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Thermodynamic systems analysis Cr–As–H₂O based on E–pH diagrams

After studying the problem of environmental pollution, it was found that the most dangerous contaminant is arsenic. Due to the fact that the properties arsenates little studied, the analysis of published data showed that a growing need for thermochemical data from each year for new manufacturing processes involving arsenic compounds. This article first introduced the E–pH diagram of the system Cr–As–H₂O at standard conditions (25 °C and 1 atm. Total pressure), where the range of existence of arsenate chromium, considered the chemical and electrode reactions produce chromium arsenate compounds of chromium and arsenic. The outcome of the conclusion about the possibility of the use of chromium compounds to output arsenic from solution in the form of a soluble, stable chromium arsenate.

Keywords: thermodynamic systems, diagrams, copper, hydrometallurgical, arsenates, chromium arsenate.

Today copper-concentrating and metallurgical enterprises are serious polluters of the environment in particular, and the hydrosphere. Some of the most dangerous pollutants are arsenic, that exists in the form of arsenates, wherein the trivalent form of arsenic compounds are the most toxic and widespread in nature [1].

In the extraction, enrichment and metallurgical processing of copper sulphide ores, arsenic is concentrated in waste of production, especially in a copper electrolyte, used during the refining copper and wastewater [2]. Due to the small demand for arsenic it's necessary to excrete it to low-toxic and poorly soluble forms, that useful for disposal or recycling.

During the burial there is a risk of toxicants entering the groundwater and surface water. In open water, located in areas of occurrence of buried waste content of toxic arsenic compounds can reach several milligrams per liter units, and in groundwater — tens and even hundreds of milligrams.

At the present time, experimentally established the enthalpy of formation, combustion heat, Gibbs energy, entropy and other thermodynamic characteristics of many, but not all chemical compounds. The number of experimental thermochemical work from year to year increases significantly, but to an even greater extent there is growing need for thermochemical data for new technological production processes and to settle other issues [3].

The gap between the required and available type of this information constrains not only development of the synthesized compounds, but also the development of many of the theoretical sections of chemistry, especially the theory of the structure of relationships and properties of substances. This leads to an increase in the role of computational methods that are based on a small number of experimental sufficiently reliable data allow us to calculate the thermodynamic characteristics for other compounds in the same class.

The aim of this study is to prove the existence of the thermodynamic insoluble precipitate chromium arsenate (CrAsO₄) and determination of the region of stability of the compound.

In accordance with the objectives of the study purpose of this system were as follows:

- calculation based on thermodynamic data, according to a known method described in [4], participating in the system of ions and molecules of redox potential using the Nernst equation;
- building on the basis of the calculated data chart E–pH Cr–As–H₂O system.

Thus, the object of study is the system Cr–As–H₂O, and the subject of study evaluation thermodynamically probable behavior of the chemical elements and their compounds, including the minerals in contact with aqueous solutions, setting the limits of capacity and pH, in which the compound element must be sustainable, identify the chemical nature of the oxidation products.

Application of thermodynamic analysis, including charts and E–pH in the research process for the hydrometallurgical production and experimental validation of the results, given the development of a new scientific direction in the field of heterogeneous systems.

In this case, the system chosen for the thermodynamic study of the possible deposition of copper electrolyte in the form of soluble arsenic, chromium oxide stable compound (III).

In the figure first presented diagram E–pH of system Cr–As–H₂O under standard conditions (25 °C and 1 atm. of total pressure) by combining the private diagram of system As–H₂O [5] with private diagram of system Cr–H₂O [6].

All the lines on the diagram E–pH of system Cr–As–H₂O strictly correspond to the numbers of chemical equations, listed in table.

Table

Calculated equations diagrams reactions E–pH of system Cr–As–H₂O

No.	Chemical reaction	Electrode reaction
1	$2\text{H}_2\text{O}_{(l)} = \text{O}_{2(g)} + 4\text{H}^+_{(l)} + 4e$	$E = 1.23 - 0,059\text{pH}$; $P_{\text{O}_2} = 1\text{atm}$.
2	$\text{H}_{2(g)} = 2\text{H}^+_{(l)} + 2e$	$E = -0.059/2\lg P_{\text{H}_2} - 0.059\text{pH}$; $P_{\text{H}_2} = 1\text{atm}$.
3	$\text{Cr}_{(s)} = \text{Cr}^{2+}_{(l)} + 2e$	$E = -0.913 + 0,0295\lg[\text{Cr}^{2+}]$
4	$\text{Cr}_{(s)} + 3\text{H}_2\text{O}_{(l)} = \text{Cr}(\text{OH})_{3(s)} + 3\text{H}^+_{(l)} + 3e$	$E = -0.654 - 0,059\text{pH}$
5	$\text{Cr}^{2+}_{(l)} + 3\text{H}_2\text{O}_{(l)} = \text{Cr}(\text{OH})_{3(s)} + 3\text{H}^+_{(l)} + e$	$E = -0.136 - 0,059\lg[\text{Cr}^{2+}] - 0,177\text{pH}$
6	$\text{Cr}^{2+}_{(l)} - e = \text{Cr}^{3+}_{(l)}$	$E = 0.4 + 0,059\lg[\text{Cr}^{3+}] - 0,059\lg[\text{Cr}^{2+}]$
7	$\text{Cr}^{3+}_{(l)} + 3\text{H}_2\text{O}_{(l)} = \text{Cr}(\text{OH})_{3(s)} + 3\text{H}^+_{(l)}$	$\lg K = \lg[\text{Cr}^{3+}] - 3\text{pH}$; $\text{pH} = 1.2$
8	$\text{HCrO}_4^-_{(l)} + \text{H}^+_{(l)} = \text{CrO}_4^{2-}_{(l)}$	$\lg K = \lg[\text{CrO}_4^{2-}] - \lg[\text{HCrO}_4^-]$
9	$\text{H}_2\text{CrO}_{4(s)} = \text{HCrO}_4^-_{(l)} + \text{H}^+_{(l)}$	$\lg K = \lg[\text{HCrO}_4^-] - \lg[\text{H}_2\text{CrO}_4]$; $\text{pH} = 0.75$
10	$\text{AsH}_{3(g)} = \text{As}_{(s)} + 3\text{H}^+_{(l)} + 3e$	$E = -0.24 - 0,059\text{pH}$
11	$\text{H}_3\text{AsO}_{4(l)} = \text{H}_2\text{AsO}_4^-_{(l)} + \text{H}^+_{(l)}$	$\lg[\text{H}_2\text{AsO}_4^-] / \lg[\text{H}_3\text{AsO}_4] = 2.2 - \text{pH}$; $\text{pH} = 2.2$
12	$\text{H}_2\text{AsO}_4^-_{(l)} = \text{HAsO}_4^{2-}_{(l)} + \text{H}^+_{(l)}$	$\lg[\text{HAsO}_4^{2-}] / \lg[\text{H}_2\text{AsO}_4^-] = 7.0 - \text{pH}$; $\text{pH} = 7.0$
13	$\text{HAsO}_4^{2-}_{(l)} = \text{AsO}_4^{3-}_{(l)} + \text{H}^+_{(l)}$	$\lg[\text{AsO}_4^{3-}] / \lg[\text{HAsO}_4^{2-}] = 11.54 - \text{pH}$; $\text{pH} = 11.54$
14	$\text{CrAsO}_{4(s)} + 4\text{H}_2\text{O}_{(l)} = \text{AsO}_4^{3-}_{(l)} + \text{CrO}_4^{2-}_{(l)} + 8\text{H}^+_{(l)} + 3e$	$E = 2.32 - 0.097\lg[\text{CrO}_4^{2-}] - 0.097\lg[\text{AsO}_4^{3-}] - 0.157\text{pH}$
15	$\text{CrAsO}_{4(s)} + 4\text{H}_2\text{O}_{(l)} = \text{HAsO}_4^{2-}_{(l)} + \text{CrO}_4^{2-}_{(l)} + 7\text{H}^+_{(l)} + 3e$	$E = 2.09 - 0.097\lg[\text{CrO}_4^{2-}] - 0.097\lg[\text{HAsO}_4^{2-}] - 0.138\text{pH}$
16	$\text{CrAsO}_{4(s)} + 4\text{H}_2\text{O}_{(l)} = \text{H}_2\text{AsO}_4^-_{(l)} + \text{CrO}_4^{2-}_{(l)} + 6\text{H}^+_{(l)} + 3e$	$E = 1.96 - 0.097\lg[\text{CrO}_4^{2-}] - 0.097\lg[\text{H}_2\text{AsO}_4^-] - 0.118\text{pH}$
17	$\text{CrAsO}_{4(s)} + 4\text{H}_2\text{O}_{(l)} = \text{H}_2\text{AsO}_4^-_{(l)} + \text{HCrO}_4^- + 5\text{H}^+_{(l)} + 3e$	$E = 1.83 - 0.097\lg[\text{HCrO}_4^-] - 0.097\lg[\text{H}_2\text{AsO}_4^-] - 0.098\text{pH}$
18	$\text{CrAsO}_{4(s)} + 4\text{H}_2\text{O}_{(l)} = \text{H}_3\text{AsO}_{4(l)} + \text{HCrO}_4^- + 4\text{H}^+_{(l)} + 3e$	$E = 1.79 - 0.097\lg[\text{HCrO}_4^-] - 0.097\lg[\text{H}_3\text{AsO}_4] - 0.079\text{pH}$
19	$\text{CrAsO}_{4(s)} + 4\text{H}_2\text{O}_{(l)} = \text{H}_3\text{AsO}_{4(l)} + \text{H}_2\text{CrO}_{4(l)} + 3\text{H}^+_{(l)} + 3e$	$E = 1.86 - 0.097\lg[\text{H}_2\text{CrO}_4] - 0.097\lg[\text{H}_3\text{AsO}_4] - 0.059\text{pH}$
20	$\text{As}_{(s)} + \text{Cr}(\text{OH})_{3(s)} + \text{H}_2\text{O}_{(l)} = \text{CrAsO}_{4(s)} + 2\text{H}^+_{(l)} + 2e$	$E = -0.06 - 0.059\text{pH}$
21	$\text{As}_{(s)} + \text{Cr}^{3+}_{(l)} + 4\text{H}_2\text{O}_{(l)} = \text{CrAsO}_{4(s)} + 8\text{H}^+_{(l)} + 5e$	$E = 0.12 + 0.0118\lg[\text{Cr}^{3+}] - 0,094\text{pH}$

Diagram analysis of E–pH system Cr–As–H₂O can draw the following conclusions. Arsenic in the oxidation area is advantageously in the form of arsenic acid and its derivatives, which are also quite stable compared to arsenous acid and in the area of water sustainability, but in reducing area it's occupies by solid arsenic and arsenic.

From the chromium compounds in the field of oxygen stability coexist H₂CrO₄ (line 9), HCrO₄⁻ (line 8), CrO₄²⁻ (line 13), that is most stable valence of chromium compounds (VI). In the water area chromium is predominantly as hydroxide (Cr(OH)₃), which can also exist in the reducing region, while metallic chromium (line 4) and ion Cr³⁺ (line 6), is stable only in the reducing region.

How can be seen from the chart at standard conditions, as chromium arsenate is stable mostly in water and oxidizing environment (In the ranges of potential from –0.7 to 1.8). In an environment of stability oxygen chromium arsenate is decomposed into arsenic acid and its derivatives (H₃AsO₄ (line 18), H₂AsO₄⁻ (line 17), HAsO₄²⁻ (line 15), AsO₄³⁻ (line 14)) and chromic acid and its derivatives (H₂CrO₄ (line 19), HCrO₄⁻ (lines 18, 17), CrO₄²⁻ (lines 16, 15, 14)). Nevertheless, it should be noted that a test compound may also be marginally stable in a reducing environment. In hydrogen the chromium arsenate mainly decomposes into elemental arsenic and chromium oxide (III) (line 20) and in the acidic into an ion Cr³⁺ (line 21). pH medium does not affect the stability of the chromium arsenate, which occupies a large pH range (0 to 14).

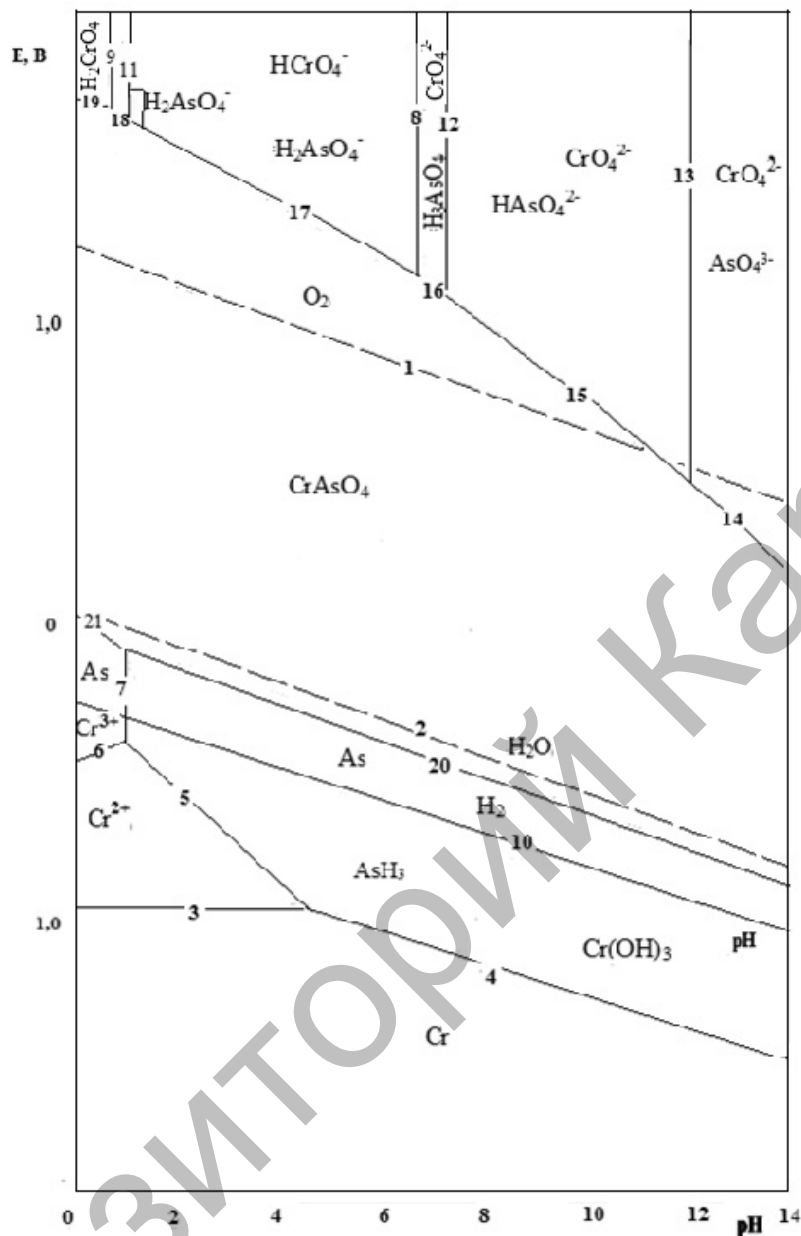


Figure. Diagram E–pH system Cr–As–H₂O at 25 °C and 1 atm.

Thus, the thermodynamic analysis system Cr–As–H₂O under diagram E–pH can be concluded that secreted arsenate chromium exhibits stability over a wide pH and potential range, and allows the use of chromium oxide (Cr₂O₃) as a precipitant arsenic and consequently dispose acid solutions of copper production.

References

- 1 Копылов Н.И. Проблемы мышьяксо­дер­жащих отвалов / Под ред. Г.А. Толстикова. — Новосибирск: Гео, 2012. — 182 с.
- 2 Бортникова С.Б., Гаськова О.Л., Бессонова Е.П. Геохимия техногенных систем. — Новосибирск: Гео, 2006. — 169 с.
- 3 Касенов Б.К., Алдабергенов М.К., Пашилкин А.С. Термодинамические методы в химии и металлургии. — Алматы: Рауан, 1994. — 126 с.
- 4 Гаррелс Р.И., Крайт И.А. Растворы, минералы, равновесие. — М.: Мир, 1968. — 386 с.
- 5 Жамбеков М.И. E–pH диаграмма системы As–H₂O // Вестн. Караганд. ун-та. Сер. Химия. — 1997. — № 3. — С. 106–108.
- 6 Справочник химика / Под ред. Б.П. Никольского. — Л.: Наука, 1965. — Т. 3. — 1008 с.

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Е–рН диаграмма негізінде Cr–As–H₂O жүйесінің термодинамикалық талдауы

Қоршаған ортаның ластану мәселесін зерттеу барысында негізгі ластаушылардың бірі күшәла екендігі анықталды. Арсенаттардың қасиеттері аз зерттелгендіктен, әдеби шолу жүргізу кезінде күшәла қосылыстары қатысындағы жана өндірістік үрдістерге термохимиялық нәтижелер қажет екендігі белгілі болды. Мақалада алғаш рет стандартты жағдайларда (25 °С және 1 атм. жалпы қысымда) Cr–As–H₂O жүйесінің Е–рН диаграммасы тұрғызылып, хром арсенатының тұрақтылық аймағы, хром және күшәла қосылыстарынан хром арсенатын алудың химиялық және электродтық реакциялары зерттелді. Нәтижесінде күшәланы хром тотығын пайдалану арқылы ерітінділерден қиын ерігіш, тұрақты хром арсенаты түрінде алуға болатындығы туралы қорытынды жасауға болады.

Кілт сөздер: термодинамикалық жүйелер, диаграммалар, мыс, гидрометаллургия, арсенаттар, хром арсенаты.

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Термодинамический анализ систем Cr–As–H₂O на основе диаграмм Е–рН

Изучена проблема загрязнения окружающей среды. Установлено, что наиболее опасным загрязнителем является мышьяк. В связи с тем, что свойства арсенатов мало изучены, в результате анализа литературных данных выявлено, что с каждым годом растет потребность в термодинамических данных для новых производственных процессов с участием соединений мышьяка. В статье впервые представлена диаграмма Е–рН системы Cr–As–H₂O при стандартных условиях (25 °С и 1 атм. общего давления), где определена область существования арсената хрома, рассмотрены химические и электродные реакции получения арсената хрома из соединений хрома и мышьяка. По итогам работы сделан вывод о возможности использования соединений хрома для вывода мышьяка из растворов в виде труднорастворимого, устойчивого арсената хрома.

Ключевые слова: термодинамические системы, диаграммы, медь, гидрометаллургия, арсенаты, арсенат хрома.

References

- 1 Kopylov N.I. *Problems of arsenic containing dumps*, Ed. by acad. G.A. Tolstikov, Novosibirsk: Geo, 2012, 182 p.
- 2 Bortnikova S.B., Gas'kova O.L., Bessonova Ye.P. *Geochemistry of technogenic systems*, Novosibirsk: Geo, 2006, 169 p.
- 3 Kasenov B.K., Aldabergenov M.K., Pashinkin A.S. *Thermodynamic methods in chemistry and metallurgy*, Almaty: Rauan, 1994, 126 p.
- 4 Garrels R.I., Christ I.A. *Solutions, minerals, equilibrium*, Moscow: Mir, 1968, 386 p.
- 5 Zhabekov M.I. *Bull. of Karaganda University. Chemistry ser.*, 1997, 3, p. 106–108.
- 6 Reference of chemist, Ed. by B.P. Nikolsky, Leningrad: Nauka, 1965, 3, 1008 p.