
Phase transformations and thermodynamics of binary systems $\text{Fe}_2\text{O}_3 - \text{V}_2\text{O}_5$ and $\text{Fe}_2\text{O}_3 - \text{MnO}$ at high temperatures

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Abstract: The phase transformations and thermodynamics of the binary systems of $\text{Fe}_2\text{O}_3\text{-MnO}_2$ as well as $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ have been investigated. Pure oxides, waste vanadium catalyst (containing ~4.12% V_2O_5) and manganese carbonate ore concentrate containing ~44.56% MnO have been used for preparation of the mixtures. The purpose of these investigations was to study phase transformations, some thermodynamic characteristics of waste products, containing Fe-Mn-V-Si-O and further producing real Fe-Mn-V alloys from this products. Two methods have been used to study these systems. Four mixtures were prepared for the investigation: mix 1 - pure oxides - V_2O_5 , Fe_2O_3 , SiO_2 ; mix 2 - waste vanadium catalyst, Fe_2O_3 ; mix 3 - pure oxides - MnO_2 , Fe_2O_3 , SiO_2 ; mix 4 - manganese concentrate, Fe_2O_3 . Phase transformations have been defined by DTA and X-ray analysis up to 1473K. The formation of new phases FeV_2O_4 and MnFe_2O_4 (Jacobsite) in the samples can be formed up to this temperature only if in the initial materials there is waste vanadium catalyst and manganese concentrate. In the temperature range 853K – 953K solid solution between Fe_2O_3 and Mn_2O_3 is formed (for pure oxides – mix3) and then it decomposes peritectically at 1203K. The oxygen potential, respectively Gibbs energy in the temperature range 1073K – 1173K has been calculated using EMF method with reference electrode Ni/NiO. Gibbs energy values for mix 1 and mix 2 are very close compared to the theoretical indications calculated for Fe_2O_3 . Gibbs energy for mix 3 is in compliance with the data of manganese oxide.

Keywords: DTA Analysis, EMF Method, Gibbs Energy

1. Introduction

The systems Fe-Mn-O and Fe-V-O have been discussed by a number of authors. They have studied the systems from different aspects.

Lina Kjellqvist and Malin Selleby [1] assessed the ternary system Fe-Mn-O. A part of the binary Mn-O system was reassessed. The thermochemistry of iron manganese oxide spinels was studied by Sophie Guillemet-Fritsch et al. [2]. Takashi Miyano and Nicolas J. Beukes [3] discussed quantitatively the phase relations in the system Mn-Fe-Si-O. The phase relations involve major oxide minerals of the ores, namely, braunite, braunite II, hausmannite, bixbyite, jacobsite, and hematite. They were constructed under quartz-deficient conditions, using existing and estimated thermodynamic data and mineral assemblages from the ores.

Phase equilibrium of the $\text{Mn}_x\text{Fe}_y\text{O}$ system ($\text{Fe}/\text{Mn} = 2$) was studied in the temperature range 1223 – 1393K and in the oxygen partial pressure interval from 101 to 105 Pa by measuring the electrical conductivity of the weight of the sample [4].

To define the Fe-Mn-O and Fe-V-O systems not only by Mössbauer spectroscopy and X-ray analyses [6, 7] were used but also they were analyzed thermogravimetrically [4, 5, 10].

Thermodynamics of these systems has been studied by a number of authors [8, 9, 12, 13, 14] Jacob, K. T. and Alcock, C. B. [12] calculated the measurements using solid oxide galvanic cells incorporating $\text{ZrO}_2\text{-CaO}$ and $\text{ThO}_2\text{-YO}_{1.5}$ electrolytes by the help of electromotive force (EMF). Toshihide Tsuji et al. [4] calculated the standard enthalpy and entropy changes per one mole oxygen for the phase boundary reaction between spinel and spinel+hematite on the basis of thermogravimetric data.

The system Fe₂O₃-MnO-V₂O₅-SiO₂ is included in the chemical composition of the waste products of the chemical and metallurgical industry.

Vanadium catalyst is used for the sulfur acid production. It is deposited as a waste product after its deactivation and this product is charged again with a fresh catalyst. Annually between 500 and 1000 tons of vanadium catalyst are released from sulfur acid production and at the same time it contains significant quantity of deficit vanadium. The toxicity of the vanadium causes certain environmental problems which is an additional consideration to look for ways to utilize this valuable waste product. Vanadium catalyst utilization is too expensive and it is also inefficient.

The ore-bed in the region of the village of Obrochishte (Varna area) contains large stocks of relatively poor manganese carbonate ore (Mn nearly 23 %). Despite the great number of experiments for its use, it was utilized as an addition to manganese agglomerate in the production of manganese alloys. Bulgarian manganese ore and waste vanadium catalyst cut down the production cost of Mn-V ferroalloy production (electro ore-smelting process) considerably.

In the present work, the phase changes in the systems Fe-V-O and Fe-Mn-O were studied at heating up to 1473K. Pure oxides of iron, manganese, vanadium and waste materials (waste vanadium catalyst and manganese concentrate) were used as initial materials. Some thermodynamic characteristics of those systems were determined. The main purpose is further obtention of real complex Fe-Mn-V alloys from these waste products.

2. Experimental

2.1. Materials and Apparatus

The nominal chemical composition (mass %) of the manganese concentrate is shown in Table 1. The nominal chemical composition (mass %) of waste vanadium catalyst is shown in Table2.

Table 1. Chemical composition of manganese concentrate, %.

MnO	CO ₂	FeS ₂	Fe ₂ O ₃	P ₂ O ₅	SiO ₂	MgO	CaO	Al ₂ O ₃
44,56	19,33	2,25	1,79	0,31	12,4	2,00	3,90	2,10

Table 2. Chemical composition of waste vanadium catalyst, %.

V ₂ O ₅	Fe ₂ O ₃	SiO ₂	K ₂ O	Na ₂ O	Al ₂ O ₃	SO ₃
4,12	3,4	57,12	6,71	3,93	0,82	23,88

Pure Fe₂O₃, MnO, V₂O₅, SiO₂ oxides were also used as initial materials. Their quantities are in such correlations as those in manganese concentrate and waste vanadium catalyst.

Four mixtures were prepared for the experiments.

Mix 1 – pure oxides (mass.%) - V₂O₅ – 5.0 g; Fe₂O₃ – 25.0g ; SiO₂ – 70.0g.

Mix 2 - waste vanadium catalyst 121.35 g and Fe₂O₃ - 21 g. (21g Fe₂O₃ is different from the needed quantity of iron in

the mixture).

Mix 3 - pure oxides (mass.%) MnO – 45.0g (55.15g MnO₂); SiO₂ 13.0g; Fe₂O₃ – 42.0g.

Mix 4 – manganese concentrate 100g and Fe₂O₃ – 40.21g (40.21g Fe₂O₃ is different from the needed quantity of iron in the mixture).

The samples were prepared as tablets with $\phi = 8.0\text{mm}$ and $P = 1.9\text{atm}$ for a thermodynamics study of the systems.

The mixtures were investigated by DTA method within the temperature range 293K-1473K using thermogravimetical apparatus STA PT1600 with specifications: temperature range -150 – 1750°C; heating rate 0.1 to 100°C/min; measuring range - $\pm 25.2500\text{mg}$; accuracy - $\pm 1\%$ full scale.

The samples initial weight was as follows: mix 1 – 56.3 mg; mix 2 – 59.2 mg; mix 3 – 57.8 mg; mix 4 – 55.5 mg. The heating rate was 10°C/min. The obtained derivatograms were registered as well as the differential changes of temperature as the mass changes.

The mixtures were studied also by EMF method within the temperature range 293K-1173K. The basic arrangement of the experimental cell 2 was the same as in paper [15]. Ni/NiO was used as a reference electrode.

The following galvanic cells were used in this work
 $\text{Pt}|\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5$ and $\text{Fe}_2\text{O}_3\text{-WVC} || \text{ZrO}_2(\text{CaO}) || \text{Ni, NiO}|\text{Pt}$
 $\text{P}'_{\text{O}_2} \quad \text{P}''_{\text{O}_2}$

WVC- waste vanadium catalyst

$\text{Pt}|\text{Fe}_2\text{O}_3\text{-MnO}_2$ and $\text{FMC} || \text{ZrO}_2(\text{CaO}) || \text{Ni, NiO}|\text{Pt}$
 $\text{P}'_{\text{O}_2} \quad \text{P}''_{\text{O}_2}$

FMC- Fe₂O₃- Mn concentrate

The Delta G°(T) (Ni O) values were reported by a number of authors [16-18]. The values of delta G°_T(Ni O) have been cited in this paper



$$\Delta G(f)(\text{o})(\text{NiO}) = -233651 + 84,893 T, \text{ J / mol}$$

2.2. DTA Results and Discussion

On Fig.1 a derivatogram of mixture 1 (pure oxides Fe₂O₃, V₂O₅ and SiO₂) is shown. The analysis of DTA curves shows the presence of intense endothermal effect at almost about 108° C (381K) and two rather weak intension endothermal effects at 672° C (945K) and 882° C(1155K). The first one corresponds to the sample mass losses in the table (with 13.33%) that is a result from dehydration processes (evaporation of dampness). The other two endothermal effects reflect most probably the polymorphous transition of SiO₂ in α -cristobalite and α Fe₂O₃ in γ Fe₂O₃. The following one is not well defined; the shallowed endothermal effect at temperature about 1155°C (1428K) relates to the sample melting. On the TG curve in that temperature range the mass change is not marked or if it is, the values are too low. The supplementary X-ray analysis, on Fig. 2, shows that in the obtained product the phases of Hematite (Fe₂O₃) have been fixed as well a low amount of cristobalite. The typical interplanar reflection of chemical composition between iron

and vanadium was not registered. This result demonstrates keeping of vanadium (V^{5+}) oxidation degree and also the data of binary system V_2O_5 - Fe_2O_3 that shows absence of chemical compounds between them.

If the above results are compared to thermal changes and phase formation of mix 2 (with waste vanadium catalyst) on Fig.3 it is seen, that at low temperatures about $104^\circ C$ ($377K$) and $202^\circ C$ ($475K$) two endothermic effects are observed in accordance with mass loss – 6.24 % and 2.00%. Those two effects are results of the physical dampness separation as well of the residual waste sulfur in the vanadium catalyst. In the temperature range from $580^\circ C$ ($853K$) up to $750^\circ C$ ($1023K$) one exothermic effect is marked as a result of solid-phase interaction between the oxides and the formation of ferrovandium FeV_2O_4 [19]. In contrast to mixture 1, where vanadium is as V_2O_5 , in the mixture 2 (with waste vanadium catalyst) it is present in lower degree of oxidation which makes possible the formation of FeV_2O_4 . These suppositions are confirmed by the X-ray analysis data, shown on Fig. 4, where apart from Hexagonal Quartz, Tetragonal Cristobalite, Rhombo Hematite FeV_2O_4 is also found. In the temperature range $580 - 750^\circ C$ the mass sample is decreased by 7.84%, which shows that the gas SO_3 separation is possible because it is about 24% in the initial chemical composition of the catalyst. Mix 2 melts at temperature about $1192^\circ C$ ($1465K$).

On Fig.5 a derivatogram of mixture 3 (pure oxides the Fe_2O_3 - MnO_2 - SiO_2) is shown. On DTA curve two endothermic effects and one exothermic are observed. The dampness separates at temperature about $77^\circ C$ ($350K$). The exothermic peak begins at temperature about $380^\circ C$ ($653K$) and the end is at temperature about $580^\circ C$ ($853K$), and its maximum is at temperature about $480^\circ C$ ($753K$). In that temperature range the formation of a solid solution between Fe_2O_3 and Mn_2O_3 takes place. A transformation from a peritectic type that decompose at about $950^\circ C$ ($1223K$) [20] to a solid solution between $Mn_2O_3 + Mn_3O_4$ is possible.

The temperature of the peritectic decompose is close to that on the experimental DTA curve ($T \sim 941^\circ C$) ($T \sim 1214K$) where the endothermic effect appears. In that temperature range, the sample mass begins to increase (by 4,52%). The most possible reason for that is the dissociation of MnO_2 by the scheme: $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ because we add MnO_2 to the mixture instead of MnO . The X-ray analysis, shown on Fig. 6, confirms the above statement because orthorhombic Mn_2O_3 , rhombic hematite Fe_2O_3 , tetragonal hausmannite (Mn_3O_4) are present in the outputs as well as tetragonal α -cristobalite. At temperature about $1131^\circ C$ ($1404K$) sample melting can be seen.

On Fig.7 the derivatogram of mixture 4 (Fe_2O_3 and Mn concentrate) is shown. On DTA curve, the same effects as in mix 3 are observed. The dampness evaporates at temperature about $88^\circ C$ ($361K$) and an endothermic effect is registered. In the temperature range $380 - 480^\circ C$ ($653K - 753K$) solid solutions are formed between iron and manganese oxides.

Endothermic effect appears at about $580^\circ C$ ($853K$) as a result of CO_2 separation that is contained in the manganese concentrate, obtained from poor carbonate ore. That fact is confirmed by TG curve as well, where the sample mass is reduced by 15.9 %, in comparison with mix 3. In the temperature range from about $680^\circ C$ ($953K$) to about $940^\circ C$ ($1213K$) three endothermic effects are observed with weak intensity respectively weak mass change. Those effects most probably are a result of Jacobsite $MnFe_2O_4$ formation [20, 7]. Sample melting can be seen at about $1179^\circ C$ ($1352K$). The X-ray analysis, on Fig.8, shows that in the output of mix 4 phases – tetragonal Hausmannite (Mn_3O_4), Rhombic Hematite (Fe_2O_3) and cubic Jacobsite ($MnFe_2O_4$) are present.

2.3. EMF Results and Discussion

The overall cell reaction could be written as the sum of the reactions occurring at the cathode and anode. The cathode reaction was



The anode reaction was



where Me_3O_4 is Fe_3O_4 (magnetite) or Mn_3O_4 (hausmannite); MeO is FeO (hematite), MnO or V_2O_3 .

The apparent partial pressure of the oxygen (generated by the concentrate) could be determined by the equation

$$E = 2,3.RT/nF(\log_{10}(P'_{O_2})_{ref} - \log_{10}(P'_{O_2})_{exp}) \quad (3)$$

where E is – the measured EMF, [V]; R is – the gas constant, $8,314 [deg K^{-1}mol^{-1}]$; n depicts the number of electrons taking part in the reaction; F – Faraday constant, $96500 [kJ C g.equivalent^{-1}]$; $\log_{10}(P'_{O_2})_{ref}$ – oxygen pressure of the reference electrode; $\log_{10}(P'_{O_2})_{exp}$ – oxygen pressure of the system studied.

Using the Ni/NiO reference electrode the partial pressure of the oxygen in the mixtures was

$$\log_{10}(P'_{O_2})_{exp} = -E.n.F/2,3.R.T - 24406/T + 8,867 \quad (4)$$

The results obtained are listed in Table 3 and Table 4. The results of EMF were obtained as average values of a number of measurements in the course of more than 30 min for every temperature under investigation.

Figures 5 and 6 represent the temperature dependence of $\Delta G(T)$ on the obtained experimental data. The compared graphs on Fig.9 show very close Gibbs energy values for mix 1 and 2. The X-ray analysis of mix 1 output shows the presence of Hematite (Fe_2O_3) whereas in mix 2 output apart from Hematite (Fe_2O_3) there is also FeV_2O_4 . So we can compare experimental data for ΔG with the data for Fe_2O_3 [21] and the data for FeV_2O_4 [12].

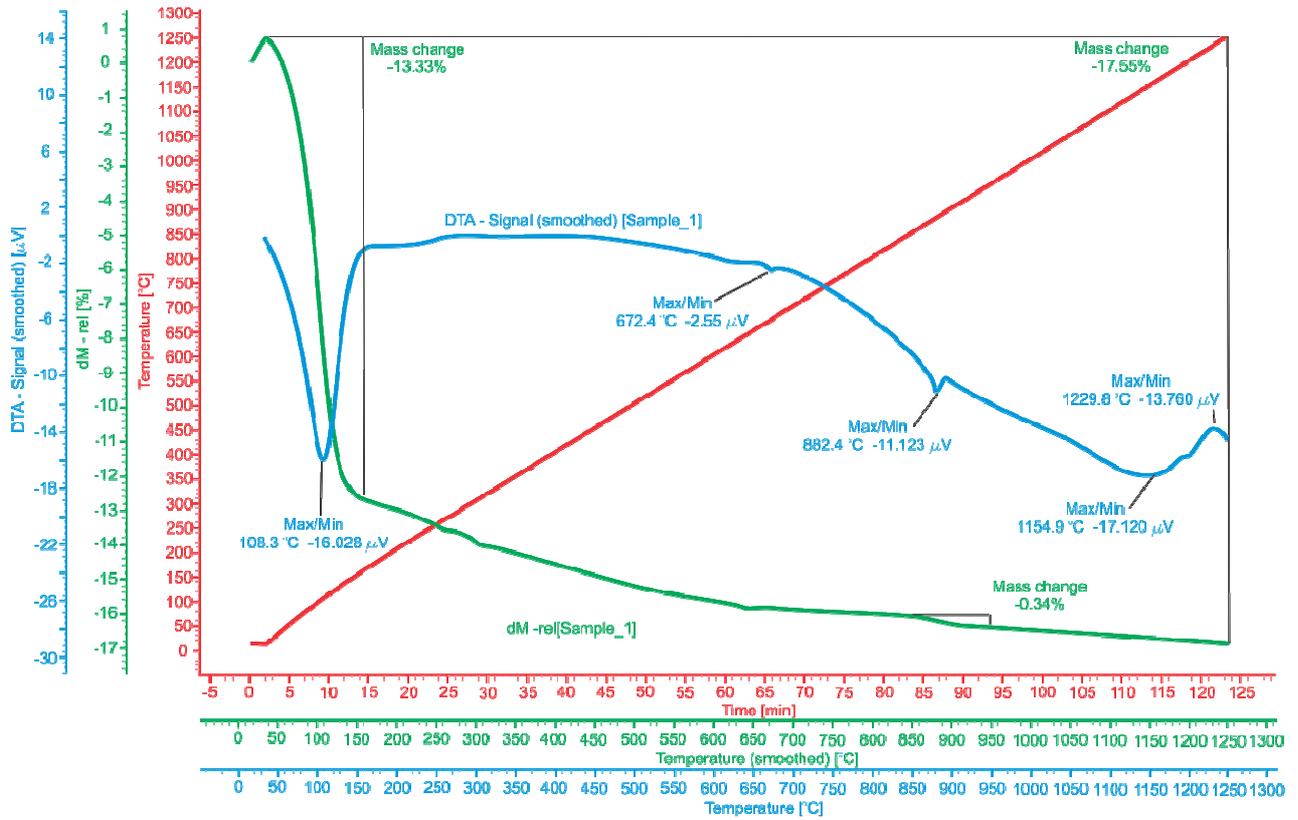


Figure 1. Derivatogram of mix 1 (pure oxides Fe_2O_3 , V_2O_5 and SiO_2).

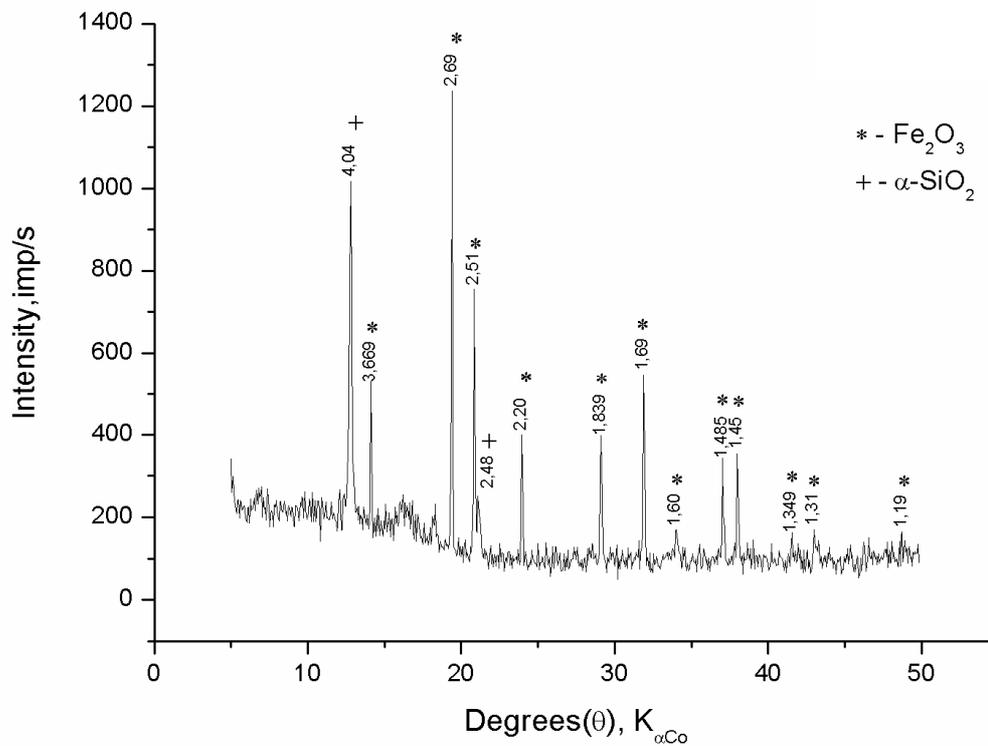


Figure 2. X-ray analysis of mixture 1 (pure oxides Fe_2O_3 , V_2O_5 and SiO_2).

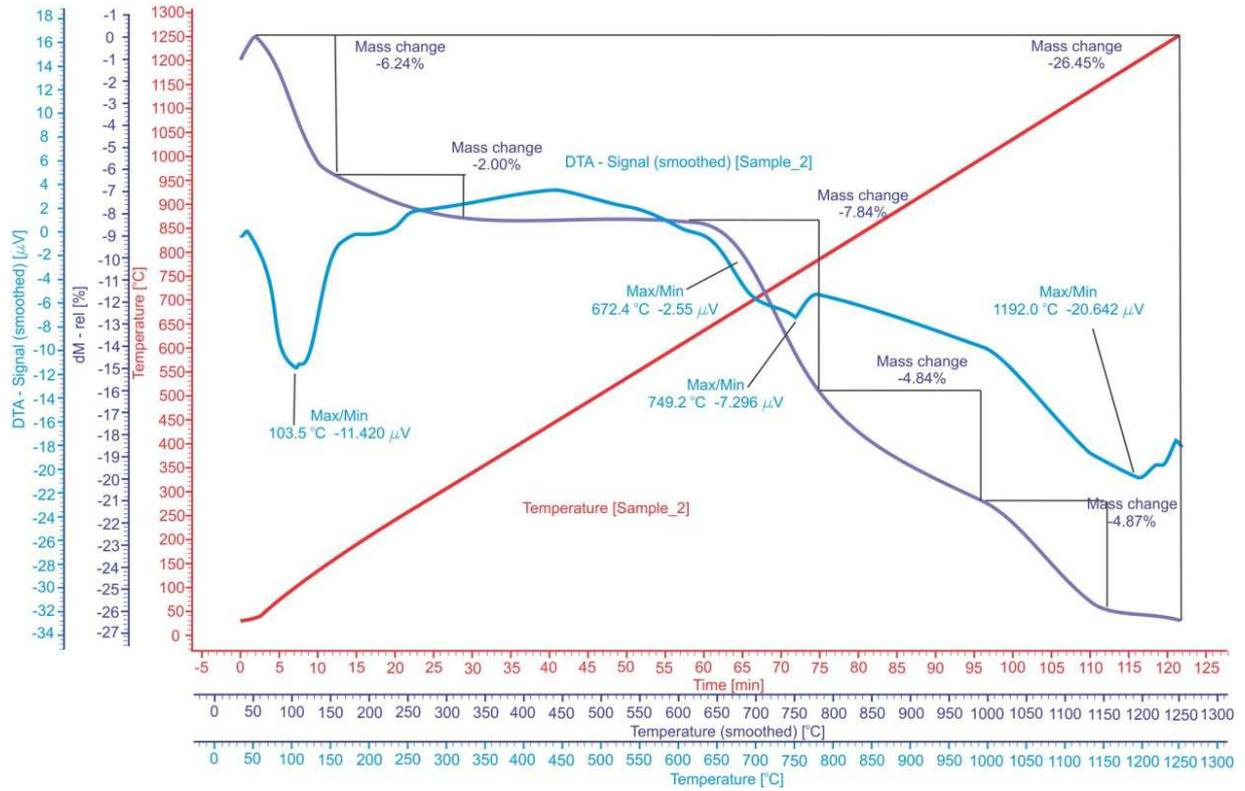


Figure 3. Derivatogram of mix 2 (Fe_2O_3 – waste vanadium catalyst).

Hematite

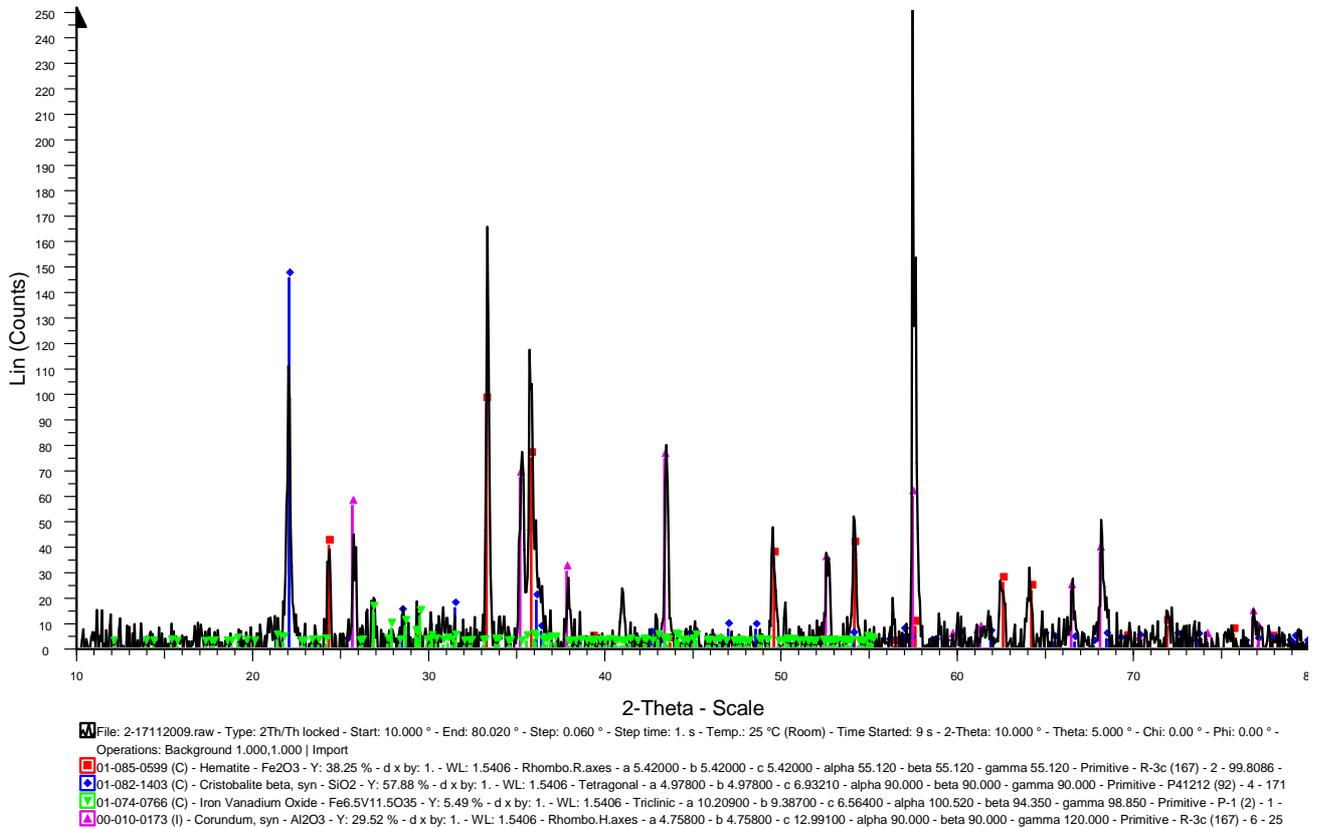


Figure 4. X-ray analysis of mixture 2 (Fe_2O_3 – waste vanadium catalyst).

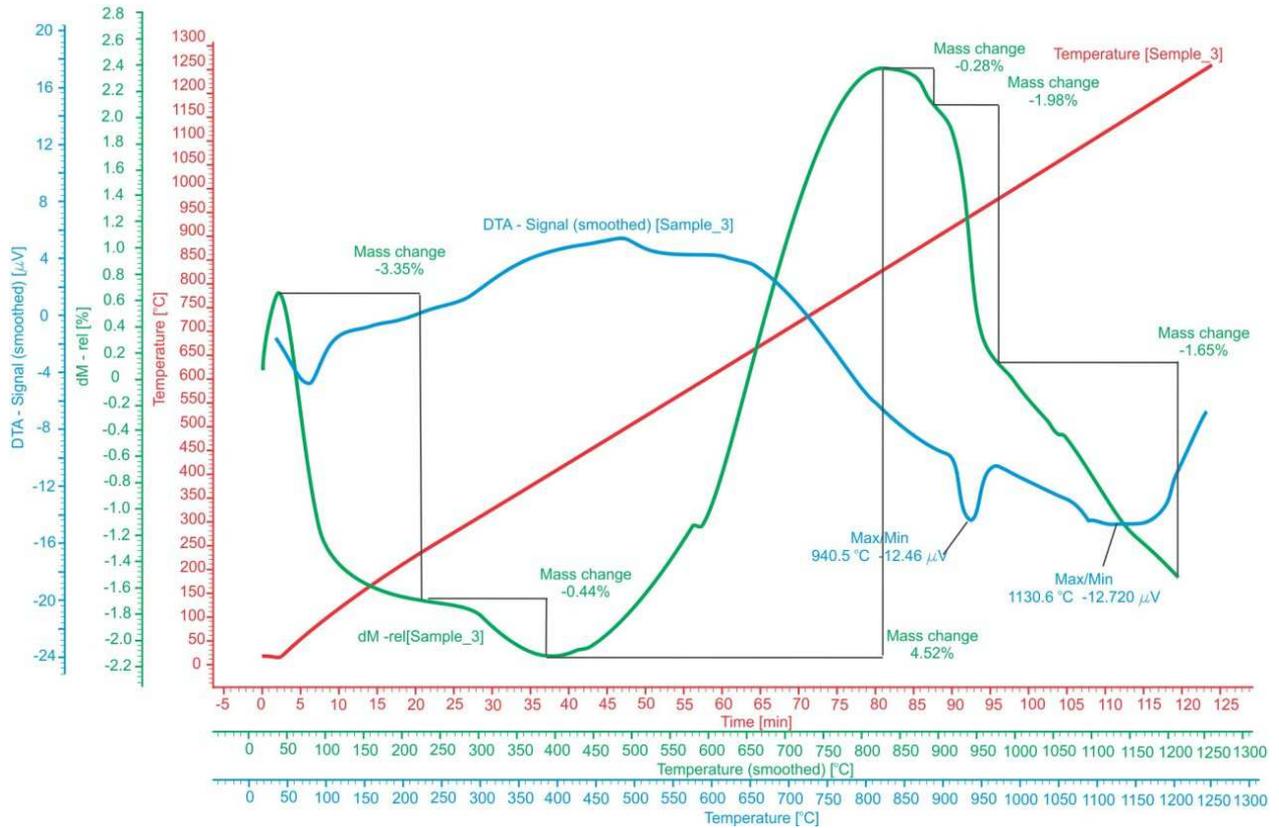


Figure 5. Derivatogram of mix 3 (pure oxides Fe_2O_3 , MnO_2 , SiO_2)

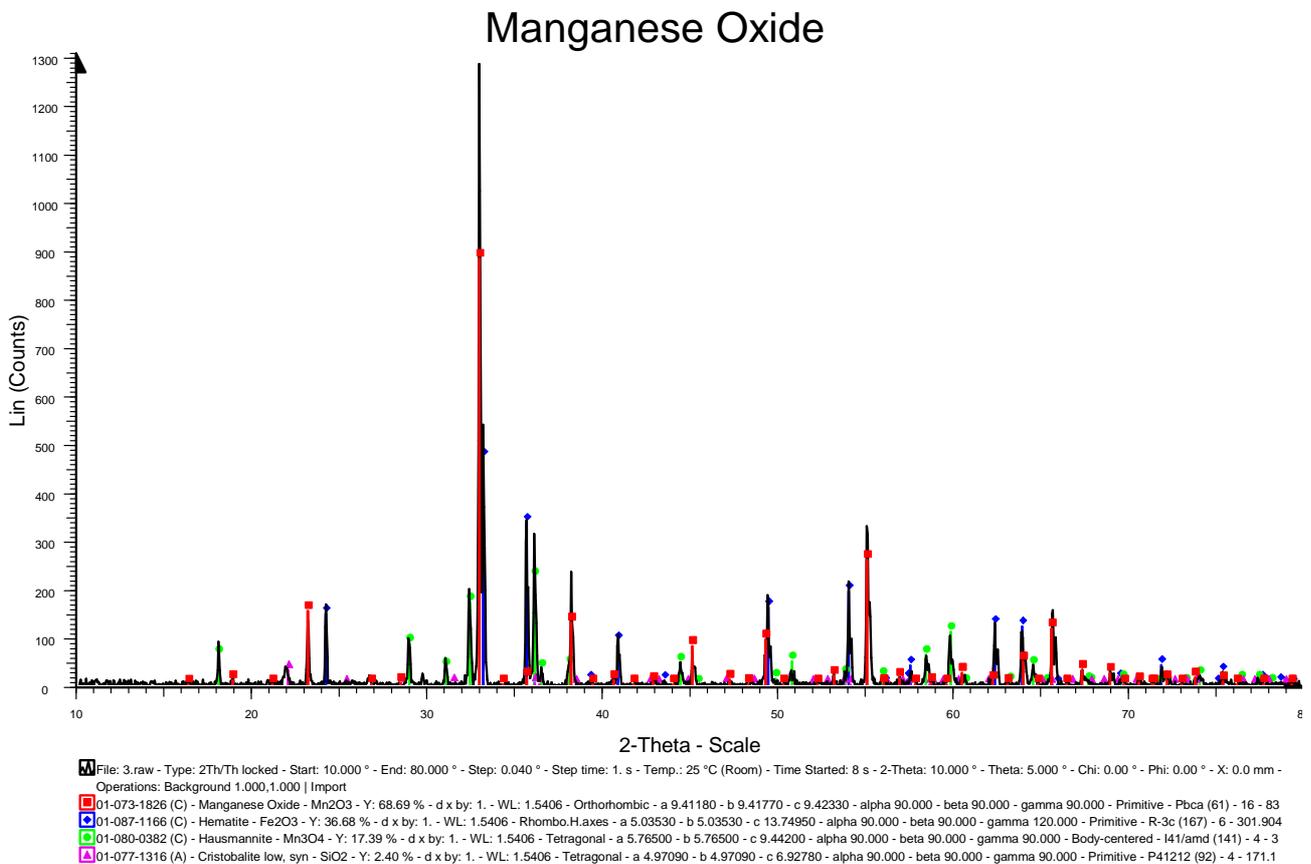


Figure 6. X-ray analysis of mixture 3 (pure oxides Fe_2O_3 , MnO_2 , SiO_2).

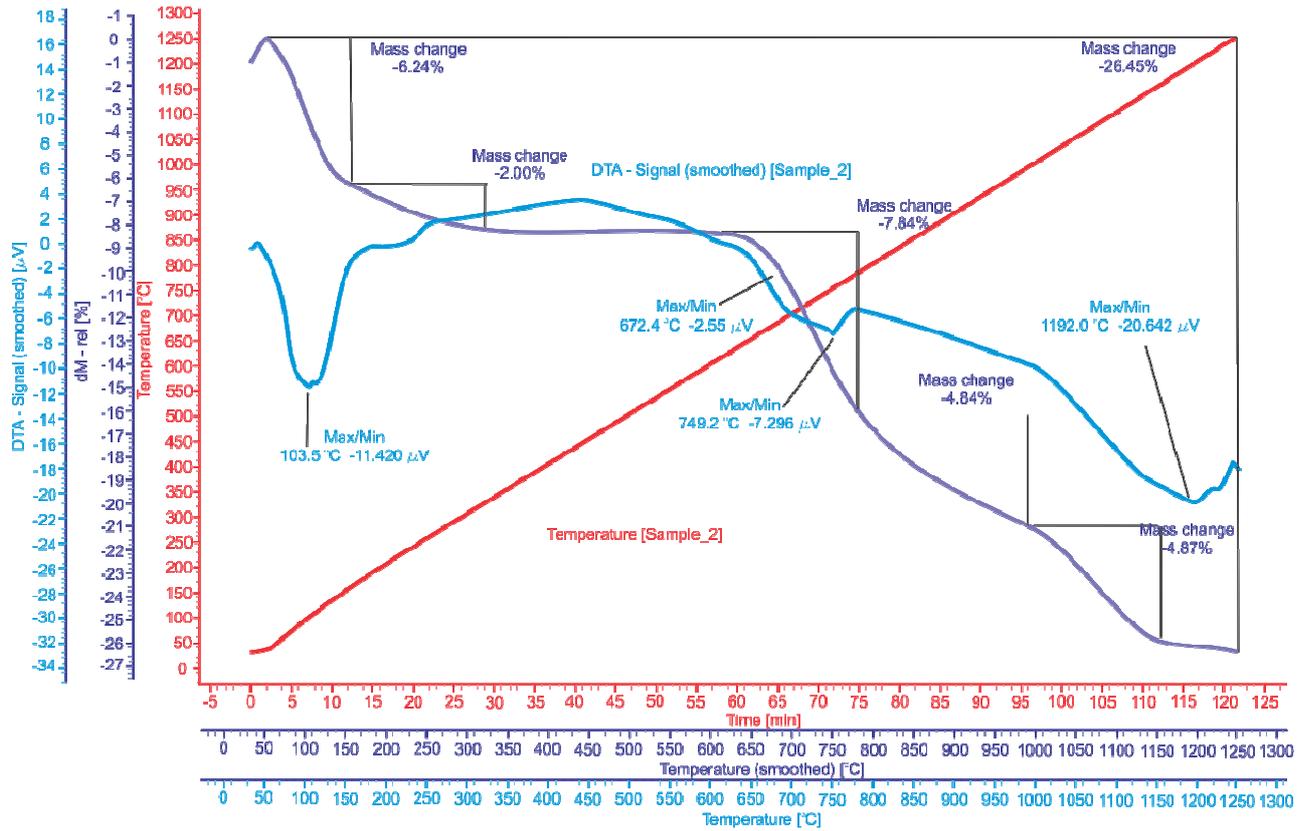


Figure 7. Derivatogram of mix 4 (Fe_2O_3 - manganese concentrate).

Jacobsite syn, precipitated

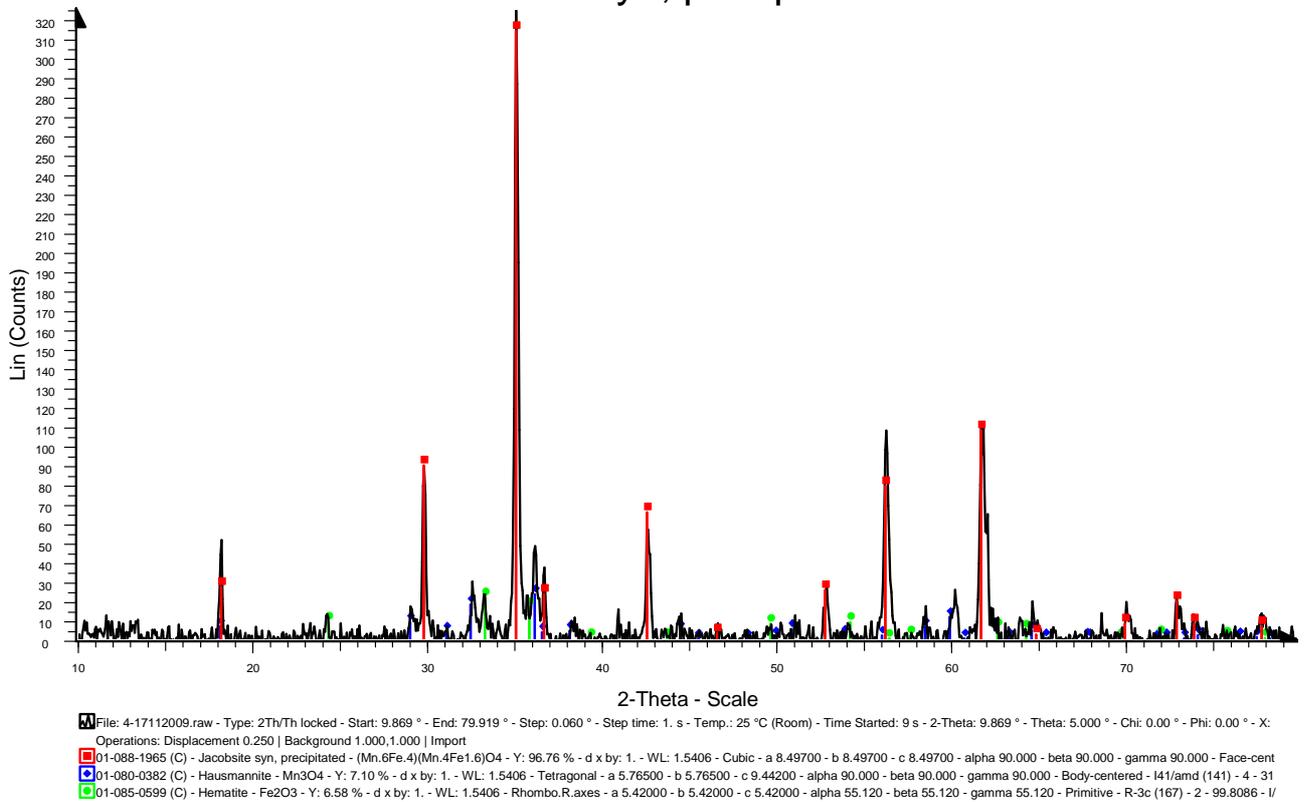


Figure 8. X-ray analysis of mixture 4 (Fe_2O_3 - manganese concentrate).

Table 3. Gibbs energy values depending on temperature for mix 1 and 2.

Mix 1 Ref. Electrode Ni/NiO				Mix 2 Ref. Electrode Ni/NiO			
T, K	E, V	log ₁₀ (P _{O₂)_{exp.}}	Delta G(T), J/mol	T, K	E, V	log ₁₀ (P _{O₂)_{exp.}}	Delta G(T), J/mol
1083	0,328	-12,9639	- 268345	1083	0,327	-12,9453	- 267959
1103	0,331	-12,7033	- 267805	1103	0,330	-12,6849	- 267419
1123	0,333	-12,4339	- 266880	1123	0,332	-12,4159	- 266494
1143	0,334	-12,1563	- 265569	1143	0,333	-12,1386	- 265183
1163	0,336	-11,9056	- 264643	1163	0,335	-11,8883	- 264258
1173	0,338	-11,8007	- 264567	1173	0,335	-11,7491	- 263409

Table 4. Gibbs energy values depending on temperature for mix 3 and 4.

Mix 3 Ref. Electrode Ni/NiO				Mix 4 Ref. Electrode Ni/NiO			
T, K	E, V	log ₁₀ (P _{O₂)_{exp.}}	Delta G(T), J/mol	T, K	E, V	log ₁₀ (P _{O₂)_{exp.}}	Delta G(T), J/mol
1073	0,342	-13,3896	- 274597	1073	0,329	- 13,1449	- 269579
1098	0,346	-13,0572	- 274019	1098	0,333	- 12,8181	- 269002
1133	0,348	-12,5523	- 271821	1133	0,337	- 12,3563	- 267575
1163	0,350	-12,1487	- 270047	1163	0,339	- 11,9577	- 265801
1173	0,350	-12,0073	- 269198	1173	0,340	- 11,8351	- 265339

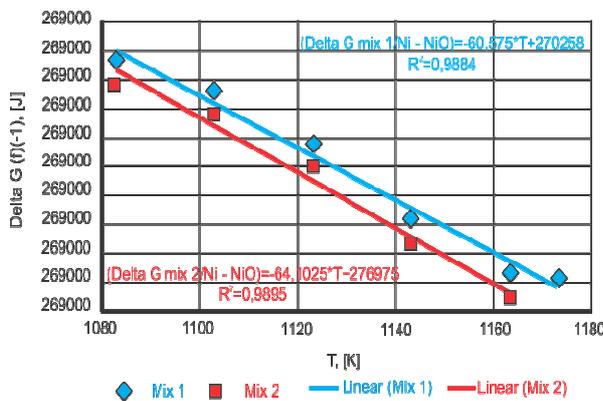


Figure 9. Comparative graphs for temperature dependence of deltaG for mix 1 and mix 2.

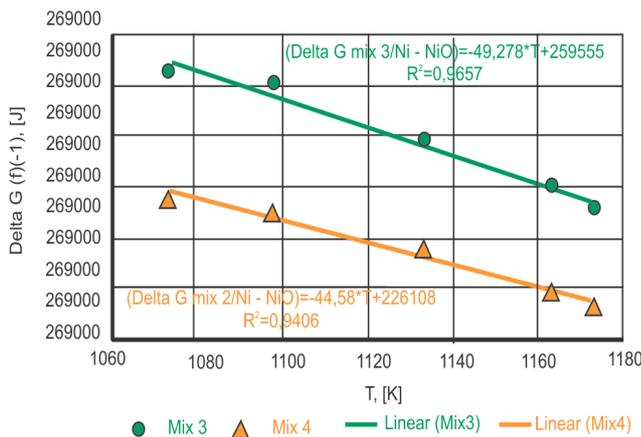


Figure 10. Comparative graphs for temperature dependence of delta G for mix 3 and mix 4.

The compared graphs on Fig.10 show lower Gibbs energy values for mix 4 than for mix 3. The X-ray analysis of mix 3 output shows presence of Mn₂O₃, Fe₂O₃, Mn₃O₄. So we can compare experimental data for Delta G with the

data for Mn₂O₃, Mn₃O₄ [9]. In the product of mix 4 there is Mn₃O₄ Fe₂O₃ and Jakobsite (MnFe₂O₄). Probably its formation is the cause for the lower value of Gibbs energy in mix 4.

3. Conclusion

As a result of the carried out experimental study the following more important conclusions can be drawn:

The phase transformations reaching up to 1473K and the formation of new phases of FeV₂O₄ and MnFe₂O₄ (Jakobsite) in the samples can be formed only if in the initial materials there is a waste vanadium catalyst and manganese concentrate.

A solid solution between Fe₂O₃ and Mn₂O₃ is formed (for pure oxides – mix3) in the temperature range 853K – 953K and then it decomposes peritectically at 1203K.

Based on the experimental results of the heating of different mixtures containing oxides of iron, manganese and vanadium the relationship of Delta G^o_T = f(T) for the temperature range 1073K – 1173K was obtained, using EMF method with a reference electrode Ni/NiO. Gibbs energy values for mix 1 and mix 2 are very close compared to the theoretical indications calculated for Fe₂O₃. Gibbs energy for mix 3 is in compliance with the data of manganese oxide.

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