.033 %. Solar power engineering belongs to young high-tech field of knowledge [23, 32–35]. There are various possible methods of the solar energy implementation. It is known that solar energy reaching the Earth's surface is 0.14 W/cm /min or 98.075–8.370 J/(cm · min). Our planet land area is equal to $148.847 \cdot 10^6$ km. Total amount of solar energy supplied to the 17 land during 1 hour equals $1.25 \cdot 10^{17}$ Wh. Only 1 % of the planet land area ($1.488 \cdot 10^{16}$ cm^2) being isolated and adjusted to trap solar beams with the help of solar energy concentrators with 15–50 % efficiency, it is possible to obtain $3.67 \cdot 10^{15}$ kJ of energy during 1 hour, and $2.57 \cdot 10^{16}$ kJ under averaged 7-hour exposure [33].

It is possible to obtain $1.75 \cdot 10^{14}$ kWh of electric energy for the same 7 h, when using photoconverters with 20 % — efficiency [33–35].

Proceeding from the predictions the authors [25] suppose that the 21st century will be the age of solar energetics. According to predictions up to 2005 the total power of the solar plants operating in the Mediterranean littoral countries will be 3500 — 13 500 MW which will allow decreasing the hydrocarbon fuel (oil, gas) consumption in the region by 4–15 %. Thus, the electric power generation by the solar power plants in Greece, Spain, and Portugal is $870 \cdot 10^3$, $290 \cdot 10^3$, and $255.2 \cdot 10^3$ MWh/yr, respectively. The Comissariat on solar energy assimilation in France planned to heat 30 % of Civil buildings, generating $174 \cdot 10^3$ MWh by 2000. Solar collectors which can satisfy the agriculture requirements (90 %) for warm water are designed and manufactured in Germany. The total power of photoelectric converters has reached 65 MW in 30 countries of the world. The share of the USA and Japan makes 2/3 of this amount.

Essential success in the field of solar radiation conversion into electricity was achieved under the construction and manufacturing of solar batteries for spacecrafts (SC) and Earth artificial satellites (EAS) [36]. In such a case great numbers of the single photoelectric converters (PEC) are connected as series-parallel units and then as a solar battery. Electromotive force of a single PEC is equal to 0.5–0.55 V, while short circuit current is 35–40 mA/cm^2 of PEC. Power of a single solar battery can be 5–10 kW. The efficiency of Inp-based PEC exceeds 20 %, and that of Si-based PEC — 15–20 % with operation resource — 10 years. Solar batteries may be manufactured of separate modules with the power of 10 kW. In this case power of 10-module solar battery, for example SGTU-10 of the first generation, can reach 100 kW. The batteries SGTU-250 and SGTU-100 with power from 250 to 1000 kW and specific power — 100–250 W/kg are constructed. Photoelectric converters of solar energy into electricity with power of 10 000 MW for space-Earth transmission are elaborated in the USA.

In conclusion of the chapter we would like to make some prediction concerning the energy carriers genesis in the 21st century. It is shown in Fig. 7 how the numbers of the used energy carries will change in the 21st century in %. Basing on analysis of the existing tendencies it may be supposed that by the end of this century the consumption of bituminous coal as energy carrier will increase to 27 %. Under these conditions a half of the mined coal (13.5 %) will be consumed to produce hydrogen used for production of liquid synthetic fuel and will be used as gaseous fuel. The share of oil as energy carrier will be no more than 2 % in 2100, while the amount of consumed gas will decrease to 10 %. The share

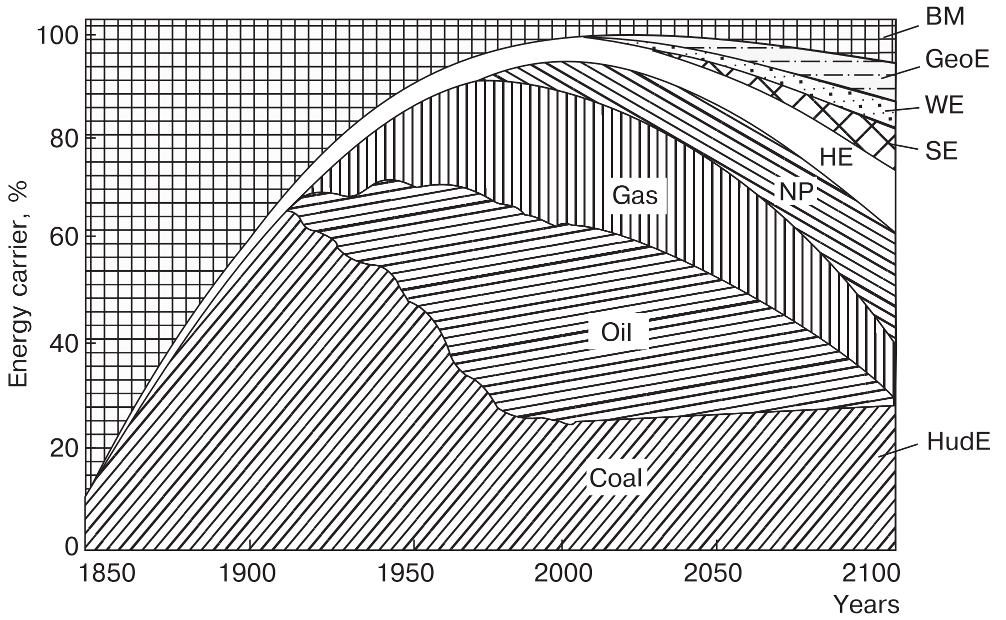

Fig. 7. Change of consumed energy carriers with time (in %) in the period of 1850–2000 and prediction for 2000–2100. BM — biomass; GeoE — geothermal energetics; WE — wind power engineering; SE — solar energetics; HE — hydraulic power engineering; HydE — hydrogen energetics

of nuclear energetics and hydraulic power will increase to 20 and 14 %. The share of renewable energy sources will be (biomass — 6 %, geothermal energy — 6 %; wind power engineering — 8 %, solar energetics — 7 %) 27 %.

It would be noticed that the development of energetics is a continuous process of perfecting technologies, attempts to make them more ecologically pure (depending on economy potentialities). Thus, much time is required to develop «ideal» ecologically pure technologies and their stabilization. One can only hope that in the 22nd century the mankind will master «pure» thermonuclear synthesis of energy, i.e. synthesis without nuclear side reactions resulting in formation of radioactive isotopes (induced radioactivity) in structural elements contacting with thermonuclear plasma. Such problem solution requires enthusiasm of researchers and engineers like that in the international teams of the USSR and USA in the period of creation of nuclear (and thermonuclear) arms under the condition of military opposition of two superstates. This problem solution requires colossal economic investments. But these investments, however high they would seem, will be less, than annual expenditures for energetics development all over the world.

New power plants with the total power of 100–110·10^9 kW are annually put in operation now. Among them (milliards of kW): 34.2 — thermoelectric stations with steam-turbine plants and 30.6 — TES with gas-turbine plants; 10.8 — hydroelectric power stations, 9.7 — diesel TES, 4.5–6.0 — nuclear power plants, the rest — RES plants which require, like any power production, great capital investments. It is considered that by the end of the first half of the 21st century the total world power generation will reach $29 \cdot 10^{13}$ kWh/yr. Such power amount is thought to be enough for the civilization could exist on the Earth.

In the present $26 \cdot 10^{13}$ kWh/yr are generated in total as a result of combustion of the fossil organic fuel by TES and nuclear fuel by NPP. This is 71.5 times less than energy produced annually in nature as a result of living vegetative mass CO_2 consumption. Milliards and hundreds of millions years ago the amount of biologic mass on the Earth was several orders higher. The fossil organic heat carriers represent solar energy, buried for the tens and hundreds of millions years, the energy is contained in once alive organisms (phyto- and citoflora) [37]. The planet land vegetation absorbs annually $6.7 \cdot 10^{17}$ kJ of solar energy; allowing for the ocean green algae this energy amount increases up to $6.7 \cdot 10^{17}$ kJ [38], which is equivalent to $1.86 \cdot 10^{16}$ kWh. We think that this process of the organic mass preservation took place as a result of the global catastrophe 285–350 Ma ago, which provided conditions for the formation and accumulation of hydrocarbon fuel in the Earth's bowels. And this most important source of energy, created occasionally by nature during hundreds of millions up to a milliard years, is consumed by the mankind not in the best way and for the exceptionally short period of time.

REFERENCES

[1] S.P. Kapitsa, Bull. Rus. Acad. Sc., 3 (1998) 234.

[2] Great Soviet Encyclopaedia, 3rd ed., USSR, Moscow, 17 (1974) 28.

[3] N. Nakichenovich, Energy: Economics, Technology, Ecology, No. 12 (1998) 2.

[4] J. Goldenberg, M.M. Brown, N.D.D. Duset, et al. Energetics and Problems of Stable Development. Estimate of the World Energetics. Survey. — UNO Development Program, 2003.

[5] V.I. Subbotin, Bull. Rus. Acad. Sc., N 12 (2001), pp. 1–59–1068.

[6] E.P. Velikhov and P. Robinson, Energy: Economics, Technology. Ecology, N 2(2003) 33.

[7] L.P. Kozin and S.V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv, 2002.

[8] H.-H. Rogner and A. Popecku, Energy and the Challenge of Sustainability. World Energy Assessment, 2000, 30.

[9] K.Ya. Kondratiev and K.S. Losev, Bull. Rus. Acad. Sc., Vol. 72, No. 7 (2002) 592.

[10] Zh.A. Medvedev, Bull. Rus. Acad. Sc., Vol. 72, N 1 (2002) 57.

[11] E.A. Kozlovsky and M.I. Shchadov, Raw-Mineral Problems of National Security in Russia, Mining Univ. Publ. Moscow, 1997.

[12] V.I. Vernadsky, Proc. Acad. Sc. USSR, No. 12 (1990) 127.

[13] N.G. Basov, V.I. Subbotin and L.P. Feoktistov, Bull. Rus. Acad. Sc., Vol. 63, No. 10 (1993) 878.

[14] A.Yu. Gagarinsky, I.V. Gagarinskaya, Energy: Economics, Technology, Ecology, No. 6 (2002) 2.

[15] L.I. Bennet, G.I. Laue, B.A. Semenov and R. Skoldebrant, The World Energetics, Energoizdat, Moscow, 1985.
[16] A.A. Beschinsky and D.B. Wolfberg, The World Enerhetics, Energoizdat, Moscow, 1985.
[17] H.-H. Rogner, A. Popecky, Energy and the Challenge of Sustainability, World Energy Assesment 2000.
[18] Adamov E. // Russian Economical J. No. 5–6 (2000) 80.
[19] L.F. Kozin and V.I. Trefilov, Rare-Metal Industry of Ukraine. Problems and Prospects. Prepr. Kyiv, 1998.
[20] Statistical Year-Book of Ukraine for 2001, Tekhnika, Kyiv, 2002.
[21] Yu.S. Vasiliev, Bull. Rus. Acad. Sc., Energetics, No. 1 (2003) 50–57.
[22] N.V. Vershinsky, The Ocean Energy, Nauka, Moscow, 1986.
[23] A.F. Dyakov, Bull. Rus. Acad. Sc., Energetics, No. 4 (2002) 13.
[24] S. Sawfer and O. Zaborsky (eds.), Biomass of Energy Source, Mir, Moscow, 1985.
[25] Ukraine: Efficiency of Minor Energetics, EC-Energy Centre, Kyiv, 1998.
[26] Yu. Matveyev, Zelena Energetyka (Green Energetics), No. 4 (2002) 14.
[27] V. Larin, Energy: Economics, Technolohy, Ecology, No. 3 (2001) 29.
[28] Yu. Matveev, Zelena Energetyka (Green Energetics), No. 1 (2002).
[29] M. Khvorov, Naukovy svit (Scientific World), No. 2 (2002) 14.
[30] Renewable Energy World, No. 3 (2002).
[31] Brennstoffspiegel, No. 11 (2000).
[32] Yu.V. Pleskov, Photoelectrochemical Conversion of Solar Energy, Khimiya, Moscow, 1990.
[33] E.B. Kuzminsty, G.Ya. Kolbasov, Ya.Yu. Tevtul, and N.B. Golub, Nontraditional Electrochemical Energy Conversion Systems, Akademperiodyka, Kyiv, 2002.
[34] D. Lott, Direct Energy Conversion, Mir, Moscow, 1975.
[35] N.S. Lidorenko, Proc. Rus. Acad. Sc., Energetics, No. 1 (2003) 98.
[36] A.I. Kiselev, A.A. Medvedev, and V.A. Menshikov, Cosmonautics on the Border of Millenis. Results and Prospects, Mashinostroyenie, Moscow, 2001.
[37] G.N. Petrov and N.A. Yasmanov, Bull. Rus. Acad. Sc., Vol. 68, No. 2 (1998) 132.
[38] F.T. Yanshina and A.I. Yanshin, Ibid, Vol. 70, No. 3 (2000) 243.

Chapter 3

Energy Resources of Fossil Fuels in the World

3.1. Fossil energy resources on the base of hydrocarbons

The organic fuel reserves are divided into proven volumes and predicted volumes of new reserves for future exploitation with a probability of 50 % [1]. Volumes of proven reserves of organic fossil fuel and promising geological fuel resources on the Earth (from estimates of Geological Service of the USA is 10^9 t of conventional fuel — t c. f.) [1] are presented in Table 9.

Total promising reserves of organic fuels (coal, oil and natural gas) are estimated by the author of the work [1] as $6.69 \cdot 10^{12}$ t c. f. The authors of the work [2] estimate promising reserves of fossil fuels of the world as $(8.5–13.0) \cdot 10^{12}$ t c. f., i.e., something higher. Of these reserves 90 % belong to hard fossil fuels (coal and its derivatives), 5–6 % to oil and 4–5 % to natural gas. According to [3, 4] the predicted reserves of organic fuel are estimated as those of the order of 10^{13} t c. f., including coal (above 80 %), oil and gas together below 20 %.

The mining coefficient for coal is taken as 30–50 %, production coefficient for oil — 30–50 %, for natural gas — 50–80 %. Specialists think that solution of the problem of increasing oil production of the deposits is more complex than the space flight. Besides the use of expensive equipment, one shall know regularities of oil- and gas-containing beds occurrence, their occurrence depths, bed intrinsic pressure, etc. According to the data of geological prospecting, oil occurs in Ukraine at twice more depths than in the bowel of Russia.

Table 9

Volumes of proven and predicted reserves of organic fuels in the world, 10^9 t

Energy carriers	Volumes of proven mined reserves	Future reserves; probability 50 %	Full reserves total
Oil	210	110	320
Natural gas	180	180	360
Bitumen containing sands	260	470	750
Bituminous coal	984	4250	5264
Total	1634	5010	6694

As a whole, the predicted reserves of organic fuel in the Earth bowel are estimated as $4–6 \cdot 10^{12}$ t c. f., including oil $–130–200 \cdot 10^9$ t. The recent data are in relatively good agreement with the total world proven oil reserve, which were determined as $139.664 \cdot 10^9$ t on 01.01.1998 [5]. The reference literature contains data that the world oil reserves are $272 \cdot 10^9$ t, and so, they exceed twice the proven world reserves given in [6, 7] and are something less than the data given in Table 9. It would be noticed that geological oil prospecting brings surprises. Let us cite the data for the USA, Russia and China. Thus, the prospected oil reserves in the USA with the probability of 65 % $220.3 \cdot 10^9$ t in 1999 were [70], (the share of Russia is 4.72–5.0 %) of the world oil reserves [8, 9] and 30 % of hard coal (including 12 % of coking coal)[1] [7], and reserves of natural gas and oil in China are 1.2 and 2,4 % of the world reserves, respectively [10].

Distribution of oil, natural gas and coal reserves in the world regions [8, 9] established from the recent data as of 01.01.2001 is given in Table 10.

It is evident that the Near East countries (Saudi Arabia, Iraq, UAE, Kuwait, Iran, Katar, Oman, Yemen, Bahrein, Syria, Israel, etc.) possess maximum quantity of oil — 66.46 %, then Southern America and Caribbean basin

Table 10

Proven reserves of oil, natural gas and coal in the world regions as of 01.01.2001

World region	Proven reserves						
	Oil		Natural gas		Coal, 10^9 t		
	10^6 t	%	10^9m^3	%	hard	brown	EJ*
Northern-America,	7996.9	5.32	7328.7	4.90	674	201	25638
Southern America and Carribean Basin	12860.0	9.25	6926.7	4.63	37	2	11.43
Western Europe	2322.6	1.67	4498.5	3.01	337	11	10196
Central and Eastern Europe and CIS countries	7977.2	5.74	56693.3	37.93	3131	765	114153
Africa	10121.3	7.28	11161.8	7.47	181	< 1	5303
Near East	92377.2	66.46	52521.6	35.14	1	1	58
South-Eastern Asia, Australia and Oceania	5940.8	4.27	10339.3	6.92	659	108	16438
Total	138996.1	100.0	149470.0	100.0	5021	1089	178959
OPEC countries	110013.8	79.15	66475.6	44.47	139	67	6030

* EJ equals $1 \cdot 10^{18}$ J

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[1] Large unaccounted oil reserves are supposed in the North of Western Siberia (Continental shelf and land), exceeding considerably presented share reserves of oil in Russia.

(Argentina, Barbados, Bolivia, Brazil, Venezuela, Guatemala, Ecuador, Columbia, Cuba, Peru, Surinam, Trinidad and Tobago, Chile) — 9.25 %, Africa (Algeria, Angola, Gabon, Egypt, Libya, Nigeria, Republic of Congo, etc.) — 7.28 %, Eastern Europe and CIS countries — 5.74 %. The share of the USA, Canada and Mexico is 5.32 % of oil. The share of Venezuela (of 15129.5 mill.m^3 — 9.25 % of world reserves) is 12221.1 mill.m^3, i.e. 80.78 % of the region reserves. Most industrially developed countries of Western Europe possess only 1.67 % of the world oil. The share of Russia is about 4.72–5.0 % of the world oil reserves. Total amount of oil is $138.9961 \cdot 10^9$ t which differs by 0.478 % from the data of 01.01.1998 and this is determined by current oil production which is 0.24–0.25 % of world reserves a year.

The natural gas distribution in the world regions is also nonuniform. Here, as is seen from Table 2, the share of Russia is 32.21 %, Near East countries — 35.14 %, Africa — 7.47 % and USA — 3.17 %. The USA have exploited actively their oil deposits, beginning from the 19th century. During 100 years from 1859 to 1959 the USA had produced 12500 mill.t of oil [8]. The prospected reserves of oil and gas in the USA in the beginning of 1969 were: oil 4139 mill.t, and natural gas-$8132 \cdot 10^9$ m^3. In 1969 the USA produced 510 mill.t of oil and in 2000 — only 317 mill.t.

Coal distribution on the planet is nonuniform. The share of the countries of Central and Eastern Europe and CIS countries is 63.8 % of coal ($3896.0 \cdot 10^9$ t, of them 18 % — brown coal).

The share of CIS countries is 61.8 % of coal ($3776 \cdot 10^9$ t, 20 % of them — brown coal). The countries of Northern America (Canada, USA, Mexico) possess 14.3 % of coal (875·10 t, 23 of them — brown coal). The countries of the South-Eastern Asia, Australia and Oceania possess only 12.5 % of coal ($767 \cdot 10^9$ t, 16 % of them — brown coal).

How long will organic fossil fuel reserves last on the planet? The world consumption of energy resources grows continuously. If in 1980 it was 8.5–10, in 1996 — 13.7, then by 2000 it approached to $20 \cdot 10^9$ t c.f/yr. According to predictions concerning Arabian oil supplied to the world market by Arabian countries even under the intensive oil production it will last 150 years (55 % of all world reserves), and Russian oil will last only 50 years [11]. But as it will be shown below that is a rather optimistic prediction. A half of oil produced is refined to produce the motor fuel now, 1/3 of which being consumed in the USA [12].

In 1980 the Earth population which was $4.5 \cdot 10^9$ consumed $8.7 \cdot 10^{13}$ kWh of energy, in 1996 $5.72 \cdot 10^9$ persons consumed $11.15 \cdot 10^{13}$ kWh. In 1998 $5.919 \cdot 10^9$ people consumed $7.869 \cdot 10^6$ t of oil equivalent (o. e.) of organic fossil fuels [76], which is equivalent to $91.52 \cdot 10^{12}$ kWh (1 o. e. is equivalent to 11630 kWh). It is predicted that in 2020 and 2050 energy consumption by population (at that time 7.4 and $10.15 \cdot 10^9$ people) will be $16.0 \cdot 10^{13}$ and $25.8 \cdot 10^{13}$ kWh, respectively, that will correspond to the consumed power per capita in 2020 — 2.46, and in 2050 — 2.91 kWh [7]. The above quantity of electric energy may be calculated in terms of equivalent consumption of organic fuel (1 t c. f. = 81.39 kWh) which will be equal to $1.97\cdot10^{10}$ t c. f. in 2020, and $3.17\cdot10^{10}$ t c. f. in 2050, to produce the corresponding amounts of electric energy.

Under the average power consumption of 261 kW per capita the energy consumption will be 22863.6 kWh/yr. The total average energy consumption by the planet population ($7.76\cdot10^{9}$) in the period of 2020–2050 will be $17.742\cdot10^{13}$ kWh that is equivalent to $2.18\cdot10^{10}$ t c. f. The authors of [7], when calculating time of hydrocarbon fuel reserves exhaustion, took that the shares of oil and gas in the obtained value of consumed energy ($17.742\cdot10^{13}$ kWh/yr.) are 30 % each, while hard fuel share is 40 %. The share of other energy sources (NPP and renewable sources) was 30 %. Under such calculation the amount of energy from oil and natural gas is $5.32\cdot10^{13}$ kWh/yr. or $6.536\cdot10^{9}$ t c. f./yr. each. When using the values of oil and gas reserves given in Table 9 and allowing for inevitable losses during energy conversion, even taking into account possible development of new methods for energy conversion with efficiency no lower than 70 % one can simply calculate that oil reserves for the mankind are only $320\cdot10^{9}$ t c. f., i.e. $0.7/6.536\cdot10^{9}$ t c. f. a year and they will last 34.3 years, while natural gas reserves are $360\cdot10^{9}$ t c. f., i.e., $0.7/6.536\cdot10^{9}$ t c. f./yr. and they will last 38.5 years.

However, real consumption of energy carriers is nonuniform and calculations ambiguous. Thus the author of the work [4] used the energy consumption value equal to $20\cdot10^{9}$ t c. f. a year to calculate total reserves of organic fuel (oil, natural gas and coal) and showed that the total volume of hydrocarbon fuel (coal being the major fuel) will last 200 years. In Canada, Norway, the USA and Russia 13.5; 13.0; 11.2 and 8.8 t.c. f., are consumed per capita, respectively. Thus, in certain countries the reserves of most intensively used hydrocarbon energy sources, first of all oil, can be exhausted in a shorter period of time.

The proven oil reserves, its annual production in 2000 in some countries from the data of [8], and integral time of oil production (τ) calculated by the authors (that is the period of time when one or another country demands for oil may be satisfied by its own reserves) are presented in Table 11. As is evident the Saudi Arabia possesses the greatest oil reserves in the world ($42212.8\cdot10^{6}$ m^3 of oil). Oil production in this country was $468.0\cdot10^{6}$ m^3 in 2000, which exceeds 1.35 times oil production in the USA and 1.27 times — in Russia. The proven oil reserves in this country will last 88.1 years under the above production rates. The proven oil reserves in Iraq of 17887.5 mill. m^3, UAE — 15550.2 and Kuwait — 14946.0 (mill. m^3) under annual production of 155.6; 129.3 and $103\cdot10$ mill. m^3 will last for $\tau = 115.0$; 120.3; and 145.1 years, respectively.

It also follows from the data of Table 11 that the proven oil reserves in industrially developed states will last for short periods of time: UK — 5.4 years, Canada — 6.5; Norway — 8.0, Denmark — 8.2; USA — 10.2 years.

Table 11

Proven reserves, annual production in 2000 [8] and calculated time of oil consumption in some countries of the world

Country	Proven reserves 10^6 m^3	Oil production in 2000 $10^6 m^3$	Calculated time of oil consumption/yr.	Country	Proven reserves 10^6 m^3	Oil production in 2000 $10^6 m^3$	Calculated time of oil consumption/yr.
Great Britain	795.4	147.2	5.4	China	38.16.0	188.9	20.2
Canada	748.3	116.0	6.5	India	751.7	37.1	20.3
Norway	1502.1	147.2	8.0	Russia	7723.1	368.6	21.0
Denmark	170.0	20.7	8.2	Ukraine	62.8	2.8	22.4
USA	3460.6	337.9	10.2	Kazakhstan	861.3	36.4	23.7
Columbia	409.8	40.0	10.2	Nigeria	3577.5	115.5	31.0
Turkmenistan	86.8	8.3	10.5	Algeria	1462.8	46.4	31.5
Uzbekistan	94.4	8.8	10.7	Romania	226.8	7.1	31.9
Australia	460.3	41.8	11.0	Katar	2092.0	39.5	52.9
Azerbaijan	187.3	15.0	12.5	Libya	4690.5	81.7	57.4
France	23.1	1.7	13.6	Iran	14263.3	20.7	68.9
Belarus’	31.5	2.1	15.0	Venezuela	12221.1	176.1	69.4
Germany	60.4	3.5	17.3	Saudi Arabia	41212.8	468.0	88.1
Italy	98.9	5.3	18.7	Iraq	17887.5	155.6	115.0
Brazil	1287.9	66.1	19.5	UAE*)	15550.2	129.3	120.3
Angola	860.5	43.1	20.0	Kuwait	14946.0	103.0	145.1

* United Arabian Emirates (Abu Dhabi, Dubai, Ras -el-Haima, Sharjah).

Taking into account proven oil reserve and total oil production we obtain rather optimistic time of oil production in the world τ = 42 years. Such a conclusion is in agreement with the data of Fig. 7 — in the first half of the 21st century oil reserves can be exhausted. But the situation with oil in the world in the current century can be much worse. Let us make the following calculation. Exclude 10 countries (Saudi Arabia, Iraq, UAE, Kuwait, Nigeria, Algeria, Katar, Libya, Iran, Venezuela) possessing great proven oil reserves infrastructure of oil production ($\Sigma Q = 127903.7 \cdot 10^6$ m^3), developed m^3/yr and are major oil exporters ($\Sigma\, \upsilon_\tau = 1335.8 \cdot 10^6$). Then calculate the integral time of production for the countries poor in oil ($\Sigma Q = 35167.5 \cdot 10^6$ m^3), 90 countries possess weak infrastructure of its production ($\Sigma\, \upsilon_\tau = 2543.9 \cdot 10$ m^3/yr). Calculation shows that the proven oil reserves in 90 countries will last only 13.8 years.

The economy of numerous countries in Western Europe and Ukraine is closely related to energy resources (oil and gas) of Russia. Oil production in Russia in 1989 was $555 \cdot 10^6$ t (17.8 % of the world production), in 1990 — 516

(16.5 %), in 1991 — 461.6, in 1996 — only $301 \cdot 10^6$ t, in 1998 — $303 \cdot 10^6$ t and in 2000 — $313.3 \cdot 10^6$ t (9.47 %) . The main reason of oil production decrease in Russia is the decrease of capital investments in the oil industry: price escalation for the construction and services of building industry, attending oil — gas complex, larger investments for production of pipes and oil-gas production equipment, etc. But the decrease of oil production has not resulted in the decrease of oil export to far foreign countries [13]. The, oil export was: 1990–$83.5 \cdot 10^6$ t (16.2 %), 1998 — $136.8 \cdot 10^6$ t (45.1 %, 2000 — $134 \cdot 10^6$ t (42.5 %) . The share of Russian oil export to the world market has increased from 2.67 % in 1990 to 3.93 % in 2000. Further increase of oil export to the world market is planned in the future. Russia possesses relatively poor oil reserves of $7.723 \cdot 10^9 m^3$ (4.72 — 5 % of the world reserves) and rather developed infrastructure on oil production ensuring oil production of $368.6 \cdot 10^6$ m^3 a year. Under such productivity Russia can exhaust its oil reserves during 21 years (Table 11).

Oil is used in the advanced industrial countries as the most valuable raw materials in petrochemistry synthesis (PCS) at oil-refining and chemical plants. The cost of PCS products (light oil products, chemicals, raw materials for production of synthetic rubber, plastic materials, etc.) surpasses 7–20 times the cost of raw oil [13]. Today, oil is the basic raw material for production of gasoline, diesel and aviation fuel, lubricating oils and valuable chemical products [14]. Artificial deficit of hydrocarbon raw materials was created in Russia in the period of economic reforms conducted in the branches of heat power complex, and the amount of work for petrochemical plants lowered to 20–39 %. This resulted in organization of foreign companies refining Russian hydrocarbon raw materials and importing much more expensive petrochemistry products. That is why the high-tech countries do not export oil since they think it unprofitable. But oil export gives «quick money». The former USSR which received $200 \cdot 10^9$ dol. from 1973 to 1985 but has not created the advanced oil-refining branch, new working places, etc., can serve as an example. Western Europe, Japan and China possess comparatively small reserves of oil and natural gas [15]. As was noticed above, in China with population close $1.5 \cdot 10^8$ (25 % of the world population) oil reserves are 2.4 %, natural gas — 1.2 % of the world reserves [15]. Annual import of oil and gas from Russia to the 9 regions of Western Europe and Asia can be from 1.7 to $3 \cdot 10^9$ t (Gt of o. e.). The volume of natural gas exported from Russia to Western Europe can exceed $1 \cdot 10^9$ t o. e./yr.

According to productions the profit from oil export from the countries of Near East and Northern Africa to developing countries of Asia will not change relative to 1990 and will be $140 \cdot 10^9$dol./yr. [15]. The rates of increase of oil production in the world are reflected in Table 12 of [14]. In the opinion of its author the mankind rather quickly, only during the 20th century, has consumed the world reserves of oil — the most valuable raw material of chemical industry

Table 12

Real and future oil production (10 barrels and m) in the world in different periods

Oil	Years						
	Before 1900	1901–1920	1921–1940	1941–1960	1961–1980	1981–2000	2001-2020 (prediction)
barr. *	0.54	6.47	27.24	73.39	266.41	445.23	1081.79
m^3	0.08586	1.029	4.33	11.67	42.36	70.79	172.00

* 1 barrel of oil – 159l.

which was created on the Earth during hundreds of million years. The whole oil limit in the world according to [16] under «unfavourable prediction» will be exhausted by 2020.

Proceeding from presented calculations on can draw a conclusion that in 13.8 — 20 years oil will be inaccessible for most countries. The shortage of oil and other hydrocarbon energy carriers will especially adversally affect the economy of developing countries. Therefore, the countries with small volumes of their own hydrocarbon resources would speed up the development of alternative renewable energy sources — construction of small, mean and big hydraulic power stations, creation of plants for conversion of the wind and solar energy into electric energy and hydrogen (solar-hydrogen energetics), as well as the plants for production of synthetic liquid fuel (SLP) from coal for autotransport. Even in 1985 the authors of [17] predicted that the mass production of SLP on the basis of fossil coal (hard or brown) will begin in 20–25 years.

According to scholars' estimates, the world reserves of hard and brown coals ($7.6 \cdot 10^{12}$ t, 75 % of them being concentrated in the territory of Russia, Ukraine and the USA) can satisfy the world population requirements during 250–300 years.

It is considered that the overwhelming part of hard fuels (coals, resins, etc.) is concentrated northwards of the latitude of 40° North and is concentrated in Russia, Ukraine, Canada and USA. It is China which is rich in coals in the Southern hemisphere. The share of the world reserves of hard energy carriers in these countries is 90 %.

The authors of [18] predict growth of commercial coal mining in the world from $3705 \cdot 10^6$ t in 1996 to $4125 \cdot 10^6$ t in 2000 and to $7700 \cdot 10^6$ t in 2025. The world electric energy which was generated in 1999 with the use of coal and was 37 % will increase to 40 % in 2010. It is considered that the amount of coal used per capita is the most important indicator of the country energy safety. The USA with population of $280 \cdot 10^6$ mined $950 \cdot 10^6$ t of coal, i.e., 3.3 t per capita, the USSR mined $750 \cdot 10^6$ t of coal, i.e., 2.5 t per capita, and in contemporary Russia

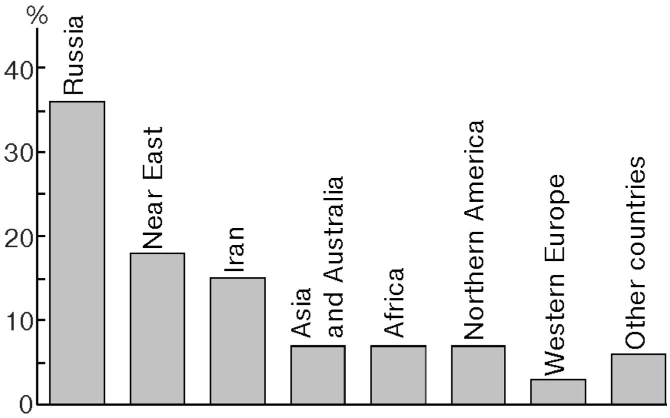

Fig 8. Distribution of resources of natural gas among the world regions

they mine $260 \cdot 10^6$ t, i.e., 1.7 t per capita, while in the Czech Republic with population of $10.3 \cdot 10^6$ they mine $50 \cdot 10^6$ t, which is 4.7 t per capita. Index of coal consumption per capita in Germany is 6.6 t, in Poland 5.8 t, in Kazakhstan — 5 t per capita. Coal mining in Ukraine was $81 \cdot 10^6$ t in 2000, which corresponds to 1.67 t per capita (Ukraine population is $48.4 \cdot 10^6$).

These data show that even hard fossil organic energy carriers, as well as oil and natural gas are nonuniformly distributed among countries. Hence, arises the probability of conflicts among states for the sphere of influence on the fuel markets, first of all oil market, as well as for the possession of other mineral resources. This global problem of the third millenium and its role in the stable peace on the Earth can augment in the future.

When calculating the terms of oil and gas consumption, the authors of [4] did not take into account nuclear energetics with its great potentialities in decreasing the organic fuel consumption. As it was noticed above, about 16–18 % of electric energy are generated today at nuclear power plants. The share of hydroelectric energy is 17 %, that of renewable sources — about 1 % of energy (geothermal energy — 0.5 %, solar, wind and biomass energy — 0.1 % each [11]), i.e. 36 % in total. The rest of the world electric energy (64 %) is produced by the combustion of fossil fuels — natural gas, oil, bituminous coal, slates, turf.

The world reserves of natural gas are $2.83 \cdot 10^{14}$ m^3 which corresponds to 4.7 % of total reserves of organic fuel (reserves of hard and brown coal — 88.8 %, oil — 5.2 %, residual petroleum — 0.8 %, slates — 0.5 % [11]. From the data of the authors [8] the proven reserves of natural gas in the world are 1.89 times lower and are $1.495 \cdot 10^{14}$m^3 (Table 10). According to the data of other authors [19], the natural gas reserves on our planet are several times higher and are estimated by experts in the volume of $(2.6–5.0) \cdot 10^{14}$ m^3. Under rational rates of production the natural gas will last 110–120 years. It is predicted that in 2030 the consumption of natural gas will be $830 \cdot 10^9$m^3. The distribution of natural gas resources between the regions of the world was shown on Fig. 8. with the use of

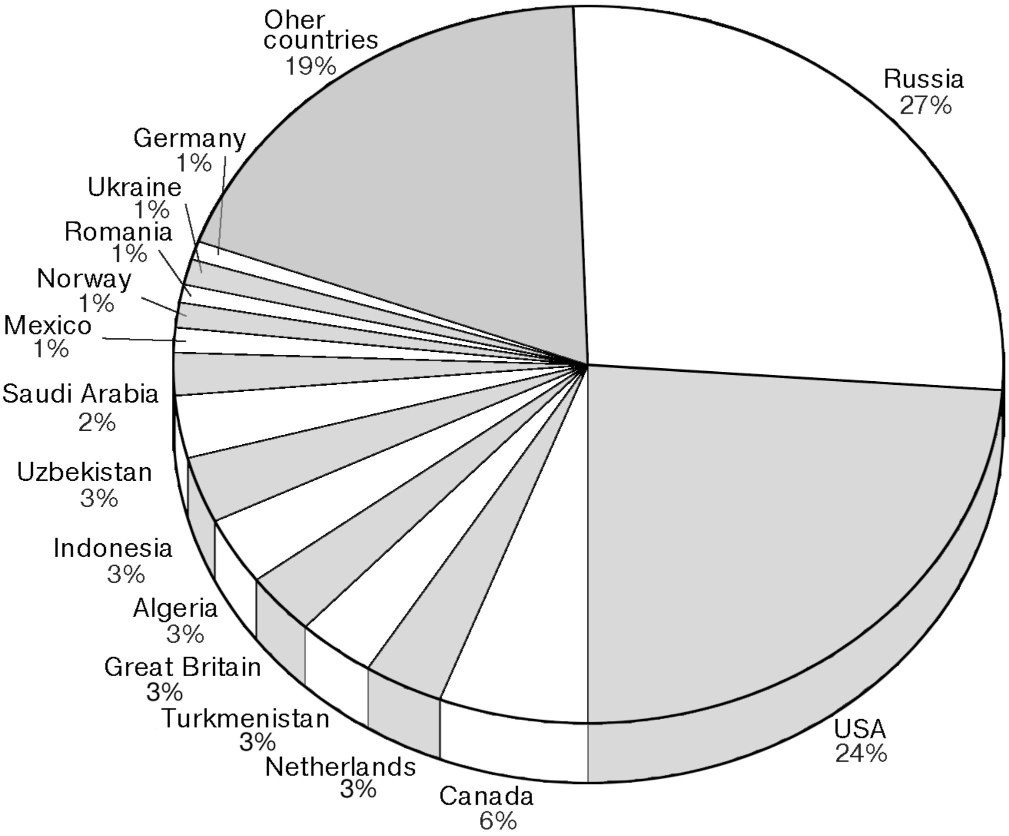

Fig. 9. Share of defferent countries in the world production of natural gas

the data of work [20]. It is seen that Russian Federation possesses 36 % of the world reserves of natural gas, the Near East — 17 %, Iran — 15 %, Asia and Australia, Africa, Northern America — 7–8 % each.

The share of China is 1.2 %. Prospected reserves of natural gas in Australia are above 10^9 m^3, which corresponds to the level of the country providing with gas for 100 years [21]. Further increment of natural gas in Australia is predicted approximately as 65 %. Prospected reserves of natural gas in Russia reach $48.9 \cdot 10^{12}$ m^3, while total potential resources are estimated as $235.6 \cdot 10^{12}$m^3. According to the estimate of [20], unprospected resources of gas are $164.8 \cdot 10^{12}$ m^3, 43.1 % of which fall to the shelf zone. Primary potential resources of natural gas in the continental shelf of the World Ocean are estimated as $52.5 \cdot 10^{12}$ m^3.

The share of various countries in the world production of natural gas is shown in Fig. 9. It is evident that Russia and the USA are leaders of natural gas production in the world. As to Ukraine, Germany, Romania, Norway and Mexico, their share is only 1 %. In 1991, $815.0 \cdot 10^{12}$ m^3 of natural gas were produced in CIS countries; $642.2 \cdot 10^{12}$m^3 were produced in Russia. In 2030 the production of natural gas in Russia will depend on the taxation system, and under «soft» conditions of production restrictions will be 635–735, and under «strict» conditions it will be 750–800·10^{12}m^3 [22]. It would be emphasized that in the recent years the prospected reserves of natural gas in Russia are estimated as 170 and additional resources as 240·10^9 t c. f. On conversion to the future the continuously worked reserves will satisfy the requirements during 60 years, with regard for additional resources — during 160 years. Specialists in geological prospecting think that only a little share of the regions with predicted deposits of natural gas (about 2/3 of such holes are in the USA and Canada) have been investigated till now. As compared to Northern America the rest of the planet has not been sufficiently prospected. According to some estimates of geologists only 25–30 % of the territory have been surveyed and «statistical sufficiency» of natural gas reserves can considerably increase. Besides, there are also huge reserves of methane in a form of the so-called crystallohydrates.

Geological enterprise *Zakhidukrgeologiya* in Ukraine (Lvov and Chernovtsy Regions) have discovered 23 deposits of natural gas; 17 of them with reserves above 60·10^9m^3 of gas were put in industrial operation. The greatest gas reserves are concentrated in the Lentya and Gayi deposits of Lvov Region, Ruski Komarivtsi and Solotvin in Zakarpatia, Chornoguz in Chernovtsy regions and Lokachyn in Volyn. A new gas field has been opened on the Azov Sea shelf by SSC *Chernomorneftegaz*. It is considered that southwards of the Sea of Azov one can observe «high efficiency» as to natural gas. There are well-known gas-bearing deposits in the Chernigov, Poltava, Sumy and Kharkov Regions of Ukraine especially in the Dnieper-Donets Depression which, from the data of the National Energetics Program for 1996–2010, contain 900·10^6 tons. Only SGE *Ukrgeofizika* has discovered 250 deposits of oil, gas and other resources in the recent decades. Geological parties are engaged in prospecting 100 regions promising for oil and gas. Unfortunately oil- and gas-bearing potentials of the Ukraine bowel are not developed intensively and need to be realized.

As follows from Table 10, Russia possesses huge reserves of natural gas. Trends and amounts of gas export from Russia to the Eurasian countries by 2050 are shown in Fig. 10 [15]. It is evident that Russia supplies gas to Europe (450·10^6 t of oil equivalent — o. e.), India (150), China (190) and Japan (75·10^6 t o. e.). It is supposed that profit of Russia from gas export is 30·10^9 dol./yr.

It follows from the above stated that Russia possesses great raw-material base, production and high-tech potential, a unique single gas supply system and fixed system of gas delivery both to the internal and foreign markets.

In 1998 total volume of Russian gas export to Europe was [93] 120.5·10^9 m^3 [23]. The open stock company (OSC) Gazprom possesses a package of contracts for the delivery of about 2.7·10^{12} m^3 of natural gas to far foreign countries. Currency receipts from the export of Russian gas — is one of the major sources for replenishment of the profitable part of the Russian state budget, as well as for financing the investment projects. That is why, Russia can do

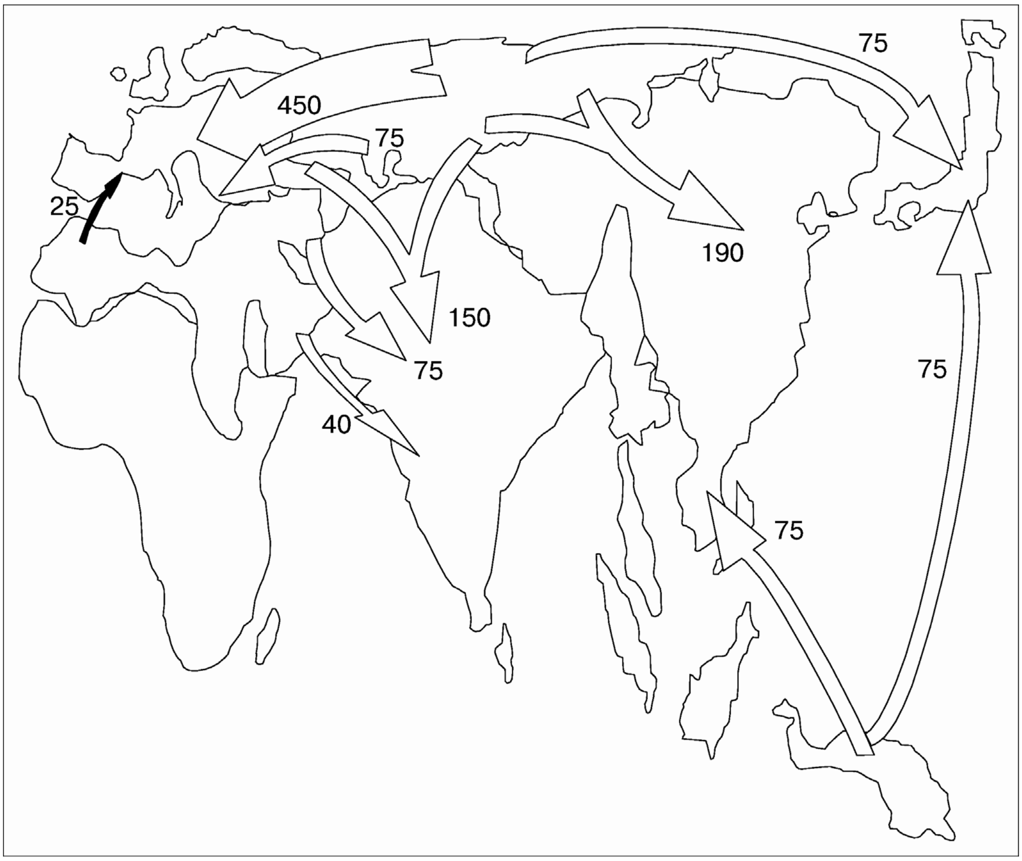

Fig. 10. Trends and amounts of natural gas export from Russia to Eurasian countries by 2050 [15]. A black arrow indicates the directions of export of gaseous natural gas, light arrows — liquefied gas, figures — volumes of gas export in millions of tons of o. e.

without the investments of ICP and other international financial organizations and states whose investments to energetics (nuclear power), gas-, oil- and coal-production industry in the nearest thirty-years period are estimated within 13–20·10^{12} dol. (in prices of 1990). Power strategy of Russia up to 2020 predicts the growth of natural gas production to 7000·10^9 m^3. The share of Russian *Gazprom* will be 530·10^9 m^3 of natural gas, while the share of other independent gas-producing enterprises will be 170·10^9 m^3. Volumes of necessary investments to the gas and oil branches of Russian industry for the period to 2020 are estimated as 3·10^{12} dol. each [15], while the USA are going to import 776·10^6 t of oil in 2010 and 837·10^6 t in 2015.

Russian Stock Company (RSC) EEC also possesses great economic potential. Most its power plants use natural gas and mazut which home price is 5–6 times as low as the world price, and this creates favourable conditions for industry development and for decreasing its production competitiveness. Gas and mazut are produced at oil- and gas-bearing deposits of Siberia, the cost of their reserves being estimated by experts as 33·10^{12} dol. [24].

The situation with energy carriers delivery from Eurasian countries being analyzed, such a conclusion inevitably comes to mind [15], that there exist some «weak points» in the problem of investments to Eurasian energetics. These are, first of all, the «conscious risks for investors in the Caspian Region and Russian Federation», as well as «long terms of recoupment of investments to the construction of large transcontinental systems of gas transportation» (pipelines, equipment for gas liquefaction, pump works, etc.).

And what about the reserves of oil and natural gas in the countries of Western and Eastern Europe? The prospecting and production of oil and natural gaz in Western Europe have been carried out from times immemorial [8]. It is of interest that the oil-bearing deposit Peschelbron in France is worked in mines from 1813. On the whole in Europe, except for CIS countries, the amounts of produced oil and gas were inconsiderable. Before the World War II the deposits of industrial oil were found in the Carpathians (Romania, Poland), as well as in France and Germany. Oil deposits were also found in the regions of Hungary and Austria before the war beginning. In the post-war years oil- and gas-bearing deposits were found in Netherlands, Bulgaria, Yugoslavia, Albania and Spain. The proven reserves in the East-European countries are as follows (10^6 t): Poland — 18.3; Albania — 26.2; Byelarus — 31.5; Hungary-17.4; Croatia — 14.7; Czech — 2.4; Slovakia — 1.4, etc.

The first place in oil production in Europe belonged for a long time to Romania where maximum production (1969) was $13.25 \cdot 10^6$ t of oil and $22 \cdot 10^9 m^3$ of natural gas; PEG occupied the second place — $7.9 \cdot 10^6$ t of oil, the third place Austria — $2.72 \cdot 10^6$ t of oil, the fourth place belonged to France — $2.5 \cdot 10^6$ t of oil. Maximum oil production in Ukraine, including gas condensate, was $13.9 \cdot 10^6$ t in 1970, natural gas — $60.9 \cdot 10^9$ m^3, and in 1975 — $12.8 \cdot 10^6$ t and $68.7 \cdot 10^9 m^3$, respectively. Current oil production in Ukraine is $3.7–3.8 \cdot 10^6$ t and that of gas $17.9–18.1 \cdot 10^9 m^3$ [25].

After proving rich Gronningen deposit of natural gas in Netherlands and oil and natural gas deposits in the territorial waters of Norway and UK in the Northe and Norwegian Seas, Norway became the first country as to reserves of oil and natural gas among West-European countries. Proven oil and gas reserves in the territorial waters of Norway were $290 \cdot 10^6$ t of oil and $227 \cdot 10^9$ m^3 of natural gas. By the present, Norway has produced $172 \cdot 10^6$ t of oil and $112 \cdot 10^9 m^3$ of gas. The extraction of the above amounts of oil and gas caused the subsidence of sea bottom within the limits of Ecofisk deposit.

Oil and gas deposits in the territory of Western Europe are distributed in the south within the Alpine folded belt and in the north within the Epipaleozoic platform [8]. Eleven oil-and-gas-bearing provinces in total have been distinguished in Western Europe. The North Sea oil-gas-bearing province, being the major oil-and-gas-producing zone in Western Europe, possesses the richest deposits of oil and natural gas. Above 100 oil deposits and above 80 gas fields have been discovered within the limits of the North Sea. The opened deposits are highly productive and produce 24 % of oil and 30 % of natural gas from the world production. Total reserves of oil and natural gas fit for production are estimated as $7.5 \cdot 10^9$ t, 4 milliard of which are the share of oil.

According to the data of [26], 126 oil deposits with proven industrial reserves equal to $427.9 \cdot 10^6$ t and with predicted geological reserves within $1229 \cdot 10^6$ t have been found in the territory of Ukraine. Ukraine possesses industrial reserves of oil and gas in the bowel of the Southern (the Black Sea, Crimean shelves, the Sea of Azov, Peri-Azovian area and its shelves, Odessa and Zaporozhie Regions), Western (Ivano-Frankovsk, Zakarpatian, Chernovtsy and Lvov Regions) and Eastern (Poltava, Sumy, Kharkov, Chernigov, Lugansk, Donetsk and Dniepropetrovsk Regions) regions. In the Eastern region, in the opinion of I. Chebanenko, about 90 % of oil-gas-producing enterprises of Ukraine are located in the main oil-bearing Dnieper-Donets aulacogen (DDA). A giant Markovskoe oil-and-gas-bearing deposit with reserves of $150–200 \cdot 10^6$ t (Lugansk Region of Ukraine and Rostov Region of RF) was found in the north of DDD in the stripe 50 km wide and 4000 km long. The fossil fuel occurs in 20 beds. The Gashinevskaya-1 hole, 3670 m deep, which gives 264 m^3 of oil daily has been bored in the Ukrainian Shield south-eastwards of Kharkov.

Promising reserves of oil and gas are in the region of Zmeiny Island, in the western part of the Black Sea shelf at the Crimean coast as well as in the Azov Sea water area. That is a part of the oil and gas geological belt of the Earth, embracing Romania, Ukraine, including the Crimea and Black Sea, Caspian area, Kazakhstan, Siberia and united by a single mechanism of oil and gas formation. Geological enterprise *Zakhidukrgeologiya* has opened 10 oil deposits in Lvov and Chernovtsy Regions during 20 years. Six of them, possessing the reserves of $6.4 \cdot 10^6$ t, were put in industrial operation. Oil deposits of Poltava Region are also in operation. Interesting information concerning oil reserves in the bowel of Ukraine is presented in [27]. According to the data of geologists 200 oil deposits have been prospected in Ukraine which is only 20 % of predicted treasures. Great reserves of oil have been preserved in the East-Sarata and Zhovty Yar oil deposits of Ukraine. Oil and gas deposits have been found comparatively recently in the Poltava and Sumy Regions. Their reserves will last for 50 years of intensive exploitation. Only in 2000 the enterprise *Okhtyrkaneftegaz* gave 40 % of produced Ukrainian oil and 8 % of natural gas. According to [8] the proven reserves of natural gas in Ukraine are $1121.3 \cdot 10^9$ m^3. But development of oil- and gas-producing industry is hampered by the absence of acceptable laws which could stimulate production of hydrocarbons which are vitally important for Ukraine [26]. The processes of oil and gas production are science-intensive processes requiring essential capital investments, and they must develop continuously. Proceeding from the principles of national security the home energy resources of any country would be no less than 50 %.

Availability of vast oil and gas fields in Ukraine was never a secret, moreover, in the early 20th century Ukraine occupied the third place in oil production. As was noticed, the Ukrainian researchers predicted the increase of production of oil and natural gas with the lowest prime cost in the former USSR. These projects were not realized because of the discovery of huge oil reserves in Tyumen and Siberia in the 60's.

Besides oil and natural gas hydrocarbons, there are rich deposits of hard and brown coals in the bowel of Ukraine. It is predicted that coal reserves in Ukrainian deposits will last 450–500 [28] to 500–600 years [29]. Geological enterprise *Zakhidukrgeologiya* has doubled reserves of the Lvov-Volynian coal basin. The south-western region with coal reserves of $1.1 \cdot 10^9$ t has been found and partially prospected. Reserves of Lyubelya 9 deposit were estimated as 0.8, Tyaglov deposit — $0.3 \cdot 10^9$ t. Methane reserves ($3 \cdot 10^9$ m^3) have been found for the first time in the region of Tyaglovska-1 mine. There are also great reserves of methane in the coal basin of Donbas. Its production and use as fuel for power plants, in motor transport and communal services can be organized rather quickly with low capital investments; besides, this will help to avoid traumatism, often with lethal outcome in the mines of Donbas and Lugansk Region because of methane explosions. It would be noticed that about $20 \cdot 10^9$ m^3 of gas are produced from coal beds in the USA.

The authors of the patent [30] propose a method of methane extraction when mining outburst-dangerous and high-gas-content coal beds. The essence of discovery lies in the hole boring from the earth surface to gas-bearing coal bed. Then the holes are connected with the vacuum pipeline and methane is pumped out. Geodynamical blocks as the areas with homogeneous geological structure are distinguished on the ground map under preparation to methane pumping-out. The holes are bored in the zones of the coal-bearing rock-mass expansion, since methane is under high pressure there.

The «methane» problem in coal industry is described in detail in the works [30, 31]. It is shown that the problem includes three interrelated aspects: 1) to ensure coal production safety which is considered by miners as «struggle with methane»; 2) to create conditions for highly-productive work of advanced mechaised complexes for taking off the restrictions as to gas factor as a result of intensive degasation of mines; 3) to organize technological process of methane extraction from coal beds for it could be used as autonomous energy resource. Predicted resources of methane in the coal beds are $32.7–60 \cdot 10^{12}$m^3 in Russia, which corresponds to a half of the world reserves of methane equal to $113 \cdot 10^{12}$m^3. In Ukraine $18 \cdot 10^{12}$m^3 of methane are contained only in the Donets coal basin. Eastern Donbas is the region with especially high methane content. An analysis of coal beds has shown that methane resources in Eastern Donbas are $1.3 \cdot 10^{12}$m^3. Great reserves of this gas are contained in the Lvov-Volyn coal basin. Methane content in the coal beds is usually 15 to 25 m of methane for 1 t of coal. Its pressure in the beds can reach 13.2 MPa (130 atm.). At the depth of 0.56–0.78 km methane pressure is 6–12 atm. Coal beds are good collectors. Pneumohydraulic methods of gas yield stimulation as well as the methods of supesonic and vibration-wave effects used in production of oils extracted with difficulty [31] are promising for industrial extraction of methane from the above beds. The Research Centre of Gas Industry of the A.A. Skochinsky Institute of Gas Dynamics is a pioneer in development of methane utilization technologies during coal production. This institute has elaborated the process of methane extraction by the method of crossing holes and introduced the method at 10 mines. Great contribution to solution of the problem of gas extraction and its catalytic oxidation with obtaining thermal energy was made by the Boreskov Institute of Catalysis of the Siberian Department of the Russian Academy of Sciences.

One would dwell on the effect of methane on the environmental conditions in coal-mining regions. This gas always accompanies the coal mining. After coal working the mine operation is stopped by «dry» or «wet» method. Methane emission proceeds under each of them. Complete mine flooding is followed by the methaning of ground waters which creates problems with drinking water for the whole regions. Methane pumping-out from coal beds is highly profitable and promising, and besides, the problems with drinking water can be avoided.

It would be noticed that systematic searches for industrial oil-and-gas-bearing deposits on continental shelves of the seas and at the bottom of seas and oceans of the world were started in 1954. Since then, above 20000 marine oil-gas-bearing holes have been bored all over the world. Only in the period from 1982 to 2002 thousands of oil and natural gas deposits were found both on continental shelves (Northern and Southern America, Western Europe, Russia, etc.), and at the bottom of seas and oceans of various regions of the world (North and Norwegian Seas, Gulf of Mexico and Persian Gulf, sea regions of Brasilia, Suez Strait, seas of the Arctic zone of America and Russia, North of Western Siberia, etc.). The deposit Bazzard with prime oil reserves of $137 \cdot 10^6$ t [32] has been found in Great Britain. For the recent 5 years 812 marine deposits of oil and natural gas with total reserves of $7 \cdot 10^9$ t of hydrocarbons were put in operation all over the world. Exploitation of 1180 more deposits with proven reserves estimated as $13.7 \cdot 10^9$ t of hydrocarbon fuel is predicted from 2002 to 2006. In 2001 capital investments to deep-water subjects in the world were $5.6 \cdot 10^9$ dol., and by 2005 they will increase to $10.6 \cdot 10^9$ dol./yr. Shelves of Western Africa are also rich in oil [32]. Oil-prospecting vessel *Glomar Challenger* has bored sedimentary rocks and salt dome under water thickness of 3400 m and found oil-and-gas-bearing deposit in the Atlantic Ocean. In the western part of the Mediterranean Sea, northwards of Alexandria, a gas-bearing bed 75 m thick was discovered after boring the 2455 m deep hole under water thickness of 1070 m in 60 km from the sea coast. A deposit of natural gas containing 98.4 % of methane with gas reserve of $330 \cdot 10^9$ m^3 [8] was discovered in the British sector of the North

Sea. It would be noticed that sensational discoveries in the field of geology of fossil fuels — oil and natural gas — occur even in our time. Thus, great reserves of oil were found in Eastern Kasalgan (Kazakhstan) on the shelf of the Caspian Sea. Kazakhstan plans to increase thrice oil production in the nearest years and to reach the level of $200 \cdot 10^6$ t a year by 2010. Oil reserves in Kazakhstan can be considerably extended due to the oil reserves at the bottom of eastern part of the Caspian Sea.

Export potentialities of the countries of Central Asia — Azerbaijan, Kazakhstan, Turkmenistan, Armenia, Georgia, Kirghizia, Tajikistan and Uzbekistan as oil suppliers to Asian-Pacific region (APR) against a background of energy requirements of this region were considered in the work [33]. In 2001 the share of oil import in APR was $1.7 \cdot 10^6$ t/day which corresponded to 0.63 % with respect to the required $268 \cdot 10^6$ t/day of oil. An analysis of energy resources in the countries of Central Asia shows that 92 % of oil reserves of this region are concentrated in two countries — Azerbaijan and Kazakhstan, and natural gas — 40 % in Turkmenistan, and 55 % in Kazakhstan and Uzbekistan. That is 2 % of the world prospected reserves of oil and 5 % of prospected reserves of natural gas. In 2001 — 192 thou.t/day of oil and $308 \cdot 10^6$ t/day of natural gas (5 % of the total world production) were produced in the countries of Central Asia. It is planned to increase oil production to 465.8 thou.t/day by 2010, and to 548 thou.t/day by 2015, production of natural gas will be 476 and $560 \cdot 10^6$ t/day, respectively. In 2001 oil export by the countries of Central Asia was 116 thou.t/day. It is predicted that by 2010 and 2015 oil export will increase to 342.5 thou.t/day and 411 thou.t/day, and export of natural gas to $196 \cdot 10^6 m^3$ and $252 \cdot 10^6$ m^3/day, respectively.

Thus, the world reserves of oil and natural gas can be considerably augmented at the expense of not completely prospected deposits of continental shelves of the seas, as well as oil- and gas-bearing deposits at the bottom of seas and oceans of the world. Thus the present proven reserves of oil, natural gas and coal would be considered relative and, as far as the known deposits are exhausted, the sea and shelf deposits will play a dominating role in providing countries with hydrocarbon fuel and raw materials for oil-refining enterprises.

Besides coal and oil the world is rich in turf. At UNO conference of 1981 in Nairobi turf was considered as the alternative fuel instead of vanishing energy carriers [31, 34]. Turf is available in all continents of the world, and it is concentrated in 40–50 countries. The total area of peat bogs in the world is $500 \cdot 10^6$ ha and occupy 3–5 % of the Earth land. The world reserves of turf fit for working are $3 \cdot 10^9$ t. The peat bogs area in the USA and Canada is 40 and 56 million hectares, respectively. There are also vast peat bog areas in Europe; big reserves of turf have been found in Finland, Ireland, Sweden, Poland, Germany, European part of Russia, Ukraine as well as in Siberia. Above two thousand of deposits with a reserve of $2.171 \cdot 10^9$ t of turf have been discovered in Ukraine. About a half of these reserves is concentrated in Volyn, Rovno and Chernigov Regions. According to estimations 57 t of turf is equivalent, as to its efficiency to 200 m^3 of wood which can be obtained from 1 ha of forest. Turf production in Ukraine in 1960, 1970, 1980, 1990, 1995 and 2000 was (mill. t): 4.7; 4.1; 1.6; 1.1 and 0.4 mill.t, respectively [25]. Turf may be successfully used to obtain synthetic liquid fuel (SLF) and synthetic combustible gas. Processes of hydration, pyrolysis and synthesis of SLF by the Fischer-Tropsch method, synthesis of methane, methanol and ethanol are developed now. The world consumption of turf is 35 mill.t which corresponds to 0.43 % of the world energy production.

Let us appeal to consumption dynamics of the basic hydrocarbon energy carriers of the world — coal, oil and natural gas presented in Fig. 11. Data of the author of [12], embracing the period from 1950 to 1998, were used to plot Fig. 11. It is evident, that the consumption of coal and natural gas in 1995–1998 reached the saturation limit — it has been established under consumption of $2210 \cdot 10^6$ t (o. e.) of natural gas (Fig. 11, (curve *ML*) and $2236 \cdot 10^6$ t of o. e. of coal (curve *KL*)). These data do not agree with the author's [35] prediction, supposing the fall of coal consumption in the 80's and that of oil — in 2000, and natural gas in 2040. Oil consumption, as is seen from Fig. 11, up to 1973 (curve *EF*) increased gradually. After 1973 one can observe the fall in oil consumption, determined by energy crisis, from 2690 mill.t o. e. (in 1983) to 2619 mill.t o. e. in 1975 (curve *GF*), then one can observe growth in oil consumption up to 1979 (2998 mill.t o. e.) (curve *GH*) and then a protracted decrease (curve *HI*) of oil consumption (which is also connected with energy crisis of 1977–1978) up to 1985 (2654 mill.t o. e.). Beginning from 1986, there begins a protracted increase of oil consumption (curve *IJ*), which continues till now, the consumption of 3423 mill.t o. e. being achieved in 1998 [12]. The increase of oil consumption can be expected in the nearest 20 years up to achieving that about 4000 mill.t o. e.

Difference in oil and natural gas consumption is connected with the infrastructure of these energy carries delivery to a consumer. Natural gas is delivered on a large scale from Norway and Russia and Western Europe by pipelines. The volumes of gas consumption in Western Europe have been stabilized. The volumes of coal in the world, delivered by railway and sea transport have been also stabilized. It would be noted that in numerous countries the coal demand is satisfied by the working of home deposits.

Thus in 1994, coal mining in China was 1210 mill.t, in the USA — 935, in Australia — 270, in South African Republic — 195, Germany — 257 mill.t. In 1990 and 2000 1420 and 1960 mill.t of coal, respectively, were used for electric energy and heat production.

Only in metallurgy industry 280 mill.t. of coking coals were used in 1990 and 320 mill. t. in 2000. It was planned to consume 18 mill.t of coal in 1990, and

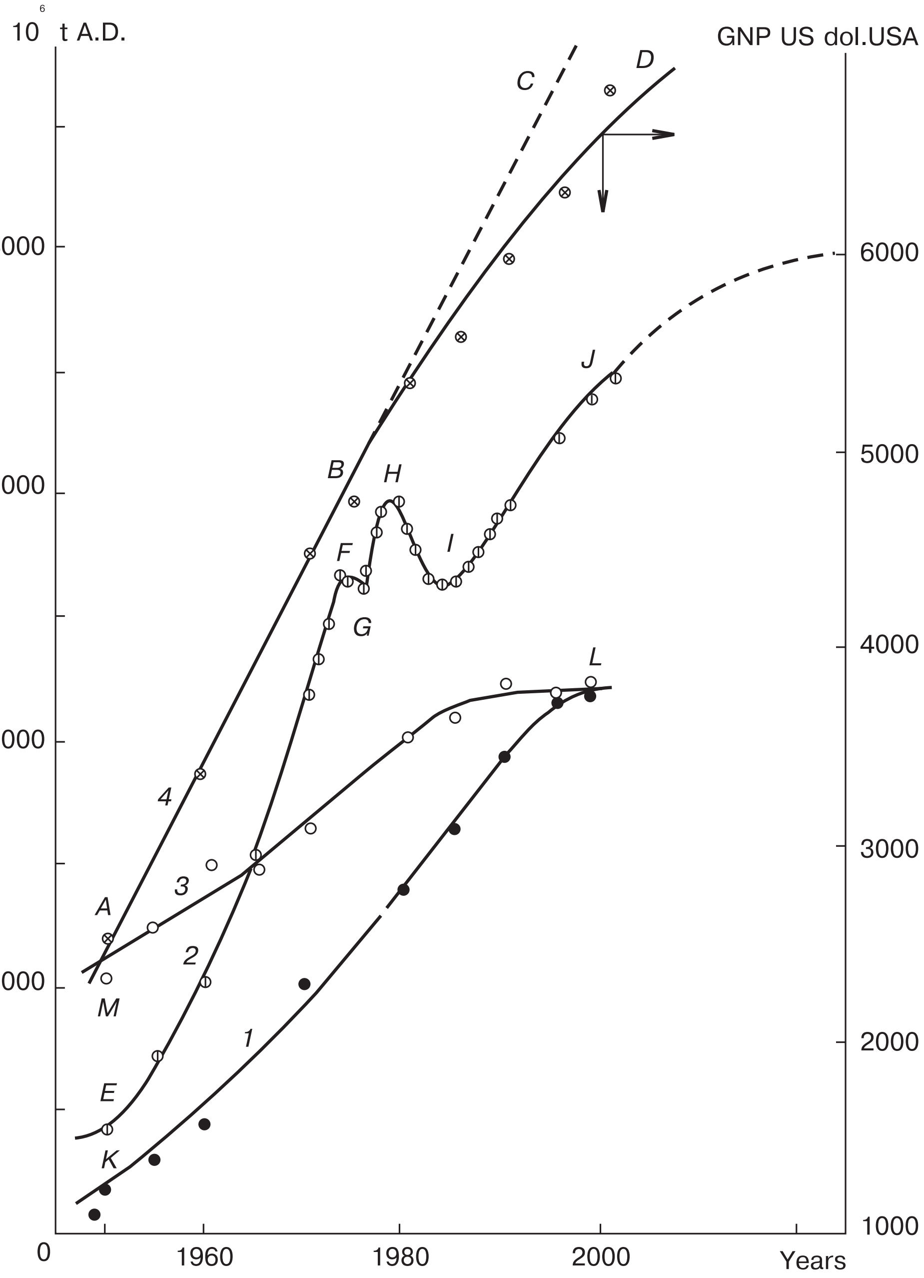

Fig. 11. Dynamics of consumption of the basic fossil hydrocarbon energy carriers of the world — coal (*1*), oil (*2*) and natural gas (*3*) in the period of 1950–1998; prediction up to 2020 and dependence of global GDP (*4*) on time: 1950–2000

120 mill.t in 2000 for production of liquid synthetic fuel. Large volumes of coal were used in chemical, electrotechnical and other branches of industry.

Goal mining and demand growth in the USA are predicted from 1997 to 2020 [36]. Coal mining in the USA will increase by 0.9 % a year and will increase from 1.099 in 1997 to $1275\cdot10^9$ t in 2020, and consumption from 1.030 to $1.275\cdot10^9$ t, respectively.

It is also planned in the USA to increase coal export to the countries of the world. Coal mining in Germany will decrease by 30 % in 2005; it is from 42 to 30 mill.t [37]. The volumes of imported coal will increase by 38 %, from 25 to 40 mill.t, respectively.

Coal mining in the USSR was 425.5 mill.t in 1988; in Russia, 215 mill.t were mined in 1998 and 257.9 mill.t in 2000. It is planned to bring the coal mining level in Russia to 300 mill.t in 2005, to 335 mill.t in 2010, and to 430 mill.t in 2020. The share of coal in electric energy production will increase from 34.1 % in 2000 to 63.5 % in 2020 [38]. Nowadays the structure of fossil hydrocarbon fuel consumption in Russia is as follows: oil — 23 %, natural gas — 58 %, coal — 19 % [39].

Coal mining in Ukraine in 1970, 1975, 1980, 1990, 1995, 1996, 1997 and 1998 was 207.1; 215.7; 197.1; 83.8; 60.5; 76.9 and 77.2 mill.t, respectively [40]. The maximum of mining of 215.7 mill.t was reached in 1975. The difference between coal mined in 1980 as compared with that in 1970 was 10 mill.t. Two power units (1977, 1978) Chernobyl NPP and one power unit at Rovno NPP with total power of 2.402 MW were constructed at that time. Electric power production by the newly built NPP power units compensated energy shortage from lowering the coal mining. Coal mining in Ukraine has decreased 2.79 times now as compared to 1975; and 2.13 times as compared with 1990. As far as the nuclear energetics developed in Ukraine, the load to coal industry decreased (see, Chapter 4).

It follows from the above data as well as from the analysis of the situation with energy carriers in the world that in the first quarter of the 21st century oil will be used as energy carrier side by side with natural gas and coal. In the second quarter of the 21st century people will use only natural gas, coal, nuclear-hydrogen energetics and alternative sources of energy (wind energetics, photoelectric converters, solar-hydrogen energetics, etc.). Natural gas, coal, hydrogen and nuclear hydrogen energetics as well as the great numbers of alternative renewable energy sources will be used as energy carriers in the second half of the 21st century. Hard and brown coal, turf, nuclear-hydrogen and hydrogen energetics will be probably used as energy carriers in the 22nd century, if the problem of thermonuclear energetics will not be solved. Oil and gas will be inaccessible as energy carries because of high prices; they will be used in the 22nd century only as raw materials for chemical synthesis.

3.2. Hypothesis of Hydrocarbon Fuels Origin on the Earth

The authors of the monograph were always interested in the oil origin problem. How could oil with its density 0.75–0.95 g/cm^3, i.e., less than that of water could be found under the 1–10 km thick layer of minerals, sand or clay and not to come to the earth surface like water? Two well-known conceptions of oil origin — inorganic (abiogenic) and organic (biogenic) — do not answer the above question. D.I.Mendeleyev, V.B.Perfilief, Member of the National Academy of Sciences of Ukraine, are founders of inorganic conception of oil and gas origin. D. I. Mendeleyev suggested the theory of oil formation as a result of interaction of water, penetrating the Earth bowel, with incandescent metal carbides. Careful study of the composition and properties of oils does not always agree with that theory. Oil, as to its chemical composition contains 83–87 % of various hydrocarbons (methane homologs and cyclic hydrocarbons), 11–14 % of hydrogen, small amounts of nitrogen, sulphur, bound oxygen and phosphorus. According to the conception developed by V. B. Perfiliev oil and gas formed at very high pressures and temperatures under the earth crust from available cosmogenic hydrogen and carbon oxide by Pischer-Tripsch reactions [5, 41]. Allowing for the fact that deep fractures always dissect simultaneously both the sedimentary thickness, and Earth crystalline crust and even the deeper Earth's bowel, oil and gas migrate along these fractures «forming oil and gas deposits on their upward path». That is why oil and gas can occur at no matter how great depth, and their deposits are formed not as a result of gravitation, since the difference in water, oil or natural gas density cannot be the motive force of their migration and accumulation in porous bodies [5, 41].

In accordance with organic (biogenic) conception, oil and natural gas were formed on the Earth as a result of metamorphic transformations of plants and animal remnants buried in the sedimentary rock deposits [42–45]. There are three necessary geological components of the appearance of biogenic oil deposits in the sedimentary rocks: availability of oil-maternal rocks; the layer of collector in a form of porous rocks capable to accumulate great amounts of oil and gas; mineral rocks, low-permeable for water, oil and gases, performing the function of the covering layer, great reserves of organic substance being accumulated under it. It is considered that microoil is formed as a result of metamorphic transformations of the plant and animal remnants in the sedimentary oil-maternal rocks [46]; it is also called primary oil or protooil [48]. Primary oil, natural gas or both migrate from the formation locality to the collector and rock-cover which interrupt their further motion — that is the way of accumulation of oil and other hydrocarbons. Hence, it is concluded that oil and gas deposits were formed as a result of migration, transport, and are the deposits of secondary occurrence. Their thickens depends on the amount of organic substances in sedimentary rocks. But the question remains unsolved: could how great masses of organic remnants get under the 1–10 km thick layer of sedimentary rocks which, following a simple logic, are formed during a long periods of time.

The shortcomings of both inorganic and organic conceptions of oil origin are considered by the author of the review paper [47]. When analyzing a deep crisis in the theory of organic oil origin, the author comes to a conclusion that «it is high time for arising a new, more universal theory of genesis of oil hydrocarbons and formation of oil and gas deposits on their basis».

It seems to us that the formation mechanisms of oil, natural gas and coal on the Earth are of a single nature. We think that about 285–300 million years ago (during Carboniferous) the extremely luxuriant vegetation and diverse animal life existed on our planet. There were high trees with 50 % of hydrogen, huge plants and animals. The atmosphere contained high amounts of carbon dioxide and water vapour. The Earth's axis was vertical to the orbit of its revolution around the Sun and there were no cool seasons hampering growth of biota. In the estimate of most scientists the Universe age is 15–18, the Sun — 5 and the Earth — $4.6 \cdot 10^9$ years. The ideas of life origin on the Earth are rather contradictory. Some researchers think that primitive forms of life appeared $1.4 \cdot 10^9$ years after the planet formation. On the expiry of 300 million years there arised blue-green algae. The first live cells — prarepresentatives of the animal kingdom were formed about $3 \cdot 10^9$ years ago (it is too long period of time, in our opinion). During following 1.1 — $1.2 \cdot 10^9$ years (Paleozoic era) the Earth surface was covered with forests of tree ferns, lepidodendrons, cordaites, ginkgo, conifers, etc. Various beast-like reptiles (theropsides), fish, crustaceans, pangolins lived on the land and in the sea. Paleozoic era was changed by Mesozoic; there appeared new species and types of flora and fauna. Kainozoic era began 67 million years ago. Life flourished during all these periods on the Earth. Mammals continued their evolution. Predatory animals, rodents, horses, monkeys, mammoths and giant elephants, sea cows, lancet and whiskered whales appeared in Paleogene; deers, giraffes, antelopes, seals, venomous snakes perissodactils, austrabopitecs appeared in Neogene. Anthropogenic epoch came about 2 million years ago and lasts till now. It is divided into Pleistocene or Glacial epoch (2 — 0.025 Ma B.C.) and Holocene which began 25 thousand years ago and lasts now. Such big mammals as mammoths, woolly rhinoceros, cave-dwelling bears and lions, sabre-tooth tigers and giant elephants died out in Pleistocene. There appeared Homo sapiens. In the beginning of Holocene Homo sapiens domesticated some animals (horses, cows, sheeps, dogs, cats, various birds, etc.) and exterminated many other animals (moa, dronts, quaggas, aurochs, Steller's cows, etc.).

In accordance with other point of view, life on the Earth existed even $4 \cdot 10^9$ years ago [48]. These data follow from discoveries in the field of paleontology. This field of science was developed during about 150 years by researchers who affirmed that life came out of water to the land in Paleozoic about 400 million years ago. The Precambrian geology was considered the prehistory one, and this threw doubt upon the truth of Darwin's theory of evolution. According to the data of Academician B. S. Sokolov [48] the notions on life origin on the Earth «radically changed after discovering the Vendian system with most ancient fauna of skeletonless organisms, Vendothenial flora and various microfossils (acratarchs, fungi, groups of vague origin) both in Vend and underlying complexes of Riphean and even more ancient Precambrian (about 4 Ma ago)». According to conclusions of today's researchers in Precambrian paleontology, basing on the analysis of fossil deposits of unique value, life manifestations were rather diverse in that period. Such views radically change the settled prognostic knowledge concerning the biosphere evolution, including the stages of gradual formation of molecular oxygen and then the protective ozone layer from ultraviolet radiation, embracing hundreds of MA. It follows from the conception of Academician B. S. Sokolov [48], that the Earth biosphere contained oxygen no less than $4 \cdot 10^9$ years ago. There are the suppositions of some scientists that the Earth biosphere existed no less than $3.6 \cdot 10^9$ years.

It follows from the above stated that both vegetative and animal life could flourish on the Earth milliards of years ago. Concentration of CO2 in the atmosphere was approximately 0.4 %, nitrogen and oxygen content were close to the present ones (see, Table 8.2). Most researchers consider that before Carboniferous period life evolution on the planet proceeded unjustifiably slowly. In our opinion, the Earth had the multimeter vegetation cover with a lot of animals in water and on the land long before the Carboniferous period.

In that period stellar galaxies were at the stage of formation. The enlargement of star clusters, birth of new planets and celestial bodies took place in the Universe. That was accompanied by release of great amounts of energy. This energy could give any celestial body a velocity sufficient to surmount gravity forces (of interstellar attraction) and to start its free flight. The process of formation of larger celestial bodies, as it was noted in the work [49] «is efficient in dense central parts of globular clusters where get the massive members of the clusters as a result of dynamic mass segregation of the order of 10^9 years».

«The decrease of its (star's) potential energy leads to the increase of the motion velocity in the cluster» and the system «acquires higher and higher speed of recoil which becomes at last sufficient for leaving the cluster. This speed is about 40 km/s for the typical globular cluster». The celestial body speed equal to 40 km/s exceeds 2.5 times the solar escape velocity (16 km/s).

Our planet could collide with such celestial body during the Carboniferous period. As the result of collision with huge wandering celestial guest — a «loose» body which was asteroid or some other spatial body (Fig. 12) — the Earth had suffered a very strong impact which resulted in the Earth's axis shift by about 23.5°. Before this impact the Solar rays were always directed perpendicularly to the equator and parallel to all the Earth surface. It was always summer on our planet. As the result of the impact and shift of the Earth's axis the climate was radically changed. There arised the season cyclicity: summer was changed by autumn, autumn by winter, winter by spring, spring by summer. Besides, after the collision with the celestial body, owing to its mass and the colossal amount of released energy, the planet surface was covered by 1–10 km thick layer of inorganic substances, silicate and carbonate rocks which isolated, in our opinion, the organic matter from oxygen. A milliard years ago our planet looked as a single

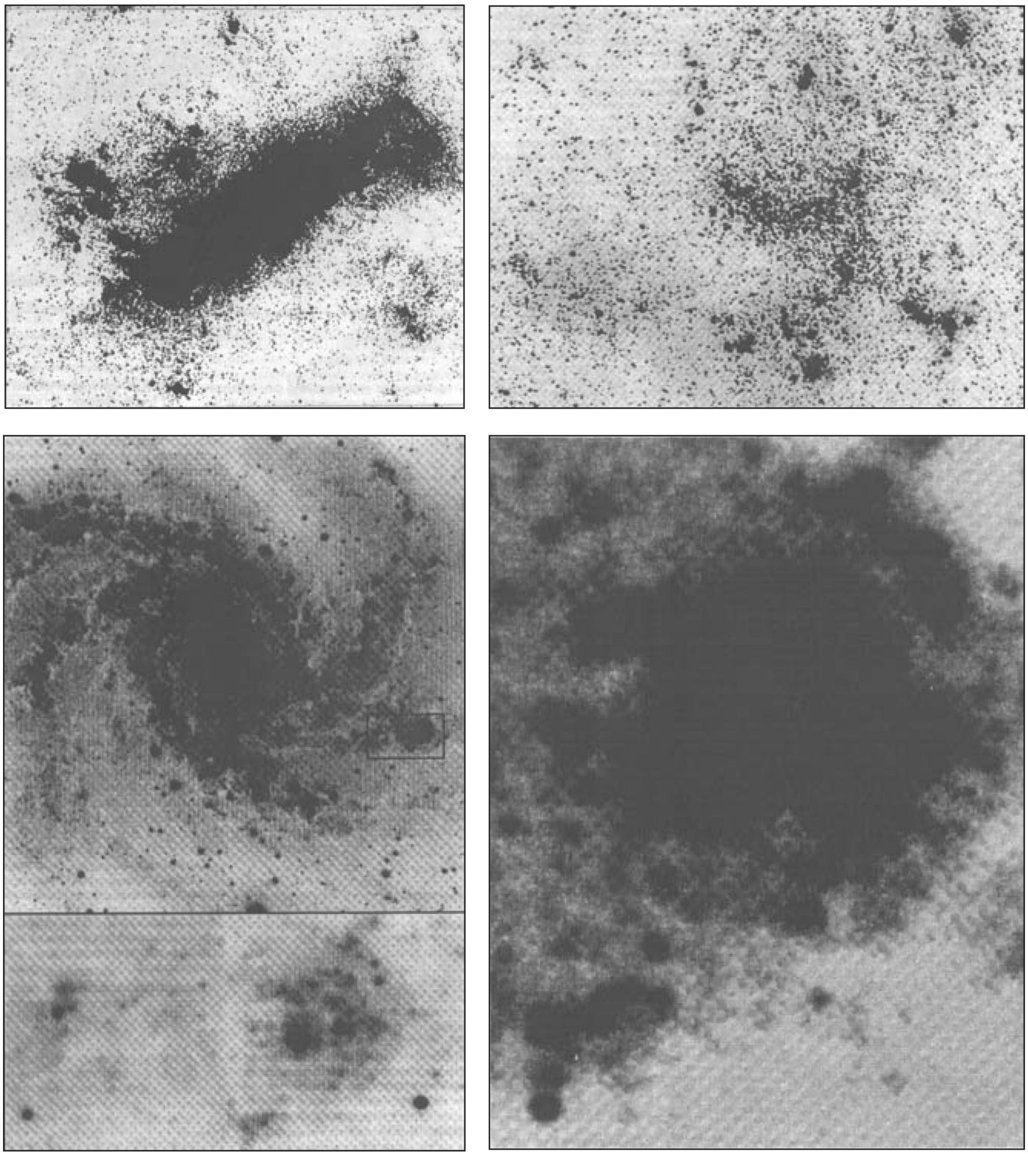

Fig. 12. Schematic structure of dust-like clouds in the space

supercontinent Pangea[1]. Structure of this super-continent surrounded by waters of a single ocean is shown in Fig. 12, *a*; 12 *b* — a moment of planet Earth-Pangea collision with a celestial body.

The main impact fell on the North hemisphere. Those are the regions of the present Northern Europe, including Byelorussia, Ukraine, as well as Siberia, Northern America, etc. As a result, biota was covered by a thick layer of sedimentary deposits. Availability of violent vegetation and various animals in one or

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[1] Another version of events movement is also possible A "loose" celestial body could cover already separated Earth's continents, but the essence of our hypothesis is the same.

another region of the Earth at the moment of collision caused the conditions for formation of the reachest oil- and gas-bearing basins which contained «gas and gas-condensate deposits», as well as bituminous coals [97]. Thus, the seams of rocks saturated with oil which could be extracted on industrial scales were found as a result of the boring in Murmansk Region of Russian Federation [5].

In accordance with the data of the work [51] thickness of the cover layer of oil-bearing strata reaches 4.5–5 km in the central part of Siberia and 1.2–3.5 km in its southern part. Small reserves of hydrocarbon raw materials in China and the South-East of Asia as a whole can be explained by geophysical landscape. About 70 % of its territory is at true altitude of 1500–4000 m and above in latitude 43°–22° north which has determined poor flora and fauna and, as a result, small volume of «preserved» biota, which provided for formation of only 1.16–1.20 % of hard coal in the territory of China. That is why China and Indostan practically have not natural gas and oil now.

Only inconsiderable oil deposits were found in the north-east of China and in the shelf of the South China Sea. Oil reserves in China are 3.6 and coal reserves $115 \cdot 10^9$ t. It is possible that in China, like it is in Ukraine, the layer of mineral cover was thicker than in other planet regions and so, oil occurs at considerable depths.

The celestial body covered to higher extent the Northern and Southern America continent. The process of mass distribution of a «loose» body, which also contained huge amounts of ice, on the Earth surface proceeded over a long period of time, but this process was incommensurably shorter than those of gas, oil and coal formation (Fig. 13). As a result the conditions were created on the Earth for appearance of the largest oil-and-gas-bearing deposits in the territories of the present-day states: in Russia (Western Siberia) [52], in Kazakhstan (Southern Mangyshlak, Eastern Kasalgan on the shelf of the Caspian Sea), in Vietnam and Malaysia (the Sound shelf), in Iran, Iraq, Livia (Sirtran basin), in North-Eastern Africa, USA (California and Gulfcoast basins), in Venezuela (Maracaibo basin), in Brazil (Sergip basin), as well as in Ukraine (Dnieper-Donets Depression, Carpathian foothills), etc. About 500 oil-gas-bearing deposits were found as a whole in the Northern and Southern America, in the North of Europe (the North Sea shelf near Norway sea-coast), Africa, Asia and Australia as well on the continental shelf of the Atlantic, Indian and Pacific Oceans. Among the above deposits 40 are giant ones (10 — gas fields, 6 — oil-gas fields and 24 oil-bearing ones).

The same regions are known as coal-bearing ones. In accordance with the hypothesis advanced by German scholar A. Vegener (1915), the breaking of supercontinent Pangea and slow drift of separate continental blocks to their present location began about 200 million years ago (after geocatastrophe which provided inhabitants of the Earth with hydrocarbons, — authors' note).

Time of 214 million years B. C. is indicated as the beginning of planet Earth continents drift in the work [53]. It is supposed that giant asteroid, 5 km in diame-

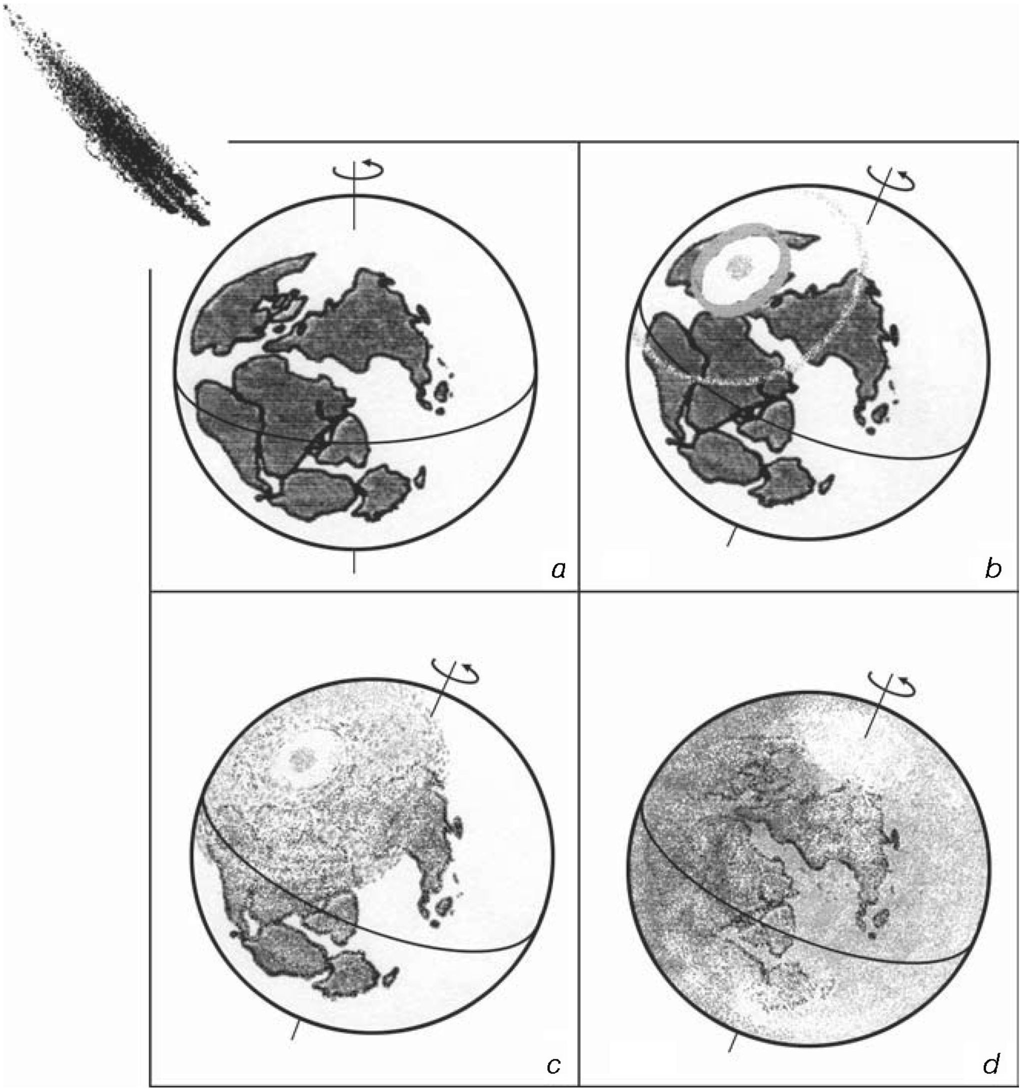


Fig. 13. Mechanism of the geocatastrophe and burial of flora and fauna on planet Earth-Pangea by the space «guest»

ter, «crashed to the Earth with velocity of 16 km/s». When overcoming the atmosphere resistance the asteroid got incandescent and its surface layer was partially melted. Under this collision Pangea, a single continent on planet Earth, was broken with a powerful impact while the asteroid exploded as a result of the impact «tectonic plates shifted», planet Earth «was set in motion which also consisted in the drift of continents». The asteroid impact centre was in the territory of Quebec in Canada; it formed a crater 100 km in diameter. One can see this crater formed 214 million years ago even now from space. The scheme of the asteroid convergence with the Earth and of explosion, as the authors imagine it, is shown in Fig. 14. As is evident, great amount of energy is released under the impact and kinetic energy of motion passes into that of the asteroid body destruction by the explosion.

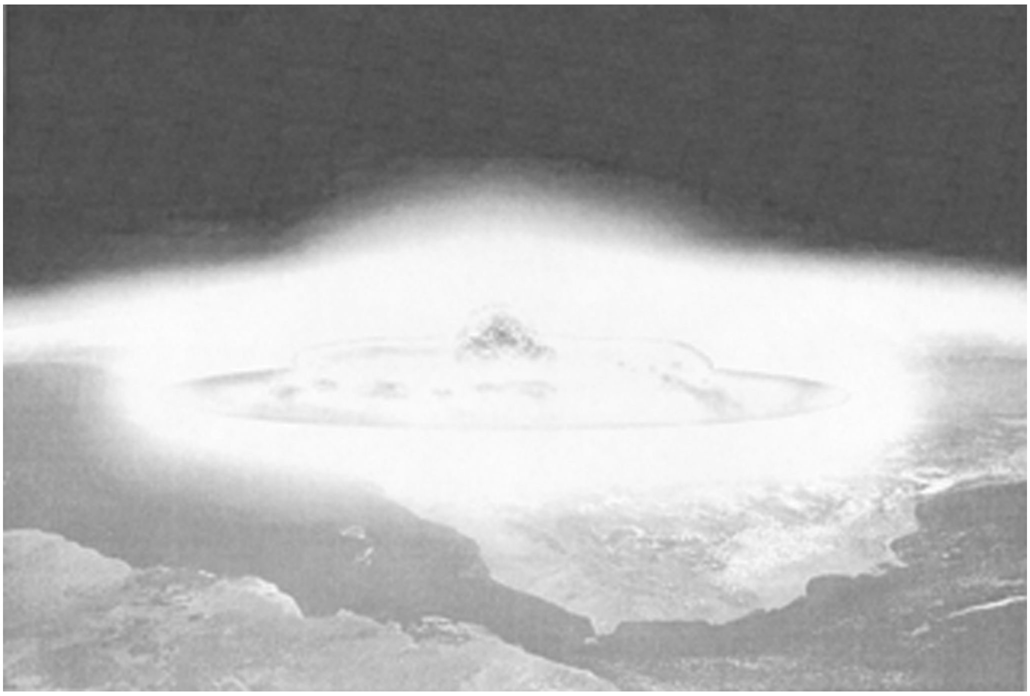


Fig. 14. A scheme of collision of the monolithic asteroid with planet Earth.

According to the data of [53] «melted stones and fragments» were formed as a result of energy released under the asteroid impact against the Earth; the fragments ascended high in the atmosphere and reached the territory which than became the British Isles. Glassy particles and dust caked at high temperature covered the Earth by the layer 2 km thick. These data were confirmed by paleontological excavations of sedimentary rocks on the Avon lakeside, where a layer of glassy particles was found at the depth of 8 m. Chemical and phase analysis confirmed that the vitrified fragment could form under the fall of big asteroid or comet on the Earth. The ideas developed in the work [53], which was published six months after the publication of our monograph [54] are similar to the ideas on planet Earth collision with a «loose body». The «ideas float in the air», indeed.

According to our hypothesis huge amount of hydrocarbon (live) matter was buried under the surface layer formed on planet Earth. According to [55, 56] the amount of live matter (plants, animals) in the biosphere is 10^{20}–10^{11} t now. By the time of the catastrophe, which resulted in the beginning of oil, natural gas, bituminous coal and slates, the amount of live matter was several orders higher and was 10^{22} t. It was that organic matter formation which became a basis for oil and gas depots which genesis continued millions of years. From the data of [57], the total mass of the formed live matter during all the Earth history equals 10^{27} g (10^{21} t). This value is only 6 times less than the Earth mass ($5.679 \cdot 10^{21}$ t).

One can approximately estimate the mass of the «loose» body which fell on the Earth and covered it by the 5-km layer at an average.

Take the then Earth radius as that by 5 km less than the present one (6378.533±0.437 km) [58] and was equal to 6373.533±0.437. Calculations show (the loose body density being taken no less than 2 g/cm^3; the Earth density is 5.919±0.004 g/cm^3), that the mass of 5-km layer which covered the Earth reaches $5.108 \cdot 10^{21}$ kg which equals only 0.0854 % of the Earth mass $(5.979 \pm 0.004) \cdot 10^{24}$ kg now). However the celestial body moved from the space outside the solar system with the escape velocity equal to $\upsilon_{2c} = 11.2$ km/s, or even with the solar escape velocity of $\upsilon_{3c} = 16$ km/s. All this as well as the considerable mass of the body being taken into account, the latter possessed the colossal motion energy. The «guest» motion energy Wc may be calculated from the equation

$$W_c = 1/2\, m\, \upsilon_{ik}^{2}, \qquad (1)$$

where m — is the mass of the space «guest»; υ_{ik} — is the second ($i = 2$) or third ($i = 3$) cosmic speed.

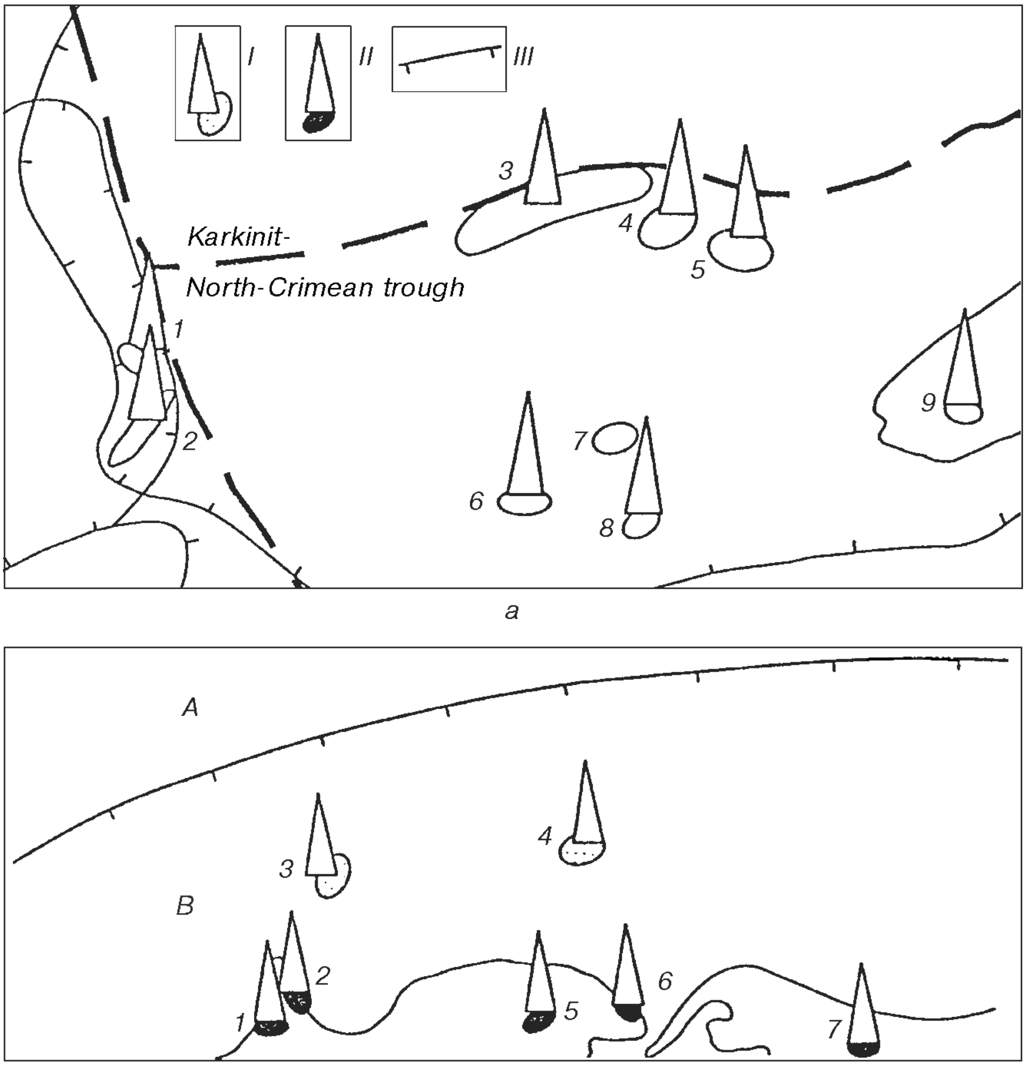
Calculations have shown that at $m = 5.108 \cdot 10^{21}$ kg, $\upsilon_{2c} = 11.2$ km/s $W_c = 3.205 \cdot 10^{20}$ kJ at $\upsilon_{3c} = 16$ km/s $W_c = 6.538 \cdot 10^{20}$ kJ. When the «guest» collided with planet Earth it was the energy of $(3.205–6.538) \cdot 10^{2}$ kJ which resulted in the geocatastrophe — the shift of the Earth axis and distribution of additional 5-km thick layer of minerals, dolomites, quartzites, silicates, aluminates, etc. on the Earth's surface. The formed dust-like clouds hid the Earth from the Sun and closed the access of solar beams to the Earth surface, isolated the planet from the major source of energy. There arised the conditions of the «dust», and then «aerosol» winter; as a result, the Earth was covered by the kilometer-thick glaciers. The diverse groups of animals, including heat-loving mammoths which lived in Siberia, perished. This period lasted for many hundreds of Ma, when the Earth's crust, oceans and seas were formed and continents separated. The mechanism of burying the vegetation and animal kingdom on planet Earth by the space «guest» was shown on the scheme in Fig. 12, *c*, *d*.

The organic matter buried under the mineral cover took part in the processes of oil and gas formation with distribution of primary oil deposits in the ravines-traps with complex mechanisms of their substitution by intensively generated gaseous hydrocarbons. The organic matter was isolated from air oxygen, the main oxidizer — the biota «sanitarian», and thus, it turned into oil and natural gas and sometimes — into bituminous and brown coals during millions of years owing to the planet heat and catagenesis processes. Natural gaseous and liquid products of oil and gas formation were distributed both across the material Earth's surface and along it, since they were subject to high pressure, being compressed by the dense layer of rocks which formed the air tight cover. During centuries and even millions of years gaseous and liquid products of oil and gas formation could drift roaming on the surface of the Siberian platform and, maybe, Ukrainian Shield, as well as other continents of the Northern hemisphere and formed a «cover» of fossil hydrocarbons (oil, gas, carbon) of planet Earth, including Siberia, Alaska, Canada, USA, Mexico, North of Europe (Norway), Byelorussia, Ukraine, Southern America, Africa, the Antarctic, etc. Oil and gas products, which suffered great pressure of the mineral cover, could also form cone-like elevated tectonic zones. The appearing beds of bituminous and brown coal, as well as bituminous products both could remain at the places of their origin and sublimate to the zones with milder conditions (temperature, pressure). It has been established that in Ukraine [59] in the zone of the Dnieper-Donets Depression, oil is covered by the stratum of anthracite underlied with 2-km layer of methane gashydrate which proven reserves are about $27 \cdot 10^{12}$ tons (that is 20 % of methane reserves in the world). Allowing for the fact that 1 ton of the gas hydrate gives 200 m^3 of gas, this amount of gas will be enough to feed Ukraine for 250 years.

The main oil-gas-producing region in Ukraine is considered to be geologically bound to the Dnieper-Donets aulacogen (DDA) embracing Dniepropetrovsk, Donetsk, Lugansk, Poltava, Sumy, Kharkov, Chernigov regions [59]. About 90 % of oil-gas-condensate reserves of hydrocarbons in Ukraine are concentrated in these deposits. The oil and gas band 170 km wide and 750 km long extends from the boundary with Russia to the boundary with Byelorussia. In the northern edge of DDA oil and natural gas are the multilayer accumulation of rocks in the band 35–100 km wide and 500 km long extending from the north-west to the south-east. The oil-bearing band extends from the Markove oil deposit in the east to Turutyne deposit in the west. Oil- and gas-bearing deposits are usually concentrated at the depths of 800 to 4500 m, and in the Dniepropetrovsk Region — at the depth of 5000–5500 km and above. Power of the first bored Gashinevian hole is 264 m^3/day [59].

The stated hypothesis being true, it would be of predictive character. Firstly, it follows from the stated hypothesis and practical knowledge available, concerning oil and gas production, that oil- and gas-bearing basins can occur at great depths. Secondly, this hypothesis explains coal formation in the bowel of Antarctic continent and in Arctic Regions (Spitzbergen), Northern America (Canada and USA), oil in the North and Norwegian Sea, etc. Thirdly, in terms of the above stated hypothesis, the investigations of oil and gas content in the North of Ukraine, DDD zones, territories of the north-western shelf of the Black Sea and Azov Sea water area are of special interest. From the data of the work [16] the primary predicted resources of hydrocarbons in the Sea of Azov water area 343.8 mill.t c. f.

Two new oil and gas deposits have been discovered in the water areas of the Black Sea and Sea of Azov: the Bezymyannoe and North-Kazantip deposits,



a

b

Fig. 15. Sketch maps of the north-western shelf of the Black (*a*) and Azov (*b*) seas according to [16]. Hydrocarbons deposits:
I-gas and gas condensates; II-oil; III-boundaries of tectonic elements; *a*: I. *1.* — Bezymyannoe; *2* — Odessa; *3* — Golytsya; *4* — South-Golytsya; *5* — Schmidts; *6* — Shtormovoe; *7* — Arkhangelskoe; *8* — Krymska; *9* — Olenevskoe; *b*: I. *1.* — Semenovskoe; *2* — Aktashskoe; *5* — Voikove; *6* — Borzove; *7* — Stara Tytarivka; II. *3* — North-Kazantip; *4* — North-Kerch; *A* — Middle Azovian Uplift; *B* — Indol-Kuban trough (gas reserves in the hole 3 according to the category $C_1 + C_2$ were $3262 \cdot 10^6$ m^3)

respectively. The Bezymyannoe gas deposit is distributed in the north-western part of the Black sea, the sea depth in the deposit region being 37–39 m [16]. The Bezymyannoe gas deposit is a part of the oil-and-gas-bearing Romano-Black Sea region. A map of north-western Black Sea shelf according to [16] is presented in Fig. 15 (*a*).

Depth of the bored holes is 1185, 2258 and 2055 m. Gas-saturated beds of these holes give gas inflow 94.49; 78.6 and 96.1 tou. m^3/day. Methane content in gas is 94.6–95.6 %, ethane and higher hydrocarbons 1.7–2.9 %. Bed pressure at the depth of 1081 (hole 1) was 11.72 MPa (116 atm.).

North-Kazantip gas condensate deposit (Fig. 15) is among well-known oil-gas and gas condensate deposits of the north Azov Sea water area, characterized by the extended sublatitudinal uplift of the Scythian platform — the Azov Ridge, as well as by the North-Azov and Indol-Kuban troughs [16].

Depth of occurrence of the folded basement is approximately estimated as that of 8 km, while the deposits thickness in the Maikop district reaches 5 km.

Three holes have been bored in the North-Kazantip gas condensate deposit. Hole 1 is 1115 m deep, with industrial gas inflow of 84.5 thou. m^3/day, hole 2 is 1400 m deep, gas condensate mixture flow rate about 91 thou. m^3/day, hole 3 was bored to the depth of 260 m.

Calculations have shown that gas reserves of the North-Kazantip gas-condensate deposit reach $40 \cdot 10^9$ m^3. Other gas condensate and oil-gas-bearing deposits evidencing for the great prospects of gas- and oil-bearing water area of the Sea of Azov are also given in Fig. 13. We think that the deposits with high oil-gas-bearing potential are much deeper. Thus the development of geological-prospecting works in the water area of the Black Sea and Azov Sea shelf is rather promising.

3.3. Energy, Economy and Gross Domestic Product

The World Energy Council predicts that by 2020 the world energy consumption will increase by 50–75 %, and the world energy generation will increase more than twice by 2050. Population growth tendencies [60] prove that by 2050 the population number will reach $8.9 \cdot 10^9$. It is considered that energy generation is the socioeconomic foundation of the state [12]. It is planned that the world demand for hygrocarbon energy carriers will increase thrice by 2050 as compared to 2000. The gross domestic product (GDP) will increase respectively [22]. It was in 1976 that Academician P.L. Kapitsa indicated to GDP dependence on the consumption of energy resources [61]. When analyzing interrelation between energy consumption and GDP values for different countries P.L. Kupitsa established the existence of a simple proportion between them: thus «the material welfare of people deprived of energy resources will decrease».

To raise living standards of citizens in one or another country it is necessary to increase the consumption of energy. It is generally accepted to use such indices as GDP per capita or integral sum of gross national product (GNP) as the integral index of economic development of countries. The idea of consumption of the manufactured useful product supplied to the market and bought by someone is assumed as a basis of the GDP and GNP category. The manufactured product purchase price is a true evaluation of its usefulness [62]. Gross domestic product is a function of high-tech productions and efficiency of energy consumed for the product. The higher is energy generation and the less is its consumption per the production unit in the country, the higher is GDP in the first approximation. We say about the first approximation since the absolute value of GDP depends on the volume of knowledge and intelligence put into this product on the one hand and energy consumption efficiency under its creation on the other hand. Hence there appear sprouts of a new epoch in the third millennium. This question is still under discussion [62]. A number of experts-analysts think that the economy of knowledge differs essentially from the industrial type economy, when accumulation of treasure was connected with primary material resources. The latter is contradicted by the experience of Japan where assimilation of new ideas, knowledge, inventions was ranked as state policy after the World War II, and this allowed them to create high-tech production of new materials for different branches and to develop on their basis electronic engineering, information systems, instrument engineering, motor industry, etc. The first dosen of states with the highest GDP per capita in the world (GDP in dol. per capita) looks as follows: Switzerland (33515), Denmark (31001), Japan (29143), Austria (27322), Norway (28150), USA (25931), FRG (25322), Belgium (25321), Netherlands (24328), Sweden (23899). Each of these states occupies certain niche in industrial development and is a leading one in one or another high-tech branch spreading its influence on relative branches in other countries, redrawing the economic map of the world (*Microsoft* (USA), Sony (Japan), *Ford* (FRG), *Mersedes* (FRG), etc).

Dependence of GDP on energy resources consumption in 1968 (*a*) and in 1998–2000 (*b*) is presented in Fig. 16. Statistical data from [84, 110] were used when plotting dependences. It is from Fig. 16 that GDP (dol. per capita at the rate of 1993) is closely connected with energy resources consumption by population of the planet (Q t of c. f.) man — tons of conventional fuel per capita) — the higher and more efficient is energy resources consumption, the higher is GDP.

The GDP — Q dependence deviation from the regression line for different countries is conditioned by the difference in efficiency of energy resources consumption [54]. Countries distributed above the regression line or on the regression line possess high efficiency of energy consumption. In 1968 Switzerland had the highest efficiency of energy consumption in the world (Q/GDP = 4.6). France and Israel shared the second and third places (3.1, each). Countries below the regression line are characterized by low energy consumption efficiency. The USA, Canada, Australia, Belgium, FRG, Great Britain, Russia, etc., belong to such countries, as is seen from Fig. 16, *a*. In 1968, energy consumption efficiency in Russia was equal to (6000/4000 = 1.5 [63]), i. e., it was lower than in the USA (2.1 [22]). Low energy consumption and, as a result, weak

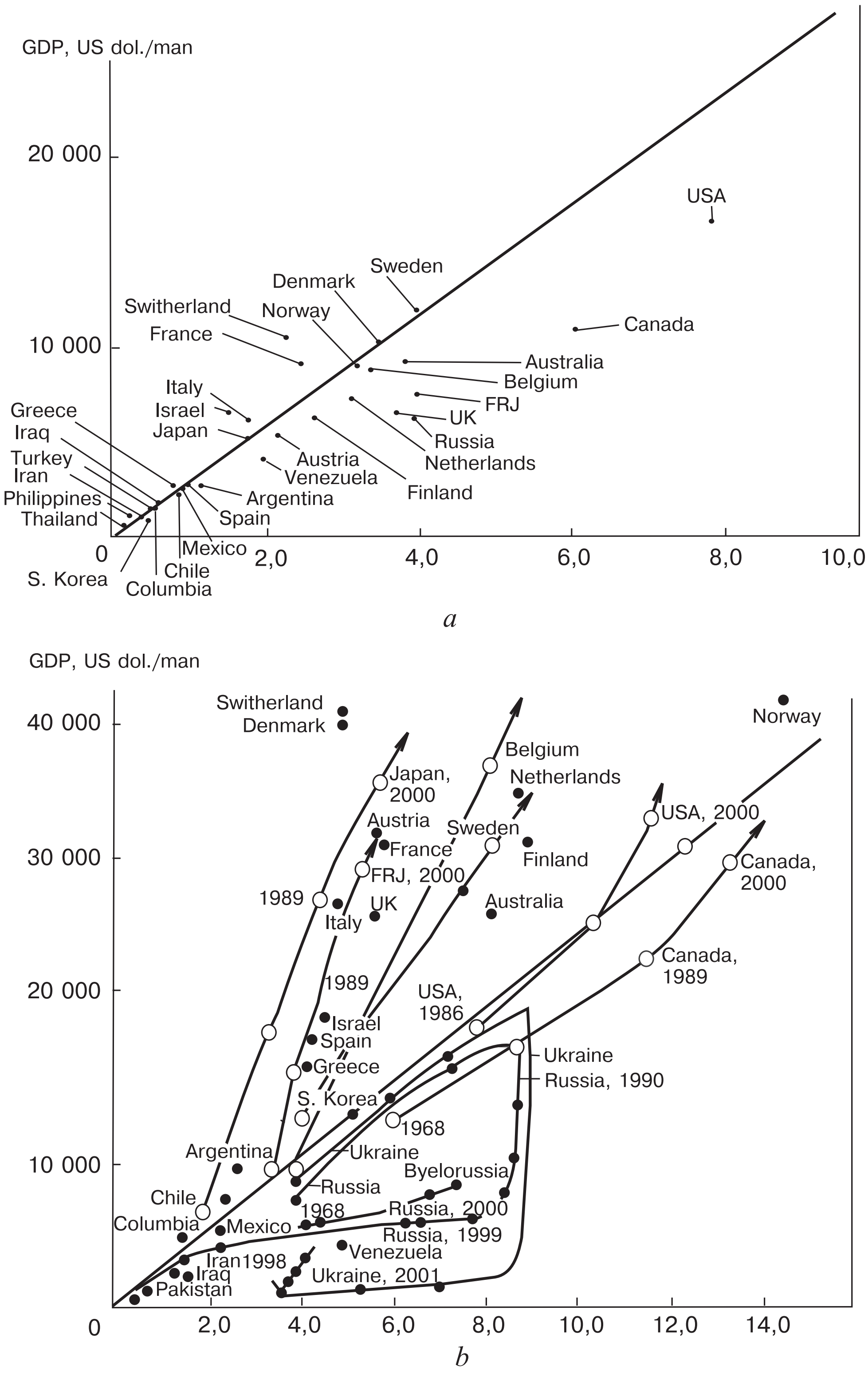


Fig. 16. GDP relation with energy resources consumption, t of c.f/man in the world countries in 1968 (*a*) and in the period of 1968–1998–2000 (*b*)

economy, low GDP values and, as thus, low living standards are characteristic of the underdeveloped countries.

The dependence GDP — Q in the world countries for the period embracing about 30 years (1968–2000) is presented in Fig. 16, *b*. As is evident even in this case the above dependence is characterized by the great spread of GDP and Q values. A comparison of the data of Fig. 16, *a* for 1968 and 16, *b* for 2000 shows that the two-fold and above increase of GDP during this period is possible for industrially developed states: Austria-6.2; Japan-5.8; Netherlands-4.9; Norway-4.7; Belgium-4.1; Denmark-4.0; France-3.75; Switzerland-3.5; FRG-3.3; Canada-28; Sweden-2.6; USA-2.1, etc. These countries have succeeded to achieve extremely high GDP with moderate use of energy resources. It is interesting that these countries do not possess their own essential resources of oil and gas and have to develop science-intensive, high-technology productions which do not require high energy consumption.

The underdeveloped countries and CIS countries, formed after disintegration of the former USSR are distributed below the regression line. GDP of underdeveloped «resourse» countries has increased several times during the period under consideration owing to energy consumption growth, though it (GDP) still remains too low. Chile 3.4 times (from 2118.6 to 4033.0 dol./man); Columbia — 3.3 times (from 1382.4 to 2201.0 dol./man); Iran-3.2 times (from 1222.9 to 2341.0 dol./man); Indonesia-2.4 times (from 390.4 to 912.0 dol./man); Mexico-1.7 times (from 2261.8 to 3934.9 dol./man). The consumption of energy resources in Iraq has become something higher, and as a result GDP has also increased, but it is still low (1331.0 dol./man). Energy consumption in Pakistan being increased from 0.0653 to 0.4056 t of. c. f., the GDP decreased from 531.7 to 462.0 dol./man [22]. The same picture is observed in Philippines: energy consumption increased from 0.2042 to 0.4393 t of c. f., while GDP has decreased from 1153.4 to 938.0 dol./man, as well as in Venezuela: Q has increased from 1.9953 to 5.7110 t of c. f., while GDP decreased from 3.9959 to 3.3070 dol./man. The latter evidences for the weakness of economy in these countries. Unefficient use of energy is characteristic of the developing countries, and, as a result, certain growth of energy consumption per capita leads to a very slow growth of GDP or even to its fall, as is observed for the case of Pakistan and Philippines.

Ukraine, Byelorussia and Russia are also below the regression line, though in 1970–1990 their GDP value corresponded to the level of medium-developed countries. A catastrophic decrease of GDP in Ukraine and Russia occurred in 1990 caused by changes in the social system of these countries. As is evident from Fig. 16, *b*, the curve GDP-Q of Ukraine and Russia has a loop-like dependence, bending towards the decrease of energy consumption and fall of GDP. Such a loop dependence of GDP-Q characterizes the economic depression of industry. It would be noticed that the loop trend of GDP-Q curves does not occur in civilized countries. Such a sharp decrease of GDP which was observed in Ukraine and Russia is possible only under a sudden economic depression with a collapse of industry under revolutions which can lead to the large-scale misappropriation of state-owned property and loss of working places, to mass unemployment with absence of economic discipline in the country, and capital export. A considerable drop of GDP per capita in the CIS countries was favoured by cancellation of personal savings by Governments of these countries. Rather large sums were accumulated on the State Bank accounts by citizens who followed the call «keep your money in the saving bank of the USSR». The deposits made by citizens with the rate of interest of 1.5 % and 3 % were used in the USSR as investments to industry and agriculture which permitted making certain contribution to the extended reproduction (that was the participation of depositors in the country development). The amounts of cancelled deposits, which exceeded hundreds of million dollars were used to create the networks of privatizational commercial companies, banks and other economic structures with plungered primary capital. The Supreme Council and the Cabinet of Ukraine as well as the governments of Russia and other CIS countries annually face the question of deposits return raised by CIS peoples. As a result the governments allocate scanty sums and this evidences for the fact that they will need at least half a century to repay the deposits, and depositors will rather die than receive their money. Some CIS countries, Latvia, Lithuania, Estonia and partially Byelorussia have not admitted the collapse of their Industries. One can observe development of economy and annual GDP increase by 7.0–11.6 % in these countries. Beginning from 1990 the GDP in China increased annually by 10 %.

The GDP-Q dependences for Ukraine, Russia and Byelorussia are presented in Fig. 16, *b*. It is evident that both Ukraine and Russia belong to the developing, «resource» countries. «The lack of power resources, their high cost played the fatal role in the collapse of industry and degradation of agriculture, growth of unemployment, decrease of revenues» in Ukraine [88] and resulted in the population impoverishment and drop of GDP.

The GDP per capita in Ukraine, Byelorussia and Russia is presented in Table 13. A swift drop of GDP was characteristic of Ukraine and Russia in 1990. The impetuous decrease of GDP and thus, the decrease in living standards, were also favoured by the severance of economic relations between CIS countries, refusal of planned economy characteristic both of the socialist countries and of a number of branches of industry (defence industry, fuel-power complex, metallurgy industry, etc.) of the world leading countries: the USA, France, England, Japan, Germany [44, 43]. It was owing to the State Plan by Chancellor Adenauer and Minister of Finance Hekchard that Germany with its war-ravaged industry was restored to life for about 10 years with minimum investments of $4 \cdot 10^3$ US dollars. As to Ukraine, we have practically destroyed the fuel-power complex — the base of economy, have not preserved the FPC-servicing industry; we are afraid of cold winter which can put Ukraine on the edge of national catastrophe,

Table 13

Gross Domestic Product (dol. per capita) of Ukraine, Byelorussia and Russia in 1990, 1994, 1998 and 2001

Year	Ukraine		Byelorussia	Russia
1990	5500		6250	6700
1994	2500		4300	4270
1996	1250	[64]*)	—	—
1998	841	"	4800	3800
1999	637	"	—	—
2001	347	"	5000	5000

* Data of GDP values calculated from the gross national product (GNP) by M. Pavlovsky [64], Doctor of Sciences (Economics), not allowing for «shadow» economy.

we have got into debts ($13 \cdot 10^9$ US dollars), impoverished people of Ukraine, lost 70 % of industry [64], destroyed our science, sold out fleet, began selling out the district power systems.

It is evident from the data of Fig. 16, *b*, where one can see a tendency to GDP-Q dependence change in Russia described distinctly by the «hysteresis loop of Russia economy» also repeated by Ukraine, that from 1968 to 1990 there proceeded a proportional increase of GDP both in Ukraine and Russia with the increase of Q, and, beginning from 1991, owing to the destruction of the planned system of management of the basic branches of industry, one could observe the fall of GDP, decrease of the efficiency of power resources utilization and as a result, the decrease of living standards.

The dependence of the global GDP (4) on time in the period of 1950–2000 is shown in Fig. 11, curve *4*. As is evident, linear dependence of GDP on time was observed up to 1973 (section *AB* of the curve *4*) — time of the beginning of energy crisis of 1973–1974 [12]. After 1973 one can observe the decrease of oil consumption up to 1975. Then, beginning from 1976, oil consumption smoothly increased up to 1979, then one can observe a fall in oil consumption up to 1985 because of the energy crisis of 1977–1978. A smooth increase of oil consumption begins from 1986. Changes in oil consumption led to the deviation of curve *BD* section (curve *4*) of the global GDP from the linear dependence of section *BC* (Fig. 11, curve *4*). It would be noticed that with the beginning of energy crises, the dependence oil consumption — GDP delayed in the change of the global GDP, determined by the corresponding oil reserves accumulated by consumers, as well as by oil refining at oil-refining plants. Data of Fig. 11 as a whole demonstrate close correlation of the global GDP and, as a consequence, the world living standards with the level of consumption of energy carriers.

The lifetime (l) dependence on the GDP integral index in the coordinates·l — GDP/man (Fig. 17). A distinct functional dependence·l — GDP/man is observed: the more is GDP the longer is the life of the country citizens. The highest life duration is observed in Japan — 79.5 years [65]. In the countries of «golden milliard»·τ_l, as is seen from Fig. 17, is equal to 75.9–78.3 years: UK, Canada and Sweden 78.3 years each, Netherlands and Norway — 77.7 years; Italy and France — 77.6 years; the USA — 77.1 yr., FRG — 75.9 yr. Life duration (τ_l) in Tzarist Russia was 32 years in 1896–1897, in the USSR it was 44.4 years in 1926–1927; 68.6 years in 1958–1959; 69.5 years in 1971–1972, and 69.5 years in 1986 [66]. Life duration in Russia has decreased to 64.4 years now [65].

In 1998, the average life duration in the world was 66 years. Average life duration in the developed countries was 75 years, in the under-developed countries — 64 years [12].

Unfavourable socio-economic processes which took place in Ukraine in the recent decade (low GDP, lack of energy resources, economic instability, low wages below the subsistence minimum, continuous «creeping» increase in prices, delays in payment of wages, etc.) led to the sharp decrease of population reproduction in Ukraine and to the decrease of population number in Ukraine.

From the data of State Statistics Committee of Ukraine, natural increase in population was –7.5 (minus) and migrational increase –0.9 per 1000 people in 2000. The population number in Ukraine has decreased from 52 to 48.4 million

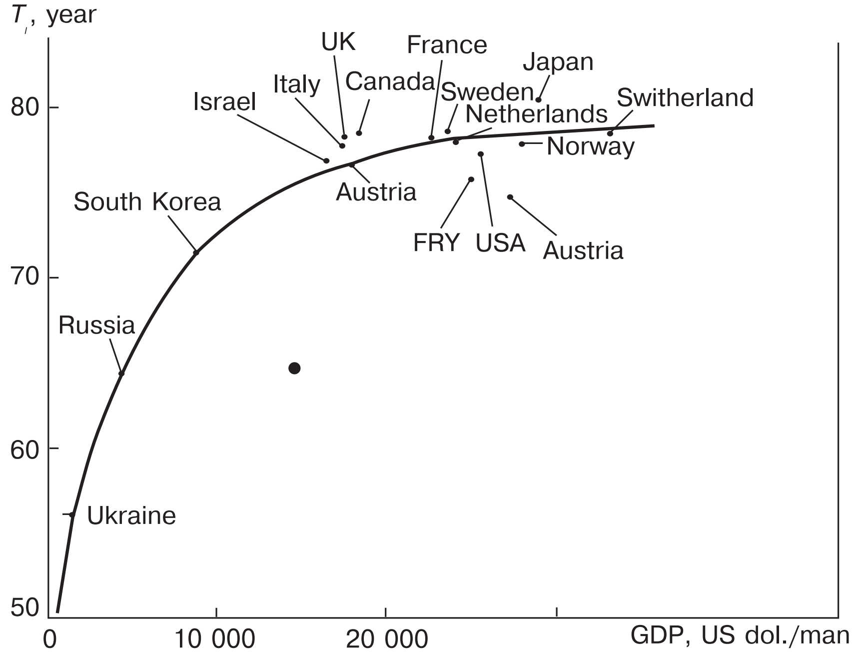


Fig. 17. Dependence of life duration (τ, years) in some countries of the world on the GDP value

people for the recent decade. According to predictions [67] under such development only 25–32 million people can remain in Ukraine by 2050.

Ukraine, the country with good climate, fertile soil, rich mineral resources and industrious people, has to change radically the socio-economic situation, following examples of development of advanced countries all over the world. The population number in the world has increased more than twice during the last 50 years; it increased from $2.5 \cdot 10^9$ in 1900 to $6.02 \cdot 10^9$ as of December 31, 2000. Grain production has increased twice, energy consumption — 4 times, production grow rates have increased 7 times during the same 50 years and, thus, they have surpassed the planet population growth rate which has provided the rise in the living standards of people [68].

When analyzing regularities of production and consumption of energy carriers in different countries all over the world, economic development and growth of GDP one can make the following conclusions: most advanced countries not only have increased production of the fossil energy carriers in the last decades of the 20th century but also increased the efficiency of its use, which has resulted in more intensive economical development, growth of population welfare and GDP. Special attention is given now to development of resource-saving technologies which permit saving about 20–25 % of primary energy carriers. At the same time availability of energy-consuming branches of industry in some countries (e. g. multitonnage and technologically obsolete metallurgy and chemical industry in Russia, Ukraine, China) decreases the efficiency of energy use and is accompanied by harmful ejections in the environment. These conclusions are characteristic not only of the countries oriented to production and sale of resources (Russia, Kazakhstan, Ukraine, Kirghizstan, etc.) but also of the advanced countries — the USA, Canada, UK which, though possessing the highest level technologies, cannot compete as to energy consumption efficiency in industry (characterized by the value of GDP per capita) with some West-European countries and Japan.

REFRENCES

[1] D.B. Volberg, Teploenergetika, No. 8 (1999) 5.

[2] H.-H. Rogner, A. Han, Energy: Economics, Technology, Ecology, No. 3 (1999) 8.

[3] Global Environment Outlook 2000, UNER. Earth scan Publ. Ltd, London, 1999.

[4] V.A. Kirillin, Sciemce Future, Iss. 16 (1983) 3.

[5] E.F. Shnyukov and V.A. Krayushkin, Geol. J., No. 1 (1999) 109.

[6] J. Laherrere, Petrol Rev., Vol. 53. No. 625 (1999) 24.

[7] N.V. Selivanov, Probl. Sc., No. 7 (2000) 44.

[8] B. Mayevsky, N. Yevdoshchuk and O. Lozinsky, Oil-Gas Provinces of the World, Naukova Dumka, Kyiv, 2002.

[9] H.-H. Rogner, Energy and the Challenge of Sustainability. World Energy Assessment, 2000.

[10] Yu.V. Kondratyuk. Cosmonautics. Encyclopaedia, Sovetskaya Entsiklopediya, Moscow, 1985.
[11] A. Han, L. Langlois, and M. Jiru, Energy, No. 11 (1998) 9.
[12] K.Ya. Kondratyev, Bull. Rus. Acad. Sc., Vol. 74, No. 9 (2000) 788.
[13] I.Yu. Yegorov-Tismenko, N.M. Baikov, Energy: Economics, Technology, Ecology, No. 12 (1998) 2.
[14] O.V. Krylov, Bull, Rus. Acad. Sc., Vol,70, No. 2 (2000) 136.
[15] N. Nakichenovich, Energy: Economics, Technology, Energetics, Ecology, No. 12 (1998) 2.
[16] N.I. Yevdoshchuk, N.K. Ilnitsky, P.N. Melnichuk, and V.P. Klochko, Geology of Oil and Gas, No. 2 (2000) 2.
[17] A.A. Beschinsky and D.B. Wolfberg, Energetics of the World, Energoizdat, Moscow, 1985.
[18] V.N. Kochetkov and A.A. Novoseltsev, Ecologic problems of coal-mining branch in the region under transition to sustainable development. Proc. Int. Scient.-Practical Conf., Kuzbasvuzizdat, Kemerovo, Vol. 1 (1999) 125.
[19] BWK, No. 7 (2000).
[20] A.N. Dmitrievsky, Bull. Rus. Acad. Sc., Vol. 67, No. 10 (1997) 893.
[21] Western Australia, Petrol. Rev., Vol. 51, No. 604 (1997) 212.
[22] A.E. Kontorovich, N.L. Dobretsov, N.P. Liverov, et al. Bull. Rus. Acad. Sc., Vol. 69, No. 9 (1999) 771.
[23] Export Strategy of Gazprom, Gas Ind., No. 7 (1989) 37.
[24] E. Adamov, Rus. Econom. J., No. 5/6 (2000) 80.
[25] Statistical Yearbook of Ukraine for 2001, Tekhnika, Kyiv, 2002.
[26] I.I. Muzychko, Oil and Gas of Ukraine. Naukova Dumka, Kyiv, 1997.
[27] B. Ustimenko, Pravda Ukrainy, May 16, 2000.
[28] N. Galkin, Zerkalo nedeli, August 21, 1999.
[29] A. Shidlovsky, Bull. NAS of Ukraine, No. 5/6 (1998) 64, No. 3 (2001) 29.
[30] D.V. Yakovlev, A.N. Shabarov, E.V. Goncharov, et al. Patent l136850, Russia MPK^{6}E21D43/00, 43/30, Bull. No. 25 (1999).
[31] Yu.N. Melyshev, Energy: Economics, Technology Ecology, No. 6 (2000) 8.
[32] J. Westwood and R. Knight, Oil and Gas J., Vol. 100, No. 33 (2002) 22.
[33] Wu Kang and Fesharaki Fereidun, Oil and Gas J., Vol. 100, No. 31 (2002) 18.
[34] S. Hannus and V. Poivonnen, Energetics of the World, Energoizdat, Moscow, 1985.
[35] N.N. Ponomarev-Stepnoy, Energiya, No. 12 (1997) 5.
[36] World Coal, Vol. 7, No. 12 (1998) 6.
[37] BWK: Branst. — Warme-Kraft, Vol. 50, No. 11/12 (1988) 8.
[38] Ugol (Coal), No. 8 (2001) p.
[39] K.Ya. Kondratyev, K.S. Losev, M.D. Ananicheva and I.V. Chesnokova, Bull. Rus. Acad. Sc., Vol. 73, No. 1 (2003) 3.
[40] Statistical Yearbook of Ukraine for 1998, Tekhnika, Kyiv, 1999.
[41] Porfiriev, Scientist, Geologist, Redagogue, Scient. Publ. Inst. Geol. Sc., Kyiv, 2000.
[42] M.I. Gebki, Science of Oil, Gostoptechizdat, Moscow, 1932.
[43] I.O. Brod, V.A. Klubov, Bull. Moscow Univ., No. 10 (1948) 21.
[44] N.B. Vassoyevich, Ibid., No. 5 (1975) 3.
[45] A.A. Trofimchuk, V.I. Molchanov, V.V. Paraev, Geology and Geophysics Sib. Branch, Russian Acad. Sc., Iss. 39, No. 5 (1998) 673.

[46] N.B. Vassoyevich, Proc. VNIGRI, Iss. 132 (1959) 131.
[47] I.I. Chebanenko, Ged. J., No. 1 (1991) 120.
[48] B.S. Sokolov, Bull. Rus. Acad. Sc., Vol. 70, No. 7 (2000) 589.
[49] Yu.N. Yefremov, Ibid., No. 4 (2000) 314.
[50] M.S. Arabadzhi and V.S. Melnichuk, Secrets of Earth's Depths, Nedra, Moscow, 1983.
[51] I.D. Polyakova, Lithology and Chemistry of Oil-Gas-Bearing Thicknesses of Liberian Platform, Nauka, Moscow, 1981.
[52] S.G. Neruchev, E.A. Rogozina. Lithology and Geochemistry of Oil-Gas-Bearing Thicknesses of Siberian Platform, Nauka, Moscow, 1981.
[53] Jounal of Real Stories, No. 11 (2002) 59.
[54] L.F. Kozin, S.V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv, 2002.
[55] F.T. Yanshina, A.L. Yanschim, Bull. Rus. Acad. Sc., Vol. 7, No. 3 (2000) 243.
[56] M.I. Budyko, A.B. Ronov, A.L. Yanshin, The Atmosphere History, Gidrometeoizdat, Leningrad, 1985.
[57] Geoecology, No. 5 (2000).
[58] I.S. Kulikov, Isotopes and elements properties: Reference Book, Metallurgia, Moscow, 1990.
[59] I. Chebanenko, V. Krayushkin, M. Yevdoshchuk, Bull. NAS of Ukraine, No. 3 (2001) 41.
[60] G.N. Petrov, N.A. Yasmanov, Ibid., No. 2 (1998) 132.
[61] P.L. Kapitsa, Science and Mankind. Znanie, Moscow, 1976.
[62] V.L. Makarov, Bull. Rus. Acad. Sc., No. 5 (2003) 450.
[63] N.L. Dobretsov, A.E. Kontorovich and V.V. Kuleshov, Bull. Rus. Acad. Sc., Vol. 71, No. 10 (2001) 867.
[64] M. Pavlovsky, Golos Ukrainy (Voice of Ukraine), March 9, No. 43 (1999).
[65] D.E. Davydynts, Problems of Statistics, No. 8 (2002) 73.
[66] Minor Medical Encyclopaedia, Vol. 2, Sovetskaya Entsiklopedia, Moscow, 1989.
[67] M. Podzharsky, Bull. NAS of Ukraine, No. 11 (2002) 2.
[68] K.Ya. Kondratyev, K.S. Losev, Bull. Acad. Sc., Vol. 72, No. 7 (2002) 592.

Chapter 4

Nuclear Energetics

1. Nuclear electroenergetics

Uranium was discovered by M. Klatron (Germany) in 1789 in uranium-organic ore (resin) and isolated in a form of UO_2. Uranium was obtained in a form of metal in 1841. Uranium radioactivity was discovered by Beckerel in 1986. In 1938, O. Gun, F. Strassmann. and L. Meitner (Germany) as well as Frederick Jolio-Curie (France) splitted uranium-235 nucleus. G. N. Flerov and K. A. Petrzhak (USSR) soon established (1940) that the disintegration of uranium-235 nuclei by neutrons proceeds as avalanche (spontaneously, without external effect) and is accompanied by the mass defect in accordance with A. Einstein and release of about 75.3 mill. kJ for each gram of disintegrating nuclei. Such quantity of energy is released in explosion of 18t of trinitrotoluene. These discoveries are considered the most important achievements of the 20th century. They started intensive development of nuclear physics, chemistry, and then energetics. There appeared an idea to use the avalanche development of uranium-235 nuclei disintegration with release of huge amounts of energy to create a nuclear bomb. Realization of the idea of the nuclear bomb was preceded by the study of kinetics of disintegration reaction of certain uranium ($^{235}_{92}U$) nuclei in atomic boilers with neutron moderators of nuclear reactions (graphite, heavy water, etc.). These atomic boilers were the prototypes of nuclear power plants (NPP). Solution of the problem of nuclear bomb resulted in creation of nuclear industry. In the USA 125 thousand people were engaged in the development of nuclear bomb project. About 357 thou. people took part in solution of the nuclear bomb problem in the USSR where they tried to remove the temporal factor of lag.

The first nuclear bomb in the USA was tested in the Nevada Desert of the State of New Mexico on July 16, 1945. The nuclear bombs were exploded for military purposes over Japan cities Hiroshima and Nagasaki on August 6 and 9, 1945. The explosions of nuclear bombs and hundreds of thousand victims of peaceful population accelerated Japan capitulation (September 2, 1945) and led to the completion of the World War II.

The beginning of nuclear energetics in the USSR is referred to 1943, the year of foundation of Laboratory N 2 — the basis for creation of I. V. Kurchatov Institute of Atomic Energy, the most powerful scientific center of the world significance.

The first nuclear bomb in the USSR was tested on the proving ground near Semipalatinsk in Kazakhstan on August 29, 1949. That was the reference point of the opposition of two great powers — the USA and the USSR. After termination of the World War II 128 thousand nuclear warheads were produced [1]: 70 thousand in the USA and 50 thousand in the USSR. Such quantity of nuclear charges is sufficient for the 10-fold annihilation of biologic life on the Earth. Joint treaty efforts of the USA and the USSR have led to the decrease of the nuclear warheads quantity from 69 478 in 1986 to 31 535 in 2000. But the present nuclear store still remains huge, corresponding to 5000 Mt. However, the opposition has not come to the end. Nowadays only Russia and USA keep on a war footing about 46 000 nuclear warheads capable to take lives of hundreds of million people.

Accumulation of enormous reserves of nuclear charges both maintains the destructive process for the mankind and freezes huge amounts of nuclear power resources. That is why that side by side with nuclear arming there arised the process of nuclear power use for peace purposes — the construction of nuclear power plants. Beginning from the 60's and up to the middle 80's nuclear energetics which became a high-tech branch of science and technology took passed ahead other technologies of high-power energy production both in the USSR and other developed countries of the world. During 25 years the nuclear energetics stood out as an independent branch of nuclear industry — nuclear power industry being developed in 43 countries of the world. An analysis of potentialities for generation of great controlled amounts of energy proves that there is no alternative of energetics [2–6], since each uranium $^{235}_{92}U$ atom nucleus fission is followed by release of 2.5 neutrons possessing high average energy equal to 2 MeV. The fission of 1 kg of uranium-235 is followed by the release of $2.5{\cdot}10^7$ kWh ($9{\cdot}10^{13}$ J) of energy which is equivalent to energy released under combustion of $2.5–10^3$ of hard coal with ash content 10–12 %. The fission of $^{235}_{92}U$ atom nuclei proceeding as follows:

$$^{235}_{92}\mathrm{U}+{}^{1}_{0}\mathrm{n}\left|\begin{array}{l} \rightarrow {}^{90}_{38}\mathrm{Sr} + {}^{144}_{54}\mathrm{Xe} + 2{}^{1}_{0}\mathrm{n}; \\ \rightarrow {}^{93}_{36}\mathrm{Kr} + {}^{140}_{56}\mathrm{Ba} + 3{}^{1}_{0}\mathrm{n}; \\ \rightarrow {}^{95}_{42}\mathrm{Mo} + {}^{139}_{57}\mathrm{La} + 2{}^{1}_{0}\mathrm{n}; \end{array}\right| \qquad (2)$$

is accompanied by formation of nuclei «fragments» — isotopes with rigid γ- and soft β- and α-radiations. Energy of neurons, as well as γ-, β- and α-radiations of fission fragments is 6 % of full energy released under the fission of uranium nuclei. For the proceeding of the self-sustaining reaction, it is necessary that at least one of the formed 2.5 neutrons caused the fission of $^{235}_{92}U$ nucleus. Thus uranium-235 content in heat-releasing, element must be enough to maintain the continuous nuclear reaction. In this connection it is uranium enriched by 3–4.4 % of $^{235}_{92}U$ which is used as fuel in the power thermal (fast) reactors of NPP. Natural uranium contains 0.718–0.72 % of $^{235}_{92}U$ which half-period ($T_{1/2}$) is $T_{1/2} = 0.7 \cdot 10^9$ years; content of isotope uranium-234 is 0.0056 % ($T_{1/2}$ = 0,252 mill. yr). Critical mass of the layer (sphere) with 90 % enrichment with uranium-235 equals 50 kg. Critical mass of the highly pure uranium-235 is 242 g [7]. Content of $^{235}_{92}U$ in natural uranium is 99.274 % with $T_{1/2} = 4 \cdot 47 \cdot 10^9$ years. Thus the content of uranium-238 in natural ores exceeds 137.88 times the content of uranium-235. The process of enrichment of natural uranium with nuclide $^{235}_{92}U$ is rather power-intensive. At the initial stage of development of nuclear production they used the diffusion methods for uranium enrichment which was then changed by more efficient methods of centrifugal separation of isotopes which lowered the cost of uranium fuel [8]. The enterprises of *Sredmash* mastered the production of hundreds of thousand centrifuges being unique even now. Today they develop a new generation of centrifuges which have no analogues in the world as to separating ability [8].

To sustain the nuclear chain reaction it is necessary to moderate the so-called fast neutrons, formed under fission by the equation (4.1) and possessing high average energy (2MeV), before they broach the nuclei of $^{235}_{92}U$ atoms evoking no nuclear reaction. They will be absorbed by the nuclei of $^{235}_{92}U$ atoms, by regulating rods-inhibitors (cadmium and hafnium rods) and reactor casing which will lead to the «damping» of fission process. Fast neutrons being moderated one can escape the arrest of nuclear chain reaction of $^{235}_{92}U$. Ordinary water (H_2O), graphite, and beryllium oxide. and heavy water (D_2O) are used as neutron moderators. The latter is the best moderator but proceeding from economic and technical reasons they use natural water and graphite. Thus the nuclear reactors using natural water for neutron moderation are called light-water ones.

Primary optimism under development of nuclear energetics as to uranium reserves and long-term solution of energy problem was changed by pessimism since thermal nuclear reactors at NPP work on uranium nuclide — uranium-235 ($^{235}_{92}U$), which reserves in nature are limited. Hence it follows that allowing for the future prospect such nuclear electroenergetics is not promising. Natural uranium-238 ($^{235}_{92}U$) in heat-releasing elements of NPP reactors under irradiation with thermal (slow) neutrons is not subject to fission reaction and practically remains a ballast, since only its inconsiderable part turns into plutonium $^{238}_{94}Pu$. But further investigations have shown that uranium $^{235}_{92}U$ undergoes nuclear reactions of fission under its irradiation by fast neutrons and first turns into neptunium $^{233}_{93}Np$, which then after the exposure during a month ($T_{1/2}$ = 2.34 days), turns into plutonium $^{233}_{94}Pu$ — the efficient nuclear fuel. This process can be presented as follows:

$$^{238}_{92}U + ^{1}_{0}n \rightarrow ^{239}_{92}U + \beta + Q \rightarrow ^{239}_{93}Np + \beta \rightarrow ^{239}_{94}Pu + \beta. \qquad (3)$$

The reactors where synthesis of plutonium nuclei was performed were called reactors breeders. As to nuclear properties $^{233}_{94}Pu$ ($T_{1/2}$ = 24.1 thou. years, critical mass 10 kg) is like to $^{235}_{92}U$ (see above about nuclear properties of uranium-235) since it is subject to fission when irradiated by slow neutrons. When using uranium-plutonium nuclear fuel there appears or possibility of nuclear fuel reproduction. The reaction (4.2) is of the greatest importance for mankind. Thus uranium-plutonium nuclear cycle well-developed by the nuclear military-industrial complex can become the basis for the nuclear energetics of the future. The first nuclear fast reactors-multipliers were developed and put in operation in the USSR (NPP of 350 MW in the 70's and Beloyarskaya NPP of 350 MW in the vicinity of Yekaterinburg, Russia). Fast nuclear reactors also function now in other countries, in particular, there are two analogs in France — *Fenix* and *Super-Fenix* as well as in Japan. In 1965 a new fast industrial reactor was put in operation in the USA. But there was an accident in the process of operation caused by errors in the reactor design. The NPP was dismounted and all works in the field of NPP with fast reactors were stopped. A failure in starting the NPP with fast reactor with liquid-metal cooling put on guard some other countries engaged in nuclear energetics. It would be noticed that in the USSR there also occurred some failures under starting the fast reactor BN-350, e.g., leaks in steam generators. But the use of three-circuit scheme, specific for nuclear reactors with liquid-metal carriers (in this case — liquid sodium) permitted to cope with the leak in steam generators. In the future the binary alloy of highly pure lead and bismuth with composition ensuring melting temperature 165–180 °C was used as heat-carrying agent in nuclear reactor. Under the accident such liquid-metal carrier «congealed» and did not interact with water.

More powerful fast reactors were designed in Russia: the reactors BN-800 and BN-1600. Plutonium with depleted uranium which great amounts have been accumulated, were to be used as nuclear fuel in the above reactors. That was the so-called uranium-plutonium cycle. About 20 % of reserves of depleted uranium in the world have been accumulated in Russia [9]. In 2000 all the NPP of the world produced about 1140t of plutonium. This amount is 4.56 times higher than that of plutonium equal to 250t which was obtained at the peak of «cold» war for production of nuclear weapons.

Power (thermal or electric) generation in fast reactors starts from the conversion of nuclear fuel by the scheme (4.2): natural uranium $^{235}_{92}U$ is irradiated and converted into neptunium $^{239}_{93}Np$ with half-time $T_{1/2}$ = 2.35 days. For full conversion of $^{238}_{93}Np$ into $^{239}_{94}Pu$ the irradiated fuel elements with $^{235}_{92}U$ are extracted from nuclear reactors and kept during 10 half-periods (about a month). Then the content of fuel elements is subject to chemical dissolution in the corresponding reagents (mainly in nitric acid) and to extractional (5–30 % tributylphosphate in inert solvent) or to ion-exchange separation. Under these conditions plutonium ${}^{239}_{94}Pu$, primary uranium ${}^{235}_{92}U$ are isolated in required chemical forms and the formed fragment elements (radioactive isotopes) are separated. Under extractional separation of plutonium and uranium (PUREX-process) they achieve high degree of finite products purification. Plutonium ${}^{239}_{94}Pu$ is used for production of nuclear charges, while it could be used as nuclear fuel (see, below). Uranium isotopes ${}^{238}_{92}U$ and ${}^{236}_{92}U$ oxides are blended for obtaining the preset composition of nuclear fuel used for production of fuel elements. At modern nuclear fuel plants all the processes of separation of uranium ${}^{238}_{92}U$ and ${}^{235}_{92}U$ and plutonium ${}^{239}_{94}Pu$ isotopes compounds are mechanized and automated. Under the successive use of ${}^{238}_{92}U$ and ${}^{239}_{94}Pu$ as nuclear fuel one can observe a 1000-fold increase of the nuclear cycle efficiency. Further development of nuclear power industry has shown that energy resources for nuclear plants with fast reactors using uranium-239 as nuclear fuel are practically inexhaustible (distribution of uranium-235 in the Earth crust is comparable with molybdenum and boron).

How many centuries will nuclear fuel last for the world NPP? Uranium distribution in the Earth crust is $2.9 \cdot 10^{-4}$ %. If uranium-235 resources are about 10^7 t, then those of uranium-238 in the Earth crust exceed them more than 2 orders ($> 2–5 \cdot 10^9$t). But when determining real uranium resources one proceeds from economic component of its extraction from the ore, including gravitational enrichment, dissolution with sulfuric acid or nitric acid and its extraction by tributylphosphate in hydrocarbons with further reextractional. As a result concentrated uranium solutions are obtained, uranium oxides UO_2, U_3O_8 being precipitated from them. Uranium oxides are used for the following process stage using fluoride method of separation of isotopes uranium-235 and uranium-238 and production of fuel elements on the basis of uranium-235 of fuel elements on the basis of the systems uranium-235 + uranium-238 for fast reactor NPP.

Table 14 includes proven uranium reserves (based on geological investigations and supposed (probable, based on incomplete geological data) reserves of uranium mined from rich and poor ores of some countries of the world regions. In the former case expenditures for uranium production are below 80 dol./kg, in the latter — 80–150 dol./kg [10]. It is seen from Table 14 that the first place in simple uranium production (expenditures < 80 dol./kg of uranium) is occupied by the Pacific OECD countries — 615000t, the second place belongs to former Soviet Union — 564500 t, the third place — Sub-Saharan Africa — 453600 t, and the fourth place to North America but by the sum of poor and rich ores.

Total reserves of rich uranium deposits in the world are 2 315 300 t, and accounting for reserves of more expensive uranium (80–130 dol./kg) total reserves are 3 200 100 t.

Table 14

Proved uranium resources (in tons) in rich ores (cost of uranium extraction about 80 dol./kg), and in poor ores (80-130 dol.kg) [10]

World region	Costs < 80 dol./kg	Costs < 80-130 dol./kg	TOTAL
North America	258000	402000	660000
Latin America and Caribbean	608000	702000	1310000
Western Europe	600000	724000	1324000
Central and Eastern Europe	n.a.*	n.a.	n.a.
Former Soviet Union	n.a.	n.a.	n.a.
Middle East and North Africa	15000	310000	325000
Sub-Saharan Africa	38000	146000	526000
Pacific Asia	24000	26000	50000
South Asia	319000	4000	323000
Central Asia	n.a.	n.a.	n.a.
Pacific OECD	300000	40000	340000
Total	2162000	2354000	4156000

n.a.* — not available

Besides these reserves, there are 5 100 400 t of uranium in the world, which mining costs 130–260 dol./kg; and 12 127 000 t of uranium which mining is evaluated as more than 260 dol./kg. Huge uranium reserves occur in waters of seas and oceans. Uranium being obtained from sea water with extraction degree of 20%, resources of marine uranium will be $n \cdot 10^9$ t.

Thorium, which can be turned into fissing uranium-233 by the reaction

$$^{232}_{90}\mathrm{Th} + \mathrm{n} \rightarrow {}^{233}_{90}\mathrm{Th} \rightarrow \beta \rightarrow {}^{233}_{91}\mathrm{Pa} \rightarrow {}^{233}_{92}\mathrm{U}, \tag{4}$$

also can be used as nuclear fuel. Thus, the isotope torium-232 by the reaction (4), like uranium-238 isotope turning into plutonium-239, turns into the isotope U-233. Nuclear properties of isotope uranium-233 are analogous to properties of the isotope uranium-235.

Besides, thorium is thrice more distributed as compared to uranium. Its content in the Earth crust makes 0.0012 %. Monazite sands (Ce, La, Th…) PO_4 where thorium content reaches 10–12 mass % are the main source of thorium. Besides in minerals: thorite $ThSiO_4$ about 77 % of ThO_2 and in thorianite (Th, U)O_2 — about 45–99 % of ThO_2. Considerable amounts of thorium occur in bauxites; it is concentrated in «red slames» under their processing [11].

Thorium resources in some regions of the world are presented in Table 15 [10]. As is evident, Western Europe occupies the first place as to thorium reserves (1 324 000 t), the second place belongs to Latin America and Caribbean

Table 15

Proven thorium resources in different regions of the world (in tons) [10]

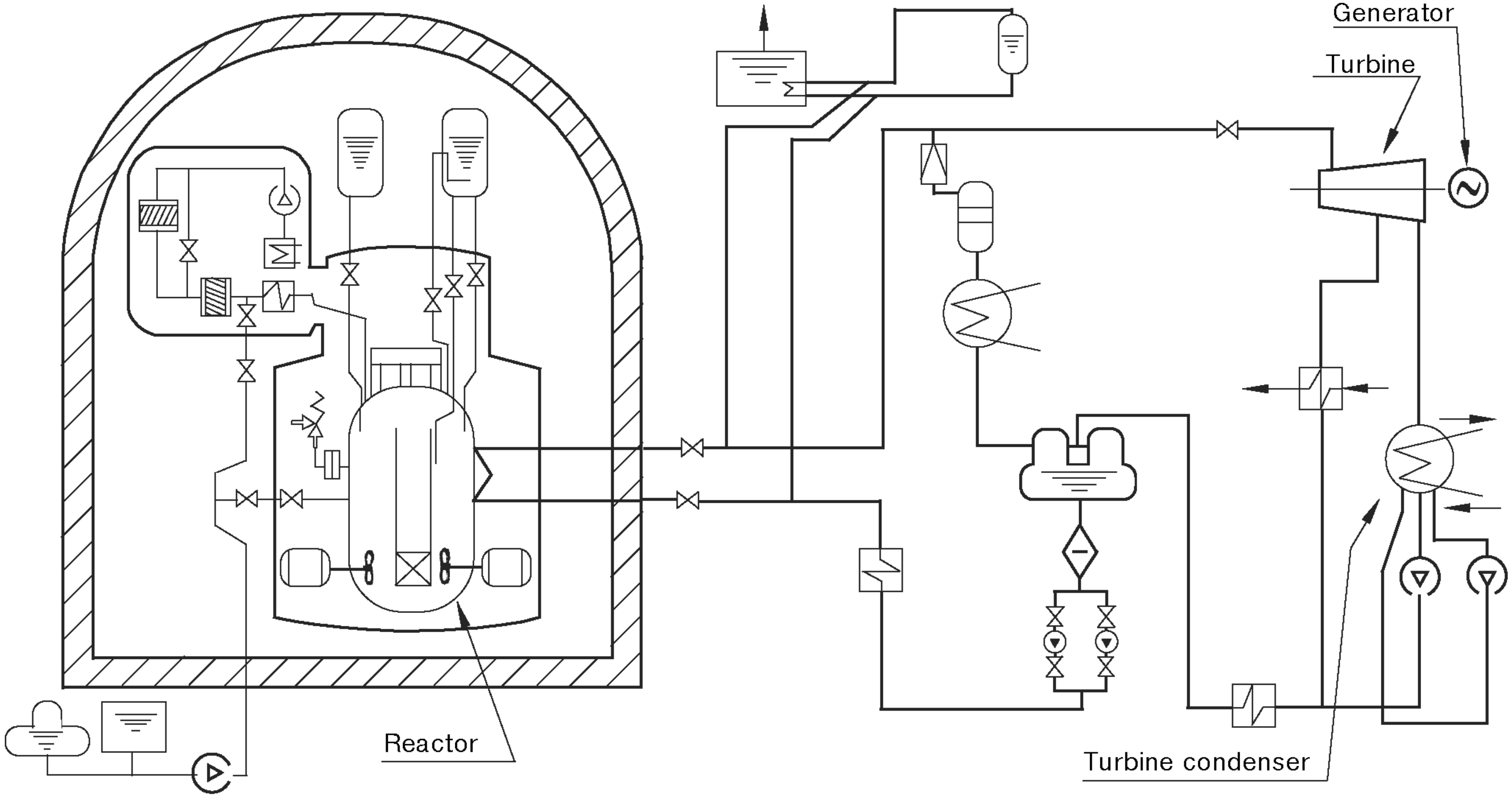
World Region	Expenditures < 80 dol./kg	Expenditures 80–130 dol./kg	Total
North America	420 000	251 000	671 000
Latin America and Caribbean	136 400	5600	142 000
Western Europe	37 300	53 500	90 800
Central and Eastern Europe	14 000	25 800	39 800
Former Soviet Union	564 300	210 200	774 500
Middle East and North Africa	21 000	8400	29 400
Sub-Saharan Africa	453 600	96 000	549 600
Pacific Asia	0	16 800	16 800
South Asia	5000	52 000	57 000
Central Asia	49 300	65 300	114 600
Pacific OECD	615 000	99 600	714 600
Total	2 315 900	884 200	3 200 100

(131 000 t), the Third one to North America (660 000 t). Total reserves of thorium in the world are 4 516 000 t.

In the opinion of most outstanding nuclear scientist the use of closed nuclear-fuel cycles will save the nuclear fuel for NPP for «thousands of years» [12].

Introduction of natural uranium-238 as fuel for fast nuclear reactions as well as the use of plutonium (weapon plutonium or that accumulated by nuclear reactors) as secondary fuel creates a precedent of practically inexhaustible power resource for the future centuries of human life on our planet. Thus the nuclear energetics of the future will use in its technological processes the initial non-deficient uranium-238, convert it into plutonium-239 and use the latter as nuclear fuel, i.e. it can form the closed nuclear fuel cycle (CNFC). Natural uranium, containing uranium isotopes 234, 235 and 238, will be used in nuclear reactions at NPP with fast reactors. Natural uranium will be used as nuclear fuel without preliminary enrichment and without isolation of plutonium. After 95–96 % burning-out of nuclear fuel the radioactive waste will be discharged by automata — robots, and stored in eternal burials (see, below). It follows from above mentioned that nuclear thermal-neutron electroenergetics has no long-term prospects.

Nuclear scientists of the leading countries in the world comprehend that the mankind provision with energy is the global problem which solution is possible only with availability of the reactor of the third millennium. That is why the «nuclear states» develop national and, which is characteristic of the present



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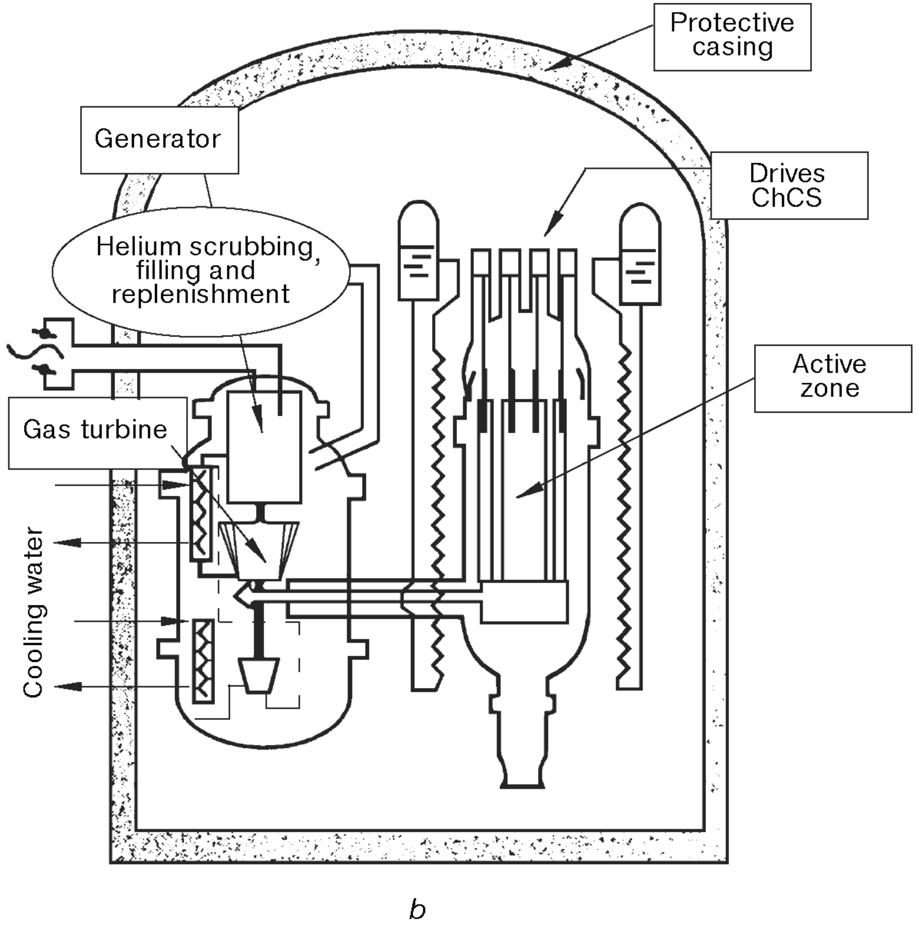


Fig. 18. Schematic thermal diagram of nuclear power unit of NPP with steam-turbine cycle VPBER-600 (*a*) and nuclear power unit NPP with gas-turbine cycle GT-MGR (*b*) [3]

world, international programs of creation of nuclear reactor of the 20th century. Thus, the USA, Japan and Russia develop «European» water-moderated reactor, Russia and the USA — high-temperature helium reactor (HTHR) with the use of high-temperature helium heat carrier with gas turbine. Russia and Japan improve fast nuclear reactors. The burning-off variants in heat-releasing elements (fuel elements) of not only uranium-238, but also thorium-232, which reserves will last during all the third millennium.

Though nuclear power industry is a young branch of industry, one would distinguish evolutionary and revolutionary projects of new NPP [13]. Evolutionary projects concern further improvement of NPP in operation, increasing their resource potentialities, use of new equipment and raising reliability of safety systems. New designs preventing from leakage of nuclear fission products in the environment are introduced under the construction of new NPP. The project VPBER-600 based on ideology of integral nuclear reactor is considered a revolutionary design. As is seen from Fig. 18, *a*, the first loop of integral, reactor is closed in a separate casing. Such a decision concerning the data of the work [13] permits decreasing the neutrons flow to the casing during the operation time to, approximately, 10^{17} n/cm^2. Availability of the reactor safety casing excludes a possibility of dewatering of the active zone, and consequently prevents from the accident.

By the work [13] the project of high-temperature reactor with helium heat carrying medium (HTHR) developed at the Design office of machine-building (DOMB, Novy Novgorod city) jointly with *General Atomics* belongs to revolutionary ones. A schematic thermal diagram of nuclear power unit of NPP with gas-turbine cycle GT-MGR is given in Fig. 18, *b*. A single-loop reactor turbogenerator set with energy generation no less than 47 % is provided in the project; both uranium and plutonium-239, including weapon plutonium, may be used in this nuclear reactor. The use of plutonium in nuclear energetics is the most important problem, being of epochal significance. Since the time of formation of nuclear energetics Russia and most leading nuclear countries (France, Japan, England, Germany) developed a conception of closed nuclear fuel cycle (CNFC). The first CNFC in the world was brought to a commercial level in Russia 15 years ago [9]. With that end in view a plant for processing the spent nuclear fuel with productivity of 400 t/year (plant RT-1 at integral plant *Mayak*) was put in operation in 1971. Uranium. plutonium and neptunium compounds and «fragmental» radioactive elements are extracted using the developed technology of fuel processing with obtaining certain fractions. Secondary uranium, after correcting uranium-235 content in it, is directed again for production of fuel elements. As is seen from Fig. 19, plutonium is also used for production of heat-releasing elements in CNFC.

France, Japan, England, Germany, Belgium have accumulated 10–15 years experience of design, production and operation of CNFC with the use of

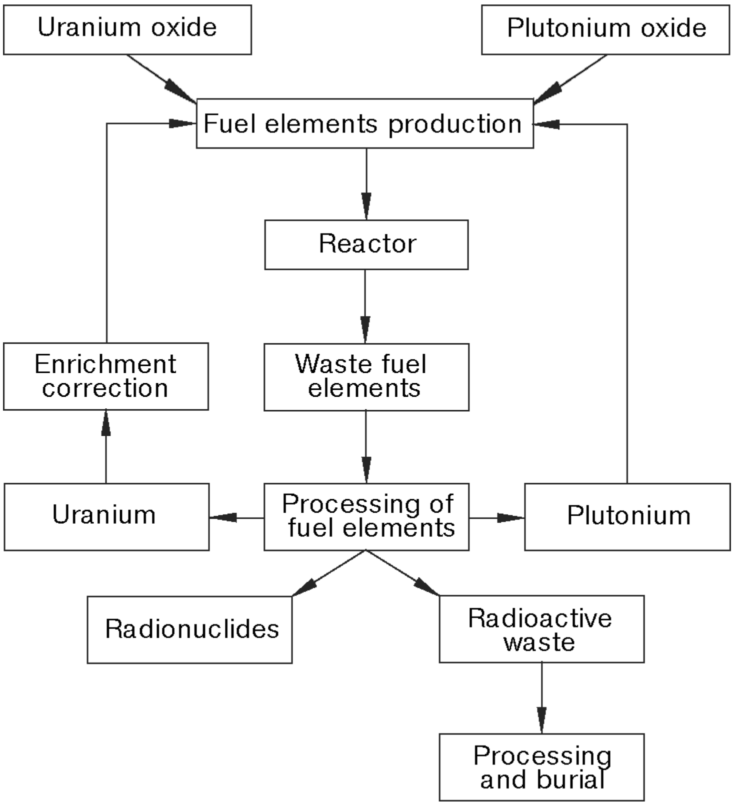


Fig. 19. Scheme of closed nuclear fuel cycle

uranium-plutonium fuel in water moderated reactors. Uranium-plutonium fuel is used in fast reactors in France and Japan. Reactors in France, Germany, Belgium and Switzerland (n = 33) work on 30 % of such fuel; 22 more reactors will soon also partially work on such fuel. The amount of plutonium fuel in the world grows steadily. During the «cold war» the extracted plutonium was used for production of nuclear weapons and this plutonium became the bomb material. After disintegration of the USSR plutonium extracted from spent fuel began accumulating. Its reserves exceed 30 t now and continue increasing. The reduction of some kinds of nuclear weapons raised reserves of «weapon plutonium» which have reached 50 t and from «half-official information» the amount of surplus plutonium reaches 100–200 t only in Russia [6]. These reserves contain a considerable share of «weapon plutonium» from Ukraine which has given up nuclear charges of strategic rockets to Russia. The «weapon plutonium» is more valuable than power plutonium extracted from spent fuel. The power plutonium contains nuclides of $^{239}_{94}Pu$ and $^{240}_{94}Pu$, the amount of plutonium-239 being 35–36 %, plutonium-240 about 20–40 %. Plutonium-240 has the more cross-section for neutrons capture and a half-life (with release of α-radiation) $6.54 \cdot 10^3$ years. Total content of plutonium isotopes in power material reaches 55–60 %. The «weapon plutonium», containing 93.5 % of plutonium-233, simply turns into oxide form used for production of fuel elements. Though the weapon plutonium is 4 times more expensive than 80-per-cent uranium-235, the former is a rather promising fuel for nuclear energetics. Nowadays, even the countries, possessing no «weapon fuel», are interested in the problem of this fuel use. These are Japan, Switzerland and Canada. They conduct intensive works on the use of plutonium fuel in operating light-water reactors WMER-1000 where about 30 % of uranium fuel may be changed by plutonium [9]. The case is not so simple with plutonium fuel, its storage in particular. Storage of 1 kg of plutonium costs 1.5 thousand US dollars a year. Modern storehouse for plutonium which costs 300 millions US dol. is built in Russia. It is also difficult to store plutonium charges dismounted of war-heads. Plutonium-gallium alloy allowing to fix plutonium delta-phase is used to make nuclear charges. The above elements form a congruently melting compound $PuGa_2$ (T_{melt} = 1570 K), as well as a whole series of congruently melting compounds (Pu_2Ga, Pu_5Ga_3, PuGa, Pu_2G_7, $PuGa_6$ etc.).

Alloying in the system Pu-Ga is accompanied by exothermal effect. Thus, formation enthalpies ΔH_{form} of intermetallides Pu_3Ga, $PuGa_2$ and $PuGa_6$, respectively, equal — 158.2; –180.0 and –238.0 kJ/mol [14, 15]. For plutonium using as nuclear fuel it would be subject to deep treatment for even traces of gallium, since the latter possesses high reactivity not only in respect of plutonium but also of many other metals.

Separation of plutonium-gallium alloy into initial components, possessing close physico-chemical properties is a difficult problem. In our opinion, having the experience of separation of multicomponent alloys with obtaining highly pure metals, one can cope with this problem, either using other new methods of separation, or even other metals-partners, which can be removed with the less labour expenditures.

A comparison of melting temperatures of plutonium and gallium, given in Table 16 (913 and 302 · 90 K, respectively) shows that the plutonium-gallium alloy can be separated crystallographically, e. g., by fractional crystallization, and on the final stage — by the zone melting. The latter process is highly efficient after the removal of impurity traces (here, low contents of gallium). It follows from a comparison of boiling temperatures of plutonium and gallium (3567 and 2476 K, respectively) that the plutonium-gallium alloy can be separated by the method of vacuum rectification. Plutonium separation from this alloy by water solution electrolysis at 30–40 °C (see, values of standard potentials given in Table 16) as well as in the form of the metal phase under electrolysis of Pu-Ga system salt melts (see, physico-chemical data of salt melts and Pu-Ga system alloys [14, 15] is rather efficient.

As to the use of other metals-partners for production of the required plutonium alloys, the delta-phase may be successfully fixed by means of zinc or aluminium. Plutonium-zinc alloys may be separated both using the methods of crys-

Table 16

Standard electrode potential, melting and boiling temperatures of zinc, plutonium and metals of III b subgroup of D.I. Mendeleev's periodical system

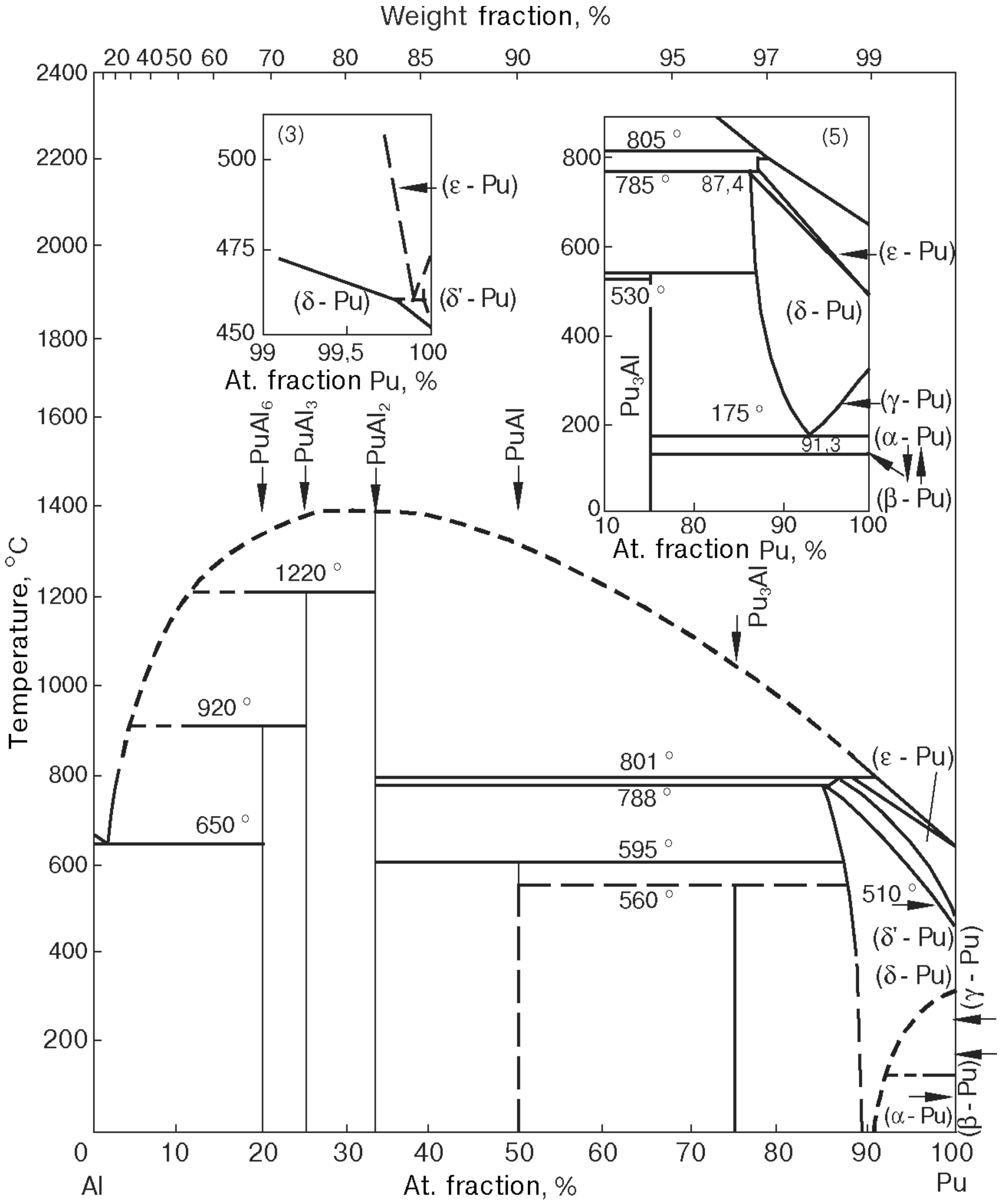
Metal	E°, V	$T_{\text{melt.}}$, K	$T_{\text{boil.}}$, K	Metal	E°, V	$T_{\text{melt.}}$, K	$T_{\text{boil.}}$, K
Pu	–2.031	913	3567	Mg	–2.363	922	1363
Al	–1.662	933 · 61	2767	Zn	–0,763	692 · 73	1180
Ga	–0.529	302 · 30	2476	Cd	–0,4029	534 · 18	1040
In	–0.343	429 · 76	2232	Pb	–0,126	600 · 60	2021
Tl	–0.3363	577	1746	Cu	+0.337	1357.6	2836

tallophysics, and rectification and by electrolysis. As is seen from Table 16 the difference between boiling temperatures of plutonium and zinc is $\Delta T = 2387$ K, which evidences for high efficiency of separation of plutonium-zinc alloys not only by rectification but also by a simpler method — distillation. That may be also done by electrolysis from melted salts at relatively low temperatures (800–1000 K). State diagrams of the binary systems Pu-Al, Pu-Ga and Pu-Zn are shown in Fig. 16 [16–18]. As is evident, a stable delta-phase, analogous to that formed in the system Pu-Ga, is also formed in the given binary systems Pu-Al and Pu-Zn [19–21].

Formation of congruently melting compounds of $PuAl_2$ ($T_{\text{melt.}} = 1813$ K), $PuGa_2$ (1537 K), $PuZn_2$ (1208), $Pu_{13}Zn_{58}$ (1201 K) and a broad range of incongruently melting compounds $PuAl_3$, PuAl, Pu_3Al, $PuGa_3$. PiGa, Pu_2Ga_3, Pu_3Ga, Pu_3Zn_{22}, Pu_2Zn_{17} etc., is characteristic of the systems Pu-Al, Pu-Fa and Pu-Zn, polymorphous transformation is characteristic of most of them.

The systems Pu-Al and Pu-Zn peculiarity is that their secondary components (Al, Zn), as compared to gallium, have a lower commercial cost and are more adaptable. Aluminium and zinc are several hundreds of times less expensive than gallium. Thus the use of aluminium and zinc as a delta-phase stabilizer is more profitable compared with gallium. The boiling point of aluminium ($T_{\text{boil.}} = 2767$ K) is higher than that of gallium ($T_{\text{boil.}} = 2476$ K) which is of important target value. Besides, aluminium is plutonium corrosion inhibitor and can protect the latter from intercrystalline corrosion. Highly-pure plutonium can be transferred to oxide form for production of fuel elements.

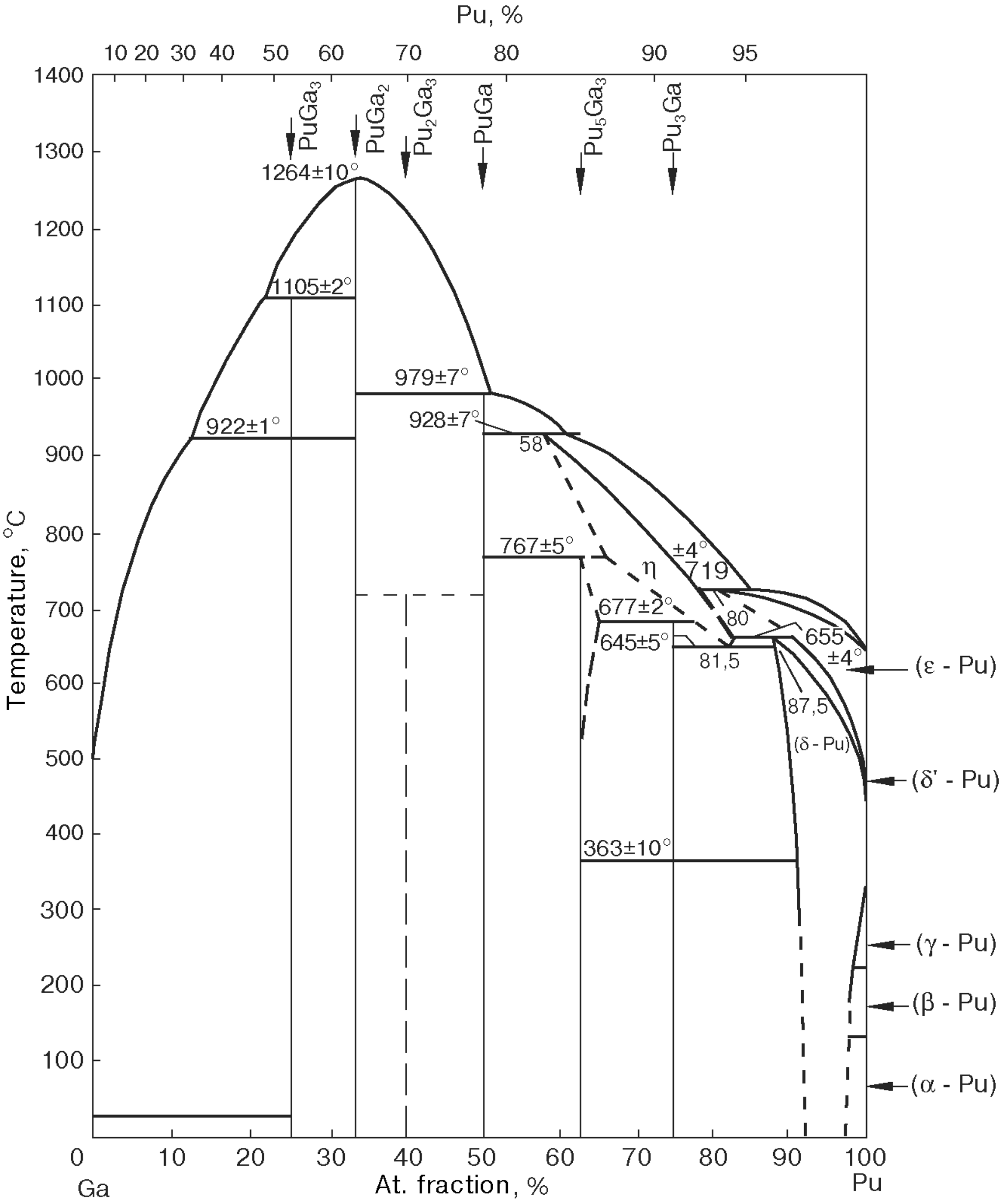
It would be noticed that not only economic but also ecological problems are solved the nuclear fuel based on plutonium-239 and uranium-238 being burnt in the fast reactors. Thus only about 1 % of nuclear fuel energy potential being realized in the thermal reactors, the especially high extent of fuel combustion (almost 90 %) is achieved in fast reactors. In the latter case the spent nuclear fuel may be buried without its preliminary processing. The amount of



a

spent fuel, when using plutonium fuel, is 5–6 times less compared with the spent fuel in thermal reactors. The design of fast reactor which is built from structural materials, meeting the most strict safety requirements, excludes completely a possibility of the active zone melting and creation of emergency situations.

In a number of projects of NPP improvement they consider a hydride scheme with available subcritical mass of active (nuclear) materials and external source of neutrons which helps to produce a flow of neutrons evoking a nuclear reaction. The external flow of neutrons can be a combination of fast



b

and slow reactors. Unfortunately, Ukraine which is one of the leading nuclear states of the world with rich intellectual legacy takes no part in the above projects.

Nuclear technologies of the 21st century would be based on the following decisions and their fulfillment:

- change of thermal nuclear reactors by reactors-breeders with closed nuclear fuel cycle;
- choice of optimal design and construction of new fast reactors-breeders providing nuclear fuel reproduction in a closed nuclear fuel cycle;

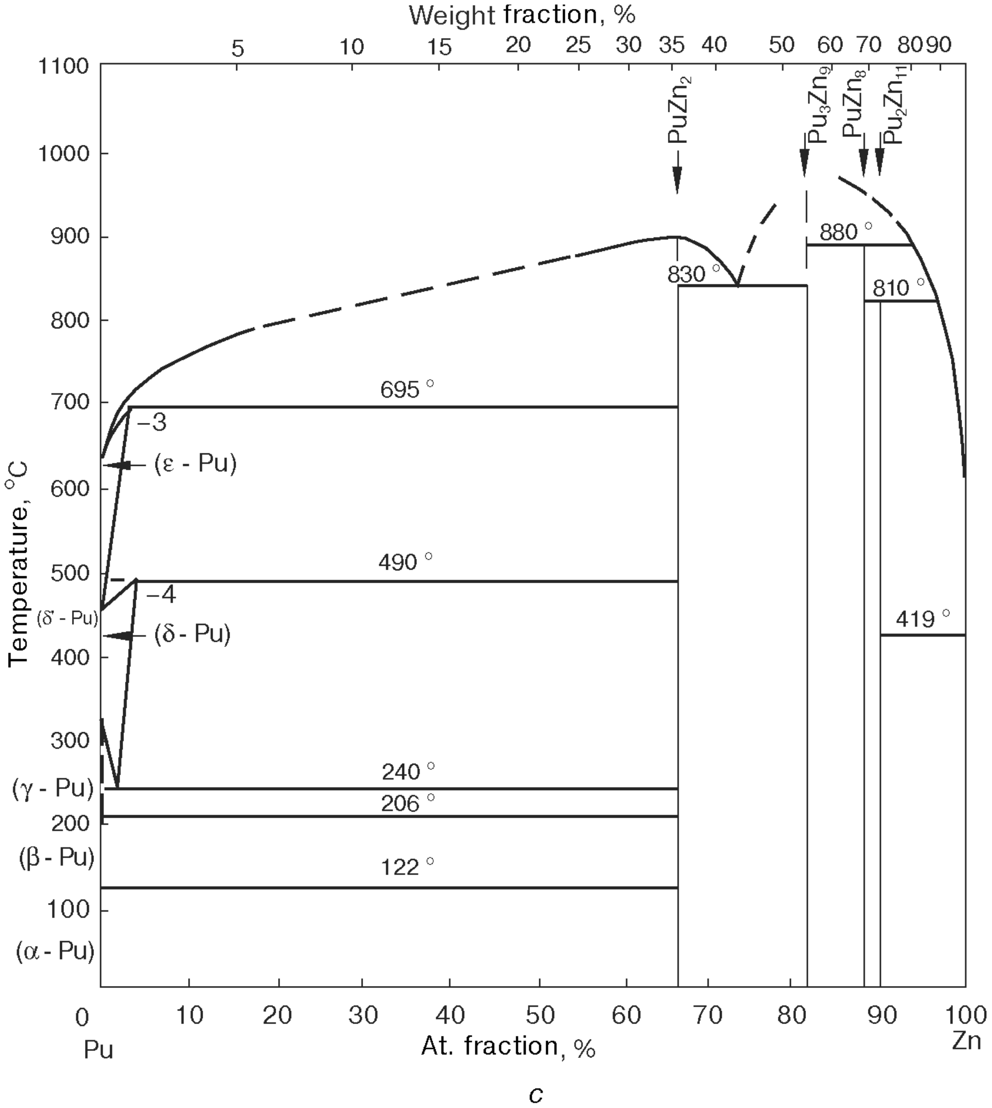
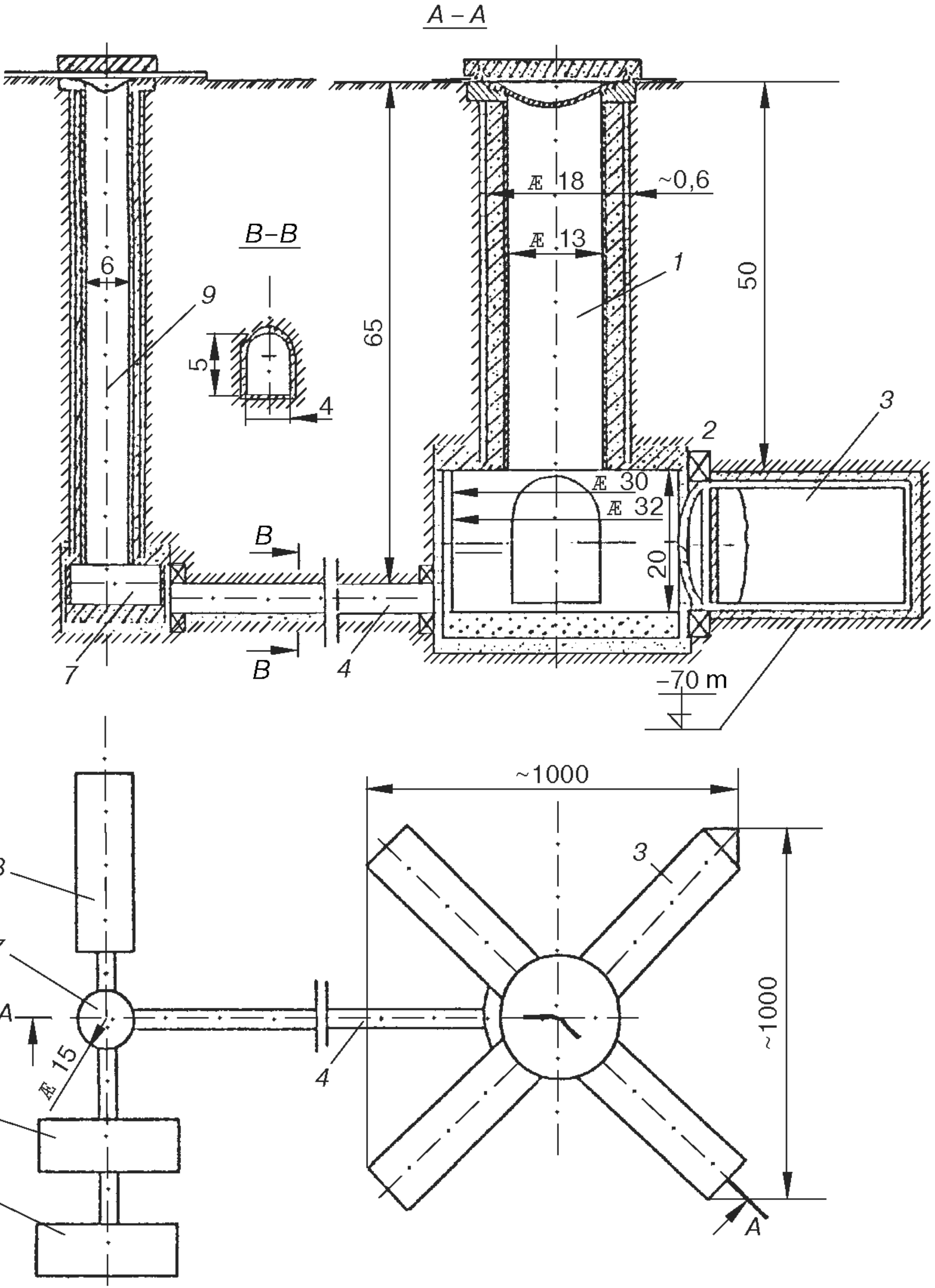


Fig. 20. State diagrams of binary systems Pu-Al (*a*), Pu-Ga (*b*) and Pu-Zn (*c*) possessing a stable delta phase

- creation of nuclear fuel cycle technologies excluding the stage of plutonium release from the technological process;
- conversion of nuclear military potential of countries — members of «Nuclear Club» and uniting their efforts for development of International nuclear power technology of the 21st century;
- target solution of the outlined crisis ecological problems of nuclear energetics owing to active financial support of the countries — members of «Nuclear Club»;
- choice of the most acceptable conception for utilization of nuclear fuel and building material, first of all, for the destructed fourth unit of the Chernobyl NPP and its practical realization (for Ukraine).

The decision of the ecological problem of nuclear energetics is the most important task of the first century in the third millennium. The conception of creation and construction of underground nuclear thermoelectric stations (UNTES) with provided strict requirements to safety of the objects of nuclear-fuel cycle (NFC) [22–25] is of interest in this respect. The UNTES under development consist of three technologically related enterprises: power generating (nuclear reactor, steam- and turbogenerator), technological plant for gathering, processing and conditioning of radioactive waste (RW), a set of mines for storage of processed RW and spent nuclear fuel. The efficient multibarrier protection of personnel and environment by unbroken frames nonpermeable for gases and rock radiation is realized in this case. The characteristic feature of UNTES, as the objects of civil building, is considerably lower level of ecological risk as compared with the overground NPP. Probability of emergency at UNTES decreases, owing to multibarrier protection based on isolation of properties of high-strength rock massifs chosen with allowance for mining-geological, structural-tectonic and hydrogeological conditions of removal and peculiarities of plants arrangement. Even under hypothetic accident at UNTES, the amount of emissions from the active reactor zone will be considerably less than at overground NPP. The most important feature of UNTES is the secured geological safety during its operation determined by changelessness of physico-chemical properties of the rocks enclosing nuclear reactors, their resistance to the outer and inner effects, stability of geological environment. The latter is determined by different-scale factors, such as: seismic and geodynamic stability of the region, stability of hydrogeological conditions of the surface and ground waters in the structural blocks providing the lowest levels of their filtration. Each of the above factors is taken into account when choosing place for UNTES location. Projects of underground nuclear plants (UNP) of different classes have been developed: trench, mine, tunnel, tunnel — builtup (module coastal UNP), mine with a basin in a form of chambers, mine with torroidal lower basin, etc. [22]. The mine and tunnel variants of UNTES have been designed for the Belgorod Region adjacent to the Kharkov Region.

Consider the design peculiarities of the mine UNTES [22] (Fig. 21). It is seen from the figure that all the underground part of the mime station of NPP consists of two functional groups of premises built from ferroconcrete and intended for the reactor modules and technological operations with spent nuclear fuel (SNF) and radioactive waste (RW). Each group of premises is provided with a vertical shaft. The shaft *1* of central chamber *2* is faced by metal corrosion-resistant coating. Its clear diameter is 13 m and height 50 m. The central chamber 30 m in diameter and 20 m high is connected with four symmetrically arranged autonomous tunnels about 45 m long which are partitioned into compartments *3* with dimensions 12 × 8 m. Nuclear module reactors (NMR) are



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arranged in the compartments. The latter are connected through a central chamber *2* by transport-technological tunnel (TTT) with technological chamber *7* and with premises for processing of liquid radioactive waste (LRW) *6*, storage of processed LRW *5* and temporary store of SNF *8*. Transport-technological tunnel *4* is connected with the Earth surface by a vertical shaft *9* with clear diameter 6 m. Containerized SNF and RW, i. e. «dirty products», are transferred along this shaft for fine processing and storage in special «eternal» storages. «Fresh» fuel

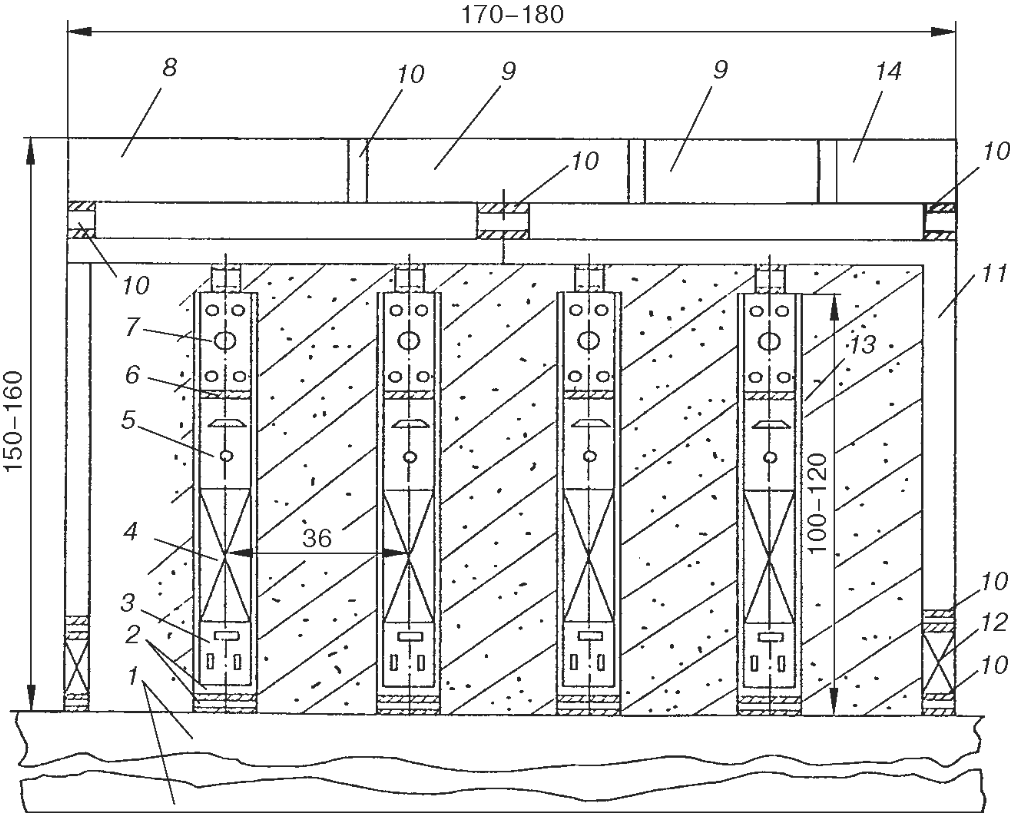

Fig. 21. Lay-out diagram of the underground part of UNTES of the mine (*a*) and tunnel (*b*) types [22, 23]

and discharge materials are supplied from the surface to underground space along the major shaft *1*.

Tunnels of nuclear module reactors (NMR) and compartments *3* are separated from the central chamber *2* by firm and dense gates. Personnel come in the NMR through special sluice-chamber. Entrances to TTT, premise of technological chamber *7*, as well as premises for processing of liquid waste *6* and for storage of processed LRW *5* are sealed in the same way. All the premises belong to the zone of strictly controlled operation conditions. All pipes with operation media and cables connecting the underground and overground (steam-turbine and power-generator plants) parts of UNTES pass through the central chamber *2* and peripheral volume of the mine between inner metal facing and ferroconcrete wall of the shafts. There are two lifts in the shafts for transfer of personnel. The shaft collars are also sealed with a firm lid.

A tunnel variant of UNTES, considered in detail in the works [22, 23], is also of practical interest. It is considered that the tunnel variant is more preferred for the plain Belgorod Region than the mine one. As is seen from Fig. 21, *b* the underground tunnel station has a transport-erection site *1*, four or above operation tunnels 100–120 m long provided with firm and dense gates *2*. Electrotechnical unit *3*, boiler units *4*, turbogenerator units *5*, protective gates *6* of nuclear module reactors are arranged in the tunnels. The tunnel UNTES has a «wet» storage for «cooling» of waste fuel elements *8*, technological premises *9, 13* for processing of radioactive waste, separated from other premises by sluice chambers *10* and decontamination center *12*. Cargo transfer is performed along TTT *11*. Temporary storage of RW is executed in unit *14*. Peculiarities of underground construction of UNTES are considered by the authors of [22, 25].

Further construction development was reflected in the design of the state Research Centre of Russia — Acad. A.N. Krylov Central Scientific Research Institute (SRCR CSRIKr) [26]. It is supposed that this design corresponds completely to the strategy of development of Nuclear Electric Power Engineering directed to caution of safe and comfortable conditions for population dwelling near UNTES which generates electric power. In a given case the total installed power of UNTES is 300 mW. UNTES consists of four unified autonomous nuclear power modules of 75 Mw each. The series ship nuclear reactors, which have shown themselves to advantage on nuclear cruisers of *Petr Velikiy* type (Russia), are used as power modules. The ship nuclear energetics began developing simultaneously with NPP [27]. These nuclear reactors are simply replaceable and not large in size. Each power module is arranged, as it has been described above, in a sealed shaft 12 m wide, 16 m high and 100 m long. The shafts are arranged at the depth of 50 m and have a rather thick natural roof above them. The shafts are built following the tunnel construction technology used in various branches of industry and military engineering.

The electric power of one electromodule, let in the network with central heating load of 50 Gcal /h, is about 63 MW. The number of hours of continuous work — 8 000 h a year (about 11.1 month). The fuel campaign of the ship nuclear reactors is 27 000 h (3.08 yr). Water is mainly used as cooler [27]. The achieved operation resource of the nuclear power unit on the ice breaker *Arktika* in operation was 150 000 h (above 17 years), and it is planned to continue its operation resource to 175 000 hours (total resource will be 20 years) [27]. The estimated coefficient of the installed power is 0.8, operation term of nuclear reactor 30 years, and that of the shafts above 100 years [26]. UNTES by the project of [26] can be built in short terms (4–5 years), since the construction of shafts and manufacturing, mounting and testing of electromodule equipment at the plants are carried out simultaneously. The ready-made power modules are supplied to the shaft and installed for operation there. The design of UNTES SRCR CSRIKr is provided is multimodule system of underground NPP permitting to construct electric stations with any preset power by increasing the number of power modules. The UNTES data possess maneuverability — the delivered power (thermal and electric) can be 5 to 100 % of the nominal power by which they are distinguished from NPP, operating in the basic conditions only. Use of the systems with complete automation of autonomous operating control of parameters of power modules, logic systems and algorithms, self-operating devices for putting into action the safety systems, double fastening systems, etc., allowed providing absence or scarcity of people under station operation. Absence of people under work of nuclear reactors of NPP is the present approach to solution of the problem of reliable or safe operation of NPP.

The proposed ship power plants for UNTES possess considerable advantages over reactors for NPP [26, 27]. Nuclear energetics, as was noticed by the author [26], being an unprecedented step in scientific-and-technological development of mankind, requires an «adequate improvement of technological discipline, filigree engineering design, rigorous following service and records, the highest culture of engineering thinking». The ship nuclear power plants have been designed at such high engineering level with simultaneous use of specially created structural materials, possessing high radiation and corrosion resistance. Thus, they are reliable and safe and UNTES constructed with their use by the design of SRCR CSRIKr could be considered the basis of energetics of the 21st century, if it were not for one shortcoming.

In the ship nuclear reactors of SRCR CSRIKr the fuel cycle is based on the use of uranium-235 enriched to 99 . 9%. It is because of the lack of uranium-238 in nuclear reactor that plutonium (Pu-239) and its isotopes (plutonium-240, 241, 243) are not produced. Hence, the amount of radioactive waste is 35 times lower. But if all the nuclear stations will use 99.9-per-cent uranium-235 as nuclear fuel which amount was about 133 times less, than of uranium-238, then the nuclear industry will soon feel the shortage of nuclear fuel.

4.2. High-temperature liquid-salt reactors

Interest for high-temperature liquid-salt nuclear reactors arised in the Ox-Ridge National Laboratory of the USA in 1947, and then attracted attention of researchers in many other nuclear countries: Japan, France, USSR. An analysis of physico-chemical properties of high-temperature liquid-salt reactors (HTLSR) and long-term experimental check of a number of their experimental designs permitted relating them to the reactors of the future nuclear-hydrogen energetics [30, 31]. HTLSR seem to be free of fuel elements, these are the third-generation reactors. Functions of fuel and salt heat-carrier in these reactors are combined in one working medium -melted salt based on halogenides (often fluorides) of alkali and alkali-earth metals circulating in operating channels (e. g., mol. share, %; LiF (55) — BeF (66) — BeF_2 (29) — ZrF_4 (5) — UF_4 (0.2)) and three-component systems on the basis of lithium, sodium and potassium carbonates, containing salts of the corresponding nuclear fuel. Designs of liquid-salt nuclear reactor with high thermal power with the use of salt melt are developed in the USA, France and Japan. The salt melt composition mol. share %: LiF (65) — BeF_2 (29.1) — ZrF_4 (5) — UF_4 (0.9), and for the reactor-breeder the recommend the following salt composition, mol. share, %: LiF (71.7) — BeF_2 (16) — ThF_4 (12) — UF_4 (0.3) [32, 33].

The design of thermal reactor breeder MSBR with electric power of 1 GW [33] is the most known one. The layouts and parameters of HTLSR are considered in the works [34–36].

Eutectic melt of sodium fluoroborate and sodium fluoride under molar ratio 92:8 plays the role of heat-carrying medium in the intermediate loop in liquid-salt nuclear reactors. The investigations have shown that binary systems of fluorides with following composition, mol. share, %; LiF (48) — BeF_2 (52) for working temperatures above 658 K [32, 33] can be used as solvents of nuclear fuel fluorides for reactors-breeders. The melting point of salt compositions for HTLSR as a whole must be low and equal 773–873 K for medium-temperature reactors and 973–1073 K — for high-temperature ones. The melts would possess optimal viscosity (3–7 sP at 973 K), high heat conductivity (0.003–0.005 cal/(cm · s · °C)) and heat capacity (0.21–0.67 cal/(g · °C)), permitting their use as efficient heat-carrying agents [35].

The salt melts are also developed for higher temperatures, up to 1573 K [37]. The melts based on fluorides of alkali and alkali-earth metals are radiation- and heat-resistant systems with low viscosity, high heat capacity, exceptionally low pressure of nonsaturated vapours (< 1Pa at $T = 1073$ K). Their considerable demerit is a capacity to corrosion interaction with metals of the casing and ancillary devices (pump channels, pipes, structural members) [30]. Even nickel-molybdenum alloys containing, %: Mo — 16, Cr — 7, Fe — 5, Ni — 72 proved to be irresistant to corrosion in fluoride media. That was the reason for developing HTLSR where isotropic pyrographite is used as the only structural material [31].

The design of high-temperature liquid nuclear reactors and their heat releasing liquid elements as well as resistance of structural materials to high-temperature corrosion are considered in the works [30, 31, 34–38]. Such structure case and pipes are mounted of graphite parts tightly connected by graphite tissue and special glues. The case is covered with a jacket of the corresponding metal providing the whole reactor strength. Nanotechnologies of synthesis of boron carbides, aluminium carbides and nitrides with high melting temperatures are developed in the recent time. Using the principles of slip casting, these materials can be compacted with obtaining articles of any shape, they can be sintered to produce high-strength parts. In our opinion the above materials can be successfully used under the construction and erection of high-temperature liquid-salt reactors.

The process of heat and electric energy generation using high-temperature liquid-salt reactors (HTLSR) is exceptionally simple. Uranium enriched with uranium-235 (0.3 mol % UF_4) plutonium-239 (~ 1.0 mol % PuF_3) is used as fissionable material, and in reproducing cycle of, e. g., uranium-233 they use thorium-232 (10–12 mol % ThF_4) [35]. The HTLSR structure consists of the reactor, two-loop heat exchanger, pumps of the first and second loop, steam generator, turbogenerator, system of chemical processing and finishing of salts. In HTLSR the fuel mixture of preset composition is pumped through the active zone with graphite rods, performing the function of moderators. Energetic properties of the active zone depend on the ratio of volumes filled with salt and graphite rods. Heat is supplied to steam generator through salt of the second loop. Thermal energy efficiency, depending on the environment temperature, is 48–56 %, resulting efficiency of the nuclear-power plant HTLSR can reach 50–60 %, and thermodynamic quality of the reactor is 0.95–0.98 [31].

High reliability of high-temperature liquid salt reactors is their characteristic feature that is explained by the following circumstances [30]. Firstly, the nuclear power plants with HTLSR are safe, since: a) nuclear fuel with salt melt is supplied continuously to the active zone; b) the reactors design allows achieving a hundred-fold temperature heat Δt_1 between salt and outer wall of graphite channel; in this connection the reactor heat is transferred to heat exchanger at a temperature close to maximum that ensures high thermodynamical quality of HTLSR as a heat source; c) stable estimated temperature and heat transfer at low pressures both in the reactor itself and in the first loop are preserved in the active zone as a result of continuous circulation of the salt melt and replenishment with fresh fuel as well as continuous removal of fragments (in accordance with technological conditions). Secondly. high degree of independence of NPP with HTLSR is determined by the fact that nuclear fuel is thoroughly processed, fragmental elements are separated and localized according to technologies, excluding a necessity of fuel elements transfer «there and back». The latter creates favourable conditions for ecology preservation in the region. Thirdly, electric energy and heat generated at NPP with HTLSR can be successfully used: a) to obtain hydrogen on great scales by electrolysis of water solutions and water vapours [32, 39–42]; b) to produce hydrogen by thermochemical methods [33–45]; c) to decompose water in the process of coal gazification and natural gas conversion. In connection with the above stated NPP with HTLSR can play a decisive part in creation of highly productive complexes of nuclear-hydrogen energetics [see, Chapter 6].

The demertits of NPP with HTLSR include; a) high activity of the first salt loop which determines a necessity to use equipment providing the remote control of the technological process; b) high velocity of tritium production reaching approximately 1Ci /(MW·day).

It would be noticed that the programs on creation of NPP with HTLSR are intensively developed. Theoretical basis of the melted media use for HTLSR consists of physical chemistry and high-temperature coordinational chemistry (HTCC) [33, 39, 46–50]. Investigations in the field of HTCC have shown that in all the enumerated cases fluoride complexes of the type of $[BeF_4]^{2-}$, $[UF_6]^{2-}$, $[ThF_7]^{3-}$, $[ZrF_6]^{2-}$, $[BF_4]^{-}$, etc., are formed in ion-diluted complex-forming metals. Total properties of these complexes in solvents LiF, NaF are determined by necessary physico-chemical and thermophysical properties of energetic fuel and heat carrier: density, heat capacity, heat conductivity, viscosity, elasticity of vapour, etc. Using knowledge obtained in researches in the field of HTCC one can also create apriori the salt melts possessing extremely low corrosion activity to structural materials of nuclear reactors of safe NPP with HTLSR (51–52). Use of the melt compound Li_2 $[BeF_4]$ melt in the hypothetic thermonuclear reactor is rather original [51, 52] and multifunctional: it can be used as heat transferring agent, carrying heat to electrogenerator, fuel reproduces of thermonuclear synthesis ($^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{4}_{2}He$), etc. The complex compound $Li_2[BeF_4]$ melt possesses satisfactory heat conductivity, favours additional accumulation of the nuclide $^{6}_{3}Li$ at the expense of nuclear reactions of beryllium, etc.

It would be noted that the developing nuclear HTLSR are reactors of the future and can be successfully used in nuclear-hydrogen energetics. Electric energy generated by these reactors may be used to produce hydrogen by means of high-temperature electrolysis of water vapours, while thermal energy of HTLSR may be used to produce hydrogen synthesis-gas and liquid synthetic fuel from coal. As a whole, nuclear reactors HTLSR being the third generation reactors can make a considerable contribution to development of industrial nuclear-hydrogen energetics.

4.3. Thermonuclear energetics

The «eternal» source of cheap and ecologically pure high-power energy can be obtained when solving the problems of controlled thermonuclear fusion (CNF) and creation of thermonuclear reactors (TNR) and thermonuclear power plants (TNPP). Great efforts were made both in the USSR and USA (as well as in some other countries) to search for decisions in the path of creation of practical thermonuclear energy generators which implementation in industrial practice was planned by the end of 2000 [51]. But it would be noted that when creating CTF, though the energy source will be «eternal», it will not be pure, since by thermonuclear reaction between deuterium and tritium

$$D + T = \alpha + n + Q \qquad (5)$$

α-particles and neutrons (n) are synthesized which possess high energy (14 MeV) and interact with surrounding materials with radioactivity induction in them which does not differ from fragmental one. Thus, the ecologic risk will be also higher under development of thermonuclear energy [53], since it is determined by the product of quantity of formed radioactive substances by the accident probability.

Ecologically pure minimal thermonuclear energy, $Q_1 = 3.26$ MeV, theoretically may be generated from reactions of nuclei coalescence of He (reaction 6) and nuclei of isotope ^{6}Li

$$^{3}\mathrm{He} + {}^{3}\mathrm{He} = {}^{4}\mathrm{He} + 2\,^{1}\mathrm{H} + Q_1 \qquad (6)$$

However for practical realization of this reaction (6) it is necessary to learn to synthesize ^{3}He on industrial scales [54] and for the reaction (7) — to separate Li and D isotopes (reaction 7)

$${}^{6}_{8}\mathrm{Li} + \mathrm{D} = {}^{4}_{2}\mathrm{He} + {}^{4}_{2}\mathrm{He} + Q_2 \qquad (7)$$

as well as maximum thermonuclear energy $Q_2 = 22.37$ MeV (isotope content ^{6}Li = 7.4 mass. %, ^{7}Li = 92.6 mass. %). Thermonuclear energy for military purposes is realized in thermonuclear bomb (hydrogen bomb), the ordinary nuclear bomb serving as a primer. Under the explosion of thermonuclear bomb energy releases during seconds. Nobody has succeeded in inventing the smouldering charge of «thermonuclear bomb», though there are a lot of examples of «thermonuclear charge» action in nature: the sun, milliards of stars, etc., converting hydrogen into helium-4 (^{4}He). The reaction of hydrogen conversion in the centre of the sun proceeds at a temperature of 13–15 mill. °C at hydrogen density about 100 g/cm^{3} [54]. Under the Earth conditions they have learnt to heat plasma, containing thermonuclear fuel (hydrogen, cleuterium, tritium), to 100 mill. °C. Nowadays there exist researches concerning solution of the problem of obtaining — for at least milliardth fractions of a second — hydrogen density in plasma close to «solar» density of hydrogen.

Side by side with the well known, but unsuccessful, examples of CTF realization for nuclear energetics, scientists search for absolutely new approaches. Thus they have developed the theory of the bubble thermonuclear bomb and made experiments on collapsing the microbubble of 20–30 kHz and amplitude 1–15 bar [55]. By the author's ideology a microbubble with deuterium vapours, may be considered as a microhydrogen bomb «exploded» due to the energy released under the microbubble compression with achieving the temperature in its centre about 50 °C · 10^{6}. Calculations have shown that in the moment of compression and spherical shock wave convergence to the microbubble centre there forms a superhot superdense plasmoid 50–80 mm in diameter with about $20 \cdot 10^{9}$ deuterium nuclei in it. Calculations demonstrate that the plasmoid temperature can reach 100 °C · 10^{6}, density 100 g/cm^{3} (the value close to hydrogen density in the centre of the Sun at 20 °C · 10^6, and pressure 100 · 10^9 bar. This superdense plasmoid exists for a very short period of time — fractions of picosecond. But despite of a short lifetime of such a microbubble (as calculations show) the bubble energy accumulation possesses a considerable resource of stability [55]. In experiments with deuterated acetone it was revealed that the tritium nuclei formation rate is approximately equal to 7 · 10^3 nuclei a second. The features of neutron radiation with energy close to estimated and equal to 2.5 MeV were also observed. Strong compression under bubbles collapse and temperature growth to $n \cdot 10^8$ K, corresponding to proceeding conditions of the reactions of nuclear synthesis accompanied by mass defect was proved as well. A possibility of executing the processes of thermonuclear explosion in microbubbles theoretically predicted by Russian scientists, was realized experimentally in the laboratory of the National Nuclear Centre of the USA in Oak Ridge (Tennessee). Scientists need 3–4 years and about 5 million dollars to create experimental supersonic thermonuclear reactor for estimating prospects of the method and proposed theory [55].

The above expenditures are a triffle compared with those of 30 · 10^9 dol. for theoretical and experimental works in heating and retaining of plasm in *tocamak* plants (tocamak-thoroidal chamber with magnetic field) — the idea proposed by Academician Lev Andreyevich Artsimovich [56]. The *tocamak* resembles a huge step-down transformer consisting of the closed iron core and primary winding, a high-power a. c. pulse being periodically skipped through the winding by the discharge of capacitor battery [57, 58]. The only closed turn of the vacuum chamber is used at the secondary winding. The vacuum chamber in filled with deuterium at low pressure. The battery discharge is followed by gas break down, ionization and heating to high temperature 10 000 000–15 000 000 °C., i. e., there appears plasma. In «the largest tocamak T-10» the plasma current reached 600 000 A, and volume of plasma made about 4 m^3. A strong magnetic field [57] is used for plasma stabilization. At a temperature of 10 000 000 °C and extremely low plasma density (about 10^{14} deuterium ions and electrons in 1 cm^3) the plasma particles collide rarely while flying hundreds of meters between collision. It is natural that multiple fusion of nuclei does not occur under such conditions. Investigations have shown that both deuterium DD-reactions and deuterium-tritium DT-reactions are of interest for thermonuclear synthesis in tocamaks. In the former case nuclei of ^{3}He + neutron or triton (tritium nuclei) + proton are formed in plasma. In the latter case there forms α-particle with energy 3.5 MeV and neutron with energy 14.1 MeV. Energy which arises in the reactions of thermonuclear fusion is determined by the probability of components collision in plasma and depends on the used systems, temperature and energy of colliding nuclei. For DT-reaction in plasma the «ignition» temperature of the reaction of controlled thermonuclear fusion (CTF) is 10 times lower, than under «ignition» of DD-reaction of synthesis. Tritium does not occur on the Earth and thus to use it in thermonuclear fusion we need the process of industrial production of tritium, for example, by lithium nuclei irradiation with neutrons. There is a variant of tritium reproduction from lithium when irradiating the latter with the neutron flux under fusion of tritium and dueterium nuclei in the process of DT-reaction of CTF. It is considered that the amount of lithium in nature is sufficient to meet the requirements of thermonuclear energetics for a millennium.

Deuterium is more accessible for proceeding the reaction of CTF both from the point of view of energetics and its distribution in nature.

The authors of [58] think that for implementing CTF it is necessary to heat DT-mixture to 100 000 000 °C. But there are no guarantees, since the intensity of CTF reaction is determined both by plasma temperature and its density. It is considered that for DT-reaction in thermonuclear reactor at 100 000 000 °C plasma density would be no less than 10^{14} ions of deuterium and tritium in 1 cm^3. Since thermonuclear fusion of helium nuclei from hydrogen nuclei proceeds in the bowel of stars and the Sun at considerably lower temperature ($10–20 \cdot 10^6$ °C) at pressure of $100 \cdot 10^9$ bar and density 100 g/cm^3, we think that the pressure of ionizing inert gas (He, Ne, Ar, Kr or Xe) being increased in the second loop (under batched supply of deutetium), a rather high temperature and required plasma density can be achieved for implementing the controlled thermonuclear reaction of DD-synthesis under the Earth conditions.

It would be noticed that as a result of theoretical researches and R&D works the data were obtained necessary for the construction of the research thermonuclear experimental reactor (RTER). The reactor construction will be started in 2003. A program of experiments made by the joint group of scientists from Russia, USA, European Community and Japan is meant for 20 years. During this period of time they will obtain results necessary for the construction of a prototype of thermonuclear reactor.

Considerable success has been achieved in Russia in the field of creation of hybrid nuclear-thermonuclear reactors with obtaining the programmed pulse-periodical neutron fluxes by means of laser thermonuclear fusion [53]. A scheme of «absolutely safe» hybrid-thermonuclear reactor is presented in Fig. 22. It combines in one aggregate a nuclear (separating) and thermonuclear (initiating) parts. The NPP major parts — laser with energy 200 kJ, subcritical targets and working mass of uranium-238 called a subcritical blanket. In the offered variant of hybrid reactor one can observe synthesis of neutrons from deuterium and tritium with the help of laser initiation by thermonuclear reaction (4) and formation of the preset quantities of α-particles. The latter are absorbed in heat-releasing chamber of uranium-238 (the combustion chamber called a blanket), the same quantity of neutrons n with energy 14 MeV undergoes a reaction of nuclear fission with uranium-238. Under these conditions plutonium is not accumulated since it reacts immediately with neutrons. If 10 fissions occur with participation

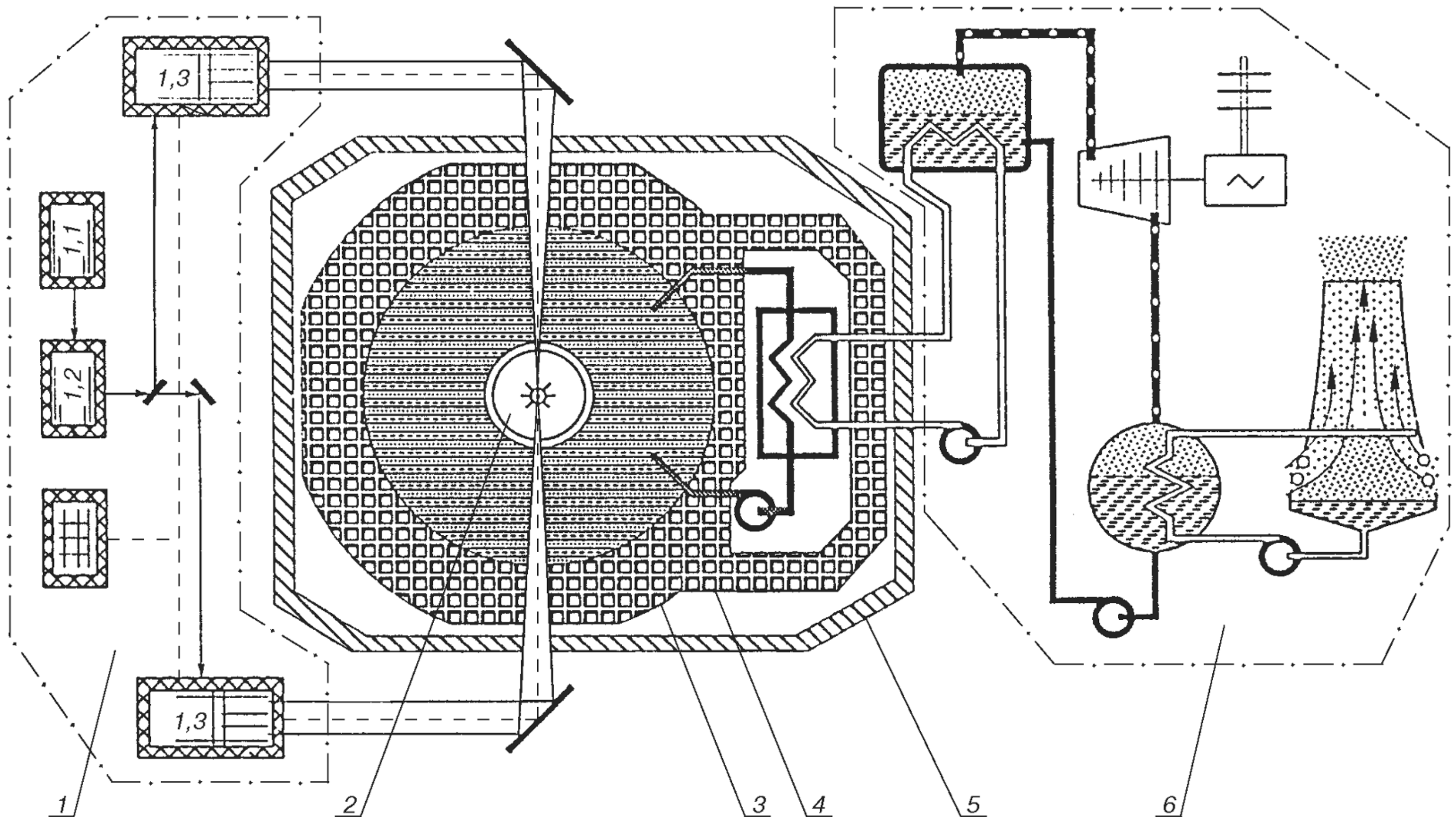

Fig. 22. Scheme of hybrid nuclear-thermonuclear reactor [53]:
1 — laser amplifier; 1.1. — master oscillator, 1.2 — preamplifier, 1.3 — laser-driver; 2 — thermonuclear chamber with a target; 3 — blanket; 4 — radiation protection; 5 — antiaccident shell (containment); 6 — steam-turbine unit

of one neutron without the break of the reaction chain, the 100-fold amount of energy releases in the uranium blanket compared with thermonuclear part serving as the ignition and providing energetics at the level of 1 %. So, such hybrid reactors are safe. The used uranium-238 allows the subcriticality to be supported at the given level: uranium-238 as if lends the absorbed neutrons for some time since in several days the neutron absorption products are recycled in a form of active atoms of plutonium-239. The electric plant power depends on the power of laser and can be decreased to dozens of MW. So, such hybrid reactors can be used in very different fields of human activity — from expeditions to the Antarctic continent and to the North Pole to those to little towns, etc. Power flows in the hybrid nuclear-thermonuclear reactor (NTR) are shown in Fig. 23. To raise the NTR efficiency it is necessary to increase efficiency of semiconductor lasers on the basis of Al_{1-x} Ga_yAs by approximately 60 % and their lifetime to 10^8–10^{11} bursts which is quite real in the opinion of the authors of the work [53]. The decrease of neutrons yield under the combustion of thermonuclear targets would be also prevented. The neutron yield for the functioning of hybrid NTR would be 10^{16}–10^7 neutrons during 1 laser pulse. In the near future the USA scientists want to achieve the target combustion with the thermonuclear power yield at the level of gigajoule and radiation of 10^{20}–10^{21} neutrons per one pulse.

The idea of a group of physicists from the All-Union Research Institute of Technical Physics (the former Chelyabinsk-70) concerning the industrial use of thermonuclear explosions for electric power generation in the so-called microexplosion combustion kettle (MECK) is of great interest; the kettle scheme is given in Fig. 24. The general idea of MECK consists in performing explosions of small thermonuclear devices (thermonuclear ammunition can be used there) in special well-protected and large steel high-strength tanks, the heat-carrying agent — liquid sodium — being continuously pumped in them. The process of production and explosion of such thermonuclear devices has been brought to commercial level. Sodium heating as a result of thermonuclear microexplosion allows its continuous pumping-out from MECK, to transfer heat to turbines (by one- and two- loop pattern) and pump the sodium heat agent back to the explosion kettle. The unburnt fuel, combustion products, pulverized structural materials and worked fission material are removed by liquid sodium and would be filtered and separated from the agent that is the method demerit. But the method also has a number of advantages:

- MECK is deprived of the problems which solution term cannot be reliably predicted;
- the process can be simply stopped at any moment since the explosions occur with intervals of dozens of minutes;
- great safety (sounds something unexpected, but it is to be allowed for that MECK is created for continuous work under continuous low-power ther-

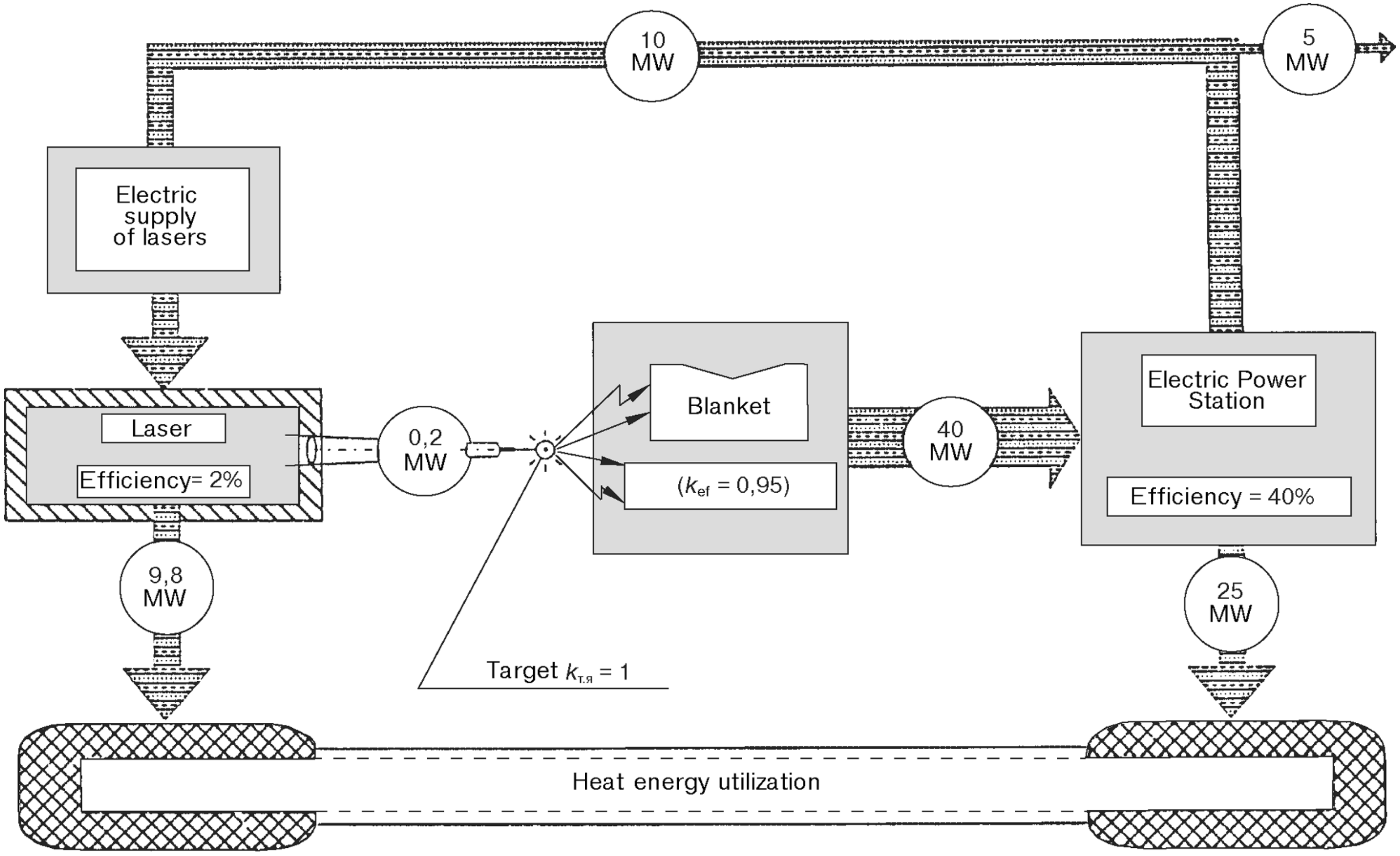

Fig. 23. Energy fluxes in «absolutely safe» hybrid-nuclear-thermonuclear-reactor [53]

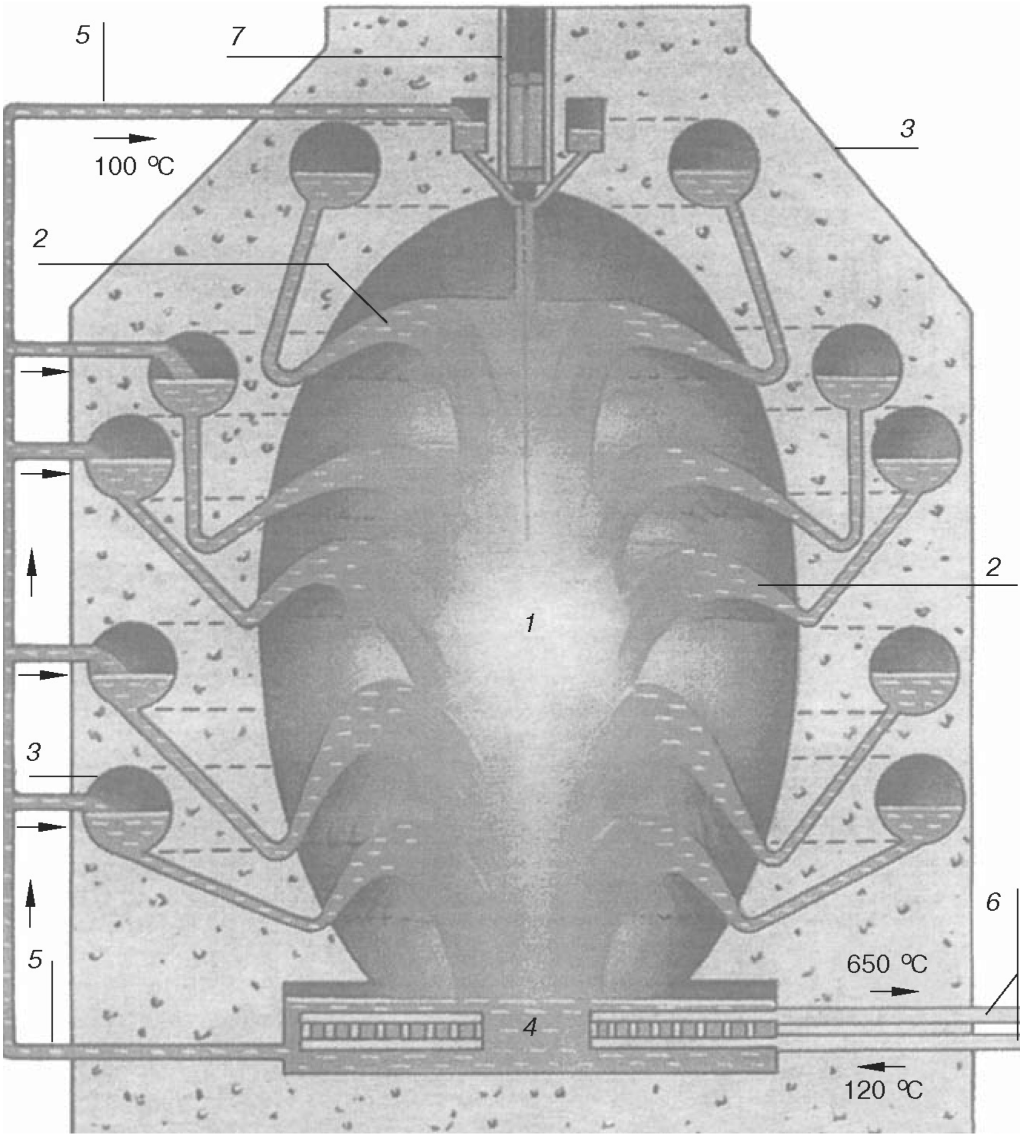

Fig. 24. Scheme of thermonuclear explosions for electric power generation in the explosion combustion kettles:
1 — explosion of thermonuclear explosion device; *2* — a «screen» of liquid sodium; *3* — accumulating tanks with cold heat-carrying agent; *4* — hot heat-carrying medium in heat exchanger; *5* — liquid sodium supply to accumulating tanks; *6* — the second loop of heat-exchange; *7* — channel of introduction of the explosion thermonuclear device

monuclear explosions and the whole structure strength is designed for such conditions);

- high temperature of the explosion allows tritium to be excluded from the reaction, operating with deuterium only;
- according to authors' estimate, cost of electric energy produced by the MECK system must be lower that that generated under combustion of organic fuels.

It follows from the above stated that a great volume of researches have been carried out in the field of controlled thermonuclear fusion; great investments and efforts of scientist and engineering staff were directed to fulfillment of the task of creation of continuously functioning thermonuclear source of energy. All that resulted in the theory of thermonuclear «combustion» of light elements (deuterium and tritium) and designers have obtained experimental proofs of reality of these processes, though the DT-reactions functioning stability in CTF has not been achieved. The problem complicacy gave birth to a sad joke among physicists that «thermonuclear energy is that of the future and always remains it».

It follows from the above stated that the works in the field of «thermonuclear explosions» are carried out in the following major promising directions:

- «slow» thermonuclear fusion in plasma in magnetic field of the tocamak type devices;
- microthermonuclear explosion (ignition) in the tritium-deuterium drop with a powerful pulse of several lasers focused on it;
- microthermonuclear explosion in the tritium-deuterium bubbles in the supersound field;
- development of hybrid nuclear-thermonuclear reactors with low power;
- realization of thermonuclear explosions for electric energy generation in the kettles of explosive combustion.

Though the authors of the work [55] think that the thermonuclear fusion energy is not the power technology of the early 21st century however investigations in the field of controlled thermonuclear fusion are carried out in the leading countries of the world. Researchers also develop the systems of automatic control of parameters of thermonuclear plasma to learn high-accuracy controlling the reactions of thermonuclear fusion. Thermonuclear energetics, possessing high-energy potential will be rather used with success in the late 21st century to produce hydrogen and synthetic liquid fuel which will meet the requirements of motor transport and agricultural machines in fuel.

4.4. Ecologic safety of nuclear energetics

The ecologic safety of nuclear energetic is based on two aspects: power production safety at NPP and reliability of nuclear waste burying.

The former aspect is the safety of thermal and electric power production at modern NPP. Nuclear energetics in numerous countries in its current form does not undoubtedly belong to the number of highly reliable power production systems. Its development was essentially moderated after a series of accidents and catastrophes, and up to 2000 the nuclear power industry remained in the state of stagnation. That caused the search of more reliable operation principles of engineering systems and structures of nuclear plants.

There are the designs of underground thermal electric stations (UNTES) [22–25], as well as the nuclear heat supply plant (NHSP) [60] arranged in the mountain massifs or under the ground in the parent rocks. Such plants, owing to peculiarities of physics of nuclear reactors are characterized by the guaranteed level of protection from the external natural and technogenic effects as well as high resistance to internal emergencies. Safety characteristics of the underground NHSP with the basin reactor as a promising pure source of thermal energy for CIS countries, especially for Ukraine and Russia are rather favourable.

The all-round theoretical analysis of the underground NHSP has shown that the reliable heat removal from the reactor is provided under all its operation conditions and even at the supposed serious emergencies, and radioactive emissions in the air and surface environment are absolutely excluded. Under the accident caused by the switch-off of the external electric power supply, the released heat is dissipated in the reactor basin water, mountain massif and the atmosphere of underground premises, and water in the basin is not heated to boiling. The active zone is cooled owing to natural circulation of heat transfer medium, and thermal loads, which could lead to the equipment break-down, are absent. The underground part of NHSP is characterized by the best economic indices compared to TES on organic fuel [60].

At the sessions of IAEA after the Chernobyl catastrophe they gave much attention to the sharp increase of the role of «human factor» in the general level of nuclear plant safety. The index of safety control functioning has been taken as quantitative characteristic of NPP safety. This index is denoted through Y per one reactor a year at an average [61]. The first place as to the minimum value of this index, as is seen from Fig. 25 (data of [61] have been ordered by us) belongs to NPP of Japan ($\Psi = 0.02$), the second one — to Germany ($\Psi = 0.2$), the third to Russia ($\Psi = 0.5$). NPP in the USA, France and South Korea share the fourth place, the Great Britain occupies the fifth place, and Ukraine — the last, sixth place ($\Psi = 1.1$), the largest value exceeding 55 times the safety control functioning index of Japanese NPP ($\Psi_{\text{Ukraine}} // \Psi_{\text{Japan}} = 55$). It is seen from Fig. 25. that for Japanese NPP the safety control functioning index Ψ per one reactor equals 0.02, and in this connection two comparatively inconsiderable emergencies in the reactor breeder (sodium leakage) and at the plant for processing the nuclear fuel in 1977 shocked general public of the country. The Ψ value is in direct relation to NPP safety, since the latter depends on qualification of specialists, introduction of technical novelties in electromechanical and test equipment. In the period from 1992 to 1996 NPP of Russia lowered their Ψ 16 times. These achievement are determined by positive changes in the composition of fuel, introduction of additional protective absorbing elements, by increasing the operation culture, creation of simulators of 1000 possible emergencies for operators. The NPP operators had good training and retraining using multifactor simulators; they can act

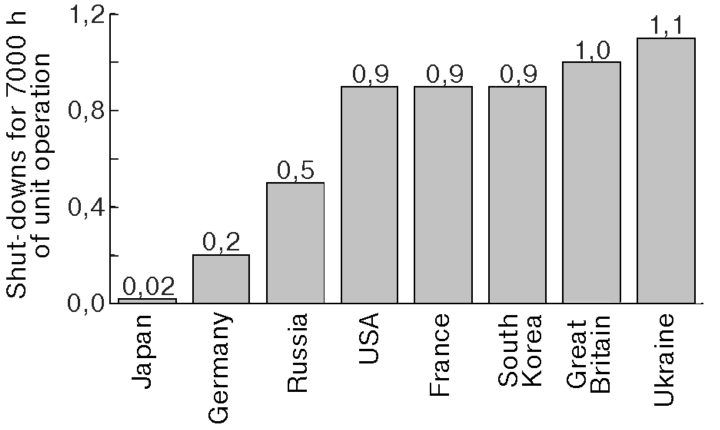

Fig. 25. Automatic emergency stops (per 7000 h of the work of NPP reactor) in different countries of the world and in Ukraine in 1995 and in Russia in 1996

in any situation which may arise at NPP in the process of their operation. In the opinion of Academician V.N. Mikhailov, Minister of Nuclear Power of Russian Federation [61], the safety index of Ukrainian NPP is considerably lower that that of Russian NPP (Fig. 25). The Minister thinks that Power Ministry of Russia has rather close relations with Nuclear Industry of Ukraine and gives Ukraine new and new designs necessary for modernization of NPP which are introduced with a delay of 1–1.5 years [61]. In creation of reactors of the 21st century special attention is paid to a possibility of immediate and reliable arrest of the nuclear reaction is of the highest interest among numerous variants. There, the subcritical mass of the reactor active materials is introduced in the reaction with the help of the external source of neutrons. The latter can be arrested immediately under emergency. The external source can be created by different methods, for example, by combination of fast and slow reactors, owing to the inertial thermonuclear explosion and accelerator of charged particles — the so-called electric explosion [61]. In the last of the mentioned cases protons pick up speed in the proton accelerator to high energies (about 1 GeV) and knock out neutrons from a heavy target; neutrons get to the reactor and induce nuclear reaction. The accelerator being switched off the nuclear reaction is arrested automatically. The design of the safe nuclear reactor is made by a powerful international cooperation with participation of European Union, USA, Japan and Russia.

The second aspect of ensuring ecologic safety is the burying of radioactive waste. It also has a decisive effect on the fate of nuclear energetics, since the problems of burying radioactive waste touches ecology and leads to fear among public and, as a result, to enstrangement of the idea of nuclear energetics as an alternative energy source for future generations. When using modern nuclear technologies, the formed radioactive waste at the scale of countries require almost annual (and forever) organization of new burials for them that is connected with the extending paradygm of the environment pollution. Small volume of RW serves as their advantage, that simplifies the construction of continuously operating (permanent) burials. Some specialists think that NPP waste would be buried at uranium deposits, i. e., returned to the place they were mined [63]. From the experience of Switzerland and Norway, it is more expedient to bury radioactive waste in the burials of geological type: in bedrocks or «deep geological formations» [64]. A typical Sweden system of storage of the spent nuclear fuel is given in Fig. 26.

Both the methods of «dry» and «wet» 10–100-year storage of the waste nuclear fuel are used in Sweden. Under dry method radioactive waste are stored under the ground in granite rocks and thick-walled copper containers, under wet storage — in the ponds in tanks under water.

To bury radioactive waste in the sea water one needs information about corrosion of steels used to make containers. It has been established in special experiments that minimum thickness of the container walls would be 33 mm even under the storage terms of 1000 years. The radioactive radiation power depends on time of the waste allowance. Calculations show that spent fuel being kept in the storage during 6–9 months, 30–40 and 1000 years, power release will decrease and will be 2000; 1.0 and 0.1 kW/t. The spent fuel kept during 30–40 years its radioactivity will decrease 2000 times, During this period of time the cost of uranium and plutonium will, undoubtedly, increase and it will be profitable to process waste and isolate plutonium and uranium from it. Thus the waste of nuclear plants may be considered as raw material for the nuclear complex of the future.

In the former USSR the spent nuclear fuel was considered as raw material. It was transported to special plants in Chelyabinsk, Krasnoyarsk, Tomsk and subjected to selective isolation of uranium and plutonium isotopes as well as to separation of «fragmental» radioactive isotopes. New more efficient technologies of selective isolation of uranium and plutonium isotopes from the spent nuclear fuel with obtaining the rest of radioactive waste have been developed for the recent 15–20 years. The waste could be reliably isolated for dozens and hundreds of years in special storages or «buried» forever in the bedrocks. It would be allowed for that about 10 % of energy in respect of the primary energy releases in the process of long-term «cooling» of RW.

In the arised Political situation of the USSR disintegration and formation of CIS countries the problem of radioactive waste would be decided on the basis of high-tech scientifically substantiated decisions made by of each country exploiting NPP. Ukraine, in correspondence with the *State Program of Treating Radioactive Substances (RS) in Ukraine in 2001-2020,* would choose the area for constructing the centralized storage of highly-active nuclear waste (CSHNW), make its design and begin its building. It is proposed to complete the erection of the underground laboratory for works with RS, and in 2021 to put in operation the first turn of CSHNW [65].

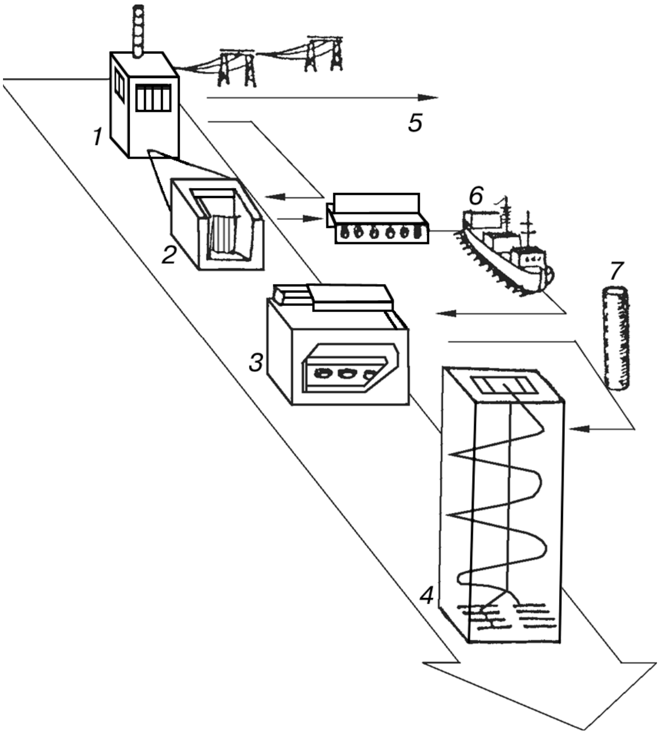

Fig. 26. Typical Sweden system of storage of the spent nuclear fuel [64]:
1 — nuclear fuel in operating reactor of NPP (5 yrs, 30 MW); *2* — spent nuclear fuel in cooling pond near the reactor (6–9 months 2 MW/t); *3* — central underground storage of the spent nuclear fuel after 30–40 yrs., (1kW/t); *4* — storage of geological type at the depth of 500 m after 1000 years (0.1 kW of residual power release); *5* — Final burying of radioactive waste of NPP; *6* — waste delivery in a special container on the vessel; *7* — transfer of radioactive waste into copper container for burying

Nowadays Ukraine has six special sites called burials for storage of RW. They are under the authority of State Enterprise *Radon*. Geography of special integrated plants-burials for RW is rather wide: Kyiv burial (the vil. of Pirogovo near Kyiv), Kharkov, Odesa, Donetsk, Dniepropetrovsk, Lvov burials. At these special objects RW are placed in containers, stored for certain time and then, in accordance with agreements with Russia, they are given up for selective processing aimed at separation of uranium $^{235}_{92}U$, $^{238}_{92}U$, plutonium $^{239}_{94}Pu$ nuclides and at obtaining pure compounds of nuclear fuel for reuse. Multistage standard chemical technologies of the Russian nuclear complex are used for these operations. NPP of Ukraine produce great amounts of RW containing primary amounts of nuclide $^{238}_{92}U$, about 50 %-burnt $^{235}_{92}U$ and formed radioactive fragments of $^{y}_{x}Me$ and $^{233}_{93}Np$ turning into plutonium $^{239}_{94}Pu$.

Since Ukraine is a nuclear state, possessing 16 nuclear power units (three units were in operation at Chernobyl NPP after the accident: the first and second units of this NPP were stopped in 1993–1997, and the third unit on December 15, 2000), generating great amount of RW; it is necessary to build specialized plants for their selective processing. Permanent storage of RW at six special plants is inexpedient for the state possessing NPPs with 16 nuclear units. Radioactive waste would be selectively separated at specialized plants, to release from RW the «fragmental» radioactive elements and nuclear fuel — uranium ${}^{235}_{92}$U, ${}^{238}_{92}$U and plutonium ${}^{239}_{94}$Pu nuclides with conditioning of ${}^{235}_{92}$U by enrichment up to the standard for making heat-releasing elements — fuel elements. It is necessary to develop more efficient methods of enrichment of uranium isotopes, to search for new technical decisions with the use of extraction and ion-exchange processes of hydrometallurgy to isolate «unburnt» uranium ${}^{235}_{92}$U, ${}^{238}_{92}$U, plutonium ${}^{239}_{94}$Pu nuclides and to obtain pure compounds of nuclear fuel components fit for fuel elements production. Selectively separated «fragmental» RW may be subjected to special treatment, e. g., vitrification aimed at their preservation and transfer into nonsoluble and nonvolatile compounds and «eternal» burying in bedrocks. These technologies can be implemented at one of the bankrupt chemico-metallurgical plants, using the experience of the plant *Mayak RT-1* (Russia). The volume of works would be fulfilled in the shortest terms, that will allow introducing CPNFC at NPP of Ukraine. Use of the latter will help to facilitate the situation with nuclear fuel. In our opinion the precipitation of hydroxides of radioactive «fragmental» metals from water solutions after selective isolation of uranium and plutonium isotopes with following production of fragmental elements oxides can serve as an example of the process of isolation of radioactive waste. When fusing these oxides with sand (SiO_2) one can obtain the glass block which may be stored «eternally» and in any conditions. At Russian integrated plant *Mayak* radioactive wastes are placed in aluminophosphate matrices containing radioactive waste with radiation intensity 250 MCi [64]. The incompetent great expenditures for burying and preservation of NPP waste will cause considerable rise in the cost of the whole cycle of electric energy generation at nuclear plants.

Nuclear energetics of Ukraine faces two problems now: liquidation of the after-effects of Chernobyl accident in such a way that to prevent from the threat of RW effect to the environment in the nearest centuries and to create a closed nuclear-fuel cycle for NPP in the third millennium.

There are three variants of solution of the former problem. As to the first variant, the I.V. Kurchatov Institute of Atomic Energy has developed a conception of stabilization of the «Shelter» object with its reconstruction as the overland long-term storage of RW with operation term of 200 years in order that future generations could process RW.

In accordance with the second variant, developed by IAEA and Power Ministry of Ukraine, there is a plan to make a cut and perform utilization of the Chernobyl NPP fourth unit goaf by industrial methods using the remote controlled devices. The above plan includes excavation, sorting of materials as to intensity of radioactive emission, selective extraction of concentrates of nuclear fuel and fragmental radioactive substances (FRS), supply of extracted nuclear fuel to specialized plants for additional treatment of concentrated uranium $^{238}_{92}$U, enrichment by $^{235}_{92}$U and isolation of plutonium $^{239}_{94}$Pu, and then for manufacturing of fuel elements; the building structural materials are put to special containers and placed to special storages. Then follows recultivation of the ground surface at the spot of the fourth unit of the Chernobyl NPP.

The third variant, developed by the Center of Environment Radiochemistry of the NAS of Ukraine, provides stabilization of the «Shelter» object by mean of the floating platform, its isolation in the capsule, nonpermiable for the ground waters; and at last the construction of a capacious mine at the depth of about 1000 m under the capsule. A capsule with a platform are to be buried in the mine. It would be noticed that the conception is the further development and detailed elaboration of the idea to bury the fourth Chernobyl unit at the depth of 1000 m offered first by the famous scholar, Academician A.D. Sakharov.

This variant is close to the project of burying the «Shelter» object developed by M. Morozov, Cand. Sc. (Eng.) [65]. He proposes a method and device for the underground automatic storage of weakly radioactive structural waste for undetermined term (unlimited in time) in the vicinity of waste formation. According to his project, a shaft 8 m in diameter and 1000 m deep with a skip hoist is constructed at a safe distance from the «Shelter». The shaft communicates with special storage (burial), 35 m in diameter and 25000 m^3 in volume. This storage in intended for storing about 50 000 t of radioactive building materials. The storage has another shaft with a belt conveyer for RW descending to the burial. The shaft is arranged at an angle of 10–20° with the horizon. Charging devices for RW are distributed in the immediate vicinity of the «Shelter». The concrete, which contains binders as well as graphite and boron additives for neutrons absorption, are delivered for layered placement of concrete in the RW storage in the vertical shaft in self-discharging skips. As the storage is filled the concrete mix with RW is compacted by layers with the help of electromechanical vibrators which are preliminarily attached to the inner storage walls. Electovibrators are remotedly controlled from the Earth surface as well as all the works conducted in the storage. The elements and variants of this project are considered in the patents and publications by M. Moroz [65]. The project implementation term is 10–15 years, and total cost does not exceed 200 million dollars.

When considering the problem of liquidation of the Chernobyl accident after-effects one would notice the following. There were 196 t of nuclear fuel in the fourth unit of Chernobyl NPP. There was an explosion as a result of «unwise treatment of the atom». The popularized illusion that the most amount of nuclear fuel remained in the reactor is a mistake. The explosion occurs on reaching critical pressure. The nuclear reactor casing is extremely strong. The noncontrolled nuclear reaction started in the reactor because of its incompetent control. As a result, the reactor temperature rose swiftly, the controlling rods regulating the reaction velocity fused. Temperature elevation led to interaction of zirconium shells (T_{meltZr} = 2133 K) with water with release of hydrogen (40 g of zirconium liberate $2 \cdot 22.4 = 44.8$ dm^3 of H_2 under normal conditions). Hydrogen pressure also increased swiftly and when it exceeded the hydrostatic one (atmospheric pressure $+h/10 = x$ atm, where h is the water column height) the most amount of water was displaced from the reactor. But the rest of water proved enough for zirconium shells could react with water with release of great amount of hydrogen which created, parallel with water vapours, the colossal pressure. Zirconium shells underwent a reaction as well as nuclear fuel (uranium-235, uranium-238, plutonium-239 and radioactive fragments — products of nuclear fuel elements which underwent chain reaction) and both became a fusion of multicomponent oxides and oxycarbide power. Under such conditions, pressure in the reactor casing was distributed uniformly in all volume. When pressure in the nuclear reactor reached critical point there occurred a powerful explosion which threw up the 200-tons coverplate of the reactor in such a way that it made a hole in the unit ceiling and roof and fell vertically on the reactor. There appeared a slot which connected the inner volume of the reactor which was under high pressure, with low external pressure, and most amount of the inner nuclear content of the reactor and even parts of its graphite coating which were then found on the building roof outbursted through that slot. In September 1986 m 149.7 t of radioactive graphite blocks and its fragments were thrown off the roof by soldiers-liquidators who worked with their bare hands [67].

The instantaneous hydrogen mixing with the air under the uncovering of white-red-hot reactor interior resulted in the hydrogen-oxygen explosion characterized by high-temperature colourless flame. Thus, as a result of these two successive explosions (technogenic explosion which led to hydrogen-oxygen one) practically most part of nuclear fuel (uranium, neptunium, plutonium, ameritium isotopes, radioactive fragments) was spread in the vicinities of the fourth nuclear unit of Chernobyl NPP, and the incandescent cloud of radioactive dust rushed into the sky for many kilometers. As a result of a double successive explosion only some part of nuclear fuel sank back to the reactor. Its considerable share in a form of radioactive dust cloud got to the atmosphere and polluted great territories of European continent. If the reactor had the devices which do not let dehumidification of operating spaces of fuel elements (operation space of the reactor) even oxidation of fuel elements with release of hydrogen led to formation of the kissel-like mass and no radioactive dust was formed under the explosion. This mass could only splash out and turn into wear-resistant abrasive under its drying (caking).

The model of destruction of the fourth power unit of the Chernobyl NPP was considered by the authors of [66]. It has been noticed that it was impossible to obtain information about the nuclear reactor state immediately after the accident because of complicated radiation conditions. Only 2 years after the accident it became possible «to look for the first time into the reactor shaft through the investigation boreholes using periscope and video cameras, and to find it empty» [67].

Thus, the nuclear reactor content has been melted and bursted out in the environment, and this is in agreement with the explosion model given by the author of the book. Investigations of the authors of [66] prove that the oxides of melted fuel elements (radionuclides) were partially restored to metal state. High temperature also led to the melting of structural materials and their dispersion. Metal components of the fusion cakes took a spherical shape, because of high surface tension, and formed particles of microscopic size. Thus, spherical radioactive, particles of metal ruthenium (T_{melt} = 2250 °C) and molybdenum (T_{melt} = 2617 °C) were found in Sweden. Melted masses of fuel elements, structural materials reached high temperatures (estimated values ~ 40 000 °C) [66] and were subjected to complex physico-chemical processes: evaporation, interaction in vapours, dispersion. turning in dust. Graphite blocks and dust were on the roofs and industrial areas between the second and third power units. In the process of the explosion graphite was separated from nuclear fuel. Graphite blocks were bursted out for hundreds of meters. As to nuclear fuel, it turned into dispersed particles, as affected by temperature, and. guided by impulse, rushed high into the air, forming a radioactive cloud, which reached European countries, leaving an empty nuclear reactor.

It is a great pity that mistakes in the reactor design, and first of all in its safety control, and incompetent management led to the epochal tragedy which has taken lives of thousands of people. However, there is no alternative to nuclear energetics. It is a high-tech field with acute response to the bungling and connivance. The fourth unit, today, is the object enclosing huge amounts of uranium and plutonium isotopes, exceeding their amount in a the volume unit of the reachest deposits, as well as fragmental radioactive elements. That is why, it is necessary to build a specialized plant for the processing of building materials and remains of the Chernobyl NPP fourth power unit reactor in the 30-km Chernobyl zone. This plant could selectively isolate uranium, plutonium and ameritium isotopes, using well-known standard technologies for their practical use by production of fuel elements. Besides, fragmental radioactive elements, isolated in a form fit for nitrification could be concentrated for their «eternal» burying. That is the only way to leave pure lands and Dnieper waters to our descendants. Using the atom energy on industrial scales, we have to master niceties of the science-intensive nuclear technology. No radioactive particles (ions, atoms, molecules, compounds) in the environment — that would be the principal law in the NPP operation.

The author of the work [12] thinks that only Russia, USA and England (in our opinion France and Japan as well) possess the worthy methods now capable to compete on the market of nuclear technologies. In the recent decade one can observe the aggravated competitive struggle for the right to construct new NPP in the nearest years which will cost above $50 \cdot 10^9$ dol. About 20–25 NPP of 1000 MW each could be built for the above sum. Growth of the production powers for the period made 5.5–5.9 %, and growth of nuclear energetics only 4.4 % [67].

Markets of the regions of East and South-East Asia extending their energy powers on the basis of construction of NPP are of special interest. As it was mentioned above China alone plans to build 45–50 NPP by 2020 for to solve their domestic energy problems. Russia is active on the market of Eastern Europe, delivering nuclear fuel for NPP in Germany and Switzerland, following long-term contracts. OSC *Elemash* (Electrostal town, Russia) plans to supply nuclear fuel to NPP of Iran, China and India. The Bush-Chany power doctrine is directed to averting the energy crisis in the USA. According to the doctrine all restrictions for modernization of 110 NPP operating in the USA have been removed and it is planned to construct a new 33rd high-productive NPP. It is also outlined to construct 1000 TES on organic fuel.

As was noticed above, creation of the closed nuclear fuel cycle is the most important programmed task of nuclear power engineering of Ukraine. A new branch of nuclear industry engaged in processing of radioactive waste of nuclear fuel would be created for this purpose. It is necessary to separate small volumes of fragmental radioactive elements for «eternal» burying, to extract selectively uranium and plutonium isotopes with bringing them up to the operational mark for production of fuel elements for thermal reactors ($^{235}_{92}U$) and fast reactors ($^{238}_{92}U$, $^{239}_{94}Pu$). All these works would be made in the shortest terms that will allow closing the cycles to obtain nuclear energy and regenerate (utilize) unburnt nuclear fuel, to realize the CNFC at NPP of Ukraine and then to obtain the highest efficiency and to decrease dependence of Ukraine on the sources of power carriers.

In conclusion, compare economic indices of operation of three types of electric power plant — steam-turbine plant on coal (STC) with the modern system of cleaning the exhausts (efficiency 35 %), steam-gas plant (SGP) on natural gas (efficiency 50 %) and NPP [68]. Estimated power of power plants is 1000 MW, cost of credit — 7% a year, sale-price of realized electric energy 6 c for 1 kWh [69].

Calculations have shown that under operation below 20 years it is more profitable to use TES with SYP on gas, from 20 to 30 years — TES on coal, and after 30-years operation the least expensive energy will be generated by NPP. Hence, it is clear that as far as organic fuel is exhausted, people will comprehend that there is no serious alternative to nuclear energetics. In this connection investments to nuclear energetics will increase. As it will be shown below, it would be rather promising to use hydrogen as heat-carrying medium. Complexes of nuclear-hydrogen energetics, the new high-tech field of science and industry will be designed and constructed. Investments in ecologically pure high-tech solar-hydrogen energetics will increase; power plants with renewable energy sources (wind, hydrothermal, solar energy, sea waves and ocean tides) with hydrogen as power — carrying medium will be used as well.

REFERENCES

[1] K. Ya. Kondratyev, K. S. Losev, Bull. Rus. Acad. Sc., No. 7 (2002) 592.
[2] L. F. Kozin, VI Int. Conf. Hydrogen Material Science and Chemistry of Metal Hydrides, Ketsiveli, Yalta, Ukraine, Sept. 2–8, 1999.
[3] V. I. Subtotin, Bull. Rus. Acad. Sc., No. 12 (2001) 1059.
[4] Yu. P. Yelagin, Atom. techn. abroad, No. 1 (1999) 9.
[5] C. Marcetti, N.N. Ponomarev-Stepnoy, Energy, No. 12 (1997) 5.
[6] V. Kukhar, Nauk. Svit, No. 8 (2000) 2.
[7] W. Schroter, K.-H. Lautenschlager, H. Bibrak, and A. Schnabel, Chemic, Leipzig, VEB Fachbuchverlag, Germany. 1986.
[8] V. N. Mikhailov, Bull. Rus. Acad. Sc., No. 2 (1998) 116.
[9] F. J. Reshetnikov, Ibid., No. 2 (2000) 17.
[10] H.-H. Rogner, Energy and the Challenge of Sustainability. World Energy Assessment, 2000, B5.
[11] L. F. Kozin, V. I. Trefilov, Rare-Metal Industry of Ukraine. Problems and Prospects, Inst. Material Sc. Problems Publ., Kyiv, 1998.
[12] E. Adamov, Russian Economic J., No. 5–6 (2000) 80.
[13] Energy, No. 2 (1997) 2.
[14] A. M. Sukhotin (ed.), Reference Book on Electrochemistry, Khimiya, Leningrad, 1981.
[15] V. A. Lebedev, V. I. Kober and L. F. Yamshchikov, Thermochemistry of Alloys of Rare-Earth and Actinoid Elements: Reference Book. Metallurgy, Chelyabinsk, 1989.
[16] M. Hansen, K. Anderko, Structure of Binary Alloys, Metallurgizdat, Moscow, Vol. 1, 2, 1962.
[17] R. P. Elliot, Structures of Binary Alloys, Metallurgiya, Moscow, Vol. 1, 2, 1970.
[18] F. Schank, Structures of Binary Alloys, Metallurgiya, Moscow, 1973.
[19] N.N. Ponomarev-Stepnoy, Energiya, No. 12 (1997) 5.
[20] World Coal, No. 2 (1998) 6.
[21] BWK: Breust, Warme-Kraft, No. 11/12 (1988) 8.
[22] E. A. Kotenko, V. N. Morozov, E. L. Petrov, et al., Gorn. Zhurn., (Mining), No. 12 (1999) 18.
[23] E. A. Kotenko, V. N. Morozov, E. L. Petrov, et al., Energiya, No. 5 (2000) 11.
[24] E. L. Petrov, I. D. Sergeyev, Underground Space for Nuclear Plant. Problems of Radiation Safety, A. N. Krylov TsNII, St. Petersbourg, 1983.
[25] E.A. Kotenko, Creation of Underground Nuclear Plants, TsNIIatominform, Moscow, 1996.
[26] O. E. Muratov, Energy, Economy, Technology, Ecology, No. 11 (2002) 9.
[27] F. M. Mitenkov, Bull. Rus. Acad. Sc., No. 6 (2003) 488.
[28] Ship Nuclear Power Plants, Moscow, Atomizdat, 1976.

[29] Ship Nuclear Power Plants of Foreign Countries, Sudostroyenie, Moscow, 1994.
[30] S.S. Abolin, V. M. Novikov, V. N. Prusakov, Nuclear-Hydrogen Energetics and Technology, Iss. 1 (1978) 126.
[31] V. A. Legasov, I. G. Belousov, N. K. Yerokhin, A. S. Doronin, Ibid., Iss. 2 (1979) 85.
[32] S. V. Volkov, J. Inorganic Chem., No. 11 (1990) 2789.
[33] L. E. McNcese, M. W. Rosenthal, Nucl. News, No. 2 (1974) 52.
[34] Yu. K. Delimarsky, Ion Melts in Modern Technology, Metallurgiya, Moscow, 1981.
[35] V. R. Blinkin, V. M. Novikov, Liquid-Salt Nuclear Reactors, Atomizdat, Moscow, 1978.
[36] J.N. Yakovlev, B.F. Myasoyedov, L.D. Dukhovenskaya, Radiokhimiya, No. 5 (1979) 687.
[37] P. Fangeras, A. Lecock, J. L. Blum, Trans. Amer. Nucl. Soc., No. 20 (1975) 703.
[38] V. N. Grebennik, N. N. Ponomarev-Stepnoy, V. V. Lebedev, Nucl. — Hydrogen Energetics and Technology, Iss. 4, 23.
[39] L. F. Kozin, VI Int. Conf. Hydrogen Materials Science and Chemistry of Metal Hydrides, Ketsiveli, Yalta, Ukraine. Sept. 2–8, 1999.
[40] S. V. Volkov, Ukr. Khim. Zhurn., No. 7 (1982) 675.
[41] S. V. Volkov, V. A. Legasov, A. V. Gorodysky, et al., A.c. 811867, USSR, MKI^3 C25 B 1/02, Electrolyte for Hydrogen Production. No. 9, 1981.
[42] O. G. Zarubitsky, V. A. Legasov, A. V. Gorodysky, et al., A.c. 1025184 USSR, MKI^3 C25 B1/02, Method of Hydrogen Production, No. 23, 1983.
[43] L. F. Kozin, V. A. Sakharenko, Ukr. Khim. Zhurn., No. 1 (1984) 9.
[44] L. F. Kozin, R. G. Sarmurzina, Zhurn. Prikladnaya Khimiya, No. 10 (1981) 21176.
[45] L. F. Kozin, Ye. O. Berezhny, B. V. Danil'tseva, VI Int. Conf. Hydrogen Materials Science and Chemistry of Metal Hydrides, Katsiveli, Yalta, Ukraine, Sept. 2–8, 1999.
[46] S. V. Volkov, Zhurn. Neorganicheskaya Khimiya, No. 1 (1980) 87.
[47] S. V. Volkov, Zhurn. Teoreticheskaya i Eksperimentalnaya Khimiya, No. 1 (1982) 3.
[48] S. V. Volkov, V. F. Grishchenko, Yu. K. Delimarsky, Coordination Chemistry of Salt Melts., Naukova Dumka, Kiev, 1985.
[49] S. V. Volkov, Zhurn. Neorganicheskaya Khimiya, No. 11 (1986) 2748.
[50] S. V. Volkov, Molten Saft Bull. Univ. de Provence, No. 35 (1988) 3.
[51] S. V. Volkov, Ion Melts and Solid Electrolytes, Iss. 4 (1983) 26.
[52] D. M. Gruen (ed.), The Chemistry of Fused Technology, Plenum Publ. Corp., New York, 1972.
[53] N. G. Basov, V. I. Subbotin, L. P. Feoktistov, Bull. Rus. Acad. Sc., No. 10 (1993) 878.
[54] V. Belokon, Inzhener, No. 9 (202) 3.
[55] R. I. Nigmatullin, Energy: Economics, Technology, Ecology, No. 3 (2003) 2.
[56] I. Larin, Energy: Economics, Technology, Ecology, No. 10 (2001) 10.
[57] B. B. Kadomtsev, Nuclear and Thermonuclear Energetics of the Future, Energoatomizdat, Moscow, 1987.
[58] B. B. Kadomtsev, V. I. Pistunovich, Nuclear and Thermonuclear Energetics of the Future, Energoatomizdat, Moscow, 1987.
[59] E. O. Adamov, V. I. Rachkov, Energy: Economics, Technology, Ecology, No. 1 (2001) 2.
[60] Press Service of RAS, Bull. Rus. Acad. Sc., No. 10 (1993) 946.
[61] V. N. Mikhailov, Bull. Rus. Acad. Sc., No. 2 (1998) 116.
[62] Yu. P. Semenov, V. M. Filin, B. A. Sokolov, et al. Bull. Rus. Acad. Sc., Energetika, No. 3 (2003)
[63] N. V. Selivanov, Problemy Nauki, No. 7 (2000) 44.
[64] E. Sobotovich, Bul. NAS of Ukraine. No. 3/4 (1998) 73.

[65] F. G. Reshetnikov, Ibid., No. 2 (2000) 117.
[66] M. Morozov, Svit, No. 17/8 (2000).
[67] A. P. Shpak, V. V. Trachevsky, V. L. Karbovsky, Actinoides in Technogenesis, Book 1, Akademperiodika, Kyiv, 2002.
[68] K. P. Chercherov. Energy: Economics, Technology, Ecology. No.6 (2002)10.
[69] K. Ya. Kondratyev, Bull. Rus. Acad. Sc., No. 9 (2000) 788.
[70] O. N. Favorsky, Bull. Rus. Acad. Sc., No. 4 (1989) 311.
[71] A. A. Makarov, World Energetics and Eurasian Energy Space, B. I., Moscow, 1998.

Chapter 5

Power Generation in the USA, Germany, Russia and Ukraine

5.1. Power Industry of the USA

The industrial and economic development of one or another country depends directly on its provision with energy carriers and on the level of its power industry. Nowadays, the world is conventionally divided into two groups of countries: the first group includes industrially developed countries, 16 % of the Earth population, 78 % of the world economy (global DGP) and 5 % of the world power consumption being concentrated in them. The first group also includes 84 % of R&D works. That is why the international markets of new expensive power technologies are controlled by the largest companies of industrially developed countries with 84 % of the world population, 22 % of the world economy, 45 % of the world power consumption, and only 6 % of R&D works.

The consumption of energy carriers (oil, natural gas, coal, renewable sources (RS), nuclear energetics) in industrial economically developed countries was $6.0191 \cdot 10^{11}$ kWh, in underdeveloped countries — $4.9781 \cdot 10^{11}$ kWh in 2000. The world production of hydrocarbon fuel (oil, natural gas, coal) reached $15 \cdot 10^9$ t of coventional fuel in 2000, that was 2.5 t c.f. per capita at an average. Power resources distribution and consumption in the world are nonuniform. The world oil consumption was $3.434 \cdot 10^9$ t c.f., in 2000, while prospected reserves grew to $140.134 \cdot 10^9$ t. The oil production in 2000 and 2020, by the estimates of International Power Agency, will be 4790 and $57\ 735 \cdot 10^6$ t, respectively. The USA consume 25 % of $15 \cdot 10^9$ t c.f. of hydrocarbon fuel produced in the world. The nature has almost deprived South Korea and Japan of power resources. Their import in these countries is 97.5 and 85 %, respectively.

Life quality (socionics) of population, as was noted in Chapter 3, characterized by the gross domestic product GDP, depends on the amount of power cousumption per capita. In 2000 the world GDP reached $43 \cdot 10^{12}$ USD, and that per capita — 7102 USD/man. Maximum GDP, equal to 42 000 USD/man at minimum power consumption, equal to 5.6 t c.f./man was reached in Switherland [1]. In Norway GDP, equal to 39 000 USD/man, was obtained under maximum power consumption in the world which was 13.6 t c.f./man. Such high energy consumption can be explained by climatic conditions (Norway is a «cold» country)

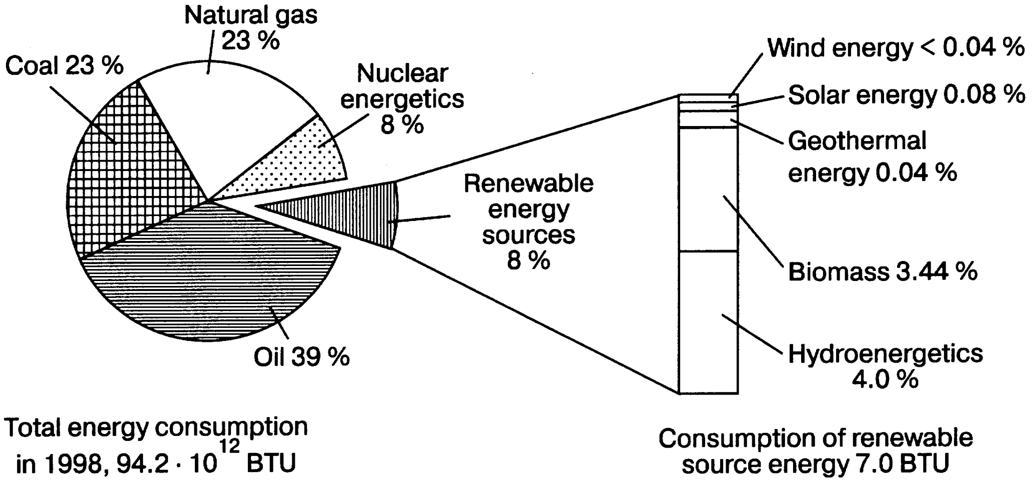

Fig. 27. Scheme of power consumption balance in the USA

and cheap electric energy. In the USA GDP was 34 000 USD/man at power consumption 11.6 t c.f./man in 2000. In the USA with only 4.3 % of the world population they consume 20 % of the world fuel and power as well as mineral resources [2]. A scheme of the consumption balance for fuel-and-power resources in the period of 1998–2000 in the USA is given in Fig. 27.

Data of the works [1–3] were used to draw this figure. Total power consumption in the USA in 1998 was 9938.1 · 10^{12} J (or 94.2 · 10^{12} Britain thermal units: 1.0 BTU is equal to 1055 J), the oil share was 39 %, coal — 23 %, natural gas — 23 %, nuclear energetics — 8 %. The share of renewable energy sources (RES) is 8 % in total, including (%): hydroenergetics — 4.0; biomass — 3.44; geothermal energy — 0.4; solar energy — 0.08; wind energy — < 0.04. The amount of electric power generated in the USA in 1998 and 1999 was 3212.2 and 3173.7 · 10^9 kWh, respectively, the share of coal in electric power generation being 57.5 and 55.7 % [3]. Solar energy conversion into electricity (photoelectrochemical systems — PhES), as well as into low-temperature (90–150 °C) or high-temperature (> 1200 °C) heat — solar collectors and stoves (SC and SS), though being a high-tech problem — is developed intensively in the USA, Germany and Russia. The total power of photoelectric systems (PhES) in the world has reached 65 MW. Two thirds of them fall on the share of the USA and Japan, and one third on Western Europe (France, Germany, etc.). Wind power plants (WPP) with total power 1.0–1.7 MW and crediting sum 1.0–3.0 · 10^9 USD/yr are installed in the USA during a year. In 2002 coal mining in the USA was 59.483 · 10^9 t. The domestic annual oil production is 323–350 million tons c.f., which is insufficient to satisfy the internal requirements, that is why import of raw oil in 1999 and 2000 was 3187 and 3320 million barrels (510–540 mill. t), respectively. Oil import in 2000 was 1.73 times more than in 1980 (1921 mill. bar.). The USA import oil and natural gas mainly from the Near East countries, Mexico, Brazil and other countries in the following annual volumes: oil — 560–580 mill. t o.e. and natural gas — 70–100 t o.e. It is predicted that in the nearest future the USA economy development will also depend on the import of energy carriers; oil import will be 776 and 837 mill. t o.e., and natural gas — 113 and 123 mill. t o.e., respectively, in 2010 and 2015. Coal import in the same years will be 15 and 17 mill. t o.e., electric energy — 5 and 4 mill. t o.e., respectively.

It is predicted that power consumption in the USA during next 20 years of the 21st century will increase by one third. It is supposed that 2/3 of coal requirements will be satisfied owing to its mining in the West of the USA. The USA will import about 1/3 of coal from the Near East and African countries and from Indonesia. Today the USA import low-sulphurous coal in the volume of 1.2 mill. t from Indonesia.

In 1997, $628.6 \cdot 10^9$ kWh were generated at 110 units of 32 NPP of the USA that was 20.1 % of the total amount of generated electric energy. In 1999 the USA shut-down 6 power units and performed some reconstructions, and thus the electric energy generation increased to $725.036 \cdot 10^9$ kWh, which corresponded to 22.8 % of the total generated power in the country. The share of energy (thermal and electric energy) generated by NPP in the USA relative to total energy is 8 %. The share of oil, natural gas and RES is 22.4 % of generated energy.

Electric power is generated by TES in the USA as well as in many countries of the world with efficiency exceeding inconsiderably 30 %. The USA government has set a task to develop and put in operation steam-gas plants with efficiency 60 %. Their designers are General Electric and Westinhouse [4]. Some foreign countries have reached efficiency 56–60 % and can reach then even 70–80 % as a result of reconstruction and successive increase of TES power. According to the State program of the USA *Sight of Energetics XXI* it is supposed to develop and realize in practice the power plants converting the organic fuel to various products and electric energy following the wasteless technologies. Energy from coal and oil will be obtained with efficiency no less than 60 %, and from natural gas with efficiency above 70 %. The fuel energy usage efficiency can be about 90 %.

It is clear from the data presented that the hydrocarbon fuel: oil, natural gas and coal, was the basic power source in the 90's of the 20th century. It is supposed that the share of electroenergetics on organic energy carriers will be on the level of 70 % in 2010–2020 [5]. In the world fuel-power balance the percentage of oil spent for power production is about 39.7 %, natural gas 23 % and hard coal 34.9 %. The share of RES in the international energetics will also increase, though slowly. As a whole, the share of electric energy in all consumed energy will be also 30 % at an average in industrially developed countries.

5.2. Power Industry of Germany

Germany is a rather power-consuming country (1.42 % (81.2 mill. people) of population, 0.26 % of territory to the world level). Consuming $1.193 \cdot 10^9$ t c.f. of primary energy carriers, power-generating plants of the country generate $3977.8 \cdot 10^9$ kWh of energy. A scheme of power consumption balance in Germany is given in Fig. 28. Oil (37.5 %), coal (24.8 %, of them 13.2 % — hard coal, 11.6 % — brown coal) and natural gas (21.7 %) are the major primary organic energy carriers. The share of nuclear power is 12.6 %, which corresponds to $5.012 \cdot 10^{11}$ kWh of electric power and heat. As to organic energy carriers, Germany possesses small reserves of oil and natural gas (about 50 deposits). The oil-gas deposit Ampfing and gas one — Easen are the largest among them. Annual natural gas production from Easen deposit is several tens of million m^3.

To meet requirements in organic energy carriers Germany imports natural gas and oil from Norway and Russia ($20.4 \cdot 10^9$ m^3 of natural gas and 14 mill.t of oil). But to avoid power dependence on other countries Germany develops intensively energetics based on renewable energy sources. With the help of RES they generated 3.4 % of the total country energy in 2002, that equaled $1.39 \cdot 10^{11}$ kWh. The greatest share of power obtained using RES falls on heat production from biomass — 1.722 %, that corresponds to $246.6 \cdot 10^{16}$ J of thermal energy of the total amount of energy generated in the country [6]. In accordance with the program of bioenergetics development in Germany in 2010, 5 % of thermal and 1.7 % of electric energy will be generated from biomass. The average amount of forest lands in Germany is 30 %, in some region it exceeds 40 %. Thus the firewood and firewood waste still remain a rather distributed form of fuel in the country-side.

The share of hydroenergetics in the country is 0.787 % ($3.132 \cdot 10^{10}$ kWh of electric energy). Wind energetics is also developed intensively in the country — its share in 2002 was 0.563 % ($2.24 \cdot 10^{10}$ kWh of electric energy). As was noted above in Chapter 2 (paragrap 2.3), 8500 wind power plants (WPP) with total power 5000 MW are working in Germany now. The WPP power in Germany equals a half of all NPP powers in Europe and one third of WPP in the world. The wind energetics is developed especially intensively in the region of lands adjacent to the North Sea, for example, in the Mehlenburg-Vorpommen, Rostok, etc., lands as well as in the northern part of Berlin region. There is a project of construction of the first off-shore WPP *Borkum West* at the distance of 45 km from the coast. The installed power of WPP is 60 MW (12 windturbines 5 MW each). The project designer is *Prokon Nord Energiesysteme GmbH* company. The investments to the first phase of the pilot project are estimated as 125–140 mill. Euro. The construction beginning is planned for 2003. The technologies being developed, it is planned to construct the off-shore WPP with total installed power 1000 MW. The installed power of WPP in Germany increases

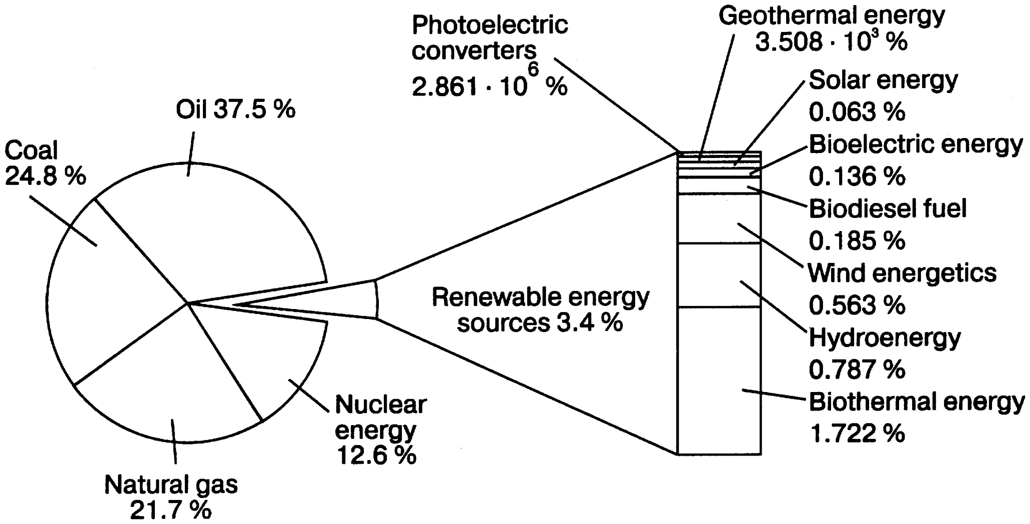

Fig. 28. Scheme of power consumption balance in Germany

annually by 40 %. The installed power of WPP reached 12 GW in 2003. It is predicted that by 2010 the installed WPP power will reach 20 GW, that will be 10 % of the country energy balance. Germany has become a recognized leader in the field of WPP. It is considered that wind energetics in Germany is the most profitable and accessible trend of the development of the branch of renewable energy sources. Today WPP make the multimilliard business in Germany.

Solar energetics (0.063 %, $2.506 \cdot 10^9$ kWh of energy) and geothermal energetics ($3.50 \cdot 10^{-3}$ %, $1.392 \cdot 10^9$ kWh of energy) are young trends of energetics for Germany as well as for Europe. And though their development is not high it is rather dynamic [6]. The first project in Germany in the field of solar energy conversion and creation of photoelectric systems (PhES) was the project «1000 Roofs» realized in 1989–1994. By this project 2250 houses were equipped with PhES, which average power was 2.6 kW and total 6 MW. The system cost was about 15 000 USD for 1 kWh. But 70 % of expenditures were compensated. In the process of the program implementation the solar systems were modernized that resulted in the decrease of their cost and favoured a considerable growth of popularity of PhES technologies. The second project in the field of PhES implemented in Germany from 1999 was called «10 000 roofs». The total power of PhES of 9 MW was realized in 1999. In 2000 Germany acquired 615 000 m^2 of solar energy converters into electricity and solar collectors to generate heat from producers of other countries, in 2001 they bought 900 000 m^2 more of solar systems. Nowadays 45.13 m^2 of solar collectors fall on 1000 dwellers in Germany [7]. Projects of solar power plants of 50 kW and 200 MW have been developed by German company *Schleich Bergermann und Purtner* [8]. The construction costs of the solar power plant of 200 MW are 1 million USD. The largest world PhES with total power 2 MW, area 63 000 m^2 has been constructed in Munchen; 7560 solar modules of photoelectric cells have been installed in that area. Solar energetics is also developed in other countries of Central Europe, especially in Austria, Greece, France. German government pursues the successive policy of the use of RES. They make State programs providing the compensation of expenses under elaboration of RES plants for generation of electric and thermal energy, and commercial stimulation of development of practical use of RES for energy generation. There exists a system of grants (interest-less) for stimulation of investigations in the field of bioenergetics. For the period of 1990–1999 about 118 mill. Euro were used for the purpose-oriented grants in Bavaria only. It is predicted that the share of RES in Germany relative to the total generated energy will increase to 12.5 % by 2010 and will reach 50 % by 2050.

5.3. Power Industry in Russia

From the data of [2] 32 % of natural gas, 12 % of oil, 12 % of hard coal and 22 % of forests are the share of Russia in the world energy sources. According to other data (see, Ch. 3) Russia possesses 5 % of the world reserves of oil. Production of primary fuel-energy resources (TES) was 1414 mill. t c.f. in 2000 [9–11], including: natural gas — $584 \cdot 10^9$ m^3, oil — $324 \cdot 10^6$ t, coal — $258 \cdot 10^6$ t. Energy production was $878 \cdot 10^9$ kWh. Of them, $130.7 \cdot 10^9$ kWh were generated by 29 NPP, $165.4 \cdot 10^9$ kWh by HES and the rest by TES and RES. Export of fuel-energy resources was $532 \cdot 10^9$ t c.f. in 2000.

A scheme of consumption balance of power resources in Russian is given in Fig. 29. It is seen that the amounts of natural gas and oil produced in 2000 are 41 % and 24.08 %, respectively, relative to the total amount of energy carriers.

Export of natural gas is 33–40 % (in 2001 — $106.5 \cdot 10^9$ m^3) and oil about 50 %. Main consumers of Russian gas in 2001 are as follows: Germany — $20.4 \cdot 10^9$ m^3, Italy — $13.5 \cdot 10^9$ m^3, Ukraine — $18.7 \cdot 10^9$ m^3. It is predicted that export of Russian gas to Turkey will increase from $3 \cdot 10^9$ m^3 in 2001 to $16 \cdot 10^9$ m^3 in 2010. As a whole, the share of Russian natural gas relative to its total consumption volume on European market is above 25 % now. Russia is also one of the main natural gas exporters to the countries of Asian-Pacific region (APR). Thus, the gas branch of Russia is one of strategic branches of the country economy, its export being a source of considerable the budget revenue.

The largest consumers of Russian oil are the following countries: Germany ($14 \cdot 10^6$ t), Italy ($11.5 \cdot 10^6$ t), Netherlands ($11.2 \cdot 10^6$ t), Poland ($9.9 \cdot 10^6$ t) and Ukraine ($12.15 \cdot 10^9$ t). Russia also exports oil to the countries of APR. The mining and consumption of hard coal in Russia is 8 %. Heat and electric power generation at NPP is 7.0 %.

The share of renewable energy sources in Russia was 19.92 %. The share of electric energy generated by HES is 18.8–19.4 % ($165.4–169.94 \cdot 10^9$), by use of biomass — 0.51% ($4.5 \cdot 10^9$ kWh), by geothermal electric power plants

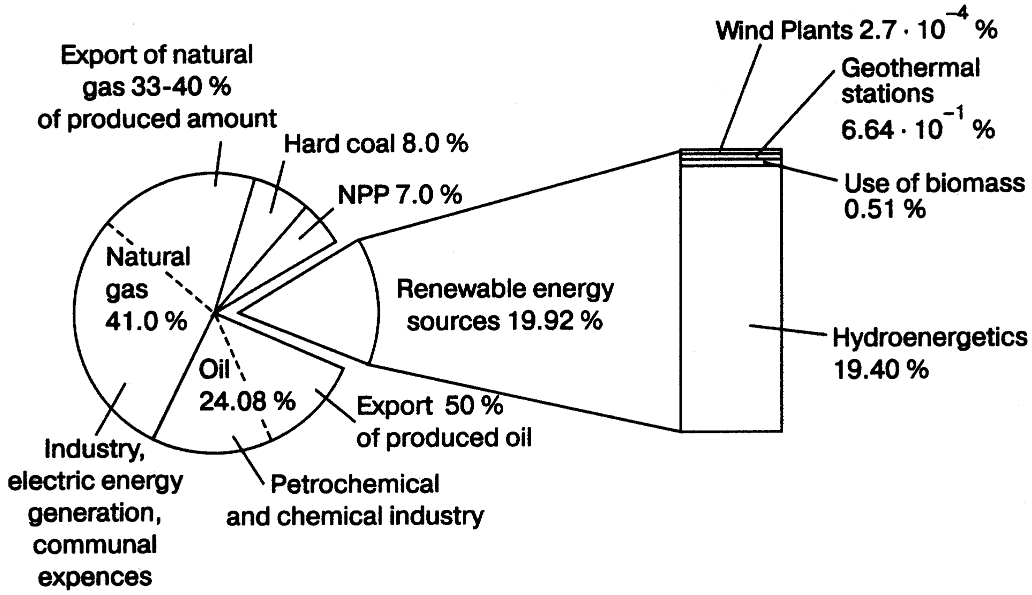

Fig. 29. Scheme of power consumption balance in Russia

($6.64 \cdot 10^{3}$ %), ($58.2 \cdot 10^{6}$ kWh) and $2.17 \cdot 10^{-4}$ % ($1.9 \cdot 10^{6}$ kWh) [11] by wind power plants. Russian RES electric power plants (wind power plants, Geo-TES, TES on biomass, minor HES) generated $6.860 \cdot 10^{9}$ kWh of electric energy in 2000, that is 0.783 % of its total generation — $878 \cdot 10^{9}$ kWh.

It is evident from the presented data that approximately 1/5 of electric energy in Russia is generated with the use of renewable energy sources. The share of electric energy generated using wind electric power plants (WPP), GeoTES, minor HES and BioHES is low. But their part in the national economy is great, since they are often arranged in unaccessible places where it is difficult to supply organic energy carriers. One can estimate the volumes of substitution of organic energy carriers by renewable energy sources under energy generation. It is known that the specific consumption of organic fuel under power generation is 380 g c.f./kWh. Then, the total volume of substituted organic fuel under generation of $6.860 \cdot 10^{9}$ kWh of electric energy in 2000 was: $6.860 \cdot 10^{9} \times 380 \cdot 10^{-6} = 2.607 \cdot 10^{6}$ t c.f. Under thermal power generation this value is about $8 \cdot 10^{6}$ t c.f. owing to RES.

Calculations have shown that the renewable energy sources in Russia have a potential equal to $270 \cdot 10^{6}$ t c.f., i.e., exceeding 25 % of domestic energy consumption [10]. These are two-three kinds of RES which use is most efficient in each territory area of Russia. For example, there are such energy zones in the territory of Russia with the area (by *Atlas of Wind Potential of Russia*) above $6.1 \cdot 10^{6}$ km^{2} where gross wind energy potential is estimated as $9.0 \cdot 10^{16}$ kWh/yr, technological — $8.3 \cdot 10^{16}$, economic — $5.4 \cdot 10^{10}$ kWh/yr. These are the coast and islands of the Arctic Ocean from the Kola Peninsula to Kamchatka

Peninsula, the Lower and Middle Volga River areas, the coast of the Baltic, Caspian and Black Seas; Karelia, Tuva, Altai, the Baikal, Far East Coast and Sakhalin Island. The wind power resources of most regions as a whole exceed hundreds of times the population demand for thermal and electric energy. All that causes the intensive researches and R&D works carried out in Russia concerning «operational» electric power stations on renewable energy sources. They attract productive powers of the military-industrial complex for creation of specialized centers of minor energetics with the use of RES.

It is predicted that power consumption in Russia will increase from 900 mill. t c.f. in 2000 to 1160 [11] and to 1840 mill. t c.f. in 2020 [12] which will be 22.5–51.1 %. Electric energy production will increase from $878 \cdot 10^9$ kWh to $1156 \cdot 10^6$ kWh, i.e., by 24 %. Results of moderate prediction version of production and consumption of fuel-energy resources of Russia and their export to other countries in 2000 and in the period of 2020–2050 made using the data of the works [11–12] are presented in Table 17. As is seen, in the period from 2000 to 2020–2050 the natural gas production will reach its shallow maximum in 2020–2030, corresponding to $700 \cdot 10^9$ m^3.

Consumption of natural gas, beginning from 2020, will regularly decrease to 488 t c.f. in 2050. Production of oil and gas condensate will decrease to $260 \cdot 10^6$ t c.f. (a decrease will be 19 % in 2050), while consumption will grow (increase by 38.4 %, compared to 2000). Coal mining in the volume of $800 \cdot 10^6$ t will provide growth of carbon energy carrier by 310 % compared with 2000.

An analysis of the data of Table 17 shows, that oil export from Russia to the international market will decrease ≈ 4 times by 2050. The latter proves that the «gas pause» both in Russia and in the world will be completed in the nearest 10–15 years and the world would transfer to the gas-coal structure of power economy already existing in the USA. From the data of the author of [13] three power-industry structures have changed in Russia during 80 years of the 20th century. The period from 1913 to 1965 was that of coal (the latter took 48–60 % in the energy balance), the years 1965–1985 were the period of oil (36–56 %, respectively) then came the period of natural gas (36–50 %). Scientific researches of the last years prove that the 21st century will become the period of coal and gas. Coal mining has increased in the world with the beginning of the new century. To lower the expenditures for coal transport by railway they began developing coal pipelines (2–3 thou. km and above) for the export of hydrocoal fuel (the hard/liquid fuel ratio 3:2). Such coal pipelines can supply energy carriers to the powerful domestic coal terminals under construction (Ust-Luga in Baltics, etc.) as well as to the countries with fuel deficit: Turkey, Greece, Italy, Germany, Denmark, etc. [13].

The water-coal fuel obtained on the basis of grinded coal, water, chemical additives, distinguished by high ecologicity, stability and plasticity can be directly burnt in boilers and boiler units of any power, operating in the power units

Table 17

Production, consumption and export to other countries of the fuel-energy resources of Russia in 2000, and prediction for 2000—2050

Index	Years				
	2000	2020	2030	2040	2050
Production total 10^6 t c.f.	1414	1625	1695	1740	1840
Natural gas 10^9 m^3	584	700	700	650	620
Oil 10^6 t	324	306	300	270	260
Coal 10^6 t	258	370	460	630	800
Hydroenergy, TWh*	168	203	218	225	228
Nuclear energy, TWh	131	206	250	340	400
Consumption total 10^6 t c.f.	890	1065	1265	1400	1540
Natural gas	434	541	539	504	488
Oil	186	241	264	289	302
Coal	59	66	66	63	56
Hydroenergy	155	183	196	191	193
Nuclear Energy	47	75	91	122	146
RES	3	8	13	16	34
Export total 10^6 t	525	500	470	390	360
Natural gas 10^9 m^3	215	235	240	230	230
Oil and oil products 10^6 t	189	137	116	67	48
Coal 10^6 t	35	18	15	13	13
Electric energy kWh	13	20	22	34	35

*T – tera – corresponds to 10^{12}; TWh equals 10^{12} Wh or 10^9 kWh.

with turbines of 300–500–800 MW. Power technologies with the use of water-coal fuel are ecologically pure processes resolving the transport-power problems of the 21st century [13]. Reserves of «high-tech» coals in Russia are 60 % of $210 \cdot 10^9$ t on the state balance. The amount of coal only in the deposits with «high-tech» reserves is sufficient to provide the annual mining in the volume no less than $500 \cdot 10^6$ t for several hundred years. According to [13] the natural gas and oil in Russia will last only for decades.

That is why it is planned to construct 1159 power plants using renewable energy sources in Russia [11] by 2020. The construction of such plants requires $47.7 \cdot 10^9$ USD. The constructed plants on RES will generate $2000 \cdot 10^9$ kWh which will cost $54.9 \cdot 10^9$ USD. The volume of substituted fuel will be $57.055 \cdot 10^6$ t c.f./yr and economic efficiency of the replaced fuel will be $28.4409 \cdot 10^9$ USD. The income from realization of energy generated using RES will be $32.9 \cdot 10^9$ USD. From the data of [12] the RES consumption for energy generation will increase 11.3 times by 2050 compared to 2000.

It would be noted that in the recent time most industrial countries of the world which energetics and, thus, industrial production, in the late 20th century were often subject to the crisis shocks (determined by the deficit and growth of prices for organic energy carriers) elaborate actively the technologies and construct power plants to generate energy with the use of RES. Economic analysis shows that even now the cost of electric energy generated with the use of RES at most power plants is at the level of cost of energy generated by traditional power sources: TES, NPP, etc. The electric energy from traditional power generators has a steady tendency to the rise in price. Thus the specific capital investments under the constructions of RES have increased from 750 dol/kWh to 1000–1100 dol/kWh, and at NPP from 1500 to 2200 dol/kW. At the same time, the construction of power plants with the use of RES is accompanied continuously by the decrease of capital investments. During the last 20 years specific capital investments to the wind plants constructed abroad have decreased from 4000 dol. for 1 kW in 1981 to 980 dol. for 1 kW in 2000. The cost of photoelectric modules has leveled down from 20000 dol. in 1980 to 3–4 thou. dol. in 2000 [10]. The price for power generated by wind plants also decreases. For example, price for power generated by RES in Denmark has decreased from 0.13 ecu in 1980 to 0.035 ecu for 1 kWh of electric energy in 1998. The cost of electric energy generated at coal TES has increased for the same period from 0.045 ecu to 0.05 ecu/kWh [10].

Broad use of RES to generate electric power and heat will decrease considerably the consumption of primary energy carriers in Russia.

5.4. Power Industry of Ukraine

Organic energy carriers and nuclear power industry. The consumption of primary energy carriers in 2001 in Ukraine was $161.5 \cdot 10^6$ t c.f., the share of natural gas, coal and coal products, oil and oil products was $88.5 \cdot 10^6$ t c.f. (44.6 %), $52.6 \cdot 10^6$ t c.f. (26.6 %), $20.4 \cdot 10^6$ t c.f. (10.3 %). In 1998 consumption of primary energy carriers was $134 \cdot 10^6$ t c.f. In this case the share of natural gas was 46.0 %, oil — 10.7 %, and coal — 27.5 %; the rest was the share of nuclear fuel and RES. Ukraine occupies the sixth place in the world as to the volume of consumed gas after the USA, Russia, Canada, Germany and United Kingdom. A detailed analysis of power resource consumption in Ukraine was performed by the authors of [14, 15]. As is evident from Table 18 of organic energy carriers only coal mining exceeds its demand (in 1998 by 21.4 %, in 2001 by 57.4 %). Only in 1995 coal deficit was 10.3 %. But it would be noticed that, beginning from 1975, one could observe a continuous decrease of coal mining and growth of consumption of natural gas and oil products. The natural gas and oil production in 2001 was $18.3 \cdot 10^9$ m^3 and $3.7 \cdot 10^6$ t, respectively [16]. The demand for natural gas in the 90's and in 2001 were $88.5–98.0 \cdot 10^9$ m^3 and oil $20.4–33.9 \cdot 10^6$ t. In this period the deficit of gas demand in Ukraine was

Table 18

Consumption of primary fuel -energy resources (FER) and electric energy generation by HES, TES, NPP in Ukraine in 1975 —2001 (10^6 t)

Resources	Years						
	1975	1980	1985	1990	1995	1998	2001
FER, total	287.4	323.1	349.4	353.0	226.3	138.1	161.5
Coal*	136/216	130/197	108/189	93/165	927/84	605/77	526/84
Gas^{2}*	136/68.7	83/56.7	113/42.9	136/28	98/18.2	88/18.0	88/18.3
Oil^{3}*	66.2/12.8	86.5/7.5	90.5/15.8	79.9/5.3	33.9/4.1	20.4/3.9	20.4/37
HES^{4}*	9.7	13.4	10.7	10.7	10.2	15.9	122
TES^{4}*	184.9	208.4	208.0	211.6	113.3	81.7	84.6
NPP^{4}*		14.2	53.3	76.2	70.5	75.2	76.2
Other fuel	13.3	14.6	16.5	15.7	6.5	5.6	4.7

* Coal, natural gas, oil — consumption in numerator, production in denominator by [16]; ^{2}* Natural gas; ^{3}* Oil and oil products; ^{4}* Electric energy generated at HES, TES, NPP, 10^{9} kWh.

80–90 · 10^9 m^3. Production and consumption of oil also sharply decreased at that time: only 3.7 · 10^6 t of oil, including gas condensate, were produced in 2001 [16]. Gas and oil demand was satisfied by import from Russia.

Because of the decrease of coal use for electric energy generation as well as for chemical and metallurgy industries, Ukraine imported huge amounts of natural gas which reached 80–86 · 10^9 m^3 [15] from Russia, beginning from 1990 [15]. In the opinion of the authors of [15] there were created «paradoxical proportion in fuel balances of Ukraine, when natural gas, 75 % of which is imported from one country (Russia), occupies the first place as to consumption volume that is about 45 % of the total consumption of primary energy resources». It is interesting that in 1990–1991, at high volumes of electric energy generation (298.5 · 10^9 kWh in 1990), the share of coal consumption was below the average world indices. The priority use of natural gas (34 %) and nuclear fuel (25 %) in Ukraine exceeded the average world indices of energetics of numerous countries. But after the disintegration of the USSR the electric energy generation at TES sharply decreased because of the gas fuel deficit.

All power stations of Ukraine generated 173.0 · 10^9 kWh of electric energy in 2001. Under these conditions TES, consuming natural gas and partially coal, have generated 84.6 · 10^9 kWh, NPP-76.2 and HES-12.2 · 10^9 kWh of electric energy. The authors [15] concerned that in Ukraine, rich with coal, the share of coal use for generation of electric energy (27.1 %) is 1.5 times lower than the world average index (39.6 % in 1990) and 2.4–2.8 times lower than this index in the USA and Eastern Europe which provide themselves with necessary volumes of coal.

Geographical position of Ukraine (in the centre of Europe), and infrastructure of gas- and oil-transport systems through its territory [14] favours its provision with natural gas and oil. Gas-transport system (GTS) of Ukraine was created as a part of a single system of Ukraine and Russia oriented to natural gas transport from the USSR to Western Europe. The GTS is 37 100 km long and is provided with the modern rather efficient equipment (compressor plants, etc.). The cost of Ukraine GTS funds is $15 \cdot 10^9$ USD. Volumes of natural gas supplied to Western Europe in 1997–2000 were $212.2–239.3 \cdot 10^9$ m^3/yr, to Turkey — $110.5–112.3 \cdot 10^9$ m^3/yr [14] during the same period. New long gas mains to Romania are constructed; routes of gas supply from Peri-Caspian region, Kazakhstan, Turkmenistan, and even Iran to Western Europe are under discussion.

The extent of oil-transport system [OTS] of Ukraine is 4750 km [14]. OTS is supplied by 37 oil-pumping plants with total power 350 000 kW. The OTS input capacity is 100 mill. t and output capacity 70 mill. t. In the recent years oil export transit was 53–55 mill. t/yr. New OTS routes are designed. The oil main Odessa-Brody, 673 km long, has been constructed. This main can allow more economical oil supply to Poland, Germany and Czechia, as well as to Ukrainian oil-refining plants.

Thermal and electric energy is generated now in Ukraine by TES (about 54.5–57.1 %), NPP (39.6–42.2 %) and HES (5.3–7.0 %) (Fig. 30). Renewable sources of energy — wind, solar (photochemical conversion), electrochemical (accumulators, fuel elements) energy in 2001 provided generation of less than 1 % of energy, and hydroenergy share was 7.05 % of electric energy, though the share of hydroelectroenergy is usually 5.3 %. Power complexes of Ukraine possess high installed powers.

The evolution of development of energy powers of HES, NPP, and TES in Ukraine in the period of 1970–1998 is presented in Fig. 31. The plot was made using the data of *Statistical Annual of Ukraine* for 1980–2001 [16].

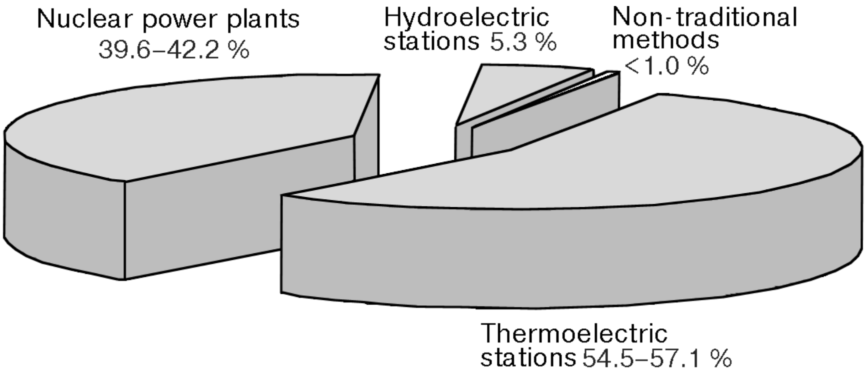

Fig. 30. Electric energy generation by NPP, TES and HES of Ukraine

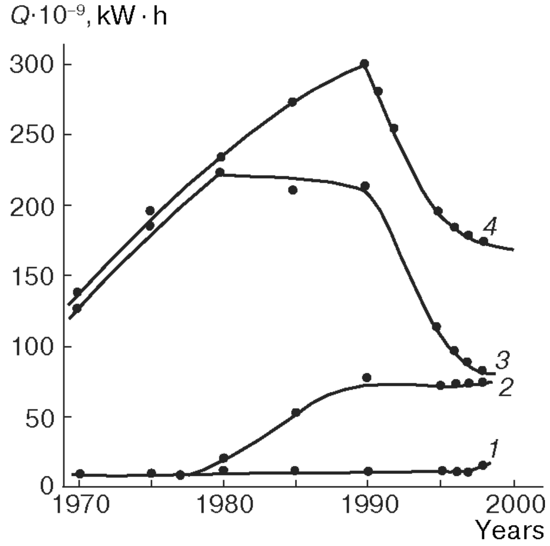

Fig. 31. Dynamics of changes of installed powers of electric energy generation by HES (*1*), NPP (*2*), TES (*3*) and total installed powers in Ukraine (*4*).

One can see a distinct, progressive growth of installed energy-generating powers of thermal electric stations up to the 1980's, and active growth of installed powers of the NPP power units up to the 90's. Five NPP were constructed in Ukraine in the period from 1977 to 1990: Zaporozhie plant with five water-moderated power reactors of WMPR-1000 type (the sixth reactor was put in operation in 1995), South-Ukrainian NPP with three reactors WMPR-1000, Rovno NPP with two reactors WMPR-440 and one reactor WMPR-1000, Chernobyl NPP with three reactors WMPR-1000, as well as Khmelnitsky NPP with one nuclear reactor WMPR-1000. Nowadays, when Chernobyl NPP three units are shut-down, the electric power of NPP decreased from 14 818 MW to 11 800 MW.

It is seen from Fig. 31, that the total quantity of generated electric energy regularly increased up to 1990. In the period from 1990 to 1995 one could observe the avalanche recession of electric energy generation by TES which was determined by the deficit of fuel as a result of lowering the supply of hydrocarbon energy carriers — oil (by 22 %), natural gas (by 35 %), turf (by 31 %), and coal (by 49 %) [16]. Electric energy generation by NPP and HES remained stable, and in 1998 it was 75.2 and $15.9 \cdot 10^9$ kWh. Nuclear energetics which arised on industrial scales in Ukraine in 1977, developed intensively, and even now, under the conditions of economic recession it occupies the most important place in the country economy. The decrease of the country provision with energy carriers (oil, natural gas and coal) and with electric energy led to the decline of industrial and agricultural production and to catastrophic decrease of the living standards of Ukrainian people. Even in 1991 Ukraine generated 5700 kWh/yr of electric energy per capita and stood among the developed states of the world

Table 19

Energy consumption per capita in different countries in the beginning of the 1990's

Country	Energy consumption, kWh	Country	Energy consumption, kWh
India	270	France	7100
China	500	Germany	7200
Iran	800	USA	12 000
Japan	5600	Norway	16 000
Ukraine	5700	Sweden	16 000
Russia	7000	Canada	16 000

(Table 19), Power availability of Ukraine exceeded the level of Japan. Even now, Ukraine occupies the fifth place in Europe and seventh place in the world as to the number of power units [17]. There are 439 nuclear reactors (from the data of the work [18] — 444, [19] — 437, [20] — 429) which continue functioning now in the world, and thus, the share of Ukraine (with population less than 1 % of the world population) is 3.66 % of nuclear energy generated in the world. Beginning from 1995 NPP of Ukraine generate $70.5–75.2 \cdot 10^9$ kWh/yr of electric energy, that is from 39.6 to 42.2 % of the total generation of electric energy ($172.8–178.0 \cdot 10^9$ kWh) in Ukraine. Only nuclear plants were put in operation in Ukraine from 1974 to 1990 (during recent 16 years).

The electric energy generation dynamics in Ukraine during the last years looks as follows: 1990 — 298.4; 1991 — 278.0; 1992 — 252.6; 1995 — 192.4; 1998 — $172.8 \cdot 10^9$ kWh (Fig. 32). The Chernobyl NPP catastrophe caused moratorium for the construction of new NPP which was in force in Ukraine from August 1990 to October 1993. The after-effects of accidents at nuclear power plants led to toughening of their safety requirements all over the world and to the decrease in construction rates. Thus, the construction and putting in operation of the sixth unit of the Zaporozhie NPP with light-water reactor WMPR-1000 continued above 9 years (from 06.1986 to 19.10.1995), instead of ordinary 4–5 years, up to 1986. The South Ukrainian and Rovno NPP possessing 3 units each, as well as Khmelnitsky NPP with 1 instead of 6 designed power units are unfinished. The estimated cost of the finishing and putting in operation of new units at the Rovno and Khmelnitsky NPP from the data of [17] is $0.840–1.3 \cdot 10^9$ USD.

Electric energy generation at thermal and city regional electric power stations (CRES) of Ukraine [21] proved to be in deep crisis. Prime cost of electric energy generated by TES and CRES is determined by their distribution near the basic fuel source — coal. The prime cost of electric energy generated by TES and CRES has rised because of fuel transporting and excessively increased railway

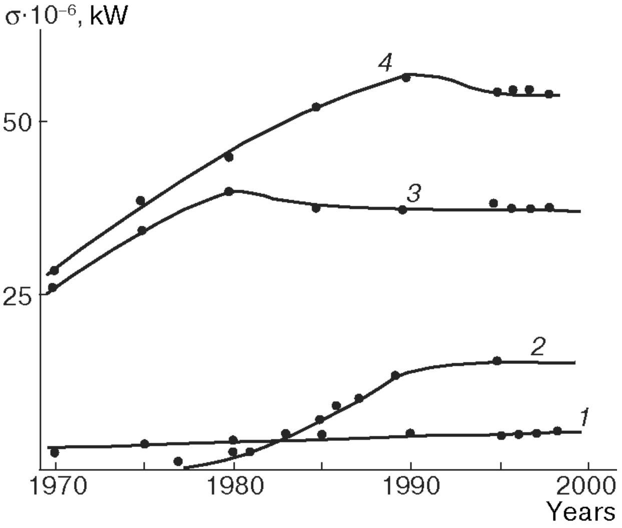

Fig. 32. Growth dynamics of electric energy generation by HES (*1*), NPP (*2*), TES (*3*) and total electric energy production in Ukraine (*4*).

cargo tariffs. That caused the construction of TES in the vicinity of coal mines in the former USSR. The two largest in Europe Zaporozhie and Uglegorsk TES, $3.6 \cdot 10^6$ kW each, have been constructed in Donbas — the centre of coal-mining region. The construction of new TES in Ukraine and in the European part of the USSR was considered unexpedient because of the lack of inexpensive local fuel. It was supposed that the available conception could be revised only with discovering the deposits of combustible slates in the European part of the USSR [22]. To meet the requirements of industry and public services of Ukraine in electric energy they relied on the construction of NPP. It was planned to build 68 nuclear reactors-«millionaires» in the territory of the USSR European part. The plans have not been realized both because of the Chernobyl catastrophe and disintegration of the USSR.

The operation resource of nuclear power units with reactors WMPR-440 and WMPR-1000 is 30 years and the operation term of the constructed reactors ends in 2010. (But there are precedents for increasing the NPP functioning to 60 years). *Energy Program of Ukraine* has been developed and adopted by the Supreme Council of Ukraine for the period before 2010. The considerable decrease of Ukraine energetics dependence on oil and gas import, decrease of expenditures for fuel and maximum reduction of harmful ejections to the environment are main tasks of the Program [23]. As follows from Table 20, Ukraine possesses only 42–50 % of domestic fuel resources. Thus the country demand for energy carriers is satisfied at the expense of import of 20 million tons of coal (though the domestic coal industry can satisfy the demand), $60–80 \cdot 10^9$ m^3 of natural gas, 12–15 mill. t of oil and 300 t of uranium fuel which cost about 10 milliard USD [17]. Only 79.4–80.7 % of

Table 20

Ukraine provision with domestic energy carriers and their import

Energy carrier	Domestic production of energy carriers		Necessary annual import of energy carriers
	10^6 t, 10^9 m^3*	%	
Coal	77.2—83.3	79.4–80.7	$20 \cdot 10^6$ t
Natural gas	18.3	24.9	$60 \cdot 10^9$ m^3
Oil	3.8	25.3—31.6	12—15 $\cdot 10^6$ t
Uranium fuel	—	—	300 t
Total	42—50	42—50	Total cost of import — 10^9 USD/yr

* Natural gas in 10^9 m^3.

demand in coal, 24.9 % — in natural gas and 25.3–31.6 % in oil are satisfied by domestic industry. Natural gas is used as energy carrier, and oil — for production of the basic kinds of oil products (gasoline, diesel fuel, reactive fuel and mazut).

Table 21 presents data on natural gas consumption in 2000 and prediction of gas consumption in electric energy production in the period of 2005–2030 from the data of the work [14]. As is evident, in 2000 24.4 % of Ukraine demand for natural gas was satisfied by domestic production. The author of [14] predicts that gas consumption in the period of 2005–2030 will increase from 70.0–71.0 to $137 \cdot 10^9$ m^3, i.e. by 48.5 %. Thus, only 18.2–21.2 % of gas consumption will be satisfied by domestic production in 2020–2030.

It follows from the data given in Table 20 and 21 that the highest share of import falls on natural gas and oil, though not only ordinary thermal but also nuclear fuel cycle are not satisfied by energy carriers in Ukraine. In this connection it is possible to decrease the dependence of Ukrainian energetics on oil, gas and coal import on condition of development of the home nuclear-fuel cycle with the use of domestic uranium deposits and reconstruction of coal industry [24].

Nuclear plants almost do not produce harmful emissions to the environment (nitrogen, sulphur, metals oxides, carbon, dioxide, ash, etc.) and thus they are more ecologically safe than TES, and the amounts of radioactive waste are low in volume and may be concentrated and buried. Safety and economicity of electric energy generation by NPP depend not only on the most strict following the process of reactors operation, but also on the fate of the spent nuclear fuel. The accumulated experience shows that economicity of electric energy production by NPP depends on efficiency of technology of nuclear fuel processing with release of unburnt fuel for its reuse and reliable burying of fragmental radioactive waste. But energy program of Ukraine for the period up to 2010 does not

Table 21

Data of natural gas consumption in 1999–2000 and prediction of gas consumption for electric energy generation in 2005–2030

Year	Domestic demand 10^9 m^3	Domestic production		Total import 10^9 m^3
		10^9 m^3	%	
2000	73.4	17.9	24.4	55.5
2005	70.0—71.0	21.3—21.8	30.6	48.2—43.7
2010	73.0—74.0	24.3—28.0	35.6	45.0—49.3
2020	118	25	21.2	93
2030	137	25	18.2	112

concern sufficiently either nuclear or thermal energetics. Only 680 000 hrn are assigned for nuclear-fuel cycle, and only 1.45 mill. hrn — for development of the methods of energy generation using RES. Such a disposition of funds is hardly rational, since: a) the amount of electric energy generated by renewable energy sources (wind, sea tide, solar and biomass energy) by predictions of International Energy Congress will reach in the world only 15–2.7 % in 2020 and b) great capital investments are needed, as it is shown below, for the construction of electric power plants with the use of RES.

Wind energetics. Northern regions of Ukraine and the shelves of the Black and Azov Seas, the Crimean perinsula possess high wind energy potential. The wind energy was historically used in Ukraine for ages. One cannot imagine Ukraine before the revolution without wind mills. In most regions of Ukraine the velocity of wind is sufficient for generation and accumulation of electric energy and provision of great rural regions and farms.

It would be noticed that WPP in their present form possess low power and thus can be used only in certain regions of Ukraine with efficient traditional energetics. Under present energy crisis in Ukraine [24] these energy sources, especially wind power plants, can function as auxiliary plants at the microlevel in the country-side. The well known standard WPP designs and decisions proposed by Kyiv Polytechnical Institute, Institute of Electrodynamics of the NAS of Ukraine and SDB *Yuzhnoe* (Dniepropetrovsk) and STC *Altex*, etc., are to be used for their development. Power of developed designs of the type VEU-0.75—VEU-10-10 embraces the range of 0.75 to 10 kW, and in those of the type AVE-25-15, AVE-100-17 and AVE-100-21 the nominal power reaches 25; 80 and 100 kW, respectively. Dniepropetrovsk *Yuzhmash* under a license with American company *Windpower* produces WPP of the type of USK 56–100 with installed power 100 kW. Besides, the components of WPP of USW-56–100 type are manufactured by 23 plants of the former military-industrial complex (MIC). The wind turbines are mounted by *Yuzhmash* plant. It is planned to make 1000 units of WPP of the above type and to arrange most of them in the Crimea, near the town of Evpatoria. Powerful and superpowerful WPP with installed power 500–2000 kW and above are used for replenishment of centralized power networks. Thus, in accordance with a complex program of wind-power industry development in Ukraine, it is planned to change the production of the licensed USW 56–100 by the licensed WPP USW 56–600 and USW 56–1000 with installed power 600 and 1000 kW.

It would be noticed that SDB *Yuzhnoe* has its own designs of WPP with power 200, 220, 500 and even 1250 kW. Most of the designs have been tested for long continuous functioning. Before 1996 SDB *Yuzhnoe* by the order of Ministry of Energetics of Ukraine has produced and delivered 40 ready-made units of WPP of 200 kW.

Let us appeal to history. Ukraine possessed high scientific and technological potential before *perestroika* — the change of the social system. Even 10 years ago, in 1993, Ukraine put in operation the Aktashian WPP with installed power 100 kW. The units of 200 and 250 kW were also made. The first wind turbine by Yu. Kondratyuk was constructed under socialism and put in operation in the Crimea in Balaklava in the 30's of the 20th century. Yu. Kondratyuk has also developed the unit designs with installed power 1000 and 10 000 kW. In the latter case two wind turbines of 5000 kW each were used at WPP. They were arranged at the first (65 m high) level and the second level (150 m high) [25]. The wind turbine of 10 000 kW was to be built in the Crimea on the Ai-Petri mountain. They even laid a foundation, but the project was not realized because of the World War II. The foundation is still preserved. Thus one can call the last 10 years and 70 years which have passed from the time of starting the first WPP the years of the «lost dreams of wind energetics» which resulted in the loss of Ukraine's priority in the branch of WPP close to its heart and … in delay. The installed power of Ukrainian wind power plants (WPP) is 40 MW now [25] that is 219 times lower than in Germany (8754 MW in 2001) and 13 times lower than in Spain (3337 MW).

Solar energetics. Solar energy is a source of life on the Earth. The Sun is a rotating spherical incandescent body (rotation period at the equator 27.275 days) with diameter 1.3919 mill. km containing 71 % of hydrogen, 26.5 % of helium, and others (carbon, oxygen, nitrogen, magnesium, sodium, silicon, iron, nickel) [26]. Average density of the Sun is 1410 kg/m^3, density in the center — 150 000 kg/m^3, and pressure $3.4 \cdot 10^{16}$ Pa [27]. Linear rotation rate at the equator — 2.025 km/s. Efficient surface temperature is 5770 K, in the center — $15 \cdot 10^6$ K. The Sun is continuously emitting energy, equal to about $4 \cdot 10^{26}$ W, to interplanetary space. The solar constant, corresponding to the amount of energy brought by solar rays for the unit of time (1 sec) at the distance of the Earth average recession from the Sun is 1.34 kW/m^2 [28] —

1.36 kW/m^2 [23]. From the data of [29] the more exact value of the solar constant equals 1.353 kW/m^2 (or 4871 kJ/(m$^2 \cdot$ h). Thermonuclear reactions with participation of hydrogen being converted into helium are the source of solar energy as it was shown in Chapter 4. Other elements (lithium, technetium) also take part in thermonuclear reactions of the Sun [26]. Average power of energy generated inside the Sun in thermonuclear reactions equals $1.88 \cdot 10^{-4}$ W/kg (0.6768 kW/kg). The Sun's mass is $(16991 \pm 0.002) \cdot 10^{30}$ kg. Hence, it is clear that a huge amount of energy is formed in thermonuclear reactions in the Sun bowel.

The solar energy flux per 1 m^2 of the surface area is 1070 kWh/m^2 in the northern part of Ukraine and to 1400 kWh/m^2 in Autonomous Republic of the Crimea [29]. Total amount of energy (thermal and electromagnetic) obtained by the Earth equal to about $173 \cdot 10^{12}$ kW is presented by the author of the work [29]. The Earth absorbs and emits certain amount of energy to the space. Thus the average Earth temperature by [27] is equal to 280 K, from other data it equals 269 K. From calculations of [25] the economically substantiated potential of solar radiation for Ukraine is $2 \cdot 10^9$ kWh/yr for electric energy production and $26 \cdot 10^9$ kWh/yr for heat supply.

Let us take the data of the work [29] to check reliability of calculations made by the authors of [25]. Estimate the flux of energy reaching the Earth surface during 1 h: $173 \cdot 10^{15} \cdot 60 \cdot 60 = 622.8 \cdot 10^{18}$ Wh. Assume that the given estimated energy arrives to the Earth for 6 h a day during only 3 months: $622.8 \cdot 10^{18} \cdot 6 \cdot 30 = 336.312 \cdot 10^{21}$ Wh or $336.312 \cdot 10^{18}$ kWh. About 30% of this quantity of energy reflect from the Earth surface without changing the wavelength [29]. About 47 % of energy are absorbed by the atmosphere and the Earth surface inducing temperature elevation. And only 23 % of energy equal to $77.35 \cdot 10^{18}$ kWh are absorbed by the Earth system components turning into the motive force of winds, tides, sea waves, storms, tsunami, «form our climate and evoke water circulation» [29].

Let us calculate how much is this energy, assimilated by the Earth atmosphere (atmosphere and surface of the Earth, river, lake, and ocean waters), comparable with energy consumed by mankind. About $20 \cdot 10^9$ t c.f. were consumed on the Earth in 2000 by population of $6 \cdot 10^9$ people [31]. Taking into account that 1 t c.f. is equivalent to 8139 kWh, we will obtain the amount of consumed energy equal to $16278 \cdot 10^{12}$ kWh/yr. Using the estimated values we obtain: $77.35 \cdot 10^{18} : 162.78 \cdot 10^{12} = 4.75 \cdot 10^5$. Thus, the amount of solar energy assimilated by the atmosphere and the Earth surface exceeds 475 000 times the amount of energy consumed on the Earth. From the data of calculations made by the author of [29], with regard for energy equivalent to $12.13 \cdot 10^9$ t c.f. consumed in 1992, the solar energy «consumed» on the Earth exceeded almost 11000 times the annual consumption of energy on the planet.

These data evidence for high power potential of solar energy on the Earth. It would be noticed that the company *Spectrolab* of *Boeing* corporation and *National Renewable Energy Laboratory* (NREL) of the Ministry of Energetics of the USA were awarded the prize of the National Energy Resources Organization for joint development of solar batteries with record efficiency of solar energy conversion into electricity. The authors have achieved the coefficient of the solar light conversion into electricity, when using a new solar battery, equal to 34 %, that is considered a new record of the world. A more perfect model of the solar battery is developed now. It is supposed that further investigations will permit overcoming the 40 % — barrier of efficiency of solar energy conversion into electricity.

The solar energy conversion into the electric and thermal energy in the regions of the Crimea, South of Ukraine and Ukraine as a whole, though being much discussed, is on the initial stage of its development. Solar energy reaching the territory of Ukraine, is characterized by high energy potential. One can assume for calculations that the average flux of the solar energy is 1235 kWh/m^2, and in Autonomous Republic of the Crimea 1400 kWh/m^2. Allowing for the area occupied by Ukraine equal to 603 700 km^2 and the solar constant (1235 kWh/m^2), time of solar exposition 6 h during 4 months (allowing for the soft climate of Ukraine) one obtains solar energy equal to $536.81 \cdot 10^{15}$ kWh. Only 23 %, i.e. $123.47 \cdot 10^{15}$ kWh will be consumed from the obtained solar energy. In 2001 Ukraine consumed 161.5 mill. t of conventional fuel that is equivalent to $1.314 \cdot 10^{12}$ kWh. Thus the calculated ratio in Ukraine will be equal to $123.4 \cdot 10^{15} : 1.314 \cdot 10^{12} = 9.4 \cdot 10^4$. Thus quantity of solar energy assimilated by the atmosphere and Earth surface in Ukraine exceeds 94 000 times the consumed quantity of primary and renewable (the divergence 8.5 %) with calculation results of the ratios of energies in the work [29].

From the data of [32] the Sun transmits annually to the territory of Ukraine $720 \cdot 10^9$ MWh of solar energy which is equivalent to $88.4 \cdot 10^9$ t c.f. Taking into account that in 2001 Ukraine consumed $161.5 \cdot 10^6$ t c.f., we will obtain the calculated ratio equal to 547. Thus, the calculation results demonstrate that solar energetics also possesses high energy potential in Ukraine. However total installed power of solar photoelectroenergetics of Ukraine is very low and is only 0.07 MW, and quantity of generated electric energy — 0.11 MWh/yr [26–33]. It is supposed to organize production of photoelectric converters (PEC) with total electric power about 1 mill. kW [27–34] by 2010. Consequently, under the existing rates of solar energy assimilation people will need a century to obtain considerable share of energy using PEC.

It would be noticed that we can make up for the lost under reasonable state policy concerning scientific-and-technological program in the use of RES to produce energy, under reasonable financial and investitious policy of attracting home capital to creation of WES and WPP, encouragement of development of WES use in the regions. On February 20, 2003, the Supreme Council of Ukraine adopted the law «On alternative energy sources», where defined principles of the use of RES in Ukraine. State management in the sphere of RES is entrusted to the Cabinet of Ministers of Ukraine and a special central body of executive power. A financial mechanism for stimulation of development of RES use for energy generation is elaborated. The program of RES use for energy generation requires great capital investments. So, it can be supposed that finances of regional production structures would play a positive role in creation of infrastructures for broad-scale energy generation by means of RES in Ukraine.

It would be noticed that more progressive laws concerning the use of RES for generation of energy were accepted in Japan, Germany, USA. In accordance with law accepted in Japan, all the power companies, beginning from May 2003, had to generate a share of electric energy with the use of renewable energy sources that is $12.2 \cdot 10^9$ kWh/yr. In 2002 the installed power of RES in Japan was 200 MW, and in 2004 it will reach 500 MW. By 2010 electric energy generation with the use of RES will be 1.35 % of its total quantity. Japan makes great efforts to solve the problems of solar energy conversion to electric energy and concentrated heat.

The second example for imitation is the resolution of the New York State Government (USA) to construct five new RES with total installed power 315 MW. The construction cost is only 17 mill. USD, and the term — 2005.

The third example is Canadian wind energetics crediting system. From December 2001 National budget of Canada provides stimulation of producers of the wind energetics. The Canadian government has set a compensation for electric energy of 12 American cents/kWh for the first 10 years for all projects in wind energetics which will be realized from April 1, 2001 to March 31, 2007. Thus, the producers of wind electric energy of Canada will receive financial support on the part of Government which will be about 260 mill. USD.

Bioenergetics. Biomass as the only and renewable energy source served the mankind during millennia. From 54 to 25 % of primary energy were obtained with the use of biomass up to the middle of the 10th century. Nowadays the biomass provides from 6–10 % [35] to 12–15 % of total energy [36]. The Earth plants form annually (by photosynthesis) the biomass equivalent to $120 \cdot 10^9$ t of oil [35]. Today, biomass is used in four trends: 1) immediate burning of wood and dry biologic waste to obtain thermal energy; 2) gasification for production of combustible gases; 3) production of ethyl and methyl alcohols to be used as motor fuels; 4) production of biogas from agricultural and domestic waste.

Biomass (mainly wood and its waste) is used as fuel in rural areas of Ukraine where biomass is the only source of thermal energy. In this connection one can face the noncontrolled felling of not only forests and forest stands but also gardens for fuel, especially in winter. Rape, maize, sunflower and straw biomass is also used as fuel. The authors of [37] have estimated the biomass potential for energy generation in Ukraine. Agricultural waste: stems of maize, sunflower and sometimes straw — are main source of biomass in Ukraine. Straw is used in cattle-breeding as fodder, lither, etc. So, straw is an unreliable source of biomass. In the recent time with a rise in price of mineral fertilizers, straw is cut during harvesting and serves as soil fertilizer. Besides, straw as well as waste of wood-working plants can be used for production of paper, board, etc.

Biomass processing with the use of processes of anaerobic fermentation with biogas production (especially using special strains of microorganisms) has not find an application. The use of biogas in the countryside requires changes in the rural mode of life established during centuries. From the data of [36] production of liquid fuels from biomass is hardly probable in Ukraine in the nearest future, since such fuels cost more than traditional liquid fuels. Only if liquid fuel will rise in price with following deficit of that for motor transport and agricultural machines the biomass will find its application to production of ethanol, methanol and their mixtures [38], biogas and dry (briquetted) fuel. The production of briquetted fuel from straw in a form of high-density «logs» (preferably square) is especially promising for the rural areas.

To decrease expenditures for biomass processing with obtaining biogas and electric energy the farmers of Denmark and Sweden as well as some regions of Germany unite and use combined plants distingushed by «progressive scaling» [36]. The plant productivity being increased, expenditures for the processing of 1 m^3 of biomass decrease. Besides, operation and maintenance of such plants is performed by highly qualified personnel. Economic stimuli have been foreseen for farmers incentive. Thus farmers receive state subsidies of 9.20 Evro for each 1 kWh of generated electric energy, when using average plants of no more than 500 kW [36].

At some large cattle-breeding farms with deficit of arable lands in foreign countries they use fermentation of manure — waste of vital functions of pigs, cattle with production of biogas. They consider animal waste the only potential source of biogas. The authors of [37] also consider manure as one more source of biomass. But livestock farming waste is valuable as organic fertilizer for raising soil fertility. Complex expensive plants allowing to generate heat and electric energy are used for the processing of cattle-breeding and poultry farms waste. The engineering-economic analysis of heat generation from biomass carried out by the authors of [37] has shown that electric energy generation using wood and straw is not profitable under available tariffs for electric energy. Besides, the equipment made abroad needs high capital investments. Thus, the cost of straw-burning mini-TEP of 1-10 MW is 8 million USD, wood-burning mini-TEP of 10 MW — 5 million USD.

Besides, power-intensity of dry biomass is higher than that of biogas produced from this mass. When biomass is fermented it releases 30 % of carbon dioxide (CO_2) which serves as the ballast, while the share of combustible volatile components is less than 60–65 %. In this connection, when using biogas with biomass application, the CO_2 ejections to the environment are higher per unit of obtained energy compared with traditional organic fossil fuel. Besides, electric energy generation with the use of biogas even at expensive mini-electric power plants endangers the environment. Efficiency of such electric power plants is lower than that of modern TEP. Besides, biogas combustion at such electric power plant can be accompanied by noncontrolled ejections of CO_2, CO, benzpyrene and other carcinogenic compounds. It would be noted that the process of biogas production is a labour- and water-consuming one (biomass: water = 1 : 20); it also requires highly qualified manual labour [38–40]. Besides, the cost of a large biogas plant is 99 980 million USD [37].

The use of renewable energy sources (RES) containing no carbon is more promising for the rural areas of Ukraine. Wind and solar energetics as well as minor hydroenergetics are such RES for energy generation.

Fuel-energy branch and its future. The reorganization of contemporary energetics is necessary to create fuel-energy branch which does not depend on the import of energy carriers in Ukraine. Nuclear and nuclear-hydrogen power plants (NHPP) (see, Chapter 4 and 6) can become a basis of the future fuel-energy complex of any industrially developed country. These plants can generate 60–70 % of electric power and heat and provide hydrogen for production of artificial fuel for motor transport and other consumers. High-temperature nuclear reactors with helium heat-carrying medium HTHR-1000 and NPP with HTLSR can allow to meet requirements of a number of high-tech productions of Ukraine for cheap hydrogen (oil cracking, coal gasification, production of synthetic motor fuels, synthesis of organic compounds and fertilizers, chemical and metallurgical enterprises). Investigations have shown that nuclear reactors of the series HTHR can provide cities and industrial complexes of ecologically pure high-temperature heat, save expensive organic fuel and improve essentially ecologic situation, especially in the cities with developed metallurgy (Dniepropetrovsk, Donetsk, Kramatorsk, Mariupol, Zaporozhie, etc.) owing to perfection of technology of power-consuming branches of industry. Inexpensive hydrogen will permit to pass to direct restoration of ore in ferrous metallurgy that will change essentially ecologic characteristics of metallurgical and chemical productions [41, 42]. A complete nuclear technological cycle, including uranium mining, enrichment to 3–4.4 % by ${}^{235}_{92}U$ for thermal plants or uranium-238 ${}^{238}_{92}U$ for NPP with fast reactor as well as modern technology of fuel element production may be realized in Ukraine, as in any developed industrial country.

In the latter case the problems with uranium fuel which arise in Ukraine could be decided. The need in uranium at NPP of Ukraine is 300 t/yr. Beginning from 1994 Ukraine receives nuclear fuel for NPP from Russia as a compensation for exportation of tactic and strategic nuclear weapon. Ukraine possesses rich deposits of uranium ores: Zheltorechensk ore field, Golovanev, Zvenigorod, Kirovograd, Gaichug structure-metallogenic zones with ore fields in Podolian, Kirovograd and Peri-Azovian subprovinces [43]. The State program has been developed and adopted in Ukraine. In accordance with the above program it is planned to create the domestic nuclear fuel complex by 2005. The complex is created on the basis of the Eastern dressing integrated works (Zheltye Vody city) for processing of ores of Zheltorechensk ore field and Peri-Dnieper Chemical Integrated works (Dnieprodzerzhinsk city) [44]. The State program consists of five chapters: the first one is dedicated to creation of uranium raw-material mining base (1994–2005) on the basis of operating infrastructure of Eastern dressing integrated works and development of a new Novokonstantinovka uranium deposit in Kirovograd region; the second chapter will be dedicated to creation of zirconium production on the basis of the Peri-Dnieper Chemical Integrated Works; the third chapter deals with the program software; the fourth and the fifth chapters are dedicated to the plans of scientific and technological and industrial support of the program. However the cost of such large-scale works is planned as 139 million USD.

To fulfill such tasks we need, besides the program, highly-qualified personnel. Thus it is necessary to restore scientific schools of «nuclear engineers» and radiochemists who worked in Ukraine before the disintegration of the USSR with the purpose to develop the construction of nuclear reactors. That would be made to remove after 2020 the reactors which have completed their term, and change them by more perfect, e.g., high-temperature gas-cooled reactors of HTHR-1000 type with helium as heat-carrying agent. It is also necessary to estimate the prospects of the construction of fast-reactor NPP in Ukraine of the type FN-800 and FN-1600. In the opinion of Russian and American specialists in nuclear power engineering the use of high-temperature helium heat-carrying medium with gas turbine is most promising while constructing NPP in Ukraine [45]. In the latter case the thermal trail of NPP can be decreased as well as thermal pollution of the environment. The authors of [46], who studied heat losses at eight nuclear plants in the water area of cooling water trails of NPP arranged on the Baltic coast, have shown that the minimum area of the thermal trail (5.9 km^2) is left by Lovis NPP (Finland), and maximum (474 km^2) — by Leningrad NPP (LNPP) in Russia.

It is also necessary to construct TES of new generations. Ukraine has high prestige as the country which can construct the best electric plants in the world. The first most powerful steam- and electrogenerators, boils and units with supercritical parameters (temperature 540 °C, water steam pressure 240 atm) supplied with the system of complete automation of technological processes [21, 24] were introduced in Ukraine. TES of new generations burn coal in circulating boiling layer with gas-turbine superstructures and packings for consumption of harmful emissions and provide additional production of 24–34 % of electric energy and heat.

TES of Ukraine use as energy-carrying agents now (%): energetic hard coal — 53, natural gas 41, mazut — 6. By the reported data of 1998 [16], the average price of hard coal for power industry is 73.77 hrn/t; allowing for the prime cost, the coal mining losses were 17 %, and electric power generation profitability at TES — 33 % with the norms of coal expenditure for generation of 1 kWh of energy equal to 365 g. The coal mining and electric energy generation being united into a single complex — the power-coal company, the prime cost of electric energy generated by the company could grow up to 17 %, and estimated profitability of electric energy generation could reach 16 %. Note, that the profitability level of electric power generation by TES of the developed countries is only 8–10 %. It would be also taken into account that the sell price in Ukraine on the path to consumer increases to 170–230 hrn, that does not stimulate coal mining. Besides, bad economic balance of coal mining and electric energy generation is proved by the ratio between the cost of coal for production of 1 kWh of electric energy and the cost of 1 kWh which is 1:2.5. Thus it is possible to raise the average «internal» price for coal with preservation of positive profitability of coal mining in the joint electrocoal company.

The situation with heat power complex (HPC) in Ukraine is aggravated by the fact that the term of TES operation is calculated as 25–30 years. This term is practically expired for most CRES and TES of Ukraine. As of 1998 95.2 % of TES power units have exhausted their estimated resource (100 000 h), including 72.1 %, and exceeded the ultimate resource (170 000 h), 53.8 % of power units are in operation above 200000 h (22.8 years of continuous work) [24]. Thus the operation term of TES exceeds the limit of physical wear and moral ageing adopted in the world practice. Degradation phenomena in fuel processes — fuel consumption increase and decrease of efficiency take place after this term.

It is time to reconstruct TES operating now in Ukraine, and even to construct new stations in some cases [21, 24]. Under the balanced sustainable economy in the state, the energetics powers are usually doubled every 15–20 years. The rates of increase of energy powers are no less than 4–6 % a year. R&D works on rational reconstruction of operating TES in Ukraine as well as the conversion of all TES to complete automation of the processes of coal burning in boiling layer, under pressure and in conditions of intracycle gasification are required. The construction of TES with the use of steam-gas cycle which construction term is twice less is especially promising. By the data of [24], we would take measures on saving the power system of Ukraine, otherwise the process of its degradation will be so fast that the deficit of generating powers can reach $7–10 \cdot 10^6$ kW by 2005. In such a case only NPP and HES will he able to function in Ukraine by 2010. Without taking urgent positive measures, all the electric energy in Ukraine would be imported beginning from 2020 that would mean the full loss of our state sovereignty [24]. Tendencies of possible

Table 22

Dynamics of changes of available powers and their deficit in the power system of Ukraine because of the lack of funds for their modernization, 10^6 kW [24]

Power system branch	Year			
	2005	2010	2020	2030
NPP (operation term 30 yr)	10.8	10.8	1	0
TES	67	1–2	0	0
TEP	3–4	1–2	0	0
HES-HNPP	4.7	4.7	4.7	4.7
Power available	24.0–30.8	17.5–22.5	5.7	4.7
Necessary operational power with regard for reserves	33–37	37–45	55–60	70–75
Operational power deficit	7–10	18.5–22.5	50–55	65–70

degradation of the fuel-energy complex of Ukraine in the course of time are reflected by the data of Table 22.

The original investigations of fundamental and applied problems of electroenergetics as well as the works in creation of powerful asynchronous turbogenerators, having no analogs in the world, have been performed at the Institute of Electrodynamics (IED) at the National Academy of Sciences of Ukraine [21, 24]. Two asynchronous turbogenerators 200 MW each are already in operation at Burshtynian TES. Researchers of IED NAS of Ukraine perform intensive investigations in the field of development of small electric stations which can be arranged in the centre of the country. Decentralization of energy sources is developed all over the world. England, where a half of electric plants are not high-power ones, can serve as an example; but allowing for their operativeness and high profitability, they can compete with the giants of the electric power industry.

Hydroelectric stations of Ukraine have almost exhausted potential resources of hydraulic energy and will, as always, generate no more than 5.0–5.3 % of electric energy. Nontraditional energy sources in Ukraine can provide at least 1–2 % of electric energy, and thus, they cannot replenish the deficit of energy which was not generated at TES and CRES. This deficit will increase because of low financing of the latter in accordance with the energy program of Ukraine for 1986–2010 insufficient for planned repairs of the capital assets of HES with 80–95.2 % wear. In the nearest years Ukraine shall develop the processes of synthetic liquid fuels production from hard coal and turf to escape stresses in agriculture. Under the available amounts of energetics financing in Ukraine one cannot answer with optimism the question of Academician A. Shidlovsky [21]: «Will Ukraine overcome the energy crizis itself?» and in what terms?

REFERENCES

[1] V. S. Arutyunov, A. L. Lapidus, Ros. Khimich. Zhurnal, vol. 47 No. 2 (2003) 23.
[2] V. I. Subbotin, Bull. Rus. Acad. Sc., Vol. 71, No. 12 (2001) 1059.
[3] U.S. Sensus Bureau, Statistical Abstract of the United States: 1999.
[4] O.N. Favorsky, Bull. Rus. Acad. Sc., Vol. 69, No. 4 (1999) 311.
[5] O.N. Favorsky, Bull. Rus. Acad. Sc., Vol. 69, No. 1 (2001) 3.
[6] G. Geletukha, T. Zhelezna, Green Energetics, No. 3 (2003) 19.
[7] Solar Energetics in Europe, Green Energetics, No. 3 (2003) 22.
[8] Novosti telposnabzheniya (Heat Supply News), No. 8 (2002).
[9] L. A. Manfutov, A. A. Troitsky, Energy Policy, Iss. 1 (2002) 3.
[10] P. P. Bezrukikh, Energy: Economy, Technology, Ecology, No. 11 (2002)2.
[11] Yu. M. Belyaev, Energy Policy, Iss. 1 (2002) 7.
[12] B. G. Sanayev, A. V. Lagerev, V. N. Khanaeva, and A. V. Chemezov, Energy Policy, Iss. 4 (2002) 16.
[13] V. M. Bykov, Energy: Economy, Technology, Ecology, No. 4 (2002) 7.
[14] I. N. Karp, Ecotechnologies and Resource Saving, No. 1 (2003) 3.
[15] S. B. Tulub, A. K. Shidlovsky, G. G. Givnyak, and M. N. Kulik, Gorny Zhurnal (Mining Journal), No. 6 (2000) 158.
[16] Statistica Annual of Ukraine, 1998, Tekhnika, Kyiv, 2002.
[17] A. Yu. Zenyuk, Energy: Economy, Technology, Ecology, No 1 (1988) 9.
[18] M. E. Kokeyev, Yu. I. Koryakin, Energy: Economy, Technology, Ecology, No. 1 (1997) 2.
[19] N. V. Selivanov, Problems of Science, No. 7 (2000) 44.
[20] K.Ya. Kondrayev, Bull. Rus. Acad. Sc., Vol. 70, No. 9 (2000) 788.
[21] A. Shidlovsky, Bull. NAS of Ukraine, No. 5/6 (1998) 64.
[22] V. A. Kirillin, Future of Science, Iss. 16 (1983) 3.
[23] O. Chernousenko, Yu. Kosyak, Energy No. 3 (1997) 11.
[24] A. Shidlovsky, Bull. NAS of Ukraine, No. 3 (2000) 29.
[25] V. Kukushkina, V. Sychevoi, A. Konechenkov, Green Energetics, No. 3 (2002) 5; 10.
[26] V. G. Fesenko, With Scholar's Eyes, Acad. Sc. USSR Publ., 1963.
[27] Complete Encyclopaedia Reference Book, Rus.Encycl. Partnership, Moscow, 2002.
[28] Cosmonautics. Encyclopaedia, Sovetskay Entsiklopedia Publ., Moscow, 1985.
[29] N. M. Mkhitaryan, Helioenergetics. Systems, Technology, Application, Naukova Dumka, Kyiv, 2002.
[30] L. L. Kistersky, I. G. Gaiduchok, Yu. V. Poluneyev, International Economic Safety. Foreign Trade, Currency-Financial and Energy Aspects, Naukova Dumka, Kyiv, 1991.
[31] L. F. Kozin, S. V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv, 2002.
[32] M. Rabinovich, I. Tolstykh, Green Energetics, No. 1 (2003) 6.
[33] Ye. V. Kuzminsky, G. Ya. Kolbasov, Ye. Yu. Tevtul, and N. V. Golub, Nontraditional Electrochemical Energy Conversion Systems, Akadem. periodika, Kyiv, 2002.
[34] V. I. Gomon, V. E. Grinshtein, A. A. Dolinsky, et al., Ukraine: Efficiency of Minor Energetics, EC Energy Centre in Kyiv, Kyiv, Ukraine, 1995.
[35] H. Armstead, P. Fraenkel, F. Murray, et al., The World Energetics, Energoatomizdat, Moscow, 1985.
[36] Jens Bau Holm-Nielsen, Green Energetics, No. 4 (2002) 6.

[37] G. G. Geletuka, T. A. Zheleznaya, S. V. Tishaev, and S. G. Kobzar, Ecotechnologies and Resource Saving, No. 3 (2002) 3.
[38] N. Martynyuk, Green Energetics, No. 4 (2002) 12.
[39] G. G. Geletukha, S. G. Kobzar, Oil and Gas, No. 3 (2001) 88.
[40] G. G. Geletukha, T. A. Zheleznaya, Ecotechnology and Resource Saving, No. 3 (1998) 3.
[41] F. M. Mitenkov, N. N. Ponomarev-Stepnoi, Energy, No. 2 (1997) 2.
[42] V. A. Ragasov, N. N. Ponomarev-Stepnoi, A. N. Protsenko, et al., Nuclear-Hydrogen Energetics and Technology. Iss. 1 (1978) 11.
[43] L. F. Kozin, V. I. Trefilov, Rare-Metal Industry of Ukraine, Problems and Prospects, Kyiv, 1998 (Prepr. IIM NAS of Ukraine. No. 479).
[44] I. Pidlusky, Kievskie vedomosti, Sept. 6, 1994.
[45] V. N. Mikhailov, Bull. Rus. Acad. Sc., Vol. 68, No 2 (1990) 116.
[46] V. I. Gorny, S. G. Kritsuk, I. Sh. Latypov, et al., Optic. Journ., Vol. 66, No. 8 (1999) 6.

Chapter 6

Hydrogen Energetics

6.1. Physico-Chemical Properties of Hydrogen and Metal Hydrides

Hydrogen is the most distributed element on the Earth and in universe. For example, the percentage of hydrogen in the Sun, Saturn and Jupiter composition is 73, 85 and 100, respectively. The percent abundance of hydrogen on the Earth is 0.14 %. The Earth weight being taken as $5.9763 \cdot 10^{21}$ *t,* hydrogen content on the Earth equals $8.367 \cdot 10^{21}$ *t.* The amount of free hydrogen on the Earth in less than $1 \cdot 10^{-6}$ portion of the atmosphere. Hydrogen if found in free (occluded) state in deposits of various salts, hard coal, rocks and in meteorites; it is also a component of volcanic gases [1]. It is supposed that when getting into the Earth atmosphere, gaseous hydrogen volatilizes steadily into space, since it is 14 times as light as the air. In the upper layers of the atmosphere hydrogen can interact with ozone O_3 or with OH type radicals with following formation of water molecules.

Water is the main hydrogen compound on the Earth ($1.4 \cdot 10^{18}$ t). Water is ecologically pure product of hydrogen oxidation and its most accessible source. Numerous organic components of the Earth — oil, natural gas, hard and brown coals, turf, resins, oils, wax, microorganisms, plants, wood — include hydrogen; most of them can serve as its sources. Molecular hydrogen is the most important intermediate component in the processes of decomposition of plant, microorganism and animal remains and organism matter degradation are performed as a result of vital activity of anaerobic and aerobic microorganisms. It is hydrogen, which often serves a source of energy in such processes. An analysis and calculations show that $2680 \cdot 10^{12}$ m^3 or 200 mill.t of hydrogen are formed and consumed on our planet only during one year.

Hydrogen content in some chemical compounds is presented in Table 23. As is seen, the hydrogen content depends on the compound nature and varies in a broad range. Considerable amounts of hydrogen are contained saturated hydrocarbons of methane series. Methane, making the base of natural gas, is used to produce hydrogen by the method of vapor-phase conversion and thermolysis. Considerable atomic fraction of hydrogen is also contained in ammonia (75 %).

As a results of small atom size (0.027–0.80 nm) hydrogen penetrates with high velocity into metals, occupies vacancies of their crystal lattices, and forms hydrides, owing to chemical activity. Thus, hydrogen possesses high diffusivity and can dissolve in numerous metals. Hydrogen dissolution in metals is ac-

Table 23

Hydrogen content in some chemical compounds

Compound	H_2 content, %		Compound	H_2 content, %	
	Total mass fraction	Atomic fraction		Total mass fraction	Atomic fraction
Hydrogen H_2	100.0	100.0	Lithium Hydride LiH	12.7	50.0
Methane CH_4	25.1	79.9	Water H_2O	11.1	66.5
Ethane C_2H_6	20.1	75.0	Lithium Alumino-hydride $LiAlH_4$	10.6	66.5
Propane C_3H_8	18.3	72.2	Yttrium cobaltohydride Yco_5H_6	9.0	50.0
Beryllium hydride Be H_2	18.3	66.5	Magnesium hydride MgH_2	7.6	66.5
Ammonia NH_3	17.3	75.0	Acetylene C_2H_2	7.3	50.0
Butane C_2H_{10}	17.3	71.4	Calcium hydride CaH_2	4.8	66.5
Pentane C_5H_{12}	14.3	70.6	Scandium hydride SeH_2	4.3	66.5
Ethanol C_2H_5OH	13.1	66.7	Sodium hydride NaH	4.2	50.0

companied by the expansion (distortion) of their crystal lattices and by change of their properties. Hydrogen diffusion coefficients in metals equal: in palladium D_0 — $2.90 \cdot 10^{-3}$ cm^2/s; in niobium D_0 — $5.0 \cdot 10^{-4}$ cm^2/s; in tantalum D_0 — $4.4 \cdot 10^{-4}$ cm^2/s at low values of activation energy 10.2 — 22.20 kJ/mol [26], in which its volume unit concentration is higher, than in liquid or even solid hydrogen ($n \cdot 10^{-22}$ atoms H/cm^3): $C^{liquid}_{H_2} = 4.2$; $C^{solid}_{H_2} = 4.593$; $C^{solid}_{LiH} = 6.23$; $C^{solid}_{MgH_2} = 6.70$; $C^{solid}_{H_{2.76}} = 6.87$; $C^{solid}_{CeH_3} = 7.00$; $C^{solid}_{ZrH_{1.96}} = 7.07$; $C^{solid}_{TiH_{1.75}} = 8.26$.

Hydrogen content in hydrides depends on the nature of hydride-forming metals. Such metal as beryllium binds the highest amount of hydrogen, thus forming beryllium hydride BeH_2. Dihydrides TiH_2 and VH_2 contain 0.15–0.20 g of H_2/cm^3, that is 2–2.5 times more than in liquid hydrogen. Thus, the metal hydrides are used in hydrogen batteries and as fuel in special units.

Hydrogen production all over the world was $6.0 \cdot 10^7$ t in 1998–1990, it reached $8.0 \cdot 10^7$ t in 1997–1998, and in the first decade of the 21st century it will exceed $(1.5–3) \cdot 10^9$ t. Hydrogen is widely used in chemical industry for production of ammonia, methanol, synthetic fuels, for deep petroleum refining, coal gazification, production of high-octane motor fuels, hydrogenation of fats and production of various chemical compounds. About 50 % of hydrogen are consumed in ammonia synthesis, 1/3 of which is used in production of nitric oxide. From 5 to 10 % of produced hydrogen are utilized in low-tonnage science-based branches of new technology and industry: electronic and pharmaceutical industry, melting of metals and alloys with preset properties, synthesis of highly active chemical compounds, etc. Liquid hydrogen is more and more used as fuel in the space and rocket facilities, while gaseous hydrogen, produced in the spaceships with the help of solar battery energy, for correction of the flight orbit.

It is supposed that about 20 % of hydrogen produced during the first decade of the 21st century will be utilized as power-generating fuel in the systems with autonomous power supply [2–6].

When hydrogen interacts with oxygen 3.5 times more heat per the mass unit is released, than under the combustion of organic fuel (natural gas, oil, coal)*. Hydrogen with oxygen form the explosive mixtures in the concentration range of 4–75 % (by H_2 volume). Hydrogen remains in solid state at a temperature of 13.813 K (T_{melt}), while at 20.258 K it boils with heat consumption and passes into gaseous state, the latter being in equilibrium with liquid hydrogen. The evaporation heat of 1 mole of liquid hydrogen at 20.258 K makes 117.152 J (454.0 kJ/kg), and sublimation heat at a temperature of 13.813 K is 0.904 kJ/mol. At temperatures of 9.6; 13.8; 15.0 and 20.26 K the hydrogen vapour pressure is 0.138; 7.65; 13.39, and 101.32 kPa, respectively.

Molecular hydrogen exists in two modifications. This is determined by difference in spinning direction of its atomic nuclei: parahydrogen (p-H_2) and orthohydrogen (o-H_2). Ordinary hydrogen is the mixture of these modifications, which concentration depends on temperature. At 25 °C (298 K) and –252.9 °C (20.35 K) the equilibrium concentration of hydrogen modifications p-H_2 and o-H_2 makes 99.71 and 0.21 %. Heat of hydrogen o-H_2 conversion into p-H_2 at 10.0; 20.258 and 70.0 K makes 1.4169; 1.4169 and 1.40248 kJ/mole, respectively. Slow spontaneous conversion to the content of o-H_2=0.21 % with release of heat occurs under hydrogen liquefaction. Dielectric constant of solids parahydrogen at a melting point $\varepsilon = 1.29660$.

Liquid hydrogen side by side with other liquid fuels (kerosene, hydrocarbons and their compounds) is more and more widely used as fuel for liquid-propellant rocket engines (LPRE) in aviation and cosmonautics. It is a colorless liquid with density 71 kg/m^3 (at –253 °C), $T_{melt.} \approx -259$ °C and $T_{boil.} \approx -252.8$ °C (Table 24). Liquid hydrogen is kept in the tanks with cryogenic stoppers, hydrogen cells and other devices, and gaseous hydrogen — in bottles, gas-holders, underground workings in compressed state. At the lowest heat of conduction 1t of hydrogen is equivalent to 4.1 t of conventional fuel.

Hydrogen and hydrocarbon compounds are high-energy ones, they possess valuable physico-chemical properties (Table 24) and are widely used in industry now. Intensive investigations on the use of hydrogen as fuel in spaceships and aviation, motor transport and industry are carried out.

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* Stechiometric mixture of components.

Table 24

Physico-chemical characteristics of hydrogen and some hydrocarbons

Parameter	H_2	CH	C_2H_6	C_3H_8
Temperature K				
melting	13.813	89.15	101.15	85.46
boiling	20.258	11.15	184.52	231.08
critical	33.15	191.15	305.42	369.95
Critical pressure, Pa	$1.297 \cdot 10^6$	$4.640 \cdot 10^6$	$4.895 \cdot 10^6$	$4.294 \cdot 10^6$
Density, kg/m^3				
gaseous at 273 K	0.1	1.6	—	—
liquid at $T_{boil.}$	71.0	416.0	—	—
solid at $T_{melt.}$	76.3	424.0	546.0	585.0
Heat m kJ/mole				
melting	0.117	0.940	2.86	3.53
evaporation	0.916	9.2801	—	—
burning	285.98	890.35	1427.83	2202.0
Combustion heat kJ/kg				
Pure matter	$142{,}97 \cdot 10^3$	$55.65 \cdot 10^3$	$47.49 \cdot 10^3$	$4994 \cdot 10^3$
Mixtures*with O_2	15899,2	8619.04	10 050.34	10 789.36
Dissociation energy eV	44.8	18.3	18.2	18.1

* Stechiometric mixture of components.

Corrosion properties of the systems hydrogen — structural metals and alloys are investigated. It appeared that low-carbon steels with high content of nickel, aluminium and copper alloys are corrosion-resistant structural materials resistant to the effect of gaseous and liquid hydrogen in the wide range of temperatures.

Metal and metalloid hydrides [4–9] considerably differ between themselves as to their physico-chemical properties. That is why, that hydride processes possess high separating capacity and are practically used in production of powders and moulds of high-melting metals (tungsten, niobium, tantalum) used as the precision melts in critical technologies (high temperatures and pressures, etc.) in cleaning of metalloids (silicon, germanium, arsenic, antimony, selenium, tellurium, sulphur, phosphorus), etc. Dependence of metal and metalloid hydrides on the position of their components in D.I. Mendeleyev's periodical element system is presented in Table 25.

Some classifications of hydrides are proposed, which allow for the character of chemical bond and their physico-chemical properties. The authors of the work [7] divide hydrides into four groups: ionic salt-like hydrides (Li—Fe, Be—Ra), hydrides of transition metals (IIIa-VIIIa subgroups, lanthanides and actinides), intermediary hydrides (Ib-IIIb) subgroups, covalent hydrides (volatile) (IVb-VIIb subgroups).

In the work [10] hydrides are subdivided into ionic, metal and covalent ones. Ionic hydrides form *s*-elements, metal — *d*- and *f*-elements; covalent (non-metal) — *s*- and *p*-elements (metalloids and degenerate metalloids). Hydrides with mixed types of bonds are formed in all the cases of mixed electron states. Thus, for the case of *s*- and *p*-electrons these are ion covalent bonds, for *s*- and *d*-electrons — ion-metal bonds, for *d*-, *s*-, and *p*-electrons — covalent-metal bonds. A conception of donor-acceptor interaction is proposed for the transition metals, lanthanides and actinides.

The metal hydrides (of transition metals Se, Y and REM) and their alloys manifest properties of the typical incorporation phases. In this case, hydrogen being dissolved in metals, the atoms of hydrogen are arranged in the metal crystal lattice vacancies and form solid solutions and hydride phases. It is seen distinctly from Table 25. that the metals of Ia-Va subgroups Cr, Co, Ni, Pb, REM and actinoids form hydrides with exothermal effect [6–29]. Hydrogen incorporation in metals is preceded by physical metal-surface adsorption of its molecules, dissociation of hydrogen molecules (H_2>2H), which is accompanied by the absorption of 432.1 kJ/mol of heat and leads to formation of the chemisorbed hydrogen atoms diffusing into the metal phase volume. Hydrogen atoms diffusions are accompanied by ionization (oxidation) reactions proceeding in parallel:

$$H_{\text{chem.}} \leftrightarrow H^{+} + e^{-} \tag{8}$$

and by reduction of hydrogen atoms:

$$H_{\text{chem.}} + e^{-} = H^{-} \tag{9}$$

the reaction (33) is accompanied by electrons transition in the conduction band and by arrangement of protons in the crystal lattice vacancies — interstitial sites of matrix lattice, by formation of a proton which radius is less than that of H atom dissolved in a metal. The metal chemisorption is accompanied by the endothermal heat effect $Q = -\Delta H$. Nonactivated (quick) chemisorption of hydrogen proceeds on Ba, La, Ti, Zr, Nb, Ta, Cr, Mo, W, Re, Fe, Co, Ni, Rh, Ir, Pd, Pt and activated (slow) one — on Ca, Sr, Mn. Hydrogen is not chemisorbed [11, 12] by such metals as K, Cn, Ag, Zn, Cd, Al, In, Sn, Pb at a temperature close to 293 K. Thermal effect of chemisorption, embracing only one atomic layer on the metal surface is from 76 to 218 kJ/mol [13], depending on the metal's nature.

The reaction (34) proceeding must result in the increase of the atomic size of the hydride-anion H^{-}, and as a consequence, of the volume of hydrogen, dissolved in the metal. Thus, it is known, that lanthanum is crystallized in the closest cubic packing with two tetrahedral vacancies surrounded by four lanthanum

Table 25

Dependence of hydrides properties on the position in D.I. Mendeleyev's periodical element system

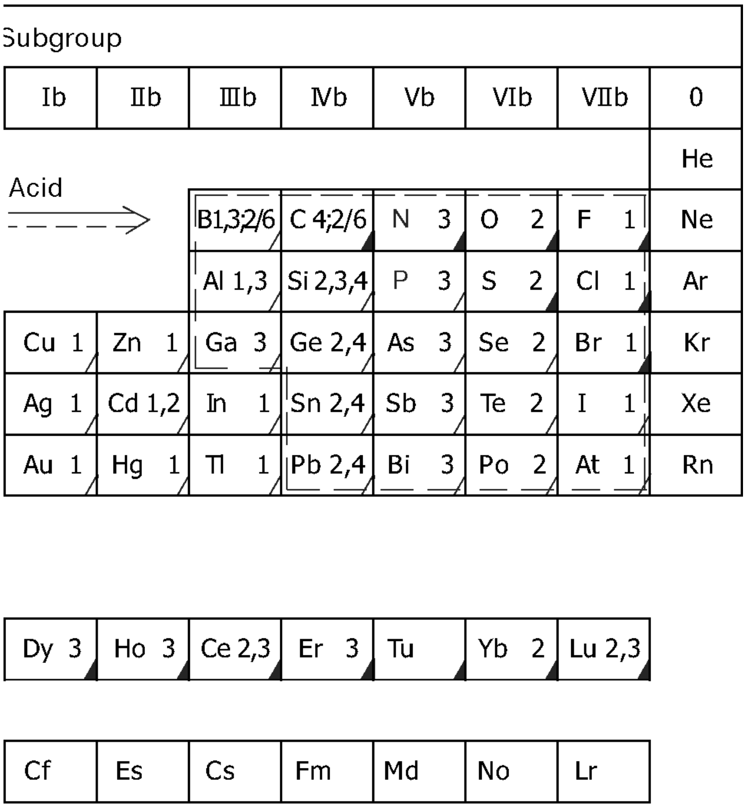
Period	Subgroup									
	Ia	IIa	IIIa	IVa	Va	VIa	VIIa	VIII		
1	H 1	Hydride character								
2	Li 1 ▲	Be 1,2 ▲	⟸ Salt-like							
3	Na 1 ▲	Mg 2 ▲								
4	K 1 ▲	Ca 1,2 ▲	Sc1,2,3 Δ	Ti* 2 ▲	V* 1,2 ▲	Cr* 1/2 ▲	Mn* Δ	Fe* Δ	Co* 1,2 ▲	Ni*0,5,1 ▲
5	Rb 1 ▲	Sr 1,2 ▲	Y 2,3 ▲	Zr* 2 ▲	Nb*1,2 ▲	Mo* θ Δ	Tc Δ	Ru Σp_i Δ	Rh* Δ	Pd 1,2 ▲
6	Cs 1 ▲	Ba 1,2 ▲	La1,2,3 ▲	Hf 2 ▲	Ta 1 Δ	W Σp_i Δ	Re Σp_i Δ	Os Δ	Ir* Δ	Pt* 1 Δ
7	Fr 1 ▲	Ra 2 ▲	Ac 2 ▲	Th 4,4 ▲	Pa 3 ▲	U 3 ▲				

Lanthanides								
	Ce 2,3 ▲	Pr 2,3 ▲	Nd 2,3 ▲	Pm 2 ▲	Sm 2,3 ▲	Eu 2 ▲	Gd 2,3 ▲	Tb 2,3 ▲

Actinoids					
	Np 2,3 ▲	Pu 2,3 ▲	Am 2,3 ▲	Cm 2 ▲	Bk 2 ▲

▲ — exothermal reaction of the element with hydrogen; Δ — endothermal reaction;
Σ_{pi} — hydrides are formed under high pressure of hydrogen; θ — hydrides are not formed;

atoms and one octahedral vacancy for each metal atom. Sizes of these vacancies are determined by simple ratios $R_T = 0.22\ R_{Me}$ and $R_O = 0.44\ R_{Me}$ [6]. Atomic radius of lanthanum is 0.186 nm, radius of free hydride-ion H^- — 0.208 nm and radius of proton — 0.024 nm. The average volume of hydrogen in transition metals and their alloys $V_H \cong 0.026$ nm^3, as a result the sphere radius equals 0.085 nm, which is something less than the zero-valent radius of hydrogen (0.090 nm) [14]. The higher hydrogen volume in REM and their alloys proves that its atoms acquire a negative charge, which value depends on the REM nature. Proceeding from the data of the work [30], radius of hydride-ion H^- in transition from Li to Cs increases from 0.137 to 0/152 nm. It is considered that the ideas of both covalent and metal bond do not allow explaining the changes of hydrogen atoms radius from 0.027 to 0/80 nm. It is supposed that the interatomic bonds in REM hydrides of MeH_2 composition are of ionic character [30]. However, as is shown below, the character of interatomic interaction in the salt-like hydrides of the elements of Ia — IIa subgroups and REM may be explained proceeding from the



Subgroup							
Ib	IIb	IIIb	IVb	Vb	VIb	VIIb	0
							He
Acid →		B1,3;2/6	C 4;2/6	N 3	O 2	F 1	Ne
		Al 1,3	Si 2,3,4	P 3	S 2	Cl 1	Ar
Cu 1	Zn 1	Ga 3	Ge 2,4	As 3	Se 2	Br 1	Kr
Ag 1	Cd 1,2	In 1	Sn 2,4	Sb 3	Te 2	I 1	Xe
Au 1	Hg 1	Tl 1	Pb 2,4	Bi 3	Po 2	At 1	Rn

Dy 3	Ho 3	Ce 2,3	Er 3	Tu	Yb 2	Lu 2,3

Cf	Es	Cs	Fm	Md	No	Lr

1, 2, 3 — the number of hydrogen atoms in a hydride molecule;
* — hydrogen solid solution in metal

principle of compression of hydride crystal lattice under the constant size of the hydride-ion H^-.

When hydrogen is dissolved in REM alloys with other metals, one can observe the lattice expansion of the metal — hydrogen solvent — because of the shift of metal atoms with respect to their equilibrium position. The process of hydrogen dissolution in metals and alloys, which is of exothermal character, results in degradation of the latter, in hydrogen brittleness, leading to spontaneous destruction [8, 15–17].

In Table 25 the numbers 1–3, as well as fractions 1/2, 2/6, etc., indicate to the number of hydrogen atoms, composing the hydride molecule. For example, lithium and other alkali metals (Na, K, Rb, Cs, Fr) form hydrides with composition LiH, NaH, KH, RbH, CsH, FrH, alkali-earth metals [4, 5] form hydrides with one and two hydrogen atoms (MeH, MeH_2), hydrides of alkali and alkali-earth metals — salt-like compounds with negatively charged hydrogen ion H^- [6–10, 18]. Scandium, yttrium, lanthanum, cerium, neodymium, praseodymium and other REM form individual hydrides *Me*H_2, *Me*H_3, and in the site between them — a phase of variable composition. Formation of monohydrides ScH, LaH and CeH occurs in the case of scandium, lanthanum and cerium. The transition form *Me* to *Me*H_2 proceeds with the lattice expansion, and transition from *Me*H to *Me*H_3 — with its compression. As hydrogen adds, the electric conduction of the hydride phase decreases, reaching the values for *Me*H_3 characteristic of semiconductors. The same behaviour is characteristic of hydrides of alkali and alkali-earth metals. Hydrogen in the hydride phase acquires electronegative charge in the case of Sc, Y, REM. The charge value increases with the amount of hydrogen. Valence transitions within the hydride phase *Me*-H characterize hydrogen interaction with free electrons, that results in formation of negative (or partially negative) hydride-ions H^- and positive triple-charged ions Me^{3+} [31]. Hence, hydrogen atoms possess negative effective charge in Sc, Y, REM hydrides. The charge is less than one in its absolute value. Proceeding from the work [6] a negative effective charge of hydrogen atoms is determined by the abstraction of some valent electrons of metal atoms from the conduction zone and their «sedimentation» on hydrogen atoms. The metal valence being increased, the partial negative charge q decreases in its absolute value. Thus, for isoelectron series LiH-CsH q = 0.50–0.59, for BeH_2 — SrH_2, q = 0.13–0.31, for AlH_3-InH_3, q = 0.05–0.12 [24, 25]. Lithium hydride is the most resistant among alkali metal hydrides. It is simply synthesized by direct action of lithium or hydrogen when heated to 983–993 K ($T_{\text{melt LiH}}$= 963 K) or at high pressure. A catalyst (naphthalene under the layer of tetrahydrofuran with dissolved $TiCl_4$) being present, lithium hydride is formed in soft conditions: under hydrogen pressure $P_{H2} \leq 101.325$ kPa (1at) and at temperatures 298–323 K [14].

The resistance of hydrides of the elements from Ia and IIa subgroups decreases from cesium to sodium and increases from beryllium to calcium. Thermodynamic properties of the elements' hydrides, ionic radii and interatomic distances in hydrides of the alkali and alkali-earth metals, Sc, Y, La, Ti and some complex alloys are given in Table 26 [7–9, 13, 27, 28].

Hydrides of transition metals of IVa–VIIa subgroups and VIII group, as well as of actinoids possess metal conductivity and are considered as alloys of hydrogen and corresponding metals in which hydrogen electrons are transferred into d-bands of the transition metal, and thus hydrogen atoms may be represented as shielded protons in the metal lattice [32, 33]. This model of hydrides is called a proton model [30]. The above metals can form solid solutions (*Me*H_n, n ≤ 1–4). In accordance with the ionic model hydrogen adds electrons extracting them from metal and forms hydride-ions H^- and metal cations [30]. From the data of [34, 35] hydrides of REM as well as of alkali and alkali-earth metals would be described by the ionic model.

Thermodynamic properties of metal hydrides are studied by the colorimetric method or by the analysis of the absorption-dissociation, pressure-

Table 26

Thermodynamic and physico-chemical properties of hydrides of the elements from Ia, IIa and other subgroups

Hydride	T_{melt} K (or T_{dis})	CH_2, %	$\Delta H°$ kJ/mol	$\Delta G°$ kJ/mol	$\Delta S°$ J/(molЧK)	$L_{Me\text{-}H}$ HM	$R_{Me_i^{z+}}$ nm
LiH	861[*1]	12.68	91.17	67.61	79.08	0.2043	0.068
NaH	694[*1]	4.20	56.43	37.65	62.760	0.2443	0.098
KH	701[*1]	2.49	57.82	41.00	66.94	0.2856	0.133
RbH	637[*1]	1.16	54.31	30.54	79.50	0.3025	0.148
CsH	662[*1]	0.75	49.87	30.54	62.76	0.3195	0.167
BeH_2	473[*1]	15.63	18.95	–	–	–	0.035
MgH_2	773[*1]	7.65	74.43	34.18	135.14	0.195	0.066
CaH_2	1347	4.76	174.26	136.45	127.19	0.232	0.099
SrH_2	1265	2.23	177.00	138.49	129.70	0.249	0.112
BaH_2	1216	1.43	190.12	153.13	125.52	0.267	0.134
ScH_2	460	4.26	208.6	155.9	148.30	0.209	0.081
YH_2	618	3.0	235.0	183.5	150.0	0.213	0.092
LaH_2	620	2.11	208.3	163.0	148.4	0.244	0.114
$CeH_{2,69}$	430	2.09	237.7	–	–	0.242	0.107
$LaNi_5H_6$[*2]	–	1.5/8.4[*3]	239.3	–	121.34	–	0.114/0.069[*4]
$TiH_{1,97}$	–	4.0	125.18	86.2	125.60	0.226	0.076
YCo_5H_6	–	9.0[*3]	212.0	–	–	–	0.092/0.072
VH_2	473[*1]	2.1	80.3	–	142.3	0.296	0.088
$LiAlH_4$	373–393	10.6	103.34	82.0	–	–	0.068/0.051
Mg_2NiH_4	–	3.8	64.43	–	121.4	–	0.066/0.069

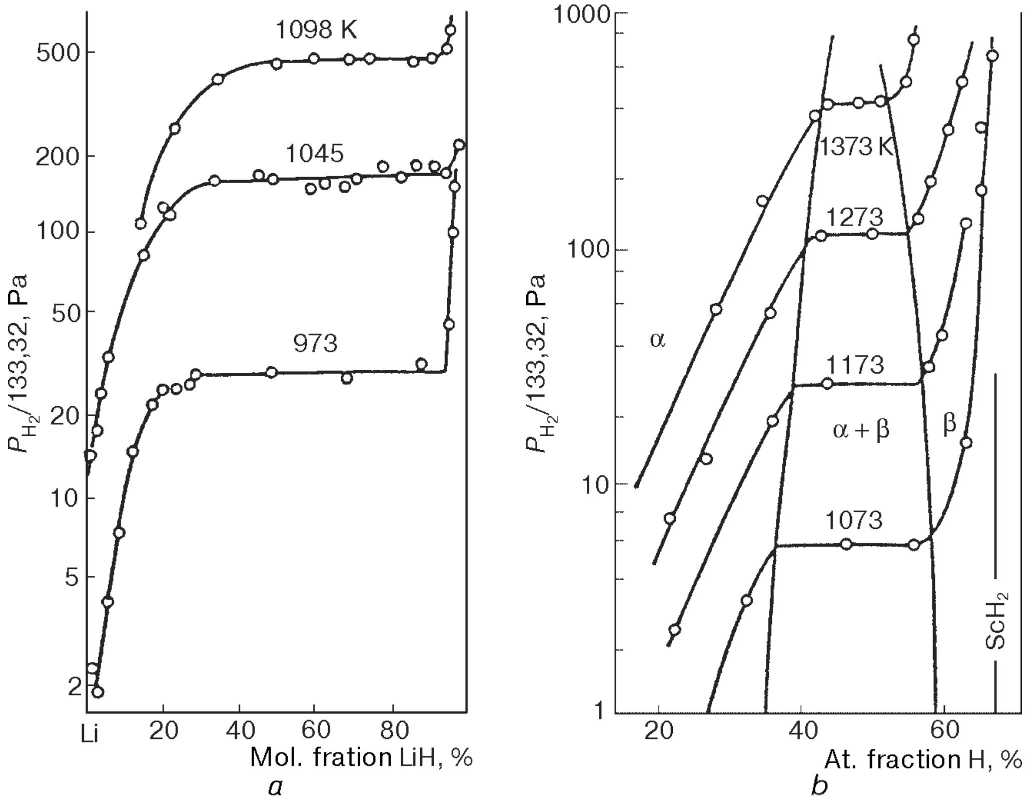
[*1] Dissociation temperature at P_{H2}=101.325 kPa (1 atm).

[*2] La Ni_5H_4.

[*3] Measured in at. shares, %/mol intermetal compound (IMC).

[*4] Radius of the second component is given in denominator.

composition-temperature curves presenting a plot of equilibrium pressure against the condensed phase composition at a constant temperature [6–10, 13, 26–30, 32]. In Fig. 33 the initial sections of curves H_2 pressure-composition evaluate hydrogen dissolution in metal without the change of crystalline lattice (α-phase is formed). The pressure being further increased, a hydride is formed which is separated as a single phase (β_1). There appears a two-phase system $\alpha + \beta_1$ characterized by horizontal sections of isotherms which extent depends on temperature. The higher is the temperature the shorter is the horizontal $\alpha + \beta_1$. At a high temperature all the metal turns into hydride and a two-phase band disappears.



Thus, with temperature elevation hydrogen solubility in metal increases, while the equilibrium pressure of hydrogen rises up to the solubility limit H/*Me* = x at T_i = const and equality of chemical potentials of the formed nonstoichiometric hydride phase $(MeH_x)m_i$ from the metal one m_{ij} saturated by hydrogen. Under these conditions m_{ij} in different phases are functions of P_{H_2}, T and the component concentration in a given phase. The value of hydrogen pressure in the system becomes constant in accordance with the phase rule

$$N = K - F + 2 \qquad (10)$$

where N is the number of the degrees of freedom; K — the number of independent components; F — the number of phases.

By the equation, the increase of the phase number F leads to the equivalent decrease of the number of the degrees of freedom. Certain equilibrium is established between the metal phase saturated with hydrogen, gaseous hydrogen and nonstoichiometric compound MeH_x at $x<MeH<n$. The equilibrium is as follows:

$$MeH + H_x \leftrightarrows MeH_x + H \qquad (11)$$

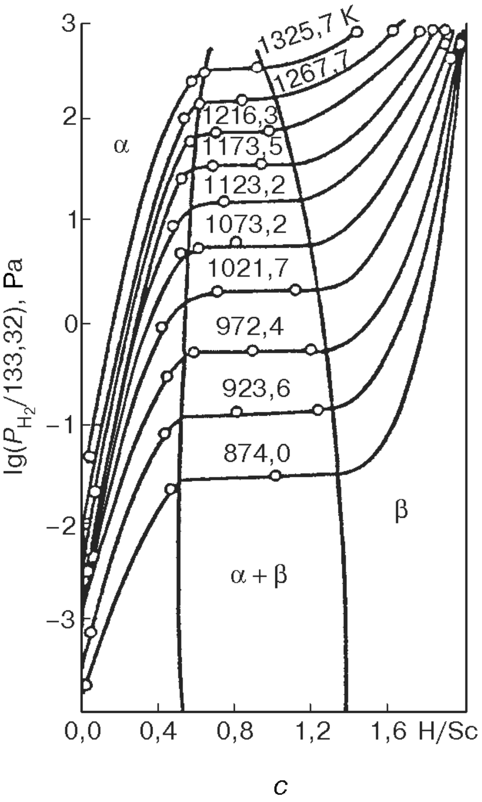


Fig. 33. Dissociation pressure isoterms in the systems, Li — LiH (*a*) [30] and Sc–ScH (*b*, *c*) [26]

Thus the horizontal line in Fig 33 evaluates the hydride dissociation pressure at a given temperature T_y and is the hydride stability function — the lower is the P_{H_2} value, the lower is the hydride stability. When reaching n>H/Me, the metal turns completely into the stoichiometric hydride MeH_n, the surplus hydrogen (P_{H_2}), equivalent to the hydride MeH_n, dissociation degree being in equilibrium with the latter. When reaching equilibrium, chemical potential of hydrogen atoms dissolved in a metal m_H is equal to the chemical potential of gaseous hydrogen [32]:

$$\mu_H = 1/2\ \mu_{H_2} = 1/2\ \mu^0_{H_2} + 1/2\ RT \ln P_{H_2}, \tag{12}$$

where $\mu^0_{H_2}$ is standard potential; R — universal gas constant; T — temperature, K.

According to Wagner [27], chemical potential corresponds to the equation:

$$\mu_H = \mu_H^0 + RT \ln\left(\frac{n}{1-n}\right) + \Delta\mu_H, \tag{13}$$

where $\mu^0_{H_2}$ is standard potential of hydrogen atoms; $RT \ln(n/(1-n))$ — configuration contribution for the ideal statistical distribution of hydrogen atoms in the crystal lattice in octahedral vacancies (positions); $\Delta\mu_H$ — a term allowing for the deviation from ideal behaviour

$$\Delta\mu_{\mathrm{H}} = \Delta\mu_{\mathrm{H}^+} + \Delta\mu_{\mathrm{e}}, \qquad (14)$$

and determined by the contribution of hydrogen electrons and protons; H-atoms in octahedral positions are protons shielded by electrons.

Under joint solution of the equations (12) — (14) the following ratio is obtained

$$\ln\sqrt{P_{\mathrm{H}_2}} = \ln\left(K\left(n/1-n\right)+1/RT\Delta\mu_{\mathrm{H}}\right), \qquad (15)$$

where K is the Siverts constant:

$$K = \exp\left[\left(\mu_{\mathrm{H}}^{0} - 1/2\mu_{\mathrm{H}_2}^{0}\right)/RT\right]. \qquad (16)$$

A dependence of solubility of the ideal two-atom gas in solid solution of the system Me-H, if gas is dissolved monatomically, is described by the Siverts equation:

$$C_{\mathrm{H}} = \sqrt{P_{\mathrm{H}_2}}\exp\left(-\Delta \mathrm{G}^{0}/RT\right) \qquad (17)$$

or

$$C_{\mathrm{H}} = \sqrt{P_{\mathrm{H}_2}}K, \qquad (18)$$

where ΔG^0 — change of Gibbs' free energy.

In the real metal systems Me-H functional dependence of gas solubility in metals is described by the ratio

$$\lg C_{\mathrm{H}} = \sqrt{P_{\mathrm{H}_2}} - A + B/T, \qquad (19)$$

where A and B are constants (Table 27).

The values of A and B constant for hydrides of alkali and alkali-earth metals, as well as for titanium, vanadium, some REM and complex hydrides ($LaNi_5H_6$, YCO_5H_6, $LiAlH_x$ and Mg_2NiH_4) are presented in Table 27. The lowest sorption-desorption temperatures are observed in hydrides of vanadium VH_2, sodium NaH, rhubidium RbH and magnesium MgH_2. Complicated metal hydrides are also known: $PdAgH_x$, $PdFeH_x$, $PdVH_x$, LiH_x, $NaBH_4$, $LiAlH_4$, Na–Al–H_4, Pd–Sc–H_x (Pd–Au) H_x, (Fe–Ni)$_x$, (Pd–Ag)H_x, (Pd–Au–Fe)H_x, (Nb–Mo)H_x, (Ti–Fe)H_x, (Pd–Al)H_x, (Pd–Al)H_x, (Pd–Eu)H_x. Laves phases $(AB_2)H_4$, where A-Zr, Ti, Hf, REM, B–V, Cr, Mn, Fe, Co, Ni, (Gd–La)Co_5H_x, (Jd–La)Ni_5H_x, $(CaNi_aCe_bAl_c)H_x$, (were $a < 7$; $0 < b \leq 0.4$; $0 < c \leq 0.6$), $(La_{1-y}Ti_yNi_5)H_{5\pm0.2}$, $La_{1-y}Si_yNi_5H_5$, $LaNi_5N_6$, $TiFeZrNbH_x$, $LaNi_xMn_y$), $LaNi_{4.7}Al_{0.3}H_x$, $TiMn_{1.5}H_x$, $LaNi_5MnAlH_x$, etc. [36–51].

Table 27

Temperature interval of equations applicability to calculation of dependence of hydrogen solubility in metals and constants *A, B, C, D*

Hydride	ΔT, K	$\lg C = 0.5\lg P_i - A - B/T$		$\lg P_{H_2} = C - D/T$	
		$-A$	$-B$	C	$-D$
LiH	773—958	4,46	–3100	14,02	10 100
NaH	573—773	3,93	180	13,62	6000
KH	613—713	3,32	—	13,32	5860
RbH	519—623	—	—	11,80	5680
CsH	613—713	—	—	9,25	4410
BeH_2	398—493	6,66	–95	—	—
MgH_2	573—853	2,45	1100	–12,12	3888
CaH_2	873—1053	—	—	12,32	9610
SrH_2	966—1169	—	—	13,22	10 400
BaH_2	1108—1223	—	—	12,75	9984
ScH_2	873—1223	4,5	–4700	12,60	10 490
YH_2	873—1223	4,06	–4250	12,64	11 869
LaH_2	873—1023	5,06	–4170	13,12	11 200
$CeH_{2,69}$	823—1023	2,6	–3900	12,75	10 760
$TiH_{1,97}$	573—873	—	—	15,62	9500
YCo_5H_6					
VH_2	283—413	2,62	–1685	9,6	4340

As was noted above, hydrogen absorption by metals and formation of hydrides are accompanied by heat release. Thus, to isolate hydrogen from the systems Me_i — H, Me_i — Me_j — H, it is necessary to consume heat, equivalent to the dissociation enthalpy of the corresponding hydride. Hydrides possessing low decomposition pressure at high temperatures are usually characterized by high absolute values of the formation enthalpy. And vice versa, hydrides with high decomposition pressure at low temperatures have low enthalpy values.

Formation of hydrides is accompanied by compression under the components interaction. The dependence of the difference of interatomic distances *Me*–H of individual components and those «bound» into hydrides on the hydrides formation enthalpy is presented in Fig. 34. To calculate interatomic distances in hypothetic molecules of MeH_i (i = 1.2), formed individual elements without compression, the element radii were taken from the works [51, 52], the hydride-ion radius was taken as that equal to 0.208 nm, the values of interatomic distances in real hydrides were taken from [30, 53] and the values of hydride formation enthalpies were presented from the data of [7–9, 28].

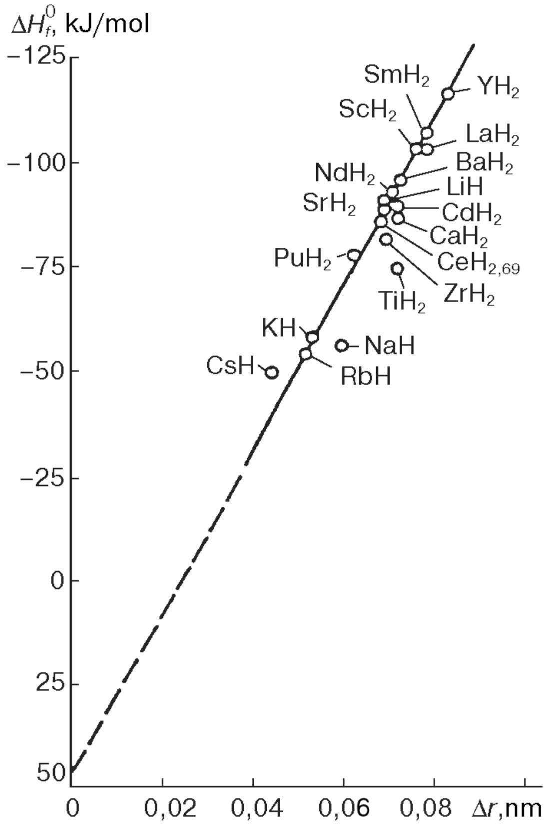


Fig. 34. Dependence of hydride formation enthalpy on the difference of interatomic radii of individual components and hydrides

When plotting ΔH_f^0 as a function of Δr the values of ΔH_f^0 were recalculated per 1 mol of hydride-ions H^-. The obtained values of ΔH_f^0 as a function of Δr (compression) were given in Fig. 34, where it is evident that the values $\Delta H_f^0 - \Delta r$ fall in a straight line. The higher is the exothermal effect of hydride formation reaction, the more is the compression and the less is the distance in the crystalline lattice $Me_i - H$.

A portion equal to 44.0 kJ/(mol H^-) is cut on the curve $\Delta H_f^0 - \Delta r$ at $\Delta r = 0$. This portion of the curve corresponds to the endothermal component of the work in compression.

It has been established [53] that both the hysteresis of P-T-x curves and its value against the rate of achieving the equilibrium state at different pressure and temperature gradient are determined by elastic stresses in the hydride (or metal) matrix. The slope of the plateau of equilibrium pressure in the region of coexistence of two solid phases is determined by the effect of the internal stress as a function of the fractional phase transformation.

It is known that nickel and stainless-steel-like alloys are hardly hydrogenized and may be used for manufacturing reactors which would work with hydrogen [54–59]. Nickel forms hydrides NiH and NiH_2. Dihydride NiH_2 posseses a face-centered lattice and dissociates even at 293–303 K. Hydrogen solubility in solid nickel in the temperature range of 623–1673 K is described by the equation [60].

$$\lg C = 0.5 \lg P_{H_2} - 2.00 - 870 / T, \tag{20}$$

in liquid nickel (1773–1973 K) — by the equation:

$$\lg C = 0.5 \lg P_{H_2} - 1.42 - 1176 / T, \tag{21}$$

For metals Au, Pd, Pt, Rh, Ru, Si. Sn, W the hydrogen solubility as a function of inverse temperature corresponds to the equation (with negative value at constant B_i)

$$\lg C_H = 0.5 \lg P_{H_2} - A_i - B_i / T, \tag{22}$$

Temperature dependence of hydrogen solubility in solid metals Hf, La, Nb, Pd, Sc, Ta, Ti, V, Y, Zr is described by the equation (19) [13, 22, 60].

The hydrides of metals of Ia and IIa subgroups actively interact with water:

$$MeH + H_2O = MeOH + H_2; \tag{23}$$

$$MeH_2 + 2H_2O = Me(OH)_2 + 2H_2, \tag{24}$$

and manifest chemical activity to oxygen.

In contrast to hydrides of the elements of Ia and IIa subgroups with ionic bond which possess high chemical activity with respect to water and oxygen, the REM, SC, Y, Ti, Zr, V, Nb, Hf, Ta hydrides are relatively chemically inert and do not interact with water and air oxygen even at high temperatures. Thus, Ta, Ti, Zr, Hf, V, Nb hydrides are widely used for production of these metals powders. The processes are based on the following reactions:

$$2\, MeMe_j + nH_2 \rightarrow 2\, MeH_n + 2Me_j,\ \text{at}\ T, P_i \tag{25}$$

$$2Me_j + 2HX \rightarrow 2Me_jX + H_2, \tag{26}$$

where Me_j — are Fe, NI, Cr, Cu, etc. impurities.

When affected by acids, these impurities dissolve and form soluble salts removed by water washing. Then highly pure powders of Ta, Ti, Zr, Hf, V, Nb hydrides are compacted and used for various purposes in power industry.

The powders, used for producing corrosion-resistant alloys with preset properties using the methods of powder metallurgy, are obtained at a temperature

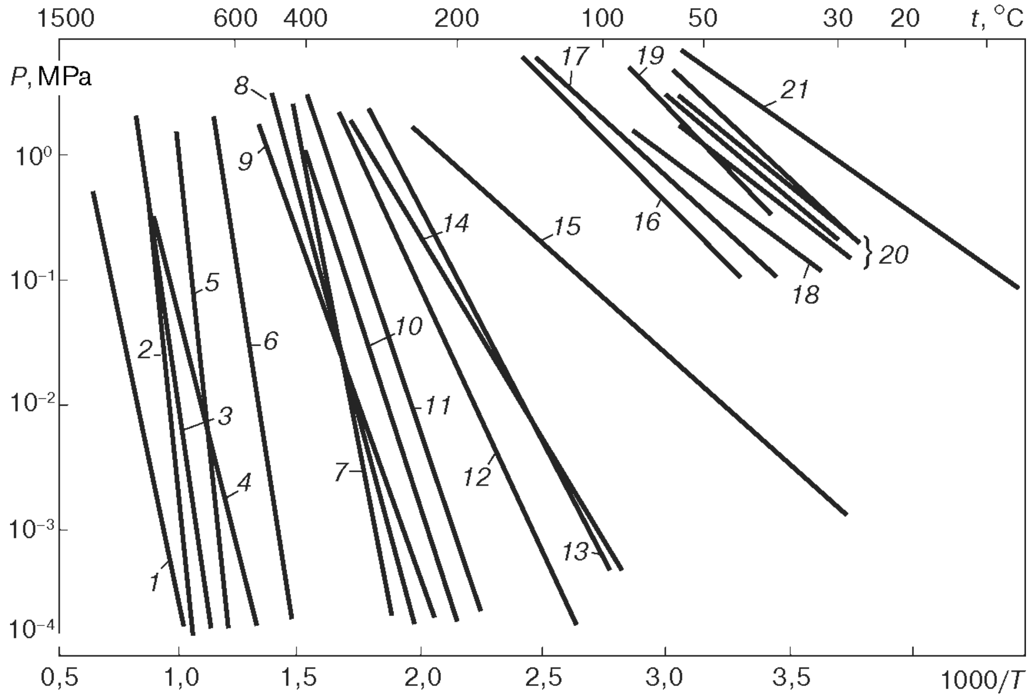


Fig. 35. Dependence of equilibrium pressure of hydrogen P_{H_2} under hydrides dissociations on the inverse temperature
1 — La–LaH_2; *2* — Ca–CaH_2; *3* — Sr–SrH_2; *4* — Ba–BaH_2; *5* — Ti–TiH_2; *7* — K–KH; *8* — Na–NaH; *9* — U–UH_3; *10* — Cs–CsH; *11* — Rb–RbH; *12* — Mg·MgH_2; *13* — MgCu·MgH_2; *14* — Mg_2Ni·MgNiH_4; *15* — Pd·Pd$H_{0.8}$; *16* — VNb–H_x; *17* — NbH·NbH_2; *18* — LaNiH_6; *19* — VH·VH_2; *20* — FeTiH_x; *21* — MnNi_5H_x

below the melting point. Hydrides of alkali-earth metals being decomposed, the metal which releases in the reaction.

$$MeH_2 \rightarrow Me + H_2 \qquad (27)$$

forms solid solution with hydride MeH_2, and in this connection the resistance of $(MeH)_x$ increases and its decomposition pressure decreases [7, 8, 22, 24, 61].

Temperature dependence of equilibrium pressure of gaseous hydrogen under dissociation of the corresponding hydrides in certain temperature range corresponds to the equation

$$\lg P_{H_2} = C_i - D / T, \qquad (28)$$

where C, D are constants (see, Table 27).

The dependence of equilibrium hydrogen pressure on inverse temperature for a number of hydrides is shown in Fig. 35. Hydrogen, formed under hydride dissociation, being removed from the closed chain, there dissociates a hydride with composition differing from its initial composition (Fig. 33)

Hydrides of IIIa subgroup elements, rare-earth metals and their alloys with Ta, Ti, Zr, Hf, V, Cr, Nb are formed under the direct hydrogen interaction with metals and alloys in certain experimental conditions (T, P_{H_2}, catalyst nature) [62]. Be, Cu, Ru, Ag, Cd, In, W, Re, Pt and Hg hydrides can be obtained at high pressures of hydrogen ($T = 100–1000$ K; $P_{H_2} \geq 100$ GPa) [63]. Resistance of hydrides of IIb subgroup elements decreases with the increase of the atom weight. Zinc hydride ZnH_2 decomposes slowly at a room temperature and decomposes intensively at 353 K [64], while cadmium hydride CdH_2 — at 293 K [65].

A capacity of some hydrides of metals (La, Y, Sc, REM) especially their intermetal alloys with other metals (Ni, Co, Ti, V) to absorb hydrogen at certain temperatures and pressures is used in the so-called hydrogen accumulators. Individual titanium and vanadium hydrides are chemically inert and thermally stable. That is also characteristic of other transition metals. Thus, it is impossible to use individual titanium and vanadium hydrides as well as other transition metals hydrides as low-temperature accumulators of bound hydrogen, since hydrogen is not mobile in them at low temperature and they are thermally resistant.

Hydrogen reactions with metal phases, containing intermetal compounds, and alloys, which components are also metals capable to form stable binary hydrides $Me\mathrm{H}_n$, [4–6,58] are used as hydrogen accumulators. It has been established that most intermetallides containing Ni, Co, Ti, Mg and La, Y or REM interact with hydrogen at relatively low temperatures (298–373 K) and pressures (0.01 – 10 MPa).

In the systems based on these alloys Me_iMe_j — H_2 the equilibrium hydrogen absorption or its release at temperature elevation and decrease of H_2 pressure in the reactor is established very quickly. That is why that hydrogen accumulators are widely used in science, technology, and industry. Special importance is attached to hydrogen accumulators for obtaining high-purity hydrogen [66–68], which is used in the precision power measurements, most technological processes of electronic industry and for obtaining great amounts of volatile hydrides.

6.2. Methods of hydrogen production

As was noted, hydrogen is used in the very different branches of industry and new technology both as a reagent and heat-carrier [70–81]. Tendencies in development of the low-tonnage technologies of hydrogen production from various raw materials prove, that in the nearest future decades hydrogen will be also able to play considerable part in power consumption. However, since the processes of gaseous hydrogen production are rather power-intensive, it is rather promising to use the thermal and electric power of NPP and NPP with high-temperature liquid-salt reactors (HTLSR) as well as power from renewable sources (see, Chapter 4). Fossil organic fuel (natural gas, hard and brown coal, combustible shales) and water which reserves are unlimited and renewable (since

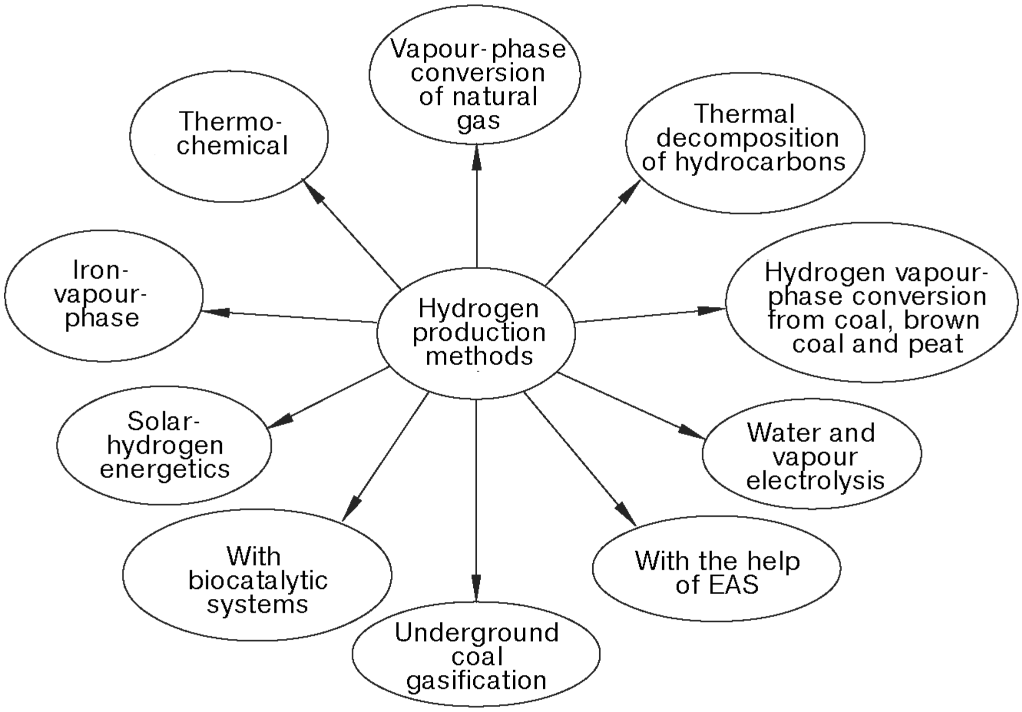


Fig. 36. Methods of hydrogen production

hydrogen under oxidation (combustion) turns into ecologically pure water) are raw materials for hydrogen production. One can distinguish 10 methods of hydrogen production now (Fig. 36).

1. Vapour-phase conversion of methane (natural gas).
2. Thermal decomposition of hydrocarbons.
3. Thermochemical cycles.
4. Vapour-phase conversion of hydrogen from hard, brown coal and turf.
5. Underground gasification of coal.
6. Iron-paraffin method.
7. Electrolysis of water and vapour.
8. Hydrogen production by means of power-accumulating substances.
9. Water photolysis with obtaining hydrogen and oxygen (solar-hydrogen power).
10. Hydrogen production by means of biocatalytic systems.

Let us consider the basic parameters of these methods.

1. **Vapour-phase conversion of methane (natural gas).** This method of hydrogen obtaining is the most large-scale and economically profitable production. Above 50 mill.t of hydrogen are produced all over the world by the method of the vapour-phase conversion. The conversion of natural gas containing 88–95 % of methane and 3–8 % of ethane is performed at a temperature above 600 °C as a results of following reactions:

$$CH_4 + H_2O \rightarrow CO + 3H_2 - 206.1 \text{ kJ}; \qquad (29)$$

$$CO + H_2O \rightarrow H_2 + CO_2 + 41.17 \text{ kJ}; \qquad (30)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 - 247.27 \text{ kJ}; \qquad (31)$$

$$C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2 - 347.3 \text{ kJ}. \qquad (32)$$

by means of water vapour and carbon dioxide. As is evident, the reactions of methane and ethane conversion by water vapour (29) and (32) proceed with heat absorption. The reaction of methane with carbon dioxide (31) with obtaining carbon oxide is also endothermal. Utilization of industrial effluents of CO_2 with obtaining carbon oxide and hydrogen can be organized on the basis of this reaction. Carbon dioxide conversion of methane according to equation (31) with obtaining dry synthesis-gas may be used for methanol synthesis by the reaction (29).

Conversion of CO by the reaction (30) is the exothermal process. To compensate the endothermal effect 25–40 % of initial natural gas are used as fuel by burning it in oxygen by the following reactions:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(\text{liq.}) + 890.2 \text{ kJ}; \qquad (33)$$

$$C_2H_6 + 2{,}5O_2 \rightarrow 2CO + 3H_2O(\text{liq.}) + 1559.7 \text{ kJ}. \qquad (34)$$

Under measured stoichiometric supply of oxygen the process of methane oxidation can be represented by the equation

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 + 318.71 \text{ kJ} \qquad (35)$$

with exothermal effect equal to $Q = 318.71$ kJ/mol CH_4. Carbon dioxide from the obtained gas mixture is removed by scrubbing with water or sodium carbonate solution. Use of the natural gas as fuel under the vapour-phase method of hydrogen production results in the rise of the obtained hydrogen price. Production of 1 t of hydrogen by the method of vapour-phase conversion of natural gas requires theoretically 2.5 t of methane. But real methane consumption is much higher. Thus, the use of such fuel as coal is more expedient, from the viewpoint of economy, because of its lower cost and great reserves [70]. It is even more efficient to perform the vapour-phase conversion of natural gas in high-temperature nuclear gas-cooled reactors HTGR-1000, which produce heat-transfer agent with temperature 1000°C. A technological scheme, combining a nuclear plant of NPP with thermochemical cycle, from the data of the work [71], is presented in Fig. 37. The scheme includes three closed cycles with possible power (heat) exchange between them.

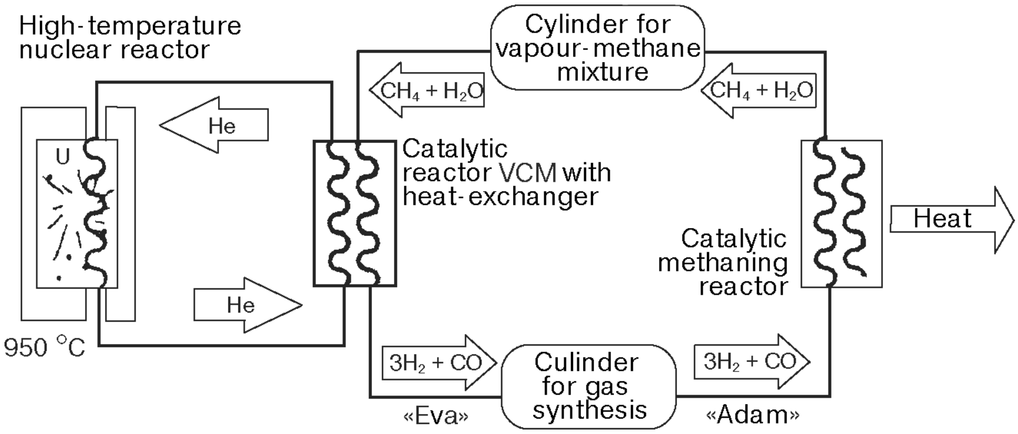


Fig. 37. Technological diagram combining nuclear plant of NPP with thermochemical cycle [72]

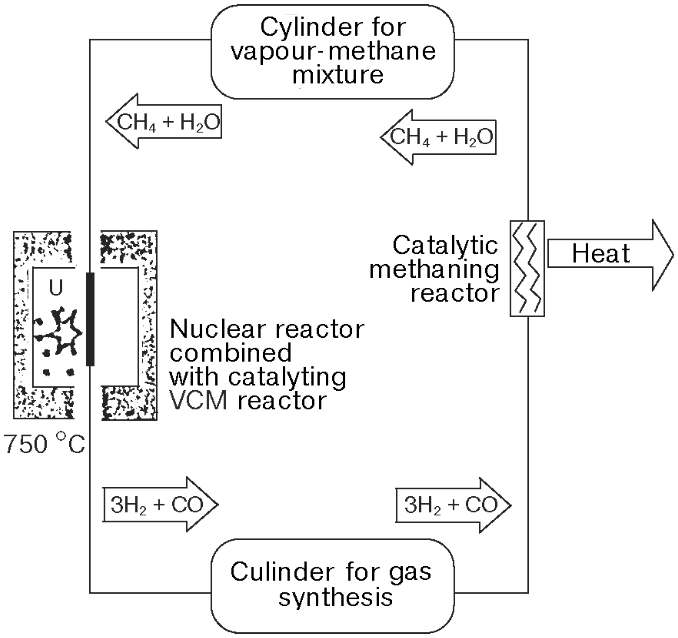


Fig. 38. Schematic technological diagram of the nuclear power plant on the basis of «Ikar» — process [82]

In the first nuclear cycle helium with temperature of 500 °C passes through the active zone of the nuclear reactor and heats to 950 °C. Then heated helium — a heat transfers agent — is supplied to heat-exchanger outside the nuclear reactor, where it transfers its heat to the second (chemical) cycle — a catalytic reactor of the vapour methane conversion in which methane is decomposed by a catalyst with formation of synthesis-gas ($3H_2$+CO). The latter is supplied to the tank-storage. Power being required, the synthesis-gas is supplied to the catalytic reactor of methaning and its heat passes through the heat-exchanger into the third cycle — a gas-turbine plant, for example.

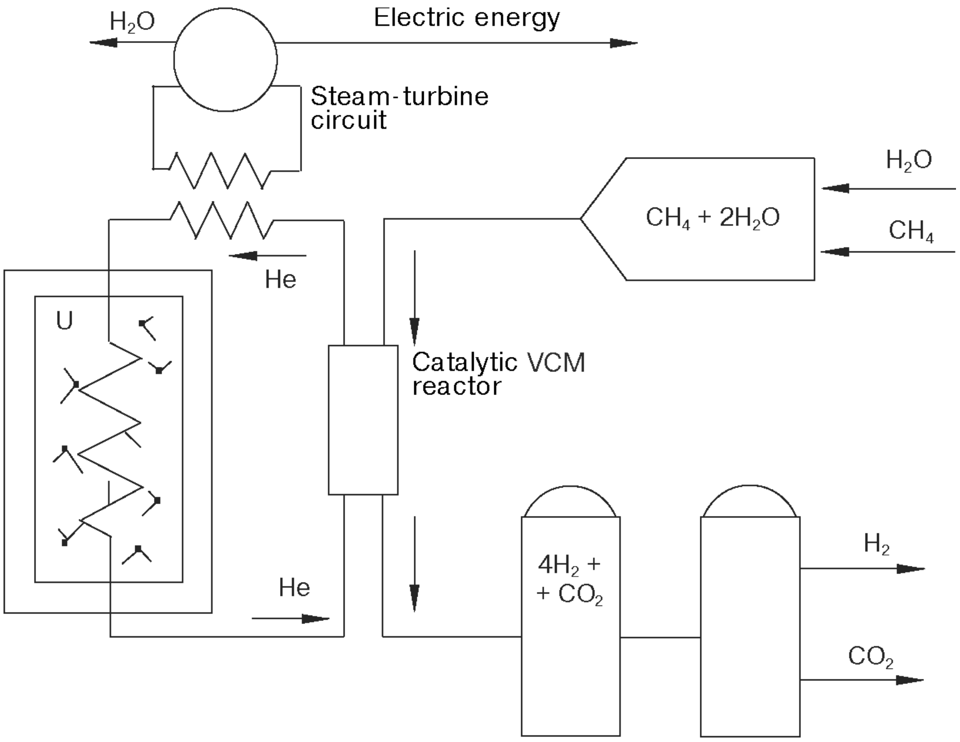


Fig. 39. Schematic technological diagram of nuclear hydrogen–power plant of vapour conversion of natural gas with production of hydrogen and electric energy generation

An interesting technology of natural gas conversion was proposed by V.N. Parmon, Academician of the Russian Academy of Sciences, and his collaborators [82]. A fundamental technological scheme of the nuclear power plant on the basis of «Ikar»-process is presented in Fig. 38. In this case the nuclear fuel is mixed with a catalyst and placed into the nuclear reactor combined with the catalytic reactor of vapour methane conversion. As a result of methane passage through the reactor active zone, the synthesis-gas is formed which is used as heat-exchange agent under methaning in the catalytic reactor. That is an original idea, but it was not allowed for, that at a temperature of 700–800 °C zirconium shell of fuel elements will interact with hydrogen, zirconium dihydride (ZrH_2) being formed according to exothermal reaction.

We think the technological scheme of the nuclear hydrogen-power plant given in Fig. 39. to be more expedient. It is characterized by a higher temperature of the nuclear high-temperature reactor HTGR-1000 with helium agent with a temperature of 1000 °C. When helium agent passes through the catalytic reactor PKM with the counter-current of components, its temperature falls to 600–650 °C, then the agent arrives to the steam-turbine loop. As a result we obtain electric-power, hot water for public services, liquid CO_2 and hydrogen sent to the consumer. Cost of hydrogen obtained by natural gas conversion is estimated as $ 4.4–8/GJ [83].

Highly efficient, manoeuvrable and ecologically safe complexes including NPP with HTLSR are rather promising to be used for conversion of natural gas.

2. Thermal decomposition of hydrocarbons. The endothermal reaction

$$CH_4 \rightarrow C(solid) + 2H_2 - 74{,}8\ kJ \qquad (36)$$

(with obtaining elementary carbon in the form of its two modifications — ash and pyrocarbon) is assumed as a basis of the thermal method of methane decomposition.

Ash is formed under homogeneous decomposition of methane, and pyrographite covering the reaction surfaces — under heterogeneous decomposition. The yield of ash (used in rubber-technological industry, in production of plastic materials and polymers, graphitized articles, in chemical production and instrument engineering) makes 40 % [84]. Methane decomposition reaction proceeds with practically complete heat absorption (74.8 kJ/mol CH_4) (decomposition extent h = 100 %). Allowing for kinetic peculiarities and positive value of Gibbs energy of reaction (36) (ΔG°_{298} = 50.8 kJ/mol CH_4) methane decomposition would be carried out at a temperature close to 1000 °C.

A new high-temperature method for pyrolysis of natural gas has been developed at the Institute of High Temperatures of the Russian Academy of Sciences. The method is based on the process of natural gas pyrolysis in «free volume» [84]. Technological scheme of the industrial plant for hydrogen production by means of pyrolysis of natural gas in «free volume» is given in Fig. 40. This process allows escaping formation of pyrocarbon in the reaction volume under decomposition of natural gas. Under hydrothermal decomposition of methane by the reactions

$$CH_4 + H_2O \rightarrow 3H_2 + CO; \qquad (37)$$

$$CO + H_2O \rightarrow CO_2 + H_2; \qquad (38)$$

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \qquad (39)$$

one can also avoid formation of solid carbon [85].

The following reaction

$$3CH_4 + CO_2 + 2H_2O \rightarrow 4CO + 8H_2. \qquad (40)$$

is possible, depending on the ratio of CO, CO_2 and CH_4 as well as on the conditions of the experiments performance.

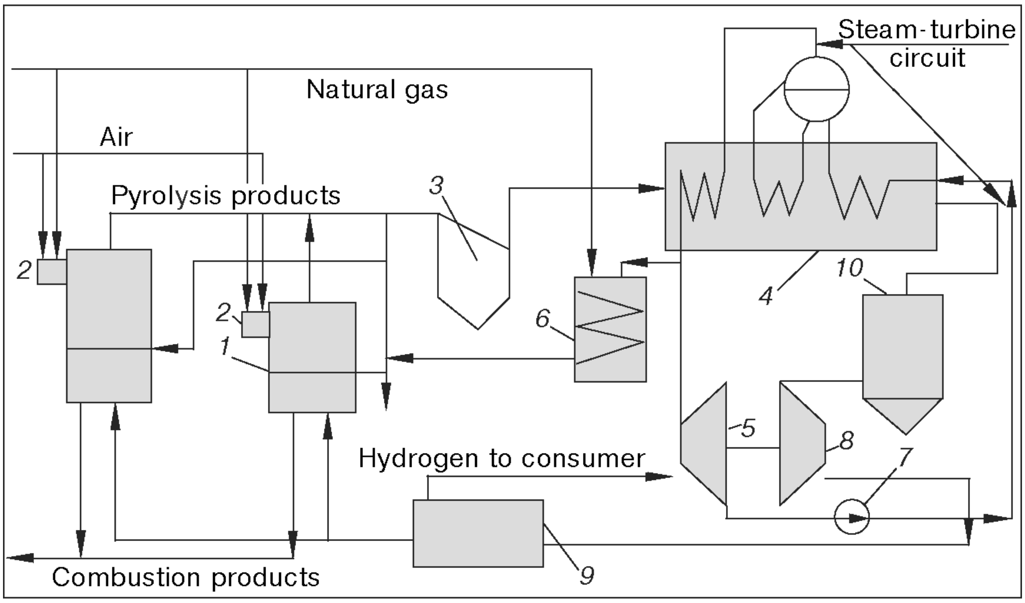


Fig. 40. Diagram of industrial plant for hydrogen production by pyrolysis of natural gas in «free volume» of regenerative heater

The reaction products may be used for catalytic synthesis of methanol, ethanol and other organic compounds.

According to technology described in the work [84], natural gas (see, Fig. 40) is heated by means of two high-temperature regenerative heaters *I* with packing in the combustion chamber *2* made of corundum balls 20 mm in diameter. The upper layers of the packing are heated in two combustion chambers *2* to the temperature of 2000–2050 K with alternation of heaters: one of them operates under heating the packing, another — under pyrolysis. Pyrolysis is carried out by mixing natural gas with gas-carrier heated in the packing to 10900–2000 K. The reaction products (H_2, C (solid)) with temperature 1600–1700 K arrive to the cyclone battery *3* where the basic quantity of deposited carbon (approximately 90 ≅ 95 % C) is separated from gaseous hydrogen.

High temperature of hydrogen is used for generation and superheat of water steam and for production of electric power in the steam-turbine cycle including steam generator *4*, steam turbine *5*, steam condenser and condensate pump *7*. The technology provides for the heating of natural gas supplied for pyrolysis with steam in the heat exchanger *6*, fine cleaning of hydrogen of deposited carbon (C(solid)) performed in the fabric filter *9*, gas-carrier circulation in the closed loop with the help of compressor *8*. Nitrogen being used as gas-carrier, the mixture is separated in the separation unit *9*. Gaseous hydrogen free from nitrogen and deposited carbon is supplied to the user.

The extent of thermal decomposition of natural gas being 100 % and efficiency for the power system with steam-power units with supercritical pressure and reheating taken close to 40.5 %, methane consumption per 1 kg of hydrogen makes 5.57 kg, with nitrogen used as heat-transfer medium, and 5.56 kg with hydrogen. In the ideal case the natural gas pyrolysis without heat losses requires only 4.7 kg of methane per 1 kg of hydrogen. Average efficiency of the processes of natural gas pyrolysis equals 75 %. Saving in methane in electric power production is 1.70 and 1.69 kg/s, when using nitrogen and hydrogen as heat transfer agents, respectively. Interesting results were obtained in the work [84] when carrying out pyrolysis of natural gas in plasma generator.

3. Thermochemical cycles. Thermochemical cycles (TChC) of hydrogen production belong to the most theoretically promising ones. The great number of cycles have been developed, but only some of them meet the requirements of thermodynamics, kinetics and power engineering. The Westinhouse cycle (Mark-2) and carbonate-halogenide one are considered most promising.

The Mark-2 cycle includes the following reactions [86]:

$$H_2SO_4 \text{ (end)} \rightarrow H_2O \text{ (gas.)} + SO_3 \text{ (347 – 400 °C)}; \quad (41)$$

$$SO_3 \rightarrow 1/2O_2 + SO_2 \text{ (780 – 320 °C)}; \quad (42)$$

$$H_2O \text{ (gas.)} \rightarrow H_2O \text{ (liq.) (100 °C)}; \quad (43)$$

$$SO_2 + H_2O \xrightarrow{\text{El.}} H_2SO_4 + H_2. \quad (44)$$

Overall reaction: $$3H_2O = 3H_2 + 1.5O_2. \quad (45)$$

In that TChC maximum temperature of thermal stage (42) is 780–920 °C, and potentials difference of standard electrode when obtaining 100 % H_2SO_4 $E° = 0.435–0.467$ V. Estimated efficiency of the given TChC equals 44 %. Power consumption to obtain 1m^3 of H_2 is close to 8 kW·h/m^3, which is considerably higher than under water electrolysis. In our opinion, the above cycle efficiency, when using worthless heat because of low values of standard potentials ($\Delta E° = 1230 – 0.451 = 0.779$ V), would be much higher (about 80 %), and power consumption to obtain 1m^3 of H_2 lower, than under ordinary water solution electrolysis with obtaining hydrogen.

The carbonate-halogenide TChC [86] combines chemical reaction with electrochemical one. The reaction of oxygen displacement by halogen was used as the chemical reaction:

$$Me_2CO_3 + X_2 \rightarrow 2MeX + CO_2 + 1/2O_2, \quad (46)$$

where *Me* — alkali metal; *X* — halogen.

The reaction of halogen production was realized at electrochemical stage:

$$2MeX + CO_2 + H_2O \rightarrow Me_2CO_3 + X_2 + H_2. \qquad (47)$$

Overall reaction: $3H_2O = 3H_2 + 1.5O_2$

Iodide NaI- and bromide LiBr-systems, where thermochemical stage proceeds at 670 and 492 °C, and electrochemical — at low value of voltage on the bath equal to 0.84 and 0.90 V, respectively, are promising for practical use.

Iron (II), (III) — oxide-chloride TChC, which efficiency is close to 73.0 % [87] seems of more interest for us. The cycle includes the following thermochemical reactions:

$$2Fe_3O_4 + 4HCl = 2FeCl_2 + 2Fe_2O_3 + 2H_2O \ (550\text{–}600\ °C); \qquad (48)$$

$$2Fe_2O_3 + 12HCl = 4FeCl_3 + 6H_2O \ (125\ °C); \qquad (49)$$

$$6FeCl_3 \rightarrow 6FeCl_2 + 3Cl_2 \ (300\ °C); \qquad (50)$$

$$6FeCl_2 + 9H_2O \rightarrow 3Fe_2O_3 + 12HCl + 3H_2 \ (450\text{–}600\ °C); \qquad (51)$$

$$3Cl_2 + 3H_2O \rightarrow 6HCl + 1{,}5O_2 \ (600\ °C). \qquad (52)$$

Overall reaction: $3H_2O = 3H_2 + 1.5O_2$

High hydrogen yield at temperatures not exceeding 600 ° is observed for the given cycle; at higher temperatures — the reaction rates are limited by mass transfer. In case of continuous use of the above cycle only Fe_2O_3 takes part in thermochemical reactions, and this reduces the number of reactions to four.

The work [88] suggests iron (II), (III) magnesium-hydroxide-chlorid mean-temperature thermochemical cycle which includes five stages of chemical reactions:

$$3FeO_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2 \ (450\text{–}900\ °C); \qquad (53)$$

$$Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O \ (50\text{–}110\ °C); \qquad (54)$$

$$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2 \ (300\ °C); \qquad (55)$$

$$Cl_2 + Mg(OH)_2 \rightarrow MgCl_2 + 1/2O_2 + H_2O \ (50\text{–}90\ °C); \qquad (56)$$

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl \ (350\ °C). \qquad (57)$$

Overall reaction: $3H_2O = 3H_2 + 1.5O_2$

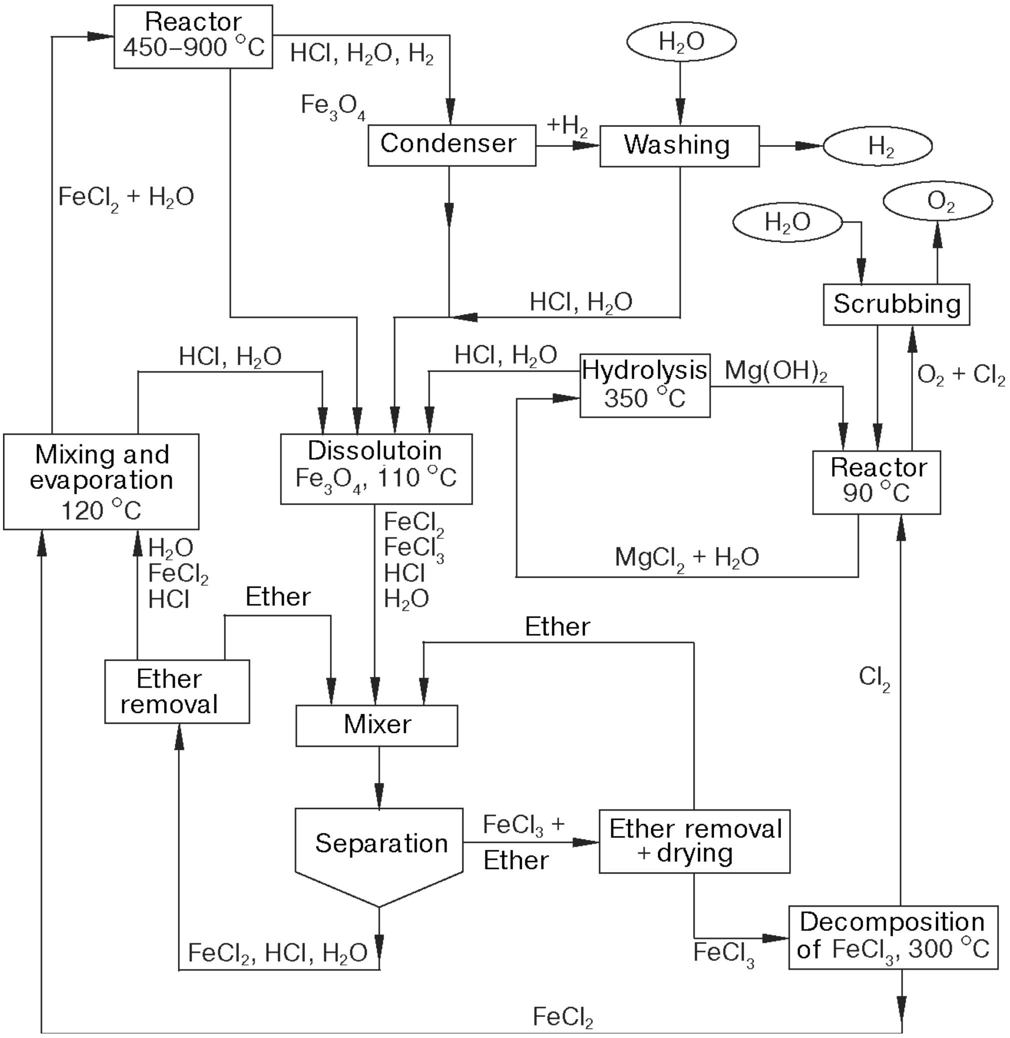


Fig. 41. Technological diagram of iron (II), (III) — magnesium-hydroxide-chloride mean-temperature thermochemical cycle [88]

A simplified flow diagram of thermochemical process is presented in Fig. 41. The diagram includes reactors, mixers, condensers, hydrolyzers. Sediments treatment by ether is provided for complete removal of moisture.

The first stage, realized at 450–900 °C by the reaction (53) of the steam-phase redox process Fe^{3+}/ Fe^{-2+} in chloride system is accompanied by the release of H_2, HCl and formation of Fe_3O_4. Temperature being elevated from 450 to 900 °C one can observe the decrease of the reaction enthalpy $\Delta H°$ from 326.3 to 284.5 kJ, and free energy $\Delta G°$ from 125.5 to 21.0 kJ.

At the second stage the reaction (54) of Fe_3O_4 dissolution in HCl, accompanied by formation of 1 mol of $FeCl_2$ and 1 mol of $FeCl_3$, proceeds at 50–110 °C. The reaction is exothermal with $\Delta H° = -209.2$ kJ. Under these conditions the change in the Gibbs standard energy makes $\Delta G° = -4.184….29.3$ kJ. At the third stage the dissociation heat of reaction (55) of $FeCl_3$ (T_{melt} = 288, T_{boil} = 315 °C) is performed at 300 °C. The reaction (55) is endothermal. Dissociation heat of solid $FeCl_3$ equals about 108.8 kJ/mol Cl_2, and dissociation of $FeCl_3$ requires only 21–25.1 kJ/mol Cl_2. Evaporation of 1 mol of solid $FeCl_3$ consumes heat of 144.3 kJ.

The reaction product — gaseous chlorine is used on the fourth stage when it is bound according to the reaction (56) by magnesium hydroxide at 50–90 °C, the reaction is accompanied by oxygen release and formation of $MgCl_2$. Change of thermodynamical parameters of $MgCl_2$ formation makes: $\Delta H°= -159.2$ kJ, $\Delta G°= -175\ldots-200.8$ kJ; for the reaction (54) $\Delta H° = 16.7$ kJ, $\Delta G° = 33.5$ kJ.

On the fifth stage $MgCl_2$ is hydrolyzed at 350 °C with obtaining hydrochloric acid HCl which is directed to the second stage. Change of termodynamical parameters of the reaction (57) of $MgCl_2$ hydrolysis makes: $\Delta H° = 16.7$ kJ, $\Delta G° = 33.5$ kJ. Thermal efficiency of iron (II), (III) — magnesium-hydroxide-chloride cycle is equal to 41 %:

$$\varepsilon_T = \Delta H_f^\circ / Q \cdot 100\ \%, \tag{58}$$

where ΔH_f° is heat of formation of 1 mol of water from hydrogen and oxygen; Q — total amount of heat for the whole process of water dissociation into hydrogen and oxygen.

Thermodynamic efficiency of iron (II), (III) — magnesium-hydroxide-chloride cycle is equal to

$$n = \beta\,(\Delta G_f^\circ / Q) \cdot 100\ \%, \tag{59}$$

where ΔG_f° — change of Gibbs free energy in formation of 1 mol of water from hydrogen and oxygen under normal conditions ($1.01325 \cdot 10^5$ Pa, 298 K); β — the factor possessing the value ≤ 1, when proceeding the process in the temperature range of 723–300 K, proved to be equal to 58.6 % at $\beta = 1$.

Interesting results were obtained when investigating copper (I), (II) — magnesiumchloride thermochemical cycle which also includes five stages of chemical reactions [88]. Copper, chlorine, hydrogen and oxygen circulate in this cycle. Their interaction may be represented by means of the following equations:

$$2Cu + 2HCl\ (aq.) \rightarrow 2CuCl\ (aq.) + H_2\ (gas.)\ (100\ °C); \tag{60}$$

$$4CuCl\ (ac.) \rightarrow 2CuCl\ (ac.) + 2Cu\ (gas.)\ (30\text{–}100\ °C); \tag{61}$$

$$2CuCl_2\ (ac.) \rightarrow 2CuCl\ (ac.) + 2Cl_2\ (gas.)\ (500\text{–}600\ °C); \tag{62}$$

$$Cl_2 + Mg(OH)_2 \rightarrow MgCl_2 + 1/2O_2 + H_2O\ (50\text{–}90\ °C); \tag{63}$$

$$MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl\ (350\ °C). \tag{64}$$

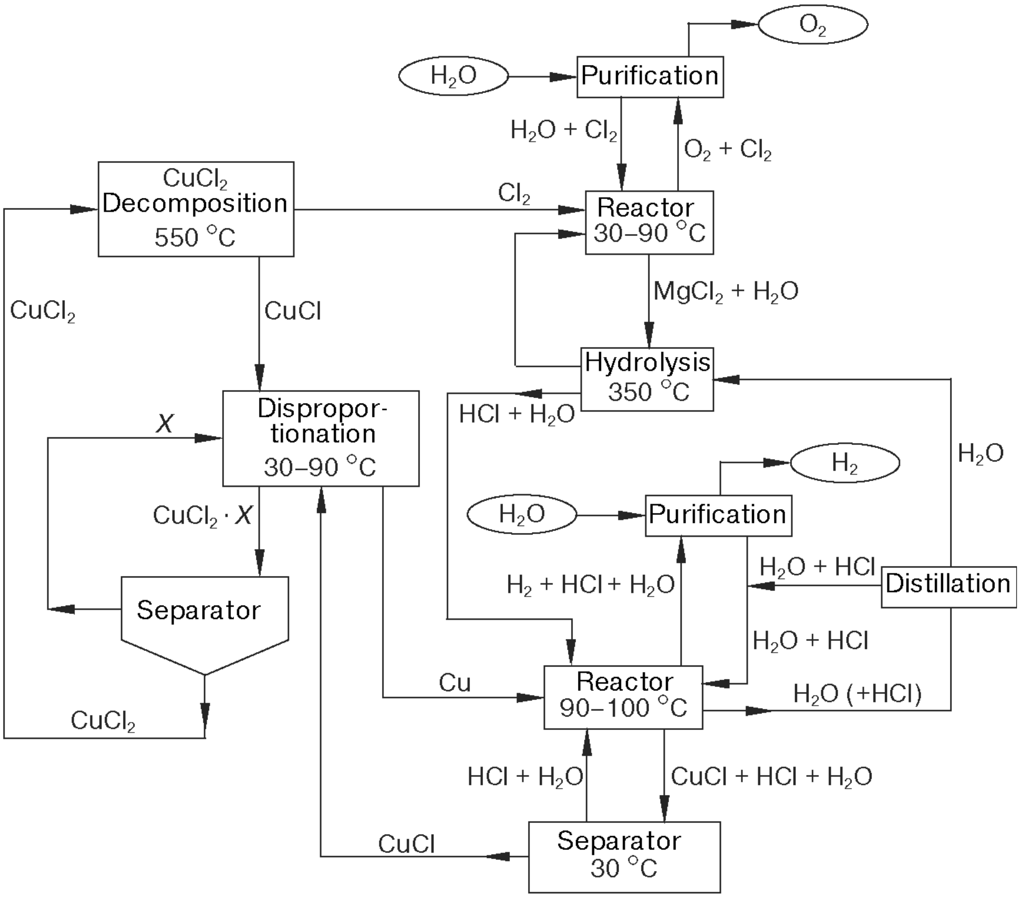


Fig. 42. Technological diagram of copper (I), (II) — magnesiumchloride average temperature thermochemical cycle [255]

Overall reaction of the cycle is the same: $3H_2O = 3H_2 + 1.5O_2$

The flow diagram of the given TChC is given in Fig. 42. The TChC instrumentation includes reactors, separators, distillation unit and hydrolyzers.

At the first stage of this cycle copper is dissolved in hydrochloric acid at 100 °C. The reaction (60) products are chloride of univalent copper and hydrogen. Changes in enthalpy and Gibbs free energy of the reaction (60) are as follows: $\Delta H° = -33.5$ kJ, $\Delta G° = 8.36$ kJ. The reaction (61) of disproportionation of copper (I) crystalline chloride is performed on the second stage in the temperature range of 30–100 °C. Two moles of CuCl (cryst.) of the first stage and 2 moles of copper monochloride of the third stage are used under these conditions. This results in obtaining metal copper which is directed to the first stage and copper (II) dichloride used on the third stage. Changes in enthalpy and Gibbs free energy of the reaction (62) make: $\Delta H° = 125.5$ kJ, $\Delta G° = 159$ kJ.

Regularities of the disproportionation reactions are considered in detail in [89].

On the third stage of TChC $CuCl_2$ is dissociated at 500 °C – 600 °C by the reaction (62). In this case changes in enthalpy and Gibbs free energy of the reaction (61) make $\Delta H° = 125.5$ kJ, $\Delta G° = 0$ kJ.

An analysis of experimental data obtained under implementation of copper (II), (III)-magnesium-hydroxide-chloride TChC has shown that the thermal efficiency $\varepsilon_T = 63$ % at $\beta = 0.85$, while thermodynamic n is approximately 53.8 %. This TChC is more efficient as compared with iron (II), (III)-magnesium-hydroxide-chloride cycle, implemented at higher temperatures. Besides, endothermal heat effects in copper (I), (II) — magnesium-chloride TChC only 41.8–62.7 kJ/mol of H_2 while in iron (II), (III) — magnesium-hydroxide-chloride TChC more than 210 kJ/mol of H_2 [88]. In the given cycle the fourth and fifth stages are realized under the same conditions as in the previous cycle.

The authors have tested the two-stage thermochemical cycle based on the combination (on the first stage) of chemical reaction proceeding at 130–150 °C.

$$Cd + H_2O \rightarrow CdO + H_2 \qquad (65)$$

with the following electrochemical reaction:

$$CdO + \text{Background} = Cd + 1/2\ O_2, \qquad (66)$$

performed in the electrolyzer in insoluble graphite, glassy carbon and other electrodes which nature depends on the background used, for example, %: KOH — 0.37; NaOH — 0.33; LiOH — 10; CdO — 12; H_2O — 8. Electrolysis proceeds at 130–300°C at cathode current density 0.2–0.5 A/cm^2. Electrochemical reaction of CdO reduction can be substituted by its carbothermal reduction.

The great number of thermochemical cycles have been offered, most of them being promising after certain revision and use of proper catalysts with the aim to lower temperatures and remove the limiting stages, and, as a results, to check the process at the pilot plants [90–93].

4. Hydrogen vapour-phase conversion from hard, brown coals and turf is the so-called Bosch process of «water gas» production. It proceeds in two stages. At the first water stage the vapour is let to pass over incandescent coke, coal etc. (temperature 1000–1100 °C). The following endothermal reactions take place under these conditions:

$$C + H_2O \rightarrow H_2 + CO - 118{,}82 \text{ kJ}; \qquad (67)$$

$$C + 2H_2O \rightarrow 2H_2 + CO_2 - 75{,}31 \text{ kJ}; \qquad (68)$$

$$C + CO_2 \rightarrow 2CO - 162{,}33 \text{ kJ}. \qquad (69)$$

Carbon oxide conversion is conducted on the second stage in accordance with the reaction

$$CO + H_2O \rightarrow H_2 + CO_2 + 130{,}3\ \text{kJ}, \qquad (70)$$

adding water and converting it into vapour; when trying to lower a temperature to optimum of 450 °C, the gas mixture is let to pass over a catalyst of iron(III) oxide activated by chromium, manganese, magnesium and potassium oxides. The reaction (70) is called the displacement reaction.

To remove CO_2 from the gas mixture, the obtained mixture is scrubbed with water under pressure or is treated by heated potassium carbonate solution binding carbon dioxide into potassium hydrocarbonate $KHCO_3$ possessing higher commercial value:

$$CO_2 + K_2CO_3 + H_2O \rightarrow 2KHCO_3 + 162{,}33\ \text{kJ}. \qquad (71)$$

The cost of hydrogen produced by coal gasification is 6.4–9.2 USD/GJ and depends little on the cost of coal, proper [83].

5. Underground gasification of coal. Ukraine has rich reserves of hard coal; thus there are broad prospects for development of the methods of coal underground gasification with obtaining a universal source of power — ecologically pure hydrogen. The process of coal gasification can be performed by means of the following reactions:

$$2C + O_2 = 2CO\ (\text{gas.}) + 221.02\ \text{kJ}; \qquad (72)$$

$$2CO\ (\text{gas.}) + 2H_2O + 2H_2\ (\text{gas.}) + 2CO_2\ (\text{gas.}) + 82.34\ \text{kJ}; \qquad (73)$$

$$2H_2\ (\text{gas.}) + 2CO_2\ (\text{gas.}) = 2H_2\ (\text{gas.}) + 2CO_2\ (\text{liq.})\ \text{or}\ P_{cr} = 7.387\ \text{Mpa};\ t_{cr} = 31\ °\text{C} \qquad (74)$$

or

$$CO_2\ (\text{liq.}) + Q\ (\text{reaction}) = CO_2\ (\text{gas.}); \qquad (75)$$

$$CO_2\ (\text{liq.}) + Q\ (\text{environ.}) = CO_2\ (\text{gas.}). \qquad (76)$$

Gaseous CO_2 separated from hydrogen (H_2(gas.)) may be also supplied to the reaction zone

$$C + CO_2\ (\text{gas.}) = 2CO - 172\ \text{kJ}. \qquad (77)$$

The major combustion reactions are (72) and (77). Heat for performing the reactions (73) and (77) can be also taken from operating NPP and TPS. Endothermal reactions of H_2, CO and CO_2 formation are possible in the coal combustion zone water vapour being available and at $Q > 0$:

$$C + H_2O = H_2\ (gas.) + CO\ (gas.) — 131.3\ kJ; \qquad (78)$$

$$C + 2H_2O\ (gas.) = 2H_2\ (gas.) + CO_2\ (gas.) — 91.13\ kJ. \qquad (79)$$

It is evident from calculations that in such a case hydrogen cost will be 5–10 times as low as of that produced following other technologies.

As it follows from the data of the work [93], the process of underground coal gasification is in operation for a long time at the station *Podzemgas* as well as at other experimental plants which use underground gas generators.

6. Iron vapour-phase method. Hydrogen is obtained with the use of iron vapour-phase method in two stages at 650–900 °C. On the first stage iron or its grinded scrap is oxidized by water vapours to magnetite by the endothermal reactions:

$$Fe + H_2O = H_2 + FeO – 23,0\ kJ; \qquad (80)$$

$$3FeO + H_2O = H_2 + Fe_3O_4 – 80,9\ kJ. \qquad (81)$$

Production of high-concentration hydrogen (98 %) and relatively simple process, especially at industrial plants, are advantages of the iron vapour-phase method. Gases with reduction properties (synthesis gas, blast-furnace gas, etc,) are side products.

On the second stage, magnetite and iron(II) oxide formed by the reactions (81), (80) are reduced by synthesis-gas at the same temperatures:

$$Fe_3O_4 + CO = 3FeO + CO_2 – 25,73\ kJ; \qquad (82)$$

$$FeO + CO = Fe + CO_2 + 17,74\ kJ; \qquad (83)$$

$$Fe_3O_4 + H_2 = 3FeO + H_2O – 80,9\ kJ; \qquad (84)$$

$$FeO + H_2 = Fe + H_2O – 23,0\ kJ. \qquad (85)$$

All the reactions are reversible, and their direction depends on temperature and concentration of reacting gases.

The authors of the work [94] have proposed a more perfect method of hydrogen production by iron-vapour method. According to this process iron redox reactions proceed separately. Elementary iron and its oxide are used as powders with particle sizes of ≤ 0.2 mm; they are transported as dust-gas mixture with vapour or synthesis-gas in a form of pseudosuspension. Iron oxidation by the reaction (76) with obtaining hydrogen proceeds at 600 °C, and reduction of iron oxides — at 700 °C. Heat for the reaction proceeding is taken by organizing maximum heat exchange of flows. The process flow diagram is given in Fig. 43. Iron — its powder after reduction in a separator *1* is supplied through one of the locks *2* to the mixer *3* where it forms pseudosuspension with overheated vapour which arrived along the pipe *4* to heat exchanger *5*. There, as a result of heating to 600 °C, there occurs iron oxidation by the reaction (76) with formation of hydrogen-vapour mixture (H_2/H_2O). This mixture with iron powder gets to the pipe-line *6* where the oxidation reactions is completed. Then, from the separator *7* the mixture H_2/H_2O flows along the pipe *8* to the condenser *9* cooled by fresh reducing gas CO/CO_2. Gaseous hydrogen and condensed water are removed from the condenser. Iron oxide powder from the separator *7* passes through one of the locks *11*, in the mixer *12* it is mixed with reduction gas *10* and flows along the pipe *13*, being supplied in a form of dust-gas mixture to the heat exchanger *14* where it is heated to 700°C. In this heat exchanger the iron oxide is reduced to metal by the reaction (84) and returns to the reactor *1* along the pipe *15*. From the reactor *1* residual gas *16* arrives for formation and overheating of vapour in the heat exchanger *17*. As a result, the iron-vapour cycle is closed, the stages of hydrogen production and conversion of the reaction product — iron

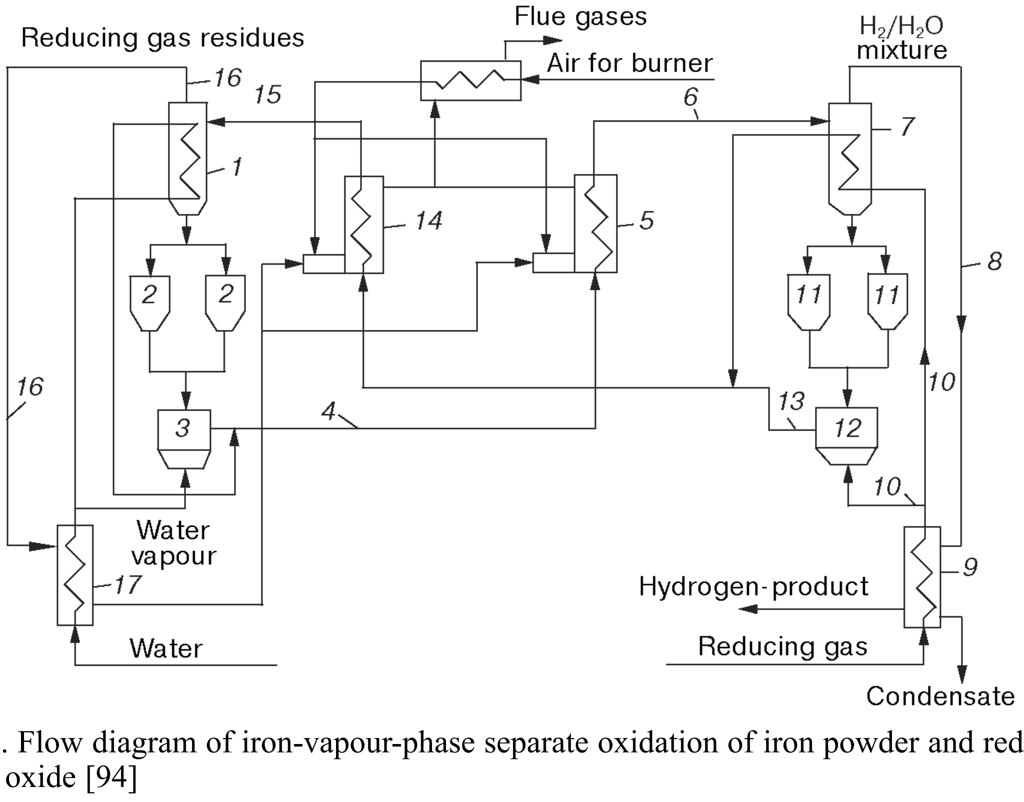


Fig. 43. Flow diagram of iron-vapour-phase separate oxidation of iron powder and reduction of iron oxide [94]

oxide — are completed. The given method serves to obtain more pure hydrogen than traditional one.

7. Water and vapour — electrolysis . There are two methods of production of electrolytic hydrogen: electrolysis of water solutions of KOH or NaOH at a temperature ≤ 100 °C [95]; electrolysis of hydrated melt of potassium hydroxide at a temperature 280–350 °C [77, 96–99] and even at 900–1000°C in case of the use of solid oxide electrolytes [100–101].

It is known that the equilibrium potential of the reaction of hydrogen deposition from acid and alkali solutions in accordance with the equations

$$H_3O^+ + 2e^- = H_2 + OH^-; \tag{86}$$

$$2H_2O + 2e^- = H_2 + 2OH^- \tag{87}$$

corresponds to the dependence

$$E_p = E^0 - 0.059\ \mathrm{pH} \tag{88}$$

at $a_{H_2O} = 1$, $P_{H_2} = P_{O_2} = 0{,}1$ MPa, $E^0 = 0$.

Theoretical value of water decomposition voltage is equal to 1.229 V at 25 °C, depends on the temperature and is described by the expression:

$$E^0 = Q/0{,}239\ zF + T\,(dE^0/dt) = 1.229\ \mathrm{V}, \tag{89}$$

where Q is thermal effect of the reaction equal to 285.838 kJ/mol at 25 °C; (dE^0/dt) — temperature coefficient equal to 0.0008 V/degree; z — quantity of electrons participating in the reaction; F — Faraday's number; T — temperature, K.

Hydrogen electrode potential decreases with temperature elevation. Fig. 44 shows the plotted dependence of equilibrium potential of hydrogen release in the temperature range 24–80 °C from the data of [102, 103] (curve *1*), at 25–80 °C [95] (curve *2*), at 400–577 °C [99] (curve *3*), at 1000 °C [100] (curve *4*), at 997 °C [103] (curves *5–8*). Water vapour electrolysis at high temperatures has its own peculiarities. At temperatures exceeding 100 °C, the ratio between partial pressure of water vapour and hydrogen pressure P_{H_2} / P_{O_2} can be equal to one, exceed one and be less than one. It is evident from Fig. 44 that experimental values of $E°$ for the reaction of hydrogen release from water vapour fall on the straight line.

The equilibrium potential of oxygen formation reaction in the acid and alkali medium at 25 °C in accordance with equations

$$4H_2O - 4e^- = 4H^+ + O_2; \tag{90}$$

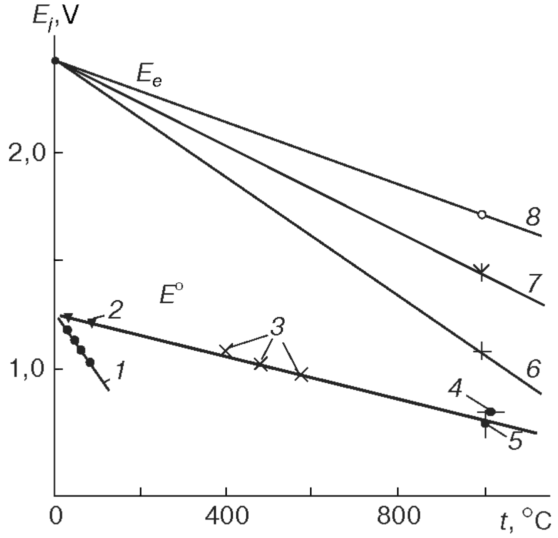


Fig. 44. Dependence of equilibrium potential of hydrogen deposition in the temperature range of 24–1000 °C from the data of [95, 99, 100, 102, 103]

$$4OH^- - 4e^- = O_2 + 2H_2O, \quad (91)$$

is described by the dependence

$$E^p_{O_2} = 1.229 - (2.303\ RT/F)\mathrm{pH} + (2.303\ RT/4F)\ \lg P_{O_2}/P_{H_2}. \quad (92)$$

In accordance with theory, it is confirmed experimentally, that the ratio P_{H_2O}/P_{H_2} being changed by an order (from 1 to 0.1 or from 1 to 10) E_E value changes by the value 0.126 V.

Voltage of hydrogen deposition on the cathode ($E_{E_{H_2}}$) depends on electrode material nature and their sum is the major component of total balance of voltage of electrochemical cell (single unit) cathode-membrane-anode, gathering in the electrolyzer section. Voltage of hydrogen and oxygen deposition in a single electrolytic cell cathode/electrode/anode corresponds to the equation

$$E_E = E^0 - RT/2\alpha F \ln P_{H_2O}/P_{H_2} + RT/2\beta F \ln P_O, \quad (93)$$

where α and β — transport factors equal to 0.5 ($\alpha > \beta = 1$);

$$E^0 = RT/2\alpha F \ln K; \quad (94)$$

K — reaction equilibrium constant

$$H_2\ (\text{gas}) + O_2\ (\text{gas}) \rightarrow H_2O\ (\text{gas. or liq.}) \quad (95)$$

Table 28

Values of overvoltage of hydrogen and oxygen deposition (mV) on various metals and materials at 25 °C

Electrode material	H_2	O_2	Electrode material	H_2	O_2
Pt	0–40	250	Ti-Ru (ORTA)	—	80
Pd	0	430	Ti-Ru (ORTA)	—	112
Ir	2	75	Graphite	290	520
Rh	30	70	Ni (galvan)	110	320
Au	20	530	Ni (alloyed)	270	60
Pt(smooth)	48	450	Cu	230	250
Ni+S(Fe)	60	260	Cd	480	430
Co	67	130	Sn	530	—
Fe	80	250	Pb	640	310
Ag	150	410	Zn	700	—
Fe (St.3)	190	250	Hg	780	—

The higher is hydrogen pressure, the higher voltage is required on the electrodes for hydrogen deposition reaction performance. The potential deviation from the equilibrium value is called overvoltage. The value of hydrogen and oxygen deposition overvoltage on different materials at low current densities are presented in Table 28. It is seen distinctly that overvoltage of hydrogen deposition on platinum group metals is of the least value. When applying nickel coating, containing sulphur on the surface of iron electrode, the overvoltage of hydrogen and oxygen deposition decreases to 60 and 260 mV, respectively. The overvoltage of hydrogen deposition (η_{H_2}) also depends on the electrode surface treatment conditions. To decrease the overvoltage of oxygen deposition (η_{O_2}) on anode they use titanium covered with a layer of ruthenium oxide, the so-called ORTA anodes. Dependence of η_{H_2} on current density i is determined by Tafel equation:

$$\eta_{H_2} = a + b \ln i, \tag{96}$$

where i — polarizing current; a, b — Tafel constants, equal:

$$a = -RT / \alpha zF \ln i_0 + RT / \alpha F \ln H^+ = -RT / \alpha zF \ln i_0 + RT / \alpha F \, pH \tag{97}$$

$$b = RT / \beta zF; \tag{98}$$

i_o — reaction exchange current.

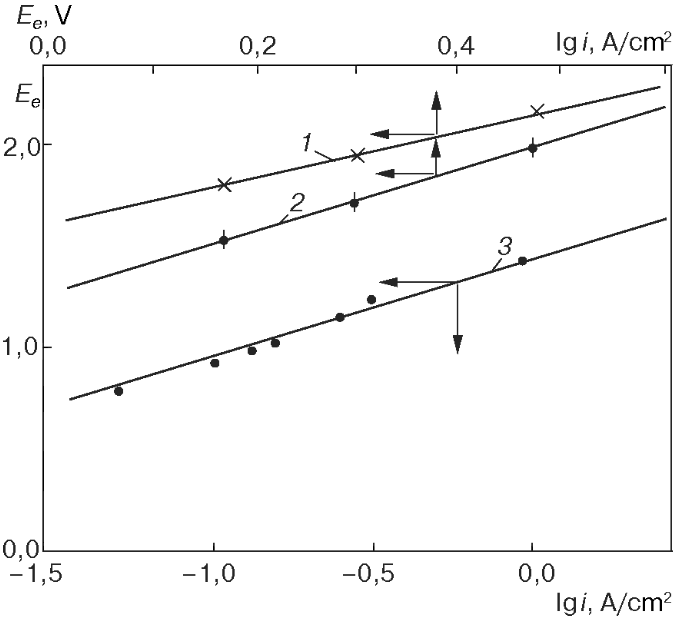


Fig. 45. Dependence of E_e on current density at temperatures 280 (*1*), 350 (*2*) [97,99] and 997 °C [103] (*3*)

The constant *a* depends very much both on the metal nature and on the nature of electrolyte and changes from 0.10 to 1.50 V. The constant *b* depends weakly on the metal nature and changes only from 1.10 to 1.50 V [104].

E_e as a function of current density (i, A/cm^2) under water vapour electrolysis on nickel electrodes in potassium hydroxide solution is shown in Fig. 45. The process was carried out at a temperature of 280, 350 [97, 99, 103, 105] and 997 °C with the use of ceramic diaphragms. The latter are based on yttrium oxide stabilized with zirconium, and possess ionic conduction, etc. [103, 106]. Products made of β-alumina are especially promising as membranes with ionic conduction. We have developed the methods of synthesis of β-alumina with the use of activated aluminium alloy [107–108]. The alloy of activated aluminium (total Al weight fraction being 88–92 % and that of gallium, indium, tin and chromium — 2–3 % each) was used for synthesis of β-alumina in the work [107]. The alloy is treated by sodium hydroxide solution corresponding to stoichiometric ratio of the sum Al_2O_3+Cr_2O_3 and Na_2O in the formed β-alumina equal to 5.33. It dissolves forming aluminium and chromium hydroxides. The obtained precipitate is separated from the mother liquor, dewatered and subjected to multistage heat treatment at 300, 500, 900 and 1200 °C. Under such conditions, according the data of X-ray phase analysis, a product is obtained which total weight fraction of β-alumina is 97 %.

Good results were obtained when using the alloy containing aluminium (95 %), gallium (3.05 %), indium (1.25 %), tin (0.65 %) and zinc (0.05 %) for synthesis of β-alumina [108]. Sodium hydroxide is also introduced in the amount corresponding to stoichiometric ratio, equal to 5.33 for Al_2O_3 and Na_2O in the formed β-alumina. The reaction of dissolution of activated aluminium was conducted in an autoclave at 250 °C during 4 h. Aluminium interacted with stoichiometric amount of water by the equation

$$2n\mathrm{Al} + 3n\mathrm{H_2O} + \mathrm{NaOH} \rightarrow \mathrm{NaOH}\cdot n\mathrm{Al_2O_3} + 3n\mathrm{H_2} \qquad (99)$$

with formation of dry product $NaOH\cdot nAl_2O_3$ taken out of the autoclave and compacted under the pressure of 1.0–5.0 t/cm^2 into membranes for chemical sources of current; then membranes were subjected to thermal treatment as described above. β-alumina was synthesized at 1100–1140 °C during 40 min. From the data of X-ray phase analysis the product contained 100 % of β-alumina. The membranes were sintered at 1660 °C for 30 min to make them mechanically strong. Specific electrical resistance of membranes of β-alumina depended on temperature, and at 300 °C it was equal to 4.1 and at 350 °C — 3.2 Ωcm.

The methods of production of solid oxide electrolytes with ionic conduction are described in the work [106]. Physico-chemical and electrochemical properties of electrolytes with ionic conduction were described in the work [106]. Physico-chemical and electrochemical properties of electrolytes based on ZrO_2 activated by admixtures of 8–10 % oxides of REE (Nd, Gd, Dy, Ho, Y, Er, Sc, etc) have been studied. Solid solutions based on binary systems of oxides ZrO_2 — Y_2O_3, ZrO_2 — Yb_2O_3, ZrO_2 — Sc_2O_3, and ternary system ZrO_2 — Y_2O_3 — Sc_2O_3 possess the best electrochemical properties. The current density being increased, voltage on a single module of electrolyzer increases (data of the works [97, 98, 103, 105] are recalculated for a single module: cathode/electrolyte/anode). Real voltage on the terminals of one section of the electrolyzer E_{e1}, as well as electrolyzer as a whole, depends on the temperature of electrolysis, nature of cathode metal and anode materials which would have as low as possible overvoltage of hydrogen and oxygen formation equal to η_k and η_a, low ohmic losses in the electrolyte, conductors, contacts and diaphragms [95–99]. Voltage also depends on the electrolyte conduction (liquid or solid diaphragms), current density and temperature. Thus, the total voltage on a single electrolyzer module in the process of electrolytic deposition of hydrogen and oxygen can be presented by the following equation:

$$E_{\mathrm{e}} = E^0_{\mathrm{K}} + E^0_{\mathrm{a}} + \eta_{\mathrm{k}} + \eta_{\mathrm{a}} + E_{\mathrm{conc.}} + E_{\mathrm{diff.}} + iR_{\mathrm{e}} + iR_{\mathrm{diaphr.}} + iR_{\mathrm{met.}}, \qquad (100)$$

where E^0_{i} — standard electrode potentials of hydrogen and oxygen; η_{c} and η_{a} — overvoltage of hydrogen deposition on cathode and oxygen on anode; $E_{\mathrm{conc.}}$, $E_{\mathrm{diff.}}$ — values of the concentration and diffusion polarizations; i — strength of current; R_{e}, $R_{\mathrm{diaphr.}}$ and R_{met} — resistance value of electrolyte, diaphragm and metal conductors and electrolyzer module contacts.

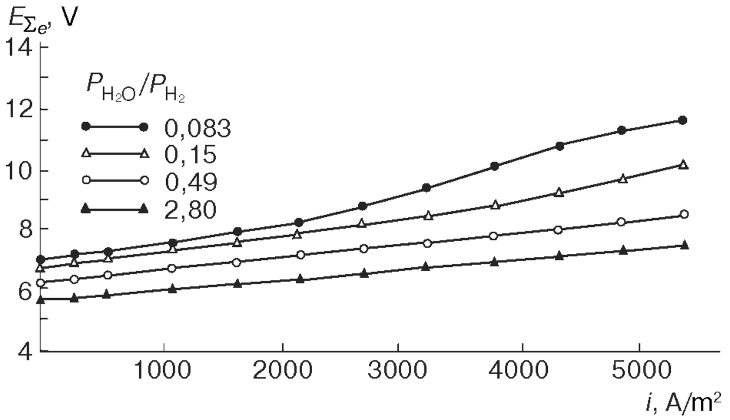


Fig. 46. Total voltage on the terminals of electrolyser including seven sections under the ratio of partial pressures P_{H_2O}/P_{H_2} = 0.083...2.80 [100].

Voltage on the electrolyzer terminals at a temperature below 100 °C usually equals 2.2–2.4 V. The temperature being increased, voltage considerably decreases on the electrolyzer terminals (at current density i = const).

The lower is the current density, the less voltage is established in the electrolyzer (see, Fig. 44., curves 6–8) and, consequently, the less amount of electric energy is consumed per production unit (of hydrogen and oxygen).

An analysis of experimental curves E_e—$\lg_i$ has shown that they are linear and with temperature elevation they shift towards the lower E_e values.

Fig. 46 demonstrates a sum of voltages E_{Σ_e} on the electolyzer of seven sections from 5 to 12 V, depending on the power of current passed through the electrolyzer and the ratio P_{H_2O}/P_{H_2}. Electric power requirements depend on voltage and strength of current passing through electrolyzer. When using catalytically active electrodes, voltage on electrolyzers decreases as well as power consumption. Fig. 47. presents minimum powers required for water dissociation by electrolysis at 100 and 1000 °C [100]. It is evident that water electrolysis power at high temperatures consists of thermochemical and electrochemical contributions. Thermochemical contribution includes the entropy component at the ratio P_{H_2O}/P_{H_2} = 0.083 – 2.80 [100]. At P_{H_2O}/P_{H_2} = 0.083 the sum of voltages E_{Σ_e} on terminals of the electrolyzer with oxide electrolyte increases, and this leads to the greater electric power consumption per the obtained hydrogen production unit. Especially sharp increase of E_{Σ_e} is observed at i = 2000 A/m^2. The increase of E_{Σ_e} with the decrease of the ratio P_{H_2O}/P_{H_2} is determined by the concentration polarization which appears because of difficult access of water vapours to the cathode surface as a result of the decrease of partial pressure of water vapours as far as they are consumed. The ratio P_{H_2O}/P_{H_2} being increased, the total value of voltage in seven electrolyzer sections decreases.

Researchers of the Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine jointly with scientists of

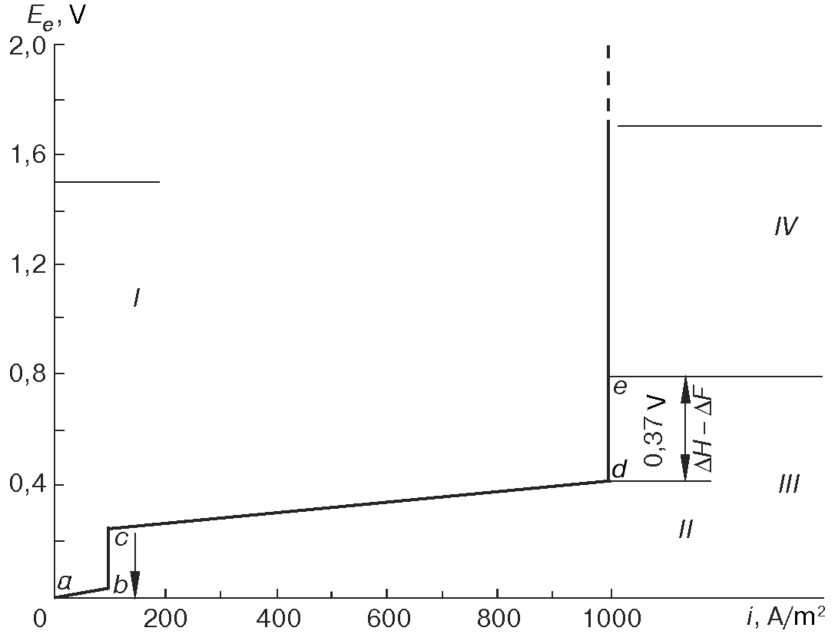


Fig. 47. Minimum powers consumed for water dissociations by electrolysis at 100 and 1000 °C [100]

I — minimum voltage required at 100 °C for supply to water with temperature 25 °C, equal to $E = 1.5$ V (*a-b-c-i*); *II* — thermal power $E_{T_1} = \Delta H - \Delta F = 0.37$ V(*d-e*); *III* — total thermal power required at 1000 °C, $E_{T_2} = 0.79$ V(a-b-c-d-e); *IV* — minimum voltage required at 1000 °C, $E_e = 0.92$ V at $P_{H_2O} / P_{H_2} = 1(e - f)$.

I.V. Kurchatov Institute of Nuclear Power have made great contribution to the theory and practice of hydrogen production by electrolysis of solvate complexes — hydrated melts of hydroxides at high temperatures [75–77, 96–99, 105].

Electrolysis was carried out in accordance with the following pattern:

$$MeOH_{(melt)}+H_2O_{(vapour)} \xrightarrow{>300\ °C} [(H_2O)Me^+(H_2O)]+H_2O{\cdot}OH \xrightarrow{0.98\ V;\ 3\ A/c^2} {\cdot}H_2,$$

where *Me* — Li, Na, K.

Methods of hydrogen production offered in the above works permit not only utilizing heat of TEP and NPP but providing higher profitableness of the process, since under electrolysis of hydrated melts the voltage of water dissociation decreases by 0.25 V (from 1.23 to 0.38 V), and the process rate increases 10 times.

To remove the concentration polarization, to rise efficiency and output of hydrogen production by high-temperature electrolysis the authors of the work [98] have developed an electrolyzer of original design (Fig. 48). It consists of a case *1*, with a perforated diaphragm *4* between anode *5* and cathode *3* made in the form of a bottomless duct. The elecrolyzer is equipped with a branch pipe *6*

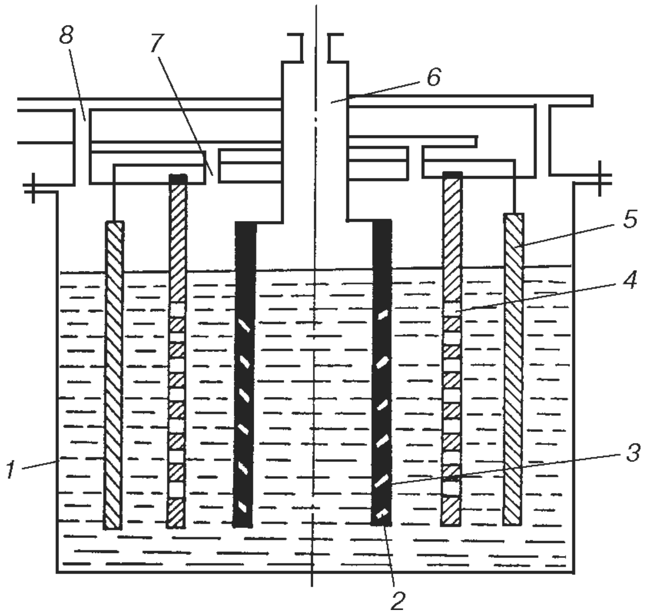


Fig. 48. Structure of electrolyser for production of hydrogen and oxygen by means of electrolysis of overheated vapour [98]

for introducing water vapour arranged over the duct *3* which functions as a cathode. Walls of the duct — cathode *3,* turned to anode *5* have slots at an angle of 45 °C. Hydrogen and oxygen are removed along the branch pipes *7* and *8*, respectively.

During the electrolyser operation intensive electrolyte circulation through the slots *2* in the cathode walls is observed because of different electrolyte density in the space cathode-membrane as a result of gas-filling, and its absence in the duct volume. Fresh portions of the electrolyte, saturated with water, are continuously supplied to the outer cathode *3* wall — the zone of electrochemical reaction of hydrogen release. Productivity of the electrolyzer of such structure surpasses 7.5–15 times that of the already known ones [98].

Hydrated melts of hydroxides of the following composition, were used as electrolyte in the above electrolyser wt. %: a) KCl 1–18; KOH 82–99; electrolysis temperature 280–350 °C [10]; b) LiOH 5–25; LiCl 33–42; KCl 33–62; electrolysis temperature 600–850 °C [77]. Hydroxide melts, containing alkali metal halogenides as additives, were saturated continuously with overheated vapour under electrolysis. The results of electrolysis of hydrated potassium hydroxide solution which contains 1–18 % of potassium chloride are presented in Table 29. [96]

Current density being 1.5–3.0 A/cm^2, the cell voltage is 1.48–1.89 V and hydrogen current efficiency — 97–99 %. Oxygen release proceeds with the same technical-and-economical indexes.

Table 29

Dependence of hydrogen current efficiency η_T and cell voltage U on current density under different content of potassium chloride and at a temperature of 350 °C according to [96]

Current density, A/cm^2	KCl content, %									
	0.2		1.0		5.0		18.0		25.0	
	U, V	η_T, %	U, V	η_T, %	U, V	η_T, %	U, V	η_T, %	U, V	η_T, %
1.5	1.51	96	1.50	98	1.49	97	1.48	98	1.59	98
2.0	1.91	95	1.61	99	1.60	98	1.55	99	1.66	98
3.0	2.29	96	1.89	99	1.81	98	1.76	99	2.16	99

Table 30

Dependence of cell voltage U_c V(g) and specific electric power consumption (W, kW·h/m^3 of H_2) on current density at different temperatures [77]

Current density, A/cm^2	Temperature, °C							
	500		600		730		850	
	U_C, V	W	U_C, V	η_T, %	U_C, V	η_T, %	U_C, V	η_T, %
0.5	1.52	3.63	1.31	3.13	0.99	2.37	0.78	1.86
0.8	1.86	4.44	1.54	3.68	1.17	2.80	0.96	2.29
1.0	2.05	4.90	1.68	4.02	1.31	3.13	1.05	2.51
1.2	—	—	1.80	4.30	1.42	3.40	1.16	2.77
1.5	—	—	1.96	4.68	1.56	3.73	1.30	3.11
2.0	—	—	2.20	5.26	1.78	4.28	1.48	3.54
2.5	—	—	—	—	2.01	4.60	1.69	4.04

High efficiency of hydrogen production has been also achieved in electrolysis of hydrated melt with the following composition, %: LiCl — 40; KCl — 50; LiOH — 10, at 500–850 °C [77]. The optimal range is 600–850 °C. High-velocity water absorption by the melt from overheated vapour proceeds within this range. But the melt corrosive effect on the bath structure materials sharply rises at temperatures above 850 °C. Table 30 presents dependences of cell module voltage and specific electric power consumption on current density under electrolytic hydrogen production in the hydrated melt of the above composition [77].

The equilibrium voltage $E°$ of a single module for hydrogen production at 1000 °C is E_{Σ_e} :7 = 5.6.:7 = 0.786 V. The obtained value of E^0 = 0.786 V at 1000 °C and i = 0 in the work [100] is in agreement within the experiment error with the data of the work [103]; where E^0 = 0.705 V at 997 °C. These data demonstrate that the electric power consumption under water vapour electrolysis is about 3 times as low as under electrolysis of aqueous alkaline solutions at a temperature below or equal to 100 °C.

The cost of hydrogen produced by electrolysis of aqueous alkaline solution is proportional to the cost of electric power and its consumption per production unit — H_2. Theoretical electric power consumption under electrolysis of aqueous alkaline solution under production of 1 m^3 of hydrogen and 0.5 m^3 of oxygen makes 2.95, while practical one makes 4.21–50 kW·h/m^3 of H_2, which corresponds to power efficiency of 60–70 %. It is evident from the data of Table 30 that under optimal temperature (850 °C) and current density 1.0 and 2.0 A/cm^2 the electric power consumption is equal to 2.51 and 3.54 kW·h/m^3 of H_2, respectively.

Power consumption under water electrolysis process being expressed in a form of electric units in certain components (stages), one can obtain the following values (Fig. 47). At $T \leq 100$ °C: the line *ab* corresponds to thermal power for heating water to 100 °C, equal to 0.0293 V, while minimum voltage for water electrolysis will be 1.50 V. For the case of water vapour electrolysis at 1000 °C the items of thermal power consumption will be as follows: *ab* — 0.0293 V for water heating to 100 °C; *bc* — 0.212 V for water evaporation at T=100–1000 °C; *cd* — 0.176 V for water evaporation at T from 100 to 1000 °C; *de* — 0.373 V for the reaction entropy component $T\Delta S$. They make 0.7093 V of thermal power in total. Electric power minimum at the stage *ef* is equal to 0.919 V. The total power consumption at high-temperature electrolysis of water vapour is 1.71 V, total power efficiency is 53.7 %. Oxygen and hydrogen current efficiency depends on the structure of electrolyzer and can reach 99.0 — 99.99 % [109].

The higher efficiency may be obtained when using «surplus» heat of NPP and TES. Under such conditions their efficiency increases. Thus, to raise the NPP

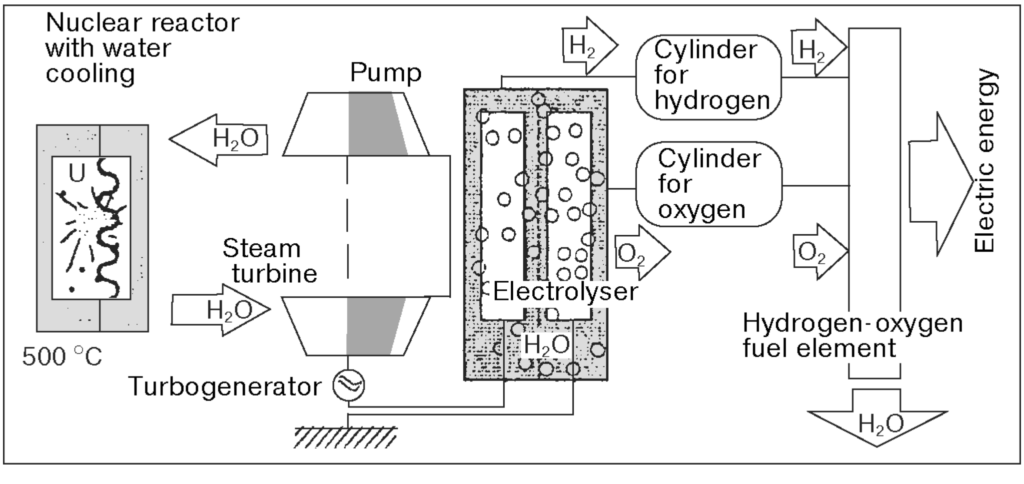


Fig. 49. Technological diagram of nuclear plant with electrochemical accumulation of surplus energy [72]

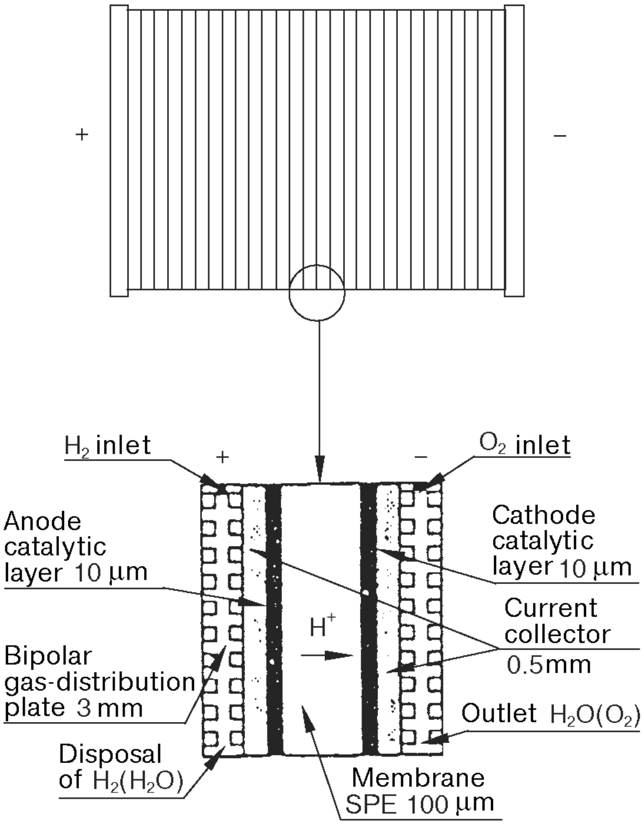


Fig. 50. Fundamental flow diagram of hydrogen-oxygen fuel cell and a cell with solid polymer electrolyte [111]

efficiency the standard nuclear plant (NP) is combined with electrochemical accumulation of surplus electric power (in a form of gaseous hydrogen and oxygen) by water electrolysis or with thermochemical cycles. A scheme of the power plant combination with water electrolysis from the data of the work [72] is presented in Fig. 49. Hydrogen and oxygen are accumulated in tanks and are used as required to produce electric power in fuel cells. A flow diagram of the hydrogen-oxygen fuel cell is presented in Fig. 50 [110]. In this cell a process of electrochemical hydrogen oxidation proceeds on anode electrocatalyst and oxygen reduction process on the cathode one. Electrocatalysts are made of platinized black applied to porous carbon-graphite current collector with hydrophobic sublayer providing for the reaction product (water) removal from the reaction zone. The membrane which lets through the hydrogen oxidation product — protons from the anode chamber to the cathode one to preserve neutrality — functions as electrolyte. The membrane electrolyte provides the electric circuit closure due to H^+ ions. The fuel element cell looks like «a puss-pastry». Since one cell voltage equals 1.0 V, then to increase voltage and power capacitance of the fuel-element (cell), the cells are connected in series as a battery with common fuel (hydrogen and oxidizer — oxygen) supply system and a common system for removal of the electrochemical reaction product (water). With this aim the cell anode and cathode are contacted with current-tapping metal bipolar plates possessing a system of gas-distributing channels [111]. Electroactive catalysts (BNi, NiS, Mn, Cr, Fe, Co, Ru, Rd, Rh, Ag, Os, Pt, Mo, Ni) are applied to the cathode surface to decrease the hydrogen release overvoltage. Power efficiency in production of electrolytic hydrogen equals 60–70 % under hydrogen current efficiency of 98–99 %, and realized efficiency of hydrogen-oxygen fuel cell reaches 50–65 % (in the future — 70 %). Thus full efficiency of nuclear power conversion into the chemical and electric fuel cell power is higher than the Carno cycle.

8. Hydrogen production with the help of energy-accumulating substances (EAS). The above methods of hydrogen production are traditional and require great capital outlays. In this connection a conception of energy-accumulating substances, which may be repeatedly oxidized and reduced, i.e. may be used as working medium when producing power, is of interest in the following works [55–58, 79, 112–132]. Energy-accumulating substances are separated into two groups: 1) EAS which give off the accumulated energy under chemical interaction with water; 2) EAS which give off the accumulated energy without chemical interaction, but as a result of physical effect.

EAS of the first group include metals with small atomic numbers (B, Be, Si, Al, Mg, Ca, Li) reduced from oxides or other compounds, which are subject to activation; metal hydrides (LiH, NaH, MgH_2, CaH_2, ScH_2, TiH_2, LaH_2, AlH_3, $LiBH_4$, $NaBH_4$, Li, $NaAlH_4$, AlH_4, B_2H_6, B_6H_{8-n} etc.), carbides, silicides, nitrides and other high-energy compounds — methanol, ammonia, hydrasin, including secondary EAS, for example, hydrogen.

EAS of the second group include substances in atomic and metastable state, high-heat-capacitance compositions which give off the accumulated energy under certain conditions in recombination processes of substances in atomic state as well as in the phase transition reactions. These are: atomic hydrogen, which power capacitance Q is equal to $2.17 \cdot 10^5$ kJ/kg, helium in metastable excited state ($Q = 4.8 \cdot 10^5$ kJ/kg), atomic nitrogen ($Q = 3.4 \cdot 10^4$ kJ/kg), boron monohydride BH ($Q = 2.6 \cdot 10^4$ kJ/kg), boron dihydride BH_2 ($Q = 2.2 \cdot 10^4$ kJ/kg), etc., as well as special alloys and some metals capable to reversible hydrogen absorption under its high pressure and to give off great volumes of molecular hydrogen ($LaNi_5H_6$, $FeTiH_x$, $LaPd_5H_6$, $LaNi_5H_6$, $Ce_3NiH_{8.4}$, YNi_5H_6, Y_3CoH_8, $MgNiH_4$, $TiCoH_4$, $ZrFe_2H_4$, $ZrCr_2H_4$, $ThNi_3H_{28}$, $TiFe_{0.7}Mn_{0.3}$, etc.) at temperature elevation. Hydrogen capacitance of hydrides, as was noted above, is extremely high and exceeds the content of hydrogen atoms 1.5–2.0 times ((6.23–8.26)$\cdot 10^{22}$ atoms H/cm^3), as compared to liquid hydrogen (($4.2 \cdot 10^{22}$ atoms H/cm^3), and solid hydrogen ($4.593 \cdot 10^{22}$ atoms H/cm^3). Metal hydrides of the second EAS group are used as the working medium of hydrogen accumulators — the hydride accumulators of hydrogen.

Processes for production of the first-group high-energy EAS for low-grade coals from the Middle Asia, Siberia, and Donbas have been proposed in a number of works. The obtained EAS may be used for production for great amounts of hydrogen. Since hydrogen consumption will reach hundreds of million tons in the nearest future, we would have great reserves of high-ash initial substances. Coals from the Kansk-Achinsk, Ekibastuz and a number of coal deposits of Donbas and Lvov region meet these requirements. The mineral part of these coals contains 13–28 % of aluminium oxides, 7.7–8 % of iron oxides, 45–59.7 % of silicon oxides, 2.9–26 % of calcium oxides, and other elements. TES slames being reduced, the highly-reactive EAS alloys may be obtained. When these alloys interact with water one can observe a high-rate release of hydrogen [4–6, 55–58, 112–127].

There are energy-accumulating substances based on aluminium, boron, silicon, magnesium and other metals used in industry and new technology. The scheme of their application is presented in Fig. 51. Aluminium-based EAS are used to obtain hydrogen from water, for production of metallized high-energy fuel, to make corrosion protectors for metal-works in the sea water, for deoxidization of steels, for making solid electrolytes based on β-alumina, for production of explosives, to increase oil and gas output under oil and natural gas production, etc. Depending on the metal nature, one or another method of activation are used. Aluminium is activated by making its alloy with small amount of indium, gallium, tin, magnesium, or mix-metal.

The activated aluminium interacts with water by the exothermal reactions:

$$2\mathrm{Al}^{*} + \mathrm{H_2O} \left| \begin{array}{l} \xrightarrow{k_1} \mathrm{AlOH} \\ \xrightarrow{k_2} \mathrm{AlH} \end{array} \right. ; \tag{101}$$

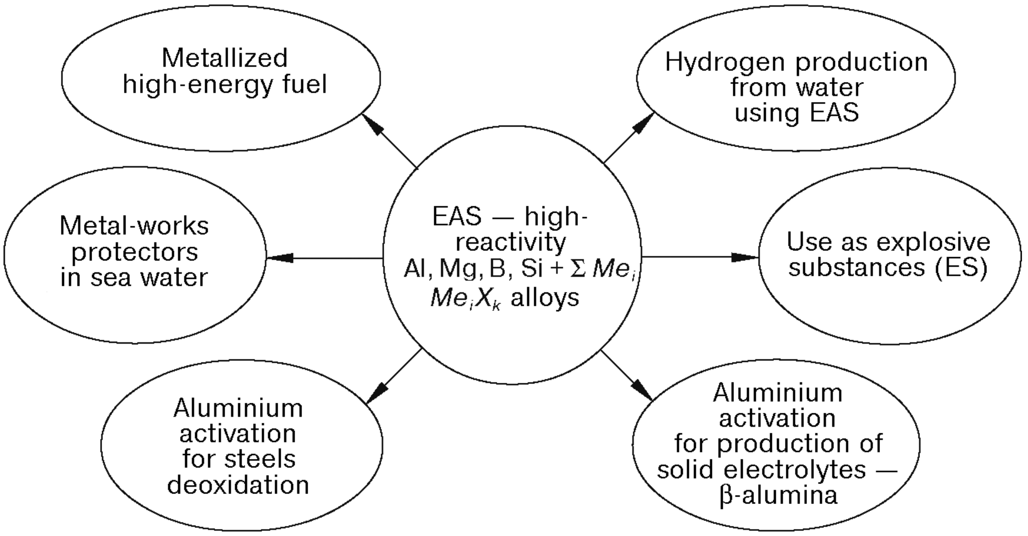


Fig. 51. Power-accumulating substances in technology of hydrogen production from water and in other field of new technology and industry

with formation of intermediates AlOH and AlH. Aluminium monohydride AlH reacts with water by the subsequent reactions:

$$\mathrm{AlH} + \mathrm{H_2O} \xrightarrow{k_3} \mathrm{AlOH} + \mathrm{H_2} \quad (102)$$

$$\mathrm{AlOH} + \mathrm{H_2O} \xrightarrow{k_4} \mathrm{AlOOH} + \mathrm{H_2} \quad (103)$$

with formation of the reaction final product (103) — boehmit AlOOH. Aluminium monohydroxide AlOH, formed by the reaction (101), also interacts with water by the reaction (103). The sum equation of dissolution of activated aluminium has the following form:

$$\mathrm{Al^*} + 2\mathrm{H_2O} = \mathrm{AlOOH} + 3/2\mathrm{H_2} + Q. \quad (104)$$

The reaction (104) rate, depending on the limiting stage (102) or (103), is described by the following equations:

$$\mathrm{w}_1 = [\{k_1k_4[\mathrm{OH}][\mathrm{OH_2}]^2 + k_2k_4k_w[\mathrm{OH_2}]\}[\mathrm{Al^*}]_s]/(k_2k_w + k_4[\mathrm{OH_2}])^2; \quad (105)$$

$$\mathrm{w}_2 = [\{k_1k_4[\mathrm{OH}][\mathrm{OH_2}]^2 + k_2k_4[\mathrm{H^+}][\mathrm{OH_2}]\}[\mathrm{Al^*}]_s]/(k_2[\mathrm{H^+}] + k_4[\mathrm{OH_2}]); \quad (106)$$

where k_w is ion product of water k_w=[$\mathrm{H^+}$][$\mathrm{OH^-}$]; Al* — activated aluminium.

An analysis of equations (104) and (105) shows, that only at $k_1 = k_2$ and [$\mathrm{OH^-}$] = [$\mathrm{H^+}$] under dissolution of activated aluminium the solution pH will not change. If $k_1 > k_2$, then [$\mathrm{OH^-}$] exceeds [$\mathrm{H^+}$] and the solution pH under dissolution of Al* will increase. Really, as is seen from Fig. 52, in the process of Al* interaction with water and chloride solutions pH increases, and thus, [$\mathrm{OH^-}$] increases too, which evidences for higher concentration of $\mathrm{OH^-}$ ions as compared with concentration of $\mathrm{H^+}$. Thus, [$\mathrm{OH^-}$] > [$\mathrm{H^+}$] and $k_2<k_1$.

Calculations show that $k_1 = = 6.6\cdot10^5{}_{\mathrm{S}}{}^{-1}$, $k_2 = 1.5\cdot10^6{}_{\mathrm{S}}{}^{+}$, k_3 and k_4 are of 10^{10}–10^{11}/($\mathrm{m^2}\cdot$s) order. The last value corresponds to ultimate rate constant values of bimolecular reactions, their rate is limited by diffusion. The lifetime of intermediate AlH molecules equals $6.6\cdot10^7{}_{\mathrm{S}}$. Oxidation reaction of activated aluminium is exothermal (Q = 15060 kJ/kg or 39200 kJ/l of aluminium). Thus, the reaction products and reacting aluminium itself are heated and aluminium oxide film forms on the surface of activated aluminium:

$$2\mathrm{AlOOH} = \mathrm{Al_2O_3} + \mathrm{H_2O}. \quad (107)$$

$\mathrm{Al_2O_3}$ is formed under certain conditions as the end product of interaction of activated aluminium with water. Thus the general reaction equation will assume the form [133, 134]:

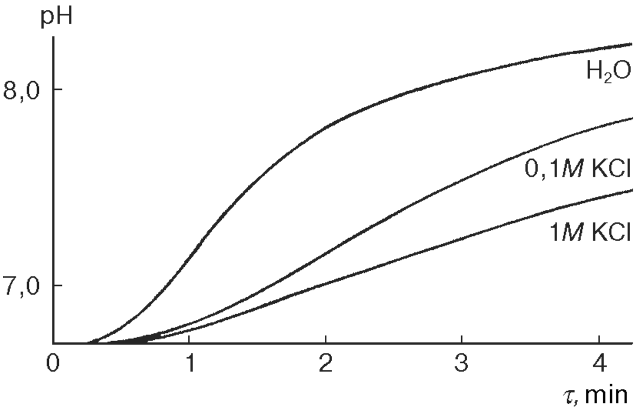


Fig. 52. Change of solution pH when aluminium activated by additions of 3 % gallium and tin interacts with water

$$2Al^* + 3H_2O \rightarrow Al_2O_3 + 3H_2. \tag{108}$$

The rate of interaction of activated aluminium with water with hydrogen liberation depends on the nature of metals-activators, their content in the alloy and temperature. Data from Fig. 53 evidence for this fact. The Figure presents kinetic curves of gallium-activated aluminium interaction with water [117, 118] as well as of aluminium activated by binary (Ga-Sn) [119] and ternary (Ga-Sn-In) [79] alloys on gallium basis. As is evident from Fig. 53, *a* the rate of gallium-activated aluminium dissolution in water with liberation of hydrogen depends on temperature. Maximum aluminium dissolution rate at 200 °C, equal to 180 of l H_2 / (m^2·min), is achieved in 12.6 min. This time corresponds to dissolution half-period of activated aluminium. Aluminium dissolution rate is considerably lower at a temperature of 50 and 100 °C. The dissolution rate of gallium-activated aluminium equal (as to hydrogen) to 180 l of H_2 / (m^2·min), is equivalent to the linear rate of aluminium dissolution of 0.0536 mm/min, which corresponds to 28.053 m/year. High-purity aluminium and its alloys are usually corrosion-resistant in pure and distilled water. Aluminium with the degree of purity 99.8–99.99 % possesses extremely high corrosion resistance owing to the passivation film on its surface [135]. Even under a short-term contact of pure aluminium surface with the air a 100–200 nm thick protective oxide layer is formed on its surface. Corrosion of 99.995 % of aluminium at 298 °K proceeds in three stages.

The amorphous oxide 500–600 nm thick film is formed on aluminium surface at the first stage. At the second stage, it turns into crystalline boehmite (AlOOH), at the third stage it turns into crystalline baierite (Al_2O_3·$3H_2O$). It is this oxide film that protects aluminium from corrosion. At a temperature elevated to 343–374 K crystalline boehmite is formed on aluminium surface instead of the amorphous layer of oxidation products. Boehmite turns soon into baierite. The formation of oxide layers on aluminium surface results in inconsiderable

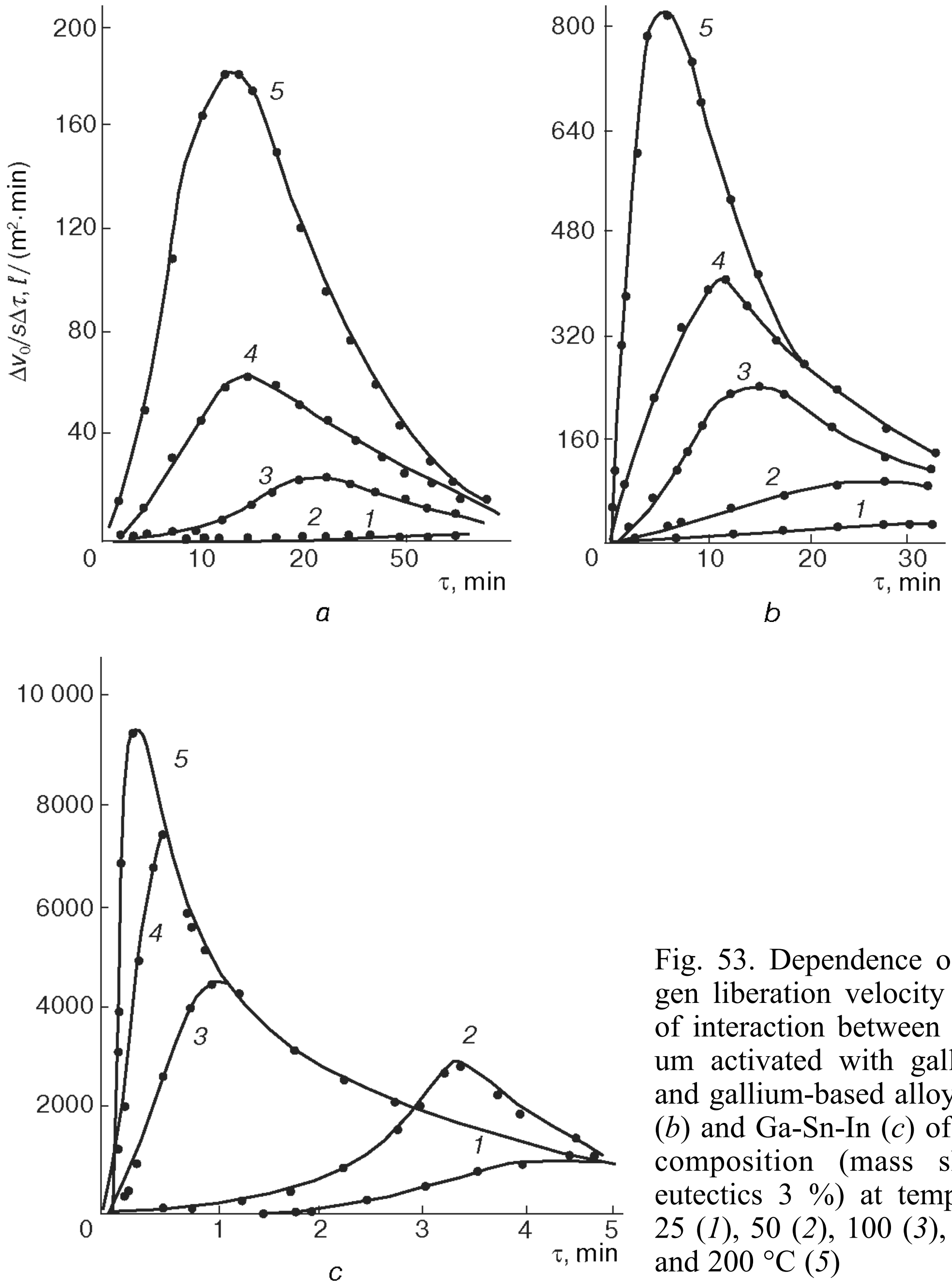


Fig. 53. Dependence of hydrogen liberation velocity on time of interaction between aluminium activated with gallium (*a*) and gallium-based alloys Ga-Sn (*b*) and Ga-Sn-In (*c*) of eutectic composition (mass share of eutectics 3 %) at temperatures 25 (*1*), 50 (*2*), 100 (*3*), 150 (*4*), and 200 °C (*5*)

increase of the mass rather than in its loss. In the process of mechanical loading most aluminium alloys — of an electronegative and thus, active metal — always interact with water, forming the oxidation products which create the adsorptional barrier layers on their surface. These layers inhibit the oxidation (corrosion) process proceeding with extremely low rate.

Aluminium alloys, loaded in water medium, fail by the mechanisms of intercrystallite cracking which is always of intercrystallite character [135]. Time of intercrystallite cracking and the cracks ontset depend on various factors. Proceeding from the available experimental data it is considered that the crack propagation velocity under loading of aluminium and its alloys is 10^{-8} cm/s. The rate of aluminium dissolution in pure water does not exceed 0.01 mm/yr. The corrosion velocity of iron-silicon-aluminium alloys (about 1 % of Si and Fe) in water is 0.005–0.015 g $(m^2{\cdot}h)$. Aluminium alloy with 0.45–90 % of Mg, 0.7–1.2 % of Si, 0.5–1.0 % of Ni possesses high corrosion resistance. Aluminium alloys containing 1–5 % of Ni, 0.3–5 % of Fe and 1–3 % of Si remain corrosion-resistant up to 300–350°C. Thus, aluminium alloy with 0.1–0.4 % of Ni and 0.5 % of Fe corrode in water at 300 °C with corrosion velocity 0.01 $g/(m^2{\cdot}h)$, which makes 0.323 mm/yr. Aluminium alloys which lose 0.1 mm/yr of their sample thickness belong to practically resistant one [136]. To raise its corrosion resistance aluminium is alloyed by additions of such metals as Mg, Cu, Zn, Si, Ti, Li, Mn and others with obtaining two-, three-, four- and five-component alloys. Multicomponent aluminium alloys, which correspond to homogenized regions of aluminium-based solid solutions possess, as a rule, high corrosion resistance to water, various oxidative media and are widely used in avionics, machine-tool industry, instrument making, etc. All the doping components form a dence oxide film on the alloy surface. This film prevents from water and oxygen penetration to the alloy surface. The alloying metals oxides (MgO, ZnO, TiO_2, ZrO_2…) are also components of the oxide film. That is why the aluminium-based doped alloys behave in solutions like aluminium.

We have stated an inverse task: to realize natural thermodynamic aluminium reactivity. It is known that the surface and volume structure homogeneity is the condition of obtaining the corrosion-resistant alloys. During crystallization of aluminium alloys most accompanying and doping metals manifest surface activity and are crystallized at crystallites' grain boundaries. That is why, the introduction of different metal additions into liquid aluminium, which additions can increase surface inhomogeneity S_d of the formed alloy, S_d being a function of volume inhomogeneity,

$$S_d = f(a_{Me} V_\delta),$$

results in realization of high reactivity inherent in aluminium. The difference of surface activity of metals-additions determines the difference of electrochemical properties of the crystalline boundaries and its central part. This difference results in the processes of dissolution and corrosion of electronegative metal — aluminium. So, the intercrystallite corrosion is the major danger for aluminium and its alloys. The corrosion can be of focal character and, at the best, it can result in the failure of expensive equipment and, at the worst, in the catastrophe with human deaths and damage to the environment.

As to its occurrence in natural minerals, aluminium takes the third place (after oxygen and silicon) and has developed infrastructure [137]. Thus, different aluminium-based energetic processes can be developed, high-reactivity aluminium-containing alloys being the working-medium in them. We have developed three types of high-reactivity alloys which display high affinity for water and perform functions of power accumulating substances [4–6, 55–58, 112–127, 133, 134]. The alloys are based on aluminium and some other metals (magnesium, boron, silicon). As is seen from Fig. 54 such alloys include low-temperature (223–273 K), medium-temperature (273–573 K) and high-temperature (573–2273 K) alloys of power-accumulating substances. Low-temperature alloys of activated aluminium interacting with ice at low temperatures are of interest for geological prospecting in the search of deposits and production of oil and natural gas. Medium-temperature alloys of EAS can be used in power production, industry and new technology. The sphere of high-temperature alloys application is rather wide — from the earth conditions to power sources of spaceships.

Low-temperature EAS. We have demonstrated in our works [79, 117–132] that if aluminium is doped with gallium, indium, tin, zinc and other metals possessing a tendency to form low-temperature eutectic then it (aluminium) will dissolve in water as a result of proceeding of intercrystallite corrosion of the volume-heterogeneous alloy, which surface boundaries are enriched with gallium. In the works [79, 118] the authors have calculated gallium distribution coefficient in the system Al-Ga which proved to be equal to 0.0526. Thus, the difference in gallium concentrations in crystallites of aluminium-gallium alloys can reach great values and, as a result, aluminium plays the role of anode in the forming micro-galvanic elements, while the interfaces of crystallite grains enriched with gallium play the role of cathode. Such a proceeding of aluminium dissolution reaction is peculiar to realization of the electrochemical mechanism [133, 134].

Secondary aluminium of AB92, AB91, AB88, AB86 grades is used for production of low-temperature alloys and compositions on their basis; gallium, indium, tin, lead of any degree of purity are used as metals-activators. These elements are introduced into aluminium, following the eutectic ratio, namely: Ga:In:Sn:Pb = 1:0.404:0.210:0.150 [131]; Ga:In:Sn:Zn = 1:0.410:0.213:0.016 [132] or mass fraction %, Al:Ga:In:Sn:Cd:Tl = 70–951:0.5–3:0.5–3:0.5–3 and sodium chloride 33–90 % with respect to the alloy mass [123, 125]. These aluminium alloys provide for hydrogen liberation in interaction with ice at 253–273 K. Hydrogen liberation velocity at 263 K is 4.4–4.5 l/kg of the composition. In the process of the composition interaction with ice the reaction thermal effect accelerates considerably the alloy dissolution and hydrogen liberation.

Medium-temperature EAS. The medium temperature EAS are in great demand in different fields of science and technology and different branches of industry. Thus, after doping aluminium with gallium the aluminium alloy acquires high reactivity with respect to water. Gallium with aluminium form

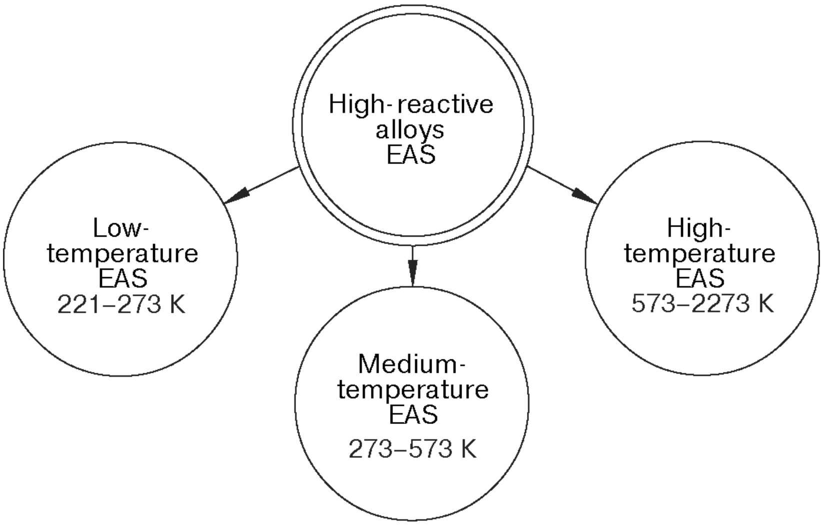


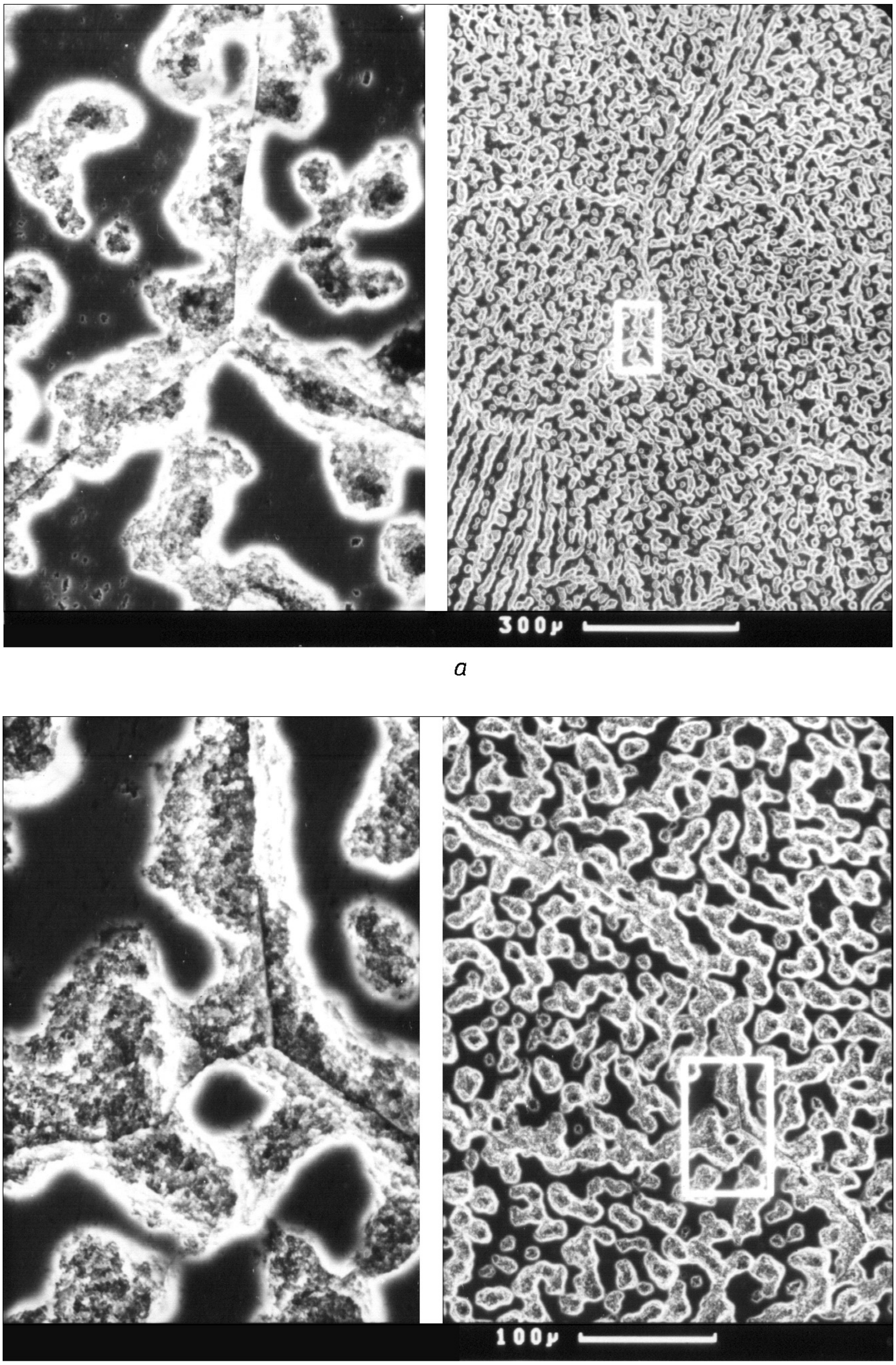
Fig. 54. Gradation of high-reactive alloys based on aluminium, boron, magnesium, silicon and other metals.

eutectics which contains 99.0 % of gallium with the melting point 26.3 °C. Aluminium solubility in solid gallium makes < 0.05 % and gallium in aluminium — about 20 %. An analysis of thermodynamic properties of the system Al–Ga proves that the affinity of homogeneous atoms Al–Al and Ga–Ga for each other in the latter is higher than between heterogeneous atoms Al–Ga.

The raster electron-microscopic photographs (with different magnification) made on a microscope *Cam-Scan 3DV* of the section specimen of Al–Ga alloy with gallium mass fraction 3.0 % pickled with Lacombe solution (mix of concentrated solutions: 3 ml of HF, 47 ml of HNO_3 and 50 ml of HCl) are presented in Fig. 55, *a*, *b*.

One can see distinctly the pickling holes determined by nonuniform distribution of gallium in crystallites volume. Boundaries of crystallites enriched with gallium and manifesting higher reactivity are also distinguishible. That is evidenced by the alloy microstructure indicated in the left part of the photograph (Fig. 55) made with a separated screen unit with a magnification of 600 power. One can see the cracks which pass along crystallites boundary and are determined by the volumetric expansion of gallium under its liquid-solid transition. The linear expansion coefficient is 3.2. It would be noticed that the linear shrinkage of aluminium is — 1.8 %. The reaction velocity constants (k_i) for aluminium interaction with water at 50, 100, 150 and 200 °C, when aluminium is activated by 3 % of gallium, equal 0.0070, 0.0290. 0.0487 and 0.0788 min^{-1}, respectively. The activation energy of hydrogen liberation reaction, equal to 17.8 kJ/mol, proves that the reaction velocity is limited by the diffusion restrictions.

The coefficient of gallium distribution in hard aluminium, as was noted above, is equal to $k_{Ga/Al} = 0.526$, which evidences for the structure heterogeneity



a

b

Fig. 55. Microstructure of Al-Ga section specimen with gallium mass fraction 3.0 %

of the system Al–Ga. Since the aluminium crystalline boundaries are enriched with gallium, then, under crystallization of the system Al–Ga, as soon as aluminium is compressed and gallium expands, there appear stresses in the alloy volume which lead to plastic deformations and difficulties in the alloy shrinkage, and this results in the onset of cracks. In the left part of Fig. 55 one can see the particles of aluminium oxidation products in the alloy Al–Ga, these particles correspond to compounds AlOOH and Al_2O_3 formed on the crystallites boundaries. Composition of the central part of crystallites and their boundaries were analyzed by he method of comparative electron analysis. The analysis results are presented in Fig. 56. The

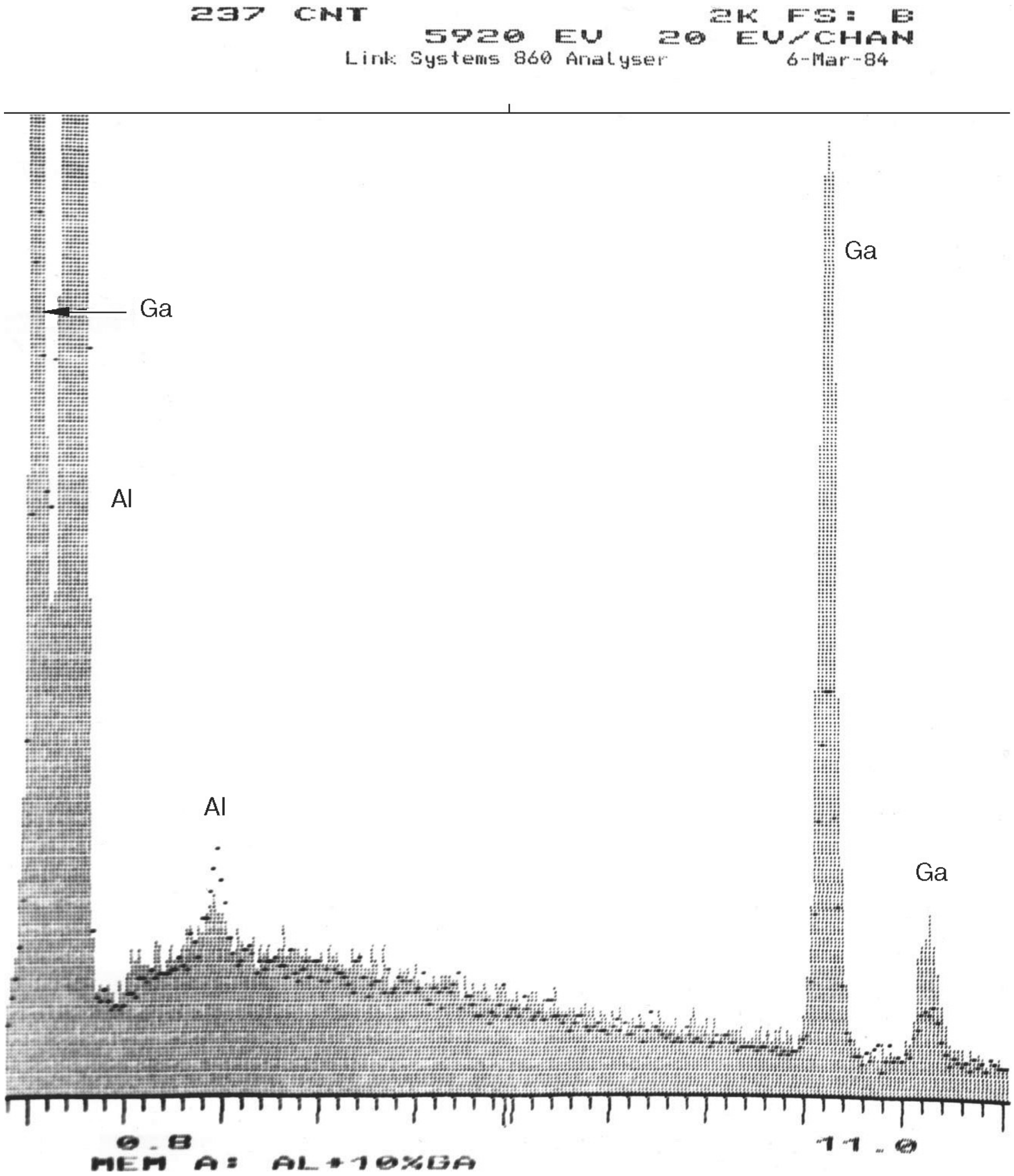
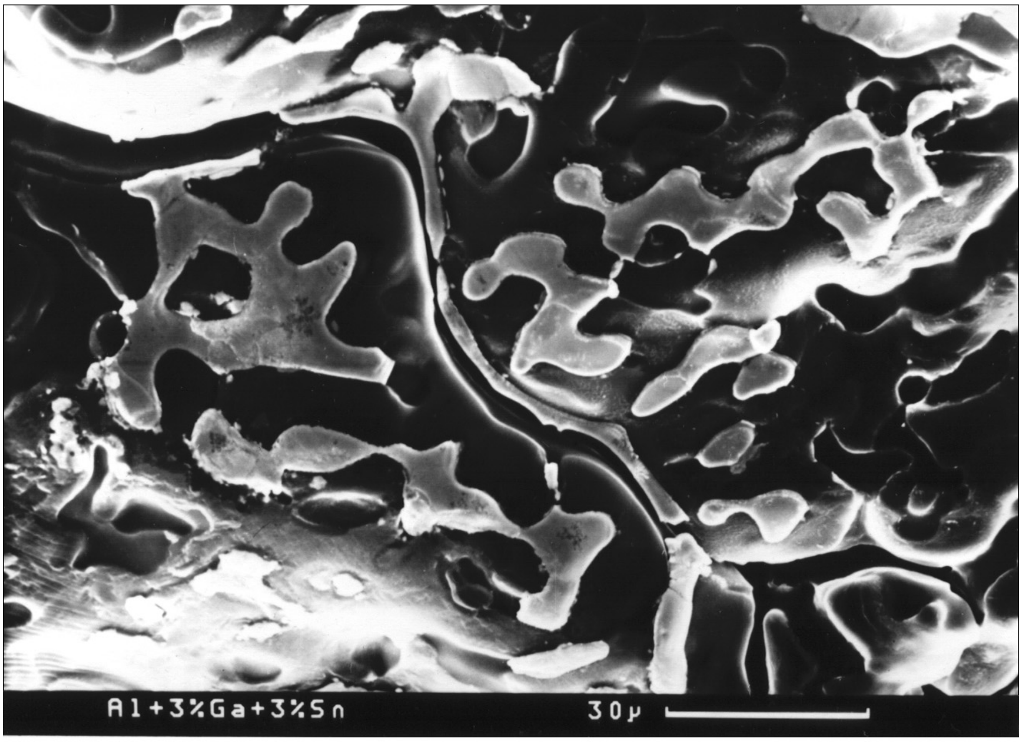
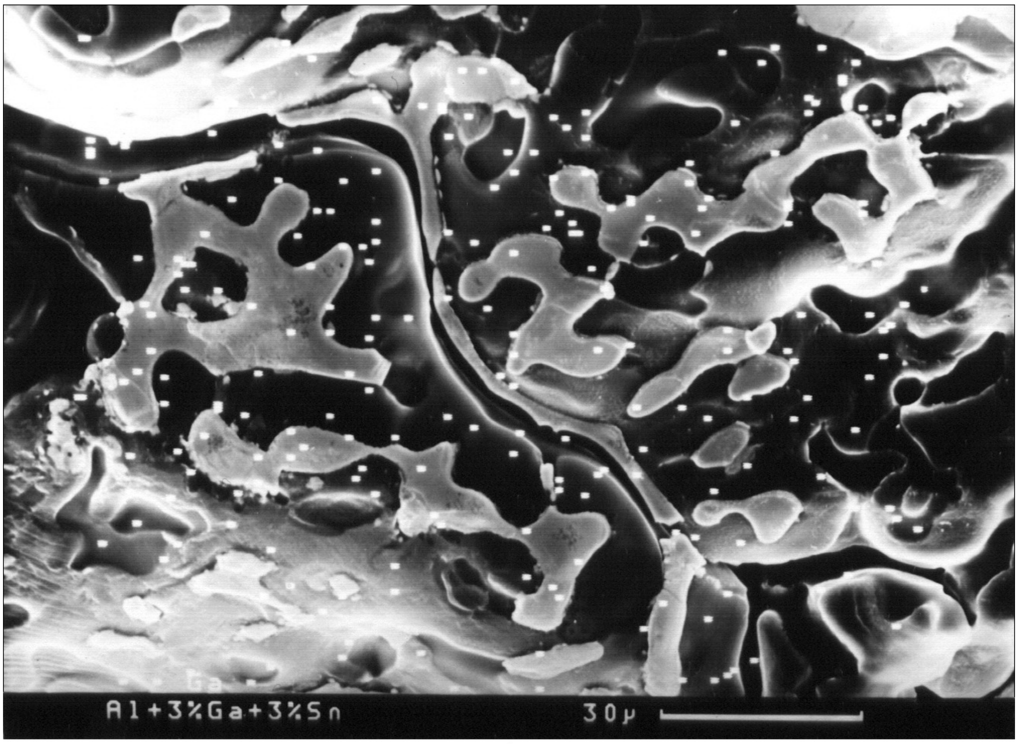


Fig. 56. Energy spectra of gallium distribution in the central part of crystallite of the alloy Al–Ga (dash-lines) and in crystallites boundaries (solid lines)



a



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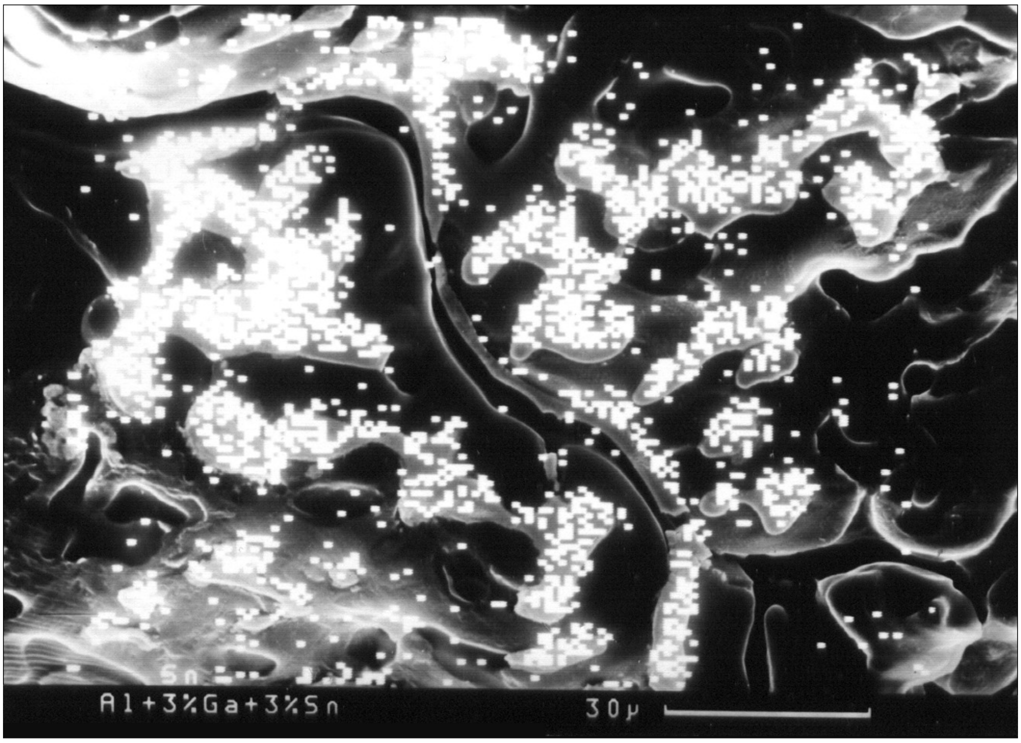


c

Fig. 57. Microstructure of a fresh fracture of aluminium alloy with gallium mass fraction 3.0 % and tin in the ordinary (*a*) and characteristic radiation of gallium (*b*) and tin (*b*)

crystallite central part spectrum is shown by separate points, and the boundaries spectrum — by solid lines. A comparison of the areas of gallium energy spectrum peaks shows that gallium content in the intercrystallite space exceeds almost thrice the content of gallium in the central part of the crystallite.

Thus microanalysis of Al–Ga alloy specimen conducted with electron microscope evidences for inhomogeneous distribution of gallium in aluminium alloy with gallium crystallized in nonequilibrium conditions. Thus, it is evident, that the aluminium alloy reactivity to water will increase with the number of its components.

Indeed, tin (3 %) being introduced as the third component into the system Al–Ga (3.0 % of gallium), and the ternary system Al–Ga–Sn being available the velocity of aluminium dissolution increases more than 5 times (Fig. 53, *b*). In this case, as it follows from the analysis of fresh fractures of the specimens obtained in deep vacuum by the electron microscope Cam-Scan cameras, the ternary alloy Al–Ca–Sn tendency to liquation and deposition of the second phase on crystallites boundaries is manifested even more as compared to the binary alloy Al–Ga (Fig. 57). An analysis of microstructure of Al–Ga–Sn specimens photographed in characteristic radiation of gallium (Fig. 57, *b*) and tin (Fig. 57, *c*) points to the nonuniform distribution of both

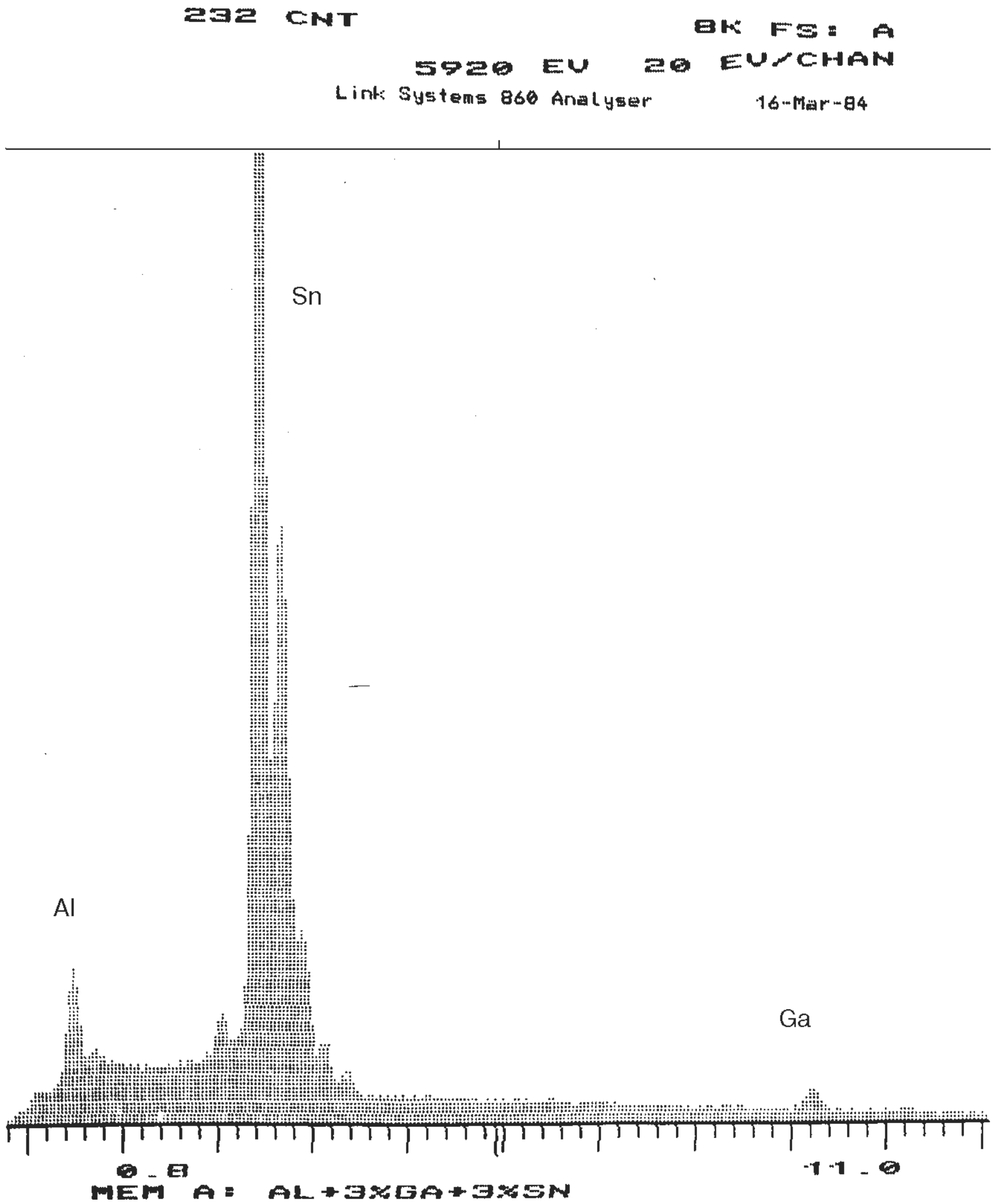


Fig. 58. Energy spectrum of metal-activators particles distributed on the surface of aluminium alloy crystallites with mass fractions of gallium and tin 3 % each

gallium and tin. Tin displays a special tendency to segregation in the crystallite boundaries of the ternary alloy. In Fig. 57 one can see a joint of all three crystallites. The second phase localization has manifested distinctly on their surface; this phase composition corresponds to the eutectics of the ternary system Al–Ga–Sn as well as to individual gallium and tin according to their distribution coefficients. Proceeding from the data of [138], the coefficient of tin distribution in aluminium $K_{S_n/\mathrm{Al}} = 0.00025$. Thus, tin deposition in the second

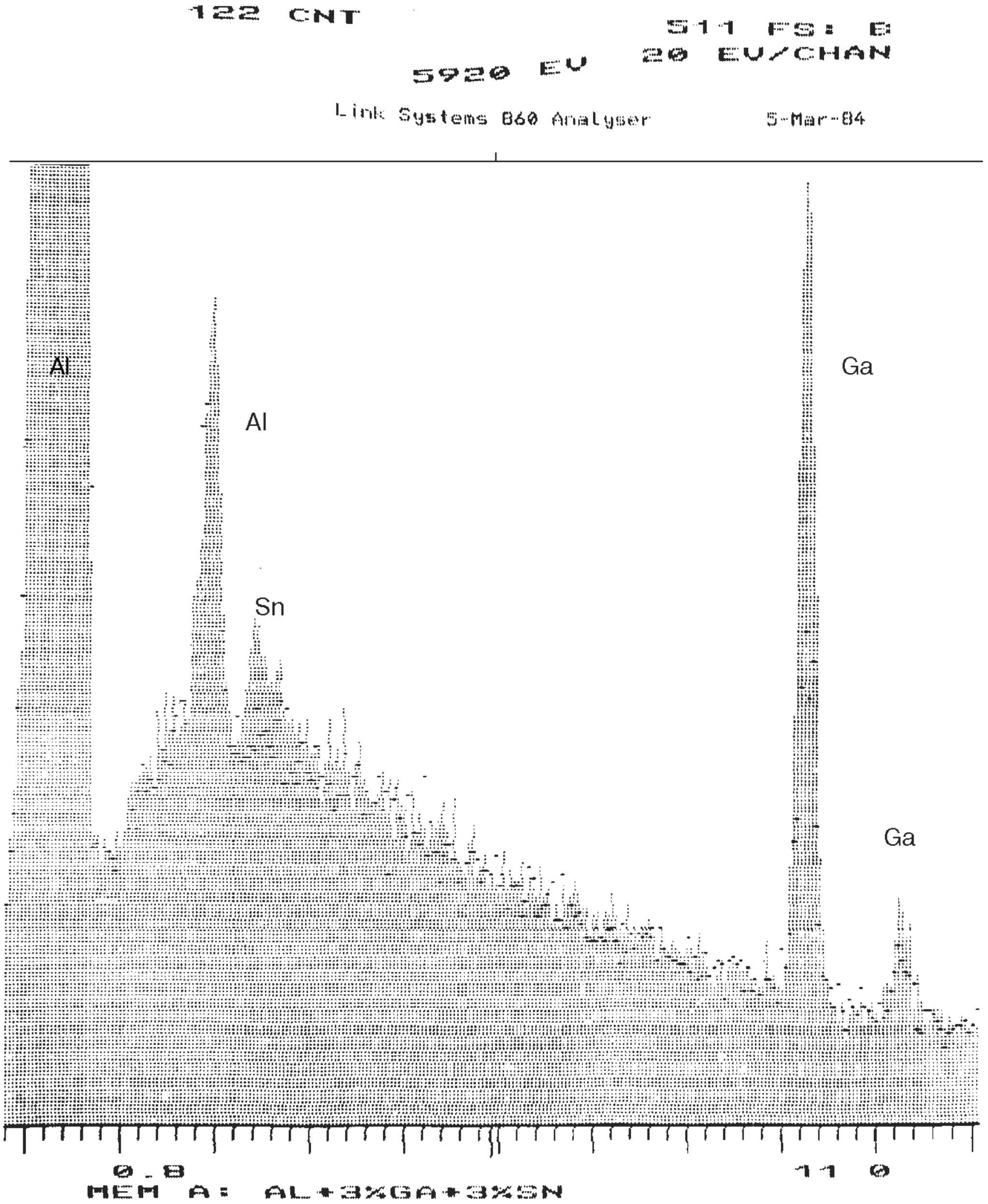
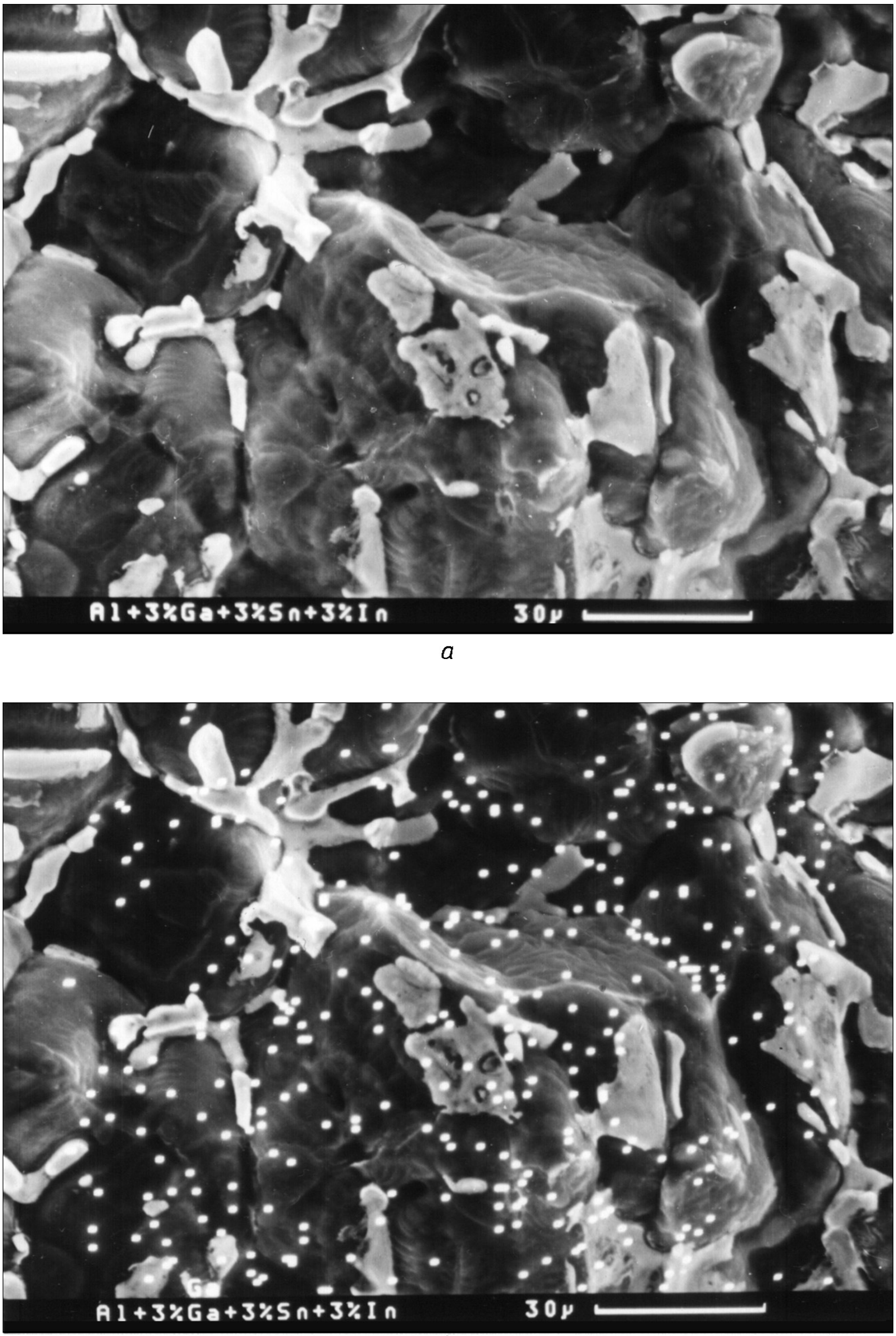


Fig. 59. Energy spectrum of the alloy Al–Ga–Sn with gallium and tin mass fractions of 3 % each in the central part of the crystallite (contour dots) and in the intercrystallite space (solid lines)

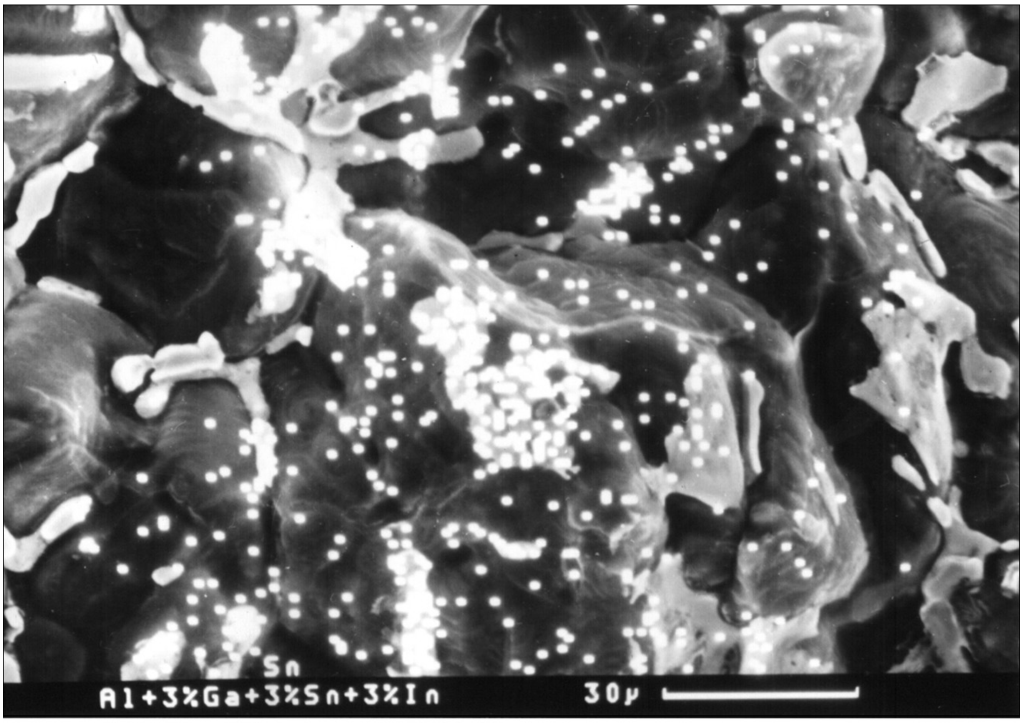
phase is natural. An analysis of Al–Sn alloys microstructure has shown that the interrupted boundaries of polyhedrons with embedded second phase depositions in a form of practically pure tin, mainly distributed in the crystallite boundaries, appear even in the alloys with 0.1–0.5 % of tin [139]. The region of solid solution in aluminium at 210 °C does not exceed the hundredths of a percent. The alloys microstructure data given in Fig. 57 demonstrate that the depositions of the second phases are not bound with aluminium by interatom-



a

b

Fig. 60. Microstructure of fresh fraction in the deep vacuum of the alloy Al—Ga—Sn—Tn specimen with mass fractions of the ternary alloy GA — Sn — In of 3 % of eutectic compo-



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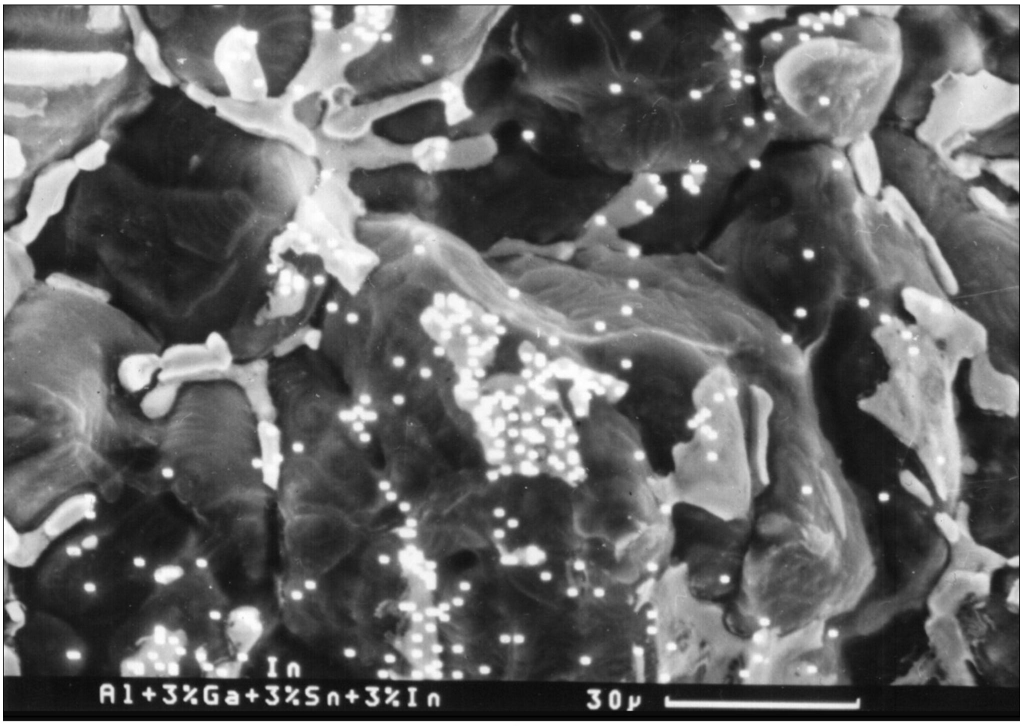


d

sition in the ordinary radiation (*a*) and characteristic radiation of gallium (*b*), tin (*c*) and indium (*c*)’ ic forces, which is evidenced for by availability of the holes formed on crystallites surface and revealed under fractures in the alloy specimen. Indeed, energy spectra of the particles localized on crystallite surfaces prove that the second phase mainly consists of tin with low amount of dissolved aluminium and gallium [Fig. 58].

The energy spectra of the Ga–Sn–In system crystallites given in Fig. 59 also evidence for nonuniform distribution of metals-activators in the aluminium matrix. In this case the spectrum of the central crystallite part is shown by single dots, while the crystallite boundary spectrum — by solid lines. A comparison of the areas of gallium and tin energy spectra peaks demonstrates that these elements content in the intercrystallite space exceeds their concentration in the central crystallite part.

Aluminium being activated by the three-component alloy Ga–Sn–In (3.0 %) of eutectic composition (with mass fractions, %: Ga — 62.0, Sn — 13.0; In — 25.0), with obtaining the four-component system Al–Ga–Sn–In, the aluminium dissolution velocity increases 51.1 times as compared to the binary system Al–Ga (Fig. 53, *c*). Microstructures of fresh fractures of Al–Ga–Sn–In alloys are given in Fig. 60. An analysis of Al–Ga–Sn–In alloy microstructure has shown that in such a case the second phases display even stronger tendency to seggregation. Indium distribution coefficient in aluminium is equal to 0.01 [140]. Thus, indium (Fig. 60, *b*), as well as tin (Fig. 60, *c*), concentrates along the crystallite boundaries. In the alloy Al–Ga–Sn–In gallium is crystallized in the boundaries and interfaces of crystallites and on the spots of the second phases deposition. The intensity of distribution of white dots, proportional to concentration of metals-activators — indium and tin, is practically similar. The latter is determined by the fact, that tin-indium ratio in the depositing second phases is close to eutectic (approximately 47.3 % of tin and 52.7 % of indium). Indeed, an analysis of the second phases has demonstrated the following relationship of the components, %: tin — 38.72, indium — 36.53, gallium — 0.41, aluminium — 24.25. The crystallite matrix usually contained, %: aluminium — 99.5, gallium — 0.285, indium — 0.131, tin — 0.084. We have also analyzed the second phases of the Al–Ga–Sn–In alloy specimen (Fig. 60, *a*). It appeared that these phases are considerably different as to composition. The second phase — *1* contained, %: indium — 70.5 %, aluminium — 4.3, gallium — 28.5, tin — 23.7. The second phase — *2* contained, %: indium — 28.5, aluminium — 4.1, gallium — 0.9, tin — 66.5. The energy diagram of the second phases, given in Fig. 61, also proves that indium, tin and aluminium are their basic components.

Investigations of the interaction rate of aluminium, activated by three-component alloy Ga–Sn–In of eutectic composition have shown (Fig. 53, *c*) that hydrogen liberation velocity in the activated aluminium-water system at 200 °C

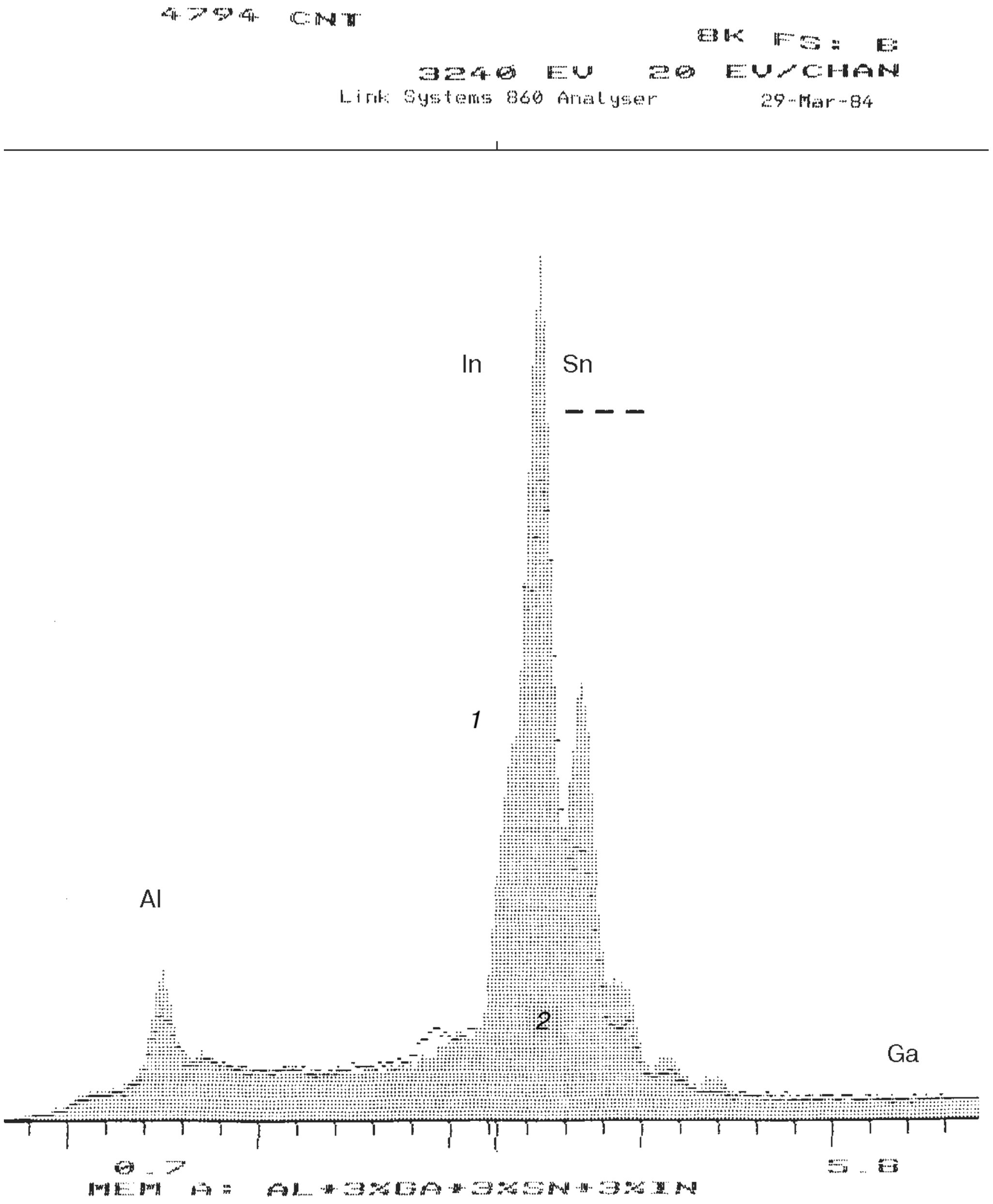


Fig. 61. Energy spectra of the second phases, rich with indium (*1* — dotted lines) and tin (*2* — solid lines) distributed on the surface of crystallites of Al-Ga-Sn-In alloy with mass fraction of three-component alloy Ga-Sn-In of 3 % of eutectic composition

is approximately 9200 l/m^2·min. One can calculate that the dissolution velocity of aluminium, activated by ternary eutectics Ga–Sn–In, equal to 9200 l H_2/m^2·min by hydrogen, is equivalent to the linear velocity of aluminium dissolution of 2728 mm/min or 1433.84 m/yr. Therefore water dissolution of the four-component alloy Al–Ga–Sn–In, containing 97 % of aluminium and only 3.0 % of eutectics Ga–Sn–In, proceeds by the «catastrophic» mechanism.

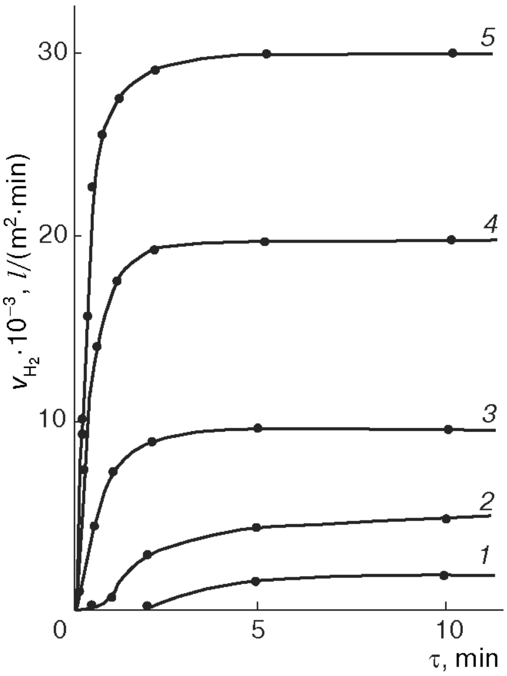
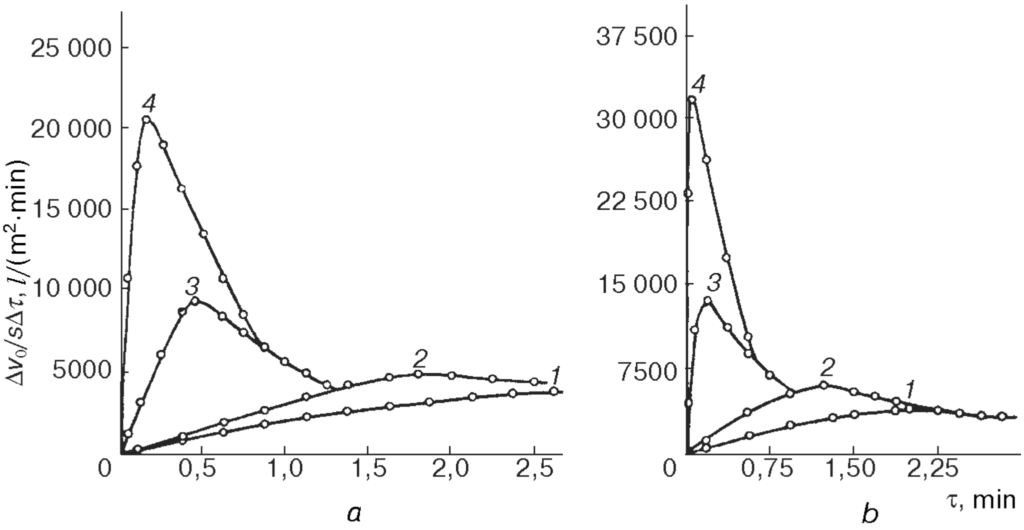


Fig. 62. Kinetic curves of hydrogen liberation as a result of aluminium interaction with water. Aluminium is activated by eutectic alloys *A* and *B* at temperatures, °C: 1–25; 2–50; 2 — 10; 4 — 200 (alloy *A*); 5 — 20 (alloy *B*)

The investigations have also shown that the number of components in the alloy-activator being increased, the rate of activated aluminium interaction with water increases immeasurably.

Kinetic curves of hydrogen liberation as a result of aluminium interaction with water are presented in Fig. 62; aluminium was activated by the four-components alloys Ga–In–Sn–Pb of eutectic composition *A*, %: Ga — 1.701, In — 0.687, Sn — 0.357, Pb — 0.255 [214] (curves *1-4*) and Ga–In–Sn–Zn of eutectic composition *B*, %; Ga-3.050, In — 1.250, Sn — 0.650, Zn — 0.050 [126] (curve *5*). As is evident, maximum hydrogen liberation velocity depends on the nature of metals-activators, and at 100–200 °C reaches its limit value of 20 000 l/(m^2·min) for the alloy *A* and 30 000 l/(m^2·min) for the alloy *B*. The maximum velocity of hydrogen release both by the alloy *A* and the alloy *B* is reached approximately in 2 min. For low temperatures (20–50 °C) the induction period (i.p.) manifests on the rate curve, and the higher is the temperature the shorter is i.p. (at 25 °C i.p. is equal to 2 min, at 50°C — 0.7, and at 100 °C — 0.05 min). At 200 °C i.p. is disappearingly small (> 0.001 min). Maximum hydrogen liberation velocities equal to 20 000 and 30 000 l/(m^2·min), were used to calculate the linear rate of dissolution of activated aluminium alloys in water. It appeared, that the linear dissolution velocity of aluminium activated by the eutectic alloy *A* makes 5.93 mm/min or 3117.0 m/yr. and of that activated by the alloy *B* — 8.89 mm/min or 4675.5 m/yr. Great amounts both of thermal power and gaseous



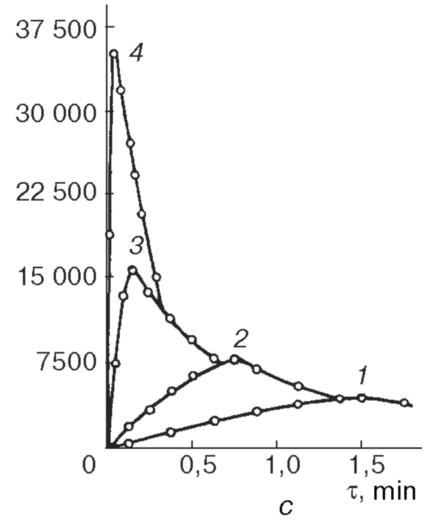


Fig.63. Hydrogen liberation velocity as a function of time under water interaction with aluminium activated by additions of Ga, Sn, I — 10 % each, and lithium — (*a*) 17.00 %; Ga, Sn, In — 3 % each and Li-21.0 % (*b*); Ga, Sn, In — 5 % each and Li — 24.5 % (*c*)

hydrogen are produced under such conditions. Aluminium dissolution in water is an exothermal reaction (6.101) which thermal effect is equal to 950.97 kJ/mol. Calculations have shown that water interaction with aluminium, activated by the alloy *A*, is accompanied by heat liberation of 283 MJ/mol and when aluminium is activated by the alloy *B* — the liberated heat equals 424.5 MJ/min.

Even higher velocities of hydrogen and heat liberation are observed under dissolution of aluminium activated by gallium, tin, indium additions with mass fraction of 3.0 % each and 17.0–24,5 % of lithium (Fig. 63) [127]. Lithium forms a broad range of solid solutions with aluminium. When introducing additions of metals-activators into the Al–Li alloy the range of solid solutions is something reduced.

Introduction of lithium into the alloy Al–Ga–In–Sn leads to formation of alloy in which intercrystallite corrosion is not observed in the grain boundaries, and this usually leads to the alloy dispersion under interaction with water. The alloy Al–Ga–In– Sn–Li interacts uniformly with water with exceptionally high rates. Under its contact with water both aluminium and lithium dissolve, lithium hydroxide being formed. The latter, in its turn, dissolves aluminium hydroxide, preventing water supply to the metal reaction surface. That is why, aluminium-lithium alloys made on the basis of activated aluminium display high (not only surface, but also volume) reactivity to water and other oxidizers (oxygen, acids, etc.).

As is seen from Fig. 63, Ga, Sn, and In (1 % each) being introduced into the alloy Al(80)–Li(17), the latter acquires high reactivity to water, and hydrogen liberation velocity at 200 °C makes 21000 l/(m^2·min). The hydrogen liberation velocity under water interaction with the alloy Al(70)–Li(21)–Ga(3)–Sn(3)–In(3) at 200 °C makes 32 000 l/(m^2·min). The content of lithium in the alloy being increased to 24.5 % and that of metals-activators to 5 % each (the alloy composition: Al(60.5)–Li(24.5)–Ga(5)–Sn(5)–In(5)) hydrogen liberation velocity reaches 36 500 l/(m^2·min). At temperatures of 25–50 °C it is equal to 5000–8000 l/(m^2·min). The processing of kinetic curves of interaction of aluminium-lithium alloys (activated by gallium, indium and tin) with water has shown that the total rate constant at 25–50 °C is equal to k_1 = 0.10–0.12 $\text{min}^{-1,}$ and at 200 °C it increases to k_1 = 4.38 min^{-1}. In this case the induction period lasts for fractions of a minute (0.25·0.10 min). The value of the effective activation energy of the reaction of activated metals (aluminium and lithium) interaction proved to be equal to 30.3 kJ/mol, which indicates to the mixed control of the rate of aluminium and lithium interaction with water under experimental conditions.

The analysis of the reaction properties of medium-temperature EAS of alloys under consideration shows that they are of interest for numerous branches of industry, fields of science and new technology. These alloys reactivity to water depends on the nature of metals-activators and structure of the formed alloys. Knowledge of regularities of the effect of the activated alloy (aluminium, magnesium, boron, silicon) structure on reactivity is of determining value for prediction of properties of the activated metals and their alloys, and, as a consequence, for the apriori development the activated aluminium alloys with preset properties (to produce high-parameter hydrogen, metal or metallized propellants, corrosion protectors for metal works, to synthesize high-temperature electrolytes based on β-alumina, etc.)

Kinetic curves of aluminium (aluminium is activated by gallium, tin, indium and other metals-activators) interaction with water, presented in Figs. 53, 62–64, possess the form charactersitic of the reactions proceeding on the solid phase surface — the topochemical reactions [141]. At low concentration of metals-activators or at low temperatures the reaction rate in the experiment beginning is low, then it grows and passes through maximum. The number of introduced metals-activators and their percentage being increased, the maximum on

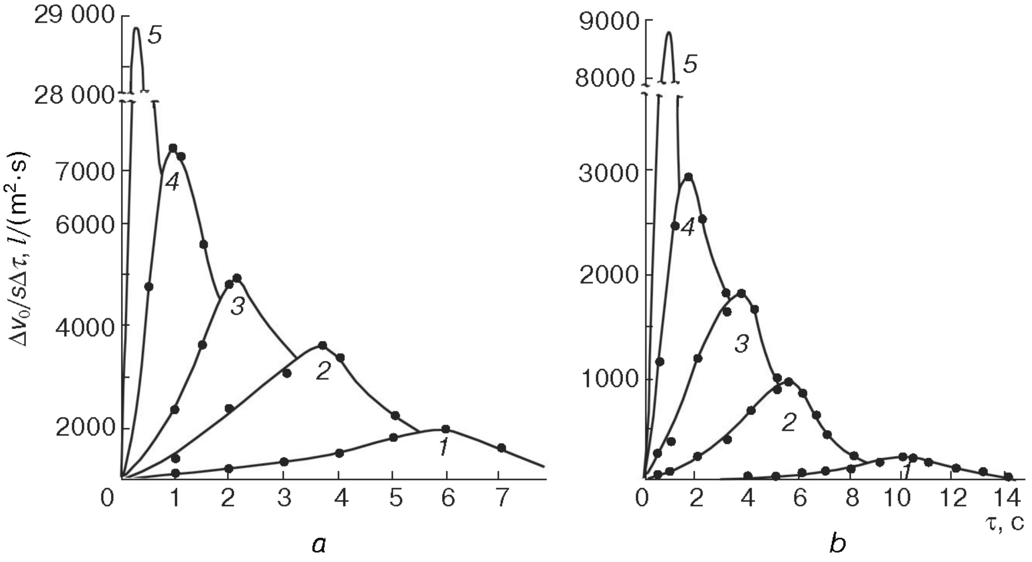


Fig. 64. Dependence of hydrogen liberation rate at temperatures of 50–300 °C on the time of activated aluminium contact with water. Aluminium of AGOIM and AMGT grades [127]: *1*–50; *2*–100; *3*–150; *4*–200; *5*–300 °C.

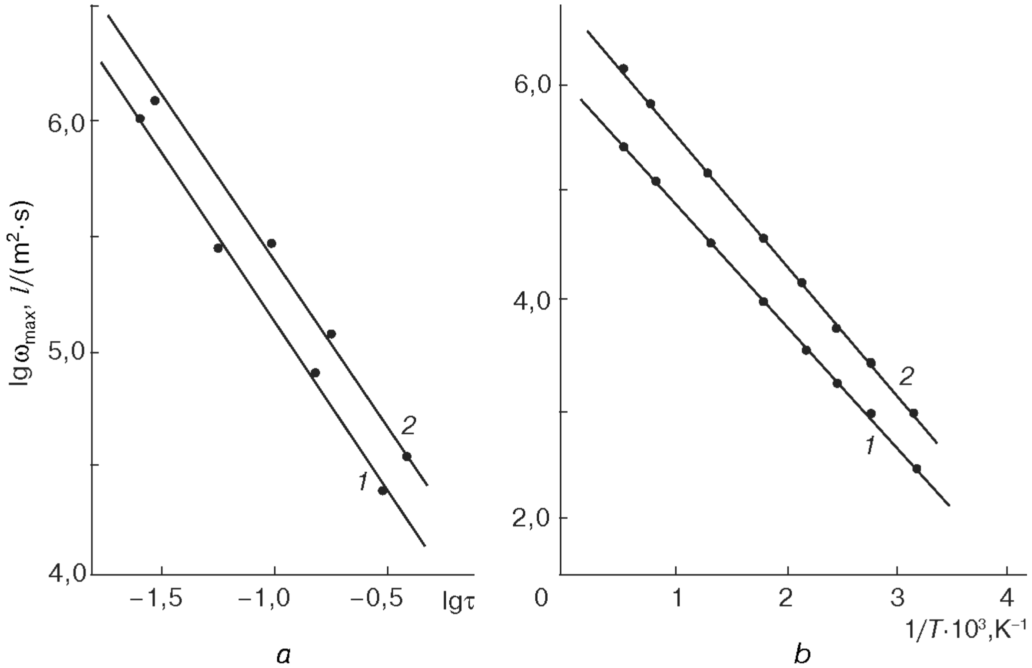


Fig. 65. Dependence of logarithms of maximum hydrogen liberation velocities on the time of contact with water vapour (*a*) and on inverse temperature (*b*)

hydrogen liberation velocity-time curves becomes more expressed and shifts towards the less time.

High-temperature EAS. The kinetic curves of high-reactivity alloy AMGT (*1*) and AGOIM (*2*) interaction with water are presented in Fig. 65 [142].

It is seen from the Figure that at 300 °C the maximum hydrogen liberation velocity is reached during fractions of a second. The dependence lg ω_{max} – lg τ for the investigated compositions of activated aluminium is shown in Fig. 65. It is evident that the maximum velocities of aluminium interaction with water are established for the hundredth fractions of a second. Thus the activated aluminium of AMGT grade interacts with water with hydrogen liberation with the rate of $1\cdot10^6$ l/(m^2·s) at 1397 °C during 0.0263 s.

The dependence of maximum hydrogen liberation velocity on the inverse temperature is linear (Fig. 65, *b*).

The calculated efficient activation energy proved to be equal to 21.25 kJ/mol which evidences for the diffusion control of the rate of aluminium reaction with water. Investigations have also shown that the rate of aluminium interaction with water depends on its particle sizes. In accordance with the data of Fig. 66, the average particle diameter being 6 μm, 21 000 l of hydrogen are released from 1 m^2 of particles surface. For the particles 2 μm in diameter the hydrogen liberation velocity reaches 35 000 l/(m^2·s). When changing the activated alloy structure one can achieve even higher hydrogen liberation velocities.

According to the investigation data, metals-activators of optimal compositions (usually in a form of eutectics) which function as alloy modifiers being introduced, the alloys acquire the fine-grained structure covered with fractures, some of them acquire brittleness.

It was established that maximum hydrogen liberation velocity depends on the average diameter of crystallites at a temperature of 473 K. A distinct dependence is observed between maximum hydrogen liberation velocity and crystallite average diameter $d_{av.}$: the less is d_{av} of crystallites the higher is the hydrogen liberation velocity (Fig. 66, *a*). To achieve hydrogen liberation velocity exceeding 21 000 l/(m^2-min) at a temperature of 473 K the size of crystals would be less than 4 μm (Fig. 66, *a*). When processing the experimental results of the relation one can observe a semi-logarithmic dependence of maximum hydrogen liberation velocity on the crystallite d_{av}. In accordance with the data of Fig. 66, *b*, the relationaship $v^{H_2}_{max} - 1/d_{av}$ is linear and is described by the equation:

$$v^{H_2}_{max} = 31605 + 18252.5\ 1/d_{av} \qquad (109)$$

It follows from the equation, that at an average size of crystallites, d_{av} of 1.0 and 0.1 μm, the maximum hydrogen liberation velocity equals 31605 and 49857 l/(m^2·min). Aluminium being crystallized in the ultrasonic field or with the use of special additions-activators, possessing surface activity in the solid-liquid system, the activated matrix metal activity may be raised to even higher extent.

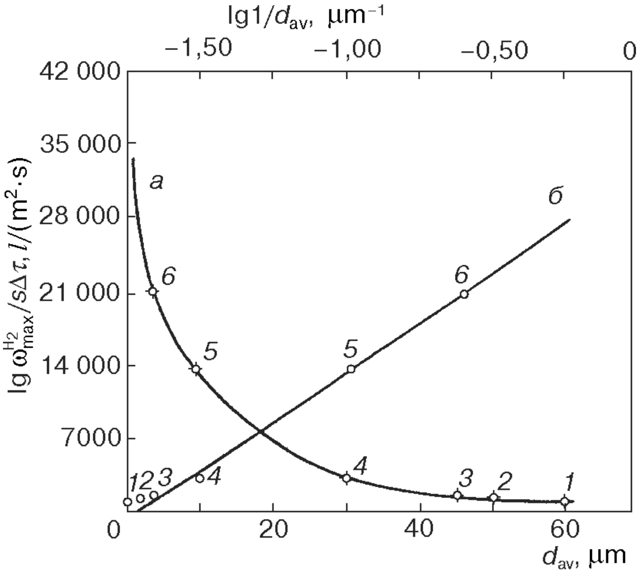


Fig. 66. Maximum hydrogen release velocity logarithm dependence on the average diameter of activated aluminium particles at a temperature of 200 °C (*a*) and logarithmic dependence lg1/d_{av} on lg $v^{H_2}_{max}$ (*b*):
1–Al–Ga; *2*–Al–Ga–Sn; *3*–Al–Ga–In; *4*–Al–Ga–Tl; *5*–Al–Ga–Sn–In; *6*–Al–Ga–Sn–In–Tl

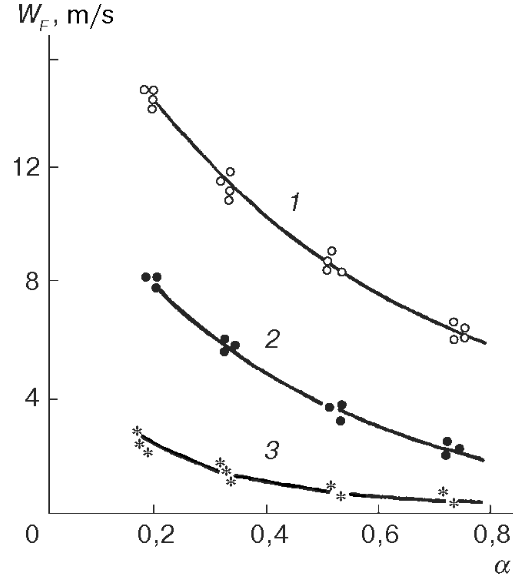


Fig. 67. Dependence of flame front velocity in the gas suspension of activated aluminium powder based on AGOIM and AMGT alloys and aluminium powder of ACD-1 grade:
1 — PMG AMGT; *2* — PMG AGOIM; *3* — ASD-1

Activated aluminium powder of AGOIM and AMGT grades possesses high activity both to water and air oxygen. The dependences of flame front velocity in the gas suspension of activated aluminium particles W_F on the oxidizer excess coefficient, when pressure in the combustion chamber operation section P_{ch} is equal to 0.1 MPa, are presented in Fig. 67.

The oxidation (combustion) velocity of aluminium powder of ACD-1 grade was also studied to compare activity. It has been established that activated aluminium of AGOIM and AMGT grades interacts with oxygen with much higher rate than the aluminium powder of ACD-1 grade. The flame front velocity in the gas suspension of ACD-1 particles P_{ch} = 0.1 MPa a = 0.15 made 1.9 m/s, and for AGOIM, produced by the same process as ACD-1, W_F = 9.2, for AMGT — 14.8 m/s. It is shown in the work [127] that extremely high combustion velocity of activated aluminium is determined by physico-chemical properties of metals-activators and aluminium. Data presented prove that activated aluminium may be successfully used for hydrogen production from water in the operative hydrogen energetics and defence engineering. More detailed methods of aluminium, magnesium, boron, silicon activation in order to give them high reactivity to water are considered in [55–58, 112–115, 118–127].

For lack of water, the ammonia conversion by the reaction of [143] is an accessible hydrogen source in the field conditions:

$$2NH_3 \rightarrow N_2 + 3H_2. \qquad (110)$$

Dependence of ammonia decomposition velocity constant on the atomic spacing in metals of group VIII which were investigated as catalysts is presented in Fig. 68. Maximum velocity in ammonia conversion belongs to ruthenium-based catalyst. Velocity constants k_i decrease in the series: Ru > Os > Rh > Ir > > Co > Pt > Pd > Fe. From the Figure data it is also clear that ruthenium possesses the least activation energy value (79.9 kJ/mol of NH_3), which evidences for kinetic control of the reaction of ammonia decomposition into molecular hydrogen and nitrogen.

The activation energy values are considerably higher for other metal catalysts, especially Fe, Co, Ni. The use of ammonia in the field conditions is rather profitable. One cylinder with ammonia contains the amount of hydrogen equivalent to that of 10 standard hydrogen cylinders at 150 atm.

9. Water photolysis with obtaining hydrogen and oxygen (solar-hydrogen energetics). Solar energy reaching the Earth surface is 8.075–8.370 J/(min·cm^2) which corresponds to about 2 kal/(min·cm^2) or 0.14 W/cm^2 [144]. Total quantity of the arriving solar energy is $1.7 \cdot 10^{17}$ W. Our planet land area is equal to $148.847 \cdot 10^6$ km^2. Only 1 % ($1.48847 \cdot 10^6$ km^2) of this area being taken and fit for trapping the solar rays, e.g., by means of photoelectrochemical converters [145–151] with 10 % efficiency makes it possible to obtain energy of $2.08 \cdot 10^{14}$ W. Power of NPP under construction and in operation makes 1.0 GW. Thus the solar energy power is equivalent to that of 100 000 NPP. That is why the problem of solar energy conversion is in the centre of attention. The increment of solar power plants made 15.9 % [152] during 1990–1998. The theory of photoelectrochemical converters of solar rays is presented by the

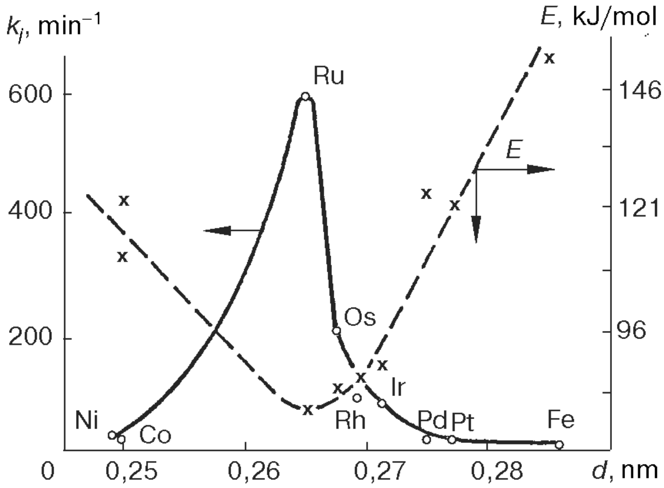


Fig. 68. Dependence of the reaction rate constant k_i of ammonia decomposition and activation energy on interatomic distance in metal-catalysts [143]

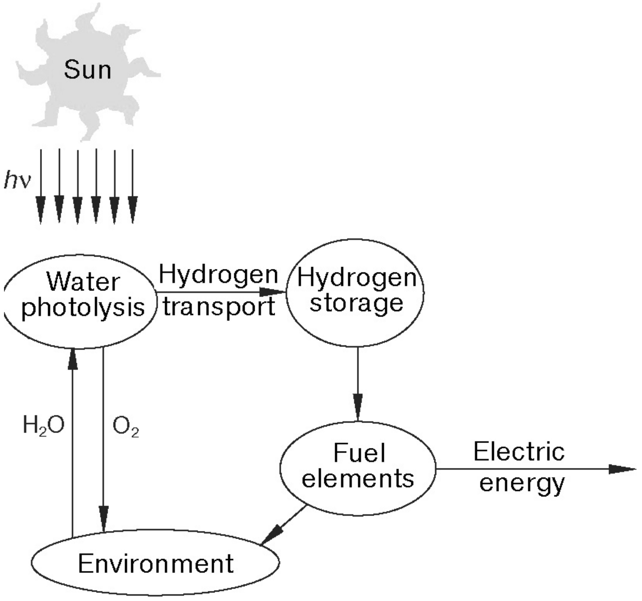


Fig. 69. Scheme of water photoelectrolysis in solar power plants with separate production of hydrogen and oxygen

authors of [145–148]. There are two approaches used, when investigating the conceptions of solar-hydrogen energy: conversion of solar energy — the light flux by means of water photoelectrolysis in the solar power plants (SPP), providing separate production of hydrogen and oxygen (Fig. 69), and the use of photosemiconductor elements with production of electric energy with its following conversion into hydrogen by water electrolysis (Fig. 70). System Ga–In–N is of interest now for photoelectrochemistry as photoelectric conductors. The system allows reaching the 34 % efficiency at no-load voltage of 0.77 V, short-circuit current of 18 mA/cm^2, filling factor 74 % and incident radiation power of 1 kW/m^2. A very low specific electric energy consumption equal to 3.84 kW·h/m^3 of H_2 was obtained in 10 kW protoelectrochemical plant made in Germany. The energy consumption was equivalent to that when producing hydrogen by means of high-temperature water elecrolysis (see, p. 6.2). Protoelectrochemical converters of solar energy with high technical-and-economic indexes were developed at the Institute of General and Inorganic Chemistry of the National Academy of Sciences of Ukraine [145, 146, 148–151]. Thus real efficiency of solar power plants on the basis of CdTe-CdSe makes approximately 24 % [145].

The highest efficiency value is observed in the range of ΔE = 1.5–1.7 eV. Photoelectrochemical converters on the basis of monocrystalline GaAs and InP with specially modified surface possess optimal forbidden band width, high photocurrent quantum efficiency (about 40–80 %) in a wide spectrum range (about 350–380 nm) and efficiency 23 % [148] and 20 % [151], respectively.

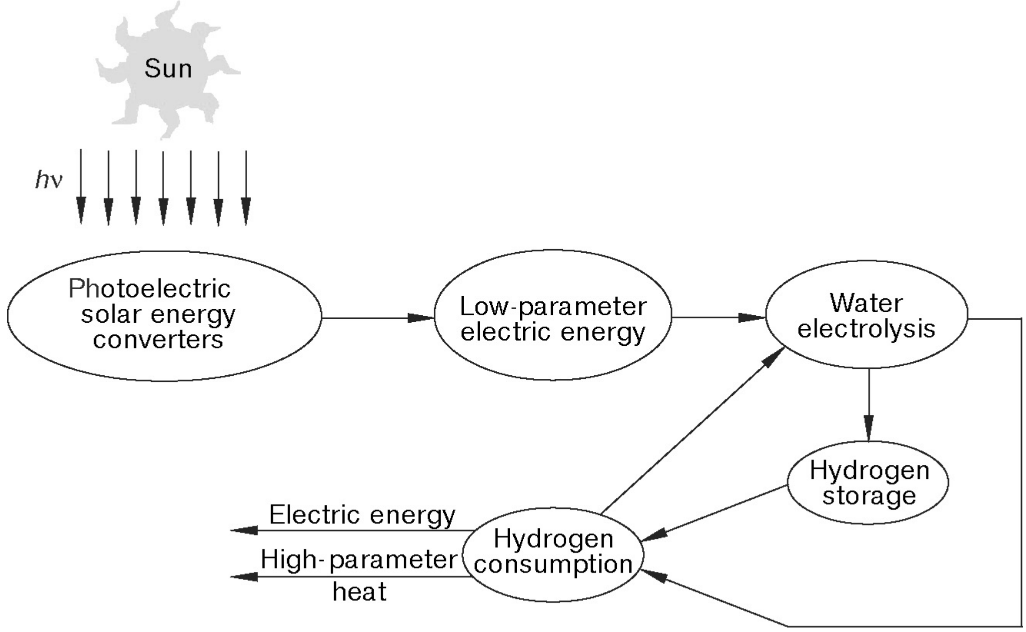


Fig. 70. Scheme of solar energy plant for electric energy generation with its following conversion to hydrogen by water electolysis

One can observe further development of investigations in photoelectrochemical conversion of solar energy into electric energy in the regenerator type device, the so-called wet-cell redox solar batteries [145–151, 153, 154]. Semiconductor compounds of $A^{II}B^{VI}$ and $A^{II}B^{V}$ type (sulphides, selenides, tellurides — ZnS, ZnSe, CdS, CdSe, CdTe) solid solutions on their base ($CdSe_{0.65}$, $Te_{0.35}$), ternary compound $CnInS_2$ and $CnInSe_2$, phosphides *n*-GaP, chalcogenides of refractory metals — molybdenum and tungsten (MoS_2, $MoSe_2$, WS_2, WSe_2, WSe_2, S_{2-x}, W_y $Mo_{1-y}Se_2S_{2-x}$) are used as electrodes in photoelectrochemical converters (PECC). Photoelectrochemical converter consists of two electrodes: illuminated semiconductor electrode and counterelectrode of inert corrosion-resistant and alloyed materials (Pt, C, Ti (Me_i Me_j)) as well as semiconductor compounds. GaAs in a form of thin mono- or polycrystalline films is widely used for making PECC electrodes. In accordance with predictions, only the USA will need 500–2000 t of pure gallium for the period of 2000–2020 for the increasing demands of semiconductors industry, optical devices, microelectronics and production of photoelectric converters of solar energy. The demand for highly-pure gallium for photoelectrical converters of solar energy is immeasurably higher in Japan.

Corrosion of semiconductor electrodes in water solutions is the most important problem of wet-cell solar batteries. Thus PECC based on the system *n* — GaAs|0.8 K_2Se_2 — 0.1 K_2Se — 1 M KOH|C is the most efficient converter of solar energy, but its service life is determined by corrosion properties of GaAs. It is established that corrosion ability of GaAs in water solutions is almost completely surpressed when using 1 M solution of K_2Se and polyselenides on its basis (K_2Se_2, K_2Se_3, K_2Se_4) as the electrolyte. The surface of PECC electrodes is treated by some metal ions, e.g., Ru^{3+}. The efficiency of GaAs-based converters reaches 15 % at the incident light power of 100 mW/cm^2, photovoltage with broken circuit — 0.78–0.8/V, short-circuit photocurrent — 24–26 mA /cm^2, filling factor — 0.65–0.75.

Solar cells with partitioned electrodes have been proposed for hydrogen production [146–149,153]. To make such semiconductor electrodes thin films of *n*-CdSe are applied by electrolysis to the support in a form of pipes from stainless steel (e.g. X19H10T). Production of hydrogen with acceptable power efficiency using solar cells requires high-intensity solar light. To raise the solar intensity one can use concentrators of solar light providing high efficiency of solar batteries.

Silicon-based solid solar energy converters are also developed intensively, their efficiency equals 12–15 %. The developed power is 1.58 kW/m^2 at $i = 42$ mA/cm^2. Solar energy converters within the conception of «solar hydrogen plantations» are rather efficient. The latter are vast areas in the zones with high level of solar radiation. The areas are mainly occupied by solar silicon cells which energy is used to produce hydrogen by water electrolysis. The design of solar power plant which energy is used to produce hydrogen and oxygen by water electrolysis is presented in Fig.71. Hydrogen and oxygen are kept separately in special gas-holders and are used to produce electric power in fuel elements at night or to produce heat when using hydrogen as fuel (see, above).

The average level of solar radiation being 3200 kW·h(m^2·yr), the solar cell efficiency 5 % and electrolysis efficiency 70 %, the energy from solar cell area of 1 m^2 is equivalent to that from 7 kg of oil a year. Hydrogen production with the help of solar cells, according to [144], is comparable with its production

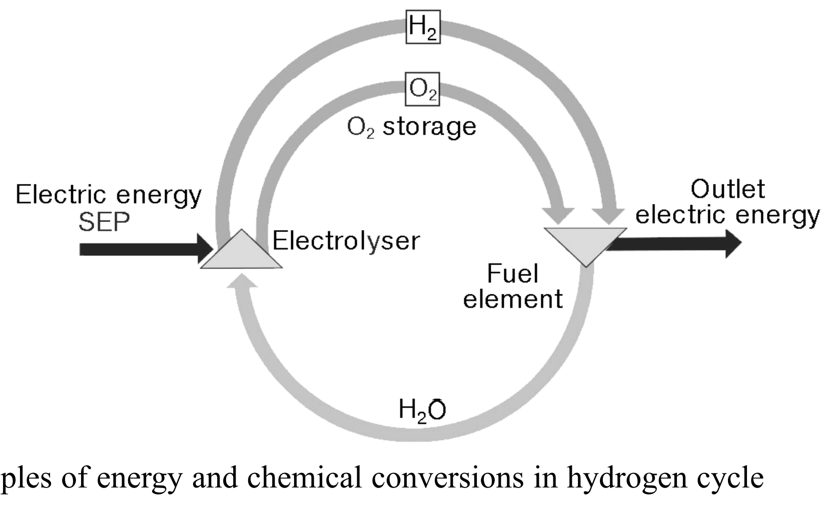


Fig. 71. Principles of energy and chemical conversions in hydrogen cycle

using nuclear energy. According to [145], the solution of the problem of partial substitution of fossil fuels in the nearest 50–100 years is possible with the use of silicon solar cells only. Cost of the electric power produced by photoelectrochemical and photoelectric converters decreases continuously. By the data of [155] the cost of single-crystalline silicon required for solid silicon phoroelectric converters was extremely high before 1973 and was equivalent to $100 000/1kW. The cost of electric energy produced using solid silicon photoelectric converter has become 100 times lower for 10 years. The less expensive methods of silicon single crystals production have been developed, which provided for the decrease of the cost of 1 kW of electric energy to 250 USD. Later on, the highly-pure polycrystalline silicon was used as the material for making solid cells for spaceships and other devices. To lower the cost of devices they began to use amorphous silicon (*p*-Si) films as well as silicon films with 1 μm thick surface layer nonuniformly alloyed with boron or phosphorus. Thus the cost of electric energy produced using silicon solid converters decreased, and now it is comparable with that of NPP energy. It would be noticed that photoelectrochemical converters (PECC) on the basis of thin films of polycrystalline cadmium selenide are 8–10 times as cheap as solid single-crystalline silicon converters [146, 147].

The total power of SPP based on photoelectric converters of solar energy is 500 MW all over the world now. Such plants of 100 MW are arranged in European countries [150]. In most cases SPP are devices for individual electric power supply to dwelling houses (75 %) in the country-side, while solid SPP are used to produce electric power for space vehicles. The USA, Germany, Japan, Mexico, Vietnam and England have the plan to make the total power of SPP established on the house-roofs 680 MW. Above 100 SPP are introduced annually in the state of California (the USA). It is supposed to mount SPP in 500 000 houses in Europe by 2010. The European Union countries and the USA have informed about the developed programs of creation of one million SPP by 2010 [64]. It was planned to mount SPP on 70 000 roofs in Japan by 2000. The expansion of SPP and renewable sources use in China would save 1.23 and by 2010 — 4.67 mill. t of conventional fuel.

There are also investigations of elaboration of film low-voltage organic converters of solar energy (CSE) with efficiency 25 % and high-voltage CSE with efficiency 50 % combined with electrolysers to produce high-parameter hydrogen, supplied by pipelines to a consumer.

10. Hydrogen production using biocatalytic systems. The volumes of biomass production under the effect of solar radiation by photosynthesis reactions are huge and make as a whole $(2–4)\cdot10^{12}$ t of carbon a year all over the Earth. According to other data the total photosynthesis productivity is $1.4\cdot10^{12}$ t a year. Continental ($6.25\cdot10^{11}$ t/yr) and tropical forests ($1.025\cdot10^{11}$ t/yr), seas and oceans ($5.3\cdot10^{9}$ t/yr) are main producers of the biomass; biomass in the volume of $1.4\cdot10^{9}$ t/yr is produced on cultivated lands, that is 76 % of the total biomass on the Earth [156]. These data do not agree with the data of the work [157], which authors insist that the amount of live matter (plants, living creatures) in the biosphere makes 10^{14}–10^{15} t now.

Production of organic fossil fuels (gas, oil, coal) makes up $1.8 \cdot 10^9$ t/yr or 0.045–0.09 % of the world annual production of the biomass ($(2–4) \cdot 10^{12}$ t carbon/yr.). The biomass photosynthesis in nature proceeds with efficiency equal to 0.1–0.3 %, which evidences for its low efficiency. The process of photosynthesis consists of numerous rather complicated reactions of carbon dioxide fixation:

$$CO_2 + H_2O + h\nu \rightarrow (CH_2O) + O_2, \quad \Delta G^0 = 477.0 \text{ kJ/mol} \qquad (111)$$

with formation of the simplest «bricks» of complex biological systems and plants:

$$6CO_2 + 6H_2O + h\nu \rightarrow (C_6H_{12}O_6) + 6O_2, \quad \Delta G^0 = 2861.9 \text{ kJ/mol.} \qquad (112)$$

It has been proved by experiments that the photosynthesis productivity is limited by physiological factors — humidity, concentration of carbon dioxide and mineral salts, etc. rather than by the light fluxes. Theoretically, the limit of photosynthesis efficiency can reach 35 %. Experimentally, the photosynthesis energy efficiency reaches 19 % for chlorella under optimal conditions. It would be noticed that CO_2 molecule is thermodynamically stable and kinetically inert. Carbon dioxide would be activated before its involving in the reactions with solution components and other ingredients. The process of carbon fixation from CO_2 or nitrogen from the air with the help of photosynthesis reactions (as affected by solar light energy), which seems so simple, proceeds by rather complicated mechanism. The plant has to extract CO_2 molecules from the carbon-dioxide diluted air, containing only 0.028 — 0.035 % of CO_2, to adsorb them on the leaf surface and, as affected by the solar energy quantum (hν) and water, to turn them into glucose and then, as a result of polymerization — into cellulose. Carbon fixation reaction consists of a set of subsequent stages, the overall reaction corresponds to the equation (112) of glucose or cellulose and molecular oxygen formation.

Photosynthesis with CO_2 fixation with water oxidation, oxygen liberation and glucose ($C_6H_{12}O_6$) formation is accompanied with the increase of Gibbs free energy (equal to 2861.9 k J/mol) and enthalpy. That is why the plant leaf is cold even during the hot sunny day. Glucose formation from initial components is ac-

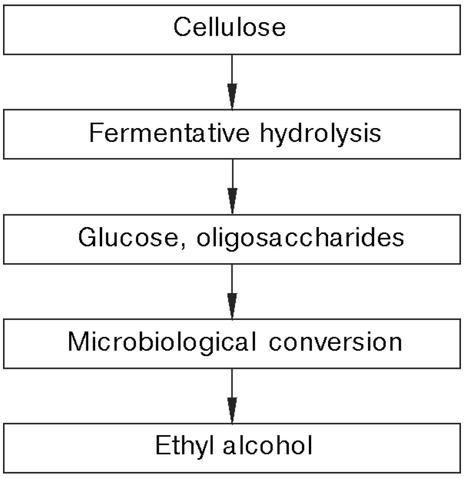


Fig. 72. Scheme of cellulose raw material conversion into ethanol

companied by the decrease of Gibbs free energy (ΔG^0 = — 908.89 kJ/mol) and enthalpy (ΔH^0 = — 1268.05 kJ/mol).

The process of photosynthesis consists of two main stages: dark and light stages. The light stage proceeds with great velocity for the time close to 10^{-12}–10^{-8} s. The light stage is followed by the successive series of reactions with transfer of electrons, formation of intermediates which undergo spontaneous reactions. The set of these reactions forms the dark stage. The dark stage reactions depend on temperature and thus limit the whole photosynthesis process. While increasing duration of one or another stage one can accelerate or deteriorate the growth rate of biota.

Cellulose — a product of glucose and oligosaccharides polymerization — is the main biological material of photosynthesis, being the greater part of biomass. Cellulose — the major component of wood and most plants — is low power-intensive fuel, so the methods of its conversion into power-intensive transportable and ecologically-pure fuel are of interest now. The scheme of cellulose raw material conversion into ethanol is presented in Fig. 72. Microbiological process of cellulose conversion may be presented with the help of the equation.

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2. \tag{113}$$

The energy conversion coefficient in this reaction is equal to 98 %. Being obtained in the amount of 20 %, ethanol may be used as fuel.

Besides, fermentative redox reactions with liberation of molecular hydrogen by biocatalysts (bk) are possible in the biological systems in correspondence with the equation

$$H_2O + bk^* \rightarrow H_2 + bkO, \tag{114}$$

$$\mathrm{bkO} \to \mathrm{bk}^* + 1/2\mathrm{O}_2. \qquad (115)$$

Biocatalysts activate hydrogen release by hydrogenases being terminal enzymes in the process of formation of molecular hydrogen by more than 100 microorganisms. There are also microorganisms which oxidize molecular hydrogen and owing to this reaction, provide metabolic processes with energy:

$$E + \mathrm{H}_2 = E\mathrm{H}^- + \mathrm{H}^+. \qquad (116)$$

Hydrogen-oxidizing microorganisms use free energy in the reaction of CO_2 reduction as well. Immobilized enzymes possess activity in molecular hydrogen liberation in accordance with the scheme [156]

$$1/nS_1 + S_2' \to S_2; \qquad (117)$$

$$S_2 + \mathrm{H}^+ \to 1/a\mathrm{H}_2 + S_2', \qquad (118)$$

where S_1 — sodium dithionite; S_2' and S_2 — oxidized and reduced forms of methylviologen; a — the number of electrons transferred from the donor S_1 to methylviologen.

The first stage — methylviologen reduction by sodium dithionite — proceeds in a moment. The second stage — hydrogen liberation — is a fermentative process catalyzed by hydrogenase.

An interesting cycle of investigations was devoted to creation of biophotolytic systems of hydrogen and oxygen production with the use of chloroplasts of higher plants, ferredoxin, low-molecular mediators (A) and bacterial hydrogenases [156]. The investigations are carried out by the schemes

$$\begin{tikzcd}
\mathrm{H_2O} \arrow[r, "\text{Electrotransport chain}"] \arrow[dr, dash] & \text{Ferredoxin} \arrow[r, "\text{Hydrogenase}"] & \mathrm{H_2}; \\
& \mathrm{O_2} &
\end{tikzcd} \qquad (119)$$

$$\begin{tikzcd}
\mathrm{H_2O} \arrow[r, "\text{Electrotransport chain}"] \arrow[dr, dash] & A \arrow[r, "\text{Hydrogenase}"] & \mathrm{H_2}. \\
& \mathrm{O_2} &
\end{tikzcd} \qquad (120)$$

Water photodecomposition is also carried out by the two-stages scheme:

$$\mathrm{H_2O} + A \xrightarrow{\text{Electrotransport chain}} 1/2\mathrm{O}_2^- + A\mathrm{H}_2; \qquad (121)$$

$$A\mathrm{H}_2 \xrightarrow{\text{Catalysis}} A + \mathrm{H}_2^-. \qquad (122)$$

In the schemes (120)–(122) the mediator A performs functions of electron carrier. The author of the work [156] has studied a wide range of low-molecular mediators and determined conditions of separation of the reaction products — hydrogen and oxygen released at different stages of biophotolysis. They have also studied the systems of water photolysis with participation of microorganisms cells which products are oxygen, liberating in the light and hydrogen liberating in darkness, following the reactions:

$$2H_2O + 2CO_2 \xrightarrow{h\nu} 2\{CH_2O\} + 2O_2; \qquad (123)$$

$$2\{CH_2O\} + O_2 \xrightarrow{\text{Darkness}} 2H_2 + 2CO_2. \qquad (124)$$

Maximum photosynthesis rate is determined by a number of factors: light flux rate, reaction centres concentration, light-absorbing layer thickness, temperature. Under real conditions the light-absorbing layer thickness is equal to 1 cm, average coefficient of molar absorption is close to $1 \cdot 10^4\ M^{-1} \cdot \text{cm}^{-1}$, and concentration of reaction centers — $5 \cdot 10^{-4}\ M/\text{dm}^3$. Under these conditions maximum oxygen productivity of photosynthesizing systems reaches (1–5) $M\ O_2\ /(\text{m}^2 \cdot \text{day})$, and hydrogen productivity (2–10) $M\ H_2\ /(\text{m}^2 \cdot \text{day})$. Photodecomposition of water being carried out with the use of chlorella suspensions with 1m^2 of illuminated surface under optimal cultivation conditions one can obtain 6 mol of oxygen and 12 mol of hydrogen a day. The efficiency of energy absorbed by photosynthesizing systems reaches 40 % (17 % of all solar energy).

The use of biologic processes at nuclear-hydrogen power plants (NHPP) for hydrogen production by conversion of natural gas with utilization of CO_2 on phytotron units of hothouse farm with obtaining biomass and food is worthy of detailed consideration. A scheme of ecologically pure power biotechnological centre on the basis of NHPP, which uses natural gas for hydrogen production, with infrastructure utilizing carbon dioxide is presented in Fig. 73 [71]. This centre uses three kinds of energy: nuclear, natural gas and solar radiation energy [71]. Nuclear-hydrogen power plant consists of the high-temperature helium reactor HTHR-1000, electrogeneration units and units of CH_4-H_2 conversion. The NHPP waste — CO_2 and low-potential heat are sent for utilization into phytotron units and methane tanks. Phytotrons assimilate CO_2 according to photosynthesis reactions (111), (112) and (113).

$$CO_2 + H_2O + 470\ \text{kJ} \rightarrow CH_2O + O_2 \qquad (125)$$

under the effect of solar radiation with obtaining biomass, oxygen and food products. Biomass is directed to methane tanks in which methane and CO_2 are synthesized by the reaction of anaerobic fermentation

$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2 \qquad (126)$$

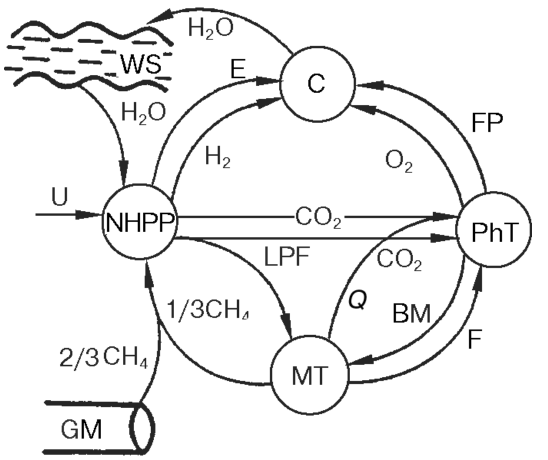


Fig. 73. Scheme of material flows of wastless energobiotechnological centre: WS — water source; C — consumer, FP — food products, PT — phytothrone; GM — Gas mains; E — electricity; *Q* — low-potential heat; BM — biomass; F — fertilizer; MT — methanetank

Methane is supplied to the NHPP cycle, and CO_2 is supplied to phytotrons and methane tanks. Composts used as fertilizers in phytotrons are waste products. The process allows to exclude CO_2 ejection into the atmosphere and to reduce by 1/3 CH_4 consumption from outside. The considered wasteless power-biotechnological centre of NHPP with infrastructure supplies electric power, hydrogen and food-products to consumers [71]. NHPP-3000 produces 1582 MW of electric energy, $11.8 \cdot 10^9 m^3$ of hydrogen, $6 \cdot 10^6 t$ of CO_2 and $3 \cdot 10^7$ GJ of low-potential heat; CO_2 and low-potential heat are provided for by hothouses of 2000 ha. As is known, the growing of biomass and food products is an order more efficient than in nature. It has been established that the increase of CO_2 concentration in the phytotron air rises 4 times the photosynthesis efficiency, which increases 2–3 times more under heating [71]. In case of NHPP the hothouses are heated by means of low-potential released heat from steam-gas turbine condenser [71].

It follows from the stated above that carbon dioxide is a reagent and it should not be ejected into the atmosphere but concentrated to obtain useful chemical products, including liquid fuel, within reasonable limits with regard for economic efficiency. Steam-gas plants can also serve as sources of CO_2. The idea of pumping CO_2-disposal from gas station in the worked out deposits of natural gas. Before methane supply to the turbine it would be subject to steam-gas conversion for to obtain 4 mol of H_2 and 1 mol of CO_2 from 1 mol of CH_4 (Fig. 74):

$$CH_4 + 2H_2O = 4H_2 + CO_2. \tag{127}$$

In this case gas energetics, native deposits being available, could be irreproachable from the viewpoint of ecological purity. But this process is also a

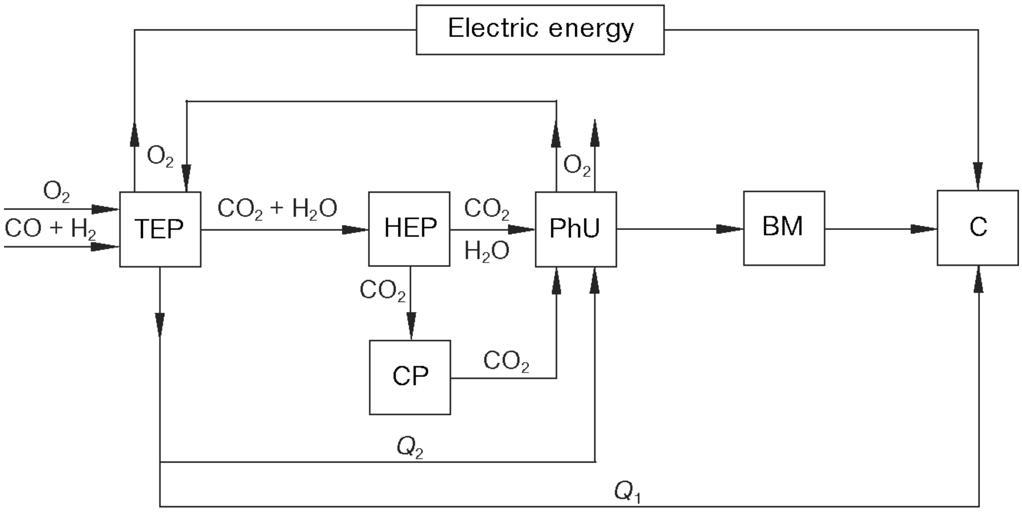


Fig. 74. Scheme of power plants using natural gas and utilizing CO_2: TES — thermoelectric stations; HEP — heat exchange plant; Q_1 — high-potential heat; Q_2 — low-potential heat; CP — compressor plant; PU — phytotrone unit; BM — biomass and food products; C — consumer

half-measure in the historical aspect of any state, since the explored reserves of natural gas all over the world will last several tens of years. It would be also kept in mind that it is a rather complicated engineering task to pump huge amounts of CO_2 in the underground cavities of worked-out deposits. But there appeared a comparatively recent information about Norwegian project on pumping considerable amounts of carbon dioxide in the worked out holes of underground deposits in the North Sea. As is known the natural gas from marine deposits of Norway contains CO_2 of extremely high concentration and the explorers have to separate CO_2 from methane and eject it in the air. The designed capacity of the Norwegian pump-in system is about 200 t of gas daily. It would be kept in mind that even partial CO_2 pumping in the worked out deposits (the more so as such deposits possess all the necessary equipment) can create accumulators for its long-term storage. New methods of processing and utilization of CO_2 from such storage with obtaining chemical products can be found in the course of time. For example CO_2 can be fixed by means of microorganisms with biomass production; CO_2 can be also used to synthesize liquid hydrocarbon fuel. Great prospects for all coal electric power stations and TES as a whole will appear with the wide use of liquid CO_2, e.g., to increase oil extraction from its deposits.

Besides, we think that the potentialities of CO_2 circulation in nature are far from being exhausted. This opinion is in agreement with conclusions made by Academicians V. I. Vernadsky and A. L. Yanshin on the favourable influence of CO_2 concentration increase in the atmosphere up to 0.13–40 % [158] on the plant kingdom and humanity. According to V. I. Vernadsky the plant kingdom of the Earth can process greater amounts of CO_2 than those contained in the atmosphere air today, and what is more, CO_2 may be used as the fertilizer raising the level of agricultural crops yields by 30–40 %, and bringing the wheat harvest to 100 c/ha; the increase of CO_2 concentration in the air will lead to the acceleration of cultivated plants ripening by 7–8 days. The diversity of biologic life on our planet has lifted the restrictions for the main resource of its development — carbon dioxide which always takes part in circulation, assimilation and dissimulation in plants; CO_2 is reproduced under anaerobic biomass decomposition, and accumulated in the biosphere reservoirs (plants) under the effect of solar radiation [158–161]. It would be noticed that the development of wasteless ecologically pure integral energobiotechnological centres on the basis of nuclear-hydride power plants will permit using only natural gas as organic fuel and raw-materials for production of hydrogen and food products. On the other hand, in case of natural gas and oil deficit (which is predicted by many researchers and economists) it is possible to elaborate a wasteless process for hydrogen production from hard and brown coals, turf with complete utilization of CO_2 in phytotrons with obtaining food products and biomass for methane tanks and complete exclusion of CO_2 ejections into the environment.

When producing hydrogen, methane and other power resources using bioenergetic processes, one can use plants, utilize agriculture wastes, wood and its processing waste. It is rather simple to obtain synthesis-gas from the biomass:

$$C_6H_{12}O_6 + 3H_2O \rightarrow 3CO_2 + 3CO + 9H_2, \qquad (128)$$

Synthesis-gas is high-energy fuel. Hydrogen, methane, methanol, ethanol and other organic derivatives can be produced from synthesis-gas by well-known methods. Methanol and ethanol can be used as liquid synthetic motor fuel for the tractor fleet and motor transport of agricultural regions. It is expedient to grow crops possessing great biomass and being food products, for example, maize and sorgo. There are a lot of examples in literature on the use of biomass as raw material for energetics. Thus, in 1999–2000 there appeared many publications on efficiency of methanol, ethanol and dymethyl ester use as motor fuels produced from agricultural raw materials. It is considered that the above organic compounds can substitute gasoline and diesel fuel in the 21st century in a number of the world regions, e.g., in South America.

Late in 1998, B. Klinton, President of the USA, issued an edict about substitution of coal, oil, natural gas and uranium by ecologically pure, renewable biological power resources. It is supposed that under three-fold increase of the use of bioenergetics and bioproducts resources the release of gases creating «hothouse effect» will decrease annually by 100 mill.t. Budgetary financing for the development of bioenergetics and other ecologically-pure energy sources in the USA for 2000 was 242 mill. US dollars.

6.3. Hydrogen, coal, turf and synthetic gasoline. Nowadays, 64 % of the world energy are obtained by combustion of fossil fuel — natural gas, oil, coal, shales, turf. Natural gas and oil being preferable, they are used in chemical industry to synthesize the whole range of organic compounds. Such kinds of fuel as gasoline, solar oil, kerosene and labricating oils are produced from oil. Oil processing all over the world increases continuously (1978 — 3.084; 1998 — $3.429 \cdot 10^9$t). The greatest volumes of refined oil fall on the USA (854 mill.t), then follow Japan (258 mill.t), Germany (136 mill.t), and France (92 mill.t). Russia and Ukraine have reduced considerably oil refining. Russia processed 419 mill.t in 1978, 199 mill.t — in 1998, Ukraine — 62 and 10.4 mill.t of oil, respectively. In accordance with the national power program of Ukraine till 2010 and the program «Oil and Gas of Ukraine, 1992–2010» annual oil demand in our state is 47 mill.t; the demand for oil products in 2000 and 2005: gasoline — 9.8 and 9.9 mill.t, diesel fuel — 16.6. and 16.8 mill.t lubricating oil — 916 thou.t, respectively.

Present transport facilities: aviation, motor cars, diesel locomotives, ships are main consumers of oil products. Motor transport consuming a half of produced fuel has not substituted completely oil products by alternative and ecologically pure fuels (with the use of fuel elements, accumulators, natural gas, hydrogen, solar batteries, etc.) the motor car production all over the world grows continuously, and in 1997 it achieved almost 41 mill. units; their number in operation exceeds 500 million. Allowing for the total number of planes, stationary diesel electric power plants, sea-going and river vessels, the total power of internal combustion engines may be evaluated as $10 \cdot 10^9$ kW. This number exceeds 3–4 times the total power of the world electric power plants and proves that natural oil reserves for providing transport vehicles with liquid fuel (gasoline, solar fuel, aviation kerosene) will last for a rather short period of time. Researchers and economists predict, as we repeatedly wrote as well, that oil reserves will be exhausted no more than in 10 [162], 30 [163], 50 years [164, 165]. What is the alternative? Where can one find a source of liquid fuel even if for 500 years? Synthetic motor fuels and fuel gases which may be obtained from considerably richer deposits of coal, turf, shales and biomass can become such a source.

Historical information. The history of research and development of the methods for production of liquid and gaseous fuels from coal lasts for about 100 years. The investigations on production of synthetic liquid fuels (SLF) from coal were carried out even in the early 20th century, because of motor fuel deficit as a result of poor exploration of oil fields. Fifteen plants with the project power of 1.1 mill.t of liquid fuels a year were constructed and put in operation in different countries in the years before the World War II, nine of them worked in Germany. Maximum output of SLF plants in Germany (I. G. Farbenindustrie, 1927–1945) was 600 thou.t in 1944 (Fischer-Tropsch process). The SLF production to meet the needs of army in war-time in Germany was subsidized in the amounts corresponding to the processing of more than 1 mill.t of half-coke resins. The plants for motor fuel synthesis from coals were built in 1950–1955: in the USSR (Novocherkassk plant of synthetic products), in FRG (plant of motor fuels in Bergkamen), in South Africa, Malaysia, GDR, China, USA.

In South African Republic (SAR) three phases of plants of *Sasol* — a company on production of SLF — were constructed and put in operation in 1957–1982. The *Sasol* company built the complex *Sasol* II — *Sasol* III in 1972–1982 in Transvaal. The complex processes annually 12–14 mill.t. of coals and synthesizes 2 mill.t of motor fuels. The SAR technologies are based on steam-oxygen coal gasification with production of carbon oxide and hydrogen which serve raw material for synthesis of liquid fuels by the perfected Fischer-Tropsch process (second generation technology). The process for production of methanol, which is well developed in industry and proved to be the motor transport fuel in the countries of South America, can be alternative to the Fischer-Tropsch process.

Plants producing synthetic motor fuels work in Malaysia (*Shell* company), New Zeland (*Mobil* company), etc. The USA, FRG and Japan companies develop new methods and build plants which can process 250–6000 t of coal a day with productivity from 350 m^3 of gaseous fuel to 3000 t of synthetic oil a day. Cost of SLF from coal is within $ 200/t [164], which is lower than current market prices for liquid fuel, since the price of raw oil varies within $21–37 for a barrel.

Beginning from 1980, the USA develop their power programs which provide for fundamental investigations in the field of creating methods for SLF production from coal, shales and biomass, their development on the industrial scales. The amount of financing for the investigations in synthetic liquid fuels production makes $88–100 \cdot 10^9$ USD during 10 years. FRG will spend $6.5 \cdot 10^9$ Deutsche Marks during 4 years for production of synthetic fuels from coal.

The increase of the world prices for power carriers (gas, oil, motor fuel, condensate) has called considerable interest to the construction of not only powerful integrated plants for production of SLF, but also to small autonomous plants capable to produce motor fuel for the enterprises connected with excavation, transportation and processing of solid hydrocarbon raw materials [166]. Such enterprises, besides meeting the country needs, can realize fuel with the purpose of making a profit.

Great interest to mastering the SLF technologies is determined by the fact, that unlike the natural reserves of oil and gas, the world reserves of fossil coal are rather rich; that is why the future belongs to synthetic fuel from coal, slates and biomass. However the amount of coal produced in Ukraine does not meet the requirements of the modern fuel-power complex of the country, that is determined by the fact that our state has no modern mines and their construction requires considerable capital investments in the nearest 5–7 years. It is impossible to excavate hard coal in amounts required for our country because of the backwardness of home coal industry. Ukraine is also rich in turf. Turf is low-energy fuel, which is rich in organic compounds. Hydrogen content in turf is 59 %, that is why turf can serve both as fuel and raw material for chemical industry. Turf was used in Ukraine and in Russia during the fuel crisis of the 20–30's of the 20th century (Shadrinsk hydroelectrostation, for example). However, coal and turf may be used both for production of hydrogen, being high-energy fuel, and SLF. Allowing for great reserves of bituminous coal in Ukraine, it is expedient to organize the large scale production of synthetic gasoline and fuel gas from coals of the Donets [167], Lvov and Chernovtsy coal basins. Methods of synthesis of gasoline, lubricating oils, fuel gases and a whole range of organic compounds from coal, fuel shales and turf have been developed at the Institutes of the National Academy of Sciences of Ukraine (L. Pisarzhevsky Institute of Physical Chemistry, Kyiv; Institute of Physico-Organic Chemistry and Coal Chemistry, Donetsk), Academy of Sciences of Byelorussia (Institute for Problems of the Use of Natural Resources and Ecology), Academy of Sciences of Russia (A.V. Topchiev Institute of Petrochemical Synthesis, Institute of Fuel Fossils, Institute of Chemistry of Carbon Materials, Institute of Power Problems of Chemical Physics).

As is known, Ukraine, possessing rich deposits of hard coal, turf, shales, is poor in oil and natural gas, i.e., today's basic energy resources. (According to our hypothesis, the bowels of Ukraine are rich in deep-occurring oil and natural gas). As a result of their higher technological effectiveness, oil and natural gas are used more actively both for obtaining energy and chemical production. Owing to dependence on foreign oil and gas the «shadow» of energy crisis threatened Ukraine even in the period of soft winter of 1999–2000. The question was: «Will Ukraine overcome the energy crisis?» [168]. Thus, any nature cataclysms (extremely cold winter, earthquakes) as well as armed conflicts in the countries exporters of oil and natural gas can put Ukraine on the verge of national catastrophe and bring cruel sufferings and hardships to its people. To avoid all this we have to develop on the industrial scale the methods of processing the solid fuels (hard coal, turf) turning them into synthetic gasoline, synthesis gas, methane, ethylene, etc., to conduct the research works on development of highly efficient technologies of SLF production from solid fuel fossils. The latter are distinguished by carbon content (anthracite contains 90 % of carbon, hard coal — 67–68 %, turf — 50–60 %). Oxygen and nitrogen content in hard coal is 4.5–10 %, in turf — 34–39 %. Thus the efficiency of one or another method of liquid fuel synthesis depends on the nature of solid fuel fossil. Since hydrogen content (5–6 %) in solid fuels is considerably lower than in oil, their liquefaction consists in hydrogen introduction into the fuel under the effect of catalysts (nickel, cobalt, platinum and others on different carriers), high temperatures and pressures [165, 166, 169–172]. To process coals, oil shales and biomass the methods of thermal decomposition,

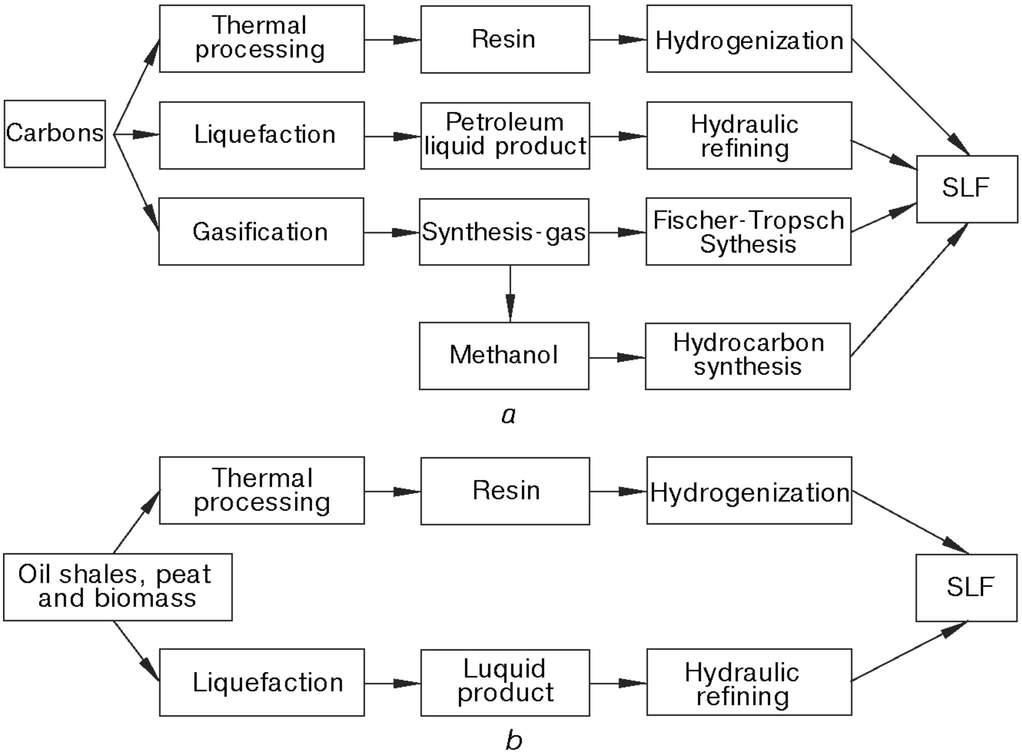


Fig. 75. Schematic diagram of production of synthetic liquid and gaseous fuels from coal (*a*), fuel shales, turf and biomass (*b*)

liquefaction, gasification and hydrogenization under pressure are used (Fig. 75) with obtaining liquid oil products or a product of vapor-phase coal disintegration synthesis gas. Methanol is obtained from synthesis-gas:

$$CO + 2H_2 = CH_3OH, \quad (129)$$

as well as dimethyl ester:

$$2CO + 4H_2 = CH_3OCH_3 + H_2O; \quad (130)$$

$$3CO + 3H_2 = CH_3OCH_3 + CO_2, \quad (131)$$

as well as the products of Fischer-Tropsch synthesis n [– CH_2 –], oxosynthesis, etc [169, 170]. Liquid and gaseous fuel, ammonia, different hydrocarbons are obtained from synthesis-gas and products of thermal decomposition of coals. Investigations of the reaction

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad (132)$$

are of special interest for carbon-chemical processes. The reaction is used in nuclear-hydrogen energetics [170].

Thermal processing of coal is used for obtaining basic products — the coke and semicoke, as well as liquid and gaseous side products. The equipment used for this process is rather simple. Specific and complex equipment is used for the multistage processes of coal liquefaction and vapor-phase gasification of fuel shales, turf, and biomass.

Volumes of SLF production by direct liquefaction and gasification of coals and other solid fuels, as a whole, depend on the situation in the world oil market. Beginning from the period of oil crisis of 1973, most countries have created national programs of researches on development of efficient methods for SLF production from coals, fuel shales, turf and biomass and their use on industrial scale. One could observe a heightened commercial interest to organization of the large-scale production of SLF. A good many of the SLF production processes considered below have been realized in the developed countries all over the world [169, 170]. Most researchers, economists and political figures think that the development of fundamental investigations and production infrastructure for SLF and various chemical products from coal is the most important task for the states being aware of the deficit of natural oil. Ukraine also belongs now to the states with limited resources of produced oil which does not meet the country requirements for industry, agrarian complex and transport.

Thermal processing of solid fuels. The methods of thermal processing of coals and shales are based on pyrolysis performed in reactors or other installations without air access. In the process of pyrolysis giant molecules of solid fuel are splitted into low-molecular fragments; the process is accompanied by condensation, dialkylation, aromatization, etc. Thermal decomposition of coal and shale is conducted by low- and high-temperature methods. Low-temperature pyrolysis, called low-temperature carbonization, is realized at 500–580 °C, high-temperature pyrolysis (carbonization) — at 900–1050 °C. In the process of pyrolysis, depending on temperature, there occurs transformation of coal organic part into liquid or gaseous hydrocarbons. Artificial liquid and gaseous fuel, being transportable and more valuable than initial coal, are obtained under low-temperature pyrolysis of coal. Semicoke (60–70 %), resin (10–20 %), gas of low-temperature carbonization (8–20 %) and tap-water (3–9 %) are the basic products of low-temperature pyrolysis. Resin serves as raw material for further processing into motor fuel, solvents and different organic compounds. Gas of low-temperature carbonization is used (after cleaning) as ash-free and smokeless high-energy fuel as well as raw-material for production of methanol, methane and other compounds. Semicoke contains about 10 % of volatile substances; it is used as raw-material for gasification and production of hydrogen, coke and solid fuel.

Coke and coke-oven gas are produced at high-temperature pyrolysis (900–1050 °C) of coal without air access. The coke, possessing 50 %-porosity and mechanical strength, is used in metallurgy industry. The coke-oven gas has the following compositions, %: H_2 — 55–60; CH_4 — 22–29; CO — 5–7; C_mH_n — 4–5; N_2 — 2–3; CO_2 — 1.5–2.0. After cleaning from volatile organic compounds, separation of the coke resin (4 % of initial raw-material), and condensation of volatile aromatic hydrocarbons used for organic synthesis and refining of motor fuels, the coke-oven gas is used as high-energy fuel. The combustion heat of the coke-oven gas is approximately 20 MJ/m^3. The coke resin serves as the source of motor fuel, oil and other organic compounds.

To increase the yield of organic volatile components and to decrease pyrolysis temperature to 250–500 °C the liquefaction is carried out in the mix of coal, formic acid and tetraline [171, 172]. Under these conditions they obtain low-boiling fractions of liquefaction of coals, oils, asphaltenes, preasphaltenes and solid residues. Coals impregnated with alkalis [173] are subject to liquefaction to increase the motor fuel output. Investigations of the authors of the work [174] have shown that in the system coal — *Me*OH the pyrolysis temperature decreases to 220–250 °C; the breaking of the bonds –C–C– and –C–O–C– increases; recombination of radicals is suppressed, and ion-radical fragments are stabilized which leads to the increase of the motor fuels and oils yield.

Under thermal decomposition of turf the composition of hydrocarbons obtained depends on thermolysis conditions [175].

Hydrogenization of solid fuels. The process of coals hydrogenization depending on their nature (hard, brown coals) is performed in two or three stages under continuous hydrogen passing through the catalytic system at the pressure of 70 MPa and temperature 400–450 °C. The system catalyst is a mixture of iron oxides and sulphates with sodium sulphite [165]. The upper limit of hydrogen content is usually 82 %. Liquefaction of brown coals in the hydrogen flow is carried out at pressure of 250–300 MPa and temperature 400–430 °C. Gasoline fraction, lubricating oils and other organic components are obtained as a result. Octane numbers of gasolines, which are usually equal to 55–70 units, are elevated by additional organization. To obtain aromatic hydrocarbons the mean-phase oils are subject to liquid hydrogenation under pressure of 500 atm and at a temperature of 480–530 °C with the presence of special catalyst. The degree of liquefaction of solid coal organic phase is equal to 90–95 %, output of liquid products — 60–65 %, gaseous — 24–30 %, hydrogen demand — 75 %.

The motor fuel is also formed under liquefaction of brown coals in the mixture of solvents, e.g., tetraminemethanol with presence of iron catalyst and hydrogen donor at 350–400 °C [176]. The catalysts have been developed which permit liquefying coals at relatively low pressures (100–200 atm) and temperatures (150–200 °C) with high yield of hydrocarbons (52–58 %). As a result, such SLF as gasoline, diesel and boil fuel, lubricating oils, phenols, aromatic hydrocarbons, etc., are obtained from solid fuel. Computations show that synthetic gasolines and lubricating oils from bituminous coal are cheaper now than gasoline and oils from petroleum.

Synthesis of hydrocarbons from carbooxide and hydrogen is realized by the Fisher-Tropsch method which was elaborated in 1925–1926 developed in industry in 1936 and is actively used nowadays. The synthesis is performed in relatively moderate conditions: pressure about 10–30 atm, temperature 170–240 °C with presence of cobalt, iron-copper or other catalyst on the basis of transition metals of group VIII of the periodic system. The composition of products for hydrocarbons synthesis from CO and H_2 depends on the catalysts nature. The process may consist of two and more stages which include production of synthesis-gas [177] and its catalytic transformation into hydrocarbons [178]. Catalytic stages of hydrocarbons formation are considered as the reactions of reduction of carbon oxide oligomerization:

$$mH_2 + nCO \rightarrow C_nH_{2m}O_n. \tag{133}$$

There are three of the Fisher-Tropsch synthesis reactions: dissociative; polymerization-condensation; polymer chain growth [173]. Dissociative mechanism is based on the consecutive set of reactions with limiting first stage:

$$CO \rightarrow CO_{ads} \rightarrow CO_{ads} + O_{ads}; \tag{134}$$

$$C_{ads} + xH_{ads} \rightarrow CH_{x\ ads}; \tag{135}$$

$$nCH_{x\ ads} \rightarrow [–CH_2–]_n + nH_{(x-2)ads}. \tag{136}$$

Under polymerization-condensation mechanism the growth of hydrocarbon chain proceeds by condensation of intermediates by the following reactions pattern:

$$CO_{adc} + H_2 \rightarrow [CHOH]; \tag{137}$$

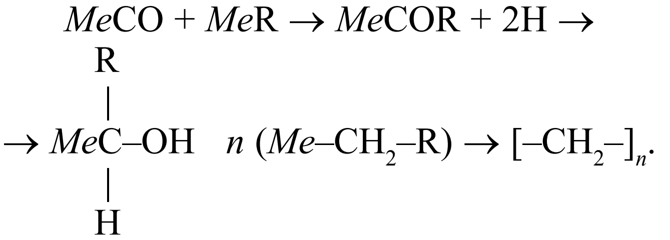
$$2[CHOH] \rightarrow [HC–C–OH] + H_2O; \tag{138}$$

$$[HC\text{-}C\text{-}OH] + H_2 + H_{adc} \rightarrow [H_3C–CH–ON]; \tag{139}$$

$$[H_3C–CH–OH] + H_{adc} \rightarrow [H_3C–CH_2–OH]; \tag{140}$$

$$2[H_3C–CH–OH] \rightarrow [H_3C–CH(OH)–CH(OH)–CH_3]. \tag{141}$$

Under growth mechanism of the polymer chain the molecule of CO adsorbed by a catalyst is introduced in *Me*-C bond between the surface atom of the metal and first carbon atom of the adsorbed hydrocarbon chain:



$$MeCO + MeR \rightarrow MeCOR + 2H \rightarrow$$

$$\rightarrow Me\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\text{–OH} \quad n\,(Me\text{–}CH_2\text{–}R) \rightarrow [\text{–}CH_2\text{–}]_n. \qquad (142)$$

In real processes the mechanisms of oligomerization reactions are more complex and represent a combination of three above mechanisms.

The extent of CO and H_2 transformation into liquid fuel makes 60–70 %, total conversion extent — 95 % [165]. When using the iron-copper tabletted catalyst, the motor fuel synthesis proceeds in two-stages. On the first stage pressure is of 2–3 MPa and temperature of 230–240 °C. The degree of CO conversion is 65–79 %, and catalyst productivity — 50–80 kg/($m^3 \cdot h$). On the second stage — in the reactor with pseudoliquefied melted iron catalyst — the degree of CO conversion reaches 90 %, and catalyst productivity — 150 kg/($m^3 \cdot h$). The yield of gasolines at the first stage is 25, on the second — 55 %. The total yield of gasolines is 80 %. Besides, high-quality diesel fuel (15 %), heavy paraffin oil and valuable high-melting paraffins are obtained. High yields of liquid hydrocarbons (C_5–C_{15}) by the Fisher-Tropsch synthesis method were obtained at 230 °C when using cobalt-dioxide catalysts [179]. Cobalt catalysts are considered most promising for hydrocarbons synthesis at pressure of 0.1–2.0 MPa and temperature — 120–130 °C. Under these conditions one can obtain selectively linear alkanes C_nH_{2n+2}. Maximum yield of liquid fuels (hydrocarbons) has made 208.5 g from 1 nm^3 of synthesis-gas [178]. The temperature being elevated to 260 °C, methane formation rate increases. Selectivity of the Fischer-Tropsch synthesis reaches 99 % when using gas mixture of CO, H_2 and the third component (ammonia, dimethylamine, piperidine) and promoted (Al_2O_3, BaO) melted iron catalysts on magnetite basis [129].

Production of 1t of gasoline by the Fisher-Tropsch method requires 5–6.5 t of conv. fuel. Thus raw materials make the greatest contribution to the real cost of motor fuels and other hydrocarbons (60 %). The authors of the work [165] think that profitableness of the processing of solid fuel fossils into liquid fuels is observed when coal/oil ratio is about 1:10–1:14.

Allowing for the observed tendencies to the increase in the world market prices for oil and for its limited reserves, one can predict that economic expediency of solid fuel conversion into liquid will rise in the nearest future. When considering long-term prognosis it becomes clear thet there is no alternative to synthetic motor fuels in some 30–50 years. Synthetic liquid fuels can be also obtained from electrolytic hydrogen and carbon oxide (for example, limestone decomposition product). Economic efficiency of the motor fuel production can

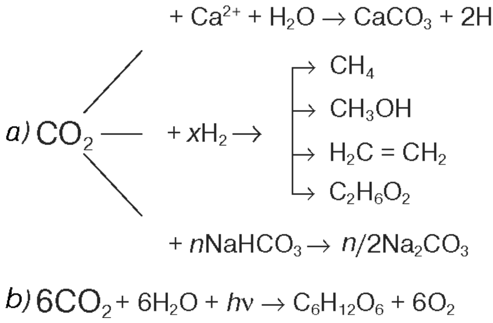


Fig. 76. Scheme of carbon dioxide dissolution in the ocean water and its use in the reactions of organic synthesis (*a*) and photosynthesis (*b*)

be calculated by the final product. Cost of 1 t of gasoline is approximately 2000 hrn, and the cost of 6.5 t of coal at sale price 73–100 — 475–650 hrn.

Expenditures for manpower payment and for equipment depreciaption make 35 % of the ready-made production value or 700 hrn. Thus, the profit from 1t of gasoline without payment of profit tax is 650–825 hrn. Cost of lubricating oils, paraffins and other synthetic oil products obtained as side-products was not taken into account.

The Fischer-Tropsch method is efficient not only for production of SLF but the whole range of hydrocarbons (ethylene, propylene, butylene, α-olefines, aromatic hydrocarbons, oxygen-containing compounds, etc.) as raw materials for oil-chemical industry [178]. Hence, it follows that the organization of synthetic motor fuel production in Ukraine from the solid fuel is promising not only for economically profitable SLF-based business but also for the supply of raw materials for organic synthesis industry. Thus, it is necessary to expand fundamental investigations for development of the methods and production processes for the third-generation SLFs and raw-materials for petrochemical industry [130].

A scheme of carbon dioxide dissolution in the ocean water and industrial use of CO_2 in the reactions of organic synthesis of methane (CH_4), methanol (CH_3OH), ethylene ($H_2C = CH_2$), ethanol C_2H_5OH, ethylenglycol ($C_2H_6O_2$), etc., is presented in Fig 76.

Methane and methanol synthesis from H_2, CO_2 and CO proceeds by the reactions under pressure of 2.8–20–30 MPa:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O,\ \Delta H^0_{298} = -165\ \text{kJ},\quad T \cong 300\ °\text{C},\ P \cong 2.8\ \text{MPa}; \tag{143}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O,\ \Delta H^0_{298} = -206\ \text{kJ},\quad T \cong 300\ °\text{C},\ P \cong 2.8\ \text{MPa}; \tag{144}$$

$$CO + 2H_2 \rightarrow CH_3OH,\ \Delta H^0_{298} = -11\ \text{kJ},\quad T \cong 350\text{–}400\ °\text{C},\ P \cong 20\text{–}30\ \text{MPa}. \tag{145}$$

The reaction (143) and (144) are realized using nickel-aluminium, the reaction (145) — zink-chrome catalyst. Methane and methanol are produced on great scales. Sodium (potassium) carbonate is used to bind CO_2 in technological processes:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3, \qquad (146)$$

commercial sodium (potassium) hydrocarbonate being obtained under these conditions. CO_2, CO and H_2 are also widely used in the motor fuel synthesis.

Hydrogen which is also capable to perform the power-carrier functions was one of reagents in the considered processes of synthetic fuel production, thus it is necessary to develop actively such alternative energy-producing technologies. As to its power capacity, hydrogen exceeds several times all the compounds which can serve as fuel: natural gas — 2.6 times, liquid oil hydrocarbons — 3.3 times, hard coal 5 times, methanol 6.6. times, cellulose — 8.5 times, etc.

REFERENCES

[1] M. Freemantle, Chemistry in Action, Part 2, Mir, Moscow, 1991.
[2] D. Dini, Int. J. Hydrogen Energy, No. 11/12 (1983) 897.
[3] I. Felkle, H. Alefeld, Hydrogen in Metals, Vol. 1, Mir, Moscow, 1981, 379.
[4] V.P. Barmin, I.L. Warshavsky, Science Future, Iss. 15 (1982) 64.
[5] I.L. Warshavsky. Energy-Accumulating Substances and Their Use, Naukova Dumka, Kyiv, 1980.
[6] K.N. Semenenko, Hydrogen — the Base of Chemical Technology and Energetics of the Future, B.i., Moscow, 1979.
[7] A.F. Zhigan, D.S. Stasinevich, Hydride Chemistry, Khimija, Moscow, 1969.
[8] Hydrogen in Metals, Ed. G. Amfeld, I. Felkle, in 2 Vols., Mir, Moscow, 1981.
[9] K. Makkey, Hydrogen Metal Compounds, Mir, Moscow, 1968.
[10] G.V. Samsonov, Rep. Acad. Sc. USSR, Vol. 208, No. 3 (1973) 621.
[11] D. O.Hoyard, B. M. Trapnell Chemisorplion, Butterworth, London, 1964.
[12] Chemisorption and reactions on Metalic Films / Ed. J. R. Anderson, Acad. Press., New York, 1971.
[13] Ya.D. Kogan, B.A. Kolpachev, Yu.V. Levinsky, et al., Contsants of Metals Interaction with Gases: Ref. Book, Metallurgiya, Moscow, 1987.
[14] L. Shihtsien, K. Weik, L. Hezhong // Hydrogen Syst. Pap. Int. Symp. (7–11 May, 1985), Beijing; Oxford, Vol. 1, 1986.
[15] Yuh. Fukai // J. Less-Common Metas. Vol. 172–174, No. 1 (1991) 8.
[16] B.A. Koplachev, Hydrogen Brittleness, Metallurgiya, Moscow, 1985.
[17] P.V. Geld, R.A. Ryabov, E.S. Kodes, Hydrogen and Imperfections of Metal Structure, Metallurgiya, Moscow, 1979.
[18] E. Huster // Galvanotechnic, Vol. 83, No. 1 (1992) 109.
[19] H. Herd, Introduction in the Chemistry of Hydrides, Izd. inostr. lit., Moscow, 1955.

[20] M.E. Kost, A.L. Shilov, V.I. Mikheyeva, et al., Compounds of Rare Elements. Hydrides, Borides, Carbides, Phosphides, Chalcogenides, Pseudohalgenides, Nauka, Moscow, 1983.
[21] V.I. Mikheyeva, Studies in Theoretical and Applied Inorganic Chemistry, Nauka, Moscow, 1971.
[22] O.M. Barabash, Yu.N. Koval, Structure and Properties of Metals and Alloys: Ref. Book, Naukova Dumka, Kyiv, 1986.
[23] Manual in Inorganic Synthesis, Ed. H. Bauer, in 6 vol., Mir, Moscow, 1985.
[24] Yu.V. Levinsky, p-I-x-Diagrams of State of the Binary Metal Systems, Ref. Book, Vol. 1, Metallurgiya, Moscow, 1990.
[25] G. Blument, Z. Engels, I. Fitz, et al., Unorganicum, Vol. 1, Mir, Moscow, 1984.
[26] D. Blackledge, Metal Hydrides, Ed. V. Miller, D. Blackledge, G. Libowitz, Atomizdat, Moscow, 1973.
[27] F. Wagner, G. Wortmah, Hydrogen in Metals, Mir, Moscow, 1981.
[28] M.M. Antonova, Properties of Metal Hydrides: Ref. Book, Naukova Dumka, Kyiv, 1975.
[29] G. Libowitz, Material Study and Energetics Problems, Ed. G. Libowitz, M. Wittingham, Mir, Moscow, 1982.
[30] G. G. Libowitz, T. Gibb // J. Phys. Chem, Vol. 60, No. 4 (1956).
[31] A.Yu. Zenyuk, Energiya, No. 1 (1998) 9.
[32] Ch.B. Meidzhy, Metal Hydrides, Ed. W. Miller, D. Blackledge, G. Libowitz, Atomizdat, Moscow, 1973.
[33] E. Wix, H. Brodoff, H. Zuchner, Hydrogen in Metals, Mir, Moscow, 1981.
[34] A. K. Switendick, Solid State Communs, Vol. 8, No. 18, (1970).
[35] A. K. Switendick, Int. Quant. Chem, No. 5, (1971) 459.
[36] L. K. Heung, T. Motyka, W. A. Summers, Proc. 4 Intern. Symposium on Hydrogen Power-Theoretical and Engineering Solutions, Stralsund. 9–14 Sept., 2001.
[37] L. E. A. Berlouis, P.Honnor, P. J. Haii, S. Morris, S. B. Dodd//Proc. 4 Intern. Symposium on Hydrogen Power-Theoretical and Engineering Solutions, Stralsund. 9–14 Sept., 2001.
[38] T. Klassen, W. Oelerich // 4 Intern. Symposium on Hydrogen Power-Theoretical and Enginttring Solutions, Stralsund. 9–14 Sept., 2001.
[39] V.I. Verbitsky, A.L. Shilov, and N.T. Kuznetsov, Journ. Inorg. Chem., Vol. 34, Iss. 9 (1989) 2401.
[40] V.N. Verbitsky, E.A. Movlev, Bull. Acad. Sc. USSR, No. 3 (1991) 37.
[41] E.I. Sokolova, L.N. Padurets, A.L. Shilov, et al., Journ. Inorg. Chem., Vol. 33, Iss. 2 (1988) 275.
[42] R. P. Mitrofanova, Yu. I. Mikhailov, N. N. Maltseva, Ibid.Iss. 9 (1989)2207
[43] Chui Hua, Li Qingfu, Chui J. // Hydrogen Syst. Pap. Int. Symp. (Beijing, 7–11 May 1985) Oxford 1986.
[44] E. Kaldis, M. Tellefsen, R. Bischof, J. Less-Common Metals // Vol. 130, No. 2 (1987) 542.
[45] S.Ono, K. Nomura, E. Akiba, R. Bischof., et al. Vol. 113, No.1 (1985) 113.
[46] Hydrogen Syst. Pap. Int. Symp. (Beijing 7–11 May 1985) — Beijing: Oxford, 1986. — Vol. 1 — P. 383.
[47] D.G Ivey, D. O. Northwood, Z. Phys Chem. (BRD). Vol.147, No.1/2 (1986) 191.

[48] Q. Jiuxin, D. Xiaoping, Z. Chaogui, Y. Yupu, Int. J. Hydrogen Ener., Vol. 11, No.2 (1986) 129.

[49] Jong-Man Park, Jai-Y Lee // Mater. Res. Bull, Vol. 22, No.4 (1987) 455.

[50] Y. Suzuki, Me Lellan // Acta met, Vol. 34, No.1 (1986) 125.

[51] Patent 4631170 USA, MKI C.01 B 6/24, NKI 42/455, Publ. 23.12.1986.

[52] L.F. Kozin, Physico-Chemistry and Metallurgy of Highly Pure Mercury and Its Alloy, Naukova Dumka, Kyiv, 1992.

[53] A.L. Shilov, Zhurn. Fiz. Khim., Vol. 43, Iss. 4 (1989) 1114.

[54] A.G. Konyaeva, Ibid., Vol. 64, Iss. 10 (1990) 2856.

[55] L.F. Kozin, V.A. Sakharenko, Ukr. Khim. Zhurn., Vol. 50, No.1 (1984) 9.

[56] L.F. Kozin, V.A. Sakharenko, A.N. Budarina, Ibid., No.2 (1984) 16.

[57] L.F. Kozin, A.N. Budarina, Zhurn. Prikl. Khim., Vol. 64, No.7 (1991)1429.

[58] B.A. Troshenkin, Circulation and Film Evaporators and Hydrogen Reactors, Naukova Dumka, Kyiv, 1985.

[59] Appl. 60–137801 Japan, MKI4 C 01 B 3/00, G17 C 11/00, Yamadzi Yakukadzy, Publ. 22.07.1985.

[60] E. From, E. Hebhardt, Gases and Hydrogen in Metals, Metallurgiya, Moscow (1980).

[61] R. E. Bischof-Furrer. Untersuchungen an Hydriden der Seltenen E: Abh. Dokt. Naturwiss.Eidgenoess.Techn.Hochsch, Zuerich, 1984.

[62] E.Ya. Pesina, O.N. Pavlov, Metal Hydrides, 1985.

[63] A. Drissen, H. Hemmes, R. Griessen, Z. Phys. Chem. (BRD). Vol. 143, No.1. (1985) 145.

[64] Yu.I. Mikhailov, N.N.Maltseva, N.S. Kerdova, N.T. Kuznetsov, 9 All-Union. Meet. on Therm. Anal.; B.i., Kyiv, 1985.

[65] K.M. Mackey, Comprehensive Inorganic Chemistry: In 5 Vol., Pergam. Press, Oxford, New York. 1973.

[66] B. Tarasov, S. Shilkin, Production, Properties, Analysis and Use of Compounds with Molecular Crystal Lattice for New. Techn., Theses, Novgorod, 1991.

[67] Appl. 63144102 Japan, MKI4 C 01 B3/56, B 01 D 53/14. Kosiba Khirosi, Publ. 16.08.88

[68] B.M. Andreyev, A.N. Borisenko, A.V. Kruglov, Hihgly Pure Substances, No. 1 (1992) 12.

[69] Appl. 2137702 Japan, MKI5 C 01 B 3/56. Hydrogen Cleaning, Jonedzaki Takakhiro, Nasako Kanlzi, Publ. 28.05.90.

[70] V.A. Legasov, G.A. Kotelnikov, V.K. Popov, Nuclear-Hydrogen Energetics and Technology, Atomizdat, Moscow, 1978.

[71] V.V. Pozdeyev, V.K. Shiryaev, S.P. Dobrovolsky, Ros. Khim. Zhurn., No. 3 (1993) 18.

[72] Yu.I. Aristov, S.I. Prokofiev, Yu.Yu. Tanashev, et al., Energiya, No.1 (1999) 9.

[73] L. F. Kozin. // VI int. Conf. «Hydrogen materials science and chemistry of metal hydrides», Katsiveli, m. Yalta, Ukraine, Sept. 2–8, 1999.

[74] L.F. Kozin, D.V. Sokolsky, Yu.F. Balybin, Direct Conversion of Thermal Energy into Electric One and Fuel Elements, No. 2 (1975) 136.

[75] S.V. Volkov, Zhurm. Neorg. Khim., No. 1 (1990) 136.

[76] S.V. Volkov, Ukr. Khim. Zhurn., No. 7 (1982) 675.

[77] L.F. Kozin, S.V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv, 2002.

[78] E.E. Shpilrain, S.P. Malyshenko, G.G. Kuplenov, Introduction into Hydrogen Energetics, Ed. V.A. Legasov, Energoatomizdat, Moscow, 1984.

[79] L.F. Kozin, V.A. Sakharenko, Ukr. Khim. Zhurn., No. 10 (1084) 9.
[80] L.F. Kozin, S.V. Volkov, Grenoble.
[81] Yu.V. Pleskov, Photoelectrochemical Transformation of Solar Energy, Khimiya, Moscow, 1990.
[82] Yu.I. Aristov, S.I. Prokofiev, Yu.Yu. Tanashev, et al., Energiya, No. 2 (1999) 7.
[83] J. O'M. Bockris, F. Gutmann, W. Graven. Hydrogen Ebergy Progr. IV. Proc. World Hydorgen Energy Conf. 4th. Pasadena, Calif., 13–17 June, 1982. Vol. 4, Oxford et al., 1982.
[84] V.M. Zaichenko, E.E. Schpilrein, Energia, No.6 (1998) 2.
[85] Inorganic Reaction and Methods. — Vol. 16. Edit J. J. Zuckerman, A. D. Norman, VCN Publishers, New York (1991).
[86] G. I. Novikov, Hydrogen Energy Progr., Proc. 3rd Word Hydrogen Energy Conf., Tokyo, 23–24 June, 1980, Oxford, 1981.
[87] I.G. Belousov, Nuclear-Hydrogen Energetics and Technology, Atomizdat, Moscow, 1990.
[88] R. H. Mentorf, R. E. Hanneman // Science. Vol. 185 (1974) 311.
[89] L.F. Kozin, Electrodeposition and Dissolution of Multivalent Metals, Naukova Dumka, Kyiv, 1989.
[90] Yu.K. Delimarsky, Ion Melts in Modern Technology, Metallurgia, Moscow, 1991.
[91] J. E. Funk, R. M. Reinstorm, Ind. Eng. Chem. Porc. Res. Develop. Vol. 5 (1966) 336.
[92] I.G. Belousov, Nuclear-Hydrogen Energetics and Technolohy, Atomizdat, Moscow, 1980.
[93] A.E. Bezhanishvili, K.N. Zvyagintsev and E.V. Kreinin, Chemistry of Hard Fuel, No. 6 (1962) 109.
[94] Pat. 251537, DDR. МКИ C 01 B 3/10/M. Heinz, K. Horst, S, Manfred.- Publ.
[95] L.M. Yakimenko, I.D. Modylevskaya, Z.A. Tkachek, Water Electrolysis, Chimiya, Moscow, 1970.
[96] A.c. 811867 USSR, MKI3 C25 B 1/02. Electrolyte for Hydrogen Production, S.V. Volkov, V.A. Legasov, A.V. Gorodyssky, et al., 1981.
[97] A.c. 80.76.71 USSR, MKI3 C25 B 1/02. Hydrogen Production Method, O.G. Zarubitsky, N.F. Zakharchenko, G.R. Sunegin, V.G. Budnik, Publ. 1981.
[98] A.c. 811868 USSR, MKI C25 B 1/04., Electropolyzer for Hydrogen Production, A.V. Gorodyssky, V.A. Legasov, S.V. Volkov, et al., Publ. 1981.
[99] O.G. Zarubitsky, Zhurn. Prikl. Khim., Vol. 68, No.5 (1995) 718.
[100] F. J. Salzano, G. Skarerdas, A. Mezzina // Int. J. Hydrogen Energy, Vol. 10, No. 12 (1985) 801.
[101] J. Divisek, H. W. Nurnberg, Grundlagenforsch. Energietechnol. Jahresber, 1982.
[102] J. Calvalho, G. Tremiliosi-Filho, L. A. Avaca et al., Hydorgen Energy Progress VI — Pergamon Press N. Y., Oxford a.o. Vol. 1 (1986) 250.
[103] W. Donits, G. Dienrich, E. Erdle et al., Ibid. Vol.1 (1986) 271.
[104] A. R. Rotinyan, K. I. Tikhonov, I. A. Shoshina, Theoretical Electrochemistry, Khimiya, Leningrad, 1981.
[105] O.G. Zarubitsky, N.F. Zakharchenko, Hydrogen Material Science and Hydride Chemistry, Proc. VI Int. Conf., Yalta, Katsiveli, 2–8 September, B.i., Kyiv, 1999.
[106] M.V. Perfiliev, A.K. Demin, B.L. Kuzin, et al., High-Temperature Water Electrolysis, Nauka, Moscow, 1988.

[107] A.c. 1358329 USSR, MKI4 C 01 F 7/04, Method of b-Silica Production, L.F. Kozin, B.I. Daniltsev, V.A. Sakharenko, Publ. 1987.
[108] A.c. 1192280 USSR, MKI4 C 08 F 7/04. Method of b-Silica Production, L.F. Kozin, B.I. Daniltsev, V.A. Sakharenko, Publ. 1985.
[109] B.V. Galkin, G.A. Grishaeva, A.P. Germanovich, et al., Problems of Nuclear Science and Technology, Ser. Nuclear Eng. and Technol., No. 1 (1991) 29.
[110] N.V. Korovin, Electrochemical Energetics, Energoizdat, Moscow, 1991.
[111] N.N. Fateyev, Energiya, No. 12 (1998) 11.
[112] A.N. Podgorny, I.L. Warshavsky, A.V. Priymak, Hydrogen and Energetics, Naukova Dumka, Kyiv, 1984.
[113] A.N. Podgorny, I.L. Warshavsky, A.I. Mishchenko, et al., Nuclear-Hydrogen Energetics, Naukova Dumka, Kyiv, 1980.
[114] R. F. Alimova, L. F. Goltsova, Garkusheva V. F. et al, Int. J. Hydrogen Energy, Vol. 10, No. 12, (1985) 861.
[115] A.N. Podgorny, I.L. Warshavsky, A.I. Mishchenko, et al., Nuclear-Hydrogen Energetics and Technology, Atomizdat, Mscow, 1980.
[116] K.N. Semenenko, Bull, Rus. Acad. Sc., No. 10 (1993) 895.
[117] A.c. 618920 USSR, MKI4 C 01 F7/04. Method of Hydrogen Production, D.V. Sokolsky, L.F. Kozin, R.G. Sarmurzina, et al., Publ. 1978.
[118] L.F. Kozin, R.G. Sarmurzina, Zhurn. Prikl. Khimii, Vol. 54, No. 10 (1981) 2176.
[119] A.c. 618921 USSR, MKI4 C 01 F 7/04, Method of Hydrogen Production, D.V. Sokolovsky, L.F. Kozin, R.G. Sarmurzina, et al., Publ. 1978.
[120] A.c. 1512159 USSR, MKI4 C 22 C 21/00. Aluminium-Bused Alloy for Hydrogen Production from water, L.F. Kozin, V.A. Sakharenko, B.I. Daniltseva, V.G. Gopienko, Publ. 1989.
[121] A.c. 1241636, MKI4 C 01 B 3/08. Method of Hydrogen Production, L.F. Kozin, A.V. Gorodysky, V.A. Sakharenko, Publ. 1986.
[122] A.c. 1051966 USSR, MKI4 C 22 C 21/00. Aluminium-Based Alloy for Hydrogen Production, L.F. Kozin, V.A. Sakharenko, Publ. 1983.
[123] A.c. 1108773 USSR, MKI4 C 22 C 21/00. Aluminium-Based Alloy for Hydrogen Production, L.F. Kozin, V.A. Sakhasenko, B.A. Troshenkin, Publ. 1984.
[124] A.c. 1360000 USSR, MKI4 B 22 F 1/00. Method of Aluminium Powder Activation, L.F. Kozin, V.A. Sakharenko, B.I. Daniltsev, V.G. Gopienko, Publ. 1987.
[125] A.c. 1591510 USSR, MKI5 C 22 C 21/90, 1/05. Aluminium-Based Composition Material for Hydrogen Production, L.F. Kozin, V.A. Sakharenko, B.I. Daniltsev, I.L. Warshavsky, Publ. 1990.
[126] A.c. 1111405 USSR, MKI4 C 01 B 3/08, Composition for Hydrogen Production by Water Decomposition, L.F. Kozin, A.V. Gorodysky, V.A. Sakharenko, et al., Publ. 1984.
[127] L.F. Kozin, V.A. Sakharenko, B.I. Daniltsev, Zhurn. Prikl. Khim., Vol. 68, No. 9 (1995) 1433.
[128] L.S. Glebov, G.A. Kliger, Ibid., No.6 (1992) 49.
[129] I.V. Kalechits, Chemical Encyclopaedia. — Sov. Entsiklopedia Publ., Moscow, Vol. 4, 1995.
[130] V.A. Legasov, Kommunist, No. 1 (1976) 72.
[131] V.A. Legasov, G.A. Kotelnikov, V.K. Popov, Nuclear-Hydrogen Energetics and Technology, Atomizdat, Moscow, 1978.

[132] V.V. Pozdeyev, S.P. Dobrovolsky, V.K. Shiryaev, Nuclear Energy, Vol. 66, Iss. 5 (1979) 347.

[133] L.F. Kozin, A.V. Gorodysky, V.A. Sakharenko, Kinetics and Burning. Chernogolovka, Nauka, Moscow, 1986.

[134] L.F. Kozin, A.N. Buderina, Zhurn. Prikl. Khimii, Vol. 62, No. 12 (1989) 2665.

[135] Corrosion. Reference Book, Edit. L.L. Schraer, Metallurgiya, Moscow, 1981.

[136] Aluminium Alloys. Reference Book, Edit. H. Nilsen, V. Hufnagel, H. Ganulis, Metallurgiya, Moscow, 1979.

[137] B.I. Kogan, Rare Metals, Nauka, Moscow, 1978.

[138] V.I. Vigdorovich, V.V. Krapukhin, I.F. Chernomordin, Bull. Acad. Sc. USSR, Metallurgy and Fuel, No. 4 (1960) 99.

[139] T.A. Badaeva, R.I. Kuznetsova, Proc. Acad. Sc. USSR, No. 2 (1950) 507.

[140] L.A. Niselson. G.A. Yaroshevsky, Interphase Distribution Coefficients, Nauka, Moscow, 1992.

[141] L.F. Kozin, A.V. Gorodysky, V.A. Sakharenko, Chemical Physics of Burning and Explosions. Kinetics and Burning, Materials of VIII All-Un. Sympos. on Burning and Expiosion, Chernogolovka, Moscow, 1986.

[142] I.L. Warshavsky, Nuclear-Hydrogen Energetics and Technology, Atomizdat, Moscow, Iss. 3 (1980) 123.

[143] D.V. Sokolsky, L.F. Kozin, T.V. Kuzora, et al., Proc. Acad. Sc. USSR, Vol. 230, No.3 (1976) 620.

[144] O.A. Melnikov, With Scientist's Eyes. Nauka, Moscow, 1993.

[145] R. Dahlbeng // Int. J. Hydrogen Energy. Vol. 7, No. 2 (1982) 121.

[146] G.Ya. Kolbasov, A.V. Gorodysky, Processes of Photostimulated Charge Transfer in the Systems Semiconductor-Electrolyte, Naukova Dumka, Kyiv, 1993.

[147] G.Ya. Kolbasov, Photoelectric Processes and Structure of the Interface Semiconductor-Electrolyte on compounds of AIIBVII and AIIIBV Type; Abstract of Thesis for Doctors degree, IGIC NAS of Ukraine, Kyiv, 1990.

[148] Yu.V. Pleskov, Photoelectrochemical Conversion of Solar Energy, Khimiya, Moscow, 1990.

[149] Ye. V. Kuzminsky, G. Ya. Kolbasov, Solar Energy Materials and Solar Cells. Vol. 56. (1999) 93.

[150] S. H. Pawar, P. D. Pawar // Indian J. Pure and Appl. Phys. Vol. 34, No. 7 (1996) 504.

[151] G.Ya. Kolbasov, I.A. Rusetsky, Ukr. Khim. Zhurn., Vol. 66, No. 5 (2000) 27.

[152] K.Ya. Kondratiev, Proc. Rus. Acad. Sc., Vol. 70, No. 9 (2000) 788.

[153] M. Sharon, P. Veluchamy, C. Natarajan, D. Kumar // Electrochim. Acta. Vol. 36, No. 7. (1991) 1107.

[154] Energy: Economy, Technology, Ecology, No. 8 (1998) 8.

[155] O. M. Bokris, Environment Chemistry, Khimiya, Moscow, 1982.

[156] S.D. Varfolomeyev, Energy Conversion by Biocatalytic System, Moscow Univ. Publ., Moscow, 1981.

[157] F.T. Yanshina, A.L. Yanshin, Bull. Rus. Acad. Sc., Vol. 70, No. 3 (2000) 243.

[158] H.L. Yanshin, Bull. Rus. Acad. Sc., Vol. 64, No. 12 (1994) 1081.

[159] V.S. Golubev, Ibid., Vol. 67, No. 12 (1997) 1104.

[160] V.G. Gorshkov, Energetics of Biosphere and Environment State Stability, VINITI, Moscow, 1990.

[161] V.G. Gorshkov, Physical and Biological Grounds of Life Stability, VINITI, Moscow, 1995.

[162] M.A. Styrikovich, A.K. Arsky, Science Future, Znanie, Moscow, 1983.

[163] V.N. Grebennik, N.N. Ponomarev-Stepnoi, V.V. Lebedev, et al., Nuclear-Hydrogen Energetics and Technology, Iss. 4., 2000.

[164] A.N. Bashkirov, G.A. Kliger, Science Future, Znanie, Moscow, 1981.

[165] D. Greenhopt, Future of Nuclear Energetics, Moscow, 1990.

[166] N.S. Safonov, T.V. Lisichkin, Ros. Khim. Zhurn., Vol. 45, No. 4 (2001) 72.

[167] I.I. Chebanenko, Geol. Zhurn., No. 1 (1999) 120.

[168] A. Shvidkovsky, Visnyk Ukrainy, No. 5/6 (1998) 64; No. 3 (2001) 29.

[169] O.V. Krylov, Ros. Khim. Zhurn., No. 4 (2001) 53.

[170] S.D. Pirozhkov, V.D. Kapkin, A.Yu. Krylova. Results of Science and Technology. Ser. Technology of Organic Substances, VINITI, Moscow, 1987.

[171] V.G. Lipovich, V.V. Zemskov, V.P. Medvedeva, Khimiya Tverd. Topliva, No. 4 (1990) 91.

[172] V.V.Zemskov, V.G.Lipovich, V.P.Medvedeva, et al., Ibid., No.6(1991)92.

[173] C.R. Chow, Fuel, Vol. 62, No.3 (1988) 317.

[174] V.A. Kucherenko, V.A. Sapunov, T.I. Zubova, et al., Khimiya Tverd. Topliva, No. 4 (1992) 96.

[175] V.E. Rakovsky, General Chemical Technology of Turf, Gosenergoizdat, Moscow, 1949.

[176] M.F. Polubentseva, V.V. Duganova, B.A. Bazhenov, et al., Khimiya tverd. topliva, No. 6 (1997) 62.

[177] P. Osterkamp, E. Wagner, G. Ross, Ros. Khim. Zhurn., Vol. 54, No. 1 (2000) 34.

[178] A.L. Lapidus, A.Yu. Krylova, Ibid.

[179] I.T. Chashechnikova, V.M. Borotyntsev, G.I. Golodets, Khimiya tverd. topliva, No. 6 (1991) 40.

Chapter 7

Hydrogen as Ecologically Pure and Unique Energy Carrier and Reagent

7.1. Hydrogen fuel and economy

Hydrogen is the only ecologically pure fuel and reagent which oxidation product by reactions

$$2H_2\ (g.) + O_2\ (g.) \rightarrow 2H_2O\ (g.) + 483.6\ kJ\ (241.8\ kJ/mol\ H_2O) \quad (7.1)$$

$$2H_2\ (g.) + O_2\ (g.) \rightarrow 2H_2O\ (l.) + 571.6\ kJ\ (285.8\ kJ/mol\ H_2O) \quad (7.2)$$

is water vapor or liquid water. The process of hydrogen combustion is not accompanied by the ejection of impurities characteristic of combustion of hydrogen fuel (oil derivatives) and bituminous coals as is described above. The only impurity formed in negligible concentrations is nitrogen oxide (from air) absorbed by water vapors. Molecular hydrogen possesses high power capacity (125 MJ/kg) exceeding more than 3 times power capacity of 1 kg of high-quality gasoline (40.1 MJ/kg). When burned, 1t of hydrogen releases heat in the amount equivalent to the combustion heat of 3.5 t of hydrocarbon fuel. Hydrogen in general possesses universal properties: it is a reducing agent, energy carrier and fuel. Besides, reserves of any organic fuel (oil, natural gas, coal) on the Earth are exhaustible, while hydrogen reserves are inexhaustible and they may be referred to the category of infinite. Additional hydrogen may be found in nature in oxidized state, water being its most distributed compound. To make hydrogen an energy carrying and reducing agent it would be restored and converted in gaseous or liquid state, convenient for its utilization. Hydrogen as an energy-carrying agent possesses valuable property. In the system hydrogen-oxygen the former as an energy-carrying agent is not subject to destruction, and in this connection its repeated use, if necessary, is possible in the redox cycles with renewable energy sources with the help of reduction and following oxidation.

Hydrogen is used in great amounts in production of ammonia, in deep processing of oil, production of high-octane motor fuel, production of SLF, in gasification of coal and turf, synthesis of methanol and different organic compounds, as well as in electric power generation by its oxidation in fuel cells of power units

(PU) [1–3]. Considerable volumes of liquid hydrogen are used as the rocket fuel, in small volumes — in high-tech low-tonnage branches of industry and science; electronic industry, special metallurgy of tantalum, tungsten, niobium and other high-purity metals [4], as well as in food industry [5].

Hydrogen production in the world was in mill.t: in 1990 — 60, in 1995 — 72, in 2000 — 83. An analysis of the data from [6] shows, that hydrogen production grows with time by the logarithmic law lg v_{H_2} – τ (years). As is seen from Fig. 77, data about hydrogen production in the USA and industrially developed countries (IDC) fall well on the straight lines lg v_{H_2} – τ. The latter evidences for the high rate of creation of hydrogen infrastructure in the world and development

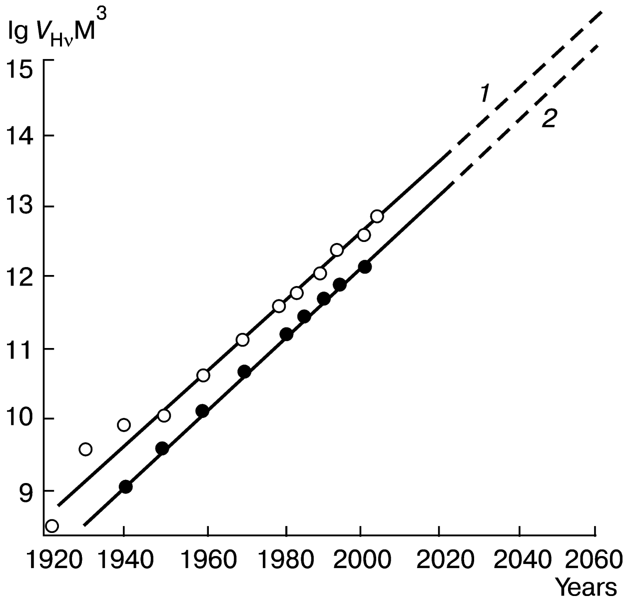


Fig. 77. Dependence of hydrogen production ($n \cdot 10^{12}$ m^3) in 1980–2000 and prediction for 2010–2050 in industrially developed countries (IDC) (*1*) and USA (*2*)

Table 31

Data of hydrogen production in 1980–2000 and prediction for the period of 2010–2050 ($n \cdot 10^{12}$ m^3)

Year	IDC	USA	Year	IDC	USA
1980	0.389	0.176	2010	14.1	4.4
1985	0.627	0.282	2020	43.7	15.8
1990	1.00	0.450	2030	131.8	45.7
1995	1.60	0.720	2040	436.5	125.9
2000	3.63	1.415	2050	1445.4	562.3

Note: IDC – Industrially developed countries.

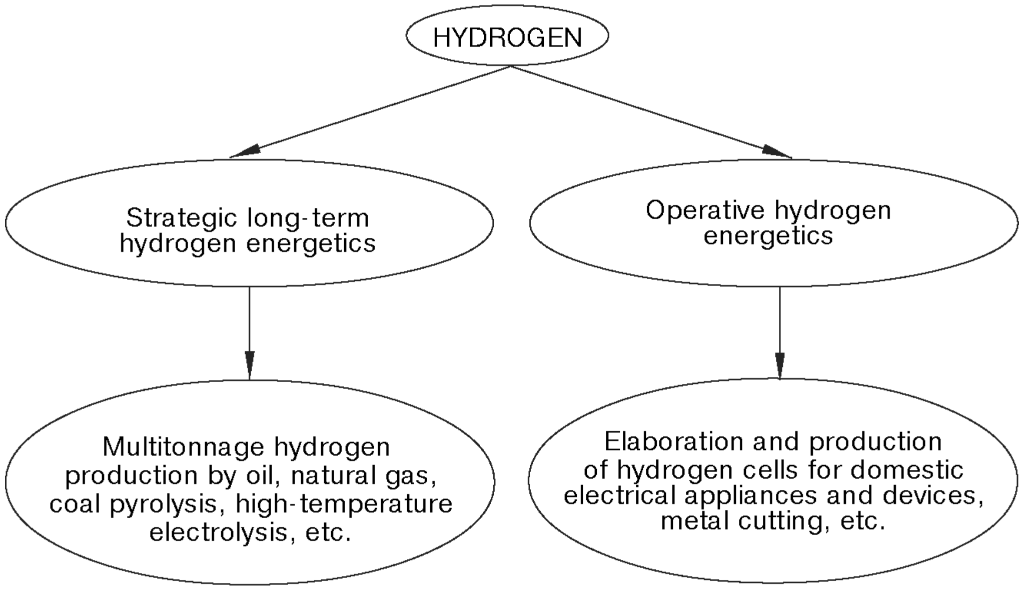


Fig. 78. Hydrogen energetics development trends

of the new branch of industry — «hydrogen economy» [7, 8]. The linear dependence lg $v_{H_2} - \tau$ allows predicting the volumes of hydrogen production in the USA and industrially developed countries for the period of 2010–2050. The data about hydrogen production in 1980–2000, according to [6], and our data of production for 2010–2050 are presented in Table 31. As is evident hydrogen production during the next half a century, compared to 2000, would rise 578 times in IDC and 375 times in the USA. Calculations have shown that the share of hydrogen produced in the USA is 39–45 % of that produced in other countries.

A gap between production volumes decreases with time and the prediction shows that in 2050 hydrogen production in the USA will be 39 % ($5.623 \cdot 10^{14}$ m^3) of the world one ($1.4454 \cdot 10^{15}$ m^3). But it would be noted, that the USA still intensify the works in the field of hydrogen energetics, making milliard investments to hydrogen production and consumption.

The demand for high-energy and ecologically pure fuel resulted in the appearance of hydrogen energetics (HE). Hydrogen energetics includes the systems which unify industrial production, housing and communal services, transport, power complexes for hydrogen production, storage and supply to a consumer along the appropriate mains or in other way with the use of the corresponding infrastructure. Academician V. A. Legasov, leader in the field of hydrogen energetics in the USSR [9–11], carried out investigations in this trend. Hydrogen energetics develops in different directions. Nowadays (Fig. 78) one can distinguish two trends: strategical long-term HE and tactical operative HE. Strategical hydrogen energetics is based on high-productivity processes and methods of low-tonnage production of hydrogen, its large-scale use in industry, aviation, motor

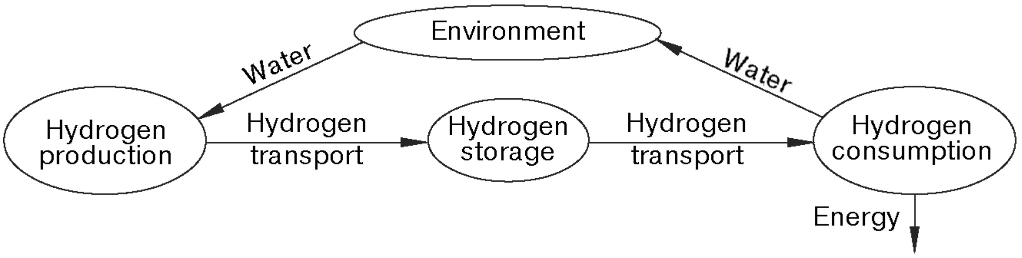


Fig. 79. Scheme of hydrogen energetic system of hydrogen production, storage and consumption

transport; the tactical one is based on the use of hydrogen properties in special installations to solve general service problems.

A scheme of hydrogen energetics system, presented in Fig. 79, includes infrastructures of hydrogen production, its storage and use connected between themselves by hydrogen-transport mains. As is shown in the works [12, 13], transport of energy by hydrogen mains is more efficient than transmission of electric power, compressed air, hot water and vapor (540 °C) and even conversion gas. The hydrogen pipe-main capacity at the distance L = 1000 km is 12.8 GW/m^2, conversion gas at L = 200 km — 1.35, hot water at L = 30 km — 0.28, and technological steam at L = 20 km — 0.11 GW/m^2. Electric power plants, transport, industry and communal-general service as well as aviation and space technology can be hydrogen consumers.

A comparison of basic operation indices of different modern power generators and their construction cost presented in Table 32 leads to unambiguous conclusion on considerable advantages of electric energy generation by steam-gas, gas-turbine plants and nuclear-hydrogen power plants. Average thermal efficiency of TES on natural gas in Ukraine and in Russia makes 25–30 % [14]. TES low efficiency is determined by the use of steam turbines, which have exhausted their estimated resourse. Thermal efficiency of TES in the USA is 35 %, in England — 38 %, Japan — 41 % [14]. To increase TES efficiency it is necessary to substitute steam turbines by steam-gas plants (SGP). In modern SGP, besides high efficiency of gas turbine, the total system efficiency can be increased to 52–54 and even to 70 % at the expense of the use of gas flow from turbine in a steam generator. To create modern SGP-TES (steam gas plants at thermoelectric stations) Russia has to invest 55–70·10^9 US dollars. In this case electric power generation will rise from 260 to 416 milliard kWh and electric power efficiency will equal 77 % and its cost will be twice lower than at the available TES [14].

New structural heat-proof materials created in the recent years in the research laboratories of the world on the basis of the so-called viscous ceramics and new metal alloys (e.g., on the basis of hastalloy, nickel-manganese steels or chrome alloys) permit increasing temperature on the turbine blades by 100–500 °C, which increases efficiency of the steam-gas turbines [15]. It has

Table 32

Comparison of basic parameters under different methods of electric power generation

Parameter	TYPE OF PLANT					
	SGP	GTP	TES	NPP	NHPP	FE
Efficiency, %	50–65	44–65	25–37	30–35	50–65	>70
Cost of 1 kW of installed power, $	600–1000	1100–1600	1000–1700	2000–3000	1000–1500	800–1000
CO_2 discharge at equal power, %	50	75	100	0	0	0
Radioactive contamination, %	1–2	1–2	100	1	1	0

Note: SGP — steam-gas plants; GTP — gas-turbine plants; TES thermoelectric stations; NPP — nuclear power plant; NHPP — nuclear-hydrogen power plants FC — fuel cells.

been established that the elevation of gas operation temperatures of GTP (from 1100 to 1600 °C) and pressure in the cycle (from 15 to 45) the efficiency increases from 33 to 44 %. Use of the intermediate air cooling under compression, intermediate heating of gas under the expansion, as well as heat regeneration provide for the increase of GTP efficiency from 44 to 56 %. The vapour cycle of GTP being complicated gradually by regeneration of the exhaust heat, by introduction of a portion of steam into the turbine tract, one can reach the efficiency of 65 %. The combining of gas turbines with high- and medium-temperature electrochemical power generators, the so-called fuel elements (FE), allows reaching the electric efficiency of 65–75 % [15–17] in such installations. Fuel elements themselves possess rather high efficiency equal to 70–80 %.

The steam-turbine plants at modern TES of the USA are combined with gas-turbine ones and TES operate with efficiency no lower than 60 % and equipment utilization efficiency (EUE) no less than 70 %. A highly efficient modern gas turbine plant designed by mechanical engineers of Research and Production Association (RPA) *Mashproekt* (Nikolaev, Ukraine) and Rybinsk Motor Plant (Russia) is worthy of concern. The GTP power is 110 MW and its rotor is about 2 m in diameter; its efficiency — 62 %. Combined or steam-gas plants with 58–60 % efficiency are created in the advanced countries to increase the power production efficiency. Power production plants in Ukraine possess EUE of 35–37 %, in Russia — 45 %, i.e. it is also relatively low. And this takes place when the construction of electric power plants costs $0.6–2.0 \cdot 10^3$ US dollars for 1 GW [14]. The equipment utilization factor in Japanese Power Company TEPCO reaches 84 %.

When substituting steam turbines at TES by the steam-gas plants [14] one can increase efficiency from 32–34 to 52–54 % and power production almost twice. It is evident that the increase of efficiency is connected directly with ecology: the higher is the efficiency the less heat losses are and the less are the ejections into the atmosphere. When natural gas in burnt in the air, the environment pollution by the combustion products is minimized, since only CO_2, partially CO and NO_2 get into the atmosphere, sulphur oxides being absolutely absent. Thus gas energetics is promising and competitive from the viewpoint of ecologic safety, the native developed gas deposits being available. The cost of energy produced by NPP in Russia is less by 30 % than that of energy produced by TES on natural gas [18]. It would be kept in mind that most TEP of RSC «SPS»[*] use natural gas which home price is 5–6 times as low as the world market price. Economic efficiency of gas energetics is rather questionable for Ukraine, which pays for natural gas the world prices and even more. It is clear now, that gas energetics in Ukraine has the future, provided that the country will develop its own deposits of natural gas and methane of coal basins. The reserves of coal deposits being utilized and coal production in Ukraine put in order with ensuring its competitiveness, it is possible to realize the processes of nuclear-hydrogen energetics by creating power-saving technologies and conversion of some NPP into NHPP with CO_2-closed biological cycle. It is NHPP which permit creating wasteless power-biotechnological centres and raising both energy and heat production efficiency [13].

The electric power and heat production efficiency can be raised even with the use of expensive imported natural gas, if only NHPP ensures utilization of CO_2 with obtaining the biomass and food products (see, Chapter 6, p. 6.1). There are NHPP which use hard and brown coals as hydrocarbon source and possess well-adjusted system for automation of technological processes and for CO_2 utilization in biotechnological cycles and hydrogen utilization in science-intensive technologics of hydrogen energetics. These NHPP possess great prospects.

The conception of «hydrogen energetics» and «hydrogen economy» was formulated in the 70's of the last century, which were the years of crisis in energetics and ecology. It became clear then that organic fuel is not eternal and so, it is necessary to care for the environment in order to preserve life on the Earth, reducing the atmosphere pollution. Hydrogen was proposed as the organic fuel (natural gas, oil, and coal) alternative. The power system using the alternative ecologically pure hydrogen as fuel in industry, transport and communal-general service was called hydrogen energetics.

Hydrogen power system (Fig. 80) possesses the developed infrastructure of hydrogen production, storage and utilization [16]. Great volumes of hydrogen, reaching hundreds of million tons, are used, as was noticed above, in the fuel and chemical oil-refining and coal-processing complexes, in ammonia synthesis, in numerous chemical and metallurgical processes. Hydrogen can be more widely

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[*] Russian Stock Company «Single Power System».

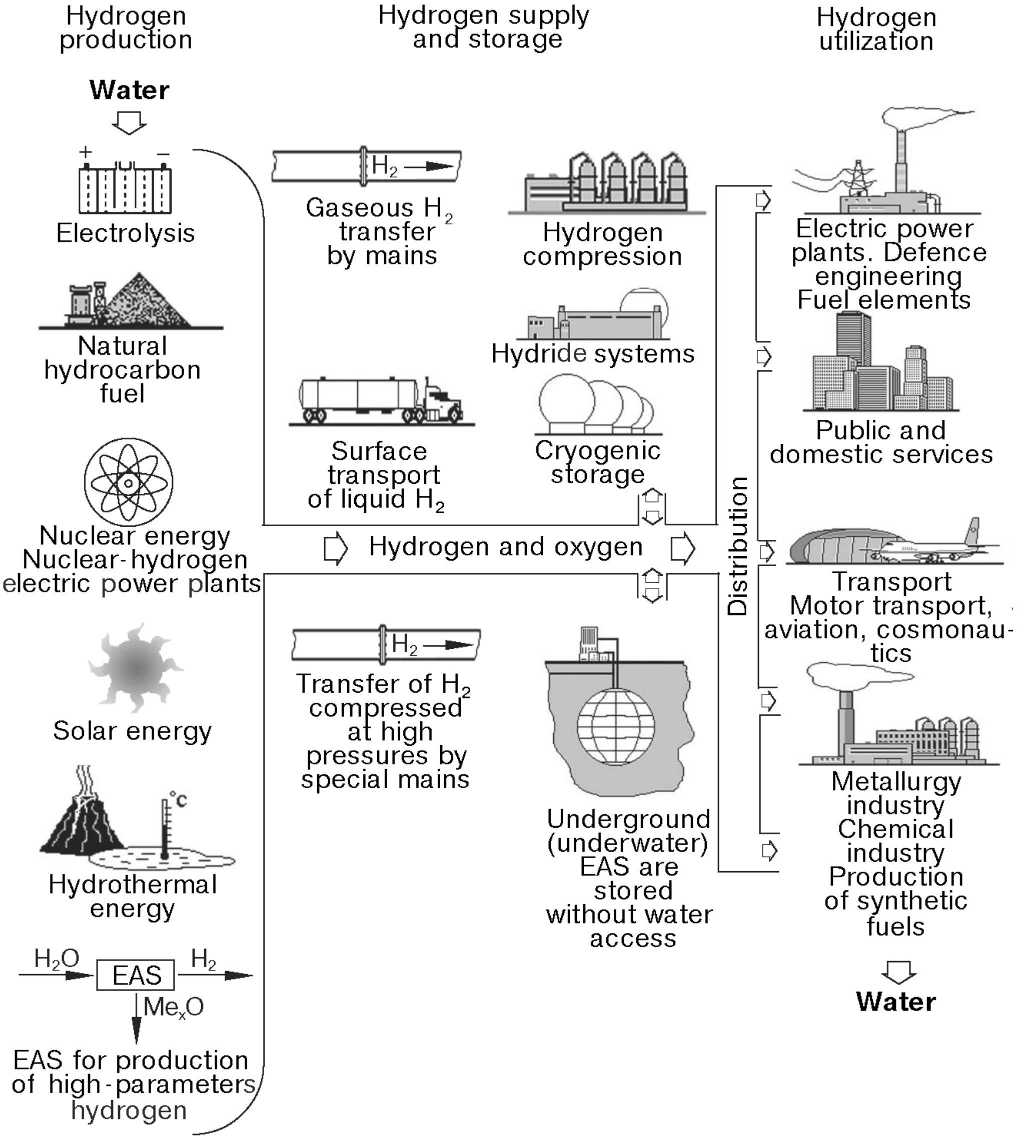


Fig. 80. Infrastructure of hydrogen energetics

used as fuel at electric power plants, in aviation and astronautics, transport, industry and communal-general service. It may be used as heat-transfer agent in power-generation cycles and as a reducing agent in metallurgical industry, and especially as a reagent in liquefaction of solid fossil fuel in order to obtain synthetic liquid motor-fuels and lubricating oils (see, Chapter 6), etc. [19–26]. The ever-increasing volumes of hydrogen are used in electrochemical current generators with power of 0.1–2.0 MW [27, 28].

Hydrogen is transported by hydrogen mains or by cryomotor transport; it is stored in gas holders under pressure, in a form of liquid hydrogen in the tanks with cryogenic plugs, as well as in hydride accumulators. It is promising to store hydrogen in the underwater and underground stores (Fig. 81 *a*, *b*) with hydro-

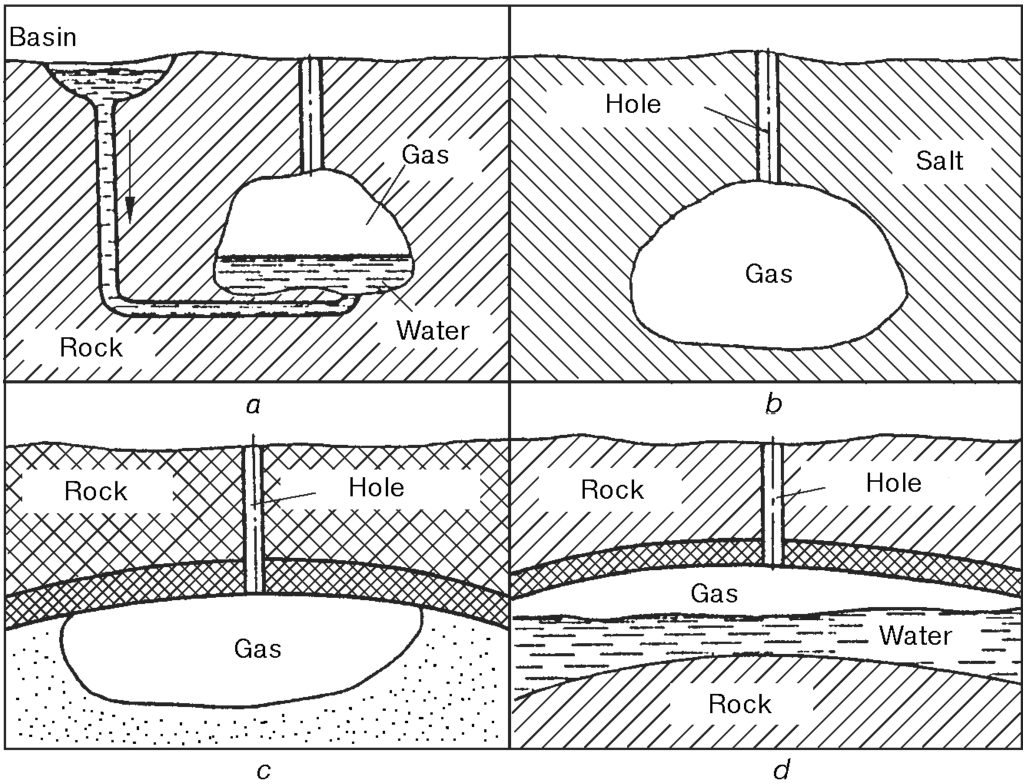


Fig. 81. Possible kinds of underground and underwater storages for compressed hydrogen

static compensation of gas pressure. The worked out deposits of natural gas and oil (Fig. 81 *c*, *d*) may be used as underground storages of hydrogen. The cost of construction of underground and underwater gas-holders is 0.1–0.3 US dollars for 1 kW of electric energy. The recoupment terms are 3–4 months. A survey of the existing and prospective methods of hydrogen storage is given in the work [29].

Hydrogen energetics is a resistant power system independent of the choice of original energy source (water, natural gas, nuclear-hydrogen processes). This system is mobile, renewable and multipurpose. The application of high-temperature electrolysis of water vapours using waste heat of NPP and NHPP is especially promising in hydrogen energetics for production of great volumes of pure hydrogen, while power-accumulating substances are used for tactical purposes and operative production of high-parameter hydrogen — power-accumulating substances (see, Chapter 6) [30–32].

7.2. Aviation and spacecrafts

The demand for organic fuel in transport aviation is comparable now with fuel consumption by motor transport. Because of ecologic problems more and more investigations are devoted to the use of liquid hydrogen as fuel in aviation and liquid hydrogen in combination with liquid oxygen in rockets (Space Shuttle, USA; H-1, Japan, etc.). Hydrogen is used in astronautics for spacecrafts *Apollo*, *Energy, Buran* and other giant rockets and space shuttles (X-33, RLW, USA; TU 2000, and H-1, Russia) capable to supply large useful cargo to the near-Earth orbit and to provide a possibility of interplanet flights.

Liquid hydrogen as fuel for liquid-fuel reaction engines (LRE) was first proposed by K.E. Tsiolkovsky in 1903. It is considered that it is hydrogen which will be used as fuel in the future both in ordinary and in supersonic aviation. Liquid hydrogen will be used in the supersonic aviation for cooling the plane airframe [33].

Great contribution to development of hydrogen energetics in as applied to aviation, space engineering and space flights was already made in the mid-70's by outstanding scientists and their collectives: V. A. Legasov, N. D. Kuznetsov (I. V. Kurchatov Institute of Nuclear Energy, Moscow), V. P. Barmin (SPA *Kriogenmash*), A. N. Podgorny, I. L. Warshavsky (Institute for Machine-Building Problems of the Ukr. SSR), V. P. Glushko (Institute of High Temperatures), A.N. Frumkin (Institute of Electrochemistry, Acad. Sc. of the USSR, Moscow) and other brilliant scientists. The programs of creation of the rocket-space complexes *Energia-Buran* and *N-1*, aviation complex TU-155 were realized with active participation of such high-tech world scale corporations as Scientific-Production Association *Kriogenmash*, V. P. Barmin Design Office of Defence Machine Building, P. I. Baranov Central Institute of Aircraft Machinery, A. N. Tupolev Aircraft Scientific-Industrial Complex, SPA *Energia*, State Institute of Aircraft Industry and many other organizations.

As a result, modern equipment for cryogenic fuel systems on the basis of liquid hydrogen was designed and manufactured. Efficient hydrogen liquefiers with power-consumption 22kWh/kg of H_2 were developed and produced.

The tank-trucks of about 45 m^3 with diurnal losses from 0.8 to 1.2% and tank cars of about 100 m^3 with diurnal losses of 0.5 % [34] have been constructed and produced for the transport of liquid hydrogen. Cryogenic pipe-mains 400 mm in diameter and 1 km long with the corresponding systems ensuring the control and safety of operations with liquid hydrogen were run for filling up the space complexes. They have also developed and produced highly efficient heat-exchange apparatus, machine equipment (compressors, highly productive vacuum pumps, ejectors, etc.), instrumentation and means for ensuring safety, systems of remote control and observation of any technological processes related to liquid and gaseous hydrogen.

Problems of power supply and support of spaceships and rocket complexes put into preset orbits were decided by the collective of SPA *Kvant* headed by N. S. Lidorenko, the famous scientist. New technological processes of large-scale production of liquid and comprimed hydrogen, methods of storage of great volumes of liquid hydrogen, transportation and distribution of hydrogen, methods of hydrogen use in aviation, rocket and space facilities were developed as a result of the conducted investigations.

The required infrastructure has been created with regard for physico-chemical properties. As a result, unique aircraft (model NK-88) and rocket engines, space complex *Energia-Buran*, plane-laboratory TU-155, rocket-space complex N-1, which function on hydrogen fuel, have been created. All the equipment and rocket-space complexes were successfully tested on the Earth, in the air and in space (*Energia-Buran*, 1988; TU-155, 1988–1989; N-1, 1989).

The conducted tests have demonstrated that hydrogen and oxygen may be used with success as fuel for putting the rocket complexes and spaceships into the desired orbits. Under these conditions, hydrogen and oxygen obtained by electrolysis immediately on spacecrafts may be used for the orbit correction.

Special attention was given to ecology of space- and aircrafts flights. The organic fuel combustion in aviation and spacecrafts was shown to lead to the great ejections of carbon (CO, CO_2), nitrogen (NO, NO_2) oxides in the environment and to the destruction of the ozone layer of the upper troposphere boundary. Hydrogen use in aviation and spacecrafts lowers hundreds and thousands times CO, CO_2, NO, NO_2 ejections in the atmosphere. The disturbing effect of flights on the ozone layer is preserved, since great amounts of hot steam call the shift of ozone disproportionation reaction equilibrium towards formation of molecular oxygen:

$$2O_3 + nH_2O = 3O_2 \cdot nH_2O \tag{145}$$

This reaction is exothermal and spontaneous in the presence of the third component. Hydration of molecular oxygen at $t > 0$ °C intensifies the reaction equilibrium accentuation to the right.

Liquid hydrogen has indisputable advantages as fuel for aviation and spacecrafts: high energy content, small molecular weight, high fluidity, acceptible viscosity, the ability to evaporate in the combustion chamber, high burning characteristics, combustion efficiency, a possibility to store liquid hydrogen in the space port, airport, in missile carrier and plane containers, lack of harmful ejections. High liquid hydrogen mass efficiency which exceeds 2.8–3.0 times that of kerosene would be referred to as its merit. Hence there is the gain in specific fuel consumption when using supersonic engines on hydrogen. Broad limits of ignition are characteristic of hydrogen mixed with the air and oxygen.

Hydrogen combustion in the liquid-propellant rockets and gas turbine engines proceeds without carbon deposit in the combustion chamber. Low energy required for hydrogen ignition with the presence of oxidizer (oxygen, air) favours the simple control for the launch of jet engine at various heights and at various outer temperatures. High hydrogen efficiency permits a 2/3 decrease of the required fuel reserve on board, and thus it is possible to decrease the plane

Table 33

Comparison of operation characteristics of subsonic aircrafts working on kerosene and liquid hydrogen [36]

Characteristics	Subsonic aircraft filled up		Characteristic changes, %
	with kerosene	with liquid hydrogen	
Maximum commercial load*, kg	25000	25400	
Flight distance, km	6000	6100	
Cruising speed, Mach's number	0.820	0.820	
Take-off mass, kg	195 000	145 000	26
Maximum landing mass, kg	108 700	97 880	10
Mass of field fuel, kg	62 300	21 200	65.9
Volume of fuel tanks m^3	82.7	313	278
Wing area, m^2	322	263	18.2
Specific load on the wing, kg/m^2	606	552	8.9
Specific fuel consumption, kg · h/kg**	0.677	0.26	76.1
Wing span, m	47	43	8.5

* Calculated for 272 passengers and 739 kg of cargo.

** Per 1 kg of thrust.

take-off mass which, in its turn, leads to the decrease of the engine mass and size, the plane and wing sizes as a whole. Being 30 times as high as in kerosene, the heat absorbing ability of liquid hydrogen allows using it in the cooling systems of the engine parts and in the plane as a whole [26]. A comparison of operation characteristics of subsonic aircrafts working on kerosene and liquid hydrogen [36] is presented in Table 33. As is evident, the aircraft filled with liquid hydrogen shows better tactical and technologic-and-economic characteristics as compared to the aircraft on kerosene.

Its take-off mass is less by 20 %, landing mass — by 10 %, and the mass of filled fuel — by 65.9 %. The wing area, load and span are less in the plane filled with hydrogen by 18.2; 8.9 and 8.5%, respectively. Economic characteristics include specific consumption of fuel which is by 76.1 % lower in case of liquid hydrogen. The decrease of necessary fuel reserve (and as a result a decrease of take-off mass and increase of useful load) is determined by high calorific power of hydrogen. The merits of hydrogen as fuel for aviation and cosmonautics are described in detail by A.N. Podgorny [19]. The mass of hydrogen fuel in modern planes is usually thrice more than that of the useful cargo. Thus in *Boeing-707* the fuel reserve is 80 t while the useful cargo weighs only 15 t. If kerosene (80 t) will be changed by 30 t of liquid hydrogen, the useful load may be increased to 60 t. According to [19] the growth of the plane flight speed is accompanied by the decrease of specific impulse of engines. In this connection the use of hydrogen as fuel is especially promising for the supersound aircrafts, since under hydrogen combustion the specific impulse of engines increases 2.5–2.7 times compared to planes on kerosene. Thus, engines on hydrogen permit performing more economic flights of the aircrafts with higher Mach's numbers (MN) than those on ordinary fuels. Optimization of parameters of the aircrafts on hydrogen, has shown that the highest flight distance is reached when M = 6, optimal value for the aircrafts on ordinary fuel is M = 3. The flight distance of the plane on liquid hydrogen is 1.5 times more at equal take-off mass.

According to the work [19], owing to low emissive power of hydrogen flame, the thermal state of the combustion chamber walls of the liquid-propellant rocket engine (LPRE) improves. The efficient engine cooling by means of hydrogen allows the operation process in LPRE to be organized at higher gas temperatures than in front of turbine and at high pressure in the compressor, that permits to additionally decrease the specific consumption of fuel by 15–20 % and to increase the specific thrust. Under these conditions the engine operation resource increases by 25% at simultaneous decrease of labour capacity and cost of the power plant maintenance. Low values of energy and broad limits of ignition of hydrogen mixed with air provide the no-failure operation under the engine starting at various height and at different temperatures of the environment.

It would be noted that the aircraft on liquid hydrogen has only one negative structural peculiarity — the volume of its fuel tanks exceeds 2.78 times that of the ordinary aircraft. Physico-chemical and energetics peculiarities of hydrogen as the energy-carrying agent require high carefullness when operating with the internal combustion engine (ICE) and liquid-propellant rocket engine (LPRE) on hydrogen. High hermetics of the tank and pipes, their strength, selection of materials resistant in the medium of liquid and gaseous hydrogen are required because of possible hydrogen losses. The planes and aircrafts on hydrogen would be equipped with the systems of control for the presence of even low concentrations of hydrogen and with automated fire safety systems.

A comparative analysis made in the work [26] of the ordinary transport aeroplane for 400 passengers with the flight range of 10 000 km, and supersonic plane for 234 passengers with the flight range of 7800 km on hydrogen and kerosene has shown that the use of hydrogen as fuel promotes the gain in fuel reserve about 64–75 %, in plane mass — about 25–51 %, in engine thrust to 12–49 %. The plane being transferred to hydrogen fuel (instead of kerosene), the flight range for the subsonic aeroplane will increase 2.0–2.1 times, for supersonic one, 1.6–1.7 times. Relative characteristics of supersonic two-cycle engines on kerosene and hydrogen during supersonic flight (H = 18 km, Mach number M = 2.2) at T_g = 1600 K, m = 1.5–1.8; k = 13–16 (T_g — gas temperature in front of turbine; k — pressure rise extent in the compressor) are presented in Fig. 82. It is seen that the hydrogen engine provides for the 1.5 times higher thrust

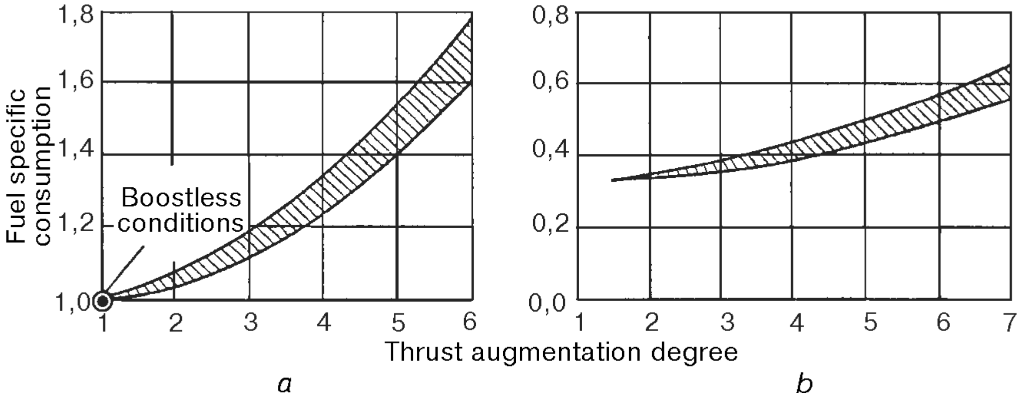


Fig. 82. Relative characteristics of supersonic two-loop engines on kerosene (*a*) and hydrogen (*b*) [26]

in flight without afterburner, which improves the efficiency of flight on afterburner.

There was also considerable success in using liquid hydrogen fuel in new designs of the subsonic and supersonic passenger aeroplanes. A demonstration flight of the passenger plane TU-155 on liquid hydrogen was performed in April, 1988 in the USSR. Works on creation of passenger aerobus with the engine on hydrogen fuel have been carried out in Germany from 1990. The NASA space programs widely use liquid hydrogen or its mixture with solid hydrogen as fuel for spacecrafts.

It would be noticed that the development of hydrogen energetics will permit the flights of piloted spacecrafts to the solar system planets, first of all to the Mars and Venus, to be realized in the 21st century. The use of hydrogen and oxygen as fuel simplifies the life-support of the crew under the long-term space flights. The matter is that the climate and atmosphere content are rather far from being like to those of the Earth. For example, on the Mars, efficient temperature is 216 K (temperature variations near the surface $\Delta T = 20–30$ K), while oxygen content in volume fractions is only 0.15 % (at 95 of CO_2, 2.7 of N_2, 1.6 of Ar). Oxygen is a component of soil elements (mass, %): SiO_2 — 45, Fe_2O — 18, Al_2O_3 — 5, MgO — 8, CaO — 5, SO_2 — 8. Thus the renewable energy source being available, the future astronautes will be able to produce oxygen from various raw materials on planet Mars. The flight of astronautes to the Mars will allow to answer the question: «Does life exist on the Mars?». Special investigations have proved availability of water on planet Mars — the condition necessary for life origin and development. Excessive amounts of carbon dioxide available on the Mars are required for the support of bacterial life. Thus, scientists think that bacterial life exists on the planet now [37]. Low temperature on contemporary Mars, according to I. A. Rezanov [37] could not extinguish life on the Mars. Great amounts of bacteria were found on our planet in its permafrost. On the

Mars with permafrost of 2 km and above, in the opinion of our scientists, «the living bacteria are developing both within this layer and under it, where underground waters are undoubtedly available».

Composition and properties of the Venus atmosphere as well as of its clouds have been investigated with the help of spacecrafts of the type of *Venera 1 — Venera 10* launched in the USSR. It has been established that the Venus is surrounded with dense atmosphere containing (vol. share, %): CO_2 — 96, $N_2 \sim 4$, CO — $3 \cdot 10^{-3}$, $SO_2 \sim 1.5 \cdot 10^{-2}$, O_2 — $5 \cdot 10^{-4}$, water vapours H_2O — 0.1–0.4 %; the upper contents of H_2S, CO_2, O_3, NO, NO_2, etc., molecules were determined as well as the efficient temperature of 230 K on the surface, diurnal temperature variation near the surface $\Delta T = 1$ K, and at the height of 50–80 km $\Delta T = 15$–20 K; the atmosphere pressure near the surface equals 9 MPa; gas density is 60 times as high as in the Earth atmosphere. Planet Venus possesses dense helium-hydrogen atmosphere at the height of 500–700 km. Above 700 km one can observe a hydrogen corona which is less dense than the Earth's one. The period of the Venus revolution about the Sun is 224.7 Earth days (243 Venusian days), the duration of the solar day is 116.8 Earth days. The research stations of the Earth inhabitants being organized on the Venus, oxygen may be obtained from CO_2 and water — by water vapour sorption.

The structures of spacecrafts (SC) of the series *Venera-1-Venera-16* were continuously improved [38]. If the carrying capacity of the first SC *Venera 1* (launched on February 12, 1961) was 643.5 kg, the mass of SC *Venera-16* launched to the orbit on June 7, 1983, was 5300 kg. SC *Venera* were equipped with a complex of scientific equipment, permitting to analyze automatically the atmosphere, aerosols, surface rocks, characteristics of solar radiation, electrical activity in the atmosphere, pressure, temperature and other parameters and to transmit the measurement results to the Earth. Solar batteries and power propulsion plants provided the airborne energy and engine correction energy.

The spacecrafts *Mariner-1, Mariner-2, Mariner-5* [38] were launched for the Venus investigation by the USA. The spaceship *Mariner-10* was launched in 1973 to investigate the Venus and Mercury from the fly-by trajectory. The SC mass was 526 kg. The spacecraft *Mariner-10* was launched on 03.11.1973, and on 05.12.1974 it flew by the Venus at the distance of 5770 km and transferred to the Earth about 3700 photographs of the cloud cover of the planet, including data about the atmosphere circulation. Then, after a perturbational maneuver in the Venus gravitation field, SC *Mariner-10* entered a heliocentric orbit passing around the Mercury. These passages around the Mercury (at distances: ~ 750, 48 000 and 318 km) were used for investigations, and about 3000 photographs with resolution about 50 m were transferred to the Earth. It has been established that the planet is rich in craters, resembling the lunar ones, but less deep. The Mercury has the rarefied helium atmosphere and considerable magnetic field (magnetic field intensity at the equator ~ 0.14 A/m and at the poles — ~ 0.56 A/m).

It is clear from all stated above that when using hydrogen fuel in combination with plasma hydrogen-nuclear plants one can create the research stations of the solar system planets.

In connection with ecological problems researchers investigate more and more widely a possibility of the use of liquid hydrogen as fuel in aviation as well as liquid hydrogen in combination with liquid oxygen in the rocket engineering (*Space Shuttle*, USA, H-1, Japan, etc.), in cosmonautics for spaceships *Apollo* (USA), *Energia-Buran* (USSR) and other giant rockets and space systems of multiple use (X-33, RLW, USA, TU 2000, N1, Russia) capable to deliver large useful cargo to the Earth's orbit and to provide a possibility of interplanetary flights. Hydrogen and oxygen obtained by electrolytes are often used as fuel on spaceships for the flight orbit correction.

7.3. Motor transport

Studies on hydrogen utilization in the internal combustion engines (ICE) have been carried out from the mid-20th century. ICE on hydrogen fuel were used for the airships *Zeppelin* in 1928 under the flight across the Mediterranean Sea [19]. During the blockade of Leningrad, in the period of the Great Patriotic war, about 600 vehicles worked on hydrogen fuel. In 1942 300 ICE from Moscow Antiaircraf Defense Service also worked on hydrogen fuel. Hydrogen from the barrage balloons, which had worked out their term, served as the fuel source. The history of development of the studies on hydrogen utilization in ICE has been considered by the authors of [19, 39–41]. Structure peculiarities of gasoline engines whose waste gas toxicity depends on the composition of petrol-air mixture with excess-air coefficient $\alpha = 0.7–1.4$ do not permit creating the fuel combustion conditions ensuring ecological purity of waste gases. That is why most researchers want to find ecologically safe fuel. It is hydrogen. It possesses a number of peculiarities as compared to gasoline or other hydrocarbon fuels for ICE. Physico-chemical properties of hydrogen against those of gasoline are presented in Table 34 [22, 42]. As is evident, wide concentration limits and low ignition energy, high combustion and flame spread rates are characteristic of hydrogen. These fuel properties permit new organization of the ICE operation process on hydrogen [40, 41, 43].

Wide ignitability range of hydrogen mixed with air and oxygen allows performing high-quality control of the combustion process in the internal-combustion engine. Allowing for high cost of hydrogen, A.N. Podgorny and I.L. Warshavsky used hydrogen as an additive to ordinary fuels [19, 40, 43]. Such a method has opened a new approach to organization of the operation process in ICE. Hydrogen possesses such physico-chemical properties as high combustion

Table 34

Physico-chemical parameters of fuels based on hydrogen and gasoline

Parameter	Hydrogen	Gasoline
Ignition energy MJ	0.02	0.25
Quenching distance, cm	0.06	> 0.25
Ignition temperature °C	585	440*
Ignition limit vol. fraction, %	4.7–74.2	0.59–7.1
Diffusion coefficient cm^2/s	0.63	0.08
Flame front spread velocity, cm/s	270	30
Low heating value		
kJ/kg	1.21 · 105	4.44 · 104
kJ/mol	1.078 · 104	—
Stechiometric quantity of air Per 1 kg of fuel		
kJ/kg	34.2	14.5
kJ/mol	2.38	—
Calorific power of fuel mixture at б = 1 In mixture with		
Air, kJ/m^3	3.19 · 103	3.71 · 103
Oxygen, kJ/kg	1.34 · 104	—

* Combustion temperature (CT) of methane equal to 538 °C is also lower than that of hydrogen. Gasoline combustion temperature by [40] equals 257 °C.

and flame propagation velocity, wide concentration limits of burning, as well as high diffusion mobility in the mixture hydrogen-air-gasoline vapours, and this results in the acceleration of burning (combustion) reaction of air-hydrogen-gasoline mixtures. It has been established, that under introduction of 5 %-addition of hydrogen mass to gasoline of lower grades the maximum power of ICE GAS-24 and VAZ-2101 remains at the level of the base engine. Even under 1–6 %-addition of hydrogen to gasoline the fuel efficiency increases by 30–40 % and thus, fuel consumption decreases [44].

The use of hydrogen additions removes one more shortage of motor engines, determined by the sharp decrease of ICE efficiency from 30 to 10 % at partial loads of the engine at cross-roads under operation in the city as well as under the decrease of the motion velocity. Hydrogen addition being introduced in gasoline, the ICE efficiency rises to 30–40 %. The latter is determined by the fact that the limit inflammation value for hydrogen is wider than for gasolines. The hydrogen inflammation limits are in the range of 4.7–74.2 % in volume, and for gasoline — 0.59–7.1 (Table 34) [44]. Hydrogen addition introduced even in the volume of 1% practically leads to 10-fold decrease of emission of CO, NO_2,

CH_4 and other hydrocarbons in waste gases. Hydrogen additions to the fuel systems of ICE increase the detonation resistance of the formed fuel system by 8–10 points by the octane number scale. The 10 %-addition of hydrogen to the fuel system increases the detonation capacity by 13–15 points and fuel, as to its properties, corresponds to the highest grades of gasolines: AI-93 and AI-98. Hydrogen additions being introduced to ordinary hydrogen fuel, the fuel efficiency rises and ejections of ecologically harmful substances considerably decrease.

Achievements in the field of nanotechnologies simplify considerably the problem of hydrogen use in cars. In the work [44] hydrogen was stored on board a car in hydrogen accumulators on the basis of hydrocarbon nanostructures. Hydrogen pressure in accumulator was 10 MPa. Mass content of hydrogen was 7 %, that exceeded thrice hydrogen content in accumulators on the basis of intermetallide Fe-Ni, used in transport [36]. The systems of ICE feeding with hydrogen-gasoline mixtures and hydrogen are considered in the works [19, 20, 39–41].

The profound theoretical and experimental investigations of the operation process of ICE on hydrogen and gasoline-hydrogen mixtures were conducted as well. The formation mechanism of harmful impurities was investigated depending on the external and internal formation of hydrogen-air mixtures. Data on the influence of hydrogen additions on the degree of increasing the fuel efficiency and the level of harmful impurities ejection in the environment [40] are presented for various kinds of fuel in Table 35.

Investigations conducted at the Institute of Industrial Machine-Building Acad. Sc. of the Ukr.SSR resulted in creation of hydrogen accumulators both on the basis of metal hydrides [40, 45], and energy-accumulating substances (EAS) [46], in creation of universal feeding systems for motor-car ICE providing their

Table 35

Increase of fuel efficiency depending on hydrogen addition [19]

Fuel kinds	Level of harmful impurities g/km			Increase of efficiency, %
	CO	C_nH_m	NO_2	
Gasoline (GAS-24), Russia	8.0	2.3	2.0	—
Natural gas (Toyota, Japan)	1.7	0.49	1.01	2–3
Mixture of gasoline with hydrogen (GAS-24)	0.5	0.4	0.1	20
Mixture of gasoline with hydrogen (RAF-2203). Latvia	0.8	0.6	0.2	25
Hydrogen (Ford B053, USA)	—	—	0.205	20–25

stable operation independent of the nature of fuel — hydrogen, gasoline or their mixtures.

The methods of onboard storage of hydrogen in a vehicle were developed by the beginning of the 80's. In cooperation with other organizations they manufactured the auxiliary systems for the ICE operation on hydrogen and benzohydrogen mixtures and tested the motor cars models: VAZ *Zhiguli*, AZLK *Moskvich*, GAZ-24 *Volga* and GAZ-69, lorries ZIL-130, microbuses RAF and UAZ.

It was supposed that hydrogen as fuel of motor transport ICE will be widely used by 2000 [19]. The use of hydrogen in the form of additives to hydrocarbon fuels would be the first step to hydrogen use in the motor transport. This method could decide in the main the problem of the environment pollution with toxical emissions under fuel combustion in ICE.

ICE efficiency in the whole range of workloads at high effective power has been established when investigating ICE work on hydrogen with variable degree of compression. The indicated efficiency of ICE on hydrogen was 37.5–43 %; from the data of [270, 271] it was 41–52 % and exceeded that of ICE on gasoline (32–46 %) under the same operational parameters (the number of engine revolutions, indicated pressure, air excess). Detonation resistance of hydrogen-air mixtures of different composition and its dependence on the degree of compression have been studied. The shock way propagation velocity for the hydrogen-air mixture with $n = 1.3$ has been established as 680 m/s. This value is considerably lower than the shock wave velocity under detonation estimated by the value 2–4 km/s. The process of hydrogen combustion in ICE, proceeding with flame front spread velocity of 200–300 m/s, evidences for detonationless combustion of hydrogen [23]. When burned in ICE, hydrogen forms water vapours and only certain amount of nitrogen oxides. Sulphur and carbon oxides are absent. Thus, the use of hydrogen as fuel for ICE simplifies essentially the problem of waste gas toxicity.

Hydrogen may be used as fuel for ICE both in gaseous and liquid states, the same is with hydrogen bound with hydride compounds lightly dissociating with hydrogen release, e.g.: $LaNi_5H_6$, $TiFeH_{1.9}$, $MgNiH_4$, $MnNi_5H_6$, VH_2, $VNbH_3$ used in hydrogen accumulators [19, 34, 40, 41, 45]. Hydrogen density in metal hydrides (as was noticed in Ch.6) are considerably higher than in liquid hydrogen.

A large series of studies on the use of hydride accumulators as the hydrogen source in motor engines converted to hydrogen fuel have been carried out [22, 23, 49]. Such a proposition was put forward by Meijer in 1970 [50]. Necessary amount of hydrogen can be purposefully released from hydrogen accumulators with time, changing the temperature. This property of hydride accumulators permits introducing hydrogen with high efficiency into the motor fuels (see, above) as 5–15 mass % hydrogen addition (from gasoline consumption).

Interesting results were obtained when using hydrogen as diesel fuel. It appeared that 4.3–5.3 % of hydrogen being added to diesel fuel, lowers the fuel consumption by 15–20 %. The amount of nitrogen oxides, carbon oxide, hydrocarbon, and especially carcinogenic 3,4-benzpyrene, free radicals and ash waste also decreased (by 30 %). That is why it is considered that hydrogen possesses great prospects as to its use as the motor fuel for city transports, since it is harmless for the environment. That is the acute problem of the present. Leading research institutes and the largest manufacturers of various kinds of the motor transport, fuel elements have been working over this problem decision during many years. The networks of gas-filling stations are developed in Germany, France, USA. From the data of [51] the Bundeswehr (Germany) considers a possibility to use hydrogen fuel on the ships and tanks.

The increase of ICE fuel efficiency without lowering the operational characteristics, the decrease of waste gas toxicity and search for new types of fuels and energy are urgent problems of the present. Some firms (in particular *Daimler Chrysler, BMW, EnBW* (Germany), *Volvo* (Sweden) *Ford* (USA), *Ballard Power System Inc*. (Vancouver, Canada), *Mazda*, *Honda*, *Toyota* (Japan), *Renault* (France)) try to use fuel cells on hydrogen as well as galvanic cells [2, 28, 52], photoconverters of solar energy into electric one [53], etc., as energy sources in the perspective and experimental prototypes of motor cars. The greatest success has been reached when using fuel cells on hydrogen with protein-exchange membrane — a solid polymer electrolyte [54]. Five types of FC are distinguished depending on the nature of used electrolytes: with alkali electrolyte (AFC), phosphoacid (PAFC), solid-polymer (SPFC), melted carbonate (MCFC) and solid oxide (SOFC) electrolytes [54–57]. The USA firms (*United Technology, Fuel Cell*), Canadian *Ballard* and firms in Japan have elaborated fuel elements with solid-polymer and phosphoacid electrolytes, conducted long-term pilot-industrial testings of the power plants (PP) of 12 to 11 000 kW and brought them to the world market. The power plants of 100–250 kW used in the motor transport are in the greatest demand.

The *Daimler Chrysler* company has reached considerable progress now in the field of creation of electric motor cars. First vehicles on hydrogen fuel were created by the company in the 80's. It planned to develop production and supply to the market of various transportation facilities on hydrogen by 2004. To reach the objective the leading companies in one or another branch of «*hydrogen*» motor industry make production alliances, corporations. The *Ballard Power System* (Canada), which has already made three generations of electric motor cars with fuel cells on hydrogen, takes leading positions on the American continent. The firm is the world leader in manufacturing fuel cells on hydrogen. The *Daimler Chrysler* corporation (Germany) also takes key positions in motor industry. These two leading corporations (*Ballard Power Systems* and *Daimler Chrysler*) have formed a joint venture XCELLSIS to develop the transport vehicles on hydrogen fuel capable to win the market. Creation of standardized systems of fuel cells (batteries) and auxiliary equipment for electric motor car is a strategic task of this venture. The *Ford Motor* company (USA) joined this alliance the same year. As a result, that ternary alliance formed a joint venture ECOSTAR — the leading producer of motors for the power units of electric motor cars on hydrogen fuel [54].

It would be noted that even in 1982 the Scientific Productive Company (SPC) *KVANT* (Moscow) and *RAF* (Riga) created the first in the world experimental hydrogen microbus *KVANT-RAF* [34]. The microbus *KVANT-RAF* was ecologically pure and demonstrated high technical and economical characteristics in tests. Basing on the results of tests of the pilot prototypes of the motor cars and buses on hydrogen fuel, made (reconstructed) in different organizations, the Ministry of Motor Industry of the USSR made a decision about production and further operation in the cities of the USSR of the pilot lot of microbuses *RAF* (200 units), operating on hydrogen and benzohydrogen mixtures. However this decision was not realized because of the political reorganization processes (1990–1991).

Today, the principle of the use of the bound hydrogen and hydrogen feeding the fuel cells (FC) in the power plants proved most expedient for the motor car transport from a set of different tested methods. Nowadays hundreds of «hydrogen» buses and thousands of cars on hydrogen fuel are driven along the streets of dencely populated cities of the world. Hydrogen is stored at gas-filling stations for cars and buses in a form of compressed gas or liquid hydrogen. Thus in Berlin, the first station for filling buses on fuel cells with hydrogen was opened at the bus station of the transport enterprise *Berliner Verkehrs-Betriebe* (BVB) in October 2002. Hydrogen is stored at filling stations both as the compressed gas and in liquefied form at cryogenic temperatures (T_{melt} of H_2 is 13.813 K (–259.337 °C); $T_{\mathrm{boil.}}$ of H_2 is 20 258 K (–252.892 °C)). The equipment for hydrogen storage was supplied by the well-known company *Linde*. Gaseous hydrogen is obtained with the help of electrolysis plant. The pilot buses will work in three climatic zones of Europe: Berlin, Lisbon, and Copenhagen. The obtained experience will be used in development of the vehicles on hydrogen fuel. In 2003 the *BVG* company plans to open one more hydrogen fuel-filling station [58].

It was informed [59] that by the end of 2002 30 buses of *Citaro* model will be in operation in 10 European cities. Fuel cells on hydrogen will be used in these buses as the power unit. The project of such a bus of *Nobus* model was developed in 1997 by *Mercedes* Company (Germany). The compressed hydrogen stored in 7 cylinders of 150 l each on the roof serves as fuel in this case. Fuel cell supplies current to 2 electric motors of 75 kW each. The *Daimler Chrysler* corporation invested $16\cdot10^9$ USD in the project of European bus *Citaro*. The power of electromotive power unit of the bus is 300 kW. Reserve of *Citaro* bus motion is 200–300 km.

The *Volkswagen* company (Germany) has produced a motor car equipped with FC on hydrogen. Power consumption by a vehicle on FC is equivalent to consumption of 5.2 l of gasoline for 100 km, that is by 40 % less than in standard *Volkswagen* with analogous parameters of the running gear (8.5 l) and the body. *BMW* Company (Germany) has also made a vehicle on fuel cells which was highly appreciated at a summit on sustainable development in Johannesburg.

Automobile companies of the USA and Japan carry out active works in the field of hydrogen energetics. *Ford* company represented a car on FC ready for series production. A small lot of 40 hybrid motorcars on the basis of *Ford Focus* model is planned to be produced for testing and operational development. The motor cars will be equipped with FC and accumulators which are supposed to be used in the process of the electric motor car operation as additional energy sources.

On December 1, 2002, Japan motor industry companies *Toyota* and *Honda* solemnly handed Japanese consumers dozens of cars on FC they have produced. The head of *Honda* H. Iosino soon left for Los Angeles to conquer the American market. A ceremony of passing hydrogen motor cars to their first users in the USA took place there. Six *Toyota* cars were given the California University and five cars the city of Los Angeles. It is planned that *Toyota* and *Honda* companies will master production of motor cars on FC filled with hydrogen.

Data presented prove that Germany, USA and Japan make actively researches and R&D work on development of efficient ecologically pure models of cars and buses with power units on the basis of electric motors, supplied with electric power generated by FC on hydrogen. To intensify scientific investigations and R&D in the field of works on creation of hydrogen engine and hydrogen infrastructure G. Bush, President of the USA, announced recently about the allocation of $1.7 \cdot 10^9$ USD for these purposes.

7.4. Hydrogen as Chemical Reagent and Nuclear Element

In D. I. Mendeleyev's periodical system hydrogen occupies its place in a square number 1 of the first period which is sometimes called preliminary period. This period includes two elements — hydrogen ($_1$H) with the atomic number one and helium ($_2$He) with the atomic number two. Hydrogen has three isotopes possessing the same nuclear charge (1+) and different mass: atomic hydrogen with atomic mass equal to one ($^1_1$H); hydrogen isotope $^2_1$H called deuterium ($^2_1$D) — heavy hydrogen, and the isotope H — tritium — superheavy hydrogen 3.0170. The average atomic mass of hydrogen is 1.00794, deuterium — 2.0147, tritium — 3.0170. Hydrogen isotope $^1_1$H content in natural waters equals 99.9844 %, deuterium $^2_1$D — 0.0156 %, tritium — traces. The same hydrogen / deuterium ratios are contained in the atmospheric water vapours. The content of tritium ($^3_1$T in the atmosphere is about $1 \cdot 10^{-7}$ %. Tritium is formed in the atmosphere as a result of the collision of deuterium and atoms of light hydrogen isotope; ${}^{1}_{1}\mathrm{H}({}^{2}_{1}\mathrm{D}, \beta^{-}){}^{3}_{1}\ \mathrm{T}$ [60]. Deuterium is synthesized in the atmosphere at the expense of neutrons formed as a result of continuous effect of spatial rays on the atmosphere components. According to [60] the intensity of space radiation is rather high that ensures the falling of one neutron on 1 cm^3 of the Earth globe every other second. The space radiation is even more intensive in the upper layers of the atmosphere. Tritium is formed there by the reaction of the basic nitrogen isotope ${}^{14}_{7}\mathrm{N}$ interaction (its content in nitrogen is 99.635 %) with neutrons of the space ray:

$$ {}^{14}_{7}\mathrm{N} + {}^{0}_{1}n = {}^{3}_{1}\mathrm{T} + {}^{12}_{6}\mathrm{C}, \tag{150} $$

$$ {}^{14}_{7}\mathrm{N} + {}^{0}_{1}n = {}^{3}_{1}\mathrm{T} + 3_{2}\,{}^{4}\mathrm{He}. \tag{151} $$

The atoms of tritium formed by any of the presented reactions, are radioactive (β-emitters) and relatively stable — their half-life is 12.26 [61] — 12.34 years [62]. Under radioactive decomposition tritium emits β-particles and converts to helium-3

$$ {}^{3}_{1}\mathrm{T} = {}^{3}_{2}\mathrm{He} + \beta, \tag{152} $$

being of great importance for thermonuclear synthesis (see, below).

The reaction of tritium synthesis from deuterium under the effect of neutrons proceeds not only in the atmosphere but also in water in the light-water nuclear reactor, as well as in water used for cooling nuclear reactors. The cooling water contains usually about 0.02 % of $\mathrm{D_2O}$ and becomes radioactive not only due to the appearance of radioactive isotope of oxygen ${}^{19}_{16}\mathrm{O}$ in it (See, Chapter 9) but also under direct addition of neutrons to deuterium; ${}^{2}_{1}\mathrm{D}({}^{0}_{1}\mathrm{n}, \gamma)\ {}^{3}_{1}\mathrm{T}$.

It would be noticed that tritium was synthesized for the first time by the bombardment of deuterium compounds by deuterium ions D^{+}. Tritium is obtained in big volumes by the bombardment of the isotope lithium-6 in nuclear reactor by fast neutrons [62]. Deuterium was obtained by electrolysis of heavy water ($\mathrm{D_2O}$). In the reaction of two deuterium nuclei interaction there proceeded their disproportionation by the reaction

$$ 2\,{}^{2}_{1}\mathrm{D} \to {}^{3}_{1}\mathrm{T} + {}_{1}\mathrm{H}^{+} \tag{153} $$

with the formation of tritium (${}^{3}_{1}\mathrm{T}$) and protium (${}_{1}\mathrm{H}^{+}$).

As to its chemical properties, hydrogen displays high reactivity inherent in alkali metals and halogenides [60], hydrogen being close to them by the degree of oxidation 1- (H^{-}) and formation of molecular hydrogen $\mathrm{H_2}$ (an analog to molecular halogens Γ_2; Γ – F, Cl, Br, I). That is why, D. I. Mendeleyev placed hydrogen both in the first and seventh groups of the Periodical system.

Hydrogen is widely distributed on planet Earth and as to the number of atoms it occupies the second place [17.25 %]. Hydrogen forms compounds with many chemical elements, including the compounds which migrate in the Earth crust with high velocity. The basic mineral of hydrogen — water composes 90 % of the Earth crust mass. Hydrogen is a component of the hard and brown coals, slates, oil and natural gas. Oil and natural gas may be changed by hydrogen in the future. By 2050 hydrogen share in the economy will be 62 % and that of liquid organic fuel only 11 %. The estimated predictions show that the share of liquid fuel in economy can be 2.2 %, by 2075 while the share of hydrogen will be 73.3 %. So, it may be supposed that the future in energetics and economy belongs to hydrogen. Even by 2000 such companies as *Electrometallurgie GmbH*, *Energy Convertion Devices, Ergenics*, *Ovonics* produce on large scales hydrogen batteries, electrohydrogen computer batteries, electric car batteries, heat pumps, hydrogen storage, air conditioning. High reactivity and power intensity of hydrogen are used by numerous companies of the world which work in the field of development of hydrogen energetics and hydrogen economy on the basis of hydrogen power systems for electric energy generation, motor and sea transportation, in air- and spacecrafts [63, 64].

One more peculiarity of hydrogen as the atmosphere component would be noticed. Hydrogen content in the Earth atmosphere is only $5 \cdot 10^{-5}$ vol. %. Hydrogen continuously gets into the atmosphere, as a result of the functioning of bacteria of biomass hydrogen fermentation. Hydrogen is not accumulated in the atmosphere, since, possessing the least specific weight, it passes to the upper layers of the atmosphere. At the heights of 150–20 km the atmosphere circulation proves insufficient for continuous uniform mixing of the air environment. Thus, the atmosphere is divided into zones enriched by one or another component. From the data of [38] atomic oxygen dominates at the height of 150–180 km. Molecular oxygen dissociates at the height of above 100 km, nitrogen above 200 km. Above 200–220 km there is the beginning of the zone of «prevalence of light helium atoms, and especially hydrogen». It remains unclear how hydrogen penetrates through the high-thickness zone (30 km) of atomic oxygen. The rate of hydrogen interaction with oxygen with pressure increase to 10^7–10^8 Pa is $(1.5–1.6) \cdot 10^{-4}$ sec [65]. Hydrogen also displays high affinity for atomic nitrogen forming the layer which exceeds 50 km in the upper atmosphere. Deuterium formation under the effect of neutrons on atomic hydrogen, synthesis of tritium and ditritium under the bombardment of nitrogen ${}^{14}_{7}N$ nuclei by neutrons, as well as high chemical affinity of hydrogen for atomic oxygen and nitrogen ($\Delta GH_2O = -237.24$ kL/mol, $\Delta GH_2O_2 = -120.4$ kJ/mol, $\Delta GNH_3 = -16.71$ kJ/mol, etc.) create the protective barrier to the effect of space radiation on planet Earth. The interaction velocity of atomic and molecular hydrogen with oxygen and atomic nitrogen increases under ultraviolet and space neutron irradiation. Thus the hydrogen «cap» or hydrogen «cover» shrouding the Earth atmosphere plays an important part in protection of Earth's biota from the «affecting» extraterrestrial radiation. This problem will be considered in detail in Chapter 8.

Atomic hydrogen possesses especially high reactivity. It takes part in numerous reactions where molecular hydrogen is inert. Two new forms of hydrogen are distinguished: H^- (hydride-ion) and H^+ (protium). The reduction properties of H^- ion and atomic hydrogen $H^O{}_{(\Gamma)}$ are close to the reduction properties of alkali metals, which is evidenced by reaction potentials given below [66].

$$H_2 + 2e = 2H^-, \qquad E^0_{H_2/H^-} = -2.25\ V, \tag{154}$$

$$H_2 + e = H, \qquad E^0_{H^+/H^-} = -2.1065\ V, \tag{155}$$

$$H_2O + e = H_{(\Gamma)} + OH^-, \qquad E^0_{H_2O/H} = -2.9345\ V, \tag{156}$$

$$Na^+ + e = Na, \qquad E^0_{Na^+/Na^-} = -2.714\ V, \tag{157}$$

$$K^+ + e = K, \qquad E^0_{K^+/K^-} = -2.925\ V, \tag{158}$$

$$Rb^+ + e = Rb, \qquad E^0_{Rb^+/Rb^-} = -2.925\ V, \tag{159}$$

$$Cs^+ + e = Cs, \qquad E^0_{Cs^+/Cs^-} = -2.923\ V, \tag{160}$$

Most hydrides of metals and metalloids are formed under the contact with atomic hydrogen. Metals of the group VIII of D. I. Mendeleyev's Periodical system have affinity for the adsorption of molecular hydrogen and, as a result of hydrogen atomization — for catalytic acceleration of chemical reactions of hydrogenization of organic compounds. Hydrogen is chemosorbed by metals: Pt, Pd, Rh, Ni, Fe, etc. [67–73]. Under the chemosorption the ratio between chemosorbed molecular ($H_2{}^{\delta+}$) and atomic hydrogen ($H^{\delta+}$, $H^{\delta-}$) depends on the nature of a metal and conditions of its preparation as a catalyst [67–73]. Hydrogen, as a reagent, plays an important role in the processes of natural gas conversion into multitonnage liquid simply-transportable chemical products. Oil and liquid fuels reserves being exhausted, the role of hydrogen increases in production of methanol, dimethyl ester, synthesis of liquid alkanes by the Fischer-Tropsch reaction, etc.

It has been established that methanol can be used both in the mixture with gasoline and separately as the substitute of diesel fuel, etc.

Gaseous hydrogen obtained by electrolysis and other methods exists in a form of two-atom H_2 molecules. Two-atom molecules of H_2 possess the strong interatomic bond. The reaction of two-atom hydrogen molecule dissociation is accompanied by energy absorption

$$H_2 + 2H + 429 \text{ kJ/kmol } [6] \tag{161}$$

The extent of H_2 dissociation at pressure of 0.101 MPa and temperature (T, K): 300; 1000; 3000 and 5000 is equal to (CH_2, %) — $1 \cdot 10^{-34}$; 0.0009; 7.85 and 95.5, respectively [6]. Molecular hydrogen displays properties of a strong reducing agent at high temperatures, reacting with metal oxides, metals, metalloids.

Hydrogen is a wonderful ecologically pure chemical energy carrier. As it follows from the reactions (147) and (148) water is a finite product of hydrogen oxidation with oxygen. The oxidation reaction proceeds too slowly at low temperatures, at 800 K — with an explosion. The burning being initiated by a spark, flame — it is accompanied by an explosion. The batching of hydrogen and oxygen when they are supplied to the chamber results in the controlled process with obtaining thermal energy. Complete combustion of 1 volume of hydrogen requires 2.335 volumes of the air. Atomic hydrogen initiates the process of hydrogen combustion in oxygen. Thin hydrogen jet being supplied to the environment atmosphere the friction of hydrogen/air interfaces results in hydrogen self-ignition with formation of the jet of invisible high-temperature flame. Hydrogen combustion mechanism, when oxygen or gaseous halogenides (F_2, Cl_2, Br_2, I_2) are used as oxidizers, is the chain mechanism. The following elementary acts are established under hydrogen combustion in oxygen at 823 K [62]:

$$O_2 + H_2 = 2OH, \tag{162}$$

$$OH + H_2 = H_2O + H, \tag{163}$$

$$H + O_2 = OH + O, \tag{164}$$

$$O + H_2 = OH + H \tag{165}$$

with total reaction

$$O_2 + 2H_2 = 2H_2O \tag{166}$$

At a temperature of 473 K hydrogen restores CO_2 by catalytic reaction (catalyst Cu_2O)

$$4H_2 + CO_2 = CH_4 + 2H_2O \tag{167}$$

with methane formation [62]. At 873 K molecular hydrogen reacts with coke with methane formation (CH_4), and at 2273 K — with acetylene (C_2H_2) formation.

The reaction of hydrogen combustion in oxygen is used for a long time for obtaining high temperatures. Hydrogen flame reaches 5000 °C in a special Langmuir burner which uses energy of atomic hydrogen recombination into molecular hydrogen. The present hydrogen torches using plasma balloons and plasma torches on H_2 and O_2 permit reaching 10 000 °C [60].

At the same time hydrogen isotopes may be even better «physical nuclear energy carriers». As was shown in Chapter 4, tritium is potential nuclear fuel for thermonuclear reactors which use the reaction between deuterium and tritium (D–T). It would be noticed that the reaction of thermonuclear D–T synthesis is not ecologically pure since helium-4 and neutrons are its products. Neutrons released in thermonuclear reaction, as was shown in Chapter 4, induce radioactivity in the structure materials of thermonuclear reactors. As a result, a thermonuclear reactor of synthesis also becomes biologically dangerous like the fission-type reactor. In this connection the idea of «ecologically pure thermonuclear synthesis» becomes leveled [74].

Thus the authors of [74] suppose that after the creation and completion of the thermonuclear reactor based on the D–T reaction, the development of thermonuclear energetics shall be directed to the mastering of assimilation of ecologically pure thermonuclear reactions (6), (7), as well as the reaction D — $^{3}_{2}\mathrm{He}$ (deuterium — helium-3 isotope).

$$\mathrm{D} + {}^{3}_{2}\mathrm{He} = {}^{4}_{2}\mathrm{He}\ (3.6\ \mathrm{MeV}) + \mathrm{H}^{+}\ (14.7\ \mathrm{MeV}) \qquad (168)$$

Fusion of deuterium and helium-3 nuclei occurs in this reaction with formation of α-particles of $^{1}_{2}\mathrm{He}$ and protium with total release of energy, equal to 18.3 MeV. It is considered that the main advantage of this reaction of thermonuclear synthesis is a considerable decrease of neutrons and deuterium accumulation by parasitic thermonuclear reaction of disproportionation D–D (see, reaction (153)).

Since there are no reserves of helium-3 on the Earth then the task to organize helium-3 production on space bodies is stated for the energetics with its participation could be realized. One of such conceptions is helium-3 production by processing of the Moon ground. Helium-3 being produced on the Moon, the expenditures for equipment supply to the Moon surface and helium-3 transportation to the Earth [74] will make considerable share of its cost. The alternative methods of helium-3 production on asteroids and other small bodies of the solar system are considered as well. The authors of the work [74] have fulfilled the project investigations on the estimation of necessary equipment, its delivery to the surface of celestial body, required energy and time for production of about 100 kg of helium-3 and its delivery to the Earth. To illustrate one of the possible variants of solution of the considered problem the authors of [74] present results of estimation of the basic engineering parameters of the transport system for the delivery of automatic complex for helium-3 production to the asteroid Fortune and supply of produced helium-3 to the Earth.

In the light of above stated we think it more pragmatic to realize thermonuclear synthesis of helium-3 at special plants on the Earth surface. Under the Earth conditions 0.00013 % of helium-3 accompany the major isotope of helium-4 (99.99987 %). It would be noticed that more rich complex deposits containing helium-3 are known in the territory of CIS countries.

7.5. Hydrogen and Industry

Hydrogen is widely used today as a reagent in chemical, petrochemical and food industries, metallurgy, microelectronics. About 95 % of hydrogen is used as a reagent in chemical and petrochemical industry, including, %: in ammonia production — 52, in oil reforming and cracking, hydrorefining of motor fuels — 38; in methanol production — 6, production of hydrochloric and nitric acids, synthetic resin, polymers, hydrogenation of fats, production of SLF by coal hydrogenation, etc. — 4. The volume of hydrogen used in chemical and petrochemical world industry in 1971, 1980 and 1990, was $7.68 \cdot 10^{10}$, $1.50 \cdot 10^{10}$, and $3.98 \cdot 10^{11}$ m^3, respectively. By the predictions the volume of hydrogen consumed in 2002 in the above branches of industry all over the world will make about 10^{12} m^3. The following amount of hydrogen was consumed in the USA in 2000 (10^9 m^3): 102 — for ammonia production, 108 — for oil refining, 62 — for synthesis of synthetic fuel, 56 — for methanol production and 40 in metallurgy. The total amount of hydrogen produced and consumed in the USA in 2000 was $368 \cdot 10^9$ m^3 [6, 75, 76]. The works on hydrogen use for coals liquefaction with the obtaining of liquid synthetic motor fuels and lubricating oils (see, below) are carried out all over the world. Hydrogen is used in metallurgy for production of rare metals by their reduction from oxides: molybdenum, tungsten, niobium, tantalum, etc. Scientific and experimental works are conducted on iron production by direct reduction from ores with the use of reducing gases produced at NHPP heated to 1200–1500 °C and containing H_2O + CO or H_2 [77]. Nuclear-metallurgic and nuclear-technological complexes producing electric power, high-potential heat and high-temperature reducing gases, synthesis-gas and hydrogen are developed all over the world. Their use in ferrous metallurgy is especially promising. Only the use of high-potential heat and reducing gases in steel and pig iron metallurgy will permit saving 30–40 % of cox and improving ecologic situation in numerous industrial regions [78]. It has been shown that, when using heat from complex power-radiation plant, hydrogen cost will be twice as low as the cost of hydrogen produced by other methods.

When expanding hydrogen consumption accompanied by the growth of demand, new processes will be developed for production of hydrogen and mixtures containing it (synthesis gas), which will lead to considerable increase of its production volumes and as a result, to the decrease of the cost for hydrogen and hydrogen-containing gases. As a result hydrogen would be able to substitute most energy sources and other kinds of fuel. The role of hydrogen in energetics will considerably increase. The transfer of high-pressure gaseous hydrogen and natural gas, their storage and distribution have considerable economic advantages over the electric energy. The basic advantage consists in a possibility to store them in great amounts and volumes.

Considerable volumes of hydrogen are used in microelectronics and laser technology, wave optoelectronics and other fields of new technology. High-purity hydrogen is widely used in research institutes when conducting investigations in the field of electrochemistry, synthesis of organic polymers, coal gasification with the aim to obtain synthetic motor fuels, lubricating oils, organic compounds, etc.

7.6. Hydrogen in Everyday Life

Hydrogen is more widely used in everyday life as power carrier in various power appliances and first of all in the devices of nontraditional energetics. Electric energy is obtained in these devices by means of photo-converters of solar, wind or sea tide energy. This energy is either directly used or converted into the power carrier — hydrogen. The latter may be accumulated in metal hydrides, pumped into the underground individual storages to be used as fuel for stove plates, heating systems, etc. [79, 80]. There are some prospects in hydrogen use as fuel in catalytic heat generators where hydrogen burns with colourless flame at low temperatures (200–220 °C) without polluting the environment. Nitrogen oxides are not formed at low temperatures and water is the only product of such hydrogen oxidation. Hydrogen mixtures with oxygen, containing no more than 4 % of hydrogen, are used for complete hydrogen combustion in catalytic generators. In this case one can observe its complete combustion. When using heat exchangers one can achieve almost 100 % use of the released heat, since it is not lost with the smoke gases [36]. Thus power devices based on the principle of catalytic hydrogen combustion are of considerable interest in hydrogen use for everyday life purposes [81].

The process of catalytic hydrogen combustion is ecologically pure and may be used successfully in the stove plates with hydrogen fuel for cooking, in absorptional refrigerators with hydrogen torch, module hydrogen systems of extermination of domestic garbage. Water, hydrogen oxidation product, is used for domestic purposes [81].

A scheme of the dwelling house with alternative power supply with hydrogen as energy-carrying agent supplied from hydrogen main is presented in Fig. 83. Such buildings will be constructed in the nearest future. In this case hydrogen will be used both for electric energy generation by means of the fuel

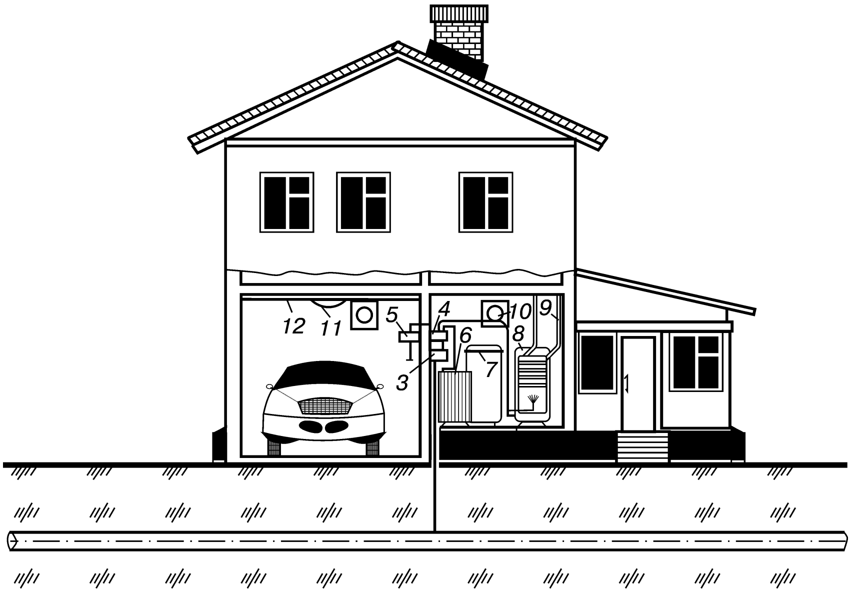


Fig. 83. Scheme of power supply to individual house with hydrogen as power carrier: *1* — hydrogen line; *2* — hydrogen supply; *3* — hydrogen meter; *4* — hydrogen distributor; *5* — charging unit for electric motor car on fuel cells; *6* — electric battery on fuel cells; *7* — metal hydride cylinder; *8* — hydrogen boiler; *9* — hot water supply to distribution boiler, placed on the attic; *10* — illumination provided by fuel cells and accumulators; *11* — ventilation system; *12* — automatic garage gate

cell battery and as fuel for heating dwelling houses. As is seen from Fig. 83, hydrogen from hydrogen line *1* arrives along the individual line *2* to the gas meter 3 and then to hydrogen distributor *4*, and then to the charging unit (for filling working chambers or balloons) for electric motor car on fuel cells *5*, to electric battery on fuel cells *6* generating electric energy and providing illumination in the house, farm buildings; metal-hydride cylinder *7*, hydrogen boiler *8*, etc.

The obtained electric energy is used not only for illumination but also for electronics, TV, domestic appliances, etc. functioning. Hydrogen is also used for filling the working chambers (or cylinders) of electric motor car on fuel cells. Hydrogen will be obtained by means of photoconverters of solar energy in the countryside with lack of hydrogen infrastructure [82]. Hundreds and thousands of such farms have been constructed in southern regions of the USA and France rich with sun light and wind. These farms are of interest for country population as models of «alternative energetics» of the future [80].

The «alternative energetics» plant produces during daylight hours (when using photoconverters) or round-the-clock (in case of wind energy utilization) more electric energy, than it is necessary for the farm, house or small industry object. The excess electric energy is accumulated in the current or hydrogen (energy carrier) cells. The latter is pumped into the underground hydrogen storage or accumulated under pressure in the hydride cells. In case of need hydrogen is converted into thermal energy by simple combustion in the power plant or even into electricity by means of FE. The absorbed hydrogen can be stored in hydrogen cells for indefinitely long time; it may be consumed continuously generating electric energy into FE or it may be used as hydrogen fuel in the corresponding devices (heat engines, heat-treating furnaces, etc.).

Heat production by hydrogen combustion in the power plants for heating houses, air conditioning, water heating is a highly efficient and ecologically pure process. The use of hydrogen energy under field conditions of geological survey, space flights is especially promising. Hydrogen FE are also very efficient sources of heat and electric energy which total efficiency reaches 80 %. International corporation of fuel elements (IFE) jointly with the firm *Toshiba Corporation* produce for commercial purposes the electric plants on FE with power of 200 kW [25]. The firm *United Technologies Corporation* develops and tests electric power plants on the basis of FE with power of 4.5 and 1.1 MW.

In the chapter conclusion it would be noted that the considered use of hydrogen as highly efficient fuel for aviation, cosmonautics, in motor car building, in industry and everyday life does not exhaust hydrogen potentialities as energy carrying agent. Hydrogen properties as energy-carrying agent allowed to look into the sea and ocean abyss. The underwater devices with FC on hydrogen as well as nonatomic submarines with auxiliary air-independent power unit on FC supplied with hydrogen in addition to traditional diesel-electric plant were tested in the USSR in the late 80's. The power unit on hydrogen FC is intended for increasing the underwater autonomicity and secretiveness of submarines [83]. The resource of the secret submarine being under water with the use of FC energy exceeds 15 days and depends only on design peculiarities of the SM and power of EP on FC. The use of energy-accumulating substances as hydrogen source in EP of submarines is more promising [46].

REFRENCES

[1] N. V. Korovin, Electrochemical Energetics, Energoatomizdat, Moscow, 1991.
[2] S. V. Volkov, V. D. Prysyazhny, Cold Burning. Naukova Dumka. Kyiv, 1972.
[3] Fuel Cell Handbook (Fifth Edition), Science Applications Interrelational Corporation Morgantown, West Virginia, 2000.
[4] L. F. Kozin, S. V. Volkov, Chemistry and Technology of Highly Pure Metals and Metalloids, In 2 Vol., Naukova Dumka, Kyiv, 2002, 2003.
[5] D. V. Sokolsky, K. A. Zhubanov, Hydration of Vegetable Fats, Nauka, Alma-Ata, 1972.
[6] Hydrogen: Properties, Production. Storage, Transportation, Use. Handbook, Edit. D. Yu. Gamburg, N. F. Dubrovkina, Khimiya, Moscow, 1989.
[7] J. O. M. Bocris, Int. J. Hydrogen Energy, No. 7 (2002) 719.
[8] J. O. M. Bocris, A. J. Appleby, Environment, Vol. 13, No. 1 (1971) 51.

[9] V. A. Legasov, N. N. Ponomarev-Stepnoy, A. N. Protsenko, et al., Nuclear-Hydrogen Energetics and Technology, Iss. 1 (1978) 11.

[10] V. A. Legasov, Kommunist, No. 1 (1976) 72.

[11] V. A. Legasov, G. A. Kotelnikov, V. K. Popov, Nuclear-Hydrogen Energetics and Technology, Iss. 1 (1978) 37.

[12] V. V. Pozdeev, V. K. Shiryaev, S. P. Dobrovolsky, Ros. Khim. Zhurn., No. 3 (1993) 18.

[13] V. V. Pozdeev, S. P. Dobrovolsky, V. K. Shiryaev, Atom-energiya, Iss. 5 (1979) 347.

[14] O. N. Favorsky, Bull. Rus. Acad. Sc., No. 1 (2001) 3.

[15] S. Mazzetti, N. N. Ponomarev-Stepnoy. Energiya, No. 12 (1997) 5.

[16] A. c. 843667 USSR, MKI^3 H 01 M 10/39. Chemical Current Source / I. V. Matyashchuk, S. V. Volkov, L. S. Leonova, Publ. 1991.

[17] A. c. 1575868 USSR, MKI^5 H 01 M 10/39/ Chemical Current Source / S. V. Volkov, I. V. Metyashchuk, V. T. Vorogushin, O. B. Babushkina, Publ. 1989.

[18] E. Adamov, Ros. Ekonom. Zhurn., No. 5/6 (2000) 80.

[19] A. N. Podgorny, Hydrogen Energetics, Znanie, Kyiv, 1988.

[20] A. N. Podgorny, I. L. Warshavsky, A. I. Mishchenko, et al. Nuclear-Hydrogen Energetics, Naukova Dumka, Kyiv, 1980.

[21] R. F. Alimova, L. F. Goltsova, N. F. Garkuscheva, et al., J. Hydrogen Energy, No. 12 (1985) 861.

[22] A. N. Podgorny, I. L. Warshavsky, A. I. Mishchenko, et al., Nuclear-Hydrogen Energetics and Technolohy, Iss. 2 (1980) 197.

[23] K. N. Semanenko, Bull. Rus. Acad. Sc., No. 10 (1993) 885.

[24] P. Osterkamp, E. Wagner, G. Ross, Ros. Khim. Zhurn., No. 1 (2000) 34.

[25] F. Barbir, T. N. Viziroglu, Ros. Khim. Zhurn., No. 3 (1993) 7.

[26] N. D. Kuznetsov, Nuclear-Hydrogen Energetics and Technology, Atomizdat, Moscow, Iss. 3 (1980) 161.

[27] D. Dini, Int. G. Hydrogen Energy, No. 11/12 (1983) 897.

[28] N. N. Fateev, Energiya. No. 12 (1998) 11.

[29] V. A. Yatzys, M. V. Lototsky, Hydrogen Materials Science and Chemistry of Carbon Nanomaterials. ICH MS' 2003/VIII, Int. Conf., Sudak, Crimea, Ukraine, Sept. 14–2, 2003.

[30] L. F. Kozin, VI Int. Conf. Hydrogen Materials Science and Chemistry of Metal Hydrides, Katsiveli-Yalta-Ukraine, Sept. 2–8, 1998.

[31] L. F. Kozin, S. V. Volkov, Grenoble.

[32] L. F. Kozin, Ya. O. Berezhny, B. I. Daniltsev, VI Int. Conf. Hydrogen Materials Science and Chemistry of Metals Hydrides, Katsiveli-Yalta-Ukraine, Sept. 2–8, 1999.

[33] J. O. M. Bocris, Chemistry of the Environment, Khimiya, Moscow, 1982.

[34] S. P. Makyshenko, Energy: Economy, Technology, Ecology, No. 7 (2003) 33.

[35] O. N. Favorsky, A. M. Starik, Bull. Acad. Sc., No. 8 (2003) 689.

[36] D. Davins, Energy, Energoatomizdat, Moscow, 1985

[37] I. A. Rezanov, Bull. Rus. Acad. Sc., No. 4 (2001) 356.

[38] Cosmonautics, Encyclopaedia, Moscow, 1985.

[39] I. L. Warshavsky, Energy-Accumulating Substances and Their Use, Naukova Dumka, Kyiv, 1980.

[40] I. L. Warshavsky Nuclear-Hydrogen Energetics and Technology, Atomizdat, Moscow, 1980.

[41] A. N. Podgorny, I. L. Warshavsky, A. I. Priymak, Hydrogen and Energetics, Naukova Dumka, Kyiv, 1984.

[42] W. D. Van Vorst, R. L. Woolley, Hydrogen: Its Technology and Implications, Vol. 4, CRS Press, Doca Raton, Florida, 1979.

[43] A. N. Podgorny, I. L. Warshavsky, A. A. Makarov, et al., Use of Hydrogen Fuel in Internal Combustion Engines, IPMASH Acad. Sc. Ukr. SSR, Kharkov, 1977.

[44] A. L. Zacharow, V. I. Kostikov, A. S. Kotosonov, et al., Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, ICHM 2003/VIII Int. Conf. Sudak-Crimea Ukraine, Sept. 14–20, Kyiv, 2003.

[45] B. A. Troshenkin, Circulation and Film Evaporators and Hydrogen Reactors, Naukova Dumka, Kyiv, 1985.

[46] L. F. Kozin, S. V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv.

[47] G. R. Rikardo, High-Speed Internal Combustion Engines, Gostransizdat, Moscow, 1932.

[48] N. V. Olmichen, D. I. Paper, 1942.

[49] R. Wisswall, Hydrogen in Metals. Applied Aspects, Mir, Moscow, 1981.

[50] R. L. Meijer, Philips Tech Rev., 1970.

[51] Erdol-Erdgas-Kohle, Bd. 117, No, 1 (2001) 492.

[52] A. c. 722454 USSR, MKI^2 H 01 M 6/14/ Nonwater Electrolyte for Low-Temperature Current Source / S. V. Volkov, I. V. Matyashchuk, V. A. Vasilenko, et al., Publ. 1979.

[53] V. Goloborodko, Signal, No. 2 (2000) 28.

[54] N. A. Levchuk, Energy: Economy, Technology, Ecology, No. 2 (2001) 35.

[55] N. V. Korovin, Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, ICHMS' 2003, VIII Int. Conf. Sudak-Crimea-Ukraine, Sept. 14–20, 2003, Kyiv, 2003.

[56] N. V. Korovin, Bull. Rus. Acad. Sc., Energetics, No. 4 (1977) 49.

[57] I. E. Baranov, V. N. Fateev, S. A. Grigoriev, V. D. Rusanov, Hydrogen Materials Sciences and Chemistry of Carbon Nanomaterials, ICHMS' 2003, VIII Int. Conf. Sudak-Crimea-Ukraine, Sept. 14–20, 2003, Kyiv, 2003.

[58] Energy: Economy, Technology, Ecology, No. 7 (2003) 40.

[59] Ph. Herissel, Vie rail et transp., No. 2767 (2000) 4.

[60] V. I. Spitsyn, L. I. Martinenko, Inorganic Chemistry, Part 1, Moscow Univ. Publ., Moscow, 1991.

[61] I. S. Kulikov, Isotopes and Element Properties, Reference Book, Metallurgiya, Moscow, 1990.

[62] R. A. Lidin, V. A. Molochko, and L. L. Andreyeva, Chemical Properties of Inorganic Substances, Chemistry, Moscow, 2000.

[63] T.N. Veziroglu, Hydrogen Energy Progress XII, Proc. 13th World Hydr. Energy Conf., Beijing, China, June 12–15, 2000.

[64] S. Verhelst, L. Sierens, Hydrogen Energy Progress XII, Proc. 13th Hydr. Energy Conf., Beijing, China, June 12–15, 2000.

[65] Qunli Hai, Chand Wahg, Poilan Wang, Hydrogen Energy Propress XII, Proc. 13th World Hydr. Energy Conf., June 12–15, 2000.

[66] Reference Book in Electrochemistry, Edit. A.M. Sukhotin, Znanie, Leningrad, 1981.

[67] D. V. Sokolsky, Hydrogen in Solutions, Publ. Acad. Sc. Kaz. SSR, Alma-Ata, 1970.

[68] D. V. Sokolsky, Optimal Hydrogenization Catalysts in Solutions, Publ. Acad. Sc. Kaz. SSR, 1962.

[69] V. V. Goncharuk, L. I. Kamalov, G. A. Kovtun, E. S. Rudakov, and V.K. Yatsimirsky, Catalysis. Mechanisms of Homogeneous and Heterogeneous Catalysis, Claster Approaches, Naukova Dumka, Kyiv, 2002.
[70] D. V. Sokolsky, G. D. Zakumbaeva, Adsorption and Catalysis on VIII Group Metals in Solutions, Nauka Kaz. SSR, Alma-Ata, 1973.
[71] D. V. Sokolsky, Ya. A. Dorfman, Coordination and Hydration, Nauka Kaz. SSR, Alma-Ata, 1975.
[72] G. D. Zakumbaeva, Interaction of organic Compounds with VIII Group Metals Surface, Nauka Kaz. SSR, Alma-Ata, 1978.
[73] N. M. Popova, L. V. Babenkova, G. A. Savelieva, Adsorption and Interaction of the Simplest Gases with VIII Group Metals in Solutions, Nauka Kaz. SSR, Alma-Ata, 1979.
[74] V. D. Yuditsky, A. S. Gribkov, S. E. Belovolov, Bul. Rus. Acad. Sc., Energetics, No. 3 (2003).
[75] V. N. Grebennik, N. N. Ponomarev-Stepnoy, V. V. Lebedev, et al., Atom-Hydrogen Energetics and Technology, Iss. 4 (1981) 23.
[76] A. N. Bashkirov, G. A. Kliger, Future of Science, Znanie, Moscow, Iss. 14 (1981) 50.
[77] N. N. Rykalin, V. A. Lega sov, A.I. Manokhina, et al., Atom-Hydrogen Energeitcs and Technology, Atomizdat, Moscow, Iss. 2 (1979) 16.
[78] Ya.M. Kolotyrkin, A.Kh. Breger, E.A. Borisov, Ibid.
[79] T.N. Veziroglu, Int. Hydr. Energy, Vol. 12, No. 2 (1987) 59.
[80] K.N. Semenchenko, V.N. Verbetsky, Ros. Khim. Zhurn., Vol. 37, No. 2 (1993) 70.
[81] K. Ledjeff, Hydrogen Energy Progress, VIII, Perg. Press, Oxford, 1990.
[82] N. Bak, J. Novotny, M. Rekas, C.C. Sorell, Int. J. Hydrogen Energy, Vol. 27, No. 10 (1002) 991.
[83] K.Yu. Ignatiev, A.V. Yurin, Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, IC HMS' 2003, VIII Int. Conf. Sudak-Crimea-Ukraine, Sept. 20, 2003.

Chapter 8

Ecology and Environment

Above 780 · 10^9 t of coal, 276.963 · 10^9 t of raw minerals and 8.5 · 10^{12} t of primary power transfer agents are mined from the Earth bowel for the following processing and consumption. The industrial and power plants as well as transport vehicles burn 5.1 · 10^9 t of conventional fuel of hard and brown coal, above 5.34 · 10^9t of oil and oil products, 3.0 · 10^9 t conv. fuel of natural gas. Above 25–30 · 10^9 t of oxygen from the Earth atmosphere are consumed for fuel combustion and other purposes. As a result about 30 · 10^9 t of carbon, nitrogen, sulphur, etc., oxides are ejected into the atmosphere. As early as in the mid-80's of the 20th century Academician A. P. Aleksandrov estimated annual emitted from operating power plants only as 200–250 mill. t of ash, 60 mill. t of suplhur oxides and predicted (even allowing for the overestimation — before the Chernobyl catastrophe — of developing nuclear power industry) the increase of these figures to 1.5 · 10^9 t and 400 mill. t, respectively, by 2000. Thus the ultimate decrease of combustion products (CO_2, CO, NO_x, SO_2, Me_iX_j, etc.), called greenhouse gases, ejections in the atmosphere is the most important task of heat power complexes (HPC) which utilize hydrocarbon fuel. To decrease the amount of contaminating combustion products in the environment it was proposed to install special accelerators on the chimneys of HPC plants. The above accelerators form electron beams which treat sulphur and nitrogen oxides and bring them to the level below maximum permissible concentration (MPC). Hydrochemical treatment of fuel gases by ammonia converts gases-contaminants into sulphates and nitrates used as fertilizer components; as a result gases are decontaminated to the level of MPC. The basic components of dry air at the sea level are given in Table 36. Oxygen content in the air exceeds about 635 times the content of carbon dioxide (8.87 · 10^{15} molecules of CO_2/cm^3). The so-called minor components (Ne, Kr, Xe, O_3, H_2, CH_4, CO, N_2O, etc.) of mainly natural origin are present in the 10 km thick air layer (troposphere). The content of minor components in the troposphere in given in Table 37. Only sulphur dioxide, as a man-made impurity, is introduced in the Table.

The content of metal oxides and other elements which usually exceeds many times MPC in the atmosphere of the regions of one or another plant location, as well as very dangerous ejections and effluents of lead, cadmium, mercury, chrome, manganese, etc., compounds into the atmosphere and environment (soil, rivers, lakes) are not presented in Table 37. Lead tetraethyl used as the anti-

Table 36

Basic components of dry air at the sea level [1, 2]

Component	Molecular weight	Content, %	Concentration of molecules in 1 cm ^{3} (n.c.)
N_2	28.02	78.08	$2.098 \cdot 10^{19}$
O_2	32.00	20.98	$5.629 \cdot 10^{18}$
Ar	39.95	0.934	$2.510 \cdot 10^{17}$
CO_2	44.01	0.033	$8.87 \cdot 10^{15}$
Ne	20.183	$1.2 \cdot 10^{-3}$	$3.25 \cdot 10^{14}$
H_2	1.0797 (H)	$1 \cdot 10^{-2}$	$1.20 \cdot 10^{13}$
He	4.0026	$4 \cdot 10^{-3}$	$1.08 \cdot 10^{15}$
SO_2	64.0628	$1 \cdot 10^{-4}$	$2.69 \cdot 10^{13}$
CH_4	16.043	$2 \cdot 10^{-4}$	$5.38 \cdot 10^{13}$
O_3	47.9982	$5 \cdot 10^{-5}$	$1.34 \cdot 10^{13}$
Xe	131.299	$8.6 \cdot 10^{-6}$	$2.31 \cdot 10^{12}$
NO_2	46.00552	$5 \cdot 10^{-6}$	$1.34 \cdot 10^{12}$
Ra	222.0176	$5 \cdot 10^{-8}$	$1.38 \cdot 10^{10}$

detonation additive to the aviation and motor engine gasolines threatens essentially the urban population. Lead is ejected into the atmosphere by the motor transport in a form of oxides (the combustion product components) as well as in a form of very toxical unburnt tetraethyl lead [3]. Motor transport is the source of lead ejections into the atmosphere in the amount of 70 %. The motor transport pollutes the ecosystem not only with lead but also with nitrogen oxides (NO, NO_2), carbon oxides (CO, CO_2) and even ozone (O_3). Aviation and space-rocket complex occupy the second place in the atmosphere pollution with lead. The third place belongs to the enterprises of ferrous and nonferrous metallurgy, chemical plants and glassworks, plants producing chemical sources of current and lead accumulators, varnish-and-paint and defence branches of industry.

The amounts of pollution of the air basin of European and CIS countries, the USA and the Earth as a whole by harmful ejections are frightening. Most industrial regions and cities in Ukraine, Europe, Russia and USA are «covered» with millions of tons of harmful substances. In particular, the air of such cities as Krivoy Rog, Mariupol, Zaporozhie, Dniepropetrovsk, Kiev, Norilsk, Magnitogorsk, Moscow, Sanct-Petersbourg are polluted annually by 1.5; 0.95; 0.43; 0.43; 0.24; 2.49; 0.67; 0.298; 0.181 million tons of harmful substances, respectively. The territories of the USA, China, Russia, Japan, Germany, Great Britain, Ukraine, Italy and France are polluted annually by 1371; 835; 455; 234; 153; 125; 104 and 90 million tons of carbon dioxide ejected into the atmosphere.

The ejections of the solid fuel, oil, gas combustion products from stationary and mobile power plants have caused the acid rains as a result of sulphur,

Table 37

Content of minor components in the troposphere [1, 2]

Component	Typical ratio in mixture	Component	Typical ratio in mixture
H_2O	10^{-5}—10^{-2}	N_2O	$2 \cdot 10^{-7}$
Ne	$1.82 \cdot 10^{-6}$	H_2	$5 \cdot 10^{-7}$
CH_4	$1.82 \cdot 10^{-6}$	CO	$6 \cdot 10^{-8}$—$2 \cdot 10^{-7}$
Kr	$1.5 \cdot 10^{-6}$	Xe	$8.7 \cdot 10^{-8}$
O_3	$n \cdot 10^{-8}$	$NO + NO_2$	$5 \cdot 10^{-8}$—$2 \cdot 10^{-8}$
SO_2	$1 \cdot 10^{-5}$	N_2O	$5 \cdot 10^{-5}$

Note. Typical ratio in mixture, or volume ratio in mixture, is equal to the fraction of particles in 1 mol.

nitrogen and other oxides (SO_2, NO_2) dissolution in the condensing water vapours. Acidification of soil, water bodies and rivers leads to the destruction of biocenosis — a set of different plant, animal, microorganism species and soil enzymes. The acid rains capture and dissolve the ejections and effluents of TEP and TES or make them assimilable for biocenosis. These wastes contain great amounts of extremely harmful substances (lead, mercury, chrome, cadmium, vanadium, molybdenum, etc.) as well as metalloid oxides (carbon, sulphur, nitrogen, chlorine, etc.). When interacting with the environment components, the harmful ejections turn into biocides — the substances and compounds capable to exterminate plants and animal orgamisms. Biocides close the process of substances circulation in nature, stimulating the live organic matter transformation into simple organic and inorganic compounds by the «killing» and decomposition of a plant or animal. The emitted CO_2 takes part in photosynthesis, and, as a result, in creation of the live nature. So, that is the question: can the excessive amounts of CO_2 and CH_4 in the atmosphere lead to the so-called greenhouse effect and do the nature a lot of harm. In the opinion of Academician G.S. Golitsyn «Life is possible on the Earth only thanks to the greenhouse effect» [5]. By the data of Academicians A.L. Yanshin and V.I. Vernadsky high contents of CO_2 in the atmosphere can lead only to the biologic life flourishing on the Earth.

8.1. Greenhouse effect

Physical processes connected theoretically with the decrease of heat losses into the environment by gases which absorb the infrared radiation are assumed as the basis of the greenhouse effect. Methane, carbon oxides and water vapour belong to such gases called the greenhouse ones. Power production by TES and TEP is directly connected with the problems of ecology — pollution of the air basin by the ejections of oxidation products of fossil fuels (coals) components — sulphur, nitrogen, iron, mangenese, chrome, vanadium, etc., oxides. The process of fuel combustion and environment pollution may be presented by the following pattern:

$$\begin{aligned} &C_nH_mS_iN_jMe_{ky} + (n + i + j\ldots)O_2 \rightarrow \\ &\rightarrow (n\text{-}x)CO_2 + xCO + iSO_2 + jNO_x + kMe_yO_x + mH_2O + Q, \end{aligned} \tag{169}$$

where $C_nH_mS_iN_jMe_{ky}$ is fossil fuel; O_2 — air oxygen — fuel oxidizer; CO_2 — carbon dioxide — final fuel combustion product; CO — carbon oxide (II) — product of noncomplete fuel combustion; SO_2, NO, Me_yO_x — fuel combustion products, taking harmful effect on the environment; Q — heat released under fuel combustion.

Carbon in the amount of $5.9 \pm 0.5 \cdot 10^9$ t is ejected annually [6] into the atmosphere as a result of combustion of organic fossil fuel. Carbon dioxide CO_2 is one of the components — «bricks» of nature. In the process of photosynthesis with the help of solar ultraviolet radiation carbon of CO_2 turns into the plant kingdom cellulose by assimilation reactions. Molecular oxygen O_2 is released (renewed) in the day-time (the opposite process — dissimilation — proceeds at night) under these conditions. The assimilation reaction velocity is considerably higher than dissimilation velocity. Certain species of microorganism also assimilate CO_2. It is clear from the above stated that carbon dioxide is one of the most important components, the source of organic matter accumulation in the environment which proceeds by biochemical reactions.

The annual photosynthesis balance in the world makes 120 Gt of carbon, more than its half falls to the primary production of continents. So, if CO_2 disappears from the atmosphere plants cannot develop because of the lack of the «structure material» for creation of cellulose. Both vegetation and any other life will disappear on the Earth. Thus the approach to accumulation of carbon dioxide — one of greenhouse gases — is ambiguous. The existence of biologic life on the Earth during milliards of years proves that the basic credo of the balance is observed in the carbon dioxide cycle: the amount of formed CO_2 is equal to the amount of its consumption.

Nature, as it will be shown below, is able to successively cope with the task of maintenance of admissible CO_2 concentrations in the atmosphere. But the excessive development of technologic processes and energy generation using organic fossils, especially coals, is accompanied by the atmosphere pollution by not only great amounts of CO_2 but also by huge amounts of finely dispersed ash, oxides of heavy metals and metalloids, which poison life of biocenoses. Some researchers misunderstand the danger of nonequilibrium accumulation of CO_2 in the atmosphere. They imitate the processes of CO_2 binding in nature and develop the processes of CO_2 fixation with obtaining different organic compounds, using photochemical, electrochemical and catalytic reactions [3, 5, 7, 8]. These efforts are of one-sided benefit, since CO_2 serves as a new source of raw materials for the synthesis of organic compounds and for obtaining chemical products.

To save life on the Earth it is necessary to consider the decrease of CO_2 content in nature, which is continuously replenished and reproduced by nature at the expence of biota decomposition and to prevent from getting man-made impurities to the atmosphere. The share of man-made CO_2 in the atmosphere, as it will be shown below, is considerably less than the volume of biotic CO_2. As a result of metabolic processes and chemical effect on the biota the impurities alien for nature poison not only the atmosphere but also water resources and Earth's surface (and crust) of the Earth lithosphere. To create ecologically pure sources of energy where hydrogen is used as power transfer agent is the only way to preserve life on planet Earth.

Water vapour. Gases and compounds, which affect negatively the Earth's biota, are attributed to greenhouse gases. Water vapour would be rather considered the conventional greenhouse gas. It is owing to water and its vapours that life in its wonderful diversity could appear on our planet. In the opinion of researchers it is water where life has come from to the land. Occupying the second place on the Earth among compounds, water is the most distributed hydrogen compound. Water in the amount of 10^{18} t takes part in the hydrogen cycle — water circulation in the Earth's nature. It is in equilibrium state in three phases: water vapour, liquid water and ice. The components ratio in one or another phase depends on temperature and pressure. Pressure in the Earth atmosphere does not exceed by 10 % that equal to 1 atm. Difference between ice melting and water boiling temperatures is 100 °C. The temperature range of the environment on the Earth is approximately –70…+ 50 °C. Equilibrium between liquid water and water vapour also depends on pressure and temperature only.

The water vapour concentration increases and decreases with temperature. The surpassing of water vapour equilibrium concentration in the air atmosphere for the given temperature, being a variable function, leads to vapours condensation and to rain and snow fall-out, to the freezing of open reservoirs. Hundreds of thousands of cubic kilometers of water run off in the seas and oceans, evaporate, form clouds and fall to the Earth as rain and snow. As a result of electric discharges under the influence of hydgoren-bearing organisms and as a result of anthropogenic activity some water vapour turns into hydrogen and oxygen and dissipates in space. Water circulation in nature proceeds during millions of years and it never threatened life on the Earth (except for the glacial periods which occurred on the planetary scale and were determined by the outer effects distributed on above 20–25 % of the Earth surface).

Thus the greenhouse effect caused by water vapour and the atmosphere gases determines the protective effect of the Earth's biota. Water vapour cannot threaten life on the Earth. During millions of years its concentration in the Earth atmosphere depends on temperature only and, as a result, on geographic position of the region (continent) and season, since it is determined by the strict thermodynamic ratios, which are not the subject of this book.

A detailed analysis of the effect of physical conditions of the Earth on the life of biota is given by the authors of the work [9]. They have shown that the average global temperature of the Earth surface (15 °C) varies no more than within several degrees as compared to the observed value given in Fig. 84 in a form of shaded area and this takes place for hundreds of million years. It is temperature which ensures life on the Earth. The near-Earth temperature by [9] is determined by the balance between the incoming solar and the Earth's back heat radiation. The Earth's surface heat balance is described by the equation [9].

$$C_p dT/dt = I/4(I–A) – \sigma T^4(I–\alpha) = \mathrm{I}/4\ \alpha – \sigma T^4\mathrm{b} \approx –dU/dT; \qquad (170)$$
$$\alpha = I–A,\ b = I–\alpha,$$

where T is absolute temperature, K; I — solar constant; A — greenhouse effect coefficient; b — a constant characterizing the greenhouse effect efficiency; σ — Stefan-Boltzmann constant, equal to $5.7\cdot10^{–8}$ W ($\mathrm{m}^2 \cdot \mathrm{K}^4$); C_p — average global density of heat capacity per the Earth's surface density unit; A — albedo (ratio between the radiant flux scattered in all directions by the surface element and a flux descending to this element).

Albedo characterizes the surface reflectance. If $A = 0.10$, then 10 % of the descending radiation are scattered in all directions by the surface, and the rest 90 % — are absorbed. The right side of the equation (170) is considered by the authors of [9] as the force equal to negative gradient of the potential function U by the temperature.

The function U value was obtained by the authors by the integration of the equation (170). In the domain where a and b coefficients are constant, the equation describing functional dependence of U on a number of variables has the following form

$$U = 1/4\ aT\ [x\{x^4/5–1\} + 4/5] \qquad (171)$$

where $x = T/T_0$; T_0 — equlibrium stationary temperature;

$$T_0 = \{a1/4\sigma b\}^{1/4} \text{ at } dT/d\tau = dU/dT = 0;\ \tau \text{ — time.}$$

The stable stationary state is observed when the inequality $d^2\mathrm{V}/dT^2 > 0$ takes place. All the states in the region of constant coefficients a and b independent of temperature are stable.

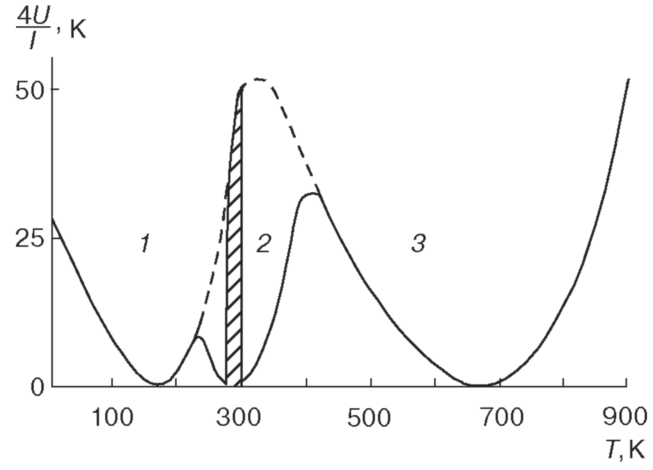


Fig. 84. Physical temperature regions on the Earth, determining complete glaciation of the planet (*1*), stable life of biota (*2*) and complete evaporation of the Earth hydrosphere with establishing the Venus temperature (*3*) [9]

From analysis of the equations (170) and (171) it follows that complete glaciation *1* and complete evaporation of water from oceans *3* (Fig. 84) corresponds to solid and gaseous states of water. Under such conditions the albedo and greenhouse effect change little with temperature, while mean global (averaged according to seasonal variations on the Earth surface) coefficients *a* and *b* in equations (170) and (171) may be considered constant. The present state of climate in the regions with liquid water temperature corresponds to mean global coefficients *a* and *b* physically varying with temperature. This state is not physically stable with respect to transition to the states *1* and *3* (Fig. 84, dash line). The observed stability of the present climate is supported by biotic regulation of the environment. As a result, the global coefficients *a* and *b* are maintained practically constant, and in this connection there appears the corresponding potential hole (Fig. 84, region *2*), separated by potential barriers (Fig. 84, solid line) from the states *1* and *3*. The transitions between states are possible near the intersection points of the corresponding curves. Under complete upset of biotic regulation the potential function is described by the dashed line. In this case the Earth climate (Fig. 84, dashed region) is on the decline leading to complete glaciation of the planet, and humanity is threatened by the global cold snap, rather than a warm spell. Thus the one-degree rise of the annual average temperature observed on the planet in the 20th century, may be changed by the one-degree fall of temperature in the next millenium.

But it would be noted that the above balance of the solar light reflection and absorption is not complete. This balance must be determined not only by the ratio between the values of the solar light reflection and absorption by the Earth surface media (waters of the seas and oceans, lakes and rivers), by ices of the

Table 38

Standard thermodynamic characteristics of the atmosphere gases

Component	Content, %	Density, g/dm^3	C_p^0	S^0	ΔG^0	ΔH^0	ΔH_{melt}	ΔH_{evap} (ΔH_{subl})
N_2	78,08	1.429	29.35	205.04	0	0	0.446	6.828
O_2	20.98	1.2506	29.10	199.9	0	0	0.721	5.59
Ar	0.934	1.7839	20.79	154.7	0	0	1.19	6.51
CO_2	0.028*	1.977	37.11	213.68	–394.38	–393.51	8.37	(25.23)
CH_4	$1.5 \cdot 10^{-6}$	0.162	35.71	186.19	–50.79	–74.85	0.94	8.178
H_2O (g)	10^{-6}–10^{-2}	0.32	33.58	188.72	–228.61	–241.82	6.009	40.66

* Corrected value.

Note. ΔH_{melt}, ΔH_{evap}, $\Delta H_{subl.}$ — molar enthalpies of melting, evaporation and sublimation of 1 mol of the substance in standard state, kJ/mol.

North Pole and Antarctic continent, by mountain glaciers (about 0.1 % of the Earth surface is covered by eternal snows and glaciers) and by continents (1/6 of the Earth surface), covered with plants, including forests, but — that is especially important for that balance — this balance would allow for the absorption of heat radiation from the Earth and Sun surface by all the atmosphere gases. It seems to us that not only water vapour, carbon dioxide and methane, called the greenhouse gases can absorb heat radiation on the Earth, but also all the molecular gases of the atmosphere. In our opinion all of them can contribute to the greenhouse effect. In Table 38 we compare thermodynamic characteristics of the atmosphere macrogases — nitrogen, oxygen with carbon dioxide, water vapour and methane which are considered responsible for the greenhouse effect on the Earth. To make it more obvious the greenhouse gases accepted in literature are given in the Table in bold print.

As is evident, the standard molar Gibbs free energy ΔG^0 and formation enthalpy of ΔG^0 and ΔH^0 of N_2, O_2 and Ar in correspondence with the principles of comparative thermodynamics are taken equal to zero. Standard molar heat capacitances of these gases are 29.35; 29.1, and 20.79 J/(mol·K), respectively. High values of standard molar entropy S^0, equal to 205.04, 199.9 and 154.7 J (mol · K), respectively, are also characteristic of them. Thus, nitrogen, oxygen and, maybe, argon can play an important part in heat transfer, they are the components of the average global density of heat capacitance per the Earth surface area unit. The role of the so-called true greenhouse gases in the transfer, and what is more, in accumulation of heat in the near-Earth atmosphere layer is not determining, since it is conditioned by the small fraction of these components in the atmosphere. Thus the mass fraction of CO_2, relative to N_2, O_2 and Ar is, respectively, 2788, 749 and 33.3 times less, while the mass fraction of CH_4 is 52 050, 13 387 and 622.7 thousand times less! The mass fraction of water vapours in the atmosphere (depending on temperature) is millions and tens of thousand times less than the mass fraction of N_2, O_2 and Ar. Thus, the contribution of the main atmospheric gases to heat accumulation and solar energy heat transfer in the troposphere to the Earth's surface, and contribution to formation of the Earth's heat shell (greenhouse effect) will be so many times higher. It is owing to relatively large mass of the Earth atmosphere ($5.158 \cdot 10^{15}$ t) and mass of water which is concentrated in the seas and oceans and accumulates heat, that the planet has not turned into the block of ice.

The latter is determined by the fact that the hydrosphere and water vapour play the most important part in preserving life on the Earth. The mass of water is 0.024 % of the Earth's mass $(1.4345–1.664) \cdot 10^{18}$ t, i. e. it exceeds the mass of the Earth's atmosphere 278–322 times. Total water reserve in the Earth's mantle equals $2 \cdot 10^{20}$ t. However water of the hydrosphere (lakes, rivers, seas, oceans) takes part in heat-transfer processes from the open surface only and thus, water is a perfect heat accumulator. Really, water vapour in the air at the Earth level is available in sufficient amount, and it is regenerated continuously (an approximate ratio of water vapour and gases of the atmosphere is 1:100). Concentration of water molecules decreases relative to the basic atmosphere gases and in the troposphere it is $3 \cdot 10^{-6}$ and in the stratosphere about $(3–10) \cdot 10^{-6}$. According to other data, the volume fraction of H_2O in the mixture of particles, depending on the season, is equal to $10^{-5}–10^{-2}$ particles in one mole [1]. Water vapour is present even in the mesosphere. It was found in a form of $H_5O_2^+$ clusters by means of mass-spectroscopy measurements. Silvery clouds formed at the height of 80 km in summer, observed in the twilight, are also water vapour manifestations in the mesosphere. As effected by solar radiation with wavelength $\lambda = 200$ nm, water molecules are subject to photodissociation in correspondence with the equation.

$$H_2O + h\nu \rightarrow H + OH^{\cdot} \qquad (172)$$

In the stratosphere and mesosphere the atomic oxygen also takes part in photodissociation reaction.

$$H_2O + O + h\nu \rightarrow OH + OH^{\cdot} + 120 \text{ kJ}. \qquad (173)$$

The reaction velocity constant equals $k = (3–5) \cdot 10^{-10}$ cm^3/s [10]. The formed $OH^{\cdot}$ radicals possess high reactivity and are sources of electrons:

$$OH^{\cdot} \rightarrow OH + e^{-}. \qquad (174)$$

In the stratosphere and mesosphere radicals OH, $OH^\cdot$ react between themselves and with other radials, with $HO_2^\cdot$ in particular, regenerating water molecules, atomic and molecular oxygen:

$$OH + OH \rightarrow H_2O + O; \quad k = 2.0 \cdot 10^{-12}\ cm^3/s; \tag{175}$$

$$O^\cdot H + H_2O \rightarrow H_2O + O_2; \quad k = 1.0 \cdot 10^{-11}\ cm^3/s. \tag{176}$$

From the data of [1] rapid processes of H_2O molecules regeneration proceed in the stratosphere and lower mesosphere, thus the photodissociation reaction little affects H_2O distribution in height. Water vapour gets to the thermosphere due to vertical turbulent motion and is subject to intensive photodissociation with formation of H atoms which are transferred upwards with a velocity sufficient to compensate hydrogen atoms losses from the exosphere.

In the stratosphere H_2O molecules formed in oxidation of hydrogen (H_2) molecules

$$O_2 + hv \rightarrow O^\cdot + O; \tag{177}$$

$$H_2 + O \rightarrow H_2O \tag{178}$$

and methane (CH_4) (see, eq. (178), etc.) are added to the reactions of H_2O regeneration from the products of water vapour molecules photodissociation.

So, water vapour is photodissociated in the atmosphere with absorption of light emission with wavelength $\lambda = 200$ nm and thus it protects the biologic life on the Earth from hard radiation.

It would be emphasized that nitrogen and oxygen react actively with photons and electrons forming various intermediates which take part in energy transfer between particles and, as a results, they protect biota of our planet from hard radiation.

Methane. As to its distribution in nature, methane occupies the second place after hydrogen. It is considered that methane/oxygen concentration ratio in the troposphere is the same as at the level of Earth's surface. The basic amount of methane getting in the atmosphere is formed on the Earth's surface in reservoirs and ocean waters during anaerobic (methane) dissociation of organic matter. Great amounts of the latter are released from the West Siberia, Belovezhian Pushcha (virgin forest) marshes, Pinsk bogs of Byelorussia and Ukrainian Polessie. The lands of Vietnam, Canada, India, South America are rich sources of this gas as well as the flood-lands of the Nile, Kongo, Mississippi, Amazon rivers and tropical areas. Huge amounts of methane (marsh gas, biogas) of biogenic origin (as a result of cellulose fermentation) get from the marshes to the atmosphere. The ratio $^{12}C/^{11}C$ proves biogenic origin of atmospheric methane: it is the same both in the atmospheric methane and biological substances. The amount of methane of biogenic origin in the atmosphere exceeds many times methane losses under production and transportation of natural gas [5].

Bioorganics dissociation velocity on the Earth's surface is $3\cdot10^{11}$ 1/(cm$^2\cdot$s) [11]. Thus, huge amounts of methane (the second greenhouse gas formed continuously as a result of decomposition of organic carbon, the major component of the Earth biota) are remade in microbiologic processes. In the stratosphere methane is oxidized as affected by radicals (OH, H_2O), atomic oxygen, NO, NO_2, molecular oxygen as well as dissociation of half-products under the effect of light emission in accordance with the equation [1,13].

$$CH_4+OH \rightarrow CH_3+H_2O,\ k = 5.5\cdot10^{-12} \exp(-1900/T)\ \text{cm}^3/\text{s}; \qquad (179)$$

$$CH_4+O \rightarrow CH_3+OH,\ k = 1.4\cdot10^{-10}\ \text{cm}^3/\text{s};\ [13] \qquad (180)$$

$$CH_4+Cl \rightarrow CH_3+HCl,\ k = 1.1\cdot10^{-11}\ \text{cm}^3/\text{s};\ [13] \qquad (181)$$

$$CH_4+H_2O \rightarrow CH_2+OH+H_2O,\ k = 1.8\cdot10^{-12} \exp(-2100/T)\ \text{cm}^3/\text{s}; \qquad (182)$$

$$CH_3+O_2+M \rightarrow CH_3O_2+M,\ k = 10^{-31}\ \text{cm}^6/\text{s}; \qquad (183)$$

$$CH_3O_2+ O_2 \rightarrow HO_2+OH+HCO; \qquad (184)$$

$$HCO+O_2 \rightarrow CO+HO_2; \qquad (185)$$

$$HCO+OH \rightarrow CO+H_2O; \qquad (186)$$

$$CH_3O_2+ NO \rightarrow CH_3O_2NO; \qquad (187)$$

$$CH_3O_2+ NO \rightarrow H_2CO+HNO_2; \qquad (188)$$

$$CH_3O_2+ NO_2 \rightarrow CH_3O_2NO_2; \qquad (189)$$

$$CH_3O_2+ NO_2 \rightarrow H_2CO+HNO_3; \qquad (190)$$

$$H_2CO_2+OH \rightarrow HCO+H_2O,\ k = 1.5\cdot10^{-11}\ \text{cm}^3/\text{s},\ 300\ \text{K}; \qquad (191)$$

$$H_2CO+O \rightarrow OH+HCO,\ k = 1.5\cdot10^{-13}\ \text{cm}^3/\text{s},\ 300\ \text{K}. \qquad (192)$$

where M is a particle participating in energy redistribution under molecules collision.

In the mesosphere methane and intermediate products of its oxidation are subject to the following reactions of photodissociation:

$$CH_4+hv \rightarrow :CH_2+H_2+2e^-;\ [13] \qquad (193)$$

$$CH_4+hv \rightarrow :CH+H+H_2+3e^-;\ [13] \qquad (194)$$

$$CH_4+M+hv \rightarrow CH_3+H^+e^-+M; \qquad (195)$$

$$H_2CO+hv \rightarrow H_2+CO; \qquad (196)$$

$$H_2CO+hv \rightarrow H+HCO; \qquad (197)$$

$$CH_3OH+ hv \rightarrow CH_3+OH; \qquad (198)$$

$$HCO+ hv \rightarrow CO+H. \qquad (199)$$

Intermediates $:CH_2$ and $:CH$ are subject to disproportionation reactions:

$$:CH_2 + :\dot{C}H_2 \rightarrow CH_4+C; \qquad (200)$$

$$:\dot{C}H + :CH \rightarrow :CH_2+C \qquad (201)$$

with formation of neutral carbon particles. By the reactions (200) and (201) methane is neutralized and introduces endothermal component into the greenstone effect absorbing by carbon (C) particles the solar radiation quanta *hv*.

A pattern of methane oxidation in the atmosphere is given in Fig. 85

The components with lifetime above 1 month are designated by squares with a double contour, those with lifetime of 24 hours — by rectangles with a single contour. These components are determined in the rain drops. Active intermediate compounds which lifetime is below 10 min are designated by circles. In the above pattern methane oxidation products CO and CO_2 look as the finite products, but in real atmosphere they are in dynamic circulation and take part in various photochemical and chemical reactions (see, eqs (202)–(208)). In the recent decade methane concentration increases continuously in the atmosphere. In the opinion of some researchers under certain conditions methane can intensify the greenhouse effect. Proceeding from current data, methane balance in the atmosphere ($1.5 \cdot 10^{-6}$ % CH_4, which is 18 666 times less than the content of CO_2) was regulated in the past and is regulated now mainly by methane-forming and methane-oxidizing bacteria living in marshes. And these bacteria have already responded to the initian heating of the atmosphere. Methane is distributed uniformly in the atmosphere and oxidizes continuously in the atmosphere as affected by atomic oxygen, radicals, nitrogen oxides and at certain stage by molecular oxygen. It is subject to photodissociation (see, above) in the mesosphere. Acetic acid is formed as a result of methane oxidation; it dissolves in water

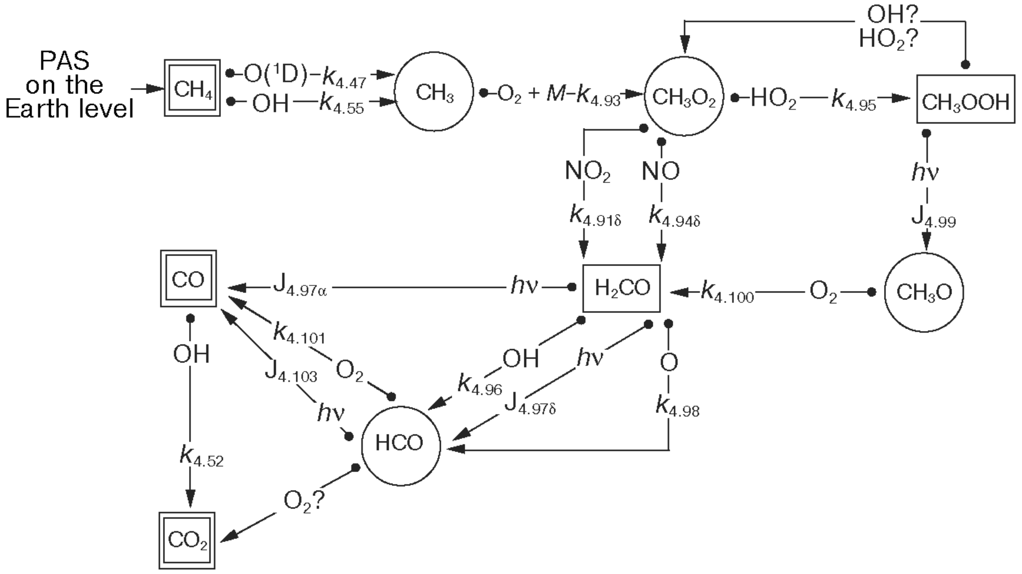


Fig. 85. Schematic diagram of methane oxidation reaction in the Earth atmosphere by [12] (PAS — permanently acting sources)

vapours and rain drops and comes back to the Earth's surface. The acetic acid lifetime is a bit more than 24 hours. Intermediates with lifetime below 10 min are also formed in the process of methane oxidation. The intermediates react between themselves and with oxidizers, and form CO, CO_2, carbonates, take part in different reactions, dissolve in water vapours and rain drops and, as a result, return to the Earth. The methane hydrogen cycle is completed to repeat under favourable conditions.

One would remember about high-volatile organic compounds, released by vegetative cover of continents and by biota of waters and oceans. It is known that milliards of tons of volatile compounds of sulphur, nitrogen, chlorine derivatives of methane (dimethylsulphide, alkylnitrares, alkanes, carbonyl compounds, alcohols, one-, di- and trichloromethane), etc., are released from sea water into the atmosphere. Do you remember the odour of forests, meadows, gardens? According to K.Ya. Kondratyev and V.A. Isidorov 25 mill. t of sulphur are released from anthropogenic and natural sources into the atmosphere, and 12–38 mill. t from the ocean waters. The mass of high-volatile organic compounds ejected into the atmosphere is $1.15–1.50 \cdot 10^9$ t. Only about $0.57 \cdot 10^9$ t of isoprene are released annually into the atmosphere. These compounds are highly reactive and interact actively with ozone, molecular and atomic oxygen, etc. However, despite of huge masses of phytogenic carbon (it is in circulation more than one milliard years) it does not make harm to nature.

Carbon dioxide. The total volume of carbon dioxide ejections in the world is currently $5.599 \cdot 10^9$ t/yr [4]. Only the USA emits into the atmosphere $1.224 \cdot 10^9$ t CO_2 and CIS countries — $1.035 \cdot 10^9$ t. But it is not CO_2 which offers main danger, but the accompanying huge amounts of ash, metal oxides, sulphur and nitrogen. Processes of methane oxidation by biochemical mechanisms and chemical oxidation of methane in the day-time in troposphere were CO_2 sources in nature for 3–4 milliard years. Methane formation and its dissociation (in accordance with the data of [14]) proceed for almost 4 milliard years; CO_2 was also formed as a result of dissociation of organic natural substances (biota) with presence of oxygen.

About 750 Gt of carbon are contained in the planet atmosphere, 1000 Gt in the ocean surface water; about 2200 Gt in the Earth's biota. This carbon content is so high, that the anthropogenic factor of CO_2 concentration growth makes only 0.14 % a year. When methane is oxidized in the troposphere, the intermediate products, such as HCO and H_2CO, can also dissolve in the rain drops or be subject to disproportionation of intermediates as affected by water vapour, by the equations

$$4HCO = CO_2 + 3C + 2H_2O; \qquad (202)$$

$$2H_2CO + 4H_2O = CO_2 + C + 4H_3O^+ \qquad (203)$$

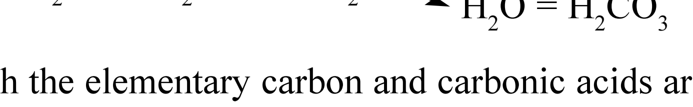
with formation of CO_2 and neutral carbon particles, being, in our opinion, of aerosol nature.

Molecules of CO_2 in the troposphere and (to higher extent) in the mesosphere may be subject to photodissociation:

$$CO_2 + h\nu \rightarrow CO + O; \qquad (204)$$

$$CO_2 + H + h\nu \rightarrow CO + OH^- + e^-. \qquad (205)$$

The reaction (8.27) under the conditions of the troposphere may be presented as that proceeding by the following reaction pattern:



$$2H_2CO + 5H_2O \rightarrow 2CO_2 + \begin{cases} \nearrow C + 4H_3O^+ \\ \searrow H_2O = H_2CO_3 \end{cases} \qquad (206)$$

according to which both the elementary carbon and carbonic acids are formed.

The process of methane oxidation in the troposphere in the day-time is the major source of CO (as well as CO_2) inflow to the atmosphere (see, Table 37), rather than the internal combustion engines, as it was considered before [1]. CO concentration in the troposphere is $(1–2)\cdot10^{-9}$ mol^{-1}. In the atmosphere CO molecules are subject to oxidation by OH radicals by the reaction

$$CO + OH \rightarrow CO_2 + H, \qquad k = 5.1\cdot10^{-13}\exp(-300/T)\,\mathrm{cm^3/s}. \qquad (207)$$

Considerably less contribution is made by the reaction with atomic oxygen:

$$CO+O+M \rightarrow CO_2+M; \quad k = 2.2{\cdot}10^{-36}\ cm^6/s. \qquad (208)$$

Carbon dioxide circulates in nature. The mechanism of carbon oxides formation by the reactions of burning with accompanying CO disproportionation by the Boudoir reaction, as well as CO_2 circulation in nature are shown in Fig. 86. Microorganisms, algae, plankton, plants, trees take part in the atmospheric CO_2 circulation; it is absorbed by the ocean water (not only molecular CO_2, but also HCO in a form of inorganic compounds), for example, by the reactions

$$CO_2+Ca^{2+}+H_2O — CaCO_3+2H^+; \qquad (209)$$

$$HCO\ +Ca^{2+}+H_2O — CaCO_3+H_3O. \qquad (210)$$

The volume of CO_2 absorbed by the ocean water (physical dissolution) is (2.0–2.6) ± 10^9 t C/yr [6]. Besides, one can also observe photochemical absorption of the atmosphere carbon by the ocean biota which is $2.4 \cdot 10^9$ t C/yr.

Thus, the ocean waters are saturated by natural microorganism species, plankton, algae, which assimilate CO_2 from the air and form the biosphere of the oceans and seas. Forests, argicultural lands, and all plants of the land biota absorb $1.3 \cdot 10^9$ t C/yr. A set of all natural species of the biosphere form the Earth's biota. Total CO_2 loss from the atmosphere as a result of its dissolution in the ocean, formation of inorganic compounds, photochemical absorption, assimilation by land biota is of about $6.0–6.7 \cdot 10^9$ t C/yr. This exceeds by $0.1–0.8 \cdot 10^9$ t C/yr the sum of CO_2 ejections in the Earth atmosphere equal to 5.9 ± 0.5, and according to [4] — $5.599 \cdot 10^9$ t C/yr. It follows from these data that the present concentration of CO_2 cannot result in quick catastrophic greenhouse effect.

In Ukraine the great share of the environment pollution also consists of such fuel combustion products as CO, CO_2, SO_2, NO, MeO_n, formed, besides industrial and transport sources in the heating systems of houses. It is noted in the work [15] that «even the giving-up of cooking in open flame using firewood or coal» will permit decreasing the air pollution level. This especially concerns densely populated Asian countries where coal is used as fuel. High concentration of polluting substances is observed in the air of densely populated city and country districts. Use of hydrogen as fuel may be one of the cardinal ways of this problem solution. The use of natural gas, which is more pure fuel as compared to coal, is a half-measure. Growth of population and development of industry which consumes the ever-increasing amount of power resources produced by thermoelectric stations on natural gas will cause quick exhaustion of gas reserves. Energy carriers on the basis of oil and coals of different genesis contain relative-

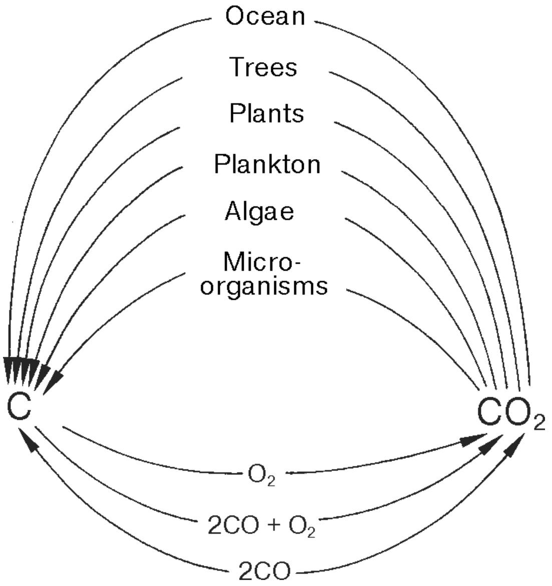


Fig. 86. Carbon dioxide circulation in nature

ly huge amount of harmful and toxic components, including radioactive ones (thorium, uranium, etc.) which disperse in the environment [4, 16–18]. In connection with the increase of operational temperatures of TES for raising their efficiency, the intensity of ejections of CO_2, SO_2, NO_x and other toxic substances into the atmosphere increases immeasurably [19].

It is considered that CO_2 concentration in the planet atmosphere continuously grows: in 1950 it was 0.027 %, in 1956 (the first world geophysical year) — 0.028 %, in 1998 — 0.035 % [20]. From the data of the work [6] CO_2 concentration has increased by 30 % during recent 100 years, which causes changes in oxygen concentration in the fourth digit, and more concretely by the value of the order of 0.05 %. From the data of Academician G.S. Golitsyn [5], carbon dioxide concentration has increased by 30 % during recent 200 years. When using the data of the work [21] concerning the changes of CO_2 concentration during the last 39 years (1960–1998), we can obtain that CO_2 concentration has changed by 12.8 %. But real contribution of CO_2 as the greenhouse gas is negligibly small because of its low concentration. The atmosphere near the Earth surface contains 78.08 % of nitrogen, 20.35 % of oxygen, 0.93 % of argon and about 0.032 % of carbon dioxide. Volume of hydrogen, helium, neon, crypton, xenon is 0.1 %. Thus the ratio of oxygen and carbon dioxide (0.028–0.035 %) in the atmosphere is 1: (0.00134–0.00167). The doubling of CO_2 content in the atmosphere is expected by the middle of the 21st century (~ 0.07–0.08 %), and this must cause its higher assimilation by vegetation and biota of the Earth as a whole according to the feedback principle. As a result, it may happen that the greenhouse effect will not occur. In our opinion one would concern the following five aspects evidencing for the extremely low probability and even improbability of the greenhouse effect manifestation on the Earth as affected by carbon dioxide.

The First Aspect. It is considered that carbon dioxide partially reflects the solar infrared radiation back to the Earth that leads to the planet heating. It is difficult to imagine that 0.032 % of CO_2 can affect the infrared radiation which reached the atmosphere layers near the Earth's surface. The Sun sends energy of $1.67 \cdot 10^{14}$ kJ/sec to our planet. From the total amount of solar radiation reaching the outer Earth's atmosphere and taken as 100 % only 43 % gets to the Earth's surface where it is absorbed by the Earth's atmosphere, hydrosphere, lithosphere and biosphere so that the solar energy losses make 57 %, 7 % of energy being reflected by the Earth's surface in the space [22]. The amount of solar energy reaching the Earth surface is 8.075–8.37 J/(min $\cdot$ cm^2) [23].

Now, compare 7 % of reflected solar energy ($1.17 \cdot 10^{13}$ kJ) and energy increment (about 5 of 0.032 % of CO_2) equal to $1.64 \cdot 10^8$ kJ, which will be confined to the circumterrestrial space as a result of absorption of infrared radiation by CO_2 molecules. This value is $4.38 \cdot 10^5$ times less than solar energy reflected from the Earth surface to the world space and is $1.02 \cdot 10^6$ times less (one million times) than solar energy reaching the Earth. In this connection the empirical approximations and arguments that the doubling of CO_2 concentration in the atmosphere will result in the increment of the circumterretrial temperature by ~ 4 °C, and that according to [24] this temperature increase by 2–3 °C will occur even in the middle of the 21st century, seem rather exaggerated. It is supposed that the temperature will rise to maximum in the polar regions and rather negligibly in the tropical belt. But the analysis of the temperature belts of the Earth shows that the temperature in Antarctics does not exceed –8 °C even in summer.

Calculations performed by Academician A. L. Yanshin show [20], that the amount of evaporated water in polar areas, the temperature being elevated by 4 °C, will be only $3.2 \cdot 10^9$ m^3 a year, while in the area of the World Ocean (320 mill. km^2) and seas the layer of this water precipitations will be only 1 cm.

Investigations performed by researchers of the West Ontario and Michigan University (USA) have shown that during the 500-years period (from 1500 to 2000) the temperature in the Earth's Northern hemisphere increased by 1.1 °C only, though more than a half of this temperature increment (0.6 °C) belongs to the recent century. From data analysis of the work [21] conducted by the authors it follows that in 1998 the average annual Earth air temperature (EAT) was higher by 0.66 °C than the long-term average temperature value equal to 13.8 °C. This increase of EAT is not determined by the anthropogenic factor, but by extremely intensive El Ninho and unprecedented warming of the Indian Ocean surface. It is supposed that the global temperature elevation may result in waters stratification and upset of the conveyor circulation of waters in the Atlantic Ocean, and, as a result, probable formation of a «new glacial epoch» [20].

The second aspect. By the data of the work [20], during recent 600 Ma carbon dioxide content in the air of our planet never exceeded 0.4 % and was at an average 0.13 %, which is 4.6–14.3 times higher than CO_2 current content equal to 0.028–0.035 %. It is established that the periods of higher CO_2 content in the atmosphere were always connected with the increase of volcanic activity and «were accompanied by the flourishing of all forms of life on the Earth». Academician A.L. Yanshin thought [20] that the increase of CO_2 content in the atmosphere within the limits of the above values (0.13 %) is an undoubtedly favourable for a man.

According to V.I. Vernadsky, the Earth plant kingdom can process much higher concentrations of CO_2, than its amount in the air of the present atmosphere. Really, the amount of the annual photochemical accumulation of carbon, for example in the territory of Russia, is 4.4 Gt, while the value of annual CO_2 emission in the atmosphere in only 3.12 Gt [23]. It is established by experiments that CO_2 content in the air (of, for example, hothouses) being doubled, all the cultural plants grow quicker and mature 7–8 days earlier than in the control experiments. According to [25] biological life on planet Earth has lifted the restrictions for the basic resource of its development — carbon dioxide, and it is renewed continuously in the turnovers of assimilation and dissimilation processes and is stored in the biosphere reservoirs. The number of biologic species consuming carbon dioxide on the Earth is very high and reaches 5 milliard, so their functioning determines the carbon cycle closing [27]. Then, in accordance with the theory of the biosphere rhythms, the biosphere after the perturbation (CO_2 concentration growth in the atmosphere) passes to a new equilibrium state in the process of damped oscillations or rhythms, i.e., it responds by its evolutionary way of development. On the ascending branch of the biosphere rhythm, by Le Chatellier principle [27], the feedback mechanism begins acting — the amount of biomass increases, CO_2 growth being thus compensated. The concentration of CO_2 in the atmosphere being lowered, the amount of biomass decreases and higher amounts of CO_2 remain in the atmosphere. According to [27], this explains the alternation of sedimentary mountain rocks on the Earth which are rich or poor in the organic matter.

There was always mobile equilibrium between biota and CO_2 on the Earth: high concentrations of CO_2 resulted in the flourishing of biota life on the Earth. The availability of CO_2 equilibrium balance determines both life appearance on the Earth milliards of years ago and preservation of the climate fit for life in the recent 4–5 million years. According to [29] the preservation of the climate fit for life on the Earth unambiguously points to the fact that «the concentration value order of such greenhouse gas as CO_2 did not change during recent milliard years». The ocean water of our planet plays considerable part in establishing CO_2 equilibrium concentration in the atmosphere. It has been established that CO_2

concentration in the atmosphere coincides with the concentration of CO_2 dissolved in the surface layer of the ocean waters and is thrice lower than that in its deep waters [29]. The latter is explained by the fact that the diffusion current of CO_2 (inorganic carbon) from the ocean depths to its surface is compensated by synthesis of organic carbon near the surface and by its submersion in the ocean depths where it decomposes. As a result the ocean biota maintains CO_2 concentration in the atmosphere, and this concentration is three times less, than it could be with the lack of biota [28].

The third aspect. In accordance with thermodynamics law the energy of infrared (thermal) radiation cannot arise from nothing or disappear without trace. When absorbing solar infrared radiation, CO_2 molecule is activated (CO_2^*) and converts the solar energy into thermal one which is uniformly distributed by $0 = C = 0$ bonds, inducing their oscillatory motion. Under the successive absorption of infrared radiation with high energy there arises high frequency of induced oscillations of the bonds. This may result in the splitting of valence bonds in CO_2^* molecule with formation of activated atomic oxygen O^+ and carbon oxide CO. This process in accompanied by energy radiation. However, the energy of infrared radiation (E_1) absorbed by CO_2 molecule exceeds the radiant energy released under the molecule splitting (E_2) by the entropy component $T\Delta S$ which depends on temperature ($E_1 << E_2$). Besides, the «heated» CO_2 molecules, in accordance with physics laws concerning heated bodies and as a result of vertical movement of turbulent flows in the atmosphere, are removed to the upper layers of the atmosphere with the temperature of 130–200 K. The «heated» molecules of CO_2 and CO_2^* are cooled there. Moreover, availability of N_2, O_2 and other molecules in the atmosphere leads to energy redistribution between molecules of CO_2 and CO_2^*. Redistributed heat ΔQ is proportional to the product of CO_2 heat capacity at constant pressure ($C_p = 0.846$ k)/(kg · K)), mass of CO_2 ($[CO_2]$) and temperature difference Δt, i.e. $\Delta Q = C_p[CO_2]\Delta t$. The estimated value ΔQ is positive but extremely low, since it is proportional to CO_2 content in the atmosphere (0.028–0.035 %). That is why such inconsiderable increase of CO_2 concentration in the atmosphere also cannot lead to the catastrophic greenhouse effect. Cold spring and summer (except for August) of 2000 and hot July-August of 2001 have demonstrated that climate depends only on the amount of energy emitted by the Sun, reaching the planet surface and assimilated by the Earth biota.

Let us cite two facts to confirm the above thesis. The beginning of winter of 2002–2003 in Europe was too severe (December 2002). Frosts reached –25–40 °C, winter crops were destroyed by frost in most European countries. But the beginning of winter of 2003–2004 proved to be rather warm. Average temperature in December was positive (3–5 °C). The latter was determined by the solar flare, the most powerful one during the whole history of observation (power-*X*20) which took place on November 5, 2003. There arised a giant cloud with milliards of tons of incandescent gases. Its volume exceeded 13 times the volume of our planet. Some share of incadescent gases rushes to the Earth and reached it 48 hours after the flare. Seven and ten days later the flares repeated but their power was lower (X7 and X10). The solar flare energy reached the Earth and was accumulated by the ocean waters and planet as a whole that provided warm spell in December 2003. Frosts came in the first decade of 2004 (–10–20°C) after the accumulated warm was consumed.

The fourth aspect. A supposition that the temperature will elevate maximally in the polar regions of the planet and negligibly in the tropics under the greenhouse effect in not always treated correctly. One would understand this supposition only in a sence that the temperature elevation can result in the violent growth of vegetation in northern regions but will not change anything in the tropics. But return to the discussion of this aspect. CO_2 concentration in the Earth atmosphere in time is distributed uniformly because of the turbulent flows. In this connection CO_2 concentration in the atmosphere coincides with that in the surface layer of waters of northern seas of Arctic and coastal waters of the Antarctic continent. Thus CO_2 concentration are identical both at the North Pole and the South Pole. So, the temperature being elevated in the tropics because of CO_2 concentration, it will also increase in the polar regions. And allowing for the cold seasons — autumn, winter and spring with characteristic overfalls of 30–70 °C, the ephemeral maximum expected 2–3 °C will disappear without trace in the variations of natural elements.

It is not still clear to what extent the warm spell of the recent 100 years is determined by natural climate system and to what extent — by the growth of concentration of greenhouse gases. The predicted negative effect of CO_2 on ecology is based on erroneous preconditions [29]. In 1985, at the International Meeting in Ottawa concerning the greenhouse effect they adopted the appeal to all countries governments to reduce the amount of burnt fuel at least by 25 % by 2000. But this appeal was not implemented though it was welcomed with enthusiasm, and in 2001 the USA renounced that recommendation. That was logic on the part of the USA. The character of changes in the world climate system is rather complicated, thus, it is impossible to explain some climate changes by the action of only one factor — the increase of CO_2 concentration. In the opinion of Academician K.Ya. Kondratyev [64] «unadmissibly schematized notions of the causes of warming underlying the «greenhouse» stereotype gave birth to not only speculative judgements of climate (e.g. the statement about the increase of frequency of meteorologic catastrophes under warming up [30]) but also to adoption of such disorientating document as *Kioto Protocol* [31–33]». The document includes recommendations on decreasing the greenhouse gases ejection in the atmosphere. The *Protocol* recommendations are almost practically unrealizable, especially for underdeveloped countries; they contain situative estimates of climate changes, and even the fulfillment of the above recommendations can only lead to negligibly small changes in climate.

It is necessary to improve the culture of burning the hard fuel — coal — for not to admit the atmosphere pollution with metal oxides, sulphur and nitrogen. Our ecology is damaged most of all by the emissions under the combustion of coals containing radioactive isotopes of potassium, thorium, radium, uranium which quality depends on ash content in them and exceeds 10 times (as to irradiation doze) their content in the ejections of normally operating NPP [34]. In the recent years different countries take part episodically in the fight for the purity of coal energy as well as for the decrease of the accompanying harmful impurities (SO, NO, Me_iO). At a number of UK enterprises it was shown [34] that the progressive methods, owing to high efficiency, cause a considerable decrease of CO_2 ejections per a watt of generated energy without considerable effect on its cost. Thus the Great Britain has imposed a tax for CO_2 ejections of 32 pound sterling for 1 ton.

Ecologically pure methods of power generation using coal are developed in the USA, Germany, Russia and other countries. It is predicted that TES of the 21st century will not use coal as fuel but its processing product — synthesis gas or hydrogen. Synthesis gas obtained by means of gasification is to be treated for sulphur, nitrogen and hard impurities and then to be used as ecologically pure fuel for gas turbines. In certain cases carbon monoxide will be converted into additional amount of hydrogen; carbon dioxide is to be separated using well-known technologies, while hydrogen will be used in electrochemical converters of chemical energy into electric one. It is also planned to develop the methods of production of synthetic liquid hydrocarbon motor fuels for autotransport, etc., using synthesis gas. That is the cardinal solution of the environment protection problem.

It is also supposed to more widely use natural gas in power generation. Natural gas is irreproachable from the viewpoint of radiation and ecologic purity, since only CO_2 and H_2O are formed under its combustion, the ejection of carbon dioxide is twice less under generation of the same amount of energy, than under coal combustion by the ordinary method. It is supposed [35] that in the 21st century natural gas will be able to satisfy the mankind demands in energy and hydrocarbon raw material.

It would be noted that the planet (land and ocean) biota can absorb the amount of CO_2 which exceeds considerably that ejected into the atmosphere under the combustion of organic fuel. Some countries (Great Britain, USA, Russia, Sweden, Austria, Australia, Germany, Japan) have performed the laboratory research on the study of the effect of high concentrations of carbon dioxide (0.033–0.066 % of CO_2) on development of cultivated plants. It appeared that the increase of CO_2 concentration in the atmosphere (habitat) takes a favourable effect on development of plants. Double concentration of CO_2 leads to the increase of the leaf surface: sorgho by 29 %, maize — by 40 %. Biomass of young plants increases to about 40 %, crop capacity rises while the terms of agricultural culture ripening decrease. Investigations have shown that cotton crop yield increases by 124 %, that of tomatoes and aubergine — by 40 %, wheat, rise and sunflower — by 20 %, pea, bean and soya — by 43 %. By some data, the average crop yield of cereals can increase by 67 %, and fodder grasses — by 95 %. The above results prove that the increase of CO_2 concentration in the atmosphere will help to decide a number of problems connected with production of foodstuffs for the predicted growth of the number of our planet population in the third millenium. It is considered that the increase of CO_2 concentration in the atmosphere will supposedly result in some rise of temperature. But from the data of the work [2] not the climate warming will prove to be a «true ecologic catastrophe», but disturbances in the circulation closeness, i.e. the already proceeding destruction of the atmosphere determined by high level of the use of biosphere resources (e.g. exhaustion of crop capacity of lands, deficite of food products). «This level evidences for the available overpopulation of the Earth and a necessity of a new socio-economic paradygm…» [2]. Experimental data described in the work [4] prove that at high concentration of CO_2 in the atmosphere biophotochemical and microbiological processes taking place in biota are more fast and productive. Thus when affected by warming and high concentration of CO_2 the biosphere resources will increase 1.5–2.0 times, while closed circulations of biocenosis will be restored with higher velocity.

It follows from the above stated that carbon dioxide plays the prime part in life preservation on the Earth. It is carbon dioxide that provides the organic life circulation on our planet. When there is surplus of CO_2, biota responds by the corresponding lowering of its content in the atmosphere and by increasing the amount of biomass on the Earth.

Thus, it seems to us that the prediction made by James Casting, professor of meteorology of the University of Pensilvania (USA) about the catastrophe threatening the biologic life on the Earth (this time from the drop of CO_2 concentration on our planet) is also inconsistent [36]. In accordance to J. Casting's statement CO_2 concentration in the Earth atmosphere will not increase but decrease with time because of CO_2 gradual absorption by calcium compounds getting in the air as a result of the mountain rock weathering. The author of this hypothesis thinks that in 500 million years CO_2 concentration in the atmosphere will be lowered to such extent that most species of the land surface plants will vanish and this will result in the destruction of biota on the Earth.

According to J. Casting, the biosphere destruction will occur long before the Sun will exhaust its hydrogen nuclear fuel which (from calculations of astrophysicists) will last $5 \cdot 10^9$ years. But in our opinion the ratio between CO_2 concentration in the atmosphere and content of calcium compounds (solid particles capable to precipitate on the planet surface) is extremely high, and this ratio tends to the increase, since the transition of heterogeneous particles of calcium compounds is a very slow process in nature. Besides, chemical activity of calcium compounds (silicates and aluminosilicates, wollastonites, anhydrides, phosphates, etc.) with respect to carbon dioxide is infinitely low at the Earth temperatures. Carbon dioxide does not remain in chemically bound state in calcites $(Ca_{0.95}Fe_{0.05})_3$, siderites $(Fe_{0.95}Ca_{0.05})_3$, as well as in natural huntites $CaMg_3(CO_3)_4$, alstonites $CaBa(CO_3)_2$, kutnahorites $CaMn(CO_3)_2$, dolomites $CaMg(CO_3)_2$ which occur most frequently in the mountain rocks [37]. Besides, calcium compounds, as a rule, are not water soluble and the rate of heterogeneous reactions, limited by the diffusion processes, is also too low.

The fifth aspect. When concluding a discussion about the role of CO_2 in the greenhouse effect, consider a quantitative side of this aspect for to answer the question: are the volumes of antropogenic CO_2, ejected in the atmosphere really critical for life preservation on the Earth. The total amount of carbon dioxide, formed under combustion of all kinds of fossil hydrocarbon fuel and ejected into the atmosphere is $5.599 \cdot 10^9$ t [4]. One can calculate what amount of oxygen is required for formation of $6.299 \cdot 10^9$ t of carbon dioxide (data about CO_2 ejections in 2000 [21]) by the reaction:

$$C + O_2 = CO_2 + Q, \tag{211}$$

where Q is thermal effects of the reaction of fossil hydrocarbon fuel combustion.

The Earth atmosphere mass is $5.13\,610 \cdot 10^{15}$ t, and the mass of free oxygen in the atmosphere — $1.5 \cdot 10^{15}$ t [38]. Allowing for atomic weights of carbon, oxygen and molecular weight of dioxide CO_2 we obtain that the combustion of 1 t of carbon requires 2.664 t of oxygen forming 3.664 t of CO_2. One ton of CO_2 contains 0.72 709 t of O_2.

Oxygen taken from the air in the amount of $4.599 \cdot 10^9$ t is consumed for formation of $6.299 \cdot 10^9$ of carbon dioxide. This amount of oxygen is only $3.053 \cdot 10^{-4}$ mass % of oxygen available in space.

However, as was mentioned above, carbon dioxide let in the atmosphere is included in natural biological (including geochemical) cyclic processes and is absorbed by vegetation. As a result the reaction of photosynthesis affected by the solar luminous energy with participation of chlorophyll helps not only to synthesize organic compounds from CO_2 and water but also to regenerate huge amounts of oxygen entering the atmosphere:

$$6\,CO_2 + 6\,H_2O \xrightarrow[\text{chlorophyll}]{\text{luminous energy}} C_6H_{12}O_6 + O_2 \tag{212}$$

From the data of the work [17] green plants by the reaction (212) not only synthesize organic compounds (it would be noted that nature creates primary matter on the Earth only by reactions of photosynthesis), but also regenerate $105 \cdot 10^9$ t of oxygen a year. Calculations show that the share of oxygen consumed in the world for energy production ($4.5799 \cdot 10^9$ t O_2/yr) makes only 4.36 mass % with respect to the amount of oxygen regenerated by the planet vegetation ($105 \cdot 10^9$ t/yr). Thus the amount of oxygen, regenerated by the planet biota exceeds about 23 times that consumed by the mankind to obtain energy from hydrocarbon fuel. Carbon dioxide is in mobile equilibrium regulated by physico-chemical processes — adsorption, chemosorption, diffusion, reactions of CO_2 exchange between the atmosphere and ocean waters, as well as waters of various genesis under seasonal temperature changes in the upper water layers; it is also regulated by formation of limestones, etc., as well as by the processes occurring in biological systems. «Inorganic» and «organic» carbon are formed as a result of these processes. The «organic» carbon mass in soils is about $2.0 \cdot 10^{12}$ t [9]. CO_2 in the amount of $1.3 \cdot 10^{14}$ t is dissolved in the oceans, seas and other reservoirs. Total mass of hydrogen in organisms equals about $8.0 \cdot 10^{11}$ t. Huge reserves of hydrocarbon raw materials of the future remaint at the bottom of oceans in the so-called gas hydrates. Methane content in gas hydrates is estimated as $2.10 \cdot 10^{14}$–$8.0 \cdot 10^{18}$ m^3 [12,40], and, it is also supposed that gas hydrates can supplement deficit of hydrocarbon raw materials in the future.

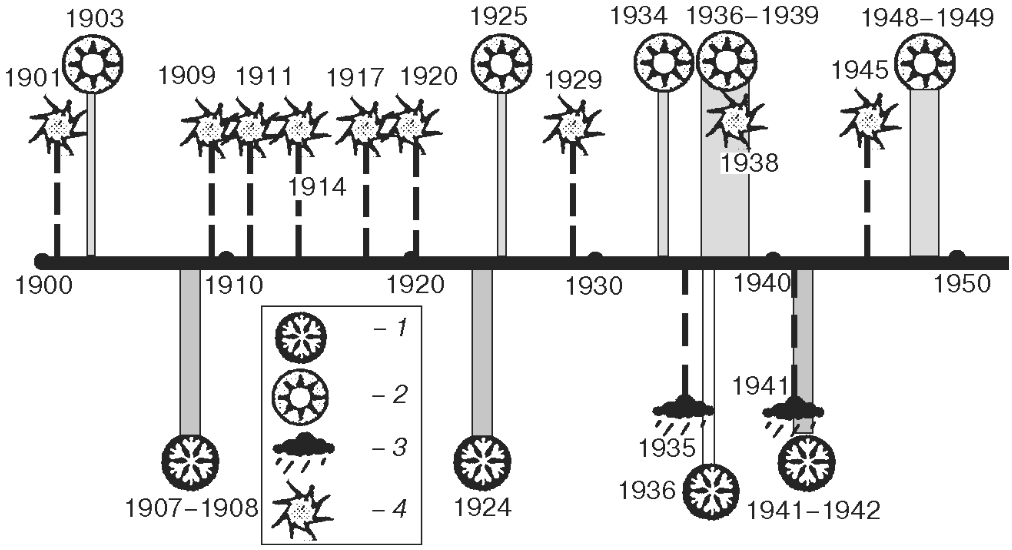
Processes of organic carbon destruction in the Earth soils, ocean and sea water, under microbiologic decomposition of organisms and volcano eruption are main sources of carbon dioxide emission into the atmosphere. Temperature variations also lead to the absorption or release of CO_2 from waters, soils, etc., that results in the change of CO_2 content in the atmosphere with time. By the data of the work [39] the mass of carbon dioxide in the atmosphere of our planet is $2.6 \cdot 10^{12}$ t which exceeds about 412 times the mass of anthropogenic carbon dioxide ($6.299 \cdot 10^9$ t) [21], entering annually the atmosphere.

Interesting calculations on photosynthesis productivity are fulfilled in the work [41]. It has been established that the on-land plant photosynthesis productivity equals $140 \cdot 10^9$ $t \cdot year^{-1}$, and that in the ocean about $190 \cdot 10^9$ t-$year^{-1}$, of dry organic matter. Under synthesis of such quantity of organic matter the atmosphere loses annually $280 \cdot 10^9$ t of CO_2 that «corresponds to the mean time of CO_2 molecules existance in the atmosphere which is equal to about 10 years» [38]. If it were not for CO_2 renewal, life on the Earth would become impossible. The main share of carbon dioxide, consumed for plants synthesis comes back to the atmosphere and hydrosphere in the processes of plant organic matter destruction occurring with formation of aerobic bacteria and other heterotrophic organisms. Comparatively little share of photosynthesized organic carbon is preserved for a long time in soil humus, sapropel, turf, methane and other combustible gases and organic substances which mass is partially consumed in the course of oxidation, and partially preserved and buried in the lithosphere. This process is characterized as the rate of organic carbon deposition which is about 30 mill. $t \cdot yr^{-1}$. The author of [39] thinks that under such rate of the organic carbon deposition the amount of carbon dioxide «in our atmosphere can disappear during 10^5 years», and that «without permanent CO_2 inflow from the deep strata of the Earth during a long period of time, comparable with historical epochs, it is impossible to preserve more or less stable concentration of atmospheric carbon dioxide». But they did not take into account the consumption of CO_2 for formation of the carbonate deposits occurring in warm shallow-water seas. By the data of [39] the rate of carbon dioxide consumption for formation of carbonate rocks in Pliocene (5 Ma B.C.) was equal to 180 mill. $t \cdot yr^{-1}$. Though CO_2 consumption for carbonates formation is something less now, nevertheless it is considerable, it agrees with the idea of James Casting, but it will not result in the catastrophe of biologic life on the Earth because of the lack of CO_2 (see, The fourth aspect).

Is there any relation between weather and greenhouse effect? It follows from the physical sense of the notion of «greenhouse effect» that it is closely related with the climate warming on the planet or great regions of the planet. Temperature differences in the regions distributed in the same latitudes will lead to storms, strong winds and cause weather instability. The «greenhouse effect» is a result of the increase of CO_2 concentration in the atmosphere, which cannot disappear during a short period of time. Consequently, the hot weather cannot be changed by the cold one immediately, as it is observed in real life.

The predicted global warming must be closely related with the mechanism of the «greenhouse effect». The «greenhouse effect» is underlied by the preservation of biogenic heat (for plant growth stimulation) released in the system (device) as a result of the proceeding of continuous microbiological processes in the underlying compost of fresh humus and soil (purposely prepared). The present «climatic» greenhouse effect is connected with episodical short-term techno-anthropogenic supply of CO_2 and other greenhouse gases into the atmosphere. It cannot be considered analogous to the «greenhouse effects» determined by «long-term interaction of the athmohydrosphere with the Earth mantle in the framework of galactic cycles of greenhouse effect on the Venus. High surface temperature on the Venus is explained by the greenhouse effect during 170–200 mill. years» [42] or carbon dioxide greenhouse effect. The duration of a solar day on the Venus is equal to 116.8 days on the Earth. The Venus is surrounded with dense atmosphere (96 % of CO_2, 4 % — N_2, $3{\cdot}10^{-3}$ % — CO; $1.5{\cdot}10^{-3}$ % — SO_2, etc.) transmitting only 3–4 % of solar emission which heats its surface. Strong opacity for the rays of the infrared self-radiation of the carbon dioxide atmosphere with water vapour ingredient prevents from the surface cooling and thus the classical «greenhouse effect» is observed.

The intensive heat exchange is observed between the Earth's heated surface, troposphere and upper layers of the atmosphere. As a result heat is carried away into the sky. This proves that the weather (climate) on the Earth depends in fact only on the amount of solar energy reaching the planet surface and absorbed



by the latter. The weather conditions in the EU countries, in Ukraine and in the European part of Russia during the 100 years period are shown schematically on Fig. 87.

Data of the work [43] and observations of the authors of this book were used when making this figure. The author of [43] has unfortunately disregarded the severe and cold winters of 1924, 1936, 1946, 1953. He has not also mentioned the dry year of 1946. We have supplemented the figure taken from the work [43] with these data. The increase of CO_2 content in the atmosphere (all the unexpected climate changes being ascribed to it because of the greenhouse effect) was not observed in more remote years. Severe winters which put numerous cities and even regions on the verge of catastrophe and determined annual climate as a whole occurred in the period between 1960 and 1980. The year of 2000 was surprising as to its contrasts. It was warm and long cold spring with cold and frequent late frosts in May, cold in June, rains in July and unusual heat of 37 °C in August, which was not observed in Kiev for almost 200 years, (the same was in 2001: cold May with late frosts, cold and rainy June and 35–41 °C in July). As to September, it «gladdened» us with precipitations which surpassed three month norms. And what is about the greenhouse effect? Where is the average annual temperature rise by 0.7° in the recent 10 years, tons of paper being covered with climatologists' publication concerning this subject.

An interesting publication appeared in Internet on September 18, 2000 where American researchers from NASA presented data obtained with the help of *Trace* — an artificial solar satellite. They considered the processes occurring on the Sun. There were photographs of flares and mighty large prominences of plasma in the Sun in the form of great «coronal loops», as well as the emissions of solar matter in the form of colossal flows of superhot, electrified gas moving away from the Sun to a distance of 300 000 miles in space. It has been established

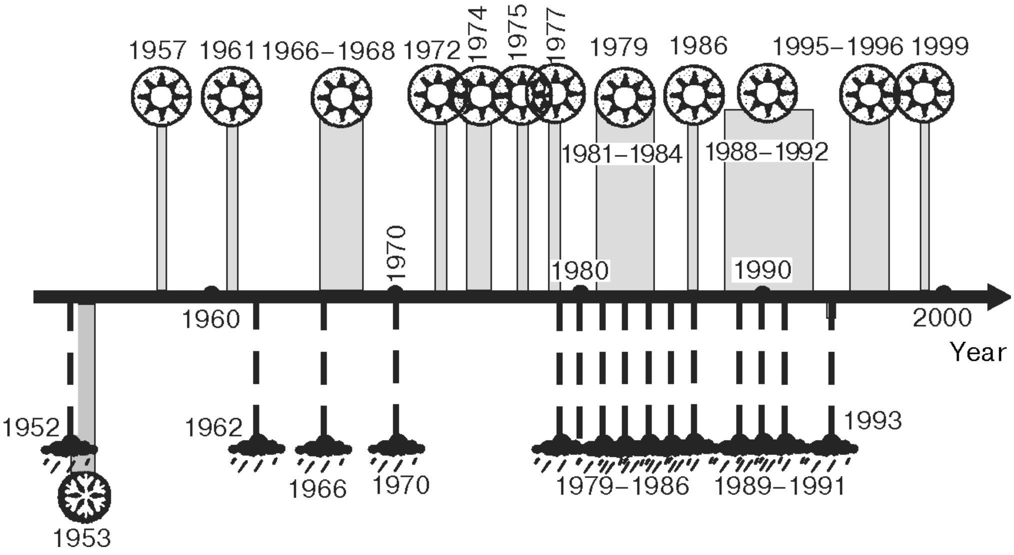


Fig. 87. Characteristic of weather in Ukraine and European part of Russia during 100 years (1900–2000): *1* — cold years; *2* — extremely warm years; *3* — damp years; *4* — dry years

that maximum temperature of the «coronal loops» is observed in the lower part of the loop at a distance of about 10 000 miles from the solar surface, the solar corona temperature being thousands of times higher than that on the solar surface. The ejections of superhot gas move away from the sun surface into space with velocity of 600 miles/s and are a result of the mighty solar storms. It is evident that gas ejections and deep eruptions of solar matter result in the unexpected losses of solar energy. Some share of this energy will not reach our planet Earth as compared to stationary conditions. The solar storm was observed again in December 2000, it was accompanied by the emissions of huge amounts of energy in space, and so, less amount of solar energy reached our planet again. This resulted in severe winter of 2000–2001 in Siberia, Canada, USA and Northern hemisphere as a whole. This helps to make sure of some artificiality of the threat from the greenhouse effect of CO_2 which influence was so favourable for plants, animals and humans for milliards of years. It is solar energy together with water and carbon dioxide which maintain the biological life and carbon circulation on the Earth in the optimal steady temperature conditions.

8.2. Ozone holes

The appearance of the ozone hole in the atmosphere over the Antarctic continent in 1973 was a real shock not only for the average citizens — «erudites» in everything concerning solar radiation threatening the Earth life but also for scientists, specialists in ecology who strived to self-assertion. Since then, this discovery has been considered in periodicals, TV and broadcast programs and even monographs as the unsolved «global problem» threatening the Earth's civilization [44]. The role of ozone in the Earth biosphere defence has been realized by the mankind in the 20th century, but it became nature's concern milliards of years ago. Ozone is formed in the atmosphere at a height of 30–50 km. Relative composition of the main atmosphere components does not change up to the height of 90–100 km, in the so-called homolayer. The atmospheric layer from 30 to 90 km is called a chemosphere because of chemical and photochemical reactions proceeding in it between practically all the components. Depending on the processes taking place in one or another layer, the Earth's atmosphere is divided into the troposphere, stratosphere, mesosphere, thermosphere, exosphere, ionosphere [45] (Fig. 88).

The interlayer boundaries are called tropopause, stratopause, mesopause, thermopause and ionopause. Troposphere is the layer of 10–12 km over the Earth surface. A regular drop of temperature with height equal to 6.5 °C per 1 km up to 10 km is observed in the troposphere. A layer with the lower boundary of 10 km in polar regions and 18 km — in equatorial ones and with the upper boundary of about 50 km belongs to the stratosphere. The main part in establishing the temperature regions in the stratosphere belongs to radiant heat transfer: temperature lowers up to 10 km, and then up to 50–60 km it grows as a result of absorption of solar UV-radiation by ozone molecules. Below 50–60 km the intensity of solar UV-radiation in the wavelength range of 180–290 km considerably decreases as a result of its absorption by ozone molecules and above this height the concentration of absorbing molecules of ozone and water vapour quickly drops. Maximum energy inflow is observed at the height of 50–60 km which leads to temperature maximum. The atmosphere layer from 50 to 80 km belongs to the mesosphere. Radiant heat transfer is the basic energy process here. The temperature drop from approximately 290 to 160 K in the mesopause point is observed in the mesosphere. The thermosphere is at the height from 90 to 400 km. Processes of absorption and conversion of energy of solar short-wave and X-ray radiation occur in the thermosphere, and this determines the increase of temperature up to 2500 K with the height from 200 to 500 km. The temperature value depends on day-time and solar activity. Solar radiation also affects the air density in the thermosphere. Thus, at the height of about 200 km the air density is 1.5–2.0 times higher in the day-time than at night.

Under the absorption of solar UV-radiation quanta with wavelength below 10 mm the atmosphere components are ionized, therefore the main ionosphere regions (D, E, F, and F_2) are distributed in the thermosphere. The thermosphere temperature above the mesopause point is called kinetic temperature. Exosphere [238, 329] is distributed over the thermosphere bounded on height by the thermopause.

The atmosphere regions from 50 to 1000 km and above are called ionosphere. As is seen from Fig. 89 the ionosphere is divided into the regions D, E, F, and F_2 characterized (depending on the height) by different electron concentration (from 10 to 10^6 el./cm^3), positive (Mg^+, Fe^+, Si^+, H_3O^+, NO^+, O_2^+, O^+, H^+,

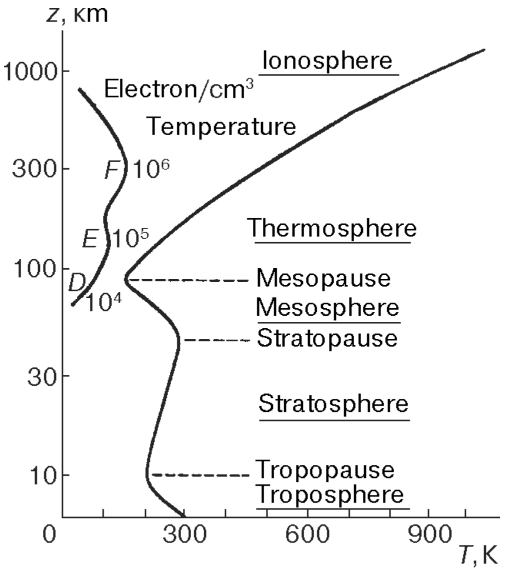


Fig. 88. Atmosphere layers and their names [1]

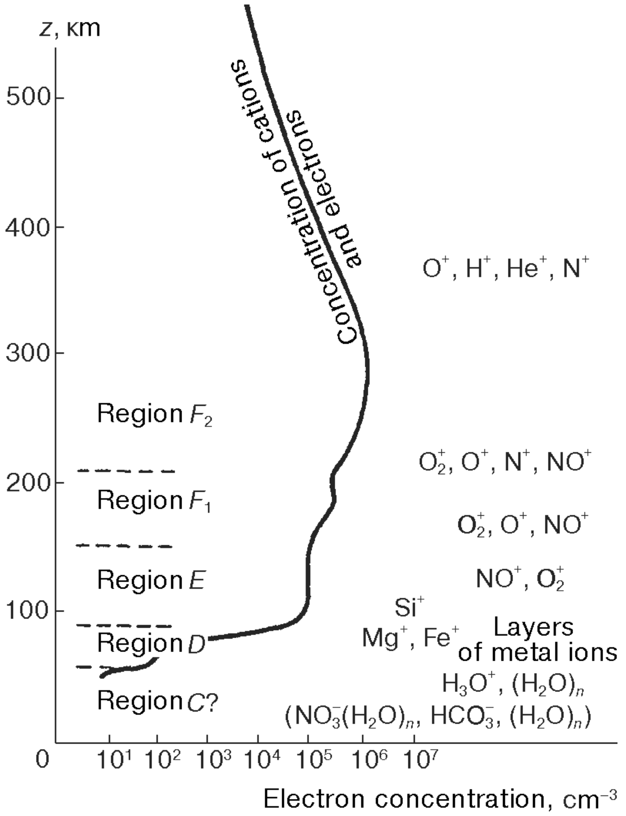


Fig. 89. Ionosphere regions and radicals distribution in them

He^+, N^+) and negative $NO_3^-(H_2O)_n$, HCO_3^-, $SO_x^{y-}(H_2O)_n$) ions in the volume unit. The region *D* stretches to 90 km on height. The electron concentration increase from 10 to 10^3 el./cm^3 in the day time is characteristic of this region. The region *E* is between 90 and 140 km and electron concentration in it is two orders higher (10^5 el./cm^3). Maximum electron concentration (about $2.5 \cdot 10^5$ el./cm^3) is observed in the region F_1 at the height of 200 km in the day-time, which is not observed at night. The electron density maximum in the region F_2 is observed at the height of 300 km.

Complex photochemical reactions with participation of oxygen, nitrogen, argon and impurities polluting the atmosphere (NO_x, SO_2, CO_2, CH_4, etc.) and with formation of atomic oxygen, nitrogen, radicals, cations and anions proceed under the effect of solar and galactic (spatial) radiation in the atmosphere up to 140 km. Both the absorption of solar radiation by atmospheric molecules and its emission by the atmosphere components as a result of fluorescence are observed in the ionosphere. Fluorescence is a result of chemical reactions between the atmospheric ionized components and recombination of excited atoms and molecules formed as affected by electrons and protons. As a result, at the height of 300 km practically all molecular oxygen turns into atomic one. Ion recombination processes (including that of atomic oxygen into molecular) lead to day and night airglow.

In the emission region of 290–170 nm up to the height of 50 km (stratospheric boundary, stratopause) one can observe the reactions of O_2 molecules photoionization with formation of atomic oxygen (Fig. 90):

$$1/2O_2(\text{gas}) + h\nu \neq 0\ (\text{gas}),\ \ \Delta H^0_{298} = 249\ \text{kJ/mol}. \qquad (213)$$

The latter interacts with molecules O_2 with formation of ozone molecules being in the excited state:

$$O_2 + O = O_3^*,\ \ \Delta H^0_{298} = 142.7\ \text{kJ/mol}. \qquad (214)$$

As a result, ozone layer with maximum ozone concentration 10^{12}–10^3 molecules/cm^3 is formed in the atmosphere at the height of 20–25 km [4], according to other data [1] at the height of 30–50 km.

When contacting or colliding with nitrogen or oxygen molecule (atom) the ozone molecules, become deactivated. Ozone — blue gas with strong smell, melting temperature –192.5 (80 K), boiling temperature –111.9 °C (163 K), critical temperature — 12.1 °C (261.05 K) and critical pressure 54.6 atm. Liquid ozone density is 1353, that of solid, at 77.4 K — 1728 kg/m^3. Ozone evaporation heat at 111.9 °C is equal to 14.67 kJ/mol, and at 183 °C it is close to 15.27 kJ/mol. Ozone dipole moment is $1.69 \cdot 10^{-30}$ Cl · m. Nuclear spacing in molecule is 127.17 pm, valence angle — 116°47′. Ionization potential of ozone O_3, equal to 11.7 eV only a bit differs from ionization potential of oxygen O_2 (12.06 eV) and water H_2O (12.61 eV) and is considerably lower than ionization potential of fluorine F_2 (15.7 eV), which evidences for ozone inertness with respect to molecular fluorine. Ozone solubility in water at 0 °C is 8.3, and at 20 °C — 4.7 (mg/l). Ozone is very much toxical (MPC = 0.01 mg/m^3) and possesses limited solubility in liquid oxygen.

According to [1] the formed layer which contains ozone at a height of 30–50 km is sometimes called ozonosphere. Besides ozone formation reactions (213) and (214) there proceed the reactions:

$$O + O_2 + \theta \rightarrow O_3 + \theta^* + 100\ \text{kJ};\quad k = 7.5\cdot 10^{-34}\ (T/300)^{-26}\ \text{cm}^3/\text{s}; \qquad (215)$$

$$O + O_3 \rightarrow 2O_2 + 390\ \text{kJ};\quad k = 1.2\cdot 10^{-11}\ \exp(-2000/T)\ \text{cm}^3/\text{s}, \qquad (216)$$

where θ^* is some third particle, for example, N_2 or O_2.

Dependence of the depth of solar radiation penetration to the atmosphere on the wavelength [46] is shown in Fig. 42. It is seen that in the wavelength range of 20–80 nm the solar radiation is absorbed by molecular nitrogen and atomic

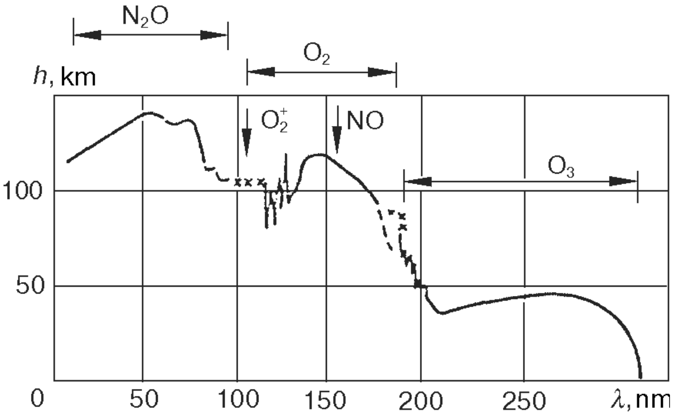


Fig. 90. Dependence of the penetration depth of solar radiation to the atmosphere on wavelength l. Radiation absorption regions are shown by arrows [46]

oxygen, in the wavelength range of 80–200 nm — by molecular oxygen, that results in its photodissociation into atomic oxygen according to the equation

$$O_2 + O^* + hv \leftrightarrows O - O^* \tag{217}$$

where O^* is atomic oxygen in the excited state.

The excited oxygen interacts actively with molecular oxygen with ozone formation

$$O_2 + O^* + hv \leftrightarrows O_3 - O, \tag{218}$$

and radicals possessing high reactivity:

$$O^* + H_2O \rightarrow 2OH. \tag{219}$$

In the wavelength range of 200–290 nm at the height of 45–47 km the solar radiation is mainly absorbed by the reactions (8.36) and (8.47). Maximum ozone concentration (1.5 mol/l) is at the height of 30 km. In the range of solar radiation wavelength of 200 < n < 320 nm there occurs ozone photodissociation by the reaction

$$O_3 + hv \rightarrow O_2 + O^*, \tag{220}$$

thus the formation and decay of ozone molecules are in the constant dynamic equilibrium. Activated ozone molecules in the troposphere and stratosphere undergo the exchange reaction with the atmosphere components — oxygen and nitrogen molecules

$$O_3^* + O_2 \rightarrow O_3 + O_2^* \tag{221}$$

$$O_3^* + N_2 \rightarrow O_3 + N_2^*, \tag{222}$$

the excited molecules of these elements being formed as a result.

Gaseous ozone is in disproportion, according to exothermal reaction with changes in the Gibbs' free energy equal to $\Delta G^0_{298} = -324.8$ kJ/mol,

$$2O_3 \rightarrow 3O_2,\ \Delta H^0_{298} = -285 \text{ kJ/mol.} \tag{223}$$

This reaction equilibrium constant calculated from the equation

$$\lg K^0_{\mathrm{p}} = a^3_{O_2}/a^3_{O_3} = -G^0_{298}/2.303RT, \quad (224)$$

proved to be equal to $K^0_{\mathrm{p}} = 8.4 \cdot 10^{56}$ (where $a^3_{O_2}$ and $a^3_{O_3}$ — activities of molecular oxygen and ozone).

The high equilibrium constant value proves that the equilibrium ozone activity (in the first approximation — concentration) is extremely low and equilibrium of the reaction (223) is shifted rightwards. Thus, the dry atmospheric air at the level of the Earth's surface contains 20.95 % of oxygen and only about (2–3) · 10^{-6} % of ozone. The reaction (223) is of the greatest importance under the establishment of the equilibrium ozone concentration in the atmosphere since, as it follows from the value ΔG^0_{298}, it can proceed spontaneously.

The region of heights from 30 to 90 km, i. e., including a part of the stratosphere and mesosphere, is called chemosphere (Fig. 30). In this region the high-velocity reactions proceed between oxygen, nitrogen, argon, and low impurities (SO_2, CO_2, CH_4, H_2O) as well as with radicals (OH, OH_2) charged with particles and ions (O^+, N^+, NO^+, H_3O^+, NO_3^-, NO_3^-, O_2^-, O^+, e^-, H^+, He^+), as well as photochemical reactions between neutral components, between particle both in the basic and excited states:

$$H_2O + hv = OH + H; \tag{225}$$

$$H^* + O_3 \rightarrow O_2 + OH; \tag{226}$$

$$OH^* + O_3 \rightarrow HO_2 + O_2; \tag{227}$$

$$O_3 + NO \rightarrow NO_2 + O_2. \tag{228}$$

Ozone, atomic oxygen and OH radicals interact actively with organic compounds (methane, olefines, etc.) [47], oxidate them by stages to CO_2 and then to carbonate-radicals taking part in the nature turnover.

Complex organic compounds are oxidized by O_3 and OH to peroxide-radicals. The latter are intermediates and undergo the reaction of organics decomposition. Ozone, atomic oxygen, OH radicals and their derivatives oxidate halogens (chlorine, bromine, iodine) to chlorates, bromates and iodates which then participate in the reactions with organic derivatives and as if reproduce the oxidative potential of initial oxidizers. In this case ozone, atomic oxygen and OH radicals perform the sanitation of both lower and upper layers of the atmosphere.

In the upper layers of the atmosphere at the altitude of 90 to 200–400 km there occur the basic processes of absorption and conversion of the energy of solar short-wave (hard) UV and X-ray radiation into the thermal energy. As a result, the temperature of atmospheric particles and radicals increases in the thermosphere depending on time of the day and solar activity. At the altitude of 200–490 km kinetic temperature increases from 200 to 1000–2000 K and then remains constant as a result of thermodynamic balance between the amount of the obtained solar energy and that emitted into the space.

Under the absorption of quanta of ultraviolet solar radiation with wavelength $\lambda < 120$ nm there proceeds ionization of the atmosphere components and this leads to formation of several ionosphere layers distributed within the thermosphere. Oxygen and nitrogen molecules, atoms, ions, radicals and electrons of the ionospheric layer move in the interplanetary space jointly with the Earth. They form the protective radiation belt of the Earth. It is the belt at the altitude of 200–400 km which provides for the Earth's biosphere protection from the fatal hard solar radiation. Thus, when energy quanta hv (photons) emitted by the Sun are absorbed by oxygen and nitrogen, there occur photodissociation reactions.

$$N_2\text{(gas.)} + hv = N\text{(gas.)} + N\text{(gas.)}, \qquad \Delta H^0_{298} = 474 \text{ kJ/mol}; \tag{229}$$

$$O\text{(gas.)} + hv = O^+\text{(gas.)} + e^-, \qquad \Delta H^0_{298} = 1569 \text{ kJ/mol}; \tag{230}$$

$$O_2\text{(gas.)} + hv = O_2^+\text{(gas.)} + e^-, \qquad \Delta H^0_{298} = 1172 \text{ kJ/mol}; \tag{231}$$

$$N\text{(gas.)} + hv = N^+\text{(gas.)} + e^-, \qquad \Delta H^0_{298} = 1883 \text{ kJ/mol}; \tag{232}$$

$$N_2\text{(gas.)} + hv = N_2^+\text{(gas.)} + e^-, \qquad \Delta H^0_{298} = 1509 \text{ kJ/mol}; \tag{233}$$

$$N_2\text{(gas.)} + O + hv = NO^+ + N + e^-, \qquad \Delta H^0_{298} = 1214 \text{ kJ/mol}. \tag{234}$$

Dissociation and ionization of the atmosphere components (molecular oxygen and nitrogen) result in the change of the atmosphere composition with altitude: atomic oxygen prevails at the altitude above 300 km.

The reactions (229)–(234) are endothermal and they are of the most importance for life support and survival on the Earth. Proceeding from positive enthalpies of formation of atomic oxygen and nitrogen as well as extremely high values of ΔH^0_{298} for the radicals O^+(gas.), O_2^2(gas.), N^+(gas.) and N_2^+(gas.) one can conclude about their high tendency to recombination reactions characteristic of gases in the state of plasma:

$$\mathrm{N(gas.)} + e^- \rightarrow 2\mathrm{N}; \qquad (235)$$

$$\mathrm{O(gas.)} + e^- \rightarrow 2\mathrm{O}; \qquad (236)$$

$$\mathrm{NO^+(gas.)} + e^- \rightarrow \mathrm{N} + \mathrm{O}, \qquad (237)$$

as well as the reactions of exchange

$$\mathrm{N{+}O_2 \rightarrow NO{+}O{+}133.5\ kJ}, \quad k_A = 1.4\cdot 10^{-11},\ \mathrm{cm^3/s}; \qquad (238)$$

$$\mathrm{N{+}NO \rightarrow N_2{+}O{+}313.8\ kJ}, \quad k_B = 1.4\cdot 10^{-11}\exp(-3570/T),\ \mathrm{cm^3/s}; \qquad (239)$$

$$\mathrm{NO_2}{+}hv \rightarrow \mathrm{NO{+}O{+}133.5\ kJ}, \quad k_C = 2.2\cdot 10^{-11},\ \mathrm{cm^3/s}. \qquad (240)$$

By the equations (8.60) and (8.61) one can calculate the constant of nitrogen oxide:

$$[\mathrm{NO}] — k_B/k_C \cong 10^{-5}\,[\mathrm{O_2}], \qquad (241)$$

in accordance with this equation NO concentration is proportional to the content of molecular oxygen [1]. Chemical and photochemical reactions of formation of positively and negatively charged particles under the effect of solar radiation and electron flow proceed in the stratosphere, mesosphere and ionosphere:

$$\mathrm{N} + hv \rightarrow \mathrm{N^+}; \qquad (242)$$

$$\mathrm{N_2^+ + O_2 \rightarrow N_2 + O}\ ; \qquad (243)$$

$$\mathrm{N_2^+ + O \rightarrow NO^+ + N}; \qquad (244)$$

$$\mathrm{O^+ + N_2 \rightarrow NO^+ + N}; \qquad (245)$$

$$\mathrm{N_2^+ + O \rightarrow N_2O^+}; \qquad (246)$$

$$\mathrm{N_2O^+ + e^- \rightarrow N_2O}; \qquad (247)$$

$$\mathrm{O_2^+ + N_2 \rightarrow NO^+ + NO}; \qquad (248)$$

$$N_2O + e^{-} \rightarrow N_2O^{-}; \qquad (249)$$

$$O + e^{-} \rightarrow O^{-}; \qquad (250)$$

$$O_3 + e^{-} \rightarrow O_2 + O^{-}; \qquad (251)$$

$$O_2 + M + e^{-} \rightarrow O_2^{-} + M; \qquad (252)$$

$$O_2^{-} + O \rightarrow O_2^{-} + O_2. \qquad (253)$$

The reactions (249) and (250) of formation of negatively charged ions are called electrons adhesion reactions and reactions (251) and (252) — those of dissociative adhesion. The reaction rate constant (253), being the basic in the domain D of the ionosphere, is equal to $k = 3.5 \cdot 10^{-10}$ cm^3/s. Ion O_3^{+} interacts actively with CO_2 by the reaction

$$O_3^{-} + CO_2 \rightarrow CO_3^{-} + O_2. \qquad (254)$$

Thus the lifetime of the ion O even at the altitude of 80 km which is relatively rich with atomic and molecular oxygen, with respect to the reaction (253), is only 0.01 s. Ozone molecules form in the ionosphere by the reaction of associative separation of the electrons.

$$O_2^{+} + O = O_3 + e^{-}. \qquad (255)$$

Such reactions affect the propagation of radiowaves in the ionosphere [1].

In the upper atmosphere layers the reactions of atmosphere components with ionospheric protons make great contribution to formation of positively charged ions and radicals:

$$H^{+} + O + O^{+} + H, \qquad k = 3.8 \cdot 10^{-10}; \qquad (256)$$

$$H^{+} + NO \rightarrow NO^{+} + H, \qquad k = 1.9 \cdot 10^{-9}; \qquad (257)$$

$$H^{+} + CO_2 \rightarrow COH^{+} + O, \qquad k = 3 \cdot 10^{-9}. \qquad (258)$$

Thus the upper layers of the atmosphere, as it was noticed above, consist of atomic oxygen, nitrogen, radicals N^{+}, N^{2+}, O^{+}, O^{2+}, NO^{+}, N_2O^{+} and N_2O molecules. The above particles form plasm. Proceeding from the data of [50, 51], plasm formation in the upper atmospheric layers (above 80 km) ensures the propagation of radiowaves and protects phyto- and cytoflora of the Earth from hard solar radiation.

Energies of formation of atomic oxygen and nitrogen molecules (E_i) are equal $E_0 = 4.11 \cdot 10^{-19}$ and $E_N = 8.2 \cdot 10^{-19}$ J/mol, respectively. Such energy in inherent in photons with wavelength λ, calculated from the equation

$$\lambda = hc / E_i, \tag{259}$$

where h is Plank constant ($6.6 \cdot 10^{-34}$ J/s); c — light velocity ($3 \cdot 10^8$ m/s); E_i — energy of atomic oxygen and nitrogen, J.

Thus, oxygen and nitrogen photodissociation proceeds under the adsorption of short-wave (ultraviolet) radiation with wavelength 120.5 and 242.0 nm. Oxygen and nitrogen ionization in the upper layers of the atmosphere up to, approximately, 50 km from the Earth's surface leads to formation of plasm consisting of ions and radicals (see, equations (229) — (237), (242)).

Ozone O_3, atomic oxygen O and radicals OH display high reactivity and are stronger oxidizers than oxygen. Standard redox potential of OH radical in the reaction

$$OH + e^- \leftrightarrow OH^- \tag{260}$$

equals $E^0 = 1.9$ — 2.02 V, and atomic oxygen in half-reaction

$$O + 2H^+ + 2e^- \leftrightarrow H_2O \tag{261}$$

possesses even higher positive value of standard potential — $E^0 = 2.422$ V.

Ozone O_3 in the half-reaction

$$O_3 + H_2O + 2e^- \leftrightarrow O_2 + 2OH \tag{262}$$

has a standard potential ($E^0 = 1.24$ V), close to the standard potential of oxygen electrode ($E^0 = 1.229$ V). Ozone is only a bit more reactive than oxygen. Consequently, the atomic oxygen O, O^* and radicals OH, OH^* in the upper layers of the atmosphere are ozone «protectors», since, being more reactive, they indergo the reaction with molecular oxygen with ozone formation by the equations (214), (215), (218), (255), as well as with other ions and molecules-restorers (CH_4, SO, SO_2, N_2, etc.). It is atomic oxygen O, O^* and radicals OH, OH^* which do not allow to simply «disintegrate» ozone molecules. Moreover, the atomic oxygen and OH radicals are capable to oxidize molecular nitrogen to oxides N_2O and NO:

$$N_2 + O \rightarrow N_2O; \tag{263}$$

$$N_2O + O \rightarrow 2NO; \tag{264}$$

$$N_2 + O^{-}H^{+} \rightarrow N_2^{-}O + H^{+}; \qquad (265)$$

$$N_2^{-}O + O^{-}H^{+} \rightarrow 2NO^{-} + H^{+}. \qquad (266)$$

Oxides N_2O and NO are non-salt-forming, they are insoluble in water (N_2O — 1.3 of volume, NO — 0.07 of the volume per 1 volume of H_2O at 0 °C) and react neither with water nor with its vapours, but create the oxidative background of the environment. That is why, that nitrogen taking part in the nature circulation during milliards of years, never did harm the Earth's ecology. Besides free nitrogen, which is absorbed by anaerobic bacteria, the Earth's airspace always contained permissible ecologically balanced concentrations of nitrogen compounds: traces of ammonia — the product of decaying of organic nitrogen-containing compounds, nitrogen oxides N_2O, NO and NO_2, traces of nitrous HNO_2 and nitric HNO_3 acids — the products of interaction between nitrogen oxides formed in the process of atmosphere electric discharges and water H_2O vapours.

Ozone in acidic solutions and media is a strong oxidizer, but its oxidizing capacity is lower than that of molecular fluorine and its compounds as it can be judged by the reaction potentials (262) and reactions

$$OH + H^{+} + e^{-} = H_2O; \qquad E^0 = 2.85\ \text{V}; \qquad (267).$$

$$O_3 + 2H^{+} + 2e^{-} = O_2 + H_2O\ ; \qquad E^0 = 2.07\ \text{V}; \qquad (268)$$

$$O_3 + 6H^{+} + 6e^{-} = 3H_2O; \qquad E^0 = 1.511\ \text{V}; \qquad (269)$$

$$O_2 + 4H^{+} + 4e^{-} = 2H_2O; \qquad E^0 = 1.229\ \text{V}; \qquad (270)$$

$$F_2O + 2H^{+} + 4e^{-} = 2F^{-} + H_2O; \qquad E^0 = 2.153\ \text{V}; \qquad (271)$$

$$F + H^{+} + e^{-} = HF; \qquad E^0 = 2.85\ \text{V}; \qquad (272)$$

$$F_2O + 2H^{+} + 2e^{-} = 2HF\ (\text{aq.}); \qquad E^0 = 2.806\ \text{V}; \qquad (273)$$

$$F_2 + 2e^{-} = 2F^{-}; \qquad E^0 = 2.866\ \text{V}; \qquad (274)$$

$$F_2 + H^{+} + 2e^{-} = HF\ ; \qquad E^0 = 2.979\ \text{V}; \qquad (275)$$

$$F_2 + 2H^{+} + 2e^{-} = 2HF; \qquad E^0 = 3.06\ \text{V}. \qquad (276)$$

Most of the presented reactions can proceed in the Earth's atmosphere under the effect of cosmic rays representing a flow of protons (H^{+}) muons (μ), electrons (e^{-}) and other particles possessing huge energy [52]. In the atmosphere, the cosmic rays when interacting with molecules and atoms of oxygen, nitrogen, other molecules of the atmosphere, form the «cascades, showers of elementary particles». The interaction of particles between themselves with formation of the excited particles and their degradation is accompanied by secondary emission. Besides ozone, the Earth's biota is protected from the hard solar and spatial degradational emission by molecular oxygen, nitrogen and their derivatives, as well as by hydrogen.

As was noted in Chapter 7, hydrogen content in the Earth atmosphere is only $5 \cdot 10^{-5}$ vol. %. Hydrogen is continuously supplied to the atmosphere as a result of the functioning of hydrogen bacteria of biomass of organic carbon. Possessing the least specific weight, hydrogen as well as helium are not accumulated in the atmosphere but move to the upper layers of the atmosphere. As is seen from Fig. 89, positively charged ions H^+, O^+, He^+, N^+ are in the ionosphere area. These ions are a product of power-consuming endothermal reactions of dissociation and ionization of molecular hydrogen, oxygen, helium, nitrogen, as well as water molecules in the process of their movement from the lower to higher atmospheric layers. In the lower atmospheric layers one can observe the intensive circulation as well as the fact that the atmospheric molecular composition remains constant up to 100 — 150 km. Ozone is contained in the range within 10–80 km with maximum concentration at a height of about 30 km. When affected by solar ultraviolet emission ($\lambda = 0.16$–0.21 μm) there occurs continuous synthesis of ozone by the reactions (215), (218), (255). From the data of L.I. Miroshnichenko the UV-rays intensity increases during solar flares and this results in the 2-fold increase of ozone concentration in the upper part of ozonosphere (above 35 km). The increase of ozone concentration leads to the decrease of the solar radiation flux supplied to the atmospheric layer below 20 km as well as to the troposphere and, as a result, it leads to the drop of the Earth surface temperature. It has been established that the double increase of O_3 concentration corresponds to the decrease of the temperature near the Earth surface by 0.8–1.2 °C. As was noted above, a regular drop of temperature to 203–208 K (minus 65–70 °C) is observed in the troposphere at a height of the tropopause — 10 km. The intensive heat exchange takes place in the troposphere. The average annual Earth surface temperature was 14.40 °C in 1990 and 1997, decreased to minimum 14.11 °C in 1992 and then in grew gradually and reached 14.40 °C in 1987 [2].

Later, as a result of the UV-radiation absorption by molecules N_2, O_2, watervapours, etc., one can observe a slow temperature rise and in the stratopause range at a height of 50–60 km (see, Fig. 83) it reaches — 2 ÷ +6 °C. In the mesosphere, as a result of the solar radiant energy consumption for the process of ionization and thermodissociation of the atmosphere components the temperature begins falling down to 160 K (–123 °C) in the mesopause. Molecular oxygen begins dissociating above 100 km in the atmosphere as affected by solar radiation, molecular nitrogen — above 200 km [45]. The lack of the atmosphere circulation at heights of 150–200 km the atmosphere separates into the zones enriched with atomic oxygen and higher — by atomic nitrogen. By the data of [45] atomic oxygen predominates in the upper atmopshere at a height of 150–180 km. Above 200–220 km there is a zone of «prevalence of light atom of helium, and especially hydrogen». High chemical affinity of hydrogen for atomic oxygen and nitrogen (ΔGH_2O = –237.24 kJ/mol, ΔGH_2O_2 = –120.4 kJ/mol, ΔGNH_3 = –16.71 kJ/mol, etc) creates a protective barrier to the cosmic radiation effect on planet Earth. The velocity of atomic and molecular hydrogen interaction with oxygen and atomic nitrogen increases under UV- and cosmic neutron irradiation. As a result, a zone of buffer protection from hard radiation is created in the upper atmospheric layers. The upper layers of the ionosphere enriched with positively charged ions H^+, O^+, He^+, N^+ protect planet Earth both from positively charged cosmic rays, their flux being decelerated by electrostatic repulsion , and from negatively charged corpusles — by interaction with the latter. Thus, we think that hydrogen and helium side by side with atomic oxygen and nitrogen play more important part in the Earth biota protection from the «affecting» extraterrestrial radiation than ozone [48,49].

Freons. The decrease of ozone concentration in the atmosphere over the Antarctic continent, compared to its content in the North hemisphere air (in the same latitudes) was detected for the first time in 1850 [54, 55]. More than a century later, in 1958, French researcher Paul Rigault and Bernar Lerois fixed even more decrease of ozone content in the air over the Antarctics. In 1974 American researchers Ch. Rowland and M. Molinat made a hypothesis that the ozone layer is destroyed by freons. Publication of the work by J. Forman in 1985, where the author explained the «ozone holes» formation over the Antarctics by the destructing effect of freons, provoked an attack on their production. It would be noticed that in the 1850's freons were not widely used in refrigerators and thus, they could not cause the decrease of ozone concentration in the ozone layer. Thus, the fact that ozone content over the Antarctics, found by J. Forman in 1985 was 1.5 times higher as compared with the data of Paul Rigault and Bernar Lerois in 1958, evidences for the inflience of other factors, including the season, on the ozone content. But after the appearance of J. Forman's work the hypothesis made by Ch. Rowland and M. Molinat was widely recognized. It was considered that the ozone holes are formed as a result of interaction of the halogen-containing compounds — freons with ozone. They stated that freons are ozone-destructing substances though atomic oxygen O, O^* and radicals OH, OH^* more quickly react with methane than with freons which, in our opinion, is more inert than most reducers.

It was offered to forbid production and use of freons in refrigerating and other branches of technology. By that time there existed a whole series of freons and such halogenorganic compounds as trichlorofluoromethane CCl_3F ($T_{melt.}$ — 111.11 °C, $T_{boil.}$ — 23.77 °C), dichlorodifluoromethane CCl_2F_2 ($T_{melt.}$ — 150 °C, $T_{boil.}$ — 29.80 °C), chloropentafluoroethylene C_2ClF_5 ($T_{melt.}$ — 106 °C, $T_{boil.}$ — 38.00 °C), bromotrifluoromethane $CBrF_3$ ($T_{melt.}$ — 143 °C, $T_{boil.}$ — 58.70 °C), etc., which were used under the grades F-11, F-12, F-115 and F-13B1 as freons — working media of refrigerators. Investigations have shown that freons possessing properties for their use in refrigerating aggregates would have considerable evaporation heats, low melting and boiling temperatures and not to promote metal corrosion, to display low toxicity, to be made with the use of ecologically safe technologies. Freons are insoluble in water and water solutions; freons are not hydrolyzed, they are inert. But there are no qualitative data concerning the kinetics and mechanisms of freons reactions with ozone. What products are formed in freons interaction with ozone? Does freon interact with ozone? It is not known how does the hard short-wave solar radiation affect this reaction. Do freons interact with harmful gas emissions (NO, NO_2, SO_2, HF, F_2) of industrial plants?

The Vienna Convention, which suggested the detailed investigation of the causes of ozone stratum exhaustion, was adopted in 1985. In 1987 the Montreal. Protocol was accepted which forbade production of ozone-hazardous substances and lobbied a new coolant R-134 made by *Dupount* Company instead of freon [55]. Ukraine signed the Montreal Protocol and pledged itself to stop the use of freons by the end of 1998 and to use only coolent R-134, which was 4 times more expensive than freons and required more electric energy (by 10–20 %) per cold unit. Besides, R-134 is toxic, forms toxical substances — fluorides and dioxines, it can initiate the greenhouse effect. It was calculated that the conversion of refrigerators in Ukraine and the use of R-134 will result in unjustified expenditures of 1 milliard dollars [55].

It is supposed that the freon adding to the air-ozone mixture and their irradiation with hard UV-rays, would result in photochemical reaction. Then ozone molecules disintegrate into molecular and atomic oxygen absorbing hard UV-radiation. Then atomic oxygen oxidizes freon and emits hard UV-rays again but with another wavelength. According to the data of [44], that was the phenomenon observed in experimental investigations which had to prove that freon could form the ozone holes. On the other hand freon lifetime in the atmosphere is equal to 130 years [4]. This can evidence for the fact that freon is resistant to ozone and other oxidizers. Such a conclusion also agrees with the values of standard electrode potentials of half-reactions of ozone, oxygen and fluorine compounds.

The attempts to substitute freons used in domestic facilities and industry were made even in the 30's, 50's and 90's. Different firms offered a lot of substitutes — freons-coolants: the above R-134 ($C_2H_5F_4$), R-125 (C_2HF_5), R-32 (CH_2F_2), R-23 (CHF_3), etc. The above freons have been characterized in [56] as «coolants-substitutes». They consume more energy as compared to freons used in industry and domestic appliances; they are toxic, ecologically hazzardous and do not meet the above requirements. An analysis of the offered coolants showed them to be more reactive not only to ozone but also to oxygen than the forbidden freons R-12 ($C_2F_2Cl_2$), R-11 (C_2Cl_3F), R-113 ($C_2Cl_3F_3$), R-114 ($C_2Cl_2F_4$), R-115 (C_2ClF_5).

According to [44] freon has nothing to do with ozone holes, and the author has made an interesting calculation to prove that. He has estimated the mass of the Earth's atmosphere which proved to be equal to $5 \cdot 10^{15}$ t., i. e., very close to the exact value of the atmosphere mass — $5.13610 \cdot 10^{15}$ t [38]. Chemical industry of the world manufactures 10^5 t of freon a year. The calculation shows that the freon produced all over the world being ejected in the atmosphere, its content of 0.01 % in the atmosphere will be reached only in a milliard years. Freon losses in the atmosphere do not really exceed 0.1 %. Thus the concentration of freons in the atmosphere will reach 0.00 001 % in one milliard years, it will be equal to $1 \cdot 10^{-8}$ % in one million years, which is below all the possible maximum permissible concentrations. And that will be only in 1 million years!!! These data prove that the problem of industrial freon and its interrelation with ozone holes are not correct. The convention which was accepted by the UNO states and prohibited the production of freons, is also underlied by erroneous preconditions and explicit conjuncture [51, 54- 57].

It is interesting to notice that in the opinion of the authors of this book the ozone holes were formed over the Antarctic continent and Arctics already during the Earth formation; the Earth had the atmosphere which contained oxygen. The ideas of oxygen appearance are contradicting. From the data of [5] oxygen appeared on the Earth 500–600 million years ago as the result of development of biogenic life. Proceeding from the recent data of paleontology, concerning the discovery of the Vendian system with the oldest fauna of large frameless organisms and availability of flora in that period, one can suppose that oxygen for their development had to exist on the Earth more than $4 \cdot 10^{-9}$ years ago. That was also the period of formation of the ozone protection of the Earth from hard solar and cosmic emission.

In accordance with observations of most researchers the ozone holes appear in winter and completely disappear («heal») in summer. We think that appearance of ozone holes is caused by the position of the North and South hemispheres of planet Earth relative to the Sun depending on the season. It is known that the Earth's axis is inclined by 23°26′30″ relative to the vertical [45]. The Earth rotation determines the alternation of day and night on its surface. The seasons change as a result of the Earth revolution round the Sun in an elliptical orbit, the constant slope of the rotation axis being preserved. The Earth's mean radius is equal to 6371.315 km, that of the Sun-695950 ± 810 km, i. e. the Earth size is 109.23 times less. Distance from the Earth to the Sun is 149.437 million kilometers [38]. When moving in the elliptical orbit the distance between the Earth and the Sun, distributed in one of the orbit foci, change from 149.457 mill. km (at perigee) to 152.083 mill. km (at aphelion). A scheme of planet Earth position relative to the Sun with summer coming in the North hemisphere and winter — in the Southern one, is presented in Fig. 8, *a*. Since the Sun dimension exceeds 109 times the Earth one and the Sun is at the distance of 149.457 mill. km, it is seen that the solar beams are directed parallel to the Earth. The Earth axis slope relative to the vertical does not allow solar emission to get the Antarctics atmosphere during winter in the South hemisphere (Fig. 91, *a*), and to the North Pole atmosphere during winter in the North hemisphere (Fig. 91, *b*). Thus, ozone is not produced in the atmosphere of the Antarctic continent and Arctics during winter in the Southern and Northern hemisphere.

As it was shown above the solar emission with wavelength below 290 nm does not reach the Earth surface but is absorbed by ozone exciting the photolysis reactions of molecules of oxygen, carbon oxides, nitrogen (218), (221), (255) with formation of atomic oxygen, nitrogen and different radicals. Since during winter in the South hemisphere solar emission is absorbed by the atmosphere components and does not reach the mesosphere, stratosphere and troposphere over the South Pole (Fig. 91, *a*) then the reactions of molecular oxygen photolysis do not proceed over the Pole and the atomic oxygen is not formed. The latter leads to the consumption of the already formed atomic oxygen and to gradual damping of ozone production by the reactions (218), (221), (255), etc. As a result, ozone from the ozone layer which maximum is at the altitude of 30 km is consumed gradually, and the ozone hole appears over the Antarctic continent. In summer the solar emission in the Antarctics (Fig. 91, *b*) reaches its atmosphere and is absorbed by the atmosphere as a result of photochemical reactions. As a consequence, ozone is produced in the South Pole atmosphere and the ozone layer is formed — the ozone hole is healed. At that time (summer in Antarctics) winter comes to the North hemisphere (the Arctic) — the solar emission does not reach the North Pole atmosphere which leads to disappearance of atomic oxygen and to stoppage of ozone formation. The ozone layer, its thickness being maximum in summer months, is gradually destructed which results in the ozone hole formation over the North Pole. That may be the miracle of appearance of the ozone holes.

The total ozone content over the territory of Ukraine is observed at 6 ozonometrical stations. These observations serve as the basis for calculating the average daily deviation of the total ozone content from the climatic norm in the units of standard deviation «S». There can exist critical and anomalous situations. Deviations of S values within 2.0–2.5 are referred to critical situation, the anomalous one is observed at $S > 2.5$, that evidences for availability of the ozone hole. Neither critical, nor anomalous situations were ever observed over the territory of Ukraine [58].

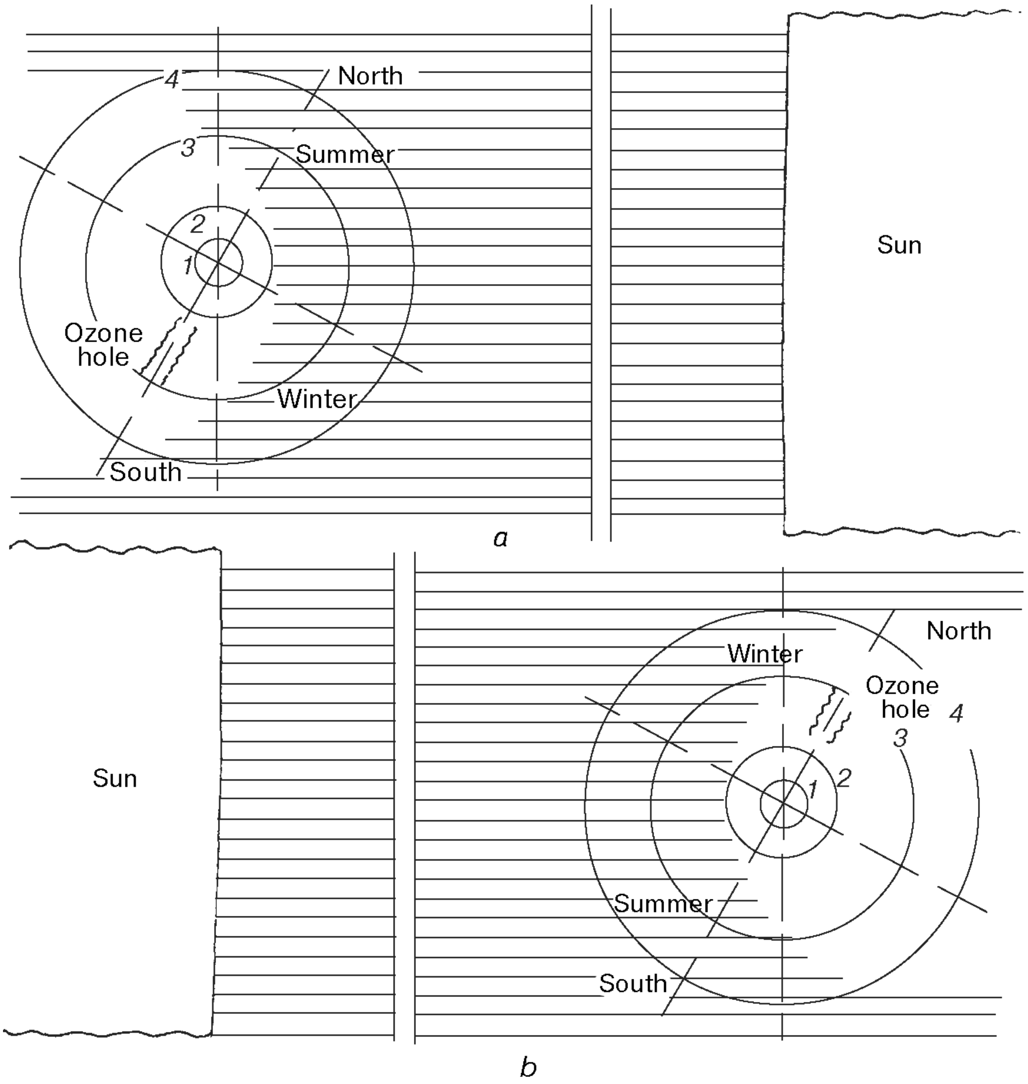


Fig. 91. Scheme of position of the Northern and Southern hemispheres of Planet Earth relative to the Sun depending on the season — the cause of ozone hole appearance: *1* — Plane Earth; *2* — troposphere boundary (tropopause); *3* — stratosphere boundary (stratopause); *4* — mesosphere boundary (mesopause)

It follows from the above stated, that ozone is formed in the upper layers of the atmosphere, and it has been is dynamic equilibrium with other atmospheric component from the time of oxygen appearance on the Earth, i. e., during several milliard years. Thus, one can state that the protective ozone «veil» of the Earth is of practically constant thickness and can be only temporarily subject to the changes as a result of natural cataclysms (volcano eruption, earthquakes, cyclopic typhoons, etc.) but it simply restores during short periods of time. That is obviously proved by Fig. 92 presenting deviations of the total ozone content from the norm by the observed data ozonometric stations of the

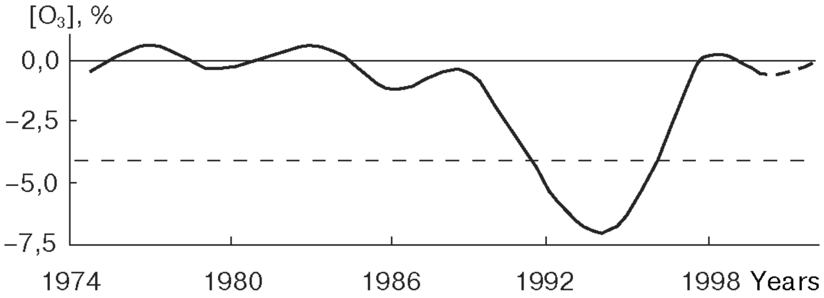


Fig. 92. Scheme of the total ozone content deviation from the norm

former Soviet Union [54]. A solid line shows a null deviation, a dash line — dangerous average ozone content deviation. One can see clearly ozone content deviation from norm observed from 1982 to 1996. In the opinion of the authors of [54] the decrease of ozone content in that period was determined by the eruption of Il Ci Con and Pina Tubo volcanoes which outbursted huge amount of chemically active aerosol, SO_2, etc., into the atmosphere. During the period of 1997–1999 total amount of ozone in the Earth atmosphere, except for the winter months over the Antarctic continent, reached the null deviation from norm. Consequently, the nature has coped with pollution during a short period of time, and a null deviation from the normal ozone content in the atmosphere has been established again.

The authors of [54] note that the concentration of ozone-destructing substances in the upper layers of the atmosphere has not changed and remained maximum for all the past period. Thus, they consider that the major postulate of the ozone problem is showing signs of breaking up. The researchers which connected considerable variations of ozone content rather with global climatic changes than with freon production proved to be right.

Such a conclusion is in good agreement with the data of analysis of the Antarctic ice delivered by the Ukrainian Antarctic Expeditions I and II. By the analysis data the Antarctic ice contains ozone destruction substances considered technogenic in accordance with the Montreal Protocol. But since the ice age is 900 years, naturally, there arises the question: can these compounds form in natural way (as a result of volcanoes eruption, degassation of the litosphere becuse the great number of fissures, formation of methane in the planet bogs and ether oils by plants, etc.)? Really, according to analysis results, the ice contained numerous chlorine and bromine derivatives of methane, CCl_4, chloroform, methylchloroform, bromoform, as well as aromatic hydrocarbons. From the data of [36], considerable concentrations of halogen-organic compounds evidence for the fact that the basic contribution to the atmosphere flow of ozone destructing compounds is made by ocean biogenic sources which produce ozone destructors included in the Antarctic ice. Thus the total ozone content in the atmospheric ozone layer of the is affected, in the first turn, by nature cataclysms and, first of all, by volcano eruptions. So, the existing ideas of the decisive effect of freons on the ozone layer thickness are obviously exaggerated. Ukraine and other countries which have not passed to new coolants would abandon the resolution to use coolant P-134a possessing unacceptable characteristics (toxicity, fire hazard, high energy consumption per cold unit, etc.) and continue special investigations on introduction of new non-toxical, fire-safe and profitable coolants.

In conclusion, it would be noticed that human technogenic activity does not take the destructive effect on the ozone layer thickness over our planet. The same is the conclusion of the members of the Antarctic expedition who state that the «ozone layer over the Earth was always and still remains unchanged» [57], that is in good agreement with a hypothesis presented in this book, the hypothesis about evolution of ozone holes over the Antarctic continent and Arctic as well as about continuous photochemical formation of ozone and natural replenishment of the Earth atmosphere by ozone.

8.3. Acid rains

The appearance of acid rains is usually connected with nitrogen- and sulphur-containing oxides. Concentration of nitrogen oxides and its compounds began to exceed their biological maximum permissible concentrations (MPC) in the atmosphere as affected by the present urbanization [4, 48]. Maximum permissible concentrations of harmful substances in the atmosphere air of settlements — maximum single (MPC_{MS}) and average daily (MPC_{AD}) are presented in Fig. 87, Table 39. Mercury with its compounds, lead with its compounds, cobalt, vanadium and others ejected with combustion products of TES operating on coal have the least MPC_{AD} among metals. When generating 1 mill. kWh of electric energy the thermal station ejects 30 t of hard particles (20 t of soot and 10 t of ash) and 18 t of gaseous substances: 15 t of sulphur dioxide and 3 t of nitrogen oxides, as well as kilograms of benzapyrene — one of the most toxical and carcinogenous chemical compounds which MPC_{AD} is 0.00 001 mg/m^3. From the data of [4], MPC of benzapyrene in the atmosphere is 0.000 001 mg/m^3, it can accumulate in the organism. Investigations have shown that in most cities of the world MPC of benzapyrene is surpassed 2 orders and above. Thus, benzapyrene concentration in Zurich reaches 0.0024 mg/m^3 (2400 times above MPC), in most USA cities — 0.002 mg/m^3 (2000 times), in Paris — 0.0007 mg/m^3 (700 times) [4]. The amount of formed benzapyrene depends on the combustion conditions of organic fuel at TES and is 1–10 mg/100 m^3 of ejected smoke for natural gas, 50–100 mg/100 m^3 for mazut and 10–50 mg/100 m^3 for coal. Total ejection of benzapyrene into the planet atmosphere is from 8 to 20 thou. t/yr.

It would be noticed that nitrogen oxides NO_x and sulphur oxides SO_2 are ejected in great amounts by thermoelectric stations and plants. Annual SO_2 ejec-

Table 39

Maximum permissible concentrations of air contamination with harmful substances [4, 17, 59]

Substance	MPCMS, mg/m^3	MPCAD, mg/m^3
Vanadium	0.001	0.002
Cadmium and its compounds	0.001	0.001
Cobalt and its compounds	0.001	0.004
Manganese and its compounds	0.01	0.001
Copper (oxides (I), (II))	0.002	0.002
Copper (sulphate (II))	0.5	0.001
Arsenic	0.01	0.002
Nickel	—	0.001
Mercury (metal)	0.01	0.0003
Mercury compounds	0.02	0.0003
Lead and its compounds	0.01	0.0003
Chrome (oxide (II))	0.0015	0.0015
Zinc (oxide)	—	0.05
Hard particles (dust)	0.5	0.15
Soot	0.15	0.005
Ammonia	0.2	0.004
Nitrogen oxide	0.4	0.06
Nitrogen dioxide	0.085	0.04
Hydrogen sulphide	0.008	—
Sulphur dioxide	0.5	0.5
Carbon monoxide	5.0	3.0
Hydrocarbons	0.03	0.005
Benzapyrene	0.0001	0.00001
Methanol	1.0	0.5
Hydrogen chloride	0.2	0.2
Sulphuric acid	0.3	0.1

tions by TES on organic fuel exceed 100, and those of nitrogen oxides NO_x — 67.6 mill. tons. The third part of SO_2 ejections being arrested to produce commodity sulphur, its amount would meet all the requirements of the world industry [4]. Only 11 industrially developed countries of Europe eject annually into the atmosphere 3.8 mill. t of sulphur dioxide SO_2 and 2.5 mill. t of nitrogen oxides (NO, NO_2). TES of the USA eject annually 50.3 mill. t of CO_2, 12 of SO_2 and 2 of NO_x, 1 of hydrocarbons and 3 mill. t of hard particles [17]. These impurities do not remain inert in the air environment. Thus, the reactive NO undergoes the dysproportionation reaction

$$3NO \leftrightarrow N_2O + NO_2 \qquad (287)$$

with formation of water-soluble nitrogen dioxide which dysproportionates into nitric and nitrous acids:

$$2NO_2 + H_2O \leftrightarrow HNO_2 + HNO_3. \qquad (288)$$

These acids are absorbed by water vapours and form «acid clouds» with following acid rains [48, 60].

Sources of nitrogen oxides are also photochemical reactions proceeding in the troposphere, stratosphere, mesosphere, and thermosphere:

$$N_2 + hv = N + N; \qquad (289)$$

$$N_2O + hv = NO^* + N; \qquad (290)$$

$$NO + hv = NO^* + e^-; \qquad (291)$$

$$NO + O_2 + hv = NO_2 + O^+ + e^-; \qquad (292)$$

$$NO_2 + hv = NO + O; \qquad (293)$$

$$NO + hv = N^* + O. \qquad (294)$$

NO concentration determined experimentally, proved to be equal to $(0.02–3.0) \cdot 10^9$ molecules/cm^3 [61]. In accordance with photochemical calculations, NO concentration in the mesosphere (80 km) is to be $10^5–10^6$ molecules/cm^3 [1]. Higher concentrations of NO and other nitrogen oxides in the mesosphere and thermosphere are determined by the proceeding of chemical reactions between nitrogen-containing components and atmosphere radicals [62–64]:

$$NO+O_3 \rightarrow NO_2+O_2+200\text{ kJ}, \quad k = 9.5 \cdot 10^{-13} \exp(-1240/T)\text{ cm}^3/\text{s} \qquad (295)$$

$$N^*+O_2 \rightarrow NO+O, \quad k = 1.4 \cdot 10^{-11}\text{ cm}^3/\text{s}; \qquad (296)$$

$$NO+O_2^+ \rightarrow NO^++O_2, \quad k = 8 \cdot 10^{-10}\text{ cm}^3/\text{s}; \qquad (297)$$

$$N_2^++O \rightarrow NO^++N, \quad k = 1.4 \cdot 10^{-10}\text{ cm}^3/\text{s}; \qquad (298)$$

$$N_2O+O \rightarrow 2NO, \quad k = 9 \cdot 10^{-11}\text{ cm}^3/\text{s}; \qquad (299)$$

$$N_2+O_2^+ \rightarrow NO+NO^+, \quad k = 3 \cdot 10^{-15}\text{ cm}^3/\text{s}. \qquad (300)$$

Even deeper NO oxidation is possible in the lower part of the stratosphere and in troposphere with participation of ozone, atomic oxygen and activated particles [64]:

$$\mathrm{NO + O_3 \rightarrow NO_2 + O_2}, \qquad k = 9.5\cdot10^{-12}\exp(-1240/T)\ \mathrm{cm^3s}; \qquad (301)$$

$$\mathrm{NO + O} + \theta \rightarrow \mathrm{NO_2} + \theta, \qquad k = 2.9\cdot10^{-33}\exp(941/T)\ \mathrm{cm^3/s}; \qquad (302)$$

$$\mathrm{NO_2 + O_3 \rightarrow NO_3 + O_2}, \qquad k = 9.8\cdot10^{-12}\exp(-3520/T)\ \mathrm{cm^3/s}; \qquad (303)$$

$$\mathrm{NO_2 + O \rightarrow NO_3^*}, \qquad k = 1.0\cdot10^{-11}\ \mathrm{cm^3/s}; \qquad (304)$$

$$\mathrm{NO_3^* + q \rightarrow NO_3 + q^*}, \qquad k = 1.3\cdot10^{-12}\ \mathrm{cm^3/s}; \qquad (305)$$

$$\mathrm{NO_3 + NO_2 \rightarrow N_2O_5 + 88\ kJ}, \quad k = 5\cdot10^{-12}\,T^{1/2}\exp(-1000/T)\ \mathrm{cm^3/s}, \qquad (306)$$

where θ and θ^* — a particle and activated particle (N, O, N_2, O_2 and others).

Concentration of NO_3 particles is in dynamic equilibrium with nitrogen monoxides

$$\mathrm{NO_3 + NO \rightarrow 2NO_2}, \qquad k = 1.0\cdot10^{-11}\ \mathrm{cm^3/s}. \qquad (307)$$

In the night atmosphere NO concentration decreases as a result of interaction with radicals, for example:

$$\mathrm{N^* + NO \rightarrow N_2 + O}. \qquad (308)$$

But in connection with the of proceeding of reactions (301), (302), (303), (304) the role of reactions (307) and (308) in NO and NO_3 disappearance is not determining. At night N_2O_5 particles formed by the reaction (306) turn into nitric oxide washed out of the atmosphere by rain [1]:

$$\mathrm{N_2O_5 + H_2O \rightarrow 2HNO_3 + 40\ kJ}, \qquad k \le 2\cdot10^{-18}\ \mathrm{cm^3/s}. \qquad (309)$$

Availability of nitric acid in the stratosphere was revealed in experiments with the help of shperes-probes. Maximum concentration of HNO was found at an altitude of 19 ± 5 km. Thus, NO_x of anthropogenic origin would not get to the atmosphere. In TES boilers nitrogen oxide (II) is formed by the reaction

$$\mathrm{N_2 + O_2 \leftrightarrow 2NO - 179.91\ kJ}, \qquad (310)$$

chain mechanism of this reaction being investigated in detail by Academician Ya. B. Zeldovich. NO_2 formation rate depends on temperature and oxygen concentration. At lower temperature there proceeds the reaction

$$NO + CO \leftrightarrow 0.5N_2 + CO_2 \qquad (311)$$

of nitrogen oxide reduction by carbon oxide. Depending on fuel nature (gas, mazut, hard coal) and its combustion conditions the concentration of nitrogen oxides in the smoke gases can vary from 150 mg/m^3 to 2 kg/m^3 [17].

Presence of sulphur compounds in the atmosphere leads to great ecological problems. Sulphur dioxide is the most distributed air pollutant since it is ejected in great amounts by TES and industrial plants. Sulphur dioxide SO_2 is highly soluble in water and, thus, it is available in the vapour of clouds. Sulphur dioxide interaction chemism, when it gets in the atmosphere, can be represented by the following set of reactions:

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^*; \qquad (312)$$

$$SO_2 + H_2O \leftrightarrow H_2SO_3; \qquad (313)$$

$$H_2SO_3 \leftrightarrow HSO_3^- + H^+; \qquad (314)$$

$$SO_2 + O^* \leftrightarrow SO_3; \qquad (315)$$

$$SO_2 + 2OH \leftrightarrow SO_3 + H_2O; \qquad (316)$$

$$SO_3 + H_2O \leftrightarrow H_2SO_4; \qquad (317)$$

$$H_2SO_4 \leftrightarrow HSO_4^- + H^+. \qquad (318)$$

The process of SO_2 genesis and its oxidation by the reactions (315), (316) is characterized by formation of highly water soluble sulphuric and sulphurous acids, which are also absorbed by water vapours, form «acid clouds» and fall as acid rains. Besides, H_2SO_3, H_2SO_4, HNO_2, HNO_3 and other acids, when interacting with metal oxides Me_yO_x, for example lead, cadmium, mercury, etc. (see, Table 39) convert them into water-soluble and vapour-soluble hydrosols and salts; sulphites, sulphates, nitrites, nitrates, etc. These compounds reach high concentrations in moisture microdrops in the atmosphere, get to the Earth surface where they are absorbed by plants and taken-up by animals, and at the final stage by a man with all grave consequences for the latter. Under the burning of 1 million tons of coal the total ejections of NO_2 and SO_2 into the atmosphere are $1.6 \cdot 10^3$ and $6 \cdot 10^4$ t, respectively, as well as thousands of tons of hard particles — oxides, soot, ashes. The latter absorb most various, including carcinogenous, substances, lower the atmosphere transparency, hasten the thawing of glaciers and, as a result, can lead to the increase of the ocean water level.

A scheme of acid rain appearance is given in Fig. 93. Not only nitrogen oxides (I), (II), (III) and sulphur (IV), lead, cadmium, mercury, manganese

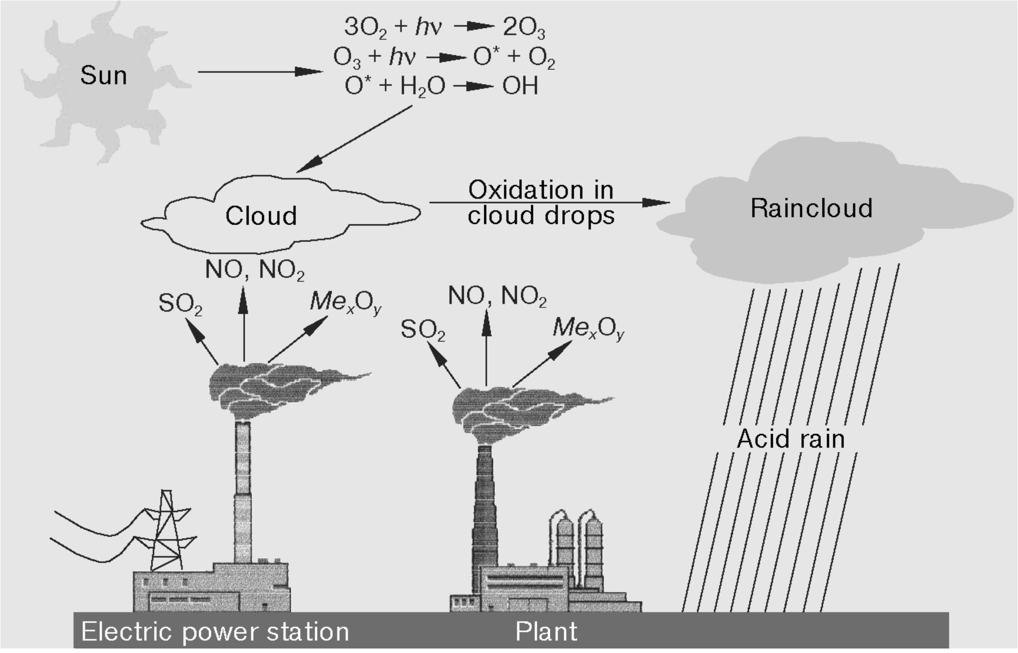


Fig. 93. Scheme of appearance of acid rains

oxides are ejected in the atmosphere from high pipes of power generation plants. Acid rains do much harm too: they promote corrosion of metal works, lead to the forest and animal perishing, to the decrease in farm crops yield and animal productivity, shorten life of people, etc. It is supposed that the intensity of acid rains, fatal for agriculture, will increase 10 times by 2000 [15]. In accordance with investigations (carried out in 50 sites) of atmosphere precipitations falling in Ukraine the latter contain not only acids but also salts of different metals. The average content of sulphates varies from 3.6 to 16 mg/l, ammonium nitrogen — from 0.6 to 2.2, nitrates — from 0.5 to 4.3, chlorides from 0.8 to 3.6 mg/l. The content of hydrocarbonates is within 0.9–12.9 mg/l, total content of sulphur — 0.06–2.2, nitrogen — 0.06–0.9 g/m^3. Considerable concentrations of sodium, potassium, calcium and magnesium salts (0.1–5.6 mg/l) are also observed in precipitations.

The highest content of metals is observed in atmospheric precipitation in such industrial city as Donetsk [58]. The atmosphere air of numerous cities of Ukraine (Mariupol, Zaporozhie, Krivoy Rog, Dniepropetrovsk, Kharkov, Lvov, etc.) contains carcinogenic compounds and harmful substances (formaldehyde, benzpyrene, phenol, ammonia), which concentrations surpass the sanitarian norms from tens to several thousand times [4, 58]. Especially high concentration of benzapyrene and nitrosoamines are observed in the regions with ferrous metallurgy and chemical industry. Population of these regions is on the verge of survival because of huge contaminations of the atmosphere by ejections of TES boilers and industrial plants. The amount of hard substances falling from the TES boilers and plant pipes on the heads of Magnitogorsk, Mariupol, Zaporozhie, Donetsk, Odessa and Kyiv dwellers are 170, 113, 70, 22, 13 and 12 tons, respectively [17]. Only in Mariupol 54 000 t of sulphur oxides, 30 000 of nitrogen oxides, and 574 000 tons of CO_2 are ejected in the atmosphere, the «lion's share» of those pollutants gets into the Azov Sea. A share of 113 000 t of hard substances as well as acid rains pollute the water area of the Sea of Azov destroying its fauna and flora. Besides, huge amounts of «acid» sewage from TES, TEP boilers, metallurgy plants get to the Sea of Azov, because of the overfilling of slime pits, mud drums, breaks of dams, etc.

To decrease innumerable damages caused by the ejected smoke gases to population and national economy as a whole various arrangements are developed for realization of «reserves» to reduce the total amount of these ejections [17]. It is considered that MPC can be achieved by better gas dispersal by means of:

a) the heightening of smoke pipes to 350–380 m;
b) increase of the pipes diameter;
c) increase of smoke gas ejection velocity from 20 to 30–4 m/s;
d) increase of the ejected gas temperature.

However, the realization of the points a) and b) is connected with the increase of capital investments and is not always possible because of the regions seismicity and for the reasons of air navigation. Realization of the points c) and d) requires the increase of the consumption of electric energy for home needs which decreases economicity of TES [17]. Besides, when realizing the arrangements by the points a)-d) the real amount of the outburst of hard particles, soot, NO_x, SO_2, SO, oxides of harmful metals, arsenic, and others into the atmosphere remains the same and, consequently, one can expect the cumulative manifestations of these harmful impurities on great areas of agricultural lands, towns and regions.

As is shown by the investigation data, the share of TES participation in the total pollution by harmful substances is especially high as to sulphur and nitrogen oxides and benzpyrene. The amount of pollutions ejected in the atmosphere depends on the nature of primary fuel. The amount of sulphur and nitrogen oxides in smoke gases increases in the transition from gas to mazut and coal. To decrease sulphur content in mazut it is subjected to desulphuration at oil-refineries by different methods: a) step-by-step vacuum distillation, selective extraction and hydrorefining; b) catalytic processing at high temperatures and pressures; c) gasification at special plants of TES. A new method is of interest, when fuel is burnt in the boiling layer of limestone (with presence of a reagent — CaO) and about 90 % of sulphur are chemically bound into nonvolatile compounds [17]. It may be used for desulfuration of solid, liquid and gaseous fuel. For its efficiency it is necessary to have the CaO regeneration system, TES provision with high amount of limestone as well as the removal of high amounts of sewage containing toxical compounds of vanadium, chrome, calcium sulphide, etc. For mazut burning in the boiling limestone layer it is necessary to reconstruct steam-generator equipment, to create new sets and systems. So, such technology can be realized only at TES constructed by special projects. It is not enough to reconstruct the operating TES, since the removal of sulphur and nitrogen oxides from smoke is impossible without the construction of special plants for their separate or joint purification.

At present, there exist plants created for dry and wet removal of sulphur oxides from the smoke gases [17]. There are four methods of TES emissions treatment for sulphur oxides (SO_2, SO_3): lime, limestone, magnesite and ammonia methods. Lime $Ca(OH)_2$, limestone $CaCO_3$ or dolomite $CaCO_3 \cdot MgCO_3$, magnesite $MGCO_3$, ammonia, etc., are used as reagents interacting with sulphur oxides. The lime and limestone methods are most studied and economically expedient. They are based on neutralization of SO_2 or sulphurous acids by lime (limestone) using wet method by the reactions

$$SO_2 + H_2O = H_2SO_3; \tag{319}$$

$$Ca(OH)_2 + H_2SO_3 = CaSO_3 + 2H_2O; \tag{320}$$

$$CaCO_3 + H_2SO_3 = CaSO_3 + CO_2 + H_2O \tag{321}$$

using dry method by the reactions

$$Ca(OH)_2 + SO_2 = CaSO_3 + H_2O; \tag{322}$$

$$CaCO_3 + SO_2 = CaSO_3 + CO_2; \tag{323}$$

$$Ca(OH)_2 + SO_3 = CaSO_4 + H_2O; \tag{324}$$

$$CaCO_3 + SO_3 = CaSO_4 + CO_2. \tag{325}$$

Principal technological scheme of smoke gas treatment for sulphur dioxide by the limestone method is presented on Fig. 94 [17]. In accordance with the scheme, the smoke gases from air heater arrive at ash trap *1* where hard particles and ash are separated, and this prevents from wear of the smoke exhauster *2*. Then gases arrive along the smoke exhauster to the scrubber *3*, irrigated by suspension and grinded limestone (and neutralization products) in water, and then they are deprived of splashes in the spray trap *4*. To increase the extent of dispersion of cleaned smoke gases the latter are heated in a heater *5* and ejected in the atmosphere. About 3 % of gaseous fuel burnt in the heater is additionally consumed for heating the cleaned gas. Then the liquid with acid reaction from the scrubber *3*, is directed to tanks *6* with limestone suspension added for neutral-

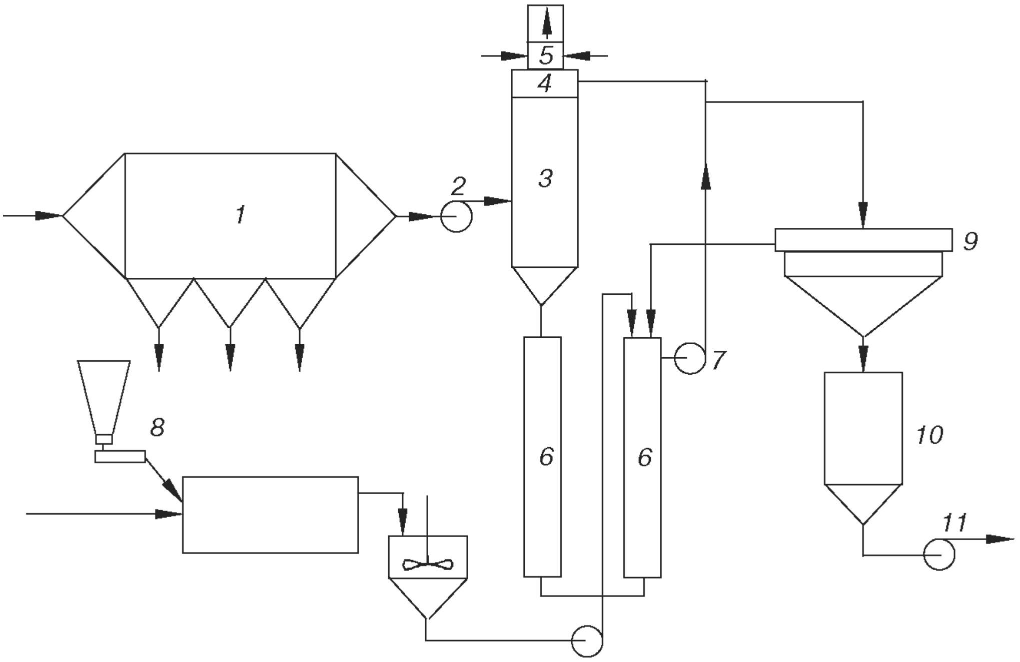


Fig. 94. Schematic technological diagram of smoke gases treatment for sulphur dioxide by limestone method [17]

ization; this suspension after settling and crystallization of $CaSO_3$ is directed by means of the pump *7* for irrigation of the scrubber *3.* Calcium sulphide and sulphate crystals as well as ash residul are accumulated in the course of time in the irrigating liquid. To maintain constant content of hard particles a share of suspension is directed to the thickener *9* supplied with a vessel for slime collection *10*, hence it is periodically discharged to ash dump with the pump *11*. The degree of smoke gas treatment for sulphur oxide is not reported.

A principle of the lime and limestone methods and their instrumentation do not differ from those described above. The ammonia method of cleaning smoke gases is based on the following reaction

$$(NH_4)_2SO_3 + SO_2 + H_2O = 2NH_4HSO_3. \qquad (326)$$

This process instrumentation is more complicated than under the limestone method [17].

A plant for joint treatment of smoke gases for sulphur and nitrogen oxides includes complex equipment and reactors. A schematic technological process of joint liquid treatment of smoke gases (JT-TES) for sulphur and nitrogen oxides developed by Leningrad State Institute of Applied Chemistry [17] is presented on Fig. 95. It consists of six basic units:

- absorbers for wet ash trapping and absorption of sulphur dioxide and nitrogen oxides;

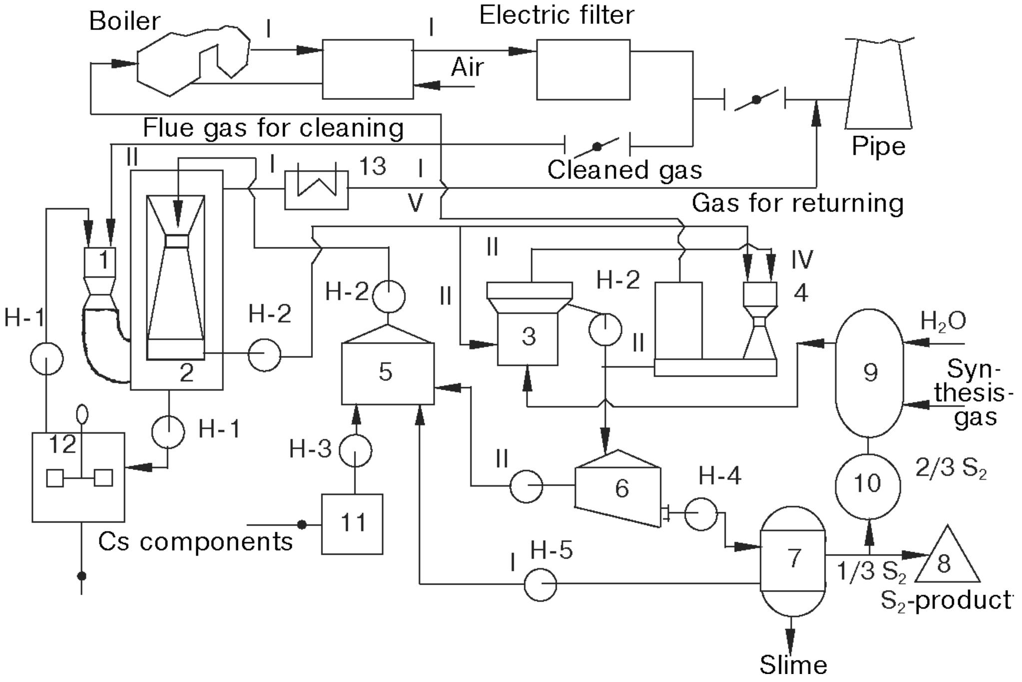


Fig. 95. Principal technological scheme of joint liquid cleaning of smoke gases from sulphuroxides and nitrogen JLC — TEP [17]. 1 — ash collection absorber; 2 — chemosorber of SO_x and NO_x; 3,4 — hydrogen sulphide absorption devices; 5 — circulation collector of the contact solution; 6 — sulphur pulp collector; 7 — sulphur melting autoclave; 8 — commodity sulphur storage; 9 — hydrogen sulphide generator; 10 — sulphur-combustion device; 11 — tank for preparation of contact solution; 12 — neutralization tank; 13 — gas heater; I–IV — operation system motion paths (I — smoke gas; II — contact solution; III — sulphur pulp; IV — hydrogen sulphide-containing gas)

- hydrogen sulphide absorbers intended for regeneration of the contact solution;
- sulphur melting unit;
- hydrogen sulphite production unit;
- unit for preparation of contact solution;
- storage of commodity sulphur.

In accordance with technological process the smoke is cleaned from ash in the ash-trapping absorber *1* and is directed to chemosorber *2* for the extraction of sulphur and nitrogen oxides (SO_x and NO_x) and then to the contact solution which irrigates the chemosorber with the help of sprayers. The contact solution is prepared in the container *11* and arrives in the chemosorber from the collector *5*. Cleaned gas from the lower part of chemosorber *2* is supplied by the pump H-2 to the spray-trap of the chemosorber (the outer case) and after heating from 13 to 80 °C is directed to the chimney.

The contact solution with absorbed sulphur and nitrogen oxides is supplied to absorbers *3* and *4*, where hydrogen sulphide H_2S is also directed as countercurrent. The reaction of SO_2 and H_2SO_3 reduction to elementary sulphur proceed there:

$$SO_2 + 2H_2S = 3S + 2H_2O; \qquad (327)$$

$$H_2SO_3 + 2H_2S = 3S + 3H_2O. \qquad (328)$$

Redox reactions between nitrogen oxides, nitric and nitrous acids, hydrogen sulphide and sulphur oxides with formation of elementary sulphur, nitrogen and ammonium sulphate also proceed in the contact solution. The contact solution containing sulphur is supplied to the sulphur pulp collector *6* where it is settled to humidity 40–60 % and then it is supplied to autoclave for sulphur melting *7*. The contact solution deprived of sulphur is supplied from autoclave to circulation collector *5*, and thus the liquid-phase loop is closed. Hydrogen sulphur is obtained in hydrogen sulphide generator *9* with the use of sulphur (they take 2/3 of sulphur after melting in autoclave *7*; 1/3 is supplied to the commodity sulphur store *8*), natural gas, water vapour, sulphur vapours, and its dioxide. Sulphur melting slime is discharged to ash dump. Losses of the contact solution components removed with melted sulphur are compensated by solution from the tank *11*. Volatile ash, extracted in absorbers, is neutralized by lime milk in the neutralization tank and discharged to ash dump.

The installation design is made for the power unit of 225 MW with a boiler on liquid fuel with steam production 670 t/h. Productivity concerning cleaned smoke gases was 962 000 m^3/h. The cleaning degree for sulphur oxides was 98–99 %, nitrogen oxides — 60–70 %.

The considered scheme of joint cleaning of smoke gases from sulphur and nitrogen oxides has a series of advantages as compared to other liquid-phase methods:

- high efficiency of cleaning;
- broad range of sulphur dioxide concentrations in smoke gases admissible for cleaning (from 0.01 to 25 %);
- production of elementary sulphur and ammonuim suplhate;
- joint efficient removal of sulphur and nitrogen oxides.

However, in our opinion, one cannot agree with the last position. The efficiency of the smoke gases separation from nitrogen oxides is only 60–70 %. At such high power unit productivity (225 MW) and low efficiency of gases separation from NO_x, one cannot succeed in saving the region from the acid rains. The technological process diagram does not demonstrate the methods of removal of bound nitrogen compounds. There is no present composition of the contact solution which probably contains lime milk, sodium and potassium hydroxides. The separation of smoke gases from sulphur and nitrogen oxides especially complex joint cleaning to concentrations, satisfying the MPC level, is the most complex problem. The latter requires high economic investments. When mazut or coal are used as fuel, the smoke gases contain extremely high concentrations of sulphur and nitrogen oxides, which exceed MPC thousand times. Even under the two-stage combustion of natural gas the content of nitrogen oxides in smoke gases reaches 364–585 mg/m^3, i. e. it exceeds MPC 6066–9750 times. The new radiation-chemical engineering methods are also characterized by low efficiency of the smoke gases separation from sulphur and nitrogen oxides. Thus the problem of acid rains and atmosphere pollution by sulphur and nitrogen oxides, being rather toxical for people and biota as a whole, still remains unsolved. Millions of TES, functioning all over the world, take the degrading effect on the environment. TES on hydrogen fuel do much damage to the fresh-water basin (occupying only 3 % of the hydrosphere) because they consume huge amounts of water [16, 17]. Concentration of sulphates, nitrates and chlorides in the discharge water of TES (at their low volumes) can reach 2000 mg/l at MPC of sulphates 240, nitrates — 45 and chlorides — 350 mg/l. That is the reason for using the closed circulating water supply with water treatment system requiring considerable labour, material expenditures and power consumption. A schematic balance diagram of the technological water supply of the Kharkov TEP-5 from the Uda River as water source and a system of additional supply from the Novobavarian reservoir [17] is given as an example in Fig. 96. From the Figure data one can see the degree of water treatment process complexity under closed water supply, the process multistage character and instrumentation requirements. Water treatment requires great amounts of reagents and energy. Pure water intake by TEP-5 under the design power of 1140 MW is 3600 m^3/h. Thus we think that there is no alternative to hydrogen energetics. The conversion of any hydrocarbon fuel with obtaining synthesis-gas, the latter being used as fuel, will help to realize ecologically pure (without ejections of harmful substances into the atmosphere) and economically profitable processes of thermal and electric power generation. A schematic technological diagram of TES on hydrogen fuel — the conversion synthesis-gas in given in Fig. 97. The power generation process is almost wasteless. Carbon dioxide (CO_2) contained in synthesis-gas is supplied from heat-exchanger to phytotron for growing the biomass and food products intended for the consumer. The consumer also obtaines generated electric energy. Oxygen released in phytotrons may be let in the atmosphere or supplied to TES boilers. Phytotrons use low-potential heat of the heat-exchange plant which also can be supplied to the consumer. Water formed under hydrogen combustion does not contain harmful impurities; it remains in the closed cycle and is used in the heat-exchange plant (it is not shown on the diagram), in phytotrons for growing the biomass and food products, for generating energy. Water vapours are condensed to liquid state and thus have no influence on the greenhouse effect. The fact of the absence of secondary energy expenditures for gas scrubbing, water treat-

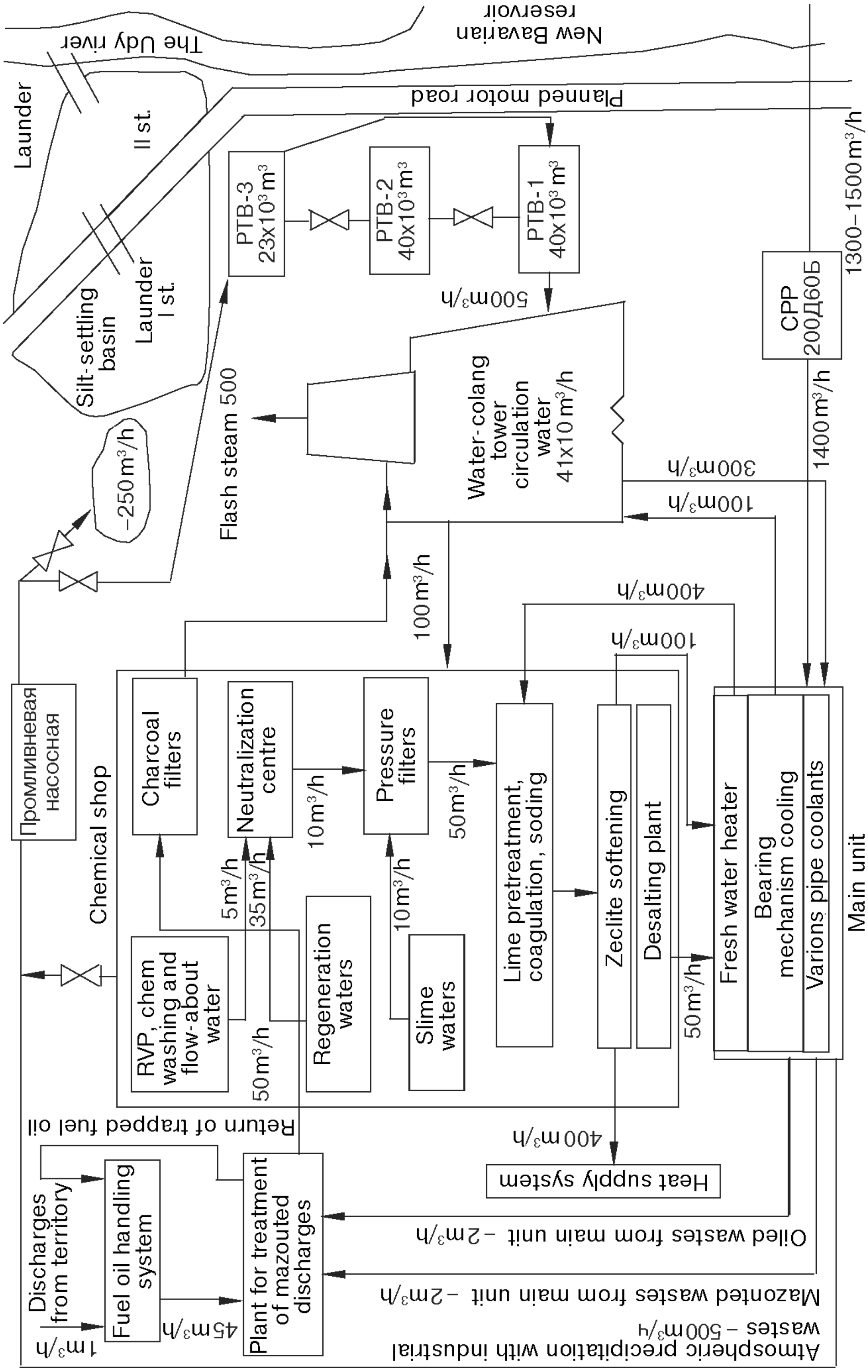


Fig. 96. Schematic technological diagram of balance water-supply of Kharkov TEP-5 [296]

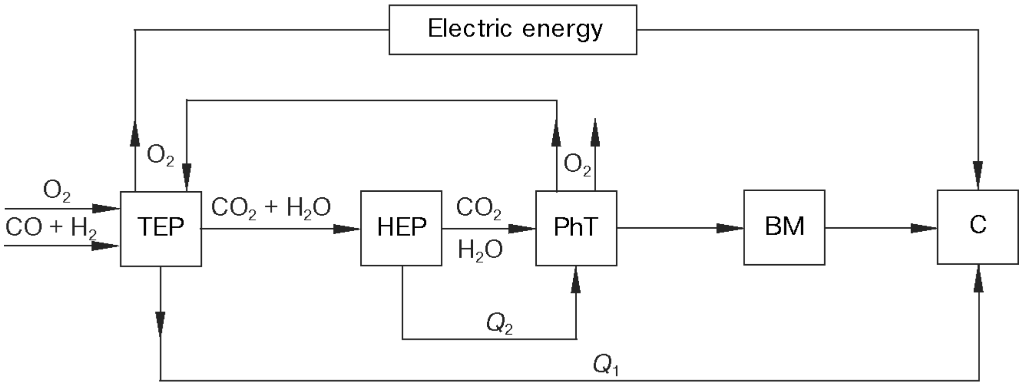


Fig. 97. Scheme of ecologically pure TES and power plants using conversion synthesis gas and utilizing CO_2: HEP — heat-exchange plant; Q — high-potential heat; Q_2 — low-potential heat; PT — phytotron; BM — biomass and food products; C — consumer

ment, etc. is important in this power generation method. Thermal energy is not dissipated in the environment (see, point 8.4). It would be noticed that the given technological diagram solves not only the problem of pure energy generation and ecology preservation but also the problem of obtaining food products, especially allowing for the quick growth of population. Hydrogen energetics can prevent from acid rains. In the light of all mentioned above we think that it is a kind of energetics of the future.

8.4. «Thermal contamination» of planet Earth

Contamination of the Earth surface and water areas by various toxical chemical compounds, heavy metals is increasing continuously. The same is with radioactive contamination of our planet. High economic expenditures can help to prevent from (or to considerably decrease) the environment contamination: you can gather (not spread) cellophane bags and tins, stop discharging nontreated waste to rivers and seas but utilize them, you can extract sulphur, nitrogen oxides and ash from industrial smokes and reburn the exhaust gases, sharply restrict the spreading of radioactive contaminations, burying radioactive waste, but it is very difficult to get rid of «thermal» pollution of the Earth. It could be possible only if all branches of industry would be converted to the use of solar energy and its direct derivatives (energy of wind, sea tides, etc.). But there exists one more idea of the authors on preservation of Earth's thermal balance: to direct the released waste heat to endothermal processes and reactions. In this case $\Delta Q_{\text{disch.}} = -\Delta H_{\text{endotherm.}} = 0$ which will ensure, theoretically, the preservation of thermal balance of the Earth.

Generated power volumes being increased, thermal contamination from the release of fuel energy conserved earlier will also play its part in modern engines and boilers. Nuclear reactors of NPP, which permanent losses are determined by production technology, also increase the planet thermal contamination and thus affect the environment.

Special procedures of thermal contamination mapping with the use of infrared scanners installed on planes, probes, satellites and spaceships have been elaborated to estimate heat losses of power plants (discharges of TES and NPP) [65]. Scanners' resolution is 3–120 m. Great experimental material concerning heat losses in the environment has been accumulated. A thermal trail from the Leningrad NPP water coolers expanding for 10 m from the coast was found in 1977. Huge thermal trails were also found in 1987 in Penemunde Bay (South Baltic) from water coolers «Nord» (East Germany). A thermal trail was fixed in 1981 in the Copor bay in the Gulf of Finland from Lovisa and Olkiluoto NPP. Analogous observations have been made in the USA at Milstone NPP (the State of Kentucky), NPP on the Hutchinson Lake (the State of Florida), etc. The authors of the work [103], with the aim to estimate the degree of the effect of NPP thermal disposals on the thermal conditions of water areas, studied NPP operating on the Baltic Sea coast: Ringhals, Barsbec, Oscarschamn and Forcemark plants in Sweden, Lovisa and Olkiluoto plants in Finland, Leningrad NPP (LNPP) in Russia, Ingalina NPP in Lithuania. As to the disposal of heat flows the considered NPP are divided into two types: those discharging their heat flows into the open sea (Ringhals, Oscarschamn, Olkiluoto plants) and into relatively isolated bays (LNPP, Lovisa, Forcemark plants). It has been established that the effect made by first type NPP on the adjacent water area ecology is weaker than that of the second-type NPP. Vast areas of heat trails (S_W) are as follows: for Forcemark NPP S_W = 20 — 165 km^2 with the heat flow Q = 310–1700 MW, for LNPP S_W = 43–474 km^2 with Q =820–13000 MW, for Olkiluoto S_W = 4.9–13.4 km^2 with Q = 36–231 MW, for Lovisa NPP S_W = 5.9–95 km^2 with Q = 48–1030 MW. Maximum heat flow density was relatively low and was equal to 55 W/m^2 (electric lamp power).

The authors of the work [65] think that «one of the basic restrictions on the power generation increase is the heat limit which arises as a result of violation of the Earth heat balance. This limit achievement is outside the 21st century». But let us compare and ponder upon the scale of thermal contaminations.

NPP and TES are generators of thermal contamination of the planet [66, 67]. The scales of low-potential heat release by modern TES and NPP in respect of the consumed heat-carrying agents are huge. Only in 1998 the amount of fuels consumed (10^9 t in oil equivalent) is as follows: coal — 2.236; oil — 3.423, natural gas — 2.210 t [64]. Of these $7.869 \cdot 10^9$ tons of fuel in oil equivalent 50–65 % (average efficiency 35–50 %), i. e. $3.93–5.11 \cdot 10^9$ tons (more than a half) are burnt and heat is emitted in the atmosphere and spent for heating the environment, of 429 NPP in the world (NPP efficiency being 35 %) two thirds (283 NPP) also «heat the sky». At the same time the low-potential heat of NPP and TES may be used for development of low-temperature chemistry and technology. There arises a vivid expediency to correlate the volumes of low-potential heat with the problems of high-temperature inorganic chemistry and plasma chemistry with the purpose to create future energy sources on the basis of electro- and plasmachemical productions [66, 67].

Nowadays both the population and industry consume annually $11.69 \cdot 10^{13}$ kWh of energy. Compare this value with obtained solar energy. Total power of the solar energy emitted in the space is about $4 \cdot 10^{23}$ kW. It provides the solar constant 1.34 kW/m^{2}at the distance of Earth average reduction from the Sun (149.457 mill. km). The planet surface total area is $5.10 \cdot 10^{14}$ m^2. The Earth is a continuously revolving sphere. Assume, that the Sun illuminates only 70 % of its surface. So, the Earth surface absorbs $5.10 \cdot 10^{14} \cdot 24 \cdot 1.34 \cdot 0.70 = = 1.15 \cdot 10^{16}$ kWh of solar energy every 24 hours and about $4.20 \cdot 10^{18}$ kWh a year. In 1998 total consumption of the fossil organic fuels in the world was $7.869 \cdot 10^9$ t in oil equivalent [21] that corresponds to $8.404 \cdot 10^{13}$ kWh of energy. The latter value is close to the amount of energy consumed by population and industry ($11.69 \cdot 10^{13}$ kWh).These values compared to solar energy absorbed by the Earth make 0.0073–0.0102 % i. e., thousandth and hundredth shares of a percent.

But our planet not only obtains the solar energy but, being in thermal equilibrium with its surrounding, consumes energy for water evaporation, atmosphere heating, emission to space, etc. In accordance with the work [4], the Earth is a relatively cold body with temperature 254 K. Radiation of such cold bodies falls on the long-wave spectral region with intesity maximum at 12 ?m. The planet total long-wave radiation is equivalent to quantity of the absorbed radiation and equals about 627.6 kJ/(cm^2 · yr) [68].

Thermal balance of the Earth surface has been studied in detail by M.I. Budyko, Member of the National Academy of Sciences of Ukraine [68]. The total quantity of the solar radiation flux is 4184 kJ (cm^2 · yr). Since the Earth is spherical, 1046 kJ (cm^2 · yr) reach the surface of the external atmosphere boundary. Allowing for the average albedo of the system Earth-atmosphere, which characterizes its reflecting ability reaching 0.40, the energy of the short-wave radiation absorbed by the Earth is 1046 · (1.0–0.4) = 627 · 6 kJ (cm^2 · yr). Since the ground albedo equals 0.14–0.15 [17] at an average, then 539.700 kJ (cm^2 · yr) of short radiation reach the Earth surface and 87.864 kJ (cm^2 · yr) (0.14 %) are reflected by the planet. Owing to the greenhouse effect (the glass-house effect by M.I. Budyko) the Earth surface obtains 539.736 kJ (cm^2 · yr) (according to [68] — 447.688 kJ (cm^2 · yr)) of radiation energy. Heat arrival is absolutely equal to its consumption. The atmosphere heat balance consists of the following components:

- the amount of heat from the absorbed short-wave radiation is 163.176 kJ (cm^2 · yr);

- the amount of heat from water vapour condensation is 234.304 kJ ($cm^2 \cdot yr$);
- the amount of heat from turbulent heat transfer of the Earth surface — 142.256 kJ ($cm^2 \cdot yr$) (the value 50·208 kJ ($cm^2 \cdot yr$) [68] is not correct because the ground albedo was accounted twice).

Total amount of heat transferred to the Earth surface reaches 539.736 $kJ/cm^2 \cdot yr$.

The items of radiational heat consumption are as follows:

- heat amount for radiation to the space — 125.52 kJ ($cm^2 \cdot yr$);
- heat amount for radiation at the ground level — 179.912 $kJ/(cm^2 \cdot yr)$;
- heat amount for water evaporation — 234.304 $kJ/(cm^2 \cdot yr)$.

Total heat consumption corresponds to its input and equals 539.736 $kJ/(cm^2 \cdot yr)$. This equality is the basis of climate stability on the Earth. One can reduce the obtained quantities of heat input and consumption to all the Earth surface $5.10 \cdot 10^{18} \cdot 539.736 = 2752 \cdot 10^{21}$ kJ/yr or $7.65 \cdot 10^{17}$ kWh/yr. Proceeding from other estimates the value of $6 \cdot 10^{18}$ kWh/yr was obtained. The divergence is less than 1 order (7.8 times) which is acceptable for such calculations.

Considerable danger for biota life is made by new pollutions: metal oxides, ash, soots, acid-forming sulphur and nitrogen oxides and other substances alien to nature circulation. When interacting with products of nitrogen and sulphur oxide hydrolysis and hydrocarbon impurities in the atmosphere, metal oxides, as well as ash, soot and dust particles of small and ultrasmoll size form new unknown stable aerosol shell over the vast planet regions. The shells do not let ultraviolet and infrared solar radiation to the Earth surface. That can lead to the regional variants of «nuclear winter» realized as a result of «aerosol cooling». It is interesting that mutual compensation of two negative factors is possible: the former is the greenhouse effect raising the Earth temperature which arises as a result of the influence of water vapours, sea and ocean water and less of CO_2 and methane on heat accumulation by decreasing the planet heat losses, and the latter is the opposite «aerosol effect» leading to the Earth cooling and its glaciation because of the limited access of the solar energy.

An analysis of the influence of human practical activity on climate changes in the early 20th century was performed in the work [69]. Fig. 98 represents the distribution of average latitudinal temperatures of the planet air obtained from the data of observations in comparison with the results of investigations made by the author of this work [69]. When calculating the sum of solar radiation falling at the outer atmosphere boundary, the radiation flow was taken equal to meteorologic solar constant 8.033 J ($min \cdot cm^2$). A divergence in the values of measured and calculated temperatures in different latitudes of the North and South hemispheres was no more than 1–2 °C. Basing on the data obtained the author of the work [69] came to a conclusion that «the increase of radiation

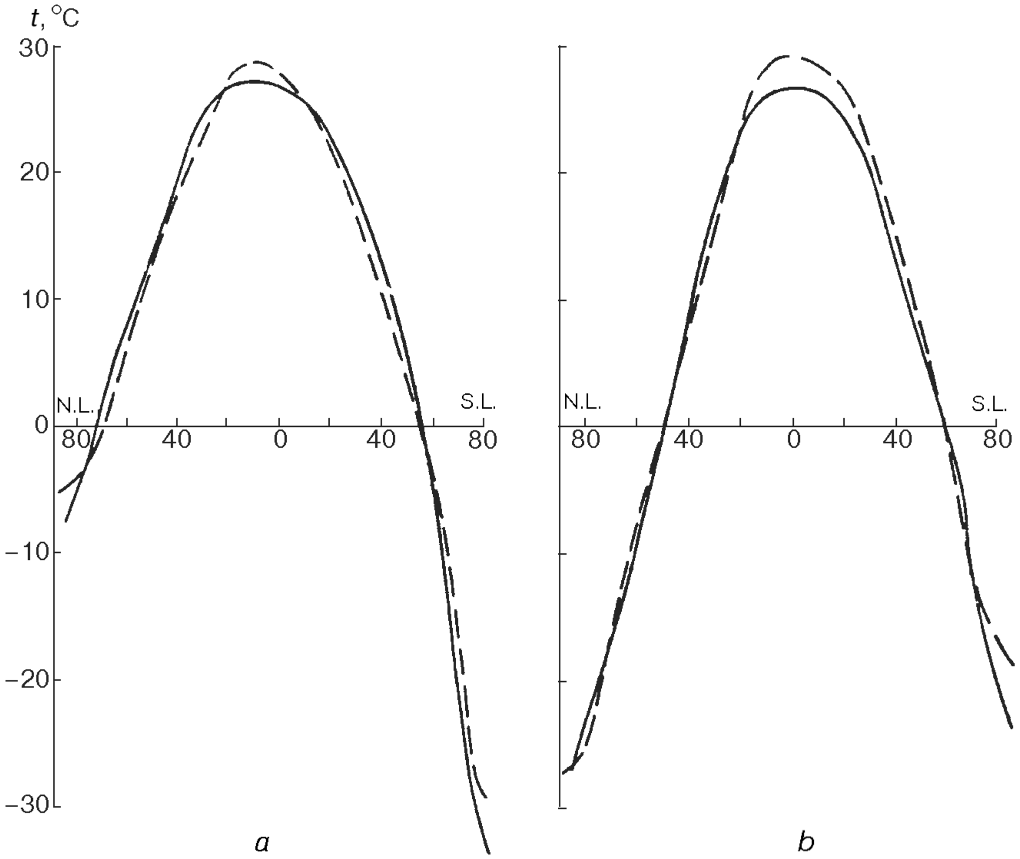


Fig. 98. Distribution of latitude average air temperatures on planet Earth from the data of the work [69]: *a* — first half-year; *b* — second half-year; solid line — observation data; dash line — calculation results

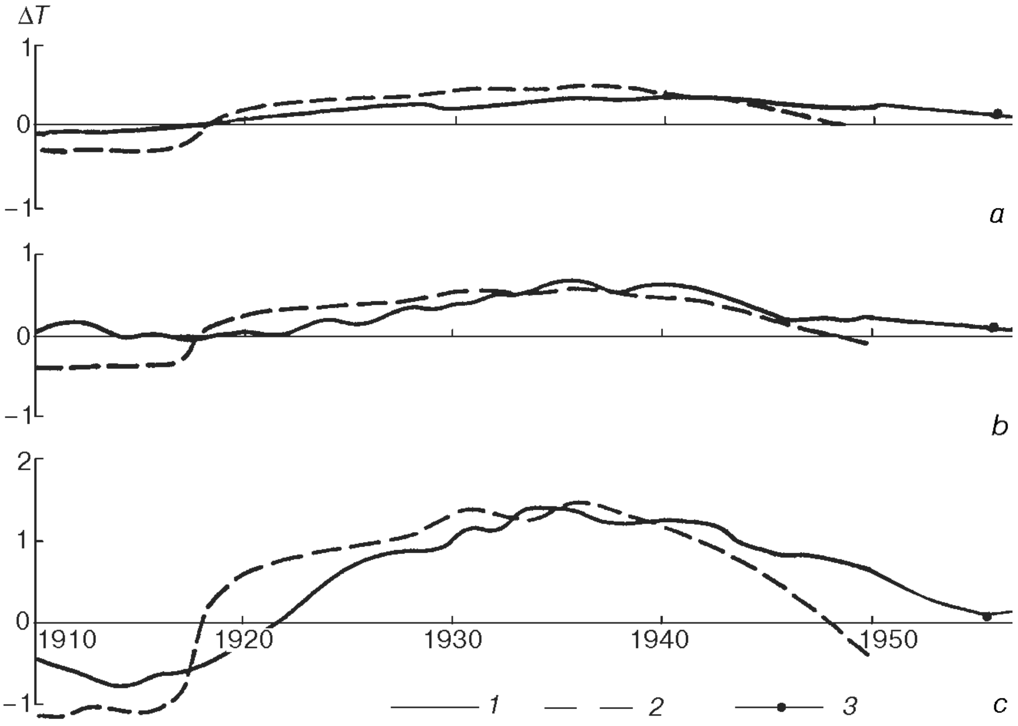
no more than several tenth of a percent would be enough to destruct the polar ices», and «that such increase of the solar radiation would be rather long-term — of the order of hundreds or thousands of years».

To find out the mechanism of the climate change it is interesting to compare temperature variations at least for the period of 100 years. Data of the work [69] are given in Fig. 99. The work dealt with temperature variations (ΔT) during 50 years of the first half of the 20th century; we have added the data of [64] concerning changes of the near-Earth air temperature during the 49-year period of the second half of the 20th century (1950–1998). The century trend of the anomalies of the average near-Earth air temperature ΔT in the North hemisphere is given in Fig. 99, *a* and in Fig. 99, *b*, *c* in the zone of 70–80 °C north for warm and cold half-years, respectively. The rise of the average annual near-Earth air temperature within 0.3–0.6 °C [21] was fixed in the 20th century. Such a broad spread of the data is determined by the absence of rather reliable data of observations over the near-Earth air temperature during the whole century. The ΔT data in Fig. 99, *a* belong to the average annual conditions, since the temperature anomalies of the warm and cold half-years according to the work [69] are not rather different. It is seen from the Figure that negative Δ*T* values were observed in the period from 1910 to 1918, then there was temperature elevation which reached its maximum in 1930–1940 and then temperature began to fall gradually [69]. In our opinion the sharp fall in temperature was observed immediately after 1940. All the world remembers the severe winter of 1941–1942. In the period of 1955–1976, proceeding from the data of [21], one could observe low values of Δ*T*, equal to 0.04–0.10. The negative value of $\Delta T = -0.03$ °C fell at 1976. Beginning from 1977 one can observe a gradual elevation of the near-earth temperature to 0.4 ± 0.2 °C. The Δ*T* value is equal to several tenth of a degree for the North hemisphere as a whole (Fig. 16, *a*) and for the warm half-year in high latitudes (Fig. 99, *b*). The Δ*T* value reached 1.5 °C in the period of 1920–1940 called «Arctics warming» during the cold half year in the zone of 70–80 °C. The Arctics warming resulted in the decrease of the area of the North sea ices by approximately 10 % [69]. The increase of Δ*T* values is determined by the higher dose of solar radiation obtained by the Earth surface. The temperature elevation in the 20–30's of the 20th century in the North hemisphere was mainly caused by the «increase of the total solar radiation reaching the Earth surface».

The century trend of direct radiation anomalies under cloudless sky during 1910–1950 obtained by the author of [69] possessed the symbate convergence with Δ*T* curve trend during the same period. It has been established that the century trend of the curve of the total solar radiation depends on optic transparence of lower layers of the stratosphere. This transparence is the function of volcanic dust content in these layers. Changes of the trend of temperature anomalies in the North hemisphere and in the analyzed latitudes during 1910–1950 were calculated on the basis of the model of thermal conditions in the system ocean — polar ices — atmosphere. The data obtained were drawn on Fig. 99 in a form of dashed curves *2*, which are arranged, as a rule, above the curves obtained using the results of observation of temperature changes with time. The extended Δ*T* curves — time for the period of 1950–1998 on the basis of the data observation of the surface air temperatures [64] — continue regularly the trend of curves of observation in the period of 1910–1950.

Basing on the analysis of the estimated century trend of temperatures in the North hemisphere in accordance with the trend of curves Δ*T*-time, plotted starting from observations, the author of [69] came to the conclusion that climate change in the early 20th century was mainly caused by considerable decrease of dust concentration in the lower layers of the North hemisphere stratosphere. This decrease of dust concentration was determined by the absence of explosive volcano eruptions during several decades and by weakened volcanic activity in the recent century as a whole.

It follows from the data of Δ*T*-time curves analysis in high latitudes of 70–80 °C during cold half-year that the solar radiation is low and does not



strongly affect thermal conditions of the atmosphere; the chief effect is made by the change of the area of polar sea ice. Ices lower considerably the air temperature in high latitudes in winter and essentially less — in summer. The air temperature in moderate and low latitudes of the North hemisphere slightly depends on their area.

Interesting results were obtained by Academician M.I. Budyko under the prediction of climate of the 21st century [69]. Special effect on ecology is made by energy generation accompanied by heat release into the environment. According to M.I. Budyko the additional released heat, which is not used by man, is not low as compared to the value of solar radiation balance of the Earth surface. One cannot agree with M.I. Budyko that the increase of energy generation from 4 to 10 % a year will result in the fact that «no later than in 100–200 years the quantity of heat created by man will be comparable with the value of radiation balance of all the surface of continents «. In the opinion of the author of [69] this additional energy will lead to the global changes of climate. Besides, additional energy generated during 100–200 years will not be accumulated but will be consumed for evaporation of water of seas and oceans, moist of land, it will be radiated in high amounts to the space, consumed for endothermal reactions of photosynthesis by plants, etc.

As was noticed, the quantity of energy obtained in the world now with respect to solar radiation energy absorbed by the Earth makes only hundredth and thousandth fractions of a percent. That is why, even ten-fold increase of energy

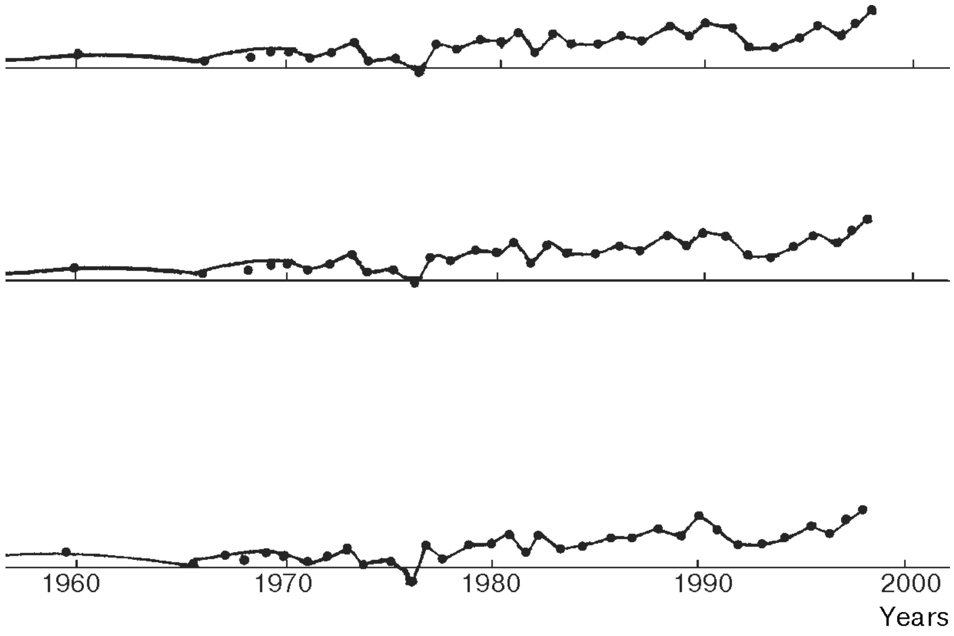


Fig. 99. Century trend of anomalies of the near-Earth air temperature: *a* — North hemisphere; *b*, *c* — zone of 70–80 °C north, warm (*b*) and cold (*c*) half-year; *1* — observation data; *2* — calculation results [69]; *3* — observation results [64]

generation will not take any effect on the global change of the planet climate, it can be significant only at a regional level. Besides, allowing for continuous consumption of hydrocarbon fuel, which had been stored by the planet biota during millions of years, it is not expedient to «warm the sky» from the point of view of economics.

The idea of possible effect of the increase of energy generation and amount of released CO_2 on the change of near-surface temperature is illustrated by Fig. 100. The ΔT values drawn on the figure were calculated from average annual near-surface air temperature in the period of 1950–1998 from the data of the work [21]. These data fall well on the prediction curve of the air temperature change under the effect of CO_2. But that is the illusory coincidence. Contribution to the elevation of average annual near-surface temperature was made by extremely intensive development of El Nigno, unprecedented growth of temperature of the Indian Ocean surface caused by intensive solar radiation [21, 70], as well as by additional solar energy of the final 11-year cycle of solar activity (explosions, outbursts of great amounts of solar energy in the space). To reflect the effect of CO_2 on the ΔT-time curve trend the author of the work [69] used the data by S. Vanabe. According S. Vanabe under the established CO_2 concentration the planetary temperature would rise by about 0.5 °C by 2000 as compared to 1970. It follows from numerous works that ΔT has changed by 0.3 °C during this period, CO_2 contribution being undetermined.

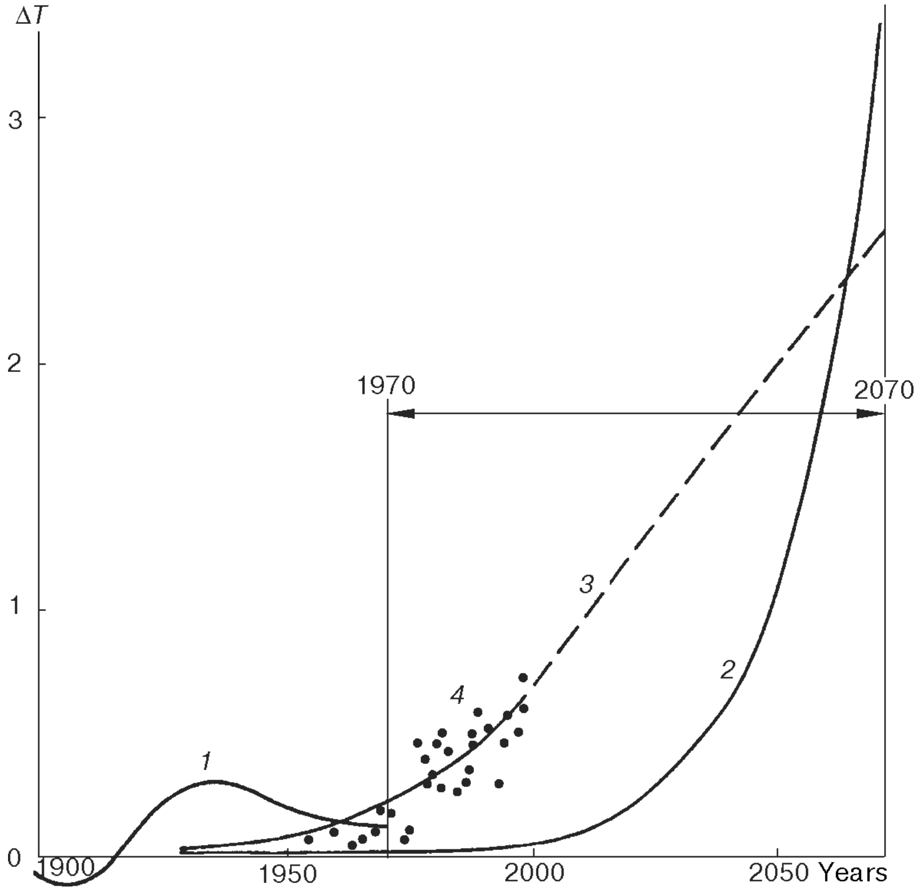


Fig. 100. Century course of anomalies of the near-Earth air temperature [327]: *1* — observation data of changes in the near-Earth air temperature in the period of 1910–1950; *2–4* — variations of D*T* determined by power generation growth (*2,3*) and CO_2 concentration in the atmosphere (*4*) in the period of 1930–2070

Under energy generation the release of heat and gaseous CO_2 (actively consumed by the Earth biota) in the atmosphere proceeds parallel with the atmosphere pollution with dust particles up to 1000 mm in size. This process may be accompanied by formation of steady layers of aerosols which, like volcanogenic particles, prevent from the solar rays penetration to the Earth surface. The absorption of aerosols by clouds amplifies the effect of solar rays reflection by clouds. Besides, when aerosols, dust particles and soot get to the atmosphere they can be accumulated and transferred at great distances, they can also aggregate, fall on the alpine and polar ices accelerating their thawing. This can lead in the future to the flooding of a share of the earth surface by waters of seas and oceans. Thus, energy generation by TES, besides the thermal component which is low (according to calculations), also introduces an indirect endothermal component capable to affect climate of the vast planet regions and leads to their glaciation. These data prove that there exists an unsteady barrier between the near-surface

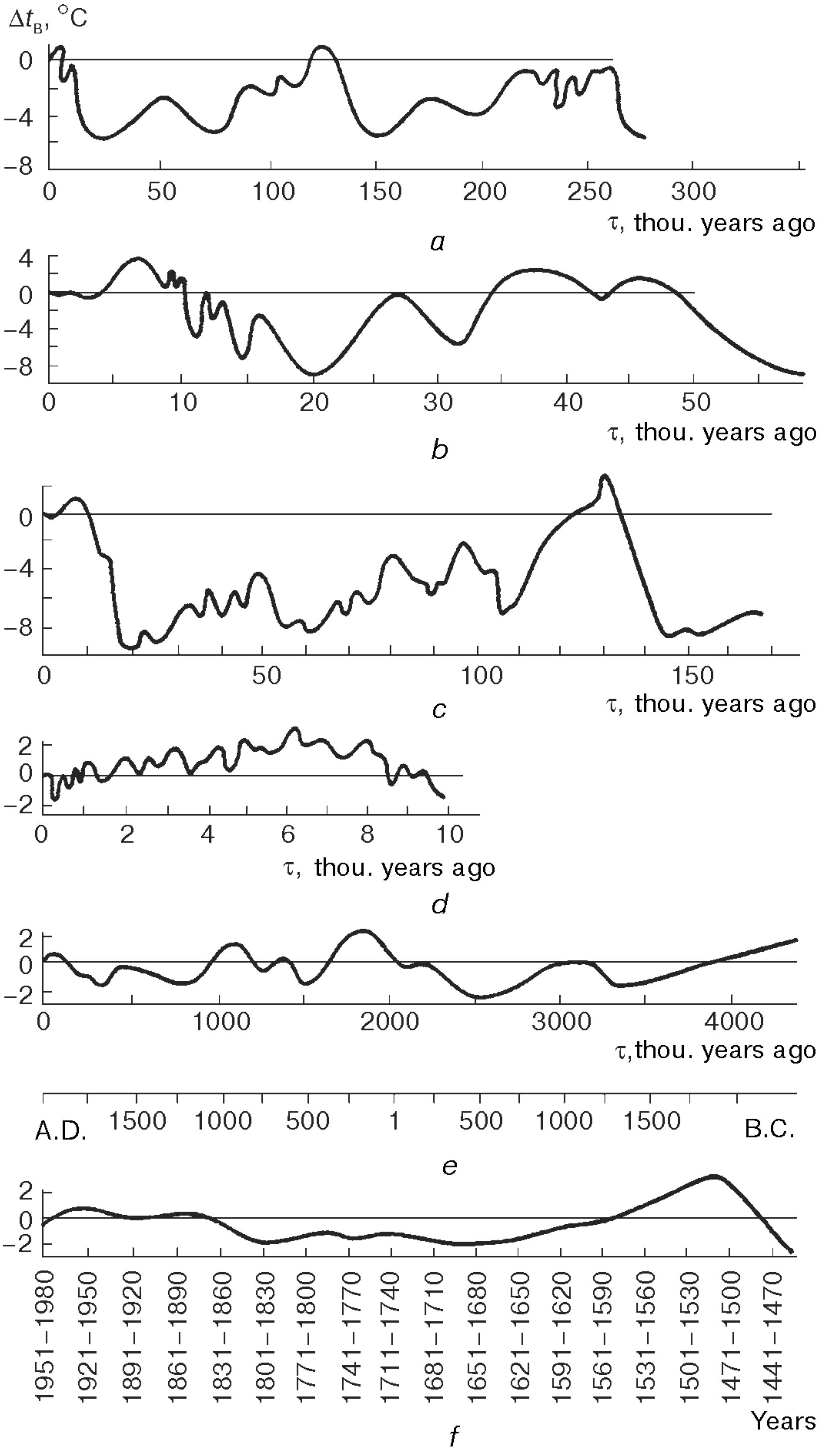
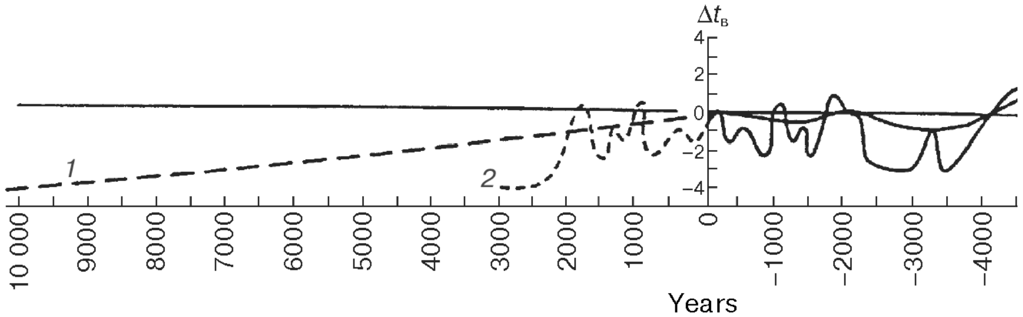


Fig. 101. Air temperature deviations of the part from modern values (D*ta*) [75]: *a* — Middle Pleistocene — Holocene, North Atlantics [72]; *b* — Late Pleistocene — Holocene, Western Siberia [73]; *c* — Middle Pleistocene — Holocene, Antarctics [74]; *d* — Holocene, European Russia, Ukraine [75]; *e* — during recent 500 years (average 30 year) territory of Russia, Ukraine [78]



temperature which maintains life on the Earth and negative temperature which can cause the planet glaciation.

A conclusion about our planet tendency to glaciation follows from the data of works which deal with the periods from 250 thousand to 1 million years [71–80]. Curves of deviation of air temperature of the past periods from its present values are given in Fig. 101. The curves of long-period changes of climate, from the data of different authors, embrace hundreds and tens of thousand years and are in good agreement with each other (Fig. 18, *a*, *b*, *c*) [72–74]. Time of cold and warm periods coincide well, independent of their duration. The cooling-off periods are longer than those of warming up. In the epochs of warming up the air temperature exceeded the present one no more than by 2–3 °C, and in the epochs of cooling off it was lower than the present temperature by 3–10 °C. If follows from short-period curves, embracing tens of thousand years (Fig. 101, *d*) [75], thousands of years (Fig. 101, *e*) [76, 77] and the last 500 years A.D. (Fig. 101,*f*) [78], that the present period is on the descending branch of the climatic macrocycle. The latter evidences for the «present-time climate trend towards the next glacial period». An analysis of Fig. 101 shows that the oscillating character of climate change is a natural feature of its development. Proceeding from the results obtained the author of the work [71] made suppositions of prediction character which follow from Fig. 102. Data of analysis of the last climatic stage of about 20 000 years served as the basis for prediction of changes in the present climate. The above stage embraces the cold epoch of Late Pleistocene with minimum 20 000–18 000 years ago and warm epoch of Holocene which began 10 500 years ago with warming-up maximum 5000–8000 years ago. It is seen from Fig. 101, *d* that one warming up wave is distinguished which continued 8000–4500 years ago when the temperature rose by 2.0–2.5 °C as compared with the present temperature [75]. It is known as the epoch of Holocene climatic optimum, and it had great influence on the nature of North hemisphere of the Earth. The analysis shows that noticeable changes in climate proceed in a form of long-period 30–40 thousand years cycles. The prolongation of the cycles of Fig. 101, *a–c* to the future, made in Fig. 102 shows that the inevitable cooling off would be expected on our planet which will lead

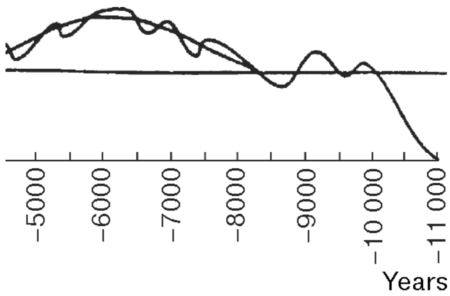


Fig. 102. Summary curve of air temperature deviations (D*ta*) from today's one during the last 10 000 years and prediction of its further course [331]: *1* — supposed descending branch of air-temperature variations of 40 thousand years ctcle; *2* — supposed short-period air temperature variations (as continuation of the same variations in historical period)

to the next glaciation period in 15–20 thousand years. The author of [71] proves convincingly groundlessness of widely distributed point of view which became an official one that climate of the 20th-21st centuries is determined by accumulation of CO_2 released in the atmosphere which evokes global warning up — the greenhouse effect. Proceeding from the ideas of some authors the average annual temperature will increase by 6–16 °C in 150–200 years as compared with the present temperature. Such a supposed warming up could be a catastrophe for the Earth.

But as it follows from the data of geological and paleontological investigations, results of isotope-oxygen analysis of plant remains and deposits, etc., such warming up was not registered during the last million years.

The problem of revealing the causes of temperature variations on the Earth is still of interest. In the first approximation these variations look as those of different periods but possess practically the same value of the air temperature deviations (ΔT_a) from the present one during thousands and hundreds of thousand years. Data of Fig. 101 *a–c* show that negative temperature variations ($\Delta t_a = -(4-9)$ °C) prevail over positive ($\Delta \mathrm{t}_a = (1-4)$ °C) deviations in the period from 20 to 250 thousand years. In our opinion temperature variations on the Earth are connected with periodic changes of the Earth and Sun orbits. It is shown in the work [79] that the space trajectories of the Sun motion relative to the centre of the solar system masses vary. In 1810 and 1990 the Sun «passed by» the mass centre. Under such «passages» the Sun is mostly affected by the tidal and inertial forces. The Sun orbit is about 0.01 of the Earth orbit diameter. Thus, the Sun motion affects both the Earth and other planets of the solar system. The obtained 22- and 11-year cycles of the Sun motion, corresponding under maximum to the highest solar activity determine climatic cycles and observed short-period rhythms in the Earth cryosphere. Depending on its place on its own orbit the Sun «attracts» (carries away) the Earth (that results in warming up) or remains indifferent to it (that leads to the cooling off). One can estimate exactly changes of the Earth orbit parameters and temperature fields on its surface by multifactor calculations allowing for the masses of the Sun, Earth and other planets of the solar system following the laws of celestial mechanics. It is considered that the change of the Earth orbit is one of the most probable reasons of periodical glacial epochs [80].

In conclusion it would be noticed that planet Earth is threatened not only by the energy crisis but also by the ecologic one because of the atmosphere pollution and man habitation ecosystem with harmful emissions of combustion products from gas, oil, hard and brown coals, oil shales, i. e.: nitrogen, sulphur and metal oxides, ash, soot and fine dust pacticles as well as thermal pollutants. Harmful emissions affect the environment and cause the acid rains, while ash, soot and fine dust particles in the planet airspace can evoke other cataclysms in the regions of human habitation.

When directing high- and low-potential heat for hydrogen production in the hydrogen energetics cycles one can both increase NPP and TES efficiency and find the ways to decrease other harmful emissions in the atmosphere — metal oxides, acid-forming sulphur and nitrogen oxides as well as ash and soot. In our opinion the problem of carbon dioxide may be really removed from the agenda now. Owing to the balance of dynamic and multicomponent natural factors, to assimilation of carbon dioxide by the Earth biota — the increase of CO_2 concentration in the atmosphere would not lead to the greenhouse effect and cannot threaten the Earth inhabitants in the visible future.

In polemics about ecology problems of the Earth which are supposed to lead to the global warming up «people disregard almost completely the functioning of natural ecosystems which regulate and stabilize the environment and climate as well as instability inherent in the Earth climate» [81] on the so-called regional level. As is witnessed by our planet history during $4.5 \cdot 10^9$ years, the global warming-up was always observed after glacial periods. The glacial periods which set in as a result of volcano eruptions, geocatastrophes caused by the Earth collisions with celestial bodies and by the change of the Earth and Sun orbit. Geocatastrophes took place on the Earth every 26–27 million years and, as a rule, led to the planet glaciation and changes in its flora and fauna. American professor U. Alvares with his colleagues advanced a hypothesis and proved, that the global catastrophe which took place 65 Ma ago and led to glaciation of the greater part of the planet was a result of the Earth collision with a large asteroid. The process of the asteroid collision with the Earth resulted in an explosion followed by the release of huge amounts of energy; great amounts of iridium, which was the asteroid component, great amounts of dust were scattered as well, and this isolated the planet from solar rays for years. Since the average planet surface temperature was equal to 264 K, that was the variant of «nuclear» winter followed by the freezing of almost all swimming and flying reptiles, as well as dinosaurs, algae and plankton [4]. But such Earth «collisions» with celestial bodies are exceptionally rare judging by the data of mathematical statistics. And the Earth collision with a celestial body of 10 km can occur every 60–100 million years, of 1 km — once every million years, about 100 m — every 5000 years, below 100 m — once every 300 years. About 200 000 tons of extraterrestrial matter particles (fortunately fine) fall on the Earth during a year [4].

The problem of the global warming-up is used now not only in scientific discussions but also in political collisions. Most scholars have doubts in reliability of data used for the prediction of the global warming-up. The data assummed as the basis fir numerous documents about changes in climate are rather indeterminate and «the main thing is that they cannot confirm validly that the rate of temperature rise in the surface air layer during the 20th century is caused by anthropogenic activity» [81]. The scholars have separated into three group as to their approach to the problem of the global warming up. The first group includes scientists and officials who support implicitly the idea of anthropogenic causes of the global warming and the Kioto Protocol. These people began and continue working on the «field» «fertilized by essential financial investments and occupied by the corresponding national and international structures». The second group includes scientists and specialists negating the anthropogenic causes of the warming-up and the global warming itself. This group scientists estimate critically the results of determination of CO_2 concentration in the past by the analysis of bubbles in the ice cores from Greenland and Antarctics. When considering such views one can sometimes divine the interests of certain industrial and economic circles. The third group includes scientists who want to find out the original causes of the global warming up. These scientists comprehend the problem complicacy and high level of responsibility for the scientific conclusions [81]. Scientists of the third group concentrate their attention on the fact that the problem of the infinite carbon dioxide emission from the atmosphere and its assimilation by the Earth biota is ignored both in the discussion about the global warming-up and in the Kioto Protocol. Thus the fixation of quotas for the lowering of CO_2 emission by decreasing the amounts of fossil fuel combustion is senseless. The authors of [81] as well as the authors of this monograph think that such a decision of the problem is groundless. We rather need quotas for the share of restoration of natural ecosystems in volumes compensating the felling in Europe and all over the world than quotas for the decrease of CO_2 emission from combustion of fossil hydrocarbon fuel. Natural ecosystems were formerly destructed in the name of industry development and for raising the living standards of citizens of one or another state, now it is made in the name of enrichment of some clans, companies and groups. They have cut 40 % of the planet forest during the 20th century. The area of Amazonian selva decreases annually by 1.25 %. The modern rates of felling being preserved, the forest will vanish from the face of the planet by the mid-21st century, as well as 30 % of oxygen supplied by these forests and by marshes [42]. Thus, the most important task for all the countries is to create conditions for restoring the forests, called the planet «lungs», in the volumes sufficient for photochemical fixation of carbon dioxide formed in the territory of one or another country in the course of its industrial activity. In this case the discussion question will not arise about the contribution of anthropogenic carbon dioxide to the observed (or rather supposed in the near future) warming up which is «rather contributed by the changes of water vapours content in the atmosphere and clouds as well as by the changes of the planet albedo» [81].

The lack of uniqueness in the question of the climate genesis on the planet and the role of anthropogenic factor in this process leads to the appearance of misinformation. Thus the data about changes in the Earth climate, its catastrophic warming, in particular, often appear in scientific literature (journal *N-ature*) and especially in mass media (BBC broadcasts). What is the cost of information of October 30, 2003, that «the climate warming thinned the Earth ice by 40 % and it is only 3 m thick now. This may result in the complete thawing of the Arctic ice in the 21st century that will raise the world ocean level by 10 m (?!) and the Golfstreem cooling, as affected by this cold arctic water, will lead to the drop of air temperature in Norway, Iceland, and other countries to –40 °C.

Firstly, if 40 % of ice have thawed and the ocean level has not essentially changed, why the thawing of the rest 60 % of ices can result in the catastrophic rise of the ocean water level?

Secondly, why the thawing of only 3 m thick Acrtic ice has to lead to the 10 m rise of water in the World Ocean?

Thirdly, how can the prime cause — the climate warming on the Earth — lead to such cooling (by this version)? And there is a lot of other absurd things.

It would be noted that the problem of the supposed anthropogenically caused climate changes is so much exaggerated that some specialists could predict that «in the 21st century the struggle apropos of this problem acquired such a strategic significance as «hot» and «cold» wars had in the 20th century [25]». In the opinion of the experts, engaged in the problem of greenhouse gases [33], the global changes of the climate on planet Earth «can become an ecologic equivalent of the cold war» [21]. The author of the work [82] thinks that «in a long prospect the measures taken for limiting the emission of greenhouse gases will not be able to remove the great anthropogenic contribution to the elevation of temperature on the planet surface». Thus, «it is time to say that the ecologic stabilization on the Earth is not possible without lowering the anthropogenic load on the biosphere, i. e., the planet population reduction by at least, one order» [82]. You can see how simple the decision of the artificial ecologic problem of planet Earth is. The planet population is to be decreased 10 times — from $6 \cdot 10^9$ to 600 million people. Who will choose one of a dozen of planet dweller deserving life, since «the search of the merited decision of this problem is the greatest challenge to civilization for the whole history of its existence» [82]. And no less.

The real solution of the Earth ecology problem is too simple. One would not pursue a shadow and make up inconceivable projects, calculate expenses for utilization of CO_2. Our planet biota coped with the ten-fold amount of CO_2 in the atmosphere in its geological past [42]. Today the Earth dwellers face the problem of restoring the destructed natural ecosystems. Calculations show that the 30 % increase of the forest areas on the planet could stop the growth of concentration of greenhouse gases without the reconstruction of energetics [81].

Power generation in the 21st century will require the careful combustion of solid fuel — coal, using the processes of gas chemistry. Ecologically pure processes of power generation from coal are developed now in the leading countries of the world. It is predicted that power generation at TES in the 21st century will proceed using the product of coal processing by its gasification — synthesis gas or hydrogen cleaned from sulphur, nitrogen and associated metals impurities. Ecologically pure synthesis-gas and hydrogen will be used as fuel for gas turbines, hydrogen energetics and electrochemical converters of chemical energy into electric one. Natural gas is intensively used in gas chemistry processes. It is supposed that the natural gas, as to its reserves, production efficiency and ecologic properties, is the most promising resource capable to satisfy the mankind requirements in energy and hydrocarbon waste in the 21st century. New processes of synthesis-gas and hydrogen production from coal and natural gas using the heat from nuclear-hydrogen energetics will be used to organize production of liquid synthetic fuels which will substitute the exhausting natural oil resources [83, 84]. That is the only way to protect the environment when generating power both from coal and natural gas in the 21st century. Active use of new gas-chemical technologies of coal and gas processing will give mankind a chance to master the controlled ecologically pure thermonuclear synthesis by the end of the 21st century.

REFERENCES

[1] M. McIvan, The Atmosphere Chemistry. — Mir, Moscow; 1978.
[2] K.Ya. Kondratyev, Bull. Rus. Acad. Sc., No. 9 (2000) 788.
[3] V.V. Snakin, Bull. Rus. Acad. Sc., No. 9 (1998) 214.
[4] A.D. Potapov, Ecology, Vysshaya Shkola, Moscow, 2000.
[5] G.S. Golitsyn, Bull. Rus. Acad. Sc., No. 11 (1998) 990.
[6] V.G. Gorshkov, K.Ya. Kondratyev, K.S. Losev, Ecology, No. 3 (1998) 169.
[7] K.P. Butin, T.V.S. Magdesieva, Rus. Khim. Zhurn., No. 1 (2000) 77.
[8] I.S. Kolomnikov, M.E. Volpin, Uspekhi Khimii, No. 47 (1978) 603.

[9] V.G. Gorshkov, A.M. Makarieva, Biotic Regulation of the Environment, Int. Sem. «Role of Virgin Biota in the Modern Conditions of the Global Environment Changes», Petrozavodsk, Karelia, Russia, Oct. 12–16, 1998 — Gatchina, 1998.
[10] H.I. Schiff, Anns Geophys, 28, No. 1 (1972) 67.
[11] S.C. Wofsy, J.C. McConnel, M.V. McElroy, J. Geophys. Res., Vol. 77 (1972) 4477.
[12] V.A. Solovyov, Ros. Khim. Zhurn., 47, No. 3 (2003) 59.
[13] V.V. Adushkin, V.P. Kudryavtsev, S.B. Turuntaev, Proc. Rus. Acad. Sc., 391, No. 6 (2003) 813.
[14] B.S. Sobolev, Bull. Rus. Acad. Sc., 70, No. 7 (2000) 589.
[15] N. Nakichenovich, Energy: Economy, Technology, Ecology, No. 12 (1998) 2.
[16] I.I. Mazur, O.I. Moldovanov, Course of Geological Engineering, Visshaya Shkola, Moscow, 1999.
[17] G.K. Voronovsky, N.P. Pereverzev, Ecology and Energetics, Kursor, Kharkov, 2000.
[18] V. Snakin, Ecology and Nature Protection, Academia, Moscow, 2000.
[19] Energetics Today and Tomorrow, Edit. A.F. Dyakov, Energoatomizdat, Moscow, 1990, 250.
[20] A.L. Yanshin, Bull. Rus. Acad. Sc., 64. No. 12 (1994) 1081.
[21] K.Ya. Kondratyev, Bull. Rus. Acad. Sc., 70, No. 9 (2000) 788.
[22] K.V. Ananichev, Problems of the Environment, Energy and Natural Resources, VINITI, Moscow, 1975.
[23] S.D. Varfolomeev, Energy Conversion by Biocatalytic Systems, Moscow Univ. Publ., Moscow, 1981.
[24] A.A. Belov, E.L. Minina, Bull. Rus. Acad. Sc., 69, No. 9 (1999) 834.
[25] A. Karnaukhov, E. Zadokhina, Komsomolskaya Pravda in Ukraine, No. 104 (2001) 6.
[26] V.S. Golubev, Bull. Rus. Acad. Sc., No. 12 (1997) 1104.
[27] V.G. Gorshkov, Energetics of Biosphere and Environment State Stability, VINITI, Moscow, 1990.
[28] V.G. Gorshkov, Physical and Biological Grounds of Life Stability, VINITI, Moscow, 1995.
[29] I.K. Larin, Khimiya I zhizn, No. 7 (2000) 10.
[30] K.Ya. Kondratyev, A.A. Grigoryev, The Earth Study from Space, Iss. 4 (2000) 3.
[31] S. Bomer-Christiansen, RGO Inf., Iss. 1 (1999).
[32] K.Ya. Kondratyev, Ecodynamics and Geopolicy. Vol. 1, Global Problems, Scient. Centre, Russ. Acad. Sc., 1999.
[33] L.R. Brown, M. Renner, B. Halweil, Vital Signs 1999. The Environment Trends That Are Shaping Our Future, World Watch Institute, W.W. Norton and Co., Inc. New York, 1993.
[34] B.C. Williams, J.T. McMullan, P. Campbell, Fuel, 73, No. 7 (1994) 1069.
[35] V.S. Arutyunov, A.L. Lapidus, Rus. Khim. Zhurn., 47, No. 2 (2003) 23.
[36] Naukovy Svit, Globus, Kyiv, No. 7 (2000) 16.
[37] R.M. Garrels, Ch.L. Criste, Solutions, Minerals Equilibrie, Mir, Moscow, 1968.
[38] I.S. Kulikov, Isotopes and Element Properties, Ref. Book, Metallurgia, Moscow, 1990.
[39] M.I. Budyko, Bull. Rus. Acad. Sc., No. 12 (1995) 1064.
[40] F.A. Kuznetsov, V.A. Istomin, T.V. Rodionova, Ros. Khim. Zhurn., 47, No. 3 (2003) 5.
[41] N.A. Yefimova, Radiation Factors of Vegetative Cover Productivity, Gidrometeoizdat, Leningrad, 1977.
[42] V.A. Zubakov, Bull. Rus. Acad. Sc., 71, No. 2 (200) 130.
[43] I. Pavlova, Arguments and Facts in Ukraine, No. 37 (2000), Sept.

[44] L. Skibinsky, Who Derives Benefit from Ozone Holes?, Uryadovy kuryer, No. 223 (1999) 6.

[45] Cosmonautics. Encyclopedia, Ed.-in-Chief V. P. Glushko, Entsyklopedia Moscow, 1995.

[46] G.I. Voronin, Systems of Air Conditioning in Aircrafts, Mashinostroenie, Moscow, 1973.

[47] R.G. Rice, A. Netzer, Handbook of Ozone Technology and Application, Vol. 1, Ann Arbor Science. England, 1982.

[48] V.N. Emokhonov, A.N. Yermakov, I.K. Larin, P.G. Filippov, Bull. Rus. Acad. Sc., Energetics, No. 3 (2002) 58.

[49] V.V. Lunin, M.P. Popovich, Physical Chemistry of Ozone, Moscow Univ. Publ., Moscow, 1998.

[50] N.V. Korovin, General Chemistry, Vysshaya Shkola, Moscow, 1998.

[51] N. Chugunov, Nauka i Zhizn, No. 9 (2000) 14.

[52] V.G. Kirillov-Ugryumov, Future of Science. Znanie, Moscow, Iss. 16 (1993) 31.

[53] Quuli Hai, Cheng Wahg, Peilan Wang, Hydrogen Energy Progress XII, Proc. BH World Hydrogen Energy Conf. Beijing, China, June, 12–15, 2000. Vol. 1–2, Published Intern. Assoc. for Hydrogen Energy, 2000.

[54] P.F. Gozhik, O.V. Bilyavsky, I.M. Krushelnitsky, O. Kostina, Nauk. Svit., No. 2 (2000) 12.

[55] I.M. Mazyrin, E.I. Mazurina, Bull. Rus. Acad. Sc., 67, No. 8 (1997) 688.

[56] E.Yu. Bezuglaya, E.K. Zacadskaya, I.V. Smirnova, Proc. Gen. Geophy. Observ., No. 549 (1998) 67.

[57] M. Das, L. Husain, J. Geophys. Res., 104, No. 17 (1998) 17.

[58] Ukraine in the context of «Agenda for the 21st Century», Edit. V.I. Vovk, Nora-Print, Kyiv, 1998.

[59] Ya.M. Glushko, Harmful Inorganic Compounds in Industrial Emissions into the Atmosphere, Khimiya, Leningrad, 1987.

[60] V. Vereshchagina, Arguments in Facts in Ukraine, No. 36 (2000).

[61] L.G. Meira, J. Geophys. Res., 76, No. 2 (1971) 202.

[62] D.F. Strobel, Ibid, No. 1 (197) 83.

[63] P. Crutzen, Can. J. Chem., 52, No. 8 (1974) 1569.

[64] N. Berces, S. Forgeteg, Irans. Faradey Soc., No. 66 (1970) 640.

[65] P.N. Alekseyev, A.Yu. Gagorinsky, N.N. Ponomarev-Stepnoy, et al., Atom. energiya, No. 1 (2000) 3.

[66] S.V. Volkov, Zhurm, neorg. khimii, 35, No. 8 (1990) 2789.

[67] Yu.P. Yelagin, State of the World Nuclear Energetics. Nuclear Eng. Abroad., No. 1 (1990) 3.

[68] M.I. Budyko, Heat Balance of the Earth Surface, Gidrometeoizdat, Leningrad, 956.

[69] M.I. Budyko, Human Effect on Climate, Hidrometeoizdat, Leningrad, 1972.

[70] T.F. Ross, C.S. Godfrey, R.R. Heim, Earth System-Monitor, 10, No. 2 (1999).

[71] N.A. Shpolyansky, The Earth Cryosphere, 5, No. 1 (2001) 3.

[72] S. Emilliani, Science, No. 3933 (1970) 168.

[73] N.V. Kind, Geochronology of Late Anthropogen by Isotopic Data, Nauka, Moscow, 1974.

[74] Trends'93, World Data Center, USA, 1994.

[75] N.A. Khotinsky, Z.V. Aleshinskaya, A.A. Sharbatyan, Proc. Acad. Sc., USSR, Ser. Geogr., No. 3 (1991) 30.

[76] V.A. Klimanov, Climate Variations in the Recent Millenium, Gidrometeoizdat, Leningrad, 1988.
[77] .G. Polozova, Ibid.
[78] M.M. Chernavskaya, Ibid.
[79] V.P. Melnikova, I.I. Smulsky, O.I. Krotov, Cryosphere of the Earth, No. 3 (2000) 3.
[80] J. Imbry, K.P. Imbry, Glacial Epoch Mysteries, Progress, Moscow, 1998.
[81] K.Ya. Kondratiev, K.S. Losev, M.D. Ananicheva, I.V. Chesnokova, Bull. Rus. Acad. Sc., 73, No. 1 (2003) 3.
[82] V.S. Arutyunov, Ros. Khim. Zhurn., 45, No. 1 (2001) 55.
[83] L.F. Kozin, S.V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv, 2002.
[84] L.F. Kozin, S.V. Volkov, Production of High-Parameters Hydrogen with Application of Energy Accumulating Substances, European Hydrogen Energy Conf., 2–5 Sept., 2003, Alpexpo, Grenoble, France.

Chapter 9

Hydrogen Energetics and Other Energy Sources in the Third Millennium

9.1. Hydrocarbon fuel

What power sources will be used by mankind in the third millennium? Hydrocarbon fuel accumulated during milliards of years — oil, natural gas, hard and brown coals — is consumed intensively by the Earth dwellers. It is considered that oil will last for 50 years, natural gas — 150–200 years, hard and brown coals — 250–300 years. And what then? An analysis of the present tendencies in development of power engineering and industry proves that the consumption of hydrocarbon fuels for power generation and in industrial and social spheres of the world states grow impetuously. By the data of [1] $250 \cdot 10^9$ t of conv. fuel were produced and consumed during the last quarter of the 20th century — the same amount of fuel was consumed during all the preceding centuries-old history of mankind. And it is hydrocarbon fuel which is the major share of consumed power resources.

Oil. Oil and natural gas are unfortunately used in the developed countries of the world to generate power though there is a broad assortment of products — from drugs to neilon, lavsan, plastic materials, etc., being much in demand which may be produced from oil. The share of oil used in the processes of petroleum chemistry composes only 3 % of its total production. The words of D.I. Mendeleyev, who said that the «oil burning is the same as stove kindling with banknotes instead of firewood» still remain prophetic.

Reserves of liquid hydrocarbon and gaseous fuels on the Earth are rather limited, but in numerous countries, including Ukraine, they still remain unprospected. The proved reserves of oil in the world are $210 \cdot 10^9$ t of c.f. by [2], in the opinion of other authors they are $138.996 \cdot 10^9$ t [3, 4] and $140.134 \cdot 10^9$ t [5]. The future predicted finds of oil fields (with probability 50 %) are $110 \cdot 10^9$ t, so total oil reserves in this case will be 320.109 t of conventional fuel. Statistical analysis of the world oil production in the 20th century and prediction for the 21st century made in the work [6], point to the exponential character of the plotted curve. Dependence of the world oil production on time which maximum falls on 2000 is given in Fig. 103, *a.* The right branch of the oil production curve, having reached maximum, drops and approaches gradually the zero. Under the extraction of 80 % ($280 \cdot 10^9$ t), $224 \cdot 10^9$ t oil will be extracted from the Earth bowel during the estimated time of 64 years. Geological oil reserves in the Earth food was $140 \cdot 10^9$ t as of 01.01.2001. As is evident from Fig. 103, *a*, this amount of oil may be produced and consumed theoretically by 2004–2050 since current annual oil production volume in the world is $(3.414–3.585) \cdot 10^9$ t. Proceeding from real total world oil reserves of $138.995 — 140.134 \cdot 10^9$ t [3, 5] and real current volumes of its production one can obtain time close to the estimated time and equal to 39.0–40.5 years (reference year 2000). When estimating oil consumption, proceeding from the amount of consumed electric power ($5.32 \cdot 10^{13}$ kWh/yr. [7]) with efficiency no less than 70 %, mankind will be provided with oil only during 34.3 years. By the prediction of O.V. Krylov, oil will completely extracted all over the world by 2020. Oil production in each separate country, for example in the USA, is also described by exponential curve with maximum. Oil production diagram of the USA, embracing the past period about 100 years, as well as its predicted production is given in Fig. 103, *b*. It is considered that geological oil reserves in the USA (about $27 \cdot 10^9$ t c.f.) will be consumed completely by 2045. It was also predicted that $23.71 \cdot 10^9$ t of oil that is 80 % of geological reserves, will be produced and consumed during the period of 1934–1998, i.e., during 65 years. If the proved geological oil reserves in the USA are $3.2876 \cdot 10^9$ t now, total amount of consumed oil ($23.71 \cdot 10^9$ t) and oil which remained intact till now ($3.2876 \cdot 10^9$ t) will just make the value close to $27 \cdot 10^9$ t of that used to calculate oil production and consumption [6].

Annual oil production in the USA is $321.0 \cdot 10^6$ t now. Under 70%-extraction home oil reserves of the USA will last only 7.2 years (see, Fig. 103, *b*). Hence it follows that the USA are short in oil reserves and, in the opinion of the author of [6], the USA position concerning oil is worse that in the world as a whole. In 1998, the USA consumed 39 % of oil 23 % of coal, 23 % of natural gas produced in the world, to generate electrical energy they also consumed 8 % of nuclear power ($628.644 \cdot 10^9$ kWh of electric power) and 7 % of renewable energy of the world. The USA produced $3122.5 \cdot 10^9$ kWh of electric power in 1998 and the share of coal was 57.3 % [8]. That is why the USA state policy is reduced to the creation of strategic reserves of oil and oil import until foreign exporters want to sell it. Though the positions of Russia something differs from that of the USA, it also has intentions to create its strategic oil reserves [9] that is advisable for any country in the world including Ukraine.

Oil pool production is an important factor. Under real conditions oil recovery depends on genesis of oil pools and many other factors and varies in the limits of 14–65 % [10]. So the methods of raising productivity of the oil wells are searched all over the world. They use the processes of water encroachment of the oil-gas pool or horizon by the supply of hot or cold water under pressure, high-temperature water vapour, compressed gases, water solutions of surfactants, etc.

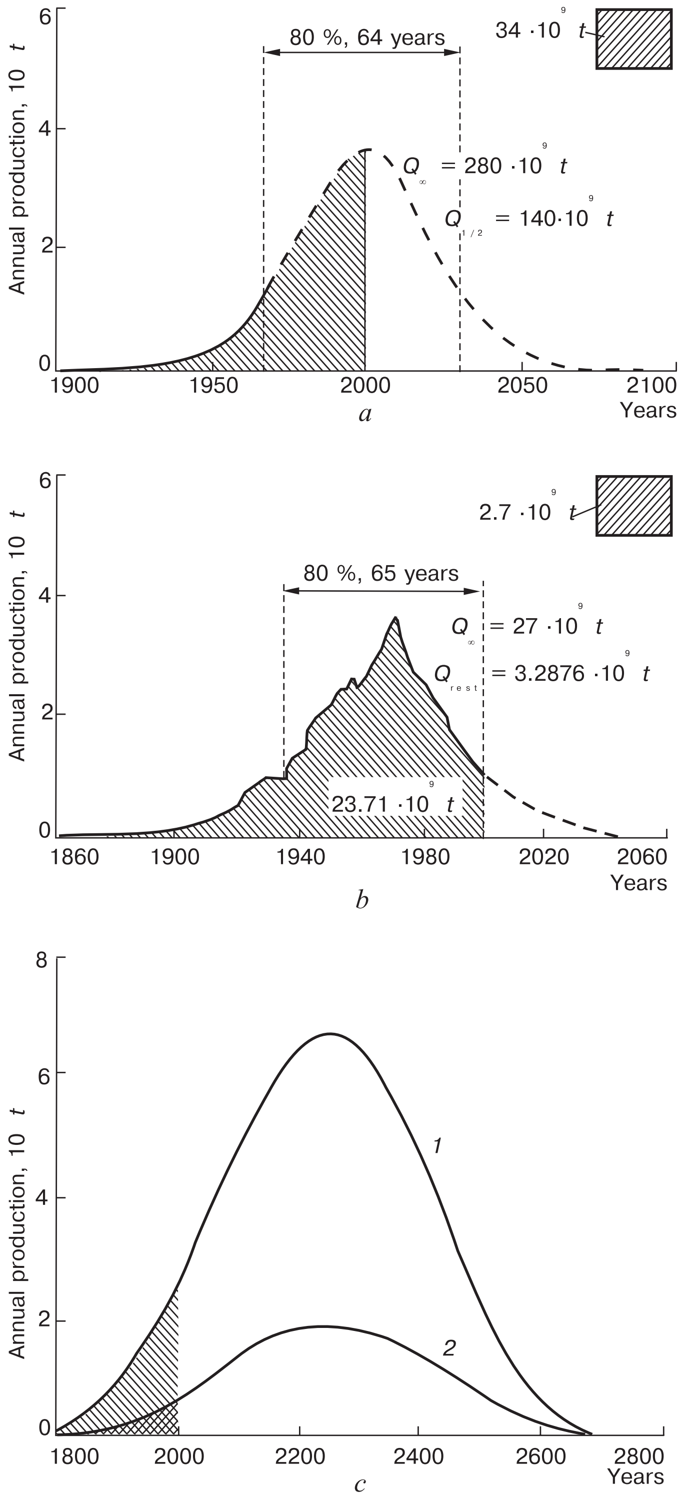


Fig. 103. Prediction of oil (a) and coal (c) production in the world under geological oil reserve $Q_\Gamma = 280 \cdot 10^9$ t (*a*), hard $Q_\Gamma = 502 \cdot 10^9$ t (1) and brown $Q_\Gamma = 1019 \cdot 10^9$ t (2) coal (c) as well as oil production in the USA (production beginning in 1980 under reserves of $Q_\Gamma = 27 \cdot 10^9$ t (b)

The process of proportional burning of oil inside the oil pool has been studied and tested; the volume gassing (CO, CO_2, H_2, H_2K vapour) under oil burning leads to oil displacement and its higher extraction, up to 74 % [10]. The processes of setting-up the external electric fields resulting in electroosmosis which increases the oil well productivity, are at the stage of research [11]. It has been established that electroosmosis raises permeability of the oil pool contiguous with a productive well, and oil recovery increases. It would be noticed that the greater volumes of oil, than those produced in the 20th century remained in the worked out oil fields. New, more efficient processes of oil production being developed in the 21st century, the oil field will be restored for additional oil production.

The time dependence curves are given in Fig. 104 which characterize the consumption of various heat carrying agents, including oil, for power generation in the world (curve 4). In the light of the past and future millennia oil and natural gas compared with other energy sources, are a «transient surprise», which has put certain power basement at mankind's disposal for people could develop transport, industrial machine building, socionics, etc.

Transport demands in liquid fuel and lubricants are satisfied today by oil processing using the newest methods.

Now, a few words about oil problems in Ukraine. Prospected oil reserves in Ukraine are $800 \cdot 10^6$ t conv. fuel without account of oil-gas-bearing fields found on the north-western shelf of the Black and Azov Seas [12]. Annual volume of oil production being 20 mill. t, such oil reserves will last only 45 years. There are six oil-refineries in Ukraine; their production capacities are about 17–20 %. Maximum level of oil refining in Ukraine reached 62 mill. t of oil in 1989, and it was reduced to 10.4 mill. t [14] (almost 6 times) by 1998. They produced 13.9 mill. t of oil in 1970 and 4.1–3.9 mill. t in 1995–1998 [14] (3.4–3.6 times less), that was 7.8–8.2 % of the amount required in Ukraine (50 mill. t; see, Table 18).

Natural gas. Proved reserves of natural gas in the world are $149.470 \cdot 10^{12}$ m^3, and full reserves (with potentially predicted reserves of $180 \cdot 10^9$ t of conv. fuel) can achieve $360 \cdot 10^9$ t of conv. fuel. Proceeding from the fact that natural gas is an associate of oil in the proportion of 1350 m^3 for 1 t of crude oil, and allowing for the proved oil reserves as of 01.01.2001 equal to $140.134 \cdot 10^9$ and $164.5 \cdot 10^9$ t [5] the natural gas reserve can be estimated as that equal to $189.181 \cdot 10^{12}$ and $222.075 \cdot 10^{12}$ m^3. These values surpass by 20.6 and 47.8 % the reserves of natural gas prospected as of 01.01.2002 by the data of [5] equal to $150.2 \cdot 10^{12}$ m^3. According to other data, total reserves (determined reserves potential resources) of natural gas in the world are estimated from 235.6 to $380 \cdot 10^{12}$ m^3 [16]. It is supposed that these reserves of natural gas in the world will last for 100 years (see, Fig. 104) [1].

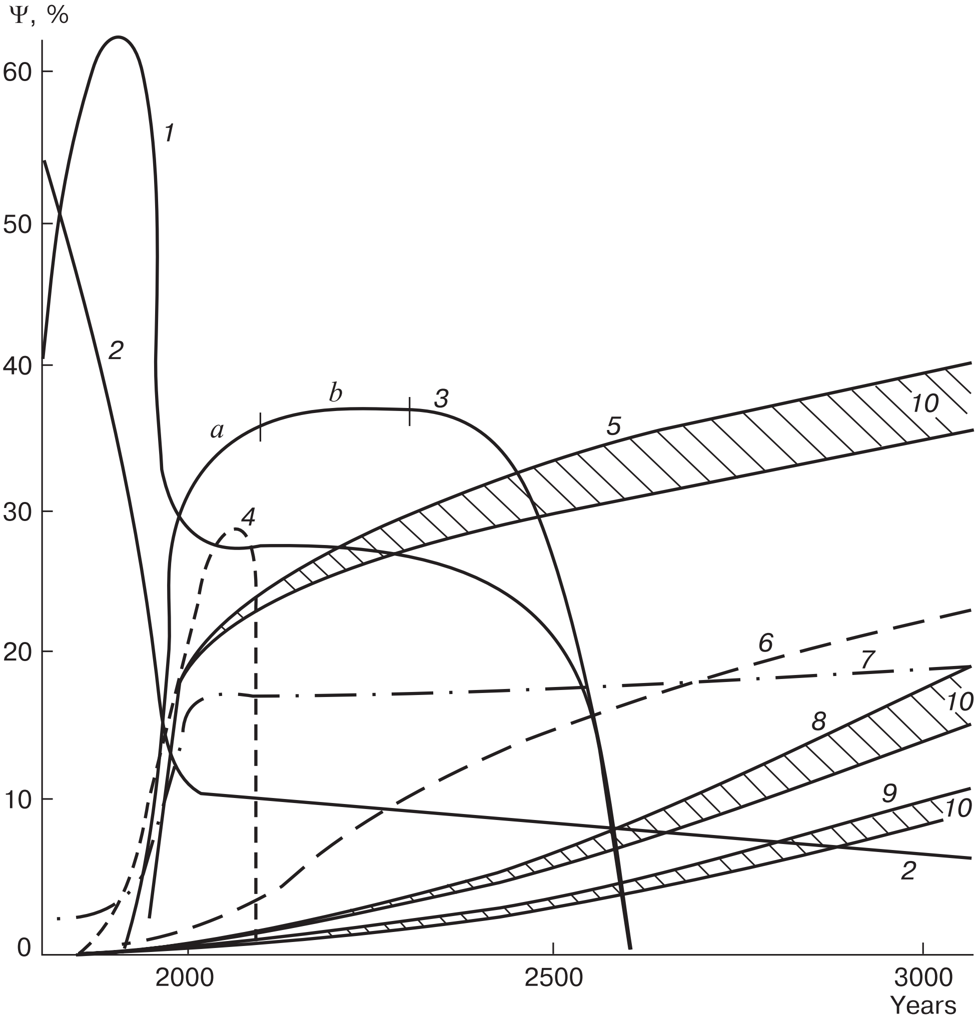


Fig. 104. Ratio of various kind of heat transfer agents used in the world for power generation: *1* — coal; *2* — biomass; *3* — natural gas (*a*); gas-hydrates (*b*); hydrogen and gaseous heat carriers from coal (*c*); *4* — oil; *5* — nuclear and thermonuclear energy; *6* — hydrogen energetics; *7* — hydroenergetics; *8* — wind energetics; *9* — photoconversion of solar energy into electric one; *10* — indeterminacy value

The proved reserves of natural gas in Russia are 48.9 · 10^{12} m^3. Gas production volume being 735 · 10^9 m^3/yr, this resource will last only for 66 year in Russia — the major supplier of blue fuel to Europe (60 % of import) and thus in Ukraine. Proved reserves of natural gas in the USA are 30 · 10^{12} m^3, though by the data of the work [16] natural gas reserves in the USA vary within the limits of 75.6–196 · 10^{12} m^3. Methane accumulation of 14 · 10^{12} m^3 was found on the sea-coast of California, in Blake Ridge region. Natural gas consumption in the USA was 616 · 10^9 m^3 in 1999, and 812 · 10^9 m^3 predicted for 2010, 868 · 10^9 m^3 for 2015. Doing justice to such a good energy carrier as gas, the USA invested 1.5 · 10^{12} USD into gas branch in 1998 [17].

If the peak of natural gas production in Ukraine fell on 1975 and it was 68.7 · 10^9 m^3, then they produced only 18.1 and 18.0 · 10^9 m^3 of natural gas in 1997 and 1998 [14], that corresponded to 20.1 and 20.0 % of the required amount, respectively (Ukraine transported 86 · 10^9 m^3 of natural gas from Russia and Turkmenia). The amount of natural gas supplied to Ukraine to support its power generation system equals 44.6 %.

But our nature presented mankind with one more energetic gift. The deposits of gas-hydrates (mainly methane) were discovered in the 70's of the 20th century in the Black (1972) and Caspian Seas (1979). The detailed investigation has shown that 1 m^3 of natural gas hydrate may contain 164 m^3 of methane, thus one water volume binds about 160 volumes of methane [15, 18, 19]. By the estimates, methane content in gas hydrates is 2 · 10^{14} to 7.6 · 10^{18} m^3 [20]. Gas methane-containing hydrates are formed and exist steadily within a broad range of pressures (from 2 · 10^{-8} to 2 · 10^3 MPa) and temperatures (from 70 to 350 K). The process of gas hydrate formation occurs with heat release and gas decomposition with heat absorption. Under the freezing of gas hydrate the specific volume of water increases by 9 %. Natural gas hydrates form the deposits where gas can remain in the solid hydrate state. In seas and oceans the thermodynamic zone of formation and stable existence of hydrates can achieve several hundred meters, but the upper boundary of methane hydrates existence is more than 260 m [15]. Submarine gas hydrate deposits are mainly confined to the deep-water shelf and ocean slope with water depth from 200 m in the prepolar regions, to 500–700 m in equatorial regions. Methane hydrate formation in the world ocean water areas begins at the bottom and reaches usually several hundred meters. The upper boundary of gas hydrate formation zone in seas and oceans is always in the water thickness and the lower one in the rocks cross-section. By the data of [15] deep-water sediments, embracing shelves, and the deposits of continental slopes and deep-water troughs are most promising zones of gas hydrates accumulation. Gas hydrate deposit formation occurs both on the part of the upper boundary, owing to the supply of new positions of organic matter and their following destructive (including microbiologic) transformation, and on the part of the lower boundary — owing to gases formed under the penetration and further transformation of the organic matter as well as owing to gases supplied from the deep bowel of the Earth. So, the thickness of gas hydrates grows both from below and from above. Depending on temperature under hydrate-saturated beds, methane can accumulate with other gas-impurities forming traditional gas fields. The same is the formation mechanism of oil deposits multiply found under the hydrate-saturated beds functioning as nonpermeable lead, isolating biota from oxygen and other oxidizers. This mechanism is analogous to that of our hypothesis of oil origin (Chapter 2).

Methane hydrate deposits also occur on land. They are usually confined to the cooled zones of the Earth crust of sedimentary type. The thickness of rocks with gas hydrate deposits can vary from 400 to 1000 m in the regions of eternal glaciation.

Two hundred gas hydrate deposits with specified well-agreed world reserves equal to $1.5 \cdot 10^{16}$ m^3 [22] and $2.1 \cdot 10^{16}$ m^3 have been discovered now. Natural gas hydrates are distributed more uniformly on the planet than oil and natural gas sources. Their development will not require superdeep wells, complicated and expensive systems for transportation of the obtained product. But it is necessary to elaborate high-tech processes using the principles of physical chemistry and chemical thermodynamics to achieve acceptable efficiency of gas (methane and nomologs) extraction equal to 80 % compared with admissible values equal to 10–60 %. It is supposed that power capacity of natural gas hydrates will be enough to generate relatively pure energy all over the world during no less than 200 years. Thus, the provision of the world energetics with gas can embrace a period of time equal to 300 years (up to 2300), and even for 500 years, when using coal to produce hydrogen.

The predictional data about energy carriers which may be used in the USA in the nearest two centuries of the third millennium (up to 2200) are given in Fig. 105, as an example.

As is evident, natural gas, coal and hydrogen will become the major energy carriers after 2050. At present the USA use 5 % of natural gas for production of hydrogen and synthetic liquid fuel [24]. Hydrogen and synthetic liquid fuel will be soon obtained with the use of coal and NPP energy. The renewable energy sources (solar, wind and hydroelectric energy), side by side with nuclear energy, will be used to produce hydrogen and to synthesize liquid synthetic fuels. Our notions about the future role of hydrocarbon fuel in energy generation agree with

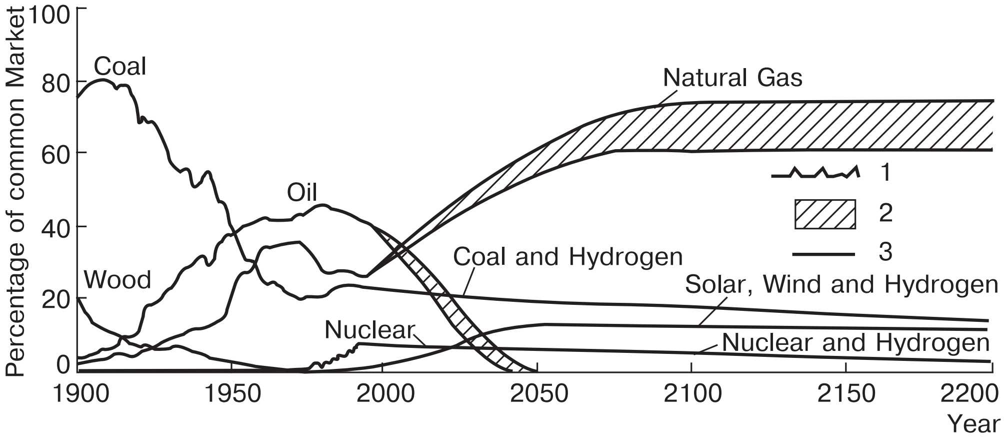


Fig. 105. Global energy carriers in the USA during 1850–2200: *1* — really consumed energy carriers up to 2000; *2* — indeterminacy value when using natural gas and coal; *3* — predicted consumption of natural gas (including gas hydrates), coal, nuclear energy and that of renewable energy sources (solar energy, wind energy, hydroelectric energy)

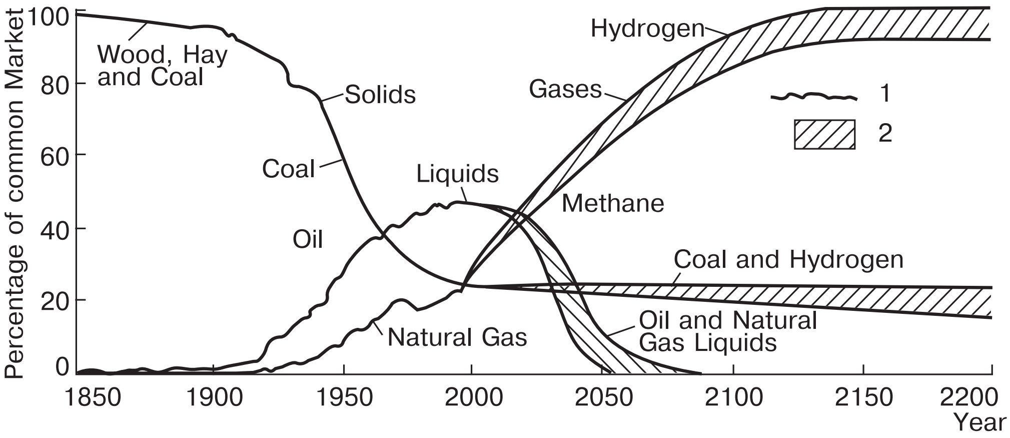


Fig. 106. Global energy carriers in the world energetics in the period of 1850–2200: *1* — really consumed energy carriers (wood and biomass, coal, oil) up to 2000; *2* — indeterminacy value when using natural gas and coal; *3* — predicted consumption of natural gas (including gas hydrates), coal, nuclear power and renewable energy sources (solar, wind, hydroelectric energy)

the data of [25]. We suppose that the role of coal as energy carrier in the USA will decrease considerably in the course of time, while the role of natural gas can increase. The large-scale use of ecologically pure fuel: natural gas as well as methane from gas hydrates, the volume of the environment contamination in the USA by sulphur and nitrogen compounds, as well as metal oxides can essentially decrease.

The same picture may be also observed as is seen from Fig. 106 in the world power system. After 2050 natural gas and methane from gas hydrates can become the major energy carriers, since oil reserves will be completely exhausted by 2050. The memory the 20th century, as extremely wasteful oil century, will be probably preserved only in historical memoirs and fantastic genre. In the 21st century natural gas and coal, including that processed into gas, containing hydrogen, will be the major sources of hydrocarbon for world chemical industry and for synthesis of the liquid fuel for motor transport and other devices on the basis of the internal combustion engines. The transition to the era of «energy gases» will be gradual [24]. Hydrogen will most probably become an intermediate and major energy carrier in the motor transport, aviation and space engineering. The nature hydrogen is not an energy source, since in remains in nature in oxidized state in a form of chemical compounds, while in free reduced state it occurs only as a product of vital activity of hydrogen microorganisms. Energy inputs are needed to produce hydrogen (gaseous, liquid). Newertheless it is predicted the hydrogen will become a universal energy carrier in the future [26, 27]. There is no alternative to hydrogen as energy carrier. When producing hydrogen from water by electrolysis, the energy input is 5.1–5.6 kWh/m^3. To decrease electric energy consumption as was shown in Chapter 7, electrolytic release of hydrogen proceeds at high temperatures. Simple but safe methods of its treatment will be created. The inhibitors, decreasing hydrogen reactivity, preventing the danger of explosions in hydrogen-air mixture and self-ignition under hydrogen outflow in the air, will be created for the large-scale use of hydrogen. Projects of supply of liquid and metal hydrogen from the nearest hydrogen stars in the space to the Earth and other extremely interesting supertasks are well-known now.

Solid hydrocarbons. The world reserves of solid fuels (in 10^9 t) are: coal — 5021–5264, bitumen-containing sands 750–1089 and turf 500 (at 40 % moisture). The highest turf reserves (10^9 t) are: in Europe — Finland (35), Ukraine (25), Byelorussia (17), Swiss (11.2); in America — USA (36.3), Canada (35); in Africa — Zair (35); in Australia (1), New Zealand (1.3). Turf reserves in Russia are $145 \cdot 10^9$ t, and production — $19.5 \cdot 10^6$ t a year. Turf production in Ukraine was 2.1 and 0.7 mill. t. in 1990 and 1997, respectively [14].

Proved reserves of coal, equal to $107 \cdot 10^9$ t conv. fuel, under production volume $1.275 \cdot 10^9$ t/yr., will be exhausted in 84 years in the USA. Predicted resources of coals in the USA deposits at the depth of 1800 m are estimated as $3.6 \cdot 10^{12}$ t. In this case calculation shows that even at higher volume of mining in the USA coal will last no more than 1000 years. Total proved coal reserves in China reached $1033.4 \cdot 10^9$ t. Annual coal mining in China being equal to $1325 \cdot 10^6$ t (1997), coal reserves in China will last for 779 years. Great reserves of coal were opened in Russia, 97 % of them are in Siberia. Open coal reserves in Siberia will last to meet the requirements in Russia for the period of 600–1000 years. The amount of open coal reserves in Siberia is enough to meet the requirements in Russia for the period of 600–1000 years. Open coal reserves in Russia surpass 400 times oil reserves and above 200 times — reserves of natural gas of Russia. Coal reserves of other countries will last, respectively (reserve/mining = year); EEC — $70 \cdot 10^6$ t / $0.246 \cdot 10^6$ / yr. = 284 years; South African Republic — 51/0.131 = 389; Australia — 25/0.101 = 247; Poland — 27/0.163 = 166; India — 13/0.123 = 106; Canada — 2/0.033 = 60; Ukraine — 42.4/0.706 = 600. Allowing for the situation with oil and gas, the role of solid hydrocarbons (coal, slates, turf) in electric energy generation must increase. Nowadays, the share of coal in electric energy generation in the world is as follows, %: Russia — 26, Ukraine — 27, USA — 57.3, Germany — 58, China — 74.6, Czechia — 75, Australia — 86, SAR — 90, Denmark — 93, Poland — 96. The average coal consumption in the world, relative to other energy carriers, is 26.9 % [28]. It is seen from Fig. 103 that the total world reserves of hard (curve 1) and brown coal (curve 2) will be exhausted only by 2500–2600. The hard and brown coals, being widely used at TES to generate electric energy, help to supply hot water and heat to cities and industrial enterprises. These coals, side by side with turf, are widely used in towns and villages for domestic needs and for heating dwelling houses. Besides, certain grades of hard coal are used to produce coke used as a reducing agent in metallurgy in pig iron and steel production. Unfortunately great amounts of carbon, sulphur and nitrogen oxides as well as metal oxides (Pb, As, Zn, Hg, Cd, Be, Cr, V), metalloids (Se, Te, Ge) and even radioactive elements (Ra, U, Th) are emitted under the combustion of hydrocarbon fuel.

New modern coal combustion processes are developed with the aim to decrease ecological danger from emissions of solid particles, acid-forming oxides of metalloids, metal oxides, including radioactive ones. The decrease of ecological danger from utilization of solid fuels will be promoted by their conversion into synthetic liquid (SLF) and gaseous (GF) fuels. The relation of coal, oil and natural gas production for energy generation in the third millennium is shown in Fig. 104. The share of coal in the balance of consumed energy was about 30 % in 2000. By our forecasts, the ratio between energies generated from coal and other kinds of heat-carrying agents will remain at the level of 28–30 % in the nearest decades. The share of gaseous carriers, as is seen from Fig. 106, will increase.

The USA consume a half of hydrocarbon fuels produced in the world now. Thus, the world prices for oil being increased — as far as its reserves are exhausted — the USA, like a number of other countries, will have to organize the large-scale production of alternative fuels from coal and natural gas, that is SLF and GF. It is in connection with the evident exhaustion of reserves of liquid hydrocarbon energy carriers, that numerous states would make every effort to develop new more efficient methods of coal processing for production of SLF and GF. There is a well-known Russian-American project of deep coal processing by soft pyrolysis with obtaining liquid hydrocarbons and ecologically pure solid fuel [29]. It is also possible to develop complex technologies of coal conversion into ecologically pure gaseous, liquid and solid fuels, as well as the use of natural gas to generate electric energy and heat at ecologically pure TES [30–32]. The methods of coal burning in the boils with circulating boiling layer and intracycle gasification of coal with only CO_2 emissions into the atmosphere are already used when constructing modern TES.

As was demonstrated by the recent researches of scientists and our analysis of their data great volumes of CO_2 emitted by TES and TEP do not threaten the Earth dwellers' life, since they are assimilated by the planet biota and are in dynamic equilibrium with it. It is CO_2 of the atmosphere and ultraviolet solar radiation which support life on the Earth. The CO_2 concentration in the atmosphere (0.028–0.033 %) and even its 5–10-fold increase will not make the determining contribution to the greenhouse effect since the latter is mainly determined by the content of water vapours (62 %), nitrogen, ozone, oxygen and other small components of the atmosphere (31 %), the share of carbon dioxide being only about 7 %. That is why some scientists, specialists in climatology are sceptical in respect of the problem of anthropogenic change of climate: they think it artificial [33–35], some other scientists call it «liberal gabble» [36]. In the opinion of the author of [35], the researchers ranking global warming among the major ecological problems of the 21st century are on the wrong track. The latter is determined by the fact that, firstly, the greenhouse warming up itself, if it takes place, will have not only supposed negative consequences, but also positive, mentioned by Academician M.I. Bydko; secondly, the action mechanism of the greenhouse effect has not been monitored in paleoclimatic practice. Paleoclymatologists have not yet decided the problem, whether the greenhouse effect caused «great warm spells of the past or it was their consequence» [35]. The authors of the work [37] negate a possibility of temperature elevation in the Earth atmosphere as a result of CO_2 concentration increase in it because of high thermal inertness of our planet. The supposed temperature elevation 20 years ago, compared with that in the 70's (by 1–2 degrees) proved to be inconsistent. Really, the fixed warm spell was equal to 0.35 °C that is 3–6 times less than it was predicted. The temperature rise velocity was measured in experiment with the help of Earth artificial sattelites (EAS) during 23 years. It was only 0.062–0.064 °C which corresponded to 0.02567 °C during a year [38]. The obtained value was 5.92 times lower compared with the value 0.367 °C postulated by Interdepartmental group of experts on the climate change (IGECC). The temperature change in the time interval from 1979 to 2001 by the data of [38, 39] is too insignificant and cannot result in the global warming up on the Earth. The CO_2 concentration in the atmosphere has increased by 38–40 % in the period of 1979–2001 compared with 1850–2001, and the insignificant change of temperature, which was really only 0.02567 °C/yr are not catastrophically dangerous.

By the data of the author of [33] natural basic climate-forming factors in the 21st century will counteract the ever-increasing greenhouse effect. It means that the «catastrophic global temperature elevation will occur neither in the present nor in the future centuries» [33]. When analyzing the mechanism of temperature elevation under natural conditions the authors of the work [37] have come to a conclusion that the overheating of green houses (the notion of greenhouse effect being introduced in analogy with them) takes place not because glass transmits visible rays and retains infrared radiation, but because the convective mechanism of heat exchange and heat transfer from soil outside the greenhouse limits is excluded from the process. The Earth is surrounded by a dense atmosphere layer, thus the average temperature of its surface must depend on the convective movement of the air masses in troposphere. Depending on the season, dense layers of clouds create a short-term positive greenhouse effect on the regional scale owing to water vapours in autumn and spring and negative (cold spell) — in summer. In the lack of the «cover» — the cloud layer — over the Earth surface — there occurs a convective removal of the troposphere heat and its scattering outside the Earth atmosphere. Heat is transferred spontaneously from the more heated body (lower troposphere layers near the Earth surface) to the less heated body — the upper troposphere and stratosphere layers as a whole. This process occurs in complete correspondence with the second law of thermodynamics by which «heat cannot flow spontaneously from the less heated body to more heated one (Clausius' formulation), but it can flow from hot to cold. Heat cannot be «preserved» in the lower layers of the troposphere, since it is transferred to more cold upper layers of the troposphere. A certain heat pump functions in nature which strives for the heat averaging (and, consequently, temperature, energy) in the throposphere and atmosphere mass as a whole.

Thus, the ever-increasing number of scientists realize that it is a mistake, thrusted by mass media, to refer CO_2 to the class of especially harmful and even toxical gases. As we have noticed, and as it is said in the work [33] CO_2 is «the most important component of global biotic circulations». The Earth flora and fauna were more rich and diverse in the periods of high concentration of CO_2. The history of our planet evidences that its vegetation was violent and rich, trees were of giant height and thickness in the epoch of high concentrations of CO_2. Today, by the data of the work [33] we live in the epoch of critically low concentrations of CO_2. In one of his predictions for the third millennium A. Clark called the increase of CO_2 concentration in our planet atmosphere the most important task of mankind. The author of the work [35] thinks that «if a man was fated to make something positive in the process of realizing the industrial revolution, it was, beyond doubt, the growth of CO_2 concentration in the atmosphere». But it does not concern the emissions of highly toxical gases — surphur and nitrogen oxides. The end products of hydrocarbon fuel combustion — great amounts of oxides of sulphur, nitrogen and other metalloids, as well as hard particles of metal oxides and radioactive elements, emitted by power producers to the environment, are a real hazard to life on the Earth. To separate these harmful and ecologically dangerous components emitted in the atmosphere the solid fuel (coal) would be subjected in the steam or underground gasification with obtaining synthesis-gas, which may be supplied to consumers by pipelines. The use of synthesis gas could decrease the load on the environment, since only water vapour and CO_2 are the end products of synthesis-gas combustion. Such a method of solid fuel utilization could increase its efficiency.

The major share of energy on our planet is generated by TES — 64 %, NPP — 18 % and HES — 17 %. These indices in Ukraine are as follows: TES produce 54.5–57.1, NPP — 33.6–42.2, HES — 5.3 %, the specific weight of power generated by NPP grows every other year because of the decrease of power generation by TES which use the hydrocarbon fuel. The share of coal in the power generation structure of our country is 27.1 %. It would be noted that the peak of coal mining in Ukraine was registered in 1975; it was $215.7 \cdot 10^6$ t. In 1980 the coal mining decreased to 164.8, and in 1998 — to $77.2 \cdot 10^6$ t that is by about 7.9 % less compared to 1940 ($83.8 \cdot 10^6$ t) [14]. The share of home coal mining in satisfying the country demand is 31.5 %, that of energy carriers — only 42 %. The rest of energy carriers based on hydrocarbon fuel — $2.0 \cdot 10^6$ t of coal,

$80–90·10^9$ m^3 of natural gas, $40–50·10^6$ t of oil are mainly exported from Russia [41].

It is clear from the above stated that the hydrocarbon fuel — natural gas, gas hydrates, hard and brown coals, turf, etc. — will still play a determining part in the fuel-power balance of most countries in the first half of the third millennium. Oil will meet the demands of power industry and transport only in the first quarter of the 21st century. The «leavings» of oil will be consumed by chemical industry of the 21st century with obtaining high-tech production (medical and chemical preparations, plastic materials, food products, etc.). Reserves of natural gas and gas hydrates will last for minimum three centuries of the third millenium, which will be called «the power gas era». Under such conditions, natural gas will last for one century and gas hydrates for two other centuries. Solid hydrocarbons (hard and brown coals, bituminous sands, turf, etc.) will allow to continue «the power gas era» no less than for one-two centuries up to 2500–2600. Highly efficient methods with high efficiency of solid hydrocarbon energy conversion into liquid and gaseous energy carriers, including those based on liquid and gaseous hydrogen for domestic needs, industry on land and air transport, spacecrafts, etc.

9.2. Nuclear and hydrogen energetics

The hydrocarbon fossil fuel is finite, thus, the high-tech nuclear-hydrogen power industry is one of the alternative ways of energetics development on our planet; it is based, e. g., on high-temperature reactors HTHR-1000 and fast reactors FN-350, FN-600 (including a design of the reactor FN-800 [42]). The use of the latter reactors is more expedient, since they reproduce nuclear fuel — plutonium. By the end of 2000 the number of functioning nuclear power units in the world increased to 439, and their total electric power was 352.121 GW (netto) [43]. In 2000 Brazil connected one more nuclear unit to its power network, India — 3, Pakistan — 1, Czechia — 1, Slovakia — 1. Total electric power of seven nuclear units, put in operation, is 3275 MW. There reactors have been built and function now in China, six more reactor are being constructed. Ministry of Energetics of China has a plan to construct and put in operation 50 more nuclear reactors by 2020.

The post-Chernobyl syndrome has inhibited the development of nuclear power systems in almost all countries of the world. Growth of nuclear industry was only 4.4 % compared with 1990. And only power crisis of 2000 in the USA caused the appearance of the Bush-Chainy doctrine of 2001. In accordance with this doctrine it is planned to build one more, the 33d NPP in the nearest future. In the USA 110 power units generating $628.644·10^9$ kWh/yr. functioned at 32 NPP in 1997. This amount of electric power was 20.1 % of total electric power generated in the country (TES, HES, etc.). Two nuclear reactors are constructed in Taiwan. France, where the share of electric energy produced by NPP is 77.21 %, is building two more high-power nuclear rectors. Finland plans to erect NPP with a total value of $2.5 \cdot 10^9$ Euro. In 2001 the government of Japan approved the plan of construction of two NPP and removed a ban for modernization of those in operation. By the end of 2010 this country plans to construct from 16 to 25 new NPP. Russia constructs new NPP in Chelyabinsk region, in Khabarovsk and Primorie areas, erects new units at Voronezh, Beloyarsk, Leningrad, Kola and Smolensk NPP, as well as finishes the units at Kursk, Kalinin and Balakovo NPP. It is planned to finish and put in operation a unit at Rostov NPP.

By predictions of IAEA made in 1998, total power of NPP in the world will reach 570 GW by 2020, and 1100 GW — by 2050 [44]. The NPP, being constructed now, have perfect safety systems. The designs of promising high-power nuclear reactors of 1500–1750 MW are developed now. The French-German project of the nuclear reactor EPR of 1750 MW, the boiling reactor of BWP 90 type of 1500 MW developed by the firms of Sweden and Finland, Russian projects of the reactor HTHR-1000 and a breader with tin heat carrier Brest-1200 are considered the most promising ones.

As is evident from Fig. 104 (curves 5), a share of nuclear power industry will be 30–34 % by 2500, in respect of other power sources, and 38–40 % by 3000. It is clear now that the nuclear reactors are more ecologically safe than TES when normal operation conditions are provided and all technological regulations observed. There are two standards of NPP operation safety — German and Japan ones. When following either of them, the nuclear power industry safety is guaranteed. Nuclear energetics is extremely economical, since it uses acceptible raw materials from the Earth bowel; their amount will last of several millennia. To generate energy at NPP they use uranium and plutonium — raw materials which «are not fit for any other purpose» [45].

So, what is the part of nuclear and thermonuclear energy in the development of energetics all over the world in the third millennium? It is generally accepted that the learning of the atom secret and realization of its huge energy both in military spheres and in peaceful construction is the outstanding achievement of the 20th century. It may be supposed that thermonuclear energetics will also make certain contribution to the nuclear power industry by 2500, and its share by 3000 will exceed that of nuclear energetics. Investigations in the field of development and practical realization of the reactions of thermonuclear synthesis are carried out in many countries all over the world: in Russia, USA, Japan, China, France though their activity is decreasing.

The share of nuclear energetics in power generation in one or another state depends on the number of factors: the level of the national science development, degree of the country energetics dependence on power resources, the state provision with energy carriers (hydrocarbon, hydroenergetic, geothermal, wind and solar energy, etc.), and efficiency of their practical use. Nuclear power industry of France, USA, Japan can be demonstrative in this respect. France occupies the first place in the world as to energy generation by NPP — 77.21 %. There is a certain «cult of nuclear power» in this country, that is connected with the deep respect of French citizens to home outstanding nuclear scientists — Pierre Curie, Maria Sklodovsky-Curie, Jolio Curie et al.

Nuclear reactors of Japan generate 35.86 %, the USA — 20.1 %, Russia — 13.1–15 % of electric energy. But the USA and Russia have succeeded in creation of great amounts of the most powerful nuclear weapons. NPP generating above 42 % of electric energy make great contribution to the power industry of Ukraine. It is planned to create a home closed nuclear-fuel cycle with the aim to increase power generation efficiency of NPP.

It is especially promising to combine the functioning of NPP with nuclear-hydrogen energetics. NPP operation possesses its specificity. NPP are highly efficient only when they operate in steady conditions and generate fixed quantities of electric energy in accordance with the load curve. In reality, consumers need different quantity of energy depending on the season (in summer and winter, in spring and autumn) and day-time (day or night). Thus, the amount of energy (heat and electric energy) generated by the nuclear units of NPP depending on the volume required by consumer, would be continuously regulated. But such incessant loading and unloading of nuclear power units is inexpedient from the viewpoint of economy and technology. The way out the situation is in putting in operation manoeuvring plants for production of gaseous or liquid hydrogen pumped into tanks-storages including underground storages. Depending on the relief (availability of highlands, mountains, ravines), water may be supplied to hydroaccumulating electric stations which also can produce great amounts of hydrogen.

Complex nuclear-hydrogen [6, 26, 46–60] and purely hydrogen energetics [24, 46, 61–103] can provide for the economy development on out planet on the basis of energy selfsupport for hundreds of years. They possess high economic potential and characterized by purity of generated energy. The amount of energy released in fission of 1 g of is 0.957 MW·day and that released under burning of 1 g of hydrogen is $3.4\cdot10^{-7}$ MW·day. Thus, chemical calorific power of hydrogen is approximately $3\cdot10^{6}$ times less than that of uranium-235. Energy equal to 3.9 MW·day is released under thermonuclear synthesis by the reaction (6) (Chapter 2) in terms of 1 g. A simple calculation shows that energy released in thermonuclear synthesis surpasses $11.47\cdot10^{6}$ times the calorific power of hydrogen. The calorific power of hydrogen in its turn is higher than that of hydrocarbons. The heat release under combustion of 1 t of hydrogen is 2.5 times more than under combustion of 1t of hydrocarbon fuel. Besides, in contrast to hydrocarbon fuel hydrogen may be obtained again when consuming certain amount of energy, e. g., electric energy generated by NPP or by renewable energy sources. That is why hydrogen is a universal heat carrying agent and hydrogen-based energetics will protect the environment from contaminations typical of power producers using coal and oil since only water vapour is the end product under hydrogen combustion in power plants, and liquid water under its oxidation in fuel elements.

Thus, hydrogen which may be produced in different ways (see, Chapter 6), natural gas and methane from gas hydrates can be the energetic fuel of the future. One can produce synthetic liquid (SLF) and gaseous fuels (SGF) in industrial volumes by the Fischer-Tropsch catalytic method using hydrogen and CO, hard and brown coals, slates and turf (to produce $CO + H_2$). The providing with SLF and SGF in the future will depend on the rates of consumption of solid hydrocarbons and they would last to 2500–2600. To produce SLF, SGF and hydrogen it is economically expedient to use thermal energy of high-temperature nuclear reactors and fast reactors with creation of nuclear-hydrogen power complexes (NHPC). The problem of creation of NHPC is of current interest since natural reserves of liquid hydrocarbon fuel on the Earth, as it was said above, will hardly last to the first half of the 21st century. The discovery of huge reserves of methane in gas hydrates can provide the Earth dwellers with hydrocarbon fuel for 200 years more up to the 23rd century. But as soon as the reserve of oil — the major source of liquid hydrocarbon raw material, natural gas and methane gas hydrates — are exhausted, the SLF and hydrogen would become the alternative fuel for motor transport and aviation in the future. In this case SLF could be obtained on large scales from hard and brown coal, turf, but only using hydrogen obtained by means, e. g., of energy accumulation substances (EAS) and water [71–105]. Solid hydrocarbons and EAS can provide the plants producing SLF and hydrogen with raw materials for hundreds of years. In the following centuries the mankind will master the SLF, SGF and hydrogen production for internal-combustion engines by conversion of materials of biogenic origin, specially cultivated plants and biomass (Fig. 104, curve 2). Possible ways of development of hydrogen energetics are considered in the works [26, 105]. The processes of hydrogen energetics are developed especially intensively in the USA, China, France, Great Britain, Germany and other countries [106, 107].

In view of afore-cited it is necessary to develop intensively both theoretical researches of conversion of soil hydrocarbons in SLF and hydrogen and to create production technologies on their basis and to assimilate them on industrial scales. Electrolysis (especially at high temperatures), chemical redox cycles and other methods considered in Chapter 6 may be used to produce hydrogen using heat of NPP or electric energy generated by them. Creation of the nuclear-hydrogen complex is closely connected with engineering characteristics of nuclear reactors generating thermal energy and electric energy as well as with efficiency of hydrogen production processes as well as farther use of hydrogen as energy carrier. Engineering characteristics of nuclear reactors depend on the type of nuclear reactions proceeding in the reactor (thermal reactor — HTHR-

1000, or fast reactors — FN-300, FN-600, FN-800, BOR-60; see, Chapter 4), physico-chemical properties of the reactor liquid heat carrying agent (water under high pressure, lead-bismuth alloy, melted sodium), determining maximum operation temperature in the reactor operation zone and a number of other factors [108]. It is known that nuclear-power plants «Buk» and «Topol» were installed in spacecrafts [103].

Let us recur to the energy problems of NPP. To increase efficiency of NPP of a new generation with reactions HTHR-1000 as the heat-carrying agent of the first loop it is promising to use helium, of the second loop — universal ecologically pure heat carrier — gaseous hydrogen. High-temperature heat of these nuclear reactors would be used in metallurgical and chemical processes, e. g., for direct production of high-quality steels (by the reaction $Fe_2O_3 + 2H_2 = = 2Fe + 3H_2O$) production of SLF, gasification of coals for production of SGF providing minimum thermal pollution of the environment. To decrease thermal pollution of the Earth atmosphere in the future, it is necessary to master using the low-temperature heat of TES, TEP, and both thermal and fast reactor NPP. The latter will not soon have alternative because of the limited reserves of hydrocarbon fuel and their exhaustion. We have to mention the works on creation of new efficient energy accumulators with the aim to increase the utilization factor of the installed NPP power (from 60 to at least 80 %). The construction of underground nuclear TES with closed nuclear-fuel cycles with rectors HTHR-100, BN-600, BN-800, Brest-1200 is rather promising for the countries possessing home uranium. The fast reactors burn completely nuclear fuel on the basis of uranium and plutonium without additional complex and chemical processing and thus they do not affect the radiation background of the environment.

The extremely important problem of any NPP operation is the inadmission of changes in the planet radiation background. An analysis of radioactivity balance shows that the total number of radioactive decays in fuel decreases during operation of nuclear reactors, since the formed nuclei undergo the less number of splittings. In this connection the most important problem of nuclear energetics consists in perfecting the methods of utilization (processing) of the exhausted radioactive fuel of nuclear fast reactors with separation of nuclides $^{235}_{92}U$, $^{238}_{92}U$, $^{239}_{94}Pu$ (for repeated use) with extraction of small amount of fragmental radioactive elements for burying them in special storages. The crisis-less energetics of the future requires performing the works on transformation of the contemporary nuclear-energetics with fast reactors to the large-scale nuclear energetics with failure-proof fast nuclear reactors [27, 108, 110, 111].

The large-scale nuclear energetics based on the fast reactors possesses the highest potential of both resource and anthropogenic (deliberate) resistance [108]. Heat conducting nitrides uranium-239, plutonium-239 or their composites (containing certain ratio of components, and liquid lead or lead-bismuth alloy as heat carrying agent) being used as fuel, the power of a cylindrical fast reactor may be led to the level of 2400–2500 MW (el.) [111]. A thin-walled cylindrical pipe being used in the fast reactor under the same technological conditions there are no physical limits for increasing power. Nuclear fast reactor (NFR) is 1000 times more efficient, in the resource respect, than thermal (slow) reactor. Nuclear fuel for NFR is not subjected to isotope separation. Natural uranium (see, Chapter 4) which is practically completely burnt in the process of the reactor operation is used as fuel for NFR. In contrast to slow reactors and breeders, plutonium is not separated from the exhausted fuel of NFR, since it burns up in the process of power generation. Hence, the anthropogenic deliberate factor — the act of terrorism — is excluded.

γ-Active oxygen nuclide ${}^{19}_{8}O$, formed under neutron irradiation of water molecules in water-moderated power reactors of the type WMPR-440, WMPR-1000 used at NPP of Ukraine is especially dangerous for people and animals [112, 117]. The exchange processes under the contact of activated water molecules with air oxygen:

$$H_2{}^{19}_{8}O + O_2\,(\text{solution}) \rightarrow H_2O + {}^{19}_{2}O = 0\ (\text{solution}) \qquad (329)$$

$$H_2{}^{19}_{8}O + O_2\,(\text{gas}) \rightarrow H_2O\ (\text{solution}) + {}^{19}_{8}O = 0\ (\text{gas}) \qquad (330)$$

lead to formation of radioactive gaseous molecular oxygen ${}^{19}_{8}O = 0$ (gas), which, when getting into the atmosphere makes harm to everything alive and consuming oxygen (half-period of the nuclide ${}^{19}_{8}O$ T1/2 = 30s, complete decay — 5 min.). High-temperature helium reactors HTHR-1000 are deprived of this shortage characteristic of the light-water reactors of WMPR type.

It would be noted that the post-Chernobyl syndrome has not affected the military construction. The construction of nuclear-powered vessels (cruisers and aircraft carriers), nuclear submarines, equipped with rockets with nuclear heads is continued is this field with the same rates. There occur tragedies (submarines *Tresher, Komsomolets K-123* and submarine cruiser *Kursk*) which take away hundreds of human lives. But there is no alternative to nuclear power sources in the military branch of autonomous-transport. A problem of spaceflight outside the solar system on spacecrafts with polonium sources or other nuclear power systems is under discussion. It is considered that such a flight is possible when using great amount of energy contained in small volume [1–8, 114]. To induce acceleration of a spacecraft from the first to the third space velocity (42 km/s), it is necessary to spend 715 kJ of energy per each gram of mass. Real energy reserve would be even higher and be 1 MJ/g. Such a source of energy — polonium ${}^{210}_{84}Po$, being α-emitter (energy of α-particles 5.3 MeV), possessing specific energy content $2.45 \cdot 10^9$ J/g, that is about $1.7 \cdot 10^5$ times more than in the most efficient liquid rocket fuel based on chemical interaction $H_2 + O_2$. Polonium energy sources were used on spacecrafts *Lunokhod-1, Lunokhod-2*, etc.

A fantastic thermonuclear source of cheap and ecologically pure high-power energy is not still realized, though great collectives of scientists work over its creation. The eternal source of energy may be obtained when deciding the problems of controlled thermonuclear synthesis (CTS) and creation of thermonuclear reactors (TNR) and thermonuclear electric power plants (TEPP). The searches of decisions on the path of creation of thermonuclear power generation have not led to positive results. It would be noted that when mastering the CTS this energy source will not be pure, since not only helium atom nuclei (a-particles) but also neutrons are released as a result of thermonuclear reaction of deuterium and tritium. The neutrons induce radioactivity in the reactors material which does not differ from fragmental radioactivity [115]. Thus the ecologic risk in development of thermonuclear energy is still high. But researchers continue searching for the alternative energy sources. Thermonuclear reaction of helium-3 is promising in this respect. It is realized on the colliding beams, bending under the effect of strong magnetic fields [116]. Both the bombarding and formed electrically charged atoms are not radioactive, since they do not release neutrons.

This also opens a possibility of direct conversion of nuclear energy into electric one avoiding the stage of its conversion into thermal energy, that is peculiar to NPP. It is considered that the problem of CTS will be cardinally solved in the second half of the 21st century.

In this respect, the hybrid nuclear-thermonuclear reactors intended for production of the programmed impulse-periodical neutron synthesis are rather promising for nuclear energetics [115]. In this case a nuclear (separating) and thermonuclear (synthesizing) parts are combined in one aggregate-reactor. They permit regulating with time the neutron synthesis velocity in the thermonuclear reaction of deuterium and tritium and producing the preset quantity of a-particles which are absorbed in doses in the heat-releasing chamber from uranium-238 and induce the reaction of its nuclear fission. Plutonium is not accumulated, since it reacts immediately with neutrons with energy liberation. The electric plant power depends in the laser power, it can be decreased to dozens of megawatt. Thus, such hybrid reactors may be used in various spheres — from expeditions to the Antarctics and North Pole to providing with energy of small towns, etc. The hybrid reactors are absolutely safe, and this guarantees their future. Stationary power plants of such type may be successfully combined with hydrogen production following thermochemical cycles. Hydrogen may be used as fuel in various stationary and transport devices.

Allowing for the ecologic purity of production of electric and thermal energy from nuclear-hydrogen and hydrogen power plants it would be noted that hydrogen, as the unique fuel, has no alternative. Being able to produce hydrogen fuel in industrial amounts and to cope with thermonuclear energy, mankind can avoid the approaching energy crisis and develop under energetic self-sufficiency on planet Earth for numerous millennia. The large-scale solution of the problem of hydrogen energetics in the nuclear-hydrogen energy cycle all over the world will require decades, and solution of the problem of thermonuclear energy for the Earth-dwellers — will require even centuries. Radiation purity of thermonuclear plants under their functioning is the most important problem of their creation (see, Chapter 4 and 7). Thermonuclear plants would not be dangerous from the viewpoint of neutron liberation in power generation reaction, nuclear burst and radioactive outburst. The emission of radioactive products of uranium nuclei fission outside the NPP, as it follows from experience accumulated during 50 years, create the radiation danger for everything alive for hundreds of years. Neither physico-chemical method can annihilate the emitted and scattered radioactivity. But scientists have found the physical method of processing of radioactive elements. These are the transmutation processes. Under certain conditions, one can dismantle the nucleon of one or another element and make it a long-lived or short-lived isotope. The process of transmutation is not a sufficiently studied method. It is not clear yet, whether the separation of isotopes is required for transmutation and the transmutation regime is required for each isotope element. What is physical efficiency (yield of transmuted elements) and economic component of transmutation of great masses of isotopes? [27, 108].

Proceeding from the laws of nuclear physics, radioactivity is dependent on time and corresponding nuclear reactions only. In the 40's of the 20th century mankind entered the nuclear-thermonuclear era. Today, the nuclear-thermonuclear war can become the last crime on the Earth [27]. Moreover, even global nonnuclear war can result in the destruction of NPP, radiochemical plants, storages of radioactive waste, plants producing heat-liberating elements and create the threat for human lives in some countries and huge regions. The level of mankind development would correspond to the scales of nature forces mastered by Homo sapiens able not to admit the outburst of broad-scale tragedy which can take away lives of not millions but milliards of planet Earth dwellers.

Academician V.I. Subbotin [27] has noted that the opponents of nuclear energetics, as a rule, are not specialists in nuclear science, they see only negative in it and demand to close all the NPP in operation. However, the closing of nuclear-power plant also requires great expenditures for the discharge of nuclear fuel, its storage, observations over the «cooling down» of fuel elements. Nuclear and radiation danger will remain in the discharged fuel for a very long time. Structural materials of NPP in the process of its functioning acquire the induced radioactivity (under the effect of neutrons), which does not disappear during years and decades, are to be guarded and thus, consume material resources and energy.

It is clear from afore-stated that the stopped NPP does not generate electric energy and heat but requires financial investments during a long period of time. We would cite the paper by V.I. Subbotin [27]: «mankind in hunting for super-arms entered the nuclear tunnel and has the only exit now: to make nuclear energetics maximum safe, to create ideology of broad-scale use of nuclear energy». Nuclear energy. as a point of fact, is the most pure power technology in the world, provided that you follow all technological conditions. The basic requirement to NPP — nuclear fuel processing method would be wasteless. The worked out fuel elements would be extracted from nuclear reactors, «cooled» in special settling basins and sent for processing at specialized nuclear-chemical plants. Technological operations at those plants would be automated. Human-free technologies would be attracted for separating radioactive products from waste nuclear fuel. Mechanical operation would be performed by robots, controlled by operator. Thus the man's contact with radioactivity could be avoided. Radioactivity is inevitable evil of nuclear energetics. By [27] «energy of fission of heavy nuclei will be claimed as the most important source of energy of the 21 st century», in our opinion of the third millennium as well, only if the chain nuclear reaction will be controllable».

It would be noted that creation of nuclear weapons and development of «peaceful atom» in the USA and USSR were carried out rather successfully and the leading part rather belonged to political conjuncture than to technical and technological expediency of nuclear processes. Researches in the field of nuclear energetics are rather dull now in the advanced nuclear states. For example, nobody develops extremely safe nuclear-energy plants of different power which could be placed both near large and small towns. Nuclear energetics with the use of fast reactors is not developed. The amount of uranium-238 isotope which captures fast neutrons is 133 times more in nature than of uranium-235 isotope. Thus the fuel resources of uranium-238 isotope is above 130 times higher than those of uranium-235, and they (with account of clark, as well as the reaction of plutonium-239 formation with reproduction coefficient from 1 to 1.3 and its burning) are unbounded (see, Chapter 4.1). Thus the large-scale nuclear energetics for millennia is rather possible with the use of fast reactors with participation of uranium-238, than thermal reactors with participation of uranium-235.

The USA, UK, Germany have not acute necessity to develop more complicated and high-tech nuclear energetics than TES on hydrocarbon fuel. In the formed energetic situation the demand of industrial states in nuclear and thermonuclear energy will not appear until the «cheap oil in the Near-East country» [27] will exist. The same situation is observed in the European countries which consume hydrocarbon fuel from Russia (60 %) and Norway [~35 %].

The next example from [27] is rather descriptive. About 200 000–400 000 t of depleted uranium (uranium-235) are kept at storages of Russia. This uranium may be burnt in fast-reactors with production of $(16–32) \cdot 10^{21}$ J of heat. This heat amount surpasses by 17.0–46.6 % the total amount of heat which can be produced when burning oil and gas from deposits all over the world [200–300 $\cdot 10^9$ t of oil; $Q_1 = (7.6–11.4) \cdot 10^{21}$ J, and 146 000 $\cdot 10^9$ m^3 of natural gas:

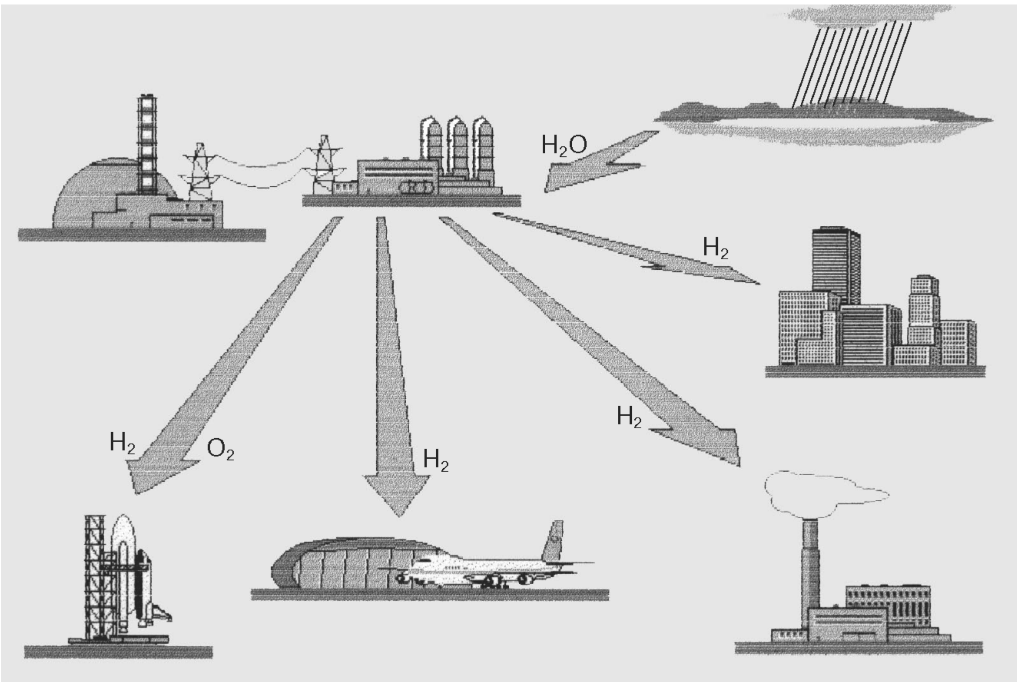


Fig. 107. Nuclear-hydrogen cycle in power industry and infrastructure of hydrogen use

$Q_2 = 5.68 \cdot 10^{21}$ J; $Q_\Sigma = (13.28–17.08) \cdot 10^{21}$ J]. Consequently, potential energy which can be used in nuclear thermal (slow) reactors, of one and the same order with energy, which can be obtained when burning all world reserves of oil and gas.

The given estimate of 200 000–400 000 t of depleted uranium in Russia is minimum, since the major mass of uranium-235 and plutonium-239 is included in nuclear weapons both in Russia and in the USA. There are considerable reserves of uranium and plutonium nuclear fuel in the USA, Japan, China, South Korea, Pakistan, India, North Korea, France, SAR, Canada, etc. Really, by [27] Russia possesses, besides depleted uranium-238, about 100–200 t of weapon plutonium-233 and 1000–2000 t of highly enriched uranium-235, which may be used as fuel in nuclear energetics. Those 100–200 t of plutonium can become the starting nuclear fuel for putting in operation of 100–200 nuclear fast reactors. Besides, special storages of nuclear states contain highly radioactive fuel, discharged from plutonium converters, reactors of NPP, nuclear submarines, nuclear ice-breackers, nuclear cruisers. The major mass of uranium-235 has not been burnt in this waste fuel. Uranium-235, uranium-238 and high-background actinoids may be used again as nuclear fuel after radiochemical separation of the waste fuel from fission products.

Infrastructure of the city of the future is given in Fig. 107. Nuclear-hydrogen energy cycle is used there for production of electric energy and hydrogen; and the infrastructure of hydrogen use in domestic life, industry, aviation, astronautics, motor transport with utilization of low-temperature heat Q is developed. Air oxygen (or liquid oxygen are used as hydrogen oxidizers when the former is used as fuel. Ecologically pure product — water which is condensed in special devices — is formed in the process of hydrogen burning. It may be used for various needs, it is supplied into the atmosphere and comes back to the Earth as rain or snow, i. e., it circulates.

9.3. Renewable energy sources

Wind power plants. Investigations in the use of renewable energy sources (energy of the wind, Sun, sea waves, ocean tides, hydrothermal waters, etc.) were insufficiently intensive in the 20th century. Thus, their share in the balance of energy used in the world does not exceed 1 %. For example, the share of wind electric power plants WPP in the world is only 0.7 %, though this level reaches 1.5–10 % in some countries. From 1990 to 1998 the increment of the wind electric power plants was 22.2 %, conversion of solar energy into thermal and electric energy — 15.9 %, development of geothermal and hydroenergy — 1.9 and 4.3 %, respectively [120]. They have built 12 WPP, includind 12660 WPI in the USA with total power of 1900 MW. Specific capital investments in the construction of these WPP were 1200–1500 USD/kW. The ISA plan to construct wind electric power plants of 50 JW by 2010 [121]. The share of electric energy generated by WPP will be 10–15 % in European countries by 2010. The increment of electric power of WPP in Germany reached 790 MW in 1998 under the total power of 2800 MW that is 1% of energy generation within the country. Nowadays, Germany has brought the electric power generation by WPP to 10 % of its total quantity. Total power of NPP in India is 900 MW, it increased by 84 % in Spain in 1998 and was 830 MW. The WPP power in Denmark has reached 1400 MW that corresponds to above 8 % of electric energy generated in the country. In 1998, Denmark manufactured about 50 % of all wind turbines developed in the world, and this has brought the country the profit of about $1 \cdot 10^5$ USD [120]. The pilot prototypes of WPP of 300 kW–1.5 MW are elaborated and manufactured in Russia. Service term of such WPP is 20 years. WPP of 10–100 kW are manufactured for dwelling houses, farms and pumping stations. Designs of WPP of 2.5 MW with diameter of wind-wheels of 10 m are developed in the USA.

Ukraine plans to put in operation WPP of 1900 MW. Six WPP with total power of 156 MW (Saki, Novoazovsk, Donuzlav, etc.) are constructed now in our country. In accordance with plans, WPP will provide 2.5 % of the annual electric power consumption in Ukraine in 2010. The volume of electric energy generated by renewable energy sources (RES), by the National Energy Programe would excess $10 \cdot 10^9$ kWh by 2010 (5–6 % of the total amount of electric energy). Potentialities of electric energy generation by WPP in Ukraine are above

$500 \cdot 10^9$ kWh/yr. [119]. Thus, it seems to us that the rates of power increase of WPI and WPP may be more intensive, than it is shown in Fig. 9.2 (curve 8). It will be possible to reach 10 %-ratio between WPI and WPP energy even in the first century of the third millennium.

Conversion of solar radiation energy. Solar energetics as independent field of knowledge appeared 50 years ago caused by the need in power for the Earth artificial sattelites, spacecrafts, piloted orbital stations like *Salut, Mir,* designed automatic interplanetary stations, etc. Solar radiation energy, using photoelements, is directly converted into electric or, using focusing parabolic reflection mirrors, into thermal energy. Solar photoenergetics is a high-tech and material-consuming branch [121–144]. Ecological purity and inexhaustibility of the energy source for millions of years are characteristic of the photoelectric method of solar energy conversion into electric energy. It has been established that the nature of initial materials of photoconverting elements, their chemical purity (no more than 1 atom of impurity per 10^9 atoms of the basic component) and crystalline structure. Photoelements on the basis of amorphous and crystalline silicon, cadmium sulphide, and gallium arsenide are most widely used, their best prototypes efficiency being 16–24 %. To meet the ever-increasing demands of semiconductor industry in gallium arsenide used in the opto- and microelectronics, as well as for making photoelectric converters, for the period of 2000–2020 only the USA will need 500–2000 t of highly-pure gallium (99.99999 % Ga) [121]. The demand in highly-pure gallium, indium and arsenic used for synthesis of gallium and indium arsenides for solar energy convertes into electric and in optoelectronics is immeasurably higher in Japan. Japan plays the leading part in development of photoenergetics. Usually, the increment of installed powers of photoelectric devices (PED) is above 100 MW/yr. Total power of PED in Japan is 317 MW [122].

The efficiency of photoelectrochemical converters of colar energy on the basis of cadmium selenide (CdSe) exceeds 20–25 % [123–129]. Thin-film converters of solar radiation on the basis of cadmium telluride (CdTe) and copper-indium diselenite $CuInSe_2$ possessing efficiency 15 and 17–25 % respectively [130–133] are rather promising. The use of thin films of compounds CdTe and $CuInSe_2$ in the solar energy converters is determined by the striving to decrease the cost of photocells for the mass production. Thin films of semiconductor compounds are obtained by the method of electrolysis [122–133].

Solar cells with efficiency 15 % are created using the band polycrystalline and amorphous silicon. Theoretically possible efficiency of photoconverting devices of solar radiation is close to 50 %. The construction of photocells on heterostructures with the use of solar radiation concentrators permits achieving efficiency close to 30 %. Experimental prototypes of photoconverting devices have been manufactured possessing efficiency 36 %, and a task is set to exceed efficiency equal to 40 %. Photoelectric converters manufactured in series have efficiency 5–15 % (statical converters) and 15–25 % (dynamic converters). The prime cost of 1 kW of installed electric power, generated by the solar cell, is 4–7 thou. USD for 1 kW. Works on creation of thin-film photoconverters with specific cost of electric energy was 250–530 USD for 1 kW are carried out with success in the USA, Japan, France, Germany, Russia. Calculations show that economic expediency of solar energy conversion into electric requires to raise efficiency by 30 % and to bring the specific production cost of panels with photocells to 60 USD/m^2 [6]. According to predictions total power of solar power plants (SPP) will be 5 JW by 2010. A complex of solar batteries of 25–100 kW with operation voltage 15–112 V and temperature from -30 to 300 °C [117, 136] has been developed for orbital space station operating for a long-time. The area of photoconverting panels is 48–930 m^2, they can resist to inertial load on the orbit of 1–3*g*.

Works on creation of space solar radiation station (SSRS) for remote electric energy transfer to consumers on the earth are of theoretical and practical interest. For example, it is of interest to directly convert solar radiation into laser one, and to convert the obtained electric energy into electromagnetic wave and to transmit it to the Earth in the microwave range [6,137,138]. Calculations show that receiving antenna with the area of about 3 km^2 can ensure the receiving of electric power « 3 JW under radiation intensity 1 kW/m^2 [6]. Creation of solar power plants transmitting energy to the Earth is the most important and unprecedented, as to its scale, problem. SSRS, which can transmit energy to the Earth have been developed and tested till now, possess the power of output radiation 1–10 MW, efficiency 12–16 % and system specific mass 14–31 kg/kW. Solar power plants of 50 JW are developed [139]. Solar high-temperature electromotive plants with photoelectric converters for long-term flights are of special interest for cosmonautics [140].

The intensively developed on-land photoelectric converters of solar energy into electric or thermal energy are intended for the use in rural regions, in individual dwelling houses, helio-hothouses, heliodryers, cattle-breeding complexes [123–137, 141]. In accordance with the data of Fig, 104 (curves), the share of solar energetics will not exceed 3–3.5 % in respect of other sources in 2500 and 10 % — by the end of 3000, because of high science intensity and great material expenditures per the power unit of converted energy. Photocatalytic and chemical methods of solar energy conversion for hydrogen and oxygen liberation from water have a certain prospect [135, 142–145]. As geological reserves of coal, slates and turf are consumed, SES will be developed intensively to provide energy generation not only at regional but also at intercontinental and interstate level. SES plantations will be constructed in Sahara, Kara-Kums and other solar regions both for generation of electric energy and for hydrogen production and transportation by pipes. For example, characteristics of the systems of hydrogen production and supply to stationary power plants generating electric energy and heat by means of fuel elements have been analyzed in [146]. Prospects of development of hydrogen energetics by 2025 have been considered in respect to Germany. The following sources of hydrogen production have been analyzed: conversion of natural gas, partial oxidation of heavy oil products, coal and biomass gasification. Special attention has been paid to the technique of solar energy conversion in North Africa by means of solar cells, tower receivers and parabolic mirrors for electric energy production. Electric energy was used for water electrolysis with obtaining gaseous hydrogen, which is predicted to be transported through Sicilia to Germany by pipes. Distribution of both gaseous hydrogen and its liquefaction and distribution of liquid hydrogen will be carried out in Germany.

Use of biomass energy. Biomass as energy source is used from times immemorial. In Eurasia, wood, side by side with coal, was the major energy source even 100 years ago. An analysis (Fig. 104, curve *2*) shows that people obtained 25–54 % of primary energy from biomass to the middle of the 20th century. Nowadays biomass serves to produce 12–15 % of total energy [146–147]. The most share of biomass is used in the developing countries, mainly in rural districts. Intensive felling for fire-wood is observed in the same countries. The share of biomass use for energy production is lower in the developed countries. Thus, $2.1{\cdot}10^{18}$ J of energy from consumed $82.3{\cdot}10^{18}$J, that corresponds to 2.6 % of its total volume [147], are obtained from biomass in the USA. It is possible to cultivate on commercial basis the fast-growing (3–5 years) trees (poplar, ash and willow, etc.) on inconvenient and non-arable lands for their further use as fuel for TES [148]. The wood of the above tree varieties has relatively high combustion heat values (20.7–20.8 MJ/kg). They can also use culture sowings with high vegetative mass (rape, maize, etc.) the combustion heat obtained under combustion of vegetative remains is $(1.5\text{–}4.0){\cdot}10^{18}$J/year [147].

Much attention is given lately in this country to organic waste of different branches of industry which volume is $7.5\text{–}10{\cdot}10^{9}$ t/yr. of dry matter. Various pilot power biostations and plants are constructed for their processing by the method of bioconversion (using special strains of microorganisms), thermochemical conversion and gasification with obtaining electric energy and biogas. The biomass is used to produce ethanol, biogas and dry (briquetted) fuel. In the future, the greater part of biomass would be used to produce organic fertilizers and to increase soil fertility because of the increase of population number. Thus the relative share of the biomass used to generate primary energy in the third millennium would decrease compared with other kinds of energy. As is seen from Fig. 104 (curve *2*), it will decrease from 10–12 % in 2000 to ~6 % in 3000.

Possible utilization of the discharge low-potential heat of NPP, TES and TEP, which takes harmful effect on the regional scale, has not been discussed in this chapter. Low-potential energy of NPP, TES and TEP may be used efficiently to produce hydrogen, biomass, and a series of food products, vitamins as well as synthetic liquid fuel on their basis.

Use of the World Ocean Energy. The conversion of energy of seas and oceans is especially concerned in the countries with insufficient home fuel resources. Thirteen million pound sterling were allocated in Great Britain in 1976–1981 for investigations on mastering ocean energy and use of the ocean waves energy. Expenditures for the ocean energy mastering were increased by an order in the late 90's. Prime Minister of Great Britain T. Blair thinks that energy of tidal waves washing the shores of England exceeds ten times the country current demands in energy [148]. Investigations in the field of taming the tidal waves are also carried out in Japan, Norway, Russia [150]. A possibility to obtain energy with no harm to ecology energy in numerous coastal regions of the world. It is supposed that the best principle of waves conversion will be assumed as a basis of the future powerful wave electric plants capable to satisfy 30–50 % of the country demand in energy. The pilot wave electric power plants generating 2–5 million kWh of electric energy have been built in numerous countries.

The World Ocean accumulates energy of various kinds. By the estimates of specialists, the accessible share of the World Ocean energy which may be practically used under the achieved level of conversion technology exceeds many times the future energy consumption level which will be $(10–50) \cdot 10^{13}$ kWh/yr. in the first half of the 21st century. The energy reserve of the World Ocean wave flow equal to 10^{21} J under flow density 1.5 m with a period 8 s and average length 20 m will be enough to meet energy requirement «of all the world in 2050 and may be during all the 21st century» [151]. Only on the shores of Kamchatka the tidal mave energy is equal to about 10^{19} J/yr.

The World Ocean is a giant accumulator of solar energy. The temperature gradient energy is estimated as $10^{21}–10^{23}$ J. The installed power of oceanic electric power station with water surface of 18 million km^2 (water volume $1.8 \cdot 10^{15}$ m^3) is $6.96 \cdot 10^{12}$ W [152]. This energy may be obtained by means of modern thermal converters. The area of equatorial belt of the World Ocean of 5 mill. km^2 can serve to produce 3 times more energy, than all the power plants in the world can produce today [152].

It is considered that reserves of thermal energy of the world ocean will last for thousands of years under the energy consumption level which will be reached in the 21st century [150]. Salinity, like other properties of the World Ocean and sea waters may be also used for conversion into electric energy, but their development is still insufficient. However, energy resources of the World Ocean will be in demand for the benefit of future generations of the Earth dwellers.

In conclusion of this paragraph one would also dwell on the problem of energy and transport of the future. Search of alternative propellers for transport facilities on accessible kinds of energy will be a special problem in the third millennium. Technological revolution in motor industry will require great capital investments for organization of practically new industrial branches. Even now, such giants of motor industry as *General Motors, Ford Motor*, and *Daimler Chrysler* have invested milliards of dollars to shift the vehicles to the motors operating on electricity, hydrogen and natural gas. Hydrogen fuel is distinguished by delivering great traction and almost zero emission of harmful combustion into the atmosphere, and, in the opinion of experts from these corporation, the future belongs to hydrogen [153]. By predictions, the mass production of vehicles working on hydrogen with be organized in the nearest decades of the 21st century. At the same time if SLF production from hard coal and turf will be developed with passing-on the baton to the process of biologic materials conversion into SLF and hydrogen, such modernized ICE would function for centuries. Rather interesting works on creation of compact hydrogen motors with great specific traction are carried out by Japanese firm *Honda* and French *Renault* and *Peugeot*. The processing of cocco-nuts copra into oils on the base of esters by French company *Motul* [154] is a bright example of production of high-quality labricating oils from vegetative raw materials. Ecologically pure two-contact free-piston Diesel-generator on hydrogen with efficiency above 50 % is offered in works [155, 156].

9.4. World demand in energy in the 21st century and third millennium

How can one estimate the world demand in energy with regard for population number growth? The consumption of conventional fuel per capita and GDP in a number of world countries by the data of [157] is given in Table 40. As is evident, the highest specific energy consumption is peculiar to three countries — Canada, Norway and the USA, the very low energy consumption efficiency equal to 1.4–2.3 USD/man being characteristic of them and average value of GDP 18813–25931 USD/man.

Switherland has maximum GDP corresponding to 33 515 USD/man and the highest energy consumption efficiency, equal to 6.0 USD/man. It is evident from the data of Table 40 that average GDP for 15 countries by results of 1995 reaches 24 055 USD/man, average energy consumption 8062 kg conv. fuel/man, and consumption efficiency — 3.33 USD/kg conv. fuel.

In accordance with the data of [120, 158] the population number growth on the globe will be stabilized at the level of $12 \cdot 10^9$ in 2100. So, under the average value of energy consumption of 8602 kg conv. fuel one can calculate the energy consumption in 2100 by 12 milliard people. By this calculation $Q = 9.67 \cdot 10^{10}$ t conv. fuel. One ton of conv. fuel being equivalent to 8139 kWh, the estimated amount of energy required for 12 milliard people will be $78.74 \cdot 10^{13}$ kWh. The energy consumption value equal to $16.0 \cdot 10^{13}$ and $25.8 \cdot 10^{13}$ kWh, respectively, was given for 2020 and 2050 in Chapter 3. It was accepted that the power consumed per capita is 2.46 kW in 2020 and 2.31 kW —

Table 40

Gross domestic product (USD/man), electric energy consumption (kg. conv. fuel/man), efficiency of energy consumption (USD/kg conv. fuel) by results of 1995

Country	GDP	Energy consumption	Energy consumption efficiency E*
Canada	18 813	13382	1.4
Norway	28150	13179	2.1
USA	25931	11321	2.3
Russia	13721	8743	1.9
Australia	18112	8279	2.2
Netherlands	24238	8246	3.0
Sweden	23899	8245	2.9
Belgium	25321	7874	3.2
Finland	22711	7401	3.1
Denmark	31001	6049	5.1
Japan	29143	5779	5.0
FRG	25322	5677	4.5
Switherland	33515	5576	6.0
France	22937	5475	4.2
Great Britain	17922	5711	3.1
average	24055	8062	3.33

*E = GDP/energy consumption, USD/kg conv. fuel.

in 2050 [8]. By the data of the work [159], the world energetic power per capita will be 5.8, 8.3 and 3.6 kW in 2020, 2050 and 2100, respectively, and in the following years it will be stabilized at the level of 10 kW per capita. Thus the world energy consumption will be $43.95 \cdot 10^{13}$, $76.18 \cdot 10^{13}$ and $102.55 \cdot 10^{13}$ kWh in 2020, 2050 and 2100, respectively.

The difference between the calculation data for the period of about 2100, obtained from coal energy demand in 1995 ($78.74 \cdot 10^{13}$ kWh) and predicted for 2100 ($102.55 \cdot 10^{13}$ kWh), is only 23 %. The authors of the work [159], when estimating the growth of the world demand for energy have made an additional adjustment for the future equal to 10 kW/man, determined by the restricted resources of the Earth and of energy requirements for their repeated use — water freshening, production of hydrogen and food products, etc.

We think that energy consumption efficiency being increased, the volume of energy generated in the third millennium after 2100 will stabilize at the level of $(78–100) \cdot 10^{13}$ kWh with the exhaust of reserves of hydrocarbon heat carriers.

It is seen from the data of Fig. 104 that after 2000 hydrocarbon fuel will be completely exhausted and vanish from the face of the Earth. Nuclear and thermonuclear energy, hydrogen energetics, hydroenergetics, including that of the

World Ocean (wave tides) wind energetics and photoconversion of solar energy into electric one will be main energy sources. It may be supposed from the consumption curve run in the third millennium that the share of nuclear and thermonuclear energy will be 38–40 %, hydrogen energetics 24 %, hydroenergetics 18 %, wind energetics 10 %, photoelectric converters of solar radiation energy into electricity — 6 %, and a share of biomass — 4–5 %. It would be noted that hydrogen energetics in which hydrogen performs the functions of heat carrying agent will require the primary energy consumption — energy of nuclear and thermonuclear power plants, hydroenergetics, etc. The plants utilizing biomass as fuel will be the only sources of CO_2 emission into the atmosphere. One may also hope that science development in the future millennium will lead to the discovery of new more power-intensive energy sources, which may be found only in science fiction now.

REFRENCES

[1] V.V. Bushuev, Energy Policy (Russia), Iss. 4 (2002)35.
[2] D.B. Wolberg, Teplotekhnika, No. 8 (1999)5.
[3] B. Mayevsky, N. Yevdoshchuk, O. Lozinsky, Oil-Gas-Bearing Provinces of the World, Naukova Dumka, Kyiv, 2002.
[4] Hans-Holger Rogner, Energy and the Challenge of Sustainability. World Energy Assessment, 2000.
[5] Erdol-Erdgas-Kohle. — Bd. 1/8, No. 7–8 (2002)32.
[6] D. Dowins, Energy, Energoatomizdat, Moscow, 1985.
[7] N.V. Selivanov, Probl. Nauki, No. 7 (2000)44.
[8] Enetrgy, US Census Bureau. Statistical Abstract of the United States, 1999.
[9] L.K. Silvestrov, V.M. Korenev, Energiya: Economy, Technology, Ecology, No. 5 (2000)9.
[10] I.O. Artemshuk, M.I. Baranovsky, S.F. Bilyk, et. al. Oil and Gas of Ukraine, Naukova Dumka, Kyiv, 1997.
[11] K.P. Tikhomolova, Electroosmosis, Khimiya, Leningrad, 1989.
[12] A.I. Vorobyev, Rec. NAS of Ukraine, No. 5 (2003)101.
[13] G. Burlaka, Ekonomika Ukrainy, No. 7 (2000)20.
[14] Statistical Annual of Ukraine for 1998, Tekhnika, Kyiv, 1999.
[15] Ya.F. Makogon, Ros. Khim. Zhurn., Vol. 47, No. 3 (2003)3.
[16] J. Krason, Offshore. Int. Ed., 59, No. 4 (1999), 96, 162, 164.
[17] Producers want gas strategy, Hart's E. and P., 73, No. 2 (2000)17.
[18] F.A. Kuznetsov, V.A. Istomin, T.V. Rodionova, Ros. Khim. Zhurn., Vol. 47, No. 3 (2003)3.
[19] S.Sh. Byk, Yu.F. Makogon, V.I. Fomina, Gas Hydrates, Khimiya, Moscow, 1980.
[20] V.A. Solovyev, Ros. Khim. Zhurn., Vol. 47, No. 3 (2003)59.
[21] Yu.F. Makogon, Ros. Khim. Zhurm., Vol. 47, No. 3 (2003)70.
[22] K.A. Kvenvolden, Chem, Geol., Vol. 41, No. 1, 1988, 41.
[23] K.A. Kvenvolden, Potantial Effect of gas hydrate on human welfare. Prec. NAS USA, 1999, 96.
[24] S. Dunn, Intern. J. Hydrogen Energy, Vol. 27, No. 2 (2002)235.

[25] R.A. Hefner, Intern. J. Hydrogen Energy, Vol. 27, No. 1 (2002)1.
[26] L.F. Kozin, S.V. Volkov, Hydrogen Energetics and Ecology, Naukova Dumka, Kyiv, 2002.
[27] V.I. Subbotin, Bull. Rus. Acad. Sc., 71, No. 12 (2001)1059.
[28] Huang Zhijong, Hydrogen Energy Progress XIII. Proc. 13th. World Hydrogen Energy Conference. Beijing, China, June 12–15, 2000, Vol. 1–2, 2000, 233.
[29] Yu.N. Malyshev, Energy, Economics, Technology, Ecology, No. 8 (2000)2.
[30] N.S. Safonov, T.V. Lisichkin, Ros. Khim Zhurn., 45, No. 4 (2001)72.
[31] N.M. Mkhitaryan, Energy-Saving Technologies in Dwelling and Civil Construction, Naukova Dumka, Kyiv, 2000.
[32] V.V. Remizov, Gasovaya promyshlennost, No. 8 (1999)5.
[33] V.V. Klimenko, Ibid., No. 5 (2001)16.
[34] N.A. Shpolyanskaya, Kriosfera Zemli, 5, No. 1 (2001)3.
[35] A.N. Zubakov, 71, No. 2 (2001)80.
[36] S. Macilwain, Nature, No. 382 (1996)195.
[37] O.G. Sorokhtin, S.A. Ushakov, Bull. Moscow Univ., Ser. Geogr., No. 5 (1996)27.
[38] K.S. Demirchyan, K.K. Demirchyan, Ya.B. Danilevich, R.Ya. Kondratyev, Bull. Rus. Acad. Sc., Energetics, No. 3 (2002)18.
[39] K.K. Demirchyan, K.S. Demirchyan, K.Ya. Kondratiev, Bull. Rus. Acad. Sc., Energetics, No. 3 (2002)18.
[40] D. Ter Haar, H. Wergeland, Elements of Thermodynamics, Addison-Wesley Publishing Company, London, 1966.
[41] A.Yu. Zenyuk, Energiya, No. 1 (1998)9.
[42] E. Adamov, Ros. Ekonom. Zhurnal, No. 5/6 (2000)80.
[43] V.A.Makhova, L.B.Preobrazhenskaya, Energy: Economy, Technology, Ecology, No. 7 (2001)2.
[44] L.B. Preobrazhenskaya, Energy: Economy, Technology, Ecology, No. 10 (2000)8.
[45] S.N. Golubchikov, Zh.A. Grishina, Energiya: Economy, Technology, Ecology, No. 10 (2000)8.
[46] Yu.P. Yelagin, State of the World Nuclear Energetics, Nuclear Technology Abroad, No. 1 (1999)9.
[47] V.N. Mikhailov, Bull. Rus. Acad. Sc., 68, No. 2 (1998)116.
[48] F.G. Reshetnikov, Bull. Rus. Acad. Sc., 70, No. 2 (2000)117.
[49] E.E. Shpilrain, S.P. Malyshenko, G.G. Kuleshov, Introduction into Hydrogen Energetics, Energoatomizdat, Moscow, 1984.
[50] F.M. Mitenkov, N.N. Ponomarev-Stepnoi, Energia, No. 2 (1997)2.
[51] S.S. Abalin, V.M. Novikov, V.N. Prusakov, Nuclear-Hydrogen Energetics and Technology, Iss. 1 (1978)126.
[52] V.A. Legasov, I.G. Belousov, N.K. Yerokhin, A.S. Doronin, Ibid., Iss. 2 (1979)85.
[53] L.E. Mc. Ncese, M.W. Rosenthal, Nucl. News, 17, No. 2 (1974)52.
[54] P. Fangeras, A. Lecocq, J.L. Blum, et al., Trans. Amer. Nucl. Soc., No. 20 (1975)703.
[55] V.N. Grebennik, N.N. Ponomaryov-Stepnoi, V.V. Lebedev, Nuclear-Hydrogen Energetics and Technology, Iss. 4, 23.
[56] S.V. Volkov, Teor. i eksp. Khimiya, No. 1 (1982)3.
[57] S.V. Volkov, V.F. Grishchenko, Yu.K. Delimarsky, Coordinational Chemistry of Salf Melts, Naukova Dumka, Kyiv, 1985.
[58] S.V. Volkov, Zhurn, Inorg. Khimii, No. 11 (1986)2748.

[59] S.V. Volkov, Molten Salf Bull. Univ. de Provence. — No. 35 (1988)3.
[60] S.V. Volkov, Ion, rasplavy i tverd. elektrolity, Iss. 4 (1989)26.
[61] L.F. Kozin, VI Int. conf. «Hydrogen material science and chemistry of metal hydrides, Katsiveli, Yalta, Ukraine, Sept. 2–8, 1999.
[62] L.F. Kozin, D.V. Sokolsky, Yu.F. Balybin, Direct conversion of thermal energy into electric and fuel elements, No. 2 (64) (1975)136.
[63] S.V. Volkov, Zhurn. Neorg. Khimii, No. 11 (1990)2789.
[64] S.V. Volkov, Ukr. Khim. Zhurn., No. 7 (1982)675.
[65] A.c. 811867 USSR, MKI^3 S25 B1/02 Electrolyte for Hydrogen Production, S.V. Volkov, V.A. Legasov, A.V. Gorodyssky, 1981, Bull. No. 9.
[66] A.C. 1025184 USSR, MKI^3 S25 B1/02 Method of Hydrogen Production / O.G. Zarubitsky, V.A. Legasov, A.V. Gorodyssky, 1983, Bull. No. 23.
[67] S.V. Volkov, Zhurn. Inorg. Khimii, No. 1 (1980)97.
[68] L.F. Kozin, V.A. Sakharenko, Ukr. Khim. Zhurn., No. 1 (1984)3.
[69] L.F. Kozin, R.G. Sarmurzina, Zhurn. prikladnoi Khimii, No. 10 (1981)2176.
[70] L.F. Kozin, Yu.O. Berezhny, B.I. Daniltsev, VI Int. conf. Hydrogen materials science and chemistry of metal hydrates, Katsiveli, Yalta, Ukraine, Sept. 2–8, 1999.
[71] A.C. 807671 USSR, MKI^3 C25 B1/02 Method of Hydrogen Production / O.G. Zarubitsky, N.F. Zakharchenko, G.P. Sunegin, V.G. Budnik. — Publ. 1981, Bull. inv. No. 7.
[72] 187 A.c. 811868 USSR, MKI^3 C25 B1/04 Electrolyser for Hydrogen Production / A.V. Gorodyssky, V.A. Legasov, S.V. Volkov, et. al. — Publ. 1981, Bull. inv., No. 9.
[73] O.G. Zarubitsky, Zhurn. prikl. khimii, No. 5 (1995)718.
[74] F.J. Salzano, G. Skarevdas, A. Mazzina, Int. J. Hydrogen Energy, No. 12 (1985)801.
[75] J. Divisek, H.W. Nurnberg, Grundlagenforsch. Energietechnol. Jahresber, 1981–1982, Kernforschungsanlage Julish, Julich, 1982.
[76] J. Carvalho, G. Tremiliosi-Filho, L.A.Avaca et al. Hydrogen Energy Progress VI Pergannon Press, N.Y. Oxford a.o., 1986.
[77] W. Donitz, G. Dienrich, E. Erdle et al., Ibid., 271.
[78] A.L. Rotinyan, K.I. Tikhonov, I.A. Shoshina, Theoretical Electrochemistry, Khimiya, Leningrad, 1981.
[79] O.G. Zarubitsky, N.F. Zakharchenko, Hydrogen Material Science and Hydride Chemistry, Materials VI Int. Conf., Yalta, Katsiveli, 2–8 September, 1999.
[80] M.V. Perfiliev, A.K. Demin, B.L. Kuzmin, et al., High-Temperature Water Electrolysis, Nauka, Moscow, 1988.
[81] A.c. 1358329 USSR, MKI^4, S 01 F 7/04 Method of b-alumina production / L.F. Kozin, B.I. Daniltsev, V.A. Sakharenko, Publ. 1987, Bull. No. 45.
[82] A.c. 1192280 USSR, MKI^4 C 01 F 7/4. Method of b-alumina production / L.F. Kozin, B.I. Daniltsev, V.A. Sakharenko, Publ. 1985, Bull. No. 42.
[83] B.V. Galkin, G.A. Grishaev, A.P. Germanovich, et al., Problems of nuclear science and technology. Ser. Nuclear Eng. and Technol., No. 1 (1991)29.
[84] A.N. Podgorny, I.L. Warshavsky, A.I. Priymak. Hydrogen and Energetics, Naukova Dumka, Kyiv, 1984.
[85] A.N. Podgorny, I.L. Warshavsky, A.I. Mishchenko, et al., Nuclear-Hydrogen Energetics, Naukova Dumka, Kyiv, 1980.
[86] R.F. Alimova, L.F. Goltsova, V.F. Garkusheva, et al., Int. J. Hydrogen Energy, No. 12 (1985)861.

[87] A.N. Podgorny, I.L. Warshavsky, A.I. Mishchenko, et al., Nuclear-Hydrogen Energetics and Technology, Atomizdat, Moscow, 1980.
[88] K.N. Semenenko, Bull. Rus. Acad. Sc., No. 10 (1993)885.
[89] A.c. 618920 USSR, MKI^4 C 01 F 7/04. Method of Hydrogen Production, D.V. Sokolsky, L.F. Kozin, R.G. Sarmurzina, et al., Publ. 1978, Bull. No. 29.
[90] L.F. Kozin, R.G. Sarmarzina, Zhurn. Prikl. Khimii, 54, No. 10 (1981)2176.
[91] A.c. 618921 USSR, MKI^4 S 01 F 7/04. Method of Hydrogen Production, D.V. Sokolsky, L.F. Kozin, R.G. Sarmurzina, et al., Publ. 1978, Bull. No. 29.
[92] A.c. 1512159 USSR, MKI^4 S 22 C 21/00. Aluminium-based alloy for hydrogen production from water, L.F. Kozin, V.A. Sakharenko, B.I. Daniltsev, V.G. Gopienko, Publ. 1989. Bull. No. 36.
[93] A.c. 1241636 USSR, MKI^4 S 01 B 3/08. Method of hydrogen production, L.F. Kozin, A.B. Gorodysky, V.A. Sakharenko, Publ. 1986, Bull. No. 24.
[94] A.c. 1051966 USSR, MKI^4 S 22 C 21/00. Aluminium-based alloy for hydrogen production, L.F. Kozin, V.A. Sakharenko, Publ. 1983, Bull. No. 40.
[95] A.c. 1108773 USSR, MKI^4 C22 C21/00. Aluminium-based alloy for hydrogen production, L.F. Kozin, V.A. Sakharenko, B.A. Troshenkin, Publ. 1094, Bull. No. 30.
[96] A.c. 1360000 USSR, MKI^4 B 22 F 1/00. Method of activation of aluminium power, L.F. Kozin, V.A. Sakharenko, B.I. Daniltsev, V.G. Gopienko, Pull, 1987, Bull. No. 40.
[97] A.c. 1591510 USSR, MKI^5 S 22 S 21/00, 1/05. Aluminium-based compositional material for hydrogen production, L.F. Kozin, V.A. Sakharenko, B.I. Daniltsev, I.L. Warshavsky, Publ. 1990, Bull. No. 33.
[98] A.c. 1111405 USSR, MKI^4 S 01 B 3/08. Composition for hydrogen production by water decomposition, L.F. Kozin, A. V. Gorodyssky, V.A. Sakharenko, Publ. 1984, Bull. No. 32.
[99] L.F. Kozin, V.A. Sakharenko, B.I. Daniltsev, Zhurn. Prikladnoi Khimii., 68, No. 9 (1995)1433.
[100] L.F. Kozin, A.V. Gorodyssky, V.A. Sakharenko, Kinetics and Burning. Chernogolovka, Nauka, Moscow, 1986.
[101] L.F. Kozin, A.N. Budarina, Zhurn, Prikladnoi Khimii, 62, No. 12 (1989)2665.
[102] L.F. Kozin, A.V. Gorodyssky, V.A. Sakharenko, Chemical physics of combustion and explosion processes. Kinetics and burning. Materials VIII All-Un. Symp. on burning and explosion, Chernogolovka, Moscow, 1986.
[103] D.V. Sokolsky, L.F. Kozin, T.V. Kuzora, et al., Proc. Acad. Sc. USSR, 230, No. 3 (1976)620.
[104] Xu Zhengang. Wu Chnlai, Hydrogen Energy Progress XIII Proc. 13th World Hydrogen Energy Conference. Beijing, June 12–15, 2000. Vol. 1–2, Published Intern. Assoc. for Hydrogen Energy, 2000.
[105] L.F. Kozin, S.V. Volkov, Production of high-parameters hydrogen with application of energy-accumulating substances, European Hydrogen Energy Conf.. 2–5 Sept., 2003, Alpexpo, Grenoble, France. Res.: C01/20.
[106] N.A. Chernomyrdine, E.E. Shpilrain, V.M. Zaichenko, Hydrogen Energy Progress XIII Proc. 13th World Hydr. Energy Conf., Beijing, China, June 12–15, 2000, Publ. Intern. Assoc. for Hydrogen Energy, 2000.
[107] Bao De-you, Hydrogen Energy Progress XIII, Proc. 13th World Hydr. Energy Conf., Beijing, China, June 12–15, 2000, Vol. 1–2, Publ. Intern. Assoc. for Hydrogen Energy, 2000.

[108] E.O. Adamov, V.I. Rachkov, Energy: Economy, Technology, Ecology, No. 1 (2001)2.
[109] Academician V.I. Subbotin, Bull. Rus. Acad. Sc., 70, No. 4 (2000)361.
[110] L.S. Belyaev, O.V. Marchenko, Ecology, No. 11 (2001)2.
[111] V.S. Okunev, Proc. Rus. Acad. Sc., Energetics, No. 2 (2002)42.
[112] V.V. Goncharuk, E.B. Strakhov, A.M. Voloshinova Water-Chemical Technology of Nuclear Power Plants and Ecology, Naukova Dumka, Kyiv, 1993.
[113] V.M. Byakov, F.G. Nichiporov, Water Radiolysis in Nuclear Reactors, Energoatomizdat, Moscow, 1990.
[114] B.V. Petrov, A.S. Abakumov, Nuclear Energy, 85, Iss. 6 (1998)483.
[115] N.G. Basov, V.I. Subbotin, L.O. Feoktistov, Bull. Rus. Acad. Sc., 63, No. 10 (1993)878.
[116] H. Siborg, P. Nitze, Za rubezhom, No. 52 (1991)20.
[117] L. Chidester, Direct Energy Conversion, Mir, Moscow, 1975.
[118] K.Ya. Kondratiev, Bull. Rus. Acad. Sc., 70, No. 9 (2000)788.
[119] Ya. Shpak, Uryadovy. Currier, No. 187 (2000)5.
[120] K.Ya. Kondratiev, Bull. Rus. Acad. Sc., 70, No. 9 (2000)788,
[121] L.F. Kozin, S.V. Volkov, Chemistry and Technology of High-Purity Metals and Metalloids, Naukova Dumka, Kyiv, 2002.
[122] Pius Husser, Sonnenenerg. Sol., No. 5 (2001)28.
[123] G.Ya. Kolbasov, A.V. Gorodyssky, Processes of Photostimulated Charge Transfer in the Semiconductor-Electrolyte System, Naukova Dumka, Kyiv, 1993.
[124] Yu.V. Pleskov, Photoelectrochemical Conversion of Solar Energy, Khimiya, Moscow, 1990.
[125] Ye.V. Kuzminskii, G.Ya. Kolbasov, Solar energy materials and solar cells, 56 (1998)93.
[126] Ye.V. Kuzminskii, G.Ya. Kolbasov. Ya.Yu. Tevtul, N.C. Golub, Nontraditional Electrochemical Systems of Energy Conversion, Akademperiodika, Kyiv, 2002.
[127] M. Sharon, P. Veluchamy, C. Natarajan, D. Kumar, Electrochim, Acta, 36, No. 7 (1990)1107.
[128] N.M. Mkhitaryan, Helioenergetics. Systems, Technology, Application, Naukova Dumka, Kyiv, 2002.
[129] J.O.M. Bockris, Int. J. Hydrogen Energy, No. 27 (2002)731.
[130] M. Dergacheva, Nauka and Higher School of Kazakhstan, No. 20 (2003)8.
[131] M.B. Dergacheva, V.N. Stasyuk, L.A. Fogel, A.R. Abdrakhmanova, Zhurn, Prikl. Khimii, 71, Iss. 4 (1998)616.
[132] M.V. Dergacheva, V.N. Stasyuk, L.A. Fogel. 8yh Intern. Conf, of II-VI Compounds, Grenoble, France, 1997.
[133] L.A. Fogel, Electrochemical reactions with participation of Tellurium (IV) Ions and Their Rope in Processes of Electrodeposition of Semiconductor Compounds, Abstr. Cand. Sc. (Chem.), Alma-Aty Rep. Kazakhstan, 2002.
[134] S. Dovgy, Bull. NAS Ukraine, No. 11 (1999)6.
[135] T. Bak, J. Nowotny, M. Rekas, C.C. Sorell, Int. J. Hydrogen Energy, No. 27 (2002)991.
[136] V.M. Andreyev, V.A. Grilikhes, V.D. Rumyantsev, Photoelectric Conversion of Concentrated Solar Radiation, Nauka, Leningrad, 1989.
[137] A.S. Glazkov, V.A. Grilikhes, Solar Energy Conversion, Nauka, Moscow, 1985.
[138] V.A. Grilikhes, Solar Space Power Stations, Nauka, Leningrad, 1986.
[139] Cosmonautics. Encyclopaedia / Ed. Chief. V.P. Glushko, Moscow, 1985.
[140] O.I. Kudrin, Solar High-Temperature Space Energomotive Plants, Mashinostroenie, Moscow, 1987.

[141] N.V. Kharchenko, Individual Solar Plants, Energoizdat, Moscow, 1991.
[142] K.I. Zamarayev, V.N. Parmon, Energy Resources though the Prism of Photochemistry and Catalysis, Mir, Moscow, 1986.
[143] K.I. Zamarayev, V. N. Parmon, Photocatalytic Conversion of Solar Energy. Chemical and Biological Methods, P. 1, Nauka, Novosibirsk, 1985.
[144] V.N. Parmon, Photocatalytic converters of Solar Energy, Molecular Systems for Water Decomposition, P. 2, Nauka, Novosibirsk, 1985.
[145] U. Wagner, Proc. 4th Intern. Sympos. on Hydrogen Power — Theoretical and Eng. Solutions, Stralsund, 9–14 Sept., 2001.
[146] S.D. Varfolomeev, Energy Conversion by Biocatalytic Systems, Moscow Univ. Publ., 1981.
[147] Biomass as Energy Source, Tranl. from Eng., Edit. S. Sowfer, O. Zaborski, Mir, Moscow, 1985.
[148] Eur. Power News, No. 5 (1999)33.
[149] T. Blair, Bull. NAS Ukraine, No. 1 (2003)9.
[150] N.V. Vershinsky, Ocean Energy, Nauka, Moscow, 1986.
[151] D.D. Aizeks, Energy Conversions in the Oceans, Vladivostok TOI, FERC AS USSR, 1981.
[152] V.A. Troshenkin, Renewable Energy, Par I, Fort Publish., Kharkov, 2993,
[153] Motor Fuel of the Future, Avto Mir, No. 43 (2000)8.
[154] Plant Fuel for Motor. Avto Mir, No. 43 (2000)22.
[155] A.M. Rubailo, V.I. Golubev, Bull. MEI, No. 1 (2000)41.
[156] Pat. 2116476 RF, MPK 6 F02 B7/04, Power Plant, A.M. Rubilo, V.I. Golubev, Publ. 1998. Bull. No. 21.
[157] A.E. Kontorovich, N.L. Dobretsov, N.I. Laverov, Bull. Rus. Acad. Sc., 69, No. 9 (1999)771.
[158] P.L. Kapitsa, Science and Mankind, 1976.
[159] V.A. Legasov, I.I. Kuzmin, Nuclear and Thermonuclear Future Energy, Energoatomizdat, Moscow, 1987.

Conclusion

It is clear from the data of the book that organic fuel, intensively consumed by mankind, is exhaustible, especially oil and gas reserves. In the second half of 20th century 40–50 % of energy were produced when consuming gaseous and liquid hydrocarbon fuel. Fuel in the amount of 250 million tons of conventional fuel was consumed during the last 25 years of the 20th century: the same amount was consumed for the centuries-old history of mankind. An analysis of consumption and production of the rest of hydrocarbon reserves in the world has shown that oil in Ukraine will be consumed during 30–40 year in the 21st century, natural gas — during 100 years. Deposits of gas hydrates (mainly methane) discovered late in the 20th century will last for 200 year, i. e. during the 21–23th centuries. Solid hydrocarbons are to last during the 21–26th centuries, Proceeding from the volumes of consumed liquid hydrocarbon fuel, the 20th century may be called the «century of oil» and the period, passing into the 21st century and up to the 26th cent. — the promising «era of coal and energy gases» — natural gas, hydrogen, methane gas hydrates and solid hydrocarbons.

It would be noted that the accessibility and low cost of oil and natural gas in the 20th century hampered development of the broad-scale nuclear energetics. It is that dependence on foreign deliveries of oil and has that has made the economy of the countries of «golden milliard» irresistant to crises, dependent on hydrocarbon fuel exporters. In 1970–1980's the countries which consumed hydrocarbon fuel «from wheels», «from boat» or «from pipe» proved to be especially subjected to the energy crisis. There arised some tension between the states possessing hydrocarbon fuel — Iran, Iraque, Arabian countries, Venesuela, etc. Iraque possessing reserves of about $17 \cdot 10^9$ t of oil, was thrice a subject to the attacks on the part of the USA and their allies: on January 13–17. 1993 «Storm in the desert» and on December 16–20, 1998 «Shield of the Desert». The war with Iraque unleashed by the USA and UK in March 2003 and finished formally in May 2003, despite the newest armory used in military operations and occupation of Bagdad, still continues in a form of guerrilla war. Oil reserves of Iran are $13.5 \cdot 10^9$ t. Only centuries-long friendship of Russia and Iran, and diplomacy of President V.V. Putin have saved this country from the fate of Iraque. Oil reserves in Saudi Arabia surpass $40 \cdot 10^9$ t. The oil «odour» strain the USA and Great Britain in the beginning of the third millennium, since their own reserves can be consumed during the nearest 8 and 6 years, respectively.

Oil reserves being limited all over the world, mankind already in the first quarter of the 21st century will become aware of the deficit in oil refining products: gasoline, diesel fuel, lubricants, etc. An inevitable rise in price for the hydrocarbon fuel will begin long before full exhaustion of oil. It is supposed that annual expenditures for the world energetics will increase 2.5–3.0 times by the middle of the 21st century, and 4–6 times by its end compared with 2000 (the ten fold rise in price is also possible!). The period of stagnation may be delayed. But one can see that it is necessary to develop new high-tech methods for production of synthetic liquid fuels (SLF) possessing properties close or even surpassing those of oil refining products. Organization of SLF production is the most important task for industries of the developed world countries. Coal and natural gas may be used as hydrogen source for SLF (power hydrocarbons, methanol and ethanol). Sinc natural gas resources will be exhausted in the 21st century, the intensive investigations on creation of new high-tech methods with the corresponding infrastructure of efficient extraction of gas-hydrates from the botton of seas and oceans would be carried out now.

Great reserves of coal in some countries could lessen the crisis stat of the hydrocarbon economy. But only seven countries in the world possess such necessary coal reserves: the USA for > 1000 years, Russia — 800, China — 779, Ukraine — 600, South African Republic — 389, EEC — 284, Australia — 247, Poland — 166, India — 106, Canada — 100 and a number of other countries — 88–90 years. As it follows from Fig. 104, only in the USA, Russia, China and Ukraine coal will last up to 26th century, inclusive. Coal may be used in some countries for hydrogen production by gasification as fuel for TES, when generating electric energy and heat, as well as in ferrous metallurgy as a reducer when producing pig iron and high-grade steels from the iron ore. Coal and turf will be also used in the domestic life as it was centuries ago. But the operation of industrial power plants and TES on coal needs new methods of trapping the emissions of sulphur, nitrogen and metal oxides making the major harm for the environment. In this case, only carbon dioxide could be released in the atmosphere, and in the less amount compared with 2000, because of the promising possibility to change the motor transport and aviation fuel by SLF and hydrogen. It is hydrogen energetics which will favour the maximum extent of the environment protection. The motor transport shift to hydrogen fuel will help to protect the atmosphere from the emissions of carbon monoxide, benzpyrene, nitrogen oxides. Basides the bottled hydrogen, metal-hydrige-based accumulators, hydrogen nanopipes, fullerenes, as well as fuel cells on hydrogen fuel can be used for hydrogen application to motor transport. Coal, gas hydrates and natural gas may be used to produce hydrogen in different phase state (gaseous, liquid).

It may be supposed that before the complete exhaustion of oil, natural gas and gas hydrates, however difficult it is, mankind will realize that there is no alternative to nuclear and thermonuclear energetics as well as to hydrogen production using NPP and TNPP heat, and that it is the only way to survive.

Intensive development of nuclear energetics of the world was hampered by the Chernobyl catastrophe. It was neither the first not the second accident in the world, and this catastrophe, like all the other catastrophes at NPPs, would be considered the payment for premature decision under the NPP construction. The illusion of human omnipotence appeared after creation of nuclear and thermonuclear bombs capable to wipe off not only towns but also countries and nations from the face of the Earth. The «peasful» atom began walking on the planet. New NPP were springing up all over the Earth. This resulted in numerous accidents at NPP in many countries. The most substantial accidents occurred at Chernobyl NPP, Ukraine (1986), and Three-Miles-Island NPP, USA (1978).

The accidents ware followed by almost 20-years stagnation in nuclear energetics development. People distrusted the nuclear plants. The situation improving required considerable capital investments, directed to elimination of defects of «premature» nuclear energetic with slow reactors. Nuclear energetics of the future would be deprived both of the defects inherent in hydrocarbon energetics and those inherent in the «pioneer» NE with open nuclear fuel cycle. The defects of NPP with slow reactors are as follows:

a) limited resources of uranium-235 in nature; b) great mass of the waste nuclear fuel (WNF) in fuel elements, containing about 84.0–88.5 % of uranium-238, actinoids (Pu, Np, Cm, Am), fission products, 0>45 % of unburnt uranium-235 from initial 4.5 %, etc.; c) limited depth of fuel burning; d) high radioactivity of WNF; e) considerable residual energy release from WNF; f) frequency and cost of processes, etc.

One can only hope that in the second half of the 21st century, people will create the high-tech methods (as a result of conscious relation of the society to nuclear energetics), and nuclear-hydrogen, thermonuclear-hydrogen energetics will be developed basing on these methods. The nuclear-hydrogen (NHPP) and thermonuclear-hydrogen electroenergetics (TNHPP) will represent the large-scale corporations of NHPP and TNHPP in the states or in the groups of states. Since nuclear-energetics with slow reactors has no future, the society will change it by pure nuclear energetics with fast reactors and with the use of natural uranium as fuel. No later than in the second half of the 21st century the present nuclear energetics will be transformed into the large-scale nuclear energetics with failure-proof fast nuclear reactors with a closed fuel cycle. Diathermal uranium and plutonium nitrides will be used as fuel for high-temperature nuclear reactors with high-boiling heat-carrying agent. Following the nitride method not only reserves of depleted uranium accumulated by nuclear countries all over the world but also ever-growing reserves of the reactor and weapon uranium-235 and plutonium-238 (which volumes have reached astronomic values that is connected with the recession of power generation by nuclear reactors and decrease of the number of produced nuclear bombs) would be reworked. In the second half of the 21st century the high-tech methods of NHPP and TNHPP will be most ecologically pure compared with other technologies of energy generation. Thorium will be also used in the future as nuclear fuel.

The share of energy consumed by nuclear-hydrogen and thermonuclear-hydrogen energetics in the third millennium will be 38–40 % and that of hydrogen energetics — 24 %. It would be noted that hydrogen energetics where hydrogen performs the functions of heat carrying agent will reguire the consumption of primary energy generated by NPP, TNPP, HES, etc. Renewable energy sources (RES) (wind, solar, tidal, geothermal biomass energy) will be developed with the use of high technologies at the regional level. The share of energy generated by RES in the 21st century, and up to the end of the third millennium (Fig. 104) will be: hydroenergetics — 18 %, wind energetics — 10 %, photoelectric converters of solar radiation energy into electricity — 6 %, biomass — 4–5 %.

We would like to touch one more problem, i. e., the decrease of dependence of energetics and economy in many countries of the world on import of oil, gas and especially coal. As it follows from the conception developed by the authors of this look, there are rich deposits of hydrocarbons occurring at great depths (within 10 km). Thus, the already established reserves of coal in the USA equal to $107 \cdot 10^9$ t conv. fuel under the corresponding volume of mining ($1.275 \cdot 10^9$ t/yr) would be exhausted during 84 years. But it was established, by means of geological prospecting, that the predicted resources of coals at the depth of 1800 m at the USA deposits are $3.6 \cdot 10^{12}$ t. Calculations show that even under two-fold mining, compared to the current one, the USA coal will last for more than 1400 years. Total resources in China are estimated as $5.06 \cdot 10^{12}$ t, the predicted resources at the depth of about 1800 m as $4.45 \cdot 10^{12}$ t.

Thus the energetic safety of most countries will require activation of geological surveying works in the field of the opening of deposits of combustible minerals at great depths, up to economically acceptible ones with the purpose of establishing true resources of minerals of solid and other hydrocarbons. In the countries of European Community, as in many other countries of the world, coal, being widely distributed (its considerable reserves are available even on the Spitzbergen Island), is considered as a guarant of energy safety. Thus it is necessary to perform active scientific and technical developments in the sphere of coal mining and production of other accompanying hydrocarbon energy carriers, for example, methane, by different methods including the methods of underground gasification. Coal mining at great depths will be carried out in the third millennium with the use of people-free technologies with completely mechanized systems and controlled robots. The 21st century will undoubtedly become the century of high-tech energetics, industry and economy. Considerably higher reserves of coal oil and natural gas, than those already proved now, may be stored both at great depths under the Earth surface and at the bottom of seas and oceans.

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