Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 643–646. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 705–708.

Thermodynamics of Lanthanum Uranovanadate

N. V. Karyakin, E. V. Suleimanov, A. V. Knyazev, and V. V. Veridusova

Lobachevskii Nizhni Novgorod State University, Nizhni Novgorod, Russia

Received May, 22, 2002

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 $La(VUO_6)_3 \cdot 10H_2O$ 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, physicochemical 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 $La(VUO_6)_3 \cdot 10H_2O$.

To calculate the standard formation enthalpy of $La(VUO_6)_3 \cdot 10H_2O$, we determined the enthalpies ($\Delta_r H^0$) of reactions (1)–(5) of a number of compounds with 4 M aqueous hydrochloric acid at 298.15 K in a reaction adiabatic calorimeter.

$$3KVUO_6(cr.) + \text{solution 1 (solution of HCl in } H_2O) \longrightarrow \text{Solution 2}, \quad (1)$$

$$LaCl_3(cr.) + \text{solution 2} \longrightarrow \text{Solution 3}, \quad (2)$$

$$10H_2O(l.) + \text{solution 3} \longrightarrow \text{Solution 4}, \quad (3)$$

$$3KCl(cr.) + \text{solution 1 (solution of HCl in } H_2O) \longrightarrow \text{Solution 5}, \quad (4)$$

$$La(VUO_6)_3 \cdot 10H_2O(cr.) + \text{solution 5} \longrightarrow \text{Solution 6}. \quad (5)$$

The following average values were obtained, each by the results of three parallel measurements, kJ: $\Delta_r H_1^0$ –75.9 ± 6.9, $\Delta_r H_2^0$ –14.7 ± 1.5, $\Delta_r H_3^0$ ~0, $\Delta_r H_4^0$ 61.11 ± 0.78, and $\Delta_r H_5^0$ –95.4 ± 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 $\Delta_r H_6^0 = \Delta_r H_1^0 + \Delta_r H_2^0 + \Delta_r H_3^0 - \Delta_r H_4^0 - \Delta_r H_5^0 = -56.3 \pm 8.0$ kJ.

$$3KVUO_6(cr.) + LaCl_3(cr.) + 10H_2O(l.) \longrightarrow La(VUO_6)_3 \cdot 10H_2O(cr.) + 3KCl(cr.). \quad (6)$$

Then, by the Hess law, the standard enthalpy of formation of lanthanum uranovanadate is determined as follows: $\Delta_f H^0[298, La(VUO_6)_3 \cdot 10H_2O, cr.] = \Delta_r H_6 + 3\Delta_f H^0(298, KVUO_6, cr.) + \Delta_f H^0(298, LaCl_3, cr.) + 10\Delta_f H^0(298, H_2O, l.) - 3\Delta_f H^0(298, KCl, cr.)$. Using this expression, the enthalpy of reaction (6), and the standard formation enthalpies of its participants at 298.15 K ($KVUO_6$ –2451 ± 9 [2], $LaCl_3$ –1071.1 ± 0.8 [3], H_2O –285.83 ± 0.04 [3], KCl –436.56 ± 0.25 kJ mol^{-1} [3]), we obtained $\Delta_f H^0[298, La(VUO_6)_3 \cdot 10H_2O, cr.]$ –10029 ± 28 kJ mol^{-1}.

To calculate the enthalpies of partial (to tetrahydrate which is rather stable at atmospheric humidity [1]) and complete dehydration of $La(VUO_6)_3 \cdot 10H_2O$, we determined the standard enthalpies of reactions (7)–(9).

$$La(VUO_6)_3 \cdot 10H_2O(cr.) + (\text{solution of HCl in } H_2O) \longrightarrow \text{Solution}, \quad (7)$$

$$La(VUO_6)_3 \cdot 4H_2O(cr.) + (\text{solution of HCl in } H_2O) \longrightarrow \text{Solution}, \quad (8)$$

$$La(VUO_6)_3(cr.) + (\text{solution of HCl in } H_2O) \longrightarrow \text{Solution}. \quad (9)$$

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

$$La(VUO_6)_3 \cdot 10H_2O(cr.) \longrightarrow La(VUO_6)_3 \cdot 4H_2O(cr.) + 6H_2O(l.), \quad (10)$$

$$La(VUO_6)_3 \cdot 4H_2O(cr.) \longrightarrow La(VUO_6)_3(cr.) + 4H_2O(l.), \quad (11)$$

$$La(VUO_6)_3 \cdot 10H_2O(cr.) \longrightarrow La(VUO_6)_3(cr.) + 10H_2O(l.), \quad (12)$$

1070-3632/04/7405-0643 ©2004 MAIK "Nauka/Interperiodica"

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: $\Delta_r H^0_{10}$ 52.5, $\Delta_r H^0_{11}$ 65.0, and $\Delta_r H^0_{12}$ 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^0_p) of the compound in the range 80–300 K in a vacuum adiabatic calorimeter. The heat capacity of $La(VUO_6)_3 \cdot 10H_2O$ 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 $C^0_p[La(VUO_6)_3 \cdot 10H_2O] = (A + BT)C^0_p[KVUO_6]$. Its coefficients A (3.7593) and B (9.478×10^{-3}) were calculated by the least-squares method from the C^0_p values for lanthanum and potassium uranovanadates at 80–100 K. The resulting equation describes the heat capacity of $La(VUO_6)_3 \cdot 10H_2O$ 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 $La(VUO_6)_3 \cdot 10H_2O$ were calculated by numerical integration of the dependences $C^0_p = f(T)$ and $(C^0_p T^{-1}) = f(T)$ 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 $La(VUO_6)_3 \cdot 10H_2O$ are listed in the table. From the standard formation entropy of lanthanum uranovanadate: $\Delta_f S^0$[298, $La(VUO_6)_3 \cdot 10H_2O$, cr.] $–3342 \pm 5$ J mol^{-1} K^{-1} at 298.15 K and the entropies of the corresponding elements {in J mol^{-1} K^{-1}: La(cr.) 56.90 ± 0.84, V(cr.) 28.91 ± 0.33, U(cr.) 50.21 ± 0.17, H_2(g.) 130.570 ± 0.033, and O_2(g.) 205.037 ± 0.033 [3]} we obtained the absolute entropy of lanthanum uranovanadate $\Delta_f S^0$[298, $La(VUO_6)_3 \cdot 10H_2O$, cr.] $–3342 \pm 5$ J mol^{-1} K^{-1}. From the standard formation enthalpy and entropy of the compound we calculated its standard formation Gibbs function at 298.15 K: $\Delta_f G^0$[298, $La(VUO_6)_3 \cdot 10H_2O$, cr.] $–9033 \pm 29$ 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.

$$3HVUO_6 \cdot 2H_2O(cr.) + La^{3+}(s.) + 4H_2O(l.) \longrightarrow La(VUO_6)_3 \cdot 10H_2O(cr.) + 3H^+(s.). \quad (13)$$

Thus, using the $\Delta_f H^0(298)$ and $\Delta_f G^0(298)$ values for the participants of reaction (13): $HVUO_6 \cdot 2H_2O$ ($–2754.0 \pm 5.5$ and $–2476.5 \pm 6.0$ kJ mol^{-1} [6]), La^{3+} ($–707.1 \pm 0.6$ and 682.9 ± 2.0 kJ mol^{-1} [3]) and H_2O ($–285.83 \pm 0.04$ and $–237.18 \pm 0.05$ 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 $HVUO_6 \cdot 2H_2O$. Despite of a fairly high positive entropy [185 J mol^{-1} 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 $\Delta\nu C^0_p$ = const [8] [$\Delta_r H^0_{13}(373)$ 77.0 $\Delta_r G^0_{13}(373)$ 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 2.5×10^{-7} mol/kg H_2O (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 $p(CO_2)$ 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 8.3×10^{-7} mol/kg H_2O (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 $La(VUO_6)_3 \cdot 10H_2O$(cr.)

T, K	C_p^0, J mol^{-1} K^{-1}	$H^0(T) - H^0(0)$, kJ mol^{-1}	$S^0(T)$, J mol^{-1} 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 $HVUO_6 \cdot 2H_2O$, which, alongside with heating, also favors displacement of equilibrium (13) to the right.

EXPERIMENTAL

Lanthanum uranovanadate was synthesized from $HVUO_6 \cdot 2H_2O$ and 0.1 M $La(NO_3)_3$ 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 $HVUO_6 \cdot 2H_2O$ 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).

Termochemical 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 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

The work was financially supported by the Russian Foundation for Basic Research (project no. 02-03-33055).

REFERENCES

1. Chernorukov, N.G., Suleimanov, E.V., Knyazev, A.V., and Klimov, E.J., *Radiokhimiya,* 1999, vol. 41, no. 6, p. 481.
2. Karyakin, N.V., Chernorukov, N.G., Suleimanov, E.V., and Haryushina, E.A., *Zh. Obshch. Khim.*, 1992, vol. 62, no. 5, p. 972.
3. *Termicheskie konstanty veshchestv* (Thermal Constants of Substances), Glushko, V.P., Ed., Moscow: Nauka, 1965–1981, issues 1–10.
4. Kelley, K.K., Parks G.S., and Huffman H.M., *J. Phys. Chem.,* 1929, vol. 33, no. 12, p. 1802.
5. Karyakin, N.V., Chernorukov, N.G., Suleimanov, E.V., and Mochalov, L.A., *Zh. Obshch. Khim.,* 1996, vol. 66, no. 1, p. 3.
6. Karyakin, N.V., Chernorukov, N.G., Suleimanov, E.V., Alimzhanov, M.I., Trostin V.L., and Knyazev A.V., *Zh. Fiz. Khim.*, 2000, vol. 74, no. 8, p. 1366.
7. Krestov, G.A., *Termokhimiya soedinenii redkozemel'nykh i aktinoidnykh elementov* (Thermochemistry of Rare-Earth and Actinoid Compounds), Moscow: Atomizdat, 1972.
8. Karyakin, N.V., *Khimicheskaya termodinamika* (Chemical Thermodynamics), Nizhni Novgorod: Izd. Nizhegorod. Gos. Univ., 1992, part 2.
9. Shvarov, J.V., *Geokhimiya,* 1999, vol. 37, no. 6, p. 646.
10. Chernorukov, N.G., Suleimanov, E.V., and Nipruk, O.V., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 7, p. 1064.
11. Chernorukov, N.G., Suleimanov, E.V., Nipruk, O.V., and Lizunova, G.M., *Radiokhimiya,* 2001, vol. 43, no. 2, p. 119.
12. Chernorukov, N.G., Suleimanov, E.V., Knyazev, A.V., and Alimzhanov, M.I., *Zh. Neorg. Khim.,* 1999, vol. 44, no. 9, p. 1425.
13. Karyakin, N.V., Chernorukov, N.G., Suleimanov, E.V., Alimzhanov, M.I., and Trostin, V.L., *Zh. Fiz. Khim.*, 2000, vol. 74, no. 4, p. 581.