Thermodynamic modeling of the Pb + Bi melt evaporation under various pressures and temperatures

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ABSTRACT

The composition of the vapor phase and the partial pressures of vapor components have been defined at pressures from 10^2 to 10^7 Pa and in the temperature range from 500 to 3000 K. Diagrams of liquid–vapor phase equilibria for the Pb–Bi system have been constructed. A good agreement between experimental results and the carried out calculations on the Pb–Bi phase diagrams is observed.

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1. Introduction

Molten metals and their vapors have found an increasing application as working bodies and heat-transfer media in various high-temperature power installations [1]. Processes occurring at evaporation of metals are of interest for vacuum metallurgy applications (alloying, purification of metals) [2] and nuclear power engineering (purification of heat-transfer liquid metals by distillation) [3].

The lead–bismuth alloy is a perspective heat-transfer medium for nuclear power units [4]. Data on the vapor pressure and liquid–vapor phase boundaries for lead–bismuth melts at pressures from 1 to 10^5 Pa are given in the article [5], however, the composition of the vapor and the partial pressures of its components are not defined.

Such experimental researches of metallurgical systems are complicated by the reaction conditions (high temperatures, difficulties of determination of the concentration of components, etc.). The method of thermodynamic modeling is often used for the investigation of the metal melt equilibrium vaporization.

2. Computational method

The thermodynamic modeling (TM) consists in the thermodynamic analysis of the equilibrium state of systems in whole (a complete thermodynamic analysis). Here thermodynamic systems are conditionally selected material areas which interaction with environment is reduced to the exchange of heat and work. The application of TM allows to simulate quantitatively and predict compositions and properties of complex heterogeneous, multielement, multiphase systems in the wide range of temperatures and pressures, taking into account chemical and phase transformations [6–8].

Calculation methods have been developed on the basis of variational principles of thermodynamics:

(1) Of all the permissible values of moles of individual substances in the thermodynamic system, only those that minimize the thermodynamic potential of the system, correspond to equilibrium values.
(2) Of all the permissible values of the energy added by each independent component (atom), those maximizing the total contribution of energy of individual atoms to the system, correspond to equilibrium values.

The components of the system are all possible and existing substances in different aggregate states, which are formed from the elements included in the system under study. The substances which are minimum necessary for forming of this system are called thermodynamic system components. The number of components equals the number of substances in the system minus the number of independent reactions bonding these substances. At TM compounds with a multiple number of atoms forming them are considered to be condensed individual substances.

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Substances with fractional stoichiometric coefficients are assumed to be solutions. Condensed phases include compounds in the solid (crystalline or amorphous) and liquid states. Individual compounds, which have the same chemical formula, but enter into different phases, are assumed to be different composite substances. The components of the gas phase are molecules, radicals, atoms, ions, and electron gas.

Extensive thermodynamic parameters of the system, i.e. those proportional to the amount or mass of substance in the system, are volume V, entropy S, internal energy U, enthalpy H, free energy F ($F = U - TS$), and Gibbs energy G ($G = H - TS$). Intensive thermodynamic parameters, i.e. those independent of the quantity or mass of the system, are pressure P, thermodynamic temperature T, concentration, and mole and specific thermodynamic values.

Two independent parameters out of V, S, U, H, P, T, F and G and the complete original chemical composition of the system should be assigned for explicit representation of any thermodynamic system. Each pair of the independent parameters defines a characteristic function, which is "the function describing the state of the thermodynamic system of the corresponding thermodynamic parameters, whereas this system is characterized by the fact that all its thermodynamic properties can be expressed explicitly by this function and its derivatives with respect to the thermodynamic parameters" [9].

The criterion of attainment of the equilibrium state by the system is the extremum of its characteristic function. If the parameters P and T are independent, the characteristic function is the Gibbs free energy G, while the minimum of this energy in the system (G_{min}) is the criterion for reaching of the equilibrium state. Taking the parameters U and V, the characteristic function in the isolated system is the entropy S, while the maximum entropy of the system, S_{max}, is the criterion for reaching of the equilibrium state.

One of the most efficient computation programs is the TERRA program package, which is the development of the ASTRA 4 soft [6].

The calculation algorithm in this program package was developed on the basis of the following assumptions of the mathematical model:

– The point in question is closed and isolated thermodynamic systems which boundaries are impermeable to the exchange of matter, heat and work with the environment.
– Systems in the state of the external and internal thermodynamic equilibrium (complete or local) are analyzed.
– The system under study is heterogeneous and consists of several homogeneous parts (phases) separated by visible interfaces.
– The gas phase should be necessarily present in the system.
– All the gaseous individual substances (atoms, molecules, atomic and molecular ions, electron gas) are parts of one gas phase.
– The gas phase is described by the ideal gas law.
– The surface effects at the interface are disregarded; gases do not dissolve in condensed (liquid and solid) phases; there can be no condensed substances.
– Condensed substances form single-component immiscible phases or are parts of ideal condensed solutions.
– The individual substances, which have the same chemical formula, but enter into different phases, are assumed to be different components.
– The substances, which have the same chemical formula, but are in different polymorphous modifications, the crystalline or liquid state, are regarded as one component which properties change abruptly at transformation temperatures.
– The volume of condensed components is negligible.

In accordance with the second law of thermodynamics, the equilibrium of such systems is characterized by the maximum entropy (S_{max}) relative to thermodynamic degrees of freedom, which include the concentration of components in an equilibrium mixture (M_q, mol/kg), the temperature T and the pressure P:

$$S = \sum_{i=1}^{K} \left[S_i^0(T) - Rln\frac{RT}{V}n_i \right] \cdot n_i + \sum_{c=1}^{\widetilde{N}} S_c^0(T)n_c$$
$$+ \sum_{n=1}^{N}\sum_{m=1}^{N_m} \left[S_m^0(T) - Rln(n_m/n_{nm}) \right] \cdot n_m \Rightarrow S_{max} \qquad (1)$$

where n_i, n_c, n_m, S_i^0, S_c^0 and S_m^0 denote the number of moles and the standard entropy (at a temperature T and pressure of 10^5 Pa) in the gas (i) and condensed (c) phases, and in the solution (m), respectively; K is the quantity of gaseous components in the thermodynamic system; C is the quantity of condensed components in the thermodynamic system; N is the quantity of solutions in the thermodynamic system; n_{nm} is the quantity of substance moles in the m-th condensed solution; N_m is the amount of substance in the m-th condensed solution; V is the specific volume; R is the universal gas constant.

The specific volume V and the internal energy U remain to be independent variables since the conditions of the system equilibrium relative to the environment can be expressed as the equalities:

$dV = 0$ and $dU = 0$ or $V = $ const and $U = $ const.

The following additional restrictions are imposed on the tolerance range of variables when the chemical and phase equilibria are established through achievement of the maximum entropy.

(1) The total internal energy (U) of the system is constant at equilibrium:

$$U - \sum_{i=1}^{K} U_i n_i - \sum_{n=1}^{\widetilde{N}} U_c n_c - \sum_{n=1}^{N}\sum_{m=1}^{N_m} U_{nm} n_{nm} = 0 \qquad (2)$$

where U_i, U_c and U_{nm} denote the total internal energy of gaseous, condensed components, and solution per mole:

$$U = \int_{T_0}^{T} C_{V\varepsilon}dT + \Delta_f H^0(T_0) \qquad (3)$$

here $\varepsilon = i, c,$ and m. $\Delta_f H^0(T_0)$ is the formation enthalpy at T_0; C_V is the heat capacity determined at a constant volume.

(2) Conservation of the mass of all the chemical elements:

$$-M_j + \sum_{i=1}^{K} v_{ji} n_i + \sum_{c=1}^{C} v_{jc} n_c + \sum_{n=1}^{N}\sum_{m=1}^{N_m} v_{jnm} n_{mn} = 0 \qquad (4)$$

where M_j is the mole content of the j-th chemical element in the system; v_{ji}, v_{jc}, and v_{jnm} are the numbers of atoms of the j-th element in the gaseous and condensed components of the system and the solution, respectively.

(3) Charge conservation law:

$$\sum_{i=1}^{K} q_{ei} n_i = 0 \qquad (5)$$

where q_{ei} is the degree of ionization of the i-th component (for the electron gas $q_{ei} = -1$).

(4) The equation of state of a mixture of ideal gases:

$$pV - RT\sum_{i=1}^{K} n_i = 0 \qquad (6)$$

where p is the pressure.