THERMODYNAMIC MIXING FUNCTIONS OF A MULTICOMPONENT LIQUID METAL AND SLAG

The work proposes a thermodynamic model of a multicomponent condensed phase applicable to metal and slag melts. The integral and partial thermodynamic mixing functions: Gibbs energy, enthalpy, entropy, heat capacity have been obtained using configurational statistical sum. Methods for estimating of model parameters using available data on activity coefficients and heats of mixing, Wagner interaction parameters have been suggested. Using binary Fe-Mn system as an example, the high accuracy of the calculation of the mixing thermodynamic functions of the metal phase in the entire concentration range has been shown. Mixing heat capacity has been shown to comply 3rd law of thermodynamics. Suggested thermodynamic model is already being used in steelmaking control system «Master» at metallurgical plant «Zaporizhstal», and in heat projecting and control system «DesigningMelt» at XuanSteel metallurgical works (PRC).

Key words: thermodynamic model, enthalpy, entropy, heat capacity, mixing functions, statistical sum

Control systems for the melting and out-of-furnace steel processing, based on the achievements of the theory of metallurgical processes, have become widespread at enterprises of the metallurgical complex. However, there is a trend everywhere when the power of the used computing facilities cannot be fully utilized due to the lag in the level of intellectual «stuffing» and the prognostic capabilities of such systems. In particular, a huge number of fragmentary works devoted to the interaction of components in metal alloys did not lead to consensus on this issue. The routine expansion of thermodynamic functions in a Taylor series is the best that at the moment does not cause special objections, leaving behind the actual behavior of the multicomponent metal or slag phase in a wide range of concentrations. In the present work, an attempt has been made to eliminate such fragmentation in the thermodynamic description of the condensed phase.

The derivation of the thermodynamic functions of the phase is based on the thermodynamic probability of the macroscopic state of a system $N$ of different-type particles (configurational statistical sum), obtained by A.G. Ponomarenko [1]:

$$Q = \exp\left(\frac{-\varepsilon_0}{R \cdot T}\right) \cdot \prod_{i=1}^{n} \frac{\left(\sum_{j=1}^{k} n_j \cdot \exp\left(-\varepsilon_{ij} / R \cdot T\right)\right)^{n_i}}{n_i!},$$

(1)

where $\varepsilon_0$ – minimum energy, which is taken as the reference point of all interaction energies $\varepsilon_{ij}$; $R$ – universal gas constant; $T$ – absolute temperature; $n_i$ – the number of particles (moles) of the $i$-th element; $\varepsilon_{ij}$ – energy parameters of the interaction of the $i$-th element with the $j$-th;

However, a subsequent analysis of the thermodynamic functions obtained from the statistical sum (1) showed that in order to meet the Raoult limit law, it is necessary to add...
a normalizing factor to the expression for the thermodynamic probability of the subsystem of \( i \)-th particles \( \exp(-n_i) \):

\[
Q = \exp(-\varepsilon_i / RT) \cdot \prod_{j=1}^{k} \left( \frac{n_j \cdot \exp(-\varepsilon_j / RT)}{n_j!} \right)^{n_i}.
\] (2)

The addition of a normalizing factor is consistent with the conclusion presented in the book of G.A. Lorenz [2] for systems with a variable number of particles. By applying Stirling formula \( n! = n^n \cdot \exp(-n) \), we derive a simpler expression:

\[
Q = \exp(-\varepsilon_i / RT) \cdot \prod_{j=1}^{k} \left( \frac{1}{n_j!} \sum_{j=1}^{k} n_j \cdot \exp(-\varepsilon_j / RT) \right)^{n_i},
\] (3)
in which the statistical weight of the \( i \)-th energy state is assigned to one g-atom of particles of the type \( i \).

The statistical sum (2) can also be reduced to another equivalent form in which the ideal part \( N! / \prod_{i=1}^{k} n_i! \) and the non-ideal part are separated, which ensures the correspondence principle, i.e., the transition to an ideal solution in the absence of interaction between particles of different types \( (\varepsilon_{ij} = 0) \):

\[
Q = \exp(-\varepsilon_i / RT) \cdot \frac{N!}{\prod_{i=1}^{k} n_i!} \left( \sum_{j=1}^{k} x_j \cdot \exp(-\varepsilon_{ij} / RT) \right)^{n_i}.
\] (4)

Using the known relations between the partition and thermodynamic functions, an expression for the chemical potential of the \( i \)-th component has been obtained in the form:

\[
\mu_i = \mu_i^* + R \cdot T \cdot \left[ \ln(x_i \cdot \psi_i) + 1 - \sum_{j=1}^{k} x_j \cdot \psi_j \cdot \beta_{ij} \right],
\] (5)

where \( x_i \) – mole fraction of the \( i \)-the element;

\[
\psi_i = \frac{1}{\sum_{j=1}^{k} x_j \cdot \beta_{ij}}, \quad \beta_{ij} = \exp\left(-\frac{\varepsilon_{ij}}{R \cdot T}\right),
\]

\( \mu_i^* \) – chemical potential of the \( i \)-th element in a standard state.

In this model, the components of any condensed phase are the chemical elements of the periodic system, which makes it possible to adequately describe the phase without introducing any assumptions about its molecular composition. This is most relevant for non-metallic phases.

In nonmetallic (oxide, salt) liquid phases at high temperatures, there are no molecules of chemical compounds of a certain stoichiometric composition, which is confirmed experimentally, in particular, by the data of X-ray diffraction analysis of melts [3]. In this case, the principle of electroneutrality of the phase is satisfied in accordance with the atomic valency, i.e., with the average number of electrons given or received by atoms of a certain kind. The valency can be fractional or even variable [4], and the electrons act as \( k + 1 \) of the virtual component of the phase with chemical potential \( \mu_e \), which must be taken into account in Gibbs partial energies in the form of a term \( \mu_e \cdot \nu_e \). In integral functions, this term disappears. Accounting for the electronic contribution to the chemical potential of elements was first proposed by K. Wagner [5] and was discussed in detail in [1; 6] for
non-metallic phases. Note that the Gibbs-Duhem equation for any phase with an electron contribution requires the fulfillment of the principle of electro-neutrality, or the law of «simple multiple relations» (if we are talking about integer valencies). On the other hand, in the description of a metal substitution solution in which heterogeneous atoms are both donors and acceptors of collectivized electrons, the electronic contribution is compensated even in partial quantities.

In some works, the chemical potential of electrons is introduced as an indefinite Lagrange multiplier in connection with minimizing the Gibbs energy of a heterogeneous system [7], while losing its physical meaning and belonging to any phase.

The Gibbs-Duhem equation does not impose any restrictions on the energy parameters in expressions (2)–(4), allowing in the general case any sign and asymmetry \((\varepsilon_{ij} \neq \varepsilon_{ji})\), however, to meet the Raoult limit law, it is necessary and sufficient that, \(\varepsilon_{ij} = 0\) i.e. \(\beta_{ji} = \exp(-\varepsilon_{ij} / R \cdot T) = 1\).

From the point of view of the microstate of the phase, this means the indistinguishability of the atoms of the same type by their energy states. If the phase consists of atoms of various types with the same energy microstates \((\varepsilon_{ij} = 0)\), then an ideal solution is formed. In the binary non-ideal systems with a positive enthalpy of mixing, always \(\varepsilon_{12} > 0\), but with a negative one we have \(\varepsilon_{12} < 0\).

Tables 1 and 2 give formulas for integral and partial thermodynamic mixing functions. It should be noted that all of them were obtained from a single statistical sum (3) using the well-known Maxwell relations and the Gibbs-Helmholtz equation without any additional assumptions about the nature of the solutions. Therefore, they are strictly consistent with each other. Obtained formulae give a fundamental answer to the question of the enthalpy and entropy components of the Gibbs energy of the phase in the strict framework of the thermodynamic formalism.

### Table 1 – Integral and partial molar mixing functions of a multicomponent system

| Function       | Int. / part. | Symbol | Formula |
|----------------|--------------|--------|---------|
| Gibbs energy   | \(i\)        | \(G_m^M\) | \(R \cdot T \cdot \sum_{j=1}^{k} x_j \cdot \ln (x_j \cdot \psi_{ij})\) (6) |
| \(p\)          | \(\mu_m^M\)  |        | \(R \cdot T \cdot \left( \ln (x_i \cdot \psi_{ij}) + 1 - \sum_{j=1}^{k} x_j \cdot \psi_{ij} \cdot \beta_{ji} \right)\) (7) |
| Activity       | \(\gamma_i\) |        | \(\psi_i \cdot \exp \left( 1 - \sum_{j=1}^{k} x_j \cdot \psi_{ij} \cdot \beta_{ji} \right)\) (8) |
| coefficient     |              |        |         |
| Enthalpy       | \(i\)        | \(H_m^M\) | \(\sum_{j=1}^{k} x_j \cdot \Psi_{ij}, \text{de} \ \Psi_{ij} = \psi_{ij} \cdot \sum_{j=1}^{k} x_j \cdot \varepsilon_{ij} \cdot \beta_{ji}\) (9) |
| \(p\)          | \(h_m^M\)    |        | \(\Psi_{ij} + \sum_{j=1}^{k} x_j \cdot \psi_{ij} \cdot \beta_{ji} \cdot (\varepsilon_{ij} - \Psi_{ij})\) (10) |
| Entropy        | \(i\)        | \(S_m^M\) | \(\sum_{j=1}^{k} x_j \left( \Psi_{ij} / T - R \cdot \ln (x_i \cdot \psi_{ij}) \right)\) (11) |

It is interesting to note that the term \(1 - \sum_{j=1}^{k} x_j \cdot \psi_{ij} \cdot \beta_{ji}\), which plays an important role in partial functions (without it, in particular, the Gibbs-Duhem equation does not hold), disappears in integral thermodynamic functions.

As can be seen from the above formulae, suggested condensed phase model allows to describe real asymmetric metal systems.
Table 2 – Integral and partial molar mixing functions of the binary system

| Function               | Int. / part. | Symbol   | Formula                                                                 |
|------------------------|--------------|----------|--------------------------------------------------------------------------|
| Gibbs energy           | i            | $G_m^I$  | $R \cdot T \left[ x_i \cdot \ln(x_i \cdot \Psi_i) + x_2 \cdot \ln(x_2 \cdot \Psi_2) \right]$ (12) |
|                        | $p$          | $\mu_1^M$| $R \cdot T \cdot \left( \ln(x_i \cdot \Psi_i) + 1 - x_i \cdot \Psi_i - x_2 \cdot \Psi_2 \cdot \beta_{21} \right)$ (13) |
|                        | $p$          | $\mu_2^M$| $R \cdot T \cdot \left[ \ln(x_2 \cdot \Psi_2) + 1 - x_i \cdot \Psi_i \cdot \beta_{12} - x_2 \cdot \Psi_2 \right]$ (14) |
| Enthalpy               | i            | $H_m^I$  | $x_1 \cdot x_2 \cdot (\Psi_1 \cdot e_{12} \cdot \beta_{12} + \Psi_2 \cdot e_{21} \cdot \beta_{21})$ (15) |
|                        | $p$          | $h_1^M$  | $x_i^2 \cdot (\psi_1^2 \cdot e_{12} \cdot \beta_{12} + \psi_2^2 \cdot e_{21} \cdot \beta_{21})$ (16) |
|                        | $p$          | $h_2^M$  | $x_i^2 \cdot (\psi_1^2 \cdot e_{12} \cdot \beta_{12} + \psi_2^2 \cdot e_{21} \cdot \beta_{21})$ (17) |
| Entropy                | i            | $S_m^I$  | $\frac{x_1 \cdot x_2 \cdot (\psi_1 \cdot e_{12} \cdot \beta_{12} + \psi_2 \cdot e_{21} \cdot \beta_{21})}{T} - R \cdot \left( \frac{x_1 \cdot \ln(x_1 \cdot \Psi_2) + x_2 \cdot \ln(x_2 \cdot \Psi_2)}{T} \right)$ (18) |
|                        | $p$          | $s_1^M$  | $s_2^M$                                                                 |
|                        |              | $\frac{h_i^M - \mu_i^M}{T} = - \left( \frac{\partial \mu_i^M}{\partial T} \right)_p$ (19) |
| Heat capacity          | i            | $C_p^I$  | $\frac{x_1 \cdot x_2 \cdot (\psi_1 \cdot e_{12} \cdot \Psi_1^2 + x_2 \cdot \beta_{21} \cdot e_{21} \cdot \psi_2)}{R \cdot T^2}$ (20) |

To assess compliance with real systems and to calculate the parameters of the proposed model, the expressions for the thermodynamic functions of infinitely diluted solutions and the Wagner interaction parameters given in Table 3 are taken into consideration.

Table 3 – Partial molar mixing functions and interaction parameters in a multicomponent system with an infinite dilution (1st element – solvent)

| Function                       | Symbol                  | Formula                                                                 |
|--------------------------------|-------------------------|--------------------------------------------------------------------------|
| Logarithm of activity coefficient | $\ln \gamma_i^I$        | $1 - \beta_{1i} - \ln \beta_{1i}$ (21)                                  |
| Enthalpy                       | $h_i^e$                 | $-R \cdot T \cdot \left( \beta_{1i} \cdot \ln \beta_{1i} + \ln \beta_{2i} \right)$ (22) |
| Excessive entropy              | $s_i^{eE}$              | $-R \cdot (1 - \beta_{1i} + \beta_{1i} \cdot \ln \beta_{1i})$ (23)     |
| 1st order Wagner interaction parameters | $e_i' = \left( \frac{\partial \ln \gamma_i}{\partial x_i} \right)_{x_i=1}$ | $1 + \beta_{1i} - \frac{2 \beta_{1i}}{\beta_{1i}}$ (24) |
|                               | $e_j' = e_i' = \left( \frac{\partial \ln \gamma_j}{\partial x_j} \right)_{x_j=1}$ | $1 + \beta_{1i} \cdot \beta_{1j} - \frac{\beta_{1j} \cdot \beta_{1i}}{\beta_{1i}}$ (25) |
| 1st order enthalpy interaction parameters | $\eta_i' = \left( \frac{\partial h_i^e}{\partial x_i} \right)_{x_i=1}$ | $2 R \cdot T \cdot \left( \beta_{1i} \cdot \ln \beta_{1i} + \ln \beta_{2i} \right)$ (26) |
|                               | $\eta_j' = \eta_i' = \left( \frac{\partial h_i^e}{\partial x_j} \right)_{x_j=1}$ | $R \cdot T \cdot \left( \beta_{1i} \cdot \beta_{1j} \cdot \ln \beta_{1i} \cdot \beta_{1j} - \frac{\beta_{1j} \cdot \ln \beta_{1j}}{\beta_{1i}} \right)$ (27) |
Formulas (21)–(27) make it possible to obtain model parameters (β_{ij} or ε_{ij}) based on tabulated experimental data on the thermodynamic functions of dilute solutions. If the mixing functions are known for the entire range of concentrations of the binary system, we use nonlinear regression analysis and formulas (12–18) to more accurately determine the sought parameters.

If it is supposed to use a thermodynamic model of the phase in the region of dilute solutions, then the parameters can be considered symmetrical, which allows halving their number and simplifying most of the formulas (6)–(27).

Using the Fe-Mn binary system at 1863 K as an example, we demonstrate extremely accurate agreement between the results of calculating the thermodynamic mixing functions according to the proposed model and the corresponding experimental data. Table 4 presents the experimental data [8] and the calculation results. The only parameter of the model needed to calculate all the thermodynamic functions of this symmetric binary system was determined by nonlinear regression using the Gibbs integral energy of mixing in accordance with formula (12):

$$
G_i^{MP} = H_i - T \cdot S_i
$$

(28)

From the equations (21)-(27) and relation (28), the origin of the «correlations» between excessive partial functions, which is discussed in many monographs, in particular [9; 10; 11] with the reference to the works of the Guggenheim [12] and Kubashevsky [13].

Figure 1 shows the correlation between the activity coefficients of liquid alloys and the Wagner interaction parameters in the approximation of the theory of regular solutions, the quasi-chemical model, and the proposed model. With significant deviations from ideality (for example, in Fe-Si and Cd-Na systems), the proposed model explains the experimental data better. Near the ideal solutions, all three models give the same ultimate dependence ε_{ij} on \ln γ_{ij}:

$$
ε_{ij} = -2 \ln γ_{ij}.
$$

Table 4 – Experimental data [8] and calculation results of thermodynamic functions of the Fe-Mn system at 1863K

| x_{Mn} | G_{Mn}^M, J/mol | H_{Mn}^{MP}, J/mol | γ_{Mn} | h_{Mn}^{MP}, J/mol |
|--------|-----------------|------------------|--------|------------------|
| 0      | -4656           | -4642            | -32134 | -32128           |
| 0,1    | -7059           | -7052            | -22136 | -22136           |
| 0,2    | -8545           | -8545            | -16509 | -16511           |
| 0,3    | -9370           | -9377            | -12615 | -12622           |
| 0,4    | -9638           | -9645            | -9638  | -9645            |
| 0,5    | -9370           | -9377            | -7205  | -7213            |
| 0,6    | -8545           | -8545            | -5133  | -5131            |
| 0,7    | -7059           | -7052            | -3291  | -3281            |
| 0,9    | -4656           | -4642            | -1604  | -1588            |
| 1,0    | -5133           | -5131            | 0      | 0                |

As it can be seen from the presented data, the calculated activity coefficient of manganese in the entire concentration range differs from experimental values only in the fourth digit. All other calculated thermodynamic functions of the solution are also consistent with experimental data with high accuracy.

Correlation of excessive partial molar quantities. It is known [9] that excessive partial molar quantities, including at infinite dilution, are bound by the same relation $G = H - T \cdot S$ as all thermodynamic functions for a non-ideal solution as a whole:

$$
R \cdot T \cdot \ln γ_j = h_j^{MP} - T \cdot S_j^{MP}.
$$

(28)
Solubility of gases. The solubility of gases in liquid iron substantially depends on the concentration of alloying elements. The proposed thermodynamic model of the phase makes it possible to adequately describe the concentrations of dissolved gases in a wide range. As an example Figure 2 shows the results of calculating the solubility of nitrogen in liquid iron at 1873K, which repeat with good accuracy the course of the known experimental curves.

Figure 1 – Correlation between activity coefficients and interaction parameters in the suggested model of phase (1), regular solution (2) and quasi-chemical model (3). Experimental points from [9; 14]

Figure 2 – Solubility of nitrogen in liquid iron at 1873K (calculation)
To obtain the curvature of the nitrogen solubility isotherms in known solution models, it is necessary to explicitly take into account the second-order Wagner interaction parameters. The proposed phase model does not require this. Moreover, it allows one to calculate, if necessary, these parameters on the basis of experimental data on the first-order Gibbs energy parameters.

*Mixing heat capacity and compliance with the 3rd law of thermodynamics.* Using the Fe-Mn binary system as an example, we demonstrate the correspondence of formula (20) for the heat capacity of mixing to the 3rd law of thermodynamics, according to which the total heat capacity of a substance (i.e., all its components) tends to zero at temperatures close to absolute zero. Substituting the value $\varepsilon_{12} = \varepsilon_{21} = 2268.1$ J/mol in the formula (20), we obtain the dependence of $C_{pM}^c$ on the absolute temperature as shown on the Figure 3.

![Figure 3 – The temperature dependence of the molar heat capacity of mixing in the Fe-Mn alloy. Calculation according to the formula (20). Comparative heat capacity curves $C_p$ of pure $\alpha$-Mn and $\alpha$-Fe. Experimental points from work [15]](image)

As it can be seen from the graph, the maximum heat capacity of mixing in a dilute solution is achieved at a lower temperature than in a saturated solution. The value of $C_{pM}^c$ in the dilute solution is lower than that in a more saturated solution over the entire temperature range, which is to be expected. With an infinite increase in temperature, the heat capacity of mixing tends to zero in all cases, and the solution becomes ideal.

Comparing the calculated $C_{pM}^c$ curves with the experimental heat capacity points $C_p$ of the pure elements, we can estimate the total heat capacity of the alloys, which should always be higher than the weighted sum of the heat capacities of the pure components.

We note that the experimentally established fact of the «loss» of heat capacity by a substance at a finite temperature $T > 0$ finds its explanation only in the framework of quantum mechanics.

*Discussion of the results.* The proposed model of the condensed phase makes it possible to describe the thermodynamic functions of many metal systems with unprecedented accuracy (an example is the Fe-Mn system). The advantage of the model is the description of all,
without exception, thermodynamic functions of the phase from a unified position that does not require the involvement of any additional assumptions about the nature of the solution.

In addition, the adequate behavior of the mixing heat capacity at a low temperatures allows us to propose this model for describing not only liquid but also solid condensed solutions. Due to the fact that \( \beta_y = \exp(-\varepsilon_y / R \cdot T) \), all the thermodynamic functions given in Tables 1–3 are functions of temperature. This makes it possible to justifiably use them for constructing phase diagrams of condensed systems, modeling the growth of nonmetallic inclusions during cooling of melts, etc.

However, in the proposed model, there are some problems that encourage further research. As in the quasi-chemical model, the excessive entropy of a binary solution at infinite dilution cannot be positive, which is not always consistent with experimental data. For some non-ideal asymmetric systems, it is not possible to accurately predict the coordinates of the extremum of integral functions.

Conclusions. The results of thermodynamic modeling of the multicomponent condensed phase obtained in this work can be implemented in computer programs, with which one can calculate the phase and component composition of heterogeneous systems of any complexity. The proposed model is already being used in steelmaking control system «Master» at metallurgical plant «Zaporizhstal» [16], heat projecting and control system «DesigningMelt» at XuanSteel metallurgical works (PRC) [17; 18], and expected to be used in industrial process control systems for melting and out-of-furnace steel processing at a number of other metallurgical plants.

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