

ION-MOLECULAR EQUILIBRIUM TECHNIQUE APPLIED TO Cr_2O_3 AND
NiO ACTIVITY DETERMINATION. GIBBS ENERGY OF FORMATION OF
 NiCr_2O_4 .

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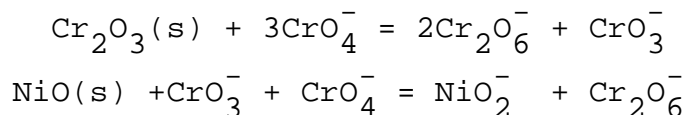
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Short title - "GIBBS ENERGY OF NiCr_2O_4 "

The method for determination of Cr_2O_3 and NiO activity in high-temperature systems based on measuring of equilibrium constants of reactions with negative ions



has been suggested. To produce measurable quantities of suitable ions in the saturated vapour small amounts of easily ionized substance (K_2SO_4 or K_2CrO_4) were added to the systems being investigated.

The activities of Cr_2O_3 and NiO have been determined for heterogeneous systems NiO - NiCr_2O_4 and NiCr_2O_4 - Cr_2O_3 and Gibbs energy of NiCr_2O_4 formation from oxides has been calculated.

1. INTRODUCTION

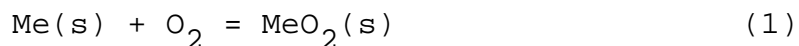
The activity measurements in the oxide systems are a remarkable

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

$$\alpha(\text{MeO}_2) = K^{\circ}(1) p(\text{O}_2) \alpha(\text{Me})$$

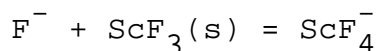
where $K^{\circ}(1)$ is equilibrium constant of reaction



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 $\text{NaF} - \text{ScF}_3$ system there are F^- and ScF_4^- ions among other ones. The following ion-molecular equilibrium can be written



Having measured the ratio of partial pressures of $\{p(\text{ScF}_4^-)/p(\text{F}^-)\}^{\circ}$ 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

$$\alpha(\text{ScF}_3) = \frac{\{p(\text{ScF}_4^-)/p(\text{F}^-)\}}{\{p(\text{ScF}_4^-)/p(\text{F}^-)\}^{\circ}}$$

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 $\text{Na}_2\text{O}-\text{SiO}_2$ ⁽⁴⁾ and $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{SiO}_2$ ⁽⁵⁾ chromates of alkali metals were used as admixture (about 3 mol %). This allowed us to provide measurable concentrations of the following ions: CrO_3^- , CrO_4^- , NaCrO_4^- , KCrO_4^- . The first three ions allowed us to determine the activity of Na_2O and the ions CrO_3^- , CrO_4^- , and KCrO_4^- - the activity of K_2O .

The aim of the present work is to extend the method of ion-molecular equilibria on the activity determination of the oxides Cr_2O_3 and NiO . It is suggested to use negative ions CrO_3^- , CrO_4^- , Cr_2O_6^- ⁽⁶⁾ for measuring of chromium oxide activity and for that of nickel oxide to use a negative ion - NiO_2^- ⁽⁷⁾.

Spinel NiCr_2O_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° , 200 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_2O_3 oxides of spectroscopic grade and phase composition was checked by the X-ray analysis.

In the vapour over Cr_2O_3 and NiO oxides as well as over NiCr_2O_4 the negative ions are absent. To generate the ions there were introduced easy-ionized compounds (K_2CrO_4 or K_2SO_4) to the investigated systems and the following negative ions CrO_3^- , CrO_4^- , Cr_2O_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 ≈ 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.

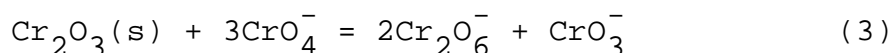
3. DETERMINATION OF Cr_2O_3 AND NiO ACTIVITIES

It has been shown that addition of potassium sulphate and

potassium chromate to the systems containing Cr_2O_3 leads to the appearance of measurable concentrations of ions in the vapour at 1200 - 1500 K: CrO_3^- , CrO_4^- , and Cr_2O_6^- . This allows us to determine the activity of Cr_2O_3 as follows

$$\alpha(\text{Cr}_2\text{O}_3) = \frac{p(\text{CrO}_3^-) p^2(\text{CrO}_6^-)}{p^3(\text{CrO}_4^-)} \frac{1}{K^{\circ}(3)} \quad (2)$$

where $K^{\circ}(3)$ is the equilibrium constant of the reaction

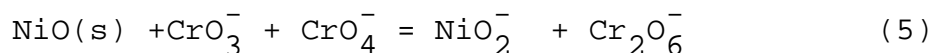


Unless specified otherwise the compounds are in the gaseous state.

Similar, in case of the systems containing NiO the addition of K_2CrO_4 gives NiO_2^- , CrO_3^- , CrO_4^- , and Cr_2O_6^- ions in measurable concentrations. It makes possible to find activity of NiO according to relation

$$\alpha(\text{NiO}) = \frac{p(\text{NiO}_2^-) p(\text{Cr}_2\text{O}_6^-)}{p(\text{CrO}_4^-) p(\text{CrO}_3^-)} \frac{1}{K^{\circ}(5)} \quad (4)$$

where $K^{\circ}(5)$ is the equilibrium constant of the reaction



The ratio of partial pressures of ions is proportional to the ratio of ion currents and can be measured by the mass-spectrometer (8)

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

were I_{mul} is the current measured on the multiplier, i is the percentage of the isotope being measured.

The equilibrium constant $K^{\circ}(3)$ was measured in the saturated vapour of the systems $\text{Cr}_2\text{O}_3\text{-K}_2\text{CrO}_4$ (exp. 1) and $\text{NiCr}_2\text{O}_4\text{-Cr}_2\text{O}_3\text{-K}_2\text{SO}_4$ (exp. 2) and $K^{\circ}(5)$ in the systems $\text{NiO-Cr}_2\text{O}_3\text{-K}_2\text{CrO}_4$ (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 $K^{\circ}(3)$ and $K^{\circ}(5)$ one can't use pure oxides Cr_2O_3 and NiO due to the absence of negative ions in the saturated vapours of these substances. That is why all the investigated systems include the admixture of easily ionized substance K_2SO_4 or K_2CrO_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 NiCr_2O_4 , a negligible solubility of NiO in Cr_2O_3 and a small (≈ 4 mole %) solubility of CrO in NiO are noted. NiO activity that is in equilibrium with NiCr_2O_4 according to the ref. (9) is equal to 0.97. Note, that NiO activity in the similar systems $\text{NiO-NiAl}_2\text{O}_4$ and $\text{NiO-NiGa}_2\text{O}_4$ also differs a little from unit up to $T = 1550 \text{ K}$ (11). K_2SO_4 solubility in NiO and Cr_2O_3 is negligible (12). That is why it is adopted in the present work that Cr_2O_3 activity in the system $\text{NiCr}_2\text{O}_4\text{-Cr}_2\text{O}_3$ and NiO activity in the system $\text{NiO-NiCr}_2\text{O}_4$ are equal to unit.

In the course of the experiment a significant vapourization of K_2SO_4 and KCr_2O_4 occurred. The absolute intensities of negative ion currents were changed by several orders and measured values of equilibrium constants did not change. It gives strong support in favour of the NiO (exp. 3 and 4) or Cr_2O_3 (exp. 1 and 2) activity is equal to unit.

The temperature dependences $K^{\circ}(3)$ and $K^{\circ}(5)$ (Fig. 1.) have been determined

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

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

Standard deviations of $K^{\circ}(3)$ and $K^{\circ}(5)$ depending on temperature

can be calculated as follows

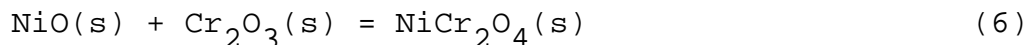
$$s\{\ln K^{\circ}(3)\} = 0.68 \left\{ \frac{1}{70} + \frac{(T^{-1} - 1356^{-1})^2}{(0.484 \cdot 10^{-3})^2} \right\}^{1/2}$$

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

Thus, the values $K^{\circ}(3)$ and $K^{\circ}(5)$ obtained allow us to measure Cr_2O_3 and 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 Cr_2O_3 - from 1 up to 10^{-5} and for NiO - from 1 up to 0.05.

4. GIBBS ENERGY OF NiCr_2O_4

Gibbs energy of NiCr_2O_4 formation from oxides has been also determined in experiments 2-4



As it was stated NiCr_2O_4 has a narrow homogeneity region (9). So in case with the experiments 2-4 it is possible to write

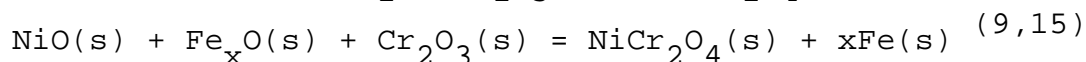
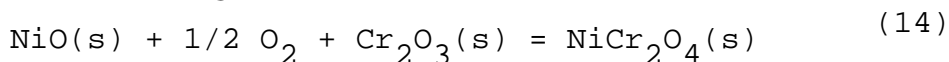
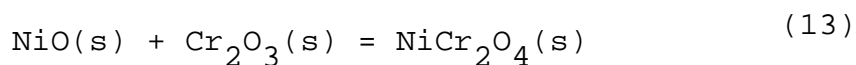
$$\Delta_r G_m^{\circ}(6) = RT \ln \alpha(\text{NiO}) \alpha(\text{Cr}_2\text{O}_3)$$

In experiment 2 in the system $\text{NiCr}_2\text{O}_4 - \text{Cr}_2\text{O}_3$ the activity of Cr_2O_3 is equal to unity and activity of NiO was measured according equation (4). In experiments 3 and 4 in the system $\text{NiO-NiCr}_2\text{O}_4$ the activity of NiO is equal to unit and Cr_2O_3 activity was measured according equation (2). The experimental data are presented in Table 3. In both cases the values of Gibbs energy $\Delta_r G_m^{\circ}(6)$ satisfactory agree between themselves.

5. DISCUSSION

In spite of a great number of investigations the situation with the thermodynamic data of NiCr_2O_4 is not single-valued.

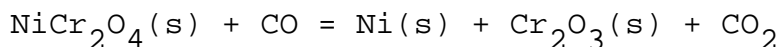
In the 60-70s a number of works have been carried out on determining of $\Delta_r G_m^\circ(6)$ by the e.m.f. method with a solid oxide electrolytes (9,13-15), where an oxygen concentration cell was used. Various electrodes of comparison were applied and Gibbs energy of the following reaction was calculated



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



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_2O_4 as well as the NiO and Cr_2O_3 in molten oxides in a calorimeter. This value at 1173K is $-5.2 \text{ kJ}\cdot\text{mol}^{-1}$ and does not agree with the e.m.f. data and the method of heterogeneous equilibria.

Thermodynamic data of NiCr_2O_4 given in the reference book (20) are based on $\Delta_r H_m^\circ(6)$ 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_2O_4 also based on the value $\Delta_r H_m^\circ(6)$ from the work (19).

Gibbs energies $\Delta_r G_m^\circ(6)$ 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 $\Delta_r G_m^\circ(6)$ and enthalpy $\Delta_r H_m^\circ(6)$ obtained in the works (9,13-17).

6. THERMODYNAMIC FUNCTIONS OF NiCr_2O_4

Gibbs energy of the reaction depends on the temperature as follows

$$\begin{aligned} \Delta_r G_m^\circ &= \Delta_r H_m^\circ(298.15 \text{ K}) - T \Delta_r S_m^\circ(298.15 \text{ K}) + \\ &+ \int_{298.15}^T \Delta_r C_{p,m}^\circ dT - T \int_{298.15}^T (\Delta_r C_{p,m}^\circ / T) dT \end{aligned} \quad (7)$$

In the case of reaction (6) entropy and temperature dependence of NiCr_2O_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_2O_4 from the reference book (20)

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

There were used enthalpies of formation, entropies and temperature dependencies of heat capacity NiO $\{\Delta_f H_m^\circ(298.15 \text{ K}) = (-239.7 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$, $S_m^\circ(298.15 \text{ K}) = (37.8 \pm 0.4) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\}$ (22) (data bank IVTAN TERMO, version of 1986) and Cr_2O_3 $\{\Delta_f H_m^\circ(298.15 \text{ K}) = (-1140.6 \pm 1.7) \text{ kJ} \cdot \text{mol}^{-1}$, $S_m^\circ(298.15 \text{ K}) =$

$(81.1 \pm 5.0) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (23).

Recalculations of the enthalpy of formation NiCr_2O_4 from oxides from the ref. (19) leads to $\Delta_r H_m^\circ(298.15 \text{ K}) = (-2.7 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{NiCr}_2\text{O}_4, \text{ s}, 298.15 \text{ K}) = (-1383.0 \pm 2.3) \text{ kJ} \cdot \text{mol}^{-1}$.

For calculation of $\Delta_r S_m^\circ(298.15 \text{ K})$ the sum of squares of deviations was minimized

$$\sum_i \{ \Delta_r G_{m,i}^\circ - \Delta_r G_{m,i}^{\circ, \text{calc}} \}^2 W_i$$

where $\Delta_r G_{m,i}^\circ$ - is an experimental Gibbs energy (Table 3); $\Delta_r G_{m,i}^{\circ, \text{calc}}$ - Gibbs energy calculated by the equation (7) and containing the unknown $\Delta_r S_m^\circ(298.15 \text{ K})$; $W_i = n_i / T_i^2$ - is the weight assigned to the experimental Gibbs energy. As a result of this calculation $\Delta_r S_m^\circ(298.15 \text{ K}) = (8.3 \pm 2.5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was obtained. This leads to $S_m^\circ(\text{NiCr}_2\text{O}_4, \text{ s}, 298.15 \text{ K}) = (127.2 \pm 5.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. On this basis thermodynamic functions of NiCr_2O_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 K_2CrO_4 and K_2SO_4 to the systems containing chrome and nickel oxide there appear ions NiO_2^- , CrO_3^- , CrO_4^- , and Cr_2O_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 NiO and Cr_2O_3 have been suggested.

NiO and Cr_2O_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 NiCr_2O_4 formation from the oxides were calculated.

REFERENCES

1. Turkdogan, E.T. Physicochemical properties of molten slags and glasses. The Metals Society, London. 1983.
2. Gusarov, A.V.; Korobov, M.V.; Sidorov, L.N. Zh. Fis. Khim., 1976, 50, 2873.
3. Sidorov, L.N.; Korobov, M.V. Mass spectrometry. 1981, 29, 199.
4. Rudnyi, E.B.; Vovk, O.M.; Sidorov, L.N.; Stolyarova, V.L.; Scakhmatkin, B.A.; Rakhimov, V.I. Fis. Khim. Stekla, 1988, 14, 218.
5. Rudnyi, E.B.; Korobov, M.V.; Vovk, O.M.; Kaibicheva, E.A.; Sidorov, L.N. High Temp. Sci. 1989, 00, 000.
6. Rudnyi, E.B.; Vovk, O.M.; Kaibicheva, E.A.; Sidorov, L.N. J. Chem. Thermodynamics, 1989, 21, 247.
7. Rudnyi, E.B.; Kusnetsova, O.V.; Kaibicheva, E.A.; Sidorov, L.N. Teplofiz. Vys. Temp. 1990, 00, 000.
8. Sidorov, L.N.; Korobov, M.V.; Zhuravleva, L.V. Mass-spectralnye termodinamicheskie issledovaniya, M., MGU, 1985.
9. Davies, H.; Smelter, W.W. J. Electrochem. Soc. 1974, 121, 543.
10. Pelton, A.D.; Schmalzried, H.; Stider, J. J. Phys. Chem. Solids, 1979, 40, 1103.
11. Kemori, N.; Katayama, I.; Kozuka, Z. Trans. J. Inst. Met. 1980, 21, 285.
12. Gupta, D.K.; Rapp, R.A. J. Electrochem. Soc. 1980, 127, 2194.
13. Schmalzried, H. Z. Phys. Chem. Neue Folge, 1960, 25, 178.
14. Tretjakow, J.D.; Schmalzried, H. Ber. Bunsenges. Phys. Chem. 1965, 69, 396.
15. Levitskii, V.A.; Resukhina, T.N.; Dneprova, V.G. Elektrokhimiya, 1965, 1, 933.
16. Levitskii, V.A.; Popov, S.G.; Gerasimov, Ya.I. In: Fisicheskaya khimiya okislov metallov. Balakirev, V.F.:

- editor. Nauka: Moscow, 1981.
17. Kunmann, W.; Rogers, D.B.; Wold, A. J. Phys. Chem. Solids. 1963, 24, 1535.
18. Lenev, L.M.; Novokhatskii, I.A. Zh. Fis. Khim. 1966, 40, 2030.
19. Muller, F.; Kleppa, O.J. J. Inorg. Nucl. Chem. 1973, 35, 2673.
20. Barin, I.; Knacke, D.; Kubaschewski, O. Thermochemical properties of inorganic substances. 1971 and supplement 1977.
21. Thermal constants of substances. Glushko, V.P.: editor. VINITI: Moscow, 1963-1982, vols. 1 to 10.
22. Gurvich, L.V. Vestn. AN SSSR, 1983, N 3, 54.
23. Thermodynamic properties of individual substances. Glushko, V.P.: editor. Nauka: Moscow, 1978-1982, vols. 1 to 4.

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

Systems	N exp.	I(NiO ₂ ⁻)	I(CrO ₃ ⁻)	I(CrO ₄ ⁻)	I(Cr ₂ O ₆ ⁻)
Cr ₂ O ₃ -K ₂ CrO ₄ 93.0:7.0	1	-	10000	1.1	0.95
NiCr ₂ O ₄ -Cr ₂ O ₃ -K ₂ SO ₄ 36.9:50.2 :12.9	2	0.25	10000	2.1	1.7
NiO-Cr ₂ O ₃ -K ₂ CrO ₄ 92.0:3.0 :5.0	3	0.51	10000	2.9	2.7
NiCr ₂ O ₄ -NiO-K ₂ SO ₄ 31.9:60.3:7.8	4	0.86	10000	3.9	3.9

TABLE 2. Equilibrium constants of reaction (3) and (5)

$\text{Cr}_2\text{O}_3(\text{s}) + 3\text{CrO}_4^- = 2\text{Cr}_2\text{O}_6^- + \text{CrO}_3^-$					$\text{NiO}(\text{s}) + \text{CrO}_3^- + \text{CrO}_4^- = \text{NiO}_2^- + \text{Cr}_2\text{O}_6^-$					
N exp.	T K	$\ln K^{\circ}(3)$	s_i	n_i	N exp.	T K	$\ln K^{\circ}(5)$	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
2	1326	10.30	0.50	3		1326	-10.04	0.24	7	
	1370	10.57	0.25	9		1413	-9.42	0.40	4	
	1413	10.65	0.45	7		1448	-8.71	0.55	3	
	1448	9.84	0.24	6		1473	-8.52	0.16	5	
	1473	9.34	0.09	6		1515	-8.08	0.10	2	
	1515	9.67	0.24	5						

$$\ln K^{\circ}(3) = \ln \frac{I(^{52}\text{CrO}_3^-)I(^{52}\text{Cr}_2\text{O}_6^-)^2}{I(^{52}\text{CrO}_4^-)^3} + 1.280$$

$$\ln K^{\circ}(5) = \ln \frac{I(^{58}\text{NiO}_2^-)I(^{52}\text{Cr}_2\text{O}_6^-)}{I(^{52}\text{CrO}_3^-)I(^{52}\text{CrO}_4^-)} + 0.809$$

s_i - calculated deviation of single values

n_i - number of measurements

TABLE 3. Gibbs energy of NiCr₂O₄ formation from oxides

N exp.	T K	ln K _I	s _i	n _i	ln α(NiO)	Δ _r G _m ^o (6)
2 ^a	1326	-11.76	0.06	2	-1.07	-11.8
	1370	-11.10	0.17	9	-0.76	-8.7
	1413	-11.09	0.13	6	-1.07	-12.6
	1448	-10.76	0.14	5	-0.98	-11.8
	1473	-10.81	0.11	6	-1.20	-14.7
	1515	-10.40	0.07	5	-1.06	-13.4
					ln α(Cr ₂ O ₃)	
3 ^b	1344	8.65	0.12	3	-0.60	-6.7
	1387	8.33	0.29	5	-0.69	-8.0
	1430	8.19	0.12	2	-0.62	-7.4
	1473	8.03	0.25	4	-0.58	-7.1
	1515	7.78	0.10	4	-0.64	-8.1
4 ^b	1209	9.52	0.32	6	-0.53	-5.3
	1255	9.21	0.00	2	-0.55	-5.7
	1291	8.65	0.32	6	-0.90	-9.7
	1300	8.87	0.53	2	-0.62	-6.7
	1326	8.45	0.18	7	-0.89	-9.8
	1370	8.46	0.17	4	-0.65	-7.4
	1413	7.90	0.12	5	-0.99	-11.6
	1448	7.86	0.40	3	-0.86	-10.4
	1473	7.92	0.13	5	-0.69	-8.5
	1515	7.41	0.53	2	-1.01	-12.7

$$a - \ln K_I = \ln \frac{I(^{52}\text{CrO}_3^-)I(^{52}\text{Cr}_2\text{O}_6^-)^2}{I(^{52}\text{CrO}_4^-)^3}$$

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

s_i - calculated deviation of single values

n_i - number of measurements

TABLE 4. Thermodynamic functions of NiCr_2O_4

T	$C_{p,m}^{\circ}$	S_m°	$H_m^{\circ}(T) - H_m^{\circ}(298.15)$
K	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\text{kJ} \cdot \text{mol}^{-1}$
298.15	148.8	127.9	0.0
300	149.1	128.8	0.3
400	161.1	173.6	15.9
500	167.7	210.3	32.3
600	172.0	241.3	49.3
700	175.4	268.0	66.7
800	178.2	291.7	84.0
900	180.6	312.8	102.3
1000	182.9	331.9	120.5
1100	185.1	349.5	138.9
1200	187.1	365.7	157.5
1300	189.1	380.7	176.3
1400	191.1	394.8	195.3
1500	193.0	408.1	214.5
1600	194.9	420.6	233.9
1700	196.8	432.4	253.5
1800	198.7	443.7	273.3
1900	200.5	454.5	293.3
2000	202.4	464.9	313.4

Fig. 1. Experimental equilibrium constants of reaction

a) $\ln K_p^{\circ}(3)$, - exp. 1, - exp. 2.

b) $\ln K_p^{\circ}(5)$, - exp. 3, - exp. 4.

Fig. 2. Gibbs energy of NiCr_2O_4 formation from oxides.

1 - Schmalzried, 2 - Tretjakow, 3 - Levitskii,

4 - Davies, 5 - Kunmann, 6 - Lenev, 7 - Barin.

- exp. 2, - exp. 3, exp. 4.