

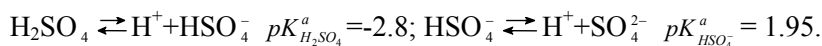
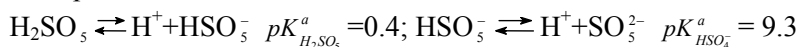
## THE DEPENDENCE OF THE OXIDATION-REDUCTION POTENTIAL OF THE SYSTEM PEROXOMONOSULFATE / SULFATE ON pH

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Oxidized  $\text{HSO}_5^-$  and reduced  $\text{HSO}_4^-$  forms of the system are weak and strong acids respectively, so along with the reactions of oxidation-reduction reactions of deprotonation proceed:



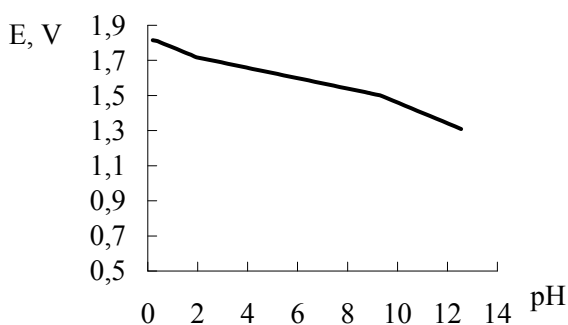
The generalized equation of electrochemical interaction of peroxomonosulfate /sulfate system is (charges of the particles here and subsequently are omitted):

$$\sum_{i=0}^2 \alpha_{\text{H}_i\text{SO}_5} \cdot \text{H}_i\text{SO}_5 + (2 + \sum_{i=1}^2 i \cdot \alpha_{\text{H}_i\text{SO}_4} - \sum_{i=1}^2 i \cdot \alpha_{\text{H}_i\text{SO}_5}) \cdot \text{H}^+ + 2\bar{e} = \sum_{i=0}^2 \alpha_{\text{H}_i\text{SO}_4} \cdot \text{H}_i\text{SO}_4 + \text{H}_2\text{O}.$$

The dependence of the oxidation-reduction potential on the pH of the system relative to the standard hydrogen electrode ( $c_{\text{H}_2\text{SO}_5} = c_{\text{H}_2\text{SO}_4} = 1 \text{ mol L}^{-1}$ ) can be expressed as:

$$E = E^0_{\text{H}_2\text{SO}_5, 2\text{H}^+/\text{H}_2\text{SO}_4, \text{H}_2\text{O}} - \frac{\partial}{2} (pK_{\text{H}_2\text{SO}_5}^a + pK_{\text{HSO}_5^-}^a - pK_{\text{H}_2\text{SO}_4}^a - pK_{\text{HSO}_4^-}^a) - \frac{\partial}{2} (2 - p + q) \cdot pH +$$

$\frac{\partial}{2} \lg \frac{c_s(\text{H}_2\text{SO}_5)}{c_s(\text{H}_2\text{SO}_4)}$ , were:  $p = \sum_{i=1}^2 i \cdot \alpha_{\text{H}_i\text{SO}_5}$ ,  $q = \sum_{i=1}^2 i \cdot \alpha_{\text{H}_i\text{SO}_4}$ ;  $\alpha_{\text{H}_2\text{SO}_5}$  and  $\alpha_{\text{HSO}_4^-}$  are mole fraction of protonized of oxidized and reduced forms.



Thus, when the solution pH changes the protolytic form of the particles changes, and, therefore, the form of the generalized equation of electrochemical interaction changes, which leads to the dependence of E on pH as shown on Fig.