**thermodynamic analysis of processes of manganese oxideS’ ionic replacement on solution in acid solutions of strong electrolytes**

 **I. G. Gorichev, D. V. Pankratov**

Moscow State Pedagogical University; 1, Malaya Pirogovskaya St., 119991, Moscow, Russian Federation, nir86@mail.ru

Total process of ionic replacement reaction at the interface «manganese oxide/solution» can be represented as next scheme:

$\frac{1-x\_{2}}{x\_{1}-x\_{2}}MnO\_{x\_{1}}+2H^{+}=\frac{1-x\_{1}}{x\_{1}-x\_{2}}MnO\_{2}+Mn^{2+}+H\_{2}O$ (1)

When (x1-x2)→0, the process is characterized by equilibrium constant: $K\_{p}=\left[Mn^{2+}\right]/\left[H^{+}\right]^{2}$.

It was found that value of Кр includes the contribution, which characterizes deviation from stoichiometry:

$f\left(x\right)={({∆G\_{i}^{0}}/{i}-{∆G\_{j}^{0}}/{j})(x-1)^{2}}/{(i-j)RT}$ (2)

where x=[O]/[Mn] in oxide phase, ∆G0i and ∆G0j – known quantities of free energy of formation manganese oxides MnOi and MnOj.

Equilibrium constant includes element, which considers interface potential (φ) on oxide/solution interphase:

$f\left(φ\right)=2F\left(x-1\right)(φ-(2,3RT/F)(pH-pH\_{0}))/2,3RT$ (3)

The numerical value of f(x) и f(φ) was found from experimental data analysis:

$lgK\_{p}=lgK\_{p}^{0}+f\left(x\right)+f\left(φ\right)=20,264-23,272(x-1)^{2}-\frac{2\left(x-1\right)}{0,059}\left(φ-0,059\left(pH\_{0}-pH\right)\right),$ (4)

where рН0 = 1,18

It follows from equation (4) that for analysis of equilibrium, which is given by the equation (1), it is necessary to take into account the interface potential on oxide/solution interphase and influence of nonstoichiometric function (2) and interface potential function (3) on kinetic parameters of manganese oxides’ dissolution. Offered regularities permit to calculate the final nonstoichiometric composition (x2) of oxide phase at various pH, φ, [Mn2+] values and lay down the methods of its regulation.