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Ruthenium redox equilibria

3. Pourbaix diagrams for the systems Ru-H₂O and Ru-Cl⁻-H₂O

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Abstract

On the basis of selected thermodynamic data, the standard electrode potentials of possible half reactions in the Ru-H₂O and Ru-Cl⁻-H₂O systems have been calculated. Using the thermodynamic approach developed by the authors, the potential - pH and potential - pCl diagrams for the considered system have been built.

Keywords

Potential - pH diagram; Standard electrode potential; Soluble and insoluble ruthenium species.

Introduction

Thermodynamic analysis is a valuable and powerful tool in predicting, comprehending, and rationalizing the stability relations in redox reaction systems. In order to create an integrated picture of the thermodynamic properties of compounds of the element in its different valence states in both aqueous and solid phases, the diagrams potential - pH (or so-called Pourbaix diagrams) are generally used [1-16]. Pourbaix diagram is very important in predicting the thermodynamic equilibrium phases of an aqueous electrochemical system. These diagrams allow the graphical presentation of the thermodynamic properties of compounds of the given element based on the solution pH and the overall metal ion concentration in solution. The diagrams $E(\text{pH})$ are compact and contain a large quantity of information, which led to their wide application in various fields of science and technology, particularly in electrochemistry [1-9], hydrometallurgy [10-13] analytical chemistry [14,15], etc. In the presence of a small number of species in the redox system the construction of such diagrams does not present difficulties. The increase in the number of components and, in particular, the appearance of poly-nuclear species, calculating chemical and electrochemical equilibria becomes laborious. Authors [16] proposed an original procedure of

calculation. Firstly, on the basis of the tabulated thermodynamic data, the thermodynamic stability areas of chemical species, depending on the solution pH for each valence state (degree of oxidation), are determined [17,18]. These areas are demarcated on diagrams by vertical lines. Then, a system of independent electrochemical equations for electrode reactions between chemical species with varying degrees of oxidation, the predominance areas of which overlap, are drawn up. The electrode potentials of these reactions are linear functions of pH, which are depicted on diagrams.

The potential - pH (*Pourbaix*) diagram constitutes an effective method of graphical representation of chemical and electrochemical equilibria, especially for systems under protolytic processes and contains as valence states oxides and hydroxides in the solid phase, protonated particles or hydroxo-complexes in solution. In addition to the "metal-water" system of a complexing agent that forms stable complexes with metal ions, the electrode potential often depends decisively on the ligand concentration C_L^0 in solution. In this case, the Pourbaix diagrams are less informative because of a large number of lines as C_L^0 functions and then the more useful are diagrams representing the dependence of the potential on C_L^0 or $\log C_L^0$. The ligand usually is taken in large excess relative to the metal ion ($C_L^0 \gg C_M^0$) and therefore C_L^0 . In particular, the influence of a number of such factors, as the medium acidity, the complexation and precipitation processes of the redox species is necessary to examine. This article has done some work in order to extend the usefulness of the Frost diagram. Since some equilibria are also some functions of the metal ion concentration C_L^0 and the solution pH, for the construction of the diagram $E(\log [L])$ the conditions $C_L^0 = \text{const}$ and $\text{pH} = \text{const}$ are assumed. In this paper, the following procedure of calculating E -pH diagram is proposed:

1. Firstly, the predominance areas of different valence forms in function of pH, $\log C_M^0$ or $\log C_L^0$ are calculated;
2. On the basis of the diagrams $\Delta G_r(n)$ [17-18], the thermodynamic stability of different valence forms toward disproportionation conditions is determined;
3. The system of electrochemical equations for electrode reactions between chemical species in different valence states, the predominance areas of which overlap, is composed;

Based on standard thermodynamic data of participating species in specific reactions, the electrode potential is calculated by the equation $E^0 \Delta G_r^0 / nF$, where ΔG_r^0 is the value of the standard Gibbs energy of electrode reaction;

The electrode potentials of these processes are calculated as a function of C_L^0 , respecting the conditions $C_M^0 = \text{const}$ and $\text{pH} = \text{const}$. The first two steps have been carried out in [17].

Theoretical considerations

The Pourbaix diagram for the Ru-H₂O system is presented in [1], but it suffers from a number of drawbacks:

- a. It is carried out on the basis of outdated thermodynamic data and their interpretation may lead to erroneous conclusions;
- b. The formation of solid phases is not taken into account;
- c. It is calculated for on metal ion concentration only.

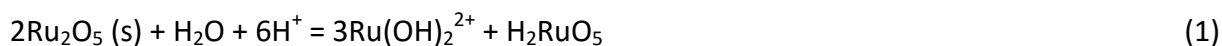
This paper aims to remove such deficiencies and calculating diagrams E -pH [16] on the basis of selected thermodynamic data [19]. In [18] it was shown that for ruthenium the disproportionation reactions are characteristic, in particular for the Ru(II), Ru(VI) and Ru(VII). In this paper the Frost diagrams are designed as a preliminary step for building E -pH diagrams.

We will examine in detail the calculation of the E -pH diagram for $C_{\text{Ru}}^0 = 10^{-4}$ mol/L. In the range $0 < \text{pH} < 14$ ruthenium for the degree of oxidations Ru(II), Ru(V), Ru(VI) and Ru(VII) is represented

by single species, Ru^{2+} , Ru_2O_5 (s), RuO_4^{2-} , RuO_4^- correspondingly, while for the valence states Ru(III), Ru(IV) and Ru(VIII), the hydrolysis is characteristic with formation of hydroxocomplexes. Ru(II) and Ru(IV), within a wide range of pH and C_{Ru}^0 , form also poorly soluble hydroxides. Authors [17,18] determined the thermodynamic stability areas of the following species for consecutive degrees of oxidation:

Ru(VIII)	H_2RuO_5	$0.00 < \text{pH} < 11.53$
	$\text{HRu}(\text{OH})_5^-$	$11.53 < \text{pH} < 14.00$
Ru(IV)	$\text{Ru}(\text{OH})_2^{2+}$	$0.00 < \text{pH} < 2.55$
	$\text{Ru}_4(\text{OH})_{12}^{4+}$	$2.55 < \text{pH} < 4.43$
	$\text{RuO}_2 \cdot \text{H}_2\text{O}$ (s)	$4.43 < \text{pH} < 14.00$
Ru(III)	Ru^{3+}	$0.00 < \text{pH} < 1.76$
	$\text{Ru}(\text{OH})_2^+$	$1.76 < \text{pH} < 4.42$
	$\text{Ru}(\text{OH})_3$ (s)· H_2O	$4.42 < \text{pH} < 14.00$

We will examine the calculation of respective values pH_D for $C_{\text{Ru}}^0 = 10^{-6}$ mol/L. From the $\Delta G_r(n)$ diagram it follows that the reaction of disproportionation of Ru(V) to Ru(VIII) and Ru(IV) occurs between the pH values 1 and 3. This process is described by the equation:



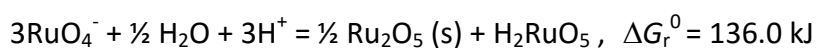
The standard Gibbs energy variation ΔG_r^0 is equal to

$$\Delta G_r^0 = \Delta G_f^0(\text{H}_2\text{RuO}_5) + 3\Delta G_f^0(\text{Ru}(\text{OH})_2^{2+}) - 2\Delta G_f^0(\text{Ru}_2\text{O}_5 \text{ (s)}) \quad \Delta G_f^0(\text{H}_2\text{O}) = 70.59 \text{ kJ}$$

For reaction (1) the isotherm equation takes the form

$$\Delta G_r = \Delta G_r^0 - 6RT \ln[\text{H}^+] + 4RT \ln C_{\text{Ru}}^0$$

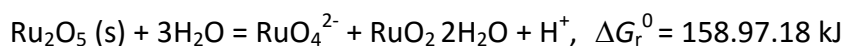
The pH_D value corresponds to the beginning of disproportionation, provided by the condition $\Delta G_r = 0$. Wherein, $\text{pH}(\Delta G_r = 0) = 1.94$ (the point A on the diagram E -pH). In the same way, we determine pH_D for the following redox couples:



$$\Delta G_r = \Delta G_r^0 + 3RT \ln[\text{H}^+] + RT \ln C_{\text{Ru}}^0, \quad \text{pH}_D(\Delta G_r=0) = 5.94 \text{ (point B)}$$



$$\Delta G_r = \Delta G_r^0 + 3RT \ln[\text{H}^+] + RT \ln C_{\text{Ru}}^0, \quad \text{pH}_D(\Delta G_r=0) = 10.57 \text{ (point C)}$$



$$\Delta G_r = \Delta G_r^0 + 2RT \ln[\text{H}^+] + RT \ln C_{\text{Ru}}^0, \quad \text{pH}_D(\Delta G_r=0) = 10.92 \text{ (point D)}.$$

Next, we will analyze the equilibria between chemical species in solution and solid phase. We will consider only the electrode potentials of redox couples, the predominance of areas of which overlap. So we get:

Ru(III) – Ru(0)		E_i^0 / V
1. $\text{Ru}^{3+} + 3\text{e} = \text{Ru}$	$0.00 < \text{pH} < 1.76$	0.599
2. $\text{Ru}(\text{OH})_2^+ + 2\text{H}^+ + 3\text{e} = \text{Ru} + 2\text{H}_2\text{O}$	$1.76 < \text{pH} < 4.42$	0.668
3. $\text{Ru}(\text{OH})_3 \text{ (s)} \cdot \text{H}_2\text{O} + 3\text{H}^+ + 3\text{e} = \text{Ru} + 4\text{H}_2\text{O}$	$4.42 < \text{pH} < 14.0$	0.631

Ru(IV) – Ru(III)

4. $\text{Ru(OH)}_2^{2+} + 2\text{H}^+ + \text{e} = \text{Ru}^{3+} + 2\text{H}_2\text{O}$	0.0 < pH < 1.76	0.831
5. $\text{Ru(OH)}_2^{2+} + \text{e} = \text{Ru(OH)}_2^+$	1.76 < pH < 2.55	0.612
6. $\frac{1}{4} \text{Ru}_4(\text{OH})_{12}^{4+} + \text{H}^+ + \text{e} = \text{Ru(OH)}_2^+ + \text{H}_2\text{O}$	2.55 < pH < 4.42	0.506
7. $\frac{1}{4} \text{Ru}_4(\text{OH})_{12}^{4+} + \text{H}_2\text{O} + \text{e} = \text{Ru(OH)}_3(\text{s}) \times \text{H}_2\text{O}$	4.42 < pH < 4.43	0.617
8. $\text{RuO}_2(\text{s}) \times 2\text{H}_2\text{O} + \text{H}^+ + \text{e} = \text{Ru(OH)}_3(\text{s}) \times \text{H}_2\text{O}$	4.43 < pH < 14.0	0.777

Ru(V) – Ru(IV)

9. $\frac{1}{2} \text{Ru}_2\text{O}_5(\text{s}) + 3\text{H}^+ + \text{e} = \text{Ru(OH)}_2^{2+} + \frac{1}{2} \text{H}_2\text{O}$	1.94 < pH < 2.55	1.222
10. $\frac{1}{2} \text{Ru}_2\text{O}_5(\text{s}) + \frac{1}{2} \text{H}_2\text{O} + 2\text{H}^+ + \text{e} = \frac{1}{4} \text{Ru(OH)}_{12}^{4+}$	2.55 < pH < 4.43	1.328
11. $\frac{1}{2} \text{Ru}_2\text{O}_5(\text{s}) + 3/2 \text{H}_2\text{O} + \text{H}^+ + \text{e} = \text{RuO}_2(\text{s}) + 2 \text{H}_2\text{O}$	4.43 < pH < 10.92	1.168

Ru(VI) – Ru(V)

12. $\text{RuO}_4^{2-} + 3\text{H}^+ + \text{e} = \frac{1}{2} \text{Ru}_2\text{O}_5(\text{s}) + 3/2 \text{H}_2\text{O}$	10.57 < pH < 10.92	2.816
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Ru(VI) – Ru(IV)

13. $\text{RuO}_4^{2-} + 4\text{H}^+ + 2\text{e} = \text{RuO}_2(\text{s}) + 2\text{H}_2\text{O}$	10.92 < pH < 14.00	1.992
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Ru(VII) – Ru(V)

14. $\text{RuO}_4^- + 3\text{H}^+ + 2\text{e} = \frac{1}{2} \text{Ru}_2\text{O}_5(\text{s}) + 3/2 \text{H}_2\text{O}$	5.94 < pH < 10.57	1.701
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Ru(VII) – Ru(VI)

15. $\text{RuO}_4^- + \text{e} = \text{RuO}_4^{2-}$	10.57 < pH < 14.00	0.586
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Ru(VIII) – Ru(IV)

16. $\text{H}_2\text{RuO}_5 + 6\text{H}^+ + 4\text{e} = \text{RuOH}_2^{2+} + \text{H}_2\text{O}$	0.00 < pH < 1.94	1.405
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Ru(VIII) – Ru(V)

17. $\text{H}_2\text{RuO}_5 + 3\text{H}^+ + 3\text{e} = \frac{1}{2} \text{Ru}_2\text{O}_5(\text{s}) + 5/2 \text{H}_2\text{O}$	1.94 < pH < 5.94	1.466
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Ru(VIII) Ru(VII)

18. $\text{H}_2\text{RuO}_5 + \text{e} = \text{RuO}_4^- + \text{H}_2\text{O}$	5.94 < pH < 11.53	0.996
19. $\text{HRuO}_5^- + \text{H}^+ + \text{e} = \text{RuO}_4^- + \text{H}_2\text{O}$	11.53 < pH < 14.00	1.678

The following expressions for electrode potentials (within the respective pH ranges) correspond to these electrode processes:

Ru(III) – Ru(0)	$E_1 = E_1^0 + RT / 3F \ln C_{\text{Ru}}^0$	0.00 < pH < 1.76
	$E_2 = E_2^0 + RT / 3F \ln C_{\text{Ru}}^0 + RT / 3F \ln [\text{H}^+]$	1.76 < pH < 4.42
	$E_3 = E_3^0 + RT / F \ln [\text{H}^+]$	4.42 < pH < 14.0
Ru(IV) – Ru(III)	$E_4 = E_4^0 + 2 RT / F \ln [\text{H}^+]$	0.00 < pH < 1.76
	$E_5 = E_5^0$	1.76 < pH < 2.55
	$E_6 = E_6^0 + RT / F \ln [\text{H}^+] - 3RT / 4F \ln C_{\text{Ru}}^0 - \frac{1}{4} RT / \ln 4$	2.55 < pH < 4.42
	$E_7 = E_7^0 + RT / 4F \ln C_{\text{Ru}}^0 - \frac{1}{4} RT / \ln 4$	4.42 < pH < 4.43
	$E_8 = E_8^0 + RT / F \ln [\text{H}^+]$	4.43 < pH < 14.0
Ru(V) – Ru(IV)	$E_9 = E_9^0 + 3 RT / F \ln [\text{H}^+] - 3RT / 4F \ln C_{\text{Ru}}^0$	1.94 < pH < 2.55
	$E_{10} = E_{10}^0 + 2RT / F \ln [\text{H}^+] - RT / 4F \ln C_{\text{Ru}}^0 - \frac{1}{4} RT / \ln 4$	2.55 < pH < 4.43
	$E_{11} = E_{11}^0 + RT / F \ln [\text{H}^+]$	4.43 < pH < 10.92
Ru(VI) – Ru(V)	$E_{12} = E_{12}^0 + 3 RT / F \ln [\text{H}^+] + RT / F \ln C_{\text{Ru}}^0$	10.57 < pH < 10.92
Ru(VI) – Ru(IV)	$E_{13} = E_{13}^0 + 2 RT / F \ln [\text{H}^+] + RT / 2F \ln C_{\text{Ru}}^0$	10.92 < pH < 14.00
Ru(VII) – Ru(V)	$E_{14} = E_{14}^0 + 3 RT / 2F \ln [\text{H}^+] + RT / 2F \ln C_{\text{Ru}}^0$	5.94 < pH < 10.57

Ru(VII)– Ru(VI)	$E_{15} = E_{15}^0$	$10.57 < \text{pH} < 14.00$
Ru(VIII)-Ru(IV)	$E_{16} = E_{16}^0 + 3 RT / 2F \ln [H^+]$	$0 < \text{pH} < 1.94$
Ru(VIII) –Ru(V)	$E_{17} = E_{17}^0 + RT / F \ln [H^+] + RT / 3F \ln C_{Ru}^0$	$1.94 < \text{pH} < 5.94$
Ru(VIII)-Ru(VII)	$E_{18} = E_{18}^0$	$5.94 < \text{pH} < 11.53$
	$E_{19} = E_{19}^0 + RT / F \ln [H^+]$	$11.53 < \text{pH} < 14.00$

Results and discussion

From the selected thermodynamic data [19], the standard electrode potentials of possible half-reactions in the Ru–Cl⁻-H₂O system have been also calculated. The calculation results of redox equilibria and the areas of predominance of chemical species in the examined system are shown in the form of diagrams potential-log[Cl⁻]. E_r^0 represents the standard electrode potential for respective redox couple, calculated in the basis of thermodynamic data [19] by the formula. $E_r^0 = -Gr^0$. Finally, the E-pH diagrams for $C_{Ru}^0 = 10^{-4}$ and $C_{Ru}^0 = 10^{-6}$ mol/L are shown in Fig. 1 and 2. On their basis the following conclusions can be made:

- With increasing of the total concentration of ruthenium:
 - The areas of stability of $\text{Ru}(\text{OH})_2^+$, $\text{Ru}(\text{OH})_2^{2+}$, RuO_4^{2-} , RuO_4^- significantly narrow;
 - The thermodynamic stability areas of the solid phase $\text{Ru}(\text{OH})_3 \cdot \text{H}_2\text{O}_{(s)}$, $\text{RuO}_2 \cdot \text{H}_2\text{O}_{(s)}$ and $\text{Ru}_2\text{O}_{5(s)}$ increase;

Ru(II) is thermodynamically unstable to dismutation in Ru and Ru(III) within the entire range of pH and CRu0 values. In [19] it is assumed that Ru²⁺ does not participate in the disproportionation process due to the preponderance of the kinetics conditions on the thermodynamic inhibition.

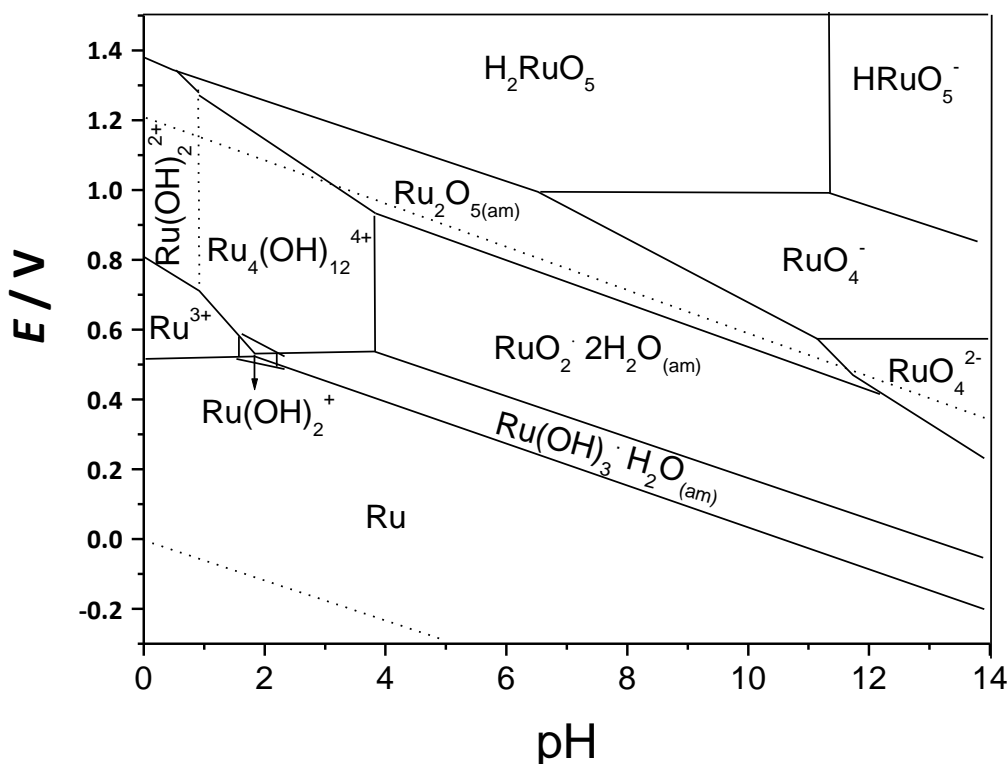


Figure 1. The potential – pH diagrams for ruthenium compounds in the system Ru-H₂O, $C_{Ru}^0 = 10^{-4}$ mol/L .

- The most stable valence state of ruthenium is Ru(IV). These results are in good agreement with existing experimental data [19].

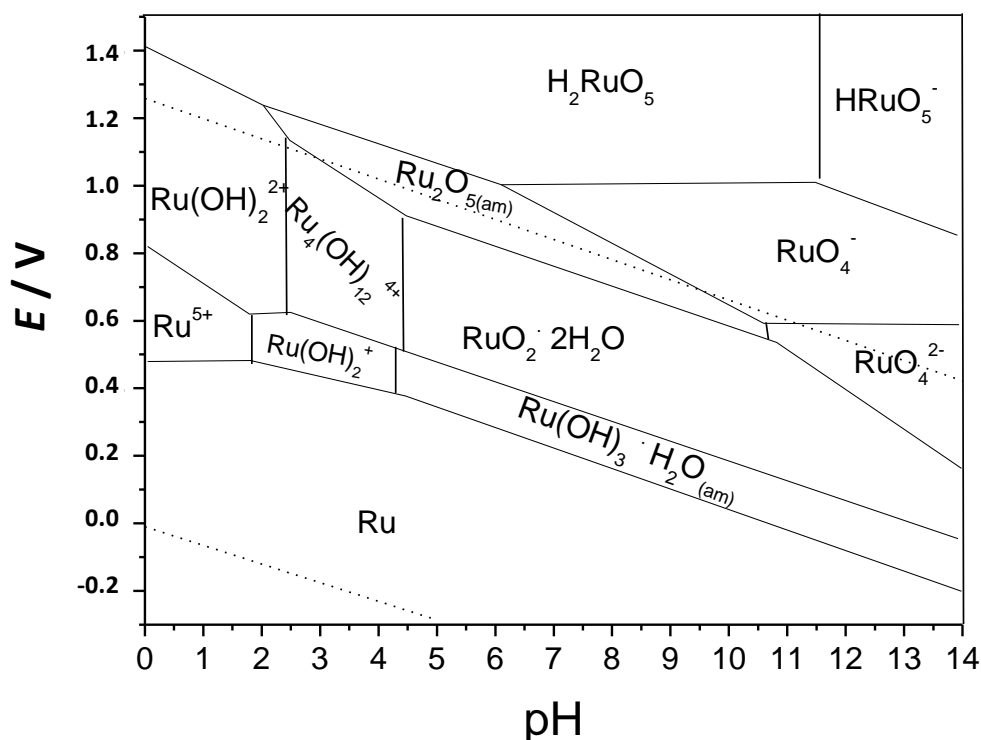


Figure 2. The potential – pH diagrams for ruthenium compounds in the system Ru-H₂O, C_{Ru}⁰ = 10⁻⁶ mol/L .

We will now examine the equilibrium between species in different valence states. Along with the reaction equation, the calculated standard electrode potential E⁰ is indicated:

Ru(III) – Ru(0)

E_i⁰ / V

1. Ru ³⁺ + 3e = Ru	log[Cl ⁻] < -2.17	0.599
2. RuCl ²⁺ + 3e = Ru + Cl ⁻	-2.17 < log[Cl ⁻] < -1.57	0.566
3. RuCl ₂ ⁺ + 3e = Ru + 2Cl ⁻	-1.57 < log[Cl ⁻] < -0.54	0.525
4. RuCl ₃ ⁰ + 3e = Ru + 3Cl ⁻	-0.54 < log[Cl ⁻] < 0.15	0.514
5. RuCl ₄ ⁻ + 3e = Ru + 4Cl ⁻	0.15 < log[Cl ⁻] < 0.30	0.517
6. RuCl ₅ ²⁻ + 3e = Ru + 5Cl ⁻	0.30 < log[Cl ⁻] < 0.40	0.523
7. RuCl ₆ ³⁻ + 3e = Ru + 6Cl ⁻	0.40 < log[Cl ⁻] < 0.50	0.531

Ru(IV) – Ru(III)

8. Ru(OH) ₂ ²⁺ + 2H ⁺ + e = Ru ³⁺ + 2H ₂ O	log[Cl ⁻] < -2.17	0.821
9. Ru(OH) ₂ ²⁺ + 2H ⁺ + Cl ⁻ + e = RuCl ²⁺ + 2H ₂ O	-2.17 < log[Cl ⁻] < -1.57	0.950
10. Ru(OH) ₂ ²⁺ + 2H ⁺ + 2Cl ⁻ + e = RuCl ⁺ + 2H ₂ O	-1.57 < log[Cl ⁻] < -1.39	1.043
11. Ru(OH) ₂ Cl ⁺ + 2H ⁺ + Cl ⁻ + e = RuCl ₂ ⁺ + 2H ₂ O	-1.39 < log[Cl ⁻] < -0.54	0.961
12. Ru(OH) ₂ Cl ⁺ + 2H ⁺ + 2Cl ⁻ + e = RuCl ₃ + 2H ₂ O	-0.54 < log[Cl ⁻] < -0.44	0.993
13. Ru(OH) ₂ Cl ₄ ²⁺ + 2H ⁺ + e = RuCl ₃ + Cl ⁻ + 2H ₂ O	-0.44 < log[Cl ⁻] < 0.15	0.915
14. Ru(OH) ₂ Cl ₄ ²⁺ + 2H ⁺ + e = RuCl ₄ ⁻ + 2H ₂ O	0.15 < log[Cl ⁻] < 0.30	0.906
15. Ru(OH) ₂ Cl ₄ ²⁺ + 2H ⁺ + Cl ⁻ + e = RuCl ₅ ²⁻ + 2H ₂ O	0.30 < log[Cl ⁻] < 0.40	0.888
16. Ru(OH) ₂ Cl ₄ ²⁺ + 2H ⁺ + 2Cl ⁻ + e = RuCl ₆ ³⁻ + 2H ₂ O	0.40 < log[Cl ⁻] < 0.50	0.865

Ru(VIII) – Ru(IV)

17. H ₂ RuO ₅ + 6H ⁺ + 4e = Ru(OH) ₂ ²⁺ + 3H ₂ O	-2.50 < log[Cl ⁻] < -1.39	1.405
18. H ₂ RuO ₅ + 6H ⁺ + Cl ⁻ + 4e = Ru(OH) ₂ Cl ⁺ + 3H ₂ O	-1.39 < log[Cl ⁻] < -0.44	1.425
19. H ₂ RuO ₅ + 6H ⁺ + 4Cl ⁻ + 4e = Ru(OH) ₂ Cl ₄ ²⁻ + 3H ₂ O	-0.44 < log[Cl ⁻] < 0.50	1.445

Finally, the electrode potential depending on the Cl^- concentration is calculated:

$\text{Ru(III)} - \text{Ru(0)}$	$(\nu = (RT / 3F) \ln 10)$	
$E_1 = E_1^0 + \nu \log C_{\text{Ru}}^0$		$\log[\text{Cl}^-] < -2.17$
$E_2 = E_2^0 + \nu \log C_{\text{Ru}}^0 - \nu \log[\text{Cl}^-]$		$-2.17 < \log[\text{Cl}^-] < -1.57$
$E_3 = E_3^0 + \nu \log C_{\text{Ru}}^0 - 2 \nu \log[\text{Cl}^-]$		$-1.57 < \log[\text{Cl}^-] < -0.54$
$E_4 = E_4^0 + \nu \log C_{\text{Ru}}^0 - 3 \nu \log[\text{Cl}^-]$		$-0.54 < \log[\text{Cl}^-] < 0.15$
$E_5 = E_5^0 + \nu \log C_{\text{Ru}}^0 - 4 \nu \log[\text{Cl}^-]$		$0.15 < \log[\text{Cl}^-] < 0.30$
$E_6 = E_6^0 + \nu \log C_{\text{Ru}}^0 - 5 \nu \log[\text{Cl}^-]$		$0.30 < \log[\text{Cl}^-] < 0.40$
$E_7 = E_7^0 + \nu \log C_{\text{Ru}}^0 - 6 \nu \log[\text{Cl}^-]$		$0.40 < \log[\text{Cl}^-] < 0.50$
$\text{Ru(IV)} - \text{Ru(III)}$	$(\nu = (RT / F) \ln 10)$	
$E_8 = E_8^0 + 2 \nu \log [\text{H}^+]$		$\log[\text{Cl}^-] < -2.17$
$E_9 = E_9^0 + 2 \nu \log [\text{H}^+] + \nu \log[\text{Cl}^-]$		$-2.17 < \log[\text{Cl}^-] < -1.57$
$E_{10} = E_{10}^0 + 2 \nu \log [\text{H}^+] + 2 \nu \log[\text{Cl}^-]$		$-1.57 < \log[\text{Cl}^-] < -1.39$
$E_{11} = E_{11}^0 + 2 \nu \log [\text{H}^+] + \nu \log[\text{Cl}^-]$		$-1.39 < \log[\text{Cl}^-] < -0.54$
$E_{12} = E_{12}^0 + 2 \nu \log [\text{H}^+] + 2 \nu \log[\text{Cl}^-]$		$-0.54 < \log[\text{Cl}^-] < -0.44$
$E_{13} = E_{13}^0 + 2 \nu \log [\text{H}^+] - \nu \log[\text{Cl}^-]$		$-0.44 < \log[\text{Cl}^-] < 0.15$
$E_{14} = E_{14}^0 + 2 \nu \log [\text{H}^+]$		$0.15 < \log[\text{Cl}^-] < 0.30$
$E_{15} = E_{15}^0 + 2 \nu \log [\text{H}^+] + \nu \log[\text{Cl}^-]$		$0.30 < \log[\text{Cl}^-] < 0.40$
$E_{16} = E_{16}^0 + 2 \nu \log [\text{H}^+] + 2 \nu \log[\text{Cl}^-]$		$0.40 < \log[\text{Cl}^-] < 0.50$
$\text{Ru(VIII)} - \text{Ru(IV)}$	$(\nu = (RT / 4F) \ln 10)$	
$E_{17} = E_{17}^0 + 6 \nu \log [\text{H}^+]$		$-2.50 < \log[\text{Cl}^-] < -1.39$
$E_{18} = E_{18}^0 + 6 \nu \log [\text{H}^+] + \nu \log[\text{Cl}^-]$		$-1.39 < \log[\text{Cl}^-] < -0.44$
$E_{19} = E_{19}^0 + 6 \nu \log [\text{H}^+] + 4 \nu \log[\text{Cl}^-]$		$-0.44 < \log[\text{Cl}^-] < -0.50$

These functions along with predominance areas of the species in solution are diagrammatically shown in Fig. 3 as the potential – $\log [L]$ diagram. Compared with diagrams E - pH, on the E ($\log [L]$) diagram a considerable number of chemical species of ruthenium(IV) is outside of the thermodynamic stability area of water (the dotted line a). Within the entire range of the $[\text{Cl}^-]$ values, $-2.20 < \log[\text{Cl}^-] < 0.50$, the valence states of ruthenium Ru(II), Ru(V), Ru(VI) and Ru(VII) are unstable with respect to dismutation processes.

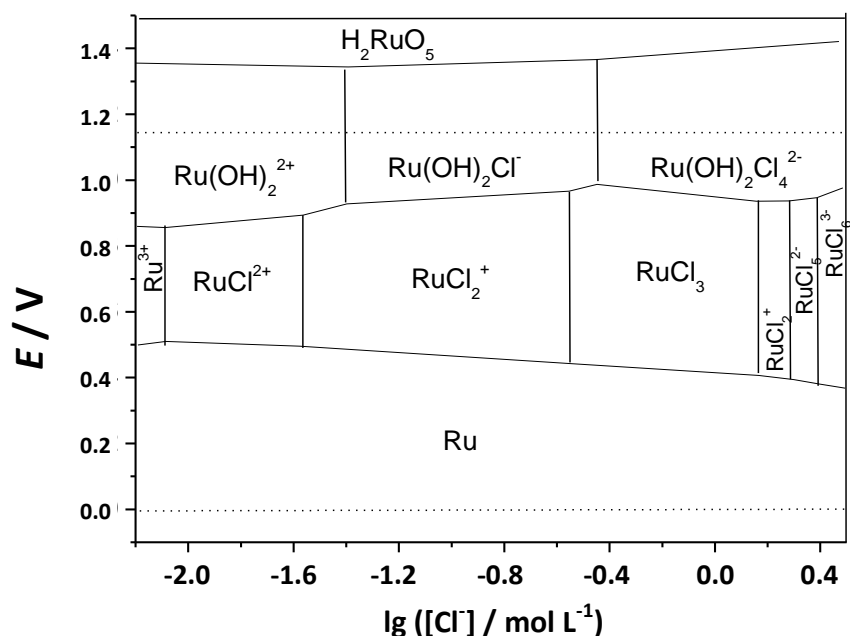


Figure 3. The potential - $\log[L]$ diagram for the system Ru-Cl-H₂O, pH 0, $C_{Ru0} = 10^{-6}$ mol/L.

Conclusions

1. On the basis of the thermodynamic data, the area of thermodynamic stability of Ru chemical species as a function of *pH* (or *pCl*) for each degree of oxidation has been determined.
2. Based on the $\Delta G_r = f(n)$ diagrams calculated for several values of *pH*, a narrow ΔpH value is determined, in which the dismutation of appropriate form takes place. Based on thermodynamic analysis, the exact pH_D value of the beginning of disproportionation (or comproportionation) is found. After that, the diagrams of heterogeneous chemical equilibria, developed by us earlier, as a function of *pH* and the total concentration of metal ion in solution, are built.
3. It is derived a system of electrochemical equations of electrode reactions between chemical species in different degrees of oxidation, the predominance areas of which are overlapped. Finally, the dependence ΔG_r or *E* on *pH* (or *pCl*) is calculated for different redox pairs. Depending on *pH* and *pE*, as well as the total concentration of inorganic ligands, the Ru compounds may undergo various transformations to produce a whole range of chemical forms in solution. The potential-*pH* and potential-*pCl* diagrams of the Ru-H₂O and Ru-Cl⁻-H₂O systems have been constructed. The calculated Pourbaix diagrams within our approach agree well with the previously reported experimental data.

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