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THERMODYNAMICS ESTIMATION OF POSSIBILITY FOR CO-OPERATION OF VI-A GROUP METALS, THEIR OXIDES AND CARBIDES WITH TUNGSTATE-CARBONATE FUSIONS

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The thermodynamics calculations of possible reactions of co-operation of metals of VI are executed - An of group, their oxides and carbides with tungstate-carbonated fusions. Thermodynamics of the balanced (convertible) systems with electrodes from the metals of VI-A group and their carbides is considered.

Keywords: VI-A group metals, oxides, carbides, tungstate-carbonate fusions, co-operation, thermodynamics estimation

Introduction. For a theory and practice of electrodeposition of metals and non-metals from fusions, and also synthesis of connections on their basis important questions there are ability of electrodes and cathode products not to corrode in fusions, which their electrodeposition is carried out, and also existence of balanced electrode potentials of electrode or cathode product.

The purpose of work was a thermodynamics estimation of possibility of co-operation of VI-A group metals, their oxides and carbides with tungstate-carbonated fusions.

Methods of experiment. As an electrolyte for the platinum-exogenous electrode of comparison in tungstate fusions chose fusion Na_2WO_4 -0.2 mole. % WO_3 . The methods of measuring of balanced potentials of platinum-exogenous electrodes in detail are described in works [1-4].

Results and their discussion. In literature there are works [5-8], sacred to the chemical action of metals of the mentioned group, their oxides and carbides with tungstate-molybdate fusions. Presently there is not single opinion of composition of such fusions, and also temperature intervals of existence of balances. The therefore defined value can have a thermodynamics calculation of Gibbs energy possible reactions of VI-A group metals, their oxides and carbides with tungstate (molybdate) fusion. For calculations chrome, molybdenum, tungsten, oxides of molybdenum and tungsten (IV), carbides of molybdenum and tungsten, were chosen.

Calculations showed that VI-A group metals of with large probability can co-operate with tungstate-molybdate-carbonated fusions. Thus by the preferable form of existence of ions for chrome, molybdenum and tungsten there will be their dimeric complexes in fusion. The carbides of molybdenum and tungsten with large

probability can co-operate with carbonate fusions and with considerably less - with ditungsten-dimolybdate-carbonated fusions.

Thermodynamics of the molten electrochemical systems with electrodes from the VI-A group metals and their carbides. At flowing in the system of convertible process in isothermal conditions at permanent pressure change of Gibbs energy (ΔG), enthalpy (ΔH) and entropies (ΔS) is connected by correlation

$$\Delta G = \Delta H - T \cdot dS . \quad (1)$$

It is known from thermodynamics, that

$$\Delta S = \left(\frac{\partial \Delta G}{\partial T} \right)_p , \quad (2)$$

then Gibbs-Helmholtz equation is just:

$$\Delta G = \Delta H + T \cdot \left(\frac{\partial \Delta G}{\partial T} \right)_p . \quad (3)$$

Decrease of energy of Gibbs for electrochemical system equal to maximal work ΔA , which the system can to commit, and this maximal work is equal to voltage work of the system on the quantity of the last electricity, id est. *ZFE*:

$$-\Delta G = \Delta A = ZFE . \quad (4)$$

Electric work, accomplished by the system, can be anymore, less than or equal to the change of enthalpy depending on the sign of temperature coefficient of voltage.

Convertibility of electrochemical reactions on the corresponding metallic and carbidic electrodes of $M(MO_2) \mid Na_2WO_4-MO_3(M-Mo, W)$; $Cr_2O_3 \mid NaCl-Na_3AlF_6-K_2CrO_4$, $M \mid NaCl-Na_3AlF_6-Na_2MO_4(M-Mo, W)$, $Mo_2C \mid Na_2WO_4-MoO_3-Li_2CO_3$; $WC \mid Na_2WO_4-WO_3-CO_2$ does not cause doubts. The oxygen electrodes applied as electrode comparisons are $Pt(O_2) \mid Na_2WO_4-0.2WO_3$ and $Pt(O_2) \mid NaCl-Na_3AlF_6-0.1Na_2MO_4(M-Cr, Mo, W)$ in molten environments, unlike aquatic solutions, are convertible electrodes. Potential of such electrodes is determined by partial pressure of oxygen and activity of oxygen-containing ions. For measuring under surplus pressure carbon dioxide was first applied convertible tungsten electrode of comparison of $W \mid Na_2WO_4-0.2WO_3$, potential of which does not depend on pressure, and determined by activity of tungsten ions. Diffusive potential on the border of two molten phases for these electrodes of comparison in the case of the use $\beta-Al_2O_3$ of diaphragms insignificantly small and does not influence on the values of voltages of the systems.

Conclusions. On the basis of the executed thermodynamics calculations probability of flowing of possible reactions of co-operation between VI-A group metals, by their oxides, carbides and components of tungstate-carbonated fusions is appraised. Possibility of existence of the balanced (convertible) systems is well-proven by correlation of the electrochemical measuring and thermodynamics calculations with electrodes from the VI-A group metals and their carbides. These systems are perspective for realization of processes of high temperature electrochemical synthesis in conditions, near to balanced, and sediment of galvanic coverages.

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