ION-MOLECULAR EQUILIBRIUM TECHNIQUE APPLIED TO Cr$_2$O$_3$ AND NiO ACTIVITY DETERMINATION. GIBBS ENERGY OF FORMATION OF NiCr$_2$O$_4$.

RUDNYI E.B., KAIBICHEVA E.A., SIDOROV L.N.

Department of Chemistry, Moscow State University, Moscow, 119899, U.S.S.R.

VARSHAVSKII M.T., MEN A.N.

The Institute of Metallurgy, Ur. Depart. Academy of science of USSR, Sverdlovsk, 620219, U.S.S.R.

Short title - "GIBBS ENERGY OF NiCr$_2$O$_4"

The method for determination of Cr$_2$O$_3$ and NiO activity in high-temperature systems based on measuring of equilibrium constants of reactions with negative ions

\[
\text{Cr}_2\text{O}_3(s) + 3\text{CrO}_4^- = 2\text{Cr}_2\text{O}_6^- + \text{CrO}_3^-
\]

\[
\text{NiO}(s) + \text{CrO}_3^- + \text{CrO}_4^- = \text{NiO}_2^- + \text{Cr}_2\text{O}_6^-
\]

has been suggested. To produce measurable quantities of suitable ions in the saturated vapour small amounts of easily ionized substance (K$_2$SO$_4$ or K$_2$CrO$_4$) were added to the systems being investigated.

The activities of Cr$_2$O$_3$ and NiO have been determined for heterogeneous systems NiO - NiCr$_2$O$_4$ and NiCr$_2$O$_4$ - Cr$_2$O$_3$ and Gibbs energy of NiCr$_2$O$_4$ formation from oxides has been calculated.

1. INTRODUCTION

The activity measurements in the oxide systems are a remarkable
branch of the high temperature chemistry due to the such subject of interest as slags, magmas, silicate glass melts and oxygen containing ceramics.

At present the method of e.m.f. with a solid oxide electrolytes or the method of heterogeneous equilibria are usually applied to determine an oxide activity (1). In both cases the oxygen partial pressure and activity of metal have to be measured and oxide activity is calculating according to relation

\[ \alpha(\text{MeO}) = K^0(1) \cdot p(\text{O}_2) \cdot \alpha(\text{Me}) \]

where \( K^0(1) \) is equilibrium constant of reaction

\[ \text{Me(s)} + \text{O}_2 = \text{MeO}_2(s) \quad (1) \]

To eliminate the additional experiments of \( \alpha(\text{Me}) \) measurements one choose the systems whith the metal activities is equil to unit or known from literature.

The new approach was developed recently and was called "ion-molecule equilibrium method" (2,3). This method is based on the measurements of the negative ion - molecule equilibria in the saturated vapours of high temperature systems.

Let us consider the example of ScF\(_3\) activity determination given in Ref. (3). In the saturated vapour of NaF - ScF\(_3\) system there are F\(^-\) and ScF\(_4^-\) ions among other ones. The following ion-molecular equilibrium can be written

\[ F^- + \text{ScF}_3(s) = \text{ScF}_4^- \]

Having measured the ratio of partial pressures of \( \{p(\text{ScF}_4^-)/p(F^-)\}^0 \) ions in the system where activity of ScF\(_3\) is equal to unit and by determining similar ratio in any other system, the activity of ScF\(_3\) can be found

\[ \alpha(\text{ScF}_3) = \frac{\{p(\text{ScF}_4^-)/p(F^-)\}}{\{p(\text{ScF}_4^-)/p(F^-)\}^0} \]
Thus, the availability of ions that allow us to write a suitable ion-molecular equilibrium is a necessary condition for determining of activity by the method concerned. In cases when there are no such ions in the vapour of the system investigated, they can be generated by introducing a small amounts of easily ionized substance. Previously, at the investigation of silicate systems $\text{Na}_2\text{O-SiO}_2$ \(^{(4)}\) and $\text{Na}_2\text{O-K}_2\text{O-SiO}_2$ \(^{(5)}\) chromates of alkali metals were used as admixture (about 3 mol %). This allowed us to provide measurable concentrations of the following ions: $\text{CrO}_3^-$, $\text{CrO}_4^-$, $\text{NaCrO}_4^-$, $\text{KCrO}_4^-$. The first three ions allowed us to determine the activity of $\text{Na}_2\text{O}$ and the ions $\text{CrO}_3^-$, $\text{CrO}_4^-$, and $\text{KCrO}_4^-$ - the activity of $\text{K}_2\text{O}$.

The aim of the present work is to extend the method of ion-molecular equilibria on the activity determination of the oxides $\text{Cr}_2\text{O}_3$ and $\text{NiO}$. It is suggested to use negative ions $\text{CrO}_3^-$, $\text{CrO}_4^-$, $\text{Cr}_2\text{O}_6^-$ \(^{(6)}\) for measuring of chromium oxide activity and for that of nickel oxide to use a negative ion $-\text{NiO}_2^-$ \(^{(7)}\).

Spinel $\text{NiCr}_2\text{O}_4$ is the object of the investigation. The selection of nickel chromite is stimulated both by its practical significance and by the disagreement of its literature data known in literature.

2. EXPERIMENTAL

The work has been carried out by the mass-spectrometer MX-1303 \((60^\circ, 200\ \text{mm})\), re-equipped for studying of ion-molecular equilibria \(^{(8)}\). Vapourization of the system was carried out of platinum effusion Knudsen cell (diameter 12 mm, height 12 mm) and negative ions of the saturated vapour were measured. The ratio of the effusion hole area to the evaporation area was
approximately 400. The resistance furnace was used for heating. The temperature was measured by Pt/PT-Rh thermocouple (10%Rh) with the accuracy of ±4 K and was kept constant with the accuracy of ±1 K during measurements.

Nickel chromite was synthesized by caking NiO and Cr$_2$O$_3$ oxides of spectroscopic grade and phase composition was checked by the X-ray analysis.

In the vapour over Cr$_2$O$_3$ and NiO oxides as well as over NiCr$_2$O$_4$ the negative ions are absent. To generate the ions there were introduced easy-ionized compounds (K$_2$CrO$_4$ or K$_2$SO$_4$) to the investigated systems and the following negative ions CrO$_3^-$, CrO$_4^-$, Cr$_2$O$_6^-$, and NiO$_2^-$ were observed at 1200-1500 K. The ion currents were measured on a channel electron multiplier.

The systems under study and its mass-spectra are presented in Table 1. Let us note that negative ions given are a result of the thermal ionization and are in the equilibrium with the condensed phase.

The experiment was planned in such a manner that the several mass spectra were taken at the same temperature and after the series of measurements at other temperatures the run was repeated. The duration of one series is about $\approx$ 15 min and the interval between series corresponding to the same temperature is more than an hour.

In the course of the experiment easy-ionized admixture almost completely vapourized and this was confirmed by a significant decrease (up to the background) ion current intensities to the end of measurements.

3. DETERMINATION OF Cr$_2$O$_3$ AND NiO ACTIVITIES

It has been shown that addition of potassium sulphate and
potassium chromate to the systems containing \( \text{Cr}_2\text{O}_3 \) leads to the appearance of measurable concentrations of ions in the vapour at 1200 - 1500 K: \( \text{CrO}_3^-, \text{CrO}_4^- \), and \( \text{Cr}_2\text{O}_6^- \). This allows us to determine the activity of \( \text{Cr}_2\text{O}_3 \) as follows

\[
\alpha(\text{Cr}_2\text{O}_3) = \frac{p(\text{CrO}_3^-) p^2(\text{CrO}_6^-)}{p^3(\text{CrO}_4^-)} \frac{1}{K^o(3)}
\]

where \( K^o(3) \) is the equilibrium constant of the reaction

\[
\text{Cr}_2\text{O}_3(s) + 3\text{CrO}_4^- = 2\text{Cr}_2\text{O}_6^- + \text{CrO}_3^- \quad (3)
\]

Unless specified otherwise the compounds are in the gaseous state.

Similar, in case of the systems containing \( \text{NiO} \) the addition of \( \text{K}_2\text{CrO}_4 \) gives \( \text{NiO}_2^- \), \( \text{CrO}_3^- \), \( \text{CrO}_4^- \), and \( \text{Cr}_2\text{O}_6^- \) ions in measurable concentrations. It makes possible to find activity of \( \text{NiO} \) according to relation

\[
\alpha(\text{NiO}) = \frac{p(\text{NiO}_2^-) p(\text{Cr}_2\text{O}_6^-)}{p(\text{CrO}_4^-) p(\text{CrO}_3^-)} \frac{1}{K^o(5)}
\]

where \( K^o(5) \) is the equilibrium constant of the reaction

\[
\text{NiO}(s) + \text{CrO}_3^- + \text{CrO}_4^- = \text{NiO}_2^- + 2\text{Cr}_2\text{O}_6^- \quad (5)
\]

The ratio of partial pressures of ions is proportional to the ratio of ion currents and can be measured by the mass-spectrometer

\[
\frac{p(A^-)}{p(B^-)} = \frac{I_{\text{mul}}(A^-)}{I_{\text{mul}}(B^-)} \frac{M(A^-)}{M(B^-)} \frac{i(B^-)}{i(A^-)}
\]

where \( I_{\text{mul}} \) is the current measured on the multiplier, \( i \) is the percentage of the isotope being measured.

The equilibrium constant \( K^o(3) \) was measured in the saturated vapour of the systems \( \text{Cr}_2\text{O}_3-K_2\text{CrO}_4 \) (exp. 1) and \( \text{NiCr}_2\text{O}_4-\text{Cr}_2\text{O}_3-K_2\text{SO}_4 \) (exp. 2) and \( K^o(5) \) in the systems \( \text{NiO}-\text{Cr}_2\text{O}_3-K_2\text{CrO}_4 \) (exp. 3) and \( \text{NiCr}_2\text{O}_4-\text{NiO}-K_2\text{SO}_4 \) (exp. 4). The
values obtained are presented in Table 2. When measuring the equilibrium constants $K^0(3)$ and $K^0(5)$ one can’t use pure oxides $\text{Cr}_2\text{O}_3$ and $\text{NiO}$ due to the absence of negative ions in the saturated vapours of this substancies. That is why all the investigated systems include the admixture of easy ionized substance $\text{K}_2\text{SO}_4$ or $\text{K}_2\text{CrO}_4$.

Phase equilibria in the system Ni-Cr-O have been studied in the ref. (9). The authors (10) carried out the calculations of the phase diagram on the basis of the available thermodynamics data. A narrow region of homogeneous spinel $\text{NiCr}_2\text{O}_4$, a negligible solubility $\text{NiO}$ in $\text{Cr}_2\text{O}_3$ and a small ($\approx 4$ mole %) solubility $\text{CrO}_3$ in $\text{NiO}$ are noted. $\text{NiO}$ activity that is in equilibrium with $\text{NiCr}_2\text{O}_4$ according to the ref. (9) is equal 0.97. Note, that $\text{NiO}$ activity in the similar systems $\text{NiO}-\text{NiAl}_2\text{O}_4$ and $\text{NiO}-\text{NiGa}_2\text{O}_4$ also differ a little from unit up to $T = 1550$ K (11). $\text{K}_2\text{SO}_4$ solubility in $\text{NiO}$ and $\text{Cr}_2\text{O}_3$ is negligible (12). That is why it is adopted in the present work that $\text{Cr}_2\text{O}_3$ activity in the system $\text{NiCr}_2\text{O}_4-\text{Cr}_2\text{O}_3$ and $\text{NiO}$ activity in the system $\text{NiO}-\text{NiCr}_2\text{O}_4$ are equal to unit.

In the course of the experiment a significant vapourization of $\text{K}_2\text{SO}_4$ and $\text{KCr}_2\text{O}_4$ occurred. The absolute intensities of negative ion currents were changed by several orders and measured value of equilibrium constants did not change. It gives strong support in favour of the $\text{NiO}$ (exp. 3 and 4) or $\text{Cr}_2\text{O}_3$ (exp. 1 and 2) activity is equal to unit.

The temperature dependences $K^0(3)$ and $K^0(5)$ (Fig. 1.) have been determined

$$\ln K^0(3) = 9734/T + 3.28 \quad T = 1163-1515 \text{ K}$$

$$\ln K^0(5) = -14330/T + 0.93 \quad T = 1255-1515 \text{ K}$$

Standard deviations of $K^0(3)$ and $K^0(5)$ depending on temperature...
can be calculated as follows

\[
s\{\ln K^0(3)\} = 0.68 \left\{ \frac{1}{70} + \frac{(T^{-1} - 1356^{-1})^2}{(0.484 \cdot 10^{-3})^2} \right\}^{1/2}
\]

\[
s\{\ln K^0(5)\} = 0.52 \left\{ \frac{1}{43} + \frac{(T^{-1} - 1393^{-1})^2}{(0.281 \cdot 10^{-3})^2} \right\}^{1/2}
\]

Thus, the values \(K^0(3)\) and \(K^0(5)\) obtained allow us to measure \(\text{Cr}_2\text{O}_3\) and \(\text{NiO}\) activities in different systems. As it was mentioned above for this purpose it was necessary to make the addition of chromate or sulphate of alkali metal to generate suitable ion-molecular equilibria. According to our estimations the range of measurable activity makes up for \(\text{Cr}_2\text{O}_3\) – from 1 up to \(10^{-5}\) and for \(\text{NiO}\) – from 1 up to 0.05.

4. GIBBS ENERGY OF \(\text{NiCr}_2\text{O}_4\)

Gibbs energy of \(\text{NiCr}_2\text{O}_4\) formation from oxides has been also determined in experiments 2-4

\[
\text{NiO}(s) + \text{Cr}_2\text{O}_3(s) = \text{NiCr}_2\text{O}_4(s)
\]

(6)

As it was stated \(\text{NiCr}_2\text{O}_4\) has a narrow homogenity region (9). So in case with the experiments 2-4 it is possible to write

\[
\Delta_r G_m^0(6) = RT \ln \alpha(\text{NiO}) \alpha(\text{Cr}_2\text{O}_3)
\]

In experiment 2 in the system \(\text{NiCr}_2\text{O}_4 - \text{Cr}_2\text{O}_3\) the activity of \(\text{Cr}_2\text{O}_3\) is equal to unity and activity of \(\text{NiO}\) was measured according equation (4). In experiments 3 and 4 in the system \(\text{NiO}-\text{NiCr}_2\text{O}_4\) the activity of \(\text{NiO}\) is equal to unit and \(\text{Cr}_2\text{O}_3\) activity was measured according equation (2). The experimental data are presented in Table 3. In both cases the values of Gibbs energy \(\Delta_r G_m^0(6)\) satisfactory agree between themselves.
5. DISCUSSION

In spite of a great number of investigations the situation with the thermodynamic data of NiCr$_2$O$_4$ is not single-valued.

In the 60-70s a number of works have been carried out on determining of $\Delta_r G^0_m(6)$ by the e.m.f. method with a solid oxide electrolytes (9,13-15), where an oxygen concentration cell was used. Various electrodes of comparison were applied and Gibbs energy of the following reaction was calculated

$$\text{NiO}(s) + \text{Cr}_2\text{O}_3(s) = \text{NiCr}_2\text{O}_4(s)$$  \hspace{1cm} (13)

$$\text{NiO}(s) + \frac{1}{2}\text{O}_2 + \text{Cr}_2\text{O}_3(s) = \text{NiCr}_2\text{O}_4(s)$$  \hspace{1cm} (14)

$$\text{NiO}(s) + \text{Fe}_x\text{O}(s) + \text{Cr}_2\text{O}_3(s) = \text{NiCr}_2\text{O}_4(s) + x\text{Fe}(s)$$ \hspace{1cm} (9,15)

The results are presented in Fig.3., where the dependence $\Delta_r G^0_m(6)$ on temperature is shown. The values $\Delta_r G^0_m(6)$ obtained by the e.m.f. method are at $T = 1273$ K in the interval from $-25$ up to $-32$ kJ·mol$^{-1}$. Work (15) differs greatly, the value $\Delta_r G^0_m(6)$ is $-80$ kJ·mol$^{-1}$ and $\Delta_r S^0_m(6)$ has another sign. In later work (16) the same author gives another dependence $\Delta_r G^0_m(6)$ on temperature that satisfactorily agree with the others.

Another applied method is heterogeneous equilibria (17-18).

Gibbs energy of the reaction (6) was calculated from the experimental value of the equilibrium constant of reaction

$$\text{NiCr}_2\text{O}_4(s) + \text{CO} = \text{Ni}(s) + \text{Cr}_2\text{O}_3(s) + \text{CO}_2$$

The results of the two works do not agree. The authors (18) note that they could attain equilibrium only from one side.

Muller and Kleppa (19) determined the reaction enthalpy by dissolving NiCr$_2$O$_4$ as well as the NiO and Cr$_2$O$_3$ in molten oxides in a calorimeter. This value at 1173 K is $-5.2$ kJ·mol$^{-1}$ and does not agree with the e.m.f. data and the method of heterogeneous equilibria.
Thermodynamic data of NiCr$_2$O$_4$ given in the reference book (20) are based on $\Delta_r H_m^O(6)$ obtained in work (19) and heat capacity estimation made by authors. In the reference book "Thermal constants of substances" (21) there is enthalpy value of NiCr$_2$O$_4$ also based on the value $\Delta_r H_m^O(6)$ from the work (19).

Gibbs energies $\Delta_r G_m^O(6)$ obtained in the present work agree with the data on calorimetry (19) and are close to the predicted values in the reference book (20). All this data can’t be adjusted to the Gibbs energy $\Delta_r G_m^O(6)$ and enthalpy $\Delta_r H_m^O(6)$ obtained in the works (9,13-17).

6. THERMODYNAMIC FUNCTIONS OF NiCr$_2$O$_4$

Gibbs energy of the reaction depends on the temperature as follows

$$\Delta_r G_m^O = \Delta_r H_m^O(298.15 \text{ K}) - T \Delta_r S_m^O(298.15 \text{ K}) +$$

$$+ \int_{298.15}^{T} \Delta_r C_p,m^O \,dT - T \int_{298.15}^{T} (\Delta_r C_p,m^O/T) \,dT$$

In the case of reaction (6) entropy and temperature dependence of NiCr$_2$O$_4$ heat capacity are unknown. Because it is not possible to calculate simultaneously both entropy and heat capacity from the experimental data available, we decided to use the estimation of temperature dependence of heat capacity NiCr$_2$O$_4$ from the reference book (20)

$$C_p,m^O/(J \cdot K^{-1} \cdot \text{mol}^{-1}) = 165.3 + 17.87 \cdot 10^{-3} (T/K) - 21.05 \cdot 10^{-5} (T/K)^2$$

There were used enthalpies of formation, entropies and temperature dependencies of heat capacity NiO ($\Delta_f H_m^O(298.15 \text{ K})=-239.7 \pm 0.5$ kJ$\cdot$mol$^{-1}$, $S_m^O(298.15 \text{ K}) = (37.8 \pm 0.4)$ J$\cdot$K$^{-1} \cdot$mol$^{-1}$) (22) (data bank IVTAN TERMO, version of 1986) and Cr$_2$O$_3$ ($\Delta_f H_m^O(298.15 \text{ K})=-1140.6 \pm 1.7$ kJ$\cdot$mol$^{-1}$, $S_m^O(298.15 \text{ K}) = (57.6 \pm 0.7)$
Recalculations of the enthalpy of formation \( \text{NiCr}_2\text{O}_4 \) from oxides from the ref. (19) leads to \( \Delta H_m^0(298.15 \text{ K}) = (-2.7 \pm 1.5) \text{ kJ mol}^{-1} \) and \( \Delta_f H_m^0(\text{NiCr}_2\text{O}_4, \text{s, 298.15 K}) = (-1383.0 \pm 2.3) \text{ kJ mol}^{-1} \).

For calculation of \( \Delta S_m^0(298.15 \text{ K}) \) the sum of squares of deviations was minimized
\[
\sum_i \left( \Delta_r G_m^0, \text{calc}_i - \Delta_r G_m^0, \text{i, exp}_i \right)^2 w_i
\]
where \( \Delta_r G_m^0, \text{i, calc} \) - Gibbs energy calculated by the equation (7) and containing the unknown \( \Delta_r S_m^0(298.15 \text{ K}) \); \( w_i = n_i / T_i^2 \) - is the weight assigned to the experimental Gibbs energy. As a result of this calculation \( \Delta_r S_m^0(298.15 \text{ K}) = (8.3 \pm 2.5) \text{ J K}^{-1} \text{ mol}^{-1} \) was obtained. This leads to \( S_m^0(\text{NiCr}_2\text{O}_4, \text{s, 298.15 K}) = (127.2 \pm 5.8) \text{ J K}^{-1} \text{ mol}^{-1} \). On this basis thermodynamic functions of \( \text{NiCr}_2\text{O}_4 \) in the interval of temperatures 298.15 - 2000 K (see Table 4) were calculated.

7. SUMMARY

It has been found that at adding of \( \text{K}_2\text{Cr}_2\text{O}_4 \) and \( \text{K}_2\text{SO}_4 \) to the systems containing chrome and nickel oxide there appear ions \( \text{NiO}^-, \text{CrO}_3^-, \text{CrO}_4^-, \) and \( \text{Cr}_2\text{O}_6^- \).

The reaction equilibrium constants (3) and (5) have been determined in the temperature interval of 1200 - 1500 K. On this basis the methods allowing to determine the activities \( \text{NiO} \) and \( \text{Cr}_2\text{O}_3 \) have been suggested.

\( \text{NiO} \) and \( \text{Cr}_2\text{O}_3 \) activities for two heterogeneous regions \( \text{NiO} - \text{NiCr}_2\text{O}_4 \) and \( \text{NiCr}_2\text{O}_4 - \text{Cr}_2\text{O}_3 \) were measured and Gibbs energy of \( \text{NiCr}_2\text{O}_4 \) formation from the oxides were calculated.
REFERENCES


TABLE 1. Mass-spectra of negative ions (relative units, 1473 K)

<table>
<thead>
<tr>
<th>Systems</th>
<th>N exp.</th>
<th>I(NiO&lt;sup&gt;−&lt;/sup&gt;)</th>
<th>I(CrO&lt;sup&gt;3−&lt;/sup&gt;)</th>
<th>I(CrO&lt;sup&gt;4−&lt;/sup&gt;)</th>
<th>I(Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;−)</th>
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<tr>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;−K&lt;sub&gt;2&lt;/sub&gt;CrO&lt;sub&gt;4&lt;/sub&gt; 93.0:7.0</td>
<td>1</td>
<td>-</td>
<td>10000</td>
<td>1.1</td>
<td>0.95</td>
</tr>
<tr>
<td>NiCr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;−Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;−K&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; 36.9:50.2:12.9</td>
<td>2</td>
<td>0.25</td>
<td>10000</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>NiO−Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;−K&lt;sub&gt;2&lt;/sub&gt;CrO&lt;sub&gt;4&lt;/sub&gt; 92.0:3.0:5.0</td>
<td>3</td>
<td>0.51</td>
<td>10000</td>
<td>2.9</td>
<td>2.7</td>
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<td>NiCr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;−NiO−K&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt; 31.9:60.3:7.8</td>
<td>4</td>
<td>0.86</td>
<td>10000</td>
<td>3.9</td>
<td>3.9</td>
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</tbody>
</table>
TABLE 2. Equilibrium constants of reaction (3) and (5)

\[
\begin{array}{cccccc}
\text{Cr}_2\text{O}_3(s)+3\text{CrO}^-=2\text{Cr}_2\text{O}_6^++\text{CrO}^- & \text{NiO}(s)+\text{CrO}^-+\text{CrO}_4^- = \text{NiO}_2^++\text{Cr}_2\text{O}_6^- \\
\hline
\text{N} \quad \text{exp.} & \text{T} \quad \text{K} & \ln K^0(3) & s_i & n_i & \text{N} \quad \text{exp.} & \text{T} \quad \text{K} & \ln K^0(5) & s_i & n_i \\
1 & 1163 & 11.82 & 0.35 & 3 & 3 & 1344 & -10.10 & 0.14 & 3 \\
& 1209 & 11.20 & 0.42 & 6 & 1430 & -9.12 & 0.20 & 2 \\
& 1229 & 11.23 & 0.21 & 5 & 1473 & -9.13 & 0.41 & 4 \\
& 1264 & 11.02 & 0.09 & 3 & 1515 & -8.65 & 0.32 & 4 \\
& 1300 & 10.47 & 0.26 & 6 & & & & \\
& 1344 & 10.50 & 0.12 & 3 & & & & \\
& 1387 & 10.88 & 0.49 & 3 & 4 & 1255 & -10.20 & 0.00 & 1 \\
& 1473 & 10.00 & 0.21 & 2 & 1291 & -10.02 & 0.18 & 6 \\
& 1515 & 9.85 & 0.26 & 3 & 1300 & -9.76 & 0.43 & 2 \\
& & & & & 1326 & -10.04 & 0.24 & 7 \\
2 & 1326 & 10.30 & 0.50 & 3 & 1413 & -9.42 & 0.40 & 4 \\
& 1370 & 10.57 & 0.25 & 9 & 1448 & -8.71 & 0.55 & 3 \\
& 1413 & 10.65 & 0.45 & 7 & 1473 & -8.52 & 0.16 & 5 \\
& 1448 & 9.84 & 0.24 & 6 & 1515 & -8.08 & 0.10 & 2 \\
& 1473 & 9.34 & 0.09 & 6 & & & & \\
& 1515 & 9.67 & 0.24 & 5 & & & & \\
\end{array}
\]

\[
\ln K^0(3) = \ln \frac{I(52\text{CrO}_3^-)I(52\text{Cr}_2\text{O}_6^-)^2}{I(52\text{CrO}_4^-)^3} + 1.280 \\
\ln K^0(5) = \ln \frac{I(58\text{NiO}_2^-)I(52\text{Cr}_2\text{O}_6^-)}{I(52\text{CrO}_3^-)I(52\text{CrO}_4^-)} + 0.809 \\
\]

\( s_i \) - calculated deviation of single values \\
\( n_i \) - number of measurements
### TABLE 3. Gibbs energy of NiCr₂O₄ formation from oxides

<table>
<thead>
<tr>
<th>N exp.</th>
<th>T (K)</th>
<th>ln Kᵢ</th>
<th>sᵢ</th>
<th>nᵢ</th>
<th>ln α(NiO)</th>
<th>ΔGᵢ ^{o}(6)</th>
<th>ln α(Cr₂O₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2⁵</td>
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</tr>
<tr>
<td></td>
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\[ a - \ln Kᵢ = \ln \frac{I(\text{52CrO}_3^-)I(\text{52Cr}_2\text{O}_6^-)^2}{I(\text{52CrO}_4^-)^3} \]

\[ b - \ln Kᵢ = \ln \frac{I(\text{58NiO}_2^-)I(\text{52Cr}_2\text{O}_6^-)}{I(\text{52CrO}_3^-)I(\text{52CrO}_4^-)} \]

sᵢ - calculated deviation of single values
nᵢ - number of measurements
### TABLE 4. Thermodynamic functions of NiCr$_2$O$_4$

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Fig. 1. Experimental equilibrium constants of reaction

a) $\ln K^0_p(3)$, - exp. 1, - exp. 2.
b) $\ln K^0_p(5)$, - exp. 3, - exp. 4.

Fig. 2. Gibbs energy of NiCr$_2$O$_4$ formation from oxides.

1 - Schmalzried, 2 - Tretjakow, 3 - Levitskii,
4 - Davies, 5 - Kunnmann, 6 - Lenev, 7 - Barin.
- exp. 2, - exp. 3, exp. 4.