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# BRIEF COMMUNICATIONS

# Standard Enthalpy of Formation of Nickel Trifluoride by Isothermal Calorimetry

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Abstract—The change in enthalpy in reactions of NiF<sub>3</sub>(s) with water and aqueous solution of potassium hydroxide are measured in the isothermal calorimetry mode at 298.15 K. The standard enthalpy of formation  $\Delta_{\rm f} H^{\circ}$  of nickel trifluoride was found to be  $-816 \pm 6$  kJ/mol.

*Keywords*: isothermal calorimetry, enthalpy of formation, water, nickel trifluoride. **DOI:** 10.1134/S0036024412030296

## **INTRODUCTION**

As part of our research program, we are interested in the thermodynamic and structural (NiF<sub>3</sub> or Ni[NiF<sub>6</sub>]) properties of hexafluoronickelates(IV) [1– 4] which are promising oxidative reagents. Here we present our work on determining the enthalpy formation of NiF<sub>3</sub>(s) from calorimetric experiments.

#### **EXPERIMENTAL**

The studied samples of nickel trifluoride were synthesized by V.B. Sokolov and A.V. Ryzhkov at the Kurchatov Institute National Research Centre. The specimens were found to be homogeneous (single phase) and stoichiometric (accuracy,  $\pm 1\%$ ) from the results of X-ray diffraction phase and quantitative chemical analyses, respectively.

The thermochemical measurements were performed using an isothermal calorimeter [5] with a thermometric and calorimetric sensitivity of  $1.2 \times 10^{-5}$  K and 0.01 K, respectively. The accuracy of maintaining temperature via a thermostat was  $\pm 0.005$  K. A semiconductor resistance thermometer of 77350  $\Omega$  was used at 298.15 K to monitor changes in temperature (3500  $\Omega$  per 1 K).

It was established in a series of experiments that the interaction of 1 mol of nickel trifluoride with water or aqueous potassium alkali yields 0.5 mol of gaseous oxygen (accuracy,  $\pm 1\%$ ).

## **RESULTS AND DISCUSSION**

The results from our calorimetric experiments are given in the table below. It should be noted that the difference between the heat capacity of the investigated centimolal solutions and the heat capacity of water was beyond the measurement error, and the calorimeter's heat capacity  $(0.1601 \pm 0.0003 \text{ J}/\Omega)$  was therefore used for all heat calculations. This was determined by monitoring changes in the resistance of the thermistor after filling the calorimetric cell with 120 g of water and passing known amounts of electric current thought the heater. The systematic error in measuring the heat capacity of the calorimeter did not exceed  $\pm 0.1\%$ .

The reaction of NiF<sub>3</sub> with water yielded a pale green solution, while the interaction with aqueous potassium hydroxide resulted in a suspension from which a greenish precipitate easily soluble in mineral acids was formed when left standing.

Extra precautions were taken while working with KOH solutions to avoid contamination with carbonates.

A number of chemical analyses were performed to determine the composition of the reaction mixtures after conducting the calorimetric experiments. The concentration of fluoride ions was thus established by titration with thorium nitrate and sodium alizarin sulfonate as an indicator (accuracy,  $\pm 1\%$ ). Titration with standardized solutions of HCl or KOH was used to find the total basicity or acidity, respectively, of reaction solutions (accuracy,  $\pm 0.5\%$ ). Titration with a standardized Trilon B solution was performed (accuracy,  $\pm 1\%$ ) to determine the concentration of nickel(II) ions in the investigated solutions (obtained directly from calorimetric experiments or prepared by dissolving Ni(OH)<sub>2</sub> precipitate in an acid).

Our analyses allowed us to conclude that water is oxidized into molecular oxygen upon the reaction of nickel trifluoride with aqueous solutions. The other products were HF and  $NiF_2$  when reacting with pure

$R_0, \Omega$	δ, Ω	$-\Delta R, \Omega$	q, mg	<i>Q</i> , J	$-\Delta H$ , kJ/mol
Water					
77570.17	16.26	195.75	40.28	31.34	90.0
77 593.54	18.41	208.43	45.41	33.37	85.0
77599.23	23.76	212.55	42.79	34.03	92.0
77589.76	20.84	201.06	39.83	32.19	93.5
77 505.37	-14.93	209.93	41.15	33.61	94.5
77496.88	-21.87	251.28	50.04	40.23	93.0
77568.45	15.25	190.13	40.95	30.44	86.0
77510.59	-19.66	197.50	43.29	31.62	84.5
77486.46	-25.52	245.91	47.94	39.37	95.0
77601.81	20.68	203.00	41.09	32.50	91.5
KOH solution					
77612.38	32.15	334.23	35.78	53.51	173
77644.87	36.42	349.03	38.94	55.88	166
77568.19	-15.56	286.51	32.16	45.87	165
77 531.27	-29.51	371.96	40.29	59.55	171
77637.83	40.74	392.50	42.76	62.84	170
77625.76	32.62	306.37	34.81	49.05	163
77 522.34	-35.39	323.17	35.63	51.74	168
77631.95	38.68	327.98	38.77	52.51	171
77519.71	-39.47	365.90	40.95	58.58	166
77642.11	40.78	345.47	37.86	55.31	169

Results from calorimetric experiments (298.15 K) on the reaction between  $NiF_3(s)$  and water and  $NiF_3(s)$  and 0.05 molal solution of KOH

Note:  $R_0$  is the initial resistance of the thermistor,  $\delta$  is the correction factor for heat transfer,  $\Delta R$  is the corrected value of temperature change, q is the sample weight, Q is the amount of reaction heat produced,  $\Delta H$  is enthalpy of the reaction,  $\sigma$  is the standard deviation, and  $t_{0.05}$  is the Student *t*-distribution parameter; for water:  $\Delta H_{av} = -91$  kJ/mol,  $\sigma = 1$  kJ/mol,  $\sigma t_{0.05} = 3$  kJ/mol; for solution of KOH;  $\Delta H_{av} = -168$  kJ/mol,  $\sigma = 1$  kJ/mol,  $\sigma t_{0.05} = 2$  kJ/mol.

water, and KF,  $Ni(OH)_2$  precipitate, and excessive KOH if a potassium alkali solution was used.

The thermochemical equations of studied reactions are therefore

NiF<sub>3</sub>(s) + 17921H<sub>2</sub>O(l) = NiF<sub>2</sub>(soln1)  
+ (1/4)O<sub>2</sub>(soln1) + HF(soln1)  
+ 17920 · 5H<sub>2</sub>O(soln1);  
$$\Delta H = -90.5 \pm 2.8 \text{ kJ},$$
  
NiF<sub>3</sub>(s) + 18KOH(soln, KOH · 1111H<sub>2</sub>O)  
= Ni(OH)<sub>2</sub>(s, freshly precipitated)  
+ 3KF(soln2) + 1/4O<sub>2</sub>(soln2)  
+ (1/2)H<sub>2</sub>O(soln2) + 15KOH(soln2);  
 $\Delta H = -168 \pm 2 \text{ kJ}$ 

where soln1 is the  $NiF_2 \cdot HF \cdot 17920.5H_2O$  and soln2 is the  $3KF \cdot 15KOH \cdot 19998.5H_2O$ .

The direct calorimetric measurements in [1, 2] showed that there are no interactions in the NiF<sub>2</sub>-

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HF-H<sub>2</sub>O and KOH-KF-H<sub>2</sub>O systems that would exceed  $\pm 0.4$  kJ per mol of NiF<sub>2</sub> or KF in a range of concentration range similar to ours. According to [1], the oxygen that evolved during the reaction stayed dissolved in the water when the amount of hexafluoronickelates(IV) reacting with aqueous solutions was less than  $3.4 \times 10^{-4}$  mol. In light of this and the low concentration of working solutions, it is reasonable to assume that the enthalpies of formation of NiF<sub>2</sub>, HF, KF, KOH, and H<sub>2</sub>O under the conditions of the given calorimetric experiments are the same as the heat of formation of these compounds in pure water [6]. The uncertainties of all the intermediate variables were considered in calculating the corresponding errors. The standard enthalpies of formation of NiF<sub>3</sub>(s) at 298.15 K were therefore found to be  $-817 \pm 7$  and  $-814 \pm 9$  kJ/mol for reactions (1) and (2), respectively, yielding an average value of  $-816 \pm 6$  kJ/mol.

## CONCLUSIONS

A comparison of our thermochemical data with the enthalpies of formation of other hexafluoronickelates(IV) [1–4] along with our analysis of the literature data on the heat of formation of di- and trifluorides of *d*-elements [6] allow us to conclude that nickel trifluoride compound exists in the Ni[NiF<sub>6</sub>] molecular form.

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