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Abstract

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ON THE STRUCTURE OF THE SURFACE LAYER OF MOLTEN NIOBATES

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In the investigations of A. N. Frumkin and co-workers (^{1,2}), as well as in the works of other authors (^{3}), it was established that capillary-active substances form a double electric layer at the air–water interface. The arrangement of charges in it is determined by the orientation of polar molecules and by the preferential adsorption of ions of one sign or another.

There are grounds to suppose that on the surface of solid (^{4}) and liquid (^{5}) oxides, as well as in aqueous solutions (^{6,7}), it is energetically more favorable for oxygen anions to be present. However, the possibility is not excluded that large monovalent cations of alkali metals may partially displace oxygen ions from the surface of the melt (^{8}) and reverse the arrangement of charges in the double layer.

For an experimental verification of this, we studied the change with composition of the surface tension (σ) and the potential (ε_s) at the boundary with air in the systems $Cs_2O–Nb_2O_5$, $K_2O–Nb_2O_5$, and $CaO–Nb_2O_5$ at 1500°C.

The experiments were carried out in a carbon-resistance furnace, into which a quartz tube was inserted to isolate the cell from the reducing atmosphere. The starting reagents were pure cesium and potassium carbonates, calcium oxide, and niobium pentoxide containing 1.5% (TiO_2, SiO_2, Fe_2O_3, and Ta_2O_5) and 0.55% K and Na.

The surface tension was determined by the maximum bubble-pressure method (^{9}), with oxygen serving as the working gas. A corundum tube with an internal diameter of 4 mm was raised, together with the melt wetting it, to 1.5 mm above its surface, and the pressure was measured in this position. The chosen procedure was checked on water and on molten chlorides, $PbCl_2$ and KCl.

In studying the surface potential (ε_s), the Gouy-Frumkin method (^{10}) was used, for which the following circuit was assembled:

$$\mathrm{Pt} \,|\, \mathrm{Nb_2O_5} \,|\, \mathrm{O_2} \,|\, \mathrm{Pt} \,|\, \mathrm{O_2} \,|\, \mathrm{Nb_2O_5} + \mathrm{MeO} \,|\, \mathrm{Pt}.$$

In it, the end platinum electrodes contacted the melts Nb_2O_5 and Nb_2O_5 + MeO, which were in separate crucibles made of ZrO_2. The middle electrode, enclosed, like the others, in an alundum tube, was continuously washed with oxygen.

The total potential at boundaries 6 (ε) and 5 (ε_s) was measured with a PPTV-1 potentiometer relative to the gas electrode (ε_r) and was always positive, i.e.,

$$\Delta\varepsilon = \varepsilon + \varepsilon_s - \varepsilon_r > 0.$$

Since at 1500° the atmosphere in the furnace is sufficiently ionized, no radioactive substance was used (^{10}). Constancy of the potential was checked with respect to a standard electrode immersed in Nb_2O_5. In most–

in most cases the quantity (boundaries 1, 2, 3)

$$\Delta\varepsilon_0 = \varepsilon_0 + \varepsilon_s^0 - \varepsilon_r$$

remained practically unchanged. The time required to reach steady values was often about 40 min.

To estimate the difference of electrochemical potentials at boundaries 1 and 6, $\Delta\varepsilon_1 = \varepsilon_0 - \varepsilon$, the crucibles were brought together and a liquid bridge was formed between them with the aid of a thin layer of Nb_2O_5. Neglecting the diffusion potential (^{11}), it was assumed that the electromotive force of such a cell was equal to $\Delta\varepsilon_1$.

Using the quantities $\Delta\varepsilon^0$, $\Delta\varepsilon$, and $\Delta\varepsilon_1$, the difference of surface potentials was calculated:

$$\Delta\varepsilon_s = \varepsilon_s^0 - \varepsilon_s = \Delta\varepsilon_0 - \Delta\varepsilon - \Delta\varepsilon_1.$$

As is seen from Fig. 1, when K_2O and Cs_2O are added up to 10 mol. %, the quantities σ and $\Delta\varepsilon$ decrease sharply, and then slowly decrease with increasing concentration of Me_2O*. By contrast, when CaO is introduced into the melt, the surface tension increases, while the quantity $\Delta\varepsilon$ changes hardly at all. This course of the curves indicates the capillary activity of the cations Cs^+ and K^+, in contrast to the ion Ca^{2+}.

Fig. 1. Isotherms of surface tension and change in surface potential. 1, 2, 3–$\sigma = f(N)$ for the systems Nb_2O_5 with Cs_2O, K_2O, and CaO, respectively; 4, 5, 6–$\Delta\varepsilon = f(N)$; 7, 8, 9–$\Delta\varepsilon_1 = -f(N)$; and 10, 11, 12–$\Delta\varepsilon_s = f(N)$ for the same systems.

The increase in the values of $\Delta\varepsilon_s$ indicates that the potential at the surface of the melt (ε_s) becomes less positive with increasing concentration of Me_2O. At

10 mol. % this decrease is about 65 mV for Cs_2O, 45 mV for K_2O, and only 2 mV for CaO.

It is known (^{12}) that platinum in an oxygen atmosphere becomes covered with its ions and itself becomes positively charged, i.e. $\varepsilon_r > 0$. Since in our case $\Delta\varepsilon_1$ and $\Delta\varepsilon_s$ are positive, it may be assumed that the outer plate of the surface layer of the melt is also formed chiefly by oxygen anions. Since its charge decreases as ε_s falls, the adsorbed cations Cs^+ and K^+ must replace oxygen anions, and not niobium ions, in the double layer. In other words, the cations Cs^+ and K^+ are located in the outer plate, i.e. at the boundary of the melt with the gas. To estimate what part of the adsorbed cations is located at this boundary, their surface concentrations (N_s) were calculated by two methods. In one of them the Gibbs equation for ideal solutions was used:

$$\Gamma = -\frac{N(1-N)}{RT}\,\frac{\partial\sigma}{\partial N}.$$

* Since the initial niobium pentoxide contained 2.3 mol. % ($K_2O + Na_2O$), the actual concentrations of Me_2O were higher.

The adsorption values Γ thus obtained for 10 mol. % of added oxides are given in Table 1. The surface concentrations (N_s) of the oxides, calculated from the values of Γ and from the geometrically possible numbers of moles (n) per 1 cm^2, are also given there: $\Gamma = n(N_s - N)$. In the second case the values of N_s were determined from the change in the charge (Δq) of the surface, on the assumption that the double layer at the surface is close to a plane capacitor. Knowing the value of $\Delta\varepsilon_s$ and taking $C = 15$ mF/cm^2 (^{13}), we obtain:

Table 1

Comparison of the values of N_s calculated from $\Delta\sigma$ and $\Delta\varepsilon_s$

Oxide	N	$\Gamma \cdot 10^{10}$ mol/cm^2 (from σ)	N_s (from σ)	N'_s (from ε_s)	N'_s/N_s
Cs_2O	0.1	2.45	0.436	0.0228	0.052
K_2O	0.1	3.18	0.415	0.0112	0.027
CaO	0.1	−0.52	0.072	0.0003	0.004

$$\Delta q = \Delta\varepsilon_s C,$$

whence

$$N'_s = \frac{\Delta q}{2nN_0e}.$$

Here N_0 is Avogadro' s number, e is the charge of the electron, and the factor 2 takes into account the number of ions in the molecule Me_2O.

As is seen from the data in Table 1, the values of N_s' are many times smaller than N_s, which can hardly be attributed to measurement error or to the approximate nature of the calculations. The noted discrepancy between N_s' and N_s indicates that the Me^+ ions entering the double layer replace chiefly niobium cations, located deeper from the surface, rather than oxygen anions. Only a small fraction of the Me^+ ions displaces O^{2-} anions from the surface. In other words, the adsorbed Me_2O oxides are oriented toward the surface mainly by oxygen anions and only to an insignificant degree by Me^+ cations. An analogous picture was observed (^{2}) also in aqueous solutions, where the actual potential ε_s was likewise smaller than that calculated for complete orientation of the dipoles.

It is interesting to note that the ability to replace O^{2-} anions decreases from Cs^+ to K^+ and practically disappears for Ca^{2+} (see Table 1). In other words, it decreases with an increase in their electrostatic potential.

The difficulty of displacing oxygen ions from the surface of the melt is due to their easy polarizability (^{5}). A one-sided deformation of the electron cloud of O^{2-} anions by niobium cations located somewhat farther from the surface leads to a considerable decrease in the effective charge of the oxygen ions (for example, from $2e$ to $1e$). As a result, the energy of their bonding with the surface proves comparable to, and even somewhat smaller than, that of the large singly charged cesium and potassium cations.

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