ISSN 0040-6015, Thermal Engineering, 2012, Vol. 59, No. 13, pp. 984–993. © Pleiades Publishing, Inc., 2012.
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Chemical Thermodynamics and Indifferent States

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Received July 10, 2011

Abstract—A more general procedure to compute the compositions and thermodynamic properties of complex systems, based on which a new modernized version of the TETRAN software was developed, is suggested. A new alternative method to evaluating the possibility of formation of indifferent states in chemically interacting heterogeneous systems based on the above-mentioned procedure is given. The number of free intensive thermodynamic parameters decreases because of the formation of indifferent states. The detailed investigation of the formation of indifferent states in the system consisting of the condensed sodium chloride and atmosphere of vapors formed during the evaporation of this substance is presented as an example. Concrete computations are confirmed by the comparison with the experimental data.

DOI: 10.1134/S0040601512130083

INTRODUCTION

The problem of calculation of thermodynamic properties and compositions of the substances of a closed (exclusive) system consists of the derivation of equations of chemical thermodynamics for concentrations of various substances, the development of the computer method of their solution, and subsequent calculations of compositions and thermodynamic properties. In this case, the mathematical formulations of the problem and algorithms of computations depend on the concrete properties of the system, the state of the question on the starting information on the properties of the system, and limitations and assumptions used when deriving the equations. In this work, we represent the modernized procedure [1] of deriving the equations of chemical thermodynamics of multicomponent and multiphase reacting systems, which is the development of approaches suggested by Gerasimov et al. [2, 3]. Currently, other approaches to the discussed question are also known, for example, [4–7], etc. However, the investigations represented below finally refer to all mentioned works, if the closed systems are considered in them.

According to general statements of chemical thermodynamics, the properties of the closed system depend on the values of free thermodynamic parameters such as pressure, temperature, volume, etc. According to the Duhem theorem [8], the number of such free parameters is limited regardless if these parameters are intensive or extensive quantities. The question of the possibility to select the form of free parameters is determined by the Gibbs phase rule, according to which, the number of free intense parameters is $w = 2 + c' - r$, where c' is the number of independent components in the system, and r is the number of the phases in the system. We understand the set of such components, which differ only by the chemical formula irrespective of the phase where they are present, as independent components. It is seen from the presented relationship that the number of independent components $w \geq 2$. For example, if $w = 1$, p and T cannot be simultaneously selected as independent intensive variables. However, in some cases, indifferent states can appear in systems [8, 9], which results in a decrease in the number of independent intensive parameters. According to [8], the states of the system that differ from the starting state by the mass of at least one phase, but in which all weight fractions of components in each phase remain invariable, are indifferent. In contrast with [9], this problem is considered in connection with the represented procedure of the calculation of thermodynamic properties of complex heterogeneous chemically reacting systems. We derived the conditions of appearance of indifferent states for chemically reacting systems in the general form, which are coordinated with the suggested computational procedure of the properties of such media. We considered the concrete cases of appearance of indifferent states in the temperature range from standard to 3000 K for Ar-containing systems. Indifferent states appear in the system involving sodium chloride plus atmosphere of vapors of this substance consisting of Na, Cl, NaCl, Na_2Cl_2, Na_3Cl_3, Na_2, and Cl_2 under the condition $N_{Na}/N_{Cl} = 1$, where N_{Na} and N_{Cl} are the numbers of moles of Na and Cl in the vapors. As a result of appearance of indifferent states in this system, the number of intensive free parameters decreases to unity. When calculating the compositions, volume V and temperature T were selected as free thermodynamic parameters. Particularly, the vapor pressures depending on temperature are determined as a result of calculations in coincidence with the experimental data. We also found other results and made some general conclusions on the possibility of specifying various free parameters when calculating the thermodynamic properties and composi-