USE OF THE ION-MOLECULE EQUILIBRIA METHOD FOR DETERMINING THE ACTIVITY OF ALKALI OXIDE IN SODIUM SILICATE MELTS

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The aim of the present study was to make use of the method of ion-molecule equilibria (IME) [1, 2] for determining the thermodynamic activity of oxides of alkali metals in glassy systems. As the subject of the investigation we chose the Na_2O-SiO_2 system for which there is already a series of experimental studies on the determination of the thermodynamic properties carried out using various methods [3-9] (see also [10] and the references therein). This choice made it possible to establish the reliability of the data obtained using the IME method in the study of glassy systems.

Method of Ion-Molecule Equilibria. The IME method is a combination of Knudsen's effusion method and the mass-spectral recording of ions formed inside the effusion chamber [1, 2].

The material to be studied in placed in the effusion chamber. At high temperatures (~1000 K) ions appear in the vapor as a result of thermal ionization. The concentration of ions is not very large ($\approx 10^2-10^7$ cm^{-3}) and is six to eight orders of magnitude less than that of the neutral evaporation products ($\approx 10^{10}-10^{15}$ cm^{-3}), but quite sufficient for the mass-spectral recording. The ions formed, unlike in other ionization methods, are in equilibrium with the condensed and gas phases. This makes it possible to determine the equilibrium constants of the ion-molecule reactions in which they participate.

In most cases the IME are used to determine the thermodynamic characteristics of ions: the enthalpy of formation; the energies of the dissociation; the electron affinity; and the ionization potentitals [1, 2, 11]. However, where the thermodynamic characteristics of the ions are well known (previously determined), the IME can be used to determine the partial pressures of the neutral components of the vapor [12, 13] and the activity of the independent components [14].

Use of IMR for Determining the Activity of Alkali Metal Oxides. Let us now consider this case using the example of sodium oxide. Let the ions CrO_3^-, CrO_4^-, and $NaCrO_4^-$ exist in the vapor of the experimental system. We shall write the reaction as follows (the material is in the gas-phase state unless otherwise indicated):

$$CrO_3^- + \frac{1}{2} O_2 = CrO_4^- \quad (K_1). \tag{1}$$

$$CrO_4^- + Na = NaCrO_4^- \quad (K_2). \tag{2}$$

$$Na_2O_{liq} = 2Na + \frac{1}{2} O_2 \quad (K_3). \tag{3}$$

The thermodynamic characteristics of CrO_3^-, CrO_4^-, and $NaCrO_4^-$ have been previously determined [15, 16], i.e., the equilibrium cosntants K_1 and K_2 are known. Then from the ratio of the partial pressures of CrO_4^- and CrO_3^-, $NaCrO_4^-$ and CrO_4^- we can calculate the partial pressure p of oxygen and sodium:

$$p(O_2) = \left[\frac{p(CrO_4^-)}{p(CrO_3^-)} \frac{1}{K_1} \right]^2, \quad p(Na) = \frac{p(NaCrO_4^-)}{p(CrO_4^-)} \frac{1}{K_2}.$$

Using K_3 (calculated from the handbook data [17]), we obtain the desired connection between the activity of sodium oxide and the partial pressures of the ions:

$$a(Na_2O) = \frac{p(NaCrO_4^-)^2}{p(CrO_3^-)p(\overline{CrO_4^-})} \frac{1}{K_1 K_2^2 K_3}.$$ (4)

The question then arises of what is to be done if the required ions are not in the experimental system. In that case, it is necessary to make some small additions of impurity materials (<0.02 mole fraction) to the system to make sure the required ions appear. However, the next question arises: how far will these additions affect the activity to be determined?

Ultimately, the extent of the effect of the addition can be established only by experiment having planned the test specially. However, to evaluate the order of magnitude of this effect let us now consider a model example. Let there be an N-component system (X_1' is the mole fraction of component 1; a'_1 is the activity of component 1; X'_2 is the mole fraction of component 2; and so on). To this system we add n moles of the impurity material (the additive). An N + 1-component system is ow obtained (X''_1 is the mole fraction of component 1; a''_1 is the activity of component 1, ..., $X_{N+1} < 0.02$-0.04 is the mole fraction of the added component). We propose the following: 1) the activity of the added material obeys Henry's law, $a_{N+1} = K_{N+1}X_{N+1}$; 2) with this addition all activities apart from the defined a_1 remain unchanged, $a'_i = a''_i$, i, 2, ..., N. Let us integrate the Gibbs—Duhem equation:

$$X_1 d \ln a_1 + X_2 d \ln a_2 + \ldots + X_{N+1} d \ln a_{N+1} = 0.$$

The second condition gives

$$X_1 d \ln a_1 + X_{N+1} d \ln a_{N+1} = 0.$$

Taking into account that the mole fraction of the first component depends on that of the additive as follows:

$$X_1'' = X_1'(1 - X_{N+1}),$$

we obtain

$$\frac{a_1''}{a_1'} = (1 - X_{N+1})^{1/X_1'}.$$ (5)

On these assumptions, when the concentrations of the first component in the original mixture is $x'_1 = 0.90$ mole fractions, the addition of $X_{N+1} = 0.02$ mole fractions leads to a decrease of ~2% in the activity of a_1; in the case of $X'_1 = 0.10$ mole fractions, a_1 decreases by 18%. We must point out that in the case of oxide systems containing alkali metal oxides (systems with a strong chemical interaction) there is every justification for assuming that all activities of all the components of the original system when the additive is present will only decrease, i.e., Eq. (5) will give the maximum estimate for the decrease in the activity a_1.

Experiment. The work was carried out on an MX-1303 mass-spectrometer modified for the study of ion—molecule equilibria [1]. The materials were evaporated from a Pt crucible (diameter 12 and height 14 mm). The ratio of the evaporation area to that of effusion was ~150. The temperature was measured using a Pt—PtRh (10% Rh) thermocouple. The accuracy of the temperature was maintained constant using a VRT-3 temperature controller with an accuracy of up to 1 K. The ion currents were recorded by a VÉU-6 secondary-electron amplifier.

Five compositions in the Na_2—SiO_2 system with a concentration of 0.10 to 0.50 mole fractions of Na_2O were studied over the temperature interval of 1255-1557 K. No negative ions were recorded directly in the vapor of the systems and therefore potassium chromate was added. The additive was carefully ground with the components of the system in an agate mortar. In the new conditions CrO_3^-, CrO_4^-, and $NaCrO_4^-$ ions appeared in the saturated vapor over the melts of the system; these ions were recorded using the mass-spectrometer (Table 1). The temperatures and duration of the experiment were chosen so that the change in the concentration of Na_2O as a result of the evaporation of Na_2O should no exceed 0.003 mole fractions.

To solve the problem of the effect of the addition of the chromate on the activity of sodium oxide we took the following steps. Two experiments in which a different amount of potassium chromate additive was used were carried out with each composition. The relative amount of the additive was varied by 4-6 fold (Table 1). The experiment was also carried out in a special way. At a constant temperature we obtained a series of mass-spectra (several sets of ion currents of CrO_3^-, CrO_4^-, and $NaCrO_4^-$). We then established another temperature and recorded the new series of mass spectra and so on. In this case we established the initial temperature after a certain time. As a result, we had a series of mass spectra recorded at the

TABLE 1. Mass–Spectrum of Negative Ions in the Vapor over Na_2O–SiO_2 at 1430 K with an Addition of Potassium Chromate (relative units)

Experi-ment No.	Concn., mole fraction		$I(CrO_3^-)$	$I(CrO_4^-)$	$I(NaCrO_4^-)$
	Na_2O	K_2CrO_4			
I	0.103	0.020	100 000	29	1.2
II	0.103	0.003	100 000	23	1.1
III	0.254	0.0022	100 000	75	2.3
IV a	0.254	0.0018	100 000	59	1.8
V	0.303	0.0511	100 000	83	8.5
VI	0.303	0.0128	100 000	30	4.7
VII	0.402	0.0018	100 000	73	29
VIII b	0.402	0.0038	100 000	38	25
IX	0.500	0.0205	100 000	91	254
X	0.500	0.0010	100 000	31	175

Note: a denotes mass spectrum recorded at 1473 K; b denotes the addition of potassium chromate.

same temperature. The measurement time for one series was ~5 min and the interval between two series at the same temperature was ~20 min. This made it possible to use single-factor dispersion analysis for comparing the results [18].

Processing of Results. From each of the mass-spectra of the ion currents we calculated the term Y_{ij} proportional to the activity of Na_2O which is exactly equal to

$$Y_{ij} = \ln \frac{I(NaCrO_4^-)^2}{I(CrO_3^-) I(CrO_4^-)}.$$

We changed from ion currents to partial pressures in accordance with the formula in [1, 2]:

$$\frac{p(A^-)}{p(B^-)} = \frac{I(A^-)}{I(B^-)} \frac{M(A^-)}{M(B^-)}, \tag{6}$$

where M is the molecular mass.

By combining Eqs. (4) and (6) we obtain the calculation equation:

$$\ln a(Na_2O) = Y - \ln K_1 K_2^2 K_3 + \ln \frac{M(NaCrO_4^-)^2}{M(CrO_3^-) M(CrO_4^-)}. \tag{7}$$

For each composition of the Na_2O–SiO_2 system at each temperature we recorded several series of measurements of $Y_{ij}(X_{Na_2O} = const, T = const)$. The suffix j denotes the mass spectrum number in the i-th series: $j = 1, \ldots, J_i$; i is the number of the measurement series: $i = 1, \ldots, I$. In this case a range of series were obtained for one amount of additive and a range of series was obtained for another amount (I refers to the total number of series). Before the calculation, in accordance with Eq. (7) the corresponding Y_{ij} were averaged ($\Sigma_i J_i$ points)

$$\langle Y \rangle = \frac{\Sigma_i \Sigma_j Y_{ij}}{\Sigma_i J_i}.$$

Also using the single-factor dispersion analysis [18] we calculated the intraseries standard deviation:

$$s_p = \left[\frac{\Sigma_i \Sigma_j (Y_{ij} - \langle Y_i \rangle)^2}{\Sigma_i J_i - I} \right]^{1/2}$$

and the interseries standard deviation:

$$s_h = \left[\frac{\Sigma_i (\langle Y_i \rangle - \langle Y \rangle)^2 J_i}{I - 1} \right]^{1/2},$$

where $\langle Y_i \rangle = \Sigma_j Y_{ij}/J_i$ is the average for the i-th series. All these values are given in Table 2.

The intraseries standard deviation s_p characterizes the average spread of the log ratio of the ion currents in the series and is conditioned by the instabilities of the instrument.

TABLE 2. Activity of Sodium Oxide in the System Na_2O-SiO_2

Concn. of Na_2O, mole fraction	T, K	$\langle Y \rangle$	s_h	s_p	$\Sigma_i J_i$	I	$\ln a\,(Na_2O)$
0.103	1430	—14.56	0.49	0.36	24	8	—22.62
	1473	—14.82	0.47	0.41	25	8	—22.51
0.254	1430	—13.98	0.23	0.25	7	3	—22.04
	1473	—14.22	0.21	0.20	9	4	—21.91
	1515	—13.34	0.38	0.48	6	3	—20.68
	1557	—13.24	—	0.02	2	1	—20.24
0.303	1344	—12.09	0.67	0.42	5	2	—20.93
	1387	—11.96	0.25	0.32	8	4	—20.40
	1430	—11.72	0.16	0.18	9	5	—19.78
	1473	—11.39	0.26	0.12	9	4	—19.03
	1515	—11.23	0.04	0.08	4	2	—18.57
0.402	1255	—9.04	0.30	0.20	8	4	—18.75
	1344	—9.02	0.48	0.13	10	5	—17.86
	1387	—9.05	0.45	0.04	8	4	—17.49
	1430	—8.92	0.34	0.13	4	2	—16.98
	1473	—9.33	0.16	0.27	4	2	—17.02
0.500	1255	—5.39	—	0.54	2	1	—15.10
	1300	—5.10	0.03	0.39	4	2	—14.36
	1344	—4.61	0.17	0.09	7	4	—13.45
	1387	—4.55	0.24	0.20	6	3	—12.99
	1430	—4.78	0.33	0.29	4	2	—12.84
	1473	—4.81	—	0.06	2	1	—12.50

Note: See the section "processing of results" for the symbols.

In other words, a measure of the error in the reproducibility of the IME method and with $s_p \approx$ 0.2-0.3 corresponds to the spread of 20-30% in the ratio of the ion currents.

The interseries standard deviation s_h shows the spread of the average $\langle Y_i \rangle$ in the series relative to the total average $\langle Y \rangle$, i.e., from the values of s_h we can estimate the agreement between results obtained in different series and with different additions of potassium chromate. In our case the values of s_h do not differ significantly from s_p (according to Fisher's criterion [18]). This means that the measurements in different series agree within the error of reproducibility. Hence we may state that a change in the activity of Na_2O due to the chromate additive is less than the statistical error of the measurement (20-30%). This is also in agreement with the evaluations using Eq. (5).

Table 1 gives the mole fraction of chromate additive in the preparation of the specimen. In the course of the experiment the mole fraction of potassium chromate decreases, in our view as a result of its high volatility and the main part of the chromate must evaporate at the initial stage of the experiment.

Using $\langle Y \rangle$ we calculate from Eq. (7) the activity of Na_2O at a given temperature (Table 2).

The thermodynamic data necessary for calculating the equilibrium constants of Eqs. (1) and (2) are given in Table 3. A more detailed experiment and a description of the treatment results for a composition with 0.30 mole fractions of Na_2O have been given in [19].

Figure 1 shows the activities of Na_2O obtained in this study in the Na_2O-SiO_2 system. For comparison the results of the determination of the activity of Na_2O in this system using an emf method [3-5], a flow method [6], and high-temperature mass-spectrometry with ionization by electron impulse (HTMS) [7-9] are also shown. The values of the activities of Na_2O are in good agreement one with another.

Discussion of Results. 1. Field of Application of the IME method. To determine the activity of Na_2O on IME method with the participation of negative ions CrO_3^-, CrO_4^-, and $NaCrO_4^-$ were used. Up to the present many similar ons have been observed: SO_2^-, SO_3^-, SO_4, MSO_4 (M = Li, Na, K, Rb, Cs), CrO_3^-, CrO_4^-, $MCrO_4^-$ (M = Na, K) and their thermodynamic character-istics have been determined (Table 3). This makes it possible to extend the proposed method to the determination of the activity of all alkali metal oxides and also when multicomponent systems with several alkali metal oxides, for example, $Na_2O-K_2O-SiO_2$ are studied. In this case, for each composition the activities of the alkali metal oxides will be determined inde-pendently.

TABLE 3. Thermodynamic Properties of Negative Ions Required for the Determination of the Activity of Alkali Metal Oxides

Ions	ΔfH_0^0, kJ/mole	Φ_{1300}^0	Φ_{1500}^0
		J/mole · K	
SO_3^-	-601 ± 7	304.5	313.8 ± 3.7
SO_4^-	-743 ± 9	332.3	344.3 ± 6.0
$LiSO_4^-$	-1041 ± 11	352.9	367.3 ± 6.3
$NaSO_4^-$	-976 ± 11	375.9	390.8 ± 7.3
KSO_4^-	-992 ± 11	386.3	401.3 ± 7.8
$RbSO_4^-$	-982 ± 11	402.1	417.2 ± 8.1
$CsSO_4^-$	-998 ± 13	412.2	427.3 ± 10
CrO_3^-	-670 ± 20	316.9	325.9 ± 4.0
CrO_4^-	-782 ± 24	340.3	352.5 ± 5.8
$NaCrO_4^-$	-974 ± 15	396.0	411.7 ± 7.4
$KCrO_4^-$	-997 ± 15	403.1	421.8 ± 9.7

Note: Choice of values has been described in [20].

The main defects of the proposed method are associated with the fact that small additions (of sulfates or chromates) must be made to the system to be studied. Nevertheless, all the equivocacy which arises can be eliminated by carrying out an experiment on the proposed system which a subsequent use of the single-factor dispersion analysis.

2. Errors in IME. It has already been pointed out that the evaluation of the error in the reproducibility in the value of $\ln a(Na_2O)$ is the intraseries standard deviations $s_p \approx$ 0.2-0.3 which corresponds to a 20-30% reproducibility of the activity. To calculate the total error it is necessary that the error in the equilibrium constant K_1, K_2, and K_3 be added to s_p. To evaluate the latter error is fairly complicated since a simple calculation from the errors in the enthalpy of formation and the reduced Gibbs potential (Table 3) according to the law of propagation of errors leads, of course, to far too high results. In our case such a calculation leads to $s(\ln K_1) = 3.7$, $s(\ln K_2) = 3.1$, and $s(\ln K_3) = 0.25$. Such an evaluation can be used only for Eq. (3) since in this case the enthalpy of formation and Φ_T^0 of the participants in the reaction are known with sufficient accuracy and have been independently determined. For Eqs. (1) and (2) these evaluations are much too high: the enthalpies of these reactions were ultimately determined from equilibrium constants experimentally determined with sufficient accuracy: $s(\ln K) \approx 0.12$ but the large error in the enthalpies of formation of the participants is due to the inaccuracy of the thermodynamic function which were used.

We now give an example of a more accurate calculation of the error using reaction (1). This reaction is a linear combination of two reactions:

$$SO_3^- + CrO_3^- = SO_4^- + CrO_4^-, \tag{8}$$

$$SO_4^- + \frac{1}{2}O_2 = SO_3^- \tag{9}$$

and $\ln K_1 = \ln K_8 + \ln K_9$. The terms K_8 and K_9 were experimentally determined over the 1200-1300 K range. The error in these terms (standard deviation) allowing for a recalculation for the temperatures of our experiment is $s(\ln K_8) = 0.12$, $s(\ln K_9) = 0.11$. Hence $s(\ln K_1) = [s(\ln K_8)^2 + s(\ln K_8)^2]^{1/2} = 0.16$. In the same way it is possible to evaluate the error $s(\ln K_2) = 0.15$. The total error in the three equilibrium constants will be $[s(\ln K_1)^2 + 4 \cdot s(\ln K_2)^2 + s(\ln K_3)^2]^{1/2} = 0.4$. When it is taken together with the error in the reproducibility, we obtain the total error in the activity of Na_2O determined by the IMR method, $s[\ln a(Na_2O)] = 0.6$. This shows that the absolute activity of Na_2O is determined within 2:1.

3. Range of Determination of the Activity of Sodium Oxide. Let us now consider Eq. (4). The value of the products of the equilibrium constants depends only on the temperature and nature of the materials taking part in the equilibria: at 1300 K, $K_1K_2^2K_3 = 16,800$; at 1500 K, $K_1K_2^2K_3 = 2800$. The ratio of the pressures of the $NaCrO_4^-$, CrO_3^-, and CrO_4^- ions changes depending on the activity of Na_2O in the experimental system. The limits of measure-
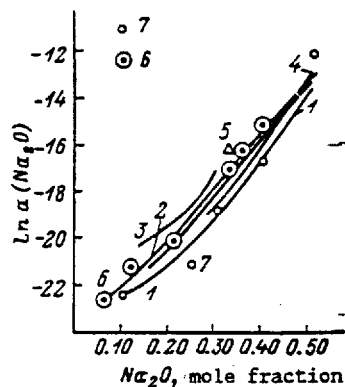
Fig. 1. Composition dependence of the log activity of Na_2O in the Na_2O—SiO_2 system at 1500 K; continuous curves illustrated data in 1) [4]; 2) [6]; 3) [8]; 4) [3]; points denote data in 5) [7]; 6) [9]; 7) our data.

ment of this ratio are determined by the sensitivity and dynamic range of the mass-spectrometer. According to our evaluations, it is possible ot determine the activity of Na_2O over a range of 1 to 10^{-14}.

4. **A Comparison between the IME Method and Others.** The emf method [3-5], flow method [6], and high-temperature spectrometry with ionization by an electron impulse (HTMS) [7-9] are currently used for the determination of the activity of Na_2O in glassy systems and melts.

The main difficulties which are encountered in the HTMS in the determination of the activity of alkali metal oxides are associated with problems of measuring the ion current of O_2^+ for determining the partial pressure of oxygen. The reason is the presence of a large impurity-ion current in this mass arising because of the ionization of residual gases. Naturally, research workers proceed as follows: they determine the partial pressure of sodium via the measurement of the ion current of Na^+ but the partial pressure of oxygen is calculated via the condition of congruency of evaporation $p(O_2) = 4p(Na)$. When using IME we replaced the badly measured ioncurrent O_2^+ by the well determined ratio of the currents of the CrO_4^- and CrO_3^- thermal ions. Moreoever, unlike the HTMS method in the study of the ion-molecular equilibria the constant of sensitivity of the change to partial pressures need not be determined since only the ratio of the ion currents is used.

In the study of two-component systems the emf and flow methods give more reliable results with a lower error than the IME, nor is there any need to make any addition to the system and there is no recalculation with the use of K_1 and K_2. However, in our view the proposed IMR method is more universal. Thus when using e.m.f. and flow methods for studying multi-component systems in the presence of several alkali metal oxides great difficulties arise. In the case of IME the study of multicomponent systems, as was already pointed out, is done in exactly the same way as in the two-component Na_2O—SiO_2-system.

Conclusions. The possibility is demonstrated of using the method of ion—molecular equilibria (IME) for determining the activity of alkali metal oxides. The IME method is used to determine the activity of sodium oxide in a melt of the Na_2O-SiO_2 system.

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