

Research Article

Thermodynamic Stability Areas of Polyvanadates of Alkaline Earth Metals

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A thermodynamic method of the global Gibbs energy variation calculation for describing heterogeneous equilibria of transformations of calcium, strontium, and barium polyvanadates, that occur in systems $\text{MeO-V}_2\text{O}_5\text{-H}_2\text{O}$, where Me is the alkaline earth element, has been developed and used. Its quintessence consists in the thermodynamic analysis of the real conditions of various processes on the basis of their total thermodynamic characteristics. On the basis of the selected thermodynamic data for involved species, the thermodynamic stability areas of solid polyvanadates towards the solution pH and vanadium and alkaline earth metal ion concentrations in heterogeneous mixtures have been established, taking into account the complex formation reactions in multicomponent heterogeneous systems. The existing experimental data confirm the results on the thermodynamic stability of polyvanadates obtained in this paper.

1. Introduction

Polyvanadates obtained by solid-phase synthesis and subsequent study of their chemical properties in water-salt systems have a huge practical significance, because regardless of the type of source of raw materials, their processing includes stages of the synthesis of final products with desired properties (high or low solubility, etc.), with the transfer of vanadium in the solution and its subsequent precipitation. The abovementioned processes are associated with extremely complex chemical equilibria, the study of which would allow the development of technological basis of a number of combined productions: obtaining technical and pure vanadium pentoxide, vanadium catalysts, dyes, etc. [1, 2]. Up to 85–87% of the total amount of polyvanadates is used in ferrous metallurgy as highly efficient and habitually an indispensable alloying additive in the production of diverse steels. About 10–12% of polyvanadates is used in nonferrous metallurgy, mainly in the form of

aluminum-vanadium alloys for alloying structural materials based on titanium, applied in space technology. Inorganic materials containing polyvanadates are used for production of optical quantum generators, ionic conductors, ferroelectrics, dielectrics, ceramics, etc. [1]. The demand for polyvanadates is projected to grow by seven percent a year till 2025 [2], thanks to the usage of vanadium-containing steels in both traditional areas and the implementation of new technologies for the manufacture of batteries [2]. The concentrations of vanadium in surface waters caused by industrial wastes are small and, in general, are within the natural content (up to $65 \mu\text{g/L}$) [3]. Literature sources provide information on vanadium concentrations in surface waters of industrial wastes up to 2 mg/L [3]. The chemistry of aqueous solutions of vanadium is complicated by the existence in solutions of numerous ions and polyions, the transition of which into an equilibrium state depends on the pH value and oxidation-reduction potentials in the systems, as well as its concentration and the content of other

elements. Thus, the composition and stability of solid phases formed in the $\text{MeO-V}_2\text{O}_5\text{-H}_2\text{O}$ system, where Me is the alkaline earth element, exhibit complex functions of the chemical composition of solution, pH, etc. Experimentally, it has been demonstrated [4–6] that depending on the conditions in the $\text{MeO-V}_2\text{O}_5\text{-H}_2\text{O}$ system, different polyvanadates $\text{MeV}_{12}\text{O}_{31}$, $\text{MeV}_6\text{O}_{16}$, $\text{Me}_3\text{V}_{10}\text{O}_{28}$, $\text{Me}(\text{VO}_4)_2$, $\text{Me}_2\text{V}_2\text{O}_7$, and $\text{Me}_3(\text{VO}_4)_2$ can precipitate. For the compounds of Ca^{2+} , Sr^{2+} , and Ba^{2+} the same authors determined the solubility products [4, 5], taking into account the mutual transformation reactions of the vanadium (V) ionic species. The coexistence areas of these polyvanadates were also calculated in the cited papers as a function of the solution pH and alkaline earth metal concentrations. At the same time, the reciprocal relationship between the solution composition and solid phases was established in the form of diagrams $\log C_V = f(\log[\text{H}^+])$ and $\log C_M = f(\log[\text{H}^+])$. This procedure is not always efficient. In particular, the solubility diagrams provide valuable information only if the solubility of solid phase is low.

In this paper, based on calculations of the global Gibbs energy variation of the dissolution-precipitation process of the polyvanadates of alkaline earth metals as a function of pH and total concentrations of vanadium and alkaline earth metals, their thermodynamic stability areas are determined. It has been proved that the value of global Gibbs energy variation under real conditions constitutes a more objective criterion for estimation of the stability areas of polyvanadates of alkaline earth metals than the solubility diagrams.

2. Theoretical Part

In a series of papers [6–8], it has been shown that as a strict criterion of solid-phase stability serves the value of the Gibbs energy variation of the solid-phase formation-dissolution process. This criterion will be applied for the determination of the thermodynamic stability areas of the alkaline earth metal polyvanadates.

The essence of the calculation method will be explained by a concrete example of equilibrium of calcium dodecavanadate with the saturated aqueous solution:



The Gibbs energy variation under standard conditions is equal:

$$\begin{aligned} \Delta G_S^0(1) = & 7\Delta G_f^0(\text{H}_2\text{O}) + \Delta G_f^0(\text{Ca}^{2+}) + 12\Delta G_f^0(\text{VO}_2^+) \\ & - \Delta G_f^0(\text{CaV}_{12}\text{O}_{31(\text{s})}), \end{aligned} \quad (2)$$

where $\Delta G_f^0(i)$ is the standard Gibbs energy of formation of the i species. The $\Delta G_f^0(i)$ values used (kJ/mol) are recalculated from the selected equilibrium constants [4, 5] and shown in Table 1. The $\Delta G_S^0(1)$ value cannot, however, serve as a characteristic of the thermodynamic stability of calcium dodecavanadate under real conditions. In the latter case, the equilibrium is described by the equation of reaction isotherm, which for Reaction (1) takes the following form:

TABLE 1: Standard Gibbs energy of formation of the soluble and insoluble species at 295.15 K [4, 5].

Species	$\Delta G_f^0(i)$	Species	$\Delta G_f^0(i)$
Ca^{2+}	-552.75	$\text{Ca}_3\text{V}_{10}\text{O}_{28}$	-9376.52
Sr^{2+}	-563.90	$\text{Sr}_3\text{V}_{10}\text{O}_{28}$	-9428.23
Ba^{2+}	-546.83	$\text{Ba}_3\text{V}_{10}\text{O}_{28}$	-9403.50
VO_2^+	-588.30	$\text{CaV}_6\text{O}_{16}$	-5031.30
H_2O	-237.24	$\text{SrV}_6\text{O}_{16}$	-5043.05
VO_3^-	-785.70	$\text{BaV}_6\text{O}_{16}$	-5029.60
VO_4^{3-}	-897.60	$\text{CaV}_{12}\text{O}_{31}$	-9295.90
HVO_4^{2-}	-979	$\text{SrV}_{12}\text{O}_{31}$	-9307.60
H_2VO_4^-	-1021.12	$\text{BaV}_{12}\text{O}_{31}$	-9293.97
H_3VO_4	-1043.95	$\text{Ca}(\text{VO}_3)_2$	-2165.56
$\text{V}_2\text{O}_7^{4-}$	-1723.94	$\text{Sr}(\text{VO}_3)_2$	-2190.70
$\text{HV}_2\text{O}_7^{3-}$	-1767.73	$\text{Ba}(\text{VO}_3)_2$	-2181.97
$\text{V}_3\text{O}_9^{3-}$	-2400.70	$\text{Ca}_2\text{V}_2\text{O}_7$	-2870.75
$\text{V}_4\text{O}_{12}^{4-}$	-3202.23	$\text{Sr}_2\text{V}_2\text{O}_7$	-2910.45
$\text{V}_{10}\text{O}_{28}^{6-}$	-7688.78	$\text{Ba}_2\text{V}_2\text{O}_7$	-2891.35
$\text{HV}_{10}\text{O}_{28}^{5-}$	-7721.88	$\text{Ca}_3(\text{VO}_4)_2$	-3553.23
$\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$	-7742.43	$\text{Sr}_3(\text{VO}_4)_2$	-3604.49
		$\text{Ba}_3(\text{VO}_4)_2$	-3574.97

$$\Delta G_S(1) = \Delta G_S^0(1) + RT \ln \frac{C_V^{12} C_{\text{Ca}}}{[\text{H}^+]^{14}}. \quad (3)$$

Note that the Gibbs energy variation in Reaction (1) strongly depends on the pH value. At the same time, Equation (3) cannot also serve as a characteristic of the thermodynamic stability of calcium dodecavanadate, because the vanadyl ion, in function of pH and C_V , is subjected to complex chemical transformations in the solution (Table 2).

Obviously, in calculating ΔG_S , all these equilibria must be taken into account. A rigorous thermodynamic analysis, developed in a series of papers [7, 8], shows the global Gibbs energy variation of Reaction (1) under real conditions, considering the equilibria (Table 2), as described by the following equation:

$$\Delta G_S(1) = (\Delta G_S^0(1)) - (RT \ln \alpha_V^{12}) + \left(RT \ln \frac{C_V^{12} C_{\text{Ca}}}{[\text{H}^+]^{14}} \right), \quad (4)$$

where α_V is the coefficient that takes into account the contribution of the equilibria (Table 2), which is determined in the following way:

$$\begin{aligned} \alpha_V = & 1 + k_1[\text{H}^+]^{-2} + k_2[\text{H}^+]^{-4} + k_3[\text{H}^+]^{-3} + k_4[\text{H}^+]^{-2} \\ & + k_5[\text{H}^+]^{-1} + 2[\text{VO}_2^+]k_6[\text{H}^+]^{-6} + 2[\text{VO}_2^+]k_7[\text{H}^+]^{-5} \\ & + 3[\text{VO}_2^+]^2k_8[\text{H}^+]^{-6} + 4[\text{VO}_2^+]^3k_9[\text{H}^+]^{-8} \\ & + 10[\text{VO}_2^+]^9k_{10}[\text{H}^+]^{-16} + 10[\text{VO}_2^+]^9k_{11}[\text{H}^+]^{-15} \\ & + 10[\text{VO}_2^+]^9k_{12}[\text{H}^+]^{-14}, \end{aligned} \quad (5)$$

where $[\text{VO}_2^+]$ is the equilibrium concentration of vanadyl ion VO_2^+ , computed for certain values of pH and C_V from the mass balance conditions:

TABLE 2: Complex chemical transformations of the vanadyl ion in the solution at 295 ± 1 K [4, 5].

Nr	Equation of reaction	log K
1	$\text{VO}_2^+ + \text{H}_2\text{O} = \text{VO}_3^- + 2\text{H}^+$	$\log K_1 = -6.98$
2	$\text{VO}_2^+ + 2\text{H}_2\text{O} = \text{VO}_4^{3-} + 4\text{H}^+$	$\log K_2 = -29.94$
3	$\text{VO}_2^+ + 2\text{H}_2\text{O} = \text{HVO}_4^{2-} + 3\text{H}^+$	$\log K_3 = -14.68$
4	$\text{VO}_2^+ + 2\text{H}_2\text{O} = \text{H}_2\text{VO}_4^- + 2\text{H}^+$	$\log K_4 = -7.30$
5	$\text{VO}_2^+ + 2\text{H}_2\text{O} = \text{H}_3\text{VO}_4 + \text{H}^+$	$\log K_5 = -3.30$
6	$\text{VO}_2^+ + 3\text{H}_2\text{O} = \text{V}_2\text{O}_7^{4-} + 6\text{H}^+$	$\log K_6 = -28.80$
7	$2\text{VO}_2^+ + 3\text{H}_2\text{O} = \text{HV}_2\text{O}_7^{3-} + 5\text{H}^+$	$\log K_7 = -21.13$
8	$3\text{VO}_2^+ + 3\text{H}_2\text{O} = \text{V}_3\text{O}_9^{3-} + 6\text{H}^+$	$\log K_8 = -13.30$
9	$4\text{VO}_2^+ + 4\text{H}_2\text{O} = \text{V}_4\text{O}_{12}^{4-} + 8\text{H}^+$	$\log K_9 = -17.51$
10	$10\text{VO}_2^+ + 8\text{H}_2\text{O} = \text{V}_{10}\text{O}_{28}^{6-} + 16\text{H}^+$	$\log K_{10} = -16.15$
11	$10\text{VO}_2^+ + 8\text{H}_2\text{O} = \text{HV}_{10}\text{O}_{28}^{5-} + 15\text{H}^+$	$\log K_{11} = -10.35$
12	$10\text{VO}_2^+ + 8\text{H}_2\text{O} = \text{H}_2\text{V}_{10}\text{O}_{28}^{4-} + 14\text{H}^+$	$\log K_{12} = -6.75$

$$\begin{aligned}
C_V &= [\text{VO}_2^+] + [\text{VO}_3^-] + [\text{VO}_4^{3-}] + [\text{HVO}_4^{2-}] \\
&\quad + [\text{H}_2\text{VO}_4^-] + [\text{H}_3\text{VO}_4] + 2[\text{V}_2\text{O}_7^{4-}] + 2[\text{HV}_2\text{O}_7^{3-}] \\
&\quad + 3[\text{V}_3\text{O}_9^{3-}] + 4[\text{V}_4\text{O}_{12}^{4-}] + 10[\text{V}_{10}\text{O}_{28}^{6-}] \\
&\quad + 10[\text{HV}_{10}\text{O}_{28}^{5-}] + 10[\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}] \\
&= [\text{VO}_2^+] (1 + k_1[\text{H}^+]^{-2} + k_2[\text{H}^+]^{-4} + k_3[\text{H}^+]^{-3} \\
&\quad + k_4[\text{H}^+]^{-2} + k_5[\text{H}^+]^{-1} + 2[\text{VO}_2^+]k_6[\text{H}^+]^{-6} \\
&\quad + 2[\text{VO}_2^+]k_7[\text{H}^+]^{-5} + 3[\text{VO}_2^+]^2k_8[\text{H}^+]^{-6} \\
&\quad + 4[\text{VO}_2^+]^3k_9[\text{H}^+]^{-8} + 10[\text{VO}_2^+]^9k_{10}[\text{H}^+]^{-16} \\
&\quad + 10[\text{VO}_2^+]^9k_{11}[\text{H}^+]^{-15} + 10[\text{VO}_2^+]^9k_{12}[\text{H}^+]^{-14}).
\end{aligned} \tag{6}$$

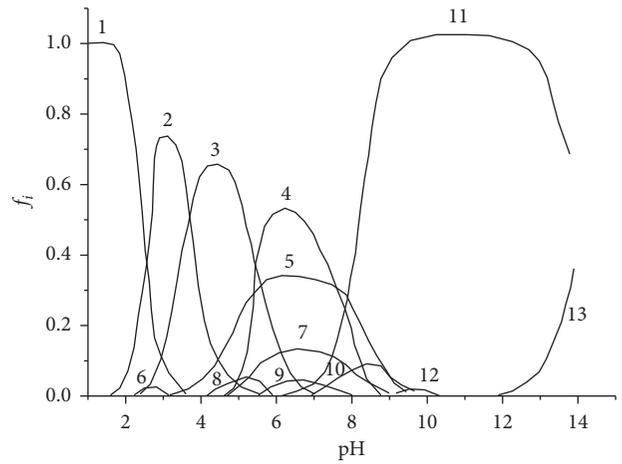
Analogous relations are valid for other vanadates. Under this approach, for $-\Delta G_S > 0$, the solid phase is thermodynamically unstable to dissolution according to Reaction (1) and vice versa; if $-\Delta G_S < 0$, the dissolution of the solid phase takes place.

3. Results and Discussion

Within the pH range where the solid phase (oxide) is thermodynamically unstable (dissolves), it is necessary to determine the areas of predominance of the soluble species in solution. In the presence of polynuclear species, it is necessary to calculate the partial molar fractions of the species as a function of pH and C_V . The last ones for vanadium compounds (V), for example, are determined in the following way [7]:

$$f_{ijn} = \frac{j[H_i V_j O_n]}{C_V} = \frac{j[H_i V_j O_n]}{\sum_i \sum_j \sum_n j[H_i V_j O_n]}. \tag{7}$$

The results of calculating these functions for vanadium (V) compounds for $C_V = 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ as a function of pH are shown in Figure 1. Based on these results, it is easy to determine the thermodynamic stability of the species in the solution as a function of pH and C_V . As one can see, in acidic media, within the pH range between 2.4 and 5.5, the species



- | | | |
|---|---|-----------------------------------|
| 1 - VO_2^+ | 6 - $\text{H}_3\text{V}_{10}\text{O}_{28}^{3-}$ | 10 - $\text{HV}_2\text{O}_7^{3-}$ |
| 2 - $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ | 7 - $\text{H}_2\text{V}_2\text{O}_7^{2-}$ | 11 - HVO_4^{2-} |
| 3 - $\text{HV}_{10}\text{O}_{28}^{5-}$ | 8 - $\text{V}_{10}\text{O}_{28}^{6-}$ | 12 - $\text{V}_2\text{O}_7^{4-}$ |
| 4 - $\text{V}_4\text{O}_{12}^{4-}$ | 9 - $\text{V}_5\text{O}_{15}^{5-}$ | 13 - VO_4^{3-} |
| 5 - H_2VO_4^- | | |

FIGURE 1: Partial molar fractions of the vanadium V(V) species for $C_V = 1 \cdot 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

$\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$ and $\text{HV}_{10}\text{O}_{28}^{5-}$ are dominant. In alkaline solutions, after $\text{pH} > 8$, the HVO_4^{2-} species prevail.

The obtained data (Figure 1) correlate well with existing experimental evidences. It is well known that high-field NMR gives high-quality structural data and quantitative information about speciation and concentration of a large variety of species in aqueous solvents [9]. Consequently, NMR ^{51}V spectroscopy measurements [10] confirm the speciation of vanadium (V) in aqueous vanadate solutions as a function of pH and vanadate concentrations. As seen in Figure 1, in alkaline solutions, tetrahedrally coordinated vanadates, metavanadate, and pyrovanadate are abundant. Decavanadate only forms when metavanadate is added to solutions of pH 3 or less. Acidification of metavanadate solutions to pH 4 or lower polymerizes all the oligomers to form V_{10} . Readjusting the pH near to 8 produces a depolymerization of V_{10} to form V_2 , V_4 , and V_5 , as it has been stated in [11–13]. As the pH of metavanadate solutions increases, V_1 and V_2 become the predominant species [14]. As reported Ralston et al. [15], in the basic pH (between 8 and 9) solution, $\text{V}_4\text{O}_{12}^{4-}$ and HVO_4^{2-} (or $\text{VO}_3(\text{OH})^{2-}$) coexist. Orthovanadates VO_4^{3-} dominate at a solution pH greater than 13 [16]. As highly basic solutions are acidified to pH values between 9 and 12, orthovanadate tetrahedral units can combine to form pyrovanadates $\text{V}_2\text{O}_7^{4-}$, $\text{HV}_2\text{O}_7^{3-}$, and HVO_4^{2-} , which are colorless [16]. Continued acidification to pH values between 6 and 9 leads to the formation of colorless or yellow metavanadates $\text{V}_4\text{O}_{12}^{4-}$, $\text{V}_5\text{O}_{15}^{5-}$, H_3VO_4 , and H_2VO_4^- [16, 17]. Additional acidification to pH between 2 and 6 causes the coordination of vanadium to change from tetrahedral to octahedral. A combination of ten octahedral units forms the decavanadate ions $\text{V}_{10}\text{O}_{28}^{6-}$, $\text{HV}_{10}\text{O}_{28}^{5-}$, and $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$, leading to orange or red solutions [16, 17].

Pervanadyl VO_2^+ is yellow and dominates at dilute concentrations in strongly acidic solutions, at pH 1.0–2.5 (Figure 1).

The calculated dependence of ΔG_S on pH for $C_V = C_{Ca} = 1 \text{ mol}\cdot\text{L}^{-1}$ for different calcium polyvanadates are shown in Figure 2.

The intersection points of the curves correspond to the boundaries of the stability areas of the respective salts. For two salts, e.g., 1 and 2, the Gibbs energy values in the given conditions are $\Delta G_S(1)$ and $\Delta G_S(2)$; in the case $-\Delta G_S(1) < -\Delta G_S(2)$, salt 1 is thermodynamically more stable, and vice versa; for $-\Delta G_S(1) > -\Delta G_S(2)$, salt 1 must transform into salt 2. In the case $\Delta G_S(1) = \Delta G_S(2)$, equilibrium is established. In Figures 3–5, the $\Delta G_S(\text{pH})$ dependence for different calcium, strontium, and barium polyvanadates are displayed for several C_V and C_{Me} values. For simplicity, only the lower boundaries of the ΔG_S values are shown.

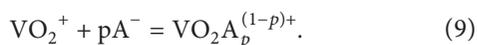
As it is evident from Figures 2–5, the thermodynamic stability of polyvanadates towards each other strongly depends on pH and total alkaline earth metal and vanadium concentrations. The most insoluble compounds are barium polyvanadates in comparison with calcium and strontium ones. With decrease in the C_V and C_{Me} concentrations, the polyvanadates become thermodynamically unstable to dissolution. From Figures 3–5, one can see that alkaline earth metal polyvanadates are thermodynamically instable when $C_V = C_{Me} \leq 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ for all the examined pH values, excepting barium polyvanadates in very acidic solutions (pH < 3.3). The last fact is not reflected in the $\log C_V = f(\log[\text{H}^+])$ and $\log C_M = f(\log[\text{H}^+])$ diagrams, that is, the main priority of the criterion proposed in this paper for assessing the thermodynamic stability of alkaline earth metal polyvanadates. The existing experimental data [4, 5, 18–20] confirm the results on the thermodynamic stability of polyvanadates obtained in this paper.

The effect of temperature on the thermodynamics stability of hydrocomplexes $\text{H}_i\text{V}_j\text{O}_n$ and solubility of polyvanadates for different temperatures are estimated on the basis of van't Hoff equation [7]:

$$\log K_2 = \frac{\log K_1 + (1/T_1 - 1/T_2)\Delta H}{2.303R} \quad (8)$$

The appropriate values of the standard enthalpies ΔH can be found in handbooks available everywhere [21–27]. Usually, it is supposed that $T_1 = 298.15 \text{ K}$ and the temperature insignificantly influences the ΔH values within the investigated temperature interval.

Vanadium in inorganic media (a mixture of an inorganic acids and their salts) may form complexes with such anions such as SO_4^{2-} , Cl^- etc. Note that the sulphate medium is important due to its industrial applications [28–32]. Schematically, if L^- denotes the ligand, the reaction of complex formation may be written as follows:



The thermodynamic equilibrium formation constant of VO_2SO_4^- at 25°C is equal to $\log K = 1.30 \pm 0.02$ [28].

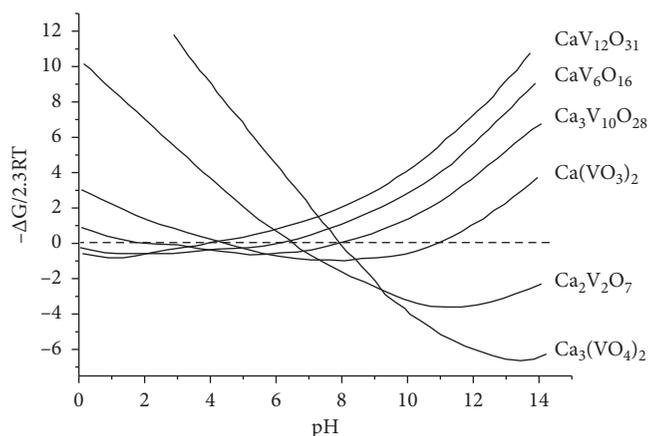


FIGURE 2: ΔG_S versus pH for different CaO–V₂O₅–H₂O systems at $C_V = C_{Ca} = 1 \text{ mol}\cdot\text{L}^{-1}$.

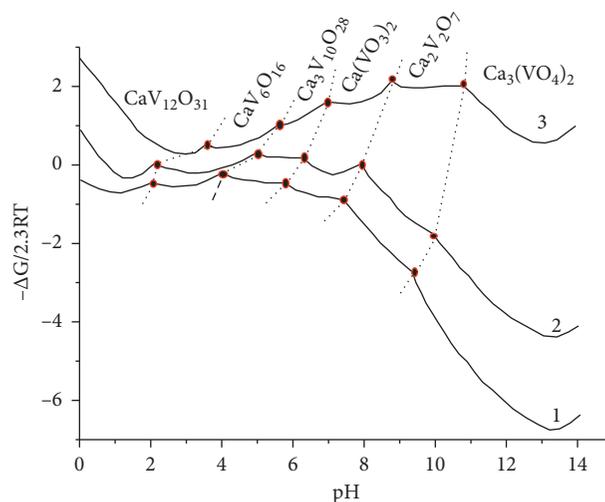


FIGURE 3: ΔG_S versus pH for different CaO–V₂O₅–H₂O systems: (1) $C_V = C_{Ca} = 1 \text{ mol}\cdot\text{L}^{-1}$; (2) $C_V = C_{Ca} = 1 \times 10^{-1} \text{ mol}\cdot\text{L}^{-1}$; (3) $C_V = C_{Ca} = 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

Consequently, the VO_2SO_4^- complexes may form in the presence of a large excess of ligand, $C_{\text{SO}_4} \gg C_V$. The contribution of anions of aqueous electrolytes on the thermodynamics stability of soluble and insoluble species can be taken into account through the alpha coefficient, in the form described in Equation (6) [7, 8].

4. Conclusions

- (i) A thermodynamic method for calculating the global Gibbs energy variation for describing heterogeneous equilibria of transformations of polyvanadates of calcium, strontium, and barium, that occur in systems $\text{MeO-V}_2\text{O}_5\text{-H}_2\text{O}$, where Me is the alkaline earth element, has been developed and applied.
- (ii) Its quintessence consists in the thermodynamic analysis of the real conditions of various processes on the basis of their total thermodynamic

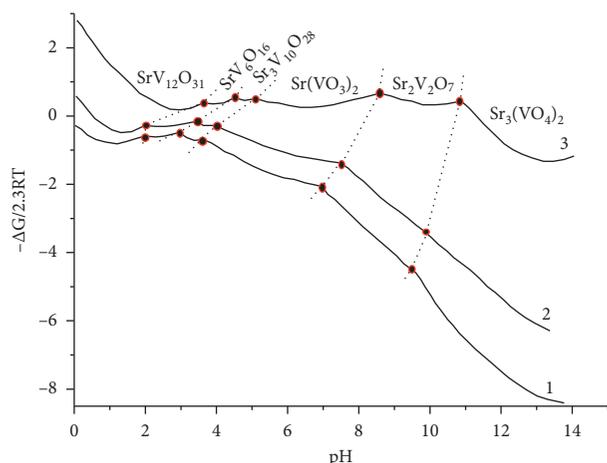


FIGURE 4: ΔG_S versus pH for different SrO- V_2O_5 - H_2O systems: (1) $C_V = C_{Sr} = 1 \text{ mol}\cdot\text{L}^{-1}$; (2) $C_V = C_{Sr} = 1 \times 10^{-1} \text{ mol}\cdot\text{L}^{-1}$; (3) $C_V = C_{Sr} = 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

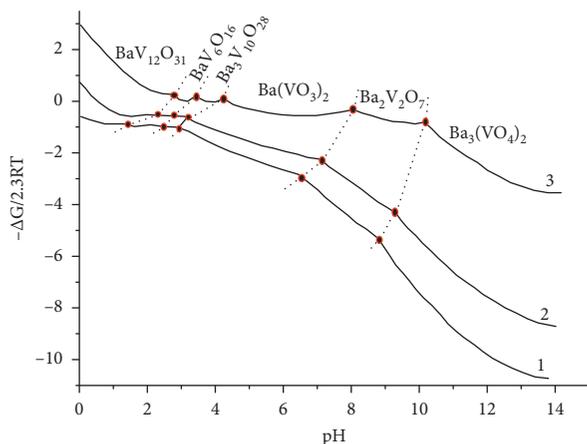


FIGURE 5: ΔG_S versus pH for different BaO- V_2O_5 - H_2O systems: (1) $C_V = C_{Ba} = 1 \text{ mol}\cdot\text{L}^{-1}$; (2) $C_V = C_{Ba} = 1 \times 10^{-1} \text{ mol}\cdot\text{L}^{-1}$; (3) $C_V = C_{Ba} = 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$.

characteristics. On the basis of the selected thermodynamic data for involved soluble and insoluble species, the thermodynamic stability areas of solid polyvanadates towards the solution pH and vanadium and alkaline earth metal ion concentrations in heterogeneous mixtures have been established, taking into account the complex formation reactions in multicomponent heterogeneous systems.

- (iii) The calcium, strontium, and barium polyvanadates are dissolved for $C_V = C_{Me} \leq 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ for all the examined pH values.
- (iv) The thermodynamic stability of soluble species as function of pH and C_V has been determined.
- (v) The obtained results, based on the thermodynamic analysis and graphical design of the calculated data, are in good agreement with the available experimental data.

Data Availability

The standard Gibbs energies of formation of chemical species used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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