

# THERMODYNAMIC ACTIVITIES OF $V_2O_3$ , MnO, AND FeO IN QUATERNARY SYSTEM $V_2O_3 - FeO - SiO_2 - MnO$

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The activities of FeO,  $V_2O_3$  and MnO in quaternary systems  $V_2O_3$ -FeO-SiO<sub>2</sub>-MnO have been investigated. Investigation of thermodynamic data of this slag system, aims extracting vanadium, from the waste and obtaining Mn-V alloy with potential industrial application. The oxygen potential in the systems was determined by the Electromotive force (EMF) method. The solid electrolyte was ZrO<sub>2</sub> (CaO), and the reference electrode - a mixture of Mo/MoO<sub>2</sub> was used as a galvanic cell. The Gibbs free energy and the activity were calculated based on experimentally obtained oxygen potential. On the basis thermodynamics of the calculations, the experimental results revealed the possibility of obtaining a complex alloy from the manganese concentrate and the vanadium waste catalyst.

*Key words:* thermodynamic, activity, quaternary systems  $V_2O_3 - FeO - SiO_2 - MnO$ , EMF method

## INTRODUCTION

Complex alloys find an ever-wider application. Significant quantities of catalysts are dumped annually. Waste catalysts have yet to be studied for a metallurgical use. The extraction of the valuable metals will have economic and ecological effects.

Studies in the present work are related to the possibility of complex pyrometallurgical processing of manganese concentrate and waste vanadium catalyst. The technological possibility of their processing demonstrates the need for additional specific thermodynamic research.

Thermodynamic studies, and in particular the determination of the activities of the components in complex systems, are essential for obtaining real alloy. The effectiveness of the  $V_2O_3$ -FeO-SiO<sub>2</sub>-MnO system depends on the activities of the respective metal oxides in this system.

The activities of individual components present in the investigated system have been considered by other authors, but in other slag systems. The EMF method with solid electrolyte is one of the main methods used in the thermodynamic study of the processes in the metallurgical aggregate and to determine the activity in multi-component systems [1]. When combining a waste vanadium catalyst and manganese concentrate, the main components of the composition are  $V_2O_5$ ;  $Fe_2O_3$ ; MnO and SiO<sub>2</sub>, which results in the formation of a quaternary system.

Thermal decomposition of divanadium pentoxide is a sequence of transformations from  $V_2O_5$  via VO<sub>2</sub> to  $V_2O_3$ . The thermal decomposition starts with the loss of

oxygen, followed by diffusion and defect formation [2]. In an inert atmosphere, the decomposition pathway is  $FeCO_3 \rightarrow Fe_3O_4$  below 1 006 K and  $FeCO_3 \rightarrow FeO + Fe_3O_4$  above 1 006 K [3]. Thermal decomposition of iron oxides scheme is  $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$  and starts at temperatures above 845 K [4, 5] and on condition that  $Fe_2O_3$  is the most unstable iron oxide among the three iron oxides, whereas FeO is the most stable one. It was found that the temperature of intensive thermal decomposition of  $Fe_2O_3$  in the inert gas environment is in the range of 1 473–1 573 K, while the thermal decomposition of  $Fe_3O_4$  could be sped up when the temperature is above 1 773 K in the inert gas [6]. The equilibrium partial pressure of oxygen ( $p_{O_2}$ ), as a function of temperature for hematite, magnetite and wüstite, increases with the increase of temperature. The thermal decomposition of hematite will accelerate at above 1 500 K.

This paper provides experimentally measurement of the activities of FeO,  $V_2O_3$  and MnO in  $V_2O_3$ -FeO-SiO<sub>2</sub>-MnO quaternary systems, of a metallurgical system, containing waste material (vanadium catalyst). The study is aimed to recycling waste vanadium catalyst and the subsequent obtaining of a complex alloy. The literary reference shows that so far such a system has not been investigated.

## EXPERIMENTAL

### Materials and equipment

The chemical composition of the vanadium catalyst and manganese concentrate, defined by weight, via ICP-OES analysis is shown in Tables 1 and 2.

Two mixtures have been prepared. Mixture 1, which is consisting of pure oxides, that are present in the system and are in analogous proportions to mixture 2. Mix-

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Table 1 **Chemical composition of the waste vanadium catalyst / wt. %**

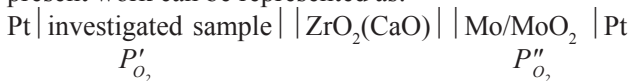
V <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>
4,12	3,4	57,12	6,71	3,93	0,82

Table 2 **Chemical composition of the manganese concentrate / wt. %.**

MnO	CO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>
44,56	19,33	1,79	0,31	12,4	3,90	2,10

ture 1 is composed of 2,5g V<sub>2</sub>O<sub>5</sub>, 22,5g MnO, 35g SiO<sub>2</sub> and 40 g Fe<sub>2</sub>O<sub>3</sub>, and mixture 2 contains 50 g waste vanadium catalyst and 50 g of manganese concentrate and 37,5 g Fe<sub>2</sub>O<sub>3</sub>. The initial materials were with fine dispersion composition. The mixtures were heated in an elevator type furnace. The test mixture was placed in a corundum crucible. The measurement of EMF was accomplished by using zirconia sensor with accuracy of error within  $\leq 0,5$ . For the galvanic cell measurements, the reference electrode of an equimolar mixture of Mo and MoO<sub>2</sub> was into the electrolyte along with a platinum wire embedded in the same which served as the electrode lead. The mixtures were heated and held for 2 hours in an inert environment or until a constant EMF value is reached.

The galvanic cell used for the measurements in the present work can be represented as:



The total cell reaction will be:



where: Me - metals of the system under investigation (Fe, V and Mn); Me<sub>x</sub>O<sub>y</sub> - oxides of the test system (FeO, V<sub>2</sub>O<sub>5</sub>, MnO)

The activity was calculated based on Nernst relationship.

$$\Delta G = -n.F.E = p.\Delta G_{\text{Me}_x\text{O}_y}^0 - m.\Delta G_{\text{MoO}_2}^0 + RT \ln(a_{\text{Me}_x\text{O}_y}^p), \quad (2)$$

where - n is the number of electrons taking part in the electrode reactions, E is the cell EMF (V) and F is Faradays constant.

## RESULTS AND DISCUSSION

The Gibbs energy data for the reference electrode was  $\Delta G_{\text{T}}^0(\text{MoO}_2)$  taken from other authors' publications [7]



$$\Delta G^0(\text{MoO}_2) = -570\,563 + 173\,T \quad \text{or}$$

$$\lg P_{\text{O}_2} = \frac{-29852}{T} + 9,051 \quad (4)$$

The thermodynamic data obtained from the phase equilibrium study in the test mixtures was determined using the oxidation potential of the system calculated according to equations (5) and (6).

$$E = \frac{RT}{nF} (\lg P_{\text{O}_2}'' - \lg P_{\text{O}_2}') \quad (5)$$

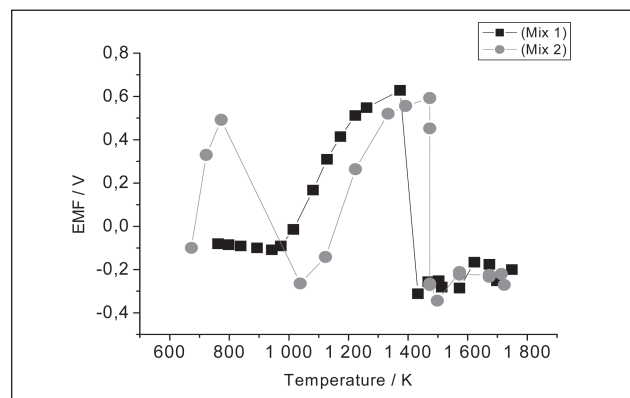


Figure 1 Dependence of EMF on temperature

$$\lg P_{\text{O}_2}' = -\frac{nFE}{RT} - \frac{29852}{T} + 9,051 \quad (6)$$

Figure 1 shows the EMF values (V) according to the temperature of the mixtures tested. When comparing the change of the electromotive force with the temperature, the two mixtures, have similar changes. Mix 2 shows a peak displacement of 373 – 423 K for higher temperatures.

The Gibbs energy changes were calculated according to equation (7).

$$\Delta G = R T \ln P_{\text{O}_2}' \quad (7)$$

From the results of the Gibbs energy change, equations for the dependence  $\Delta G = f(T)$  of the two mixtures were derived. Table 3 presents the results of the deduced Gibbs energy change equations of both, synthetic and the mixture containing waste vanadium catalyst and manganese concentrate. For the whole temperature range for both mixtures, three stages were clearly formed. The results are experimental and describe the dependency of Gibbs energy at non-isothermal heating.

Table 3 **Experimentally obtained equations of  $\Delta G = f(T)$  of the tested mixtures 1 and 2**

Temperature rang / K	$\Delta G_{\text{exp}} / \text{J/mol}$	R <sup>2</sup>
Mixture 1		
1 015-1 261 K	$\Delta G = 148\,758 - 318,4\,T$	0,9702
1 468-1 573 K	$\Delta G = -279\,210 + 125,6\,T$	0,9046
1 623-1 745 K	$\Delta G = -371\,694 + 167,5\,T$	0,9267
Mixture 2		
1 038-1 333 K	$\Delta G = 292\,323 - 396,48\,T$	0,9651
1 333-1 473 K	$\Delta G = -2,10^6 + 1\,219\,T$	0,8650
1 573-1 713 K	$\Delta G = -226\,323 + 84,8\,T$	0,9267

R<sup>2</sup> – correlation coefficient

Table 4 shows the possible reactions that occur on the cell. These reactions were described with the standard Gibbs energy change and were applied according to the Nernst equation to determine the activities. The data on the specific heat capacity Cp, enthalpy H and entropy S by O. Essin and P. Geld.

The calculated value of  $\Delta G = f(T)$  of MnO is identical to that quoted in the literature [8].

The activities of FeO, V<sub>2</sub>O<sub>5</sub> and MnO in the investigated system were calculated according to equation (2) for each reaction in Table 4. The results of the change in

Table 4 Reactions in the cell

$\text{Fe} + 1/2 \text{O}_2 = \text{FeO};$ $\Delta G^\circ = -240\,084,3 + 52,75 \text{ T}$ / J/mol	$1/2 \text{MoO}_2 + \text{Fe} = \text{FeO} + 1/2$ $\text{Mo}$
$4 \text{V} + 3 \text{O}_2 = 2 \text{V}_2\text{O}_3$ $\Delta G^\circ = -2\,533,1 + 0,652 \text{ T} / \text{J/mol};$	$3 \text{MoO}_2 + 4 \text{V} = 2 \text{V}_2\text{O}_3 +$ $3 \text{Mo}$
$2 \text{Mn} + 1/2 \text{O}_2 = 2 \text{MnO};$ $\Delta G^\circ = -386\,334 + 78,341 \text{ T} / \text{J/mol}$	$\text{MoO}_2 + 2 \text{Mn} = 2 \text{MnO} + \text{Mo}$

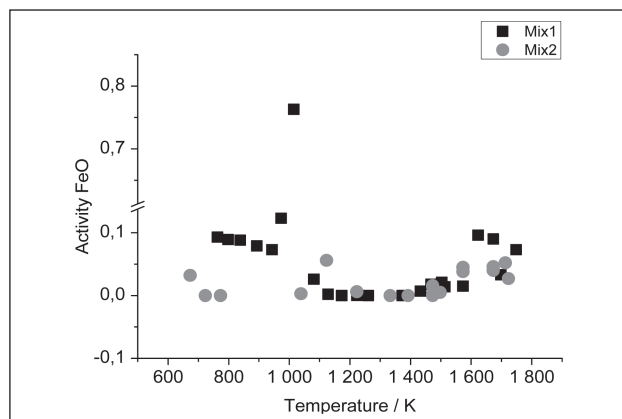
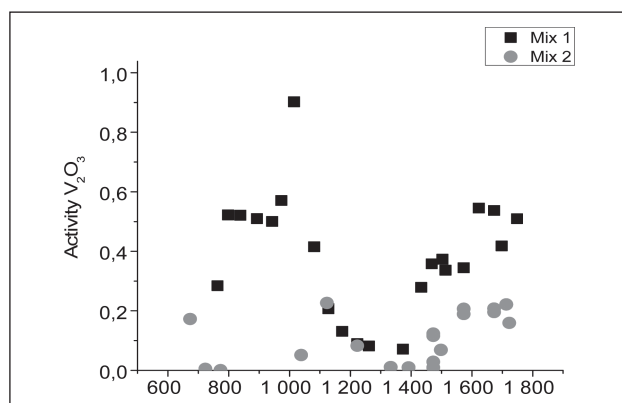


Figure 2 Change of FeO activity in mixtures 1 and 2 under heating

Figure 3 Change of V<sub>2</sub>O<sub>3</sub> activity in mixtures 1 and 2 under heating

the FeO, V<sub>2</sub>O<sub>3</sub> and MnO activities depending on temperature are presented in Figures 2 to 4.

Metal Mn-Fe solutions and MnO-FeO slag melts have a similar thermodynamic behaviour and therefore they may be assumed as ideal. This is confirmed by Table 4 for the values of delta  $\Delta G$  for Fe-FeO and Mn-MnO. That expounds their analogous behavior to the defined activities presented in Figures 2 and 4. Temperature had a negligible effect on the activity of FeO, MnO and V<sub>2</sub>O<sub>3</sub> in investigated system.

Figure 2 makes it clear that the activity of FeO is relatively low. The highest values were recorded for mixture 1 at a temperature of 1 015 K-  $a_{\text{FeO}}=0,76$ . For mixture 2,  $a_{\text{FeO}}=0,056$  at 1 123 K. As it can be seen from Figure 3, the highest activity of V<sub>2</sub>O<sub>3</sub> was recorded for mixture 1 at 1 015 K -  $a_{\text{V}_2\text{O}_3}=0,902$ . At 773 K, there was a thermal decomposition of V<sub>2</sub>O<sub>5</sub>, forming VO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>. Above 873 K, the stable oxide was V<sub>2</sub>O<sub>3</sub> [2]. Activity peaks in mixture 1 are recorded at 800 - 973 K. Depending on the diagram (Figure 5) [9], ferrovana-

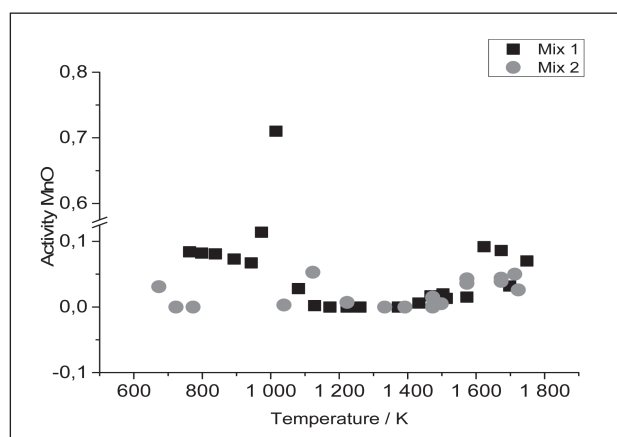
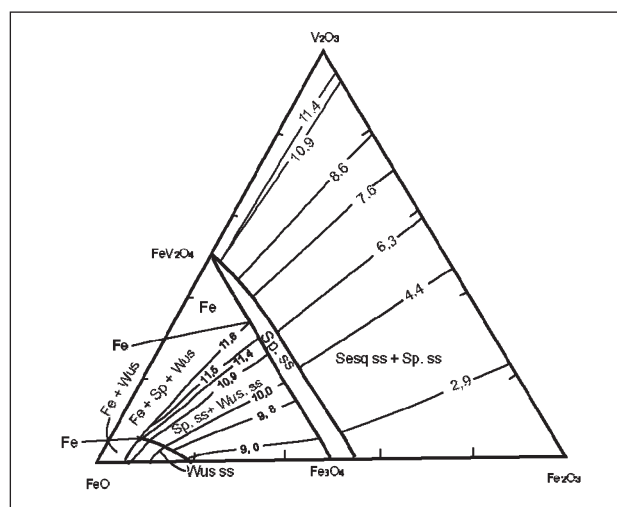


Figure 4 Change of MnO activity in mixtures 1 and 2 under heating

Figure 5 System FeO-Fe<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>3</sub> [9]

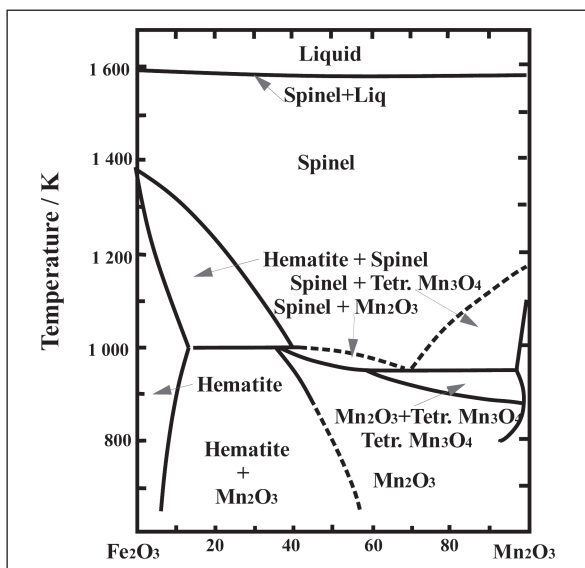
dates are possible to be obtained. The thick curves in the diagram, on Figure 5, outline the areas of the different groups of phases, and the thinner lines are isobaric of oxidithe at 1 500 K.

In the waste vanadium catalyst, its oxides have undergone multiple thermal transformations and are also present in a lower degree of oxidation, which confirms the possibility of formation of this ferrovanadate. For mixture 2, the maximum is observed at 1 123 K with  $a_{\text{V}_2\text{O}_3}=0,226$ .

Relatively high activity was also recorded for manganese oxide. For Mix 1, high activity was reported at 1 015 K and also at temperatures above 1 623 K. Analogous performance was also observed for mixture 2.

In the temperature range of 855 - 940 K a solid solution between Fe<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O<sub>3</sub> of perithetic type is formed, which decomposes at about 930 °C to a solid solution between Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>, which can also be confirmed by the Fe<sub>2</sub>O<sub>3</sub> - Mn<sub>2</sub>O<sub>3</sub> state diagram, illustrated on Figure 6 [10].

Divanadium trioxide (V<sub>2</sub>O<sub>3</sub>) has the highest experimentally observed activity. The presence of impurities affects the activity of the main components. Therefore, the activity reported for mixture 2 is lower compared to mixture 1 (containing pure oxides).



**Figure 6** System  $Mn_2O_3$ - $Fe_2O_3$  [10]

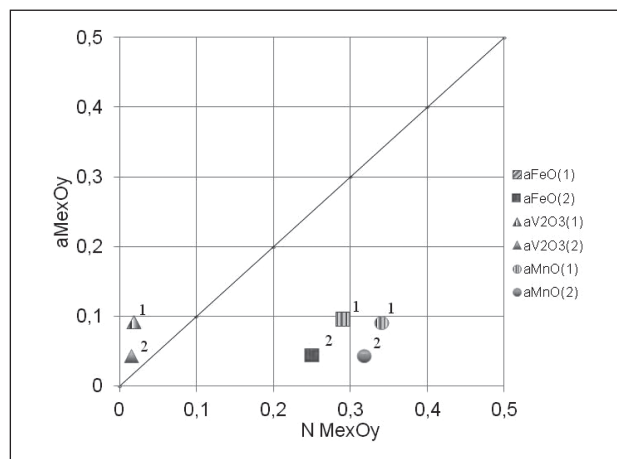
Divanadium trioxide ( $V_2O_5$ ) has the highest experimentally observed activity. The presence of impurities affects the activity of the main components. Therefore, the activity reported for mixture 2 is lower compared to mixture 1 (containing pure oxides).

Figure 7 shows the dependence of the activity of the investigated oxides on the respective concentration at 1 650 K. The values of the activity were considered against the ideal straight line to determine the probability as well as the degree of stratification. The activity during the first stage has its maximum at 1 015 K for mixture 1 and at 1 039 K for mixture 2. The solid-phase interaction processes are characteristic of this stage as well as the positive deviation from Henry's law for ideal solutions. The lowest activity was recorded during the second stage. The third stage begins from 1 650 K.

Some shifts from Henry's law at 1 650 K are observed with vanadium oxide. This can lead to insignificant stratification of this phase, which at high temperatures (1 750 K) disappears. The experimental results show the possibility of obtaining a complex alloy involving manganese concentrate and waste vanadium catalyst.

## CONCLUSION

The influence of the additional impurities present in the manganese concentrate and the vanadium catalyst on the thermodynamic properties of the studied four-component system was investigated. Experimentally, three sub-stages for investigated temperature range based on determined Gibbs energy were found out. Both mixtures have similar thermodynamic changes. Based on the experimental obtained data, the  $FeO$ ,  $V_2O_5$



**Figure 7** Dependence of  $FeO$ ,  $V_2O_5$  and  $MnO$  on their concentration in the investigated system at 1 650 K.

and  $MnO$  activities were calculated at heating up to 1 748 K. The highest activity for all oxides was recorded at 1 015 K. The thermodynamic characteristics of the synthetic mixture and the mixture containing catalyst and concentrate are highly correlated. At a suitable temperature (over 1 750 K), a complex alloy can be formed using manganese concentrate and a waste vanadium catalyst.

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**Note:** The responsible for English language is PhD Maria Todorova, Sofia, Bulgaria