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ACTIVITY INVESTIGATION OF FeO, SiO_2 AND V_2O_5 IN V_2O_5- FeO - SiO_2TERNARY SYSTEMS

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ABSTRACT

The activity of FeO, SiO_2, and V_2O_5 in V_2O_5 - FeO - SiO_2 ternary systems has been investigated. Pure oxides were used as reference mixtures, included in the system in ratios, analogous to those of mixtures, containing waste vanadium catalyst. Two mixtures were prepared: 1st mixture - V_2O_5 - FeO - SiO_2 (pure oxides), 2nd mixture - waste vanadium catalyst - FeO - SiO_2.

The oxygen potential in the systems was determined by the EMF method. The solid electrolyte was ZrO_2 (Y_2O_3), and the reference electrode - a mixture Mo/MoO_2 in 1: 1 ratio, was used as a galvanic cell. The investigations were carried out in an isothermal and a non-isothermal condition. The Gibbs free energy and the activity coefficient were calculated from the experimentally obtained oxygen potential. Equations for $\Delta G_T = f(T)$ were derived for different temperature ranges. New phases were observed in the mixture containing vanadium catalyst.

Keywords: activity, ternary systems V_2O_5 - FeO - SiO_2, EMF method.

INTRODUCTION

The investigations, related to the pyrometallurgical processing of waste vanadium catalysts are of great importance, due to its relatively high content of vanadium. Vanadium imparts hardness, tensile strength and improves the processing properties of steel. Vanadium steels are used for general engineering purposes. The addition of small quantities of vanadium imparts excellent welding characteristics. It is added to steel mainly as ferrovanadium.

In the extractive metallurgy, vanadium is used for deoxidation, alloying, modifying and desulphurization. Therefore, the production of complex alloys, including vanadium, is significant.

The use of low-grade vanadium slags for the production of ferrovanadium by steel works, is an alternative for the future of vanadium oxides. Thermodynamic calculations show the possibility of pyrometallurgical processing of such materials [1].

The effectiveness of the system V_2O_5 – FeO – SiO_2 depends on the thermodynamic activities of the metal oxides in this system. Although there is sufficient literature on the thermodynamic activity of FeO and SiO_2 [2-6], the publications on the thermodynamic activity in this ternary system is non-existent.

The EMF method is one of the main methods for activity determination in multi-compound systems. An electrochemical sensor for insertion into the slag for determining the activity of a metal oxide in it, is disclosed in the patent literature [7].

An electrochemical cell with ZrO_2 (CaO) and a Mo+MoO_2 reference electrode, was used by S. Seetharaman et al. [8]. The values of the FeO activity in metallurgical slags have been reported by a number of authors [9 - 11].

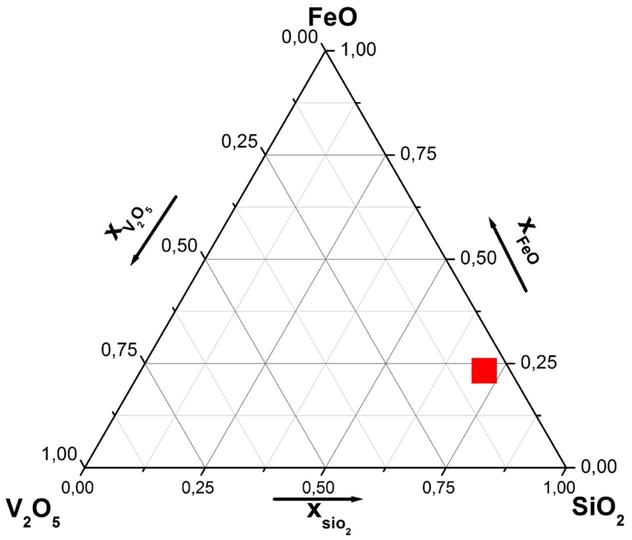

Fig. 1. The investigated area of the system V_2O_5 - Fe_2O_3 - SiO_2.

EXPERIMENTAL

Waste vanadium catalyst and chemically pure oxides of Fe_2O_3, V_2O_5, SiO_2 were used as starting materials. Two mixtures were prepared. Mixture 1 contained pure oxides - V_2O_5 - Fe_2O_3 - SiO_2, in a ratio where the quantities are in similar correlations to those in the waste vanadium catalyst - mixture 2. To assess the impact of the secondary elements present in the waste material on the thermodynamics, the parameters of the synthetic mixture of pure oxides was studied.

The investigated area of thermodynamic studies in the ternary system - V_2O_5 - Fe_2O_3 - SiO_2 is visualised in Fig. 1.

The chemical composition (mass %) of waste vanadium catalyst is shown in Table 1.

The following galvanic cells were used in this work.

$$\underset{P'_{O_2}}{\mathrm{Pt}|\ \text{investigated sample}}\ ||ZrO_2(Y_2O_3)||\ \underset{P'_{O_2}}{Mo/MoO_2\ |\mathrm{Pt}} \quad (1)$$

The schematic diagram of the cell arrangement is illustrated in Fig. 2.

RESULTS AND DISCUSSION

The Gibbs energy ΔG^o_T (MoO_2) values have been reported by a number of authors [12, 13], so they have been used to calculate Delta G (MoO_2).

$$Mo + O_2 = MoO_2 \quad (2)$$

$$\Delta G^o(\ MoO_2) = -570563 + 173.T$$

or $$\lg P_{O_2} = \frac{-29852}{T} + 9{,}051 \quad (3)$$

M. Iwase and his co-workers have developed a “shop floor” activity determination, based on the principles of zirconia sensors [11, 14].

The activity $a_{ox.}$ of a molten oxide in a molten slag is defined by the expression:

$$a_{ox.} = \left(\frac{P_{O_2\ ox.}}{P^0_{O_2\ ox.}}\right)^{1/2} \quad (4)$$

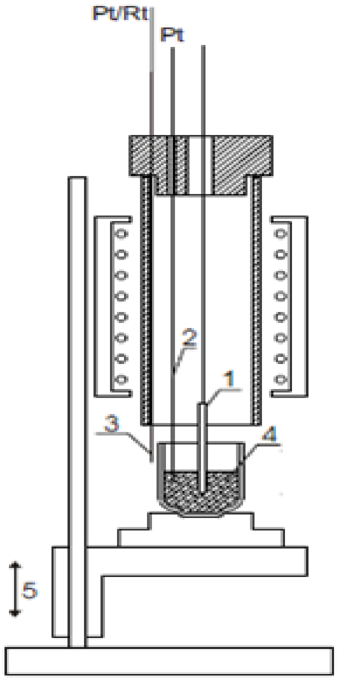

Fig. 2. A schematic diagram of the cell arrangement. 1- zirconia sensor with Mo/MoO_2 as the reference electrode; 2 - Pt-wire; 3 - thermocouple Pt-Rh/Pt; 4 - crucible with sample; 5 - elevator.

Table 1. Chemical composition of the waste vanadium catalyst, %.

V_2O_5	Fe_2O_3	SiO_2	K_2O	Na_2O	Al_2O_3	SO_3
4,12	3,42	57,12	6,71	3,93	0,82	23,88

where $P_{O_2\,ox.}$ is the oxygen partial pressure of the slag in equilibrium with the actual liquid oxide in the slag and $P^0_{O_2\,ox.}$ is the oxygen partial pressure of the slag in equilibrium with pure liquid oxide.

The measured values of the EMF galvanic cell (1) of the equipment (Fig. 1) have been used in the well known thermodynamic relation:

$$\frac{10{,}08\ .E\,(mV)}{T} = log\left(P_{O_2}ox.\right)^{1/2} - log\left(p_{O_2}ref.\right)^{1/2} \tag{5}$$

where E (mV) is EMF, T is the absolute temperature in K and $P_{O_2}ox.$ and $p_{O_2}ref$ are the equilibrium oxygen partial pressures at the oxides and reference electrodes, respectively. Combining equations (4) and (5), the following expression that relates the oxygen partial pressures to the oxide and the reference electrodes to the activity of the oxides in the slag has been obtained:

$$\log a_{ox.} = \frac{10{,}08\,.E}{T} + log\left(\frac{p_{O_2}\,ref.}{p^0_{O_2}\,ox.}\right)^{1/2} \tag{6}$$

The values of $p^0_{O_2}\,ox.$ and $p_{O_2}ref$ are constants for a particular electrode couple. The activity coefficient with respect to liquid oxide is given by the ratio:

$$\gamma_{ox.} = \frac{a_{ox.}}{N_{ox.}} \tag{7}$$

where $N_{ox.}$ is the molar part of oxides into the slag system.

Activity of FeO

The equilibrium relation of iron oxidation is based on the following reaction:

$Fe + 1/2O_2 = FeO$;

$\Delta G^0 = -240084{,}3 + 52{,}75.T$, J/mol;

$$logP_{O_2} = -\frac{12538{,}91}{T} + 2{,}75 \text{ [18]} \tag{8}$$

The total cell reaction will be:

$$0{,}5\ MoO_2 + Fe = 0{,}5\ Mo + FeO \tag{9}$$

On the basis of Equation (6), using Equations (3) and (8), the following theoretical relation of ferrous oxide activity was obtained:

$$loga_{FeO} = 1{,}78 - \frac{2387{,}1 - 10{,}08\,.E}{T} \tag{10}$$

Activity of V_2O_5

The equilibrium relation of the vanadium oxidation is based on the following reaction:

$2/5\ V + ½\ O_2 = 1/5\ V_2O_5$;

$\Delta G^0 = -322005 + 107{,}48.T$, J/mol;

$$logP_{O_2} = -\frac{16817{,}39}{T} + 5{,}61 \tag{11}$$

In this paper, the equation for Gibbs free energy change of the reaction was calculated (11) from the published thermodynamic properties [16].

The total cell reaction is as follows:

$$½MoO_2 + 2/5V = ½\ Mo + 1/5V_2O_5 \tag{12}$$

On the basis of Equation (6), using Equations (3) and (11), the following theoretical relation of vanadium pentoxide activity was obtained:

$$loga_{V_2O_5} = -1{,}08 + \frac{1891{,}4 - 10{,}08\,.E}{T} \tag{13}$$

Activity of SiO_2

The equilibrium relation of the silicon dioxide is based on the following reaction:

$Si + O_2 = SiO_2$;

$\Delta G^0 = -581900 + 221{,}8.T$, J/mol;

$$logP_{O_2} = -\frac{30391}{T} + 11{,}58 \text{ [17]} \tag{14}$$

The total cell reaction is:

$$MoO_2 + Si = Mo + SiO_2 \tag{15}$$

$$loga_{SiO_2} = -1{,}26 + \frac{269{,}5 - 10{,}08\,.E}{T} \tag{16}$$

The obtained experimental results for the ternary system V_2O_5 - FeO - SiO_2 were processed and grouped. The results for a mixture containing vanadium waste materials were compared with the synthetic mixture. The oxygen potential and Gibbs free energy change in the investigated system were calculated. Fig. 3 shows graphically the dependence of the Gibbs free energy of formation on the temperature.

With the experimental results (Fig.3), the delta G_T = f (T) equations have been deduced. The equations of mixture 1 are:

delta G_{1_1} = 177270-431.T, J/mol, (R^2 = 0.9337),
T = 1096 - 1319 K
delta G_{1_2} = -63543-57,5.T, J/mol, R^2 = 0,8655),
T = 1573 - 1761 K (17)

Both processes of mixture 2, containing vanadium catalyst and Fe_2O_3, are described by the equations:

delta G_{2_1} = -470181 + 217,13.T, J/mol, (R^2 = 0,9946),
T = 1194 - 1514 K
delta G_{2_2} = -481471+194.73.T, J/mol, (R^2 = 0,6584),
T = 1544 - 1673 K (18)

Two processes were observed in mixture 1 and mixture 2. The reversible reaction $Fe_2O_3 \leftrightarrow Fe_3O_4$, according to the theoretical calculations of delta G, occurs in a low- temperature range. In both mixtures an endothermic effect, corresponding to the formation of vanadates was observed - at temperatures 1155 K for mixture 1, and at 1022 K - for mixture 2. In the waste vanadium catalyst (as opposed to pure oxides which have V_2O_5), oxides of vanadium in the form of V_xO_y (V_2O_3, VO, V_2O_4, V_6O_{13}) and the formation of those vanadates is possible, due to its repeated thermal transformations. The X-ray diffraction analysis confirmed the presence of ferrovanadates - Iron - Vanadium Oxide - $Fe_{6.5}V_{11.5}O_{35}$. The melting point for mixture 1 was 1428 K, and for mixture 2-1465 K [18].

The activity and the activity coefficient were calculated from experimental data. Measurements were carried out under isothermal heating at temperatures 1573 K and 1673 K. The variations of parameters' range are presented in Table 2.

Fig. 4 shows the dependence of the vanadium oxide coefficient activity on time. The ferrous oxide and the silicon oxide curves are similar with the vanadium oxide shown in Fig. 4.

Fig. 5 illustrates the change of the vanadium oxide activity coefficient at non- isothermal heating up to 1760 K for both mixtures. Mixture 2, containing waste vanadium catalyst, has a higher activity coefficient than the synthetic mixture 1.

Dependence of the three oxides activity coefficients in the ternary system V_2O_5 - FeO - SiO_2 on time, at temperature 1573 K for mixture 1, is given in Fig. 6, and for mixture 2 - in Fig. 7. It was found that the vanadium oxide activity coefficient has the highest values. In the synthetic mixture 1, this parameter decreases while in mixture 2, containing waste vanadium catalyst, the activity coefficient increases with a clearly defined maximum of about 80 min, and a subsequent decrease.

The dependences of mixture 1 and mixture 2 activity coefficients for the studied oxides as a function of time

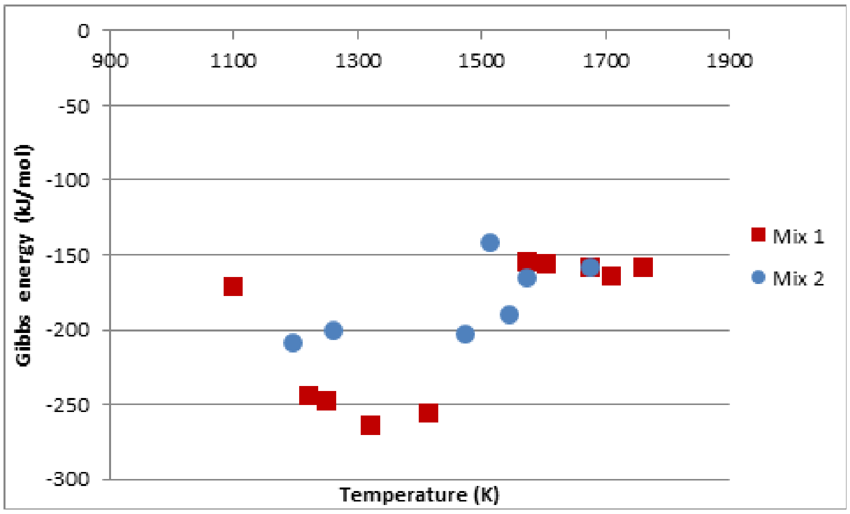

Fig. 3. Correlation between Gibbs free energy of formation and temperature. (Mix 1- synthetic mixture, Mix 2 - waste vanadium catalyst and Fe_2O_3 mixture).

Table 2. Activity ($a_{ox.}$) and coefficient activity ($\Upsilon_{ox.}$) changes.

	Mixture 1		Mixture 2	
Temperature, K	a_{FeO}	Υ_{FeO}	a_{FeO}	Υ_{FeO}
1573	0,12-0,42	0,035-4,51	0,01-0,75	0,71-2,5
1673	0,06-0,24	0,30-1,46	0,05-0,24	0,37-1,4
	a_{SiO2}	Υ_{SiO2}	a_{SiO2}	Υ_{SiO2}
1573	0,05-0,018	0,05-0,018	$7{,}3.10^{-5}$-0,034	$7{,}3.10^{-5}$-0,034
1673	0,0022-0,0087	0,0022-0,0087	0,0017-0,0086	0,0017-0,0086
	a_{V2O5}	Υ_{V2O5}	a_{V2O5}	Υ_{V2O5}
1573	0,086-0,303	5,54-19,42	0,0043-0,55	0,27-35,03
1673	0,03-0,12	1,95-7,82	0,025-0,11	1,58-6,8

at 1673 K, are presented in Figs. 8 and 9. Vanadium oxide has the highest activity coefficient values. The experimental activity coefficients of SiO_2 FeO and V_2O_5 decrease up to the 60th min and after that start increasing.

The comparison of experimental activity coefficients of both mixtures at temperature 1673K shows a minimum of the curves above the 30th min, earlier for mixture 1. After this minimum, the values of the

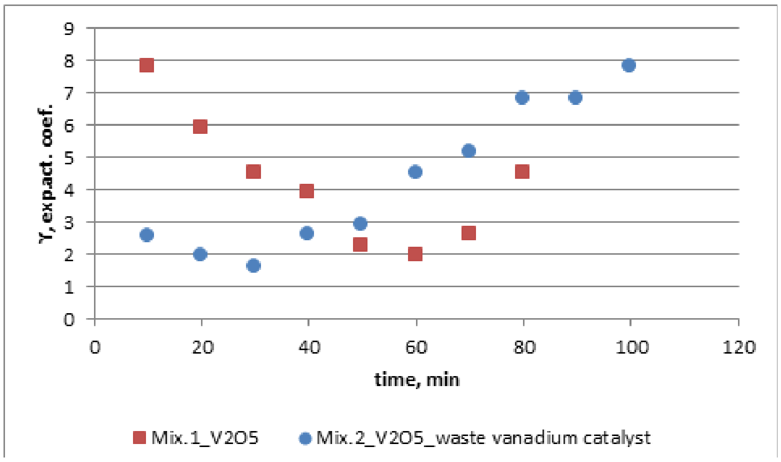

Fig. 4. Dependence of the experimental activity coefficient on V_2O_5 on time, at temperature 1673 K.

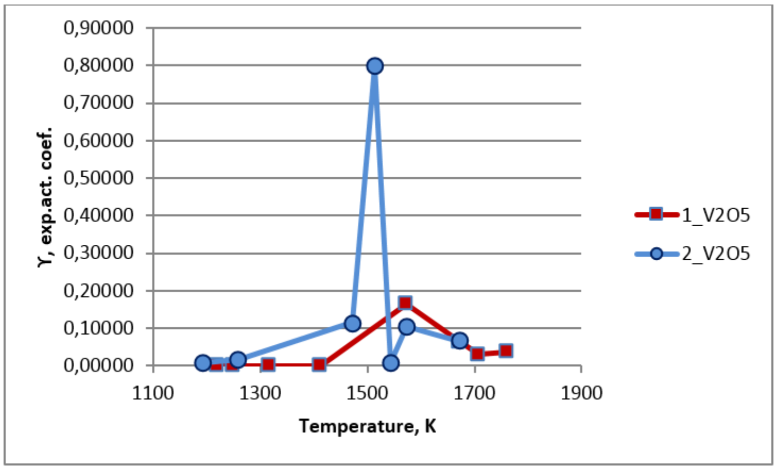

Fig. 5. Dependence of the experimental activity coefficient of V_2O_5 on temperature.

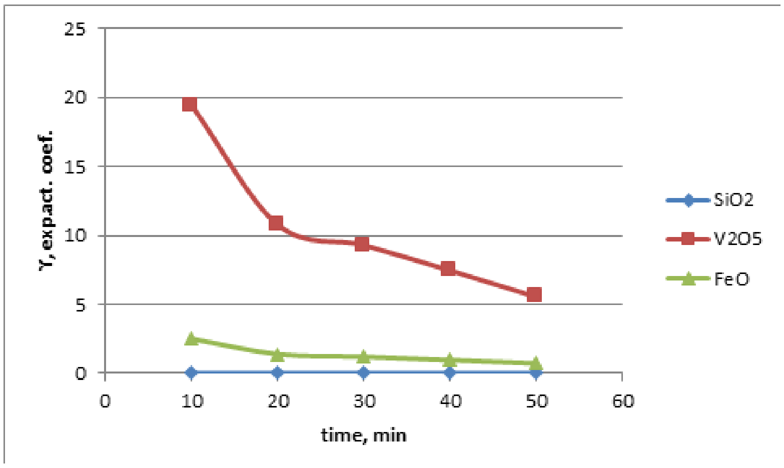

Fig. 6. Difference between the experimental activity coefficients for Mixture 1 as a function of time, in the isothermal heat treatment at temperature 1573 K.

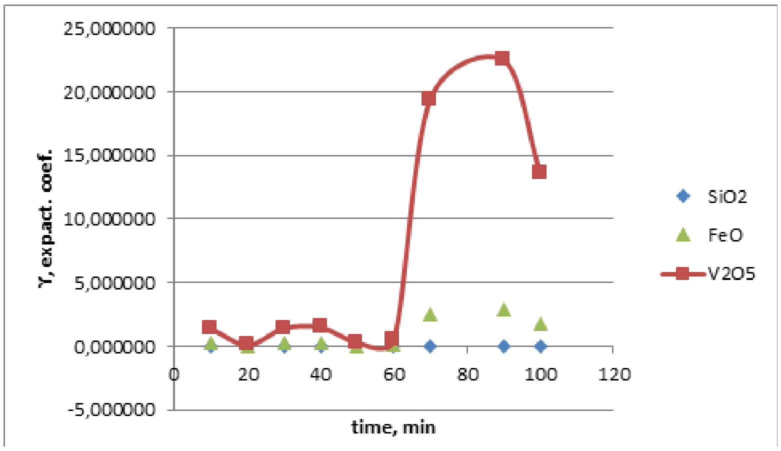

Fig. 7. Difference between the experimental activity coefficients for Mixture 2 as a function of time, in the isothermal heat treatment at temperature 1573 K.

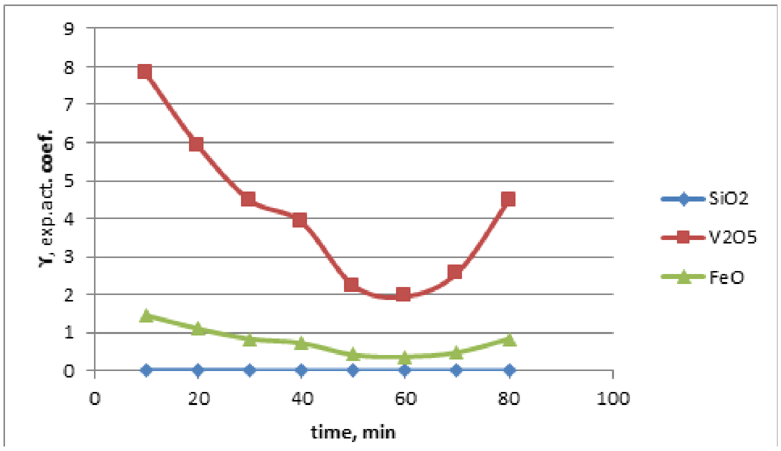

Fig. 8. Difference between the experimental activity coefficients for Mixture 1 as a function of time, in the isothermal heat treatment at temperature 1673 K.

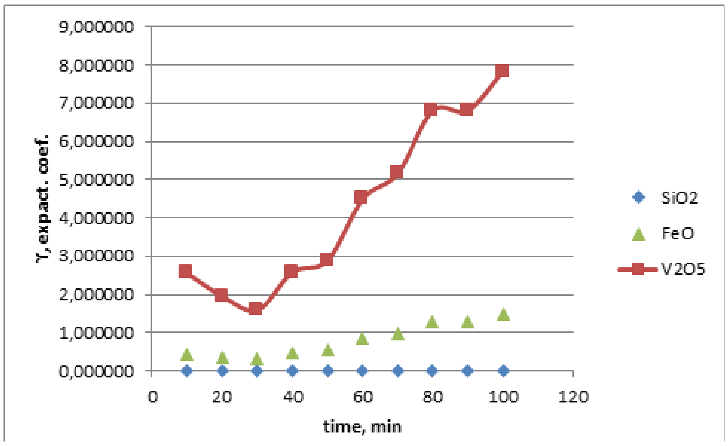

Fig. 9. Difference between the experimental activity coefficients for Mixture 2 as a function of time, in the isothermal heat treatment at temperature 1673 K.

parameters increase and the intensity of the vanadium oxide activity coefficients is the highest.

CONCLUSIONS

Activity and activity coefficients in isothermal heating at temperatures of 1573 K and 1673K were calculated from experimental data. The highest values were deduced for vanadium pentoxide, both for the synthetic mixture and for the mixture containing waste material (vanadium catalyst). The calculated vanadium oxide activity has the highest values in the mixture containing waste vanadium catalyst, at non-isothermal heating up to temperature 1760 K. The equation for $\Delta G_T = f(T)$ was obtained from the experimental data. The results show that in the ternary system V_2O_5 - FeO - SiO_2, at the studied temperatures and ratios between the oxides, two processes take place.

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