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THE REVISED POTENTIAL–*pH* DIAGRAM OF *Sc–H₂O* SYSTEM
УТОЧНЁННАЯ ДИАГРАММА ПОТЕНЦИАЛ–*pH* СИСТЕМЫ *Sc–H₂O*

Р.А. Nikolaychuk
П.А. Николайчук

Chelyabinsk State University, 129 Bratiev Kashirinykh St, Chelyabinsk, 454001, Russia

Челябинский государственный университет, Россия, 454001, г. Челябинск, ул. Братьев Кашириных, 129

E-mail: nra@csu.ru

Résumé. The thermodynamic data on the standard Gibbs energies of formation of scandium solid and aqueous species were collected and systematised. The speciation diagram for the dimerisation reaction $2ScOH^{2+}(aq) \rightleftharpoons Sc_2(OH)_2^{4+}(aq)$ was plotted. The equilibria between various hydrolysed scandium (III) species in an aqueous solution were discussed. The potential–*pH* diagrams of system *Sc–H₂O* at 25°C, air pressure of 1 bar and various activities of ions in a solution were plotted. The influence of possible electrochemical formation of scandium hydride and the effect of non-stoichiometry of scandium sesquioxide on the corrosion-electrochemical properties of scandium were discussed.

Аннотация. Собраны и систематизированы термодинамические данные о стандартных энергиях Гиббса образования различных соединений скандия в твёрдом состоянии и в водном растворе. Построена диаграмма распределения для реакции $2ScOH^{2+}(aq) \rightleftharpoons Sc_2(OH)_2^{4+}(aq)$. Обсуждены равновесия между различными гидратированными формами скандия (III) в водном растворе. Построены диаграммы потенциал–*pH* системы *Sc–H₂O* при 25°C, давлении воздуха 1 бар и различных активностях ионов в растворе. Обсуждено возможное влияние электрохимического образования гидроксида скандия и нестехиометрии сесквиоксида скандия на коррозионно-электрохимические свойства скандия.

Key words: scandium, scandium oxide, scandium hydride, scandium nitride, non-stoichiometry, scandium aqueous species, speciation diagram, activity–*pH* diagram, potential–*pH* diagram, corrosion-electrochemical behaviour.

Ключевые слова: скандий, оксид скандия, гидрид скандия, нитрид скандия, нестехиометрия, водные соединения скандия, диаграмма распределения, диаграмма активность–*pH*, диаграмма потенциал–*pH*, коррозионно-электрохимическое поведение.

1. Introduction

An interest to the chemistry of scandium significantly increased in the last five decades. With the development of microelectronics, air- and spacecraft engineering, hydrogen energetics and other high-technology branches of industry scandium began to attract an attention of researchers. Various scandium compounds are widely employed for the development of high-temperature ceramics, quantum-mechanical amplifiers, lasers, luminophores, emission materials, dielectrics, solid electrolytes, halogen projectors, catalysts, filters for quasimonochromatic rays of neutrons, emitters of β -particles *et cetèra*. Scandium-based alloys have a series of valuable properties, including thermal and mechanical stability, corrosion and radiation resistance [Horovitz et al., 1975; Komissarova, 2001]. The aqueous chemistry and the corrosion-electrochemical behaviour of scandium are very similar to that of aluminum [Brookins, 1988; Rayner-Canham, 2013; Schweitzer, Pesterfield, 2010]. The potential–*pH* diagram for scandium found its application in studying of pitting behaviour of alloys [Santamaria et al., 2013; Wloka, Virtanen, 2007] and characterisation of scandium inorganic compounds [Wang et al., 2013]. However, the existing variants of Pourbaix diagram for scandium [Brookins, 1988; Pourbaix, 1966; Schweitzer, Pesterfield, 2010; Takeno, 2005] take into account only *Sc* (hcp), Sc^{3+} (aq), $ScOH^{2+}$ (aq) and Sc_2O_3 (bcc) and do not consider another scandium aqueous species, including the polymerised forms. The goal of this study is to collect the reliable data on the



Gibbs energies of formation of the various scandium aqueous species, consider the speciation of Sc (III) species and revise the potential–*pH* diagram of Sc–H₂O system.

2. Thermodynamic data on scandium solid and aqueous species

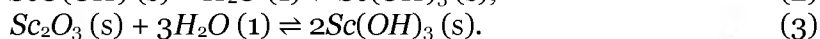
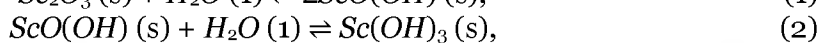
According to the phase diagram of Sc–O system [Kuprashvili et al., 1969; Predel, 1998; Diagrammy sostoaniâ ..., 2001], only one stable oxide – Sc₂O₃ – exists in the system at 298K. It has the crystal structure of body centered cube. It was reported earlier [Dufek et al., 1969, 1967; Petru et al., 1970] about the existence of scandium monoxide, ScO (s), which can be obtained by reduction of Sc₂O₃ by silicon, but the subsequent studies and the thermodynamic calculations [Work, Eick, 1972; Yudin et al., 1976] disproved this report. Upon interaction with hydrogen scandium form two hydrides, namely, ScH₂ (s) and ScH₃ (s) [Bashkin et al., 1978; Horovitz et al., 1975; Jerosch-Herold et al., 1997; Kobayashi, Takei, 1978; Kobayashi, Takei, 1980; Switendick, 1989; Komissarova, 2001]. In aqueous acidic environments scandium exists in form of the cation Sc³⁺ (aq), which with increase of the basicity of the solution can be hydrolysed to ScOH²⁺ (aq), Sc(OH)₂⁺ (aq) or Sc(OH)₄⁻ (aq) [Baes Jr., Mesmer, 1976; Schweitzer, Pesterfield, 2010]. The hydroxide Sc(OH)₃ (s) can be precipitated from a solution, but it is unstable relative to the oxide [Travers et al., 1976].

Table 1 summarises the standard Gibbs energies of formation of various scandium species. In the case when only the standard enthalpies of formation and the standard entropies of the species were present in literature [Bommer, Hohmann, 1941; Huber et al., 1963], the standard entropy of pure scandium were taken from [Gerstein, 1971] and used in calculations of the standard Gibbs energies. The standard Gibbs energy of formation of scandium (III) hydroxide was estimated from the value of the solubility product of Sc(OH)₃ (s) [Aksel'rud, 1963; Feitknecht, Schindler, 1963; Moeller, Kremers, 1945; Oka, 1938; Wood, Samson, 2006]. The standard Gibbs energies of formation of various scandium hydroxocations were estimated from the values of hydrolysis constants [Akalin, Özer, 1971; Antonovich, Nazarenko, 1968; Aveston, 1966; Biedermann et al., 1956; Cole et al., 1969; Haas et al., 1995; Kilpatrick, Pokras, 1953; Kilpatrick, Pokras, 1954; Komissarova et al., 1971; Lindqvist-Reis et al., 2006; Marques et al., 1997; Paul, 1962; Sekine, Hasegawa, 1966; Siqueira et al., 1995; Türkel et al., 1999; Wu et al., 2004; Zhuk, 1954]. The values chosen for further calculations are marked in *italic*.

3. The equilibria involving various scandium (III) compounds

3.1. The oxide, the oxyhydrate and the hydroxide

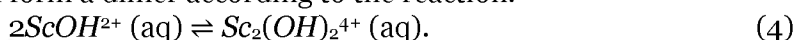
The following reactions involving the oxide, the oxyhydrate and the hydroxide of scandium (III) can be considered:



The Gibbs energy changes in the reactions (1), (2) and (3) are calculated using the values from Table 1, and the following values are obtained: $\Delta_r G_{298}^\circ (1) = 41\,940 \text{ J} \cdot \text{mol}^{-1}$, $\Delta_r G_{298}^\circ (2) = 10\,940 \text{ J} \cdot \text{mol}^{-1}$ and $\Delta_r G_{298}^\circ (3) = 63\,820 \text{ J} \cdot \text{mol}^{-1}$. The calculations show that scandium sesquioxide is the most thermodynamically stable compound, and it does not tend to be hydrolysed.

3.2. The polymerisation of aqueous ScOH²⁺

The ion ScOH²⁺ (aq) can form a dimer according to the reaction:



The Gibbs energy change in the reaction (4) from the data of Table 1 is $\Delta_r G_{298}^\circ (4) = -15\,200 \text{ J} \cdot \text{mol}^{-1}$, and the equilibrium constant is $K_{(4)} = 461.621 \cdot \text{mol}^{-1}$.

Table 1
Таблица 1

The standard Gibbs energies of formation of various scandium species
Стандартные энергии Гиббса образования различных соединений скандия

Compound	Reference state	$-\Delta_f G_{298}^{\circ}, \text{J} \cdot \text{mol}^{-1}$	Reference
Sc	s, hexagonal close packed	0	By convention
ScN	s, cubic	253 250	[Alimarin, Yung-Schaing, 1961; Komissarova, 2001]
		253 150	[Gschneider Jr., 1961; Horovitz et al., 1975]
		283 800	[Pankratz et al., 1984]
ScH ₂	s, face centered cubic	149 280	[Termičeskie konstanty vešestv, 2007]
		157 170	[Lieberman, Wahlbeck, 1965; Komissarova, 2001]
		157 300	[Horovitz et al., 1975]
Sc ₂ O ₃	s, body centered cubic	1 819 360	[Brookins, 1988; Wagman et al., 1982]
		1 819 410	[Speight, 2005]
		1 819 460	[Horovitz et al., 1975]
		1 804 110	[Pankratz et al., 1984]
		1 804 250	[Veryagin et al., 1965]
		1 819 320	[Ruzinov, Gulzanitskii, 1975; Progress in the Science ..., 2013]
		1 819 200	[Schweitzer, Pesterfield, 2010]
		1 818 930	[Termičeskie konstanty vešestv, 2007]
		1 802 030	[Jichang, Ke'ren, 1984; Komissarova, 2001]
		1 819 380	[Travers et al., 1976]
1 819 370	[Robie et al., 1979]		
Sc(OH) ₃	s, body centered cubic	1 233 300	[Brookins, 1988; Wagman et al., 1982]
		1 233 230	[Ruzinov, Gulzanitskii, 1975]
		1 233 400	[Schweitzer, Pesterfield, 2010]
		1 232 980	[Horovitz et al., 1975]
		1 226 000	[Travers et al., 1976]
		1 055 830	[Termičeskie konstanty vešestv, 2007]
ScO(OH)	s	1 007 200	[Baes Jr., Mesmer, 1976]
Sc ³⁺	aq	586 600	[Brookins, 1988; Schweitzer, Pesterfield, 2010; Wagman et al., 1982]
		586 200	[Schweitzer, Pesterfield, 2010]
		583 890	[Termičeskie konstanty vešestv, 2007]
		586 650	[Travers et al., 1976]
ScOH ²⁺	aq	801 200	[Brookins, 1988; Speight, 2005; Wagman et al., 1982]
		799 000	[Schweitzer, Pesterfield, 2010]
		799 220	[Travers et al., 1976]
		799 200	[Baes Jr., Mesmer, 1976]
		794 120	[Termičeskie konstanty vešestv, 2007]
Sc(OH) ₂ ⁺	aq	1 005 400	[Schweitzer, Pesterfield, 2010]
		1 005 500	[Baes Jr., Mesmer, 1976]
Sc(OH) ₄ ⁻	aq	1 370 800	[Brookins, 1988]
		1 380 700	[Schweitzer, Pesterfield, 2010]
		1 386 750	[Baes Jr., Mesmer, 1976]
Sc ₂ (OH) ₂ ⁴⁺	aq	1 649 750	[Termičeskie konstanty vešestv, 2007]
		1 613 200	[Baes Jr., Mesmer, 1976]
Sc ₃ (OH) ₄ ⁵⁺	aq	2 626 500	[Termičeskie konstanty vešestv, 2007]
Sc ₃ (OH) ₅ ⁴⁺	aq	2 838 220	[Termičeskie konstanty vešestv, 2007]
		2 852 200	[Baes Jr., Mesmer, 1976]



The ratio of activities of monomeric and dimeric forms is determined by the following system of equations:

$$\left\{ \begin{array}{l} K_{(4)} = \frac{a_{Sc_2(OH)_2^{4+}}(aq)}{a_{ScOH^{2+}}^2(aq)}; \\ a_{[Sc]} = a_{ScOH^{2+}}(aq) + 2 \cdot a_{Sc_2(OH)_2^{4+}}(aq). \end{array} \right. \quad (5)$$

Here $a_{[Sc]}$ is the total activity of dissolved scandium in a solution. The dependency of activities of monomeric and dimeric forms on the total activity of dissolved scandium is illustrated by Figure 1. Here curves 1 and 2 show the dependencies of the “activity fractions”

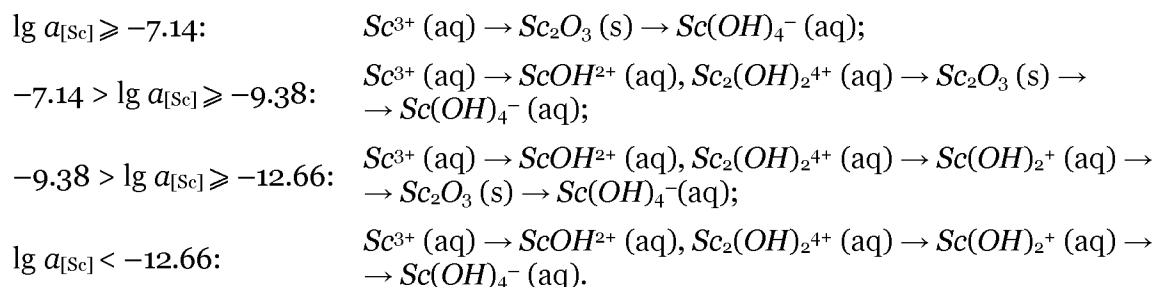
$$\frac{a_{ScOH^{2+}}(aq)}{a_{ScOH^{2+}}(aq) + a_{Sc_2(OH)_2^{4+}}(aq)} \text{ and } \frac{a_{Sc_2(OH)_2^{4+}}(aq)}{a_{ScOH^{2+}}(aq) + a_{Sc_2(OH)_2^{4+}}(aq)} \text{ on } a_{[Sc]}, \text{ and curve 3 determines the ratio } \frac{a_{ScOH^{2+}}(aq)}{a_{Sc_2(OH)_2^{4+}}(aq)}.$$

The dimeric form predominates in concentrated solutions. At $a_{[Sc]}=1$ M the ratio $\frac{a_{ScOH^{2+}}(aq)}{a_{Sc_2(OH)_2^{4+}}(aq)} = 0.067$. With decrease of the total content of dissolved scandium this ratio begins to grow. The activities of monomeric and dimeric forms become equal at $\lg a_{[Sc]}=-2.15$, and in more diluted solution the monomeric form predominates. At $a_{[Sc]}=10^{-3}$ M the ratio $\frac{a_{ScOH^{2+}}(aq)}{a_{Sc_2(OH)_2^{4+}}(aq)} = 3.43$ and at $a_{[Sc]}=10^{-6}$ M $\frac{a_{ScOH^{2+}}(aq)}{a_{Sc_2(OH)_2^{4+}}(aq)} = 2170$.

3.3. The aqueous scandium (III) species

The relative stability of other scandium (III) hydroxocomplexes depends on both pH and the activities of species in a solution. This dependence is illustrated in Figure 2.

The cation Sc^{3+} exhibits the following consecutive reactions with increase of pH depending on the activities:



Accordingly, the cation $Sc_3(OH)_5^{4+}$ has no domain of thermodynamic stability.

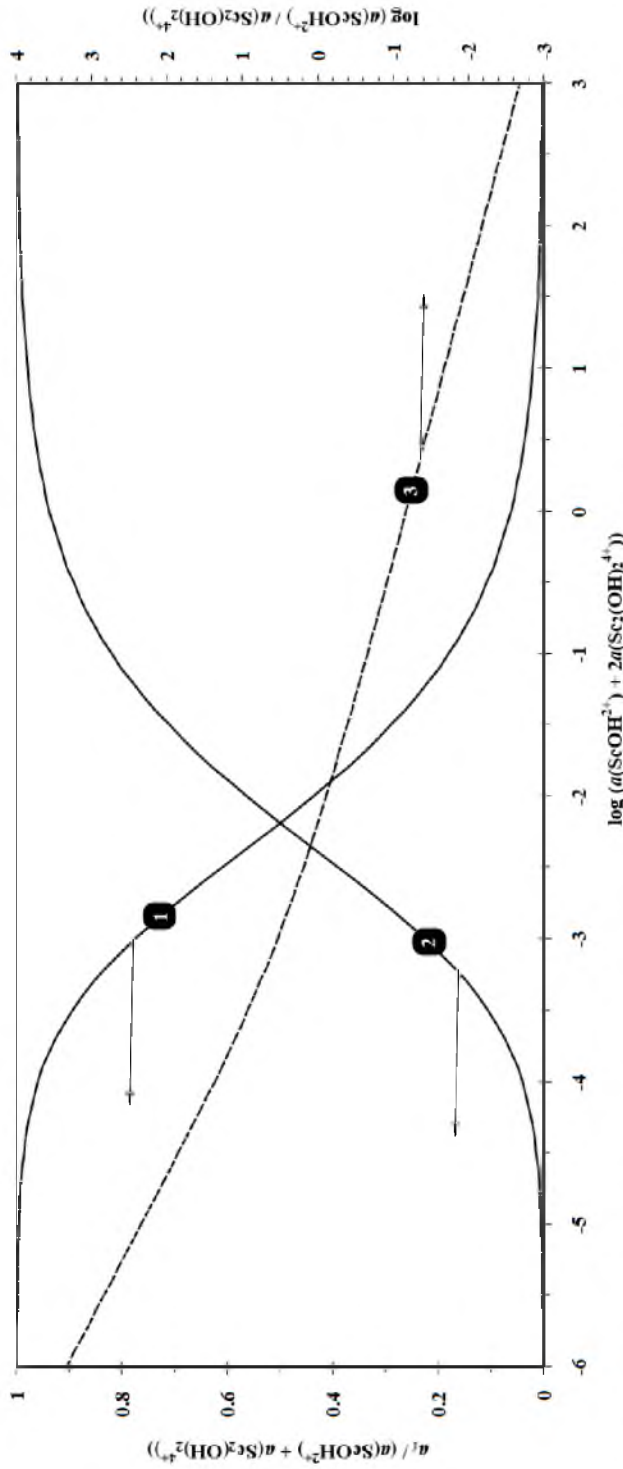


Fig. 1. The speciation diagram of the scandium (III) hydroxocations in a solution, $2ScOH^{2+} (aq) \rightleftharpoons Sc_2(OH)_2^{4+} (aq)$:

$$1 - \frac{a_{ScOH^{2+}}(aq)}{a_{ScOH^{2+}}(aq) + a_{Sc_2(OH)_2^{4+}}(aq)} = f\left(\lg(a_{ScOH^{2+}}(aq) + 2 \cdot a_{Sc_2(OH)_2^{4+}}(aq))\right), \text{ left axis;}$$

$$2 - \frac{a_{Sc_2(OH)_2^{4+}}(aq)}{a_{ScOH^{2+}}(aq) + a_{Sc_2(OH)_2^{4+}}(aq)} = f\left(\lg(a_{ScOH^{2+}}(aq) + 2 \cdot a_{Sc_2(OH)_2^{4+}}(aq))\right) \lg \frac{a_{ScOH^{2+}}(aq)}{a_{Sc_2(OH)_2^{4+}}(aq)} = f\left(\lg(a_{ScOH^{2+}}(aq) + 2 \cdot a_{Sc_2(OH)_2^{4+}}(aq))\right), \text{ right axis}$$

Рис. 1. Диаграмма распределения гидроксационов скандия (III) в растворе, $2ScOH^{2+} (aq) \rightleftharpoons Sc_2(OH)_2^{4+} (aq)$:

$$1 - \frac{a_{ScOH^{2+}}(aq)}{a_{ScOH^{2+}}(aq) + a_{Sc_2(OH)_2^{4+}}(aq)} = f\left(\lg(a_{ScOH^{2+}}(aq) + 2 \cdot a_{Sc_2(OH)_2^{4+}}(aq))\right), \text{ левая ось;}$$

$$2 - \frac{a_{Sc_2(OH)_2^{4+}}(aq)}{a_{ScOH^{2+}}(aq) + a_{Sc_2(OH)_2^{4+}}(aq)} = f\left(\lg(a_{ScOH^{2+}}(aq) + 2 \cdot a_{Sc_2(OH)_2^{4+}}(aq))\right) \lg \frac{a_{ScOH^{2+}}(aq)}{a_{Sc_2(OH)_2^{4+}}(aq)} = f\left(\lg(a_{ScOH^{2+}}(aq) + 2 \cdot a_{Sc_2(OH)_2^{4+}}(aq))\right), \text{ правая ось}$$

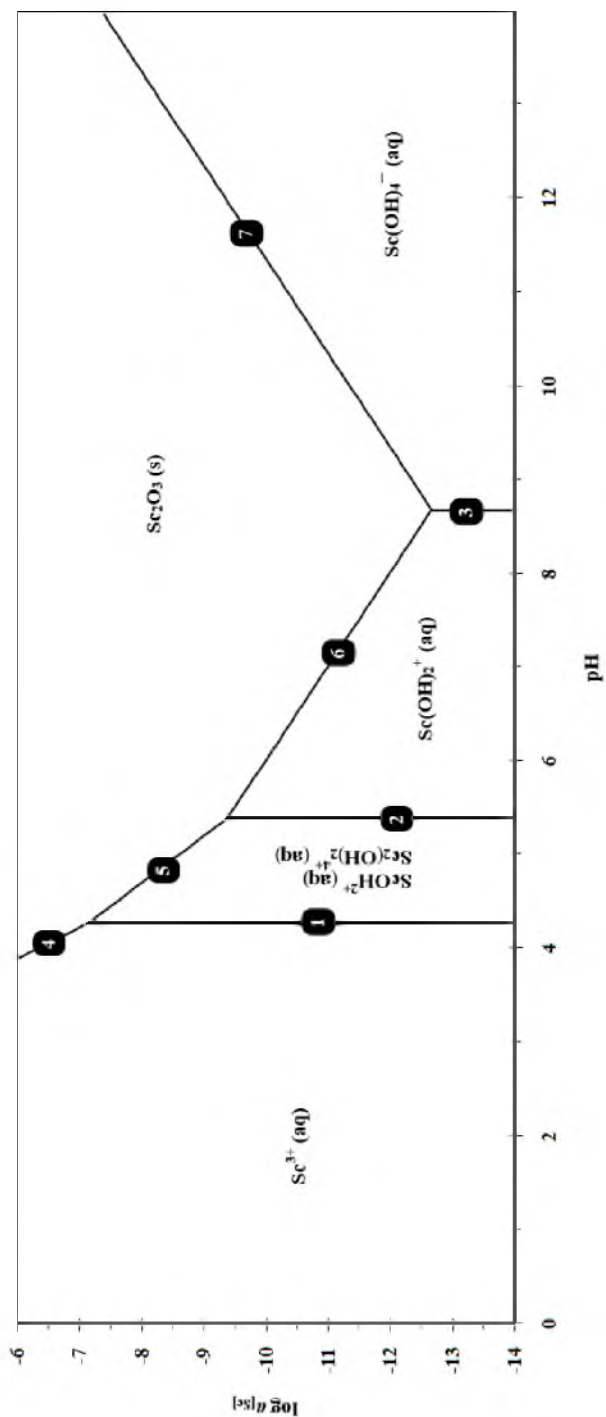


Fig. 2. The activity-pH diagram for Sc (III) species
 Рис. 2. Диаграмма активность-pH для соединений Sc (III)



4. The potential–*pH* diagram

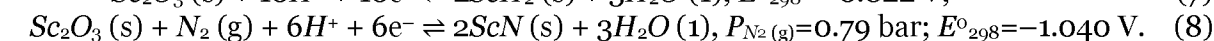
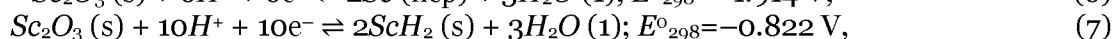
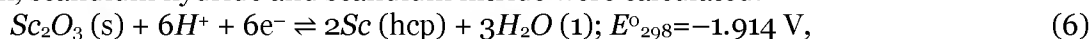
In accordance with Figure 2 the sequence of equilibria involving various scandium ions differs with alteration of activities of dissolved species in a solution. This also affects the potential – *pH* diagrams. The diagrams at various activities of ions in solutions from 10^{-6} M to 10^{-15} M are shown in Figures 3 through 6. The calculations show that for the environments, in which the activities exceed 10^{-6} M and which are of the most importance for applied chemistry, the diagrams are in good agreement with the previously published ones [Brookins, 1988; Pourbaix, 1966; Schweitzer, Pesterfield, 2010; Takeno, 2005]. The diagrams at the activities lower than 10^{-10} M currently have no practical implementation; however they are presented in order to show the influence of the presence or absence of the domains of thermodynamic stability of certain phases on the thermodynamic activities. Probably the thermodynamic prediction of the electrochemical properties of solutions at super-low activities of ions in solutions may become practically important in the future due to developing of analytical techniques and the tendency of decreasing the detection limit of substances in a solution.

The corrosion-electrochemical behaviour of scandium is very similar to that of aluminum. In the highly acidic environments (at $pH < 4$) scandium exhibits the active dissolution with formation of Sc^{3+} (aq). At higher *pH* values the protective layer consisting of Sc_2O_3 (s) is formed on the metal surface. However, in very diluted solutions, where $a_{[Sc]} < 10^{-7}$ M, the hydrolysed aqueous scandium species begin to predominate, and the domain of scandium passivity is rapidly narrowed.

5. The influence of scandium hydride and nitride

In addition to the oxide passivation, scandium can exhibit either hydride or nitride passivation. The layer of scandium hydride can be formed due to electrochemical reduction of water and interaction of metallic scandium with the forming hydrogen. When scandium is exposed in a natural water that stays in equilibrium with atmospheric air, the possible electrochemical formation of scandium nitride due to reduction of the atmospheric nitrogen should also be considered.

Using the data from Table 1 the potentials of reduction of Sc_2O_3 (s) to metallic scandium, scandium hydride and scandium nitride were calculated:



It follows from the equations (6), (7) and (8) that both metallic scandium and scandium nitride become thermodynamically unstable in presence of scandium hydride, and that scandium oxide is electrochemically reduced directly to ScH_2 (s). Therefore, the potential–*pH* diagram for scandium with consideration of scandium hydride ScH_2 (s) were calculated and presented in Figures 7 through 10. The domain of hydride passivation of scandium is present at these diagrams instead of the domain of thermodynamic stability of pure scandium. However, all the reactions involving dissolution of both metallic scandium and its hydride, occur below the potential of the standard hydrogen electrode, and therefore, do not affect the corrosion-electrochemical properties of scandium in the domain of electrochemical stability of water.

The basic chemical and electrochemical equilibria in $Sc-H_2O$ system are listed in Table 2.

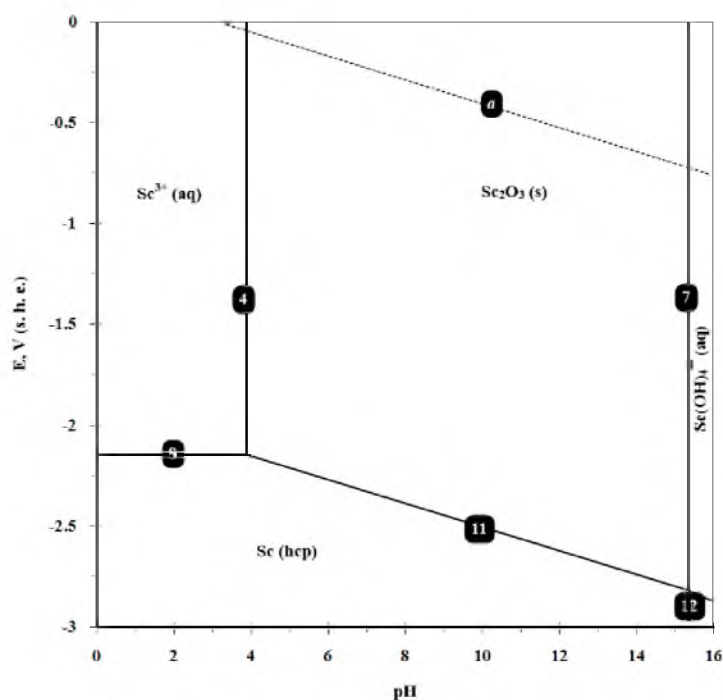


Fig. 3. The potential–pH diagram of Sc–H₂O system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-6}$ M

Рис. 3. Диаграмма потенциал–pH системы Sc–H₂O при 298K, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-6}$ M

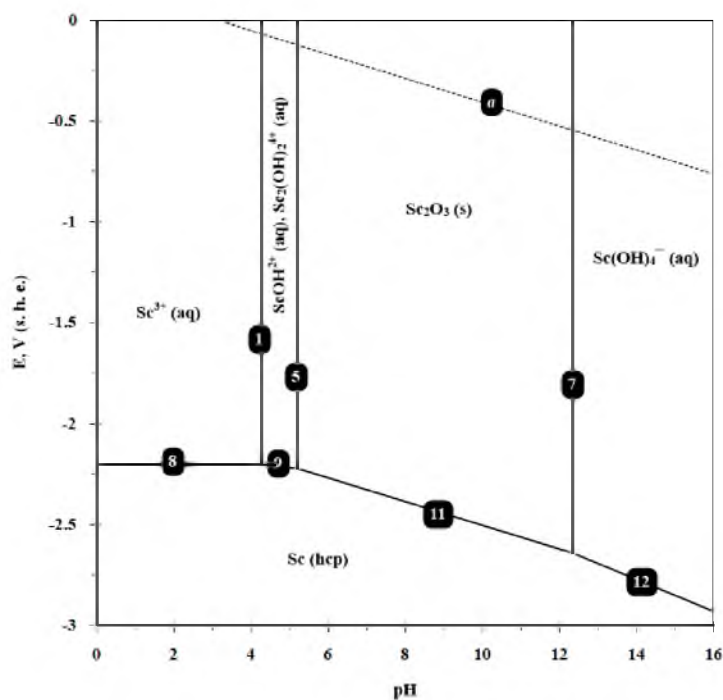


Fig. 4. The potential–pH diagram of Sc–H₂O system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-9}$ M

Рис. 4. Диаграмма потенциал–pH системы Sc–H₂O при 298K, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-9}$ M

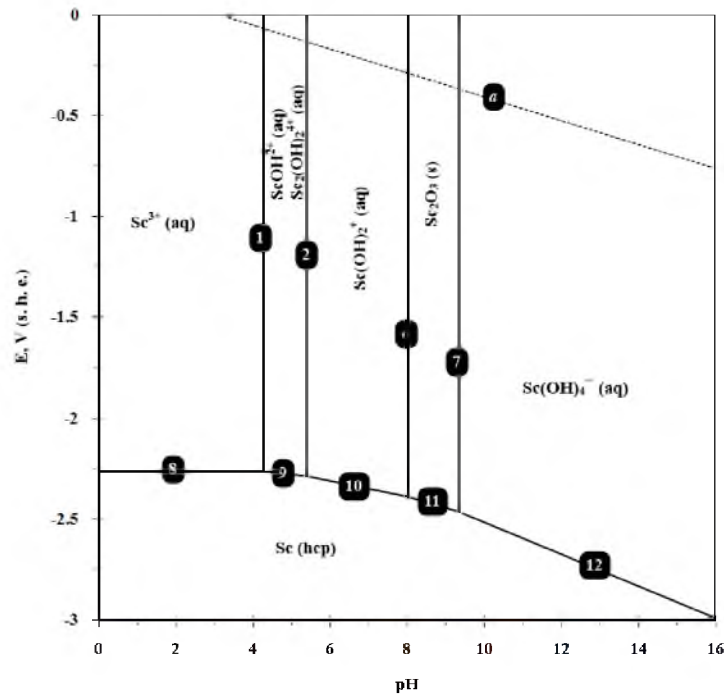


Fig. 5. The potential– pH diagram of $Sc-H_2O$ system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-12}$ M

Рис. 5. Диаграмма потенциал– pH системы $Sc-H_2O$ при 298K, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-12}$ M

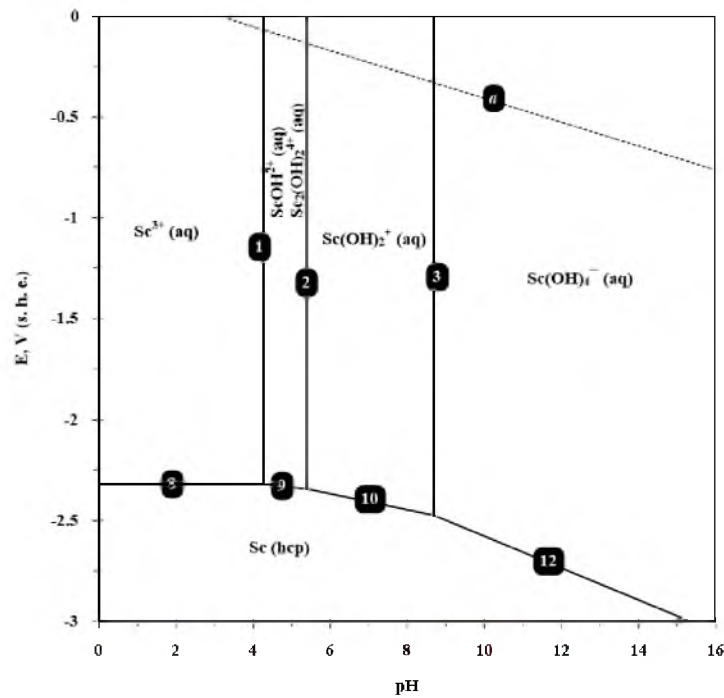


Fig. 6. The potential– pH diagram of $Sc-H_2O$ system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-15}$ M

Рис. 6. Диаграмма потенциал– pH системы $Sc-H_2O$ при 298K, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-15}$ M

Table 2
Таблица 2

Basic chemical and electrochemical equilibria in Sc–H₂O system at 298K and air pressure of 1 bar
Основные химические и электрохимические равновесия в системе Sc–H₂O при 298K и давлении воздуха 1 bar

No of line in Figures 2–10 and 12	Electrode reaction	E, V (s. h. e.) or pH of the solution
1	2	3
a	$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g); P_{H_2(g)} = 5 \cdot 10^{-7} \text{ bar}$	$E = 0.186 - 0.0591 \cdot \text{pH}$
1	$\begin{cases} ScOH^{2+} (aq) + H^+ (aq) \rightleftharpoons Sc^{3+} (aq) + H_2O (l); \\ Sc_2(OH)_2^{4+} (aq) + 2H^+ (aq) \rightleftharpoons 2Sc^{3+} (aq) + 2H_2O (l) \end{cases}$	$\text{pH} = 4.266 + \lg \frac{a_{ScOH^{2+}}(aq)}{a_{Sc^{3+}}(aq)} = 2.934 + 0.5 \cdot \lg \frac{a_{Sc_2(OH)_2^{4+}}(aq)}{a_{Sc^{3+}}^2(aq)}$
2	$\begin{cases} Sc(OH)_2^+ (aq) + H^+ (aq) \rightleftharpoons ScOH^{3+} (aq) + H_2O (l); \\ 2Sc(OH)_2^+ (aq) + 2H^+ (aq) \rightleftharpoons Sc_2(OH)_2^{4+} (aq) + 2H_2O (l) \end{cases}$	$\text{pH} = 5.387 + \lg \frac{a_{Sc(OH)_2^+}(aq)}{a_{ScOH^{3+}}(aq)} = 6.719 + 0.5 \cdot \lg \frac{a_{Sc_2(OH)_2^{4+}}^2(aq)}{a_{Sc_2(OH)_2^{4+}}(aq)}$
3	$Sc(OH)_4^- (aq) + 2H^+ (aq) \rightleftharpoons Sc(OH)_2^+ (aq) + 2H_2O (l)$	$\text{pH} = 8.673 + 0.5 \cdot \lg \frac{a_{Sc(OH)_4^-}(aq)}{a_{Sc(OH)_2^+}(aq)}$
4	$Sc_2O_3 (s) + 6H^+ (aq) \rightleftharpoons 2Sc^{3+} (aq) + 3H_2O (l)$	$\text{pH} = 1.887 - \frac{1}{3} \cdot \lg a_{Sc^{3+}}(aq)$
5	$\begin{cases} Sc_2O_3 (s) + 4H^+ (aq) \rightleftharpoons 2ScOH^{2+} (aq) + H_2O (l); \\ Sc_2O_3 (s) + 4H^+ (aq) \rightleftharpoons Sc_2(OH)_2^{4+} (aq) + H_2O (l) \end{cases}$	$\text{pH} = 0.698 - 0.5 \cdot \lg a_{ScOH^{2+}}(aq) = 1.364 - 0.25 \cdot \lg a_{Sc_2(OH)_2^{4+}}(aq)$
6	$Sc_2O_3 (s) + H_2O (l) + 2H^+ (aq) \rightleftharpoons 2Sc(OH)_2^+ (aq)$	$\text{pH} = -3.991 - \lg a_{Sc(OH)_2^+}(aq)$
7	$2Sc(OH)_4^- (aq) + 2H^+ (aq) \rightleftharpoons Sc_2O_3 (s) + 5H_2O (l)$	$\text{pH} = 21.337 + \lg a_{Sc(OH)_4^-}(aq)$

End of table 2
 Окончание таблицы 2

1	2	3
8	$Sc^{3+} (aq) + 3e^- \rightleftharpoons Sc (hcp)$	$E = -2.025 + 0.0197 \cdot \lg a_{Sc^{3+}} (aq)$
9	$\left\{ \begin{array}{l} ScOH^{2+} (aq) + H^+ (aq) + 3e^- \rightleftharpoons Sc (hcp) + H_2O (l); \\ Sc_2(OH)_2^{4+} (aq) + 2H^+ (aq) + 6e^- \rightleftharpoons 2Sc (hcp) + 2H_2O (l) \end{array} \right.$	$E = -1.941 - 0.0197 \cdot pH + 0.0197 \cdot \lg a_{ScOH^{2+}} (aq) =$ $= -1.967 - 0.0197 \cdot pH + 0.0099 \cdot \lg a_{Sc_2(OH)_2^{4+}} (aq)$
10	$Sc(OH)_2^+ (aq) + 2H^+ (aq) + 3e^- \rightleftharpoons Sc (hcp) + 2H_2O (l)$	$E = -1.835 - 0.0394 \cdot pH + 0.0197 \cdot \lg a_{Sc(OH)_2^+} (aq)$
11	$Sc_2O_3 (s) + 6H^+ (aq) + 6e^- \rightleftharpoons 2Sc (hcp) + 3H_2O (l)$	$E = -1.914 - 0.0591 \cdot pH$
12	$Sc(OH)_4^- (aq) + 4H^+ (aq) + 3e^- \rightleftharpoons Sc (hcp) + 4H_2O (l)$	$E = -1.493 - 0.0788 \cdot pH + 0.0197 \cdot \lg a_{Sc(OH)_4^-} (aq)$
13	$Sc^{3+} (aq) + 2H^+ (aq) + 5e^- \rightleftharpoons ScH_2 (s)$	$E = -0.889 - 0.0236 \cdot pH + 0.0118 \cdot \lg a_{Sc^{3+}} (aq)$
14	$\left\{ \begin{array}{l} ScOH^{2+} (aq) + 3H^+ (aq) + 5e^- \rightleftharpoons ScH_2 (s) + H_2O (l); \\ Sc_2(OH)_2^{4+} (aq) + 6H^+ (aq) + 10e^- \rightleftharpoons 2ScH_2 (s) + 2H_2O (l) \end{array} \right.$	$E = -0.839 - 0.0355 \cdot pH + 0.0118 \cdot \lg a_{ScOH^{2+}} (aq) =$ $= -0.855 - 0.0355 \cdot pH + 0.0059 \cdot \lg a_{Sc_2(OH)_2^{4+}} (aq)$
15	$Sc(OH)_2^+ (aq) + 4H^+ (aq) + 5e^- \rightleftharpoons ScH_2 (s) + 2H_2O (l)$	$E = -0.775 - 0.0473 \cdot pH + 0.0118 \cdot \lg a_{Sc(OH)_2^+} (aq)$
16	$Sc_2O_3 (s) + 10H^+ (aq) + 10e^- \rightleftharpoons 2ScH_2 (s) + 3H_2O (l)$	$E = -0.822 - 0.0591 \cdot pH$
17	$Sc(OH)_4^- (aq) + 6H^+ (aq) + 5e^- \rightleftharpoons ScH_2 (s) + 4H_2O (l)$	$E = -0.570 - 0.0790 \cdot pH + 0.0118 \cdot \lg a_{Sc(OH)_4^-} (aq)$
18	$2Sc^{3+} (aq) + xH_2O (l) + (6-2x)e^- \rightleftharpoons Sc_2O_x (s) + 2xH^+ (aq);$ $2.89 \leq x < 3$	$E = \frac{-0.419 \cdot x^2 - 0.656 \cdot x + 6.076}{x-3} - \frac{0.0591 \cdot x}{x-3} \cdot pH - \frac{0.0591}{x-3} \cdot \lg a_{Sc^{3+}} (aq)$
19	$Sc_2O_x (s) + 2xH^+ (aq) + 2xe^- \rightleftharpoons 2Sc (hcp) + xH_2O (l); 2.89 \leq x < 3$	$E = -0.419 \cdot x - 0.656 - 0.0591 \cdot pH$
20	$2Sc(OH)_4^- (aq) + (8-2x)H^+ (aq) + (6-2x)e^- \rightleftharpoons Sc_2O_x (s) + (8-x)H_2O (l); 2.89 \leq x < 3$	$E = \frac{-0.419 \cdot x^2 - 0.656 \cdot x + 4.495}{x-3} - \frac{0.0591 \cdot (x-4)}{x-3} \cdot pH - \frac{0.0591}{x-3} \cdot \lg a_{Sc(OH)_4^-} (aq)$

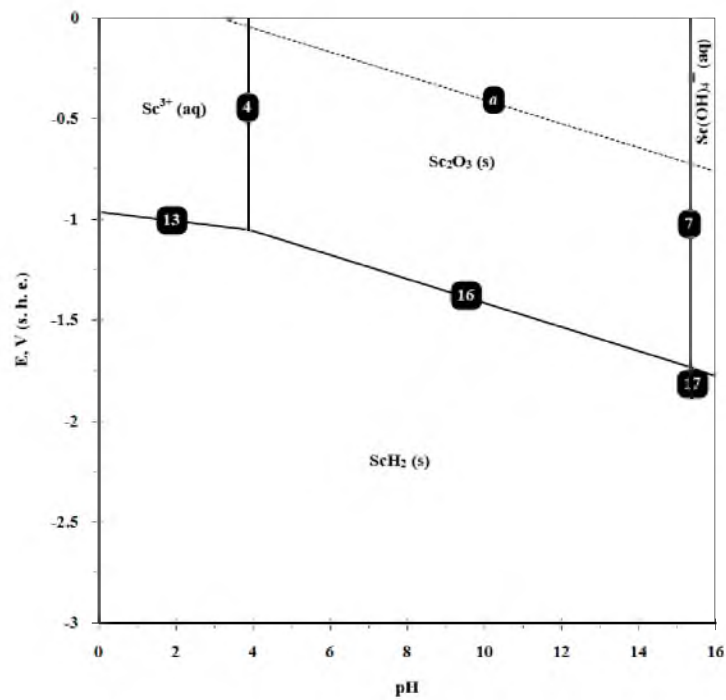


Fig. 7. The potential–*pH* diagram of *Sc–H₂O* system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-6}$ M with consideration of scandium hydride
Рис. 7. Диаграмма потенциал–*pH* системы *Sc–H₂O* при 298K, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-6}$ М с учётом гидрида скандия

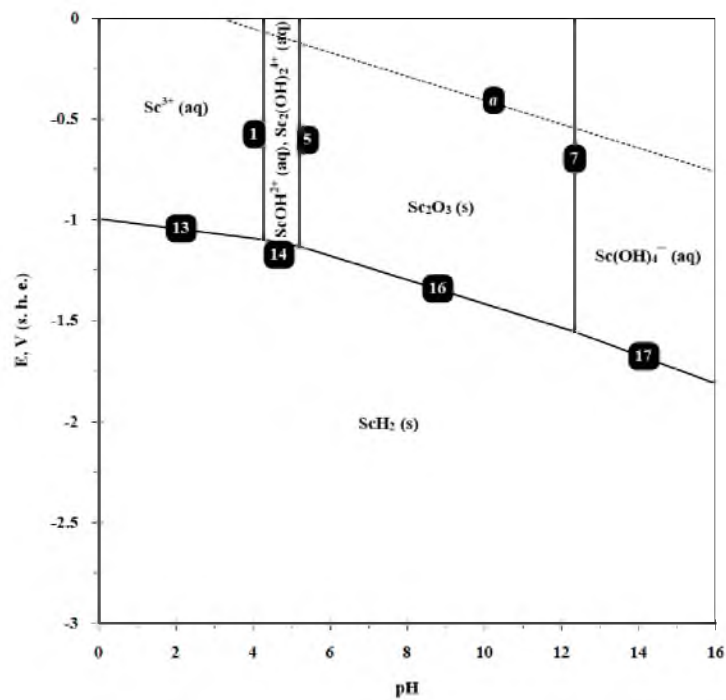


Fig. 8. The potential–*pH* diagram of *Sc–H₂O* system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-9}$ M with consideration of scandium hydride
Рис. 8. Диаграмма потенциал–*pH* системы *Sc–H₂O* при 298K, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-9}$ М с учётом гидрида скандия

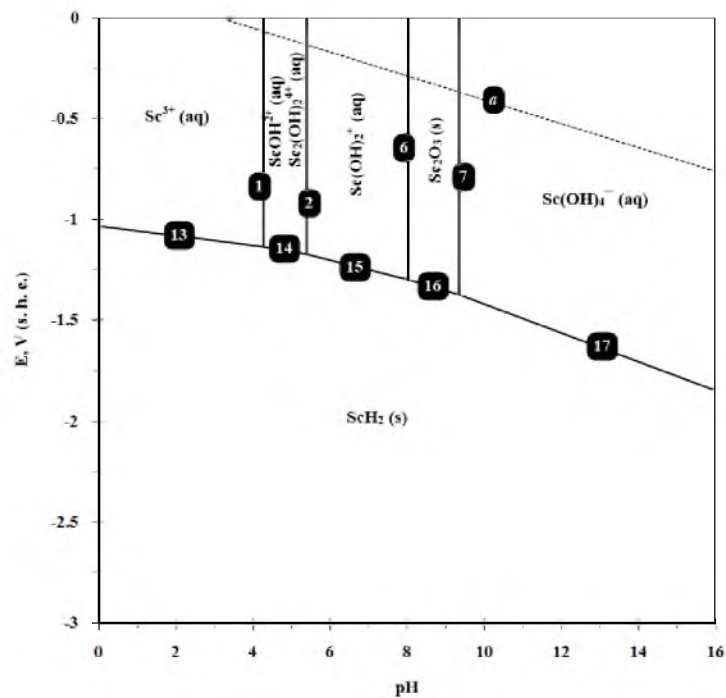


Fig. 9. The potential–*pH* diagram of *Sc–H₂O* system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-12}$ M with consideration of scandium hydride
Рис. 9. Диаграмма потенциал–*pH* системы *Sc–H₂O* при 298К, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-12}$ М с учётом гидрида скандия

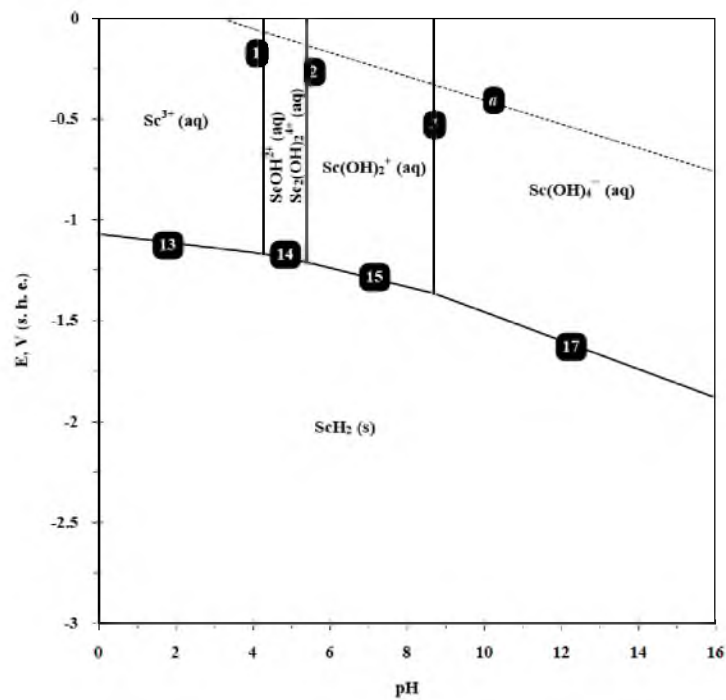


Fig. 10. The potential–*pH* diagram of *Sc–H₂O* system at 298K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-15}$ M with consideration of scandium hydride
Рис. 10. Диаграмма потенциал–*pH* системы *Sc–H₂O* при 298К, давлении воздуха 1 бар и активностях ионов в растворе $a_i=10^{-15}$ М с учётом гидрида скандия

6. The influence of non-stoichiometry of scandium sesquioxide

It was reported [Arkharov, Kichigina, 1966; Horowitz et al., 1975; Young Jr., Sienko, 1972] that scandium sesquioxide has a considerable degree of homogeneity Sc_2O_3 , $2.89 \leq x < 3$.

The standard Gibbs free energy of formation of Sc_2O_3 can be estimated according to the Gorichev's method [Gorichev, Klyushin, 1971] based on Waring – Lagrange interpolation polynomial [Meijering, 2002]. However, the implementation of this method requires reliable data on at least two different oxides of the same metal with different oxidation states. As only data on Sc_2O_3 (s) are available in literature, the standard Gibbs energy of formation of ScO (s) should be estimated.

V.A. Kireev proposed [1970] that an approximate relationship exists between the standard Gibbs energies of formation of similar compounds of transition metals and the atomic number of elements forming these compounds. Using this method, the standard Gibbs energy of formation of hypothetical scandium monoxide ScO (s) was estimated basing on the data on the standard Gibbs energies of formation of TlO (s), VO (s), MnO (s) and ZnO (s) taken from [Wagman et al., 1982]. The following relationship was found:

$$\frac{\Delta_f G_{298}^\circ (\text{MeO})}{Z_{\text{Me}}} = -233.4 \cdot Z_{\text{Me}}^2 + 13500 \cdot Z_{\text{Me}} - 205550 \text{ J} \cdot \text{m ol}^{-1}, \quad (9)$$

where $21 \leq Z_{\text{Me}} \leq 30$ is the atomic number of metal. The dependence is illustrated in Figure 11.

From this relationship the standard Gibbs energy of formation of ScO (s) was found to be equal to $\Delta_f G_{298}^\circ (\text{ScO}) \cong -525550 \text{ J} \cdot \text{m ol}^{-1}$. Using this value and that of Sc_2O_3 (s) from Table 1, the standard Gibbs energy of formation of non-stoichiometric scandium oxide was estimated by the following relationship:

$$\Delta_f G_{298}^\circ (\text{Sc}_2\text{O}_x) = -80900 \cdot x^2 - 363700 \cdot x, \text{ J} \cdot \text{m ol}^{-1}; \quad 2.89 \leq x < 3. \quad (10)$$

The hypothetical potential–*pH* diagram of $\text{Sc}-\text{H}_2\text{O}$ system at 298 K, air pressure of 1 bar and activities of ions in solutions $a_i=10^{-6}$ M taking into consideration the non-stoichiometry of scandium sesquioxide is presented in Figure 12. Thermodynamic prediction shows that the domain of thermodynamic stability of Sc_2O_3 decreases with decrease of *x*.

7. Conclusions

The dimerisation of the ion ScOH^{2+} (aq) was considered, and it was shown that the dimeric form predominates in concentrated solutions, whereas the monomeric form predominates in diluted media. The polynuclear ions $\text{Sc}_3(\text{OH})_4^{5+}$ (aq) and $\text{Sc}_3(\text{OH})_5^{4+}$ (aq) have no domains of thermodynamic stability.

The revised potential–*pH* diagrams of $\text{Sc}-\text{H}_2\text{O}$ system presented in this study, take into account the possible formation of various hydrolysed scandium species with alteration of the activities of ions in a solution. For the solutions with moderate content of scandium these diagrams are consistent with the previously published ones.

The corrosion properties of scandium are similar to that of aluminum; in most environments the passivation layer on the surface of metal consists of Sc_2O_3 (s). The possible formation of scandium hydride ScH_2 (s) shifts the borders of scandium active dissolution, but does not affect its properties in the domain of electrochemical stability of water. The scandium nitride ScN (s) is not thermodynamically stable in aqueous solutions in presence of pure scandium and scandium hydride.

An attempt to estimate the corrosion properties of non-stoichiometric scandium oxide Sc_2O_x ($2.89 \leq x < 3$) was performed. Using Kireev's method the standard Gibbs energy of formation of ScO (s) was estimated and then, using Gorichev's method the dependency of $\Delta_f G_{298}^\circ (\text{Sc}_2\text{O}_x)$ on *x* was also estimated. Thermodynamic prediction shows that with increase of the degree of homogeneity of Sc_2O_3 its domain of passivity in the potential–*pH* diagram narrows.



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