

Thermodynamics of Lanthanum Uranovanadate

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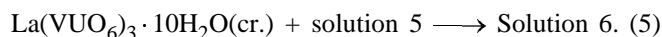
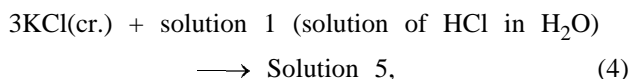
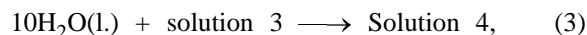
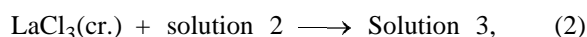
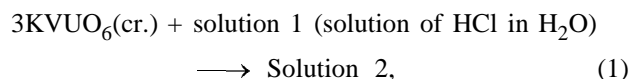
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Abstract—Temperature dependence of heat capacity in the range 80–300 K, as well as absolute entropy and standard formation enthalpy, entropy, and Gibbs function at 298.15 K were determined for $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$ by reaction and adiabatic vacuum calorimetry. Thermodynamic characteristics of dehydration, synthesis, and solution of the compound were calculated.

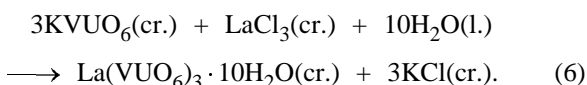
In [1] we have considered the structure, physico-chemical properties, and formation of crystalline lanthanum uranovanadate decahydrate. In this work we determined thermodynamic properties of this compound by means of reaction and adiabatic vacuum calorimetry and gave a thermodynamic description of the most practically important processes involving $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$.

To calculate the standard formation enthalpy of $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$, we determined the enthalpies ($\Delta_f H^0$) of reactions (1)–(5) of a number of compounds with 4 M aqueous hydrochloric acid at 298.15 K in a reaction adiabatic calorimeter.



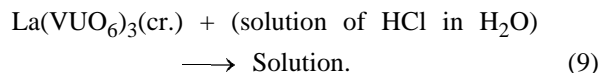
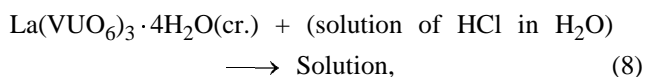
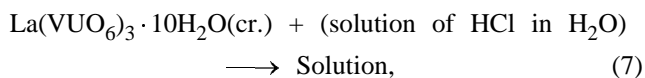
The following average values were obtained, each by the results of three parallel measurements, kJ: $\Delta_f H_1^0 -75.9 \pm 6.9$, $\Delta_f H_2^0 -14.7 \pm 1.5$, $\Delta_f H_3^0 \sim 0$, $\Delta_f H_4^0 61.11 \pm 0.78$, and $\Delta_f H_5^0 -95.4 \pm 4.0$.

Reactions (1)–(5) formed true solutions. Moreover, reagent ratios were selected so that the compositions of solutions (4) and (6) were identical. In view of this fact, the algebraic sum of reactions [(1 + 2 + 3) – (4 + 5)] gives reaction (6) whose enthalpy is $\Delta_f H_6^0 = \Delta_f H_1^0 + \Delta_f H_2^0 + \Delta_f H_3^0 - \Delta_f H_4^0 - \Delta_f H_5^0 = -56.3 \pm 8.0$ kJ.

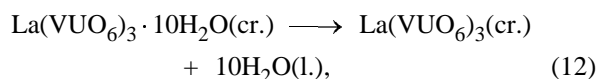
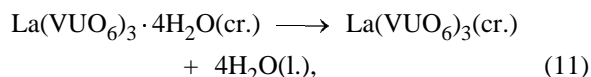
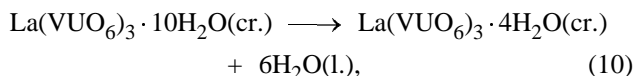


Then, by the Hess law, the standard enthalpy of formation of lanthanum uranovanadate is determined as follows: $\Delta_f H^0[298, \text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O, cr.}] = \Delta_f H_6^0 + 3\Delta_f H^0(298, \text{KVUO}_6, \text{cr.}) + \Delta_f H^0(298, \text{LaCl}_3, \text{cr.}) + 10\Delta_f H^0(298, \text{H}_2\text{O, l.}) - 3\Delta_f H^0(298, \text{KCl, cr.})$. Using this expression, the enthalpy of reaction (6), and the standard formation enthalpies of its participants at 298.15 K ($\text{KVUO}_6 -2451 \pm 9$ [2], $\text{LaCl}_3 -1071.1 \pm 0.8$ [3], $\text{H}_2\text{O} -285.83 \pm 0.04$ [3], $\text{KCl} -436.56 \pm 0.25$ kJ mol⁻¹ [3]), we obtained $\Delta_f H^0[298, \text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O, cr.}] -10029 \pm 28$ kJ mol⁻¹.

To calculate the enthalpies of partial (to tetrahydrate which is rather stable at atmospheric humidity [1]) and complete dehydration of $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$, we determined the standard enthalpies of reactions (7)–(9).



The following average values were obtained, each by the results of three parallel measurements, kJ: $\Delta_f H_7^0 -95.4 \pm 4.0$, $\Delta_f H_8^0 -147.9 \pm 4.0$, and $\Delta_f H_9^0 -212.9 \pm 4.0$. The algebraic differences of reactions (7)–(8), (8)–(9), and (7)–(9) give reactions (10)–(12).



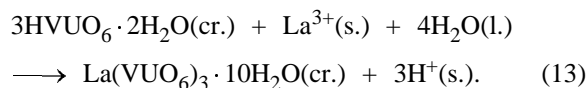
Taking into account that the difference in the enthalpies of dilution with water of crystallization for solutions obtained in the reactions are negligible, the enthalpies of reactions (10)–(12) are, according to the Hess law, kJ: $\Delta_f H_{10}^0$ 52.5, $\Delta_f H_{11}^0$ 65.0, and $\Delta_f H_{12}^0$ 117.5 or, per 1 mol of liberated liquid water, kJ: 9.0, 16.0, and 12.0, respectively. These results show that the energy of intermolecular interaction between water of crystallization and the compound is insignificant and increases as the number of the water molecules decreases.

To determine the absolute entropy of lanthanum uranovanadate decahydrate, we measured the isobaric heat capacity (C_p^0) of the compound in the range 80–300 K in a vacuum adiabatic calorimeter. The heat capacity of $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$ steadily increases over the whole range, exhibiting no apparent anomalies within the measurement error (0.2–0.3%). The heat capacities below 80 K were calculated by the Kelley–Parks method [4] using the equation $C_p^0[\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}] = (A + BT)C_p^0[\text{KVUO}_6]$. Its coefficients A (3.7593) and B (9.478×10^{-3}) were calculated by the least-squares method from the C_p^0 values for lanthanum and potassium uranovanadates at 80–100 K. The resulting equation describes the heat capacity of $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$ with an uncertainty of 0.3%. We believed that the error of the description at lower temperatures is no higher than this value. The choice of potassium uranovanadate as reference was defined by its structural similarity to the lanthanum compound [1] and by the availability of its experimental heat capacities in the range 5–300 K [5]. This way of extrapolation for structural analogs brings a fairly small contribution to the values of thermodynamic functions up to ~300 K [4].

The enthalpy of heating [$H^0(T) - H^0(0)$] and the absolute entropy $S^0(T)$ of $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$ were calculated by numerical integration of the dependences $C_p^0 = f(T)$ and $(C_p^0 T^{-1}) = f(T)$ in the range 0–300 K. The Gibbs function [$G^0(T) - H^0(0)$] of heating of the compound was calculated by the Gibbs–Helmholtz equation. The heat capacities and standard thermodynamic functions of $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}$ are listed in the table. From the standard formation entropy of lanthanum uranovanadate: $\Delta_f S^0[298, \text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}, \text{cr.}] -3342 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K and the entropies of the corresponding elements {in $\text{J mol}^{-1} \text{ K}^{-1}$: $\text{La}(\text{cr.})$ 56.90 ± 0.84 , $\text{V}(\text{cr.})$ 28.91 ± 0.33 , $\text{U}(\text{cr.})$ 50.21 ± 0.17 , $\text{H}_2(\text{g.})$ 130.570 ± 0.033 , and $\text{O}_2(\text{g.})$ 205.037 ± 0.033 [3]} we obtained the absolute entropy of lanthanum uranovanadate $\Delta_f S^0[298, \text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}, \text{cr.}] -3342 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$. From the standard formation enthalpy and entropy of the compound we calculated its stan-

dard formation Gibbs function at 298.15 K: $\Delta_f G^0[298, \text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}, \text{cr.}] -9033 \pm 29 \text{ kJ mol}^{-1}$.

The resulting thermodynamic functions of lanthanum uranovanadate allow us to characterize quantitatively, in particular, two most important processes with its participation, namely, synthesis [reaction (13)] and solution in water.



Thus, using the $\Delta_f H^0(298)$ and $\Delta_f G^0(298)$ values for the participants of reaction (13): $\text{HVUO}_6 \cdot 2\text{H}_2\text{O}$ (-2754.0 ± 5.5 and $-2476.5 \pm 6.0 \text{ kJ mol}^{-1}$ [6]), La^{3+} (-707.1 ± 0.6 and $682.9 \pm 2.0 \text{ kJ mol}^{-1}$ [3]) and H_2O (-285.83 ± 0.04 and $-237.18 \pm 0.05 \text{ kJ mol}^{-1}$ [3]), we could estimate the standard enthalpy (83 kJ), Gibbs function (28 kJ), and equilibrium constant (1×10^{-5}) of this reaction at 298.15 K.

The results obtained show that reaction (13) is endothermic. In our opinion, this is explained by a high dehydration enthalpy of the La^{3+} ion (4648 kJ mol^{-1} [7]). Partial dehydration occurs when this ion inserts into $\text{HVUO}_6 \cdot 2\text{H}_2\text{O}$. Despite of a fairly high positive entropy [$185 \text{ J mol}^{-1} \text{ K}^{-1}$], the equilibrium of reaction (13) at 298.15 K is almost completely displaced toward starting compounds. According to our experimental observations [1], this reaction can only be effected at 80–100°C. Actually, from the thermodynamic characteristics of the reaction at 100°C, calculated under the assumption $\Delta \nu C_p^0 = \text{const}$ [8] [$\Delta_f H_{13}^0(373)$ 77.0 $\Delta_f G_{13}^0(373)$ 15 kJ, K_{13} 8×10^{-3}], it follows that the considered temperature rise increases the equilibrium constant by three orders of magnitude, thus increasing the yield of the target reaction product.

The solubility of lanthanum uranovanadate in water (298.15 K, p 1 atm) was calculated by numerical equilibrium simulation using the GIBBS program complex [9]. According to the calculation results, the solubility of the compound is $2.5 \times 10^{-7} \text{ mol/kg H}_2\text{O}$ (the equilibrium pH is 7.18). It is known that the solubility of hexavalent uranium compounds in aqueous solutions is appreciably affected by carbon dioxide. In this connection we calculated the solubility of lanthanum uranovanadate in the presence of carbon dioxide at $p(\text{CO}_2)$ 10^{-3} atm which corresponds to the partial atmospheric pressure of CO_2 . The calculation showed that in the case in hand this value increases to $8.3 \times 10^{-7} \text{ mol/kg H}_2\text{O}$ (pH 5.56). The resulting data testify that the solubility of lanthanum uranovanadate in water is extremely low. It compares with the solubility of uranovanadates of mono- and

Heat capacities and thermodynamic functions of $\text{La}(\text{VUO}_6)_3 \cdot 10\text{H}_2\text{O}(\text{cr.})$

| $T, \text{ K}$ | C_p^0 , $\text{J mol}^{-1} \text{ K}^{-1}$ | $H^0(T) - H^0(0)$, kJ mol^{-1} | $S^0(T)$, $\text{J mol}^{-1} \text{ K}^{-1}$ | $-[G^0(T) - H^0(0)]$, kJ mol^{-1} |
|----------------|---|---|--|--|
| 0 | 0 | 0 | 0 | 0 |
| 5 | 1.868 | 0.003937 | 0.7776 | 0.000049 |
| 10 | 7.246 | 0.02453 | 3.330 | 0.008774 |
| 20 | 37.51 | 0.2269 | 16.17 | 0.09646 |
| 30 | 82.49 | 0.8212 | 39.65 | 0.3684 |
| 40 | 132.0 | 1.891 | 70.08 | 0.9125 |
| 50 | 183.7 | 3.466 | 105.0 | 1.785 |
| 60 | 237.6 | 5.575 | 143.3 | 3.024 |
| 70 | 283.9 | 8.186 | 183.5 | 4.658 |
| 80 | 327.5 | 11.24 | 224.2 | 6.696 |
| 90 | 377.2 | 14.80 | 266.1 | 9.147 |
| 100 | 419.5 | 18.79 | 308.0 | 12.02 |
| 110 | 463.4 | 23.20 | 350.0 | 15.31 |
| 120 | 509.4 | 28.06 | 392.4 | 19.02 |
| 130 | 550.8 | 33.37 | 434.8 | 23.16 |
| 140 | 590.5 | 39.07 | 477.1 | 27.71 |
| 150 | 628.1 | 45.17 | 519.1 | 32.70 |
| 160 | 665.0 | 51.63 | 560.8 | 38.10 |
| 170 | 707.5 | 58.49 | 602.4 | 43.91 |
| 180 | 751.7 | 65.79 | 644.1 | 50.14 |
| 190 | 794.5 | 73.52 | 685.9 | 56.79 |
| 200 | 837.6 | 81.68 | 727.7 | 63.86 |
| 210 | 882.8 | 90.28 | 769.7 | 71.35 |
| 220 | 925.5 | 99.33 | 811.7 | 79.25 |
| 230 | 964.2 | 108.8 | 853.8 | 87.58 |
| 240 | 1000.0 | 118.6 | 895.5 | 96.33 |
| 250 | 1031.0 | 128.8 | 937.0 | 105.5 |
| 260 | 1059.0 | 139.2 | 978.0 | 115.1 |
| 270 | 1081.0 | 149.9 | 1018.4 | 125.0 |
| 273.15 | 1087.9 | 153.3 | 1031.0 | 128.3 |
| 180 | 1102.0 | 160.8 | 1058.1 | 135.4 |
| 190 | 1123.0 | 172.0 | 1097.1 | 146.2 |
| 298.15 | 1138.0 | 181.2 | 1128.5 | 155.3 |
| 300 | 1141.0 | 183.3 | 1135.5 | 157.4 |

bivalent metals [10, 11] and is slightly lower than that of $\text{HVO}_6 \cdot 2\text{H}_2\text{O}$, which, alongside with heating, also favors displacement of equilibrium (13) to the right.

EXPERIMENTAL

Lanthanum uranovanadate was synthesized from $\text{HVO}_6 \cdot 2\text{H}_2\text{O}$ and 0.1 M $\text{La}(\text{NO}_3)_3$ by ion-exchange reaction (13) at 80°C within 24 h. For better crystallinity the sample was subjected to hydrothermal treatment (150°C, reactor charge coefficient 0.5). The synthesis of $\text{HVO}_6 \cdot 2\text{H}_2\text{O}$ has been described in [12]. The elemental composition and phase purity were controlled by electron microscopy on a Philips

SEM-515 instrument with an EDAX-9900 energy-dispersion analyzer (accuracy 2–5 at. %) and by X-ray diffraction (DRON-3.0 diffractometer).

Thermochemical measurements were performed using a modernized calorimeter designed by S.M. Skuratov. The experiments were carried out in a two-vessel thin-wall Teflon ampule; weighed samples were placed in the inner vessel, whereas the outer vessel was charged with a solution of hydrochloric acid. The reagents were mixed by knocking out the bottom of the inner vessel. The temperature was measured with a platinum resistance thermometer and an SHCH-516 digital voltmeter. Adiabatic conditions

were maintained automatically. The systematic bias was estimated in a series of experiments on the determination of the enthalpy of solution of potassium chloride of special purity grade in twice distilled water. The total error in the enthalpies did not exceed 1.5–2.0%.

Heat capacity measurements were performed in an adiabatic vacuum calorimeter [13]. The compound was placed in a platinum ampule ($V\ 7.5\ \text{cm}^3$). The temperature was measured with a platinum resistance thermometer. The calorimeter was calibrated by measuring the heat capacity of an ampule filled with helium up to a pressure of 8.5 kPa. The measurement procedure was tested using benzoic acid of K-1 brand as reference. The heat capacities of benzoic acid, measured in the range 80–300 K, fitted the reference values within 0.3–0.2%. The scatter of the experimental heat capacities of lanthanum uranovanadate about the fitting curve was the same.

ACKNOWLEDGMENTS

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