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Standard enthalpies of formation of $KCaH_{3-x}F_x$ with $x = 1, 1.5, 2, 2.5$

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Abstract

The standard enthalpies of formation of $KCaH_{3-x}F_x$ with $x = 1$, 1.5, 2, 2.5 were determined by calorimetry using their reaction with hydrochloric acid aqueous solution (0.5 M HCl):

$$\Delta_f H^0\ (KCaH_2F,\ cr,\ 298\,K) = -(874 \pm 38)\,kJ\,mol^{-1}$$

$$\Delta_f H^0\ (KCaH_{1.5}F_{1.5},\ cr,\ 298\,K) = -(1092 \pm 5)\,kJ\,mol^{-1}$$

$$\Delta_f H^0\ (KCaHF_2,\ cr,\ 298\,K) = -(1305 \pm 16)\,kJ\,mol^{-1}$$

$$\Delta_f H^0\ (KCaH_{0.5}F_{2.5},\ cr,\ 298\,K) = -(1524 \pm 12)\,kJ\,mol^{-1}$$

The standard enthalpy of formation of $KCaH_3$ was estimated on the basis of the experimental measurements and on the value for potassium–calcium fluoride ($KCaF_3$) noted in the literature:

$$\Delta_f H^0\ (KCaH_3,\ cr,\ 298\,K) = -(442 \pm 38)\,kJ\,mol^{-1}$$

These results show that hydride compounds are less stable than fluoride homologous.

Keywords: Hydride; Hydridofluoride; Perovskite; Standard enthalpy of formation; Calorimetry

1. Introduction

In previous works [1,2], standard enthalpies of formation of perovskite-like potassium–magnesium and sodium–magnesium hydrides and hydridofluorides were determined with calorimetric measurements and estimation methods.

In the same way, this study is based on potassium–calcium similar compounds.

2. Experimental

2.1. Synthesis

Because of the extreme sensitivity of the compounds being studied, handling and sampling are performed in a glove box under perfectly dried and deoxygenated argon atmosphere (with gas circulating system).

Hydridofluorides $KCaH_{3-x}F_x$ with $x = 1, 1.5, 2, 2.5$ were synthesised from required proportions of powdered KF, CaF_2 and CaH_2 (high purity chemicals from

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Aldrich). The powders weighed in the calculated ratios were pressed into a pellet then heated at 753 K for 2 days under 40 bar hydrogen pressure (in order to avoid any decomposition) in a stainless steel autoclave. The product of reaction was recovered and conditioned in a glove box.

2.2. X-ray powder diffraction and chemical analysis

In spite of several attempts, no single crystals of our products could be prepared.

Powder diffraction patterns were obtained with a Philips goniometer. Cu Kα radiations were used (1.5418 Å). The hydridofluoride powder is conditioned in the glove box into a sample holder equipped with a X-ray transparent polyimide film in order to prevent any air moisture.

In all cases, X-ray diffraction reveals the presence of a single phase and an absence of starting reagents.

These phases crystallise with an orthorhombic structure. Their lattice parameters were determined and refined using a less square method. They are summarised in Table 1 in which the lattice constants of the well-known fluoride ($KCaF_3$) [3] are reported for comparison.

Alkali and alkaline-earth amounts were determined by high frequency plasma [4] and fluoride ion by electrochemistry [5]. Theses results confirm composition of ours samples.

2.3. Principle of calorimetric measurements

Standard enthalpy of formation was determined by calorimetry of reaction, based on the study of the action of aqueous solution of hydrochloric acid (0.5 M HCl) on this compound. Final state was characterised according to: a sample was attacked by HCl then solid or solids, obtained after a slow evaporation are identified by X-ray diffraction.

Table 1
Cell parameters (Å) of hydridofluorides and fluoride of potassium–calcium

Parameter	Compound				
	$KCaH_2F$	$KCaH_{1.5}F_{1.5}$	$KCaHF_2$	$KCaH_{0.5}F_{2.5}$	$KCaF_3$ [3]
a (Å)	6.268	6.259	6.234	6.221	6.209
b (Å)	8.866	8.819	8.810	8.784	8.757
c (Å)	6.274	6.239	6.208	6.184	6.164

The enthalpy of reaction was determined at 298 K using a LKB 8700 isoperabolic calorimeter improved in our laboratory. Description of the apparatus and principle of measurements are detailed in previous papers [6,7].

The calorimeter is standardised using the Tris-(hydroxymethyl)-aminomethane (THAM) reaction with 0.1 M HCl. The result is in agreement with the reference value [8].

Masses of used samples varied from 5 to 15 mg (±0.1 mg) and were weighed with an electronic balance (Denver Instrument type). Hydridofluoride powder was contained in a PTFE vessel (1 cm^3) which was opened into a cell of reaction (100 cm^3). Filling of the vessels was carried out in the glove box.

2.4. Experimental results

For all measurements, the precision of energy values is better than 98%. The accuracy of final results is better than 4%.

2.4.1. $KCaH_2F$, $KCaH_{1.5}F_{1.5}$, $KCaHF_2$, $KCaH_{0.5}F_{2.5}$

Procedure is only detailed for $KCaH_2F$.

$KCaH_2F(cr)$ reacts with HCl(aq) according to:

$$\mathrm{KCaH_2F(cr) + 3HCl(aq) \rightarrow KCl(aq) + CaCl_2(aq) + 2H_2(g) + HF(aq)} \qquad \text{(r1)}$$

$\Delta_{r1}H$ is the enthalpy of this reaction:

$$\Delta_{r1}H = \Delta_f H^0\,\mathrm{KCl(aq)} + \Delta_f H^0\,\mathrm{CaCl_2(aq)} + \Delta_f H^0\,\mathrm{HF(aq)} - 3\Delta_f H^0\,\mathrm{HCl(aq)} - \Delta_f H^0\,\mathrm{KCaH_2F(cr)} + \Delta_{dil(1)}H \qquad (1)$$

Eq. (1) is used for determining the searched value $\Delta_f H^0$ ($KCaH_2F$, cr, 298 K).

$\Delta_{dil(1)}H$ is a corrective value which takes in account the initial HCl concentration decrease due to consumption of acid during the reaction. This value is determined by a method developed in the laboratory [9]. In our experimental conditions, considering the low account of used samples then a low variation of acid concentration during the reaction of dissolution, the thermal effect combined with phenomenon of dilution can be neglected.

Table 2
Standard enthalpies of formation of KCl(aq), $CaCl_2$(aq), HCl(aq) from literature [10]

	KCl(aq)	$CaCl_2$(aq)	HCl(aq)
$\Delta_f H^0$ (kJ mol^{-1})	−418.65	−877.88	−167.45

Standard enthalpies of formation of KCl(aq), $CaCl_2$(aq), HCl(aq) are known from literature [10] and summarised in Table 2. Enthalpy of formation of HF (0.001 M in our experimental conditions) in aqueous solution of hydrochloric acid (0.5 M HCl) is equal to -320.21 kJ mol^{-1} [11].

Many attempts are performed to obtain enthalpy of reaction $\Delta_{r1}H$. Results are reported in Table 3. The average value is: $\Delta_{r1}H = -(240 \pm 38)$ kJ mol^{-1}.

From Eq. (1)

$$\Delta_f H^0 \ (KCaH_2F, \text{cr}, 298\,K) = -(874 \pm 38)\,\text{kJ mol}^{-1}$$

For the others ($KCaH_{1.5}F_{1.5}$, $KCaHF_2$, $KCaH_{0.5}F_{2.5}$), HCl reacts with these compounds in the same manner.

Experimental values of enthalpy of reaction $\Delta_{r1}H$ are reported in Table 4. The average values are reported in Table 5.

According to Eq. (1), standard enthalpy of formation are calculated and summarised in Table 5.

2.4.2. $KCaH_3$

Hydride $KCaH_3$ was not synthesised. Its standard enthalpy of formation has been determined by an estimation, method previously described [2]. This method consists in taking to account only anionic substitution. So we can write:

$$\Delta_f H(KCaH_2F, \text{cr}, 298\,K) = \tfrac{2}{3}\Delta_f H^0(KCaH_3, \text{cr}, 298\,K) + \tfrac{1}{3}\Delta_f H^0\ (KCaF_3, \text{cr}, 298\,K) \qquad (2)$$

Table 3
Experimental values of enthalpy ($\Delta_r H$ in J g^{-1}) of reaction of 0.5 M HCl on $KCaH_2F$

	Mass (mg)	$\Delta_r H$ (J g^{-1})
$KCaH_2F$	4.9	−2408.2
	5.8	−2636.2
	5.4	−2261.1
	4.5	−2737.7
	5.0	−1984.5
	7.4	−2379.2

Table 4
Experimental values of enthalpy ($\Delta_r H$ in J g^{-1}) of reaction of 0.5 M HCl on the others compounds

Compound	Mass (mg)	$\Delta_r H$ (J g^{-1})
$KCaH_{1.5}F_{1.5}$	7.7	−1668.3
	8.1	−1642.5
	10.5	−1737.7
	13.8	−1690.2
	13.2	−1654.8
	10.1	−1678.8
$KCaHF_2$	5.1	−1000.0
	4.0	−1321.5
	10.8	−1140.2
	6.5	−1002.9
	8.0	−1046.3
$KCaH_{0.5}F_{2.5}$	5.9	−578.8
	13.4	−643.3
	9.4	−698.0
	11.9	−504.1
	11.1	−478.0
	15.1	−455.1

Table 5
Enthalpy of reaction and standard enthalpy of formation of synthesised products

Compound	$\Delta_r H$ (kJ mol^{-1})	$\Delta_f H^0$ (kJ mol^{-1})
$KCaH_{0.5}F_{2.5}$	71 ± 12	1524 ± 12
$KCaHF_2$	130 ± 16	1305 ± 16
$KCaH_{1.5}F_{1.5}$	183 ± 5	1092 ± 5
$KCaH_2F$	240 ± 38	874 ± 38

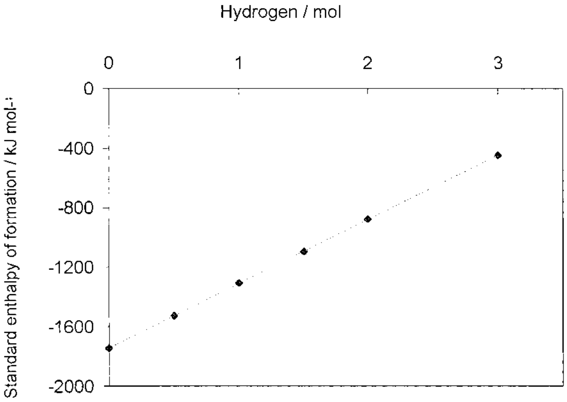

Fig. 1. Evolution of standard enthalpy of formation vs. hydrogen content in $KCaH_{3-x}F_x$ family.

The value for $KCaH_2F$ is known with preceding results. Standard enthalpy of formation of $KCaF_3$ is given in literature [12]: $\Delta_f H^0$ ($KCaF_3$, cr, 298 K) = −1754.4 kJ mol^{-1}.

From Eq. (2): $\Delta_f H^0$ ($KCaH_3$, cr, 298 K) = −(434± 38) kJ mol^{-1}.

This result agrees very well with the evolution of standard enthalpy of formation with hydrogen molar number as shown in Fig. 1.

Graphically, a value of −442 kJ mol^{-1} is obtained for $\Delta_f H^0$ ($KCaH_3$, cr, 298 K).

Obtained value from Fig. 1 agrees with obtained value by the method of anionic substitution.

3. Conclusion

Table 6 summarises the values of standard enthalpies of formation of $KCaH_{3-x}F_x$ with $x = 0, 1, 2, 3$ obtained in this work. For comparison the values for $KMgH_{3-x}F_x$ and $NaMgH_{3-x}F_x$ with $x = 0, 1, 2, 3$, [1,2] are also reported.

For these compounds, it is clearly established that substituting fluorine by hydrogen involves a drastic decrease in their stability: hydrides are more reactive than fluorides.

The evolution of $\Delta_f H^0$ does not depend on the crystalline structure of compound. In fact, only a structural factor connected to the cation size must be taken in account: standard enthalpy of formation is high for large cations and related compounds are less reactive.

Finally, evolution of $\Delta_f H^0$ depends on difference in iono-covalent character of metal–hydrogen bond. This behaviour can be assign not only to the difference on electropositivity between alkali and alkaline-earth cations but also to the difference in polarisability between fluorine and hydrogen [13].

Table 6
Comparison of standard enthalpies of formation ($\Delta_f H^0$ in kJ mol^{-1}) for $KMgF_{3-n}H_n$, $NaMgF_{3-n}H_n$ and $KCaF_{3-n}H_n$

	$\Delta_f H^0$ (kJ mol^{-1})			
	$MM'H_3$	$MM'H_2F$	$MM'HF_2$	$MM'F_3$
M = Na, M′ =Mg, [2]	−232	−718	−1221	−1716
M = K, M′ =Mg, [1]	−278	−762	−1246	−1727
M = K, M′ = Ca, this work	−442	−874	−1305	−1754

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