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Critical evaluation and thermodynamic optimization of the Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system

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ABSTRACT

A critical assessment and thermodynamic optimization of phase diagrams and thermodynamic properties of the entire Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system were carried out at 1 atm total pressure. A set of optimized model parameters obtained for all phases present in this system reproduces available and reliable thermodynamic property and phase equilibrium data within experimental error limits from 298 K to above liquidus temperatures for all compositions and oxygen partial pressures from metallic Fe saturation to 1 atm. The Gibbs energy of liquid solution was described based on the Modified Quasichemical Model considering the possible formation of $NaAlO_2$ and $NaFeO_2$ associates in the liquid state. The solid solutions wüstite, spinel, feldspar, nepheline, carnegieite, mullite, corundum, clino-pyroxene, meta-oxides and Na-β″-alumina were treated within the framework of Compound Energy Formalism. The database of model parameters can be used to calculate any thermodynamic property and phase diagram section of the present system.

1. Introduction

The Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system either in whole or in part is of significant interest in both industrial processes and natural phenomena. For example, the Na_2O–FeO–Fe_2O_3 system was studied for the cooling system of fast breeder reactors [1–6]. The Na_2O–FeO–Fe_2O_3–SiO_2 system is important for the desulfurization [7–10] and dephosphorization [7–9] of hot metal and liquid steel, the production of bioactive glasses [11–13] and coal-combustion slags [9,14,15]. The Na_2O–FeO–Fe_2O_3–Al_2O_3 system is directly related to the reduction process of bauxite with soda for the production of Al_2O_3 [16], and the production of solid-state electrodes for electrochemical cells [17–19]. The Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system possesses many well-known minerals such as wüstite, spinel, corundum, aegirine, nepheline, carnegieite, albite, jadeite, fayalite and silica (quartz, tridymite, cristobalite) of importance in geology. However, phase equilibria of this system are indeed very complex due to the change of Fe oxidation state with oxygen partial pressure and the substitution of Fe^{3+} by Al^{3+} in solid solutions. Moreover, the high vapor pressure of sodium, hygroscopicity, high viscosity of SiO_2-rich melts, and the high fluidity of Na_2O- and FeO-rich melts make the experimental study of this system quite challenging.

The purpose of the present study was to critically evaluate and optimize thermodynamic properties and phase diagrams of the Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system, which was not previously attempted. In the thermodynamic "optimization" of a system, all available thermodynamic property and phase equilibrium data are evaluated, simultaneously, to obtain a set of model equations for Gibbs energies of all phases as functions of temperature and composition. Thermodynamic property data such as activity aid in the evaluation of phase diagrams, and phase diagram measurements are used to deduce thermodynamic properties. From optimized Gibbs energy equations, all thermodynamic properties and phase diagrams can be back-calculated. Using this approach, all data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies among available data are often resolved, and interpolations and extrapolations are made in a thermodynamically correct manner. The optimized thermodynamic database which is self-consistently built from low order to high order systems can be applied to industrial processes.

Many lower order systems of Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 were already critically evaluated and optimized. For example, the Na_2O–Al_2O_3–SiO_2 [20], Na_2O–FeO–Fe_2O_3 [21], Na_2O–FeO–Fe_2O_3–SiO_2 [22], Na_2O–FeO–Fe_2O_3–Al_2O_3 [23,24] and FeO–Fe_2O_3–Al_2O_3–SiO_2 [25] systems were previously studied. In particular, as very few experimental phase diagram data were

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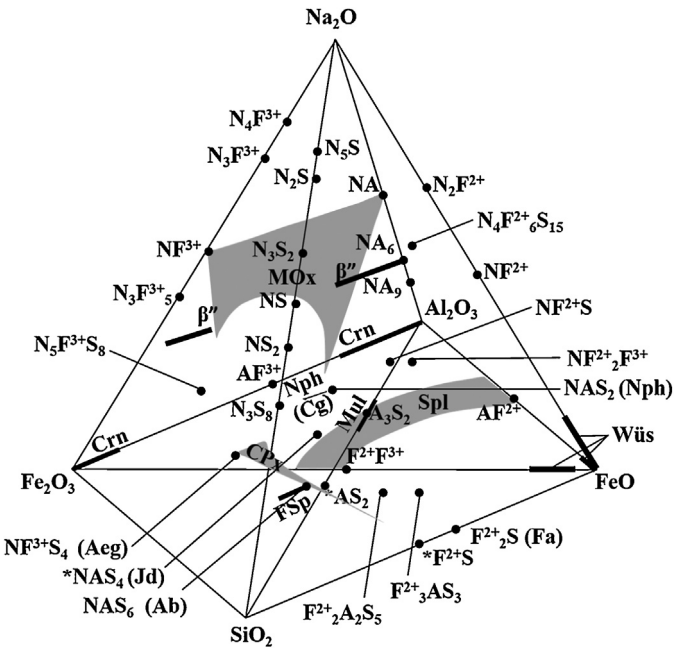

Fig. 1. Schematic diagram of the solid phases in the Na_2O-FeO-Fe_2O_3-Al_2O_3-SiO_2 system. N_4F^{3+}: $Na_8Fe_2O_7$, N_3F^{3+}: Na_3FeO_3, NF^{3+}: $NaFeO_2$, $N_3F^{3+}{}_5$: $Na_3Fe_5O_9$, N_2F^{2+}: Na_4FeO_3, NF^{2+}: Na_2FeO_2, NA: $NaAlO_2$, NA_6: $Na_2Al_{12}O_{19}$, NA_9: $NaAl_9O_{14}$, N_5S: $Na_{10}SiO_7$, N_2S: Na_4SiO_4, N_3S_2: $Na_6Si_2O_7$, NS: Na_2SiO_3, NS_2: $Na_2Si_2O_5$, N_3S_8: $Na_6Si_8O_{11}$, AF^{3+}: $AlFeO_3$, AF^{2+}: $FeAl_2O_4$, $F^{2+}F^{3+}$: Fe_3O_4, $F^{2+}S$: $FeSiO_3$, $F^{2+}{}_2S$: Fe_2SiO_4 (Fa), A_3S_2: $Al_6Si_2O_{13}$, AS_2: $Al_2Si_2O_7$, $N_5F^{3+}S_8$: $Na_5FeSi_4O_{12}$, $N_4F^{2+}{}_6S_{15}$: $Na_8Fe_6Si_{15}O_{40}$, $NF^{2+}S$: Na_2FeSiO_4, $NF^{2+}{}_2F^{3+}$: $NaFe_2O_3$, NAS_2: $NaAlSiO_4$, $F^{2+}{}_3AS_3$: $Fe_3Al_2Si_3O_{12}$, $F^{2+}{}_2A_2S_5$: $Fe_2Al_4Si_5O_{18}$, $NF^{3+}S_4$: $NaFeSi_2O_6$ (Aeg), NAS_4: $NaAlSi_2O_6$ (Jd), NAS_6: $NaAlSi_3O_8$ (Ab), Wüs: wüstite, Spl: spinel, Crn: corundum, Mul: mullite, Nph: nepheline, Cg: carnegieite, Ab: albite, FSp: feldspar, Aeg: aegirine, Jd: jadeite, Fa: fayalite, MOx: meta-oxide, CPx: clino-pyroxene, β″: β″-alumina. Phases marked with '*' are metastable.

available in the Na_2O–FeO–Fe_2O_3–Al_2O_3 system, a coupled key phase diagram experiments and thermodynamic optimization was conducted in this system to properly constrain Gibbs energies of all phases (solids and liquid) under reducing (in equilibrium with metallic Fe) and oxidizing (in air) conditions [23,24].

To describe the entire Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system at oxygen partial pressures ranging from metallic saturation to 1 atm, a set of consistent thermodynamic models and optimized parameters for all existing phases are necessary. Therefore, all previous thermodynamic models and optimized parameters of the sub-systems were integrated together using proper extrapolation techniques, especially for the liquid solution, and the nepheline, carnegieite, feldspar, and clino-pyroxene solid solutions were newly modeled to develop a thermodynamic database for this system. Many unexplored phase diagrams were predicted from the database.

2. Phases and thermodynamic models

Fig. 1 shows the solid phases, considered for the current optimization, in the Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system at 1 atm total pressure. There are many stoichiometric phases and extensive solid solutions. The solution phases present in this system are as follows:

1) Liquid solution: $NaO_{0.5}$–FeO–$FeO_{1.5}$–$AlO_{1.5}$–SiO_2, containing $NaAlO_2$ and $NaFeO_2$ associates,
2) Wüstite: FeO solid solution with limited solubility of Fe_2O_3, Al_2O_3 and Na_2O,
3) Spinel: solid solution between magnetite Fe_3O_4 and hercynite $FeAl_2O_4$ with excess solubility of γ-Fe_2O_3 and γ-Al_2O_3, structurally formulated as $(Fe^{2+}, Fe^{3+}, Al^{3+})^T[Fe^{2+}, Fe^{3+}, Al^{3+}, Va]_2{}^oO_4$,
4) Corundum: solid solution between Al_2O_3 and Fe_2O_3 with a large sub-solidus miscibility gap, structurally formulated as $(Al^{3+}, Fe^{3+})_2O_3$,
5) Nepheline: low-temperature $NaAlSiO_4$ solid solution with excess solubility of SiO_2 and limited solubility of $NaFeSiO_4$,
6) Carnegieite: high-temperature $NaAlSiO_4$ solid solution with excess solubility of SiO_2 and limited solubility of $NaFeSiO_4$,
7) Feldspar: high-temperature $NaAlSi_3O_8$ (high_albite) with limited solubility of $NaFeSi_3O_8$, structurally formulated as $(Na^+)[Al^{3+}, Fe^{3+}]Si_3O_8$,
8) Mullite: $Al_6Si_2O_{13}$ with excess solubility of both Al_2O_3 and SiO_2, and dilute $Fe_6Si_2O_{13}$, structurally formulated as $(Al^{3+}, Fe^{3+})_2{}^o[Al^{3+}, Fe^{3+}, Si^{4+}]^T\{O^{2-}, Va\}_5{}^V$,
9) High-temperature meta-oxide: a complete solid solution between γ-$NaFeO_2$ and β-$NaAlO_2$ with limited solubility of SiO_2, belonging to the tetragonal crystal system, and structurally formulated as $(Na^+,Va)[Fe^{3+}, Al^{3+}, Si^{4+}]O_2$,
10) Intermediate-temperature meta-oxide: a complete solid solution between β-$NaFeO_2$ and α-$NaAlO_2$ with limited solubility of SiO_2, belonging to the orthorhombic crystal system, and structurally formulated as $(NaFe^{4+}, NaAl^{4+}, Si^{4+})O_2$,
11) β″-alumina: Na-β″-alumina $Na_2Al_{12}O_{19}$ extending to about 90 mol% of hypothetical $Na_2Fe_{12}O_{19}$ with a large miscibility gap in the middle, and structurally formulated as $(Na^+)_2[Al^{3+}, Fe^{3+}]_{12}O_{19}$,
12) Clino-pyroxene: a complete solid solution between $NaFeSi_2O_6$ (aegirine) and $NaAlSi_2O_6$ (jadeite; unstable at 1 atm) with limited solubility of $FeSiO_3$ (ferrosilite) at 1 atm, structurally formulated as $(Na^+, Fe^{2+})^{M2}[Fe^{2+}, Al^{3+}, Fe^{3+}]^{M1}\{Al^{3+}, Fe^{3+}, Si^{4+}\}^BSiO_6$.

In the above descriptions, cations shown within a set of brackets occupy the same sublattice, and Va represents vacancy.

2.1. Stoichiometric compounds

The Gibbs energy of a stoichiometric compound (species) is expressed by:

$$G_T^o = H_T^o - TS_T^o \quad (1)$$

$$H_T^o = \Delta H_{298K}^o + \int_{298K}^{T} C_P \mathrm{d}T \quad (2)$$

$$S_T^o = S_{298K}^o + \int_{298K}^{T} \left(C_P/T\right) \mathrm{d}T \quad (3)$$

where ΔH_{298K}^o is the standard enthalpy of formation of a given stoichiometric compound from pure elements at 298 K (ΔH_{298K}^o of elemental species stable at 298 K and 1 atm are assumed to be 0 J/mol as reference), S_{298K}^o is the standard entropy at 298 K, and C_p is the heat capacity.

Nineteen binary and nine ternary stoichiometric phases were considered in the entire Na_2O–FeO–Fe_2O_3–Al_2O_3–SiO_2 system under 1 atm total pressure, $Na_{10}SiO_7$, Na_4SiO_4, $Na_6Si_2O_7$, Na_2SiO_3, $Na_2Si_2O_5$, $Na_6Si_8O_{19}$, $FeSiO_3$ (metastable), Fe_2SiO_4, $NaAlO_2$, $Na_2Al_{12}O_{19}$, $NaAl_9O_{14}$, $Al_2Fe_2O_6$, $Al_2Si_2O_7$ (metastable), Na_2FeO_2, Na_4FeO_3, $Na_3Fe_5O_9$, $NaFeO_2$, Na_3FeO_3, $Na_8Fe_2O_7$, $NaAlSi_2O_6$ (jadeite, metastable), $NaAlSi_3O_8$ (albite), $Fe_2Al_4Si_5O_{18}$, $Fe_3Al_2Si_3O_{12}$, $NaFe_2O_3$, Na_2FeSiO_4, $Na_8Fe_6Si_{15}O_{40}$, $NaFeSi_2O_6$ (aegirine, formerly named as acmite) and $Na_5FeSi_4O_{12}$. The Gibbs energies of all these stoichiometric compounds, presented in Fig. 1,