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A thermochemical study of hexaoxoiodata(VII) hydrates of the type $M_2HIO_6{\cdot}nH_2O$, where M=Cd, Cu, Zn

Xu Mingfei[a], Wan Hongwen[a,*], Hu Juncheng[a], Wang Tianzhi[a], QU Songsheng[b]

[a]Department of Chemistry, Central China Normal University, Wuhan 430079, PR China
[b]Department of Chemistry, Wuhan University, Wuhan 430072, PR China

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Abstract

The following reactions

$$2Zn(Ac)_2\cdot 2H_2O\ (s) + H_5IO_6\ (s) \rightarrow Zn_2HIO_6\cdot 1.25H_2O\ (s) + 4HAc\ (l) + 2.75H_2O\ (l)$$

$$2Cd(Ac)_2\cdot 2H_2O\ (s) + H_5IO_6\ (s) \rightarrow Cd_2HIO_6\cdot 1.25H_2O\ (s) + 4HAc\ (l) + 1.25H_2O\ (l)$$

$$2Cu(Ac)_2\cdot H_2O\ (s) + H_5IO_6\ (s) \rightarrow Cu_2HIO_6\cdot 2H_2O\ (s) + 4HAc\ (l)$$

have been studied. The molar dissolution enthalpies of the reactants and products in a certain solvent (3 M l^{-1} HNO_3) of this three reaction have been measured using an isoperibol calorimeter at 298 K. From these values, combined with auxiliary values, the standard molar formation enthalpies of $Zn_2HIO_6{\cdot}1.25H_2O$ (s), (298.2 K), $Cd_2HIO_6{\cdot}1.25\ H_2O$ (s), (298.2 K) and $Cu_2HIO_6{\cdot}2H_2O$ (s), (298.2 K) have been determined to be $\Delta_f H_m^\theta$ ($Zn_2HIO_6{\cdot}1.25\ H_2O$ (s), 298.2 K) $= -1342.11$ kJ mol^{-1}, $\Delta_f H_m^\theta$ ($Cd_2HIO_6{\cdot}1.25H_2O$ (s), 298.2 K) $= -1405.49$ kJ mol^{-1} and $\Delta_f H_m^\theta$ ($Cu_2HIO_6{\cdot}2H_2O$ (s), 298.2 K) $= -1226.08$ kJ mol^{-1}.

Keywords: Periodates; Standard molar formation enthalpy; Ispoperibel calorimetry

1. Introduction

Interest in the study of periodates has been prompted by the valuable properties they possess as electrical and corrosion inhibitions, and in chemical analyses, etc. [1]. But the current status of thermodynamic data on the periodates is far from satisfactory. The synthesis of the periodates of the type $M_2HIO_6{\cdot}nH_2O$ (M^{II}=Cu, Zn, Cd; n=2,1.25,1.25) has been described [2–3] and the solubility and related thermodynamic parameters of these periodates was reported [4]. However, the enthalpies of these substances have not been determined. The purpose of the present study is to determine the dissolution enthalpies of the reagents and products in the respective synthesis reaction. The standard molar formation enthalpies of these substances has been derived from the respective dissolution enthalpies.

2. Experimental

2.1. Chemical

All the chemicals (including the H_5IO_6, HAc, $Zn(Ac)_2{\cdot}2H_2O$, $Cd(Ac)_2{\cdot}2H_2O$, $Cu(Ac)_2{\cdot}H_2O$, HNO_3 and KCl) used were A.R. grade.

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[*] Corresponding author.

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KCl (obtained from Shanghai Reagent Factory), had a purity greater than 99.99%, and was dried in a vacuum oven for 6 h at 408 K prior to use.

2.2. Preparations and the calorimetric solvent

$Zn_2HIO_6 \cdot 1.25H_2O$ and $Cd_2HIO_6 \cdot 1.25H_2O$, were prepared and analyzed according to the method given in [2]. $Cu_2HIO_6 \cdot 2H_2O$ was prepared and analyzed according to the method given in [3]. $3\ M\ l^{-1}$ HNO_3 was chosen as calorimetric solvent for all the chemicals.

2.3. Calorimeter and calibration

All calorimetric determination were carried out in an isoperibol calorimeter as described previously [5]. The solution enthalpies of KCl in water and THAM (NBS 742a, USA) in $0.1000\ M\ l^{-1}$ HCl were determined to check the precision of the calorimetric system. The measured dissolution enthalpy of KCl (s) in water at 298.2K was 17597 ± 17 J mol^{-1}, and the enthalpy of THAM in $0.1000\ M\ l^{-1}$ HCl was -29776 ± 16 J mol^{-1} in agreement with the published data [6].

3. Result and discussion

3.1. Evaluation of the standard molar formation enthalpy of $Zn_2HIO_6 \cdot 1.25H_2O$ (s)

3.1.1. Determination of the dissolution enthalpies of the reactants and products in 3 M l^{-1} HNO_3 solvent

The results of dissolution enthalpies measurements of $2Zn(Ac)_2 \cdot 2H_2O + H_5IO_6$ (s), $Zn_2HIO_6 \cdot 1.25H_2O$ (s), HAc (l) are shown in Table 1. Using Hess' law, a thermochemical cycle was designed as shown in Table 2.

UV spectroscopy and the data of the refrangibility have confirmed that the final state 1and state 3 are thermodynamically equivalent. so, the reaction

Table 1
Dissolution enthalpies of $Zn_2HIO_6 \cdot 1.25H_2O$ (s), HAc (l), $[2Zn(Ac)_2 \cdot 2H_2O + H_5IO_6]$ (s) in $3\ M\ l^{-1}$ HNO_3 solvent at 298.2 K ($R = 996.0\ \Omega$, $I = 20.000$ mA)

System	Solvent	No.	t (s)	ΔE_s (mV)	ΔE_e (mV)	$-Q$(J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
$2Zn(Ac)_2 \cdot 2H_2O$ (s) $+H_5IO_6$ (s) ($n_1/n_2 = 2:1$)	HNO_3	1	62.2	6.8021	6.9125	24.385	−48.769
		2	63.3	6.8107	7.0410	24.394	−48.767
		3	62.7	6.8092	6.9682	24.401	−48.802
		4	65.4	6.7968	7.2671	24.369	−48.738
		5	62.5	6.8001	6.9523	24.359	−48.719
		$\Delta_s H_m^\theta[2Zn(Ac)_2 \cdot 2H_2O + H_5IO_6$ (s), 298.2 K$] = -48.758 \pm 0.014$ kJ mol^{-1}					
$Zn_2HIO_6 \cdot 1.25H_2O$ (s)	HNO_3	1	100.7	9.6970	11.2120	34.694	−69.388
		2	89.3	9.7031	9.9490	34.716	−69.434
		3	88.2	9.7212	9.8219	34.792	−69.585
		4	87.4	9.7026	9.7338	34.708	−69.416
		5	86.5	9.7171	9.6270	34.799	−69.598
		$\Delta_s H_m^\theta[Zn_2HIO_6 \cdot 1.25H_2O$ (s), 298.2 K$] = -69.484 \pm 0.044$ kJ mol^{-1}					
4:2.75 HAc (aq)[a]	$Zn_2HIO_6 \cdot 1.25H_2O + HNO_3$	1	32.1	0.9212	0.9422	3.124	−6.248
		2	33.7	0.9285	0.9915	3.149	−6.298
		3	36.1	0.9249	1.0598	3.132	−6.265
		4	33.0	0.9370	0.9668	3.183	−6.366
		5	34.0	0.9301	0.9981	3.159	−6.318
		$\Delta_s H_m^\theta[4:2.75$ HAc (aq), 298.2 K$] = -6.299 \pm 0.021$ kJ mol^{-1}					

[a] In this system $I = 10.000$ mA; n_1 — molarity of $Zn(Ac)_2 \cdot 2H_2O$ (s); n_2 — molarity of H_5IO_6 (s); t — heating period of electrical calibration; Q — heat effect; ΔE_s — voltage change during the sample dissolution; $\Delta H = (\Delta E_s / \Delta E_e) I^2 R t_e$ (M/m); ΔE_e — voltage change during the electrical calibration; (R — electro-resistance; I — current; m — mass of samples: M — molar mass).

Table 2
Reaction scheme for the standard molar formation enthalpy of $Zn_2HIO_6{\cdot}1.25H_2O$ at the temperature 298.2 K[a]

Reaction	ΔH^0 (kJ mol^{-1})
1. $Zn(Ac)_2{\cdot}2H_2O$ (s)+H_5IO_6 (s)+'A'={$Zn(Ac)_2{\cdot}2H_2O$+H_5IO_6} (soln in 'A')	−48.758±0.014
2. $Zn_2HIO_6{\cdot}1.25H_2O$ (s)+'A'={$Zn_2HIO_6{\cdot}1.25H_2O$} (soln in 'A')	−69.484±0.044
3. 4:2.75 HAc (aq)+{$Zn_2HIO_6{\cdot}1.25H_2O$} (soln in 'A')={HAc+$Zn_2HIO_6{\cdot}1.25H_2O$} (soln in 'A')	−6.299±0.021
4. $2Zn(Ac)_2{\cdot}2H_2O$ (s)+H_5IO_6 (s)=$Zn_2HIO_6{\cdot}1.25H_2O$ (s)+4 HAc (l)+2.75 H_2O (l)	27.025

[a] The solvent 'A' was 3 M l^{-1} HNO_3 (aq).

$\Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3$

enthalpy of:

$$2Zn(Ac)_2 \cdot 2H_2O\ (s) + H_5IO_6\ (s) \xrightarrow{\Delta_r H_m^\theta} Zn_2HIO_6 \cdot 1.25H_2O\ (s) + 4HAc\ (l) + 2.75H_2O\ (l) \qquad (1)$$

$$\Delta_r H_m^\theta = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 = 27.025\ \text{kJ mol}^{-1}$$

3.1.2. *Determination of the standard molar formation enthalpy of $Zn_2HIO_6{\cdot}1.25H_2O$ (s)*

According to the reaction (1)

$$\begin{aligned}\Delta_r H_m^\theta(1) = {} & \Delta_f H_m^\theta[Zn_2HIO_6 \cdot 1.25H_2O(s)] \\ & + 4\Delta_f H_m^\theta[HAc\ (l)] \\ & + 2.75\Delta_f H_m^\theta[H_2O\ (l)] \\ & - \Delta_f H_m^\theta[H_5IO_6\ (s)] \\ & - 2\Delta_f H_m^\theta[Zn(Ac)_2 \cdot 2H_2O\ (s)]\end{aligned}$$

according to [7,8]:

$$\Delta_f H_m^\theta[Zn(Ac)_2{\cdot}2H_2O\ (s)] = -1677.23\ \text{kJ mol}^{-1},$$

$$\Delta_f H_m^\theta[H_2O\ (l)] = -286.92\ \text{kJ mol}^{-1}$$

$$\Delta_f H_m^\theta[HAc\ (l)] = -486.98\ \text{kJ mol}^{-1},$$

$$\Delta_f H_m^\theta[H_5IO_6\ (s)] = -761.50\ \text{kJ mol}^{-1}$$

and the value obtained above

$$\Delta_r H_m^\theta(1) = 27.03\ \text{kJ mol}^{-1}$$

so that

$$\Delta_f H_m^\theta[Zn_2HIO_6 \cdot 1.25H_2O\ (s)\ \ 29825\ \text{K}] = -1342.11\ \text{kJ mol}^{-1}$$

3.2. *Evaluation of the standard molar formation enthalpy of $Cd_2HIO_6{\cdot}1.25H_2O$ (s)*

3.2.1. *Determination of the dissolution enthalpies of $Cd_2HIO_6{\cdot}1.25H_2O$ (s), [$2Cd(Ac)_2$+H_5IO_6] (s), Hac (l) in 3 M l^{-1} HNO_3 solvent*

Using the same method as described above, the dissolution enthalpies of $Cd_2HIO_6{\cdot}1.25H_2O$ (s), Hac (l), [$Cd(Ac)_2$+H_5IO_6] (s) in 3 M l^{-1} HNO_3 solvent were measured and are presented in Table 3.

The reaction scheme used to derive the standard molar formation enthalpy of $Cd_2HIO_6{\cdot}1.25H_2O$ (s) is given in Table 4.

State 1 and 3 are thermodynamically equivalent ,as confirmed by UV spectroscopy and refrangibility data. The reaction enthalpy of the reaction:

$$2Cd(Ac)_2 \cdot 2H_2O\ (s) + H_5IO_6\ (s) \xrightarrow{\Delta_r H_m^\theta} Cd_2HIO_6 \cdot 1.25H_2O\ (s) + 4HAc\ (l) + 2.75H_2O \qquad (2)$$

$$\Delta_r H_m^\theta = \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3 = 3.455\ \text{kJ mol}^{-1}$$

3.2.2. *Evaluation of the standard molar formation enthalpy of $Cd(Ac)_2{\cdot}2H_2O$ (s)*

The standard molar formation enthalpy of $Cd(Ac)_2{\cdot}2H_2O$ (s) has not been reported. To obtain the value, the enthalpy of dissolution of $Cd(Ac)_2{\cdot}2H_2O$ (s) in 100 ml 3 M l^{-1} HNO_3 was measured and presented in Table 3.

The dissolution process of the $Cd(Ac)_2{\cdot}2H_2O$ (s) in 3 M l^{-1} HNO_3 is

$$Cd(Ac)_2 \cdot 2H_2O\ (s) \xrightarrow{\Delta_r H_m^\theta} Cd^{2+}\ (aq) + 2Ac^-\ (aq) + 2H_2O\ (l)$$

Table 3
Dissolution enthalpies[a]

System	Solvent	No.	t (s)	ΔE_s (mV)	ΔE_e (mV)	$-Q$ (J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
$Cd(Ac)_2{\cdot}2H_2O$ (s)	3 Ml^{-1} HNO_3	1	18.6	1.0371	0.9821	7.825	−15.650
		2	19.4	1.0840	1.0615	7.844	−15.768
		3	17.9	0.9931	0.9103	7.780	−15.560
		4	18.1	1.0202	0.9412	7.816	−15.632
		5	18.8	1.0514	1.0056	7.831	−15.662
		$\Delta_s H_m^\theta[Cd(Ac)_2{\cdot}2H_2O$ (s), 298 K]=−15.654±0.017 kJ mol^{-1}					
$2Cd(Ac)_2{\cdot}2H_2O$ (s)+H_5IO_6 (s)	HNO_3	1	57.1	8.5420	8.5411	22.752	−45.502
(n_1/n_2=2:1)		2	58.3	8.5519	8.7280	22.756	−45.512
		3	59.2	8.5386	8.8510	22.752	−45.505
		4	57.5	8.8549	8.6008	22.756	−45.512
		5	57.8	8.5410	8.6454	22.749	−45.498
		$\Delta_s H_m^\theta[2Cd(Ac)_2{\cdot}2H_2O+H_5IO_6$ (s), 298.2 K]=−45.506±0.007 kJ mol^{-1}					
$Cd_2HIO_6{\cdot}1.25H_2O$ (s)	HNO_3	1	44.1	5.2409	5.2511	17.554	−35.108
		2	43.9	5.2401	5.2403	17.488	−34.976
		3	45.0	5.2487	5.3627	17.546	−35.092
		4	43.4	5.2435	5.1668	17.541	−35.082
		5	44.6	5.2503	5.3232	17.525	−35.050
		$\Delta_s H_m^\theta[Cd_2HIO_6{\cdot}1.25H_2O$ (s), 298.2 K]=−35.058±0.048 kJ mol^{-1}					
4:2.75HAc (aq)[b]	$Cd_2HIO_6{\cdot}1.25H_2O+HNO_3$	1	35.0	2.5420	2.5508	3.473	−6.946
		2	35.6	2.5431	2.5712	3.507	−7.014
		3	36.1	2.5468	2.6037	3.517	−7.039
		4	34.8	2.5412	2.5321	3.478	−6.957
		5	35.2	2.5477	2.5497	3.503	−7.006
		$\Delta_s H_m^\theta$ [4:2.75HAc (aq), 298.2 K]=−6.993±0.046 kJ mol^{-1}					

[a] Experimental condition solvent: 3 M l^{-1} HNO_3 at 298.2 K (R=996.0 Ω, I=20.000 mA.

[b] In this system I=10.000 mA; n_1 —molarity of $Cd(Ac)_2{\cdot}2H_2O$ (s); n_2 — molarity of H_5IO_6 (s).

$$\Delta_s H_m^\theta = \Delta_f H_m^\theta(\mathrm{Cd^{2+}\ (aq)}) + 2\Delta + H_m^\theta(\mathrm{Ac^-\ (aq)}) + 2\Delta_f H_m^\theta(\mathrm{H_2O\ (l)}) - \Delta_f H_m^\theta(\mathrm{Cd(Ac)_2 \cdot 2H_2O\ (s)})$$

According to [8]

$$\Delta_f H_m^\theta(\mathrm{Cd^{2+}\ (aq)}) = -152.42\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H_m^\theta(\mathrm{Ac^-\ (aq)}) = -488.86\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H_m^\theta(\mathrm{H_2O\ (l)}) = -285.49\,\mathrm{kJ\,mol^{-1}}$$

and

$$\Delta_f H_m^\theta(\mathrm{Cd(Ac)_2 \cdot 2H_2O\ (l),\ 298.2\,K}) = -15.65\,\mathrm{kJ\,mol^{-1}}$$

Table 4
Reaction scheme for the standard molar formation enthalpy of $Cd_2HIO_6{\cdot}1.25H_2O$ at the temperature 298.2 K[a]

Reaction	ΔH^θ (kJ mol^{-1})
1. $Cd(Ac)_2{\cdot}2H_2O$ (s)+H_5IO_6 (s)+‘A’={$Cd(Ac)_2+H_5IO_6$} (soln in ‘A’)	−45.506±0.007
2. $Cd_2HIO_6{\cdot}1.25H_2O$ (s)+‘A’={$Cd_2HIO_6{\cdot}1.25H_2O$} (soln in ‘A’)	−35.058±0.048
3. HAc(l)+{$Cd_2HIO_6{\cdot}1.25H_2O$} (soln in ‘A’)={ HAc+$Cd_2HIO_6{\cdot}1.25H_2O$} (soln in ‘A’)	−6.993±0.046
4. $2Cd(Ac)_2{\cdot}2H_2O$ (s)+H_5IO_6 (s)=$Cd_2HIO_6{\cdot}1.25H_2O$ (s)+4 Hac (l)+2.75 H_2O (l)	−3.455

[a] The solvent ‘A’ was 3 M l^{-1} HNO_3 (aq).

$$\Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3$$

so that $\Delta_f H_m^\theta(Cd(Ac)_2\cdot 2H_2O\ (s)) = -1685.47\,kJ\,mol^{-1}$

3.2.3. Determination of the standard molar formation enthalpy of $Cd_2HIO_6\cdot 1.25H_2O$ (s)

From the reaction (2):

$$\begin{aligned}\Delta_r H_m^\theta(2) = {} & \Delta_f H_m^\theta[Cd_2HIO_6\cdot 1.25H_2O\ (s)] \\ & + 4\Delta_f H_m^\theta[HAc\ (l)] \\ & + 2.75\Delta_f H_m^\theta[H_2O\ (l)] \\ & - \Delta_f H_m^\theta[H_5IO_6\ (s)] \\ & - 2\Delta_f H_m^\theta[Cd(Ac)_2\cdot 2H_2O\ (s)]\end{aligned}$$

and the value obtained above

$$\begin{aligned}&\Delta_r H_m^\theta(2) = -3.46\,kJ\,mol^{-1}\\ &\Delta_f H_m^\theta[Cd_2HIO_6\cdot 1.25H_2O\ (s)] \\ &\quad = -1685.47\ kJ\ mol^{-1}\end{aligned}$$

As well as [7,8]:

$$\begin{aligned}&\Delta_f H_m^\theta[H_2O\ (l)] = -286.92\,kJ\,mol^{-1},\\ &\Delta_f H_m^\theta[H_5IO_6\ (s)] = -761.50\,kJ\,mol^{-1}\\ &\Delta_f H_m^\theta[HAc\ (l)] = -486.98\,kJ\,mol^{-1}\end{aligned}$$

then,

$$\begin{aligned}&\Delta_f H_m^\theta[Cd_2HIO_6\cdot 1.25H_2O\ (s),\ 298.2\,K]\\ &\quad = -1405.49\,kJ\,mol^{-1}\end{aligned}$$

3.3. Evaluation of the standard molar formation enthalpy of $Cu_2HIO_6\cdot 2H_2O$ (s)

3.3.1. Determination of the dissolution enthalpies of $Cu_2HIO_6\cdot 2H_2O$ (s), $[Cu_2(Ac)_2\cdot H_2O+H_5IO_6]$ (s), Hac (l) in 3 M l^{-1} HNO_3 solvent

The results of dissolution enthalpies measurements of $Cu_2HIO_6\cdot 2H_2O$ (s), Hac (l), $[Cu(Ac)_2\cdot H_2O+H_5IO_6]$ (s) are shown in Table 5.

According to Hess' law, a thermochemical cycle was designed as shown in Table 6.

UV spectroscopy and the data of the refrangibility have confirmed that the final state 1and state 3 are thermodynamically equivalent. So, the reaction enthalpy of

$$2Cu(Ac)_2\cdot H_2O\ (s) + H_5IO_6\ (s) \xrightarrow{\Delta_r H_m^\theta} Cu_2HIO_6\cdot 2H_2O\ (s) + 4HAc\ (l) \qquad (3)$$

$$\begin{aligned}\Delta_r H_m^\theta &= \Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3\\ &= 34.310\,kJ\,mol^{-1}\end{aligned}$$

Table 5
Dissolution enthalpies of $Cu_2HIO_6\cdot 2H_2O$ (s), Hac (l), $[2Cu(Ac)_2\cdot H_2O+H_5IO_6]$ (s) in 3 M l^{-1} HNO_3 solvent at 298.2 K (R=996.0 Ω, I=20.000 mA)

System	Solvent	No.	t (s)	ΔE_s (mV)	ΔE_e (mV)	$-Q$ (J)	$\Delta_s H_m^\theta$ (kJ mol^{-1})
$2Cu(Ac)_2\cdot H_2O$ (s) $+H_5IO_6$ (s) (n_1/n_2=2:1)	HNO_3	1	32.8	4.0125	4.1278	12.702	−25.404
		2	31.4	4.1037	4.0526	12.667	−25.334
		3	34.1	4.0745	4.3402	12.753	−25.506
		4	33.5	4.0268	4.2435	12.665	−25.330
		5	35.0	4.2512	4.6518	12.737	−25.474
		$\Delta_s H_m^\theta[2Cu(Ac)_2\cdot H_2O+H_5IO_6$ (s), 298.2 K]=−25.410±0.027 kJ mol^{-1}					
$Cu_2HIO_6\cdot 2H_2O$ (s)	HNO_3	1	68.1	7.8725	7.9131	26.992	−53.984
		2	67.8	7.8905	7.8719	27.074	−54.148
		3	69.3	7.8521	8.0123	27.057	−54.114
		4	65.2	7.9038	7.5921	27.041	−54.082
		5	68.0	7.9128	7.9136	27.088	−54.176
		$\Delta_s H_m^\theta[Cu_2HIO_6\cdot 2H_2O$ (s), 298.2 K]=−54.100±0.038 kJ mol^{-1}					
HAc (l)[a]	$Cu_2HIO_6\cdot 2H_2O+HNO_3$	1	27.6	1.9406	1.9038	2.802	−5.604
		2	28.2	1.9726	1.9621	2.824	−5.648
		3	29.8	1.9803	2.0803	2.825	−5.650
		4	28.7	1.8912	1.9308	2.800	−5.600
		5	28.1	1.9028	1.9043	2.797	−5.594
		$\Delta_s H_m^\theta$[Hac (l), 298.2 K]=−5.620±0.015 kJ mol^{-1}					

[a] In this system I=10.000 mA; n_1 — molarity of $Cu(Ac)_2\cdot H_2O$ (s); n_2 — molarity of H_5IO_6(s).

Table 6
Reaction scheme for the standard molar formation enthalpy of $Cu_2HIO_6{\cdot}2H_2O$ at the temperature 298.2 K[a]

Reaction	ΔH^{θ} (kJ mol^{-1})
1. $Cu(Ac)_2{\cdot}H_2O$ (s)+H_5IO_6 (s)+'A'={$Cu(Ac)_2{\cdot}H_2O$+H_5IO_6} (soln in 'A')	−25.410±0.037
2. $Cu_2HIO_6{\cdot}2H_2O$ (s)+'A'={$Cu_2HIO_6{\cdot}2H_2O$} (soln in 'A')	−54.100±0.038
3. HAc (l)+{$Cu_2HIO_6{\cdot}2H_2O$} (soln in 'A')={HAc+$Cu_2HIO_6{\cdot}2H_2O$} (soln in 'A')	−5.620±0.015
4. $2Cu(Ac)_2{\cdot}H_2O$ (s)+H_5IO_6 (s)=$Cu_2HIO_6{\cdot}2H_2O$ (s)+4 HAc (l)	34.310

[a] The solvent 'A' was 3 M l^{-1} HNO_3 (aq).

$$\Delta H_4 = \Delta H_1 - \Delta H_2 - \Delta H_3.$$

3.3.2. Determination of the standard molar formation enthalpy of $Cu_2HIO_6{\cdot}2H_2O$ (s)

According to the reaction (3)

$$\begin{aligned}\Delta_r H_m^{\theta}(3) = {} & \Delta_f H_m^{\theta}[\mathrm{Cu_2HIO_6 \cdot 2H_2O\ (s)}] \\ & + 4\Delta_f H_m^{\theta}[\mathrm{HAc\ (l)}] \\ & - \Delta_f H_m^{\theta}[\mathrm{H_5IO_6\ (s)}] \\ & - 2\Delta_f H_m^{\theta}[\mathrm{Cu(Ac)_2 \cdot 2H_2O\ (s)}]\end{aligned}$$

According to [7,8]

$$\begin{aligned}&\Delta_f H_m^{\theta}[\mathrm{Cu(Ac)_2 \cdot 2H_2O\ (s)}] \\ &\quad = -1189.10\,\mathrm{kJ\,mol^{-1}};\end{aligned}$$

$$\Delta_f H_m^{\theta}[\mathrm{HAc\ (l)}] = -486.98\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_f H_m^{\theta}[\mathrm{H_5IO_6\ (s)}] = -761.50\,\mathrm{kJ\,mol^{-1}}$$

and the value obtained above

$$\Delta_r H_m^{\theta}(3) = 34.31\,\mathrm{kJ\,mol^{-1}}$$

so that

$$\begin{aligned}&\Delta_f H_m^{\theta}[\mathrm{Cu_2HIO_6 \cdot 2H_2O\ (s),\ 298.2\,K}] \\ &\quad = -1226.08\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

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