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A NEW MULTIPURPOSE THERMODYNAMIC DATABASE FOR OXIDE SYSTEMS

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A new thermodynamic database for oxides has been developed in order to perform calculations and predictions of equilibria for various scientific and industrial applications (slags, ashes, glasses, minerals, ceramics, refractories, etc.). The database containing all known phases (gas, stoichiometric compounds, solid and liquid solutions) for combinations of 27 different components provides proper descriptions for many different processes under varying conditions (temperature, pressure, overall composition) including interactions between materials and environments, and thus supports the development of new materials.

Keywords: thermodynamic assessment, CALPHAD modelling, database development, phase equilibria, oxide systems, associate model, calculations of thermodynamic properties.

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INTRODUCTION

Thermodynamic properties of complex oxide systems containing high amounts of silica, alumina, iron oxides, alkali-earth and alkali oxides, for which the measurements are experimentally difficult due to high temperatures, high volatility, high viscosity, etc., can be calculated and predicted by thermodynamic modelling on the basis of reliable experimental data and appropriate Gibbs energy models for the various phases. The available commercial databases are not always sufficient to describe the complete system containing slag, ashes, biomass, gas, coal etc., so a new database is necessary. In the past 15 years an oxide database has been developed in the framework of a series of national projects (concerning coal gasification and combustion processes) supported by funding from the German government and industrial partners [1].

THERMODYNAMIC MODELS

Detailed reports on several of the assessments of subsystems can be found in respective publications e.g. [2–4]. The thermodynamic database has to contain reliable descriptions of all relevant phases (gas, stoichiometric compounds, solid and liquid solutions) in order to perform proper calculations and predictions of thermodynamic properties and phase constellations. Stoichiometric compounds, i.e. solids with a fixed chemical formula such as Al_2O_3 or $CaSiO_3$ are modelled with a temperature dependent $G^\circ(T)$-function:

$$G^\circ = A + B\cdot T + C\cdot T\cdot \ln(T) + D\cdot T^2 + E\cdot T^3 + F/T. \tag{1}$$

In case of non-stoichiometric phase, i.e. solid and liquid solutions, the molar Gibbs energy of the solution is a three-term expression with contributions of the reference part (G^{ref}), the ideal (G^{id}) and the excess (G^{ex}) part as:

$$G_m = G^{\text{ref}} + G^{\text{id}} + G^{\text{ex}}. \tag{2}$$

Depending on the solution model chosen the three parts take on different mathematical form.

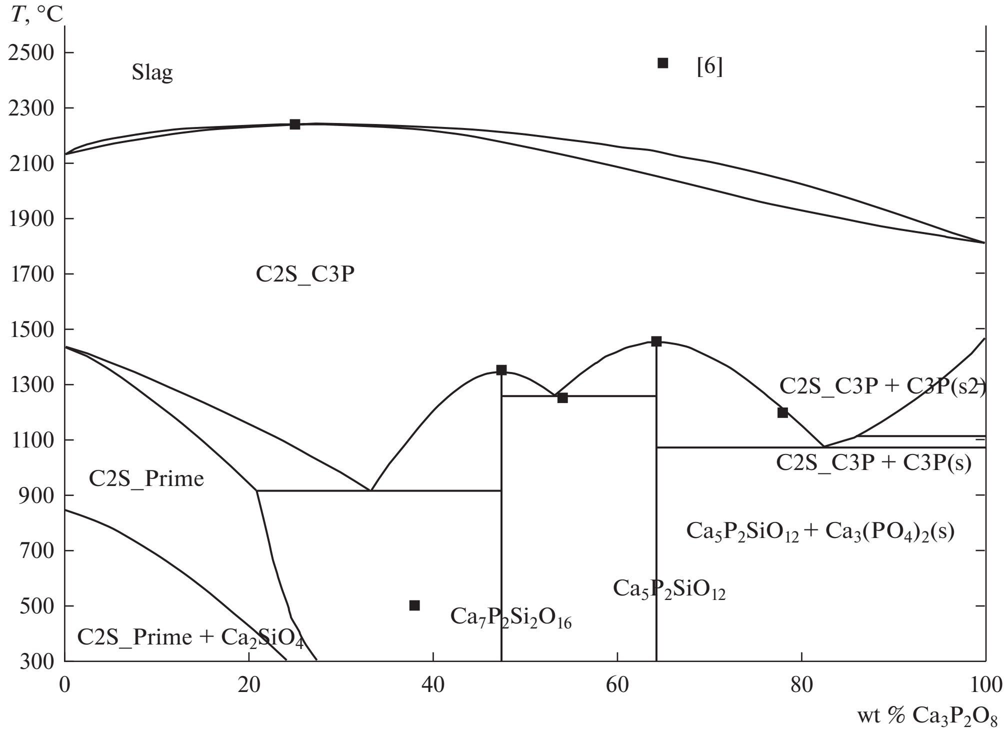

Fig. 1. Isopleth Ca_2SiO_4–$Ca_3P_2O_8$.

Solid solutions are usually treated using the multi-sublattice approach. For example, the high-temperature modifications of dicalcium silicate Ca_2SiO_4 and tricalcium phosphate $Ca_3P_2O_8$ have the same structure and Pearson symbol [5]. According to the high-temperature phase equilibria investigations [6] in the quasi-binary system Ca_2SiO_4–$Ca_3P_2O_8$ a continuous series of solid solutions is formed at steelmaking temperatures. This is termed the C2S-C3P phase with the phase formula $(Ca^{2+})_3(Ca^{2+},Va)(P^{5+},Si^{4+})_2(O^{2-})_8$. The first and fourth sublattices have fixed occupancy, while the third sublattice can be occupied by phosphor and silicon cations and the second sublattice represents an interstitial position. This formula allows describing the unsymmetrical end-members Ca_2SiO_4 (C2S) and $Ca_3P_2O_8$ (C3P) and the continuous transition between them. As shown in Figure 1, the solid solution between the two end members C2S and C3P is complete above 1500°C.

Chromium, manganese and magnesium cations are introduced on the second sublattice to describe their experimentally determined solubilities in C2S–C3P. Eke and Brett [7] reported considerable solubility also of Vanadium oxide in the α-Ca_2SiO_4. The positioning of V as a pentavalent cation on the third sublattice leads to a good reproduction of the experimental solubility as shown in Figure 2. The full thermodynamic description of the phase C2S–C3P is presented using the following formula $(Ca^{+2})_3(Ca^{2+},Mg^{2+},Cr^{3+},Mn^{2+},Va)(P^{5+},Si^{4+},V^{5+})_2(O^{2-})_8$.

The liquid phase (slag), which exhibits short-range ordering as well as ranges of immiscibility, is modelled using the non-ideal modified associate model according to Spear and Besmann [8]. The model was successfully applied for many types of systems with strong interactions [2–4]. Moreover, this model can give a reliable phase internal distribution of associate species, which is consistent with experimentally determined Q_n species distributions [9]. Fur-

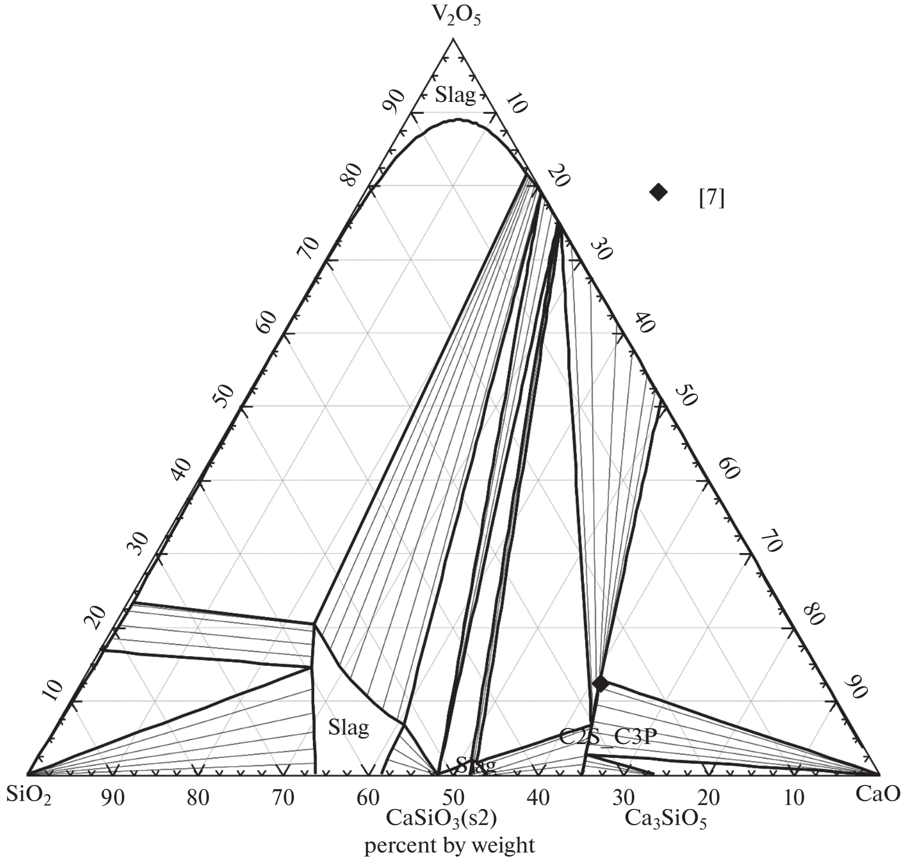

Fig. 2. Isothermal section at 1500°C in CaO–V_2O_5–SiO_2 system.

thermore, the associate model representing the internal structure of the molten slag provides an excellent basis for the modelling of melt viscosity [9]. The liquid component oxides as well as binary and ternary associate species are considered as solution components. In addition, interactions between species were introduced in order to fine tune the thermodynamic description especially in regions of immiscibility. The excess term of G (Eq. (2)) is expressed by Redlich–Kister polynomials. The associate species were given the same stoichiometries in comparable systems in order to provide a handle for their use in multi-component systems. As an example of consistent description, all P_2O_5-containing liquid species are listed in Table 1.

ASSESSMENT OF THERMODYNAMIC PARAMETERS

According to CALPHAD-type modelling all available experimental data (phase equilibria, mixing properties, activity, etc.) are critically analysed in terms of their consistency. Each phase in the system is treated by an appropriate Gibbs energy model with adjustable parameters (Gibbs energy of constituents, interaction parameters, etc.). The Gibbs energy parameters are optimised in accordance with the experimental information in order to generate a self-consistent dataset of Gibbs energies of all phases in a system.

Table 1

Liquid components (associate species) in the P-containing systems

System	Associate species with P_2O_5	Description $MeO_x : P_2O_5$
MeO_2–P_2O_5 with Me = Si, Ti	$SiP_2O_7 \cdot 2/3$, $Si_3P_4O_{16} \cdot 2/7$, $TiP_2O_7 \cdot 2/3$,	1 : 1, 3 : 2
Me_2O_3–P_2O_5 with Me = Al, Cr, Fe	$AlPO_4$, $CrPO_4$, $FePO_4$	1 : 1
MeO–P_2O_5 with Mn = Mg, Ca, Fe, Zn	$Me_3P_2O_8 \cdot 2/5$, $Me_2P_2O_7 \cdot 1/2$, $MeP_2O_6 \cdot 2/3$	3 : 1, 2 : 1, 1 : 1
Alk_2O–P_2O_5 with Alk = Na, K	$Alk_3PO_4 \cdot 1/2$, $Alk_4P_2O_7 \cdot 1/3$, $AlkPO_3$	3 : 1, 2 : 1, 1 : 1

The database, called GTOX, is under constant development and at present covers the following oxide and sulphide components: Al_2O_3–Al_2S_3–CaO–CaF_2–CaS–CrO_x–FeO_x–FeS–MgO–MgS–MnO_x–MnS–K_2O–K_2S–Na_2O–Na_2S–NiO–P_2O_5–SiO_2–SO_3–TiO_x–VO_x.

DATABASE APPLICATION

In the following examples of application calculations using the GTOX-database will be presented.

Slagging and fouling. An effective use of the world's fossil fuels is obligatory in terms of their limited supply and the worldwide increase in demand for energy. Hence, a fundamental knowledge of the thermophysical and thermochemical processes during the conversion of the fuel is necessary. Combustion and gasification request an essential understanding of the properties of the inorganic residue (ash). The high temperature causes the ash to melt and, therefore, the slag characteristically influences the conditions and limitations of the processes. The behaviour of the liquid phase (melting temperature, crystallisation on cooling) is strongly dependent on the overall composition of the fuel (coal, biomass) and, particularly, of the residual mineral part (ash). Thermodynamic calculations with reliable thermodynamic data can be helpful in modelling the processes depending on various parameters (temperature, partial pressure of oxygen, etc.). Table 2 shows the compositions of several ashes from different hard coals. Taking into account all possible transitions occurring in the system (phase formation and decomposition, melting, structure transitions, etc.) it is possible to represent the fraction (in wt %) of the liquid phase as a function of temperature (Fig. 3). The ash SKK containing the highest amount of alumina and CaO and the smallest one of SiO_2 is predicted to begin melting at higher temperature (about 870°C) compared to the other compositions. The liquidus temperature (mass fraction of liquid = 100%) is higher as well (1400°C) due to the high melting temperature of alumosilicates. The SKC composition on the other hand, with minimal content of CaO and Al_2O_3 and maximal SiO_2 has a low melting range (onset at 750 and end at 1150°C). The phase transitions can be calculated in order to describe the processes under cooling or heating at equilibrium conditions. Slagging and fouling in a coal fired power plant (formation of liquid and/or solid deposits) are determined by the composition of the condensed phases formed. Furthermore, the composition and formation temperature of solid phases influence the thermochemical and thermophysical properties of the slag (e.g. viscosity).

Dephosphorization. Dephosphorisation of steels by a metal-slag reaction is important for the steelmaking chemistry. The GTOX database can be used in this application field for the calculation of dephosphorisation equilibria between slag and iron melts determining the equilibrium distribution of phosphorus between slag and metal for basic slags of various composi-

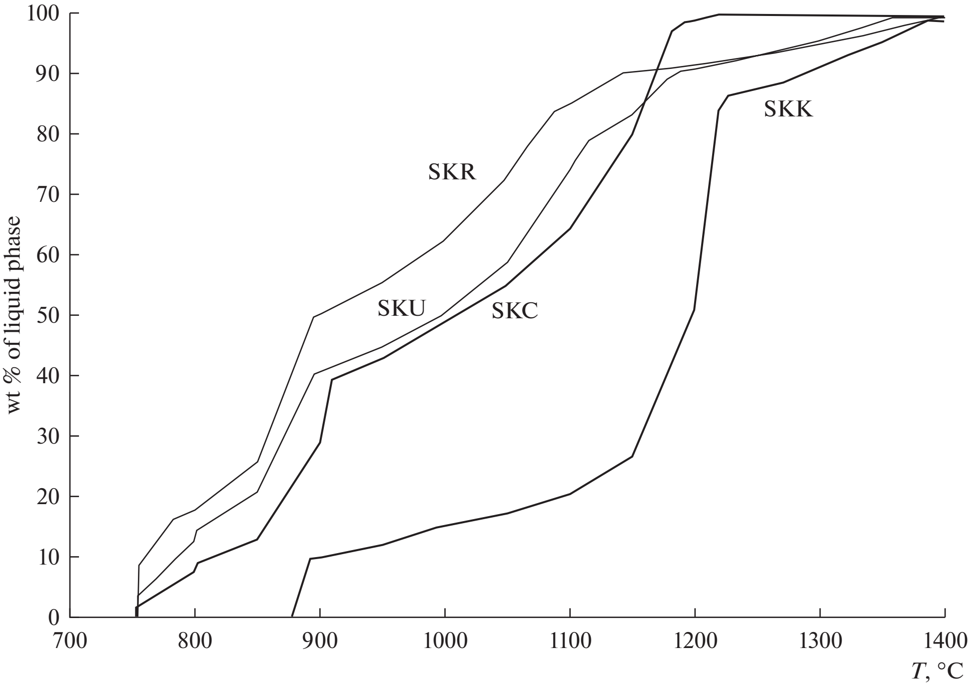

Fig. 3. Melting of different ashes (hard coals).

tions. A critical thermodynamic aspect of these processes is the equilibrium phosphorus partition ratios Lp(%P)$_{Slag}$/[%P]$_{Fe}$) between slag and metal. The ternary CaO–FeO–P_2O_5 system is a most important system for the Basic Oxygen Furnace (BOF) process. This system is characterized by a wide field of immiscibility extending in the liquid phase towards the FeO-rich corner reported by many investigators [10, 11]. The calculated isothermal section at 1600°C pre-

Table 2

Compositions (in wt %) of the ashes

Oxides	Columbia	South Africa	Russia	USA
	SKC	SKK	SKR	SKU
Al_2O_3	14.6	25.9	22.1	20.6
CaO	2.1	7.1	4.9	3.7
Fe_2O_3	15.5	15.4	6.8	14.6
K_2O	1.4	0.7	2.9	2.4
MgO	1.1	0.1	0.2	0.9
Na_2O	1.8	0.2	1.3	0.7
P_2O_5	0.1	1.5	0.5	0.2
SiO_2	60.7	45.4	57.1	52.6
SO_3	1.9	2.5	3.2	3.0
TiO_2	0.8	1.4	0.9	1.1

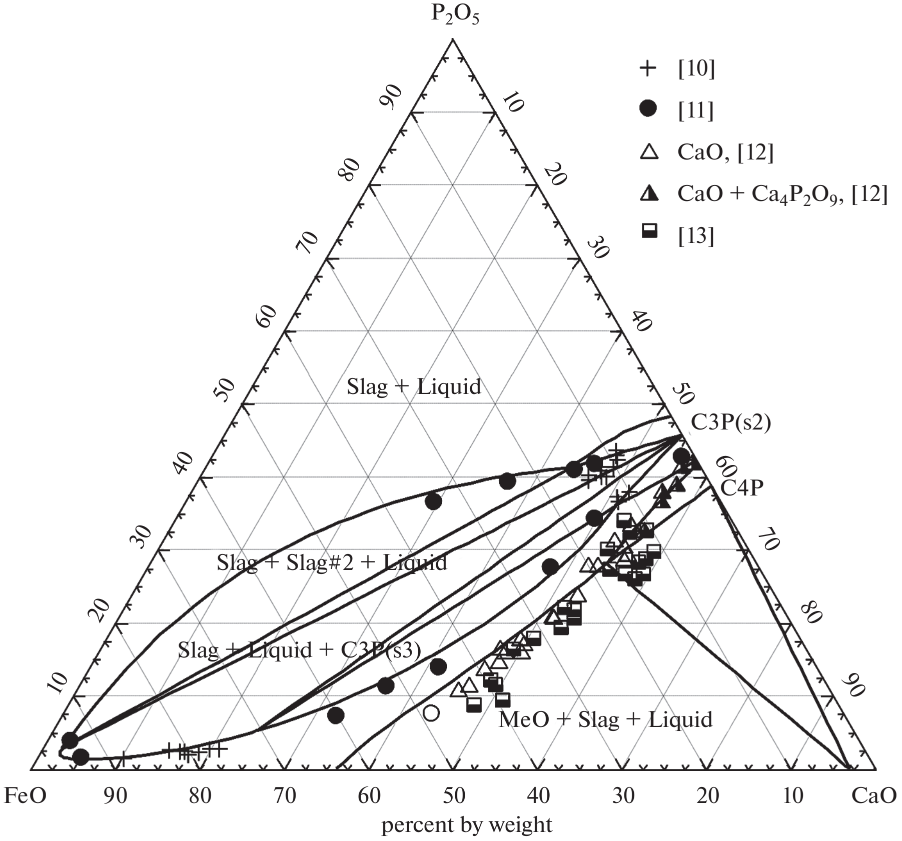

Fig. 4. Isothermal section at 1500°C in CaO–FeO–P_2O_5 system in equilibrium with Fe.

sented in Figure 4 is in good agreement with known experimental data [10–13]. The phosphorus distribution between molten slag and liquid Fe in the CaO-FeO-P_2O_5 system along the CaO saturation was studied by several researchers in the temperature range 1550–1650°C [13, 14]. Figure 5 shows the relationship between the amount of phosphorus in liquid iron and the content of FeO in CaO-saturated molten slags at different temperatures. The phosphorous concentration in liquid Fe depends on the temperature and the amount of FeO in the molten slag. It increases with increasing temperature and decreasing amount of FeO. The experimental behaviour could be well reproduced by the calculations (Fig. 5).

Inclusion of CaF_2. An other important non-oxide addition in the GTOX oxide database is Fluorspar (CaF_2) because of its wide application in ladle treatment of steel and especially electrometallurgy. The addition of CaF_2 decreases the melting temperature and furthermore the viscosity of the slags. Figure 6 shows the isothermal section at 1600°C through the Al_2O_3–CaO–CaF_2 system compared with experimental data [15, 16]. The calculated lines of saturation with CaO, Al_2O_3, CA6 and CA2 are in good agreement with experimental data, also the computed wide zone of liquid immiscibility in the high-fluoride region.

Addition of sulphur. *S*ulfur is commonly contained as an essential component in many natural and manufactured materials. Sulfide glasses can be used for high refractory index materials.

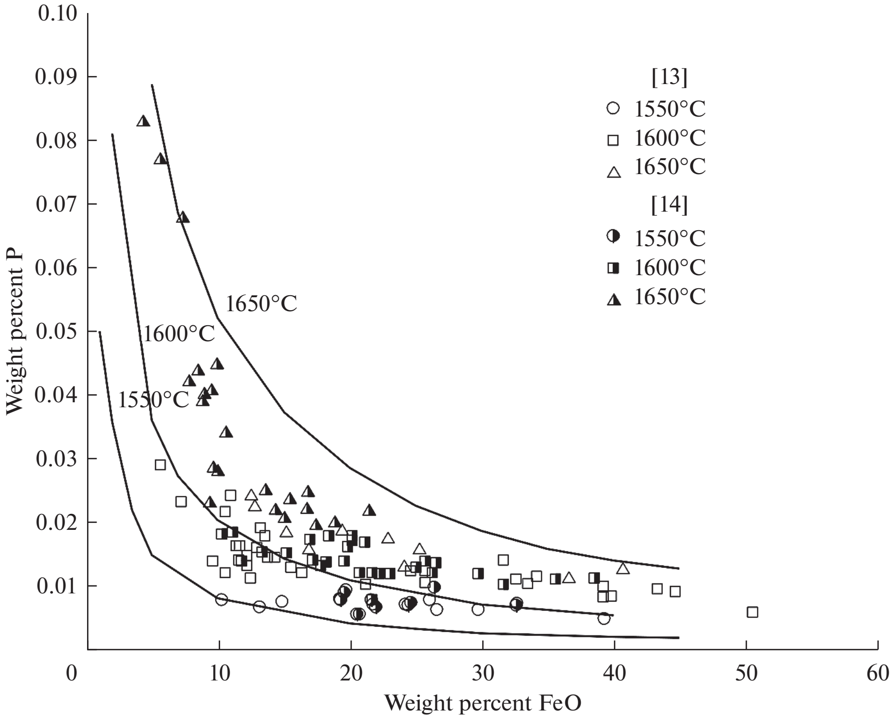

Fig. 5. Relationship between [%P] in liquid Fe and (FeO) in slag.

Sulfur species are present in radioactive and toxic wastes. Sulfides are in focus of attention due to their importance for ferrous and copper metallurgical processes. The thermal properties and stability ranges of sulfide containing systems is necessary for understanding and control of the processes of desulfurization of molten alloys and precipitation of the sulfides during the solidification process. The Ca–Cr–Fe–Mg–Mn–S sulfide sub-system in combination with corresponding oxides is part of the GTOX database (Table 3) and can be used and can be used for thermodynamic calculations [4].

Table 3

GTOX database

Contents	Year 2018
Binary systems	149
Ternary systems	131
Quaternary systems	7
Solid solution phases	117
Compounds	702
Slag Atlas pages	1001

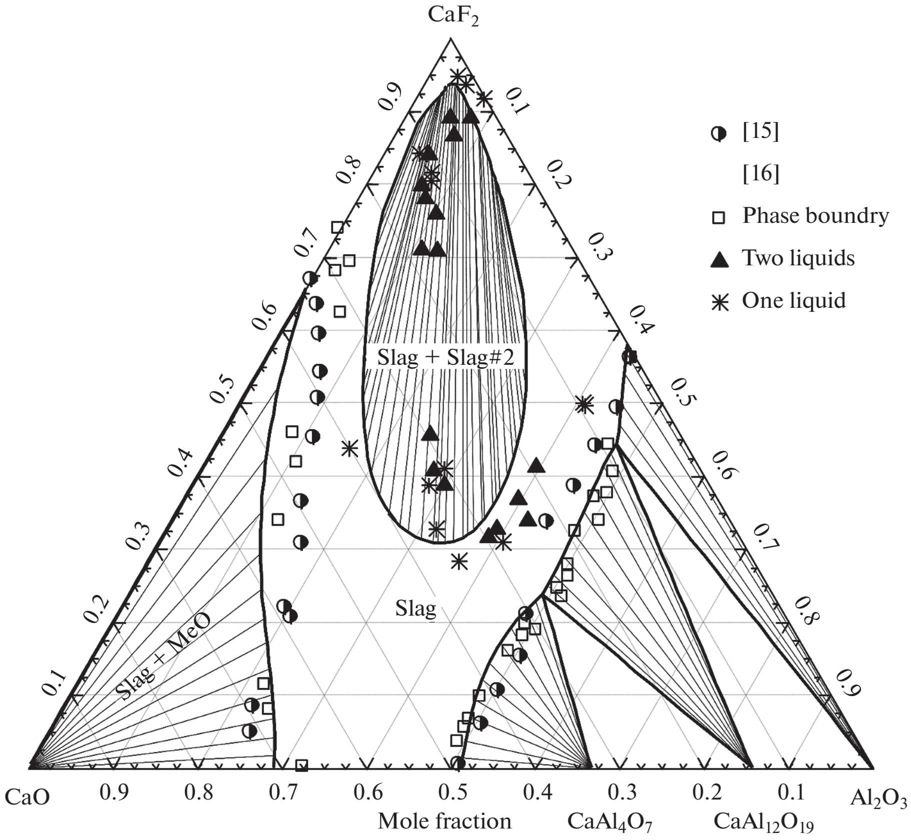

Fig. 6. Isothermal section at 1600°C in Al_2O_3–CaO–CaF_2 system.

CONCLUSIONS

A self-consistent thermodynamic database for the system Al_2O_3–Al_2S_3–CaO–CaF_2–CaS–CrO_x–FeO_x–FeS–MgO–MgS–MnO_x–MnS–K_2O–K_2S–Na_2O–Na_2S–NiO–P_2O_5–SiO_2–SO_3–TiO_x–VO_x which permits the calculation of phase diagrams and thermodynamic properties for any composition and temperature has been established. Phase diagrams calculated using this database show generally good agreement with the experimental phase boundaries. All phase diagrams assessed are presented in a Slag Atlas provided by GTT-Technologies in the framework of the HotVeGas project [17]. The database obtained is successfully used in a very wide range of applications (coal combustion and gasification metallurgy, dephosphorization, fluxing, viscosity modelling).

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