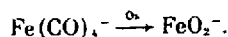# Determination of the electron affinity of FeO₂ by the ion—molecule equilibrium method

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ABSTRACT. Equilibrium constant of a reaction involving the FeO_2^- ion has been measured by the Knudsen effusion method with mass spectroscopic detection of the negative component of the vapour. The enthalpy of formation $\Delta_f H_0^\circ (FeO_2^-) = -164 \pm 13$ kJ mol^{-1} and the electron affinity $EA(FeO_2) = 266 \pm 24$ kJ mol^{-1} have been determined.

The FeO_2^- negative ion has been observed in the gas phase during the secondary ion emission accompanying the oxidation of a monolayer of the metal[1-4] and during the interaction of negative iron carbonyl ions with oxygen,[5]

$$Fe(CO)_x^- \xrightarrow{O_2} FeO_2^-.$$

In condensed phases the FeO_2^- ion is formed during the anodic oxidation of steel in concentrated solutions of alkali.[6,7]

None of these references gives thermodynamic information. The lower limit of the electron affinity, $EA(FeO_2) > 241$ kJ mol^{-1}, has been obtained[8] by photoelectron spectroscopy. On the basis of this initial value an electron affinity $EA(FeO_2) = 275$ kJ mol^{-1} has been recommended.[9] A model calculation of the chemical composition of the plasma in a MHD generator showed that at temperatures above 2000 K FeO_2^- becomes one of the predominant negative ions. However, the ion has not been detected in experimental studies.

The FeO_2 molecule and the FeO_2^- negative ion are convenient models for studying the mechanism of heterogeneous and of homogeneous catalysis[10,11] and of the reversible binding of oxygen.[12-14]

The aim of the present work was to determine the enthalpy of formation of the FeO_2^- ion and the electron affinity of the FeO_2 molecule. The results can also be used to determine the thermodynamic activity of the iron oxides in high-temperature systems. We have, for example, previously measured the activity of nickel oxide in the $NiO-Cr_2O_3$ system by studying ion—molecule equilibria involving the NiO_2^- ion.[15]

Experimental

The measurements were carried out in an MX-1303 mass spectrometer (60°, 200 mm), modified for studies of ion—molecule equilibria.[16] The systems were evaporated from a plateau crucible 12 mm in diameter and 12 mm high; the diameter of the effusion orifice was 0.7–0.8 mm. The temperature was measured with a Pt—Pt/Rh (10%) thermocouple to within ± 4 K. The ion currents were measured with a channel (VEU-6) electron multiplier. The initial preparations were of chemically pure grade; the iron oxide (Fe_3O_4) was prepared by heating Fe_2O_3 of analytically pure grade. A more detailed description of the apparatus and method has already been given.[15,16]

Measurement of the constant of ion—molecule equilibria involving FeO_2^-. Negative ions containing oxygen were generated in the vapour over the iron oxide Fe_3O_4 by introducing a small amount of an easily ionised substance (potassium chromate, or chromium oxide). The compositions of the systems and the mass spectra of their negative ions are shown in Table 1.

The use of K_2CrO_4 and Cr_2O_3 creates conditions (appropriate oxygen and electron partial pressures) for which the concentration of FeO_2^- is measurable. The effect of additives has been discussed[17] for the case of CoO_2^-.

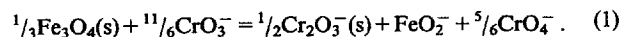We have determined the equilibrium constants for the ion—molecule reaction

$$\tfrac{1}{3}Fe_3O_4(s) + \tfrac{11}{6}CrO_3^- = \tfrac{1}{2}Cr_2O_3^-(s) + FeO_2^- + \tfrac{5}{6}CrO_4^-. \quad (1)$$

Table 1. Intensity of the ion currents (measured with an electron multiplier and corresponding to the ^{52}Cr and ^{58}Fe isotopes) in the vapour of the $Fe_3O_4-K_2CrO_4-CrO_3$ system at 1406 K.

Experiment	Composition	CrO₃⁻	CrO₄⁻	Cr₂O₆⁻	FeO₂⁻
1	88.5 : 5.0 : 6.5	1 000 000	526	193	6.7
2	89.6 : 5.4 : 5.0	1 000 000	656	128	21.1

The ratio of the partial pressures of the ions is proportional to the ratio of the measured ion currents:[18]

$$\frac{p(A^-)}{p(B^-)} = \frac{I(A^-)}{I(B^-)} \frac{M(A^-)}{M(B^-)} \frac{i(B^-)}{i(A^-)},$$

where I is the intensity of the ion current measured with the electron multiplier, M is the mass of the ion, and i is the content of the measured isotope.

The activity of the chromium oxide was determined through the ratio of the partial pressures of the CrO_3^-, CrO_4^-, and $Cr_2O_6^-$ ions:

$$a(Cr_2O_3) = \frac{p(CrO_3^-)p^2(Cr_2O_6^-)}{p^3(CrO_4^-)} \frac{1}{K_p(2)},$$

where $K_p(2)$ is the known[15] equilibrium constant of the reaction

$$Cr_2O_3(s) + 2CrO_4^- = 2Cr_2O_6^- + CrO_3^-,$$
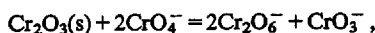
$$\ln K_p(2) = 9734/T + 3.28 \ (T = 1163 - 1515 \text{ K}).$$ (2)

The standard deviation can be calculated by the formula

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

The activity of Fe_3O_4 was taken to be unity. The validity of this assumption will be examined below.

This leads to the following formula for the equilibrium constant of the reaction (1):

$$\ln K_p(1) = \ln \frac{I(FeO_2^-)I(Cr_2O_6^-)}{I^{4/3}(CrO_3^-)I^{2/3}(CrO_4^-)} - \frac{1}{2}\ln K_p(2) + 0.505.$$

The $K_p(1)$ values thus obtained are shown in Table 2.

Table 2. Equilibrium constants of reaction (1).

T, K	$-\ln K_I$	s_I	n_I	$-\ln K_p^\circ(1)$	$\Delta_r H_0^\circ(1)$, kJ mol^{-1}
		Experiment 1			
1406	15.38	0.15	3	19.98	217.7
1430	15.44	0.14	4	19.98	221.2
		Experiment 2			
1344	14.74	0.03	2	19.50	203.4
1368	15.39	0.07	6	20.08	213.5
1387	14.34	0.00	1	18.99	203.5
1406	14.84	0.16	5	19.44	211.4
1447	14.56	0.18	5	19.06	212.6
1498	14.06	0.08	5	18.45	211.9

Notes. $\ln K_I = I(FeO_2^-)I(Cr_2O_6^-)/I^{4/3}(CrO_3^-)I^{2/3}(CrO_4^-)$; s_I is the standard deviation of a single determination; n_I is the number of determinations.

Calculation of the thermodynamic activity of Fe_3O_4 in the present system.

In the calculation of the equilibrium constant of the reaction (1) the activity of the iron oxide, the main component ($\sim 89\%$) of the $Fe_3O_4 - Cr_2O_3 - K_2CrO_4$ system, was taken to be unity, for two reasons: 1) the possible nonstoichiometry of the sample of iron oxide, and 2) the presence of $Cr_2O_3 - K_2CrO_4$ additives. Let us examine the effects of these factors separately.

Activity of the oxide in a nonstoichiometric phase.

The possible changes in the activity of Fe_3O_4 due to nonstoichiometry in the sample of oxide ($Fe_3O_{4+\delta}$) were calculated as follows.

Let the stoichiometric oxide Me_nO_m $\{a'(Me_nO_m) \equiv 1\}$ correspond to an oxygen partial pressure $p'(O_2)$ and to an activity of the metal $a'(Me)$, and the nonstoichiometric oxide $Me_nO_{m+\delta}$ to $p''(O_2)$ and

$a''(Me)$. We shall find the activity $a''(Me_nO_m)$ in the nonstoich metric composition by using the condition of compositi independence of the equilibrium constant of the reaction

$$Me_nO_m(s) = nMe(s) + \frac{m}{2}O_2.$$
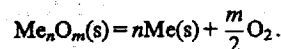
This gives

$$a''(Me_nO_m) = a''(Me)^n p''(O_2)^{m/2}/a'(Me)^n p'(O_2)^{m/2}.$$

The change in the activity of the metal can be found by integra the Gibbs – Duhem equation

$$\ln a''(Me) - \ln a'(Me) = \int_{\frac{n}{n+m'}}^{\frac{m+\delta}{m+m+\delta}} \frac{1}{1-y} d\ln p(O_2)^{\frac{1}{2}},$$

where y is the atom fraction of oxygen.

If the dependence of the oxygen pressure on the nonstoichiome is known an exact integration can be carried out.[19,20] In our cas relatively crude estimate of the change in activity of Me_nO_n needed. We therefore assumed that the dependence of the oxy partial pressure on the atom fraction of oxygen has the fc $\ln p(O_2) = ky + c$. This approximation gives the follow equation for the dependence of the activity of the oxide Me_nO_m the nonstoichiometry index:

$$\ln a''(Me_nO_m) = \frac{1}{2}\{\ln p''(O_2) - \ln p'(O_2)\} (n+m)\times$$

$$\times\left\{\frac{n+m+\delta}{\delta}\ln\frac{m+n}{m+n+\delta} + 1\right\}.$$

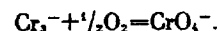Eqn. (3) can be further simplified by using the series expansion of logarithm:

$$\ln a''(Me_nO_m) \approx -\frac{1}{2}\delta \ln\{p''(O_2)/p'(O_2)\}.$$

In our experiments the partial pressure of oxygen was determi for the system

$$p(O_2) = p^x(CrO_4^-)/p^2(CrO_3^-)K_p^2(5),$$
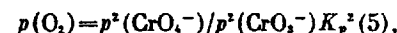
where $K_p(5)$ is the known[21] equilibrium constant of the reaction

$$Cr_3^- + \frac{1}{2}O_2 = CrO_4^-.$$

By comparing the experimental oxygen pressures with publis values (Fig. 1) we can obtain an estimate of the index δ for oxide. Hence, using this information, we obtain from formula the change in activity of Fe_3O_4 in the homogeneity reg corresponding to the composition thus determined. As can be s from the graph, for Fe_3O_4 the index δ does not exceed 1.5×10 According to our calculation the activity of pure Fe_3O_4 in this ph is 0.98.

Effect of the additive on the activity of the oxide.

To calculate change in the activity of Fe_3O_4 caused by the introduction of additive we require the phase diagram of the $Fe - Cr - K - O$ syst Since this information is not available we shall start from the ph diagram of the ternary $Fe - Cr - O$ system.[22,23] The region of s solutions of iron chromate ($FeCr_2O_4$) and Fe_3O_4 corresponds to compositions with the same $Fe:Cr:O$ ratio as the initial samp

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Petric and Jacob[24] give the activities of the oxide (Fe_3O_4) in the $Fe_3O_4-FeCr_2O_4$ system. From these data we may conclude that in our case $a(Fe_3O_4) \geq 0.8$.

committee of the High Temperatures Institute, Russian Academy of Sciences (Ed. of Translation)]. A correction of $R \ln 2$ was applied to these values to allow for the change in the degeneracy of the electronic ground state attending the transition from the uncharged molecule to the ion as a result of the appearance of an unpaired electron.
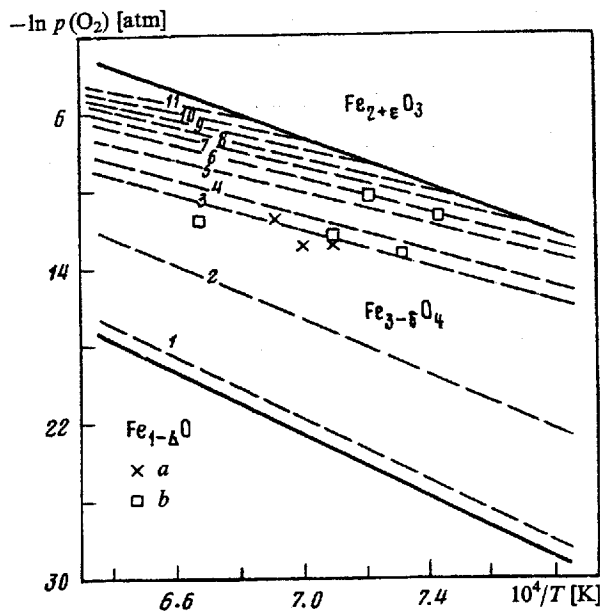
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Figure 1. Oxygen partial pressures corresponding to the nonstoichiometric $Fe_{3-s}O$ oxide[36] for different values of $10^2\delta$: 1, -0.25; 2, 0; 3, 0.25; 4, 0.5; 5, 1; 6, 1.5; 7, 2; 8, 2.5; 9, 3; 10, 3.5; 11, 4.5; a and b are the results of experiments 1 and 2 respectively.

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We note that the added potassium chromate evaporated almost completely during the experiment (the intensity of its ion currents decayed to the background level). Therefore the ratio of the measured ion currents was constant with the limits of the random error. This is additional evidence that the activity of the main component was not significantly affected by the presence of the additive.

On the whole the error in the equilibrium constant of reaction (1) attributable to our assumption on the activity of Fe_3O_4 probably does not exceed 15%, corresponding to an error of about 2 kJ mol^{-1} in the enthalpy of the reaction.

Determination of the enthalpy of formation of FeO_2^-. On the basis of the equilibrium constants of reaction (1) thus obtained the enthalpy of the reaction was determined by the third law of thermodynamics (see Table 2). The thermodynamic functions of the participants of the equilibrium needed for the calculation are given in Table 3. The Gibbs free energy of the FeO_2^- ion was calculated by the writers. Published data on the molecular constants of FeO_2^- and FeO_2 are inconsistent.[10,11,25-29] Therefore we used the reduced Gibbs free energies of the neutral FeO_2 molecule from the IVTANTERMO data bank (1986 version)[30] [the thermodynamics

Table 3. Initial thermodynamic values.

Compound	$-\Delta_f H^o_0$, kJ mol^{-1}	Φ^o_T, J mol^{-1} K^{-1}		
		1000 K	1200 K	1400 K
Fe_2O_4 (s) (Ref.30)	1106.9±2.1	217.3	248.8±0.8	276.1
Cr_2O_3 (s) (Ref.32)	1134.8±2.0	125.1	145.8±1.3*	160.2
CrO_3^- (Refs. 21, 32)	669±9	299.3	311.5±4.0	322.1
CrO_4^- (Ref.21)	781±11	318.9	333.6±5.8	346.5
FeO_2^-		286.0	294.7±7.0	302.5

The results of two experiments were processed jointly. The enthalpy of reaction (1) was found to be $\Delta_r H^o_0(1) = 213.1 \pm 16$ (1.7) kJ mol^{-1}. The full error is quoted, including the random error (shown in brackets) and the error in the choice of Φ^o_T values. Since the enthalpies of formation of the other participants are known we can calculate the enthalpy of formation of the FeO_2^- ion: $\Delta_f H^o_0(FeO_2^-) = -164 \pm 13$ kJ mol^{-1}.

The error of the enthalpy of formation calculated by the law of addition of errors was found to be higher (25 kJ mol^{-1}). This is because the enthalpies of formation of the CrO_3^- and CrO_4^- ions were obtained by solving an overdetermined system of equations,[21] and their errors are correlated mutually as well as with the errors of the reduced Gibbs free energies of these ions. A method of allowing for these correlations has been proposed.[31] The quoted error includes the reproducibility error, the error in the enthalpies of formation of the key components, and the error in Φ^o_T.

Bond energies in the anions and electron affinity of FeO_2. By combining these results with the known enthalpies of formation

Compound	O	O$^-$	O$_2^-$
$\Delta_f G^o_0$, kJ mol^{-1}	246.8±0.1	105.6±0.6	-42.5±0.8 (Ref.32)

Fe	FeO	FeO$_2$
412.8±1.3	270±13 (Ref.30)	102±20 (Ref.30)

and with the electron affinity $EA(Fe) = 15.7 \pm 3.4$ kJ mol^{-1} [33] we obtained the bond energies

Bond	Fe−O	FeO−O	FeO−O$^-$
D, kJ mol^{-1}	390±13;	401.2±7.5 (Ref.34);	415±24 539±18

Fe−O$_2^-$	Fe$^-$−O$_2$	
534±13	591±14	405±13 (Ref.35)

The electron affinity $EA(FeO_2) = 266 \pm 24$ kJ mol^{-1} thus obtained is consistent with the lower limit of this parameter [$EA(FeO_2) > 241$ kJ mol^{-1}] obtained by photoelectron spectroscopy.[8]

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Determination of the enthalpy of formation of the BiO⁻ and BiO₂⁻ ions by the ion—molecule equilibrium method

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ABSTRACT. The Knudsen effusion method with m spectroscopic detection of negative ions has been used to meas equilibrium constants involving BiO⁻ and BiO₂⁻ ions. The enthalp of formation $\Delta_f H^0_0(\text{BiO}^-) = -33 \pm 7$ kJ mol⁻¹ and $\Delta_f H^0_0(\text{BiO}_2^-$ -187 ± 10 kJ mol⁻¹ and the electron affinities $EA(\text{BiO}) = 156$ 14 kJ mol⁻¹ and $EA(\text{BiO}_2) = 311 \pm 27$ kJ mol⁻¹ have b determined.

This work is a continuation of our systematic study of thermodynamic properties of negative ions containing oxygen The energetics of negative ions must be known in order to model capture of electrons by electronegative additives in a low-tempera plasma.[3] Furthermore, the presence of negative ions in the vap of inorganic compounds allows the thermodynamic activity of ox to be determined in high-temperature systems.[4] The results obtained can be used to develop a method of determining activity of Bi_2O_3.

Experimental

The measurements were made with an MX-1303 spectrometer (200 mmHg, 60 °C), modified for studies ion—molecule equilibrium.[5,6] The temperature was measured wi Pt—Pt/Rh (10%) thermocouple, and held constant to within ± by a VRT-3 temperature regulator. The precision of the temper measurement was ±4 K. The ion currents were measured wi VEU-6 channel secondary electron multiplier.

Equilibrium constants involving the BiO₂⁻ ion. We have studie evaporation of Bi_2O_3 with small additions of Cr_2O_3 and K_2C The role of the additives was to increase the concentratio electrons in the Bi_2O_3 vapour, thus favouring the formatio measurable concentrations of BiO⁻ and BiO₂⁻ (the problem has