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BRIEF COMMUNICATIONS

Potential–pH Diagram for the Nickel–Water System Containing Nickel(III) Metahydroxide

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Abstract— The potential–pH diagram (25ºC) of the nickel–water system containing nickel(III) metahydroxide was calculated. Fields of thermodynamically stable states of nickel ions Ni^{2+}, hydronickelate ions, nickel hydroxide and metahydroxide were determined.

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It is known that the potential-determining process occurring on positive electrodes of nickel–iron, nickel–cadmium, and nickel–zinc alkaline batteries can be described by the electrochemical reaction involving nickel(III) metahydroxide:

$$NiOOH_{(s)} + H_2O + e = Ni(OH)_{2(s)} + OH^-,$$

however, this reaction is absent from the potential–pH diagram for the nickel–water system [1, 2]. Therefore we have calculated the potential-pH diagram for the nickel–water system containing nickel(III) metahydroxide at 25°C. In the calculations we used the published values [3, 4] of Gibbs standard energies for the formation of the compounds (see the table). The calculation of potentials of electrode reactions was carried out for the activities of nickel, nickel(II) hydroxide, nickel(III) metahydroxide, and water equal to 1 and the activities of ions in solutions equal to 1 and 1×10^{-6}.

The reaction passing on a nickel electrode in an acid medium containing nickel(II) ions can be written as follows:

$$Ni^{2+} + 2e = Ni_{(s)};\ \Delta\Delta G^\circ_{298} = 48.2\ \text{kJ}. \quad (1)$$

The potential of reaction (1) is described by the equation

$$E_1 = -0.250 + 0.0296 \log \{Ni^{2+}\},$$

where $\{Ni^{2+}\}$ is the activity of nickel(II) ions in solution.

At $\{Ni^{2+}\} = 1$ $E_1 = -0.250$ V and at $\{Ni^{2+}\} = 1 \times 10^{-6}$ $E_1 = -0.426$ V.

On the alkalization of the solution nickel(II) hydroxide can be precipitated.

$$Ni^{2+} + 2OH^- = Ni(OH)_{2(s)};\ \Delta G^\circ_{298} = -90.3\ \text{kJ}. \quad (2)$$

The calculated solubility product of nickel(II) hydroxide lies in the interval between the solubility products for freshly precipitated nickel hydroxide of 2.0×10^{-15} and for aged nickel hydroxide of 6.3×10^{-18} [5]. The pH value of the hydrate formation at $\{Ni^{2+}\} = 1$ is 6.09, and at $\{Ni^{2+}\} = 1 \times 10^{-6}$ it is 9.09.

Small amounts of hydronickelate ions are formed in strongly alkaline solutions as the change of the Gibbs energy of reaction (3) is positive:

$$Ni(OH)_{2(s)} + OH^- = HNiO_2^- + H_2O;\ \Delta G^\circ_{298} = 24.0\ \text{kJ}. \quad (3)$$

At the activity of hydronickelate ions $\{HNiO_2^-\} = 1$ pH of their formation is 18.2 and at $\{HNiO_2^-\} = 1 \times 10^{-6}$ it is 12.2.

Thus, the field of nickel(II) hydroxide stable existence at the unit activities of nickel and hydronickelate ions is $6.09 < pH < 18.2$, and at $\{Ni^{2+}\} = \{HNiO_2\} = 1 \times 10^{-6}$

it is 9.09 < pH < 12.2. The following reaction occurs in these fields on the nickel electrode surface:

$$Ni(OH)_{2(s)} + 2e = Ni_{(s)} + 2OH^-;\ \Delta G^\circ_{298} = 138.5\ kJ. \quad (4)$$

The potential of reaction (4) is described by the equation

$$E_4 = 0.110 - 0.0592\ pH.$$

At pH 6.09 $E_4 = -0.250$ V, at pH 9.09 $E_4 = -0.426$ V, at pH 18.2 $E_4 = -0.964$ V, and at pH 12.2 $E_4 = -0.610$ V.

In strongly alkaline solutions with pH > 12.2 reaction (5) can proceed

$$HNiO_2 + H_2O + 2e = Ni_{(s)} + 3OH^-;\ \Delta G^\circ_{298} = 114.5\ kJ. \quad (5)$$

The potential of reaction (5) is described by the equation

$$E_5 = 0.648 - 0.0887pH + 0.0296\ \log\ \{HNiO_2\}.$$

At $\{HNiO_2^-\} = 1$ and pH 18.2 $E_5 = -0.967$ V, at $\{HNiO_2^-\} = 1 \times 10^{-6}$ and pH 12.2 $E_5 = -0.612$ V.

In the field of stable existence of nickel(II) hydroxide electrochemical reaction (6) involving nickel(III) metahydroxide proceeds on the electrode surface:

$$NiOOH_{(s)} + H_2O + e = Ni(OH)_{2(s)} + OH^-;$$
$$\Delta G^\circ_{298} = -47.4\ kJ. \quad (6)$$

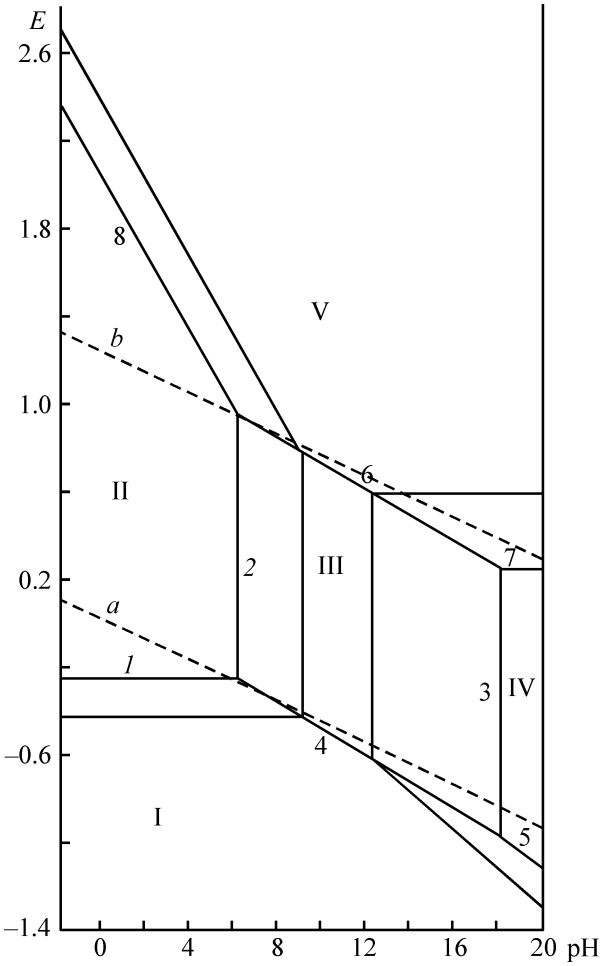
The potential of reaction (6) is described by the equation:

$$E_6 = 1.319 - 0.0592pH.$$

At pH 6.09 $E_6 = 0.959$ V, at pH 9.09 $E_6 = 0.781$ V, at pH 12.2 $E_6 = 0.597$ V, and at pH 18.2 $E_6 = 0.242$ V.

Changes of standard Gibbs energies corresponding to the formation of various substances [3, 4]

Substance	ΔG°_{298}, kJ mol^{-1}	Substance	ΔG°_{298}, kJ mol^{-1}
$Ni_{(s)}$	0	$Ni(OH)_{2(s)}$	–453.1
Ni^{2+}	–48.2	H^+	0
$HNiO_2^-$	–349.2	OH^-	–157.3
$NiOOH_{(s)}$	–325.8	H_2O	–237.2



Dependence of potential E(V) on pH for the nickel-water system containing nickel(III) metahydroxide at 25°C. (I) Ni, (II) Ni^{2+}, (III) $Ni(OH)_2$, (IV) $HNiO_2^-$, (V) NiOOH.

In strongly alkaline solutions with pH > 12.2 reaction (7) proceeds.

$$NiOOH_{(s)} + e = HNiO_2^-;\ \Delta G^\circ_{298} = -23.4\ kJ. \quad (7)$$

The potential of reaction (6) is described by the equation:

$$E_7 = 0.242 - 0.0592\ \log\ \{HNiO_2^-\}.$$

At $\{HNiO_2^-\} = 1$ $E_7 = 0.242$ V and at $\{HNiO_2^-\} = 1 \times 10^{-6}$ $E_7 = 0.597$ V.

The reaction proceeding on the electrode containing nickel metahydroxide in an acid medium can be written as follows:

$$NiOOH_{(s)} + 3H^+ + e = Ni^{2+} + 2H_2O;$$
$$\Delta G^\circ_{298} = -196.8\ kJ. \quad (8)$$

The potential of reaction (8) is described by the equation:

$$E_8 = 2.040 - 0.1776\text{pH} - 0.0592 \log \{Ni^{2+}\}.$$

At $\{Ni^{2+}\} = 1$ and pH 6.09 $E_8 = 0.958$ V, and at $\{Ni^{2+}\} = 1 \times 10^{-6}$ and pH 9.09 $E_8 = 0.781$ V.

The potential-pH diagram (25°C) for the nickel-water system containing nickel(III) metahydroxide is given in the figure. The fields of thermodynamically stable state of nickel Ni^{2+} ions, hydronickelate ions $HNiO_2^-$, and of nickel hydroxide and metahydroxide are seen in the diagram. Potentials of oxygen and hydrogen electrodes depending on pH are plotted by dashed lines *a* and *b*.

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