THE CHARACTERIZATION OF THE THERMAL BEHAVIOUR OF INORGANIC FLUORIDES USING QUASI-STATIC THERMOANALYTICAL METHODS

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Quasi-static thermal analysis is very useful for the characterization of the thermal behaviour of inorganic fluorides. The strong dependence of the thermal decomposition of hydroxonium fluorometallates, monofluorophosphates, and ammonium fluorometallates on the partial pressure is demonstrated. Non-reciprocal quasi-isobaric investigations are especially suitable to disclose this behaviour. The possibilities of characterization of the reaction mechanism using quasi-static thermal analytical methods as well as the use of these methods as synthetic variants for phase-pure fluorides are demonstrated by further examples. In this context the repression of the amount of hydrolysis products is discussed.

Keywords: inorganic fluorides, quasi-static thermal analysis

Introduction

The application of fluorides as catalysts, precursors or raw materials for fluoride glasses requires exact knowledge on thermal behaviour of these compounds. In most cases thermal decomposition and reaction of hydrolysis take place simultaneously. In literature these two parts are not consequently separated. Therefore many examples exist in which the published data on thermal stability of fluoride containing materials as well as the information on thermal decomposition reactions are in contrast to expectations based on thermodynamical estimations.

Paulik and Paulik [1], Rouquerol [2], Sörensen [3], and Bean and Oliver [4] have developed the so called reciprocal thermal analysis, the controlled transformation rate thermal analysis (CRTA). The quasi-static methods of thermal analysis are special cases of CRTA. These methods allow to work near the equilibrium state. The results of such measurements are better

comparable to thermodynamic values, and the single steps of thermal decomposition are better separated.

Up to now, these techniques are rarely used in order to characterize the thermal behaviour of inorganic fluorides. Therefore the aim of the present paper is to give some experiences and to demonstrate some particularities using quasi-static methods for studies of thermal decomposition reactions of inorganic fluorides.

Experimental

The main principle of all variants of quasi-static thermoanalytical methods is to control the reactions of thermal decomposition or transition in such a way, that at least one of the reaction parameters is not changed or only changes within narrow bonds.

Usually the quasi-static conditions are adjusted by heating control. All of the commonly recorded thermoanalytical signals like DTG, DTA, Δp and Δl can be applied as a control characteristic of the heating control system. The temperature program is changed until the selected parameter is equal or smaller as the maximum determined by the user (reciprocal form of thermal analysis). The control effect determines the denotation of the method: quasi-isobaric, quasi-isothermal, and so on [1].

A special case is the quasi-isobaric thermal analysis. Three different forms of this method exist, namely two kinds of reciprocal thermal analysis (the control characteristic is either the total pressure or a spectroscopically determined partial pressure) and one non-reciprocal form. Non-reciprocal quasi-isobaric investigations are possible using special forms of crucibles claimed by Paulik and Paulik [1]. These crucibles allow to suppress a remixing of the gaseous reaction products with the atmosphere of the furnace. In this way different values of constant partial pressures are realized in dependence on the crucible form.

Paulik and Paulik [1] already pointed out the necessity to ensure a constant concentration of gaseous reaction products during the whole transformation process as a precondition for the success of quasi-static thermoanalytical methods. Therefore combinations of quasi-static and non-reciprocal quasi-isobaric techniques are used in most cases.

Nevertheless thermal behaviour can change dramatically by varying the partial pressure of the reaction products [1]. Our experiences show that this is characteristic for inorganic fluorides.

At a partial pressure of 70 kPa or more the atmosphere above the sample is mainly determined by the gaseous reaction products. In this case one can describe the atmosphere as 'self-generated' or the conditions as non-reciprocal quasi-isobaric. It should be mentioned, that mostly no change of the reaction mechanism is detectable by further increase of the partial pressure. Therefore the comparison of the results of the non-reciprocal quasi-isobaric and the classical forms of thermal analysis discloses the influence of partial pressure on the decomposition or transformation reactions. The comprehension of all other forms of quasi-static kinds of thermal analysis also requires such measurements.

The thermal analysis was carried out with the Derivatograph Q1500D which was modified for analyzing high reactive substances [5] and coupled with a computer MC 80. A further modification makes it possible to use the DTG or DTA signal alternatively as control characteristic of the original heating control system. The following parameters were used:

Sample mass: 200–400 mg dynamic heating rate: 2,5 and 5 deg/min, quasi-static heating rate: 3 deg/min without thermal effect, 0,6%/min with DTG or DTA effect; atmosphere N_2, pumping rate 8 l/h; reference: Al_2O_3.

The samples were prepared and characterized as described in the references.

All intermediates and final products of the decomposition reactions were characterized by X-ray analysis (Guinier-method CuK_α–radiation) and by IR spectroscopy (Specord, KBr–technique) after cooling to room temperature.

Results and discussion

In a first part, results of four classes of compounds are presented demonstrating the main effects, which are caused by changing the partial pressure, and demonstrating the advantages of using of non-reciprocal quasi-isobaric investigations. The examples are selected in such a way that a lot of results of dynamic thermal analysis are available for comparisons in each case.

A second part shows the possibilities to characterize the reaction mechanism and to prepare special inorganic fluorides using quasi-static thermoanalytical methods.

Hydroxonium fluorometallates — an example of changing the decomposition temperatures under non-reciprocal quasi-isobaric conditions

Under dynamic conditions the thermal decomposition of hydroxonium fluorometallates and the evaporation proceed simultaneously [6–8]. A determination of the stability of these compounds is impossible in this case.

Using non-reciprocal quasi-isobaric conditions, the first thermogravimetric effect is shifted to a higher temperature in comparison to the dynamic measurements. An endothermal effect is separated totally from the process of evaporation as to be seen in Figs 1 and 2 (see also Fig. 6). Consequently the evaporation of HF/H_2O-azeotrope starts always at the same temperature, the first endothermal effect is a criterion of the stability of the compounds. The stability decreases in the following order: $(H_3O)_3AlF_6 \cdot 3H_2O$, $(H_3O)_2ZrF_6$, $K(H_3O)_2AlF_6$, $(K, Rb)(H_3O)_2AlF_6$, and $Rb(H_3O)_2AlF_6$ [8].
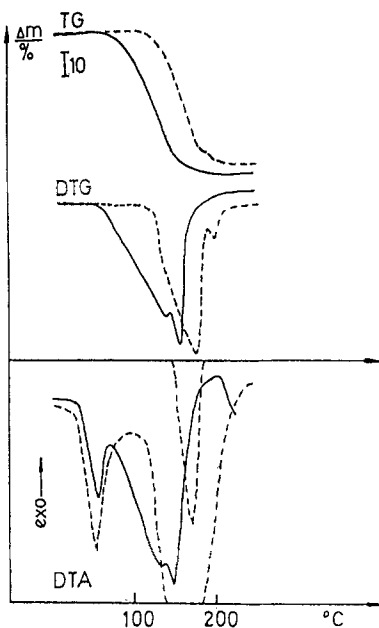
Fig. 1 The formation of $AlF_3 \cdot 0.5H_2O$ by thermal decomposition of $(H_3O)_3AlF_6 \cdot 3H_2O$ at 5 kPa (conventional) ———— and 70 kPa (non-reciprocal quasi-isobaric) — — —

The comparison of the thermal decomposition of $(H_3O)_2ZrF_6$ and $(H_3O)_3AlF_6 \cdot 3H_2O$ at 5 and 70 kPa shows the favoured formation of intermediates at higher partial pressures. In both cases, an additional ther-

mogravimetric step is detected at 160°C ((H$_3$O)$_3$AlF$_6$·3H$_2$O) and at 140°C ((H$_3$O)$_2$ZrF$_6$), respectively. At 70 kPa the decomposition can be described with the following schemes:

$$(H_3O)_2ZrF_6 \rightarrow HZrF_5 \cdot 2H_2O \rightarrow ZrF_4 \cdot H_2O \rightarrow ZrF_4 \qquad (1)$$

$$(H_3O)_3AlF_6 \cdot 3H_2O \rightarrow AlF_3 \cdot 1.5H_2O \rightarrow AlF_3 \cdot 0.5H_2O \rightarrow AlF_3 \qquad (2)$$
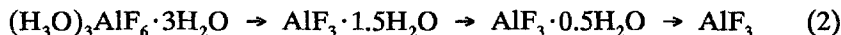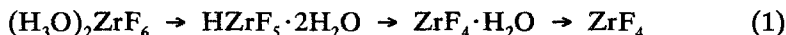
Under non-reciprocal quasi-isobaric conditions also the formation of products of hydrolysis is represented. The thermal decomposition of (H$_3$O)$_2$ZrF$_6$ leads at 5 kPa to ZrF$_4$ and a mixture of zirconium oxifluorides of the α–ZrF$_4$-type and the U$_3$O$_8$-type. ZrF$_4$ is the final product at 70 kPa; only traces of zirconium oxifluoride α–ZrF$_4$-type) are detectable.
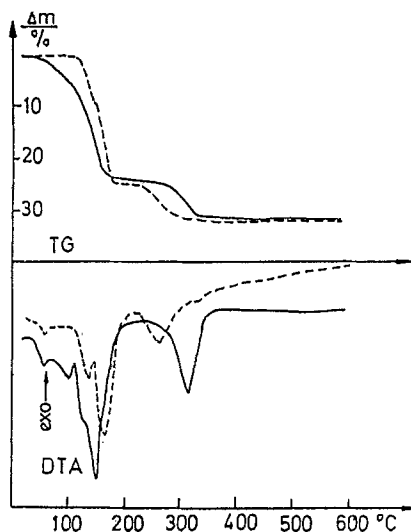

Fig. 2 Thermal decomposition of (H3O)2ZrF6 at 5 kPa (conventional) ——— and 70 kPa (non-reciprocal quasi-isobaric) — — —

In contrast to the first thermogravimetric step, the decomposition temperature of the intermediate ZrF$_4$·H$_2$O decreases from 310° to 250°C with increasing partial pressure (see Fig. 2), because ZrF$_4$·H$_2$O is stabilized by hydrolysis products which have been determined by X-ray measurements.

K2SiF6 − an example of simplification of the reaction mechanism

The thermal behaviour of K_2SiF_6 is extensively investigated by Kolditz and co-workers. The thermal decomposition of this compound leads to various products at different temperatures in dependence on the reaction conditions. A lot of side reactions have to be taken into account between 450° and 950°C, if the partial pressure of the gaseous reaction products is smaller than 70 kPa [9].

The decomposition at 70 kPa shows a simplification of the reaction sequence: side reactions are suppressed and the decomposition starts not below 900°C.

This is an example for the strong influence of the results by the variation of the partial pressure, because all part-reactions depend on this parameter in a different manner.

It is noteworthy, that the results of solid state reactions of K_2SiF_6 under non-reciprocal quasi-isobaric conditions correspond to the thermodynamical estimations.

Alkaline earth monofluorophosphates − an example of suppression of formation of hydrolysis products

The thermal decomposition of these compounds was investigated several years ago [10–12]. It was impossible to separate the thermal dissociation and the hydrolysis at that time.
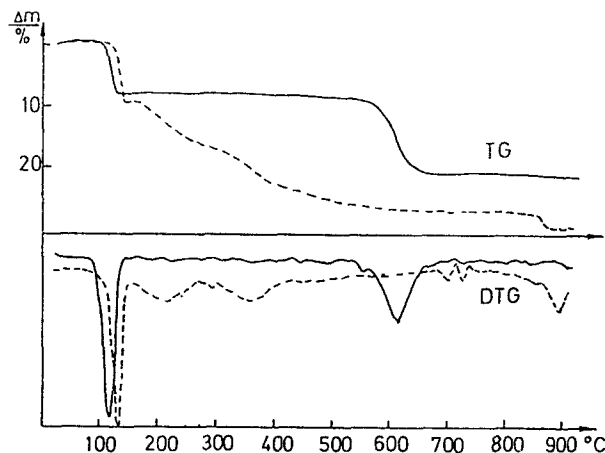

Fig. 3 Thermal decomposition of CaPO3F·2H2O − − − and SrPO3F·H2O ——— at 70 kPa (non-reciprocal quasi-isobaric)

Figure 3 shows the results of the non-reciprocal quasi-isobaric thermal analysis of $CaPO_3F \cdot 2H_2O$ and $SrPO_3 \cdot H_2O$.

The decomposition of $SrPO_3F \cdot H_2O$ takes place in two steps without any influence of partial hydrolysis on the formation of the intermediate $SrPOF_3$ at 70 kPa:

$$5\,SrPO_3F \cdot H_2O \xrightarrow{-5H_2O} 5\,SrPO_3F \xrightarrow{-POF_3} SrF_2 + 2\,Sr_2P_2O_7 \qquad (3)$$
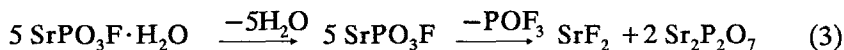
The mass loss agrees with the theoretical value. The formation of hydrolysis products is totally suppressed. At 5 kPa another pathway of decomposition is observed. HP is the main component of the gas phase after the evaporation of more than 0.7 mol H_2O and then a continuous mass loss between 150° and 450°C was observed [11]. Also the following decomposition of $SrPO_3F$ is influenced: in contrast to the two reaction steps at 5 kPa, only one decomposition step is observed at higher partial pressures.

In the case of $CaPO_3F \cdot 2H_2O$ only the first reaction step is clearly separated at 70 kPa. The mass loss agrees with the formation of $CaPO_3F \cdot H_2O$. Above 150°C the thermal decomposition and the evaporation of water and HF proceed simultaneously. At 5 kPa all these reactions take place throughout the whole decomposition, single steps are not separated. In [2] we have described the dependence of the thermal decomposition on the sample mass and the heating rate. Really this dependence is caused by the partial pressure in the intergranular cavities, which is influenced by these parameters.

Ammonium fluorometallates — an example of favoured formation of intermediates

The thermal decomposition of ammonium fluorometallates strongly depends on the partial pressure of the gaseous reaction products [5, 13]. Up to now, the thermal behaviour of these compounds has been investigated only under dynamic conditions [14, 15]. In comparison to the results of Bukovec [16] and other authors the following changes in the reaction mechanism have been detected using non-reciprocal quasi-isobaric conditions:

— the beginning of the decomposition shifted to higher temperatures [5]

—the ranges of existence of intermediates are prolonged, the reaction steps are better separated, new intermediates or special structures of them are detectable [5, 13]

— the amount of products of hydrolysis in the final products are minimized [17]

These general results should be explained by two further examples. Figures 4 and 5 show the thermoanalytical results of the decomposition of $(NH_4)_2TiF_6$ and $(NH_4)_2ZrF_6$ at 5 and 70 kPa. The curves obtained at 5 kPa agree with the results of Gaudreau [14]. Non-reciprocal quasi-isobaric measurements allow to describe the decomposition reactions more detailed.
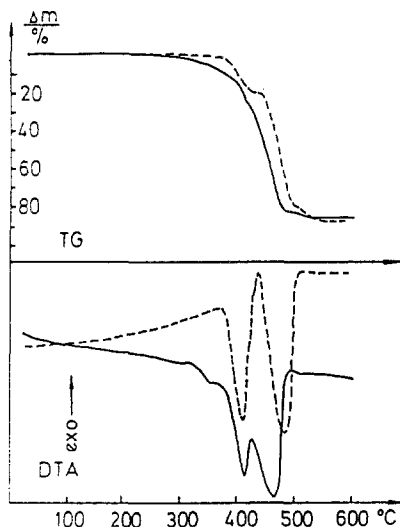

Fig. 4 Thermal decomposition of (NH4)2TiF6 at 5 kPa (conventional) ———— and 70 kPa (non-reciprocal quasi-isobaric) — — —

During the decomposition of $(NH_4)_2ZrF_6$ (Fig. 5) three further reaction steps are observed. The first thermogravimetric step is caused by partial hydrolysis, the reaction of the sample with self-generated water, and a zirconium oxifluoride (U_3O_8-type) is formed. This intermediate is refluorinated in the next reaction step. The decomposition of the intermediately formed NH_4ZrF_5 leads to another intermediate, $NH_4Zr_2F_9$, but only at heating rates <5 deg/min. The last intermediate (ca. 500°C in Fig. 5) can be described as an insertion compound ($ZrF_4 \cdot xNH_4F$ with $x \approx 0.02$); vacancies in the ZrF_4 structure are occupied by NH_4F. The final product is pure ZrF_4, the quality is not influenced by the partial hydrolysis.

Also the decomposition of $(NH_4)_2TiF_6$ (Fig. 4) under non-reciprocal quasi-isobaric conditions leads to NH_4TiF_5 as a new intermediate. This compound can only be isolated under these conditions, Table 1 gives the powder pattern. NH_4TiF_5 is hygroscopic and not stable in air in atmospheric moisture NH_4TiOF_3 is formed.
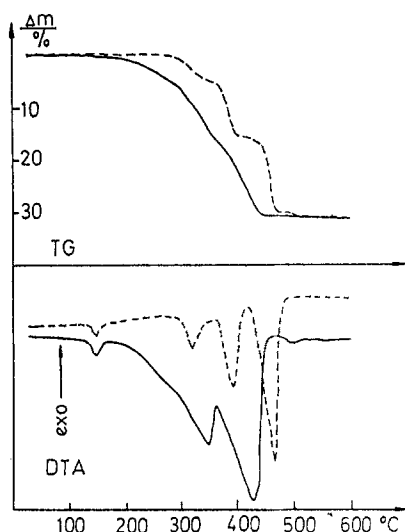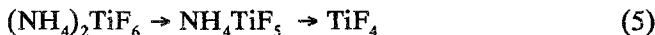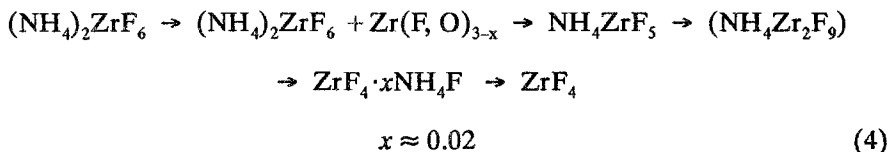
Fig. 5 Thermal decomposition of $(NH_4)_2ZrF_6$ at 5 kPa (conventional) ———— and 70 kPa (non-reciprocal quasi-isobaric/heating rate 5 deg/min) — — —

Table 1 Powder pattern of NH₄TiF₅

d / pm	I	d / pm	I	d / pm	I
684.7	11	319.1	14	202.2	4
653.4	6	311.1	3	200.1	5
578.4	100	303.3	3	198.8	7
486.4	34	289.6	5	189.3	6
480.5	7	260.6	3	188.2	3
455.2	4	252.9	4	183.4	4
431.4	5	243.4	4	181.1	12
374.4	8	226.7	14	174	4
347.6	66	222.3	3	171.8	5
343.2	50	210.3	4	162.8	5
324.7	8	207.3	12	162.2	4

The last step includes the formation of TiF_4 as well as its evaporation. The crucible is empty after the decomposition process. But the observed total mass loss is faulty, because TiF_4 is hydrolysed outside the crucible and TiO_2 is deposited on the sample holder.

The results are summarized in the following reaction schemes:

$$(NH_4)_2ZrF_6 \rightarrow (NH_4)_2ZrF_6 + Zr(F, O)_{3-x} \rightarrow NH_4ZrF_5 \rightarrow (NH_4Zr_2F_9)$$

$$\rightarrow ZrF_4 \cdot xNH_4F \rightarrow ZrF_4$$

$$x \approx 0.02 \tag{4}$$

$$(NH_4)_2TiF_6 \rightarrow NH_4TiF_5 \rightarrow TiF_4 \tag{5}$$

Characterization of f'' ? mechanism of thermal decomposition of inorganic fluorides using quasi-static methods

The characterization of reaction mechanism of thermal decomposition using quasi-static methods is based on an analysis of the temperature course in dependence on the control characteristic [1].

Two examples:

1. As shown in Fig. 6 the two endothermal reaction steps during the decomposition of $K(H_3O)_2AlF_6$ proceed quasi-isothermally if the heating process is controlled by the DTA signal. The two reaction steps are non-variant and are caused by decomposition of the compound and the following evaporation of the HF/H_2O azeotrope. In the result $KAlF_4 \cdot 0.5H_2O$ is formed [8].
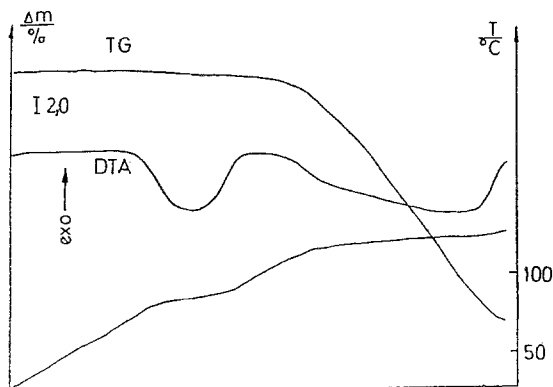

Fig. 6 Quasi-static thermal decomposition of $K(H3O)2AlF6$ DTA controlled

2. In contrast to the thermal decomposition of $(NH_4)_2TiF_6$ the vaporization of NH_4F during the decomposition of $(NH_4)_2ZrF_6$ cannot be controlled isothermally by the DTA signal. This is caused by overlapping of decomposition reaction (endothermal), partial hydrolysis and refluorination reactions (exothermal), see Eq. (4).

Quasi-static methods as a synthetic route

There are three effect of quasi-static methods which are useful for preparation of inorganic fluorides: the prolongation of the range of existence of intermediates, the formation of the thermodynamically stable compounds, and the minimization of the amount of hydrolysis products in the final products.

The *prolongation of the range of existence* of intermediates and the separation of reaction steps which normally overlap are useful for the preparation of phase-pure fluorides by partial decomposition of precursors. This way, e.g. $SrPO_3F$, $ZrF_4 \cdot H_2O$ and NH_4TiF_5 have already been obtained.

In self-generated atmosphere ($p > 70$ kPa) the *thermodynamically stable products* and intermediates are formed. Therefore $(NH_4)_3CrF_6$ as well as $(NH_4)_2[Cr(H_2O)F_5]$ and even $(NH_4)_2[Cr(H_2O)_6]F_5$ can be used for the production of water-free CrF_3, because under non-reciprocal quasi-isobaric conditions the same intermediates are formed [17].

The precondition for a successful preparation of fluorides is *the minimization of hydrolysis* products caused by structurally bonded water, adsorbed water, and water traces in the atmosphere. In general, partial hydrolysis occurring during the decomposition process cannot be suppressed completely, but the experimental conditions can be determined in such a way, that the final products contain only a small amount of hydrolysis products.

Caused by partial hydrolysis, very reactive fluorinating agents are available in the gas phase. Therefore the refluorination of all intermediately formed products is relatively easy under non-reciprocal quasi-isobaric conditions, if the ratio of the volumes of the crucible and the sample is small enough (less than 0.1 m% of the sample is allowed to evaporate in order to produce a self-generated atmosphere in the whole crucible). As a result, the amount of hydrolysis products is apparently suppressed.

But the use of self-generated atmosphere is not successful in each case. Whereas, e.g., equal qualities of AlF_3 and ZrF_4 (90−95%) are formed by the decomposition of hydrates or ammonium fluorometallates under dynamic conditions, only the non-reciprocal quasi-isobaric decomposition of the ammonium fluorometallates leads to high-purity AlF_3 and ZrF_4 (quality better than 99.5%). In comparison, the best result of quality achieved by the decomposition of the hydrates at $p > 70$ kPa is smaller than 97% [18]. These differences in quality cannot be determined by thermal analysis alone, also X-ray and chemical analysis of the final products are necessary.

The possibilities and the limits of a minimization of the amounts of hydrolysis products in the final product – using non-reciprocal quasi-isobaric conditions and complete thermal decomposition – can be estimated by a mathematical expression elaborated by Tschebull and Kepplinger [19]. This equation allows to optimize the parameters of the decomposition of $AlF_3 \cdot 3H_2O$ in such a way, that the amount of hydrolysis products reaches a minimum. The decomposition product contains more than 96% AlF_3 if the so called hydrolysis factor B is smaller than $5 \cdot 10^{-5}$:

$$m_{H_2O}/m_{AlF_3} \cdot (A/100)^{-1/2} \cdot e^{-8380/T} = B \tag{6}$$

In Eq. (6), A is the volume concentration of H_2O above the sample, m_{AlF} and m_{H_2O} the total masses of these components, and T the reaction temperature.

Due to our experience, this equation is applicable to all decomposition processes of hydrolysable compounds. The numerical conditions have to be determined for each problem separately, but the general connection is always the same.

The factor of hydrolysis can be interpreted as a part of the preexponential factor of an Arrhenius equation of hydrolysis:

$$v = dc/dt = k \cdot c$$

$$k = A \cdot e^{E/RT} = A' \cdot B' \cdot e^{-E/RT}$$

$$k = A' \cdot B$$

$$B = m_{H_2O} / m_{fluoride} \cdot (A/100)^{-1/2} \cdot e^{-E/RT} \tag{7}$$

The amount of hydrolysis depends on the relation of the total masses of water and the fluoride, on the factor $(A/100)^{-1/2}$ and on the activation energy of the hydrolysis. The factor $(A/100)^{-1/2}$ is the degree of the equilibrium between solid and gaseous reaction products and corresponds to the partial pressure of the reaction products. It describes sufficiently the effect of changing the partial pressure of the gaseous reaction products. This can be illustrated by the dependence of the decomposition point of the last intermediate on the thermal decomposition of $(NH_4)_3AlF_6$ [5].

High values of partial pressure of the gaseous reaction products are favourable to repress the amount of hydrolysis products. The factor $(A/100)^{-1/2}$ becomes nearly one if the decomposition reaction proceeds in self-generated atmosphere. Consequently B is mainly determined by the

relation of $m_{H_2O} / m_{fluoride}$ in the case of a special reaction with a fixed activation energy.

Whereas $(A / 100)^{-1/2}$ depends only on the reaction conditions, the relation $m_{H_2O} / m_{fluoride}$ is determined by the reaction conditions and the mechanism of the decomposition too. As described above, the intermediately formed hydrolysis products are refluorinated in a following decomposition step.

Only during the last decomposition step this refluorination is impossible. A small, but considerable difference between the composition of the last intermediate and the final product is the important supposition in order to obtain high-pure products. The smallest value of the factor $m_{H_2O} / m_{fluoride}$ is mainly influenced by this difference, and is not predetermined by the quantity and bond type of water in the starting material.

The importance of the intermediate $AlF_3 \cdot xNH_4F$ [5] and $ZrF_4 \cdot xNH_4F$ for the preparation of high pure AlF_3 and ZrF_4 using the decomposition of ammonium fluorometallates are obvious in this context.

Equation (7) illustrates the significance of non-reciprocal quasi-isobaric conditions for preparation and has been proved as a tool for optimizing synthesis of flurides.

Conclusions

Using quasi-static methods, thermal decomposition or transformations of fluorides take place at quasi-equilibrium conditions. The reactions occur thermodynamically controlled and the results are useful for a correlation with thermodynamical values.

As a rule, the thermal decomposition of inorganic fluorides under quasi-static conditions and dynamic conditions, respectively, are very different. The decomposition reaction strongly depends on the partial pressure of gaseous reaction products. This particularity is caused by the high reactivity of the gaseous reaction products, which make multivarious side reactions possible.

Especially, non-reciprocal quasi-isobaric techniques are useful for the investigation of thermal decomposition reactions and — via controlling of side reactions — for the preparation of inorganic fluorides.

References

1 F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23.

2 J. Rouquerol, Thermochim. Acta, 144 (1989) 209.

3 O. T. Sörensen, Thermal Analysis, Proc. 6the ICTA Bayreuth, 1980, Ed. W. Hemminger, Vol. 1, Birkhäuser Verlag, Basel 1980, p. 231.

4 C. M. Bean and R. H. Oliver, GB 1063898 (1964).

5 D. H. Menz and U. Bentrup, Z. Allg. Anorg. Chem., 576 (1989) 186.

6 U. Bentrup and L. Kolditz, J. Thermal Anal., 34 (1988) 143.

7 N. S. Nikolaev, Y. A. Buslaev and M. P. Gustyakova, Zh. Neorg. Khim., 7 (1962) 1685.

8 U. Bentrup and D. H. Menz, TAIRES 9, Jena 1989.

9 D. H. Menz, W. Wilde and L. Kolditz, J. Fluorine Chem., 24 (1984) 345.

10 VU Quang Kinh and G. Montel, C. R. Acad. Sci., 252 (1961) 3809.

11 D. H. Menz, K. Heide, Ch. Kunert, Ch. Mensing and L. Kolditz, Z. Allg. Anorg. Chem., 540/541 (1986) 191.

12 K. Heide, D. H. Menz, C. Schmidt and L. Kolditz, Z. Allg. Anorg. Chem., 520 (1985) 32.

13 U. Bentrup and D. H. Menz, Z. Allg. Anorg. Chem., 591 (1990) 230.

14 B. Gaudreau, Rev. Chim. Miner., 2 (1962) 1.

15 A. M. Rodriguez, J. A. Martinez, M. C. Caracoche, P. C. Rivas, A. R. Lopez Garcia and S. Spinelli, J. Chem. Phys., 82 (1985) 1271.

16 P. Bukovec and J. Siftar, Monats. Chem., 105 (1974) 510.

17 D. H. Menz and U. Bentrup, 13rd Intern. Symp. on Fluorine Chem., Bochum 1991, Z. Allg. Anorg. Chem., in press.

18 D. H. Menz and U. Bentrup, Fluorsymposium, Dohna 1987.

19 W. Tschebull and W. Kepplinger, FE 2837211 B2, 5.10.77.

Zusammenfassung — Quasi-statische thermoanalytische Methoden sind sehr gut für die Charakterisierung anorganischer Fluoride geeignet. Am Beispiel der termischen Zersetzung von Hydroxoniumfluorometallaten, Monofluorophosphaten und Ammoniumfluorometallaten wird der starke Einfluss von Partialdruckänderungen demonstriert. Besonders wichtig sind quasi-isobare, nicht-reziproke Verfahren für die Untersuchung dieses Verhaltens. An Beispielen wird auch die Möglichkeit der Reaktionsaufklärung mit quasi-statischen thermoanalytischen Methoden gezeigt. Die gleichen Methoden eignen sich darüber hinaus als Synthesevariante für phasenreine Fluoride. In diesem Zusammenhang werden die Möglichkeiten der Herstellung von Fluoriden mit geringem Hydrolysegrad ausführlich diskutiert.