Standard Molar Enthalpies of Formation for Ammonium/3d-Transition Metal Phosphates $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+})

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Ammonium/transition metal phosphate monohydrate $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}) compounds were synthesized by solid-state reaction at low temperature and characterized by X-ray diffraction (XRD), FT-IR, and chemical analysis. Based on Hess's law, the thermochemical cycles were designed for measuring the dissolution enthalpies of reactants and products using a solution-reaction isoperibol calorimeter at 298.15 K. From the dissolution enthalpies, the molar enthalpies of the five reactions designed were calculated individually. With these data and other auxiliary theromodynamic data, the standard molar enthalpies of formation of the title compounds were concluded as: $\Delta_f H_m^{\ominus}[NH_4MnPO_4 \cdot H_2O] = (-1925.01 \pm 0.25)$ kJ·mol^{-1}, $\Delta_f H_m^{\ominus}[NH_4CoPO_4 \cdot H_2O] = (-1754.91 \pm 0.43)$ kJ·mol^{-1}, $\Delta_f H_m^{\ominus}[NH_4NiPO_4 \cdot H_2O] = (-1755.48 \pm 0.39)$ kJ·mol^{-1}, and $\Delta_f H_m^{\ominus}[NH_4CuPO_4 \cdot H_2O] = (-1636.41 \pm 0.36)$ kJ·mol^{-1}.

Introduction

Ammonium/transition metal phosphates $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) have been investigated for over 50 years and have been widely applied as fertilizers, pigments for paint finishes for protection of metal, and fire retardants in paints or plastics.[1,2] They are a good source for macro- and micronutrients (P, N, Fe, Mn, Co, Cu, Zn) required by plants. Also, they show good flammability retarding performance both in the gas phase and in the condensed phase as a combined flame retardant. Recently, more attention has been paid to potential applications in ionic conductivity and catalyst and ionic exchange of these dittmarite-type compounds with a layered or tunnel structure. Their magnetic and intercalation properties have been investigated.[3–5] Considerable research interests are focused on new synthesis routes, particle structure, and molecular interaction of these compounds. Nieves Barros et al.[6] prepared $NH_4FePO_4 \cdot H_2O$ using a mild hydrothermal technique, and the effect of the addition of $NH_4FePO_4 \cdot H_2O$ on soil microbial activity was determined by calorimetry. Koleva[7,8] investigated the metal + water ($M^{2+} + H_2O$) hydrogen bonding and the vibrational behavior of the phosphate ions in these double phosphates for the first time. Although there have been structural and spectroscopic reports on these compounds, to our knowledge, little or no thermodynamic data are available.

Calorimetry is a universal technique widely used for the measurements of enthalpies of reaction, dissolution, dilution, and excess enthalpies in thermochemistry, which involves physical change, chemical reaction, and living biochemical metabolism in the fields of industrial and scientific research. The data of the standard molar enthalpy of formation play an important role in theoretical study, application development, and industrial production of a compound as a basis of theoretical analysis.

In our previous papers,[9,10] some metal phosphates, e.g., $NH_4MgPO_4 \cdot H_2O$ and NH_4ZnPO_4, have been prepared by solid-state reaction at room temperature. Their standard molar enthalpies of formation have also been reported. The present work is a continuation of the previous investigation on the phosphates, which deals with the synthesis of $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}) by a new method; namely, solid-state reaction at low temperature and their standard enthalpies of formation are calculated by calorimetry at 298.15 K. These fundamental thermodynamic data will be important for further studies of these compounds.

Experimental

Reagents. All the chemical reagents used were of analytical grade and made in China. KCl with purity higher than 99.99 % was dried in a vacuum oven for 6 h at 393 K prior to use.

Preparation and Characterization of $NH_4MPO_4 \cdot H_2O$. Ground $(NH_4)_3PO_4 \cdot 3H_2O$ and $MnSO_4 \cdot H_2O$, $CoSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, and $CuSO_4 \cdot 5H_2O$, respectively, were mixed together with a molar ratio of 1:1. The mixture was ground for 60 min after addition of nonion surfactant PEG-400 and then put into an oven at 40 °C for 48 h. The white crystals obtained were washed repeatedly with water until no SO_4^{2-} was detected in the filtrate. Then, the crystals were washed with ethanol and dried at 80 °C. The products were identified by XRD (D/max-2500V diffractometer, Japan) and chemical analysis for M^{2+}, P, and N content.

Calorimeter and Calibration. The isoperibol reaction calorimeter, described in detail elsewhere,[11,12] was used for the investigation. The calorimeter was calibrated by the dissolution enthalpy of KCl (calorimetric primary standard) in water at 298.15 K. The measured mean dissolution enthalpy was (17466 ± 25) J·mol^{-1} in agreement with the value of (17536 ± 9) J·mol^{-1} of ref 13.

Calorimetric Experiment. The chosen solvent for the calorimetric experiment should dissolve the chemicals in the sample

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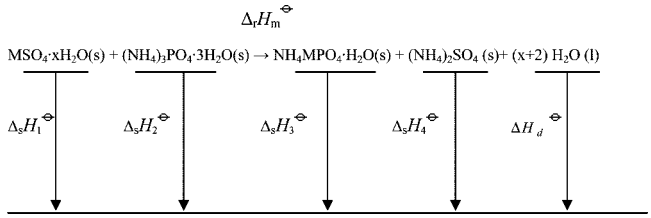

Figure 1. Scheme of the thermochemical cycle of $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}). In this work, $\Delta_s H_1^\ominus$, $\Delta_s H_2^\ominus$ are the dissolution enthalpies of two reactants in 4 mol·L^{-1} HCl at 298.15 K; $\Delta_s H_3^\ominus$, $\Delta_s H_4^\ominus$ are the dissolution enthalpies of two of the products in 4 mol·L^{-1} HCl at 298.15 K; $\Delta H_d^\ominus$ is the dilution enthalpy of water in 4 mol·L^{-1} HCl at 298.15 K; $\Delta_r H_m^\ominus$ is the enthalpy value for the designed reaction. Uncertainty $= \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)}$ in which n is the experiment times ($n = 5$); x_i is the experimental data of each measurement; and $\bar{x}$ means average of results.

Table 1. Chemical Analysis Results of $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+})

$NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+},-Cu^{2+})	determination		calculation			
	N/%	P/%	M^{2+}/%	N/%	P/%	M^{2+}/%
$NH_4MnPO_4 \cdot H_2O$	7.57	16.52	29.21	7.53	16.67	29.19
$NH_4CoPO_4 \cdot H_2O$	7.65	16.40	31.09	7.67	16.32	31.05
$NH_4NiPO_4 \cdot H_2O$	7.15	16.02	31.42	7.37	16.32	31.05
$NH_4CuPO_4 \cdot H_2O$	7.24	16.11	32.12	7.18	15.90	32.82

cell completely and rapidly, and the selection of the calorimetric solvent is very important. It has been found that the reactants and products could be dissolved completely in 4 mol·L^{-1} HCl to give the same final state. To obtain the standard enthalpy of formation for $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}), these compounds can be regarded as the product of reaction (1), and a thermochemical cycle has been designed, as shown in Figure 1. If the dissolution enthalpies of reactants ($\Delta_s H_1^\ominus$, $\Delta_s H_2^\ominus$) and products ($\Delta_s H_3^\ominus$, $\Delta_s H_4^\ominus$) were measured, the $\Delta_r H_m^\ominus$ and $\Delta_f H_m^\ominus$ of $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}) can be obtained with the aid of auxiliary data. According to Hess's law, $\Delta_r H_m^\ominus = \Delta_s H_1^\ominus + \Delta_s H_2^\ominus - \Delta_s H_3^\ominus - \Delta_s H_4^\ominus - n\Delta H_d^\ominus$ ($n = 3, 9, 8, 7$)

$$MSO_4 \cdot xH_2O(s) + (NH_4)_3PO_4 \cdot 3H_2O(s) \rightarrow NH_4MPO_4 \cdot H_2O(s) + (NH_4)_2SO_4(s) + (x+2)H_2O \quad (1)$$

Results and Discussion

Identification of Synthetic Sample. Table 1 lists the chemical analysis results of the titled compound for nitrogen, metal, and phosphorus. The results are in good agreement with the calculated values. The XRD patterns of the products are shown in Figures 2 to 5. The patterns match the standard XRD data. For $NH_4MnPO_4 \cdot H_2O$ (JC PDF50-0554), the XRD data are indexed as an orthorhombic system, with space group $Pmm2_1$: $a = 0.57289$ nm; $b = 0.88167$ nm; $c = 0.49098$ nm; and $V = 0.24799$ nm^3. For $NH_4CoPO_4 \cdot H_2O$ (JC PDF21-0793), the XRD data are indexed as an orthorhombic system, with space group $Pmm2_1$: $a = 0.5624$ nm; $b = 0.4801$ nm; $c = 0.8775$ nm; and $V = 0.23693$ nm^3 ($Z = 2$). For $NH_4NiPO_4 \cdot H_2O$ (JC PDF21-0034), the XRD data are indexed as an orthorhombic system, with space group $Pmm2_1$: $a = 0.5566$ nm; $b = 0.8760$ nm; $c = 0.4742$ nm; and $V = 0.23121$ nm^3 ($Z = 2$). For $NH_4CuPO_4 \cdot H_2O$ (JC PDF89-1303), the XRD data are indexed as a rhombic system, with space group PZ1/a: $a = 0.7390$ nm; $b = 0.7519$ nm; $c = 0.8650$ nm; and $V = 0.47923$ nm^3. All these results show the obtained products are pure $NH_4MPO_4 \cdot H_2O$ ($M = Mn^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}).

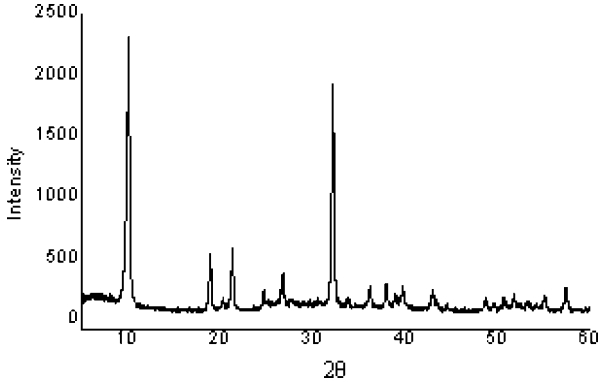

Figure 2. XRD of $NH_4MnPO_4 \cdot H_2O$.

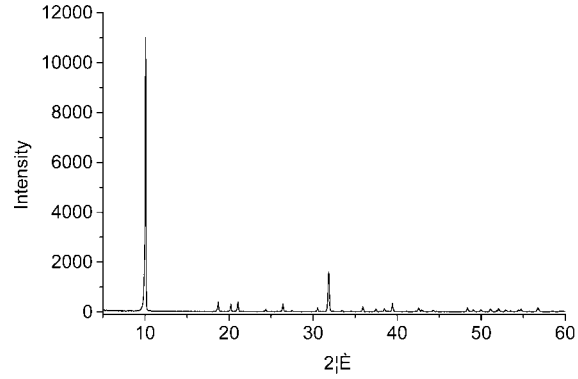

Figure 3. XRD of $NH_4CoPO_4 \cdot H_2O$.

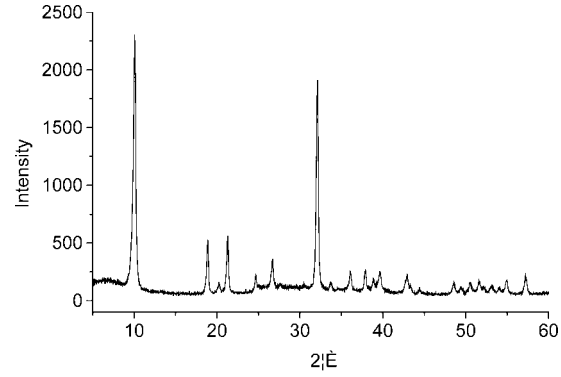

Figure 4. XRD of $NH_4NiPO_4 \cdot H_2O$.

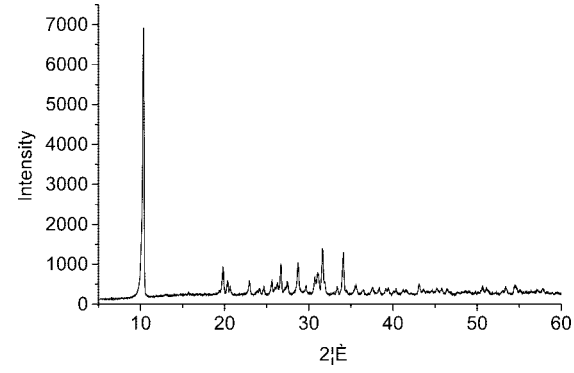

Figure 5. XRD of $NH_4CuPO_4 \cdot H_2O$.

Determination of the Molar Dissolution Enthalpies $\Delta_s H^\ominus$ and $\Delta_s H_2^\ominus$. Molar dissolution enthalpies of $MSO_4 \cdot xH_2O$ in 100 mL of 4 mol·L^{-1} HCl at 298.15 K have been measured,

Table 2. Dissolution Enthalpies of $MSO_4 \cdot xH_2O$(s) in 100 mL of 4 mol·L^{-1} HCl at 298.15 K

$MSO_4 \cdot xH_2O$	M/g	Q/J	$\Delta_s H_1^\Theta$/kJ·mol^{-1}
$MnSO_4 \cdot H_2O$	0.2535	(−4.134 ± 0.113)	(−2.570 ± 0.07)
$CoSO_4 \cdot 7H_2O$	0.4246	(69.972 ± 0.113)	(43.506 ± 0.07035)
$NiSO_4 \cdot 6H_2O$	0.3943	(56.603 ± 0.054)	(35.194 ± 0.034)
$CuSO_4 \cdot 5H_2O$	0.3745	(74.579 ± 0.090)	(46.372 ± 0.056)

Table 3. Dissolution Enthalpies of $NH_4PO_4 \cdot 3H_2O$(s) in 100 mL of 4 mol·L^{-1} HCl at 298.15 K

no.	$M(NH_4)_3PO \cdot 3H_2O$	Q/J	$\Delta_s H_2^\Theta$/kJ·mol^{-1}
1	0.3048	7.638	4.749
2	0.3048	7.670	4.769
3	0.3048	7.854	4.883
4	0.3048	7.634	4.746
5	0.3048	7.863	4.889
average		(7.732 ± 0.101)	(4.807 ± 0.073)

Table 4. Dissolution Enthalpies of $NH_4MPO_4 \cdot H_2O$(s) in 100 mL of 4 mol·L^{-1} HCl at 298.15 K

$NH_4MPO_4 \cdot H_2O$	M/g	Q/J	$\Delta_s H_3^\Theta$/kJ·mol^{-1}
$NH_4MnPO_4 \cdot H_2O$	0.2790	(−27.946 ± 0.085)	(−17.376 ± 0.053)
$NH_4CoPO_4 \cdot H_2O$	0.2850	(−41.149 ± 0.095)	(−25.585 ± 0.059)
$NH_4NiPO_4 \cdot H_2O$	0.2846	(−35.490 ± 0.116)	(−22.067 ± 0.072)
$NH_4CuPO_4 \cdot H_2O$	0.2918	(41.939 ± 0.143)	(13.039 ± 0.045)[a]

[a] The molar dissolution enthalpies for $NH_4CuPO_4 \cdot H_2O + (NH_4)_2SO_4$.

Table 5. Dissolution Enthalpies of $(NH_4)_2SO_4$(s) in 100 mL of 4 mol·L^{-1} HCl at 298.15 K

no.	$M(NH_4)_2SO_4$/g	Q/J	$\Delta_s H_4^\Theta$/kJ·mol^{-1}
1	0.1981	41.273	25.680
2	0.1982	41.252	25.649
3	0.1982	41.240	25.642
4	0.1981	41.385	25.750
5	0.1982	41.198	25.616
average			(25.668 ± 0.051)

as shown in Table 2 and Table 3. These results were calculated based on the average of five measurements.

Determination of the Molar Dissolution Enthalpies $\Delta_s H_3^\Theta$ and $\Delta_s H_4^\Theta$. The molar dissolution enthalpies of $NH_4MPO_4 \cdot H_2O$ (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}) and $(NH_4)_2SO_4$ in 4 mol·L^{-1} HCl at 298.15 K have been shown in Table 4 and Table 5. These results were calculated from the average of five measurements.

Calculation for the Standard Molar Enthalpies of Formation for $MnSO_4 \cdot H_2O$. With the aid of the auxiliary data in Table 6, the molar standard formation enthalpies of $MnSO_4 \cdot H_2O$ could be calculated from the dissolution enthalpies of these compounds through the designed eq 2. The results have been listed in Table 7.

$$\begin{aligned} &MnSO_4 \cdot H_2O(s) + H_2O(l) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + \\ &2H_2O(l)\Delta_{sol}H_m^\Theta[MnSO_4 \cdot H_2O(s)] = \Delta_f H_m^\Theta[Mn^{2+}(aq)] + \\ &\Delta_f H_m^\Theta[SO_4^{2-}(aq)] + \Delta_f H_m^\Theta[H_2O(l)] - \\ &\Delta_f H_m^\Theta[MnSO_4 \cdot H_2O(s)]\Delta_f H_m^\Theta[MnSO_4 \cdot H_2O(s)] = \\ &\Delta_f H_m^\Theta[Mn^{2+}] + \Delta_f H_m^\Theta[SO_4^{2+}] + \Delta_f H_m^\Theta[H_2O] - \\ &\Delta_{sol}H_m^\Theta[MnSO_4 \cdot H_2O(s)] = (-1380.70 \pm 0.08)\ \text{kJ·mol}^{-1} \end{aligned} \quad (2)$$

Calculation of ΔH_d. According to the literature,[15] the dilution enthalpies of 4.5 mmol, 10.5 mmol, 12 mmol, and 13.5 mmol of water in 100 mL of 4 mol·L^{-1} HCl at 298.15 K can be calculated as

$$\begin{aligned} \Delta H_{d(4.000 \rightarrow 3.996763)} &= \Delta H_{d(4.000 \rightarrow 0)} - \Delta H_{d(3.996763 \rightarrow 0)} \\ &= -4433.45 - (-4430.51) \\ &= -0.00294\ \text{kJ·mol}^{-1} \\ \Delta H_{d(4.000 \rightarrow 3.992454)} &= \Delta H_{d(4.000 \rightarrow 0)} - \Delta H_{d(3.992454 \rightarrow 0)} \\ &= -4433.45 - (-4426.58) \\ &= -0.00687\ \text{kJ·mol}^{-1} \\ \Delta H_{d(4.000 \rightarrow 3.991379)} &= \Delta H_{d(4.000 \rightarrow 0)} - \Delta H_{d(3.991379 \rightarrow 0)} \\ &= -4433.45 - (-4425.60) \\ &= -0.00785\ \text{kJ·mol}^{-1} \\ \Delta H_{d(4.000 \rightarrow 3.990304)} &= \Delta H_{d(4.000 \rightarrow 0)} - \Delta H_{d(3.990304 \rightarrow 0)} \\ &= -4433.45 - (-4424.62) \\ &= -0.00883\ \text{kJ·mol}^{-1} \end{aligned}$$

Table 6. Ancillary Data of Standard Enthalpies of Formation at 298.15 K

index	$\Delta_f H_m^\Theta$/kJ·mol^{-1}	refs
$CuSO_4 \cdot 5H_2O$(s)	−2279.65	14
$(NH_4)_2SO_4$(s)	−1180.9	14
Mn^{2+}	−220.75	14
$CoSO_4 \cdot 7H_2O$(s)	−2979.93	15
$NiSO_4 \cdot 6H_2O$(s)	−2682.823	15
SO_4^{2-}	−909.27	15
HCl(l)	(−92.31 ± 0.13)	16
H_2O(l)	(−285.830 ± 0.042)	16
$(NH_4)_3PO_4 \cdot 3H_2O$(s)	(−2554.114 ± 0.141)	17

Table 7. Enthalpies of Solution for $MnSO_4 \cdot H_2O$ in 100 mL of H_2O at 298.15 K

no.	M $MnSO_4 \cdot H_2O$/g	Q/J	$\Delta_{sol}H_m^\Theta$/kJ·mol^{-1}
1	0.0634	−14.170	−35.233
2	0.0634	−14.137	−35.151
3	0.0634	−14.148	−35.178
4	0.0634	−14.142	−35.162
5	0.0634	−14.095	−35.046
average			−35.154 ± 0.068

Calculation of Molar Enthalpy of Reaction and Standard Molar Enthalpies of Formation. Based on the obtained data, the molar enthalpy of reaction was calculated. From these values and using the various ancillary data in Table 5, the standard molar enthalpies of formation could also be calculated.

For $NH_4MnPO_4 \cdot H_2O$

$$\begin{aligned} \Delta_r H_m^\Theta &= \Delta_s H_1^\Theta + \Delta_s H_2^\Theta - \Delta_s H_3^\Theta - \Delta_s H_4^\Theta - 3\Delta H_d^\Theta \\ &= (-6.05 \pm 0.13)\ \text{kJ·mol}^{-1}\Delta_f H_m^\Theta[NH_4MnPO_4 \cdot H_2O] \\ &= \Delta_r H_m^\Theta + \Delta_f H_m^\Theta[MnSO_4 \cdot H_2O] + \\ &\quad \Delta_f H_m^\Theta[(NH_4)_3PO_4 \cdot 3H_2O] - \Delta_f H_m^\Theta[(NH_4)_2SO_4] - \\ &\quad 3\Delta_f H_m^\Theta[H_2O] \\ &= (-1925.01 \pm 0.25)\ \text{kJ·mol}^{-1} \end{aligned}$$

For $NH_4CoPO_4 \cdot H_2O$

$$\begin{aligned} \Delta_r H_m^\Theta &= \Delta_s H_1^\Theta + \Delta_s H_2^\Theta - \Delta_s H_3^\Theta - \Delta_s H_4^\Theta - 9\Delta H_d^\Theta \\ &= (48.31 \pm 0.13)\ \text{kJ·mol}^{-1}\Delta_f H_m^\Theta[NH_4CoPO_4 \cdot H_2O] \\ &= \Delta_r H_m^\Theta + \Delta_f H_m^\Theta[CoSO_4 \cdot 7H_2O] + \\ &\quad \Delta_f H_m^\Theta[(NH_4)_3PO_4 \cdot 3H_2O] - \Delta_f H_m^\Theta[(NH_4)_2SO_4] - \\ &\quad 9\Delta_f H_m^\Theta[H_2O] \\ &= (-1754.91 \pm 0.43)\ \text{kJ·mol}^{-1} \end{aligned}$$

For $NH_4NiPO_4 \cdot H_2O$

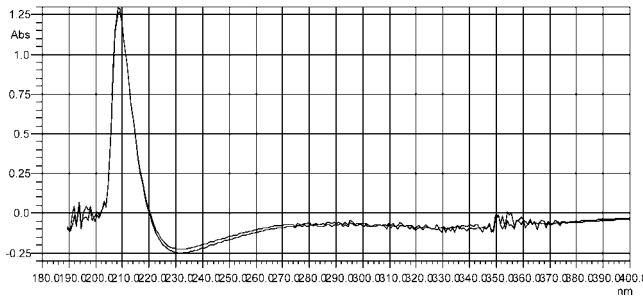

Figure 6. Ultraviolet absorption spectrometry of reactions and products in 100 mL of 4 mol·L^{-1} HCl for the thermochemical cycle of $NH_4Mn\ PO_4 \cdot H_2O$.

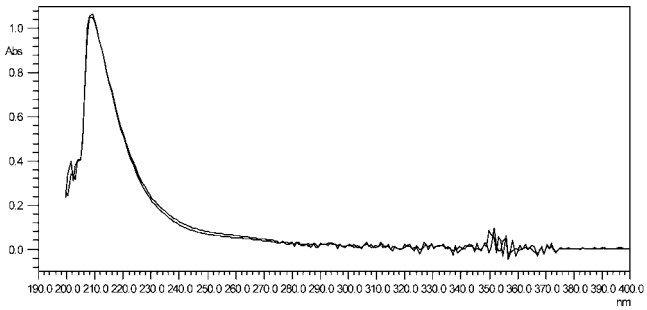

Figure 7. Ultraviolet absorption spectrometry of reactions and products in 100 mL of 4 mol·L^{-1} HCl for the thermochemical cycle of $NH_4CoPO_4 \cdot H_2O$.

$$H_m^{\ominus} = \Delta_s H_1^{\ominus} + \Delta_s H_2^{\ominus} - \Delta_s H_3^{\ominus} - \Delta_s H_4^{\ominus} - 8\Delta H_d^{\ominus}$$
$$= (36.46 \pm 0.13)\ \text{kJ}\cdot\text{mol}^{-1}\Delta_f H_m^{\ominus}[NH_4NiPO_4 \cdot H_2O]$$
$$= \Delta_r H_m^{\ominus} + \Delta_f H_m^{\ominus}[NiSO_4 \cdot 6H_2O] + \Delta_f H_m^{\ominus}[(NH_4)_3PO_4 \cdot 3H_2O] - \Delta_f H_m^{\ominus}[(NH_4)_2SO_4] - 8\Delta_f H_m^{\ominus}[H_2O]$$
$$= (-1755.48 \pm 0.39)\ \text{kJ}\cdot\text{mol}^{-1}$$

For $NH_4CuPO_4 \cdot H_2O$

$$\Delta_r H_m^{\ominus} = \Delta_s H_1^{\ominus} + \Delta_s H_2^{\ominus} - \Delta_s H_3^{\ominus} - \Delta_s H_4^{\ominus} - 7\Delta H_d^{\ominus}$$
$$= (38.19 \pm 0.13)\ \text{kJ}\cdot\text{mol}^{-1}\Delta_f H_m^{\ominus}[NH_4CuPO_4 \cdot H_2O]$$
$$= \Delta_r H_m^{\ominus} + \Delta_f H_m^{\ominus}[CuSO_4 \cdot 5H_2O] + \Delta_f H_m^{\ominus}[(NH_4)_3PO_4 \cdot 3H_2O] - \Delta_f H_m^{\ominus}[(NH_4)_2SO_4] - 7\Delta_f H_m^{\ominus}[H_2O]$$
$$= (-1636.41 \pm 0.36)\ \text{kJ}\cdot\text{mol}^{-1}$$

Determination of the Final State of the Reaction. The UV–vis spectra (see Figures 6 to 9) of the final solution of the reactants and the products could also be used to determine whether they have the same thermodynamic state. In the present experiments, reactant 1 was dissolved in 100 mL of 4 mol·L^{-1} HCl. Then reactant 2 was dissolved in the resulting solution. (1.5n) mmol (n = 3, 9, 8, 7) of water was added to 100 mL of 4 mol·L^{-1} HCl. Then, product 2 was dissolved in the resulting solution. Then, product 1 was dissolved in the resulting solution. The ultraviolet absorption spectrometry of the solution obtained by dissolving the reactant or the product in 100 mL of 4 mol·L^{-1} HCl completely overlaps with the maximum absorption wavelength. All these results show both the reactant and the product have the same dissolved state to ensure realization of the thermochemistry cycle.[18] Therefore, we believed these standard enthalpies determined by solution-reaction calorimetry were reliable.

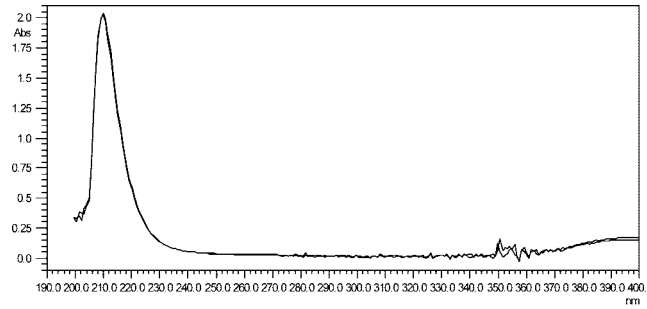

Figure 8. Ultraviolet absorption spectrometry of reactions and products in 100 mL of 4 mol·L^{-1} HCl for the thermochemical cycle of $NH_4NiPO_4 \cdot H_2O$.

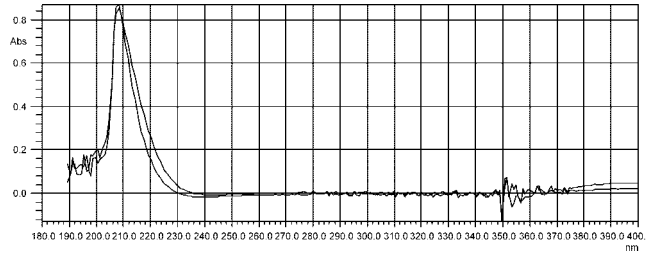

Figure 9. Ultraviolet absorption spectrometry of reactions and products in 100 mL of 4 mol·L^{-1} HCl for the thermochemical cycle of $NH_4CuPO_4 \cdot H_2O$.

Conclusions

Solid-state reaction at low temperature can be used to prepare $NH_4MPO_4 \cdot H_2O$ (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}). By designing thermochemical cycles, the standard molar enthalpies of formation of these four compounds are calculated as follow: $\Delta_f H_m^{\ominus}(NH_4MnPO_4 \cdot H_2O) = (1925.01 \pm 0.25)$ kJ·mol^{-1}, $\Delta_f H_m^{\ominus}(NH_4CoPO_4 \cdot H_2O) = (-1754.91 \pm 0.43)$ kJ·mol^{-1}, $\Delta_f H_m^{\ominus}(NH_4NiPO_4 \cdot H_2O) = (-1755.48 \pm 0.39)$ kJ·mol^{-1}, and $\Delta_f H_m^{\ominus}(NH_4CuPO_4 \cdot H_2O) = (-1636.41 \pm 0.36)$ kJ·mol^{-1}. Standard formation enthalpies of these phosphates increase with a decrease in the ionic radius of 3d-transition metal.

Literature Cited

(1) Erskine, A. M.; Grimm, G.; Horning, S. C. Ammonium Ferrous Phosphate. *Ind. Eng. Chem.* **1944**, *36*, 456–460.

(2) Carling, S. G.; Day, P.; Visser, D. Dimensionality crossovers in the Magnetization of The Canted Antiferromagnets $NH_4MnPO_4 \cdot H_2O$ and $ND_4MnPO_4 \cdot D_2O$. *Solid State Commun.* **1993**, *88*, 135–138.

(3) Vidal, B.; Jose, T. Crystallochemical Properties of $NH_4(Fe_{1-x}Mn_x)PO_4 \cdot H_2O$. *J. Agric. Food Chem.* **1994**, *42*, 105–107.

(4) Greedan, J. E.; Reubenbauer, K.; Birchall, T.; Ehlert, M.; Corbin, D. R.; Subramanian, M. A. Magnetic and Mossbauer Study of The Layered Compound $(NH_4)Fe(PO_4) \cdot H_2O$. *J. Solid State Chem.* **1988**, *77*, 376–388.

(5) Neeraj, S.; Noy, M. L.; Cheetham, A. K. Structure and Magnetic Properties of A Three-dimensional Framework Manganese(II) Phosphate, $[NH_4][Mn_4(PO_4)_3]$. *Solid State Sci.* **2002**, *4*, 397–404.

(6) Nieves, B.; Claudio, A.; Jose, A. S.; Beatriz, R.; Aranzazu, E.; Jose, R. G. Calorimetric Determination of The Effect of Ammonium-iron(II) Phosphate Monohydrate on Rhodic Eutrudox Brazilian Soil. *Thermochim. Acta* **2006**, *441*, 89–95.

(7) Koleva, V. G. Metal-water Interactions and Hydrogen Bonding in Dittmarite-type Compounds $M'M''PO_4 \cdot H_2O$ ($M' = K^+$, NH_4^+; $M'' = Mn^{2+}$, Co^{2+}, Ni^{2+}): Correlations of IR Spectroscopic and Structural Data. *Spectrochim. Acta Part A* **2005**, *62*, 1196–1202.

(8) Koleva, V. G. Vibrational Behavior of The Phosphates Ions in Dittmarite-type Compounds $M'M''PO_4 \cdot H_2O$ ($M' = K^+$, NH_4^+; $M'' = Mn^{2+}$, Co^{2+}, Ni^{2+}). *Spectrochim. Acta Part A* **2007**, *66*, 413–418.

(9) Wu, J.; Yuan, A. Q.; Huang, Z. Y.; Song, B. L.; Liao, S. Thermochemical Study on The Chiral Sodium Zincophosphate Nanocrystalline. *Chin. J. Chem.* **2006**, *24*, 453–456.

(10) Yuan, A. Q.; Liao, S.; Tong, Zh. F.; Wu, J.; Huang, Z. Y. Synthesis of Nanocrystalline Zinc Phosphate Dihydrate by Solid State Reaction

at Room Temperature and Its Thermochemical Study. *Mater. Lett.* **2006**, *60*, 2110–2114.

(11) Qu, S. S.; Wang, T. Z.; Liu, Y.; Wen, D. C.; Yu, Y.; Li, L. W.; Li, Q. G. A Thermochemical Study of The Reactions of 8-hydroxyquinoline With $Co(Ac)_2 \cdot 4H_2O$ and $Zn(Ac)_2 \cdot 2H_2O$. *Thermochim. Acta* **2002**, *381*, 61–64.

(12) Gao, Sh. L.; Fang, Y.; Chen, S. P.; Hu, R. Z.; Shi, Q. Zh. Crystallization Kinetics of $Zn(Leu)SO_4 \cdot 0.5H_2O$ in Mixed Solvent of Water and Acetone. *Acta Chim. Sin.* **2002**, *60*, 2220–2224.

(13) Montgomery, R. L.; Melaugh, R. A.; Lau, C.-C.; Meier, G. H.; Chan, H. H.; Rossini, F. D. Determination of The Energy Equivalent of a Water Solution Calorimeter With a Standard Substance. *J. Chem. Thermodyn.* **1977**, *9*, 915–924.

(14) Weast R. C. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC Press Inc: FL, 1988/1989.

(15) Dean, J. A. *Lange's Handbook of Chemistry (11th)*; McGraw-Hill: New York, 1973.

(16) Wagman, D. D.; Evans, W. H.; Parker, V. B. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Data*, **1982**.

(17) Yuan, A. Q.; Wu, J.; Chen, J.; Liang, R. L.; Huang, Z. Y.; Tong, Z. F. Thermochemical Properties and Decomposition Kinetic of Nanocrystalline NH_4ZnPO_4. *Chin. J. Appl. Chem.* **2007**, *24*, 12–16.

(18) Li, Q. G.; Qu, S. S.; Liu, Y. A Thermochemical Study on The Coordination Complex of Lanthanum Trichloroacetic Acid With 8-hydroxyquinoline. *Thermochim. Acta* **2001**, *376*, 101–107.

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