

# Component activities in $\text{SiO}_2\text{-CrO}_x\text{-MgO-Al}_2\text{O}_3$ ( $\text{MgO/Al}_2\text{O}_3=2.0$ ) slags at 1873 and 1973 K.

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## Abstract

The component activities in the  $\text{SiO}_2\text{-CrO}_x\text{-MgO-Al}_2\text{O}_3$  ( $\text{M/A}=2.0$ ) system have been obtained by the Knudsen effusion method with mass-spectral monitoring of the gas phase composition on an MS-1301 mass spectrometer. The experiments were carried out in double effusion cells.

The enthalpy of melting divalent chromium oxide,  $\text{CrO}$ , was found from experiments to be equal to 9,3 kcal/mole. Temperature dependencies of  $\text{CrO}_{(\text{g})}$  vapor pressure above quasi-solid and liquid divalent chromium oxides have been determined from experimental results and literature data:  $\lg P_{\text{CrO}[\text{CrO}_{(\text{s})}]}^{\text{subl.}} = -28038/T + 11.858$ ;  $\lg P_{\text{CrO}[\text{CrO}_{(\text{l})}]}^{\text{vap.}} = -26006.8/T + 10.82$ .

The component activities ( $\text{SiO}_2$ ,  $\text{CrO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{MgO}$ ) at 1873 and 1973 K are presented as isoactivity lines in phase diagrams.

## Literature survey

The three-component system,  $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3$ , is used for description of the slag from production of high carbon ferrochromium. Phase equilibria [1] and component activities [2] in the system have been investigated rather well. However, it remains to be explained why the  $\text{Cr}_2\text{O}_3$  content in some cases reach 8-10 %, and in other cases 4-5 %. Besides, some authors have shown, that a layer of ore is formed between metal and slag at production of high carbon ferrochromium. This ore layer refines the liquid metal by lowering its content of silicon and carbon. The ore layer consists of unmelted pieces of chromium ore floating in slag. It is well known that the solubility of  $\text{Cr}_2\text{O}_3$  is very low in the slag systems  $\text{SiO}_2\text{-MgO}$ ,  $\text{MgO-Al}_2\text{O}_3$  and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  and consequently also in the  $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3$  system at temperatures of practical interest. However, there is no limitation to the solubility of divalent chromium oxide,  $\text{CrO}$ , in the same slag system. As a result the chromium content of the slag can be increased considerably, and the ternary slag system may not be sufficient for a complete analysis of the technical process.

Toker *et al* [3] have shown the presence of a third phase in the Cr-O system between Cr and  $\text{Cr}_2\text{O}_3$ . This phase was identified as  $\text{Cr}_3\text{O}_4$  and is stable in a temperature interval from 1650°C to 1705°C. The composition of the liquid oxide phase at the eutectic temperature of 1665°C was found to be close to  $\text{CrO}$ . It is obvious from the given results that the chromium in slag melts can exist in various valence states. Many investigators have studied the valence state of chromium in different slag systems. It has been shown that equilibrium in the chromium oxide- $\text{SiO}_2$  system depends on the partial pressure of oxygen [4-6]. In air the stable state of chromium is threevalent and at equilibrium with chromium metal (or at reducing conditions) - divalent. Similar results were obtained for the chromium oxide- $\text{CaO}$  [7,8] and the chromium oxide- $\text{SiO}_2\text{-CaO}$  [9] systems. Pretorius and Muan [9] have shown, that valence state of chromium also depends on the slag basicity.

Rankin and Biswas [10] investigated the distribution of chromium between metal ( $\text{Fe-Cr-Si}$ ) and slag ( $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-FeO-CrO}_x$ ) depending on the contents of iron and silicon. They determined the chemical formula of the chromium oxide in slag as  $\text{CrO}_{1.07}$ . It corresponds to about 86 % divalent and the rest threevalent chromium.

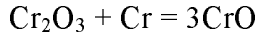
The phase diagram of the  $\text{SiO}_2\text{-CrO}_x\text{-MgO-Al}_2\text{O}_3$  ( $\text{MgO/Al}_2\text{O}_3=2.0$ ) system and the liquidus surfaces at 1600°C and 1700°C were constructed from results of our own experiments carried out earlier [11].

The purpose of the present research is an experimental determination of component activities in the  $\text{SiO}_2\text{-CrO}_x\text{-MgO-Al}_2\text{O}_3$  ( $\text{MgO/Al}_2\text{O}_3=2.0$ ) slag system at 1600°C and 1700°C.

## The experimental technique

Experimental data were obtained by use of the Knudsen effusion method with mass spectral monitoring of the gas-phase composition on a MS-1301 mass spectrometer. Double effusion cells made of Mo and covered by Ir were used. The sublimation-to-effusion area ratio was  $\geq 300$ . The sample to be investigated was placed in the first effusion cell, and a standard sample with known activity of the studied element (or elements) - in the second cell. Initially pure  $\text{Cr}_2\text{O}_3$  was used as a standard sample for determination of component activities in the slag sample №6:  $\text{CrO}=50$  %,  $\text{SiO}_2=41$  %,  $\text{MgO}=6$  %,  $\text{Al}_2\text{O}_3=3$  %; all concentrations in mass %. Sample №6 was subsequently used as a standard for the rest of samples. The temperature

was measured with an optical EOP-66 pyrometer to better than  $\pm 5$  K. The known melting temperatures of Ag, Fe and Si were used for calibrating the pyrometer. The investigated slag compositions were prepared by mixing of  $\text{SiO}_2$  or master slag ( $\text{SiO}_2=34.2$  %,  $\text{MgO}=44.8$  %,  $\text{Al}_2\text{O}_3=21.0$  %) with pure oxide components.  $\text{CrO}$  was added to the slag samples as  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_{\text{met}}$  in weight proportion according to the reaction:



In addition all samples were preheated in alumina crucibles and kept at  $1300^\circ\text{C}$  in Ar atmosphere for 5 hours.

The ionic current intensities of the gas phase components in equilibrium with a melt were determined in the mass-spectrometric experiments. Therefore the prime problem was recalculation of intensities of ion currents to partial pressures. In general the partial pressure of a component is equal to:

$$P_i = K_i \cdot I_i \cdot T; \quad (1)$$

where,  $K_i = \frac{K}{\sigma_i}$ ; - constant for element  $i$ ;

$I_i$  - Intensity of the ionic current of component  $i$ ;

$T$  - Temperature, K

$K$  - Constant of the installation;

$\sigma_i$  - Parameter of element ( $i$ ) ionization (literature values),  $10^{16} \text{ cm}^2$ .

The value of  $\sigma_{ij}$  for a compound can usually be calculated from the equation:

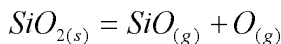
$$\sigma_{ij} = \sigma_i + \sigma_j \quad (2)$$

$\sigma_{\text{Cr}}=5.1$ ;  $\sigma_{\text{O}}=1.27$ ;  $\sigma_{\text{CrO}}=6.37$ ;  $\sigma_{\text{CrO}_2}=7.64$ ;  $\sigma_{\text{Mg}}=5.38$ ;  $\sigma_{\text{SiO}_2}=7.89$  [12, 16]

The  $\text{Cr}^+$ ,  $\text{CrO}^+$ ,  $\text{CrO}_2^+$ ,  $\text{SiO}^+$ ,  $\text{SiO}_2^+$ ,  $\text{Mg}^+$  ions were detected in saturated vapor above slag melts of the  $\text{SiO}_2\text{-CrO}_x\text{-MgO-Al}_2\text{O}_3$  system. The activities of Cr, CrO,  $\text{Cr}_2\text{O}_3$ ,  $\text{SiO}_2$  and MgO can then be calculated in the temperature interval  $1600\text{-}1700^\circ\text{C}$  as a results of the mass-spectrometric measurements of ion intensities:

### 1. Activity of $\text{SiO}_2$ :

$\text{SiO}_2$  sublimates congruently by the reactions:



$$\text{SiO}_{2(s)} = \text{SiO}_{2(g)} \quad \lg P_{\text{SiO}_2}^o = -\frac{29655}{T} + 11.56 \quad [13]$$

Then, if the vapor pressure of  $\text{SiO}_{2(g)}$  above a melt is known, its activity can easily be determined:

$$a_{\text{SiO}_2} = \frac{P_{\text{SiO}_2[\text{sample}]}}{P_{\text{SiO}_2}^o} \quad (3)$$

### 2. Chromium activity:

$$\text{Cr}_{(s)} = \text{Cr}_{(g)} \quad \lg P_{\text{Cr}}^o = -\frac{19602}{T} + 9.76 \quad [13]$$

$$a_{Cr} = \frac{P_{Cr[sample]}}{P_{Cr}^o} \quad (4)$$

### 3. CrO activity:

$$CrO_{(l)} = CrO_{(g)}$$

$$a_{CrO} = \frac{P_{CrO[sample]}}{P_{CrO}^o} \quad (5)$$

### 4. Cr<sub>2</sub>O<sub>3</sub> activity:

$$2Cr_{(g)} + 3/2 O_{2(g)} = Cr_2O_{3(s)}$$

$$a_{Cr_2O_3} = \frac{\left( P_{Cr}^2 \cdot P_{O_2}^{3/2} \right)_{[sample]}}{\left( P_{Cr}^2 \cdot P_{O_2}^{3/2} \right)_{[Cr_2O_3]}} \quad (6)$$

### 5. MgO activity:

$$MgO_{(s)} = Mg_{(g)} + O_{(g)} \quad \lg(P_{Mg} \cdot P_O) = -51399/T + 19.91 \quad [13]$$

$$a_{MgO} = \frac{\left( P_{Mg} \cdot P_O \right)_{[sample]}}{\left( P_{Mg} \cdot P_O \right)_{[MgO]}} \quad (7)$$

Cr<sub>(s)</sub>, CrO<sub>(l)</sub>, Cr<sub>2</sub>O<sub>3(s)</sub>, SiO<sub>2(s)</sub> and MgO<sub>(s)</sub> were used as a standard states at such calculations. It is necessary to mark, that in the Cr-O system [3], CrO<sub>(l)</sub> is formed at temperatures of more than 1665°C. For that reason, super-cooled liquid, CrO<sub>(l)</sub>, is adopted as standard for determination of CrO activity in slag at 1600°C.

The temperature dependence of P<sub>CrO[CrO(l)]</sub> have not been studied earlier. Therefore it was necessary to conduct preliminary tests where Cr<sub>2</sub>O<sub>3</sub> was placed in one part of a double effusion cell, and (Cr+Cr<sub>2</sub>O<sub>3</sub>) in weight ratio 1:1, in the other part of the double effusion cell. The effusion areas had the following diameters: d<sub>e(1)</sub>=0.5; d<sub>e(2)</sub>=0.09).

## Results and discussion

As already mentioned, pure Cr<sub>2</sub>O<sub>3</sub> and (Cr+Cr<sub>2</sub>O<sub>3</sub>) mixture were investigated in a preliminary test. (Cr+Cr<sub>2</sub>O<sub>3</sub>) is a heterogeneous mixture at temperatures up to 1650°C. The pure chromium is present at temperatures up to 1665°C (1938 K). Saturated vapors above both parts of the cell consist of Cr<sup>+</sup>, CrO<sup>+</sup> and CrO<sub>2</sub><sup>+</sup>, but the absolute values are different. Results are given in table 1.

The values of Cr, CrO and CrO<sub>2</sub> partial pressures were calculated from experimental results by equation (1). The coefficient *K* in this equation can be determined based on known thermodynamic values, for example for pure chromium:

$$P_{Cr} = \frac{K}{\sigma_{Cr}} \cdot I_{Cr} \cdot T$$

$I_{Cr}$  was determined by experiment at the temperature  $T$  (from the cell with  $Cr+Cr_2O_3$ ). From the literature [13]:  $\lg P_{Cr[Cr]} = -19602/T + 9.76$ , giving  $P_{Cr}^o = 0.2$  (mm Hg) at 1873 K. Then from the experimental result above ( $Cr+Cr_2O_3$ ):

$$0.2 = \frac{K}{\sigma_{Cr}} \cdot 1873 \cdot 12.6 \Rightarrow K_{Cr} = \frac{K}{\sigma_{Cr}} = 8.54 \cdot 10^{-6}$$

Then above  $Cr_2O_3$ :

$$K_{Cr} = 8.54 \cdot 10^{-6} / (0.5 / 0.09)^2 = 2.77 \cdot 10^{-7}$$

The additive scheme can be used for determination of constants for other compounds ( $CrO$  and  $CrO_2$ ):

$$\frac{K_{Cr}}{K_{CrO}} = \frac{\sigma_{CrO}}{\sigma_{Cr}} = 1.25 \Rightarrow \text{above}(Cr + Cr_2O_3) K_{CrO} = 6.83 \cdot 10^{-6}$$

$$\text{above}(Cr_2O_3) K_{CrO} = 2.21 \cdot 10^{-7}$$

$$\frac{K_{Cr}}{K_{CrO_2}} = \frac{\sigma_{CrO_2}}{\sigma_{Cr}} = 1.5 \Rightarrow \text{above}(Cr + Cr_2O_3) K_{CrO_2} = 5.69 \cdot 10^{-6}$$

$$\text{above}(Cr_2O_3) K_{CrO_2} = 1.85 \cdot 10^{-7}$$

Constants of other elements in the multicomponent system can be calculated in the same way. For an example:

$$\frac{K_{Cr}}{K_{SiO_2}} = \frac{\sigma_{SiO_2}}{\sigma_{Cr}} = 1.547 \Rightarrow K_{SiO_2} = 0.646 \cdot K_{Cr}$$

$$\frac{K_{Cr}}{K_{Mg}} = \frac{\sigma_{Mg}}{\sigma_{Cr}} = 1.055 \Rightarrow K_{Mg} = 0.948 \cdot K_{Cr}$$

Vapor pressures of different components above  $Cr_2O_3$  and ( $Cr+Cr_2O_3$ ) at various temperatures have been calculated and the results are shown in table 2.

Based on own results and literature data, it is possible to make a some important calculations given below.



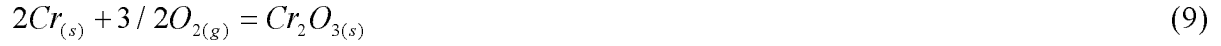
$$K_P^{1873K} = \frac{P_{CrO}^2}{P_{Cr} \cdot P_{CrO_2}}$$

$$\text{above}(Cr + Cr_2O_3), \quad K_P^{1873K} = 0.4$$

$$\text{above}(Cr_2O_3), \quad K_P^{1873K} = 0.32$$

This result is in a good agreement with literature data (0.314 [14]; 0.367 [13]). This is an indication of correct experimental technique.

⇒ For the reaction:



we have:

$$\Delta_f G_{(Cr_2O_3, s, 1873K)}^\circ = 4.576 \cdot 1.873 \cdot \lg \left( \left( \frac{8.3 \cdot 10^{-4}}{2.0 \cdot 10^{-1}} \cdot \frac{760}{760} \right)^2 \cdot P_{O_2}^{3/2} \right) = -154.9 \text{ (Kcal/mole)}$$

$$\text{Then } P_{O_2[Cr_2O_3, s, 1873K]} = 1.02 \cdot 10^{-6} \text{ (mm Hg)}$$



$$\lg K_p = \lg \frac{P_O^2}{P_{O_2}} = -\frac{26640}{T} + 9.85 \quad [13]$$

$$\text{Then, } K_p^{1873K} = \frac{P_O^2}{P_{O_2}} = 4.23 \cdot 10^{-5} \Rightarrow P_O = \sqrt{4.23 \cdot 10^{-5} \cdot 1.02 \cdot 10^{-6}} = 6.57 \cdot 10^{-6} \text{ (mm Hg)}$$



$$K_p^{1873K} = \frac{P_{CrO}}{P_{Cr} \cdot P_O} = \frac{2.55 \cdot 10^{-4}}{8.3 \cdot 10^{-4} \cdot 6.57 \cdot 10^{-6}} = 46762.4$$

from the literature [13]:  $\Delta_r H^\circ = -112.2 \text{ (Kcal/mole)}$

$$\lg K_p = -\frac{\Delta_r H^\circ}{R \ln 10} + b = -\frac{-112200}{1873 \cdot 4.576} + b \Rightarrow b = -8.421$$

Then

$$\lg K_p = \frac{24519.2}{T} - 8.421 \quad (12)$$

Using the obtained relation (12), it is possible to calculate partial pressures of oxygen above the research samples. The results of calculations are presented in a table 3.

Now considering the following reactions:



From the literature [13]:  $\Delta_r H^{o(1950K)} = 384.8 \text{ (Kcal/mole)}$

Then:  $\Delta_s H_{CrO}^{o(1950K)} = 384.8 / 3 = 128.3 \text{ (Kcal/mole)}$

And from experiment:  $P_{CrO[CrO_{(s)}]}^{subl.(1956K)} = 3.342 \cdot 10^{-3}$  (mm Hg)

We observe:

$$\lg P_{CrO[CrO_{(s)}]}^{subl.} = -28038/T + 11858 \quad (14)$$

$$\Rightarrow Cr_{(l)} + Cr_2O_{3(l)} = 3CrO_{(g)} \quad (15)$$

From the literature [15]:

$$S_{CrO(g)}^{o(1950K)} = 73.1$$

$$S_{Cr_2O_3(l)}^{o(1950K)} = 86.1$$

$$S_{Cr(l)}^{o(1950K)} = 22.2$$

$$\text{or } \Delta_r S^o = 3S_{CrO}^o - S_{Cr_2O_3}^o - S_{Cr}^o = 111$$

Activities of components above CrO at 1956 K:

$$a_{Cr[CrO]} = \frac{P_{Cr[CrO]}}{P_{Cr}^o} = 0.45$$

$$a_{Cr_2O_3[CrO]} = \frac{(P_{Cr}^2 \cdot P_O^3)_{[CrO]}}{(P_{Cr}^2 \cdot P_O^3)_{[Cr_2O_3]}} = 0.82$$

The equilibrium constant of reaction (15) is equal to:

$$K_P^{(1956K)} = \frac{P_{CrO}^3}{a_{Cr} \cdot a_{Cr_2O_3}} = \frac{\left(3.342 \cdot 10^{-3} / 760\right)^3}{0.45 \cdot 0.82} = 2.3 \cdot 10^{-16}$$

Enthalpy of reaction (15):

$$\Delta_r H^{1956K} = \Delta_r G^o + T\Delta_r S^o = -RT \ln K_p + T\Delta_r S^o = -4.576 \cdot 1956 \cdot \lg(2.3 \cdot 10^{-16}) + 1956 \cdot 111 = 357.02 \text{ (Kcal/mole)}$$

and the enthalpy of CrO<sub>(l)</sub> vaporization:  $\Delta_{vap.} H_{CrO(l)}^o = 357.02 / 3 = 119 \text{ (Kcal/mole)}$

Then the temperature dependence of vapor pressure above CrO<sub>(l)</sub> and enthalpy of CrO melting can be calculated:

$$\lg P_{CrO[CrO_{(l)}]}^{vap.} = -26006.8/T + 10.82 \quad (16)$$

$$\Delta_{melt.} H_{CrO}^o = \Delta_{subl.} H_{CrO}^o - \Delta_{vap.} H_{CrO}^o = 128.3 - 119 = 9.3 \text{ (Kcal/mole)}$$

The expression (16) can be used for calculation of partial pressures of CrO at various temperatures above a standard sample of CrO<sub>(l)</sub>. Then the CrO activity in an investigated sample can be determined from the measured partial pressure of CrO above this sample, using formula (5).

The activities of the slag components in the quasibinary system, CrO-SiO<sub>2</sub>, at 1600 and 1700°C, are shown in figure 1. Also the values of chromium activity for the present experimental conditions are given in figure 1. It appears that the Cr, CrO and Cr<sub>2</sub>O<sub>3</sub> activities increase with increasing CrO content in slag. The CrO activity reaches its maximum value (equal to unity) at a composition corresponding to pure CrO. The value of the Cr<sub>2</sub>O<sub>3</sub> activity depends strongly on the temperature. At 1600°C it increases sharply with increasing CrO concentration in the slag and becomes equal to unity at 92 mol % of CrO. At this composition the liquid slag is in equilibrium with (Cr<sub>2</sub>O<sub>3</sub>+Cr). At 1700°C the maximum Cr<sub>2</sub>O<sub>3</sub> activity is equal to 0.84. This value is reached at 100 % of CrO. The activity of SiO<sub>2</sub> in the liquid area decreases with increasing CrO content in the slag.

The results of measured component activities in the SiO<sub>2</sub>-CrO<sub>x</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> (M/A=2.0) system at 1600°C and 1700°C are shown in the figures 2, 3 and 5. In the figures the experimental results are given as isoactivity lines for the investigated components. The compositions of investigated slag samples are shown as circles.

SiO<sub>2</sub> activities obtained in the present research are presented in figure 2(a) and 2(b) at 1600°C and 1700°C respectively. Chipmans data [2] for the CrO free system, SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>, are also shown in figure 2(a) These data are shown as square symbols along the SiO<sub>2</sub>–(MgO+Al<sub>2</sub>O<sub>3</sub>) axis. These values of silica activities were adopted as initial points for the silica isoactivity lines.

The silica activity naturally depends on the content of SiO<sub>2</sub> in the slag. It increases with increasing concentration of SiO<sub>2</sub> and reaches the maximum value ( $a_{\text{SiO}_2}=1$ ) along a line corresponding to saturation compositions of SiO<sub>2</sub>. Besides, increasing temperature results in a lowering of the silica activity. This effect is obviously connected to the significant extension of the liquid area at the increase of temperature from 1600°C to 1700°C. Consequently it also gives a stronger decrease of silica activity when the slag composition moves out of the area with SiO<sub>2</sub> saturation. However, it is necessary to mark that the experiments were not conducted in the field of high SiO<sub>2</sub> concentrations at 1700°C. The silica isoactivity line,  $a_{\text{SiO}_2}=0.9$ , was estimated in order to be in harmony with the lines of  $a_{\text{SiO}_2}=0.8$  and  $a_{\text{SiO}_2}=1$ .

The results of measured values for CrO and Cr<sub>2</sub>O<sub>3</sub> activities are shown in figure 3(a) and 3(b) at 1600°C and 1700°C respectively. As can be seen, the activity of chromium oxides increase with increasing CrO concentration in the slag. The isoactivity lines for CrO and Cr<sub>2</sub>O<sub>3</sub> have different “slope” to the (MgO+Al<sub>2</sub>O<sub>3</sub>)-CrO<sub>x</sub> axis. This difference increase with increasing CrO concentration. To explain this phenomenon, a sketch is presented in figure 4. Here a segment near the CrO corner of the investigated phase diagram is shown. The ABC line represents a part of a liquidus line at some constant temperature (assume 1600°C). The liquid slag is in equilibrium with (Cr<sub>2</sub>O<sub>3</sub>+Cr) along the BC section of the liquidus line. The Cr<sub>2</sub>O<sub>3</sub> activity in this section is equal to unity. The Cr<sub>2</sub>O<sub>3</sub> activity decrease when the slag composition is changed from point B to point A. The isoactivity lines for Cr<sub>2</sub>O<sub>3</sub> are distributed to fit in with the line for  $a_{\text{Cr}_2\text{O}_3}=1$ . The CrO activity is equal to unity only at the top of the CrO corner. Then the isoactivity lines for CrO are “curved around” this corner.



Isoactivity lines for MgO are shown in figure 5. Near the (MgO+Al<sub>2</sub>O<sub>3</sub>) corner, there is an area of MgO stability where  $a_{\text{MgO}}=1$ . The MgO activity decreases when the slag composition moves out of this area. The activity of MgO can be calculated for a slag composition corresponding to equilibrium between liquid slag and the solid forsterite phase at 1600°C. This slag composition is shown in figure 5 as a square symbol on the (MgO+Al<sub>2</sub>O<sub>3</sub>)-SiO<sub>2</sub> axis. This equilibrium conditions is described by the following reaction:



$$K_P = \frac{1}{a_{\text{SiO}_2} \cdot a_{\text{MgO}}^2}; \text{ at } 1600^\circ\text{C}: K_P=50.6 \quad [15]$$

When accepting from figure 2 that  $a_{\text{SiO}_2}=0.4$  at 1600°C, we get  $a_{\text{MgO}}=0.22$ . This is in good agreement with the experimentally defined values.

## Conclusions

- 1 The enthalpy of melting divalent chromium oxide, CrO, and the temperature dependence of CrO<sub>(g)</sub> vapor pressure above this oxide have been determined from experimental results and literature data.
- 2 The component activities (SiO<sub>2</sub>, CrO, Cr<sub>2</sub>O<sub>3</sub> and MgO) at 1600°C and 1700°C have been determined from a mass-spectrometric investigation. The results are presented as isoactivity lines in the SiO<sub>2</sub>-CrO<sub>x</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> (M/A=2) phase diagram.

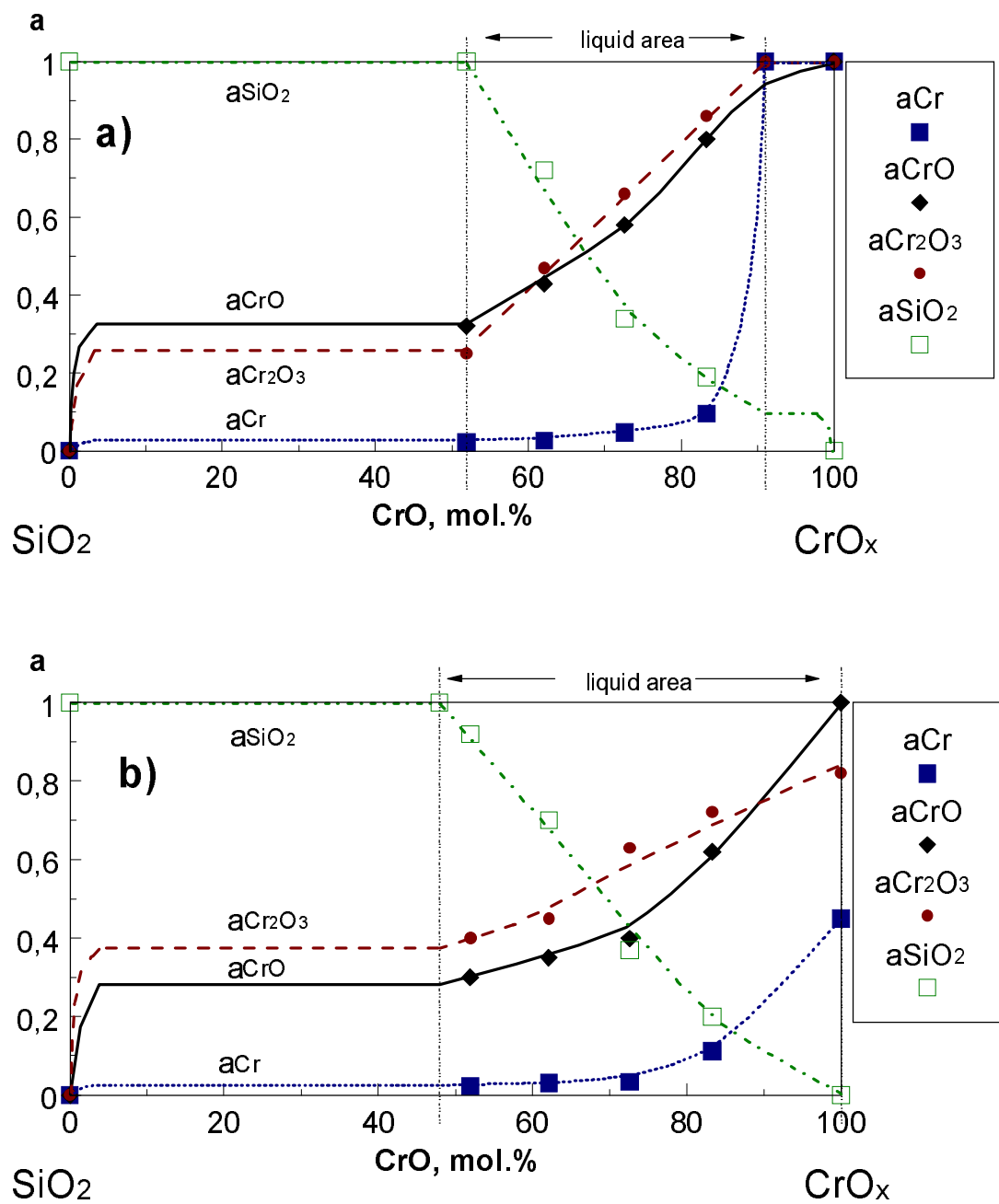
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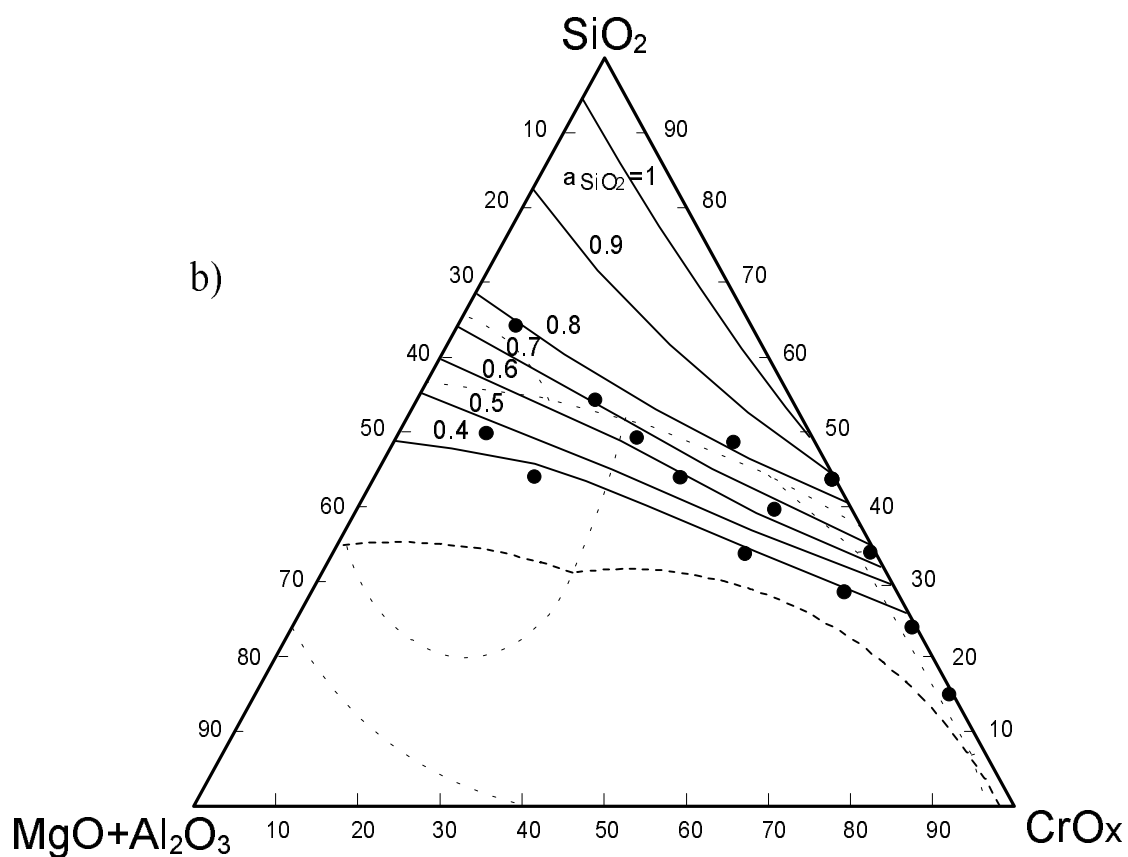
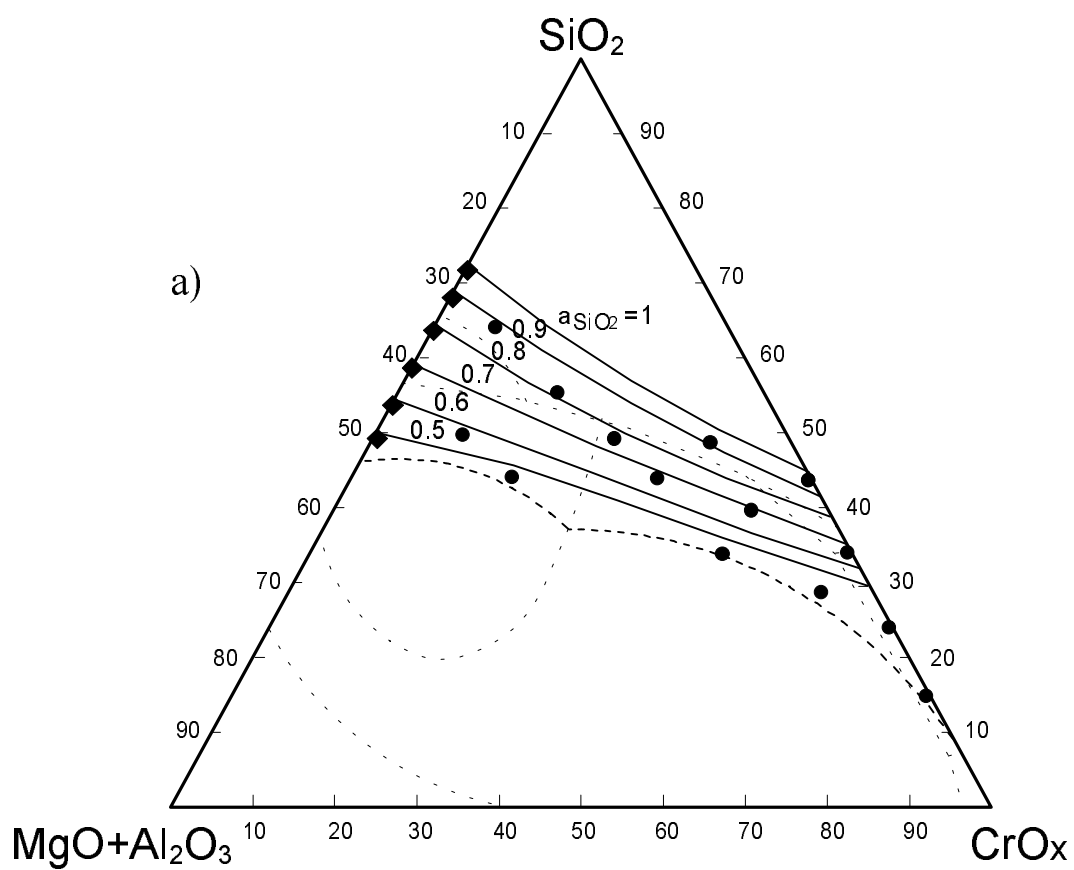
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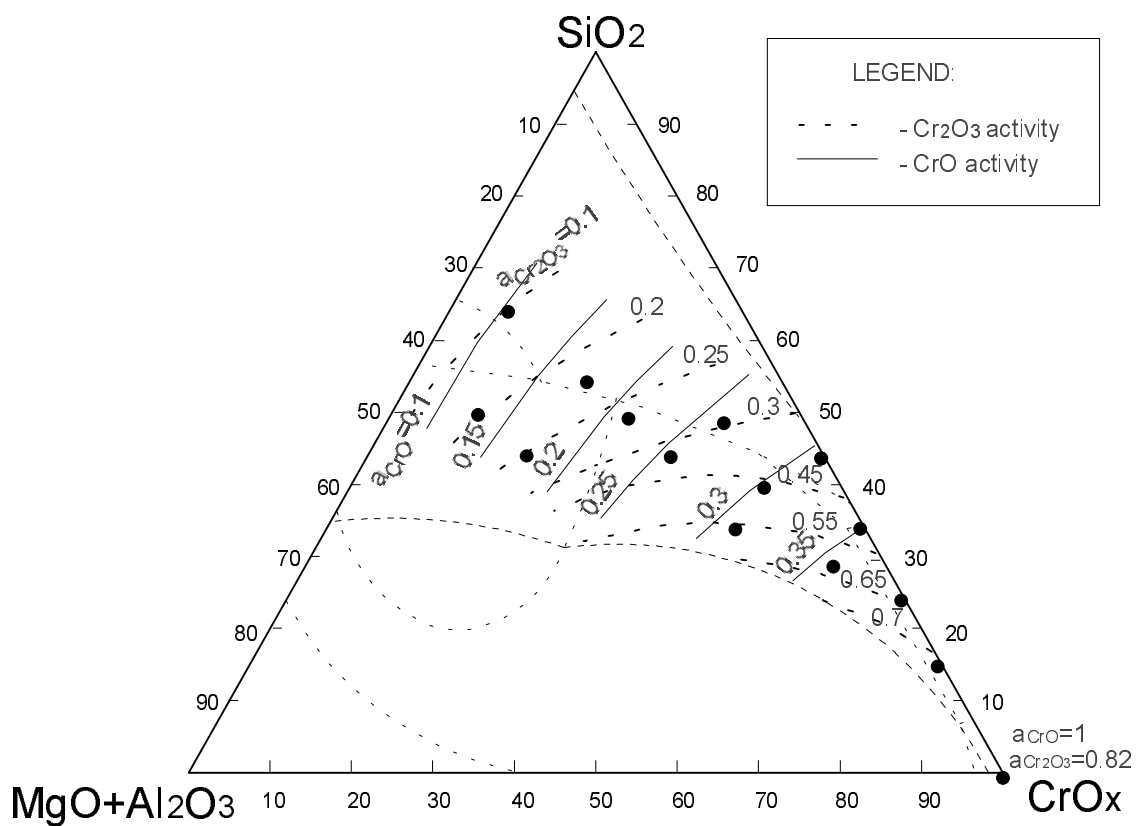
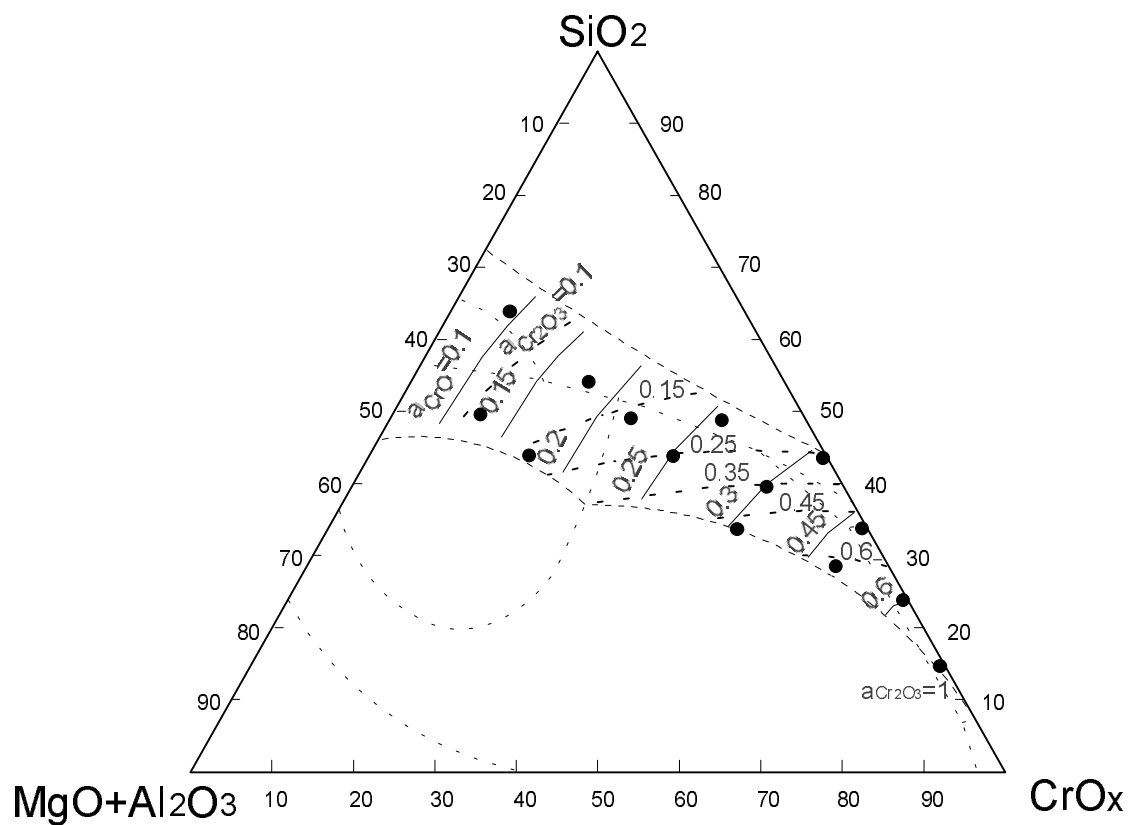
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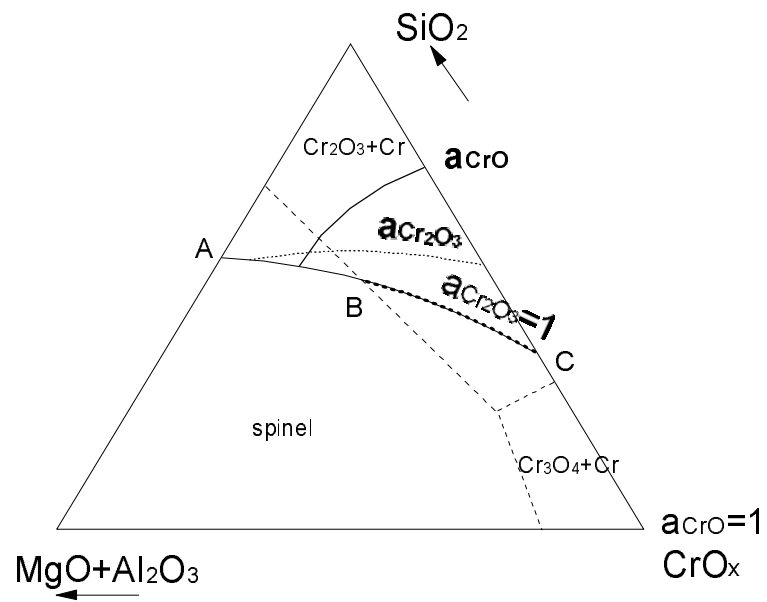
**Fig.1.** Component activities in  $\text{CrO}_x\text{-SiO}_2$  system at 1600°C (a) and 1700°C (b).



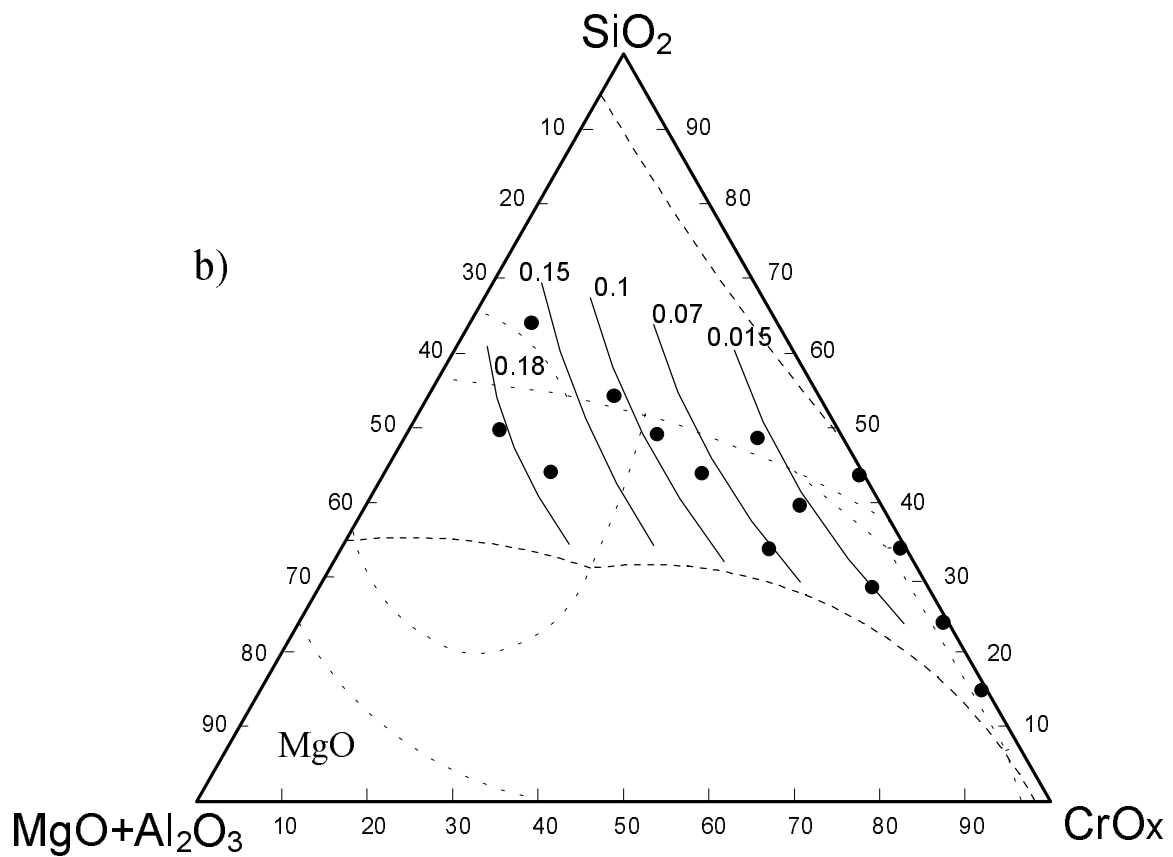
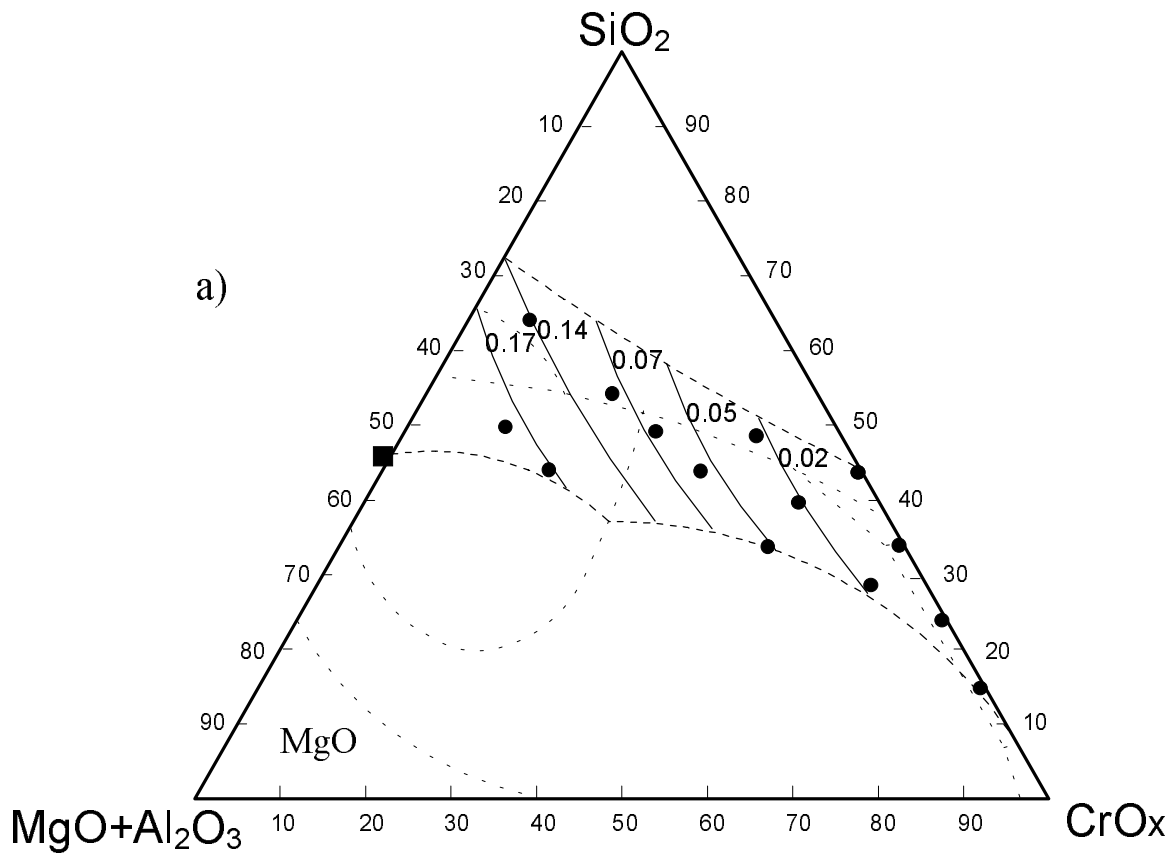
**Fig.2.** SiO<sub>2</sub> activity in SiO<sub>2</sub>-CrO<sub>x</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> (M/A=2) at 1600 (a) and 1700°C (b) (concentrations in wt.%).



**Fig.3.** Chromium oxides activity in  $\text{SiO}_2\text{-CrO}_x\text{-MgO-Al}_2\text{O}_3$  ( $M/A=2$ ) at 1600 (a) and 1700°C (b) (concentrations in wt.%).



**Fig.4.** Schematic presentation of isoactivity lines for CrO and Cr<sub>2</sub>O<sub>3</sub> in investigated slag system.



**Fig.5.** MgO activity in SiO<sub>2</sub>-CrO<sub>x</sub>-MgO-Al<sub>2</sub>O<sub>3</sub> (M/A=2) at 1600 (a) and 1700°C (b) (concentrations in wt.%).

**Table 1.** *Outcomes of experiment 1.*

Sample	Temperature, K	$I_{Cr+}$	$I_{CrO+}$	$I_{CrO_2+}$
$Cr_2O_3$	1873	1,6	0,615	0,7
	1956	6,4	2,0	3,25
	1973	8,0	2,7	4,1
$Cr+Cr_2O_3$	1873	12,5	0,125	0,003
	1956	14,6	0,25	0,0085
	1973	17,0	0,3	0,012

**Table 2.** *Vapor pressures of components (in mm Hg).*

T, K	$Cr_2O_3$			$Cr+Cr_2O_3$		
	$P_{Cr}$	$P_{CrO}$	$P_{CrO_2}$	$P_{Cr}$	$P_{CrO}$	$P_{CrO_2}$
1873	0,00083	0,000255	0,000242	0,2	0,0016	0,000032
1956	0,00346	0,000866	0,001173	0,24395	0,003342	0,000095
1973	0,00437	0,00118	0,001493	0,28652	0,004045	0,000135

**Table 3.** *Oxygen partial pressures (in mm Hg) above  $Cr_2O_3$  and  $(Cr+Cr_2O_3)$ .*

T, K	$K_{P(12)}$	$Cr_2O_3$		$Cr+Cr_2O_3$	
		$P_O$	$P_{O_2}$	$P_O$	$P_{O_2}$
1873	46759.5	6.57E-06	1.02E-06	1.71E-07	6.89E-10
1956	13013	1.92E-05	2,16E-06	1.05E-06	6.5E-09
1973	10147.7	2.66E-05	3,17E-06	1.39E-06	8.66E-09