

DISTINCTIVE FEATURES OF THERMODYNAMIC ANALYSIS IN SHS INVESTIGATIONS

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From the viewpoint of thermodynamic analysis, SHS processes differ from the majority of other high-temperature processes of inorganic synthesis by the presence of substantial temperature and chemical inhomogeneities in the reaction medium, which causes intense heat and mass transfer to proceed between separate regions of the system. Consideration of the distinctive features of the dynamics of these processes in thermodynamic analysis makes it possible to considerably increase the effectiveness of the latter in investigations of this class of systems.

Introduction. Self-propagating high-temperature synthesis (SHS) of inorganic compounds is a complex macrokinetic process that depends on many diverse parameters [1]. Since experimental and, especially, theoretical study of the SHS mechanism involves difficulties, the method of thermodynamic analysis has found wide application in SHS investigations because it permits a rapid quantitative study of the SHS process [2-4].

A distinctive feature of the thermodynamic analysis of SHS processes lies in the fact that the issue is always systems that are quite inhomogeneous in chemical composition, in temperature, and often in aggregate state, which causes intense heat and mass transfer to proceed between separate parts of the system. Obviously, a study of the equilibrium state of such a system as a whole, conducted in investigations of many other high-temperature processes, is too simplified an approach to the solution of the problem in the present case.

Distinctive Features of the Formulation of the Problem of Thermodynamic Analysis of Complicated Technological Processes. Prior to thermodynamic analysis of such a complicated process as SHS, it is necessary to qualitatively study a system in order to analyze the conditions of SHS implementation and the distinctive features of heat and mass transfer processes and to evaluate their characteristic times. As a result of such an analysis, the system is subdivided into a number of subsystems in each of which during a time comparable to the characteristic time of synthesis one may expect the establishment of some quasiequilibrium state. By the equilibrium state is meant a state of the system where a function of its thermodynamic potential is at a minimum and restrictions are imposed in the form of the laws of mass conservation of chemical elements. An adiabatic temperature is found from the solution of the equation of energy conservation in which the expression for the initial enthalpy of the system is in the left-hand side of the equation, while the total enthalpy of the synthesis products enters the right-hand side. For each subsystem, its set of thermodynamic parameters (enthalpy, pressure or volume of gaseous products, temperature, etc.) is determined and their ranges are qualitatively evaluated. In so doing, it should be kept in mind that in real technological processes the notions of a thermodynamic parameter and a governing parameter fall far short of coinciding [5]. For instance, the pressure of an inert gas that may occupy the volume of an SHS reactor is recognized as a governing parameter of the process since it exerts an influence on the combustion temperature and thereby on the properties of the end product of synthesis, but it is not a thermodynamic parameter of the system investigated since it enters none of the equilibrium equations. The inert gas in the present case serves as a medium that prevents evaporation of the gaseous products of synthesis. It is obvious that the higher its pressure, the lower the diffusion rate of evaporating gas components is, and, consequently, a smaller volume will be occupied by the components during the characteristic time of the process. Since the partial pressures of the gaseous products at the prescribed temperature and qualitative composition of the condensed phase cannot exceed some value

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determined by the temperature, a decrease of the volume entails a decrease of the mass of the products formed. Since the evaporation proceeds with absorption of heat, the temperature of the process, as a result, will increase. From the above it follows that in this case some effective volume should be taken as a thermodynamic parameter of the system, which at the given mass transfer rate, determined by the pressure of the inert gas, may be occupied by the gaseous products of synthesis. Thus, the thermodynamic parameter of the system is related, in a certain way, with the concrete governing parameter of the process. This permits one to control the change in the thermodynamic parameters in synthesis and to achieve optimal conditions of the process.

The objective to be pursued in conducting the thermodynamic analysis of SHS is to reveal tendencies in the influence of any governing parameters of the process on the behavior of the latter and on the composition of the desired products rather than to obtain concrete quantitative information on the processes involved in the synthesis. Such an approach extends substantially the domains of applicability of thermodynamic analysis in investigating complicated processes thus allowing one to combine it with kinetic considerations of the phenomena that occur in the system under investigation, as well as to use qualitative estimates of some thermodynamic constants in calculations.

Classification of SHS Systems. It is a known fact that at present self-propagating high-temperature synthesis underlies many production processes:

synthesis of inorganic compounds from elements (oxides, carbides, nitrides, borides, silicides, sulfides, etc.);

SHS from oxides involving a reduction stage;

reduction of metals from compounds in a combustion process;

synthesis of composites of inorganic compounds;

application of coatings to the surfaces of articles by gas transport reactions in the combustion medium and other processes.

According to the distinctive features of thermodynamic simulation, all these processes may be grouped into four basic types. The first type pertains to the case where all the initial reagents of the synthesis are condensed substances and the share of gaseous products is small (synthesis of carbides, borides, and silicides in binary systems); in the second type, among the reagents there is a gas, but gaseous products are formed to a small extent (synthesis of oxides, nitrides, and hydrides from elements); synthesis of the third type produces a considerable amount of gaseous products (sulfides, selenides, and tellurides), but the combustion proceeds in a closed system, while in the fourth type, on the contrary, it proceeds in an open system (e.g., in air) with considerable gas release.

For the systems pertaining to the first type thermodynamic parameters characterizing the external conditions of the process are the internal energy of the system and the volume occupied by the gaseous products formed during synthesis. The value of this volume is either assumed to be equal to the reactor volume or is evaluated as the effective volume that may be filled with gaseous products during the characteristic time of the process as a result of diffusion processes. However, for complex multielement systems, where many different components enter the composition of the gaseous products, whose transport properties differ greatly, it is sometimes difficult to choose a single effective volume for all the components. In that case, the eigenvalues of free volumes may be introduced for some components. If the reactor volume is filled with an inert gas, some portion of the released gas must be consumed for its heating. Under the assumption of slight gas release, we may consider that the gas is heated only by heat conduction. Estimating the possible heat loss and taking it into account in solving the equation of energy conservation will allow one to obtain a more exact adiabatic temperature of the system.

The systems of the second type have, as thermodynamic parameters, the enthalpy and pressure of the gaseous component of the reaction, which at the same time serve as the governing parameters of the reaction and may easily be controlled in synthesis. The foregoing concerning the role of heat loss in systems of the first type is fully valid for systems of the second type. The only difference is that in the latter case we are concerned with heating of an excessive amount of the reacting gas.

For the systems of the third type, the internal energy and the reactor volume should be taken as the thermodynamic parameters because we may anticipate that due to a large amount of gaseous products the gases manage to fill the entire free volume during the characteristic time of the process. However, in adiabatic temperature

calculations we should remember that the heat loss due to heating of the gas filling the reactor plays a greater part, as compared to the first two cases, since now the heat transfer between hot gaseous products and the colder reactor gas contributes to the heat losses. Proceeding from the assumption that the gaseous products fill the entire reactor volume, we may assume that during the characteristic time of the process the entire mass of the reactor gas is heated up to a temperature equal to the adiabatic one. In this case, it is reasonable to take account of the heat losses by including the entire mass of the reactor gas in the composition of the reagents.

And lastly the fourth type consists of the most complicated, from the viewpoint of thermodynamic analysis, systems since no notion of the actual thermodynamic equilibrium exists for them. For such systems, as a method of thermodynamic analysis we may propose the following. An equilibrium state is calculated for the case when the pressure of the gaseous products is equal to the ambient pressure. If the calculation reveals the existence of a gas phase at such values of the thermodynamic parameters (pressure and enthalpy of the mixture), then we may consider that evaporation proceeds in a convective regime. This means that the pressure of the gaseous products in the evaporation process, with the quantity of condensed phases being equal to the maximum possible quantity of the coexisting condensed phases according to the Gibbs rule, exceeds the ambient pressure and as a result the formed gases upon expansion push out the surrounding gas from the surface of the condensed phase but virtually do not enter into heat transfer with it. This proceeds until one of the condensed phases is completely evaporated. Then since the set of condensed phases is already not complete, the pressure of the gaseous products becomes a function of the volume and further expansion of these gases entails a decrease of their total pressure. When this pressure becomes equal to the ambient one, it may be considered that the convective evaporation is completed and further evaporation is possible only when the gaseous products diffuse into the surrounding gas. It is obvious that this process is considerably slower than the convective evaporation and is accompanied by heat transfer with the surrounding gas. If the effective volume that may be filled with the gaseous products during the characteristic time of the process is much smaller than that volume occupied by the gases in convective evaporation and the heat losses are small as compared to the heat consumed by the system for the convective evaporation, then the calculation may be considered completed, otherwise we should repeat it according to the scheme described for systems of the first type. In this case, as the thermodynamic parameter we will use a free volume whose value exceeds the volume determined at the first stage of the calculations. If the calculation at constant pressure shows that the gas phase is absent, we may suppose that from the very beginning the evaporation is due to diffusion. Then the thermodynamic analysis of the system may be carried out in the same manner as for systems of the first type.

Evidently, the systems of the considered types pertain to extreme cases and we may come across variants not falling within those discussed above. However, a reasonable combination of the approaches discussed makes it possible to construct a thermodynamic model for practically any process.

Results of the Thermodynamic Analysis of SHS. The thermodynamic analysis of SHS may produce information on the following questions.

1. *Is it possible to conduct synthesis in the given system from the viewpoint of the amount of heat released in the course of the reaction?* With this in mind, the adiabatic temperature of combustion is calculated as a function of mixture composition, energy of the system, and process conditions. The maximum temperature of the process may obviously be realized when the initial reagents are taken in an optimum ratio and upon completion of synthesis no unreacted substances remain in the system, otherwise they will play the role of a thermal ballast and decrease the combustion temperature of the system. For simple binary systems, the optimum ratio is, as a rule, the stoichiometric ratio of the components participating in the synthesis. However, for complex multielement systems, containing many different gaseous products formed, the optimum composition is commonly one that contains an excessive amount of the more volatile components and depends on the synthesis conditions and its temperature.

The energy of the system is determined by the initial enthalpy of the mixture, which is equal to the total enthalpy of formation of the reaction components. If the system has a source of substantial heat loss not related to mass removal, e.g., heat conduction through the reactor walls or emission etc., and the heat loss may be evaluated, then it should be accounted for in enthalpy calculations of the system. Often with the aim of conducting the synthesis in an optimum regime one must artificially decrease the process temperature. This is usually achieved by diluting the mixture of initial reagents with some amount of the end product. In this case, since the enthalpy

of formation of the end product of the synthesis is less than the total enthalpy of formation of the reagents, the enthalpy of the system decreases, thus causing a fall in the adiabatic temperature. When one fails to ignite the mixture at the normal temperature of the reagents T_0 , the batch is to be preliminarily heated to T_1 . In so doing, the enthalpy of the system increases by the difference in enthalpy of the reagents at T_1 and T_0 , thus entailing a rise in the combustion temperature.

The synthesis conditions influence the combustion temperature in a different manner, depending on the type of the process investigated. For a solid-solid system the adiabatic temperature decreases as a consequence of an increase in the amount of the gas phase in the synthesis products, which may be suppressed by increasing either the inert gas pressure in the reactor [6] or the combustion rate. Both ways cause a decrease in the effective volume occupied by gaseous products during the characteristic time of the process and, consequently, a decrease in heat loss due to evaporation. For solid-gas systems, where the governing parameter of the process is the pressure of the gaseous reagent, an increase in the latter entails the suppression of dissociation of the synthesis products at high temperatures, which, in its turn, increases the adiabatic temperature.

2. *What is the range of the thermodynamic parameters of the system for which the purest end product is formed and synthesis proceeds in an optimum regime?* At this stage of the research the main parameter is, obviously, the mixture composition. For systems with a low content of the gas phase, the regions of coexistence of different condensed phases are determined in correspondence with the stoichiometry of their formation. In so doing, one should remember that for solid-solid systems the compositions of the initial and reacting mixtures may differ. This is attributed to the limited mobility of the reagents participating in the synthesis. The ratio of the reagents in the reaction zone is in many ways determined by the mechanism of their transport to a zone where one of the reagents is transferred to the surface of another. This process may be accomplished in different ways, e.g., through the gaseous phase, by way of simple diffusion or gas-transport reactions, by melting of one of the reagents followed by its spreading over the surface of another, by diffusion through an interface or a melt, etc. The necessity of considering this circumstance in analysis of such fast processes as SHS is dictated by the fact that the characteristic times of synthesis and mass transfer processes are close. For slower processes, such as furnace synthesis of the same compounds, this factor is of no significance since the characteristic time of the process considerably exceeds that of all mass transfer processes.

The spatial inhomogeneity of the initial mixture and time restrictions of the mass transfer processes are responsible for the presence of some amount of underreacted initial substances in the end product. Their amount depends on the synthesis conditions. If these conditions are such that a sufficient amount of the gaseous phase is formed during synthesis, which is the case for a high combustion temperature and a high volume of the system, then underreacted condensed substances pass into the gaseous phase since their thermodynamic potentials are higher than those of the same substances constituting the compounds. Thus, owing to the self-purification process in the vicinity of stoichiometric compositions of the initial mixture, regions where no impurities of underreacted substances are present in the composition of the condensed products are formed. The stoichiometric composition of the initial mixture may lie outside these regions [7].

The composition of the end product may also be affected by the process temperature. This influence may be manifested indirectly, through a change in the conditions of transport of the reagents to the reaction zone and, consequently, a change in the composition of the reacting mixture and the intensity of the self-purification process of the products as well as through direct action on the synthesis of the products. For solid-gas systems an increase in the process temperature that leads to melting of the reagents or the products of synthesis hinders filtration of the gas component into the reaction zone and causes a decrease in its content in the end product and nonuniform distribution of it throughout the reaction volume. Furthermore, when the process temperature increases, the products of synthesis can undergo physical transformations, for instance, thermal decomposition of crystalline compounds, peritectic melting, etc. Some portion of the products may pass into the composition of different melts and, as a result, at the cooling stage the desired crystalline phase may fail to form or the structure of the product formed may change sharply. Thus, thermodynamic analysis of the influence of the process temperature on the composition of the end product of synthesis allows determination of the optimum region of combustion temperatures

for which the necessary rate of mass transfer of the reagents to the reaction zone and the optimum conditions of formation of the phase and the structure of the end product are ensured [8].

3. *Is it possible to improve the purity of the desired products by transferring impurities and underreacted initial substances into the composition of easily removed phases and what are the optimum conditions for its implementation?* If self-purification under optimum conditions does not result in complete purification of condensed products of synthesis from different impurities, special additives may be incorporated into the composition of the reagents to intensify the process or to bind the impurities in the composition of easily removed condensed phases. The effectiveness of one or another of the additives is determined similarly to the influence of different factors of the process on the composition of the condensed products of synthesis.

4. *What are the characteristics of the interphase equilibrium in different quasiequilibrium regions of the system investigated?* At this stage we determine the characteristics of the gaseous phase (the partial pressure of the components) as well as the composition and the amount of the melts as a function of the temperature and the qualitative composition of the coexisting condensed phases. For this, the thermodynamic parameter of the subsystem (the volume) is assumed to be such that the number of coexisting condensed phases is maximal according to the Gibbs rule. In this case, we obtain the maximum partial pressures, which, being a function of the temperature, do not depend on the volume occupied by the gas phase or on the quantitative composition of the condensed phase. The information obtained at this stage is employed for simulation of heat and mass transfer processes between different regions of the reaction space and provides the initial data for a qualitative description of the mechanism and the rate of transport of the reagents to the reaction zone. Based on the results obtained we can often predict on what reagent surface a film of the product is formed under the given conditions of synthesis .

5. *What is the effect of natural impurities, e.g., oxygen, on the interphase equilibrium characteristics in different quasiequilibrium regions of the system investigated?* In systems with weak gas release, when the partial pressures of the gaseous products are low and cannot ensure a sufficient transport rate of the reagents to the reaction zone, the presence of a small quantity of impurity oxygen, present in practically any system, may intensify this process by several orders of magnitude because of the substantially higher volatility of many oxides as compared to the pure elements [9].

Conclusion. The above principles of thermodynamic analysis of complicated rapid processes, which include SHS, are a generalization of research studies of many years conducted at the Institute of Structural Macrokinetics of the Russian Academy of Sciences [2-5, 10]. Results of these investigations as applied to the development of new technologies of inorganic synthesis have showed the sufficiently high effectiveness of this method for SHS processes. We have developed and realized on a PC a special program for calculating equilibrium characteristics in multielement heterophase systems of any degree of complexity using a data bank of thermodynamic properties of inorganic compounds based on selected information from different handbooks and data banks [11-15]. We are also preparing for publication a handbook based on the results of our systematic thermodynamic studies of different classes of SHS processes, in which all necessary information for conducting thermodynamic analysis of a large number of SHS systems in accordance with the principles discussed above will be provided.

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