



Open Access : : ISSN 1847-9286

www.jESE-online.org*Original scientific paper*

Ruthenium redox equilibria

1. Thermodynamic stability of Ru(III) and Ru(IV) hydroxides

Igor Povar[✉], Oxana Spinu*Institute of Chemistry of the Academy of Sciences of Moldova, 3 Academiei str., MD 2028, Chisinau, Moldova*[✉]Corresponding Author: ipovar@yahoo.ca; Tel.: +373 22 73 97 36; Fax: +373 22 73 97 36

Received: September 30, 2015; Accepted: February 18, 2016

Abstract

On the basis of the selected thermodynamic data for Ru(III) and Ru(IV) compounds in addition to original thermodynamic and graphical approach used in this paper, the thermodynamic stability areas of sparingly soluble hydroxides as well as the repartition of their soluble and insoluble chemical species towards the solution pH and initial concentrations of ruthenium in heterogeneous mixture solid phase–saturated solution have been investigated. By means of the ΔG –pH diagrams, the areas of thermodynamic stability of Ru(III) and Ru(IV) hydroxides have been established for a number of analytical concentrations in heterogeneous mixtures. The diagrams of heterogeneous and homogeneous chemical equilibria have been used for graphical representation of complex equilibria in aqueous solutions containing Ru(III) and Ru(IV). The obtained results, based on the thermodynamic analysis and graphic design of the calculated data in the form of the diagrams of heterogeneous chemical equilibria, are in good agreement with the available experimental data.

Keywords

Heterogeneous chemical equilibria; Sparingly soluble hydroxides; Soluble and insoluble ruthenium chemical species; Thermodynamic analysis

Introduction

Chemistry of ruthenium is characterized by some specific properties, such as the existence of various valences from 0 to 8, the relatively easy formation of stable polynuclear compounds, occurrence of various disproportionation and comproportionation processes etc. Widespread application of ruthenium and its compounds in various practical purposes serves as an impulsion for the development of the ruthenium applied analytical chemistry. Currently, selective fast and

efficient methods for determination of ruthenium were developed [1-5]. The choice of the appropriate method requires knowledge of the forms of existence of ruthenium in solution and the composition of its complex compounds. Depending on the solution pH, metal ion concentrations in solution, presence of oxidants and reductants as well as their concentration, ruthenium can exist in the form of several complexes, each exhibiting its own catalytic and voltammetric activities [6,7]. Within research of the reduction – oxidation mechanism, it is necessary to know if some coexisting species are reduced simultaneously or, conversely, the process has a “stepwise” character and one species reduces gradually [8]. The knowledge of the forms of metal ion in solution facilitates the choice of optimal sorption and extraction conditions. Therefore, the use of suitable analytical methods and procedures of ruthenium research involves a priori knowledge of its forms of existence for the interpretation of mechanisms of predominant reactions of certain species for selecting a suitable procedure.

It is known that the assessment of solubility (S) based on the value of the solubility product can lead to large misinterpretation. This is explained by the fact that the precipitate (solid phase) components in solution are subjected to different reactions of hydrolysis, complex formation etc. Generally, these secondary processes contribute to increasing the precipitate solubility [9-15]. A particularly strong influence on the precipitate solubility (S) exercises the solution pH value. Determination of the dependence of S on pH requires extensive calculations, since this method involves solving systems of nonlinear equations for mass balance (MB). However, from the solubility diagrams one cannot draw conclusions on the thermodynamic stability of the solid phase when the precipitate solubility is relatively high. Authors [9-15] proposed a strict criterion for assessing the solid phase stability, based on the Gibbs energy change value of the precipitation - dissolution process of solid phases. In general, Gibbs energy variation calculations for these systems were examined in [9].

The paper presents a thermodynamic approach for the complex chemical equilibria investigation of two-phase systems containing Ru(III) and Ru(IV) hydroxides. This approach utilizes thermodynamic relationships combined with original mass balance constraints, where the solid phases are explicitly expressed. The factors influencing the distribution and concentrations of various soluble ruthenium species were taken into account. The new type of diagrams, based on thermodynamics, graphical and computerized methods, which quantitatively describe the distribution of soluble and insoluble, monomeric and polymeric ruthenium species in a large range of pH values was used.

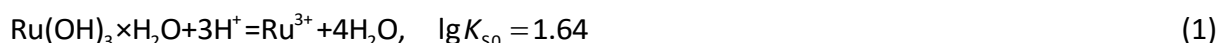
The developed thermodynamic approach is based on:

1. Analysis of thermodynamic stability areas for the solid phase;
2. Determination of the molar fractions of chemical species in heterogeneous systems precipitate-solution based on the MB equations of the method of residual concentrations (MRC).

Theory and calculations

Thermodynamic stability areas of sparingly soluble Ru(III) and Ru(IV) hydroxides

In the present paper the relations, obtained in [10], will be applied to determine the thermodynamic stability of hydroxides Ru(III) and Ru(IV) under real conditions, different from standard ones. We will expose the quintessence of this method on the example of the equilibrium of Ru(III) hydroxide with aqueous solution:



where K_5 is the equilibrium constant of reaction (1).

The variation of the Gibbs energy of reaction (1) under standard conditions is equal to

$$\Delta G_r^0 = \Delta G_f^0(\text{Ru}^{3+}) + 4\Delta G_f^0(\text{H}_2\text{O}) - \Delta G_f^0(\text{Ru(OH)}_3 \times \text{H}_2\text{O}(\text{s})) = -RT \ln K_5 \quad (2)$$

where $\Delta G_f^0(i)$ is standard Gibbs energy of formation of species i . The selected values for $\Delta G_f^0(i)$ [16] are shown in Table 1.

Table 1. The values of standard Gibbs energy of formation of ruthenium chemical species at 298.15 K

Chemical species	$\Delta G_f^0(i) / \text{kJ mol}^{-1}$	Chemical species	$\Delta G_f^0(i) / \text{kJ mol}^{-1}$
$\text{H}_2\text{RuO}_5(\text{aq})$	-391.2	$\text{HRu}_4(\text{OH})_{12}^{4+}(\text{aq})$	-1877
$\text{HRuO}_5^-(\text{aq})$	-325.4	$\text{Ru}^{3+}(\text{aq})$	173.4
$\text{RuO}_4^-(\text{aq})$	-250.1	$\text{Ru(OH)}^{2+}(\text{aq})$	-51.0
$\text{RuO}_4^{2-}(\text{aq})$	-306.6	$\text{Ru(OH)}_2^+(\text{aq})$	-280.9
$\text{RuO}_2 \times 2\text{H}_2\text{O}(\text{am})$	-691.0	$\text{Ru}_4(\text{OH})_4^{8+}(\text{aq})$	-193.5
$\text{Ru(OH)}_3 \times \text{H}_2\text{O}(\text{am})$	-766.0	$\text{Ru}^{2+}(\text{aq})$	150.3
$\text{Ru}_2\text{O}_5(\text{aq})$	-445	$\text{H}_2\text{O}(\text{aq})$	-237.19
$\text{Ru(OH)}_2^{2+}(\text{am})$	-221.8	$\text{OH}^-(\text{aq})$	-157.33

But the ΔG_r^0 value cannot serve as a characteristic of thermodynamic stability of Ru(III) hydroxide under real conditions. In this case, the equilibrium is described by the equation of isothermal reaction that for the scheme (1) takes the form:

$$\Delta G_r(s) = \Delta G_r^0(s) + RT \ln(C_{\text{Ru}}^0 / [\text{H}^+]^3) \quad (3)$$

where C_{Ru}^0 denotes the concentration of ruthenium in heterogeneous mixture. It is easy to see that the Gibbs energy change of reaction (1) depends strongly on the pH value. At the same time the equation (3) can also be applied for the determination of thermodynamic stability of the ruthenium(III) hydroxide as the Ru^{3+} ion, depending on the pH and the initial concentration of the ruthenium, C_{Ru}^0 , is subjected to complex chemical transformations in solution:

- $\text{Ru}^{3+} + \text{H}_2\text{O} = \text{Ru(OH)}^{2+} + \text{H}^+, \quad \lg K_{10} = -2.24$
- $\text{Ru}^{3+} + 2\text{H}_2\text{O} = \text{Ru(OH)}_2^+ + 2\text{H}^+, \quad \lg K_{20} = -3.52$
- $4\text{Ru}^{3+} + 4\text{H}_2\text{O} = \text{Ru}_4(\text{OH})_4^{8+} + 4\text{H}^+, \quad \lg K_{44} = -10.80$

(The hydrolysis constants were calculated from ΔG_r^0 values using the equation $\Delta G_{ij}^0 = -RT \ln K_{ij}$).

Obviously, the ΔG calculation requires accounting for all equilibria (4). A rigorous thermodynamic analysis shows that the change in Gibbs energy of reaction (1) in real conditions is described by the equation [13]:

$$\Delta G_r(s) = \Delta G_r^0 - RT \ln \alpha_{\text{Ru}} + RT \ln(C_{\text{Ru}}^0 / [\text{H}^+]^3). \quad (5)$$

Here α_i represents the hydrolysis coefficient of reactions (4) [13], defined as:

$$\alpha_{Ru} = 1 + K_{10} [H^+]^{-1} + K_{20} [H^+]^{-2} + 4K_{44} [Ru^{3+}] [H^+]^{-3} \tag{6}$$

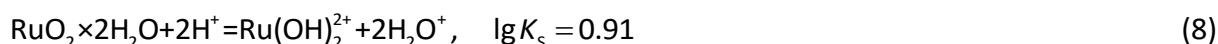
In relation (6) $[Ru^{3+}]$ is the equilibrium concentration of the ruthenium(III) ion, which is calculated for the fixed values of pH and C_{Ru}^0 from the MB equation:

$$\begin{aligned} C_{Ru}^0 &= [Ru^{3+}] + [R(OH)^{2+}] + [Ru(OH)_2^+] + 4[Ru_4(OH)_{12}^{4+}] = \\ &= [Ru^{3+}] + K_{10} [Ru^{3+}] [H^+]^{-1} + K_{20} [Ru^{3+}] [H^+]^{-2} + 4K_{44} [Ru^{3+}]^4 [H^+]^{-4} = [Ru^{3+}] \times \alpha_{Ru} \end{aligned} \tag{7}$$

The changes in equation (7) are made by using the consequence of mass action law:

$$[Ru_i(OH)_j] = K_{ij} [Ru^{3+}]^i [H^+]^{-j}$$

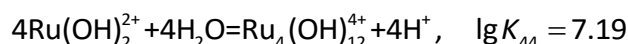
In the case of ruthenium(IV) hydroxide similar relationships are obtained. We present here only the basic equations:



$$\Delta G_r (s) = \Delta G_r^0 + RT \ln(C_{Ru}^0 / [H^+]^2) - RT \ln \alpha_{Ru} \tag{9}$$

$$\Delta G_r^0 = -RT \ln K_s$$

where α_{Ru} is coefficient of hydrolysis reactions of $Ru(OH)_2^{2+}$:



calculated by the equation:

$$\alpha_{Ru} = 1 + 4K_{44} [Ru(OH)_2^{2+}]^4 [H^+]^{-4} \tag{10}$$

The equilibrium concentration of $Ru(OH)_2^{2+}$ ion is determined for respective values of pH and C_{Ru}^0 from MB conditions:

$$C_{Ru}^0 = [Ru(OH)_2^{2+}] + 4[Ru_4(OH)_{12}^{4+}] = [Ru(OH)_2^{2+}] (1 + 4K_{44} [Ru(OH)_2^{2+}]^3 [H^+]^{-4}) = [Ru(OH)_2^{2+}] \alpha_{Ru}$$

Within this method, when $\Delta G_r < 0$ the solid phase is thermodynamically unstable towards dissolution according the schemes (1) and (8) and, vice-versa, for the values $\Delta G_r > 0$ the formation of solid phase takes place. Results of calculation of the ΔG_r dependence on pH for $C_{Ru}^0 = 10^{-6}$ and 10^{-4} mol L⁻¹ for both the hydroxides are presented graphically in Figs. 1 and 2. From these graphs it is observed that in acidic solutions Ru(III) and Ru(IV) hydroxides are thermodynamically unstable in regard to dissolution. From the $\Delta G_r(pH)_{C_{Ru}^0}$, diagrams the pH of beginning of precipitation (pH₀) corresponds to the condition $\Delta G_r = 0$.

In the case of ruthenium(III) hydroxide, $Ru(OH)_3 \cdot H_2O_{(s)}$, one obtains for $C_{Ru}^0 = 10^{-4}$ mol L⁻¹, pH 2.24 and for $C_{Ru}^0 = 10^{-6}$ mol L⁻¹, pH 4.42 (Table 2). Therefore, by increasing C_{Ru}^0 in mixtures, the pH₀ value shifts to region of acidic solutions.

For ruthenium(IV) hydroxide, $RuO_2 \cdot H_2O_{(s)}$, from the $\Delta G_r(pH)$ diagram one can see that pH₀ is 3.93 for $C_{Ru}^0 = 10^{-4}$ mol L⁻¹, pH₀ is 3.93 for $C_{Ru}^0 = 10^{-6}$ mol L⁻¹ (see also Table 2).

Table 2. Areas of thermodynamic stability of solid phases, $\Delta G_r > 0$ of the Ru(III) and Ru(IV) hydroxides in the system $\text{Ru}^{n+}\text{-H}_2\text{O}$

The precipitate composition	Area of thermodynamic stability of solid phase	
	$C_{\text{Ru}}^0 = 10^{-4} \text{ mol L}^{-1}$	$C_{\text{Ru}}^0 = 10^{-6} \text{ mol L}^{-1}$
$\text{Ru}(\text{OH})_3 \cdot \text{H}_2\text{O} (\text{s})$	$2.42 < \text{pH} < 14.0$	$4.42 < \text{pH} < 14.0$
$\text{RuO}_2 \cdot \text{H}_2\text{O} (\text{s})$	$3.93 < \text{pH} < 14.0$	$4.43 < \text{pH} < 14.0$

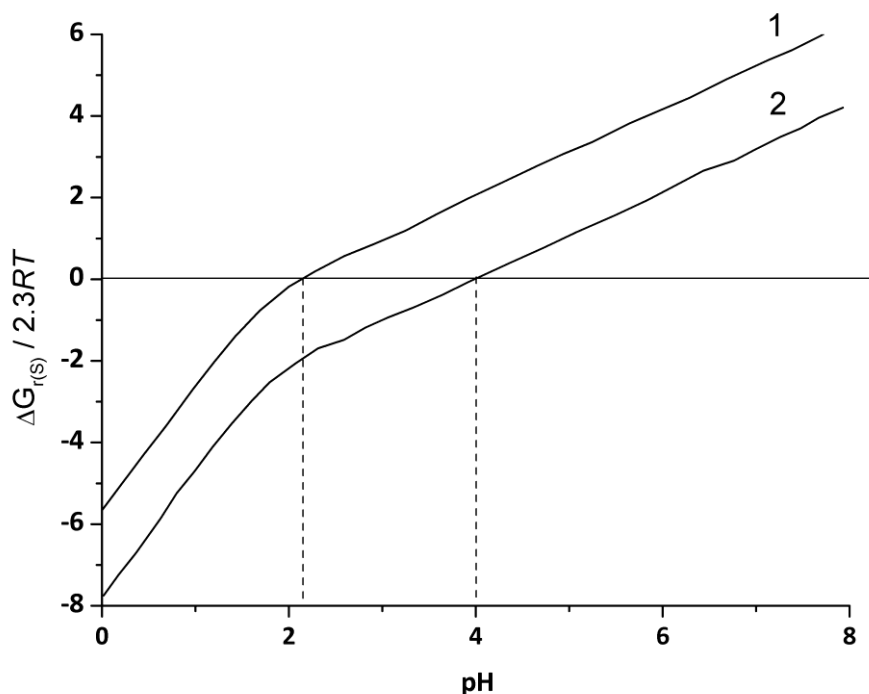


Figure 1. The dependence of the Gibbs energy change on solution pH for the precipitation-dissolution process of Ru(III) hydroxide. C_{Ru}^0 : 1 - $10^{-4} \text{ mol L}^{-1}$; 2 - $10^{-6} \text{ mol L}^{-1}$

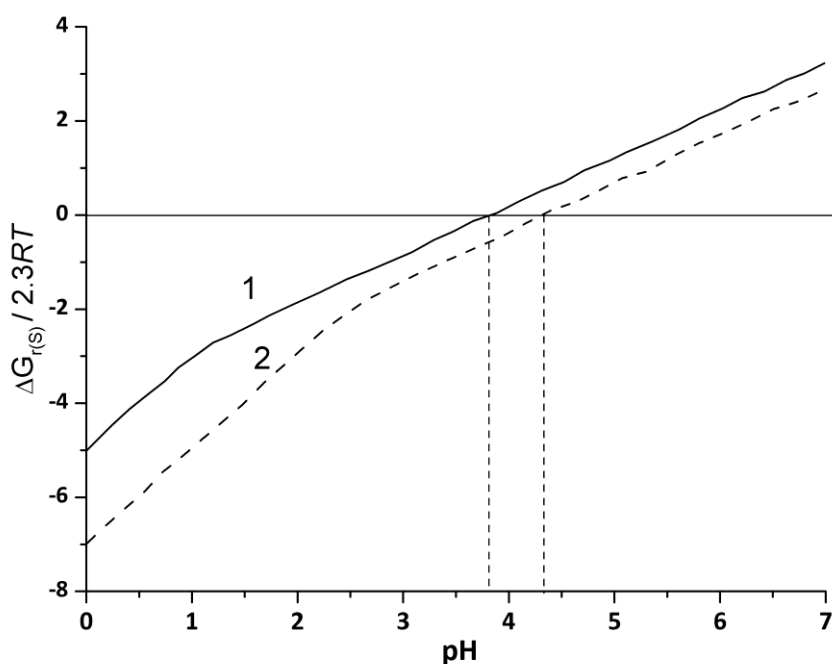


Figure 2. The curves $\Delta G_{r(s)}(\text{pH})$ of the dissolution-precipitation process of Ru(IV) hydroxide, C_{Ru}^0 : 1 - $10^{-4} \text{ mol L}^{-1}$; 2 - $10^{-6} \text{ mol L}^{-1}$

Repertition of Ru(III) and Ru(IV) soluble and insoluble chemical species towards the solution pH and initial concentrations of ruthenium in heterogeneous mixture solid phase–saturated solution

In formulating MB conditions for the precipitate components in heterogeneous mixture we have taken into consideration the quantity of each component in the solid and liquid phases (residual quantity). Knowing the residual concentration of i -th ion (C_i^r) in solution, its quantity in precipitate in a unit volume is easily calculated as the difference between the analytical concentration in the mixture (C_i^0) and that in solution. Therefore, in terms of molar concentrations,

$$\Delta C_i = C_i^0 - C_i^r$$

where ΔC_i denotes the quantity of i ion in precipitate (moles) in 1 L of solution. If this quantity is recalculated related to the mixture volume (V_{am}), then

$$\Delta m_i = m_i^0 - m_i^r$$

where Δm_i , m_i^0 and m_i^r denote the quantity of ion (in moles) in precipitate, in mixture and in volume of liquid phase, respectively. For several systems it was established [17], that this approximation can be applied for solutions up to 0.5 mol L⁻¹.

Initially, a set of possible reactions [18] in the system Ru(IV)–H₂O is taken into account:



The MB equation for Ru(IV) is written as:

$$C_{\text{Ru}}^0 = \Delta C_{\text{Ru}} + C_{\text{Ru}}^r = \Delta C_{\text{Ru}} + [\text{Ru}(\text{OH})_2^{2+}] + 4[\text{Ru}_4(\text{OH})_{12}^{4+}] \quad (13)$$

Taking into consideration equation (12), the expression for C_{Ru}^r has the form:

$$C_{\text{Ru}}^r = [\text{Ru}(\text{OH})_2^{2+}] + 4K_{4,4} [\text{Ru}_4(\text{OH})_{12}^{4+}]^4 [\text{H}^+]^{-4} = [\text{Ru}(\text{OH})_2^{2+}] \alpha_{\text{Ru}}$$

Here α_i is the coefficient of hydrolysis reactions for ruthenium:

$$\alpha_{\text{Ru}} = 1 + 4K_{4,4} [\text{Ru}(\text{OH})_2^{2+}]^4 [\text{H}^+]^{-4}$$

From equation (11) it follows

$$[\text{Ru}(\text{OH})_2^{2+}] = K_s [\text{H}^+]^2$$

Substituting this expression in (13), one gets:

$$C_{\text{Ru}}^0 = \Delta C_{\text{Ru}} + K_s [\text{H}^+]^2 + 4K_{4,4} K_s^4 [\text{H}^+]^{-4} \quad (14)$$

Results and discussion

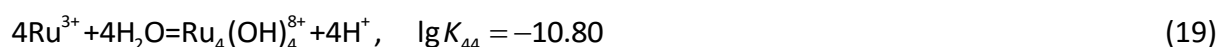
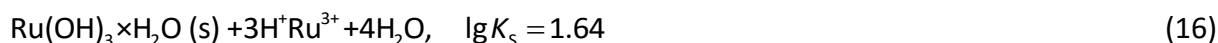
From obtained relations, ΔC_{Ru} for the set of values (C_{Ru}^0 , $[\text{H}^+] = 10^{-\text{pH}}$), can be easily determined. Further, the concentrations of the chemical species in solution are calculated. Then the molar fractions of chemical species in solution are computed. Finally, the molar fractions of chemical species in heterogeneous mixture, in function of pH for constant values of C_{Ru}^0 are determined, using the equations:

$$\gamma_s = \Delta C_{\text{Ru}} / C_{\text{Ru}}^0; \quad \gamma_{10} = [\text{Ru}(\text{OH})_2^{2+}] / C_{\text{Ru}}^0; \quad \gamma_{44} = 4[\text{Ru}_4(\text{OH})_{12}^{4+}] / C_{\text{Ru}}^0; \quad \gamma_{\text{sum}} = \gamma_{10} + \gamma_{44} \quad (15)$$

The subscript index (sum) symbolizes the sum of the all soluble species fractions containing Ru(IV). It is easily to observe that $\gamma_{\text{sum}} + \gamma_{\text{s}} = 1$.

The molar fraction of the metal ion from precipitate is defined also as the degree of precipitation [12,13]. For heterogeneous equilibria, the molar fractions of chemical species depend on the mixture initial composition, in this case of C_{Ru}^0 , even in the absence of polynuclear complexes, thus $\gamma_i = f(C_{\text{Ru}}^0, \text{pH})$. Consequently, the diagrams of repartition in heterogeneous systems (DRHS) can be plotted in coordinates $(\gamma_i, \text{pH})_{C_{\text{Ru}}^0 = \text{const}}$ or $(\gamma_i, C_{\text{Ru}}^0)_{\text{pH} = \text{const}}$. It should be mentioned that the relationships derived above is valid only within the thermodynamic stability area of the precipitate ($\Delta G_r < 0$) [9].

Analogically, DRHS are calculated for the system Ru(III)–H₂O, where the following equilibria are possible [11]:



Here, the particular equilibrium constants represent:

$$K_5^0 = [\text{Ru}^{3+}][\text{H}^+]^{-3} \quad (20)$$

$$K_{10} = [\text{Ru(OH)}^{2+}][\text{H}^+] / [\text{Ru}^{3+}] \quad (21)$$

$$K_{20} = [\text{Ru(OH)}_2^+][\text{H}^+]^2 / [\text{Ru}^{3+}] \quad (22)$$

$$K_{44} = [\text{Ru}_4(\text{OH})_4^{8+}][\text{H}^+]^4 / [\text{Ru}^{3+}]^4 \quad (23)$$

The MB equations for this system are following:

$$C_{\text{Ru}}^0 = \Delta C_{\text{Ru}} + C_{\text{Ru}}^r \quad (24)$$

$$\begin{aligned} C_{\text{Ru}}^r &= [\text{Ru}^{3+}] + [\text{Ru(OH)}^{2+}] + [\text{Ru(OH)}_2^+] + 4[\text{Ru}_4(\text{OH})_4^{8+}] = \\ &= [\text{Ru}^{3+}](1 + K_{10}[\text{H}^+]^{-1} + K_{20}[\text{H}^+]^{-2} + 4K_{44}[\text{Ru}^{3+}]^3[\text{H}^+]^{-4}) \end{aligned} \quad (25)$$

The equilibrium concentration of Ru³⁺ ion is calculated using the relation:

$$[\text{Ru}^{3+}] = K_5[\text{H}^+]^3 \quad (26)$$

From equations (24) and (25) one obtains the expression for calculating ΔC_{Ru} , then the equilibrium concentrations of the free Ru(III) ion and its hydroxocomplexes are determined. Finally, on the diagram of repartition the $\gamma_{ij}(\text{pH})$ functions are plotted for fixed C_{Ru}^0 values:

$$\gamma_{50} = \Delta C_{\text{Ru}} / C_{\text{Ru}}^0; \quad \gamma_{00} = [\text{Ru}^{3+}] / C_{\text{Ru}}^0; \quad \gamma_{10} = [\text{Ru(OH)}^{2+}] / C_{\text{Ru}}^0$$

$$\gamma_{20} = [\text{Ru(OH)}_2^+] / C_{\text{Ru}}^0; \quad \gamma_{44} = 4[\text{Ru}_4(\text{OH})_4^{8+}] / C_{\text{Ru}}^0$$

$$\gamma_{\text{sum}} = \gamma_{00} + \gamma_{10} + \gamma_{20} + \gamma_{44}$$

Therefore, the procedure of DRHS construction includes several stages:

1. The determination of the thermodynamic stability of solid phases ($\Delta C_{Ru} > 0$) in function of solution pH or C_{Ru}^0 .
2. Calculation of the molar fractions of all species γ_i in the solid phase and solution within the pH (or C_{Ru}^0) range, established at the first stage.
3. For the image integrity, outside this range, in the case of homogeneous solution, the molar fractions of chemical species are calculated by typical equations for plotting the diagrams of distribution in solutions. Usually, in the $\gamma_i(\text{pH})$ diagrams the pH values vary between 0 and 14.

By the developed diagrams, the precipitate quantity (in moles or grams), in 1 L of solution for certain pH and C_{Ru}^0 values, is easily determined. For example, from Fig. 3(b) it results that for pH 3.95 and $C_{Ru}^0 = 10^{-4} \text{ mol L}^{-1}$ the degree of precipitation $\gamma_{S0} = 0.5$, whence it follows that $\Delta C_{Ru} = \gamma_{S0} C_{Ru}^0 = 5 \cdot 10^{-5} \text{ mol L}^{-1}$ or quantity of precipitate P (in g L^{-1}) $P_{RuM}(\text{RuO}_2 \cdot 2\text{H}_2\text{O}) = 5 \cdot 10^{-5} \text{ mol L}^{-1} \cdot 169 \text{ g mol}^{-1} = 8.45 \cdot 10^{-3} \text{ g L}^{-1}$. Thus, under these conditions in one liter of solution 8.45 mg of ruthenium(IV) hydroxide is deposited.

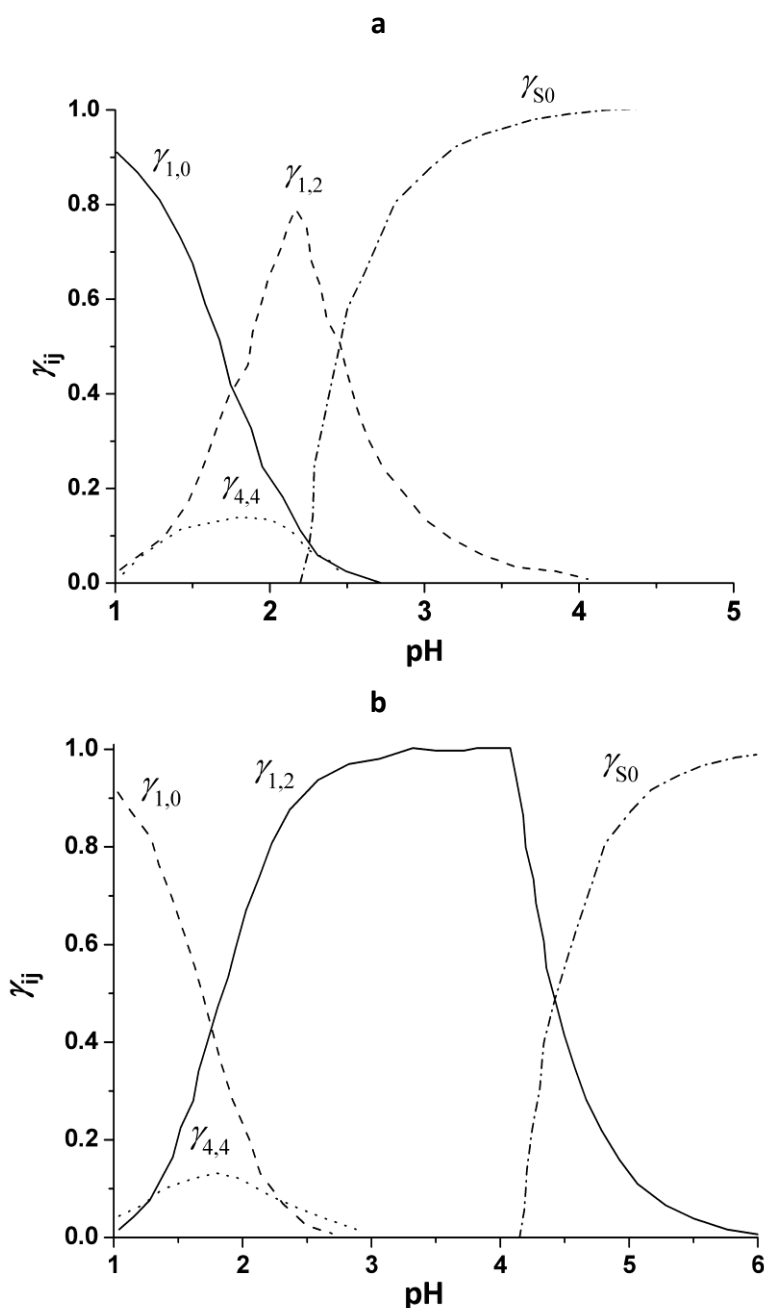


Figure 3. Repartition for the system $\text{Ru}(\text{OH})_{3(s)} \cdot \text{H}_2\text{O}$ – saturated aqueous solution, C_{Ru}^0 : a) 10^{-4} ; b) $10^{-6} \text{ mol L}^{-1}$

In Fig. 3 (a,b) and 4 (a,b) there are shown DRHS for both systems for two values of C_{Ru}^0 : 10^{-4} and 10^{-6} mol L $^{-1}$. From these diagrams, the pH regions of predominance of different Ru(III) and Ru(IV) species are depicted in Table 3.

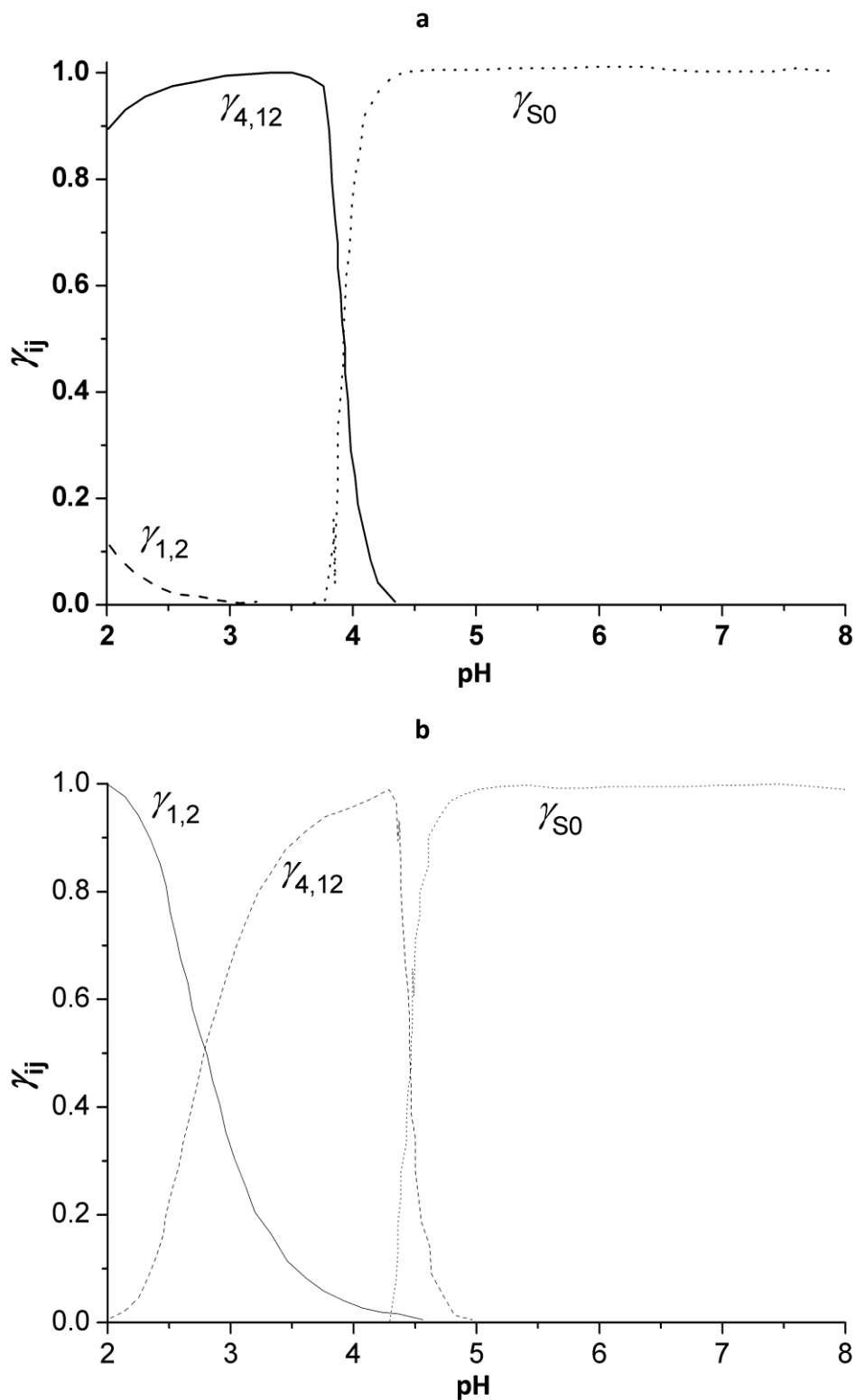


Figure 4. Repartition for the system $RuO_2 \cdot 2H_2O(s) - H_2O$; C_{Ru}^0 : **a)** 10^{-4} , **b)** 10^{-6} mol L $^{-1}$

Table 3. pH regions of predominance of chemical species in **A** - $Ru(OH)_{3(s)} \cdot H_2O - H_2O$ and **B** - $RuO_2 \cdot 2H_2O_{(s)} - H_2O$ system

System	Chemical species	pH regions of predominance	
		$C_{Ru}^0 = 10^{-4} \text{ mol L}^{-1}$	$C_{Ru}^0 = 10^{-6} \text{ mol L}^{-1}$
A	Ru^{3+}	$0.00 < \text{pH} < 1.76$	$0.00 < \text{pH} < 1.76$
	$Ru(OH)_2^+$	$1.76 < \text{pH} < 2.42$	$1.76 < \text{pH} < 4.42$
	$Ru(OH)_3 \cdot H_2O (s)$	$2.42 < \text{pH} < 14.0$	$4.42 < \text{pH} < 14.0$
B	$Ru(OH)_2^{2+}$	$0.00 < \text{pH} < 1.05$	$0.00 < \text{pH} < 2.55$
	$Ru_4(OH)_{12}^{4+}$	$1.05 < \text{pH} < 3.93$	$2.55 < \text{pH} < 4.43$
	$RuO_2 \cdot H_2O (s)$	$3.93 < \text{pH} < 14.0$	$4.43 < \text{pH} < 14.0$

Conclusions

From the obtained results the following conclusions can be drawn:

1. By means of the diagrams ΔG -pH, the areas of thermodynamic stability of Ru(III) and Ru(IV) hydroxides have been established for a number of analytical concentrations in heterogeneous mixtures. The diagrams of heterogeneous and homogeneous chemical equilibria have been used for graphical representation of complex equilibria in aqueous solutions containing Ru(III) and Ru(IV).
2. The ruthenium (III) polynuclear hydroxocomplex $Ru_4(OH)_4^{8+}$ (aq) for the considered values is not formed.
3. At increasing C_{Ru}^0 from 10^{-6} to $10^{-4} \text{ mol L}^{-1}$, the region of predominance of the ruthenium(IV) polynuclear complex $Ru_4(OH)_{12}^{4+}$ shifts to the acidic solutions and is increased by one pH unit.
4. The ruthenium(III) monohydroxide $Ru(OH)_2^+$ is formed in insignificant amounts under analyzed conditions.
5. The thermodynamic stability area of solid phases increases with growing the initial concentration of ruthenium in mixture.

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