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Aluminum dihydrogen tripolyphosphate: Thermodynamic characteristics

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ABSTRACT

For the first time solution enthalpies of Al, H_3PO_4, and $AlH_2P_3O_{10} \times 2H_2O$ in 2 mol dm^{-3} NaOH have been measured as following: $\Delta_{sol}H^\circ_1 = -404.75 \pm 4.36$ kJ mol^{-1}; $\Delta_{sol}H^\circ_2 = -189.48 \pm 0.54$ kJ mol^{-1}; $\Delta_{sol}H^\circ_3 = -238.95 \pm 3.32$ kJ mol^{-1}. On the basis of experimental data the standard molar enthalpy of formation and enthalpies of some reactions with participation of $AlH_2P_3O_{10} \times H_2O$ were calculated. The enthalpy of interaction of Al with H_3PO_4 is $\Delta_rH^\circ = -734.24 \pm 5.56$ kJ mol^{-1}. It was established that according to thermodynamic data Al_2O_3 can react with H_3PO_4 forming investigated compound at 513 K. Employed compound ($AlH_2P_3O_{10} \times H_2O$) can react with H_2O with formation of $AlPO_4$ and phosphorous acid. All the data were obtained for the first time.

1. Introduction

Layer materials with low-dimensional structure have wide set of unique properties such as ion exchange, ionic conductivity, intercalation, catalytic activity and other [1–11]. For the reason the compounds are applied in different fields of technique. In papers [1,3,5,8] the series of materials with composition $M^{III}H_2P_3O_{10} \times 2H_2O$ (where M^{III} = Al, Ga, Fe, Mn, V, Cr), which have layer structure, is examined. Aluminum dihydrogen tripolyphosphate which belongs to these classes of materials is already used as a new non-toxic white anticorrosive pigment for painting. For perspective application it is necessary to investigate physicochemical properties of $AlH_2P_3O_{10} \times 2H_2O$ in detail. In paper [1] the structure of the compound was studied for the first time. It was enough difficult to determine the structure of aluminum dihydrogen tripolyphosphate because it has complex structure.

To optimize processes of synthesis of above mentioned compound it is useful to know thermodynamic data. Thermodynamic characteristics allow one to predict interaction with different external reagents, for example, with water, to study compound stability, decomposition, etc. Consideration of literature papers showed that there are no data on thermodynamics of aluminum dihydrogen tripolyphosphate. In paper [8] the conductivity and stability of $AlH_2P_3O_{10} \times 2H_2O$ were studied. Authors [8] showed that in vapor water above mentioned compound transfer first of all in $Al(H_2PO_4)_3$ and then in $AlPO_4$.

In our paper we for the first time investigated the thermodynamic properties of aluminum dihydrogen tripolyphosphate by solution calorimetry, namely, we measured solution enthalpy, standard molar enthalpy of formation and enthalpies of reactions. In future we plan to measure thermodynamic functions for compounds $M(III)H_2P_3O_{10} \times 2H_2O$ (M(III) is metal of third group) to construct dependence "thermodynamic property-structural property". Knowledge of these relations is very important to understand the nature of properties change [12].

2. Experimental part

2.1. Synthesis and identification of sample

We used sample of $AlH_2P_3O_{10} \times 2H_2O$ which was prepared and characterized in paper [1]. $AlH_2P_3O_{10} \times 2H_2O$ was prepared from H_3PO_4 and Al_2O_3 [1]. Phosphorous acid and aluminum oxide was mixed in ratio 6:1 and heated up to 513 K (t = 24 h). Then mixture was slowly cooled to room temperature during 48 h. Forming white microcrystalline product was washed with water. According to data [1] the sample has layer structure and the layers appear to be held together by a hydrogen bonding network, principally involving the presence of two water molecules per formula unit

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within the interlamellar region, which are each hydrogen bonded to the hydroxyl groups of the hydrogen triphosphate.

Identification of sample was performed by power X-ray diffraction [1]. Rietveld analysis was performed using the GSAS program. According to power data the compound $AlH_2P_3O_{10} \times 2H_2O$ has monoclinic structure (space group P2/c) with lattice parameters: a = 0.79381(3) nm, b = 0.49188(2) nm, c = 1.16286(4) nm, β = 95.739(2)°, V = 0.45178(4) nm^3. Detailed information about structure is presented in paper [1].

Sample $AlH_2P_3O_{10} \times 2H_2O$ was characterized by chemical analysis as well. For the analysis of Al, P an atomic absorption method was used. CHN analyzator Evrovector 600 was used to determine H content. We used obtained sample, Aluminum (>99%) and phosphorous acid (Aldrich, 85%) to perform calorimetric experiments. Detailed information is presented in Table 1.

2.2. Thermochemical cycle

We have chosen solution calorimetry as method of investigation to obtain thermochemical properties of aluminum dihydrogen tripolyphosphate. For this aim it was necessary to select solvent in such a way that $AlH_2P_3O_{10} \times 2H_2O$ and initial components are solved in solvent. We checked that $AlH_2P_3O_{10} \times 2H_2O$ was not solved in hydrochloric acid but solved in NaOH. To construct thermochemical cycle we tried to solve Al_2O_3 in NaOH but it was impossible. So, we have chosen calorimetric cycle in such a way that Al and H_3PO_4 are solved in NaOH. The schema is presented in Table 2. 2 mol dm^{-3} NaOH have been chosen to perform experiments.

All experiments with aluminum were performed in dry box. It was made to avoid interaction of aluminum with oxygen and air moisture. Dry box was filled by argon. The procedure was following. Aluminum tape (99.99%) was placed into dry box. Further aluminum was crushed by special way, preliminary weighed using balance located in dry box. Then aluminum was placed in weighed glass ampoules. After that ampoules were closed by special caps, took out from box and soldered. The weight of aluminum was determined as difference of empty ampoule and ampoule with substance.

After we choose NaOH as solvent it was necessary to select concentration of alkali. Concentration should be so that all substances were dissolved with enough speed for measurements. The investigated substance ($AlH_2P_3O_{10} \times 2H_2O$) and phosphoric acid are dissolved in alkali (since 1 mol dm^{-3} concentration) very quickly (about 5 min). The crushed aluminum is dissolved since 2 mol dm^{-3} of alkali within 10 min. For this reason 2 mol dm^{-3} NaOH was selected as solvent.

2.3. Experimental technique

The enthalpies of solution were measured in the calorimeter that has been described in papers [13–16]. The calorimeter was constructed as Dewar glass vessel (250 cm^3) placed in a brass capsule. The calorimeter was closed hermetically by cover which made of brass and covered with Teflon. The thermometer for measurement of calorimeter temperature, the device for broken and washing of calorimetric ampoules, the mixer for hashing of liquid placed in calorimeter, and the heater for carrying out calibration were placed on cover. Resistance of thermometer was measured by the precision voltmeter (Schlumberger firm) Solartron 7061. Power on the heater was given by means of the precision regulator of power. Voltage and current were measured by the second precision Solartron 7061 voltmeter. The device for broken of ampoules and the heater was symmetrized to avoid the errors connected with location of heat source and calibration source (see paper [17]).

The repeatability of calorimeter on heat equivalent was 0.03% (it is standard uncertainty). Dissolution of potassium chloride in water was performed to check operation of calorimeter. The obtained dissolution heat of KCl was 17.41 ± 0.08 kJ mol^{-1} (the molality of the final solution was 0.028 mol kg^{-1}, T = 298.15 K). The type of uncertainty presented by us for dissolution enthalpy of KCl is standard uncertainty. The literature data is: 17.42 ± 0.02 kJ mol^{-1}) [18]. As it is possible to see the value which we measured is in a good agreement with literature data.

Table 2
Reaction scheme for the formation enthalpy of $AlH_2P_3O_{10} \times 2H_2O$ from Al and $H_3PO_4 \times 0.96H_2O$ at the temperature 298.15 K and pressure p = 0.1 MPa. $\Delta_rH°_4 = \Delta_{sol}H°_1 + 3\Delta_{sol}H°_2 - \Delta_{sol}H°_3$. Solution 1 is 2 mol dm^{-3} NaOH.[a]

Nr	Reaction	$\Delta_rH°_m$/ kJ mol^{-1}
1	Al + solution 1 = solution 2 + 1.5H_2	$\Delta_{sol}H°_1$
2	3($H_3PO_4 \times 0.96H_2O$) + solution 2 = solution 3 + 2.88H_2O	$3\Delta_{sol}H°_2$
3	$AlH_2P_3O_{10} \times 2H_2O$ + solution 1 = solution 3	$\Delta_{sol}H°_3$
4	Al + 3($H_3PO_4 \times 0.96H_2O$) = $AlH_2P_3O_{10} \times 2H_2O$ + 1.5H_2 + 2.88H_2O	$\Delta_rH°_4$

[a] Standard uncertainties u are $u(T)$ = 0.01 K, $u(p)$ = 0.05p, $u(c_{NaOH})$ = 0.003 mol dm^{-3}.

3. Results and discussion

Detail information on synthesis and identification of obtained compound is presented in paper [1]. Compound is individual phase with composition $AlH_2P_3O_{10} \times 2H_2O$.

We measured the following solution enthalpies for Al, H_3PO_4 (85%) and aluminum dihydrogen tripolyphosphate: $\Delta_{sol}H°_1$ = −404.75 ± 1.65 kJ mol^{-1}; $\Delta_{sol}H°_2$ = −189.48 ± 0.54 kJ mol^{-1}; $\Delta_{sol}H°_3$ = −238.95 ± 3.32 kJ mol^{-1}. $\Delta_{sol}H°_2$ was calculated for mole of 85% H_3PO_4 which equal to $H_3PO_4 \times 0.96H_2O$. Detail information is presented in Tables 3–5. The type of uncertainty presented by us here is standard uncertainty.

Table 1
Characterization of chemical samples used in this study.

Chemical name	Chemical formula	Source	State	Mass fraction purity
Aluminum dihydrogen tripolyphosphate	$AlH_2P_3O_{10} \times 2H_2O$	Synthesis	Solid	>0.99
Phosphorous acid (85 wt%)	$H_3PO_4 \times 0.96H_2O$	Aldrich	Liquid	>0.998
Aluminum	Al	Bolkan Eco Trader Ltd.	Solid	0.99
Sodium hydroxide	NaOH	Aldrich	Solid	>0.99

The following methods of analysis were used. $AlH_2P_3O_{10} \times 2H_2O$: atomic absorption method and CHN analysis; $H_3PO_4 \times 0.96H_2O$: atomic absorption method and CHN analysis; Al: atomic absorption and mass-spectrometry methods; NaOH: atomic absorption method and CHN analysis.
Atomic absorption method: spectrometer iCE3000; ways of atomization: flame, graphite furnace; methods of supply: aerosol; calibration by standard solutions; the standard uncertainty is 0.1–0.5%.
Mass-spectrometry method: EMAL-2 laser ionization mass spectrometer (F = 10–100 Hz, E = 1–10 MJ); detection limits: 10^{-4}–10^{-6} mass%; F – frequency, E – energy.
CHN analysis: analyzer Evrovector 600; standard Deviations: C – 0.065; H – 0.050.