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Corresponding Member of the Academy of Sciences of the USSR
Vikt. I. Spitsyn, A. V. Lapitskii,

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR Vikt. I. Spitsyn,
A. V. Lapitskii,
R. I. Aistova, D. Nishanov, and V. A. Pchelkin

STUDY OF THE ISOTOPIC EXCHANGE OF OXYGEN BETWEEN HEAVY-OXYGEN WATER AND CERTAIN NIOBATES AND TANTALATES

In earlier studies ($^{1-4}$) on the dehydration of various niobates, we studied the character of bound water in these compounds. The purpose of the works cited was to clarify the role of water in the structure of the salts under investigation, since different structures are ascribed to them. For niobates, Chou (^{5}) proposed the general formula $Me_xH_y[(NbO_3)_{12}(OH)_6] \cdot nH_2O$. Somewhat different structures were described in Windmeisser' s work (^{6}): $Me_{16}[(NbO_3)_{12}(OH)_4] \cdot nH_2O$ and $H_{20}[(Nb_3O_{10})_4]$. The structure of tantalates, according to Jander (^{7}), is described by the formula $Me_7[Ta(TaO_4)_4]$, and the role of water is not taken into account here. Hall, Hett, and Windmeisser (^{8}), proceeding from the assumption of identity in the structures of niobates and tantalates, proposed the structural formula $Me_{16}[(Ta_{12}O_{36})(OH)_4] \cdot nH_2O$. On the basis of X-ray studies, Lindqvist (^{9,10}) found that the structural unit of hexaniobates and hexatantalates consists of the ions $(Ta_6O_{19})^{8-}$ and $(Nb_6O_{19})^{8-}$. In the compounds he studied, the positions of water and of the cations were not determined.

All the structures cited, except those mentioned in Lindqvist' s works, while describing to one degree or another the behavior of the salts upon heating, do not concern the nature of the bond between the central atom and the oxygen atoms. In Nowacki' s opinion (^{11}), in niobates and tantalates the bond with oxygen is mainly heteropolar.

Two of us, together with Vasil' ev (^{12}), used isotopic exchange to study the structure of one of the most important aquopoly compounds of tungsten—sodium paratungstate—as well as normal sodium tungstate. We decided to apply this method to the study of the structure of certain niobates and tantalates.

The initial niobates and tantalates were prepared by the methods described earlier ($^{1-3,13}$). Analyses carried out in the usual manner showed the following composition of the salts:

sodium pentatantalate $-6.88\,Na_2O \cdot 5Ta_2O_5 \cdot 29.1H_2O$;
sodium hexatantalate $-3.92\,Na_2O \cdot 3Ta_2O_5 \cdot 26.1H_2O$;

potassium hexaniobate $-7.04\,K_2O \cdot 6Nb_2O_5 \cdot 22.0H_2O$;
potassium metaniobate $-0.96\,K_2O \cdot Nb_2O_5 \cdot 4.36H_2O$.

For carrying out the isotope-exchange experiments, water enriched in O^{18} was used (containing 1.28 at.% O^{18}). The exchange was studied at a temperature of 95° with saturated solutions of the salts listed above. The exchange time in all experiments was 5 h. Owing to hydrolysis, the solutions of the salts studied had an alkaline reaction (pH = 11–12). The procedure for carrying out the experiments is described in one of the works cited (12).

Table 1 gives the results of the isotopic exchange of oxygen between water and sodium tantalates, together with the calculated values of the O^{18} content in the solvent after complete exchange. As can be seen from the table, not only the oxygen of the bound water of the tantalates taken enters into isotopic exchange.

ates, but also all the oxygen from their anions. In addition, all the values found for the content of O^{18} in the water after exchange with sodium tantalate are characterized by values markedly lower, in comparison with the calculated ones. The indicated deviations lie outside the limits of experimental error, since the error in determining the content of O^{18} was ±1% of the measured value. The results obtained can be explained by fractionation of the oxygen isotope directed toward enrichment of the salt with the heavy oxygen isotope. A similar phenomenon was observed for sodium paratungstate (12) and certain trivalent ions (14). As is seen from the data of Table 2, in the case of potassium hexaniobate and metaniobate there is also complete exchange of oxygen from the solvent water with the bound water and with the anions of the salts taken. However, in this case no enrichment of the salt with the heavy oxygen isotope is observed. Apparently, the lower molecular weight of niobates, in comparison with tantalates, leads to such a difference. As for the tantalates studied, in this respect they approach aquopoly-tungstates.

Table 1

Isotopic exchange of oxygen between heavy-oxygen water and sodium tantalates.
(Content of O^{18} in the initial water 1.28 at. %)
(temperature 95°)

Experiment No.	Amounts taken (g): salt	Amounts taken (g): water	Content of O^{18} in water after the experiment (at. %): calculated for complete exchange of O^{18} with all oxygen of the salt (b)	Content of O^{18} in water after the experiment (at. %): found (a)	b/a
Preparation No. 1 — salt $3.92\,Na_2O \cdot 3Ta_2O_5 \cdot 26.1H_2O$					
1	0.0630	2.0150	1.27	1.22	1.04
2	0.0609	2.0410	1.27	1.22	1.04
3	0.0647	2.0219	1.27	1.24	1.02
Preparation No. 2 — salt $6.88\,Na_2O \cdot 5Ta_2O_5 \cdot 29.1H_2O$					
1	0.0390	2.0184	1.27	1.22	1.04
2	0.0375	2.0373	1.27	1.23	1.03
3	0.0363	1.9866	1.27	1.23	1.03

Table 2

Isotopic exchange of oxygen between heavy-oxygen water and potassium niobates.
(Content of O^{18} in the initial water 1.28 at. %)
(temperature 95°)

Experiment No.	Amounts taken (g): salt	Amounts taken (g): water	Content of O^{18} in water after the experiment (at. %): calculated for complete exchange of O^{18} with water of the salt (c)	Content of O^{18} in water after the experiment (at. %): calculated for complete exchange of O^{18} with all oxygen of the salt (b)	Content of O^{18} in water after the experiment (at. %): found (a)	c/a	b/a
Preparation No. 1 —salt $7.04K_2O\cdot 6Nb_2O_5\cdot 22.0H_2O$							
1	0.2196	2.0070	1.26	1.23	1.24	1.02	0.99
2	0.2237	2.0165	1.26	1.23	1.22	1.03	1.01
3	0.2296	2.0141	1.26	1.23	1.23	1.02	1.00
Preparation No. 2 —salt $0.96K_2O\cdot Nb_2O_5\cdot 4.36H_2O$							
1	0.2385	1.9910	1.26	1.23	1.24	1.02	0.99
2	0.2223	2.0032	1.26	1.23	1.23	1.02	1.00
3	0.2190	1.9439	1.26	1.23	1.23	1.02	1.00

The investigation carried out shows that in the compounds studied—sodium pentatantalate and hexatantalate, potassium hexaniobate and metaniobate—all oxygen atoms of the salts and of the bound water are accessible to isotopic exchange with the solvent water. Isotopic exchange of oxygen between

between water and the salts studied proceeds comparatively rapidly, and equilibrium is already reached within 5 hours.

Institute of Physical Chemistry
Academy of Sciences of the USSR,

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.

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