

One of the Aspects of Chemical and Thermodynamic Simulation in Solving the Complex Problems of Description of the States of Water Systems

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Abstract

The generalized approach and methodology of formulating and solving a series of direct problems of chemical equilibrium aimed at estimating the real state of substances in aqueous solutions as subsystems of natural and technological water is presented. A minimal set of the key terms is outlined in brief (locality and partial character of equilibria, physicochemical decomposition, initial system, system under investigation and so on); these terms are necessary to master the approach and the procedure, and also to use correctly the corresponding results in solving the complex problems connected with the description of the state of water systems. Examples of two implementations (estimation of the consumption and evolution of carbon dioxide during photosynthesis, breathing of hydrobionts, oxidative destruction of organic matter in surface water, partial analysis of the local states of mercury in the environment) illustrate the technology of applying this approach and the procedures, and also their self-descriptiveness. Specific results obtained within these examples are of independent interest.

1. INTRODUCTION

Problems of environmental chemistry and ecologically safe technologies have attained increasing significance in world research [1, 2]. In turn, fundamental physicochemical knowledge in combination with up-to-date complex research, natural and industrial information allows one to formulate and solve various specifically aimed series of *direct problems of chemical equilibrium* (DPCE)¹.

¹Here and below, italics indicate simple and composite terms for a minimal set of notions to the essence of which (in connection with the context) special attention should be paid to provide adequate perception of the approach and procedure described in the present paper.

In particular, the role of universal approaches to the estimation of the concentrations of *chemical forms* [3, 4] in various highly dimensional *systems under study* [3–7] as subsystems of natural and technological water (*initial systems*). In the present paper we report on the physicochemical foundations of formulation and solution of the problems of this class and illustrate the proposed procedure using some implementations.

2. PRESENT APPROACH AND MOST IMPORTANT FEATURES OF CHEMICAL AND THERMODYNAMIC SIMULATION

Constructive interpretation of the *principle of locality and partial character of equilibria* in

terms of *physicochemical decomposition, initial system, description completeness, level of detailed elaboration, system under investigation* broadens the application area and self-descriptiveness of chemical and thermodynamic simulation, for example, for the analysis of behaviour of *heavy metals* in the environment [2, 8, 9]. Relying, upon this *pair principle* on the one hand and on restrictions drawn from the existing knowledge, goals and hypotheses, on the other, the *oriented physicochemical decomposition* is performed; that is, a notion of some class of *initial systems* is formed; within these systems, definite *systems under investigation* are distinguished and characterized specifically [3–9].

In this context, the *initial system* is an *abstract portion of aqueous solution*, as a subsystem of some portion of natural water, biohydrosystem, *etc.* First, it is a *formally open system* with a definite (compatible with the accepted *completeness of description*) definition domain in the state space the dimensionality of which is $(k^* + 1)$. In other words, an arbitrary state is depicted by a vector $(T, n_1^*, \dots, n_{k^*}^*)$, where T is temperature, and n_i^* is the molar amount of the i th *independent initial component* I [7]. The total pressure as an independent variable of state is omitted in this representation because the effect of its variation is insignificant in the problems of the class under consideration. Second, this portion is *internally equilibrium* within the entire region of states associated with it. This is the implementation of the *locality principle* in this context. Third, due to *locality* (in spatial-temporal relations) the *internal equilibrium* is never absolute. It is always realized approximately; it is necessary to ensure that this would not drive the system out of the borders of the accepted completeness of description. In doing this, a part of *principally (thermodynamically) possible interconversions* of the substance often turns out to be *essentially hindered*, that is, having no significant effect on the equilibria with respect to others and on the considered characteristics of the system in general within the entire region of its states included in the field of vision. Thus the *principle of partial equilibria* is implemented.

The above consideration means that any point $(T, n_1^*, \dots, n_{k^*}^*)$ from the region in question at a reasonably chosen *level of detailed elaboration*

[10] (modern knowledge about aqueous solutions give the grounds for four levels [4, 6, 11, 12]) may be put in a univocal correspondence with a point in the simulating space with the dimensionality $(l + 1)$, (T, n_1, \dots, n_l) . In the *complete list* of the detailed components of dimensionality l , as a rule, a part of them can be chosen as k *basis components* (this may not always be done uniquely but the restriction $l \geq k \geq k^*$ is always fulfilled) [7]. Quite often, only the subsystems of the full system may turn out to be available for local partial modeling; this full system is principally in correspondence with the given *initial system* at a specific level of its detailed elaboration, that is, some *systems under investigation* $(l' < l; k' \leq k)^2$. In practice, for states of the *internal equilibrium* any point in the subspaces of $(k + 1)$ or $(k' + 1)$ dimensionality is in univocal correspondence with some point in the generating spaces $(l + 1)$ or $(l' + 1)$. Ambiguities in the above-indicated relations between the points of the basis and full spaces are possible in principle only under the significant actions of the so-called *secondary environmental effects* [4, 6, 7, 12, 13] and only for the *systems under investigation*. In the considered spaces, n_i or n_i' are molar amounts of the so-called *detailed components*. Analysis of the consequences of admissible changes in detailed elaboration levels, including questions concerning standardizing of thermodynamic characteristics accounting for the choice of the level of detailed elaboration, concentration scale (for nonunitary partial characteristics) and a method to take into account environmental effects, had been carried out for many years [4, 6, 11, 12, 14, 15]; only recently the results were generalized, formalized in rather complete form and represented compactly as a separate paper [7]. One of the reasons for the formalization method chosen by us is the fact that any *list of detailed components* of a homogeneous system (or its subsystem) can be separated (more often with a non-unique method)

²Here the upper primed index is to distinguish the *system under investigation* as a subsystem of the full one which corresponds to the *initial system* at a given level of its detailed elaboration. This circumstance is not to be confused with the designations previously used in [4–6, 10] to denote different *levels of detailed elaboration* of the same *initial system*.

into two lists: the *basis* (B_i , dimensionality: k or k') and *non-basis* [A_j , dimensionality: $(l - k)$ or $(l' - k')$]. The *basis* of homogeneous equilibria corresponding to this is

$$\sum v_{ij} B_i = A_j \quad (1)$$

where v_{ij} are the stoichiometric coefficients (they can be zero, positive, or negative). If necessary, this basis can be supplemented with the required number of heterogeneous equilibria: $\sum v_{ij} B_i = A_j$ [solid or gas for $j > (l - k)$ or $j > (l' - k')$]. In any of these representations, it is not difficult to carry out a transition from the molar amount to concentrations (for the homogeneous system or its subsystem under study) within the chosen scale. The molar scale is preferable for sequential accounting and interpretation of the so-called *full, primary* and *secondary environmental effects* and consequences of changes in the *level of detailed elaboration* [7, 10–13].

This approach, though only briefly outlined above, in general allows us to perform full formalization of all the procedures and to pose and solve diverse problem-oriented series of the so-called *direct tasks of chemical equilibrium* [4]³ using this ground and a computer in complicated cases, or other means in simple cases.

In particular, for high-dimensionality problems (with respect to l' , k'), based on CRUIZ-1 software which was a part of the software complex [21], the CRUIZ-2 version was developed for IBM-PC [22]. The procedure involves solution of $(l' - k')$ equations of the *law of mass action* (LMA) with k' restrictions in the form of *mass balance* equations and/or assignment of the equilibrium concentrations of a definite number (not more than k') of forms. The application of the *effective constants* apparatus is provided [3, 6, 23] (some authors have recently transformed this term into the notion of *lumping analysis* [24, 25]), as well as the possibility to supplement the basis of homogeneous equilibria with the required number of heterogeneous ones. Only *chemical forms* within the same solution are *reagents* in

a homogeneous system. In heterogeneous solutions, these may be either *chemical forms* comprising various *topochemically contacting solutions* based on solvents with limited mutual solubility (possibly, with separate account of the *forms* at the *interfaces* and/or specific *assemblies of macromolecules* in their δ -neighbourhood [26, 27] or *condensed or gaseous phases* [7]).

In addition, it is necessary to stress that any other approaches to solving DPCE (Lagrangian method of undetermined coefficients and mathematical programming [28], minimization of Gibbs' energy in the space of the so-called *internal coordinates* [29, 30] and the approaches involving initial restrictions for any other than P , T , n^* sets of the variables of state) are fully equivalent to the above-described approach as far as the results are concerned. However, in our opinion, they bring substantial complications into the semantic perception of the range of problems under consideration. The statement of the authors of book [28, p. 22] that a specific choice of k or k' basis components in the list of detailed components in the full system (l) or in the system under investigation (l') (that is, the choice of $(l - k)$ or $(l' - k')$ basis equilibria) in the case of the existence of versions (the number of which cannot naturally exceed the number of combinations of k from l (or of k' from l')) requires (or is equivalent to) the information on the mechanism of the process certainly cannot be accepted as a correct one. For this reason alone, the argumentation of those authors [28, pp. 22, 23] in favour of the methods based on determination of the coordinates of saddle points (Lagrangian method of undetermined coefficients, mathematical programming) as distinct from the methods based on the joint solution of the systems of equations of the material balance and the law of *mass action* for equilibria is baseless. In addition, the monographs in this area of which we are aware (for example, [31, 32]) do not pay sufficient attention to the *principle of locality and partial character of equilibria* and to the problems connected with accounting for the *secondary environmental effects* (compatible with the accepted *completeness of description*), to the principal possibility of fairly different *levels of detailed*

³This composite term was borrowed into manual [4] from the proceedings of a number of All-Union workshops [16–20]; in our opinion, their usefulness for researchers meeting the questions concerning the application of mathematics in the area of formulating and solving the problems of chemical thermodynamics is still valid.

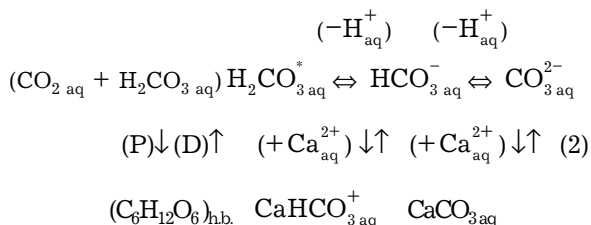
elaboration of the same aqueous systems (and also solutions based on other solvents, including mixed ones [15, 33]). Moreover, for some reason, the notion of *open systems* is usually [34, 35] connected only with “fair” possibilities and realizations of the transport of the substance through their boundaries. By doing this, the right for detailed consideration of the original Gibbs’ ideas [36] is excluded together with the application of these ideas to the solutions of any reasonably (problem-related) selected sets [2–9, 11, 12], as to some states of some open systems (that is, the right for the approach to natural waters as developed by us [2, 8, 9, 26, 27]). Specific examples of the application of the set of ideas presented above in compact form can be two realizations chosen for illustration; they have already been considered in somewhat different aspects in [8, 9]. Of course, the classes of this kind of problems with respect to their problem orientations can be extremely diverse. This relates to all cases when knowledge of the composition of the homogeneous or heterogeneous phases under consideration only in terms of phases and initial components (elements in a particular case) becomes insufficient, and acute necessity arises to get specific knowledge of real states of a substance incorporated in the phases (not only solution phases) at the level of *chemical forms* (Speciation analysis) [2–9, 37, 38].

3. EXAMPLE OF FORMULATION AND SOLUTION OF DPCE FOR ESTIMATING THE INDICES OF PHOTOSYNTHESIS, BREATHING AND DESTRUCTION IN SURFACE WATERS

The binding of carbon dioxide molecules during photosynthesis and their evolution during breathing of hydrobionts and oxidative destruction of the mort mass cause a clearly exhibited redistribution of chemical forms of the *carbonate system* (CS) of the surface water. The latter is depicted specifically in the diurnal dynamics of pH of water and on this basis allows quantitative estimation of the generally accepted integral indices of the functioning of biohydrocenoses: primary production (P), breathing and destruction (D) in terms of the amounts of consumed and released carbon dioxide [39–41]. Within the framework of Bruevich’s procedure which has already become

generally known [42], the same problem was solved using the data on diurnal dynamics of pO_2 . Our approach and procedure of formulating and solving the DPCE series provide the possibility to simplify and automate the necessary calculations, to get a clearer idea of the initial approximations and possible consequences. As a result, prerequisites for the construction of new versions are created (as the information obtained by field observations and research gets accumulated).

A simplified interconnection between the main forms of the CS and the products of life activities of hydrobionts (the general formula being $(C_6H_{12}O_6)_{h.b.}$) in the photic layers of water (*initial system*) within a period of 24 h can be represented by a scheme



This scheme represents only the main inorganic forms of the CS which according to the data reported in [43, 44] can play a significant part in calcium bicarbonate surface water. If necessary, this list can be broadened. In particular, as it has already been stressed in the works [8, 9], the problem connected with separate accounting for the presence of molecular forms of two types in solution can arise – $CO_{2\ aq}$ (clathrate-bound CO_2 molecules) and $H_2CO_{3\ aq}$ (carbonic acid molecules formed by chemical combination of CO_2 and H_2O molecules). Here, as previously [8, 9, 39–41], we will not distinguish between them; the entire set will be denoted as $H_2CO_{3\ aq}^*$ because it is this species that is called *carbonic acid*, and the standard data on the constants of chemical dissociation are assigned to this species.

In addition, in this approximation, we accepted that locally (for place and time), for water portions under consideration, other input-output flows of the *formal element* CO_3^{2-} get mutually extinguished approximately within the analyzed intervals of the day and do not make significant contribution to the equilibrium of the CS forms in comparison with the integral action of the P and D channels.

Let us take the specific information [39, 40] about the concentrations of *formal elements* [3–6, 11, 12] Ca^{2+} , CO_3^{2-} and pH in four characteristic points (two of which, the first and the last ones, can turn out to be equivalent in principle) of time of the two adjacent days (sunrise, afternoon maximum of pH, sunset, the next sunrise) with the typical data for the surface (photic) layer of the water of the Novosibirsk reservoir during summer. The *system under investigation* is composed of the forms H_2CO_3^* , H^+ , HCO_3^- , CO_3^{2-} , Ca^{2+} , CaHCO_3^+ , CaCO_3 . According to the reference data [43, 44] for the constants of the *basis of equilibria*, we obtain:

$$\text{H}_2\text{CO}_3^* \rightleftharpoons \text{H}^+ + \text{HCO}_3^-, \lg K_1^0(25) = -6.37, \\ \log_{10} K_1^\circ(25) = -6.33 \quad (3)$$

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}, \lg K_2^0(25) = -10.33, \\ \log_{10} K_2^\circ(25) = -10.25 \quad (4)$$

$$\text{Ca}^{2+} + \text{HCO}_3^- \rightleftharpoons \text{CaHCO}_3^+, \lg K_3^0(25) = 1.23, \\ \log_{10} K_3^\circ(25) = 1.15 \quad (5)$$

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3, \lg K_4^0(25) = 3.20, \\ \log_{10} K_4^\circ(25) = 3.04 \quad (6)$$

The values of $\log_{10} K_i^\circ(25)$ are standardized for the medium in the solutions under consideration (the action of the ionic force is taken into account; it is accepted to be at a level of $1.6 \cdot 10^{-3}$ in the Debye–Hückel approximation). Water temperature was 20–25 °C, so the effect of its changes was not taken into account.

Since in each of the four problems of the considered problem-directed series calculation is carried out for the independently assigned pH value, it is necessary to change the basis (3)–(6) and the constants for the effective ones:

$$\text{CO}_3^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{CO}_3, K_1^* = (K_1^\circ K_2^\circ / [\text{H}^+]^2)^{-1} \quad (7)$$

$$\text{CO}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HCO}_3^-, K_2^* = (K_2^\circ / [\text{H}^+])^{-1} \quad (8)$$

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaHCO}_3^+, K_3^* = (K_3^\circ / K_2^\circ) [\text{H}^+] \quad (9)$$

$$\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3, K_4^* = K_4^\circ \quad (10)$$

So, the initial concentrations for the calculation are those of the *formal elements*

TABLE 1

Initial data and results of calculation of the problem for pH* 8.02 (a series of four problems, see Table 2, is composed as a typical one for water samples considered in [8, 39, 40])

No.	Form of system	Initial data			
		M*		$\log_{10} K^*$ (init.)	C_{init} , mol/l
1	CO_3^{2-}	1.0	0.0	0.0	$1.30 \cdot 10^{-3}$
2	Ca^{2+}	0.0	1.0	0.0	$5.00 \cdot 10^{-4}$
3	H_2CO_3	1.0	0.0	0.54	0.0
4	HCO_3^-	1.0	0.0	2.23	0.0
5	CaCO_3	1.0	1.0	3.04	0.0
6	CaHCO_3^+	1.0	1.0	3.38	0.0
Equilibrium composition					
		M*		$\log_{10} K^*$ (transf.)	C_{equil} , mol/l
1	HCO_3^-	1.0	0.0	0.0	$1.25 \cdot 10^{-3}$
2	Ca^{2+}	0.0	1.0	0.0	$4.87 \cdot 10^{-4}$
3	H_2CO_3	1.0	0.0	–1.69	$2.56 \cdot 10^{-5}$
4	CO_3^{2-}	1.0	0.0	–2.23	$7.39 \cdot 10^{-6}$
5	CaCO_3	1.0	1.0	0.81	$3.95 \cdot 10^{-6}$
6	CaHCO_3^+	1.0	1.0	1.15	$8.64 \cdot 10^{-6}$

*The matrix of the stoichiometric coefficients.

CO_3^{2-} , Ca^{2+} and the logarithms of *effective constants of the basis* (7)–(10) for each of the specific pH values. Thus, pH is the negative logarithm of the equilibrium H^+ concentration estimated using the measured pH values (the instrumental coefficient of activity is equated with the thermodynamic one which is calculated in the approximation of the theory of Debye–Hückel).

Table 1 contains an extract from the computer output with the results of solution of one of the four problems of the above-indicated series of DPCE by means of CRUIZ-2 software for IBM-PC [22] developed within the framework of an open software complex [21].

Table 2 shows the information which is necessary for estimation of diurnal production of photosynthesis; this information was extracted from the solutions of all the problems of the series. In addition to the above-indicated approximations, due to the buffer nature of CS with respect to the *detailed components* Ca^{2+} and HCO_3^- , and low variability of their equilibrium concentrations during a day under the action of the factors under consideration,

TABLE 2

Results of simulation necessary and sufficient for estimating the diurnal production of photosynthesis

No.	pH	τ , h	$[\text{H}_2\text{CO}_3^*]_{\text{aq}}$, mol/l	$[\text{CO}_3^{2-}]_{\text{aq}}$, mol/l	$[\text{CaCO}_3]_{\text{aq}}$, mol/l
1	8.02	6	$2.56 \cdot 10^{-5}$	$7.39 \cdot 10^{-6}$	$3.95 \cdot 10^{-6}$
2	9.11	18	$2.03 \cdot 10^{-6}$	$8.09 \cdot 10^{-5}$	$4.01 \cdot 10^{-5}$
3	9.01	22	$2.61 \cdot 10^{-6}$	$6.54 \cdot 10^{-5}$	$3.30 \cdot 10^{-5}$
4	7.83	6 (30)	$4.12 \cdot 10^{-5}$	$4.52 \cdot 10^{-6}$	$2.42 \cdot 10^{-6}$

Note. On the basis of the data on $\text{pH} = \varphi(\tau)$ for constant $t = 25^\circ\text{C}$, $I = 1.6 \cdot 10^{-3}$ mol/l, $C_{\text{Ca}^{2+}} = 5.0 \cdot 10^{-4}$ mol/l, $C_{\text{CO}_3^{2-}} = 1.3 \cdot 10^{-3}$ mol/l.

the accepted assumption about constant concentrations of the *formal elements* Ca^{2+} , CO_3^{2-} can be considered to be quite correct. Because this (taking into account the fact that $[\text{H}^+]$ is much less than the equilibrium concentrations of all the other chemical forms of the system under investigation, and for the water of the class under consideration we may neglect the effect of redistribution of H^+ into the balance of other acid-base subsystems) we have an almost stoichiometric relation between the local input-output for the CO_3^{2-} ($\text{CaCO}_3 + \text{CO}_3^{2-}$) and H_2CO_3^* components in agreement with the overall equation



Therefore, the balance of consumption-evolution of CO_2^* in the analyzed system due to the set of processes P and D is made up from the calculated data of Table 2 according to equation

$$\Delta[\text{CO}_2^*] = \Delta[\text{H}_2\text{CO}_3^*] - \Delta[\text{CO}_3^{2-}] \quad (12)$$

Then, the primary production in moles of CO_2 $[\text{P}(\text{CO}_2)]$ in one litre of water according to the data shown in Table 2 can be determined approximately, similarly to [39–41], using the equation

$$\text{P}(\text{CO}_2) = \Delta[\text{CO}_2^*]_{4-3}(n_1 + n_2)/n_3 - \Delta[\text{CO}_2^*]_{2-1} - (0.5\Delta[\text{CO}_2^*]_{2-1}n_2/n_1 + 0.5\Delta[\text{CO}_2^*]_{4-3}n_2/n_3) \quad (13)$$

With the designations accepted here, the $\Delta[\text{CO}_2^*]$ values depict the contribution of P and D processes to $\Delta[\text{H}_2\text{CO}_3^*]$ (with which the changes in acidity in the series pH_1 – pH_4 are connected), while n_i values depict the

corresponding intervals of the day. In equation (13), following the assumptions of Bruevich in estimations of the oxygen balance [42], the authors of [39–41] accepted equivalently that the mean hourly CO_2 income into the water portion under consideration due to breathing and destruction is constant for 24 h and can be determined for the night period (n_3). Thus determined CO_2 income due to breathing and destruction during the period $n_1 + n_2$ is added algebraically to the decrease in CO_2 calculated using equation (12) in the region of the most active photosynthesis (n_1) and to the increment in the region n_2 , calculated according to equation (12), which is connected, according to Bruevich's assumption, with a two-fold decrease in the hourly mean rate of photosynthesis in comparison with the first region. Finally, we determine (as a positive value) CO_2 consumption for photosynthesis (P) during the entire active period of a day $n_1 + n_2$ (for example, according to the data of Table 2 we obtain $\text{P}(\text{CO}_2) = 3.8 \cdot 10^{-4}$ mol/l). In principle, within the restrictions considered for such an estimation and the initial information, some are verifiable and superfluous (in some aspects) and insufficient (in other aspects). However, more details (including analysis of errors and possible ways of mastering this procedure) go out of the range of the main problem which is the subject of the present paper.

To conclude, we are to stress that as field observations are accumulated, different specifically oriented series of DPCE can be formulated; to solve them, universally applicable (dimensionality, kind of basis, the number of fixed equilibrium concentrations, the presence or absence of heterogeneous equilibria) are the approach [6–9], software [21] and CRUIZ-2 program [22]. For example, these can be problems connected with simulation of the states of *heavy metals* in any kinds of natural water and in the atmosphere.

CHEMICAL AND THERMODYNAMIC ANALYSIS OF THE STATES OF MERCURY IN THE ENVIRONMENT

Some reference data. Having rather high Clarke (0.05 mg/kg) mercury has very low MPC: 0.5 $\mu\text{g/l}$ for drinking water, 0.01 $\mu\text{g/l}$ for the

workplace air, 0.0003 $\mu\text{g}/\text{l}$ for the air of residential areas, 0.05 mg/l in fish, 0.5 mg/kg in solid waste [45]. Within the last 100 years, because of the substantial effect of anthropogenic factors, the concentration of the scattered mercury in the atmosphere, water and other components of the environment has increased substantially (according to the data of [46], by a factor of three in the atmosphere; 70 % of modern mercury income into the oceanic water is of anthropogenic origin, which makes about 3500 t/year). According to estimates [47, 48], the emission of mercury from the surface of land and water (almost solely in the form of mercury (0), which is one of the two specific features of mercury in comparison with other heavy metals [8, 49] is about 6000 t/year (among them, more than a half is of anthropogenic origin), and it is essentially included into transcontinental transport processes. The back flux from the atmosphere is nearly equal to the emission but consists almost completely of the forms of mercury (II) [8, 49]. That is why daily income of mercury (which is the element of the first group of danger) into the organism of an average European adult person is already reaching the level of 6 μg (mainly with food) [50]. It is known that under the conditions of high diurnal doses (for humans, 0.3 mg/day) for a long time (months) mass poisoning of people and animals occurs. This is the reason for the attention of a wide range of researchers to the so-called *mercury problem*.

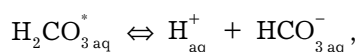
A specific aspect of the *mercury problem* is also the existence of yet unclear mechanisms of concentrating (with coefficients of up to 10^6 and more) some forms of mercury in trophic chains. For instance, even for the background mercury content in the environment, during the first years after the creation of artificial water reservoirs we observe the concentrations of highly toxic form CH_3Hg^+ to exceed the MPC in fish [51].

So, the necessity to accumulate, analyze and generalize the information obtained by field observations and in investigations of the real states of mercury in specific subsystems of the environment has been causing no doubt since long ago. (Many aspects of this problem were

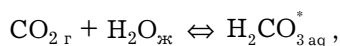
considered at the International Symposium "Regional and Global Mercury Turnover: Sources, Flows and Balances" which was held in Novosibirsk in 1995 under the initiative of the SB RAS within the SCOPE Project "Estimation of mercury distribution and its role in the environment" [52].

Some of the results obtained [8]. Actual states of *heavy metals* (in particular, mercury) in natural aqueous solutions and their participation in the material exchange with other subsystems of water and with the bordering systems are strongly affected by pH, $p\text{O}_2$, E_h . Because of this, we will briefly consider some results of analysis of the laws of pH, $p\text{O}_2$, E_h variations in fresh surface water of West Siberia. According to the data of [39–41], the main *initial component* in the Novosibirsk reservoir is calcium bicarbonate; correspondingly, the main *detailed mineralization-forming components* are bicarbonate ions and calcium cations. We also are to take into account the fact that the concentration of bicarbonate ions is in linear correlation with total salt content; their seasonal variations are at a level of 0.4–0.5 logical units. Diurnal periodic variations of $[\text{HCO}_3^-]$ are almost absent. Nevertheless, pH in the surface layer of water exhibits a clear diurnal periodic variation (8.4 ± 0.8 pH units in summer and 8.4 ± 0.4 pH units in autumn [8, 41]). In addition, water is much more acidic near the bottom, and any diurnal variations are absent there (they do not exceed 0.2 logical units.). According to the data of observations of 10 years [53], the prevailing initial component in the water of the upper Ob basin and in the lake Teletskoye is calcium bicarbonate, too. The second important component contributing into the salt content is magnesium sulphate. The pH values varied (due to the combination of diurnal and seasonal periodic changes) within the range from 6.4 to 8.7, while the *mean value* was about 7.5. It should also be noted that E_h values did not exceed 570 mV, that is, were rather low in all the cases.

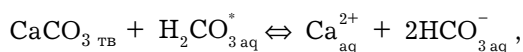
Our key statements in the interpretation of briefly considered set of data are outlined below. First, in an aqueous solution as a subsystem of natural water, at any moment and in any place (at any macropoint) there is the equilibrium:



$\text{p}K^0 = 6.37$ (25 °C), 6.52 (0 °C) [8, 43, 44] (14)
second, the buffer reservoir of the atmosphere acts permanently over the entire border of its contact with water:



$\text{p}K_{\text{r}} = 1.46$ (25 °C), 1.12 (0 °C) [8, 43, 44] (15)
third, the set of scattered contacts with calcium carbonate varieties supply calcium bicarbonate into water⁴:

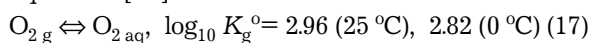


$\text{p}K^0 = 4.4$ (25 °C), 4.0 (0 °C) [8, 43, 44] (16)

Thus, pH levels and their seasonal, diurnal and spatial variations can be fruitfully interpreted taking into account equilibrium (14). In other words, they may be represented as a consequence of the levels of concentrations and their seasonal, diurnal and spatial variations for only two detailed components – H_2CO_3^* and HCO_3^- . The first one is formed not due to process (15). Quite contrary, almost universally prevailing is the discharge of the excess carbon dioxide into the atmosphere. Only in summer and in autumn, due to intense photosynthesis in the subsurface layers, stable diurnal regimes with regular variations around equilibrium (15) arise. The latter circumstance is essential among others providing correctness of approximations forming the foundations of the procedure of estimations of the primary production of photosynthesis on the basis of diurnal dynamics (see Section 3). As a diurnal mean, the main sources of carbon dioxide (consumed for photosynthesis during the period of active life of zoo and phytoplankton) of water turn out to be breathing of animal and plant organisms (including plankton) and oxidative destruction of the mort matter. The concentration of HCO_3^- is formed mainly in the overall reactions (16) and is a buffer with respect to the processes

responsible for diurnal variations of pH. Only for kinds of water not characteristic of West Siberia, other sources of the formation of HCO_3^- concentrations can be valid. However, even in these cases the above-presented key statements (with an amendment or some supplements to the third one) will remain valid.

The regime of oxygen in the surface water under consideration is relatively simple. In the majority of cases, we may restrict the consideration to the estimation on the basis of equation [43]



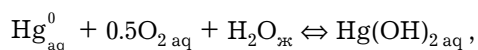
Within a more detailed approach, we may take into account not only the local consumption of oxygen both for oxidation of the organic and mineral matter in water and at the borders, and also for breathing of water organisms, but also its incoming from the photosynthesis in photic layers. However, the indicated factors have a weaker effect on the variations of the real concentration of molecular oxygen than on the variability of CO_2 concentration. This is connected with the fact that the ratio of the equilibrium (with the atmosphere) concentrations of these forms is about 20 (in favour of O_2) at 25 °C. This is one of the reasons of lower information content of Bruevich's procedure [42] in comparison with the procedure proposed by Smolyakov and co-authors [39–41] (see Section 3). The E_{h} values in water under consideration (117–561 mV, more frequently 400 mV [53]) are almost in all the cases much lower than the calculated values of the oxygen potential (756–820 mV at pH ~ 7.8 and $t = 25$ –0 °C [8, 9]). It is natural to expect that any of the subsystems determining E_{h} (but not the oxygen one) can turn out to be labile to the oxidation-reduction action on the chemical forms of heavy metals (in particular, mercury).

Partial analysis of the possible local states of mercury in water and in the atmosphere, which was performed on the basis of the above considerations and the data presented in [8], allowed us to make some specific conclusions⁵.

⁴⁴The $\text{p}K^0$ values for equilibrium (16) participated by metastable crystal hydrate $\text{CaCO}_3 \cdot \text{H}_2\text{O}_{\text{s}}$ were reported in [8]. Here we mention the data for the equilibrium with calcite. The fact that the point of the diurnal pH saw-shaped curve in summer and in autumn in the Novosibirsk reservoir corresponds with a surprising accuracy to the simultaneous realization of the equilibrium between water and calcite (exactly so!) and atmospheric CO_2 .

⁵In this case, physicochemical decomposition (separation of the full system depicting the considered initial system at the accepted level of its detailed elaboration, into autonomously analyzed systems under investigation) allowed us to make conclusions, starting from the third one, without using computer calculations.

First, in the subsystem of inorganic complexes of mercury (II) in medium (with $\text{pH} \sim 7.5$) and alkaline water ($\text{pH} \leq 9.2$), the prevailing *detailed component* is $\text{Hg}(\text{OH})_2$ (the opinion that the contribution from $\text{Hg}(\text{OH})_3^-$ complex is substantial, for example as stated in [54], is undoubtedly erroneous). For this reason, the activity of Hg^{2+} within this pH range decreases as the square with an increase in pH in the alkaline region. Second, in the acid region, especially near the lower boundary ($\text{pH} 6.4$), *detailed components* $\text{Hg}(\text{OH})\text{Cl}$ and HgCl_2 become prevailing. For this reason, the concentration of hydrogen ions here loses its ability to affect the activity of Hg^{2+} giving place to chloride ions. Third, the upper boundary of the possible concentration of the *detailed component* $\text{Hg}(\text{OH})_2$ is about 44–22 mg Hg/l H_2O , otherwise HgO_{cr} gets precipitated. Fourth, the process



$\log_{10} K^0 = 14.62$ (25 °C), 16.05 (0 °C) (18) judging from the thermodynamic data, should go almost to completeness to the right-hand side. However, it is known from the laboratory practice and field observations that this process is *substantially hindered*. This allows one, for example, to obtain saturated solutions of metal mercury without any noticeable its transformation into $\text{Hg}(\text{OH})_2$ according to (18). Because of this, in the case when elementary mercury is prevailing in water, its concentration is limited from above by 60 $\mu\text{g/l}$ (25 °C), that is, 120 MPC units (otherwise Hg_1 precipitates). In the atmosphere, the corresponding mercury content can be limited by 20 $\mu\text{g/l}$ [8]. In principle, for water, other mechanisms responsible for the predominance of the elementary form are also possible. One of them, participated by the organic matter under oxidative destruction, was mentioned above. However, it should be stressed once more that in water (and in the atmosphere) in the case of the slightest prerequisites of the elimination of hindrance, process (18) should proceed almost till completeness. In particular, in this case, the situation with the $\text{Hg}(\text{OH})_2$ to Hg^0 concentration ratio up to 10^{13} can be realized in water. Unfortunately, almost the entire set of questions connected with the characteristics and

levels of mercury bonding on the organic matter remains open [2]. However, we assume that the above-listed conclusions would not become invalid; they will certainly be useful for the complex analysis of mercury redistribution between the dissolved inorganic matter (which has already been considered) and the dissolved organic matter, colloid suspended inorganic and organic matter, etc. (the latter subsystems of water have not been considered by us yet). This is one of the clear demonstrations of the effective character of the procedures developed by us. It is natural that the set of key constants which was formed in [8] remains open for adding and verifying. In general, we hope that while the amount of research and observation data increases, the realization presented herein in brief will turn out to be useful for formulation and solution of new specific problems (first of all, in the area of chemistry of *heavy metals* in the environment, including ecological problems).

CONCLUSIONS

It is evident that the approach and the procedure of formulating and solving the problem-oriented series of DPCE of the classes under consideration are applicable to simulation of the real state of the matter not only in natural water but also in technological one, and in water subsystems inside the plant and animal organisms. It is also clear that more thorough assimilation of chemical thermodynamic simulation of the distribution of matter over *chemical forms* (including both anion and cation forms, that is, ion forms, and the forms with separated charges [13], and electrically neutral ones, among which molecules are only a partial case, and chemical forms resulting from binding the heavy metal cations on the fragments of high-molecular substances [27]) in the solutions of diverse destinations, including aprotic and mixed solvents [15, 33] can broaden the area of its application involving analytical chemistry, geochemistry, biochemistry, hydrochemistry, electrochemistry, chemical synthesis (for example, for the interpretation and optimization of synthesis processes with the participation of solutions), catalysis (both homogeneous and

heterogeneous participated by liquid and gas solutions), *etc.*

A separate and certainly very important problem includes obtaining, evaluation and arrangement of the data files that would provide the PBCE under consideration with the concentrational (finally) equilibrium constants [3–6]. Researchers in the area of environmental chemistry still survive acute lack of the quantitative information about heavy metal binding (the major part of these metals are transition and *p*-metals) with the high-molecular organic matter of water [2, 27]). In the above-indicated respects, three moments are important. The first moment is the formation of databases related to standard physicochemical conditions, usually hypothetical (ideal), and subsequent compilation of local databases for specific classes of the systems *under investigation* (separated inside the specific classes of *initial systems*). The second moment involves extrapolation-interpolation estimations of the lacking standard data and formation of the grounds to the reduction of the constants to specific (*T*, *P*, *n*^{*}) conditions. The third moment involves broadening and increase in the information content of the arsenal of regular correlations (of semi-empirical and other substantiation levels) to perform the two above-indicated classes of interpolation-extrapolation estimations.

In addition, it is an important problem to estimate the error of the results obtained by this kind of simulation [3–6]. It is appropriate mentioning here yet unemployed priority (with respect to the objective information content) of the so-called *integral estimations* or even their *separate (upper or lower) boundary values* over the *point* ones [4, 55, 56]. We permanently come across underestimation and corresponding non-involvement of the independent information (which is usually available) to compose the initial models of errors and therefore to solve the indicated problems correctly.

In general, in spite of still prevailing lack of the information obtained in research, field observations and technological applications, which is necessary for constructive formulation and solution of problem-oriented series of DPCE, we insist on the promising character of

the approach and procedure generalized in the present work for practical application.

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