Dynamics of megasystems in geochemistry: Formation of base models of processes and simulation algorithms

Article *in* Geologiya i Geofizika · January 1999

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Vol. 40, 1999

RESERVOIR DYNAMICS FOR MEGASYSTEMS IN GEOCHEMISTRY: FORMATION OF BASE MODELS OF PROCESSES AND ALGORITHMS FOR SIMULATION

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Using thermodynamic-potential minimization as a base, an approach to the formation and investigation of simulations of dynamic megasystems has been developed. By dynamic megasystems are meant natural and geoengineering systems, or reservoirs, which interact chemically and are connected with each other by direct, reverse, and through flows of matter and energy. The structure of a simulation model is formed by combining basic constituents and directive parameters. The user can choose diverse variants of aggregating systems and flow connecting the system to a single physicochemical object, i.e., into a megasystem. The evolution of megasystems can be calculated by two algorithms. In the first algorithm, two operations are performed in a unit of time: calculation of the equilibrium for all systems at a time and then transfer of matter by flows in accordance with a given matrix of macrokinetic coefficients of transfer. In the second algorithm, the megasystem evolution in time and space proceeds cyclically. In each cycle, calculation of the equilibrium for the systems and transfer of the matter by flows are performed consecutively from system to system in accordance with the number of system and matrix of macrokinetic coefficients. The number of time units is equal to the number of systems in a megasystem. The cycle of the second algorithm ends in the system with the greatest number, and the next cycle begins with the first system. The most important trait of both algorithms is separation of the flows into groups of mobile phases. The flows of aqueous solutions, gas mixture, solid materials (eolian dust, furnace charge, mineral suspensions in water), liquid hydrocarbons, organic material, etc. can be transferred from system to system. Each group of mobile phases has a matrix of macrokinetic coefficients. If required, the macrokinetic coefficients can be recalculated by built-in algorithmic operators in the intervals between time units. The proposed approach is illustrated by two examples. In the first, the tolerance of Lake Imandra (north of the Kola Peninsula) for pollution with nepheline − apatite production waste was investigated by an integral physicochemical index − pH of water, depending upon the sewage volume. In the second example, the redistribution of material in the megasystem $Al_2O_3 - SiO_2 - H_2O$ was studied. The redistribution is caused by an external energetic effect, production of a stationary nonisothermal profile at $T = 300–440$ °C and at $P = 3$ kbar. The simulation results are compared with Vidal's experimental data. The formation procedures and simulation algorithms for dynamic megasystems were realized in the form of the "Reservoir dynamics" module, included into the program complex *Selektor-C* designed in 1997. It can be employed for solving scientific problems, for engineering, and education.

Geochemistry, minimization of thermodynamic potentials, chemical and spatial mass transfer, reservoir dynamics, simulation

INTRODUCTION

Formulation and solution of problems on complete, partial, intermediate, and/or metastable equilibrium are only the initial stage of modeling based upon minimization of thermodynamic potentials [1–4]. When the

models of individual systems have been formed and the equilibrium in these systems has been calculated, the geochemist inevitably conceives the idea of creating not only the models of individual systems but simulations* of processes as well. Any natural process, as well as a technological one, is an interaction of several systems integrated into megasystems. At least, the interaction between a system and its environment is the simplest megasystem model, which consists of two systems: the system itself and the environment. Therefore, in geochemical simulation and modeling of physicochemical processes, a demand arises for creating models of megasystems which evolve in space and time. If there is no quantitative information on the rates of conversion and transport, the megasystem can be modeled qualitatively when events change sequentially in conventional units of space and time.

With each system of the megasystem regarded as a reservoir, the megasystem dynamics can be called the "reservoir" dynamics. This term is widely used in various fields.

PRINCIPLES

In the famous reservoir-dynamics models, where the equilibrium constant method is employed, the physicochemical evolution itself is described by a fixed set of chemical reactions, i.e., a scenario for the process described in advance; the scenario is dictated by a preassigned set of stoichiometric equations for the reactions. It is a very serious restriction.

Any optimal path of the megasystem evolution cannot be anticipated unambiguously. The physicochemical path of evolution is established in the course of the process. It is precisely this "detail" that settles the matter! In the equilibrium constant method no mention is made of this "detail". While the megasystem is functioning, there may occur reactions whose mechanisms have been earlier unknown. Moreover, what reaction occurs remains a mystery. Omission of a reaction or its improper prediction may sacrifice the scenario described in advance. In addition, the equilibrium constant approach proposes that calculations for chemical conversions are performed in the systems where the phases to be in equilibrium are already known. However, for geochemical models, equilibrium (or partial equilibrium) should be defined in multisystems, i.e., systems where the number of equilibrated phases is several tens of times greater than the number of independent components. There is a need to determine just which phases and which dependent components of these phases will be in equilibrium at any given stage of a dynamic process. Thus, the equilibrium constant approach does not consider properly the feedbacks between the locally temporal equilibrium and the exchange flows between reservoirs. Moreover, the flows cannot be specified in phase and component composition.

Compared with the approach based upon stoichiometric equations and equilibrium constants, the method of thermodynamic-potential minimization can better combine the models of dynamics and of chemical interaction in megasystems consisting of reservoirs which are connected with one another and with the environment by direct, reverse, and through flows of matter and energy. The initial prerequisites for this combination are as follows:

— the reservoirs that form a megasystem are characterized by rapid mixing, as related to the rates of mass transport between the reservoirs, and by rapid attainment of complete, metastable, or partial equilibrium within their volume or within the separated parts of the volume;

— the reservoirs may have various T and P;

— the mass is transported between the reservoirs by flows of physically individualized phases: liquid, gas, and solid. Each flow has its own rate of mass transfer, which can depend on the mass of the source reservoir and on its composition, which change at each step of the dynamic process;

— inside any reservoir, the dependent components, phases, and/or all or some of the independent components can be produced or lost. Besides, the TP-conditions, which are dictated by external and internal factors of state, such as mixing, heating-up, and isochoric heating, can change in time in each reservoir;

— restrictions on changes in a free energy, entropy, enthalpy, and other thermodynamic parameters of a megasystem during its evolution may or may not be introduced as dictated by the initial directives of the simulator. The matter and energy flows which connect the megasystem with the environment, i.e., with external controlling parameters, may specify the optimal path of the megasystem evolution or may produce a disturbance;

— the physicochemical evolution of the megasystem with time and space is represented as a sequence

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* Simulation is a method of investigation of real processes, based upon studying models of dynamic megasystems. Computerized experiments are performed on a model of a dynamic megasystem. The experiments may be performed in accordance with a design made beforehand. If the design of experiments is lacking, the objective of the subsequent experiment is based upon the results of the previous series of experiments.

of conditions of complete, metastable, and/or partial thermodynamic equilibrium in the reservoirs in the coordinates of kinetic and dynamic controlling factors of evolution. By kinetics is meant the evolution of physicochemical processes in time and by dynamics, that in time and space. The model pattern of dynamics in space is given by the corresponding numbering of conjugate reservoirs within the megasystem. The flows move across the reservoirs bearing corresponding numbers in accordance with the accepted scenario of the process.

Modeling is performed by a two-level algorithm. First, at the upper level, the changes in the reservoirs which depend functionally upon kinetic and dynamic parameters are calculated. Then the equilibrium in the reservoirs is calculated with regard for the changes that resulted from the realizations of the upper level of the algorithm. At each step involving two levels, determination of the equilibrium gives an estimate of the state of the reservoirs during their nonequilibrium evolution, controlled by given flows of matter and energy. The characteristics of the flows may be changed during the simulation. For example, the thermodynamic equilibrium controls the emergence of new phases and the disappearance of old ones, which cannot be predicted in advance.

Thus, the minimization method provides a constructive approach — combination of equilibrium-thermo-dynamics methods with the kinetics and dynamics of physicochemical processes.

At present, the combined approach where two functional restrictions of the evolutional process — kinetics and thermodynamics — are integrated finds adherents in geochemistry and other nongeochemical fields of scientific and practical application of physical chemistry [2, 5–14]. Rational integration of kinetics and thermodynamics permits the use of some advantages of kinetic and thermodynamic representation of complicated processes and correction of some of their faults. We can hardly add anything to the previous information on this subject. Therefore, we will mention only the most interesting publications [3, 5, 7, 14, 15–20].

This paper treats megasystems which evolve under the action of external controlling factors — input and output flows of matter and/or energy. We do not consider isolated megasystems where the redistribution of material proceeds spontaneously as a result of the smoothing-out of the chemical potentials of independent components of the systems which were initially thermodynamically incompatible. This is the subject of a separate study. In such isolated megasystems, the direction of flows is not governed by the environment but is self-established in accordance with the gradients of the chemical potentials of independent components at each elementary step of the evolution. Some questions of the isolated-megasystem evolution and a possible approach to their modeling were considered by Chudnenko and Karpov in a series of publications [2, 21, 22].

The operation of the reservoir dynamics module in the program complex *Selektor-C** can be illustrated by two numerical examples. The first example concerns the interaction of industrial waste of nepheline-apatite production with the atmosphere, slime train, and freshwater Lake Imandra on the Kola Peninsula. The second example simulates Vidal's experiment [1] on the redistribution of material in the system $Al_2O_3 - SiO_2 - H_2O$ under nonisothermal conditions.

BASIC STRUCTURE OF THE MODEL OF A DYNAMIC MEGASYSTEM
AND TWO ALGORITHMS FOR SIMULATION OF ITS EVOLUTION

A mathematical representation of dynamic megasystems and algorithms for their simulation implies formal tools of description. It requires an introduction of a system of symbols, designations, and indices and definition of vectors and matrices. Here we have a choice. We may list all details, including comprehensive identification of all constituents of heterogeneous multireservoir multisystems, as was done by Karpov [2] and Chudnenko et al. [21], or we may restrict ourselves to a sketchy representation in general terms.

The advantage of the former way is doubtless. It permits one to consider all numerous physicochemical "wheels and screws". However, this advantage is basically of a user's manual for software rather than of a scientific article. The text is crowded up with technical details, which hinder the recognition of the major peculiarities of functioning dynamic megasystems as special polysystem thermodynamic objects controlled by external factors. The second way involves a sacrifice in the completeness of description. Attempts to make the text more understandable lead to loss in some important details which cannot be represented only by words without special mathematical tools for description. Therefore, in this report we will try to be in the center of

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these two ways. We will restrict ourselves to a minimal necessary set of designations with which one can give a clear idea of the skeleton structure of dynamic megasystems and algorithms of their functioning. Such a formalized pattern provides a further, more complete and detailed, description of the component and phase compositions of heterogeneous and multiaggregate systems of a megasystem, using the terms and notions of convex programming [2, 4].

At first, let us list the input data with which models of dynamic megasystems can be formed.

1. $n(R)$ is the number of discrete intervals of time, i. e., the number of "units of time", on real or relative scales

$$R = \{r/0, 1,..., r,..., n(R)\},$$

where R is a finite set of discrete intervals of time. The evolution of the dynamic megasystem begins with the "zero" (starting) time, $r = 0$.

2. $n(Q)$ is the number of systems (reservoirs) in the dynamic system

$$Q = \{q/0, 1,..., q,..., n(Q)\},$$

where Q is a finite set of systems in the megasystem. The environment is designated by the zero reservoir, $q = 0$. Each system of the megasystem can have its own environment.

3. $v(q,r)$, $q = 0, 1,..., n(Q)$, $r = 0, 1,..., n(R)$ is the extent to which the process runs, or the coordinate of the process [23] in the q-th system in the r-th interval of time. These processes are dissolution, mixing, inflow of matter and of energy from the environment, decomposition or decay of organic material, redox reactions, etc.

Let us offer a brief explanation using a simple example. Let Φ_J be a finite set of phases in the q-th system in the r-th interval of time:

$$\Phi_J = \{\alpha/l,..., \alpha,..., n(\Phi_J)\},$$

where α is the phase index.

The molar quantity of the α-th phase in the q-th system in the r-th interval of time is designated by X_α^0, $\alpha \in \Phi_J$. In this case, if, for example, the α-th phase dissolves, the state of the q-th system in the $(r + 1)$-th interval of time corresponds to the dissolution of

$$X_\alpha^0(q,r) \cdot v(q,r+1)$$

moles of the phase α, while the number of moles in the nondissolved portion of the phase α in the $(r + 1)$-th interval of time is equal to

$$X_\alpha^0(q,r+1) = X_\alpha^0(q,r) - [X_\alpha^0(q,r) \cdot v(q,r+1)].$$

It may be supposed that $v(q,r+1)$ is the number of moles of the phase α which are involved in the interaction (in this case, dissolution) in the $(r + 1)$-th interval of time.

For chemical conversions, the gross-formula of compounds without identification of their component and phase compositions can be used. For example, the gross-formula of 10 kg of air, 100 g of granodiorite, 1000 g of H_2O with the compounds dissolved in water, etc. The form of presentation of the chemical, component, and phase compositions of systems in a megasystem is specified by the formulation of the problem. The program complex *Selektor-C* [3, 4, 24] has a simple and flexible scheme of the interaction of compounds which may be presented both in the form of individual dependent components and phases and in the form of gross-formula in which the composition of compounds and flows in independent components is fixed.

A change in $v(q,r)$ over one interval of time can be calculated from the equation

$$v(q,r+1) = v(q,r) + v1(Q,r+1),$$

where $v1(q,r+1)$ is a change in the degree to which the process runs over the $(r+1)$-th interval of time.

The logarithmic scale of a step-by-step change in $v(q,r)$ often appears to be more convenient for the description of interaction. To turn to the logarithmic scale, the following equation can be applied:

$$\xi(q,r+1) = \xi(q,r) + \xi1(q,r+1),$$

$$v(q,r+1) = 10^{\xi(q,r+1)}.$$

For example, in the case of dissolution, at the beginning of water-mineral interaction the mineral passes into the solution in minor amounts. But as the "water-minerals" system attains equilibrium, the concentration of mineral components increases. The range of the changing content of dissolved material in the "water-minerals" system from start to equilibrium can be best presented on the logarithmic scale. Therefore, at the beginning of the process we can take $\xi(q, r=0) = -7$ and then model the dissolution process to the point of saturation, taking $\xi1(q, r) = 0.5$ as a step.

Comprehensive information on how to operate with the variables v, $v1$, ξ, and $\xi1$ with which different scenarios of the evolution of systems in megasystems can be made is given in the manual of the program complex *Selektor-C*.

4. $n(P)$ is the number of groups of mobile phases:

$$P = \{p \,|\, 1, ..., p, ..., n(P)\}.$$

The group of mobile phases is something that moves from one reservoir into another. It is most often an aqueous phase with dissolved components. The aqueous stream may also contain various mineral and organic suspensions. Another common group of mobile phases is a gas mixture with dust. A special group of mobile phases is solid phases of systems, such as eolian dust, volcanic ash, and technogenic aerosol. Magmatic melts are also a group of mobile phases.

5. B is a matrix of the initial compositions of the systems of the megasystem in independent components.

$$B^{r=0} = [b_{qi}^{r=0}], \quad q=0, 1, ..., q, ..., n(Q), \; i = 1, ..., n(N_q),$$

where $n(N_q)$ is the number of independent components in the q-th system; $b_{qi}^{r=0}$ stands for the molar abundance of the independent component i in the q-th system when $r = 0$.

$$b_q^{r=0} = (b_{q1}^{r=0}, ..., b_{qi}^{r=0}, ..., b_{qn(N_q)}^{r=0})^T,$$

where $b_q^{r=0}$ is the vector of the molar quantities of independent components in the system q.

6. A_{qk}^P is a matrix of the relations of "input-output" flows for the p-th group of phases:

$$A_{qk}^P = [\alpha_{qk}^P], \; p \in P, \; q, k \in Q.$$

Let us consider the structure of the matrix A_{qk}^P (Fig. 1).

The quantity α_{qk}^P, being an element of the matrix A_{qk}^P, performs a dual function with respect to the q-th reservoir:

α_{qk}^P is the output;

α_{kq}^P is the input.

The input is distinguished from the output by the repositioned indexes. *If the former index is the output,*

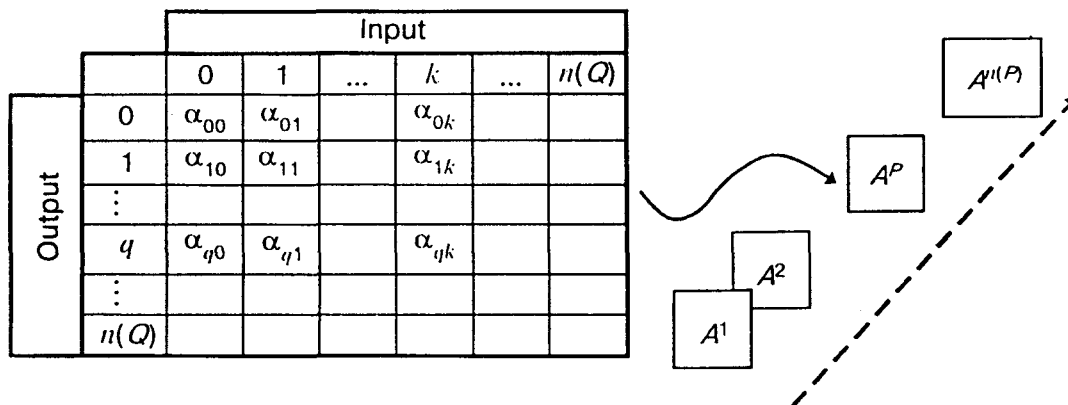|	Input					
	0	1	...	k	...	$n(Q)$
0	α_{00}	α_{01}		α_{0k}		
1	α_{10}	α_{11}		α_{1k}		
⋮						
q	α_{q0}	α_{q1}		α_{qk}		
⋮						
$n(Q)$						

(Output label on left side spanning rows)
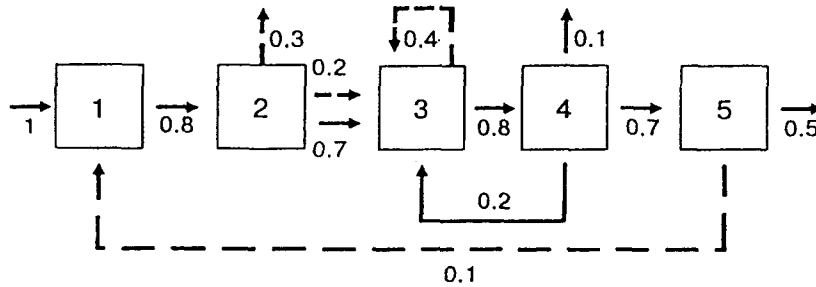
Fig. 1. The structure of the matrix A_{qk}^P.

Fig. 2. An illustrative scheme of conjugation of five systems in the megasystem by flows of two groups of mobile phases, $n(Q) = 5$ and $n(P) = 2$. The flows of the first group of mobile phases are shown by solid lines. The flows of the second group are shown by dashed lines. The numerals near the arrows are the values of α^1_{qk}, β^1_{kq}, α^2_{qk}, and β_{kq} in the matrices A^1_{qk} and A^2_{qk}. The numeral in the center of the square is the number of a system in the megasystem.

		Input					
		0	1	2	3	4	5
Output	0		1				
	1			0.8			
	2				0.7		
	3					0.8	
	4	0.1			0.2		0.7
	5	0.5					

		Input					
		0	1	2	3	4	5
Output	0						
	1						
	2	0.3			0.2		
	3				0.4		
	4						
	5		0.1				

Fig. 3. The numerical values of macrokinetic coefficients for the illustrative example of a megasystem consisting of five systems with flows of two groups of mobile phases. On the left of the figure there is the matrix A^1_{qk} (the first group of mobile phases), on the right — the matrix A^2_{qk} (the second group of mobile phases).

the latter index is the input. It is not quite convenient to distinguish visually the elements of the matrix A^P_{qk} by the position of the indices. Therefore, we will use the following symbols:

α^P_{qk} — the output from the q-th reservoir,

β^P_{kq} — the input ($\beta^P_{kq} = \alpha^P_{kq}$) into the q-th reservoir.

The quantities α^P_{qk} and β^P_{qk} account for the fraction of the p-th group of mobile phases in the systems q and k in the time interval r, which moves from the system q into the system k and from the system k into the system q.

The simplest illustration may help the reader to gain a deeper insight into the structure of the matrix A^P_{qk}, $p \in P$, which connects the flows of systems in the megasystem.

For example, let the megasystem consist of five systems connected between one another by flows of two groups of phases (Fig. 2).

Figure 3 demonstrates the matrixes A^1_{qk} and A^2_{qk} and the numerical values of α^1_{qk}, β^1_{kq}, α^2_{qk}, and β^2_{kq}.

This example readily illustrates the way of formation of the model of systems in a megasystem and the flows connecting these systems. Recall that the environment is identified by zero reservoir.

7. The compositions of the input and output flows differentiated in the groups of mobile phases for each system are as follows:

$$(b^P_\beta)^r_q = \sum_{k=0}^{n(Q)} [(\beta^P_{kq})^r \cdot (b^P_k)^r], \ p \in P, \ r \in R, \ q, k = 0, 1, ..., n(Q), \tag{1}$$

where $(b_k^P)^r$ is the vector of the molar quantities of independent components, which has dimensionality $n(N_q)$, for the p-th group of mobile phases in the k-th system in the r-th interval of time; $(\beta_{kq}^P)^r$ is the macrokinetic* coefficient of transport of the p-th group of mobile phases from the system k into the system q in the r-th interval of time; $(b_\beta^P)_q^r$ is the total molar quantity matter in independent components for the p-th group of mobile phases which were introduced into the q-th system over the r-th interval of time;

$$(b_\alpha^P)_k^r = \sum_{q=0}^{n(Q)} [(\alpha_{qk}^P)^r \cdot (b_q^P)^r], \; p \in P, \; r \in R, \; q, k = 0, 1, ..., n(Q), \tag{2}$$

where $(b_q^P)^r$ is the vector of molar quantities of independent components, which has dimensionality $n(N_q)$, for the p-th group of mobile phases in the q-th system in the r-th interval of time; $(\alpha_{qk}^P)^r$ is the macrokinetic coefficient of transport of the p-th group of mobile phases from the system q into the system k in the r-th interval of time; and $(b_\alpha^P)_k^r$ is the total molar quantity of matter in independent components for the p-th group of mobile phases which were transferred from the system q over the r-th interval of time.

Obviously, during the program realization of the algorithm of megasystem dynamics, not only the molar quantities of compounds at the input and output but also their masses are calculated.

The evolutional dynamics of a megasystem with the specific structure of interacting systems and flows and values of macrokinetic coefficients can be described by two algorithms, which are composed of operators approximating the elementary operations in each interval of time.

In the first algorithm, two operations are performed simultaneously in a unit of time in all systems of the megasystem.

The first operation is as follows. The equilibrium is computed in all systems. It may be complete, metastable, and/or partial. What type of equilibrium will be realized depends upon the input conditions of the simulator. Besides, the mass balances of the materials which remain chemically unreacted, such as mineral and organic suspensions, nonreplaced rock, xenogenic material, are taken into account.

The second operation is as follows. The materials are transported from the k-th systems into the q-th systems and, inversely, from the q-th systems into the k-th systems in accordance with the specified structure of the systems and flows and with the macrokinetic coefficients of transport, α_{qk}^P and β_{kq}^P.

Thus, when the first operation is symbolized by E (equilibrium) and the second by tr (transfer), the first algorithm can be presented in the form of the following sequence of operations in time:

time:	$r = 0$	$r = 1 ...,$	$r = n(R) - 1$	$r = n(R)$
operation:	$E \to tr$	$E \to tr ...,$	$E \to tr$	E

The general scheme of the algorithm is the following sequence of operations:

1. When $r = 0$ (the "zero" time), the initial compositions of megasystem systems, i.e., the vectors $b_q^{r=0}$ of dimensionality $n(N_q)$, are established.

2. The equilibria are computed for $n(Q)$ systems.

3. By Eqs. (1) and (2), the total molar quantities of compounds in independent components are calculated for the groups of mobile phases transported from the systems k into the systems q and, conversely, from the systems q into the systems k, i.e., $(b_\alpha^P)_q^r$ and $(b_\beta^P)_k^r$.

4. The vectors of the molar quantities of independent components, b_q^{r+1}, are calculated for $n(Q)$ systems:

$$b_q^{r+1} = b_q^r + \sum_{p=1}^{n(P)} (b_\beta^P)_q^r - \sum_{p=1}^{n(P)} (B_\alpha^P)_q^r, \; q \in Q, \; r \in R. \tag{3}$$

5. The energy parameters of the megasystem, such as Gibbs' and Helmholtz' free energy, enthalpy, internal energy, entropy, volume, and mass and volume densities of these parameters, are computed.

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* By macrokinetics is meant determination of the dependence of the amounts of material in reservoirs upon the rates of its inflow and removal. Macrokinetics describes the most important features of the material transfer through the reservoirs with no regard for a comprehensive analysis of the nonlimiting mechanisms of kinetic transformations. Besides, in the macrokinetic approach, the basic limiting processes of chemical interactions, such as dissolution, decay of organic compounds, precipitation, redox reactions, mixing of solutions, etc., are taken into account. These processes can be described in relative and/or real scales of time.

6. Check of the stability criteria, i.e., reaching a stationary regime.

7. If the specified number of the intervals of time is exhausted, the process comes to an end; otherwise, the process goes on from Operation 2.

Remark. *Between the r-th and (r+1)-th intervals, a special operator built in the algorithm can operate. This operator recalculates the macrokinetic coefficients α_{qk}^P and β_{kq}^P, when, under the conditions of the scenario of the simulator, these coefficients are not constants and are changed by external control.*

In the second algorithm, the order of operations is determined by a sequence of systems numbered 1, 2, ..., q, ..., n(Q) and by a scheme of interaction of systems and flows, which is given by the matrix A_{qk}^P. The sequence of the time intervals 1, 2, ..., r, ..., n(R) is synchronous with the numbering of the systems.

The second algorithm operates under the following scheme:

On time scale, the megasystem evolution proceeds during $n(T)$ cycles, where $T = \{t/1, ..., t, ..., n(T)\}$.

In each t-th cycle, the following sequence of operations is performed:

1. The input composition of the first system is established at the "zero" time $r = 0$ for the vector $b_{q=1}^{r=0}$ of dimensionality $n(Q)$ with consideration of the flows from the zero system $q = 0$, i.e., from the environment.

For the second algorithm, the following conditions must be fulfilled:

Condition 1. After the transition from the system q to the system $q+1$, the input flows with the macrokinetic coefficients $\alpha_{q, q+1}$ cease to operate before the current cycle is over, once the values of these macrokinetic coefficients have been taken into account for the calculation of the composition of the system $q+1$. The macrokinetic coefficients $\alpha_{q, q+1}$ of these flows moving from the system q are taken to be equal to zero until the current cycle ends.

Condition 2. After the transition from the system q to the system $q+1$, all flows entering the system $q+1$ from the subsequent systems, i.e., the systems with the number greater than $q+1$, are not taken into account in the first cycle. Hereafter the flows defined by macrokinetic coefficients $\alpha_{q, q+1}$, where $k > q + 1$, are taken from the preceding time cycle. Once these flows have interacted with the system $q+1$, the corresponding macrokinetic coefficients are taken to be zero.

It can be said that when the time interval $q+1$ ends, all flows entering the system with the number smaller than q and greater than $q+1$ are cut off according to Condition 1 and Condition 2.

2. Time $r = 1$.

3. The equilibrium in the system $q = 1$ is computed.

4. In the system $q = 1$, groups of mobile phases are discerned according to the matrix A_{qk}^P.

5. According to the matrix of relation of the systems, flows, and macrokinetic coefficients α_{qk}^P, into the groups of mobile phases, material is transported into the system $q = 2$ and other systems of the megasystem ($k > 2$ and $k > 2$).

6. The vector $b_{q=2}^{r=1}$ in the system $q = 2$ is computed.

7. Condition 1 and Condition 2 are fulfilled.

8. Time $r = 2$.

9. The equilibrium in the system $q = 2$ is computed.

10. In the system $q = 2$, groups of mobile phases are discerned according to the matrix A_{qk}^P.

11. In the groups of mobile phases the matter is transported into the system $q = 3$ and other systems of the megasystem ($k > 3$ and $k < 3$) in accordance with the matrix of relation of the systems, flows, and macrokinetic coefficients α_{qk}^P.

12. The vector $b_{q=3}^{r=2}$ in the system $q = 3$ is computed.

13. Time $r = 3$, and so on.

The cycle ends when $r = n(Q)$. In the next cycle $t + 1$, the operations of the cycle t are replicated. The process goes on before all T cycles have been exhausted. As in the first algorithm, a controlling operator can be built-in between the cycles t and $t + 1$, which recalculates the macrokinetic coefficients of the matrix A_{qk}^P.

In Fig. 4, three different variants of conjugating flows and systems are presented, which can be employed in simulations using the second algorithm.

In principle, other schemes of conjugation can be constructed. In particular, the scheme in Fig. 2 can be employed for the second algorithm when Conditions 1 and 2 are fulfilled.
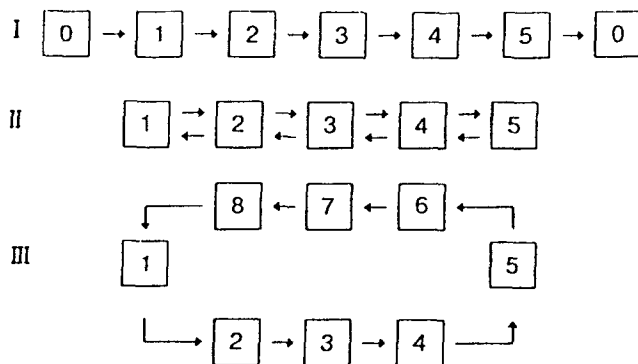
I $\boxed{0} \rightarrow \boxed{1} \rightarrow \boxed{2} \rightarrow \boxed{3} \rightarrow \boxed{4} \rightarrow \boxed{5} \rightarrow \boxed{0}$

II $\boxed{1} \underset{\leftarrow}{\rightarrow} \boxed{2} \underset{\leftarrow}{\rightarrow} \boxed{3} \underset{\leftarrow}{\rightarrow} \boxed{4} \underset{\leftarrow}{\rightarrow} \boxed{5}$

III

$\boxed{8} \leftarrow \boxed{7} \leftarrow \boxed{6}$

$\boxed{1}$ $\boxed{5}$

$\boxed{2} \rightarrow \boxed{3} \rightarrow \boxed{4}$

**Fig. 4. Different schemes of conjugating flows and systems according to the second algorithm.
I — simple sequence, when material enters the first system from the environment and moves
into the environment from the last system, i.e., the flow-through megasystem; II — sequence
with the feedbacks between adjacent systems; III — closed convective cell, i.e., rotation.**

TWO EXAMPLES OF RESERVOIR DYNAMICS IN GEOCHEMISTRY

Two relatively simple problems of reservoir dynamics are given below. The first example is taken from the geochemistry field which deals with the effect of industrial sewage on the physicochemical characteristics of fresh-water reservoirs. We have determined the limits to which Lake Imandra (north of the Kola Peninsula) may be resistant to the pollution by sewage of the apatite production (AP), using a physicochemical indicator — known values of *pH* of aqueous solutions [25, 26]. Attention was focused on the illustration of how to form and study a multireservoir simulator. The chief objective of this example is to help the reader to understand the idea of the dynamic megasystem without going into the details of physicochemical analysis. There is no way to represent the dynamic megasystem of interaction of industrial sewage of AP with Lake Imandra as a simple simulator. The completeness of physicochemical description will inevitably suffer some loss, because the model contains many independent and dependent components, mineral phases that are potentially possible in state of equilibrium, systems, and flows. Therefore, we omit input data and results of detailed physicochemical analysis of modeling because of a too large body of information. They may be published in another paper.

The second problem is a simulator of the redistribution of material in nonisothermal profile under the *TP*-conditions of hydrothermal process. The results of modeling have been qualitatively compared with Vidal's experimental data [1]. Unlike the first example, the second one is demonstrated with all input thermodynamic data. Being the geochemical illustration of how the material may be redistributed in a nonisothermal column, the second example can also be used as a convenient educative and test problem built into the base of models of the program complex *Selektor-C* [24].

We think that these two examples clearly demonstrate the general contour of our approach to formation and study of the simulators of dynamic megasystems. Based on these examples, one can construct more complicated models of reservoir dynamics.

Example 1. *The interaction of the industrial sewage of apatite production with the repository of tailings, atmosphere, and Lake Imandra.*

Lake Imandra is the largest freshwater reservoir in the north of the Kola Peninsula. For the last 60 years, it has been polluted by industrial sewage and slime from mining and metallurgical plants. Among them, the greatest amount of sewage, from 80 million m^3/year in 1992–94 to 240 million m^3/year in 1976–78 came from Apatit Co. [26].

A generalized scheme of interaction of the sewage of AP with Lake Imandra can be presented as an assemblage of interconnected systems (reservoirs) (Fig. 5). Before mixing with the Lake Imandra water, the industrial sewage passes through a technogenic deposit (slime-train) of apatite-nepheline rocks, i.e., a repository of tailings with a settling basin. A portion of the sewage is filtered through the deposit, and some portion goes over the surface of the technogenic deposit. The route of the sewage toward Lake Imandra can be modeled by three reservoirs which are partially open to the atmosphere, i.e., each of these reservoirs has an input flow from the atmosphere. Reservoirs 4 and 5 contain the surface and deep waters of the lake. In the fourth reservoir, the surface waters of the lake are mixed with the sewage of apatite production and with the seasonal
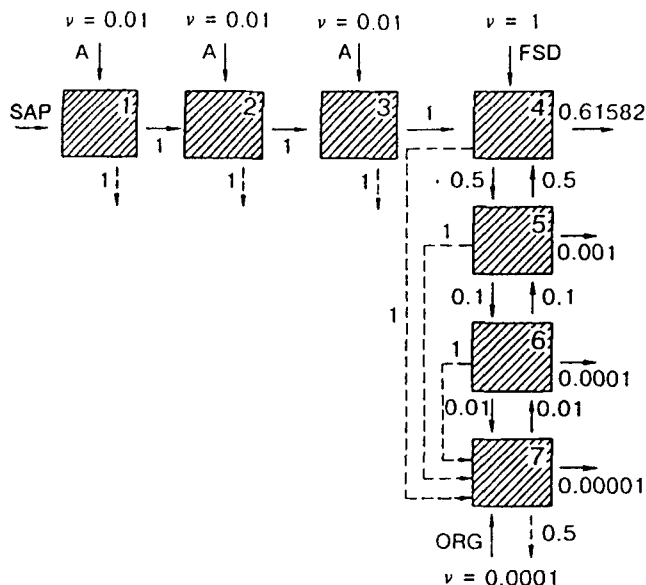
Fig. 5. The principal scheme for the seven-reservoir simulator of the dynamic megasystem "sewage of apatite production — Lake Imandra". The solid arrows are the first group of mobile phases (aqueous solution). A is the atmosphere flow which characterizes the degree to which systems are open to the atmosphere, FSD — flow of seasonal drainage, ORG — flow of the organic carbon, SAP — sewage of apatite production. Dashed arrows indicate flows of solid matter: in systems 1–3 — mineral particles precipitating into tailing repository as a result of chemical interaction of a sewage flow of apatite production with the atmosphere; in systems 4–7 — mineral suspension resulting from chemical interaction of flows and systems of precipitating into system 7. Digits at arrows are macrokinetic coefficients.

waters. A portion of the mixed waters of the fourth reservoir enters the environment. Reservoir 6 contains the near-bottom waters. Reservoir 7 is the reduced layer of the bottom sediments with the pore waters.

Reservoirs 5, 6, and 7 are connected with one another and with the surface waters through the exchange flows. The flow of a mineral suspension, which forms by chemical interaction of the flows and aqueous solutions in reservoirs 4–7, goes through reservoirs 5–7 and settles onto the bottom. Organic material in the form of solid carbon enters from the environment into reservoir 7. In this case, the "environment" should be conventionally taken as a controlling factor. In such a manner, the "organic material — water" interaction can be modeled. The lake waters have a run-off aside from the surface one; that is, reservoirs 5–7 have a small flow of the aqueous phase into the environment. Therefore, it is supposed that a portion (preassigned or known from the hydrochemical balance) of internal, near-bottom, and bottom waters can leave the water body through the Niva River (the only river flowing from Lake Imandra). Besides, it can leave the water body through the filtration into enclosing rocks, into ground and subterranean waters, etc.

Let us outline the input data for the simulator. We proceed from the assumption that the chief interaction of the sewage with Lake Imandra occurs in the surface waters (reservoir 4). The volume of the water body is 10.9 km^3 [26]. The volume of reservoir 4 is 1/10 of the water body plus 1/10 of the seasonal drainage system. The yearly volume of the sewage of AP was assessed at 80,000,000 m^3 from data for 1992–94. Let us normalize the volume of the yearly sewage of AP and the volume of reservoir 4 so that reservoir 4 would have 1 kg of pure water, ignoring H$_2$O in the dependent components of the aqueous solution. One kilogram of water is equal to 55.51 mole H$_2$O. Such normalization is convenient, because the volumetric mass of water is brought to the "molar" equivalent. When the volume of mixture (reservoir 4) is 1/10 of the volume of the lake and is normalized to 55.51 mole H$_2$O as a solvent, the yearly sewage of AP will be equal to 4.0741 mole H$_2$O plus 30.5557 mole H$_2$O of the seasonal run-off. The last number has been calculated from the data in Table 1.2 in [26].

Let us assume that the yearly inflow of the sewage and seasonal drainage-system waters into reservoir 4 and the yearly run-off from reservoir 4 into the environment provide the mass of the system (reservoir 4) to be constant with some possible fluctuations. For ease of the model, we ignore the water exchange involved

with the atmospheric precipitation onto the lake surface, evaporation, and sewage of plants. The overall water balance is considered to be controlled by the sewage of AP and by the flow of seasonal drainage system. The extension of the model of Lake Imandra on the basis of interrelated geochemical and technological flows, which are combined into a single geotechnological megasystem, should present no problem. Formation and study of such megasystems must be the subject of a special research, which, as we hope, will be performed within the coming 2–3 years.

In order to bring the simulator closer to real conditions, we have made an effort to take into account all basic dependent components which may exist in flows and systems of the dynamic megasystem of Lake Imandra at low temperatures (1–25 °C), pressures (1–5 bars), and a wide range of possible values of pH (from 1 to 12) and Eh (from 1.2 to –0.8). The list of the dependent components of the aqueous solution was made in such a way that it represents the real composition of Lake Imandra and of the sewage of AP. The total number of the dependent components of the aqueous solution is 91, including H_2O as a dependent component (a solvent). The volatile constituents are 12 dependent components. The solid phases are minerals which may potentially exist in equilibrium, such as oxides, composite oxides, hydroxides, various silicates, "cement" minerals, sulfides, sulfates, carbonates, apatites, fluorite, alunite, solid carbon (graphite), and sulfur. Altogether there are 88 dependent components, including amorphous, disordered, and hydrated phases.

Thus, the input list of the basic multisystem consists of 191 individual species. There are 18 independent components in systems 1–3: $Al - Ar - C - Ca - Cl - F - Fe - K - Mg - N - Na - Ne - P - S - Si - H - O - e$, where e is an electron. In systems 4–7, there are two additional independent components — Mn and Sr.

The thermodynamic properties were taken from three sources:

1) the thermodynamic properties of all components of the aqueous solution, including H_2O, and of a portion of solid phases and the parameters of the HKF modified equation of state [27–29] were taken from the program complex SUPCRT92 with the thermodynamic database SPRONS92.DAT [30];

2) the thermodynamic characteristics of the majority of solid phases were taken from the Robie and Hemingway's reference book [31];

3) the thermodynamic properties of gases were taken from the RPS base [32]. The individual coefficients of ion activity were calculated using the modified Debye – Huckel equation [27]. The activity coefficients of neutral species of the aqueous solution, including H_2O, were taken to be equal to unity. The fugacity coefficients and molar volumes of gases were calculated using the Lee-Kesler three-parametric equation of state [33]. The critical parameters of gases were taken from the RPS base. The equations and procedures for calculation of the coefficients of activity and of fugacity were built into *Selektor-C* in the form of program modules [24]. The gas phase is considered an ideal mixture of real gases.

The input vectors of the molar quantities of independent components for the tailings of apatite production were calculated using Dudkin's data [34] and were reduced to 100 g of technological slime. The sewage of AP was calculated using the summary in Ref. [25]; the run-off of Lake Imandra and the flow of seasonal drainage system in the monitoring area of the lake were estimated according to [26].

The dynamic model was realized according to the second algorithm. One cycle is one year. Two groups of mobile phases were separated. The first group is the aqueous solution in reservoirs 1–7. The second group is the mineral suspension formed by a chemical interaction in systems 1–7.

The ingress of the atmosphere in systems 1–3, of the flow of seasonal drainage system in system 4, and of solid carbon in system 7 is controlled by quantity which is the degree to which the process runs. Technically, the way to do this is as follows. The gross formulas for 30.5557 mole H_2O as a solvent with the corresponding number of moles of dissolved species in system 4 (the flow of seasonal drainage system), for 100 kg of the air expressed in molar quantities of elements (systems 1–3) and 1 mole of solid carbon in system 7 should be multiplied by a corresponding degree to which the process runs. In each time cycle, the ingress of mineral species, atmosphere, and solid carbon into the megasystem systems is controlled by the quantity

$$x_1^0 \cdot \nu_{iq}, \ i = 1, 2, 3; \ q \in Q, \tag{4}$$

where x_1^0 is the gross formula for 100 kg of air expressed in molar quantities of elements (sys- tems 1–3); x_2^0 is the gross formula for 30.5557 mole H_2O as a solvent with the corresponding number of moles of dissolved species in system 4 (the flow of the seasonal drainage system); x_3^0 is 1 mole of solid carbon (graphite). It must be emphasized that each system may have its own ν_{iq}, i.e., the degrees to which the process runs in systems may vary. The same species may by more abundant in one system than in another. The value of ν_{iq} is determined by the input conditions, which can be corrected during the preliminary experimental runs of the simulator.

The temperature and pressure in the reservoirs are as follows: reservoirs 1–4 — 10 °C, 1 bar; reservoir 5 — 10 °C, 2.5 bars; reservoir 6 — 8 °C, 4 bars; reservoir 7 — 4 °C, 5 bars. The mass of reservoirs 5–7 are expressed by the number of moles of H_2O (as a dependent component of the solvent) equal to 55.51. The total volume of water of all four lake systems is about 4/10 of the volume of Lake Imandra.

Let us estimate how many cycles (years) will be required for the dynamic megasystem "sewage of apatite plant — Lake Imandra" to reach a stationary state if the following data are given at the input of the simulator:

1) the run-off of apatite plant is 80 million m^3/year;

2) the flow of the seasonal drainage system is 600 million m^3/year;

3) the macrokinetic coefficients of flows are constant, and their values are given in Fig. 5;

4) the surface waters, being the reservoir of mixing, make up 1/10 of the volume of Lake Imandra. The surface, deep, near-bottom, and bottom waters make up 4/10 of the water mass of Lake Imandra.

The numerical modeling with the program complex *Selektor-C* has shown that the stationary state of the dynamic megasystem is reached in 12 years.

For simulation, the most important tool in studying the physicochemical processes is determination of the sensitivity of results to the varying parameters of the input flows. Analysis of sensitivity implies that these parameters are varied within some range, and then one can determine their influence on the desired parameters of the model. Almost in any simulator, many of the variables may be selected on the basis of rough interval data obtained by experts and/or from the preliminary runs of the simulator, which are checked and corrected against the limited bulk of input information.

Figure 6 demonstrates three variants of the established stationary values of pH (solid line) and of Eh (dotted line) in the dynamic megasystem "**sewage of apatite plant — Lake Imandra**".

In the first variant (line 1 in Fig. 6), the sewage volume is 80 million m^3/year, and the initial value of pH is 8.6 (before the sewage comes to the first reservoir). This variant simulates the current state of the lake. The obtained values of pH and Eh are close to the average profile of these parameters of the aqueous solution at the monitoring station of Lake Imandra over August — October [26].

This recent minimal volume of pollution is due to the economic decline in Russia and decrease in apatite production. In the second variant (line 2 in Fig. 6), the sewage volume is three times greater — 240 million m^3/year. This was the maximal load on Lake Imandra over 1976–78. The initial pH is 8.6. At last, in the third catastrophic variant (line 3 in Fig. 6), the sewage volume is the same as in the second variant, i.e., 240 million m^3/year. But the initial pH is 9.75, which theoretically may correspond to an emergency run-off of the sewage of apatite production.

In general, the volume of apatite production sewage of 80 million m^3/year has no profound impact on the quality of the Lake Imandra waters. However, the scales of pollution increase with sewage and reach a critical limit when the sewage volume is 240 million m^3/year. The value of pH throughout the water body increases by 0.5. The emergency sewage of high alkalinity (up to pH = 9.75) is especially dangerous. The redox potential changes considerably less.

The results obtained are rather conventional. Nevertheless, they may point out the direction for further investigation into the formation of a more detailed simulator of the thermodynamic megasystem of Lake Imandra.

Example 2. *Redistribution of material in the megasystem* $Al_2O_3 - SiO_2 - H_2O$ *under nonisothermal conditions at 300–440 °C and 3 kbar.*

In only a few of known experimental studies on the redistribution of material in thermodynamically incompatible assemblages of mineral systems, chemical conversions and spatial mass transport are treated with a quantitative control over input and output physicochemical parameters of megasystems [35–36]. Recently, Vidal [1] has published very interesting results of experiments by the "tube-in-tube" method on mineral-formation processes in the system $Na_2O - Al_2O_3 - SiO_2 - H_2O$ under nonisothermal conditions at a fixed pressure of 3 kbar. A small gold capsule (2 cm long, 2.6 mm in diameter), whose walls were drilled to enable exchanges of solution but not of solids, was filled with a starting mixture of minerals and placed into a gold tube (15 cm long, 4 mm in diameter) filled with bidistilled water, which was then welded. Between two ends of the tube, a stationary gradient of temperature was produced, and a constant pressure, set externally, was maintained. The duration of the experiments was varied within 63–152 days. The horizontal position of the tube provided a combined mechanism of spatial mass transport — thermal diffusion combined with convection.

A mixture of paragonite, pyrophyllite, and quartz in different proportions was taken as a starting material. In the long run, along the capsule a column was formed with zonally located parageneses of quartz, beidellite $Na_{0.37}Al_{2.33}Si_{3.67}O_{10}(OH)_2$, rectorite $Na_{0.67}Al_{2.67}Si_{3.33}O_{10}(OH)_2$, kaolinite, and amorphous products, which are due to the kinetic retardation of chemical conversions and the effect of metastable "supersolubility" of
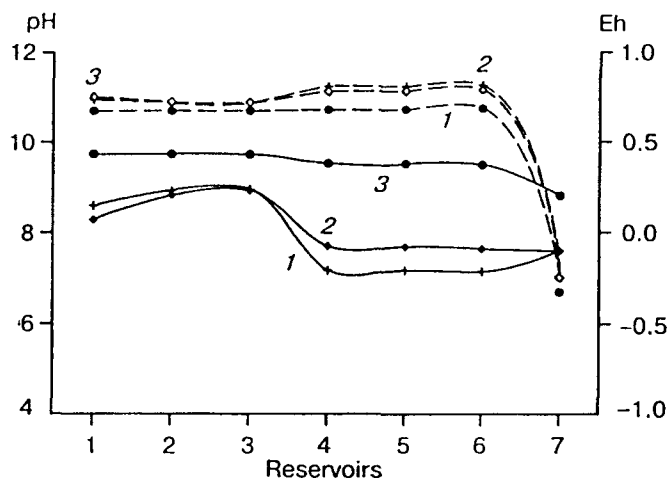
Fig. 6. Stationary values of pH and Eh for seven reservoirs of the simulator of the dynamic megasystem "sewage of apatite production — Lake Imandra". Sewage of apatite production: 1 — 80 million m^3/year, initial value pH = 8.6, 2 — 240 million m^3/year, initial value pH = 8.6, 3 — 240 million m^3/year, initial value of pH = 9.75. pH is shown by a solid line, Eh — by a dashed line.

silica under hydrothermal conditions [37, 38]. In general, the distribution of minerals along the nonisothermal column characterizes some intermediate state between the initial nonequilibrium conditions and conditions close to the stationary nonequilibrium state at the end of the experiment [1]. Despite the incompleteness of the process, the tendency toward redistribution of material in the nonisothermal columns of the megasystem $Na_2O-Al_2O_3-SiO_2-H_2O$ has been established quite definitely. In the "cold" ends of the columns, kaolinite, beidellite, rectorite, and quartz accumulate. In the "hot" ends, paragonite, pyrophyllite, and diaspore gather.

We have developed a physicochemical model of the dynamic megasystem which simulates the simplest Vidal experiment [1]. The starting mineral is pyrophyllite, i.e., the nonisothermal redistribution of material is considered in the context of the system $Al_2O_3-SiO_2-H_2O$ system. The list of the phases and components of the megasystem potentially possible in equilibrium and the input thermodynamic data are presented in Tables 1 and 2. The list involves the following dependent components of the aqueous solution and minerals: quartz, kaolinite, pyrophyllite, and diaspore. In the present example, the list of phases potentially possible in equilibrium in the system $Al_2O_3-SiO_2-H_2O$ does not involve metastable species, such as amorphous silica. Hence, we have considered the redistribution process in which only mineral phases at thermodynamic equilibrium are generated. The individual activity coefficients of ions were calculated by a modified Debye-Hückel equation [27]. The activity coefficients for the neutral components of the aqueous solution, including H_2O, were taken to be equal to unity. The modeling was performed using the program complex *Selektor-C* of 1997.

The dynamic megasystem $Al_2O_3-SiO_2-H_2O$, which simulates the nonisothermal redistribution of material, consists of five systems with temperatures of 440, 400, 360, 330, and 300 °C. The pressure in all systems is the same and equals 3 kbar. By convention, the numbering of the systems follows the decreasing temperature: system 1 is at 440 °C, system 2 at 400 °C, etc. Material is transported between the systems by a group of mobile phases — the aqueous solution, in accordance with the scheme called "the sequence with feedbacks" (see Fig. 4, II). The macrokinetic coefficients of all flows have been assumed to be equal to 0.5.

We have treated six variants of the simulator. They vary in the initial proportion of the input composition "pyrophyllite — water" and in algorithms of redistribution (Table 3).

The initial conditions for simulation by the first and second algorithms were specified so that the zero time, the equilibrium in all five systems could be calculated when the pyrophyllite—water proportion was the same. That is, the composition of all five systems of the megasystem was identical at the zero time.

Without regard for the particular algorithm by which the redistribution of material was performed and for the initial pyrophyllite/water ratio, the distribution of minerals in the nonisothermal column reaches a stationary regime in 50 units of conventional time (by the first algorithm) or in 100 cycles (by the second

Table 1

Standard Thermodynamic Properties of the Dependent Components of the Aqueous Solution of the Megasystem $Al_2O_3 - SiO_2 - H_2O$ at 25 °C, 1 bar and Parameters of the HKF Modified Equation of State [27–27]

Dependent components	$\Delta G^{\bullet}_{f298}$, cal / mole	$\Delta H^{\bullet}_{f298}$, cal / mole	$S^{\bullet}_{298}$, cal / K·mole	$a_1\,10$, cal·K / bar·mole	$a_2\,10^{-2}$, cal / mole	a_3, cal·K / bar·mole	$a_4\,10^{-4}$, cal·K / mole	c_1, cal / K·mole	$c_2\,10^{-4}$, cal·K / mole	$\omega\,10^{-5}$, cal / mole	Ref.
Al^{3+}	−116 543	−128 681	−80.80	−3.3404	−17.110	14.9917	−2.0716	10.70	−8.06	2.8711	[39]
$Al(OH)^{2+}$	−166 468	−185 096	−46.82	0.2580	−9.6965	9.6000	−2.5767	38.00	−2.60	1.7666	[39]
$Al(OH)_2^{+}$	−215 465	−241 825	−17.00	3.5000	−2.4600	6.3000	−2.8100	46.70	−1.50	0.8089	[39]
$HAlO_2^0$	−207 500	−230 730	−6.50	3.6808	1.2058	5.2761	−2.8288	39.00	2.50	0.3000	[39]
AlO_2^-	−198 700	−222 079	−7.00	3.7280	3.9800	−1.517	−2.9435	19.10	−6.20	1.7595	[39]
SiO_2^0	−199 190	−209 775	18.00	1.90	1.70	20.00	−2.70	29.10	−51.20	0.1291	[30]
O_2^0	3954	−2900	26.09	5.79	6.35	3.25	−3.04	35.35	8.37	−0.394	[30]
H_2^0	4236	−1000	13.80	5.14	4.78	3.87	−2.98	27.63	5.09	−0.209	[30]
H^+	0	0	0	0	0	0	0	0	0	0	[30]
OH	−37595	−54977	−2.56	1.2527	0.0738	1.8423	−2.7821	4.15	−10.34	1.7246	[30]

Table 2

Standard Thermodynamic Properties of Minerals of the Megasystem $Al_2O_3 - SiO_2 - H_2O$, Coefficients of Heat-Capacity Equations and Equation for Temperature and Pressure Dependence of Molar Volume of Minerals (25 °C, 1 bar)

Minerals	ΔG^0_{f298}, cal / mole	ΔH^0_{f298}, cal / mole	S^0_{298}, cal / K·mole	V^0_{298}, cm³ / mole	Coefficients of equation of heat capacity				Coefficients of equation $V = f(T, P)$			
					a	$c\,10^{-5}$	$e\,10^{-7}$	$g\,10^{-1}$	$V_1\,10^6$	$V_2\,10^{12}$	$V_3\,10^6$	$V_4\,10^{10}$
Quartz SiO2	−204 658	−217 662	9.909	22.69	19.2	−8.48	11.75	−5.74	−2.434	10.137	23.895	—
Pyrophyllite Al2Si4O10(OH)2	−125 811	−1348 179	57.217	127.60	159.16	−11.90	15.82	−140.95	−1.354	—	12.637	381.66
Diaspore AlO(OH)	−22 078	−238 857	8.439	17.76	34.23	−0.7722	1.54	−36.82	−0.599	—	29.718	—
Kaolinite Al2Si2O10(OH)4	−908 167	−984 782	48.684	99.52	125.05	−5.36	2.21	−105.8	−1.2	—	32.0	—

Note. The table was compiled by Berman's data [40]. The T-dependence of Cp is approximated by the heat-capacity equation of the type: $Cp = a + cT^{-2} + eT^{-3} + gT^{-0.5}$. The molar volumes are calculated by Berman's equation [40]: $V = V_0[1 + V_1(P - 1) + V_2(P - 1)^2 + V_3(T - 298.15) + V_4(T - 298.15)^2]$, where V is the volume as a function of T, K, and P, bars, $V_0 = V^0_{298}$. To transform $V \frac{cm^3}{mole}$ to $V \frac{cal}{mole \cdot bar}$, $V \frac{cm^3}{mole}$ should be multiplied by $0.0239 \frac{cal}{cm^3 \cdot bar}$.

algorithm). For all six variants, the mineral assemblages are the same, but the quantitative proportions of minerals in the systems depend upon their initial composition (Table 3). The greater the mass of water, the more diaspore forms in the "hot" end of the column. Generally, our calculations, as in Vidal's experiment [1], have shown that the kaolinite + quartz association forms in the "cold" end of the column, and pyrophyllite + diaspore in the "hot" end. The quantitative proportions of kaolinite and quartz in the fifth system change in accordance with the initial contents of pyrophyllite and H_2O. The less water, the more kaolinite − 68.23 wt.% for the first variant and 56.3 wt.% for the fifth one. Inversely, quartz increases with H_2O in the input composition: from 31.77 wt.% in the first variant to 42.29 wt.% in the sixth one. In the "hottest" fifth system, the input proportions of pyrophyllite and water have a more considerable effect on the mineral composition at the final stationary state: 99.99 wt.% pyrophyllite and 0.01 wt.% diaspore in the first variant, 1211 wt.% pyrophyllite and 87.89 wt.% diaspore in the sixth one. In the second, third, and fourth systems, pyrophyllite

Table 3

Stationary Composition of Five Systems of the Megasystem Al_2O_3 - SiO_2 - H_2O, Calculated at Different Initial Proportions of Pyrophyllite and H_2O by the First and Second Algorithms

Variant	Phase	System*					Initial ratio Prl—H_2O	Algorithm	Process duration	
		1	2	3	4	5			$n(R)$	$n(T)$
		440 °C	400 °C	360 °C	330 °C	300 °C				
1	Prl	99.99	100	100	100	—				
	Dsp	0.01	—	—	—	—				
	Kln	—	—	—	—	68.23	1 : 0.3427	2		100
	Qtz	—	—	—	—	31.77				
	H_2O	0.05	0.05	0.05	0.05	0.04				
2	Prl	99.00	99.81	99.49	99.87	—				
	Dsp	1.00	—	—	—	—				
	Kln	—	—	—	—	67.7	1 : 10	2		100
	Qtz	—	0.19	0.51	0.13	32.3				
	H_2O	33.1	32.6	32.52	32.59	31.38				
3	Prl	93.73	98.95	99.49	99.87	—				
	Dsp	6.27	—	—	—	—				
	Kln	—	—	—	—	65.32	1 : 55.51	2		100
	Qtz	—	1.05	0.51	0.13	32.3				
	H_2O	75.72	73.24	72.87	73.28	71.57				
4	Prl	96.62	99.78	99.15	99.8	—				
	Dsp	3.38	—	—	—	—				
	Kln	—	—	—	—	67.02	1 : 55.51	1	50	
	Qtz	—	0.22	0.85	0.2	32.98				
	H_2O	74.77	73.45	73.31	73.43	72.14				
5	Prl	21.72	95.72	88.37	96.89	—				
	Dsp	78.28	—	—	—	—				
	Kln	—	—	—	—	56.3	1 : 555.1	2		50
	Qtz	—	4.28	11.63	3.11	43.7				
	H_2O	98.62	96.38	96.08	96.41	95.62				
6	Prl	12.11	97.91	92.06	98.11	—				
	Dsp	87.89	—	—	—	—				
	Kln	—	—	—	—	57.71	1 : 555.1	1	50	
	Qtz	—	2.09	7.94	1.89	42.29				
	H_2O	98.72	96.46	96.23	96.46	95.72				

Note. Pr — pyrophyllite, Dsp — diaspore, Kln — kaolinite, Qzt — quartz; $n(R)$ is the number of units of time in the solution; $n(T)$ is the number of cycles.

*The content of minerals in percentage of the total mass all solid phases of the system. The mass of H_2O given relative to the mass of the entire system, including solid phases.

with a small admixture of quartz is a predominant product. In all variants, pH is kept constant: system 1 — pH = 4.6; system 2 — pH = 4.66; system 3 — pH = 4.72; system 4 — pH = 4.78; system 5 — pH = 4.85.

The stationary thermal gradient results in the stationary nonequilibrium distribution of material in systems of a megasystem. It is interesting to trace the manner in which the additional external source of energy, which maintains the constant temperature difference along the column, influences the change in the total Gibbs energy of the megasystem in its transition to a stationary state. This change is illustrated by Fig. 7. The Gibbs energy of the megasystems, G_Σ, (variant 3) increases and reaches a stationary state. Unlike the equilibrium thermodynamic models of systems in which the Gibbs energy decreases as the equilibrium is approached, G_Σ of nonequilibrium stationary megasystems can increase relative to its starting value owing to external factors. In our case, this occurs owing to the stationary thermal gradient in the conjugate assemblage of systems.
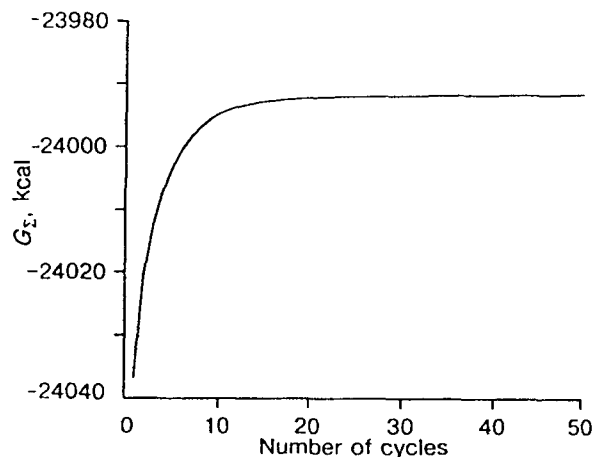
Fig. 7. Change in the total Gibbs internal energy, (G_Σ, cal) of the dynamic megasystem $Al_2O_3 - SiO_2 - H_2O$ by the second algorithm, when the initial proportion of pyrophyllite and water is 1 : 55,51 (in moles).

CONCLUSIONS

In the approach proposed, the structure of the simulator of a dynamic megasystem is formed according to the principle of combination of basic constituents of a unified set and directive parameters. The user himself can form diverse variants of aggregation of systems and flows connecting them into megasystems.

The physicochemical evolution of a megasystem can be computed by two algorithms. In the first, two operations are performed in a unit of time: the calculation of equilibrium for all systems simultaneously and then transporting of material in flows in accordance with the specified matrix of the macrokinetic coefficients of transport. In the second algorithm, the evolution in time and space proceeds cycle by cycle. In each cycle, calculation of equilibrium in systems and transporting of material are performed in succession from one system to another in accordance with their numbering and the matrix of macrokinetic coefficients. The number of the units of time in each cycle is equal to the number of systems in a megasystem. One cycle of the second algorithm ends with the system which has the greatest number.

The most important feature of both algorithms is that the flows can be separated according to groups of mobile phases. The flows of aqueous solution, gas phase, and solid compounds in the form of suspension, dust, organic material, etc. can leave (or enter) a system independently of one another. Each group of mobile phases has a corresponding matrix of macrokinetic coefficients, which can be recalculated, once each unit of time ends, by a special built-in algorithmic operator.

The scheme proposed for simulation of dynamic megasystems has been realized in the form of a special module "Reservoir Dynamics" in the program complex *Selektor-C* of 1997. It can be used for solving scientific problems, for engineering and education.

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