

ENTHALPIES OF FORMATION OF NEGATIVE IONS MnO_2^- , MnO_3^- , AND
 MnO_4^- AS DETERMINED BY ION-MOLECULE EQUILIBRIA METHOD

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running title - NEGATIVE IONS MnO_2^- , MnO_3^- , AND MnO_4^-

Admixture of potassium chromate to manganese oxide has allowed us to generate measurable concentration of negative ions MnO_2^- , MnO_3^- , and MnO_4^- in the vapors of manganese oxide at 1300 - 1500 K. Equilibrium constants with the participation of these ions have been measured and the enthalpies of formation $\{\Delta_f H_m^{\circ}(\text{MnO}_2^-, 0 \text{ K}) = (-266 \pm 13) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^{\circ}(\text{MnO}_3^-, 0 \text{ K}) = (-538 \pm 14) \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_f H_m^{\circ}(\text{MnO}_4^-, 0 \text{ K}) = (-669 \pm 17) \text{ kJ} \cdot \text{mol}^{-1}\}$, dissociation energies and the electron affinity of MnO_2 $\{\text{EA} = 292 \text{ kJ} \cdot \text{mol}^{-1}\}$ have been estimated. The use of manganese-containing negative ions to measure the activity of manganese oxides has been discussed.

Recently we have discovered that admixture of potassium chromate to cobalt, nickel, and iron oxides allowed a measurable concentration of negative ions FeO_2^- , CoO_2^- , and NiO_2^- to appear at temperatures 1300-1500 K.^{1,2} In the present work a

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similar approach has been employed with manganese oxide. As a result, conditions to register negative ions MnO_2^- , MnO_3^- , and MnO_4^- have been found and we were able to determine thermodynamic properties of these ions.

Ions like MnO_2^- are interesting in connection with studies of the mechanism of heterogeneous catalysis and the reversible oxygenation of metal complexes.^{3,4} A number of **ab initio** calculations have been carried out for MnO_4^- which is the most stable negative ion in solid and solution chemistry of manganese (VII).⁵⁻¹⁰

Gas-phase negative ions MnO_2^- , MnO_3^- , and MnO_4^- have earlier been obtained by means of electron ionization of $\text{Mn}_2(\text{CO})_{10}$ ^{11,12} and secondary-ion mass spectrometry (SIMS) of manganese surfaces covered by oxygen.^{13,14} Fokkens et al.¹² have investigated the reactions of MnO_2^- and MnO_3^- with aliphatic alcohols.

Thermodynamics of negative oxygen-containing ions of manganese is unknown.

EXPERIMENTAL

This work was performed on a magnet mass spectrometer, model MKh-1303 (Electron, Sumy, Ukraine) (60°, 200 mm), adapted to study ion/molecule equilibria. A platinum effusion chamber (diameter 12 mm, height 12 mm) was used with (0.5 to 1.2 mm) effusion orifice. The temperature was measured with a platinum/(platinum-rhodium 10%) thermocouple, the accuracy being ±4 K. Ionic currents were measured with a channel electron multiplier model VEU-6. The substances Cr_2O_3 , K_2CrO_4 , and MnO_2 of chemical grade purity were used.

MnO_2 as well as Mn_3O_4 , prepared by heating MnO_2 on the air for 3 hours at temperature 1000°C ,¹⁵⁻¹⁷ were put into the effusion chamber. In the first case, decomposition of MnO_2 with formation of Mn_3O_4 was performed in the effusion chamber itself in vacuum for two hours at temperature 750°C before beginning of the experiment. The composition of the oxide was controlled by X-ray analyses. During the experiment Mn_3O_4 underwent further decomposition with formation of non-stoichiometric MnO_{1+x} at high temperatures.

The systems under study and the mass spectra observed are presented in Table 1. Note that the ions were formed inside the effusion cell because of thermal, surface, or self-ionization. Negative ion MnCrO_5^- besides ions presented was in all the experiments as well.

A small amount of potassium chromate was added to manganese oxide to enhance the electron concentration. It was this admixture that produced the measurable concentration of negative ions MnO_2^- , MnO_3^- , and MnO_4^- in the vapors of the mixtures under study. Besides enhancing the electron concentration, K_2CrO_4 admixture gave us chromium-containing negative ions also. Since their enthalpies of formation are well-known we were able to use them as ions-"standards" to estimate enthalpies of formation of manganese-containing negative ions.

In experiment 2 currents of negative ion PtO_2^- were also measured. Its formation was due to comparatively high concentration of electrons and oxygen in the platinum effusion chamber. We had seen this ion earlier¹⁸ while the mixture $\{\text{Na}_2\text{WO}_4 + \text{Na}_2\text{SO}_4\}$ was vaporized under similar conditions from the

platinum chamber and already estimated the enthalpy of formation of PtO_2^- . Thus, the data of experiment 2 permits checking reliability of the obtained results.

The experiments were carried out on a fashion described elsewhere.¹⁹

The ratio of the partial pressures of ions was calculated from measured ion currents as follows:

$$\frac{p(\text{A}^-)}{p(\text{B}^-)} = \frac{I(\text{A}^-)}{I(\text{B}^-)} \left\{ \frac{M(\text{A}^-)}{M(\text{B}^-)} \right\}^{1/2} \frac{\gamma(\text{B}^-)}{\gamma(\text{A}^-)} \frac{i(\text{B}^-)}{i(\text{A}^-)}$$

where I is an ion current measured with the multiplier, M is the mass of the ion, γ is the multiplier gain, and i is the isotope abundance. The multiplier gain was assumed to be inversely proportional to the square root of ion mass.

COMPUTING EQUILIBRIUM CONSTANTS

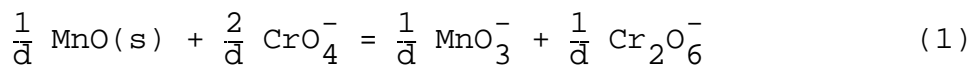
In the mathematical treatment which will follow, the logarithms of ion currents are assumed to be independent random quantities with the same variance

$$D(\ln I_{ij}) = \sigma^2$$

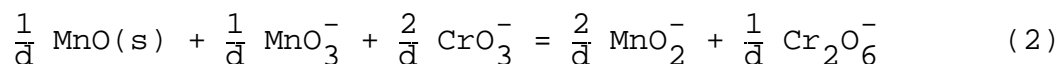
An amplifier measures ion currents with the same relative accuracy, and as a result, the logarithms of ion currents should have the same absolute accuracy.

Equilibrium inside the effusion chamber is assumed to be reached and activities of platinum Pt(s) and stoichiometric MnO(s) are assumed to be equal to unity. We will discuss these hypotheses later on.

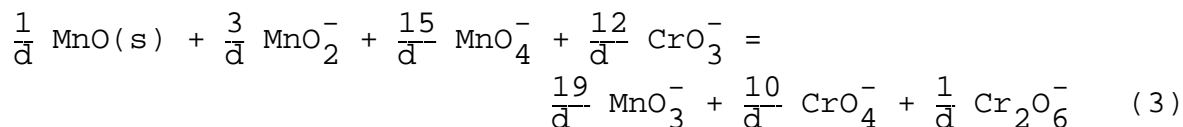
To estimate equilibrium constants four reactions were chosen as follows (they don't display the mechanism of ion formation by any means but show the mass balance only)



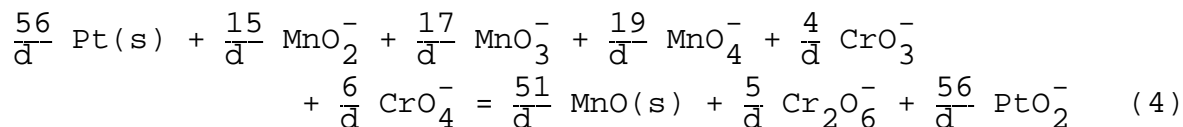
where $d = 6^{1/2}$



where $d = 10^{1/2}$



where $d = 840^{1/2}$



where $d = 4088^{1/2}$

We chose such unusual and monstrous reactions because of their useful properties which eased the following statistical processing, i.e. they comply with two equations

$$\sum_C \nu_{iC}^2 = 1$$

$$\sum_C \nu_{iC} \nu_{jC} = 0$$

where ν_{iC} is a stoichiometric number (greater than zero for products and less than zero for reagents), C is a set of all ions. This brings about that all the estimated equilibrium constants are non-correlated with each other and possess the same variance equal to that of the logarithm of the ion current

$$D\{\ln K^O(i)\} = \sigma^2$$

$$\text{cov}\{\ln K^O(i), \ln K^O(j)\} = 0$$

This problem has been discussed more thoroughly in Reference 19.

The estimated values of equilibrium constants of Reactions (1) to (4) are given in Tables 2.

Determining enthalpies of formation from equilibrium constants

The special choice of Reactions (1) to (4) brought about that the necessary hypotheses for ordinary least squares method (the logarithms of equilibrium constants are non-correlated and possess the same variance) have been met. Thus, the minimum of the following sum of squared deviations

$$SS = \sum_{ij} (\ln K_{ij} - \ln K_{ij}^{\text{calc}})^2 \quad (5)$$

over unknown enthalpies of formation should give the best estimates under the hypotheses accepted.

In Equation (5) K_{ij} is an experimentally determined equilibrium constant (i enumerates the reactions, j does the equilibrium constants of the i -th reaction), K_{ij}^{calc} is a true value of the equilibrium constant which in turn is connected with the enthalpies of formation and the entropies of all the substances in the i -th reaction

$$\ln K_{ij}^{\text{calc}} = R^{-1} (-T_{ij}^{-1} \cdot \vec{v}_i' \vec{H} + \vec{v}_i' \vec{S}) \quad (6)$$

Here \vec{H} is a vector of enthalpies of formation, \vec{S} is a vector of entropies, \vec{v}_i' is a vector of stoichiometric numbers of the i -th reaction. While Eqn (6) has been used the enthalpies of formation and the entropies were assumed not to depend on temperature and relate to the mean temperature in our experiments $T = 1400$ K.

The minimum of (5) has been found over unknown enthalpies of formation of MnO_2^- , MnO_3^- , MnO_4^- , and PtO_2^- while the enthalpies of formation of other compounds participating in Reactions (1) to (4) and all the entropies were taken **a priori** (see Table 3).

The entropy of neutral molecule MnO_2 from Reference 20 was used to estimate the entropy of negative ion MnO_2^- . Ion was assumed to have the same molecular constants except the orbital degeneracy ($g_o = 1$).

(Rigid rotator + harmonic oscillator) approximation was employed to calculate the entropy of MnO_3^- . To this end, the molecular constants such as $g_0 = 1$, $R(\text{Mn} - \text{O}) = 0.165 \text{ nm}$, $\angle \text{OMnO} = 107^\circ$, symmetry C_{3V} , $I_A I_B I_C = 2.3 \cdot 10^{-114} \text{ g}^3 \text{sm}^6$, frequencies 830, 429, 830(2), 355(2) sm^{-1} were chosen after comparative analysis of molecular constants of ClO_3^- , ClO_4^- , and MnO_4^- .^{25,26}

As in Reference 19, not the enthalpies of formation at 1400 K but quantities $\{\Delta_f H_m^0(0 \text{ K}) + \Delta_0^{1400} H_m^0\}$ (see Tables 3 and 4) were substituted into Eqn (6). This made computing a bit less complicated since the quantity $\Delta_0^{1400} H_m^0$ is easier to calculate than $\{\Delta_f H_m^0(1400 \text{ K}) - \Delta_f H_m^0(0 \text{ K})\}$. Note that both ways bring to the same results.

The procedure for finding such a minimum is described elsewhere¹⁹ and the results are presented in Table 4.

Inaccuracies of the values obtained were estimated on the same way as in Reference 19. Inaccuracies of auxiliary values from Table 3 were used as diagonal members of dispersion matrices of auxiliary thermodynamic quantities $\mathbb{D}(\vec{H}_{Ah})$ and $\mathbb{D}(\vec{S}_{AS})$ (notation from Reference 19). For auxiliary enthalpies of formation and entropies from Table 3 are correlated with each other non-zero non-diagonal members of the matrices $\mathbb{D}(\vec{H}_{Ah})$ and $\mathbb{D}(\vec{S}_{AS})$ and members of the matrix $\text{COV}(\vec{H}_{Ah}, \vec{S}_{AS})$ were also taken into account.

The values $\text{cov}[H^0(\text{CrO}_3^-), S^0(\text{CrO}_3^-)] = 21 \text{ kJ} \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-2}$, $\text{cov}[H^0(\text{CrO}_4^-), S^0(\text{CrO}_4^-)] = 44 \text{ kJ} \cdot \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-2}$, $\text{cov}[H^0(\text{CrO}_3^-), H^0(\text{CrO}_4^-)] = 57 \text{ kJ}^2 \cdot \text{mol}^{-2}$ were obtained during the combined treatment in Reference 23. Besides, nine covariances for enthalpy and entropy of Cr_2O_6^- , recorded in Table 5, were added.

They were obtained while the experimental equilibrium constants from Reference 24 were processed under the procedure of Reference 19.

The covariances among inaccuracies of the obtained values and among obtained and auxiliary values (see formulas in Reference 19) are presented in Table 5.

DISCUSSION

The activity of stoichiometric MnO was assumed to be equal to unity when the equilibrium constants of Reaction (1) to (4) were computed. In our experiments the activity of MnO actually was a little bit lower than unit because of two reasons: a) presence of admixture of chromium oxide and potassium chromate, b) manganese oxide being non-stoichiometric.

The first reason should not lower the activity of MnO more than on 10 per cent for MnO being the chief ingredient of the mixture (more than 90 mole per cent). Note that in the course of the experiments vaporization of K_2CrO_4 occurred. The absolute intensities of negative ion currents went down but this did not change the measured values of equilibrium constants.

To reckon influence of oxide non-stoichiometry we have to see at first what oxide composition was during measurements of equilibrium constants, since as we mentioned above, at high temperatures oxide decomposition occurred with formation of MnO_{1+x} .

To this end, partial pressures of oxygen in the vapors of the mixtures under study were estimated as follows

$$(p(O_2)/p^0) = \{p(CrO_4^-)/[p(CrO_3^-) K^0(7)]\}^2$$

where p° is the standard state pressure ($p^\circ = 101325 \text{ Pa}$) and $K^\circ(7)$ is the equilibrium constant of the reaction



Numeric values of $K^\circ(7)$ were computed from values of Table 3.

Figure 1 displays the experimental oxygen partial pressures combined with the stability diagram of manganese oxides. The data of Keller and Dieckmann^{27,28} for MnO_{1+x} and $\text{Mn}_3\text{O}_{4-y}$ were used to draw such a diagram (comparison and discussion of other works see in the References 27 and 28). Having compared the experimental oxygen partial pressures and the stability diagram one can say that, at lower temperatures the heterogeneous mixture ($\text{MnO}_{1+x} + \text{Mn}_3\text{O}_{4-y}$) was formed in the effusion chamber and at higher temperatures MnO_{1+x} was, where $x \approx 0.02$.

To estimate the activity of stoichiometric MnO the Gibbs-Duhem equation was applied

$$\ln a(\text{MnO}) = - \int_0^x \frac{x}{2} d \ln p(\text{O}_2)$$

Integration with Keller and Dieckmann²⁷ data gives us that the activity of MnO due to non-stoichiometry is not less than 0.95 at 1400 K on the line of heterogeneous equilibrium of MnO_{1+x} and $\text{Mn}_3\text{O}_{4-y}$ ($x = 0.029$).

As a result, we can state that the error produced by the assumption on the activity of MnO being unity is small (less than $2 \text{ kJ}\cdot\text{mol}^{-1}$ in the enthalpy of formation).

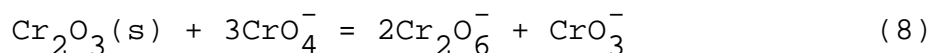
Another, even more important assumption was that equilibrium had been achieved in the effusion cell. The following facts witness that.

Let us compare the equilibrium constants (see Table 2)

estimated in different experiments with distinct composition of the mixtures. To underline the difference in composition we computed the activities of chromium oxide (see Table 6) according to the equation

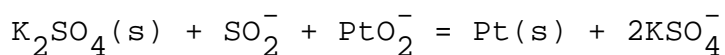
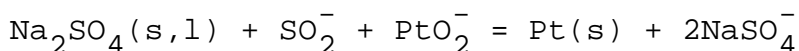
$$a(\text{Cr}_2\text{O}_3) = [\text{p}(\text{CrO}_3^-) \text{p}^2(\text{Cr}_2\text{O}_6^-)] / [\text{p}^3(\text{CrO}_4^-) K^0(8)]$$

where $K^0(8)$ is an equilibrium constant of the reaction (for more details, see Reference 24)



The activities of chromium oxide differed by almost ten times in different experiments (note the distinct ratios of ion currents of MnO_3^- and CrO_3^- in Table 1) while the measured equilibrium constants are in good agreement with each other.

The enthalpy of formation of PtO_2^- as determined in our work $\{\Delta_f H^0(\text{PtO}_2^-) = (-70 \pm 14) \text{ kJ} \cdot \text{mol}^{-1}\}$ is in a fair agreement with that from Reference 18 $\{\Delta_f H^0 = (-66 \pm 18) \text{ kJ} \cdot \text{mol}^{-1}\}$ where the equilibrium constants of the reactions



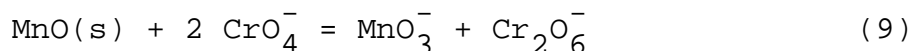
were measured. It also confirms that equilibrium has been achieved.

Using the enthalpies of formation of negative ions MnO_2^- , MnO_3^- , and MnO_4^- determined by us (Table 4) and the literature data (see Table 7) the electron affinity of MnO_2 and dissociation energies presented in Table 8 have been estimated. For comparison, the electron affinity of ClO_2 and some dissociation energies of chlorine-containing negative ions are also shown in Table 8.

Having determined the thermodynamic properties of manganese-containing negative ions we can suggest a new

approach to determine activities of manganese oxides at high temperatures by ion-molecule equilibria method.

We will give an example for stoichiometric MnO. Using literature (Table 3) and obtained (Table 4) values one can compute equilibrium constants of the reaction



Then, measuring the ratio of ion currents of CrO_4^- , Cr_2O_6^- , and MnO_3^- in the vapors of the mixture under study one is able to determine the activity of manganese oxide as follows

$$a(\text{MnO}) = [p(\text{MnO}_3^-) p(\text{Cr}_2\text{O}_6^-)] / [p^2(\text{CrO}_4^-) K^{\circ}(9)]$$

It should be mentioned that since the errors of the enthalpies of formation and the entropies presented in Tables 3 and 4 are correlated between each other (see Table 5) the error propagation law must be applied in its general form

$$R^2 D\{\ln K^{\circ}\} = \frac{1}{T^2} \{ \vec{v}' D(\vec{H}) \vec{v} \} + \vec{v}' D(\vec{S}) \vec{v} - \\ - \frac{1}{T} \{ \vec{v}' \text{COV}(\vec{H}, \vec{S}) \vec{v} + \vec{v}' \text{COV}(\vec{S}, \vec{H}) \vec{v} \}$$

Here are included, besides the errors of the enthalpies of formation and the entropies, the covariances among them {the matrix $\text{COV}(\vec{H}, \vec{S})$ and non-diagonal members of $D(\vec{H})$ and $D(\vec{S})$ }.

We will give a small numerical example for the equilibrium constant of reaction (9) at 1400 K. Were the covariances not used the greatly enhanced inaccuracy would be obtained: ± 3.4 in $\ln K^{\circ}$, which corresponds to the error in $K^{\circ}(9)$ on 3000%. Only application of the covariances from Table 5 supplies the reliable inaccuracy which is just ± 0.19 in $\ln K^{\circ}$ or 20% in K° itself.

REFERENCES

1. E.A. Kaibicheva, E.B. Rudnyi, L.N. Sidorov, I.D. Sorokin, **Zhurnal Fiz. Khimii**, 65, 919 (1991); **Russ. J. Phys. Chem.** (English translation), 65, 484 (1991).
2. E.A. Kaibicheva, E.B. Rudnyi, L.N. Sidorov, **Zhurnal Fiz. Khimii**, 66, 3153 (1992).
3. L. Vaska. **Acc. Chem. Res.** 9, 175 (1976).
4. M.H. Gubelman, A.F. Williams. **Structure and Bonding**, 55, 1 (1983).
5. J.A. Connor, I.H. Hillier, V.R. Saunders, M.H. Wood, M. Barber. **Mol. Phys.** 24, 497 (1972).
6. V.A. Gubanov, J. Weber, J.W. Connolly. **J. Chem. Phys.** 63, 1455 (1975).
7. T. Sasaki, H. Adachi. **J. Elect. Spectr. Rel. Phen.** 19, 261 (1980).
8. G.L. Gutsev, A.I. Boldyrev. **Chem. Phys. Let.** 108, 255 (1984).
9. A.V. Kondratenko, E.S. Fomin, K.M. Neiman, V.A. Nasluzov. **Optika i Spektr.** 66, 339 (1989).
10. A.V. Kondratenko, E.S. Fomin, V.I. Nemanova, S.F. Ruzankin, G.M. Zhidomirov, L.N. Mazalov. **J. Struct. Chem.** 30, 249 (1989).
11. R.R. Squires. **Chem. Rev.** 87, 623 (1987).
12. R.H. Fokkens, I.K. Gregor, N.M.M. Nibbering. **Rapid Com. Mass Spect.** 5, 368 (1991).
13. C. Plog, L. Wiedmann, A. Benninghoven, **Surf. Sci.** 67, 565 (1977).
14. H. Gnaser. **Surf. Sci.** 138, 561 (1984).
15. K. Terayama, M. Ikeda. **Trans. J.I.M.** 24, 754 (1983).

16. Q.Y. Chen, X.M. Chen. **Thermochim. Acta**, 123, 61 (1988).
17. M.C. Puerta, P. Valerga. **J. Chem. Educ.** 67, 344 (1990).
18. E.B. Rudnyi, O.V. Kuznetsova , E.A. Kaibicheva , L.N. Sidorov, **Teplofiz. Vys. Temp.** 28, 1135 (1990); **High Temp. USSR** (English translation) 28, 864 (1990).
19. E.B. Rudnyi, E.A. Kaibicheva, L.N. Sidorov. **J. Chem. Thermodynamics**, 1993, accepted for publication.
20. L.V. Gurvich. **High Temp. Sci.** 26, 197 (1989).
21. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelley. **Selected values of the thermodynamic properties of elements**. Metals Park, Ohio, (1973).
22. **Termodinamichekije Svoistva Individual'nykh Veshchestv (Thermodynamic Properties of Individual Substances)**, ed. by V.P. Glushko, vols. 1 to 4, Nauka, Moscow (1978-1982).
23. E.B. Rudnyi, O.M. Vovk, E.A. Kaibicheva, L.N. Sidorov, **J. Chem. Thermodynamics**, 21, 247 (1989).
24. E.B. Rudnyi, E.A. Kaibicheva, L.N. Sidorov, M.T. Varsavskii, A.M. Men', **J. Chem. Thermodynamics**, 22, 623 (1990).
25. A. Loewenschuss, Y. Marcus. **Chem. Rev.** 84, 89 (1984).
26. A. Loewenschuss, Y. Marcus. **J. Phys. Chem. Ref. Data** 16, 61 (1987).
27. M. Keller, R. Dieckmann. **Ber. Bunsenges. Phys. Chem.** 89, 883 (1985).
28. M. Keller, R. Dieckmann. **Ber. Bunsenges. Phys. Chem.** 89, 1095 (1985).
29. L.M. Babcock, T. Pentecost, W.H. Koppenol. **J. Phys. Chem.** 93, 8126, 1989.

TABLE 1. The mixtures under study and observed mass spectra of negative ions (relative units, 1430 K, values for the isotope ^{51}Cr are given for chromium-containing ions and for the isotope with $m/e = 227$ for PtO_2^-)

1	$0.95\text{MnO}_2 + 0.05\text{K}_2\text{CrO}_4$	MnO_2^- (16), MnO_3^- (11000), CrO_3^- (100000), CrO_4^- (150), Cr_2O_6^- (3.1)
2	$0.92\text{Mn}_3\text{O}_4 + 0.04\text{K}_2\text{CrO}_4$ $+ 0.04\text{Cr}_2\text{O}_3$	MnO_2^- (1.1), MnO_3^- (720), MnO_4^- (1.7), CrO_3^- (100000), CrO_4^- (100), Cr_2O_6^- (21), PtO_2^- (3.8)
3	$0.96\text{Mn}_3\text{O}_4 + 0.03\text{K}_2\text{CrO}_4$ $+ 0.01\text{Cr}_2\text{O}_3$	MnO_2^- (6.2), MnO_3^- (2500), MnO_4^- (5.4), CrO_3^- (100000), CrO_4^- (77), Cr_2O_6^- (9.5)

TABLE 2. Standard equilibrium constants of reactions

exp	T/K	$\ln\{K^{\circ}(1)\}$			$\ln\{K^{\circ}(2)\}$			$\ln\{K^{\circ}(3)\}$			$\ln\{K^{\circ}(4)\}$		
		s	N		s	N		s	N		s	N	
1	1344	0.37	0.00	1	-8.69	0.00	1						
	1430	0.35	0.01	2	-8.02	0.04	2						
2	1344	0.70	0.07	4									
	1387	0.49	0.13	3	-8.12	0.16	3	0.93	0.22	3	-0.54	0.00	1
	1430	0.31	0.12	2	-8.24	0.06	2	1.00	0.41	2	0.00	0.11	2
	1473	0.29	0.13	3	-8.36	0.09	3	0.95	0.10	3	-0.14	0.08	3
	1515	0.44	0.07	3	-8.16	0.23	3	0.66	0.21	3	-0.49	0.37	2
3	1300	0.67	0.08	4	-8.25	0.13	4	0.79	0.08	4			
	1344	0.61	0.09	5	-8.19	0.13	5	0.83	0.04	5			
	1387	0.49	0.08	5	-7.88	0.09	5	0.81	0.05	5			
	1430	0.74	0.07	2	-7.77	0.03	2	0.90	0.15	2			

s is the calculated deviation of single values

N is the number of measurements

TABLE 3. The auxiliary enthalpies of formation and entropies

substance	$\frac{\Delta_f H_m^O(0\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_0^{1400} H_m^O}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{H_m^O(1400\text{ K})^a}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{S_m^O(1400\text{ K})}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
MnO(s) ^b	-384.8±0.5	66.6	-318.2	137.5±3.0
Pt(s) ^c	0.0	37.5	37.5	85.1±0.5
Cr ₂ O ₃ (s) ^d	-1134.8±1.7	152.1	-982.7	268.9±1.3
O ₂ ^d	0	45.6	45.6	255.5±0.0
CrO ₃ ^{-e}	-669±9	97.5	-571.5	391.7±4.0
CrO ₄ ^{-e}	-781±11	119.9	-661.1	432.2±5.8
Cr ₂ O ₆ ^{-f}			-1237.8±18.0	600.5±12.0
MnO ₂ ^{-g}		69.4		343.2±5.0
MnO ₃ ^{-g}		97.2		384.5±5.2
MnO ₄ ^{-h}		121.9		422.7±6.9
PtO ₂ ⁻ⁱ		70.8		362.1±4.9

a - The quantity $\{\Delta_f H_m^O(0\text{ K}) + \Delta_0^{1400} H_m^O\}$ is given

b - From the data bank IVTAN-TERMO (1986 version)²⁰

c - From the reference book²¹

d - From Gurvich's reference book²²

e - From Reference 23

f - From Reference 24

g - see text

h - From References 25 and 26

i - From Reference 18

TABLE 4. The obtained enthalpies of formation

ion	$\frac{H_m^O(1400\text{ K})^a}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_f H_m^O(0\text{ K})}{\text{kJ}\cdot\text{mol}^{-1}}$
MnO_2^-	-196.3	-266±13
MnO_3^-	-441.0	-538±14
MnO_4^-	-547.2	-669±17
PtO_2^-	0.4	-70±14

^a - The quantity $\{\Delta_f H_m^O(0\text{ K}) + \Delta_0^{1400} H_m^O\}$ is given

TABLE 5. Covariances among the obtained enthalpies of formation and the auxiliary values

	$H(\text{Cr}_2\text{O}_6^-)$	$S(\text{Cr}_2\text{O}_6^-)$	$H(\text{MnO}_2^-)$	$H(\text{MnO}_3^-)$	$H(\text{MnO}_4^-)$	$H(\text{PtO}_2^-)$
$H(\text{MnO}_2^-)$			165	114	118	95
$H(\text{MnO}_3^-)$			114	188	148	112
$H(\text{MnO}_4^-)$			118	148	280	130
$H(\text{PtO}_2^-)$			95	112	130	195
$H(\text{MnO})$			0	0	0	0
$H(\text{Pt})$			0	0	0	0
$H(\text{CrO}_3^-)$	45	-11	49	54	59	54
$H(\text{CrO}_4^-)$	153	66	56	59	61	59
$H(\text{Cr}_2\text{O}_6^-)$	312	181	49	50	51	51
$S(\text{MnO}_2^-)$			35	0	0	0
$S(\text{MnO}_3^-)$			0	37	0	-1
$S(\text{MnO}_4^-)$			0	0	66	-1
$S(\text{PtO}_2^-)$			0	0	0	35
$S(\text{MnO})$			-12	-12	-12	1
$S(\text{Pt})$			0	0	0	0
$S(\text{CrO}_3^-)$	-11	-8	-1	0	1	0
$S(\text{CrO}_4^-)$	66	50	1	-2	-5	-2
$S(\text{Cr}_2\text{O}_6^-)$	181	137	16	12	8	13

$\text{cov}(H, H)$ in $\text{kJ}^2 \cdot \text{mol}^{-2}$, $\text{cov}(H, S)$ in $\text{J} \cdot \text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-2}$, $\text{cov}(S, S)$ in $\text{J}^2 \cdot \text{K}^{-2} \cdot \text{mol}^{-2}$

TABLE 6. Activities of chromium oxide

exp.	T/K	$\ln R_1$	N	$a(\text{Cr}_2\text{O}_3)$
1	1344	0.84	1	2.2e-004
	1430	-1.24	2	4.3e-005
2	1344	4.01	4	5.3e-003
	1387	3.77	3	5.2e-003
	1430	3.68	2	5.9e-003
	1473	3.67	3	7.1e-003
	1515	3.28	3	5.8e-003
3	1300	0.67	4	1.5e-004
	1344	0.75	5	2.0e-004
	1387	1.02	5	3.3e-004
	1430	2.99	2	3.0e-003

$$R_1 = \{I(\text{CrO}_3^-) I^2(\text{Cr}_2\text{O}_6^-)\} / I^3(\text{CrO}_4^-)$$

Table 7. Auxiliary enthalpies of formation to calculate dissociation energies

	$\frac{\Delta_f H_m^{\circ}(\text{O K})}{\text{kJ}\cdot\text{mol}^{-1}}$		$\frac{\Delta_f H_m^{\circ}(\text{O K})}{\text{kJ}\cdot\text{mol}^{-1}}$		$\frac{\Delta_f H_m^{\circ}(\text{O K})}{\text{kJ}\cdot\text{mol}^{-1}}$
O ^a	246.8±0.1	Mn ^b	282.4±2.1	Cl ^a	119.6±0.0
O ^{-a}	105.6±0.6	MnO ^b	162±13	ClO ^a	101.0±0.1
O ₂ ^{-a}	-42.5±0.8	MnO ₂ ^b	26±20	ClO ₂ ^a	107±6
				ClO ₂ ^{-c}	-121±10

a - From Gurvich's reference book ²²

b - From the data bank IVTAN-TERMO (1986 version) ²⁰

e - From Reference 29

Table 8. Dissociation energies and the electron affinity
(kJ·mol⁻¹)

	Mn	Cl				
EA(MO ₂)	292	229	D(MnO ₂ -O ⁻)	670	D(MnO ₃ ⁻ -O)	378
D(MO-O ⁻)	534	329	D(MnO-O ₂ ⁻)	658	D(MnO ₂ -O ₂ ⁻)	653
D(M-O ₂ ⁻)	506	199	D(MnO ₂ ⁻ -O)	519	D(MnO ₂ ⁻ -O ₂)	403

FIGURE LEGEND

Fig. 1. Experimental partial pressures of oxygen and the stability diagram of manganese oxides^{27,28}

