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A thermochemical study of the reaction of salicylaldoxime with anhydrous nickel(II) and cobalt(II) acetate

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Abstract

The solid-state coordination reaction:

 $\begin{aligned} &2\text{HSAO}(s) + \text{Ni}(\text{Ac})_2(s) \rightarrow \text{Ni}(\text{SAO})_2(s) + 2\text{HAc}(g) \\ &2\text{HSAO}(s) + \text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}(s) \rightarrow \text{Co}(\text{SAO})_2 \cdot 2\text{H}_2\text{O}(s) + 2\text{HAc}(g) + 2\text{H}_2\text{O}(g) \end{aligned}$

have been studied by classical solution calorimetry. The molar dissolution enthalpies of the reactants and the products in a certain solvent (for one reaction is in 6 mol 1⁻¹ HCl and another in a mixed solution consisting of DMSO and DMF) of this two solid-solid coordination reactions have been measured using an isoperibol calorimeter. From the results and other auxiliary quantities, the standard molar formation enthalpies of [Co(SAO)₂·2H₂O, s, 298.2 K] and [Ni(SAO)₂, s, 298.2 K] at 298.2 K have been determined to be $\Delta_f H_m^{\ominus}$ [Co(SAO)₂·2H₂O, s, 298.2 K] = -957.205 kJ mol⁻¹ and $\Delta_f H_m^{\ominus}$ [Ni(SAO)₂, s, 298.2 K] = -403.336 kJ mol⁻¹. © 1997 Elsevier Science B.V.

Keywords: Cobalt(II); Isoperibol calorimetry; Nickel(II); Salicylaldoxime; Standard molar formation enthalpy

1. Introduction

Solid state chemistry is of fundamental importance in material science. Over the years the Coordination Chemistry Institute, Nanjing University, P.R. China, has investigated many solid-state transformations of coordination compounds at ambient temperatures [1–9]. In 1992, the reaction of anhydrous nickel(II) acetate with salixylaldoxime (HSAO) was reported [8], and the solid-solid state reaction of salicylaldoxime with hydrous cobalt(II) acetate at ambient temperature was reported [9]. XRD, IR and element analyses are employed to characterize the solid products. The kinetics of isothermal solid-state reactions were investigated by electrical conductivity measurements and possible mechanisms are discussed. However, the thermochemical properties of these two solid-state reactions at ambient temperature have not been reported. The purpose of the present study is to determine the dissolution enthalpies of the reactants and the products of the two solid-state coordination reactions by solution calorimetry. The standard molar formation enthalpies of the products of the two solid-state coordination reactions were derived from the respective dissolution enthalpies.

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2. Experimental

2.1. Chemical

Salicylaldoxime is abbreviated as HSAO. All the chemicals (including the HSAO, $Ni(Ac)_2 \cdot 4H_2O$, $Co(Ac)_2 \cdot 4H_2O$, HAC, DMF, DMSO and KCl) used are of A.R. grade and obtained from Shanghai Reagent Factory.

Anhydrous nickel acetate was obtained by drying the $Ni(Ac)_2 \cdot 4H_2O$ in a vacuum oven at $90^{\circ}C$ to a constant mass [10].

KCl (obtained from Shanghai Reagent Factory), a purity greater than 99.99%, was dried in a vacuum oven for 6 h at 135° C prior to use.

2.2. Preparations

 $Ni(SAO)_2(s)$, a dark green solid, was prepared and analyzed according to the method given in Ref. [8].

 $Co(SAO)_2 \cdot 2H_2O(s)$, a reddish brown solid, was prepared and analyzed according to the method given in Ref. [9].

2.3. Calorimeter and calibration

All calorimetric determinations were carried out in an isoperibol calorimeter as described previously [11]. The solution enthalpies of KCl in water and THAM (NBS 742a, USA) in 0.1000 mol 1^{-1} HCl were determined to check the precision of the calorimetric system. The measured dissolution enthalpy of KCl(s) in water at 298.2 K was 17597 ± 17 J mol⁻¹ and the enthalpy of reaction of THAM in 0.1000 mol⁻¹ HCl was -29776 ± 16 J mol⁻¹ which are in agreement with the corresponding published data [12,13].

3. Results and discussion

3.1. The calorimetric solvent

In this experiment, 6 mol 1^{-1} HCl was chosen as calorimetric solvent for the reaction of HSAO(s) with Ni(Ac)₂(s). It is found that only the mixed solvent DMSO and DMF in a volume ratio V_{DMSO} : $V_{DMF} = 2 : 1-3 : 1$ is suitable for both HSAO(s) and

 $Co(Ac)_2 \cdot 4H_2O$. In this experiment, the ratio of V_{DMSO} : $V_{DMF} = 2.5 : 1$ was chosen.

3.2. Evaluation of the standard molar formation enthalpy of Ni(SAO)₂(s)

3.2.1. Determination of $\Delta_s H_m^{\ominus}$ [HSAO, s], $\Delta_s H_m^{\ominus}$ [Ni(Ac)₂, s], $\Delta_s H_m^{\ominus}$ [Ni(SAO)₂, s] and $\Delta_s H_m^{\ominus}$ [HAc, l] in 6 mol l^{-1} HCl solvent

The results of dissolution enthalpies measurements of HSAO(s), $Ni(Ac)_2(s)$, $Ni(SAO)_2(s)$, HAc(1) are shown in Table 1.

According to 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 2 and state 5 are thermodynamically equivalent. So, the reaction enthalpy of:

$$Ni(Ac)_{2}(s) + 2HSAO(s) \xrightarrow{\Delta_{f}H_{m}^{\ominus}(1)} Ni(SAO)_{2}(s) + 2HAc(g)$$
(1)
$$\Delta_{r}H_{m}^{\ominus}(1) \equiv \Delta H_{6} = 2\Delta H_{1} + \Delta H_{2} - \Delta H_{3} - 2\Delta H_{4} - 2\Delta H_{5} = 84.075 \text{ kJ mol}^{-1}$$

3.2.2. Evaluation of the standard molar formation enthalpy of Ni(Ac)₂(s)

The standard molar formation enthalpy of $Ni(Ac)_2(s)$ has not been reported. To obtain this value, the enthalpy of dissolution of $Ni(Ac)_2(s)$ in 100 ml 6 mol l⁻¹ was measured and presented in Table 3.

The dissolution process of the $Ni(Ac)_2$ in 6 mol l^{-1} HCl(aq) is

$$\begin{split} \operatorname{Ni}(\operatorname{Ac})_{2}(s) &+ 2\operatorname{HCl}(\operatorname{aq}) \stackrel{\Delta_{s}H_{m}^{\ominus}}{\to} \operatorname{Ni}^{2+}(\operatorname{aq}) \\ &+ 2\operatorname{Cl}^{-}(\operatorname{aq}) + 2\operatorname{HAc}(\operatorname{aq}) \\ \Delta_{s}H_{m}^{\ominus}[\operatorname{Ni}(\operatorname{Ac})_{2}, s] &= \Delta_{f}H_{m}^{\ominus}[\operatorname{Ni}^{2+}, \operatorname{aq}] \\ &+ 2\Delta_{f}H_{m}^{\ominus}[\operatorname{Cl}^{-}, \operatorname{aq}] + 2\Delta_{f}H_{m}^{\ominus}[\operatorname{HAc}, \operatorname{aq}] \\ &- \Delta_{f}H_{m}^{\ominus}[\operatorname{Ni}(\operatorname{Ac})_{2}, s] - 2\Delta_{f}H_{m}^{\ominus}[\operatorname{HCl}, \operatorname{aq}] \end{split}$$

according to Ref. [16]

$$\begin{split} \Delta_{f} H^{\ominus}_{m}[\text{Ni}^{2+},\text{aq}] &= -54.000 \text{ kJ mol}^{-1} \\ \Delta_{f} H^{\ominus}_{m}[\text{Cl}^{-},\text{aq}] &= -167.159 \text{ kJ mol}^{-1} \end{split}$$

Table 1

System	Solvent	No.	t/s	$\Delta E_{\rm s}/{\rm mV}$	$\Delta E_{\rm e}/{ m mV}$	Q /J	$\Delta_{\rm s} H_{\rm m}^{\ominus}/{ m kJ} { m mol}^{-1}$		
HSAO(s)	$6 \text{ mol } 1^{-1} \text{ HCl}$	1	150.0	4.4296	4.4880	24.754	12.377		
		2	149.0	4.4360	4.4758	24.691	12.346		
		3	149.9	4.4255	4.4900	24.703	12.352		
		4	179.8	4.4292	5.3697	24.797	12.399		
		5	149.6	4.4295	4.4872	24.692	12.346		
		$\Delta_{\mathrm{s}} H_{\mathrm{m}}^{\ominus}$ [H	$\Delta_{\rm s} H_{\rm m}^{\odot}$ [HSAO, s, 298.2 K] = +12.364 ± 0.010 kJ mol ⁻¹						
Ni(Ac) ₂ (s)	HSAO·HCl(aq)	1	329.7	9.0723	9.8371	-50.840	-50.840		
	-	2	329.4	9.0760	9.8249	-50.878	-50.878		
		3	329.9	9.0647	9.8413	-50.807	-50.807		
		4	329.7	9.0486	9.8234	-50.778	-50.778		
		5	330.2	9.0558	9.8424	-50.797	50.797		
		$\Delta_{ m s} H_{ m m}^{\ominus}$ [N	li(Ac) ₂ , s, 298.2	$\mathbf{K}] = -50.820 \pm$	0.018 kJ mol-	1			
Ni(SAO) ₂ (s)	$6 \text{ mol } l^{-1} \text{ HCl}$	1	90.11	2.2732	2.7035	-12.668	-12.668		
		2	90.43	2.2503	2.7013	-12.596	-12.596		
		3	89.61	2.2739	2.6833	-12.697	-12.697		
		4	90.31	2.2486	2.6916	-12.615	-12.615		
		5	89.33	2.2587	2.6800	-12.588	-12.588		
$\Delta_{\rm s} H_{\rm m}^{\ominus} [{ m Ni}({ m SAO})_2, { m s}, 298.2 { m K}] = -12.633 \pm 0.021 { m kJ} { m mc}$						-1			
HAc(1)	Ni(SAO)2·HCl	1	15.87	0.1900	0.5015	-1.005	-0.503		
		2	29.93	0.1673	0.9122	-0.918	-0.459		
		3	15.08	0.1853	0.4962	-0.934	-0.467		
		4	15.61	0.1750	0.4736	-0.964	-0.481		
		5	15.46	0.1763	0.4700	-0.970	-0.485		
		$\Delta_{\rm s} H_{\rm m}^{\Theta}$ [HAc, 1, 298.2 K] = -0.479 ± 0.008 kJ mol ⁻¹							

Dissolution enthalpies of [HSAO, s], [Ni(Ac)₂, s] [Ni(SAO)₂, s] and [HAc, 1] in 6 mol l^{-1} HCl solvent at 298.2 K ($R = 1672.0 \Omega$, I = 10.000 mA)

t - heating period of electrical calibration; m - mass of samples.

 $\Delta E_{\rm s}$ -: the voltage change during the sample dissolution; $\Delta_{\rm s} H_{\rm m}^{\odot} = (\Delta E_{\rm s}/\Delta E_{\rm e}) I^2 R t_{\rm e} (M/m)$.

 ΔE_{e} - the voltage change during the electrical calibration.

Q – heat effect.

(R - electro-resistance; I - current; and M - molar mass).

Table 2

Reaction scheme for the standard molar formation enthalpy of Ni(SAO)₂ at the temperature 298.2 K. The solvent "A" was 6 mol 1^{-1} HCl(aq). $\Delta H_6 = 2\Delta H_1 + \Delta H_2 - \Delta H_3 - 2\Delta H_4 - 2\Delta H_5$

Reaction	$\Delta_{\mathbf{s}} H_{\mathbf{m}}^{\ominus} / (\mathbf{kJ} \ \mathbf{mol}^{-1})$
1. HSAO(s)+"A"=HSAO(sln in "A")	12.364±0.010
2. Ni(Ac) ₂ (s)+2HSAO(sln in "A")={Ni(Ac) ₂ +2HSAO}(sln in "A")	-50.820 ± 0.018
3. Ni(SAO) ₂ (s)+"A"=Ni(SAO) ₂ (sln in "A")	-12.633 ± 0.021
4. $HAc(g)=HAc(1)$	48.288
5. $HAc(1)+Ni(SAO)_2(sln in "A") = \{HAc+Ni(SAO)_2\}(sln in "A")$	-0.479 ± 0.008
6. $Ni(Ac)_2(s)+2HSAO(s)=Ni(SAO)_2(s)+2HAc(g)$	84.075

System	No.	m/g	t/s	$\Delta E_{ m s}/ m mV$	$\Delta E_{ m e}/{ m mV}$	Q/J	$\Delta_{ m s} H_{ m m}^{\ominus}/ m kJ~ m mol^{-1}$	
Ni(Ac) ₂ (s)	1	0.2066	330.3	9.8309	9.7915	-55.448	-47.445	
	2	0.2048	329.8	9.7870	9.7843	-55.158	-47.611	
	3	0.2034	330.2	9.7050	9.7890	-54.736	-47.584	
	4	0.2011	329.6	9.5952	9.7749	-54.096	-47.554	
	5	0.2030	329.9	9.6651	9.7884	-54.465	-47.430	
	$\Delta_{\rm s} H_{\rm m}^{\odot}$ [Ni(Ac) ₂ , s, 298.2 K] = -47.525 ± 0.037 kJ mol ⁻¹							
Co(Ac) ₂ ·4H ₂ O(s)	1	0.3504	149.9	4.3333	4.4004	-25.240	17.229	
	2	0.3514	149.8	2.3679	4.4939	-24.344	-17.258	
	3	0.3499	149.6	4.3114	4.4729	-24.110	-17.163	
	4	0.3513	120.4	4.2928	3.6008	-24.000	-17.019	
	5	0.3509	120.1	4.3148	3.5880	-24.148	-17.141	
		$\Delta_{ m s} H_{ m m}^{\odot}$ [Co($\Delta_{s}H_{m}^{\odot}$ [Co(Ac) ₂ ·4H ₂ O, s, 298.2 K] = -17.162 ± 0.042 kJ mol ⁻¹					

Table 3 Dissolution enthalpies of [Ni(Ac)₂, s], [Co(Al)₂·4H₂O, s], in 6 mol 1^{-1} HCl solvent at 298.2 K.

m – mass of samples.

$$\begin{aligned} \Delta_{\mathbf{f}} H_{\mathbf{m}}^{\ominus}[\mathrm{HAc}, \ 1 \ \mathrm{mol} \ \mathrm{in} \ 2000 \ \mathrm{mol} \ \mathrm{H}_{2}\mathrm{O}] \\ &= -485.750 \ \mathrm{kJ} \ \mathrm{mol}^{-1}, \\ \Delta_{\mathbf{f}} H_{\mathbf{m}}^{\ominus}[\mathrm{HAc}, \ 1 \ \mathrm{mol} \ \mathrm{in} \ 10 \ \mathrm{mol} \ \mathrm{H}_{2}\mathrm{O}] \end{aligned}$$

$$= -161.318 \,\mathrm{kJ}\,\mathrm{mol}^{-1},$$

and $\Delta_{s}H_{m}^{\ominus}[Ni(Ac)_{2}, s] = -47.525 \text{ kJ mol}^{-1}$, measured above

so that
$$\Delta_{f}H_{m}^{\ominus}[Ni(Ac)_{2}, s] = -989.657 \text{ kJ mol}^{-1}$$

3.2.3. Determination of the standard molar formation enthalpy of Ni(SAO)₂(s)According to the reaction (1):

$$\begin{split} \Delta_{\mathbf{r}} H^{\ominus}_{\mathbf{m}}(1) &= \Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{Ni}(\mathsf{SAO})_2, \mathbf{s}] \\ &+ 2\Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{HAc}, \mathbf{g}] \\ &- \Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{Ni}(\operatorname{Ac})_2, \mathbf{s}] \\ &- 2\Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{HSAO}, \mathbf{s}] \end{split}$$

according to Ref. [14]:

$$\begin{split} &\Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}}[\mathrm{HSAO},\mathbf{s}] = -183.720\,\mathrm{kJ\,mol^{-1}}\\ &\Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}}[\mathrm{HAc},\mathbf{g}] = -434.843\,\mathrm{kJ\,mol^{-1}} \end{split}$$

as well as the above-mentioned values:

$$\begin{split} \Delta_{f} H^{\ominus}_{m}[\text{Ni}(\text{Ac})_{2},s] &= -989.657 \text{ kJ mol}^{-1} \\ \Delta_{r} H^{\ominus}_{m}(1) &= 84.075 \text{ kJ mol}^{-1} \end{split}$$

$$\Delta_{\rm f} H^{\ominus}_{\rm m} [\rm Ni(SAO)_2, s, 298.2 \, \rm K]$$

= -403.336 kJ mol⁻¹

- 3.3. Evaluation of the standard molar formation enthalpy of $Co(SAO)_2 \cdot 2H_2O(s)$
- 3.3.1. Determination of the dissolution enthalpies of $Co(Ac)_2 \cdot 4H_2O(s)$, HSAO(s), $Co(SAO)_2 \cdot 2H_2O(s)$, 1 : 1 HAc(aq) in (DMF + DMSO) solvent

Using the same method as described here, the dissolution enthalpies of $Co(Ac)_2 \cdot 4H_2O(s)$, HSAO(s), $Co(SAO)_2 \cdot 2H_2O(s)$, 1:1 (mol ratio) HAc(aq) in (DMF + DMSO) solvent have been measured and presented in Table 4.

The reaction scheme used to derive the standard molar formation enthalpy of $Co(SAO)_2 \cdot 2H_2O(s)$ is presented in Table 5.

States 2 and 7 are of thermodynamically equivalent, as confirmed by UV spectroscopy and refrangibility data. The reaction enthalpy of the reaction:

$$2HSAO(s) + Co(Ac)_2 \cdot 4H_2O(s)$$

$$\xrightarrow{\Delta_r H_m^{\oplus}(2)} Co(SAO)_2 \cdot 2H_2O(s)$$

$$+ 2HAc(g) + 2H_2O(g)$$
(2)

Dissolution enthalpies of	Co(Ac) ₂ ·4H ₂ O(s), HSAO(s), Co(SAO) ₂ ·2H ₂	O(s), 1:1 HAc	(aq) in (DMSO +	DMF) solvent at	298.2 K		
System	Solvent	No.	1/S	$\Delta E_{ m s}/ m mV$	$\Delta E_{e}/\mathrm{mV}$	<u> </u>	$\Delta_{\rm s} H_{\rm m}^{\ominus}/{\rm kJ} \ { m mol}^{-1}$
$Co(Ac)_2.4H_2O(s)$	DMSO + DMF	-	119.0	6.4321	5.3202	24.005	24.055
		2	149.2	6.4227	6.6733	24.009	24.009
		ŝ	150.7	6.4816	6.7536	24.182	24.182
		4	149.6	6.4249	6.6875	24.013	24.013
		S	119.1	6.3475	5.2472	24.089	24.089
		$\Delta_{\rm s} H_{\rm m}^{\ominus}$ [Cc	o(Ac) ₂ .4H ₂ O, s, 29	8.2 K] = 24.073 :	± 0.030 kJ mol ⁻¹	-	
HSAO(s)	$Co(Ac)_2 \cdot 4H_2O + DMSO + DMF$	-	240.1	10.7725	10.5971	-40.809	20.405
	•	2	239.7	10.7640	10.5750	40.794	-20.397
		£	209.7	10.8557	9.2445	-41.173	-20.586
		4	239.5	10.7609	10.5274	-40.933	-20.466
		S	269.1	10.7707	11.8661	-40.340	-20.420
		$\Delta_{\rm s} H_{\rm m}^{\circ}$ [H!	SAO, s, 298.2 K] =	$= -20.455 \pm 0.03$	5 kJ mol ⁻¹		
Co(SAO) ₂ ·2H ₂ O(s)	DMSO + DMF	-1	119.6	5.4115	5.2843	-20.479	-20.479
		2	119.1	5.4083	5.2908	-20.356	-20.356
		3	120.1	5.4401	5.3382	-20.464	-20.464
		4	119.6	5.4529	5.3185	-20.502	
		5	119.6	5.4325	5.3307	-20.430	-20.430
		$\Delta_{ m s} H_{ m m}^{\odot}$ [Cc	o(SAO)·2H ₂ O, s, 2	98.2 K] = -20.4(56 ± 0.025 kJ mc	ol ^{−1}	
1:1 HAc(aq)	$C_0(SAO)_2 \cdot 2H_2O + DMSO + DMF$	1	180.1	7.1844	7.9640	-27.165	-13.583
		2	194.8	7.1158	8.6118	-26.913	-13.456
		c,	180.2	7.0670	7.9581	-26.756	-13.378
		4	178.6	7.0750	7.8846	-26.796	-13.398
		5	179.7	7.1081	7.9552	-26.846	-13.423
		$\Delta_{ m s} H_{ m m}^{\odot}$ [1 :	1 HAc, 1, 298.2	K] = 13.448 ± 0).036 kJ mol ⁻¹		

Table 4

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Table 5

Reaction scheme for the standard molar reaction enthalpy of Co(SAO₂·2H₂O at the temperature 298.2 K. The solvent "B" was DMSO and DMF in a volume ratio V_{DMSO} : $V_{\text{DMF}} = 2.5 : 1$. $\Delta H_8 = \Delta H_1 + 2\Delta H_2 - \Delta H_3 - 2\Delta H_4 - 2\Delta H_5 - 2\Delta H_6 - 2\Delta H_7$

Reaction	$\Delta_{s}H_{\mathfrak{m}}^{\Theta}/ ext{kJ mol}^{-1}$
1. $Co(Ac)_2 \cdot 2H_2O(s) + "B" = \{Co(Ac)_2 \cdot 2H_2O\} (sln in "B")$	24.073±0.030
2. $HSAO(s) + \{Co(Ac)_2 \cdot 2H_2O\}(sln in "B") = \{HSAO + Co(Ac)_2 \cdot 2H_2O\} (sln in "B")$	-20.455 ± 0.035
3. $Co(SAO)_2 \cdot 2H_2O(s) + "B" = \{Co(SAO)_2 \cdot 2H_2O\} (sln in "B")$	-20.446 ± 0.025
4. $HAc(g) = HAc(1)$ (according to Ref. [14])	-48.288
5. $H_2O(g) = H_2O(1)$ (according to Ref. [14])	-44.012
6. $HAc(1) + H_2O(1) = 1$: 1HAc(aq) (according to Ref. [15])	-3.674
7. 1 : $1HAc(aq) + {Co(SAO)_2 \cdot 2H_2O}(sln in "B") = {HAc + Co(SAO)_2 \cdot 2H_2O}(sln in "B")$	-13.448 ± 0.036
8. $2HSAO(s) + Co(Ac)_2 \cdot 4H_2O(s) = Co(SAO)_2 \cdot 2H_2O(s) + 2HAc(g) + 2H_2O(g)$	222.453

$$\Delta_{\rm r} H_{\rm m}^{\ominus}(2) = \Delta H_8 = \Delta H_1 + 2\Delta H_2 - \Delta H_3$$
$$- 2\Delta H_4 - 2\Delta H_5 - 2\Delta H_6$$
$$- 2\Delta H_7 = 222.453 \,\text{kJ mol}^{-1}$$

3.3.2. Evaluation of the standard molar formation enthalpy of $Co(Ac)_2 \cdot 4H_2O(s)$

The standard molar formation enthalpy of $Co(Ac)_2 \cdot 4H_2O(s)$ has also not been reported. To obtain thin value, the same method described above was used. The dissolution enthalpy of $Co(Ac)_2 \cdot 4H_2O(s)$ in 6 mol l^{-1} HCl was also shown in Table 3.

$$\begin{split} & \operatorname{Co}(\operatorname{Ac})_2 \cdot 4\operatorname{H}_2\operatorname{O}(s) + 2\operatorname{HCl}(\operatorname{aq}) \stackrel{\Delta_s H_m^{\ominus}}{\to} \operatorname{Co}^{2+}(\operatorname{aq}) \\ & + 2\operatorname{Cl}^-(\operatorname{aq}) + 2\operatorname{HAc}(\operatorname{aq}) + 4\operatorname{H}_2\operatorname{O}(1) \\ & \Delta_s H_m^{\ominus}[\operatorname{Co}(\operatorname{Ac})_2 \cdot 4\operatorname{H}_2\operatorname{O}, s] = \Delta_f H_m^{\ominus}[\operatorname{Co}^{2+}, \operatorname{aq}] \\ & + 2\Delta_f H_m^{\ominus}[\operatorname{Cl}^-, \operatorname{aq}] + 2\Delta_f H_m^{\ominus}[\operatorname{HAc}, \operatorname{aq}] \\ & + 4\Delta_f H_m^{\ominus}[\operatorname{H}_2\operatorname{O}, 1] - \Delta_f H_m^{\ominus}[\operatorname{Co}(\operatorname{Ac})_2 \\ & \cdot 4\operatorname{H}_2\operatorname{O}, s] - 2\Delta_f H_m^{\ominus}[\operatorname{HCl}, \operatorname{aq}] \end{split}$$

according to Ref. [16]:

$$\begin{split} &\Delta_{\rm f} H^{\ominus}_{\rm m}[{\rm Co}^{2+},{\rm aq}] = -58.200\,{\rm kJ\,mol}^{-1} \\ &\Delta_{\rm f} H^{\ominus}_{\rm m}[{\rm Cl}^{-},{\rm aq}] = -167.159\,{\rm kJ\,mol}^{-1} \\ &\Delta_{\rm f} H^{\ominus}_{\rm m}[{\rm HAc},\ 1\,{\rm mol\,in}\ 2000\,{\rm mol\,}\,{\rm H_2O}] \\ &= -485.750\,{\rm kJ\,mol}^{-1}, \\ &\Delta_{\rm f} H^{\ominus}_{\rm m}[{\rm HC1},\ 1\,{\rm mol\,in}\ 10\,{\rm mol\,}\,{\rm H_2O}] \\ &= -161.318\,{\rm kJ\,mol}^{-1} \end{split}$$

 $\Delta_{\rm f} H_{\rm m}^{\ominus}[{\rm H}_2{\rm O},1] = -285.830 \,{\rm kJ}\,{\rm mol}^{-1}$

and the value $\Delta_{s}H_{m}^{\ominus}[Co(Ac)_{2} \cdot 4H_{2}O, s] = -17.162 \text{ kJ mol}^{-1}$ obtained above so $\Delta_{f}H_{m}^{\ominus}$ [Co(Ac)₂ · 4H₂O, s] = -2167.540 \text{ kJ mol}^{-1}

3.3.3. Determination of the standard molar formation enthalpy of Co(SAO)₂·2H₂O(s) From the reaction (2),

$$\begin{split} \Delta_{\mathbf{r}} H^{\ominus}_{\mathbf{m}}(2) &= \Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{Co}(\operatorname{SAO})_2 \cdot 2\mathrm{H}_2\mathrm{O}, \mathrm{s}] \\ &+ 2\Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{HAc}, \mathrm{g}] + 2\Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\mathrm{H}_2\mathrm{O}, \mathrm{g}] \\ &- \Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{HSAO}, \mathrm{s}] \\ &- \Delta_{\mathbf{f}} H^{\ominus}_{\mathbf{m}} [\operatorname{Co}(\operatorname{Ac})_2 \cdot 4\mathrm{H}_2\mathrm{O}, \mathrm{s}] \end{split}$$

and the value obtained above:

$$\begin{split} \Delta_{\rm r} H_{\rm m}^{\ominus}(2) &= 222.453\,{\rm kJ\,mol^{-1}}\\ \Delta_{\rm f} H_{\rm m}^{\ominus}[{\rm Co(Ac)}_2\cdot 4{\rm H}_2{\rm O},{\rm s}]\\ &= -2167.540\,{\rm kJ\,mol^{-1}} \end{split}$$

as well as Ref. [14]:

$$\begin{split} &\Delta_{\rm f} H^{\ominus}_{\rm m}[{\rm HSAO},{\rm s}] = -183.720\,{\rm kJ\,mol^{-1}}\\ &\Delta_{\rm f} H^{\ominus}_{\rm m}[{\rm HAc},{\rm g}] = -434.843\,{\rm kJ\,mol^{-1}}\\ &\Delta_{\rm f} H^{\ominus}_{\rm m}[{\rm H}_2{\rm O},{\rm g}] = -241.818\,{\rm kJ\,mol^{-1}} \end{split}$$

then,

$$\Delta_{\rm f} H_{\rm m}^{\ominus} [\rm Co(SAO)_2 \cdot 2H_2O, s, 298.2 \, K]$$

= -957.205 kJ mol⁻¹

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