DETERMINATION OF EQUILIBRIUM OXYGEN PRESSURES IN VAPORS OF HIGH-TEMPERATURE SYSTEMS USING THE ION-MOLECULE EQUILIBRIUM METHOD

E. B. Rudnyi, O. M. Vovk, E. L. R. Kappe,
E. A. Kaibicheva, and L. N. Sidorov

Authors of this publication suggest the application of ion-molecule equilibria for determination of oxygen pressure in vapors of macromolecular systems. The method was tested by determination of Ni oxide dissociation pressure. The necessary ion-molecular equilibria were generated by adding, to the Ni-NiO system, a small amount of easily ionized sodium metaphosphate. The oxygen pressures produced in the 1300-1473°K range are in good agreement with literature data. The paper discusses the errors and the range of the ion-molecule equilibrium method $(10^{-12}-10$ Pa). The method was compared with other methods for oxygen pressure determination.

Interaction of metal and slag melts in many cases depends strongly on equilibrium oxygen pressure. For instance, in [1] it was demonstrated that the slag sorption capacity changes considerably when the equilibrium oxygen pressure changes from 10^{-16} to 10^4 Pa. Under such conditions, it is difficult to measure equilibrium oxygen pressure by traditional methods. Therefore the present authors suggest a new method, based on the use of ion-molecular equilibria in vapors of high-temperature systems.

The method [2,3] measures the currents of ions emitted from high-temperature surfaces (thermal ionization). The method of ion-molecule equilibria uses high-temperature mass-spectrometry methods, further developed, in order to produce ionization with an electron shock, therefore it requires relatively small alteration of the existing ion sources. During the experiment, the ions are at equilibrium with neutral components of the vapor and with the condensed phase. That permits application of well-known thermodynamic relations for calculation of equilibrium oxygen pressure.

Let us analyze the definition of equilibrium oxygen pressure. We use the following example. Let us assume that, in saturated vapor of the system studied, the ions PO_2^- and PO_3^- are at equilibrium with the vapor's neutral components. Then we can write down the following:

$$p(O_2) = \left[\frac{p(PO_3^-)}{p(PO_2^-)} \frac{1}{K_2} \right]^2. \tag{1}$$

where K_2 is an equilibrium constant of the following reaction:

$$PO_2^- + \frac{1}{2}O_2 = PO_3^-.$$
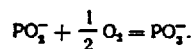
The ratio between partial pressures of the ions can be calculated from the experimentally determined ratio of ion currents in vapors of the system studied [2,3]:

$$\frac{p(PO_3^-)}{p(PO_2^-)} = \frac{I(PO_3^-)}{I(PO_2^-)} \frac{M(PO_3^-)}{M(PO_2^-)}. \tag{2}$$

where p is partial pressure, I is ionic current from an electron multiplier, and M is the ion's mass. The equilibrium constant K_2 can be calculated from previously established thermodynamic characteristics of the PO_2^- and PO_3^- ions [4].

Table 1

Logarithm of the Ratio Between the PO_2^- and PO_3^- Ion Currents in the System with Addition of $NaPO_3^*$

T, K	Y_ijk						Y_ij·
	i	j	k=1	2	3	4	
1300	1	1	4.56	4.79	4.74	4.90	4.75
1387	3	1	4.08	4.29			4.19
1344	2	1	4.68	4.71			4.69
1473	5	1	3.74	4.02	4.02		3.93
1430	4	1	4.23	4.31	4.32		4.29
1344	2	2	4.34	4.35			4.35
1300	1	2	4.67	4.68			4.68
1430	4	2	4.15	4.09	4.30		4.18
1387**	3	2	4.56	4.54	4.52		4.54
1473	5	2	4.05	4.05	4.06		4.05
1300	1	3	4.73	4.75	4.64		4.71
1344	2	3	4.45	4.45			4.45
1430	4	3	4.16	4.21	4.23		4.20
1473	5	3	3.98	3.97	3.93		3.96
1387	3	3	4.28	4.23	4.02		4.18

* The table reflects the order of the measurements (left to right and top to bottom). Designations are presented in the text, in explanations for formulas (3) and (4).
** This series was not considered in the further processing of results.

Oxygen partial pressure has already been determined by the ion-molecule equilibria method [4,5]. However, it was limited to systems whose vapors originally contained negative ions. The present work extends the application of that method to cover random systems. For that purpose, it was suggested that the required ions be generated by introducing, into the system studied, small, easily ionized dopes (oxygen-containing salts of alkali metals). The method was tested by determining oxygen partial pressure in a saturated vapor of the Ni-NiO system (NiO dissociation pressure).

EXPERIMENTAL METHOD AND RESULTS

For the investigation, an MKh-1303 (60°, 200 mm) mass-spectrometer was used, modified for the analysis of ion-molecule equilibria [2,3]. It has to be mentioned that the ion source used was not equipped with an electron gun. The Ni-NiO system studied (40 mg Ni and 180 mg NiO) was placed in a Knudsen effusion chamber (12 mm diameter, 12 mm height, 8 mm effusion orifice diameter, the ratio of evaporation to effusion surface area being 4). Let us mention that the Ni effusion chamber was one of the components of the system investigated, which excluded any unforeseen effect of that chamber on results of the experiments. The chamber was heated by a furnace with Mo wire (1300-1473°K). The temperature was maintained and measured by a VRT-3 regulator (Pt/Pt + 10% Rh thermocouple). Temperature was measured with ±4°K accuracy. The ions were registered with a VEU-6 electron multiplier.

In the Ni-NiO system's vapors per se, no negative ions were detected. In order to generate them a small (3 mg) sodium metaphosphate dope was prepared. After its introduction the PO_2^- and PO_3^- ions were detected.

The experiment was carried out at 5 fixed temperatures, the top temperature, 1473°K, being the maximum temperature for the furnace used, while the bottom one, 1300°K, was determined by the sensitivity of the mass spectrometer. The order of the experiment and measurement results are presented in Table 1, which gives logarithms of the ratios of ionic currents:

$$Y_{ijk} = \ln \frac{I (PO_3^-)_{ijk}}{I (PO_2^-)_{ijk}} \begin{cases} i = 1, \ldots, I, \\ j = 1, \ldots, J_i, \\ k = 1, \ldots, K_{ij}, \end{cases} \qquad (3)$$

which are required for the further calculation of oxygen pressure (see formulas (1) and (2)). Each value is marked by three indices which present the order number of the experimental temperature (i, the numeration goes from low to high temperature): at the i-th temperature, the series number is (j), while at the j-th temperature, it is (k).

Table 2

Equilibrium Oxygen Pressure
in the Ni-NiO System*

T, K		Y_{ij*}				Y_{i**}	$\Sigma_j K_{ij}$	$p(O_2)$	$p(O_2)$**
								$\cdot 10^*$ Pa	
1300	1	4.75	4.68	4.71		4.72	9	0.06	0.11
1344	2	4.69	4.55	4.45		4.56	6	0.28	0.46
1387	3	4.19		4.18		4.19	5	0.68	1.70
1430	4	4.29	4.18	4.20		4.22	9	3.40	5.30
1473	5	3.93	4.05	3.96		3.98	9	9.10	18.00

* Designations are explained in the text, see formulas (3) — (5).
** Calculated using the IVTANTERMO databank [7] (1986 version).

Let us analyze in more detail the order of the experiment (see Table 1). First, the measurements were carried out at 1300°K ($i = 1$, $j = 1$) where the PO_2^- and PO_3^- ionic currents were recorded four times. That comprised the first experimental series ($K_{11} = 4$). Then the temperature was set at 1387°K ($i = 3$, $j = 1$) and the next series was measured (the PO_2^- and PO_3^- currents were recorded twice, $K_{31} = 2$). Then the series at 1344, 1473, 1430°K, etc., were measured. The holding time during the measurement of one series was 20 min. After approximately 1.5 hr the measurements were repeated at the same temperatures. Three measurement series were carried out at each temperature. The total time of the experiment was 5 hr.

Intensities of the PO_2^- and PO_3^- ion currents were decreasing during the experiment, so that at the end the PO_2^- intensity was comparable to the background level. This suggests practically complete evaporation of Na metaphosphate during the experiment.

Table 1 also presents the average logarithms of the ratios of the PO_3^- and PO_2^- ion currents for every series:

$$Y_{ij*} = \sum_k Y_{ijk}/K_{ij}.$$ (4)

while Table 2 presents the general average logarithms for each temperature:

$$Y_{i**} = \sum_{jk} Y_{ijk}/\sum_j K_{ij}$$ (5)

(Index * marks the averaging).

DISCUSSION

Effect of the sodium metaphosphate addition on oxygen pressure determined. In order to determine the equilibrium oxygen pressure in the Ni-NiO system a small addition of Na metaphosphate was introduced. Therefore the first question which should be answered is: what is the difference between the measured oxygen pressure in the Ni-NiO-NaPO$_3$ system and the oxygen pressure in the Ni-NiO system, in other words, what is the difference between what has been measured and what we would like to measure?

Let us analyze the experimental data produced, from this point of view. During the experiment, Na metaphosphate had practically completely evaporated (its volatility is much higher than that of Ni or NiO). Consequently, the measurement of partial oxygen pressure during the experiment provides an unambiguous quantitative assessment of the effect which NaPO$_3$ has on the partial oxygen pressure.

Oxygen pressure is related to the ratio of the PO_3^- and PO_2^- ion currents through the following formula (produced from formulas (1) and (2)):

$$\ln p(O_2) = 2\{Y - \ln K_2 + \ln [M(PO_3^-)/M(PO_2^-)]\}.$$ (6)

Ion	ΔfH_q^0, kJ/mol	ϕ^0_{1000}	ϕ^0_{1200}	ϕ^0_{1400}
			J/(mol·K)	
PO_2^-	-645 ± 18**	262.1***	270.5 ± 2.0	277.9
PO_3^-	-943 ± 16**	277.9**	289.1 ± 3.0	298.9
SO_2^-	-400 ± 4***	269.3***	277.9 ± 1.5	285.4
SO_3^-	-602 ± 6	288.2	299.4 ± 3.7	309.3
SO_4^-	-743 ± 9	311.6	325.8 ± 6.0	338.3
CrO_3^-	-669 ± 9	299.3***	311.5 ± 4.0	322.1
CrO_4^-	-781 ± 11	318.9	333.8 ± 5.8	346.6
MoO_3^-	-637 ± 11	306.4***	318.6 ± 4.5	329.2
MoO_4^-	-900 ± 11	340.6	356.0 ± 4.9	369.4
WO_3^-	-695 ± 11	313.4***	325.6 ± 4.5	336.3
WO_4^-	-881 ± 11	341.1	356.4 ± 4.7	369.7

* $\phi_T^0 = S_T^0 - (H_T^0 - H_0^0)/T$.
** Adopted from [4].
*** Adopted from handbook [9].

At a constant temperature, oxygen pressure is directly proportional to the ratio of
the PO_3^- and PO_2^- ion currents, and the change of the ratio between them reflects the oxygen
pressure change during the experiment. Using Table 1, let us compare logarithms of the
measured ratios of the PO_3^- and PO_2^- ion currents (Y_{ijk}) at the same temperatures but at
different times. Table 2 is more comfortable to use for such a comparison, because it
presents the averages for the series (Y_{ij*}) and the general average (Y_{i**}) for each tem-
perature.

It can be seen that the logarithm of the ratio of the ion currents at a constant
temperature during the time of the experiment, remains constant within the experimental
error (with the exception of the second series, at 1387°K). This demonstrates either
that the oxygen pressure measured does not change during the experiment, or that the
$NaPO_3$ dope added has, within the experimental error, no effect on the equilibrium oxygen
pressure. The second series, at 1387°K was considered to be an experimental reject,
therefore it was not taken into consideration during further processing of the results.

A conclusion that the logarithm of the ratio between ion currents (oxygen pressure)
is independent on the time of the experiment also follows from dispersion analysis (see,
for instance, [6]) of the results produced. Dispersions within the series

$$ s_e^2 = \sum_{kij} (Y_{ijk} - Y_{ij*})^2 \Big/ \left(\sum_{ij} K_{ij} - \sum_i J_i \right) $$

and between the series

$$ s_h^2 = \sum_{ij} (Y_{ij*} - Y_{i**})^2 K_{ij} \Big/ \left(\sum_i J_i - I \right) . $$

were calculated.

The dispersion within the series, s_e^2 characterizes scattering of Y_{ijk} and of the
average for the series Y_{ij*}, i.e., it indicates reproducibility of the instrument. Dis-
persion between the series, s_h^2, on the other hand, characterizes scattering between dif-
erent series at a constant temperature; it shows the variation of the logarithm of the
ratio between ion currents with time.

In the present case s_e = 0.09 (26 translatory degrees of freedom), while s_h = 0.11
9 translatory degrees of freedom). The s_h^2/s_e^2 = 1.49 ratio equals 1.49, which is 5% below

53

Table 4

| Method	Measurement range (Pa)	Characteristic
Statistical		
a) direct	$1 - 10^4$	Measurement of the total pressure with a parameter
b) indirect	$10^{-4} - 10^4$	Measurement of a gas characteristic related to pressure
Effusion Knudsen's	$10^{-3} - 10$	Measurement of the mass loss or torsion angle of a quartz fibre
Flow	$10 - 10^4$	Measurement of the amount of material removed by a neutral gas flow
Heterogenous equilibria	$10^{-13} - 10^3$	Determination of the ratio of the partial pressure of CO/CO_2 or H_2/H_2O which are at equilibrium with the system studied
High-temperature mass-spectrometry with electron shock ionization	$10^{-3} - 10$	Measurement of the O_2^- ion flow formed by electron bombardment of a molecular beam
Ion-molecular equilibria	$10^{-13} - 10$	Measurement of the ratio of ion flows of oxygen-containing ions which are at equilibrium with the system studied

Fisher's distribution quartile ($F_{0.05;9;26} = 2.27$). This suggests that, with 95% probability, one can accept the hypothesis about constancy of the ratio of ion currents at a constant temperature.

NiO dissociation pressure. Table 2 presents the equilibrium oxygen pressures calculated (formula (6)) using the average logarithms of the ratios (Y_{1**}) of PO_3^- and PO_2^- flows. Digital values of the equilibrium constant K_2 were calculated, using thermodynamic characteristics of ions (see Table 3). It has to be mentioned that further on, when using these values, they have to be given an importance proportional to $\sum_i K_{ij}$, the number of measurements at a given temperature.

For the sake of comparison, Table 2 also presents oxygen pressures in the Ni-NiO system calculated using the IVTAN-TERMO databank [7] (1986 version):

$$\ln p(O_2) = -2 \ln K_{10} = 2\Delta_f H_0^\circ(NiO, \bullet)/T -$$
$$- 2 \phi_T^\circ(NiO, \bullet) + 2 \phi_T^\circ(Ni, \bullet) + \phi_T^\circ(O_2).$$

where K_{10} is the equilibrium constant of the following reaction:

$$Ni (s) + \frac{1}{2} O_2 = NiO (s).$$
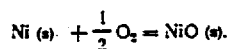
Experimental values of equilibrium oxygen pressures agree with the literature data within the factor of 2, which, in our opinion, can be considered a good level of agreement. Thus, comparison with the literature data showed that the method proposed here is applicable for determination of the equilibrium oxygen pressure in high-temperature systems.

Range and error in determination of equilibrium oxygen pressure, using the ion-molecular equilibrium method. In order to use the ion-molecule equilibria method for determination of oxygen pressure, it is, first of all, necessary to have a measurable ion concentration (over 10^3 ion/cm^{-3}) in vapors of the system studied. At present, several pairs of negative ions are known, with the help of which oxygen pressure can be determined (see Table 3). In order to receive the required ions, small amounts of a phosphate, sulfate, chromate, molybdate, or tungstate of an alkali metal can be added. Selection of the appropriate dope and its amount depends on the nature of the system studied: on its chemical and emission properties (the output energy). The present experiment suggests that, if a correct dope has been selected, the method of ion-molecule equilibrium can be used for determination of the oxygen equilibrium pressure up to 10^{-13} Pa (see, for instance, [4]). The maximum oxygen pressure which can be determined is 10 Pa, because at higher pressures, effusion conditions for the molecular beam emission would be destroyed.

The error of the oxygen pressure determination depends on three factors: a) effect of the dope on oxygen pressure; b) reproducibility error; and c) error of the equilibrium constant (K_c) used.

The dope effect can be determined by a specially planned experiment (for instance, as was done here). In the present case, it was shown that the dope has a smaller effect than the reproducibility error. The measure of the reproducibility error are values s_1 and s_2, which determine that the error in the measurement of the ratio between ion flows is 7%, while in the measurement of oxygen pressure it is 15%.

It is quite difficult to determine the K_2 error, because a direct calculation, using the error distribution law applied to thermodynamic data (see Table 3), produces over-estimated results. That is so because the errors of the formation enthalpies and of Φ_T^u presented in Table 2, are too much interrelated. In order to determine the correct K_2 error, it is necessary to remember that K_2 can be calculated directly from experimental equilibrium constants determined in [4]. That method determines that the K_2 error is 60% which results in the error of the oxygen pressure within the limit of the factor of 2.5.

Thus, the main contributor into the oxygen pressure determination is the K_2 error. The following method can be suggested for increasing correctness in the oxygen pressure determination: to measure the ratio of PO_3^- and PO_2^- ions for a known oxygen pressure. Then, at a constant temperature

$$p(O_2) = p^0(O_2)\left[\frac{p(PO_3^-)}{p(PO_2^-)} \Big/ \frac{p^0(PO_3^-)}{p^0(PO_2^-)}\right]^2.$$

where index "zero" refers to the state with a known oxygen pressure. This application of ion-molecular equilibria does not require any information on thermodynamic properties of negative ions.

Comparison of the method of ion-molecular equilibria with other methods for oxygen pressure determination. Table 4 presents determination methods for the partial oxygen pressure. It has to be mentioned that the statistical methods, the Knudsen effusion method, the flow method, and the method of heterogeneous equilibria have limited fields of application, because they can be used only when the vapor consists of one component only: oxygen. They cannot be used for systems with complex vapor compositions.

High-temperature mass-spectrometry with electron shock ionization is the most universal method applicable for any systems, however it has a limited dynamic range. The main difficulty is that the O_2^+ ion flow forms not only because of ionization of a molecular beam, but also because of ionization of residual gas. The necessity to separate the signal from the background considerably limits the possibility of determining low oxygen pressures.

The method of ion-molecule equilibria overcame these problems. In that method, the O_2^+ ion, which is hard to measure, is replaced by the ratio of ion flows (for instance, PO_3^- and PO_2^-), which are easy to measure. In its principles, the method of ion-molecule equilibria resembles the monomer-dimer method, and other mass-spectrum methods, based on the measurement of a ratio rather than the absolute values of ion flows. That helps to avoid determination of the instrument's sensitivity constant.

Of all the methods presented in Table 4, the method of ion-molecule equilibria is similar to the method of heterogeneous equilibria, however its reaction is not with neutral vapor components but with negative ions.

REFERENCES

1. V. A. Grigoryan, L. N. Belyanchikov, and A. Ya. Stomakhin, Theoretical Principles of Electric Steelmaking Processes [in Russian], Metallurgiya, Moscow, pp. 84 and 135, 1987.
2. L. N. Sidorov, M. V. Korobov, and L. V. Zhuravleva, Mass-Spectral Thermodynamic

Investigations [in Russian], Izd-vo MGU, Moscow, 1985.

3.   L. N. Sidorov, L. V. Zhuravleva, and I. D. Sorokin, "High temperature mass spectrometry and studies of ion-ion, ion-molecule, and molecule-molecule equilibria," Mass Spectr. Rev., vol. 5, p. 73, 1986.

4.   E. B. Rudnyi, O. M. Vovk, L. N. Sidorov, et al., "Formation enthalpy of PO_2^-, PO_3^-, and $NaPO_2$," Teplofizika Vysokikh Temperatur, vol. 24, no. 1, p. 62, 1986.

5.   E. V. Rudnyi, L. N. Sidorov, L. A. Kuligina, and G. A. Semenov, "Heterolytic dissociation of potassium chromate in the gas phase and the electron affinity of chromium oxides," Int. J. Mass. Spectr. Ion Proc., vol. 64, p. 95, 1985.

6.   G. Scheffe, Dispersion Analysis [Russian translation], Nauka, Moscow, 1980.

7.   L. V. Gurvich, "IVTANTERMO as an automated system of the data on thermodynamic properties of materials," Vestn. AN SSSR, no. 3, p. 54, 1983.

8.   E. B. Rudnyi, O. M. Vovk, E. A. Kaibicheva, and L. N. Sidorov, "Formation enthalpies of oxygen-containing anions of group VI elements in the gas phase, and the electron affinity of CrO_3, MoO_3, and WO_3," J. Chem. Thermodyn., vol. 21, no. 3, 1989.

9.   V. P. Glushko (Editor), Thermodynamic Properties of Individual Materials. Handbook, Nauka, Moscow, 1978-1982.

Submitted 5 April 1988   Moscow