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Overview of the applications of thermodynamic databases to steelmaking processes

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ABSTRACT

Computerized thermodynamic databases for solid and liquid steel, slags and solid oxide solutions, for large numbers of components, have been developed over the last three decades by critical evaluation/optimization of all available phase equilibrium and thermodynamic data. The databases contain model parameters specifically developed for molten slags, liquid and solid steel and solid oxide solutions. With user-friendly software, which accesses these databases, complex chemical reactions and phase equilibria occurring throughout the steelmaking process can be calculated over wide ranges of temperature, oxygen potential and pressure. In the present article, the thermodynamic models and databases for molten slag and liquid steel included in well-known thermochemical packages and their applications to complex steelmaking processes involving molten slag, steel, inclusions, refractories and gases are reviewed.

1. Introduction

Steelmaking comprises consecutive high-temperature chemical processes to refine liquid steel and to attain a narrow chemical composition for specified steel grades. In particular, clean steels with a low level of gaseous impurities such as C, S, P, N, H and O and non-metallic inclusions can be produced by the elaborate control of the chemical reactions involving liquid steel, slags, inclusions, refractories and gases. However, the reactions are often difficult to understand due to their complexity. Usually, to understand the complex chemical phenomena and solve practical problems in pyrometallurgical processes, a large body of experimental data must be obtained at great expense. In order to reduce the time and expense required for the experiments, and to understand the chemical reactions more fully, thermodynamic calculations based on accurate thermodynamic databases have been used actively in recent years.

Thermodynamic modeling has been actively pursued together with the improvement of computational techniques and software. Based on a proper thermodynamic model for every phase of a given system, all available thermodynamic and phase equilibrium data for the system are critically evaluated simultaneously in order to obtain one self-consistent set of model equations for the Gibbs energies which best reproduce the data for all phases as functions of temperature and composition. This technique has come to be known as thermodynamic "optimization (modeling)". Where data are lacking for a multicomponent system, the models and optimized model parameters for low-order (binary and ternary) subsystems can be used to provide good estimates. In this way, the thermodynamic databases are developed. The databases are then used, along with Gibbs energy minimization software, to calculate the conditions for multicomponent equilibrium.

The selection of proper databases for a given system is a prerequisite for accurate thermodynamic calculations. The databases must be thermodynamically self-consistent; otherwise, very erroneous results can often occur. Computerized thermodynamic databases for solid and liquid steel, slag and solid oxide solutions, for large numbers of components, have been developed over the last three decades by critical evaluation/optimization of all available phase equilibrium and thermodynamic data. The well-known thermochemical software packages with large thermodynamic databases for steelmaking processes are CEQCSI [1], FactSage [2], MPE [3], MTDATA [4] and Thermo-Calc [5]. The user-friendly software makes it possible to perform versatile thermodynamic calculations within the accuracy of the experimental data even for regions of composition and temperature where no experimental data are available.

In the present review article, the thermodynamic models and databases for oxide and liquid steel in large thermochemical packages and their applications to complex steelmaking processes involving molten steel, slag, inclusions, refractories and gases will be reviewed.

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2. Thermodynamic models

In recent years, large thermodynamic databases for multicomponent oxide and alloy systems have been developed by what has come to be known as the 'Calphad technique'. Thermodynamic and phase equilibrium data for binary and ternary subsystems are critically evaluated and thermodynamic models are chosen for each phase based on their crystal structure. The model parameters are optimized to reproduce all reliable experimental data within experimental error limits. The databases are accessed by the Gibbs energy minimization software to calculate thermodynamic properties, phase diagrams and chemical reactions for multicomponent systems. Apparently, a thermodynamic model that adequately describes the enthalpy, entropy and Gibbs energy of the solution as functions of temperature and composition is the most essential for the development of large thermodynamic database for multicomponent systems. To be useful for this purpose, a model must be sufficiently realistic to have a good predictive ability, but not be so complex as to be mathematically intractable. In the present study, thermodynamic models frequently encountered in steelmaking applications involving molten slag, solid oxide solutions and liquid Fe solution will be reviewed without delving into the mathematical details.

2.1. Molten slag (liquid oxide)

Molten silicate slags are ionic liquids with complex network structure. The silicate tetrahedra network can be gradually broken down with addition of metal oxides, MO (network modifier), as represented schematically by the reaction

$$(\vdots\mathrm{Si{-}O{-}Si}\vdots) + \mathrm{MO} = (\vdots\ \mathrm{Si{-}O{-}}\ \mathrm{M}^{2+}\mathrm{{-}O{-}Si}\ \vdots). \quad (1)$$

This silicate network breaking reaction (depolymerization reaction) can be simulated as

$$\mathrm{O}^0 + \mathrm{O}^{2-} = 2\mathrm{O}^- \quad (2)$$

where O^0, O^- and O^{2-} represent the bridged, broken and free oxygens. In the CaO–SiO$_2$ system, for example, the SiO_2 tetrahedra network can be gradually broken down with the addition of CaO, and the bridged oxygen bonds can be almost completely broken at the orthosilicate (Ca_2SiO_4) composition.

Toop and Samis [6] were the first to calculate the Gibbs energy and activities of oxides in binary silicate melts using the equilibrium constant of the depolymerization reaction (2). Yokokawa and Niwa [7,8] adopted the depolymerization reaction (2) and calculated the configurations of silicon atoms on the quasi-lattice in binary silicate melts. The configuration (entropy) and Gibbs energy of the melts are dependent on the strength of the depolymerization reaction (2). The activities of MO and SiO_2 were properly calculated in binary MO–SiO_2 melts. The model was also successfully extended to ternary silicate solutions such as the CaO–MnO–SiO_2, CaO–MgO–SiO_2 and CaO–FeO–SiO_2 melts with the ideal solution assumption between basic oxides. Kapoor and Frohberg [9] developed a similar model to describe the ternary CaO–FeO–SiO_2 silicate melts with the assumption of a non-ideal solution between basic oxides.

Masson et al. [10] developed a model that considers the formation of various silicate chains.

$$\mathrm{SiO}_4^{4-} + \mathrm{Si}_n\mathrm{O}_{3n+1}^{2(n+1)} = \mathrm{Si}_{n+1}\mathrm{O}_{3n+4}^{2(n+2)-} + \mathrm{O}^{2-}. \quad (3)$$

The amount of different silicate chains in molten silicates can be calculated from the equilibrium constants of reaction (3). Masson et al. [10] optimized the equilibrium constants of the reaction (3) for various binary silicate systems and calculated the activity of the MO. Gaskell [11] extended the concept of Masson et al. and calculated the Gibbs energy of binary silicate melts by introducing an appropriate entropy of mixing term based on the Guggenheim equation for mixing of anions in linear and branching chains.

Lin and Pelton [12] proposed an ionic model for binary MO–SiO_2 melts. The entropy of solution was calculated over the entire composition range based on the random distribution of O^{2-}, O^- and O^0 over quasi-lattice sites in binary silicate melts. The main model parameter was ΔG for reaction (2) which was described as a function of SiO_2 concentration. The value of ΔG was determined to reproduce the phase diagrams of binary silicate systems as well as thermodynamic properties of the melt. The complex silicate chain structure proposed by Masson et al. [10] could be calculated a posteriori. The model has been extended to ternary MgO–FeO–SiO_2 and CaO–NiO–SiO_2 silicate systems by Romero and Pelton [13,14].

These structure-related models for molten slags have been further developed and adopted in the presently available thermodynamic packages. The best-known models are the Associate Model, the Cell Model, the Modified Quasichemical Model and the Reciprocal Ionic Liquid Model. As the similarities and differences between these models were recently reviewed by Pelton [15], no detailed mathematical formulations of the models will be discussed in the present study.

2.1.1. The Modified Quasichemical Model

The Modified Quasichemical Model (MQM) was introduced by Pelton and Blander [16,17]. The most recent version of the model is discussed in a series of articles [18–21]. The MQM has been used for the FACT slag database of FactSage [22]. The silicate network breaking reaction (reaction (2)) can be equivalent to the following quasichemical reaction among second-nearest-neighbor pairs.

$$(\mathrm{M{-}M}) + (\mathrm{Si{-}Si}) = 2(\mathrm{M{-}Si}) \qquad \Delta g_{\mathrm{MSi}} \quad (4)$$

where (i–j) represent (i–O–j) pairs in molten slags. (M–M), (Si–Si) and (M–Si) are equivalent to free (O^{2-}), bridged (O^0) and broken (O^-) oxygen, respectively, in reaction (2). The short-range ordering in molten silicate is taken into account through the above quasichemical reaction. The molar Gibbs energy of the reaction Δg_{MSi} is the main model parameter, which is expanded as an empirical polynomial in composition and temperature. The configuration entropy is given by randomly distributing the pairs over imaginary pair sites. The molar Gibbs energy of the binary MO–SiO_2 solution can be expressed as

$$\begin{aligned} G^m = {} & (x_{\mathrm{MO}} g^o_{\mathrm{MO}} + x_{\mathrm{SiO_2}} g^o_{\mathrm{SiO_2}}) + (Z_{\mathrm{M}} x_{\mathrm{MO}} + Z_{\mathrm{Si}} x_{\mathrm{SiO_2}}) \\ & \times (x_{\mathrm{MSi}} \Delta g_{\mathrm{MSi}}/4) + RT(x_{\mathrm{MO}} \ln x_{\mathrm{MO}} + x_{\mathrm{SiO_2}} \ln x_{\mathrm{SiO_2}}) \\ & + RT \frac{(Z_{\mathrm{M}} x_{\mathrm{MO}} + Z_{\mathrm{Si}} x_{\mathrm{SiO_2}})}{2} \left(x_{\mathrm{MM}} \ln \frac{x_{\mathrm{MM}}}{Y^2_{\mathrm{MO}}} \right. \\ & \left. + \ x_{\mathrm{SiSi}} \ln \frac{x_{\mathrm{SiSi}}}{Y^2_{\mathrm{SiO_2}}} + x_{\mathrm{MSi}} \ln \frac{x_{\mathrm{MSi}}}{2 Y_{\mathrm{MO}} Y_{\mathrm{SiO_2}}} \right) \end{aligned} \quad (5)$$

where x_{MM}, x_{SiSi} and x_{MSi} are the pair fractions, Z_M and Z_{Si} are the second-nearest-neighbor coordination numbers of M and Si (Z_{Si}/Z_M is the valency ratio of Si and M cations), and Y_{MO} and $Y_{\mathrm{SiO_2}}$ are weighted mole fractions defined as $Y_{\mathrm{SiO_2}} = (1 - Y_{\mathrm{MO}}) = Z_{\mathrm{Si}} x_{\mathrm{SiO_2}}/(Z_{\mathrm{M}} x_{\mathrm{MO}} + Z_{\mathrm{Si}} x_{\mathrm{SiO_2}})$. The values of pair fractions at equilibrium at any overall composition $x_{\mathrm{SiO_2}}$ are determined by setting $\partial G/\partial x_{\mathrm{MSi}} = 0$. This results in an equilibrium constant for reaction (4):

$$x^2_{\mathrm{MSi}}/(x_{\mathrm{MM}} x_{\mathrm{SiSi}}) = 4 \exp(-\Delta g_{\mathrm{MSi}}/RT). \quad (6)$$

Due to the coordination numbers Z_M and Z_{Si}, the maximum second-nearest-neighbor ordering of the M–Si can occur at $x_{\mathrm{SiO_2}} = Z_{\mathrm{M}}/(Z_{\mathrm{M}} + Z_{\mathrm{Si}})$. For example, the maximum ordering for the CaO–SiO_2 slag occurs at the Ca_2SiO_4 composition. The very