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## PROGNOSTICATION AND PRACTICAL REALIZATION OF ACID-BASIC CO-OPERATIONS FOR THE ELECTRODEPOSITION OF METALS AND THEIR CONNECTIONS IN TUNGSTATE FUSIONS

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On the base of thermodynamic calculations for possible reactions between sodium tungstate and oxygen-containing compounds of boron, carbon, phosphorus, sulfur and VI-A groups metals was estimated the probability of these reactions. Experimental test of expressed assumptions by potentiometry and IR-spectroscopy was carried out.

Key words: acid-base co-operations, melts, electrodeposition, metals, compounds

*Introduction.* In electrochemistry of aquatic solutions it is known about influence of acidity of solutions, the determined by concentration of hydrogen ions, on electrochemical kinetics. Influence of acid-basic balances on electrochemical kinetics in haloganide-oxygen fusions is studied by Yu.K. Delimarskiy and V.I. Shapoval [1,2]. Authors marked that complete cathode renewal of oxianions to the metal or non-metal was carried out in acid electrolytes in presence oxygen ion acceptors.

Change of ionic composition of oxide fusions on the basis of tungstates and molybdates of alkaline and alkaline-landed metals renders substantial influence, both on electrode processes and equilibrium and on composition of cathode products.

### *Methods of experiment*

Probability of flowing of possible reactions of co-operation between the metals of VI-A group, by their oxides, carbides, tungstates and oxychemicals of the boron, carbon, phosphorus and sulphur was appraised on the basis of calculations of change of sample energy of Gibbs ( $\Delta G_T$ ).

As an electrolyte for the platinum-oxygen electrode of comparison in tungstate fusions we chose fusion  $Na_2WO_4$ -0.2 mole. %  $WO_3$ . The methods of measuring of balance potentials of platinum-oxygen electrodes in detail are described in works [3,4].

For authentication of connections in fusions applied the methods of infrared Spectroscopy and рентгенофазового analysis of the chilled samples. IR-spectrums got on the spectrophotometer of «SPECORD 75 IR», sciagrams – on the x-ray photography diffractometer of «DRON-4.0». At the use to infrared Spectroscopy the methods of removal of spectrums, expounded in-process [16] followed.

*Results and their discussion. Thermodynamics estimation of probability of co-operations of different connections with tungstate fusions.* In literature is present small information about the chemical co-operating of tungstate fusions with different oxychemicals. We executed the thermodynamics calculation of possible reactions of co-operation of different connections with the sodium tungstate.

It is set that from the group of boron-containing oxygen connections with tungstate fusion the sodium metaborate must not co-operate probably. From the group of phosphorus-containing of oxygen connections sodium phosphate must not co-operate with tungstate fusion. From the group of sulfur-containing oxygen connections with tungstate fusion the sulfate of sodium must not co-operate probably.

*Confirmation of possibility of control acid-basic properties of tungstate fusion from data of potentiometry method, x-ray phasic analysis and infrared spectroscopy of the cooled samples.* For explanation of experimental dependences of action of tungstate fusions in balance and non-balance conditions it is possible to offer the next model of ionic composition of these fusions. We will examine oxychemicals as attended acids-grounds. We will suppose that in fusion of  $Na_2WO_4$ , mainly, there are existing in an equilibrium inter se ions of  $Na^+$ ,  $WO_4^{2-}$ ,  $W_2O_7^{2-}$ ,  $O^{2-}$  and they can be examined as molten polytungstate electrolytes of composition  $2Na^+ + WnO_{2n+1}^{2-}$ , where  $n > 1$ . Through such «quasichemical» approach is possible explanation of displacements of interionic balances' in these fusions.

For the supervision of change of activity of ions of oxygen in tungstate fusion it is possible to use cells with oxygen electrodes:

$$Pt, O_2/(1 - n) Na_2WO_4 - A(\mathcal{I}) O^{2-}/(-Al_2O_3/0.8Na_2WO_4-0.2WO_3/O_2, Pt, \quad (1)$$

where  $A(\mathcal{I}) O^{2-}$  – an acceptor (donor) oxygen ion.

In cleanly tungstate fusion there is an balance  $2WO_4^{2-} \Leftrightarrow W_2O_7^{2-} + O^{2-}$  with the constant of balance  $K$ :

$$K = \frac{[WO_4^{2-}]^2}{[W_2O_7^{2-}][O^{2-}]} . \quad (2)$$

From equation of ionic balance on tungsten, using the methods of calculations [20], we get eventual equations of potential of oxygen electrode  $E$  from the concentration of oxide of the boron  $B_2O_3$ :

$$E = E^* + \frac{2.3R \cdot T}{2F} \cdot \lg \left( \frac{K \cdot nB_2O_3}{1 - 2nB_2O_3} \right) = E^{**} + \frac{2.3R \cdot T}{2F} \cdot \lg \left( \frac{nB_2O_3}{1 - 2nB_2O_3} \right) ; \quad (3)$$

$$E = E^* + \frac{2.3R \cdot T}{2F} \cdot \lg \left( \frac{K \cdot 2nB_2O_3}{1 - 4nB_2O_3} \right) = E^{**} + \frac{0,69R \cdot T}{2F} \cdot \lg \left( \frac{nB_2O_3}{1 - 4nB_2O_3} \right) . \quad (4)$$

According to equations (3) and (4) the pre-logarithmic coefficients of these dependences must make at the temperature of 1173 K 0.116 and 0.035 V respectively. It ensues from experimental data, that in the investigated range of concentrations of oxide of the boron a pre-logarithmic coefficient of dependence (3) is 0.111-0.120 V, and motion of dependence (4) has nonlinear character.

For authentication of connections of refractory metals in fusions of tungstate of sodium, containing different donors and oxygen ion acceptors, IR-spectrum and sciagrams of the chilled samples compared with spectrums and sciagrams of clean matters. As the last used fusion cakes of chemical reagents of chomates, molybdates and tungstates. Fusion cakes of dichromat, dimolybdates and ditungstates got by sintering of chomates, molybdates and tungstates with the corresponding oxides of metals (VI). As a result possibility of formation of dimeric particles is confirmed at adding to fusion of sodium tungstate oxygen ion acceptors.

### *Conclusions*

1. On the basis of the executed thermodynamics calculations probability of flowing of possible reactions of co-operation is appraised between the metals of VI-A group, by their oxides, carbides, sodium tungstate and oxychemicals of the boron, carbon, phosphorus and sulphur.

2. By electrochemical and structural methods we are get experimental confirmation of possibility of adjusting of acid-basic properties of tungstate fusion by these connections.

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