

# Thermodynamic Analysis of Endogeneous Fluid Systems: The Paradigm Shift of the 21st Century

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**Abstract**—At the end of the 20th century, the methods of equilibrium thermodynamics in studying natural fluid systems were replaced by synergetics, a more general paradigm. The main difference of the synergetic approach is its interdisciplinary character, and one of its achievements is understanding the role of governing parameters in particular fluid systems and introducing the concept of endogeneous fluid systems as polystationary systems.

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The role of fluids in endogeneous processes is widely-known; therefore, the estimate of the fluid conditions of any process that forms rocks or ores is one of the fundamental problems of the Earth sciences. The estimate of the fluid conditions includes information on the composition and physicochemical parameters of a particular fluid that cause this process to occur. In this case, it is especially important to know the initial composition of the fluid, since this is a starting parameter for all subsequent physicochemical calculations, experiments, and computer modeling. The common property of all fluidized systems of the Earth is that they are nonlinear, mostly nonequilibrium open stationary systems.

In the 1930s the well understood experimental studies at high  $T$  and  $P$  were brought to the theory of studying natural high-temperature fluid systems, and closed (isolated) fluid mineral systems became the objects of study. The principles and methods of equilibrium chemical thermodynamics were used as the main mechanism of these systems [1, 2]; that is, the complex natural systems were divided into separate parts that were studied by the methods of equilibrium chemical thermodynamics in sufficient detail.

The principles of equilibrium thermodynamics, when the three main classes of the thermodynamic systems were considered, such as equilibrium, local-equilibrium (stationary), and non-equilibrium, dominated in the detailed studies [3].

The detailed study of natural objects showed that they mainly represented nonequilibrium systems, whose separate parts were studied in terms of nonequilibrium chemical thermodynamics [4]. The works by D.S. Korzhinskii [2] stand out among the works in

which attempts were made to carry out physicochemical analysis of natural local-equilibrium (stationary) systems. Fetishization of a certain state led researchers astray from detailed analysis of natural fluid systems that were nonequilibrium in general; although as early as 1976 it was emphasized that "... at the same time the systems can be equilibrium with respect to certain parameters and nonequilibrium by other parameters" [5].

The end of the 20th century and especially the beginning of the 21st century were marked by the inflow of absolutely new scientific and factual materials, which made it possible to cross principally new frontiers in ore-formation problems, i.e., the equilibrium paradigms, which were based on classical chemical thermodynamics, were replaced by synergetics, a more general paradigm, that fast won the leading positions in the early 1980s.

This happened first of all because synergetics had a disciplinary character. The author of synergetics H. Haken [6] wrote, "Synergetics studies systems that consist of many subsystems of the most different nature... Synergetics shows how the interaction between subsystems leads to the appearance of the spatial, time, or spatial–time structure in the macroscopic systems." Is this not a geological formulation of the problem of studying geological processes and their derivatives? The leading scientist and specialist Yu.A. Danilov [7] emphasized several features of the synergetic approach:

—the interdisciplinary (supradisciplinary) scientific area;

—the study systems that consist of a great many parts, components, or subsystems that interact with each other; the word "synergetics" means a "combined action," which emphasizes the consistent operation of the parts that is reflected in the behavior of the system as a whole;

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—the science of self-organization; the consideration is often carried out at a level where the system processes and structures are seen as self-occurring due to self-organization without a leading and guiding “hand” from outside;

—the identification a few order parameters that influence the values that characterize the state of the system and that, in turn, can influence the order parameters;

—the evolution is a series of alternating structures: the structures lose stability, disintegrate, and are replaced by new ones under certain conditions (the values of the order parameters).

We turn our attention to the concept of “order parameters” or a “mode.” Since in synergetics we deal with an open system that exchanges matter, energy, and information with the medium, then for each state of such open systems we identify the main parameters that determine the state of such open systems. But due to the fact that such systems can change from one state to another, each case has a few order parameters that influence the values that characterize the state of the system and that, in turn, can influence the order parameters.

As an example, we consider the ore-bearing fluid (for instance, hydrothermal) system. A temperature is definitely the first order parameter, since high-, medium-, and low-temperature systems are identified purely empirically. It is natural that as the temperature decreases, such systems lose their energy potential, and their governing parameters change when, as part of a new system, other governing parameters start playing a major role, for example, the oxygen conditions change to the sulfur conditions, and consequently the oxide forms change to sulfide forms. We can present plenty of such examples. For each particular case, we should identify the main governing parameters (or modes) that can consecutively replace each other, which will influence the composition of mineral clusters that are deposited from a particular fluid.

Since we are focusing on ore-formation processes, we consider several aspects that occur in the high-temperature fluid systems. The high-temperature chemical technology of separating complex multicomponent mixtures saw a quality jump between the 20th and 21st centuries. The key point of the new approach is that, in these systems, thermodynamically isolated reactions were selected earlier; where the state of components depended on the pairs, which were often selected arbitrarily, some of them were components of the initial fluid, and others were a part of reaction products. This means that the chemically active pairs and the products of their interaction were selected arbitrarily from the left and right sides of such a linear equation, respectively. The reactions under consideration were autonomous and mostly did not depend on the rest of the fluid components. In the multicomponent systems, however, the state of the latter is, in gen-

eral, determined by the entire set of system components. Therefore, a principally new approach was developed in the chemical technology of multicomponent fluid systems, which first of all include oil, based on synergetic analysis of the behavior of multicomponent systems and recent computer technologies [8–10]. The new method is based on the approach to such systems from the perspective of a well-developed theory of stationary systems. All natural systems, and first of all, fluid ore-bearing systems, exist in a stationary state for a certain time, which is characterized by many components in different physical forms. Ore-bearing fluid hydrothermal systems conform to them the most. Since these systems are characterized by a transition from one stationary state to another quality state, these systems are considered as polystationary against the background of a change in the governing parameters, and the method itself determines the characteristics, and often the location of such polystationary systems. The natural fluid systems pass through a cascade of stationary transitions from the initial to the final ones.

Therefore, the methods of polystationarity are widely used not only in chemical technology, but also to analyze any multicomponent systems based on the required thermodynamic data, when a megasystem is considered to be a single stationary system consisting of many parts, components, or subsystems that interact with each other.

It was emphasized in [5] that “it is especially important that at the same time the systems can be equilibrium with respect to certain parameters and nonequilibrium by other parameters.”

The sign of equality between the locally equilibrium and stationary systems was first placed by K.P. Gurov [4].

Detailed mineralogical studies of the microstructures in minerals from ore hydrothermal deposits point to the oscillatory deposition of minerals from ore-bearing fluids that was earlier recorded by A.G. Betekhtin, O.D. Levitskii, et al., in [1]. In particular, they presented the examples of zonal deposition of ore minerals within one sample, when oxides and sulfides, for example, cassiterite  $\text{SnO}_2$  and stannite  $\text{Cu}_2\text{FeSnS}$ , were deposited complementarily.

Without giving a definition for this phenomenon, polystationarity phenomena are recorded many times during detailed study of rare-metal shallow deposits.

As an example we take the rare-metal W–Bi–Mo–Be Kara-Oba deposit in Central Kazakhstan, which is located in the apical segment of the shallow leikogranites. The deposit has been studied quite well and is exposed by mine workings. The mineralization is localized in quartz veins. The earliest ones are flat quartz–molybdenite veins with no other ore minerals, where molybdenite clusters reach 20–30 cm. These quartz–molybdenite veins are intersected by extended (over 1 km) quartz–tungsten veins (without molybdenite) with high contents of bismuthine and native

Bi. A special place is occupied by quartz–cassiterite veins, in which tungsten is found very infrequently. In this case, we have a polystationarity process in which the mineral fluid systems were formed with different composition from the same magma chamber due to the process of polystationarity.

The properties of geological high-energy open nonlinear nonequilibrium properties depend on their state. The violation of the superposition principle is the most common feature in such systems. We know that the superposition principle consists in the fact that “additivity of reasons leads to additivity of consequences” [11]. The analysis of the geological fluid nonlinear systems that are far from the state of equilibrium unambiguously points to the fact that the superposition principle is not retained in them. The inappropriate reaction between the impact force and the response in the system to this impact is the most typical feature of nonlinear systems. Nondetermination of the development is one of the most important properties of these systems, since their multivariance depends on many factors, including one in which the system can develop simultaneously in several alternative ways behind the bifurcation point. The violation of the superposition principle leads us to the sphere of uncertainty, when it is hard to predict which way or several alternative ways the system will go. Under these conditions, even insignificant fluctuations can “detonate” large-scale phenomena. First of all, this concerns finely disperse (down to the nanoscale) supercritical fluidized systems that exist at high  $T$  and  $P$ .

Since all fluidized geological processes are irreversible, they are considerably prone to structurization, i.e., the creation of new structural ensembles. It is the fluidized geological media that strike us with the variety of structuring forms upon irreversible development of natural processes. The synergetic analysis makes it possible to reveal the “governing parameters” that

caused the appearance and the existence of particular structures.

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