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The role of chemical factors in the evolution of natural systems (chemistry and ecology)

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ABSTRACT. Certain trends in the development of chemical and related sciences as regards the solution of ecological problems are described. Apart from the discussion of traditional chemical problems associated with the development of resource-saving and low-waste technologies and sensor systems for the monitoring of the natural environment, the physicochemical aspects of the dynamics of a wide variety of natural systems are analysed and the role of the chemical factor in their evolution is elucidated. The idea of parameters defined as limiting permissible amount of waste and limiting permissible concentrations, characterising respectively the self-protecting properties of the environment and individual organisms was introduced on the basis of non-linear models of non-equilibrium thermodynamics. The dynamic equations describing the states of eco-systems in the presence of external stochastic chemical factors are discussed. Problems concerning the influence on the evolution of natural communities of mass transfer processes in the interior of the Earth and in various layers of the atmosphere are analysed. The idea that the Earth–atmosphere system as thermodynamically open is developed and the possible role of anthropogenic factors in the initiation of natural catastrophies is discussed.

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I. Introduction

The Earth's biosphere, which embraces the lower part of the atmosphere, the hydrosphere, and the upper part of the lithosphere with its rich and wide variety of ecological localised regions and eco-systems, was formed under conditions where the Earth was strongly acted upon both from space (electromagnetic radiation over a wide frequency range, solar and stellar wind, gravitational effects of the sun, the moon, and the planets, and collisions with macroscopic objects—asteroid fragments and comets), and from the inner regions of the Earth (terrestrial magnetism, movements of the lithospheric plates and of the Earth's core, material ejected in major volcanic eruptions). The unity (physicochemical, biochemical, geochemical, and cosmochemical) between eco-systems and their environment arising under these conditions[1–5] was responsible for the modulating and modifying variability[6] of organisms subjected to variations in the intensity and form of extraneous factors. The evolution of terrestrial communities provided examples of the stability of living matter accompanied by the variability of its forms even under the conditions of global catastrophies. Since the 30's of the present century and especially during the last decades, the biosphere has been subjected to the influence of anthropogenic factors having anomalously high (compared with those obtained previously) local intensities and sometimes exhibiting new essential features. According to Matros and Noskov,[7] in terms of the amount of sulphur dioxide (~150 million tonnes annually) and hydrocarbons (~70 million tonnes annually) evolved, industry has already become comparable to natural sources and as regards carbon monoxide (~300 million tonnes annually) it surpasses them. The parameters of other types of anthropogenic contaminants ejected into the natural environment and their amounts are also not encouraging.[8] The greatest risk associated with anthropogenic contaminants and influences (in contrast to the natural ones) involves their locally high concentrations, harmful to living matter, or their locally enhanced levels (for example, radioactive and elecromagnetic radiation). Indeed, despite the large integral radiation dose received by the biosphere from cosmic rays and the natural breakdown of radioactive elements in the Earth's core, the overall background of damaging radiation is low and is not dangerous to eco-systems. Whereas the material ejected by volcanoes contains large amounts of harmful components (for example, SO_2), it is usually scattered over large areas because, these components reach an extremely great height. Thus, the relationship between the appearance of silvery clouds at a height of approximately 80 km and the powerful eruption of Vesuvius preceding this phenomenon led to the conclusion that large amounts of water vapour are ejected into the mesopause by the eruption.[11] Sulphur compounds have also been detected in the silver clouds.[12]

In the anthropogenic evolution of harmful components, their scattering in the atmosphere, the hydrosphere, and in the soil does not occur on such a scale and the local concentrations (or harmful radiation) can exceed by many orders of magnitude the natural background. An even greater danger is associated with the ejection into the biosphere of substances foreign to living organisms—xenobiotics, including those which did not exist previously in nature. Such substances are dioxins, formed in the manufacture of organochlorine derivatives.[13] They already constitute a global risk to humanity and civilisation as a result of the possibility of the long term contamination of the entire biosphere by these substances.

Under these conditions, ecology and other sciences which may participate in the solution of complex ecological problems assume first class importance.[14] In this communication, an attempt is made to present the principal relationships through which such interaction between chemistry and ecology can occur and is already occurring. However, before proceding to the discussion of the essential features of the problems, certain general explanations are necessary.

In connection with the development of acute ecological problems, during the last decade the concept of "ecology" has been extended and it is now regarded as an interdisciplinary synthetic science and protection of the environment from pollution, the development of low-waste resource-saving technologies, the construction of purifying equipment, and planned utilisation of the Earth's resources are included in it. Naturally, ecology employs data from most varied disciplines, but this refers to the methodological and not the idealogical aspects of the science.[15,16]

Ecology is a component of biological science, dealing with the study of the structure and functioning of systems at a superorganism level (eco-systems or biogeocenoses) as regards their relationship with one another and with the environment.[1-5,15-17] This means that any ecological development should include the analysis of the state or dynamics of biological communities in their living environment. Separate components are traditionally investigated in this connection within the framework of genetics, physiology, and anatomy; the level of individual cells is investigated in cell biology; the mechanisms of the interaction of molecular components in the environment and various types of radiation with submicroscopic elements of living systems (biological membranes and their fragments), a wide variety of enzymes, parts of the heredity apparatus, etc. are studied in biochemistry and molecular biology; the state of the environment, including the effects of radiations and particles of different kinds on such environment (liquid, gaseous) is investigated in various branches of chemistry (analytical, inorganic, organic, chemistry of macromolecular compounds, colloid, physical, and radiation), physics (chemical, the physics of the condensed medium, nuclear, molecular, biological), and mathematics.[18] Thus the effecive solution of ecological problems implies that specialists in adjacent disciplines possess the necessary professional knowlege and that each executes his own concerted "manoeuvre".

In particular, in the construction and analysis of models of the evolution of eco-systems—ecological modelling,[19] there arises, together with the formulation of the problem and the elucidation of the main factors to be taken into account in the model (the ecological problem), a set of physicochemical, physical, and biochemical problems associated with the determination of the essential features (genesis) of the parameters in the equations and their dependences on the state of the environment, which may change, as well as mathematical problems associated with the necessity to analyse the corresponding systems of equations (in the general case non-linear), the determination of stationary states of the eco-system and the conditions of bifuraction transitions,[20] etc.

The aim of the present article is to present in a general form (accompanied by specific examples with which the author is most familiar) the possible relations between chemistry and ecology in order to elucidate the aspects of chemical science, of greatest current interest, which assist in the solution of ecological problems. Evidently in such formulation of the problem the role of chemical science should consist primarily in the development of nature-protecting and resource-saving technologies with analytical monitoring of the composition of the entire industrial waste and of the quality of the final products and articles. The ecological problems then involve the study of the influences of such waste on eco-systems with the elucidation of the possible ecological modulations and modifications[6] to prevent the possible eco-system degradation process. Naturally, it is essential to describe adequately the self-protecting possibilities of the eco-systems themselves, the buffer properties of their environment, the ecological resources of the biosphere as a whole, and its "tolerance of abuse".[21,22] This is particularly important bearing in mind the objectively existing tendencies to expand industrial manufacturing processes, to develop further the exploitation of useful mineral products, and to influence actively the biosphere.

The ecological resources are usually estimated empirically and are characterised by experimental (for the given region, a specific season, etc.) limiting permissible amount of waste (LPW) and limiting permissible concentrations (LPC). However, the discovery of the genesis of these parameters and the elucidation of the responses to various anthropogenic influences of the living systems themselves as well as the purifying possibilities inherent in inorganic nature make it possible to forecast on a sounder basis and more comprehensively the consequences of harmful influences of anthropogenic factors on eco-systems and to prevent these influences. As shown below, chemical science can analyse successfully and partly solve such problems.

II. Nature-protecting chemical technologies

The scale and nature of man's industrial activity has to be interrelated with the possibilities of modern science and technology and cannot permit a disturbance of the state of the environment of the planet's eco-system. This means that technological waste (gaseous, liquid) from industry must be sufficiently diluted as regards corrosive components and components harmful to living systems, so that, despite the wide variety of substances of anthropogenic and non-anthropogenic origin constantly ejected into the natural environment, the "buffer capacity" of the environment is maintained, i.e. the rates of degradation or elimination from turnover cycles (accompanied by irreversible "storage") should ensure the conversion of harmful substances into safe ones, which participate in natural turnovers. At the same time certain stationary concentrations of corrosive components not exceeding the LPC should be established in the environment (see Section IV).

The discovery of the mechanisms of the binding, detoxification and transformation (chemical, radiochemical, photochemical, microbiological) of harmful substances in the environment and also their elimination (filtration, micro-and ultra-filtration, reverse osmosis[23,24]) or their decomposition products constitutes an important problem in the protection of nature, since requirements as regards the LPW and the anthropogenic contaminants of the environment (LPC) in each specific region must be worked out on precisely this basis.

High local pollution of the environment by heavy metals, in the first place lead, cadmium, mercury, and arsenic,[25] accumulating in living organisms, is especially dangerous. Metals and metalloids enter the atmosphere with aerosol and vapour-phase industrial waste, as a result of dust rising from the soil, as a consequence of the arrival of dust from space, during volcanic eruptions, etc.[26] At the same time the metals present in rain water enter the soil and open water containing areas where the vast majority of heavy metal ions are adsorbed on microscopic suspensions of mineral origin which form part of the composition of medium and fine silt particles

0.05–0.005 μm in size (up to 70–80% of the total content in water).[27]

There are a wide variety of technological processes for the elimination of heavy metals from industrial aqueous waste and water in open water containing areas. Membrane (including membrane-sorption[23,24] and membrane-extraction[28]) and radiation-sorption methods for the detoxification of contaminated waters are effective. Such procedures are frequently used in combination with traditional chemical treatments with active agents (Cl_2, NH_3, O_3) and physical treatment (heating, UV radiation). There is now a possibility of synergism in the action of the above factors.[29] Irradiation alters the chemical (microbiological) composition of the system, i.e. leads to the disruption or conversion of the contaminants in water, which makes it possible to remove them subsequently from the medium being purified.

The solutions of the problem of the detoxification of aqueous waste by the removal of heavy metals may also be based on the use of the characteristic features of their complex formation reactions with a wide variety of ligands in the given medium. The formation of the so called secondary bonds,[30] whose strength is intermediate between covalent and van der Waals bonds, frequently plays an important role in such complex formation. The formation of secondary bonds by heavy organometallic cations with the functional groups of biopolymers is responsible for the poisoning of living organisms by heavy metals [for example, Hg(II)]. At the same time, the secondary bonds between Au(I) and organic ligands are formed in many medicinal drugs exhibiting a high therapeutic effect.

Other examples of the use of modern advances in chemical science for the detoxification of natural and technological waters may be found in other reviews of the present issue (see also Refs. 31 and 32). Naturally the number of unsolved problems is still very large. Cellulose-paper industries, non-ferrous metallurgical undertakings, power engineering, and the industrial manufacture of caustic soda and chlorine are serious sources of the pollution of the environment. The ejection into the atmosphere of Freons, which help to disrupt the Earth's ozone layer protecting the biosphere against the harmful effects of UV radiation, is a well known ecological danger.[33,34]

It is important to note that the advances achieved in chemical technologies makes it possible to reduce the amount of waste and achieve a saving of energy and materials in many industries. In particular, the harmful components discharged into the atmosphere (under conditions where they become highly concentrated during the purification process) may become sources of a valuable raw material for other industries. At the present time, large streams of effluent gases, containing admixtures of harmful components (SO_2, NO_x, HF, H_2S, CO) are ejected into the atmosphere in many industries.[35] In particular, the amount of sulphur dioxide discarded into the atmosphere in individual copper-zinc undertakings exceeds 1000000 tonnes per year. Nevertheless in the processes involving the neutralisation of gaseous waste containing SO_2, H_2S, and HF in small amounts (<1%) the sulphur- and fluorine-containing waste is hardly utilised.

One of the possible schemes (Fig. 1) for the detoxification of local gaseous waste (their volume is relatively small), which contains harmful components (SO_2, HF, HCl, NO_x, CO, H_2S), is described below. It involves their neutralisation with ammonia and the utilisation of the useful components, using a membrane unit whereby the excess ammonia is returned to the cycle. In the presence in the initial gaseous stream of the least reactive components (NO_x, CO, H_2S), it is necessary to introduce a catalytic reactor into the scheme[35] in order to neutralise these components with ammonia.

This scheme provides for the absorption of the excess ammonia (usually the amount of the excess ammonia may be approximately 10–20% of that supplied for neutralisation) by dilute aqueous ammonia solutions followed by the extraction of the absorbed ammonia and its return (with regulated amounts of water vapour) to the neutralisation reactor. Ammonia is extracted from the ammonia solution by passing a small proportion αI ($\alpha \ll 1$)

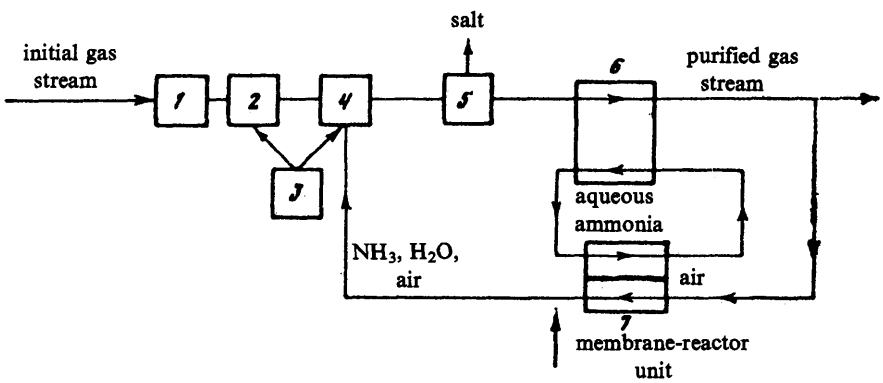


Figure 1. Schematic illustration of the process involving the neutralisation with ammonia of the corrosive components of gaseous waste in the membrane unit for the return of ammonia to the cycle.[36] The principal components of the block scheme: *1*, filter for preliminary purification of the gas mixture; *2*, catalytic purification unit (in the presence of NO_x, CO, and H_2S in the gas); *3*, source of ammonia; *4*, turbulent reactor for the neutralisation of corrosive components with moist ammonia supplied in stoichiometric excess; *5*, system for the trapping of the aerosol formed with isolation of the salt product; *6*, system for scrubbing with water to remove excess ammonia from the effluent gas stream, including a water absorber with supply to the latter of dilute aqueous ammonia (2–4%) (at the outlet the ammonia concentration is 4–5%); *7*, membrane unit (aqueous ammonia at a concentration of 4–5% is supplied to the interfibre space).

of the purified gas stream *I* through hollow fibres,[36–38] the ratio of the concentrations of ammonia and water at the outlet from the membrane unit being regulated by the gas-dynamic gas flow regime within the fibre.[36,37] For gas flow rates of approximately 10^2-10^3 $m^2\ h^{-1}$ and for a content of acid components of about 1 vol. %, the membrane elements should return ammonia in an amount $\lesssim 1.0$ m^3 $NH_3\ h^{-1}$, which is an entirely acceptable task in view of the functional characteristics of the hollow fibre membranes developed for this purpose on the basis of a perfluorinated sulphonic acid cation-exchange material of the Nafion type.[38]

The salt compounds removed from the mixing reactor (trapped in the form of aerosols) may be of interest as a raw material. In particular, the neutralisation of sulphur dioxide with ammonia in the presence of water vapour results in the formation of salts of sulphurous and sulphuric acids, which can be used either for the preparation of mineral fertilisers or for the liberation of ammonia (on thermal decomposition of the salts, on electrolysis of their solutions) with return of the ammonia to the cycle. This imparts to the given technology a low-waste character. Naturally, problems associated with the development of the optimum design of the mixing reactor with a system for the trapping of aerosols and for the removal of solid or highly concentrated liquid products arise in the application of this type of technology.

In fact, each liquid or gaseous industrial waste can be and should become a source from which valuable components can be extracted (or returned to the cycle): scarce heavy metals (Cu, Cr), organic components, acids, and alkalies. The advances in chemical science give grounds for the hope that new highly effective nature-protecting and resource saving technologies will be achieved:[39,40]

In discussing problems associated with the ejection of harmful components into the environment, it is important to discover whether these components are scattered uniformly throughout space (as molecular or ionic impurities) or are concentrated on some type of carriers (for example, aerosols, a wide variety of submicroscopic colloid particles, etc.). It is well known that simple knowledge of the chemical composition of the environment does not permit the understanding of many of the phenomena in inorganic nature. The combination of even small fractions of certain components of the environment (water molecules, other inorganic molecules or atoms, organic molecules) into colloid formations influences fundamentally a wide variety of physicochemical processes in the environment. Aerosols, the amount of which (in terms of weight) in the atmosphere is small (microgramme amounts in a cubic metre of air) and are at the level of the content of rare gases (xenon, krypton), determine not only many properties and phenomena (including the generation of sky glow, rainbows, and false suns as well as the climate in different regions of the Earth) but also the forms and rhythms of life on our planet, which we are witnessing.[41]

Furthermore, aerosols as well as colloid impurites in aqueous media can sorb harmful components in the environment, giving rise thereby to their anomalously high concentration: the concentrations of these components averaged over the volume of the aerosols can exceed by many orders of magnitude the corresponding average values in the environment. Such concentration processes play a dual role. On the one hand, the environment is freed from harmful components (including carcinogenic, radioactive, etc. components) with their "storage" in a relatively small number of macroparticles. On the other hand, these "depositories" represent a serious danger to individual persons so that development of methods for the individual protection of organisms against the harmful effect of active aerosols[42] and other colloid particles has acquired great importance as regards the protection of nature.

The development of methods for exerting controlled chemical, physical, and physicochemical influences on the environment in order to initiate such processes leading to the storage of individual components of the environment in a colloid-chemical depository is extremely urgently required. One can, for example, spray into the atmosphere special aerosols or introduce into an aqueous medium specific complex forming agents, after which the resulting complexes can be concentrated by ultrafiltration.[43] Various flocculation,[44] coagulation, etc. procedures are effective.

One of the methods whereby aqueous systems can be specifically acted upon may be the so called "magnetic treatment". Although this type of preparation of water for use in steam boilers in order to diminish the amount of scale formed during their functioning has long been known,[45] the attitudes to various procedures for the magnetic treatment of aqueous systems (the establishment of a flow of water through a permanent magnet with an induction of approximately $1-10^3$ Oe,[46,47] exposure to a variable electromagnetic field in the frequency range $1-10^3$ Hz [24]) have been extremely cautious in view of the controversial nature of the theoretical interpretations of the effects of such treatments.

Nevertheless, certain ideas about the results of the action of magnetic fields on real aqueous systems have already been formulated. According to Michelson,[46] when a moving solution supersaturated with hard salts is exposed to a magnetic field, crystallisation results in the formation of particles with a crystallographic structure differing (looser) from that arising in the absence of the magnetic field, so that there is a change in the ratio of the rates of crystallisation in the bulk of the solution and on the inner surface of the thermal apparatus (the latter is undesirable).

Further progress in the discovery of the mechanisms of the action of magnetic fields on aqueous systems will be associated with the formulation of experiments with the necessary analytical backup, including the monitoring of the content of ionogenic impurities (starting from water with a specific resistance of 18 N Ω cm) and of the number of colloid particles (for example, when microfiltration membranes with a pore size of approximately $0.1-0.2$ μm are used) in the aqueous medium.[48] Various hypothetical models of the mechanisms of such influences can have undoubted heuristic value in this connection.[49]

III. Chemical membrane sensors

The application of nature-protecting and resource-saving technologies is possible only when special systems for the industrial monitoring of the quality of the products and waste and also for continuous monitoring of the environment with analysis of specific industrial gaseous and liquid waste (for chlorine-containing hydrocarbons, organic solvents, pesticides, heavy metals, etc.) are present at all the stages and cycles of the manufacturing processes. A wide variety of systems for the detection of chemical signals are usually employed; traditional, analytical systems (based on specific chemical reactions, in particular colour reactions) and modern sensor systems which permit high-speed and continuous monitoring of the chemical composition of the medium up to the determination of the lowest possible concentrations of the components.[50–52] The sensitive elements in the recording system of the sensor are usually sputtered layers of metal oxides (ZnO, TiO_2, NiO, etc.) whose

resistance changes on chemisorption of electron-donating or electron-accepting components,[53] field transistors sensitive to chemisorption processes on the locking valve,[50] ceramic layers formed from mixtures of oxides ($Cr_2O_3-Al_2O_3-V_2O_3-Ti_2O_3$, α-$Fe_2O_3-SnO_2$, etc.)[54] whose electrical conductivity changes on sorption of certain components, light guides where conditions for total internal reflections are altered on sorption of specific components on the surface which thereby influences the propagation of the light signal,[55,56] and thin metallic layers (Al, Cu) in which surface plasmons, sensitive to the adsorption of specific components, may be excited in the IR range.[57]

The characteristic concentrations of the components measured by the above procedures depend on the type of molecules, the method of measurement, and the composition of the medium and lie in the range $10^{-8}-10^{-4}$ M. In individual cases, a higher sensitivity can be attained: antigen concentrations of approximately 2.5×10^{-9} M have been measured[57] with the aid of an IR biosensor; proteins in solution at a concentration of approximately $10^{-11}-10^{-12}$ M have been detected using opto-biosensors with excitation of surface plasmons;[58] using in the recording system sensitive bioelements (of the blue crab) in which electrical pulses are generated during the "recognition" process, an aminoacid concentration of approximately 10^{-13} M has been measured.[59] For comparison, we may point out that insects can distinguish the molecules of sex attractants when their content relative to other molecules in air is in the proportions $1:10^{17}$.[60]

The use of solid state systems for chemical sensors makes it possible to diminish greatly the size of the latter by accommodating on a single crystal or transistor several sensitive elements together with electronic circuits for the preliminary treatment of the signal and the storage and processing of information. Highly sensitive electrochemical sensors,[61,62] in which electrocatalytic reactions of components adsorbed on the electrodes take place, are widely used.

The progress in the creation of chemical and electrochemical sensors is at present very appreciable.[50-52] Sensors for the determination of the concentrations of ions (H^+, K^+, Na^+, Ca^{2+}, Ag^+, NH_4^+, Fe^{2+}, Cu^{2+}, Ni^+, Cd^+, Pb^+, F^-, Cl^-, Br—, NO_3^-), gas molecules (H_2, O_2, NH_3, CO_2), and biologically active substances (glucose, urea, quaternary ammonium compounds, sucrose, lactose, lysine, ethanol, penicillin, pyruvate, lactate, organophosphorus compounds, carbolates, psychotropic substances) have been developed and are widely used.[63-66] Thus semiconductor sensors based on metal oxides (ZnO, TiO_2, NiO) make it possible to measure microamounts of oxygen in gases ($10^{-5}-10^{-1}$ vol. %), to determine the concentrations of organic and inorganic gases and vapours (alcohol, acetone, ammonia, nitrogen oxides, carbon monoxide), and to detect free atoms and radicals (H, O, N Cl, OH, CH_3, C_2H_5, NH, NH_2) with a sensitivity up to 10^6-10^8 of active species in 1 cm^3.[53] Nevertheless the requirements (decrease in the levels of measurable concentrations of the components in liquid and gaseous media, greater selectivity, high speed, stability of characteristics) which must be met by such systems are continuously becoming more stringent, which is associated with the creation of new industries where components dangerous to eco-systems may be synthesised and also with some progress in establishing the harmful influence of components which had been previously regarded as safe. This entails the appearance of new virtually uninvestigated problems associated with the possible observation of synergistic effects when the eco-system is acted upon simultaneously either by a mixture of harmful components or by individual components against the background of fields of different nature (electromagnetic fields in different frequency ranges, low-frequency sonic fields).

The study of effects of this type will probably lead to a revision of the established values of the LPC (for different regions of the Earth and for different times of the year). This means that work on the improvement of chemical sensors should continue and chemical science should help in progress in this field. Together with the problem of the chemical composition of the environment (in the first place the determination of the content of harmful components), it is necessary to formulate the problem of the adequate description of the state of the environment—the provision of a more complete set of its characteristics influencing the evolution of an individual person and the eco-system as a whole. Therefore, apart from purely chemical sensors which permit the determination of the chemical composition of the environment as well as temperature and pressure sensors, it is necessary to employ other procedures for monitoring the state of the environment (for example counters for aerosol particles and radioactive radiation, sensitive receivers for electromagnetic radiation).

In this section, we shall discuss only problems associated with the increase in the sensitivity of the action of chemical sensors. Problems involving an increase in the selectivity of the detection of individual mixture components by solid state sensors are of extremely great current interest because the selectivity of many of the existing systems is low. Thus the change in the resistance of semiconducting oxide films depends only on the electron-donating or electron-accepting properties of the chemisorbed components. Therefore the overall change in resistance on sorption of several components makes it difficult to reach unambiguous conclusions about the contributions of individual components. The causes of the change in the charge on the gate of a field transitor on chemisorption of several components simultaneously are also difficult to analyse. The selectivity of such sensor devices can be significantly increased using as one of the elements special layers, partitions, or coatings which separate the medium being analysed from the recording system. Such composite devices are usually referred to as membrane sensors. If the partition (in particular, a porous one) contains biologically active compounds, enzymes, fragments of individual cells, immobilised antigens for the detection of the corresponding antibodies, fragments of membranes with chromophoric groups, etc., one refers to membrane biosensors.[55,56,67]

Coatings modifying the surface of the recording system increase the efficiency of the analysis in cases where the transfer of the components through the membrane layer is the rate-limiting stage of the overall irreversible process involving the detection of these components, namely in the appearance of stationary currents associated with electrochemical reactions of the components of the mixture analysed (O_2, H_2, alcohols, etc.),[68] in transient processes during the establishment of the state of equilibrium on sorption of components by the sensitive elements of the device, in enzyme-catalysed chemical and biochemical reactions,[66] in the generation of photocurrents whose magnitude may depend on the sorption of the components of the medium,[69] on irreversible "storage" or chemical binding of the permeating components in information accumulating systems, etc. Materials (organic and inorganic) usually employed in the membrane technology can be used for the formation of membrane coatings on the surfaces of sensor elements. The main difficulty then consists in the deposition of membrane coatings with an optimum thickness: sufficiently thin so that the response time does not exceed a certain required value and at the same time sufficiently thick so that the transfer through the coating (or the

transient processes in it for non-stationary analytical methods) should remain the rate-limiting stage of the entire irreversible process leading to the detection of the component with its chemical or electrochemical transformation. One of the optimum solutions apparently involves the creation of fairly compact submicroscopic barrier membrane layers with $d \simeq 0.01\,\mu m$.[70]

In this case it is possible to achieve anomalously high selectivities with respect to the target components for a relatively short delay time τ ($\tau \simeq d^2D \simeq 1$ s for diffusion coefficients D characteristic of vitreous polymeric materials) in the detection of a chemical signal. The possibility of attaining high selective detection parameters will be demonstrated on a model example.[71] We shall assume that the barrier layer is formed on the basis of a film with a thickness d and consisting of a material with a permeability constant $\Pi_{0i} = \gamma_{0i}D_{0i}$ in which repelling (for the permeating component i) force centres are distributed at random. We shall represent the repulsion potential of this species i, at a distance r from the centre, by the expression

$$U_i(r) = U_{0i}(b_i/r)^{m_i},$$

where b_i is the characteristic distance and m_i is a numerical parameter. Suppose that n is the concentration of such centres, whereupon, under conditions such as $d \ll d_{0i}$,

$$d_{0i} = [(U_{0i}/k_BT)^{1/m_i} b_i n^{1/3}]^{m_i-2} n^{-1/3},$$

we have the following expression for the permeability constant:[71]

$$\Pi_i \simeq \Pi_{0i} \exp\left[-\pi\Gamma\left(1-\frac{2}{m_i}\right)(U_{0i}/k_BT)^{2/m_i} b_i^2 nd\right]. \qquad (1)$$

A similar situation occurs also in other model representations of the potentials of the repelling centres.

The case considered corresponds to the transfer process (below the permeation threshhold) of the components i.[24] For a lower density of the scattering centres, where the transfer process "above the permeation threshold" obtains (for further details, see Refs. 24 and 71), we have the following features:

(1) for $d \lesssim L_i$ (L_i is the correlation length characterising the topology of the path followed in the transfer of the species i in the given material[24]), we have $\Pi_i \simeq d^{3-D_{fi}}$—fractal transfer ($D_{fi}$ is the fractal dimension);

(2) for $d \gg L_i$, we have Π_i = const.—diffusional transfer.

The significance of the theoretical relations (1) for low values of d is that at high repulsion potentials the species effectively pass through the membrane only in those regions where the fluctuating force field is weakened by the lower local concentration of repelling centres (in the region of a "defect" in the packing of the centres. Since the parameters of the repulsion potentials for species of different nature are different, the selectivity of such a membrane depends exponentially on its thickness. Therefore it is possible, in principle, to achieve for the target component an anomalously high selectivity combined with a high (owing to the small thickness) permeability. So far this is merely a theoretical prediction of the unique possibilities for the selective isolation of mixture components with the aid of submicroscopic barrier membrane structures. These may be layers of organic or inorganic (for example, polyphosphazenes) materials obtained in different ways (the Langmuir–Blodgett method, plasma-chemistry, photochemistry, electrochemistry, alkoxo-technology, etc.). The Langmuir–Blodgett method, which makes it possible to achieve in the layer a specified array of individual molecules (for example, the formation of alternating oriented donor and acceptor layers separated by a distance of 2–3 nm) is especially promising.[72–75]

The technology used for the creation of such barrier structures and ultrathin layers should be at the highest level of sophistication. Such ultraclean technology (as regards materials and the concentrations of impurities and aerosols in the preparation chamber) should employ the experience and methods of the electronic industry. The sensitivity of such membrane systems with respect to the component being detected can probably be increased if the signal is recorded with one-sided excitation of the recording system (on photoexcitation of a semiconductor film, on transition of the membrane to the conductivity switching state,[24] etc.).

In the case of electrochemical sensors, the electric field behaves as an additional controlling factor, which determines the transfer of species, by altering its strength in the layer, one can apparently regulate the "permeation" regime for individual components—below or above the threshhold. Analysis of the voltage–current characteristics of such electrochemical systems with barrier membrane layers over a wide range of potentials can therefore yield exhaustive information about the impurities present in the electrolytic medium.

IV. Physicochemical principles of the modelling of the state of eco-systems

One of the main tasks in ecology consists in the discovery of the dynamic changes in the eco-systems taking into account the wide variety of life cycles, complex interactions, and internal controls (including positive and negative feedback) in food chains.[76] The classical deterministic models characterise the simplest of the situations, such as the dynamics of the growth of population in a closed environment, taking into account the fertility parameters, the real living area, etc., described by a logistic equation,[77–79] the dynamics of the mutual relations between the predator and prey taking into account the "search efficiency", the "successful" encounters between the predator and the prey, etc., described by the Lotka–Volterra equation.[76,80]

Such models make it possible to discover the main principles governing the existence and coexistence of consumers in eco-systems and to understand in what way and how rapidly anthropogenic factors can interfere in the natural characteristic features of the development of populations. The possibilities of modern computers have made it possible to expand significantly and increase the sophistication of deterministic models and to introduce into the latter various functional relationships, including a wide variety of food chains,[81,82] and to elaborate the interactions between consumers and the environment, including the situation when the latter contains toxicants.[83–85] There has also been a growth of the spatial scale of eco-systems susceptible to modelling: from levels corresponding to individual lakes[86] to the level corresponding to large regions (with dimensions up to 500 km).[84] The results of such model calculations make it possible to plan and prosecute more purposefully on a well-founded basis man's economic activity and to develop a strategy for saving ecologically endangered regions.

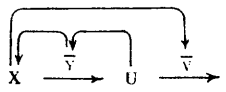
However, a number of fundamental problems arise in such modelling.[78] Each investigator is faced by the necessity to select certain arbitrary boundaries of eco-systems and boundary conditions, which influences the characteristic features of the evolution of the system, its stationary states, and naturally

introduces elements of subjectivity. The second more fundamental problem consists in the non-linearity of deterministic equations for the dynamics of eco-systems, which gives rise to the virtual unpredictability and the pseudo-random nature of the behaviour of such systems over a long time interval owing to the exceptional sensitivity of the solutions to the selection of the initial conditions, which can never be fixed or measured with sufficient accuracy. High-dimensional systems, such as the real eco-systems with a wide variety of internal feedbacks (positive and negative, including feedbacks with lag) and external influences, exhibit a random behaviour to a large extent with transitions between various stationary states. An impression is created that the greater the number of real factors underlying the model, the greater the chance of a transition during analysis to chaos or at least to instability.[78]

All the foregoing means that the very formulation of the model must be designed not so much to discover the multifactor influences on eco-systems but rather to establish the possibilities of the eco-system (with all its complex inter-relationships) as regards its preservation and its reponse to individual factors. In particular, these can be the response of eco-systems to changes in the state of the environment, for example, under the influence of electromagnetic radiation and on introduction of toxicants and sources of radioactive contamination. In the latter cases, the analysis of ecological models makes it possible to represent more effectively the physicochemical and biochemical significance of the LPC and LPW, including the nature of the change in the states of consumers at concentrations of harmful substances exceeding the LPC and of the "ecological reserves" of the system which determine the values of the LPW. Evidently the equations describing the evolution of eco-systems must take into account the possibility of the transfer of consumers to new states with altered properties (in particular with an altered content of harmful substances). We shall examine all these problems in somewhat greater detail.

1. Models of the evolution of eco-systems subjected to the action of toxic substances. The limiting permissible amounts of waste

To illustrate the general principles governing the allowance for the effect of toxic components on the evolution of eco-systems, we shall examine, following Kreikenbohm and Bohl,[83] a model example of a system comprising two interacting populations Y and V of microbions in the food chain:



Here X is the substrate of the organism Y which is a toxicant of the organism V, this being reflected in the above scheme by the direction of the arrow from X to V. It is assumed that, at low concentrations of the substrate, the latter undergoes degradation (consumption by the organism Y), i.e. the "environment is purified" by the removal of the substance X. However, with increase in its concentration, the substrate suppresses the functional activity of Y and thereby limits the formation of the product U, which in its turn inhibits the activity of Y. The scheme presented can, for example, describe the functioning of the phenol degrading bacteria (X = phenol, toluene, unsaturated hydrocarbons, aliphatic acids),[83] which are inhibited by the substrate X itself at its elevated concentrations (in the case examined by the above workers,[83] for $x \gtrsim 5$ mM). Their metabolic partners—the bacteria V (methanogens)—completely cease to form the products of the conversion of their substrate U (methane) at concentration $x \gtrsim 20$ mM.

The evolution of such microbiological populations can be described by the following dynamic system of formal chemical kinetic equations:[83]

$$\dot{x} = -\frac{\mu_1(x, u)}{\gamma_1} y + \tilde{D}(x_R - x), \tag{2a}$$

$$\dot{y} = [\mu_1(x, u) - \tilde{D}]y, \tag{2b}$$

$$\dot{u} = \frac{\mu_1(x, u)}{\gamma_1} y - \frac{\mu_2(x, u)}{\gamma_2} v - \tilde{D}u, \tag{2c}$$

$$\dot{v} = [\mu_2(x, u) - \tilde{D}]v, \tag{2d}$$

$$\gamma_1 > 0,\ \gamma_2 > 0,\ \tilde{D} > 0,\ x_R > 0,$$

where x and u are respectively the concentrations of the substrates X and U in the given medium, x_R is the concentration of the substrate on the surface of the source (we postulate that the substrate enters the medium by dissolving at a rate $\tilde{D} = \alpha S$, α being the rate constant for the dissolution of the substrate X and S the surface area of the substrate), y and v are respectively the densities of the populations of Y and V in the culture medium, $\mu_1(x, u)$ and $\mu_2(x, u)$ are parameters (for their model representation, see Kreikenbohm and Bohl[83]) which determine the rates of change of the densities of the populations of Y and V, and γ_1 and γ_2 are parameters relating the changes in the concentrations of the populations of Y and V to the concentrations of the substrates X and U. The second terms in Eqns. (2b) and (2d) model the effects of inhibition by the substrate X. We may draw attention to the fact that in the scheme described by Eqns. (2a)–(2d) purely concentration effects are considered without taking into account the possible changes (see below) in the functional parameters of the kinetic scheme in an evolutionary dynamic process.

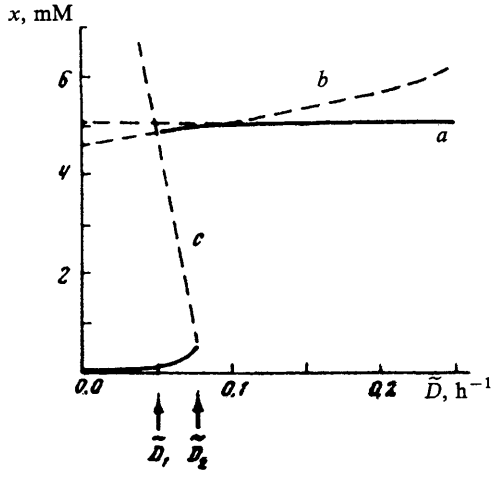


Figure 2. Bifurcation diagram for Eqns. (2a)–(2d).[83] The continuous lines along branches *a*, *b*, and *c* characterise the stationary states of the substrate.

Kreikenbohm and Bohl[83] analysed the stability of various stationary states of the system of non-linear equations (2a)–(2d). The rate of introduction of the substrate-toxicant X into the medium was examined as the controlling parameter. Fig. 2 presents the bifurcation diagram in the plane $(\tilde{D}, x)$ corresponding to the system (2a)–(2d) and constructed using a certain set of parameters.[83] The continuous lines on all three branches *a*, *b*, and *c* characterise the stationary states of the substrate X attained for any evolution of the system beginning in the vicinity of these states (stable states). The range $\tilde{D}_1$, $\tilde{D}_2$) represents the region of bistability. From the ecological point of view, the "bacteriological reactor" described functions well, provided that the system is in the region of stability of the branch *c*. The magnitude of the perturbation forcing the system components to evolve to the standard state on the branch *b*, in which the system is no longer capable of ensuring to the required extent the degradation of the toxic substance X, is thereby determined in the model.

Evidently, in a comparative analysis the parameter $\tilde{D}$ may characterise different types of toxicants added to the medium by sources with the same area of dissolving surface but with different rates of dissolution. At the same time, the differences in the value of $\tilde{D}$ can be caused by the different amounts of a definite toxicant present in the medium, i.e. by different areas of the source adding the toxicant at a specific rate. When the medium contains only one kind of toxicant, this provides grounds for relating the parameter $\tilde{D}$, for which there is a transition from the stable branch *c* to the stable branch *b*, to LPW—the limiting permissible amount of waste component injected into the medium, which is determined by the area S_{lim} injecting the toxicant. When the output of the source of the harmful component exceeds the limiting value, so that $S > S_{\text{lim}}$, the bacteria Y are no longer able to cope with the "processing" of the toxicant. In this case irreversible changes may occur in the eco-system (see below).

2. Models of the functioning of protetcing systems of the organism. Limiting permissible concentrations

As mentioned in the Introduction, living systems have been subjected throughout the entire course of evolution to powerful one-sided influences of different kinds. Under these conditions, specific protecting systems should have arisen in organisms, preventing the lethal effect of at least low concentrations of xenobiotics and other harmful components and small doses of a wide variety of harmful radiation.

Evidently such stability of biosystems in relation to changes in the parameters of the environment is possible up to a certain limit. When this is exceeded, the functional stage of the organism changes and there is then a possibility of ecological consequences for the entire eco-system owing to the existing interrelations, including food chains. Such deviations of the states of individuals from the norm can be naturally attributed to structural rearrangements in individual components or systems of the organism (enzymes, membranes, respiratory or photosynthetic chains). The Ageev–Vershubskii model,[87] proposed previously to describe the cooperative phenomena associated with the rearrangement of the polymer matrix in uptake–release processes in binary media containing surface-active and inactive components, may prove useful in this instance.

We shall consider the evolution of the structural changes in certain components of the living system occurring on uptake of a toxicant by this component. In conformity with Ageev and Vershubskii,[87] we shall consider the equations governing the evolution of two coupled quantities characterising the state of the component being examined: the concentration $c(t)$ of the toxicant component taken up by the component and the structural parameter $a(t)$ defined as the current values of the fraction of the total volume V_0 of the component undergoing structural rearrangements on uptake. We assume that $0 \leqslant a(t) \leqslant a_{\max} < 1$, where $a_{\max}$ is the fraction of the volume of the component in which the given structural changes can occur on uptake of the toxicant. We assume further that the volume $(a_{\max} - a)V_0$ which has still not been transformed and the volume $V_0(1 - a_{\max})$ which does not undergo structural rearrangements participate in the uptake process (the rate constants for the corresponding uptake processes will be designated by γ and η), while the release of the toxicant into the medium takes place via the volumes $(a_{\max} - a)V_0$ and a_0V_0 with release rate constants β and α respectively. Let k be the rate constant for the structural rearrangements which may occur in the volume $a_{\max}V_0$ of the component on uptake of the toxicant. Evidently the physical significance of the constants α, β, γ, η, and k can be discovered by constructing models at a more elementary level, taking into account the nature of the influence of the toxicant molelcules on components of the living system and specifying in detail the characteristics of the mechanism of the structural transformations occurring in the components.

According to Ageev and Vershubskii,[87] the system of equations for the evolution of the parameters $c(t)$ and $a(t)$ can be expressed as follows:

$$\dot{c} = \gamma\left[1 - \left(\frac{c}{c_s}\right)^n\right](a_{\max} - a) + \eta(c_{0s} - c)(1 - a_{\max}) - \\ - \beta c(a_{\max} - a) - \alpha c a, \qquad (3a)$$

$$\dot{a} = -ka\left[a^2 - a_{\max} \cdot a + \frac{1}{4}a_{\max}^2 \frac{c_{\max} - c}{c_{\max} - c_{\min}}\right] \\ \text{when } c \leqslant c_{\max}, \qquad (3b)$$

$$\dot{a} = 0, a \equiv a_{\max} \text{ when } c > c_{\max}, \qquad (3c)$$

where c_s and n are respectively the uptake saturation concentration and the parameter of the dynamics of the uptake of the toxicant by components of the system which can undergo a change in their structure on uptake, c_{0s} is the uptake saturation concentration of the fragments whose structure does not change on uptake of the toxicant, and $c_{\max}$ and $c_{\min}$ are the critical concentrations of the toxicant at which abrupt transitions of the system to the state with a rearranged structure (from the initial non-rearranged state) and to the state with the initial structure (from the state with a rearranged structure) respectively begin.

In order to determine the entire set of the possible stationary states of the system (3a)–(3c), it is necessary to analyse the phase diagram of the model (Fig. 3) in the states space (a, c).[87] The intersection of a zero isocline $c = 0$, which is unique for the specified system of parameters α, β, γ, and η family of the possible curves I–IV of this type with various branches of the zero isocline $a = 0$ (the equation of state of the structure) corresponds to the stationary solutions on the phase plane. There is a possibility of the intersection of the three stable branches of the equation of state MA, GB, and BE with curves I, III, and IV respectively. An unstable solution of the system with the generation of the limiting cycle DABG and the appearance of an auto-oscillatory state in the alteration of the structure corresponds to the intersection of curve II with the unstable branch GA. Fig. 4 illustrates the kinetics of the attainment of a stationary state in the regions MA, GB, and BE by the toxicant concentrations.

Within the framework of this model, the contact between the component of the living system and the environment does not alter its structure provided that the uptake concentration of the toxicant does not exceed c_{max}. Following the dynamic attainment of the critical concentration of the toxicant taken up ($c = c_{max}$), processes inolving a rearrangement of the structure of the component begin and either reach an oscillatory state (for system parameters giving rise to the type II zero isoclines) with periodic variation (from 0 to a_{max}) of the structure of the component and of the concentration of the toxicant taken up (from c_{min} to c_{max}) or are completed by the establishment of a stationary state (a_{st}, c_{st}) of the system. For parameters giving rise to the zero isocline I, the system returns to the initial non-rearranged structural state (0, c_1), in the case of the zero isocline (III) the state (a_3, c_3) is generated, while in the case of the zero isocline (IV) the state produced is a_{max}, c_4).

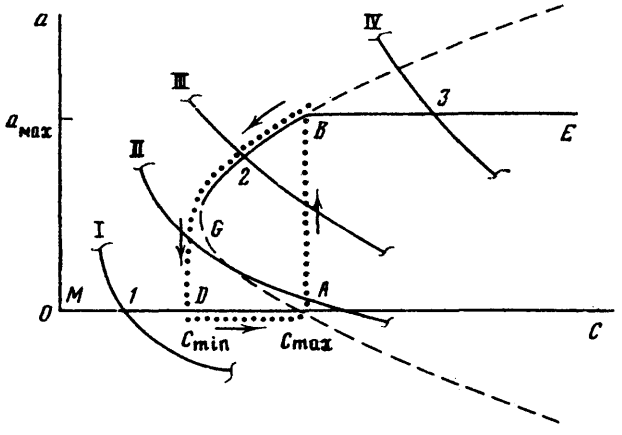


Figure 3. Phase portrait of the model.[87] Dashed lines—unstable or non-realised branches; circles—possible location of limiting cycle. The arrows indicate the direction of motion of the representative point. The numbers of solutions *1*–*3* correspond to the numbers of the regions of existence of the stationary regimes (see also text).

Thus, if the concentration c_{max} is attained in the component of the system considered for certain concentrations ρ_{lim} of the toxicant in the external environment, then it is natural to relate ρ_{lim} to the limiting permissible concentration LPC. In other words, the LPC for different individuals may be defined as the concentrations of harmful components of the external environment for which the organism undergoes a transition to another state which is different from the normal state. Such changes in states can be either reversible or irreversible depending on whether the state returns or does not return to the initial state when the harmful components are removed from the medium. In the former case, one may speak of ecological modulations, while in the latter we have ecological modifications and degradation of the system.[6] The state of the organism can then be characterised in terms of different features (the contents of the harmful component, the rate of metabolic processes, the changes in the functional activities of various systems of the organisms, disturbances in the hereditary apparatus), etc. Evidently the deviations of the states of individuals from the norm give rise to general changes in the evolution of eco-systems. In particular, an increase in the content of the harmful component (carcinogen) in certain individuals can constitute a risk to predators feeding on the given individuals, etc. This should be reflected in the system of equations for the evolution of the eco-system as a change in the "level of quality" of the predator's food. A possible scheme for the construction of equations for the evolution of eco-systems taking into account the modulating or modifying changes occurring in them under the influence of fluctuating external factors is presented below.

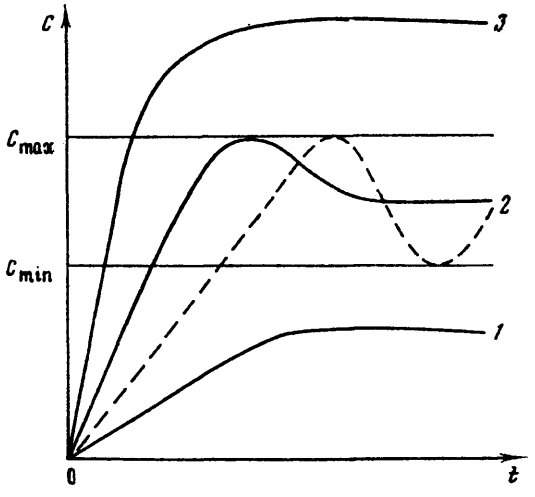


Figure 4. Characteristic form of the kinetic curves for the attainment of a stationary regime by the toxicant concentrations.[87] The numerals opposite the curves correspond to the numbers of the regions of existence of the stationary regimes; the possible occurrence of oscillatory kinetics is indicated by the dashed line.

3. Equations of the dynamics of eco-systems with allowance for various states of individuals

A general approach to the modelling of ecological modifications can be formulated on the basis of kinetic equations for space–time distribution functions of the subsystems in the overall space of the characteristic parameters with introduction of functions of random sources and sinks modelling the characteristics of the changes in state both as a result of the internal activity of the above subsystems and due to factors external to the systems.[20] The deterministic nature of the kinetic equations makes it possible to determine beforehand the nature of the possible states and to estimate their relative stabilities, while the fluctuation influences on the system determine the occurrence of one of several possible states in the vicinity of the bifurcation point.[77]

Since biological systems are highly non-equilibrium and open systems, in the analysis of their evolution it is necessary to take into account two fundamental factors. Firstly, the probability of the transition of the system to one of the stable states beyond the bifurcation threshhold of the thermodynamic branch when some

kind of controlling parameter λ is altered depends on the specific state of the system in the given time interval. The population of the species, the solar activity, the ionisating radiation dose, the amount of dissolved organic matter of allochthonous or autochthonous origin (if one is dealing with aqueous systems) etc. may be considered as the controlling parameter.

Secondly, the evolution of the highly non-equilibrium eco-systems can be effectively acted upon by weak external factors. In principle, without exerting any effects on equilibrium systems, such factors can determine the preferred selection of a particular stationary state beyond the bifurcation point ("forced bifurcation"[20]). Such factors may be, in particular, electromagnetic radiation in different frequency ranges (starting from weak low-frequency influences[88]), changes in the qualitative composition of the environment, etc. The accumulation of the changes occurring under these conditions and the subsequent fluctuation influences of diffeent kinds may lead either to slight but fundamental changes in eco-systems or to new bifurcation transitions.

Evidently the modelling of the evolution of eco-systems involves major fundamental and mathematical difficulties. Each eco-system is a multicomponent object with a multiplicity of internal feedbacks (including negative feedbacks) and subjected to multifactor influences of a wide variety of different types. The state of each system can be described by the distribution function $f(t, \mathbf{r}, \Gamma)$, where t is the time, $\mathbf{r}$ the radius-vector, and Γ the set of parameters determining the state of the given system. For a quantitative analysis of the equations for the evolution of the system (kinetic equations for the function f), complicated in many instances *a priori* by the uncertainty and the ambiguity in the overall parameters Γ, it is convenient to employ characteristics introduced in the mathematical description of random motion in mechanical and hydrodynamic systems.

Conservative systems are usually considered for which an element of the phase space undergoes a change in shape after a time but retains its volume, and dissipative systems for which the volume of the element of the phase space contracts during motion, i.e. structure formation in the system takes place as a result of an external excitation with increase in the controlling parameter. Dissipative systems are coherent. They behave as a single whole as if each species were "informed" about the state of the system as a whole. Under these conditions, a decrease in the controlling parameter in classical dissipative systems leads reversibly to the initial state of the conservative system.

In eco-systems the situation may be fundamentally different. The changes occurring in communities under conditions of the reversible alteration of certain controlling parameters may be reversible and irreversible, i.e. may be characterised by a kind of "hysteresis". The irreversible changes in eco-systems, including those characterised by a decrease in the volume of elements of a generalised phase state ($\mathbf{r}$, Γ) will be defined here as ecological modulations. The irreversibility of the changes occurring in the eco-system shows that the magnitude of the controlling parameters has exceeded the adaptive possibilities of the biocenosis. Here one should refer to ecological modifications and, when metabolic and ecological regression processes have developed,[6] to eco-system degradation processes. Evidently in each specific case it is necessary to determine in addition the minimum level of irreversible changes, indicating the occurrence of ecological modulations and modifications and of ecological regression. In particular, one can detect changes in the genetic apparatus.

So far several systems are known (mechanical, hydrodynamic, etc.) for which it is possible to describe analytically the phenomena involving the appearance of dissipative structures under the influence of controlling factors (the constraining force on excitation of the motion of a pendulum, the temperature difference in the Benard system, the energy introduced into the Henon–Hales system,[77] etc.). In ecological systems one cannot even be certain about the adequacy of the description of stationary states and difficulties arise even in the modelling of the deterministic behaviour of such systems. We shall therefore refer only to qualitative analysis of the characteristics of the evolution of communities.

The nature of the transition to bifurcation points and the factors which determine such transitions to new levels of organisation of communities are of interest. In this case, it may prove sufficient to analyse a relation for the correlation function of fluctuations ("correlator") which is simpler than for the distribution functions $f(t, \mathbf{r}, \Gamma)$:

$$\delta g_a = \int \langle \delta f_a(t_1; \mathbf{r}_1, \Gamma_1) \delta f_a(t_2; \mathbf{r}_2, \Gamma_2) \rangle \mathrm{d}\Gamma_1 \, \mathrm{d}\Gamma_2 \,, \tag{4}$$

where $\delta f_a = f_a - \bar{f}_a$, where $\bar{f}_a$ is the stationary distribution function for the subsystem a. The symbol $< \ldots >$ denotes averaging over all possible states of the subsystem. In the case of spatially homogeneous systems, the averaging involves integration with respect to one of the radius-vectors and one of the times. Here one introduces the variables $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and $\tau = t_1 - t_2$. In particular, the average residence time of substances in a flow reactor is the external controlling parameter for the classical Belousov–Zhabotinskii reaction—the oxidation of malonic acid in the presence of cerium sulphate and potassium bromate where spectroscopic methods detect oscillations in the concentrations of Ce^{3+} and Ce^{4+} as a function of time. In this case the function $\delta g(\mathbf{r}, \tau) = \delta \bar{g}(\tau)$ introduced is a measure of the correlation between the successive changes in the Ce^{4+} concentration detected from the selective light absorption by these ions. For a regular motion, the function $\delta \bar{g}(\tau)$ is constant or oscillates, while in the chaotic regime $\delta \bar{g}(\tau)$ decreases rapidly (frequently exponentially) with time.[77,89]

Naturally the equations describing the evolution of the function $\delta g(\tau)$ are in general complex and difficult to analyse but the use of the phenomenological approximations to the correlation times, usually employed for such equations, may become a basis for the qualitative analysis of the models of eco-systems. Indeed, solutions of the equations for the function f when the system is acted upon by stochastic factors should be treated either in terms of generalised functions[90] or, following the Langevin method,[91] in terms of probabilities—as functions of the density of the probability of the occurrence of various values of f. At the same time, analysis of the relaxation equations, which are naturally not as informative as the equations for f, may prove an easier task. Here it is more convenient to analyse the equations for the Fourier components:

$$\delta \varphi_a(\mathbf{k}, \omega) = \int_{-\infty}^{+\infty} \int \delta g_a(\mathbf{r}, t) \exp[-i(\mathbf{kr} - \omega t)] \, \mathrm{d}\mathbf{r} \, \mathrm{d}t. \tag{5}$$

This is partly associated with the simple analytic form of the Fourier components of external stochastic influences.

We shall now quote the simplest example of the introduction of relaxation equations for correlators in a linear approximation, where the "equation of motion" for the function $\delta \tilde{f}_a(t)$ assumes the form

$$\frac{\mathrm{d}}{\mathrm{d}t} \delta \tilde{f}_a = -\sum_b \lambda_{ab} \delta \tilde{f}_b, \tag{6}$$

where λ_{ab} are constant coefficients. Correlators of the quantities $\delta\tilde{f}_a$ satisfy the same linear equations:[92]

$$\frac{d}{dt}\langle\delta\tilde{f}_a(t)\delta\tilde{f}_c(0)\rangle=-\sum_b\lambda_{ab}\langle\delta\tilde{f}_b(t)\delta\tilde{f}_c(0)\rangle,\quad t>0 \quad (7)$$

(the subscript c in this system of equations is of arbitrary significance). When the system departs appreciably from equilibrium and also when it is acted upon by random factors capable of displacing it from the initial stationary state, the equations describing the devleopment of the system prove to be non-linear.

The simplest non-linear equations with feedback,[76,93,94] in which account is taken of interspecies interactions and also of influences of abiotic factors on the system, are usually analysed in relation to the evolution of eco-systems. A way of describing the state of the system, differing somewhat from that in the literature,[76,93,94] is described below. It makes it possible to use the above synergistic approaches[20,77] for the analysis of the evolution of eco-systems taking into account all the existing internal interrelations (including positive and negative feedbacks) and external factors.

The state of eco-systems may be characterised by the presence of a definite number of trophic levels. We shall attribute to each organism of the given eco-system two numbers (ij). The order of the trophic level will be designated by the index i ($i = 1, 2, \ldots, l$), starting from the highest-order level of consumers ($i = 1$) and ending with the level of producers ($i = l$). The numbering of individuals in each trophic level i will be specified by the index j ($j = 1, 2, \ldots, N_i$), where N_i is the number of individuals in the level i. We shall assume that each individual is in one of several possible states (these states s may be characterised from the standpoint of physiology, biochemistry, etc. depending on the formulation of the problem and the level of the problem considered).

Let θ_{ij}^s represent the relative populations of each of the states $s(ij)$ for individuals (ij) subject to the normalisation condition

$$\sum_s\theta_{ij}^s=1.$$

Under these conditions, certain stationary states of the population $\theta_{ij}^{s_0}$ correspond to the state of the eco-system in the norm. The states s_0 and the corresponding values of $\theta_{ij}^{s_0}$ depend in the general case on the natural age of the entire eco-system and on its previous history and vary with fairly large characteristic times in conformity with the programmed most probable evolution of the given eco-system up to its significant modification with transition to a climatic state. Since we are interested in evolutionary changes associated with the influence of external factors of the community and occurring over a much shorter time than that of natural succession, we shall consider the evolution of an eco-system as a quasi-stationary process and shall not introduce explicitly the time variation of s_0. We shall represent the equations for the evolution of the eco-system in the form

$$\frac{d\theta_{ij}^S}{dt}=\sum_{i'j';s'}\hat{D}[\theta_{ij}^s|\{\theta_{i'j'}^{s'}\}]+$$

$$+\sum_{s'}\hat{L}[W(ij;s'\to ij;s)\theta_{ij}^{s'}-W(ij;s\to ij,s')\theta_{ij}^s]+(g_{ij}^s-r_{ij}^s), \quad (8)$$

where $\hat{D}$ is a non-linear operator defining the evolution of the eco-system as a consequence of the internal interrelations present in it under standard external conditions ensuring natural evolution. The second term, characterised by the action of the linear operator $\hat{L}$, defines the influence on the evolution of the system by the fluctuations of external factors in time and the influence of factors of a new kind (for the given eco-system) expressed in terms of the probabilities W of the transition of the system from the state s to adjacent states s' and the reverse transition from the possible state s' to the state s.

For example, when biocidic ionogenic additives are introduced into the environment, ionic impurities are incorporated into a wide variety of components of the organism, in particular into the active ion transport systems, which can influence fundamentally the kinetics of their functioning as a consequence of changes in the initial distributions of local electrostatic fields in the vicinity of ionic channels in a biological membrane and also the possible conformational rearrangements in the protein–lipid complexes.[24] This factor may be taken into account by altering the probabilities $W(ij;\ s\to ij,\ s')$ in Eqn. (8) and it should influence the populations θ_{ij}^s and hence the evolution of the entire eco-system. Evidently the influence of ionising radiation on the structural elements of biological systems can be described similarly [in terms of the change in the probabilities $W(ij;\ s\to ij,\ s')$].

The time-variable quantities such as the pH, intensity of the thermal and UV radiations, concentration of nutrient substances (if one is dealing with aqueous cenoses), etc. may behave as the fluctuating factors in Eqn. (8). The inclusion of "new" factors in the second term implies the possibility of a significant influence by the latter on the evolution of the eco-system. The third term in Eqn. (8) characterises the rate of change of the population θ_{ij}^s as a consequence of external sources (g_{ij}^s) and sinks (r_{ij}^s) and contains a component rapidly fluctuating in time. Therefore, in the second and third terms it is sometimes convenient to differentiate fluctuation components and to represent them by generalised functions, for example:

$$g_{ij}^s-r_{ij}^s=\sum_k a_{ij;k}\theta(t-t_k),\quad \theta(x)=\begin{cases}1 \text{ when } x>0\\ 0 \text{ when } x<0\end{cases} \quad (9)$$

or

$$g_{ij}^s-r_{ij}^s=\sum_k b_{ij;k}^s\delta(t-t_k). \quad (10)$$

Here $\delta(x)$ is a delta-function.

Assuming that the second and third terms are perturbing factors, it is possible to analyse the devleopment of the eco-system under the conditions where these factors operate, provided that the evolution of the unperturbed system, expressed in a general form by a system of non-linear equations for the populations $\overline{\theta}_{ij}^s$, is assumed to be known, i.e. the relations $\overline{\theta}_{ij}^s=\overline{\theta}_{ij}^s(t)$ are known. In order to obtain these relations in each specific case, it is necessary to set up and solve the corresponding model system of non-linear equations whose parameters can be obtained in the course of special studies. As pointed out above, we shall be interested in the variation of the differences $\delta\theta_{ij}^s=\theta_{ij}^s-\overline{\theta}_{ij}^s$ as a function of time. We do not assume that these changes are small in the general case ($\delta\theta_{ij}^s\lesssim 1$). As a consequence of the non-linear inter-relations in the system, the change in the populations of states s (with the transition $s_0\to s_1$) for the individuals (ij) may influence significantly the evolution of the entire system as a consequence of the influence of "weak" factors.

Evidently a fully defined state s_0^ξ should correspond to each set ξ of external factors (natural for the given eco-system). If one may formulate the concept of a mutually unambiguous correspondence between the states s_0^ξ and the state of the environment, then the

changes in the values of s_0^{ξ} (transition to adjoining states s from the state s_0) will be qualified as a modulation transition. On the other hand, if irreversible changes in the states s_0 take place (for example, there is a transition to the state s' accompanied by a change in hereditary structures), then we shall refer to the modification or degradation of the states of (ij). In this case fundamental changes may occur in the entire eco-system owing to the existence in the latter of internal interrelations. The problems of the evolution of the eco-systems involve precisely the discovery of the possibilities of such irreversible changes detected via the functions $\delta\theta_{ij}^{s'}(t)$. As mentioned above, it is more convenient to analyse the evolution of correlators

$$\delta g_{ij}^{ss'}(t)=\langle\delta\theta_{ij}^{s}(t)\delta\theta_{ij}^{s'}(0)\rangle,$$

where s' is any of the possible states or components of the specific spectrum $\delta\varphi_{ij}^{ss'}(\omega)$.

V. The influence of mass transfer processes in the earth–atmosphere system on the state of the biosphere

The preservation of life on Earth under the conditions of continuing intense anthropogenic influences may depend to a large extent on a series of global factors influencing the evolution of large eco-systems (seas and oceans and part of the continents). Here we have in mind the phenomena occurring not only in the Earth's biosphere but also in the upper layers of the atmosphere and in the deep layers of the Earth. These are in the first place the turnover of water and of biologically important elements (C, O, N, P, and certain others) in nature. The occurrence of the corresponding cycles is varied and, apart from the movements of water in the atmosphere and streams of subterranean waters carrying a wide variety of inorganic and organic components, it may involve the circulation of water in the oceans[95,96] and the turnover of the oceanic crust (its formation from melts in the reservoir in the Earth's mantle accompanied by their partial degassing with subsequent subduction of the oceanic lithosphere[97]).

1. Processes in the upper layers of the atmosphere

In this Section we shall discuss the possibility of the existence of fairly intense flows of water, the molecules and cluster of which can entrain also other inorganic and organic components in the upper atmosphere, into the stratosphere and further into the ionosphere and space. The discovery and quantitative analysis of the magnitude of such directed fluxes of substances is essential for the construction of models of the evolution of large eco-systems and for the understanding of the evolution of the entire biosphere as a whole.

The evident influence of the upper layers of the atmosphere on the evolution of biological communities is demonstrated by the ozone layer, which protects biocenoses against the harmful effects of intense UV radiation.[33] The conclusion of international agreements limiting the manufacture and large-scale employment of Freons, which, without reacting with the tropospheric radicals, enter freely the stratosphere, has in fact been associated with the global nature of the danger of the breakdown of the ozone layer on photodissociation of the Freons in the stratosphere.

Many inorganic and organic compounds have been detected in the upper atmosphere at heights of approximately 100 km,[98–100] which indicates the unsuitability of equilibrium barometric ideas for the determination of the density and composition of the atmosphere. At the heights indicated, water may be present in anomalously large amounts, forming silvery clouds, and the sources of this water are by no means always associated with volcanic eruptions. Seasonal changes in the relative concentrations of sodium and potassium in the silvery clouds have been detected, agreeing in the summer with the ratio characteristic of sea water.[99] This shows that sodium and potassium enter the silvery clouds with the wind-driven sea water spray and points to terrestrial rather than cosmic (as a consequence of the interaction of the solar wind and the ionosphere) causes of the appearance of silvery clouds at the heights indicated.

The rate of supply of a wide variety of components from the troposphere to the upper layers of the atmosphere is determined primarily by the turbulent mixing of the atmosphere at least up to heights of approximately 110 km.[101] Evidence for the existence of intense migrations of air masses at heights of 80–90 km (the rate of the wind-induced displacements is approximately 1–2 km h^{-1}) was obtained, in particular, by analysing the form of the silvery clouds and also on the basis of spectroscopic data.[102] A possible source of the turbulence, ensuring the transport of components indicated, is internal gravitational waves propagated from the regions of active meteorological processes occurring in the lower atmosphere (fronts, zones of increased activity) and also from mountainous regions.[101]

The transport of water to the upper atmosphere can be effected by charged water clusters in the electric fields arising between storm clouds in the ionosphere.[98] According to estimates,[98] approximately 1 g of H_2O can be transported with ionic clusters containing 10 H_2O molecules from an area of 1 km^2 per hour with a characteristic overall current of approximately 0.1 A. This corresponds to the water content in a silvery cloud with a volume of approximately 1 km^3 and made up of ice particles approximately 0.12 μm in diameter at a concentration of ~0.1 of a particle per cm^3. Evidently such "upward rain" or "rain on the ionosphere" should eliminate aerosol particles and gaseous components dissolved in water from the atmosphere.

The subsequent transfer of the water molecules and the impurity species, which partly dissociate and ionise, to the upper layers of the ionosphere can occur under the influence of convective plasma streams developing in the ionosphere–magnetosphere system as it drifts through crossed electric and magnetic fields. The electric fields in the boundary regions of the ionosphere arise regardless of the possible fields between powerful storm clouds and the ionosphere.[103,104] Analysis has shown[105] that various types of distribution of the large-scale electric field may arise in the ionosphere–magnetosphere system. A definite type of convective movement of the plasma corresponds to each distribution. The characteristic inhomogeneities existing under these conditions, whose extent in space is approximately $10-10^3$ km,[106] may influence strongly the kinetics of the removal of the components to the upper layers of the ionosphere, including the region of the exosphere (above 500 km) where processes involving the thermal heating of the species as a result of the absorption of UV quanta by oxygen and nitrogen molecules from sunlight take place vigorously. A proportion of the molecules and atoms then acquire thermal velocities exceeding 11.2 km s^{-1}, which is sufficient to drive the species outside the limits of the Earth's atmosphere.

The removal of components of the Earth's atmosphere (predominantly water molecules and the oxygen atoms and ions formed as well as nitrogen atoms and molecules) outside the limits of the Earth's gravitational field occurs also on interaction of the solar wind—the stream of charged particles (predominantly protons,

helium nuclei, and electrons) emitted by the sun—with the external layers of the ionosphere, which form the boundary of the magnetosphere and are turned towards this stream.[103] In the transition layers, formed at the boundary of the region of the strong magnetic field (magnetosphere) and the rapidly moving plasma, strong electric fields arise.[107,108] These fields can induce magnetospheric convection—the acceleration of plasma streams, which promote the removal of neutral and charged components into the region of the direct influence of the solar wind, which "blows off" the atmospheric species into space. The high energy components of the solar wind penetrate the atmosphere down to heights of 40–60 km, so that the processes involving the "blowing off" of species can proceed with different efficiencies as a function of the thickness of the atmosphere—from the mesosphere up to heights exceeding approximately 1000–1500 km, where appreciable concentrations ($\sim 10^2$ cm^{-3}) of oxygen and nitrogen ions have been detected by modern instruments.[109] The possibility of the operation of this mechanism of the removal of atmospheric species into space is indicated by data concerning the effect of the solar wind on cosmic rays. Under conditions where the Earth crosses part of the recurrent high-speed stream of solar wind, part of the stream of cosmic rays "intended" for the Earth is driven off and does not reach the Earth.[110]

The efficiency of the "blowing off" effects increased with increase in the velocity of the particles in the solar wind, provided that their energy is sufficient for the generation of secondary particles and the formation of particle showers, since large overall momenta can then be transmitted to the species (ions, molecules, and clusters) in the atmosphere. It has therefore been of interest to analyse the phenomena occurring on the sun and responsible for the increase in the velocity of the particles of the solar wind. It has come to be assumed that the high-speed streams of the solar wind arise in the coronal holes or in unipolar magnetic regions with an open configuration of the magnetic field.[111] Another possibility for the generation of high-speed streams of the solar wind may be associated with the non-stationary processes in the active regions of the sun or in the vicinity of active formations.[111–113] The acceleration of the protons emitted by the sun is induced, in particular, by the formation at distances of approximately 2000 km from the sun's surface, where the temperature and density decrease sharply, of magnetohydrodynamic Alfven waves,[114] into which the non-linear acoustic waves generated by the layers of the sun's photosphere are transformed.

The generation of streams of the solar wind having anomalously high energies, up to relativistic values, has in fact been attributed to the Alfven waves arising in powerful solar eruptions. The fact that the energies E_p of the protons emitted by the sun can be $E_p \lesssim 3000$ MeV is indicated by the streams of neutrons (these are formed in the atmosphere together with π-mesons) having energies up to 1000 MeV after certain solar eruptions (for example on 21st June, 1980 and on 3rd June, 1982).[115,116]

Since the high speed streams of the solar wind can intensify the "blowing off" of the components of the atmosphere into space, the elucidation of adequate mechanisms of the formation of such streams and of the relation with the visible phenomena and processes on the sun (see also the footnote on p. 1197 below) is important for the analysis of the processes involving the partial "replacement" of the components of the atmosphere and its purification (see below), which influence the evolution of the Earth's biosphere. This is of particularly great current interest in connection with the intensification of the anthropogenic influences on the Earth's ionosphere by powerful electromagnetic radiations, by chemical substances emitted during the flights of ultrasonic aeroplanes, and by the ignition of powerful rockets[117,118] and also in connection with the possibility of stimulating the processes in the ionosphere (for example, on excitation in the latter of plasma-wave discharges[119]).

Naturally, the fluxes and composition of the components carried away from the Earth vary with time and depend on many factors. The discussion in the present Section of the entire set of problems of the "upward mass transfer" beyond the limits of the Earth's gravitational influence appears essential, because it is not clear *a priori* which of the stages of the transport of the components of the atmosphere (primarily water, oxygen, and nitrogen) into space is rate-limiting. It might be thought that each of the stages considered above may under certain conditions prove to be rate-limiting. In the next Section, we shall discuss the range of problems associated with the discovery of the processes occurring in the inner regions of the Earth, which are responsible for the current stable state of the atmosphere despite the processes involving the "cleaning" of the atmosphere by the removal of its components into space, described above.

2. Processes in the inner regions of the Earth

The deep layers of the Earth exert not only a direct influence on the eco-system (during earthquakes or on emission into the atmosphere of the products of volcanic activity) but also an indirect influence, determining the Earth's magnetic field. The influence of the magnetic field on the evolution of eco-systems is exerted when it acts on the functioning of biological objects[24,88,120] and also on the state of aqueous systems as living environments.[24,48,49]

It will be shown below that processes associated with the generation of the Earth's magnetic field can also lead to ecological consequences. According to existing ideas,[121–125] the observed magnetic field is caused by the convective movement, arising in the course of the Earth's rotation, of the conducting medium—the Earth's liquid metal core enclosed in a spherical layer with dimensions $0.19\ R_0 < R < 0.57\ R_0$ between the mantle and the solid inner core (R_0 is the Earth's radius). An obligatory condition for the functioning of this mechanism ("the dynamo-mechanism") is the gyrotropic nature (reflecting non-invariance) of the convective streams in which either right-hand screw or left-hand screw motions should predominate. Mathematically this is expressed by the non-zero value of the average helicality of the streams generated: $\langle \mathbf{v}\,\mathrm{rot}\,\mathbf{v}\rangle \neq 0$, where $\mathbf{v}$ is the local flow rate vector. The Earth's magnetic field has a poloidal (meridional) component with lines of force in the meridional plane and a toroidal (azimuthal) component in which the lines of force run along the latitudes. Under these conditions, only the meridional field has a radial component and extends into the environment. The convective movements in the liquid-metal core, with different angular velocities of the rotation of its different layers, lead to the transformation of the magnetic field indicated, including the interconversions of the components specified above.[121,122] The energy consumed under these conditions on dissipation in the functioning of the dynamo is evolved in the gravitational separation processes in the Earth's liquid core—in the precipitation of heavy substances, in the first place iron, at the lower limit of the liquid core and of light substances, containing the elements S, O, and Si, at its outer limit.

It is important to emphasise that the dynamo-mechanism is merely a mechanism of the intensification of certain seeding magnetic fields, which are generated in the Earth's liquid core. According to Dolginov,[122] the most probable mechanisms of the

generation of such fields are associated with galvanoelectric phenomena, in particular with the "battery" effect. The latter is characteristic of the Lorentzian plasma[92] when the electron concentration and pressure gradients are not parallel. Under the conditions on Earth, the battery field is naturally associated with the large-scale irregularities in the temperature and chemical composition at the interface between the mantle and the liquid core. The changes in the magnitude and sign of the geomagnetic field which occurred in the course of geological epochs (such data are obtained from the analysis of the magnetisation of ancient rocks) are associated, according to Dolginov,[122] with the change in the composition of the interface as a result of the exchange of material between the mantle and the core (cf. Ruzmaikin et al.[124]).

Despite the comprehensive development of the theory of terrestrial magnetism, the question of the nature of the convection in the Earth's core, the nature of the seeding magnetic fields, has still not been unambiguously solved. We shall consider below one of the possible hypotheses[24] concerning the nature of the seeding geomagnetic field, from which follow a series of global consequences related to the evolution of the Earth's eco-systems and to the characteristic features of the formation of a number of useful minerals, the optimum search for and the rational employment of which constitute an important aspect of man's nature-protecting activity.

It has been postulated[24] that in the region of the boundary between the outer part of the Earth's liquid metal core and the lower mantle, where high pressures are combined with shift deformations and the breakdown (regrinding) of rocks, endothermic chemical reactions take place. One of the initial reactants (hydrogen) is dissolved at high concentrations ($\sim 10^{24}$ cm^{-3}) in the Earth's liquid metal core (this hypothesis does not conflict with the possible ideas concerning the formation of our planet).[126]† According to this hypothesis, the Earth's core is a fairly capacious source of hydrogen, which has been active in the course of more than two billion years, i.e. throughout the existence of the hydrosphere. For the densities of the hydrogen dissolved in the Earth's core indicated above, its mass ($\sim 2 \times 10^{26}$ g) exceeds the overall mass of hydrogen in the hydrosphere (1.8×10^{23} g) by three orders of magnitude. This hypothesis is justified by the multiplicity of the consequences arising from it (see below), some of which are apparently susceptible to direct tests. Under the conditions indicated, the hydrogen, which is present in the atomic ionised state in a melt of catalytically active iron-group elements and other heavy elements, can effectively reduce the metal oxides MO_x in the lower mantle with formation of water:

$$MO_x + xH_2 \dashrightarrow M + xH_2O, \qquad (11)$$

and can interact with the metal carbides in the lower mantle, forming methane:

$$M_pC + 2H_2 \dashrightarrow CH_4 + pM. \qquad (12)$$

Water arises also on interaction of hydrogen with the oxygen approaching the core–mantle interface. The products formed as well as the helium and nitrogen emerging from the core are removed to the upper layer of the mantle and then into the Earth's crust.

†Another consequence which may follow from the above model[126] is that helium, nitrogen, and oxygen are dissolved (in smaller amounts than hydrogen) in the Earth's core.

Presumably the interface between the Earth's core and the mantle is not an ideal sphere. It is more likely to be "indented" in a radial direction from the centre and is non-uniform as regards the composition of the rocks at the boundary with the liquid core. In view of the high rates of the catalytic processes indicated, convective mass streams may be initiated in a number of regions of such a non-uniform boundary in the liquid phase of the core. They may be responsible for the transfer of hydrogen to the reaction zones and the temperature gradients generated in endothermic chemical reactions [in the first place on occurrence of reaction (11)] may give rise to certain spatially fixed dissipative structures. Owing to the establishment of non-uniform (with respect to the interface) temperature jumps

$$\Delta T(\mathbf{r})|_{s_i} = T_{s_i}(\mathbf{r}) - T_0 < 0,$$

where $T_{S_i}(\mathbf{r})$ is the local temperature of the lower mantle–liquid core interface (the surface S_i) and $T_0 \equiv T_{S_0}$ is the temperature "at the bottom" (the surface S_0) of the convective zone considered, structures of a mixed type can be formed—Benard[77] and Marangoni[127] structures. Evidently, owing to the non-uniformity (chemical, temperature-dependent) of the surface, asymmetric irregular dissipative structures (humps, eddies) should arise. Such irregularity gives rise to a non-zero average helicality of the streams of the liquid-metal medium generated, which is essential for the generation of the seeding magnetic field.

Owing to the presence of a temperature gradient in the radial direction in such convective structures the temperature in each section parallel to the interface varies within the limits of the cell[77] from a certain maximum quantity at the cell boundary S_u, where the convective stream is directed from the bulk of the core upwards towards the interface, to the minimum value at the boundary S_d, where the stream is directed downwards—into the bulk of the core. Conditions are thereby created for the occurrence of thermodiffusion streams (the Soret effect) of the highly mobile electronic component in the direction from the boundary S_u to the boundary S_d. As a result of this, electric fields $\mathbf{E}_c$, compensating the thermal diffusion electron stream, arise in the region between the above boundaries. These fields must be characterised not only by the components $E_c^{\perp}$ normal to the S_u and S_d surfaces (as a consequence of the Soret effect) but also by the components $E_c^{\parallel}$ parallel to the above surfaces (owing to the variation of the average temperature in the radial direction). Under these conditions, double electrical layers are formed at the boundaries S_u, S_d, S_i, and S_0 and also in the sections S_m through the convective zone where the quantities $T(\mathbf{r})|_{S_m}$ are characterised by local minima or maxima.

It is to be expected that the redistribution of the labile electron density as a consequence of the Soret effect and the generation of the electric fields $\mathbf{E}_c$ lead to additional stabilisation of the dissipative structures. In addition, owing to the appearance of the electric field component $E_c^{\parallel}$, closed circuits L are formed in each dissipative cell, in which eddy currents flow:

$$\oint_L \mathbf{E}_c \, d\mathbf{l} = -\frac{1}{c}\frac{d}{dt}\int_S \mathbf{B} \, d\mathbf{S} \neq 0,$$

where $\mathbf{B}$ is the electromagnetic induction vector, $d\mathbf{l}$ a differential element of the closed circuit L, and S the surface resting on the circuit L.

Evidently in the dissipative cell adjoining the cell under consideration an eddy current flowing in the opposite direction is generated. However, owing to the non-uniformity, mentioned above, of the convective structures formed, in the system investigated the induced resultant magnetic field can be regarded, together with other fields analysed,[122] as a seeding field. The orientation of the circuits L will depend on the geometrical characteristics of the chemical non-uniformities of the interface and on the differential rate of rotation of the liquid-metal phase of the core in the region of the formation of the dissipative structures considered.‡

Evidently the geomagnetic field (when the model considered is adequate) must be associated with the convective mass streams in the Earth's core, of maximum spatial extent, which are generated on reduction of oxides (the commonest compounds in the mantle) accompanied by the formation of water. In a critical analysis of this hypothesis, it is essential to take into account the available data concerning the distribution of water in the Earth's crust and in the hydrosphere during different geological eras and the stochastic changes in the Earth's magnetic field occurring in the given model as a consequence of the decrease in the rate of the chemical reaction (either as a consequence of the exhaustion of the oxides at the core–mantle interface or due to the limitation of the product removal stages). At the same time, data concerning the stochastic nature of the changes in the geomagnetic field apparently give rise to conclusions about the structure of the liquid core–lower mantle interface and about the kinetics of the endothermic reactions occurring in this region and initiating the formation of dissipative structures in the Earth's liquid core. This makes it possible in its turn to predict further changes in the geomagnetic field, which is of undoubted importance for ecological modelling.

A further series of consequences with an ecological and nature-protecting bias follow from the foregoing and refer to problems of the formation of useful minerals. The discovery of the mechanisms of the formation of deposits of ores, petroleum, gas, and coal is useful not only from the standpoint of an effective search for them but also for the rational mining and exploitation of these deposits, which is particularly important since the Earth's resources are already to a large extent exhausted. A theory of the mixed inorganic and organic nature of the formation of petroleum can be established on the basis of the hypothesis that processes (11) and (12) occur.

The methane generated in reaction (12) may participate in the chain of further catalytic incomplete oxidation (with participation of water and oxygen molecules) and hydrogenation processes. These reactions, occurring in the submicropores of the rocks in the Earth's lower mantle at more moderate temperatures than those corresponding to the formation of methane, lead to the synthesis of alkanes (possibly via the formation of CO,[129] alkenes, alkadienes, alkynes, arenes, and acenes,[130–134] which are the simplest components of petroleum.

The subsequent pathway leading to the conversion of the above components into more complex and heavier petroleum fractions involves the transfer of the components via a system of transport channels under the influence of static pressure gradients into regions where their organic (possibly in the presence of fossil residues of organic and bio-organic nature "stored" in these regions) and microbiological transformation takes place under the conditions of diagenesis.

Numerous special studies have been devoted to the problems of the biochemistry and geochemistry of petroleum formation.[135–141] The proposed scheme apparently makes it possible to reconcile the theories of the organic and inorganic origin of petroleum. Firstly, it incorporates naturally organic and microbiological reaction stages,[138–140] including those discovered in the study of petroleum biomarkers.[140] Secondly, the scheme developed here makes it possible to understand the inorganic origin of petroleum and gas in deep deposits.[141] It is regarded as established[142] that the existence of petroleum and gas deposits requires that the deposit be provided with an additional supply of natural gases, in the first place methane, from deeper regions with their partial outflow and scattering in the Earth's troposphere ("ascending mass transfer"), where the hydrocarbons are oxidised to CO_2 in photochemical reactions. The inflow of gaseous hydrocarbons together with hydrogen and helium into bore holes driven into a crystalline foundation has been detected at depths of 2–12 km.[130,143]

Analysis of maps of known petroleum and gas deposits (with discrimination between them as regards type and age) with the aim of their possible inclusion in a single system of "pores" (sites where petroleum and gas have accumulated) and "channels" (transport ways) would be of undoubted heuristic interest from these standpoints. Such systems of pores and channels should begin in the region of the interface between the liquid-metal core and the lower mantle, should pass through the mantle and the Earth's crust, and should terminate in the deposits. The transport pathways may include channels with submicroscopic dimensions and also macrocracks (fluid breaks),[144] through which the continuous hydrcarbon phase is transported. It is evidently necessary to analyse maps on different scales in order to discover the "self-resembling" scale-invariant fractal rules.[145]

Naturally the specification of the proposed scheme in a more concrete form must reflect the genetic relation between the latest shifts of the Earth's crust and the formation of various types of accumulations of petroleum and gas and also the dependence of the phase and chemical compositions of the hydrocarbon deposits on the direction and activity of the latest displacements and on the intensity of the heat flux. Data obtained by deep seismic probing in tectonic studies have shown (this does not conflict with the model) that the Earth's crust is subdivided into blocks of differnt shape and size as a consequence of the formation of vertical and inclined zones with breaks and cracks, many of which can be traced as far as the upper mantle.

Ore formation processes can be considered similarly. They are known to depend largely on the distribution in the Earth's crust of convective fluxes of geothermal waters and on the mineral composition of the rocks through which water is transported to the core-forming zones. When water interacts with the rocks, the composition of the fluid, including the isotope composition of the oxygen in water, evolves. The latter factor provides an effective instrument for the analysis of the ore formation processes. In particular, conclusions have been reached for specific deposits concerning the nature of the structure of the fluid fluxes on the way to the ore formation zones, about the amount of water which has passed through a wide variety of rocks during specific periods of time, about the rate of cooling of rocks, about the features of the

‡ Electric fields of the type indicated can also be generated in the convective region of the sun and in the relatively stable convective structures of the solar atmosphere.[128] These fields not only ensure an additional stability of the structures in the solar plasma but also act as a factor accelerating charged particles (protons, electrons), causing an increase in the energy of the particles of the solar wind (external effect) and non-isothermal nuclear synthesis in the region of the lower boundary of the convective zone (internal effect).

spatial distribution of temperature in the ore formation zones for different times, and about the sequence of the formation of various sections of the deposits.[146–148]

In the general case, the picture of the formation of ore deposits must be supplemented by ideas concerning the genesis of geothermal sources and about the features of the water–rock interaction, which determines, in particular, the rates of filtration, microfiltration, ultrafiltration, and reverse-osmotic penetration of water streams into the Earth's mantle. Subterranean waters are usually considered in terms of a single system of the natural water turnover: evaporation from the surfaces of open water-containing areas—accumulation in the atmosphere—precipitation—stages involving the transport of water incident on soils to subterranean storage areas and further to open water-containing areas, etc. In conformity with Eqn. (11), the water turnover system must be expanded by including in it the sources of water active in the region of the liquid core–lower mantle interface and the systems of transport channels in the Earth's mantle.

As already mentioned, a branched network of pores and channels with different characteristic dimensions, used for the ascending transport of water under the influence of internal pressure gradients, may be formed in the mantle, which is inhomogeneous as regards composition, structure, and the extent of cracks and breaks. Such water is included in the region of the Earth's crust in the normal system of the water turnover.[130,131] The topology of such waterways from the Earth's core can be characterised by the correlation length L_E, which is comparable to the Earth's radius. Conclusions, of heuristic value, about the location of subterranean water streams[149] and the principal breaks through which the hydrosphere is additionally supplied with water follow from the fractal nature of the transport of liquid fluid through the Earth's mantle.

Such analysis, supported by experimental research, may prove useful not only for the rational utilisation and preservation of natural resources already discovered but also for the more effective search for new useful minerals and for the development of general concepts concerning the rational utilisation of natural resources in the future. Indeed, the very processes involved in the search for useful minerals and the mining of deposits already discovered cause harm to nature, damaging local ecological areas. In the initial stages of the utilisation of natural resources, these features exert a lesser influence. The present exploitation of the depths of oceans in order to collect iron–manganese concretions[150,151] as a rich source of copper, nickel, cobalt, and other metals does not constitute a danger to the natural environment. On the other hand, the continuation of the vigorous exploitation of coal and petroleum and gas deposits leads to the breakdown of the natural balances in terms of the solid, liquid, and gaseous components in major subterranean reservoirs, which is riddled with serious consequences, primarily owing to the disturbance of local natural ecological areas.

As regards petroleum and gas as well as fresh water, humanity has approached the stage where it has become necessary to curtail the extraction of these substances to amounts which can be made good under natural conditions. The development of the concept of the "limiting permissible utilisation" (LPU) and the introduction of the corresponding norms as regards the restoration of the given substance in nature has become a matter of urgency. For the solution of such problems, it is necessary to specify adequately the mechanisms of the formation and "ripening" of useful minerals and to approach an understanding of the conditions governing the initiation and acceleration of these processes under natural conditions. One cannot rule out the possibility that it is already necessary to think about "laying down" petroleum and gas deposits for our descendants using for this purpose the deposits which have already been "worked out" but which have retained the entire natural system of "subterranean communications", including the transport systems in the Earth's mantle. It may be that for this purpose it is necessary to introduce into the remaining bore holes certain substances and micro-organisms and to employ other methods involving chemical, biochemical and physical influences.

3. The Earth as a thermodynamically open system

We shall consider yet another important comment. If it is supposed that the formation reactions of water and certain organic chemical compounds from inorganic components are still continuing, then the quasi-stationary level of the World oceans is achieved owing to the existence of a definite flux of water molecules and oxygen atoms and ions from the Earth into space. These molecules entrain other components of the atmosphere, including larger organic molecules (urea, aminoacids, nucleotides, etc.) and clusters (the possible mechanisms of the "blowing off" of such molecules into space were discussed in Section V.1). Evidently the experimental observation of such quasi-stationary fluxes, provided that they exist, would make it possible to refine certain conceptual ideas about the turnover of water and other biologically important elements (N, C, P, etc.) in nature and also the models of the evolution of eco-systems on a global scale [for example, from a study of the purification processes in the atmosphere after major volcanic eruptions, especially since the components of the eruptions can reach the stratosphere (see Section I), in the analysis of the consequences of global radioactive contaminations, in the nuclear winter scenarios,[152] etc.].

It was emphasised above that the directed streams of the molecules of water and other substances into the stratosphere and then into space should serve as an additional (acting together with the turnover of the given substances, processes leading to the degradation and photodegradation of harmful substances, etc.) factor cleaning the atmosphere, because, together with such streams, harmful components can also be carried away outside the limits of the Earth's gravity.

In order to estimate the amounts of water lost by the Earth, we shall assume that throughout the existence of the hydrosphere (2 billion years) the content of hydrogen in the Earth's core diminished by 0.1%, i.e. that the loss of hydrogen per year was approximately 10^{14} g. The average amount of water carried away into space is then about 10^{15} g per year (the flux is $\sim 10^{11}$ H_2O molecules cm^{-2} s^{-1}) for an overall mass of the hydrosphere of approximately 1.6×10^{24} g and of the atmosphere of approximately 0.5×10^{22} g. We may note that the average fluxes of solar wind particles incident on the Earth are $\sim 10^{10}-10^{12}$ particles cm^{-2} s^{-1}. The generation on the sun of ultrafast streams of protons and electrons leads to an increase of the above quantities by 2–3 orders of magnitude with evident consequences for the process involving the "blowing off" of the particles of the atmosphere.§

When the Earth is considered as a thermodynamically open system involved in energy and material exchange with cosmic space, a number of theoretical problems, requiring model justification, arise. In particular, it is necessary to establish the mechanism of the

§Bearing in mind the ecological problems considered in this article, we may point to the possible analogy between the brief intense external influences purifying the Earth's atmosphere and the cleaning effect of large precipitations of water in St. Petersburg.

generation of the addition momentum ΔM in the Earth–atmosphere system in order to compensate for the difference between the flux of material ΔM_{out} lost from the Earth into space and the flux ΔM_{in} of material (flowing from space to the Earth)—meteor streams and components of the solar wind. There exist also other mechanisms "perturbing" the dynamic behaviour of the Earth–atmosphere system. One of the factors is associated with the position of the Earth in its orbit, since the overall vector of the Earth's orbital velocity and the velocity of the solar system in the Galaxy and the Metagalaxy change in the course of the year. This leads to seasonal variations in the rate of rotation of the Earth about its axis, which is the reason for changes in the elastic stresses within the Earth's crust.[153] One should also note the variable nature of the tidal forces associated with the inconstancy of the moment of the lunar and solar gravitational forces, which leads to oscillations in the Earth's axis (nutation).[153] Fluctuating influences on the Earth's motion are also exerted by processes on the sun, some of which have definite cyclic features.

The dynamic equations describing the Earth–atmosphere system must take into account the entire set of the perturbing external factors indicated and must include terms corresponding to the "sources" and "sinks" of the momentum in order to ensure stable motion of the Earth as a thermodynamically open system. Under these conditions, the entire solar system must be regarded as a complex hierarchy of self-organising subsystems saturated by energy sources and involve a surprisingly large number of collective processes.[154] The stable states of the Earth–atmosphere system occur in the vicinity of local minima in certain generalised functionals with stabilisation of the overall momentum of the Earth and the atmosphere in the vicinity of the mean value. Apparently such local minima characterise the overall stage of the entire solar system as well as the "resonance" stabilisation of the moon, the exotic "reverse" rotation of Venus,[155] and the rings in the satellite systems of the giant planets.[154]

It is important to note that the momentum of the sun (about 2% of the momentum of the entire solar system corresponds to the sun, while the mass of the latter is 99.9% of the total mass) as well as the momentum of each planet in the solar system as a single whole do not remain unaltered during the changes in the relative positions of the sun and the planets.[156] The centre of gravity of the solar system can shift from the central regions of the sun almost by $2R_{\odot}$, where $R_{\odot}$ is the radius of the sun, i.e. outside the limits of the sun. The stability of the states of the Earth and other elements of the solar system indicated above can therefore be partly due to entirely deterministic (in terms of location, in terms of the time of inclusion) internal local rearrangements in each of the celestial bodies, manifested for planets by "planet-quakes", by local rearrangements in the ionosphere ("ionosphere-quakes"), and by volcanic activity, and for the sun of the local processes in its surface region. The latter may include the generation of sunspots, leading to the necessary correction of the intrinsic momentum of the sun and its atmosphere. From this standpoint, numerical calculations of the variations in solar activity (of the relative number of sun spots—the Wolf number or the "indices of solar activity", determined by the flux of the wave type radiation from the sun in the radiowave ranges from metres to centimetres—usually at a wavelength of 10.7 cm[156]) merely as a consequence of a change in the relative positions of the sun and the planets and also the discovery of the sun—planet contribution to the initiation of natural catastrophes on our planet (as a consequence of the effects due to the changes in the momentum of the Earth in the Solar System and the attractive forces from other celestial bodies) may be of definite heuristic value.

It is noteworthy that the changes in the water regime within large regions, in particular the oscillations in the levels of large lakes without outflow (the Caspian and Aral seas and the Balkhash and Chany lakes), associated with natural long-period variations in the rate of rotation of the Earth,[157] as well as the movements of the tectonic plates in the course of the Earth's geological evolution may lead to a spatial rearrangement of the sources and sinks of the momentum i.e. to a change in the location of the regions with the highest seismic and volcanic activities. There is a possibility of a simultaneous "switching on" of atmospheric and intraterrestrial sources and sinks of the momentum, leading to major natural catastrophes, which have been described since ancient times: "... there was a violent earthquake and the sun went black... and the stars of the sky fell onto the Earth... and all the mountains and islands were shaken from their places" (Book of Revelation by John the Evangelist: **6**, 12–6, 14).

It is important to note that external influences leading to catastrophes can also be anthropogenic. One should probably consider major nuclear tests, the ignition of powerful rockets, and sharp changes in the hydrological regions associated with the construction of large dams. Furthermore, unsystematic and extravagant development of the Earth's resources (water, useful minerals) disturbs the complex system of natural hydrothermal and other communications which govern the mass transfer processes (the transport of water and simple inorganic and organic compounds) in the Earth's crust, which is essential for natural processes leading to the formation of new and the long term existence of present deposits of natural resources. The mass redistributions occurring may influence also the geological activity of individual regions and can also initiate natural catastrophes.

In view of the objective necessity for the further utilisation of natural resources and the expansion of the scale of industrial and agricultural products, humanity is forced to develop a strategy for its existence. The prediction of possible situations, including natural catastrophes, on the basis of mathematical models describing the changes in the Earth–atmosphere system under the influence of stochastic external factors becomes important in this connection. In the future, it will actually be possible to refer to a system of measures directed to weaken undesirable natural phenomena and their partial regulation or even complete elimination—by launching special powerful rockets or by nuclear explosions in deep bore holes.

The development of such approaches requires an adequate analysis of the existing and new data concerning the relationships[158] between anthropogenic activities in various regions, supported by experimental justification of the proposed concept—by the study of chemical processes at high temperatures, pressures, and shear deformations, by the study of mass transfer processes in the upper layers of the atmosphere, etc. We may note that direct experimental information about the mass fluxes blown off from the ionosphere into space, characterising the additional purifying capacity of the atmosphere, may be obtained from a comparative analysis of the components of the solar wind incident on the Earth after interaction with the Earth's atmosphere. The mass fluxes carried away from the Earth into space contain definite information about our planet since their composition includes fragments of organic and bioorganic molecules.

It may be thought that all planets with liquid metal cores in all the star systems of the Universe are thermodynamically open (naturally to different extents) systems "breathing" into space.[21,22]

One could imagine also exceptional situations—occurring in explosions of "nova" or "supernova" stars—where instead of "breathing" the corresponding planetary systems are destroyed with ejection of the contents of their atmospheres into space. Admittedly, such a fate does not threaten our planet. The detection in space of regions with an increased concentration of fragments of organic molecules may be an indication of the catastrophes which occurred on other worlds.

Thus one may speak of a dynamic unity of the Earth and the surrounding cosmic space, which means that the enigmas concerning the appearance of living organisms on Earth shift from a purely terrestrial level to a cosmic level. Life, having arisen (or having been created) anywhere, might have embraced those regions of the Universe where the necessary conditions for their development existed. We thus arrive at a more concrete specification of Vernadskii's general ideas[1] concerning the interaction of the inorganic matter of the planet and of the living matter at all the space-time levels of the organisation of the material world, the constant interaction of cosmic organic matter with the living matter on planets, and the wide-scale distribution of living matter throughout the Universe and its cosmic importance.

VI. Conclusion

The efforts of chemical science in connection with problems of ecology have been traditionally directed to current developments in the resource-saving and low-waste technologies and towards an improvement of the efficiency of the system of monitoring of the natural environment. At the same time, the possibilities of chemistry and related sciences in the solution of ecological problems may be expanded. In this section we shall deal with one class of hitherto poorly developed problems whose ecological importance is apparently not fully recognised. This concerns the electromagnetic pollution of the natural environment.[88,159] As a consequence of the experimental theoretical complexities in the problems arising, many of the postulates described below have still not been fully formulated in modern science and should be regarded as controversial.

At the present time, the spectral density of anthropogenic sources of electromagnetic radiation (EMR) within many frequency ranges, primarily in the radio-frequency ranges, exceeds by several orders of magnitude the natural background (generated by the radio emission from the sun, the planets, and other cosmic sources, by phenomena in the Earth's atmosphere, etc.) and by the intrinsic spectral noise in natural radiation receivers (native biological systems, including the human brain and nervous system).

At the same time, many effects on biological systems by the EMR in various frequency ranges, starting from fractions of Hz and up to SHF (wavelength $\lambda \simeq 1 - 10$ cm) and EHF ($\lambda \simeq 0.1 - 1$ cm) ranges. Together with therapeutic effects of EMR in different ranges on man,[88,159] specific (non-thermal) negative effects have been observed after prolonged irradiation, so that limiting permissible levels (LPL) of exposure to EMR have been established. The LPL for irradiation by radiowaves under industrial conditions is 10 μW cm^{-2} in the USSR, 1 mW cm^{-2} in Canada, 10 mW cm^{-2} in the USA and a number of other countries.[159] The existing scatter in the established norms (by up to 3 orders of magnitude in terms of power!) indicate an inadequate level of the current understanding of the specific features of the effect of EMR in different ranges on biological systems—on the human brain and nervous system. On the other hand, the discovery of all the factors influencing the state and functional activity of man, in the first place the functioning of his brain, constitutes a fundamental condition for the existence of civilisation. It is not fortuitous that the United States Senate and Congress have declared the decade starting on 1st January, 1990 as the "decade of the brain".

The human brain, being a non-equilibrium system of the organism, is most capable of "switching over" its state ("forced bifurcation") under the influence of weak external (light, sonic, etc.) signals. The brain is apparently the most highly organised multiparameter dynamic system, each state of which is established as a coherent (concerted) set of ensembles comprising ten and more neurons and characterised by a definite set of metastable levels. The transitions between such generalised states occur via a system of alternatives[77] under the influence of weak signals. The wide variety of states of the brain system is indicated by the virtually "non-deletable" and readily recalled memory, including visual images, manifested by man's creative activity during normal life and in dreams.

Man's light and sound receptor systems, which transmit information to the brain, as well as the olfactory biochemical reception systems, possess a uniquely high sensitivity. It has been shown experimentally that the radio frequency EMR also exerts a direct influence on the sensitive highly non-equilibrium systems of the brain.[159] In biological systems there are no specialised receptor organs for radio signals (in contrast to light signals). One may therefore think that the primary mechanisms of the reception of radio waves are fairly non-specific and are the same for all biosystems.

These influences can be exerted either through a change in the state of the aqueous component of the biosystems, in which the activity of free, non-bound water may be altered under the influence of the radio frequency EMR [49] or through a change in the functional state of the ionic channels in biological membranes as a result of an increase in the degree of hydration of the channels and the consequent loss of selectivity relative to the transfer of ions of different kinds.[24] Further studies should establish with a greater certainty not only the primary mechanisms of the effect of EMR at different frequencies on man but also the systems for further processing in the brain of the information carried by such radiation.

This is of particularly great current interest, since negative influences on man can be exerted not only by anthropogenic sources of EMR but also by major fluctuations in the natural radio frequency EMR background. In particular, the increase in solar activity with increase in the relative number of sun spots and eruptions on the sun, responsible for the increased intensity of the solar wind and streams of plasma clouds away from the sun, leads not only to an increase in the intensity of the intrinsic solar EMR in the radio frequency ranges (type I–V radio waves) but also to the generation of magnetospheric holes and subholes with strong variations in the geomagnetic field on interaction of the streams of solar plasma with the Earth's magnetosphere and ionosphere. A broad spectrum of electromagnetic waves is then excited in the Earth's magnetosphere: "holes" and "swellings" ($\sim 10^5 - 10^2$ Hz); stable and irregular geomagnetic pulsations ($\sim 10^{-2} - 10$ Hz); atmospheric noise ($\sim 1 - 10^2$ Hz); low-frequency radiation ($\sim 10^2 - 10^4$ Hz). This is a consequence of a wide variety of phenomena in magnetospheric holes and subholes: turbulent movements in the magnetospheric plasma, the development of plasma instabilities, the generation of intense electric currents amounting to tens of thousands of amperes in the ionosphere (at heights of approximately 100 km), etc.[109,156] The negative

influences of such magnetic holes on the state of human beings are well known. Although solar activity can be partly associated with the relative positions of the sun and the planets (see Section V), each planet is a source of its characteristic radiation in the ultralong radio frequency range, generated on interaction of the solar wind and the streams of solar plasma with the planet's magnetosphere and atmosphere. Presumably, further progress in the science of the brain, the discovery of the mechanisms of the reception of weak information-containing electromagnetic signals by the organism, will make it possible to understand better all the influences exerted by cosmic space and the environment on man.

We shall make yet another comment. The history of science has shown how difficult it is to predict the true course of scientific progress. It is sufficient to recall the classical statement by Lord Kelvin on the eve of the XXth century, concerning two "small clouds" (the negative results of Michelson's experiments, anomalies in the absorption spectrum of an absolutely black body) which at the time precluded the formulation of physical science in a "final form". The theory of relativity and quantum mechanics were created on this basis. The century coming to its conclusion involved the formulation of its own problems and puzzles. One of the "little clouds" as regards physicists has already been specified: the fact that the measured flux of "solar" neutrinos is smaller almost by a factor of three than the value predicted within the framework of the standard model of the sun. The paradox of the situation consists in the fact that, together with brilliant astrophysical discoveries of the nature of many stellar and quasi-stellar objects separated from the sun by billions of light years, we have the state of affairs where the processes in our Star are still not fully understood!

Here one would wish to mention two other major "clouds" (which arose many centuries before Lord Kelvin's "little clouds"), whose internal essential features have so far been poorly understood, so poorly that many scientists do not consider them seriously. This concerns astrology as the science of relations between the state and evolution of individual living organisms (including man) and eco-systems, on the one hand, and the relative disposition of celestial bodies, on the other, as well as telepathy as the science of processes involving the transfer of information without special signals and technical means (including "thought transfer") at a distance in which the organism makes use of his own memory system and the system for the reproduction of visual images.

We have already discussed above the possible relation between solar activity and the relative positions of the sun and the planets. The fairly well established influence of the state of the sun on the functioning of living systems should be effected primarily through the low-frequency variable magnetic field and different radio frequency ranges generated by the EMR. The problem of how the above radio emissions influence the human psyche and state of health remains, however, unsolved. As regards information signals from bio-objects, including man, if one does not introduce into consideration new postulates (in conformity with Occam's principle), in particular the hypothesis of the existence of "hitherto unknown biofields",[160] one may assume that the transmission and reception of such signals are effective also at radio frequencies, most probably in the centimetre and decimetre ranges.[159] At the present time the thermal radio emission by man (in the ranges indicated and at longer wavelengths — in the decametre, kilometre, etc. ranges), the intensity of which is rigorously related to the temperature of the emitting internal organs, is used effectively for diagnosis at a distance. This also applies to the equilibrium emission by the body in the IR range ($\sim 8-14$ μm).[161] The latter is characterised by a high power (~ 10 mW cm^{-2}) so that the power of the radiation emitted by the entire human body in the IR range exceeds 100 W.[162]

Evidently, for the transmission of information signals by the human brain in radio frequency ranges as well as the establishment of the highest sensitivity for the reception of weak signals, it is necessary that macroscopic ($\sim 1-10$ cm) domain structures, all the neurons of which function in a coherent regime, be formed in the brain. In this case the power of the transmitting signals may exceed by several orders of magnitude the equilibrium thermal background. There are no fundamental prohibitions of the existence of such "telepathic communication" — neither as regards energy characteristics nor as regards the possible highly specific individual sensitivity of natural systems. Naturally, there are major difficulties in the experimental location of the signals transmitted by the brain, which is partly associated with the fairly random character and virtual non-controllability of the most striking manifestations of spontaneous telepathy. There exist also fundamental difficulties in the understanding of the mechanism of the coding of information in the domains of the active medium of the brain capable of being stimulated, the transformation of information into radio wave signals, the reception of the signals in the receiving systems, etc.

In such hypothetical approaches to astrology and telepathy, the problems of these sciences acquire the same essential features and should be solved by discovering the mechanisms of the reception by man of weak information signals in different radio frequency ranges. The question arises whether the "clouds" mentioned above will develop and whether astrology and telepathy will become established as natural scientific disciplines or whether they will still remain for a long time *terra incognita* which will excite the imaginations of impressionable investigators and laymen.

Enigmas in nature have always existed and will exist. Furthermore, the level of the recognised lack of knowledge increases (or at least does not diminish) as reliable knowledge accumulates. Scientific progress is partly effected through this process involving the recognition by man of the depth of his lack of knowledge. However, even regardless of the difficulties concerning astrology and telepathy discussed above, the discovery of information communication, manifested in the reception by living organisms of low-frequency variable magnetic fields and radio frequency EMR, is one of the new and important aspects of ecological science.

This review represents an attempt to analyse the wide variety of problems arising in the formulation of the concept of the survival of humanity combined with the choice of ecological priorities and the aim is to draw the attention of chemists as well as specialists in other fields (ecologists, medical practitioners, biochemists, physicists, and mathematicians) to the possibilitiy of a joint search for and solution of general and what are apparently the most important problems to everyone at the present time — the problems involved in saving the home.

What future awaits us? "Then I saw a new heaven and a new earth; the first heaven and the first earth had disappeared now and there was no longer any sea" — wrote John the Evangelist (Book of Revelation: **21**, 2). What was the new world seen by the Evangelist? After all, the New Testament is threaded by the idea of the multivariability of the future, the understanding of the world as a subject with which humanity has a dialogue and as an open system with an "open future".[163] Not only destructive but also creative, cleansing forces are active in the world (the "white horse", Book of Revelation: **6**, 2, 19, 11) and the scales in the hands of the rider on the "black horse" (Book of Revelation: **6**, 5) can serve as a

symbol of the uncertainty of the ways in which man and humanity as a whole will develop.

This view on the world is adequate, especially now that wide use is made of technologies which can do irreparable harm to the biosphere and when nuclear and chemical weapons have accumulated in amounts sufficient for the complete annihilation of civilisation. The visions of John the Evangelist may prove to represent reality, as already demonstrated by the Chernobyl catastrophe: "... and a huge star fell from the sky, burning like a ball of fire, and it fell on a third of all rivers and streams; this was the star called wormwood and a third of all water turned to bitter wormwood, so that many people died from drinking it." (Book of Revelation: **8**, 10; **8**, 11).

Humanity stands at the crossroads and the face of the "new" Earth will in fact depend on the choice of priorities (ecological, social, ideological etc.) in the development of a survival strategy: either a path will be found and followed to the convergence of world social-political systems, so that the history of humanity does not break off, or civilisation will be destroyed and will be reborn after many thousands or millions of years (possibly "without a sea"?).

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