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# Standard enthalpy of formation of $[Ni(NH_3)_6]Cl_2(cr)$ as determined by solution-reaction calorimetry "

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The standard molar enthalpy at 298.15 K was determined by solution-reaction calorimetry for the reaction:  $NiCl_2(cr) + 6NH_4Cl(cr) = [Ni(NH_3)_6]Cl_2(cr) + 6HCl(g)$ . From the standard molar enthalpy of reaction, the standard molar enthalpy of formation of  $[Ni(NH_3)_6]Cl_2(cr)$  was derived. The derived value is in reasonably good agreement with a value given in the NBS tables of chemical thermodynamic properties, which was based on the analysis of the equilibria:  $NiCl_2(cr) + NH_3(g) = [Ni(NH_3)]Cl_2(cr), [Ni(NH_3)]Cl_2(cr) + NH_3(g) = [Ni(NH_3)_2]Cl_2(cr).$ 

## 1. Introduction

Recently, a (gas + solid) reaction-calorimeter has been constructed in the authors' laboratory.<sup>(1)</sup> To test its performance, the reaction:  $NiCl_2(cr) + 6NH_3(g) =$  $[Ni(NH_3)_6]Cl_2(cr)$ , was conducted, the calibration being made by electrical energy supplied to a built-in heater. The derived standard molar enthalpy of reaction at 298.15 K was numerically smaller by  $10.3 \text{ kJ} \cdot \text{mol}^{-1}$  (2.5 per cent) than the value based on the standard molar enthalpies of formation of the related compounds given in the literature.<sup>(2)</sup> The literature standard molar enthalpy of formation of [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub>(cr) had been obtained from an analysis of the equilibria: NiCl<sub>2</sub>(cr)  $NH_3(g)$ =  $[Ni(NH_3)]Cl_2(cr), [Ni(NH_3)]Cl_2(cr)$ +  $NH_3(g)$  $[Ni(NH_3)_2]Cl_2(cr)$ , and  $[Ni(NH_3)_2]Cl_2(cr) + 4NH_3(g) = [Ni(NH_3)_6]Cl_2(cr).^{(3)}$ The present study was performed to examine the accuracy of the literature value by another method.

### 2. Experimental

A desirable method for the preparation of anhydrous nickel dichloride is probably the vacuum sublimation of raw nickel dichloride obtained by the dehydration of nickel dichloride hexahydrate. However, the sublimed nickel dichloride dissolved in

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water very slowly. So, finely powdered nickel dichloride was prepared by the dehydration of nickel dichloride dihydrate, obtained by the partial dehydration of the hexahydrate, at 473 K for 4 h, under a nitrogen stream containing hydrogen chloride. Anhydrous nickel dichloride thus obtained was kept under vacuum at 433 K over potassium hydroxide to remove remaining hydrogen chloride. The sample was analyzed gravimetrically for nickel using dimethylglyoxime as a precipitant and for both cobalt and iron by an atomic-absorption spectroscopic method. The results were  $w(Ni) = (0.4472 \pm 0.0001)$  (three determinations),  $w(Co) = 2.3 \times 10^{-5}$ , and  $w(Fe) = 6 \times 10^{-6}$ , where w is the mass fraction and the uncertainty is the standard deviation of the mean, while the calculated value of w(Ni) for NiCl<sub>2</sub> is 0.4529. The infrared spectrum of the sample showed weak absorption bands at 725 cm<sup>-1</sup>, 1615 cm<sup>-1</sup>, and 3400 cm<sup>-1</sup>, characteristic of nickel dichloride dihydrate. Hence, the deviation of the observed mass fraction of Ni from the calculated value is attributable to the presence of a small amount of the dihydrate as an impurity. The density used for the buoyancy correction to the weighing was  $3.521 \text{ g} \cdot \text{cm}^{-3}$ .<sup>(4)</sup>

Sublimed nickel dichloride  $\{w(Ni) = 0.4510,$  $w(Co) = 8 \times 10^{-6}$ and  $w(Fe) = 6 \times 10^{-6}$  was reacted with dry ammonia at 101 kPa, at 393 K for 12 h and then at 373 K for 60 h, in a Pyrex-glass tube to prepare hexammine nickel dichloride. The product was exposed to a nitrogen stream for 1 h to remove excess ammonia. The amount of ammonia reacted with nickel dichloride was determined by back-titration of the aqueous solution of the complex containing both excess hydrogen chloride and ammonium chloride  $\{c(NH_{4}Cl) = 1 \text{ mol} \cdot dm^{-3}\}$  with aqueous sodium hydroxide. Under this condition, the effect of the formation of  $[NiNH_3]^{2+}$  on the titration is negligibly small even at the equivalence point. The derived result was  $n(NH_3)/n(Ni) = (5.979 + 0.006)$  (five determinations), where the uncertainty is the standard deviation of the mean; the calculated value for  $[Ni(NH_3)_6]Cl_2$  is 6.000. The density used for the buoyancy correction to the weighing was 1.4808 g  $\cdot$  cm<sup>-3</sup>.<sup>(5)</sup>

The reaction used for the determination of the standard enthalpy of formation at 298.15 K of  $[Ni(NH_3)_6]Cl_2(cr)$  was

$$\operatorname{NiCl}_{2}(\operatorname{cr}) + 6\operatorname{NH}_{4}\operatorname{Cl}(\operatorname{cr}) = [\operatorname{Ni}(\operatorname{NH}_{3})_{6}]\operatorname{Cl}_{2}(\operatorname{cr}) + 6\operatorname{HCl}(g).$$
(1)

The standard molar enthalpy change  $\Delta_r H_m^\circ$ , of reaction (1), was derived from the equation:

$$\Delta_{\rm r} H_{\rm m}^{\circ} = \Delta H_{\rm m}(2) + \Delta H_{\rm m}(3) - \Delta H_{\rm m}(4) - \Delta H_{\rm m}(5) - \Delta H_{\rm m}(6),$$

where  $\Delta H_{\rm m}(i)$  (i = 2 to 6) refers to the thermochemical processes:

 $6NH_4Cl(cr) + 3204HCl \cdot 358069H_2O(sln) = 6NH_4Cl \cdot 3204HCl \cdot 358069H_2O(sln), \text{ (solution A), (2)}$ 

 $NiCl_2(cr) + solution A$ 

= NiCl<sub>2</sub>  $\cdot$  6NH<sub>4</sub>Cl  $\cdot$  3204HCl  $\cdot$  358069H<sub>2</sub>O(sln), (solution B), (3)

 $6HCl(g) + 669H_2O(l) = 6HCl \cdot 669H_2O(sln),$ (4)

$$\Delta_{\rm f} H^{\circ}_{\rm m} \{ {\rm Ni}({\rm NH}_3)_6 {\rm Cl}_2, {\rm cr}, 298.15 {\rm K} \}$$
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$$6HCl \cdot 669H_2O(sln) + 3204HCl \cdot 357400H_2O(sln) = 3210HCl \cdot 358069H_2O(sln), \text{ (solution C)}, \text{ (5)}$$

and

$$[Ni(NH_3)_6]Cl_2(cr) + solution C = solution B.$$
(6)

 $\Delta H_{\rm m}(4)$  was calculated from the literature,<sup>(2)</sup> and  $\Delta H_{\rm m}(5) = 0$ . Calorimetric experiments were carried out for reactions 2, 3, and 6, by use of an LKB 8700 isoperibol solution calorimeter. The calorimetric solutions were prepared by the dilution of standard hydrochloric acid solution (Wako,  $c = 0.499 \text{ mol} \cdot \text{dm}^{-3}$ ). The enthalpy change for a calorimetric process was calculated by the equation:  $\Delta H = -\varepsilon \Delta R/\langle R \rangle$ ,<sup>(6)</sup> where  $\varepsilon$  is the energy equivalent of the calorimeter obtained by electrical calibration,  $\Delta R$  is the change in the resistance of the thermistor corrected for heat exchange with the surroundings and for subsidiary temperature rise, and  $\langle R \rangle$  is the mean resistance during the reaction period.

# 3. Results and discussion

Results of the calorimetric experiments are summarized in table 1. Corrections due to the presence of impurities in the samples were made for the observed values of  $\Delta H_m(3)$  and  $\Delta H_m(6)$ .

TABLE 1. Results of solution-reaction calorimetric experiments; n, amount of substance dissolved based on the assumption that the samples are absolutely pure;  $\Delta R$ , change in the thermistor resistance in a hypothetical adiabatic process;  $\langle R \rangle$ , mean resistance during a reaction;  $\varepsilon$ , energy equivalent;  $\Delta H$ , observed enthalpy change; s, standard deviation of mean.  $\Delta H_m(i)$ , molar enthalpy of reaction for process i based on n(A)

n(A)	$10^{3}\Delta R$	3	$\Delta H$	$\Delta H_{m}(i)$
mmol	$\langle R \rangle$	Ĵ	J	kJ · mol <sup>−1</sup>
$i = 2; A = NH_4Cl(cr)$				
1.85180	-2.794	10664	29.80	96.54
1.93278	-2.796	11059	30.92	95.99
1.93698	-2.771	11126	30.83	95.50
			mean: 96.01; $s = 0.30$	
$i = 3$ ; $A = NiCl_2(cr)$				
0.285694	2.257	9857	-22.25	-77.87
0.283892	2.267	9726	-22.05	- 77.67
0.293392	2.242	10134	-22.72	- 77.44
			mean: $-77.66; s = 0.12$	
$i = 6; A = [Ni(NH_3)_6]$	]Cl <sub>2</sub> (cr)			
0.312101	5.3855	10730	- 57.786	-185.16
0.316338	5.3539	10859	- 58.138	-183.78
0.312106	5.6329	10228	- 57.613	-184.59
0.316098	5.3900	10858	- 58.525	-185.15
0.311764	5.2884	10877	- 57.522	-184.50
0.317788	5.3968	10951	- 59.100	-185.97
			mea	an: $-184.86$ ; $s = 0.30$

From the elemental analysis and the infrared measurement, the composition of the NiCl<sub>2</sub> sample used for the determination of  $\Delta H_m(3)$  was estimated to be  $\{0.9537\text{NiCl}_2(\text{cr}) + 0.0463\text{NiCl}_2 \cdot 2\text{H}_2\text{O}(\text{cr})\}$ . Hence, the molar enthalpy of solution of NiCl<sub>2</sub>  $\cdot 0.0926\text{H}_2\text{O}(\text{cr})$  into solution A is  $-78.66 \text{ kJ} \cdot \text{mol}^{-1}$ . The molar enthalpy of solution  $\Delta H_m(7)$  of NiCl<sub>2</sub>  $\cdot 2\text{H}_2\text{O}(\text{cr})$  into solution A was estimated by the scheme:

 $NiCl_2 \cdot 2H_2O(cr) + solution A$ 

= 
$$NiCl_2 \cdot 6NH_4Cl \cdot 3204HCl \cdot 358071H_2O(sln)$$
, (solution D), (7)

$$\operatorname{NiCl}_{2} \cdot 2\operatorname{H}_{2}O(\operatorname{cr}) = \operatorname{NiCl}_{2}(\operatorname{cr}) + 2\operatorname{H}_{2}O(\operatorname{I}), \tag{8}$$

$$NiCl_2(cr) + solution A = solution B,$$
 (3)

and

$$2H_2O(l) + solution B = solution D,$$
 (9)

It follows that

$$\Delta H_{\rm m}(7) = \Delta H_{\rm m}(8) + \Delta H_{\rm m}(3) + \Delta H_{\rm m}(9), \tag{10}$$

and, to a good approximation,

$$0.9537\Delta H_{\rm m}(3) + 0.0463\Delta H_{\rm m}(7) = -78.66 \text{ kJ} \cdot \text{mol}^{-1}.$$
 (11)

 $\Delta H_{\rm m}(8)$  was calculated to be 45.21 kJ·mol<sup>-1</sup>,<sup>(2)</sup> and  $\Delta H_{\rm m}(9)$  can be taken to be zero. By solving equations (10) and (11) simultaneously, there were derived:  $\Delta H_{\rm m}(3) = -80.75 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta H_{\rm m}(7) = -35.54 \text{ kJ} \cdot \text{mol}^{-1}$ .

From the results of titrations on the  $[Ni(NH_3)_6]Cl_2$  sample, the composition was estimated to be  $\{0.9948[Ni(NH_3)_6]Cl_2 + 0.0052NiCl_2 \cdot 2NH_3\}$ . The molar enthalpy change for the solution of  $NiCl_2 \cdot 5.979NH_3(cr)$  into solution C is  $-184.58 \text{ kJ} \cdot \text{mol}^{-1}$ . The molar enthalpy of solution of  $[Ni(NH_3)_2]Cl_2(cr)$  into solution C was estimated by the scheme:

$$\operatorname{NiCl}_{2} \cdot 2\operatorname{NH}_{3}(\operatorname{cr}) + 4\operatorname{NH}_{4}\operatorname{Cl}(\operatorname{cr}) + 2\operatorname{HCl}(g) = \operatorname{NiCl}_{2}(\operatorname{cr}) + 6\operatorname{NH}_{4}\operatorname{Cl}(\operatorname{cr}), \quad (12)$$

$$2HCl(g) + 223.1H_2O(l) = 2HCl \cdot 223.1H_2O(sln),$$
(13)

$$2HCl \cdot 223.1H_2O(sln) + 3208HCl \cdot 357845.9H_2O(sln) = solution C,$$
 (14)

 $NiCl_2 \cdot (NH_3)_2(cr) + solution C$ 

= NiCl<sub>2</sub> · (NH<sub>3</sub>)<sub>2</sub> · 3210HCl · 358069H<sub>2</sub>O, (solution E), (15)

 $4NH_4Cl(cr) + solution E$ 

 $6NH_4Cl(cr) + 3208HCl \cdot 358069H_2O(sln) = 6NH_4Cl \cdot 3208HCl \cdot 358069H_2O(sln), \text{ (solution G)}, \text{ (17)}$ 

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and

 $NiCl_{2}(cr) + solution G$ = NiCl\_{2} · 6NH\_{4}Cl · 3208HCl · 358069H\_{2}O(sln), (solution E). (18)

 $\Delta H_{\rm m}(15)$  is given by

$$\Delta H_{\rm m}(15) = \Delta H_{\rm m}(12) + \Delta H_{\rm m}(17) + \Delta H_{\rm m}(18) - \Delta H_{\rm m}(13) - \Delta H_{\rm m}(14) - \Delta H_{\rm m}(16), (19)$$

where  $\Delta H_{\rm m}(12) = -182.18 \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(2)</sup>  $\Delta H_{\rm m}(13) = -147.38 \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(2)</sup> and  $\Delta H_{\rm m}(14) = 0$ . The following relations hold approximately:  $\Delta H_{\rm m}(16) = (2/3)\Delta H_{\rm m}(2)$ ,  $\Delta H_{\rm m}(17) = \Delta H_{\rm m}(2)$ , and  $\Delta H_{\rm m}(18) = \Delta H_{\rm m}(3)$ . It follows that  $\Delta H_{\rm m}(15) = -83.55 \text{ kJ} \cdot \text{mol}^{-1}$ . By substituting this value into the equation:

$$0.9488\Delta H_{\rm m}(6) + 0.0052\Delta H_{\rm m}(15) = -184.53 \text{ kJ} \cdot \text{mol}^{-1}, \tag{20}$$

the corrected value for  $\Delta H_{\rm m}(6)$  is  $-(185.11\pm0.75)$  kJ·mol<sup>-1</sup>.

In this paper, it was assumed that an uncertainty associated with the standard enthalpy of formation given in reference 2 is 10 times the last digit of the value, and the final overall uncertainties were calculated by combining twice the standard deviations of the means of the observed quantities with the estimated uncertainties of the literature values using the error-propagation equation.

Consequently,  $\Delta_r H_m^\circ$  for reaction (1) was evaluated as  $\Delta_r H_m^\circ(298.15 \text{ K}) = (642.52 \pm 0.82) \text{ kJ} \cdot \text{mol}^{-1}$ . From this value, using  $\Delta_f H_m^\circ(\text{NiCl}_2, \text{cr}) = -305.332 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $\Delta_f H_m^\circ(\text{NH}_4\text{Cl}, \text{cr}) = -314.43 \text{ kJ} \cdot \text{mol}^{-1}$ , and  $\Delta_f H_m^\circ(\text{HCl}, \text{g}) = -92.307 \text{ kJ} \cdot \text{mol}^{-1}$ ,<sup>(2)</sup> the molar enthalpy of formation of  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2(\text{cr})$  was derived:  $\Delta_f H_m^\circ\{[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2, \text{cr}, 298.15 \text{ K}\} = -(995.6 \pm 1.0) \text{ kJ} \cdot \text{mol}^{-1}$ , where the uncertainty was evaluated as described above. This value agrees with the value given in reference 2 ( $-994.1 \text{ kJ} \cdot \text{mol}^{-1}$ ), at least, within the sum of the uncertainties. Thus, the accuracy of the latter value was reconfirmed by the present solution-reaction calorimetric experiments, and this led to the recalibration of the (gas + solid) reaction-calorimeter, which gave a satisfactory result.

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