Translated from *Uspekhi Khimii* **60** 2332–2361 (1991) U.D.C. 502.7:504.06:577.1

Certain physicochemical principles of eco-systems and their expression in the form of material inequalities for different levels of initial information

N V Sokolov
Institute of the Problems of Water, USSR Academy of Sciences

ABSTRACT. The usefulness of estimates of the contents of various components of ecological systems and subsystems in the form of material inequalities is demonstrated with the aid of the principle of the threshold nature of the action of chemical substances on producers and consumers. The principle of the coupled material-characteristic imbalance is formulated, according to which the unknown part of the mass of the ecological system can be estimated with the aid of inequalities expressing the relations between the masses of the components and their contributions to the overall characteristics of the system as a whole. The possibilities of using material inequalities for different levels of initial information for the monitoring of eco-systems and for the planning of physicochemical nature-protecting measures are demonstrated.

The bibliography includes 40 references.

Contents

I. Introduction 1205
II. Universal rules for the compositions of ecological systems and subsystems expressed in the form of inequalities 1206
III. Specific rules for the compositions of homogeneous ecological subsystems 1210
IV. Specific rules for the compositions of heterogeneous ecological subsystems 1210
V. Analysis of the deviations from the limiting possible contents of substances and rates of chemical reactions 1212
VI. Specific features of the estimation of the changes in disperse ecological subsystems when nature-protecting measures are taken 1214
VII. The principal rule for the compositions of simple and complex two-component and multicomponent ecological systems and subsystems 1216
VIII. Measures ensuring that the limiting permissible amounts of liquid and gaseous harmful waste discharged into the environment are not exceeded for different levels of initial information 1218

I. Introduction

Monitoring on the global and regional scale and prediction of the changes in the state of eco-systems and planning of nature-protecting measures necessitates the large-scale and operative estimation of the contents of various components, phases, fractions, and constituents of ecological systems and subsystems and also the determination of the rules governing their compositions.

An ecological system represents a territorially (spatially) isolated integral elementary unit of the biosphere all the components of which are closely related to one another, or a certain assembly of such units.[2]

By an ecological subsystem, we shall understand a part of the eco-system which is imagined to be isolated or which has real physical boundaries and which can contain or not contain producers, consumers, and substrates. Ecological subsystems defined in this way can include waste water before and after purification, liquids contained in closed water supply systems, solid waste stored on military proving grounds and contaminating the lithosphere, various solutions and heterogeneous mixtures undergoing chemical changes in industrial and natural processes, as well as individual living organisms and their components. Under these conditions, one of the features of ecological subsystems is the possibility of their ultimate interaction with the environment and the living organisms present in it. Thus, various substances can enter natural water-containing areas even from a closed water supply system when its hermetic seal fails, while waste aerosols and industrial waters in general lead to daily contamination of the atmosphere and hydrosphere. It is seen from the definition that, in contrast to the eco-system itself, its ecological subsystem can be both homogeneous and heterogeneous, can consist of one component or of a very large number of components, and can be part of nature or an artificially produced mixture.

The principle of the threshold nature of the effect of chemical substances on producers and consumers[1–14] is in the first place the reason why it is useful to estimate in the form of material inequalities the liquid and gaseous waste entering the environment. Secondly, the methods for the large scale monitoring of the states of the atmosphere, the hydrosphere,[15–22] and the lithosphere should not themselves promote additional anthropogenic contamination by chemical substances. Thirdly, when they are applied, one must achieve the most effective utilisation of the initial information collected at considerable material expense. Fourthly, these methods should not entail the destruction or negative changes in biological objects.

The difficulty of collecting detailed information about the state of ecological systems and subsystems and of its subsequent utilisation[23,24] necessitates the establishment of universal characteristics of the compositions of such systems. These characteristics must be suitable for practical use even in the absence of complete data and in the presence of different levels of the initial information.

Thus large scale monitoring and prediction of the state and chemical evolution of ecological systems and subsystems as well as the planning of nature-protecting measures[24–30] require the discovery of the principal rule governing the composition which is applicable to the entire wide variety of information conditions encountered in practice. The specific features of ecological requirements (the principle of the threshold nature of the effect of chemicals contaminating the environment) indicates the suitability of the inequalities in the search for such a rule.

II. Universal rules for the compositions of ecological systems and subsystems in the form of inequalities

The chemical processes in ecological subsystems frequently take place under the conditions of random oscillations in temperature, pressure, the concentrations of reactants, the activity of the catalyst and inhibitors, the magnetic field strength, and other parameters. Furthermore, as already mentioned, there is frequently no exhaustive information about the ecological subsystem. These features necessitate the establishment of new general rules which determine the relations between the amounts of reactants and products in chemical reactions in both homogeneous and heterogeneous ecological subsystems.

Bearing in mind the specific features of ecological subsystems and the principle of the threshold nature of the influence (of various factors), we shall attempt to compare, under the conditions of incomplete initial data, the unknown amount of the system component with a quantity which can be readily calculated theoretically or determined experimentally. We shall explain the idea of this approach by a simple example. Evidently, the overall mass of substances with a molecular weight not less than the specified value cannot be greater than the mass of the entire system. Having divided the left-hand and right-hand parts of the trivial inequality corresponding to this claim by the specified molecular weight and having taken into account the fact that one then obtains on the left-hand side a quantity which exceeds the total number of moles of such substances, we obtain as a result a new relation according to which the total number of moles of substances with a molecular weight not less than the specified value, existing in a certain ecological subsystem (isolated volume), cannot be greater than the ratio of the total mass of the system to the specified molecular weight at any instant during chemical reactions.

Using the definition of the concentration and of the average density, it is easy to demonstrate with the aid of the above rule that the molar concentrations of substances in a certain volume of space where chemical reactions take place cannot be greater at any instant than the ratio of the average density of the entire system at this instant to the molecular weights of the corresponding substances.

The possibility of applying this rule can be illustrated in relation to the industrial synthesis of sulphuric acid by the contact method.[31] This substance exerts a powerful negative effect when it enters the environment. Suppose that an aqueous solution of sulphuric acid with a density of 1841 kg m^{-3} is introduced into the absorption tower. Then, according to the rule established, the concentration of sulphuric acid in the solution entering the tower is $\leqslant$18.79 kmol m^{-3}. If after the reaction with SO_3 and cooling of the liquid phase, the density of the resulting solution is 1838 kg m^{-3}, then, on the basis of the assertion formulated above, we find that the concentration of sulphuric acid in the resulting solution is less than or equal to 18.76 kmol m^{-3}. If the initial sulphuric acid solution contains 98.2% H_2SO_4, then the concentration of sulphuric acid was 18.45 kmol m^{-3}. The final solution with the density indicated at 15 °C can represent 99.3% sulphuric acid and its concentration will be 18.62 kmol m^{-3}. As can be seen from the values obtained, the results are in full agreement with the rule established above.

Thus the general rules postulated above make it possible to estimate at each instant the amounts of both the starting materials and the products present in any isolated volume even for a minimal amount of information available about the chemical reactions and about the influence of numerous random factors and mass-exchange processes.

In order to obtain an expression whereby the weight fractions of the substances in ecological subsystems can be estimated, we write

$$\frac{m_k(t)}{M_\Sigma(t)} \leqslant \sum_{i=k}^{i=l(t)} \frac{n_i(t)\mu_k}{M_\Sigma(t)} \leqslant \mu_k n_{sp}^{\cdot}(t), \qquad (1)$$

where $M_\Sigma(t)$ is the mass of the entire ecological subsystems at time t, $n_i(t)$ and $m_i(t)$ are the number of moles and the mass of the ith substance in the ecological subsystem at time t, μ_k the molecular weight of the kth substance, $l(t)$ the number of substances present in the subsystem at time t, i the summation index such that at a fixed time t the inequalities

$$\mu_1 \leqslant \mu_2 \leqslant \mu_3 \leqslant \ldots \leqslant \mu_{i-1} \leqslant \mu_i \leqslant \mu_{i+1} \leqslant \ldots \leqslant \mu_{l(t)}, \qquad (2)$$

hold, k a fixed value of i, and $n_{sp}^{\cdot}(t) = \left[\sum_{i=1}^{i=l(t)} n_i(t)\right] \Big/ M_\Sigma(t)$, the specific number of moles (the average characteristic of the ecological subsystem) equal to the ratio of the total number of moles of all the substances present in the ecological subsystem to their overall mass.

Eqn. (1) makes it possible to formulate the following theorem:

Theorem 1. *For any chemical reactions in ecological systems and subsystems, the weight fraction of a given substance at any instant cannot exceed the product of the specific number of moles at the given instant and the mole fraction of the given substance.*

Having multiplied the terms of the inequalities (1) by the average density† of the entire ecological subsystems $\bar{\rho}(t)$, we obtain an expression which makes it possible to estimate the concentrations of the components of the ecological subsystem from a minimal amount of data. It permits the formulation of the following rule.

The weight concentration of any reactant cannot be greater than the product of the specific number of moles, the average density of the system at the given instant, and the mole fraction of the substance.

Having used the idea of the material imbalance in relation to the mole fractions of the components of an ecological subsystem, we set up a sequence of inequalities:

$$\frac{n_k(t)}{\sum_{i=1}^{i=l(t)} n_i(t)} \leqslant \sum_{i=1}^{i=k} \frac{n_i(t)\mu_i}{\mu_k \sum_{i=1}^{i=l(t)} n_i(t)} \leqslant [\mu_k n_{sp.}(t)]^{-1}, \qquad (3)$$

where $n_i(t)$ is the number of moles of the ith substance and μ_i is the molecular weight (the weight of one mole) of the ith substance.

† The average density of the ecological subsystem is equal to the ratio of the mass of the entire subsystem to its volume.

Using Eqn. (3), we formulate the second theorem.

Theorem 2. *The mole fraction of a given substance in any reactions in ecological subsystems and subsystems at any instant cannot be greater than the reciprocal of the product of the specific number of moles and the mole fraction of the given substance.*

Since the weight and mole fractions of a substance cannot be greater than unity, their estimates are limited by the values of the products: for the weight fractions $\mu_k n^{\circ}_{sp}(t) \leqslant 1$ and for the mole fractions $\mu_k n^{\circ}_{sp}(t) \geqslant 1$. The expressions for their estimation can therefore be usefully combined into a single universal inequality:

$$\frac{|1-\mu_k n^*_{sp}(t)|+\mu_k n^*_{sp}(t)-1}{2[\mu_k n^*_{sp}(t)-1]} n \frac{n_k(t)}{\sum_{i=1(t)}^{i=t} n_i(t)} + \frac{|1-\mu_k n^*_{sp}(t)|+1-\mu_k n^*_{sp}(t)}{2[1-\mu_k n^*_{sp}(t)]} \frac{m_k(t)}{\sum_{i=1(t)}^{i=t} m_i(t)} \leqslant \leqslant \frac{\mu_k n^*_{sp}(t)[|1-\mu_k n^*_{sp}(t)|+1\mu_k n^*_{sp}(t)]}{2[1-\mu_k n^*_{sp}(t)]} + +[\mu_k n_{sp\cdot}(t)]^{-1} \frac{|1-\mu_k n^*_{sp}(t)|+\mu_k n^*_{sp}(t)-1}{2[\mu_k n^*_{sp}(t)-1]}. \quad (4)$$

Consequently the contents of the components in ecological subsystems can be estimated from minimum amounts of physicochemical data when the specific number of moles in the system is known. The new average characteristic introduced here—the specific number of moles—can be fairly readily determined in the case of homogeneous liquid ecological subsystems from the decrease in the freezing point of the solution, or the increase in its boiling point, or osmometrically; for gaseous solutions, this quantity is unambiguously expressed in terms of the pressure, density, and temperature.

A series of practical problems concerning the protection of the environment necessitate the estimation of the content of substances with a molecular weight greater (smaller) than the specified value. For this purpose, using the principle of material imbalance, we shall set up similarly a sequence of inequalities replacing the unknown masses and numbers and moles of the components by larger quantities. As a result, we obtain the third and fourth theorems which are formulated as follows.

Theorem 3. *The sum of the weight fractions of substances with molecular weights smaller than or equal to the specified value at any instant in eco-systems and ecological subsystems cannot be greater than the product of the specific number of moles at this instant and the specified molecular weight.*

Theorem 4. *The sum of the mole fractions of substances with molecular weights greater than or equal to the specified value in ecological systems and subsystems at any instant cannot be greater than the reciprocal of the product of the specified molecular weight and the specific number of moles.*

Thus an objective relationship has been established between the content of the component in the system, the specific number of moles, and the molecular weight. These rules make it possible to differentiate the space of the values of the possible weight and mole fractions of the components constituting the ecological subsystems (Figs. 1 and 2).

Situations are frequently encountered where, apart from the average characteristic of the ecological subsystem (the specific number of moles), data concerning its quantitative composition at a given instant are also known. In order to establish the general rules for the compositions of multicomponent systems applicable for this level of initial data, we shall again make use of inequalities. The method of achieving this aim is expressed in the form of the principle of the coupled material-characteristic imbalance; *the unknown part of the mass of the ecological subsystem can be estimated by comparing the inequalities expressing the relations between the masses of the components and their contributions to the overall characteristic of the entire subsystem.*

We shall write the inequality relating the number of moles of the kth component to the total number of moles in the subsystem:

$$m_k(t)/\mu_k+[M_\Sigma(t)-m_k(t)]/\mu_{max} \leqslant N_\Sigma(t), \quad (5)$$

where μ_{max} is the maximum molecular weight of the component and $N_\Sigma(t)$ the total number of moles of all the substances constituting the system.

We supplement Eqn. (5) by the expression relating the mass of the component to the overall mass of the system through the number of moles of the remaining substances multiplied by the minimum molecular weight, namely

$$m_k(t)+[N_\Sigma(t)-m_k(t)/\mu_k]\,\mu_{min} \leqslant M_\Sigma(t). \quad (6)$$

By dividing inequalities (5) and (6) by the mass of the entire system, we obtain, after algebraic rearrangements, relations which make it possible to estimate in the following manner the contents of the components in ecological systems from the specific number of moles when the qualitative composition is known:

$$\frac{m_k(t)}{M_\Sigma(t)} \leqslant \begin{cases} \mu_k \dfrac{n^*_{sp}(t)\mu_{max}-1}{\mu_{max}-\mu_k} \\ \text{when } \mu_k n^*_{sp}(t) \leq 1, \\ \mu_k \dfrac{1-\mu_{min} n^*_{sp}(t)}{\mu_k-\mu_{min}} \\ \text{when } \mu_k n^*_{sp}(t) > 1. \end{cases} \quad (7)$$

The regions where the estimating inequalities, constituting formula (7), are applicable were determined on the basis of the condition $m_k(t)/M_\Sigma(t) \leqslant 1$.

In order to derive relations between the mole fractions of the components and an average physicochemical characteristic of the entire system, we shall take into account the fact that $n_k(t)/N_\Sigma(t) = m_k(t)/[\mu_k n^{\circ}_{sp}(t) M_\Sigma(t)]$. We then obtain from formula (7)

$$\frac{n_k(t)}{N_\Sigma(t)} \leqslant \begin{cases} \dfrac{n^*_{sp}(t)\mu_{max}-1}{n^*_{sp}(t)(\mu_{max}-\mu_k)} \\ \text{when } \mu_k n^*_{sp}(t) \leq 1, \\ \dfrac{1-\mu_{min} n^*_{sp}(t)}{n^*_{sp}(t)(\mu_k-\mu_{min})} \\ \text{when } \mu_k n^*_{sp}(t) \leq 1. \end{cases} \quad (8)$$

With the aid of inequalities (4), (7), and (8), it is possible to estimate the weight and mole fractions of the components for two levels of incomplete information.

Calculations based on the universal rules established for the compositions of ecological systems in the presence and absence of qualitative analytical data, carried out with the aid of a computer by

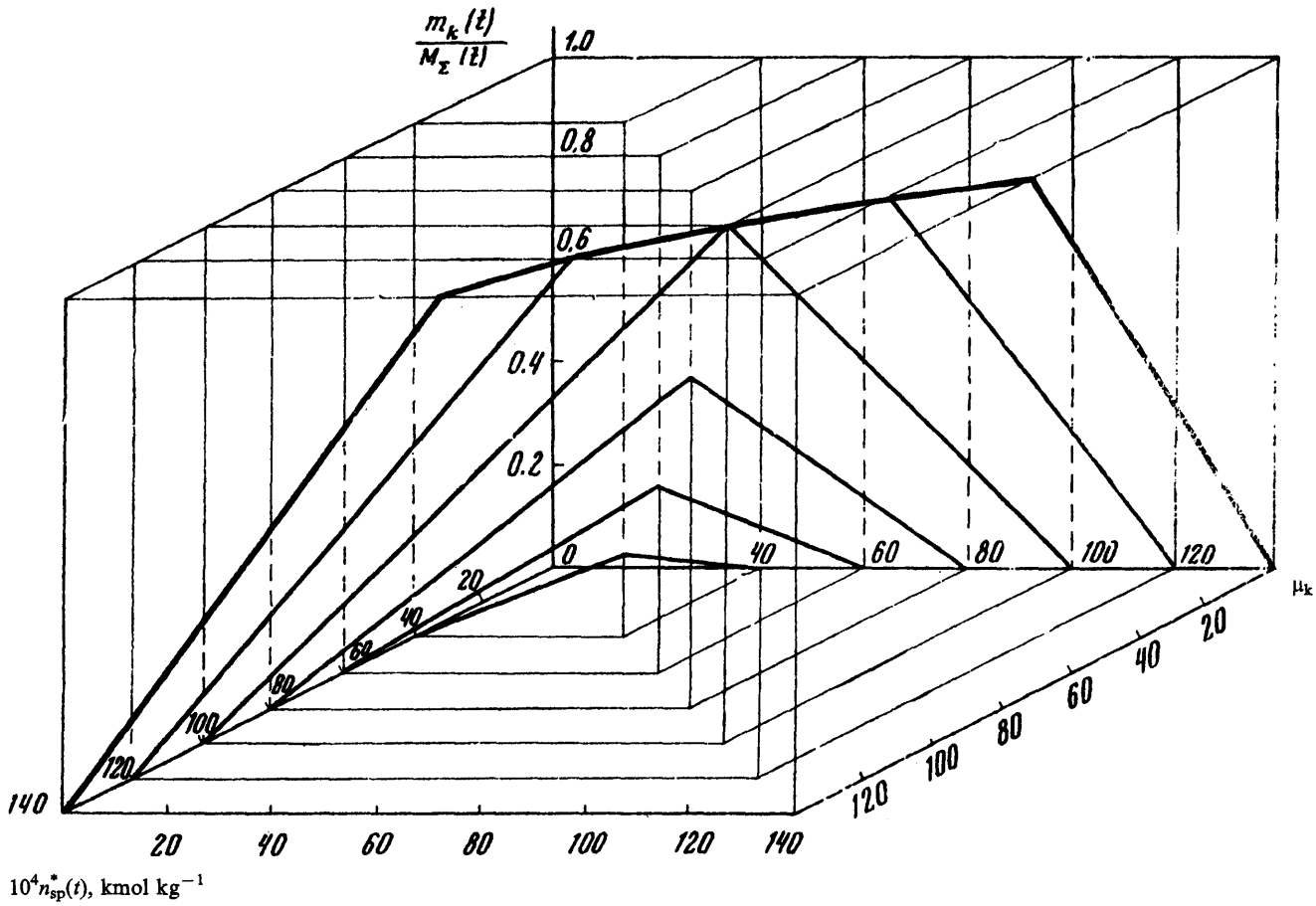


Figure 1. The space of the possible weight fractions of substances constituting eco-systems.

means of a specially developed algorithm and a program written in the BASIC language and based on it, confirmed the possibility of their practical employment. The high degree of generalisation of the above inequalities makes it possible to take into account any chemical, physical (including nuclear) and physicochemical changes in open, closed, and isolated ecological systems and subsystems, taking into account the effects associated with mass-exchange processes. Yet another important feature of these expressions is their low information requirement, i.e. the possibility of their practical application for a small amount of initial data.

Since in certain cases it is simpler for homogeneous and heterogeneous systems to measure experimentally the specific heat and the specific volume than to determine the specific number of moles of the ecological subsystem, we shall find inequalities relating the partial molar quantities and composition for these levels of information.

For this purpose, applying the principle of the coupled material-characteristic imbalance, we set up an inequality for heat capacities using the partial molar heat capacity of the kth component in the following form:

$$C_k^m \frac{m_k(t)}{\mu_k} + [M_\Sigma(t) - m_i(t)] \left(\frac{C^m}{\mu}\right)_{min} \leqslant C_\Sigma(t), \qquad (9)$$

where C_k^m is the partial molar heat capacity of the kth component, $C_\Sigma(t)$ the overall heat capacity of the entire ecological subsystem at time t, and $(C^m/\mu)_{min}$ is the minimum ratio of the partial molar heat capacity to the molecular weight (the minimum partial specific heat).

The inequality coupled with formula (9) is obtained by expressing the mass of the components with the aid of infinitesimal amounts of heat absorbed by them on raising the temperature of the entire ecological subsystem by an infinitesimal amount. Thus,

$$\frac{\mu_k \delta Q_k}{\delta T C_k^m} + \frac{(\delta Q_\Sigma - \delta Q_k)}{\delta T} \left(\frac{C^m}{\mu}\right)^{-1}_{max} \leqslant M_\Sigma(t), \qquad (10)$$

where δQ_Σ is the infinitesimal amount of heat absorbed by the entire ecological subsystem, δQ_k the infinitesimal amount of heat absorbed by the kth component, δT the infinitesimal rise in the temperature of the system on absorption of heat, and $(C^m/\mu)_{max}$ the maximum ratio of the partial molar heat capacity to the molecular weight of the given system (the maximum partial heat capacity).

On dividing inequalities (9) and (10) by the mass of the system and taking into account the fact that

$$\delta Q_\Sigma = M_\Sigma(t) \delta T \overline{C}_{sp}(t) \text{ and}$$

$$\overline{C}_{sp}(t) = C_\Sigma(t)/M_\Sigma(t),$$

we obtained a relation between the specific heat of the entire system

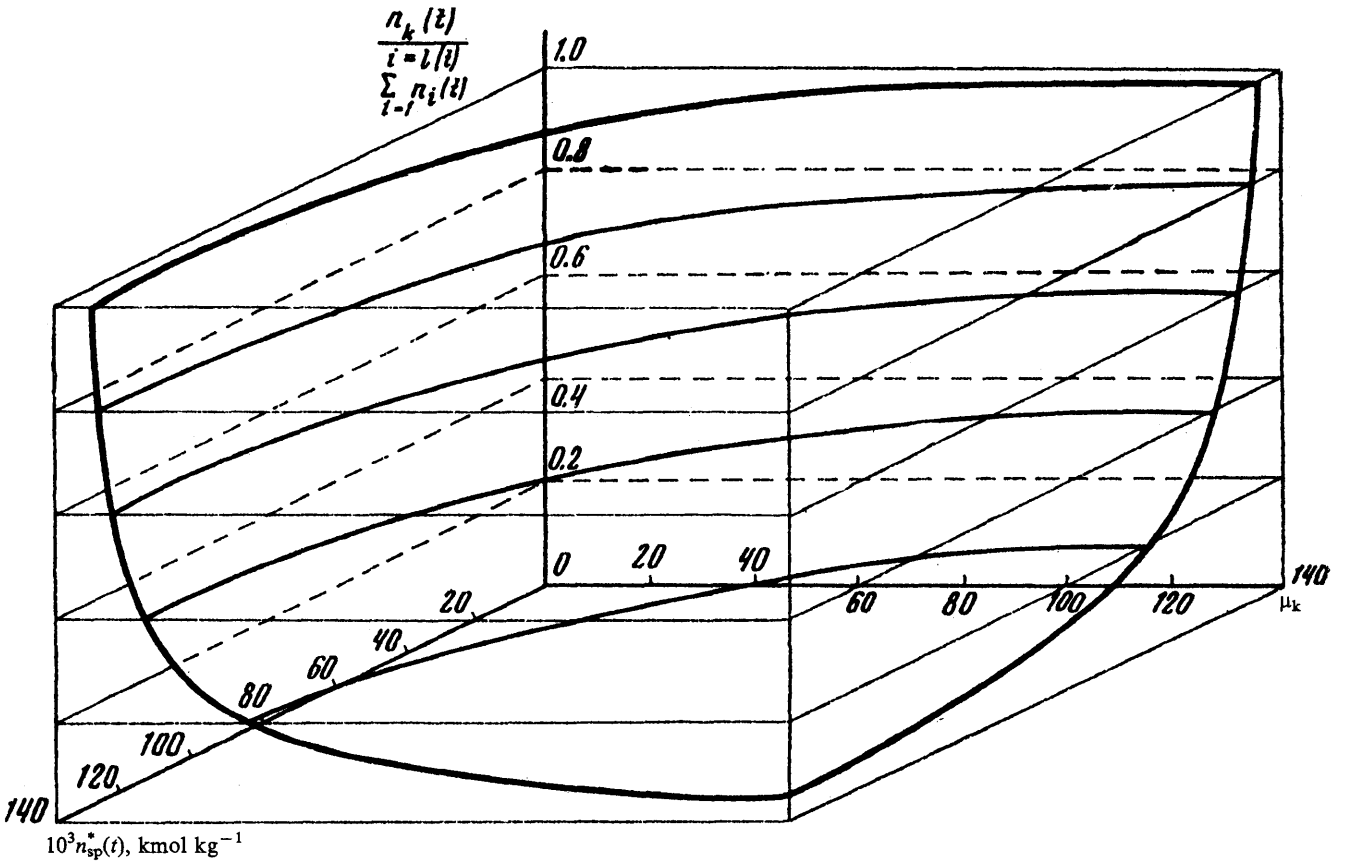


Figure 2. The space of the possible mole fractions of the substances constituting ecological systems. The surface of the maximum possible mole fractions of the substances in the eco-systems is differentiated.

$\bar{C}_{sp}(t)$ and the partial molar heat capacity and the content of the given component:

$$\frac{m_k(t)}{M_x(t)} \leqslant \begin{cases} \dfrac{\bar{C}_{sp}(t) - (C^m/\mu)_{min}}{C^m_k/\mu_k - (C^m/\mu)_{min}} \\ \text{when } \bar{C}_{sp}(t)\mu_k/C^m_k < 1, \\ (C^m/\mu)_{max} - \bar{C}_{sp}(t) \\ (C^m/\mu)_{max} - C^m_k/\mu_k \\ \text{when } \bar{C}_{sp}(t)\mu_k/C^m_k \geq 1. \end{cases} \tag{11}$$

The following rule follows from Eqn. (11):

The weight fraction of any component in a differentiated ecological system (subsystem) at a given instant cannot be greater than the ratio of the product of its molecular weight and the specific heat of the entire system (subsystem) to its partial molar heat capacity.

It can be used when the partial molar heat capacities of the other components constituting the ecological system are unknown. For example, the average specific heat of a human being, constituting a complex ecological subsystem, is 3.59 kJ kg K^{-1}.[32] Consequently, on the basis of this value of the specific heat of the ecological subsystem, one can conclude that the human organism contains not more than 86% of water. This result corresponds to the real situation, since according to Lightfoot,[32] the weight fraction of water in the human organism is 0.75.

We shall make use of the concept of the partial molar volumes of the components in order to obtain new relations. By setting up an inequality with the partial molar volume, we obtain a relation implying that *the weight fraction of any component at a fixed instant cannot be greater than the ratio of its molecular weight to the product of its partial molar volume and the average density of the entire system at this instant.*

For the case where the range of variation of the partial molar volumes is known, we set up two coupled relations for the imbalance of the volume and mass and, on combining them, we obtain, after algebraic rearrangements,

$$\frac{m_k(t)}{M_x(t)} \leqslant \begin{cases} \dfrac{1/\bar{\rho}(t) - (v^m/\mu)_{min}}{v_k{}^m/\mu_k - (v^m/\mu)_{min}} \\ \text{when } \nu^m_k/\mu_k > 1/\bar{\rho}(t), \\ \dfrac{(v^m/\mu)_{max} - 1/\bar{\rho}(t)}{(v^m/\mu)_{max} - v_k{}^m/\mu_k} \\ \text{when } \nu^m_k/\mu_k < 1/\bar{\rho}(t), \end{cases} \tag{12}$$

where $\bar{\rho}(t)$ is the average density of the ecological subsystem at

time t, $(v^m/\mu)_{min}$ and $(v^m/\mu)_{max}$ are the minimum and maximum ratios of the partial molar volume to the molecular weight, and v_k^m is the partial volume of the kth component.

Inequalities which make it possible to express under conditions of incomplete data a relation between the numbers of the components, their specific heats of combustion, and the specific heat of combustion of the entire ecological system can be set up similarly by establishing material inequalities for the imbalances in the masses of the components and in the heat of combustion. It is then possible to demonstrate, in particular, that *the weight fraction of any substance in the ecological subsystem at a given instant cannot be greater than the product of the specific heat of combustion of the system and the ratio of the molecular weight to the molar heat of combustion of the given substance.*

In order to discover the relation between the specific radioactivities of physicochemical systems and their content of radioactive isotopes when incomplete data are available, inequalities were set up expressing the imbalance in the overall radioactivity in terms of the weight fractions of the substances and the masses. It was then shown that the *weight fraction of the radioactive isotopes cannot be greater than the ratio of the specific radioactivity of the physicochemical system at a given instant to the specific radioactivity of the isotopes.*

III. Specific rules for the compositions of homogeneous ecological subsystems

We shall find the general relations for a series of readily determined mean statistical characteristics of homogeneous systems such as refractive index, the radiation attenuation factor, etc., on the one hand, and their contents of the components, on the other.

With the aid of the generalised Debye equation, a relation was found between the refractive index of a homogeneous system n and the content of the kth component:

$$\frac{m_k(t)}{M_\Sigma(t)} \leqslant \begin{cases} \left[r_{max} - \dfrac{n^2-1}{(n^2+2)\bar{\rho}(t)}\right] \Big/ (r_{max}-r_k) \\ \text{when } r_k \leqslant (n^2-1)/[(n^2+2)\bar{\rho}(t)], \\ \left[\dfrac{n^2-1}{(n^2+1)\bar{\rho}(t)} - r_{min}\right] \Big/ (r_k - r_{min}) \\ \text{when } r_k > (n^2-1)/[(n^2+2)\bar{\rho}(t)], \end{cases} \tag{13}$$

where r_k is the specific refraction of the kth component and r_{max} and r_{min} are the maximum and minimum specific refractions of the substances constituting the homogeneous system.

With the aid of the equations set up for the imbalance of the molecular refraction and the number of atoms, it proved possible to estimate the maximum possible number of atoms in the molecules from the relative refractive index under the conditions of incomplete information.

The fact that the fraction of radiation absorbed can be readily measured for homogeneous systems makes it possible to compare it with the contents of substances in multicomponent systems under the conditions of incomplete information. A relation which makes it possible to formulate the following rule can be obtained from the Lambert–Bouguer–Beer Law.

The molar concentration of each component in solution cannot exceed the ratio of the logarithm of the attenuation factor for incident radiation attenuated by a layer of solution of unit thickness to the molar extinction coefficient.

By applying the principle of the material-characteristic imbalance to cases of the absorption of radiation, it is possible to establish the following relation:

$$\frac{m_k(t)}{M_\Sigma(t)} \leqslant \begin{cases} \left[\dfrac{1}{\rho(t)L}\ln\dfrac{I_0}{I} - \varepsilon_{min}^{sp}\right] \Big/ (\varepsilon_k^{sp} - \varepsilon_{min}^{sp}) \\ \text{when } \varepsilon_k^{sp} \geqslant [\bar{\rho}(t)L]^{-1}\ln I_0/I, \\ \left[\varepsilon_{max}^{sp} - \dfrac{1}{\bar{\rho}(t)L}\ln\dfrac{I_0}{I}\right] \Big/ (\varepsilon_{max}^{sp} - \varepsilon_k^{sp}) \\ \text{when } \varepsilon_k^{sp} < [\bar{\rho}(t)L]^{-1}\ln I_0/I, \end{cases} \tag{14}$$

where L is the thickness of the layer through which radiation passes, I_0 and I are the intensities of the incident and transmitted radiation, ε_{max}^{sp} and ε_{min}^{sp} are the maximum and minimum specific extinctions, and ε_k^{sp} is the specific extinction of the kth component.

Setting up similarly the inequality for electrical conductivity, we note that *the number of equivalents in a unit volume of any substance, dissociating into ions in solution, cannot be greater than the ratio of the specific conductance of the homogeneous system to the equivalent conductance of the given substance at infinite dilution.*

For systems containing high-molecular-weight compounds, we find, by setting up material imbalance inequalities, the relation between the viscosity-average, number-average, and weight-average molecular weights, on the one hand, and the distribution of the fractions of the macromolecules, on the other. It has been possible to show that *the weight fraction of macromolecules with a molecular weight greater than or equal to the specified value cannot be greater than the ratio of the viscosity-average molecular weight to the specified value raised to the power equal to the parameter of the Mark–Houwink equation, while the numerical fraction of macromolecules with a molecular weight greater than or equal to the specified value cannot be greater than the ratio of the viscosity-average molecular weight to the specified molecular weight.*

IV. Specific rules for compositions of heterogeneous ecological subsystems

When heterogeneous systems are examined, new tasks, involving the determination of their phase and fractional composition and also of the measure of the fragmentation of phases arise. Therefore, in order to establish the general characteristics of the phase composition of heterogeneous systems, we shall set up relations for the imbalance of the volume and mass, expressing them with the aid of the average density of the entire system and the minimum and maximum densities of its constituent phases. As a result, we obtain a relation between the volume fraction of a particular part of the system and the average density of the heterogeneous system in the following form:

$$\frac{V_k^p(t)}{V_\Sigma(t)} \leqslant \begin{cases} [\bar{\rho}(t) - \rho_{min}]/(\rho_k - \rho_{min}) \\ \text{when } \rho_k > \rho(t), \\ [\rho_{max} - \bar{\rho}(t)]/(\rho_{max} - \rho_k) \\ \text{when } \rho_k \leqslant \bar{\rho}(t), \end{cases} \tag{15}$$

where $V_k^p(t)$ is the volume of the kth phase (fraction), $V_\Sigma(t)$ the volume of the entire heterogeneous system, and ρ_k the density of the kth phase.

Consequently, *the volume fraction of the phase (fraction) of the heterogeneous system cannot be greater than the ratio of the deviations*

of the average density of the entire heterogeneous system and the density of the given phase (fraction) from the minimum or maximum density of the heterogeneous system.

From the inequalities expressing the material-volume imbalance, we obtain

$$\frac{m_k^p(t)}{M_\Sigma(t)} \leqslant \begin{cases} \dfrac{1/\bar{\rho}(t)-1/\rho_{max}}{1/\rho_k-1/\rho_{max}} \\ \text{when } \rho_k < \bar{\rho}(t), \\ \dfrac{1/\rho_{min}-1/\bar{\rho}(t)}{1/\rho_{min}-1/\rho_k} \\ \text{when } \rho_k \geqslant \bar{\rho}(t), \end{cases} \tag{15a}$$

which makes it possible to formulate the following rule:

The weight fraction of the phase (fraction) of an ecological heterogeneous subsystem cannot be greater than the ratio of the deviations of the average specific volume of the entire ecological heterogeneous subsystem and the specific volume of the given phase (fraction) from the minimum or maximum specific volume of the subsystem.

As an example, we shall consider the application of this rule to the determination of the weight fraction of one of the components of DNA from the crab *Cancer borealis*. The average density of this DNA in CsCl solution is $\bar{\rho}(t)$ = 1694 kg m^{-3}, while its maximum density is 1700 kg m^{-3} or the density of the satellite band is 1681 kg m^{-3}. We shall estimate from Eqn. (15a) the weight fraction of the satellite band. Here $m_k^p(t)/M_\Sigma(t) \leqslant 0.313$, which corresponds to the real situation (according to experimental data for centrifugation in a density gradient,[32] the relative amount of the minor component of the DNA of the crab *Cancer borealis* in 0.3). The average density of mouse DNA is 1700 kg m^{-3}, while the maximum density is 1701 kg m^{-3}. Then, according to the rule, the weight fraction of the part with the density of 1690 kg m^{-3} is $\leqslant$0.09 and according to experimental data[33] it is approximately 0.08. Thus the experimental results indicate that the relations established can be applied in practice to heterogeneous ecological subsystems.

In the special case where the maximum and minimum specific volumes of phases constituting the system are unknown, it follows from Eqn. (15a) that *the weight fraction of the phase (fraction) of the ecological heterogeneous subsystem cannot be greater than the ratio of its density to the average density of the entire ecological heterogeneous subsystem.*

We shall use the latter postulate to predict the content of water in an ecological subsystem—an active silt representing a complex heterogeneous system containing micro-organisms and solid disperse particles with the aqueous dispersion medium surrounding them. Comparison of the high-speed estimates of the moisture contents of the active silt with the water contents found as a result of drying (Table 1) shows that in all cases the deviation of the high-speed estimates of the moisture content of the active silt from the exact value hardly exceeds 1.21%. The slightly greater moisture content determined by drying compared with the maximum possible value specified by the high-speed estimates in two cases out of 19 can be explained by errors of the measurement.

Consequently one may assume that the relation established between the weight fraction of the phase (fraction) of the ecological heterogeneous system and the ratio of its density to the average density of the entire system does indeed hold in practice and permits high-speed estimates of the moisture content of the active silt—a specific ecological subsystem used in purification plant for the protection of the environment against substances dissolved in waste water.

Table 1. High-speed estimates of the moisture content of an ecological subsystem (active silt) obtained under the conditions of incomplete information and the moisture contents found by a drying procedure*.

Average density of active silt, kg m^{-3}	Density of water, kg × × m^{-3}	Observed moisture content of the active silt, %	High-speed estimate of the moisture content of the active silt, %	Relative error of the high-speed estimate, %
1000.8	996.3	99.12	$\leqslant$99.52	0.40
1009.2	1002.3	99.13	$\leqslant$99.32	0.19
1002.4	993.8	99.29	$\leqslant$99.14	−0.15
1002.4	994.3	99.24	$\leqslant$99.19	−0.05
1001.24	998.8	99.24	$\leqslant$99.76	0.52
998.72	998.62	99.06	$\leqslant$99.99	0.93
1001.43	998.80	99.15	$\leqslant$99.74	0.59
1000.57	998.23	99.35	$\leqslant$99.77	0.42
1002.27	998.80	98.65	$\leqslant$99.65	1.01
1003.33	998.71	98.35	$\leqslant$99.54	1.21
1000.94	994.76	99.23	$\leqslant$99.38	0.15
998.96	994.70	99.25	$\leqslant$99.57	0.32
997.9	994.62	99.02	$\leqslant$99.67	0.65
999.48	995.78	98.94	$\leqslant$99.63	0.69
1001.72	992.88	99.01	$\leqslant$99.12	0.11
999.48	996.40	99.25	$\leqslant$99.69	0.44
996.93	995.84	99.40	$\leqslant$99.96	0.56
997.38	996.86	99.34	$\leqslant$99.94	0.60
999.11	996.11	99.30	$\leqslant$99.70	0.40

* The experiments were performed under the author's supervision in the Academy of Communal Economy.

We now set up the inequality for the imbalance of specific heats:

$$m_k^p(t)C_{p_k} + [M_\Sigma(t) - m_k^p(t)]C_{p_{min}} \leqslant M_\Sigma(t)\bar{C}_{sp}(t), \tag{16}$$

where $m_k^p(t)$ is the mass of the kth phase, $C_{p_k}^{sp}$ the specific heat of the kth phase, and $C_{p_{min}}^{sp}$ the minimum specific heat of the phases. The mass imbalance can be formulated as follows with the aid of the specific heats:

$$m_k^p(t) + [M_\Sigma(t)\bar{C}_{sp}(t) - m_k^p(t)C_{p_k}^{sp}]/C_{p_{max}} \leqslant M_\Sigma(t). \tag{17}$$

After rearrangements and combination of formulae (16) and (17), we arrive at the following postulate:

The weight fraction of a given phase, in a heterogeneous system, cannot be greater than the ratio of the deviations of the specific heat of the entire heterogeneous system and of the partial specific heat of the given phase from the minimum or maximum specific heats of the phases of the heterogeneous system.

Using the principle of the material-characteristic imbalance, we shall establish the general characteristics of the fragmentation of phases and of the size distribution of particles. By solving this problem with the aid of a sequence of inequalities, we obtain relations equivalent to such assertions.

The weight fraction of a part (fraction) of a heterogeneous system cannot be greater than one third of the product of the specific surface

of the entire system, the density of the disperse phase, and the maximum radius of the particles of the given part; the weight fraction of any part (fraction) of particles of a fragmented phase cannot be greater than the product of the specific number of the particles and the mass of the particle of maximum size in the given part (fraction).

Analysis of the adsorption of a multicomponent mixture can also be carried out under conditions of incomplete information with the aid of the idea of material imbalance. It was found that

$$\Gamma_k(t) \leqslant \begin{cases} (V_\Sigma(0)\bar{\rho}(0) - \bar{\rho}(t)V_\Sigma(t)]/(\mu_k S_{sp} M_\Gamma), \\ \text{provided that the qualitative composition of the mixture of adsorbates is known;} \\ \dfrac{[N_\Sigma(0) - N_\Sigma(t)]\mu_{max} - [V_\Sigma(0)\bar{\rho}(0) - V_\Sigma(t)\bar{\rho}(t)]}{M_\Gamma S_{sp}(\mu_{max} - \mu_k)}, \\ \text{when the qualitative composition of the mixture adsorbate is known if} \\ \mu_k < [V_\Sigma(0)\bar{\rho}(0) - V_\Sigma(t)\bar{\rho}(t)]/[N_\Sigma(0) - N_\Sigma(t)]; \\ \dfrac{\bar{\rho}(0)V_\Sigma(0) - \bar{\rho}(t)V_\Sigma(t) - \mu_{min}[N_\Sigma(0) - N_\Sigma(t)]}{M_\Gamma S_{sp}(\mu_k - \mu_{min})}, \\ \text{when the qualitative composition of the mixture adsorbate is known if} \\ \mu_k \geqslant [V_\Sigma(0)\bar{\rho}(0) - V_\Sigma(t)\bar{\rho}(t)]/[N_\Sigma(0) - N_\Sigma(t)]. \end{cases} \quad (18)$$

Here M_Γ and S_{sp} are the mass and specific surfaces of the adsorbent and $\Gamma_k(t)$ is the degree of adsorption of the kth component from the mixture of adsorbable substances at time t. Thus it is possible to analyse the adsorption process under conditions of a small amount of initial data.

V. Analysis of the deviation from the limiting possible contents of substances and rates of chemical reactions

For a number of problems of the protection of the environment, it is necessary not only to indicate the ranges of the possible contents of substances but also to achieve point predictions of all the quantities and to estimate the possible deviations. Theoretical analysis led to the derivation of formulae demonstrating that, for any prespecified absolute or relative deviation of the content of a component from its maximum possible value, there may exist ecological subsystems such that the real deviation is equal to the specified deviation. This means that the points corresponding to the different ecological subsystems can continuously fill the space of the possible contents of the components determined by the ratio of the average characteristic of the system to the isotypical measure of the properties of the components.

We shall make use of the universal characteristics of the compositions for the point estimates of the contents of the components in ecological subsystems. For a minimum amount of initial data, it is useful to postulate that the point estimate x_{est} of the weight fraction of components with $\mu_l > \mu_k$ is given by

$$x_{est} = 1 - n^*_{sp}(t)\mu_k/2. \quad (19)$$

The relative error of this estimate is

$$\frac{|x_{est} - \sum_{\mu_i > \mu_k} m_i(t)/M_\Sigma(t)|}{\sum_{\mu_i > \mu_k} m_i(t)/M_\Sigma(t)} \leqslant \frac{n^*_{sp}(t)\mu_k}{2[1 - n^*_{sp}(t)\mu_k]}. \quad (20)$$

In the case where qualitative analytical data are also available, the point predictions are refined. It follows from the relations established that in this situation the point estimate of the weight fraction of substances with specific heats greater than or equal to the specified value C^{sp}_k can be obtained with the aid of formula

$$x^c_{est} = 1 - (1/2)[\bar{C}_{sp}(t) - C^{sp}_{min}]/(C^{sp}_k - C^{sp}_{min}), \quad (21)$$

subject to the relative error

$$\frac{|x^c_{est} - \sum_{c_i^{sp} \geq C_k^{sp}} m_i(t)/M_\Sigma(t)|}{\sum_{c_i^{sp} \geq C_k^{sp}} m_i(t)/M_\Sigma(t)} \leqslant \frac{\bar{C}_{sp}(t) - C^{sp}_{min}}{2[C^{sp}_k - \bar{C}_{sp}(t)]}. \quad (22)$$

The non-equilibrium concentrations of reactants and products in the system can also be estimated with the aid of the equilibrium constants for closed homogeneous systems. For this purpose, the equilibrium value of the chemical variable is determined from the solution of the equation containing the equilibrium constant and the initial concentrations of the products and reactants of the chemical reaction.[33] With the aid of this variable, the point predictions of the concentrations of reactants and products and *a priori* estimates of their errors are found.

Table 2. ***A priori*** **estimates of the absolute errors of the point estimates of the rates of chemical reactions for a known ratio of the reactant concentrations.**

Reaction	Order of reaction	Rate constant for reaction	Overall concentration of reactants, kg m^{-3}	Absolute error of the point prediction of the rate of reaction kmol m^{-3} s^{-1}	*A priori* absolute estimate of the error of the prediction of the rate of reaction, kmol m^{-3} s^{-1}
Interaction of triphenylmethyl chloride with methanol	3	4.48×10^{-3} m^3 kmol^{-1} s^{-1}	31,281	$3.407 \cdot 10^{5}$	$\leqslant 3.545 \cdot 10^{-5}$
$NO_2 \rightarrow NO + (^1/_2)O_2$	2	100.6 m^3 kmol^{-1} s^{-1}	$1.84 \cdot 10^{-3}$	$7.9 \cdot 10^{-8}$	$\leqslant 8 \cdot 10^{-8}$
$C_6H_5-C\equiv C-COOH + I_2 \rightarrow C_6H_5-CI= =CI-COOH$	2	1.02×10^{-3} m^3 kmol^{-1} s^{-1}	10,039	$2.965 \cdot 10^{-7}$	$\leqslant 3.465 \cdot 10^{-7}$
Thermal decomposition of dioxane	1.5	5.8×10^{-3} m$^{1.5}$ kmol$^{-0.5}$ s^{-1}	1.45	$1.23 \cdot 10^{-5}$	$\leqslant 1.23 \cdot 10^{-5}$
$CH_2CHBrCOO^- + OH^- \rightarrow Br^- + CH_2CH(OH)COO^-$	2	5.73×10^{-4} m^3 kmol^{-1} s^{-1}	77.786	$6.069 \cdot 10^{-5}$	$\leqslant 6.193 \cdot 10^{-5}$

In order to predict the results of the change in the compositions of ecological systems and subsystems under the conditions of incomplete information, it is essential to analyse the possible deviations of the rates of chemical reactions from their maximum values. As a result of a theoretical study, it has been shown that, by virtue of the limitations to the densities of solutions and to the overall pressure of the mixture of gases, under real conditions the rates of chemical reactions have a relative maximum. It was found that, when account is taken of the first limitation, the rate of the chemical reaction reaches its relative maximum value for molar concentrations of the reactants directly proportional to the ratio of the kinetic orders with respect to these substances to their molecular

weights and, for a limited maximum total pressure of the gas mixture in the reactor, the rate of a chemical gas-phase reaction reaches its maximum value in the case where the partial pressures of the reactants are in the same proportions relative to one another as the kinetic orders with respect to these substances.

The possible ranges of the rates of chemical reactions thus established permitted point predictions of their values and the estimation of the absolute errors of such predictions under conditions of incomplete information. Table 2 presents the results of such predictions. The rate constants for the calculations were taken from Emanuel' and Knorre.[34] In all the cases analysed, such predictions proved justified.

Formulae for the estimation of the concentrations and mass of the products formed as a result of the reactions in ecological subsystems and also inequalities for the *a priori* estimation of their accuracy were derived with the aid of the maximum possible rates of chemical reactions.

In all cases of practical importance, parallel chemical reactions occur when measures are taken for the protection of nature and in respiration, digestion, and other processes where the organisms interact with the components of the environment. Under such conditions, a sequence of the following inequalities can be written for the estimation of the weight fractions of the reactants forming a monotonically non-decreasing sequence of reactivities:

$$\sum_{i=1}^{l_s} m_i(t) \leqslant \sum_{i=1}^{j-1} m_i(0) + [1-\varkappa_j(t)] \sum_{i=j}^{l_s} m_i(0) \leqslant$$

$$\leqslant [1-\varkappa_j(t)] \sum_{i=1}^{l_s} m_i(0) + \varkappa_j(t)\mu_{j-1} \sum_{i=1}^{j-1} m_i(0)\mu_i^{-1} \leqslant$$

$$\leqslant \left\{1-\varkappa_j(t)\left[1-\mu_{j-1}\sum_{i=1}^{l_s} n_i(0) \Big/ \sum_{i=1}^{l_s} m_i(0)\right]\right\} \sum_{i=1}^{l_s} m_i(0), \quad (23)$$

where $\varkappa_j(t)$ is the degree of conversion of the jth substance at time t; $1 \leqslant j \leqslant l_s$; l_s is the number of reactants forming the reactivity sequence.

The following rule follows from Eqn. (23):

The weight fraction of the substances in the mixture, which form a series with monotonically non-decreasing reactivities and which have not entered into parallel chemical reactions, cannot be greater than the sum of the quantity supplementing the degree of conversion of any one substance in the given mixture up to unity and the product of this degree of conversion, the molecular weight of the preceding substance in the reactivity series, and the specific number of moles of the initial mixture of substances forming the given series.

In the case where there is a monotonically non-increasing reactivity, another sequence of inequalities is valid:

$$\sum_{i=1}^{l_s} n_i(t) \leqslant [1-\varkappa_j(t)] \sum_{i=1}^{j} n_i(0) + \sum_{i=j+1}^{l_s} n_i(0) \leqslant$$

$$\leqslant \sum_{i=1}^{l_s} n_i(0)[1-\varkappa_j(t)] + \varkappa_j(t) \sum_{i=j+1}^{l_s} n_i(0) \leqslant$$

$$\leqslant \left\{1-\varkappa_j(t)\left[1-\sum_{i=j+1}^{l_s} n_i(0)\mu_i \Big/ \left(\mu_{j+1}\sum_{i=1}^{l_s} n_i(0)\right)\right]\right\} \sum_{i=1}^{l_s} n_i(0) \leqslant$$

$$\leqslant \left\{1-\varkappa_j(t)\left[1-\sum_{i=1}^{l_s} m_i(0) \Big/ \left(\mu_{j+1}\sum_{i=1}^{l_s} n_i(0)\right)\right]\right\} \sum_{i=1}^{l_s} n_i(0). \quad (24)$$

On the basis of Eqns. (24), we formulate a new rule:

The overall mole fraction of substances which have not entered into parallel chemical reactions by time t and which form a series with monotonically non-increasing reactivities cannot be greater than the sum of the quantity supplementing up to unity the degree of conversion of any of the substances constituting the reactivity series and the ratio of this degree of conversion to the product of the molecular weight of the next substance, after the chosen one, and the specific number of moles of the initial mixture of substances constituting the reactivity series.

We shall make use of the rules established for the occurrence of parallel chemical reactions in order to obtain point estimates of the results of chemical reactions of this type. Here one can write

$$\frac{m_{re}^{est}(t)}{\sum_{i=1}^{l_s} m_i(0)} = 1 - \frac{1}{2}\{1 - x_j(t)[1 - \mu_{j-1}n_{sp}^{s}(0)]\}, \quad (25)$$

where $m_{re}^{est}(t)$ is the point estimate of the overall mass of the substances constituting the reactivity series and entering into chemical reactions and $n_{sp}^{s}(0)$ is the specific number of moles of these substances at $t = 0$.

It follows from Eqns. (23) and (25) that the relative error of such a point estimate must satisfy the inequality

$$\frac{|m_{re}^{est}(t) / \sum_{i=1}^{l_s} m_i(0) - \sum_{i=1}^{l_s}[m_i(0) - m_i(t)] / \sum_{i=1}^{l_s} m_i(0)|}{\sum_{i=1}^{l_s}[m_i(0) - m_i(t)] / \sum_{i=1}^{l_s} m_i(0)} \leqslant$$

$$\leqslant \frac{1 - \kappa_j(t)[1 - \mu_{j-1}n_{sp}^{s}(0)]}{2\{\kappa_j(t)[1 - \mu_{j-1}n_{sp}^{s}(0)]\}}. \quad (26)$$

A point estimate of the mole fraction of the substances which have reacted is obtained similarly using Eqns. (24).

Various mixtures of petroleum products, members of genetic and homologous series, etc., entering the environment and present in various ecological subsystems, belong to the set of substances forming series with monotonically non-increasing or monotonically non-decreasing reactivities in parallel chemical reactions.

Point estimates of the results of parallel chemical reactions in ecological system can be refined, provided that data for μ_{min}^{s} and μ_{max}^{s}—the minimum and maximum molecular weights of the substances constituting sequences with monotonically non-decreasing or monotonically non-increasing reactivities—are available. Since

$$\sum_{i=1}^{j-1} m_i(0) \leqslant \mu_{j-1} \sum_{i=1}^{j-1} n_i(0),$$

it follows that, on the basis of the imbalance of the number of moles in the mixture, we obtain

$$\sum_{i=1}^{j-1} m_i(0)/\mu_{j-1} + \left[\sum_{i=1}^{l_s} m_i(0) - \sum_{i=1}^{j-1} m_i(0)\right] \Big/ \mu_{max}^{s} < n_{sp}^{s}(0) \sum_{i=1}^{l_s} m_i(0).$$

Consequently,

$$\sum_{i=1}^{j-1} m_i(0) \Big/ \sum_{i=1}^{l_s} m_i(0) \leqslant \frac{n_{sp}^{s}(0) - 1/\mu_{max}^{s}}{1/\mu_{j-1} - 1/\mu_{max}^{s}}.$$

On the basis of the latter expression, we find the relation for the case of a monotonically non-decreasing reactivity of a mixture with known values of μ^s_{max} and μ^s_{min}:

$$\sum_{i=1}^{l_s}[m_i(0)-m_i(t)]\Big/\sum_{i=1}^{l_s}m_i(0)\geqslant\varkappa_j(t)\left[1-\frac{n^s_{sp}(0)-1/\mu^s_{max}}{1/\mu_{j-1}-1/\mu^s_{max}}\right].$$

This makes it possible to obtain the point estimates

$$m^{est}_{re}(t)\Big/\sum_{i=1}^{l_s}m_i(0)=1-\frac{1}{2}\left\{1-\kappa_j(t)\left[1-\frac{n^s_{sp}(0)-1/\mu^s_{max}}{1/\mu_{j-1}-1/\mu^s_{max}}\right]\right\},$$

and an *a priori* estimate of the modulus of the relative error:

$$\frac{|m^{est}_{re}(t)-\sum_{i=1}^{l_s}[m_i(0)-m_i(t)]|}{\sum_{i=1}^{l_s}[m_i(0)-m_i(t)]}\leqslant\left\{1-\kappa_j(t)\left[1-\frac{n^s_{sp}(0)-1/\mu^s_{max}}{1/\mu_{j-1}-1/\mu^s_{max}}\right]\right\}\Big/$$

$$\Big/2\kappa_j(t)\left[1-\frac{n^s_{sp}(0)-1/\mu^s_{max}}{1/\mu_{j-1}-1/\mu^s_{max}}\right].$$

For the case of the monotonically non-increasing reactivity of the mixture, we obtain after similar steps

$$\sum_{i=1}^{l_s}[n_i(0)-n_i(t)]\Big/\sum_{i=1}^{l_s}n_i(0)\geqslant\kappa_j(t)\left(1-\frac{1/n^s_{sp}(0)-\mu_{min}}{\mu_{j+1}-\mu^s_{min}}\right).$$

Consequently the number of moles of the reactive substances constituting a mixture with monotonically non-increasing reactivity can be estimated with the aid of the expression

$$n^{est}_{re}(t)\Big/\sum_{i=1}^{l_s}n_i(0)=1-\frac{1}{2}\left\{1-\kappa_j(t)\left[1-\frac{1/n^s_{sp}(0)-\mu^s_{min}}{\mu_{j+1}-\mu_{min}}\right]\right\},$$

subject to the guaranteed relative error

$$\frac{|n^{est}_{re}(t)-\sum_{i=1}^{l_s}[n_i(0)-n_i(t)]|}{\sum_{i=1}^{l_s}n_i(0)}\leqslant\left\{1-\kappa_j(t)\left(1-\frac{1/n^s_{sp}(0)-\mu^s_{min}}{\mu_{j+1}-\mu^s_{min}}\right)\right]\Big/$$

$$\Big/2\kappa_j(t)\left(1-\frac{1/n^s_{sp}(0)-\mu^s_{min}}{\mu_{j+1}-\mu^s_{min}}\right).$$

VI. Specific features of the estimation of the changes in disperse ecological subsystems when nature-protecting measures are taken

The disperse particles entering the environment, formed as a result of man's industrial activity, exert an appreciable negative influence on consumers and producers. In order to predict the amount of disperse contaminants entering the hydrosphere and the atmosphere together with waste water and gaseous waste, it is necessary to establish the efficiency of the purification of such waste water and gaseous waste as a result of nature-protecting measures. A characteristic of the process involving the removal of disperse particles from an ecological subsystem is the degree of separation (purification) $\varkappa_s$ — a quantity indicating the weight fraction of the disperse phase trapped by means of technical nature-protecting procedures. Another parameter — the relative loss ε — is equal to the weight fraction of the residual disperse phase particles in the liquid or gas after purification. There exists a simple relation between the degree of separation (purification) and the relative loss:

$$\varkappa_s=1-\varepsilon.$$

If after the completion of the application of nature-protecting measures, no compression or rarefaction of the purified liquid and gaseous media occurred, then the relative loss is equal to the ratio of the output and input weight concentrations of the disperse phase.

Taking into account the specific features of the disperse systems and using a probability (statistical?) treatment of the separation process, we formulate an expression for the degree of separation $\varkappa_s$ in the form

$$\varkappa_s=\int_o^\infty P_{11}(r,t|\mathrm{B})dF_1(r), \tag{27}$$

where $F_1(r)$ is the integral size distribution function of the particles of the disperse phase at the instant when the disperse system is introduced into the separation apparatus and $P_{11}(r,\ t|\mathrm{B})$ is the conventional probability of the separation (of entry into the collector designed for the disperse phase) by time t of a molecule present in particle having a radius r on entry into the apparatus subject to the condition that all the particles and molecules of the disperse medium enter the collectors for the phases undergoing separation.

In the separation of heterogeneous systems in continuous operation apparatus, the particles may become dispersed owing to the presence of velocity gradients in the streams and their impact against the inner surfaces of the apparatus and against one another. The fine particle fragments formed (other characteristics remaining unchanged: density and charge) are in most cases more difficult to separate than the whole particles. If the comminution takes place only at the instant when the particles are introduced into the apparatus, then the efficiency of the separation will be smaller than for gradual dispersion to the same extent. Therefore

$$\varkappa_s>\int_o^\infty P_{11}(r,t|\mathrm{B}\cap\mathrm{Con})dF^{fr}_1(r), \tag{28}$$

where $F^{fr}_1(r)$ is the integral size distribution function of the particles after grinding and $P_{11}(r,\ t|\mathrm{B}\cap\mathrm{Con})$ is the conventional probability of the separation of particles which have retained their initial dimensions subject to the condition that they enter one of the separation zones (one of the collectors).

For further exposition, we introduce the concept of the quasi-size of the separation of order α. We shall define the quantity r_{s_α} as the radius of a particle such that the relation

$$P_{11}(r,\ t|\mathrm{B}\cap\mathrm{Con})\geqslant 1-\alpha,$$

is valid for $r\geqslant r_{s_\alpha}$. It follows from this definition that in the general case r_{s_α} depends on the current time t. The application of the concept of the quasi-size of the separation makes it possible to take into account the experimentally observed effects involving the loss of individual large particles owing to random influences, eddies, and streams of dispersion media, while finer particles are fully separated.

Using r_{s_α}, we can formulate the following inequality:

$$\int_o^\infty P_{11}(r,t|\mathrm{B}\cap\mathrm{Con})dF^{fr}_1(r)\geqslant(1-\alpha)\int_{r_{s_\alpha}}^\infty dF^{fr}_1(r). \tag{29}$$

Then

$$\varkappa_s\geqslant(1-\alpha)[1-F^{fr}_1(r_{s_\alpha})]. \tag{30}$$

In its turn, we have

$$\int_o^{r_{s_\alpha}} dF_1^{\text{fr}}(r) \leqslant r_{s_\alpha}^n \int_o^{r_{s_\alpha}} r^{-n} dF^{\text{fr}}(r) \leqslant r_{s_\alpha}^n \int_o^{\infty} r^{-n} dF_1^{\text{fr}}(r), \tag{31}$$

whereupon

$$\overline{r_{\text{fr}}^{-n}} = \int_o^{\infty} r^n dF_1^{\text{fr}}(r) \text{ and } \int_o^{r_{s_\alpha}} dF_1^{\text{fr}}(r) = F_1^{\text{fr}}(r_{s_\alpha}). \tag{32}$$

Ultimately, we have

$$F_1^{\text{fr}}(r_{s_\alpha}) \leqslant \overline{r_{\text{fr}}^{-n}} r_{s_\alpha}^n. \tag{33}$$

Consequently,

$$\varkappa_s \geqslant (1-\alpha)(1-\overline{r_{\text{fr}}^{-n}} r_{s_\alpha}^n). \tag{34}$$

The universal relation for the degree of separation thus demonstrated is valid for any form of the size distribution function of particles. This inequality is applicable to both continuous and periodic heterogeneous system separation processes. For its practical employment, it is essential to determine the quantity $\overline{r_{\text{fr}}^{-n}}$ for any positive value of n. For this purpose, we express $\overline{r_{\text{fr}}^{-3}}$ in terms of the particle concentration ν_{fr} after fragmentation. In the case of particles of arbitrary shape, the particle concentration is

$$\nu = \frac{C_o}{\beta_s \rho_1} \int_o^{\infty} \frac{dF_1(r)}{r^3} = \frac{C_o \overline{r^{-3}}}{\beta_s \rho_1}, \tag{35}$$

where β_f is a coefficient equal to the ratio of the volume of the particle to that of the cube having its characteristic dimension (for spherical particles, $\beta_f = 4/3\pi$) and C_0 is the concentration of the particles of the disperse phase.

If the particles of the disperse phase are insoluble in the dispersion medium, then the particle concentration after fragmentation can be found from the formula

$$\nu_{\text{fr}} = \beta_p C_o \overline{r^{-3}} / (\beta_f \rho_1), \tag{36}$$

where β_p is the fragmentation coefficient indicating by what factor the number of particles has increased on dispersion.

It follows from Eqn. (36) that $\nu_{\text{fr}} = \beta_p \nu$. On the other hand,

$$\nu_{\text{fr}} = C_o \overline{r_{\text{fr}}^{-3}} / (\beta_f \rho_1).$$

Hence

$$r_{\text{fr}}^{-3} = \beta_p \beta_f \rho_1 \nu / C_o. \tag{37}$$

We shall refer to the ratio ν/C_0 as the specific number of particles and shall denote it by n_{sp}. We may note that the product $\beta_f \rho_1 r_{s_\alpha}^3$ is none other than $m_p(r_{s_\alpha})$—the mass of a particle whose radius is equal to the quasi-size of the separation. Then on substituting Eqn. (37) in the inequality (34), we obtain

$$\varkappa_s \geqslant (1-\alpha)[1-\beta_p m_p(r_{s_\alpha})\nu/C_o]. \tag{38}$$

We express $\overline{r^{-1}}$ with the aid of the specific surface. For particles of arbitrary shape,

$$S_{\text{sp}} \geqslant 3\rho_1^{-1} \int_o^{\infty} r^{-1} dF_1(r). \tag{39}$$

This inequality is converted into an equality in the case of spherical particles with an ideally smooth surface. Therefore

$$\overline{r^{-1}} \leqslant S_{\text{sp}} \rho_1 / 3. \tag{40}$$

For $\overline{r_{\text{fr}}^{-1}}$, one can also write

$$\overline{r_{\text{fr}}^{-1}} < S_{\text{sp}}^{\text{fr}} \rho_1 / 3 \text{ or } \overline{r_{fr}^{-1}} < \beta_s S_{\text{sp}} \rho_1 / 3,$$

where $S_{\text{sp}}^{\text{fr}}$ is the specific surface after dispersion and β_s is a coefficient showing by what factor the specific surface has increased owing to the fragmentation of the particles. With the aid of the latter inequality, we obtain from Eqn. (34)

$$\varkappa_s \geqslant (1-\alpha)[1-\beta_s S_{\text{sp}} \rho_1 r_{s_\alpha}/3]. \tag{41}$$

When the separation process is effected as a result of the work performed by external forces A, the particles may undergo deformation and fragmentation and an amount of heat Q may be evolved. We denote by $m_1^+(t)$ the mass of the disperse phase entering the apparatus at time t; ΔH_{def} is the change in the internal energy of the heterogeneous system on deformation of the particles. For systems which do not contain highly disperse fractions, one can write for the process under stationary conditions

$$A = \Delta U_{\text{def}} + Q + m_1^+(t)[S_{\text{sp}}^{\text{fr}} - S_{\text{sp}}]\sigma. \tag{42}$$

Hence

$$S_{\text{sp}}^{\text{fr}} = (A - \Delta U_{\text{def}} - Q)/[\sigma m_1^+(t)] + S_{\text{sp}}. \tag{43}$$

Subsequently

$$\beta_s = (A - \Delta U_{\text{def}} - Q)/[\sigma S_{\text{sp}} m_1^+(t)] + 1. \tag{44}$$

Thus the coefficient β_s, taking into account the phenomenon of dispersion during separation, can be found from simple energy relations. It is seen from Eqn. (44) that, other conditions being equal, the coefficient β_s diminishes with increase in the specific surface of the heterogeneous system entering the apparatus, i.e. the intensity of the comminution diminishes with increase in dispersity.

In the absence of dispersion, the coefficient $\beta_p = \beta_s = 1$ and formulae (38) and (41) assume the following form:

$$\varkappa_s \geqslant (1-\alpha)[1-n_{\text{sp}} m_p(r_{s_\alpha})], \tag{45}$$

$$\varkappa_s \geqslant (1-\alpha)(1-S_{\text{sp}} r_{s_\alpha} \rho_1/3). \tag{46}$$

The quantities r_{s_α} can be determined not only theoretically but also experimentally. A suspension (emulsion or aerosol) resistant to aggregation and having a known grain size distribution must be used for the experiment.

When random influences are negligible, for example, when coarsely disperse particles are deposited in the gravitational field, one can assume that all the particles larger than a certain radius r_{s_o}, called the size of the separation, are fully separated. When this condition holds, we find from the inequalities (45) and (46), having put $\alpha = 0$ in the latter,

$$\varkappa_s \geqslant 1 - n_{\text{sp}} m_p(r_{s_o}), \tag{47}$$

$$\varkappa_s \geqslant 1 - S_{\text{sp}} r_{s_o} \rho_1/3. \tag{48}$$

In the analysis of separation processes, the concept of the relative loss (breakthrough) ε is frequently employed. By definition, $\varepsilon = 1 - \varkappa_s$. From the inequalities (47) and (48), we obtain

$$\varepsilon \leqslant n_{\text{sp}} m_p(r_{s_o}), \tag{49}$$

$$\varepsilon \leqslant S_{\text{sp}} \rho_1 r_{s_o}/3. \tag{50}$$

The results of the theoretical study, expressed by the inequalities (45) and (46), can be usefully formulated in the form of the following theorems:

Theorem 5. *The relative loss (the ratio of the output and input weight concentrations) of the disperse phase cannot be greater than the sum of the specified probability and the product of the quantity supplementing to unity the specified probability, the specific number of particles, and the mass of the particle which is not separated with the specified probability.*

Theorem 6. *The relative loss (the ratio of the output and input weight concentrations) of the disperse phase cannot be greater than the sum of the specified probability and one third of the product of the specific surface, the quantity supplementing to unity the specified probability, the density of the disperse phase, and the radius of the particle which is not separated with the specified probability.*

In order to estimate the maximum possible degree of separation, we introduce the concept of the quasi-size of the loss r_{e_α} of order α. The quantity r_{e_α} will be defined as the radius of the particles such that the probability $P_{11}(r, t|\mathrm{B}\cap\mathrm{Con}) \leqslant \alpha$ for $r < r_{e_\alpha}$.

Taking into account the possibility of the fragmentation of particles, we obtain with the aid of r_{e_α}

$$\varkappa_s \leqslant \int_0^\infty P_{11}(r, t \mid \mathrm{B} \cap \mathrm{Con})\, dF_1(r) \leqslant$$
$$\leqslant \alpha \int_0^{r_{e\alpha}} dF_1(r) + \int_{r_{e\alpha}}^\infty P_{11}(r, t \mid \mathrm{B} \cap \mathrm{Con})\, dF_1(r). \qquad (51)$$

Since $P_{11}(r, t|\mathrm{B}\cap\mathrm{Con}) \leqslant 1$, it follows that

$$\int_{r_{e\alpha}}^\infty P_{11}(r, t \mid \mathrm{B} \cap \mathrm{Con})\, dF_1(r) \leqslant \int_{r_{e\alpha}}^\infty dF_1(r). \qquad (52)$$

We therefore have

$$\int_0^\infty P_{11}(r, t|B\cap\mathrm{Con})\, dF_1(r) \leqslant 1 - F_1(r_{e_\alpha}) + \alpha F_1(r_{e_\alpha}). \qquad (53)$$

Since

$$F_1(r_{e_\alpha}) \geqslant 1 - \int_{r_{e\alpha}}^\infty (r/r_{e\alpha})^n\, dF_1(r) \geqslant 1 - r_{e\alpha}^{-n} \int_0^\infty r^n\, dF_1(r), \qquad (54)$$

it follows that

$$F_1(r_{e_\alpha}) \geqslant 1 - \overline{r^n}/r_{e_\alpha}^n. \qquad (55)$$

Consequently

$$\varkappa_s \leqslant \alpha + (1-\alpha)\overline{r^n}/r_{e_\alpha}^n. \qquad (56)$$

On the basis of the results obtained, we formulate the following theorem:

Theorem 7. *The degree of separation of a disperse system cannot be greater than the sum of the order of the quasi-size of the loss and the product of the quantity supplementing to unity the order of the quasi-size and the ratio of the initial nth order moment of the random particle radius to the quasi-size of the loss raised to the nth power.*

With the aid of the relations demonstrated, one can also obtain point estimates of the degree of separation of disperse systems with an improved accuracy. Bearing in mind that, when $\alpha = 0$, the relative loss $\varepsilon \leqslant \overline{r^{-n}} r_{s_0}^n$, we can write expressions for the point estimate of the degree of separation:

$$\varkappa_{\mathrm{est.}} = 1 - \overline{r^{-n}} r_{s_0}^n/2, \qquad (57)$$

and for the *a priori* estimate of the modulus of its relative error:

$$\frac{|\varkappa_s - \varkappa_{\mathrm{est.}}|}{\varkappa_s} \leqslant \frac{r_{s_0}^n \overline{r^{-n}}}{2\varkappa_s} \leqslant \frac{r_{s_0}^n \overline{r^{-n}}}{2(1 - r_{s_0}^n \overline{r^{-n}})}, \qquad (58)$$

where $n = 1$, we obtained from the last two relations

$$\varkappa_{\mathrm{est.}} = 1 - S_{\mathrm{sp}} \rho_1 r_{s_0}/6 \text{ and}$$

$$\frac{|\varkappa_s - \varkappa_{\mathrm{est.}}|}{\varkappa_s} \leqslant \frac{S_{\mathrm{sp}} \rho_1 r_{30}}{6 - 2 S_{\mathrm{sp}} \rho_1 r_{s_0}}, \qquad (59)$$

and, when $n = 3$, they assume the following form:

$$\varkappa_{\mathrm{est.}} = 1 - n_{\mathrm{sp}} m_{\mathrm{p}}(r_{s_0})/2 \text{ and}$$

$$\frac{|\varkappa_s - \varkappa_{\mathrm{est.}}|}{\varkappa_s} \leqslant \frac{n_{\mathrm{sp}} m_{\mathrm{p}}(r_{s_0})}{2[1 - n_{\mathrm{sp}} m_{\mathrm{p}}(r_{s_0})]}. \qquad (60)$$

As was in fact to be expected, all the experimental points obtained by different workers[35–38] lie close to the line of the predicted degrees of separation and none fall into the cross-hatched regions of impossible values (Figs. 3 and 4). The closer were the points in Fig. 4 plotted from the experimental values to the abscissa axis, the more accurate was the *a priori* point estimate of the degee of separation of the disperse systems.[38]

VII. The rule for the compositions of simple and complex two-component and multi-component ecological systems and subsystems

Comparison of the rules established above for the compositions of homogeneous and heterogeneous ecological subsystems makes it possible to discover their general features and to proceed to the solution of the problem of the discovery and formulation of the main rule for the compositions of ecological systems and subsystems, generalising the results obtained in the theoretical study.

All the inequalities for the contents of substances, demonstrated for both homogeneous and heterogeneous systems, can be reduced to the following form provided that qualitative analytical data are available:

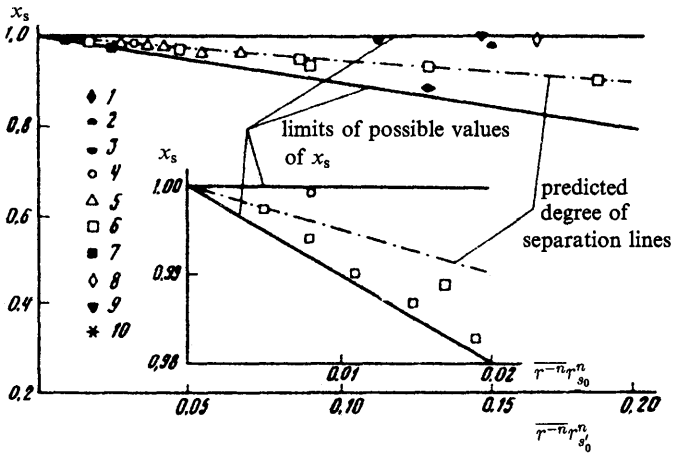
$$\mathfrak{D}_i(t) \leqslant (\overline{\mathrm{S}}(t) - \mathrm{S_b})/(\mathrm{S}_i - \mathrm{S_b}), \qquad (61)$$

where $\mathfrak{D}_i(t)$ is the fraction (weight, mole, or volume fraction) of the component, phase, or part (fraction) of the ecological subsystem, $\overline{\mathrm{S}}(t)$ is an average physicochemical characteristic of the system, $\mathrm{S_b}$ is the boundary value (minimum or maximum) of the isotypical measure of the property of the given substance of the system, and S_i is a measure of the property of the ith component.

The inequality (61) is equivalent to the following formulation of a theorem:

Theorem 8. *The fraction of any component [phase, part (fraction)] of ecological systems and subsystems cannot be greater than the ratio of the deviations of the average characteristic of the entire system (subsystem) as a whole and the isotypical measure of the property of the component, phase, or part (fraction) from their maximum or minimum value.*

Varieties of the expression for the fraction are unambiguously related to the method of averaging the physicochemical characteristic of the ecological system (subsystem). For example, if this is the specific number of moles, then $\mathfrak{D}_i(t)$ will be the weight fraction and if it is the average density $\bar{S}(t)$ then $\mathfrak{D}_i(t)$ will be the volume fraction.



Point	System being separated (purified)	Separation apparatus
1	Aqueous oil emulsion	Ultracentrifuge
2	Tobacco dust	Sleeve filter, No. 2 cloth fabric
3	Tobacco dust	Sleeve filter, No. 5114 nitron fabric
4	Water drops	Cyclone
5	Kaolin suspension	Centrifugal "Plava-E" separator
6	Suspension of poly (vinyl chloride)	Tubular centrifuge
7	Kaolin suspension	Tubular centrifuge
8	Quartz glass suspension	Cup-type centrifuge
9	Suspension of Ammophos sludge	Settling tank
10	Coal powder	Sifting screen

Figure 3. Point estimates of the degree of separation (purification) of disperse systems.

On combining the entire set of relations established, we obtain the following equation:

$$\mathfrak{D}_i(t) = K_i(t)\bar{S}(t)/S_i, \qquad (62)$$

which reflects the principal rule for the compositions of multicomponent ecological subsystems and eco-systems:

The relative amounts (contents) of substances, phases, fractions, parts, and subsystems in any ecological systems (subsystems) can be numerically estimated at any instant by comparison with the ratios of the average (overall) characteristic of the system (subsystem) to the isotypical measures of the properties of the substances, phases, fractions, parts, and subsystems multiplied by coefficients which are always smaller or equal to unity and do not increase by discrete increments together with the uncertainty of the estimate with increase in the level of the reliable initial information.

For the practical employment of the principal rule for the compositions of ecological subsystems and systems, it proved necessary to calculate the coefficients in Eqn. (62). An algorithm was therefore developed for the calculation of these coefficients for different levels of the initial data and a block scheme was set up. For cases of incomplete information, it proved possible to derive formulae permitting the calculation of the coefficients of the principal rule. The possibility of determining the coefficients $K_i(t)$ from thermodynamic and kinetic parameters for higher levels of initial data was demonstrated.

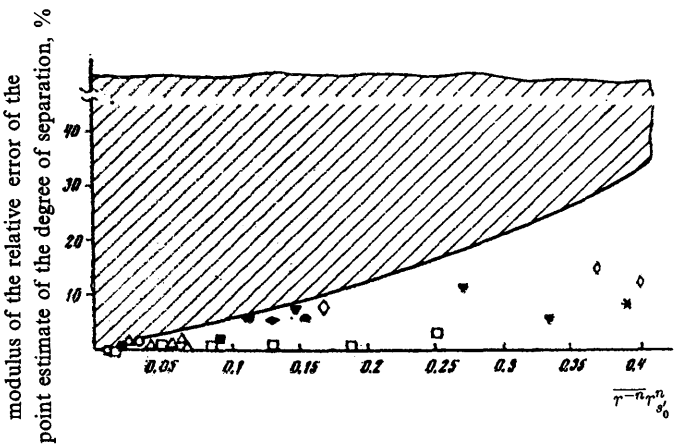


Figure 4. The region of the possible values of the modulus of the relative error of the point estimates of the degree of separation of disperse systems with an improved accuracy. For the designations of the points, see Fig. 3. The cross-hatched region represents the impossible values of the modulus of the relative error (of the points estimates of the degree of separation with an improved degree of accuracy).

On the basis of the principal rule established for the compositions, it was found possible to represent graphically the changes in the compositions of multicomponent ecological systems and subsystems in terms of their variables $\bar{S}(t)$, S_i, and $\mathfrak{D}_i(t)$.

With the aid of the main rule established for the compositions, it has been shown that *the overall (average) characteristic of the entire system (specific heat, specific number of moles, density, specific volume, specific heat of combustion, etc.) is equal* to the product of the isotypical characteristics of the components, their weight fractions, and the reciprocals of the coefficients of the principal rule governing compositions.

The principal rule for the compositions of ecological systems and subsystems can be used not only for the determination of the compositions of the eco-system but also for the solution of certain problems of the protection of the environment, including the organisation of the monitoring and measures ensuring that the limiting permissible concentrations of toxic substances are not exceeded.

Using the author's own experimental data for the specific heats of solution of two- and three-component powders and the specific volume of a specific ecological subsystem (active silt) as well as the literature data,[39,40] the coefficients of the principal rule for the

compositions of eco-systems and ecological subsystems have been found for zero uncertainty in the estimates of the contents of the components. The results of the calculations are presented in Table 3, from which it is seen that, in conformity with the principal rule for the compositions established, all the coefficients are not more than unity.

Table 3. The coefficients of the principal rule for the compositions of ecological systems and subsystems for zero uncertainty in the estimates of the contents of the components.

Ecological subsystem	Components	Average characteristic	Content, weight fraction	$K_i(t)$
Three-component powder	KNO_3,	Specific heat of solution	50.0	0.64
	$CuSO_4 \cdot 5H_2O$,		33.3	0.07
	KCl		16.7	0.17
Two-component powder	KNO_3,	Ditto	33.3	0.94
	$CuSO_4 \cdot 5H_2O$		66.7	0.31
Aqueous solution of methanol	H_2O,	Specific volume of solution	45.8	0.40
	CH_3OH		54.2	0.60
Aqueous HNO_3 solution	H_2O,	Specific heat of solution	80.0	0.95
	HNO_3		20.0	0.05
Gas mixture	$H_2+O_2+H_2O$	Specific number of moles	3.0	0.29
			47.0	0.28
			50.0	0.55
Man	H_2O	Specific heat	75	0.87
Active silt	H_2O	Specific volume	99.12	0.996
	H_2O	Ditto	98.35	0.988

VIII. Measures ensuring that the limiting permissible amounts of liquid and gaseous waste polluting the environment are not exceeded for different levels of initial information

The increasingly acute ecological crisis makes it essential that the following requirement is rigidly adhered to: that the limiting permissible norms as regards gaseous and liquid waste products[2,12] contaminating the hydrosphere and the atmosphere must not be exceeded. The existence of different levels of initial information makes it much more difficult to satisfy this requirement.

According to the definition of the limiting permissible amounts of liquid and gaseous waste, the condition that the limiting permissible concentration of the ith toxic substance in the eco-system is not exceeded is specified by the relation

$$C_i^-(t) \leqslant (\mathrm{LPLW}_i \text{ or } \mathrm{LPGW}_i)/Q(t), \tag{63}$$

where $Q(t)$ is the productivity of the apparatus for the detoxification (purification) of liquid or gaseous waste, $C_i^-(t)$ the concentration of the toxic ith component at the outlet from the detoxification apparatus to the environment, LPLW_i and LPGW_i are the limiting permissible amounts of liquid and gaseous waste, and t is the current time.

For further exposition, we shall make use of the concept of the protection factor (PF_i) for the environment introduced by the present author.[12] By definition, this quantity shows by what factor the weight fraction of the ith toxic component has diminished during the detoxification process as a result of separation and chemical reactions.

The concentration of the ith toxic component at the inlet to the detoxification apparatus can be represented in the following form with the aid of the principal rule for compositions:

$$C_i^+(t) = K_i(t)\bar{\rho}_+(t)\bar{S}_{sp}(t)/S_i^{sp}, \tag{64}$$

where $\bar{\rho}_+(t)$ is the average density at a given instant t of the liquid or gaseous mixture subjected to detoxification.

Using the concept of the protection factor, we shall represent the condition that the limiting permissible concentration is not exceeded in the following way:

$$\frac{K_i(t)\bar{\rho}_-(t+t_r)S_{sp}(t)}{S_i^{sp}PF_i} \leqslant \frac{(\mathrm{LPLW}_i \text{ or } \mathrm{LPGW}_i)}{Q(t+t_r)}, \tag{65}$$

where $\bar{\rho}_-(t + t_r)$ is the average density of the mixture (for example, water or air being purified) entering the environment at time $t + t_r$ after detoxification and t_r is the residence time of the mixture in the detoxification apparatus.

We shall call the ratio $\mathrm{LPLW}_i/[Q(t + t_r)\bar{\rho}_-(t + t_r)]$ the dimensionless limiting permissible amount of liquid waste and $\mathrm{LPGW}_i/[Q(t + t_r)\bar{\rho}_-(t + t_r)]$ the dimensionless limiting permissible amount of gaseous waste. We shall designate them by DLPLW_i and DLPGW_i. The physical significance of the quantities introduced is fairly simple: they indicate the maximum permissible weight fraction of the toxic substance in the liquids and gases entering the environment after detoxification (purification).

Using the concept of DLPLW_i and DLPGW_i, one can write on the basis of Eqn. (65)

$$PF_i \geqslant \frac{K_i(t)\bar{S}_{sp}(t)}{(\mathrm{DLPLW}_i \text{ or } \mathrm{DLPGW}_i)S_i^{sp}}. \tag{66}$$

The last relation proves the following theorem.

Theorem 9. *The protection factor for the environment not less than the product of the reciprocal of the dimensionless limiting permissible amount of liquid (gaseous) waste, the coefficient of the principal rule for compositions, and the ratio of the average specific characteristic of the homogeneous or heterogeneous mixture being detoxified to the isotypical measure of the properties of the toxic component guarantees that the limiting permissible concentration (LPC) is not exceeded.*

Thus, on the basis of the theorem formulated, it is possible to determine the protection factors for the environment which guarantee *a priori* that the limiting permissible concentration is not exceeded for different levels of initial information.

In particular, in the presence of a minimal amount of data, when only the values of $\bar{S}_{sp}(t)$ and S_i^{sp} are known, we have the following expression according to the sequence of inequalities for the detoxification of waste waters and bearing in mind that $K_i(t)$ is always less than or equal to unity:

$$C_i^-(t) \leqslant \frac{K_i(t)\bar{\rho}_-(t+t_r)\bar{S}_{sp}(t)}{S_i^{sp}PF_i} \leqslant \frac{\bar{\rho}_-(t+t_r)\bar{S}_{sp}(t)}{S_i^{sp}PF_i} \leqslant \frac{\mathrm{LPLW}_i}{Q(t+t_r)}. \tag{67}$$

According to the analogous sequence of inequalities for the detoxification of gaseous waste, we obtain a relation for the estimation of the protection factor (in the presence of a minimal amount of information) guaranteeing that the limiting permissible concentration is not exceeded:

$$PF_i \geqslant \frac{\bar{S}_{sp}(t)\bar{\rho}_-(t+t_r)Q(t+t_r)}{(\mathrm{LPLW}_i \text{ or } \mathrm{LPGW}_i)S_i^{sp}}. \tag{68}$$

If S^{sp}_{max} and S^{sp}_{min}, the maximum and minimum specific partial measures of the properties (characteristics) of the components, are known, then it follows from formulae (61) and (62) that the coefficient of the principal rule for compositions $K_i(t)$ can be estimated as follows:

$$K_i(t) \leqslant \begin{cases} \dfrac{\bar{S}_{sp}(t) - S^{sp}_{min}S^{sp}_i}{S^{sp}{}_i - S^{sp}_{min}\bar{S}_{sp}}(t) \\ \text{when } S^{sp}_i \geqslant \bar{S}_{sp}(t), \\ \dfrac{S^{sp}_{max}\bar{S}_{sp}(t)S^{sp}{}_i}{S^{sp}_{max} - S^{sp}{}_i\bar{S}_{sp}(t)} \\ \text{when } S^{sp}{}_i < \bar{S}_{sp}(t). \end{cases} \tag{69}$$

For this level of information, we obtain from formula (69) the relation ensuring unconditionally that the LPC is not exceeded:

$$PF_i \geqslant \begin{cases} \dfrac{\bar{\rho}_-(t+t_r)Q(t+t_r)[\bar{S}_{sp}(t) - S^{sp}_{min}]}{(LPLW_i \text{ or } LPGW_i)(S^{sp}_i - S^{sp}_{min})} & \text{for } S^{sp}_i \geqslant \bar{S}_{sp}(t) \\ \dfrac{\bar{\rho}_-(t+t_r)Q(t+t_r)[S^{sp}_{max} - \bar{S}_{sp}(t)]}{(LPLW_i \text{ or } LPGW_i)(S^{sp}_{max} - S^{sp}_i)} & \text{for } S^{sp}_i > \bar{S}_{sp}(t). \end{cases} \tag{70}$$

Formulae (69) and (70) are special cases of the more general formula (66).

The protection factor can be expressed as a function of temperature, the concentration of added reagents, the residence time, the length of the apparatus, and other technological and design parameters of the detoxification process and apparatus. Therefore, expressing one of such quantities as a function of the reciprocal of the protection factor, it is possible to determine from the inequality (66) the values of the technological or design parameter guaranteeing the satisfaction of the ecological requirement that the limiting permissible amounts of liquid or gaseous waste are not exceeded. For example, if the detoxification of the ith toxic component is described by a first-order chemical reaction equation, then the following expression holds for the protection factor:

$$PF_i = \phi(T) = \exp\,[At_r \exp\,(-E_a/RT)], \tag{71}$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant, T the temperature and $\varphi(T)$ a function of temperature.

Having expressed the temperature T as a function of the reciprocal of the protection factor $\varphi^{rec}(PF_i)$ and then using the inequality (66), we obtain a relation for the determination of the absolute temperatures which must be maintained in the chemical waste water detoxification reaction in order to guarantee that the limiting permissible amount of liquid waste is not exceeded:

$$T \geqslant -E_a/R \ln\left[\frac{1}{At_r}\ln\frac{K_i(t)\bar{S}_{sp}(t)}{DLPLW_iS^{sp}_i}\right]. \tag{72}$$

In another special case, for the detoxification of disperse contaminations with an unknown distribution of grain sizes (by the separation of the disperse particles), using the inequality already established

$$\varepsilon \leqslant \alpha + (1-\alpha)\overline{r^{-n}_{fr}}r^n_{s_\alpha},$$

and theorem 9, we can formulate a sequence of inequalities guaranteeing that the limiting permissible concentration of the disperse phase is not exceeded:

$$\frac{1}{PF_{i_d}} \leqslant \alpha + (1-\alpha)\overline{r^{-n}_{fr}}r^n_{s_\alpha} \leqslant \frac{LPGW_{i_d} \text{ or } LPLW_{i_d}}{Q(t+t_r)C^+_{i_d}(t)} \leqslant$$

$$\leqslant [(DLPGW_{i_d} \text{ or } DLPLW_{i_d})S_{i_d}]/[K_{i_d}(t)\bar{S}_{sp}(t)]. \tag{73}$$

Here the subscript d indicates that the corresponding characteristics refer to the disperse phase. Consequently

$$r_{s_\alpha} \leqslant \sqrt[n]{\left[\frac{[DLPGW_{i_d} \text{ (or } DLPLW_{i_d})]S^{sp}{}_{i_d}}{K_{i_d}(t)\bar{S}_{i_d}(t)} - \alpha\right] \Big/ [(1-\alpha)\overline{r^{-n}_{fr}}]}. \tag{74}$$

Eqn. (74) makes it possible to find the quasi-sizes of the separation which guarantee that the limiting permissible concentration of the disperse phase is not exceeded. After this, it only remains to select the apparatus for the purification of waste water or a dust trapping device with r_{s_α} satisfying this expression.

For known values of the input concentrations (weight and particle concentrations) of the disperse phase and in the absence of effects associated with the fragmentation of particles, the inequality (74) (for $n = 3$) assumes the following form:

$$r_{s_\alpha} \leqslant 3\sqrt{\left[\frac{LPGW_{i_d} \text{ (or } LPLW_{i_d})}{Q(t+t_d)C^+_{i_d}(t)} - \alpha\right] \Big/ [(1-\alpha)\beta_f\rho_1 n_{sp}]}. \tag{75}$$

Thus the successive employment of the principle of the coupled material-characteristic imbalance has made it possible to obtain a series of inequalities for the estimation of the contents of substances in ecological systems and subsystems for different levels of initial information and to formulate the principal rule for the compositions of such systems. The results obtained can be applied both for high-speed large-scale monitoring and for the design and technical measures to protect the environment, whose aim is to reduce the amounts of different toxic substances entering the hydrosphere, atmosphere, and lithosphere.

References

1. V P Voloshin *Okhrana Morskoi Sredy* (Protection of the Marine Environment), Sudostroenie, Leningrad, 1987, 208 pp
2. D P Nikitin, Yu V Novikov *Okruzhayushchaya Sreda i Chelovek* (The Environment and Man), Vys. Shkola, Moscow, 1986, 415 pp
3. G V Stadnistkii, A I Rodionov *Ekologiya* (Ecology), Vys. Shkola, Moscow, 1988, 272 pp
4. G I Sidorenko, E A Mozhaev *Sanitarnoe Sostoyanie Okruzhayushchei Sredy i Zdorov'e Naseleniya* (The Sanitary State of the Environment and the Health of the Population), Meditsina, Moscow, 1987, 128 pp
5. A V Mikheev, V M Galushin, N A Gladkov, et al. *Okhrana Prirody* (Protection of Nature), Prosveshchenie, Moscow, 1987, 256 pp
6. G I Rumyantsev *Nauchno-Tekhnicheskii Protsess i Metodicheskie Voprosy Gigienicheskogo Reglamentirovaniya Vrednykh Faktorov Okruzhayushchei Sredy* (Scientific-Technical Progress and Methodological Problems of the Establishment of Hygienic Norms for Harmful Factors in the Environment), Izd. IMMI, Moscow, 1984, 46 pp

7. A V Mikheev, V M Konstantinov *Okhrana Prirody* (Protection of Nature), Vys. Shkola, Moscow, 1986, 256 pp
8. G P Bespamyatnov, Yu A Krotov, Handbook *Predel'no Dopustimye Kontsentratsii Khimicheskikh Veshchestv v Okruzhayushchei Srede* (Limiting Permissible Concentrations of Chemicals in the Environment), Khimiya, Leningrad, 1985, 528 pp
9. Yu A Ershov, T V Pleteneva *Mekhanizmy Toksichnogo Deistviya Neorganicheskikh Soedinenii* (The Mechanisms of the Toxic Effects of Inorganic Compounds), Meditsina, Moscow, 1989, 272 pp
10. I F Livchak, Yu V Voronov *Okhrana Okruzhayushchei Sredy* (Protection of the Environment), Stroiizdat, Moscow, 1988, 191 pp
11. I S Autsypovich, L Ya Popenko *Okhrana Okruzhayushchei Sredy na Predpriyatiyakh Myasnoi i Molochnoi Promyshlennosti* (Protection of the Environment in the Undertakings of the Meat and Milk Industry), Agropromizdat, Moscow, 1986, 255 pp
12. N V Sokolov *Dokl. VASKhNIL*, 1990, (3) 31
13. L A Petrosyan, V V Zakharov *Vvedenie v Matematicheskuyu Ekologiyu* (Introduction to Mathematical Ecology), Izd. Leningrad. Gos. Univ., Leningrad, 1986, 224 pp
14. P Raven, R Evert, S Eichhorn *Modern Botany* (Translated into Russian) (in two volumes), Mir, Moscow, 1990, Vol. 2, 344 pp
15. *Gigiena Okruzhayushchei Sredy v SSSR/Ezhegodnye Publikatsii ob Issledovaniyakh Sovetskikh Avtorov* (The Hygiene of the Environment in the USSR. Annual Publications about the Research of Soviet Workers), Meditsina, Moscow, 1987, 288 pp
16. I D Rodziller *Prognoz Kachestva Vody Vodoemov—Priemnikov Stochnykh Vod* (Prediction of the Quality of Water in Water-Containing Areas Serving as Sewage Dumps), Stroiizdat, Moscow, 1984, 263 pp
17. V M El'terman *Okhrana Vozdushnoi Sredy na Khimicheskikh i Neftekhimicheskikh Predpriyatiyakh* (Protection of Air in Chemical and Petrochemical Undertakings), Khimiya, Moscow, 1985, 160 pp
18. I M Elshin *Stroitelyu ob Okhrane Okruzhayushchei Sredy* (Information for the Builder Concerning the Protection of the Environment), Moscow, 1986, 136 pp
19. Yu S Drugov, A B Belikov, G A D'yakova, V M Tul'chinskii *Metody Analiza Zagryaznenii Vozdukha* (Methods for the Analysis of the Contaminants in Air), Khimiya, Moscow, 1984, 384 pp
20. Ya M Grushko *Vrednye Organicheskie Soedineniya v Promyshlennykh Vybrosakh v Atmosferu* (Harmful Organic Compounds in the Industrial Gaseous Waste Discharged into the Atmosphere), Khimiya, Leningrad, 1986, 207 pp
21. S B Iokhel'son, F Ya Rovinskii *Reka Moskva: Chistaya Voda* (The Moscow River: Pure Water), Gidrometeoizdat, Leningrad, 1985, 152 pp
22. D Williams *Principles of the Monitoring of Marine Pollution* (Translated into Russian), Sudostroenie, Leningrad, 1984, 136 pp
23. G I Marchuk *Matematicheskoe Modelirovanie v Probleme Okruzhayushchei Sredy* (Mathematical Modelling in the Problem of the Environment), Nauka, Moscow, 1982, 320 pp
24. V A Vavilin *Nelineinye Modeli Biologicheskoi Ochistki i Protsessov Samoochishcheniya v Rekakh* (Non-Linear Models of Biological Purification and Self-Purification Processes in Rivers), Nauka, Moscow, 1983, 158 pp
25. L A Kul'skii *Teoreticheskoe Obosnovanie Tekhnologii Ochistki Vody* (Theoretical Foundations of the Technology for the Purification of Water), Naukova Dumka, Kiev, 1968, 127 pp
26. Z S Razumovskii, G L Medrish, V A Kazaryan *Ochistka i Obezzarazhivanie Stochnykh Vod Malykh Naselennykh Punktov* (The Purification and Disinfection of Sewage in Small Populated Areas), Stroiizdat, Moscow, 1986, 173 pp
27. E D Babenkov *Ochistka Vody Koagulyantami* (Purification of Water by Coagulants), Nauka, Moscow, 1977, 356 pp
28. S V Yakovlev, Ya A Karelin, Yu M Laskov, Yu V Voronov *Ochistka Proizvodstvennykh Stochnykh Vod* (Purification of Industrial Waste Waters), Stroiizdat, Moscow, 1985, 335 pp
29. *Ekologicheskaya Biotekhnologiya* (Ecological Biotechnology), Khimiya, Leningrad, 1990, 384 pp
30. R Ya Agranonik *Tekhnologiya Obrabotki Osadkov Stochnykh Vod s Primeneniem Tsentrifug i Lentochnykh Fil'tr-Pressov* (Technology of the Treatment of Sewage Deposits Using Centrifuges and Belt-Driven Filter Presses), Stroiizdat, Moscow, 1985, 144 pp
31. A G Amelik, A I Melekhov, I E Zubova, V N Zaitsev *Obshchaya Khimicheskaya Tekhnologiya* (General Chemical Engineering), Khimiya, Moscow, 1977, 400 pp
32. E N Lightfoot *Transport Phenomena in Living Systems* (Translated into Russian), Mir, Moscow, 1977, 520 pp
33. D Freifelder *Physical Biochemistry* (Translated into Russian), Mir, Moscow, 1980, 583 pp
34. N M Emanuel', D G Knorre *Kurs Khimicheskoi Kinetiki* (Textbook of Chemical Kinetics), Vys. Shkola, Moscow, 1984, 463 pp
35. *Izmel'chenie i Klassifikatsiya* (Comminution and Classification), GNT Izd. Lit. po Chernoi i Tsvetnoi Metallurgii, Moscow–Leningrad, 1950, 82 pp
36. E A Shtokman *Ochistka Vozdukha ot Pyli na Predpriyatiyakh Pishchevoi Promyshlennosti* (Elimination of Dust from Air in the Food Industry), Pishchevaya Promyshlennost', Moscow, 1977, 304 pp
37. *A Surface and Colloid Science*, Plenum Press, New York, 1978, Vol. 10
38. N V Sokolov *Khim. Prom.*, 1987, (1) 39
39. F Daniels *Getman's Outlines of Physical Chemistry* (Translated into Russian), Moscow, 1941, 628 pp
40. N V Sokolov *Dokl. Akad. Nauk SSSR*, 1990, **315**(6) 1423