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KINETICS OF THE THERMAL DECOMPOSITION OF ALKALINE EARTH METAL HYDROFLUORIDES

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The thermal stability of alkaline earth metal hydrofluorides was studied by means of a Derivatograph. The values of the activation energy, reaction order and rate constant were determined. The comparison of the kinetic parameters of the decomposition process for the complete series of hydrofluorides studied led to a certain regularity in the differences in their thermal stabilities and its correlation with the strength of the hydrogen bond in their structure.

The interaction of the alkaline earth metal fluorides with hydrogen fluoride leads to the formation of compounds of composition $MeF_2 \cdot nHF$ (Me = Ba, Sr, Ca) [1], named hydrofluorides. The results of the investigation of barium, strontium and calcium hydrofluorides by NMR [2, 3], IR spectroscopy [4, 5] and refractometry [6] have shown that their formation is due to hydrogen bonds of the type $F-H \ldots F$, similarly to the alkali metal hydrofluorides [7] where the anions HF^-_{n+1} are present in their structure. The strength of the hydrogen bond in the series of hydrofluorides decreases from barium to calcium and with the increasing number of HF molecules present.

The majority of hydrofluorides are unstable and can easily be reconverted to the corresponding fluorides by removing hydrogen fluoride. However, their thermal stability has not been thoroughly studied so far, due to the special properties of hydrofluorides and the difficulties in the experimental work with these compounds. The data reported in the literature mainly concern the thermal stability of alkali metal bifluorides $MeF \cdot HF$ [8–11]. The information on the thermal stability of the alkaline earth metal hydrofluorides is not completely available. The results of the investigation of the thermal stability of alkaline earth metal hydrofluorides are reported in this paper.

The studied compounds were prepared on the basis of the data on the ternary system $HF-MeF_2-H_2O$ [1]. The following reagents were used: hydrofluoric acid (of special purity); anhydrous hydrogen fluoride, purified by rectifying; metal fluorides (analytical grade). Excess hydrogen fluoride was removed in a desiccator. The compounds prepared from the aqueous solutions of HF were dried in a desiccator over phosphorus pentoxide. Some compounds were prepared by decomposing hydrofluorides of higher HF content. The compounds were analysed for hydrogen fluoride by titration with standard alkali solution, for the metal by weighing in the form of the fluoride or sulphate (Table 1).

Table 1

Composition of alkaline earth metal hydrofluorides

Compound	HF content weight %		MeF_2 content weight %	
	calculated	found	calculated	found
$BaF_2 \cdot 4.5\ HF$	33.92	34.54	66.08	65.50
$BaF_2 \cdot 3\ HF$	25.49	25.20	74.51	74.52
$BaF_2 \cdot 2\ HF$	18.58	18.85	81.42	80.25
$BaF_2 \cdot HF$	10.24	10.50	89.76	89.76
$SrF_2 \cdot 2.5\ HF$	28.47	29.05	71.53	70.70
$SrF_2 \cdot 2\ HF$	24.15	24.15	75.85	75.37
$SrF_2 \cdot HF$	13.74	13.53	86.26	86.54
$CaF_2 \cdot 2\ HF$	33.86	33.06	66.14	67.10

The kinetics of the decomposition of hydrofluorides was studied by thermogravimetry (TG) under dynamic conditions. This method was chosen after the preliminary studies of these processes carried out under isothermal and dynamic conditions. It was found that if the decomposition was carried out under constant temperature, the weight loss curve did not show the staged mechanism of the process due to the very small differences in the thermal stabilities of hydrofluorides of different HF content, while it was suggested that the decomposition of the majority of the hydrofluorides had to proceed through the formation of intermediates.

The thermal curves were recorded by means of a Derivatograph of the Paulik–Paulik–Erdey type. 0.3–0.7 g samples were heated at the rate of 6°/min up to 300° in a platinum crucible, since the decomposition process was known to finish by this temperature. The reproducibility of the measurements with different series of the prepared samples was satisfactory. The loss of weight during the heating of hydrofluorides corresponded within the limits of error to their hydrogen fluoride content. When the sample contained excess HF due to adsorption, it was possible to distinguish the losses of weight on the thermogravimetric curve due to the removal of bound hydrogenfluoride and of excess HF.

The thermal analysis of alkaline earth metal hydrofluorides shows that their decomposition sometimes proceeds in stages.

The thermogravimetric curve of $BaF_2 \cdot 4.5\ HF$ is the most complicated one (Fig. 1) and shows three endothermic effects corresponding to the consecutive removal of hydrogen fluoride according to the scheme:*

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* The temperatures of the endothermic effects in the reaction scheme correspond to the time of maximum rate of reaction (T_s).

$$BaF_2 \cdot 4.5\ HF \xrightarrow[95^\circ]{-2.5\ HF} BaF_2 \cdot 2\ HF \xrightarrow[100^\circ]{-HF} BaF_2 \cdot HF \xrightarrow[227^\circ]{-HF} BaF_2. \qquad (1)$$

The decomposition of $BaF_2 \cdot 3\ HF$ (Fig. 2) proceeds through the following stages:

$$BaF_2 \cdot 3\ HF \xrightarrow[98^\circ]{-HF} BaF_2 \cdot 2\ HF \xrightarrow[112^\circ]{-HF} BaF_2 \cdot HF \xrightarrow[215^\circ]{-HF} BaF_2. \qquad (2)$$

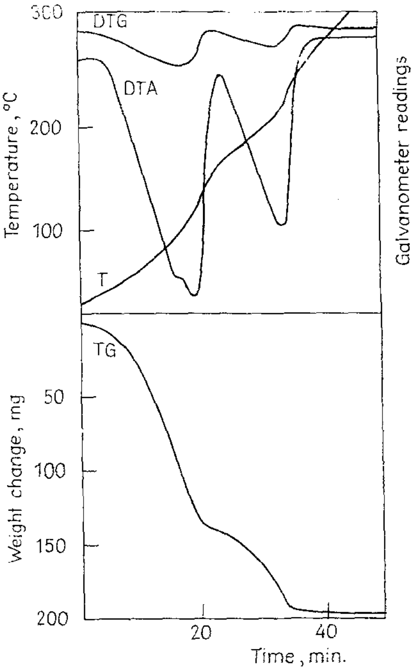

Fig. 1. $BaF_2 \cdot 4.5\ HF$

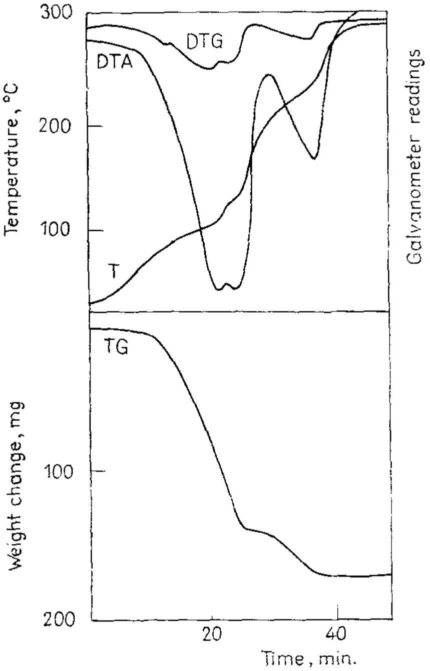

Fig. 2. $BaF_2 \cdot 3\ HF$

The shapes of the TG curves of $BaF_2 \cdot 4.5\ HF$ and $BaF_2 \cdot 3\ HF$ clearly show the different thermal stabilities of the hydrofluorides formed as intermediates of the decomposition.

It is interesting to note that among the decomposition products of the hydrofluorides $BaF_2 \cdot nHF$ ($n = 4.5$; 3), the phase $BaF_2 \cdot 2\ HF$, previously unknown, was found. Our data proved the remarkable thermal stability of this compound and gave us the possibility to prepare it in the pure state by decomposing barium hydrofluorides with higher HF content. There are two endothermic effects on the thermogravimetric curve of $BaF_2 \cdot 2\ HF$ (Fig. 3) prepared as mentioned above:

$$BaF_2 \cdot 2\,HF \xrightarrow[100^\circ]{-\,HF} BaF_2 \cdot HF \xrightarrow[207^\circ]{-\,HF} BaF_2 . \qquad (3)$$

The thermal stabilities of the hydrofluorides $BaF_2 \cdot 4.5$ HF and $BaF_2 \cdot 3$ HF, as indicated by their thermogravimetric curves, differ only slightly; therefore the phase $BaF_2 \cdot 3$ HF cannot be considered as an intermediate of the decomposition of $BaF_2 \cdot 4.5$ HF.

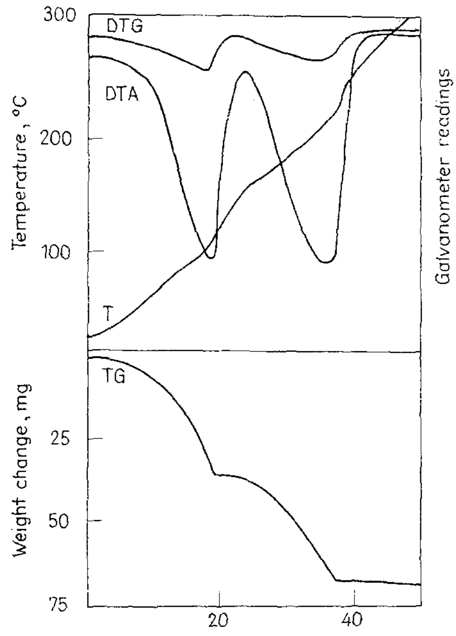

Fig. 3. $BaF_2 \cdot 2$ HF

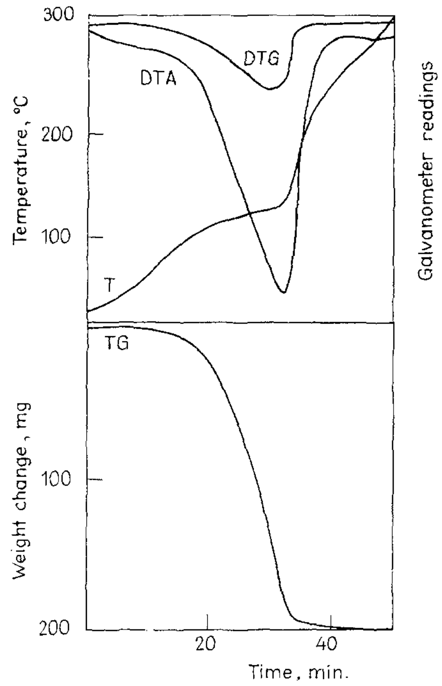

Fig. 4. $BaF_2 \cdot$ HF

In the series of barium hydrofluorides, $BaF_2 \cdot$ HF (Fig. 4) which has the highest decomposition temperature is the most stable:

$$BaF_2 \cdot HF \xrightarrow[224^\circ]{-\,HF} BaF_2 . \qquad (4)$$

The formation of $BaF_2 \cdot$ HF during the decomposition of the hydrofluorides $BaF_2 \cdot$ nHF ($n = 4.5$; 3; 2) is indicative of the high stability of the former. The slight differences in the values of T_s obtained during the decomposition of the hydrofluorides of different composition are apparently due to the structures of the hydrofluorides formed in the course of decomposition.

Strontium hydrofluoride $SrF_2 \cdot 2.5$ HF (Fig. 5) at first gives off 0.5 molecule of HF; the resulting $SrF_2 \cdot 2$ HF (Fig. 6) decomposes without the formation of intermediates

$$SrF_2 \cdot 2.5\,HF \xrightarrow[82^\circ]{-0.5\,HF} SrF_2 \cdot 2\,HF \xrightarrow[145^\circ]{-2\,HF} SrF_2 . \qquad (5)$$

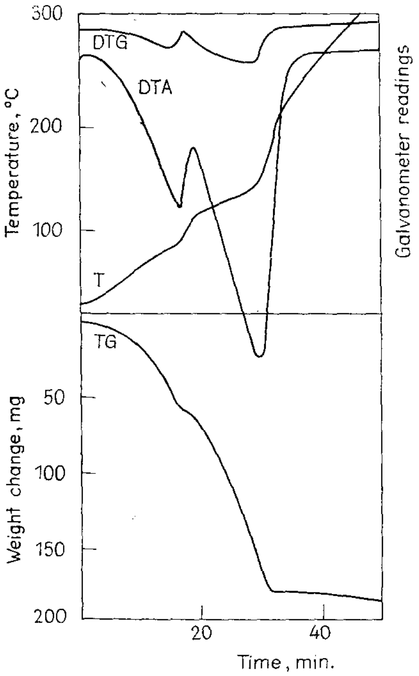

Fig. 5. $SrF_2 \cdot 2.5$ HF

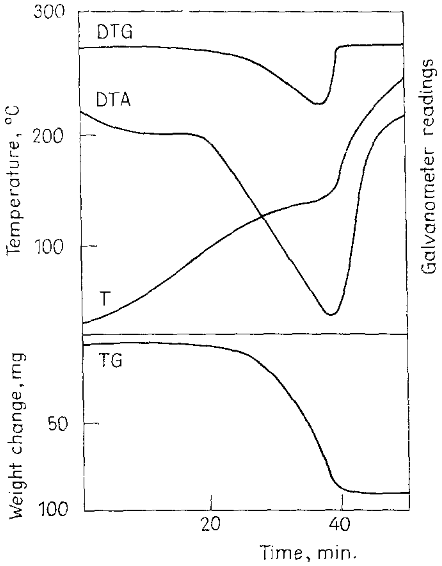

Fig. 6. $SrF_2 \cdot 2$ HF

The fact that in this case the hydrofluoride $SrF_2 \cdot$ HF does not form, is probably due to the peculiarities of the hydrofluoride structures. As was shown by NMR and IR spectroscopy, there are two different anions, F^- and HF_2^-, in the structure of the compounds $MeF_2 \cdot$ HF. As the hydrogen bond in strontium hydrofluorides is weaker than in barium hydrofluorides, $MeF_2 \cdot$ HF with its unsymmetrical cation environment is less stable in the case of strontium. Obviously, that is why the formation of the compound with such a composition during the decomposition of $SrF_2 \cdot 2$ HF is less favoured than from $BaF_2 \cdot 2$ HF.

The same reasons obviously stipulate that the hydrofluoride of composition $MeF_2 \cdot$ HF in general does not exist in the case of calcium. In the hydrofluoride $CaF_2 \cdot 2$ HF the two molecules are identical and form two bifluoride ions. The decomposition of this compound proceeds similarly to that of $SrF_2 \cdot 2\,HF$, but its decomposition temperature is lower, 130° (Fig. 7).

The decomposition of $SrF_2 \cdot HF$ proceeds in the solid phase of the system $HF - SrF_2 - H_2O$ [1], unlike the decomposition of the corresponding barium hydrofluoride. In this case the reaction mechanism is complex, and is characterized by three maxima with marked differences in the decomposition rates and in the values of the temperatures of the endothermic effects, 114°, 155°, 252°, on the curve (Fig. 8). No simple explanation for this experimental fact could be found. The staged mechanism of the decomposition was also observed for potassium bifluoride [12, 13].

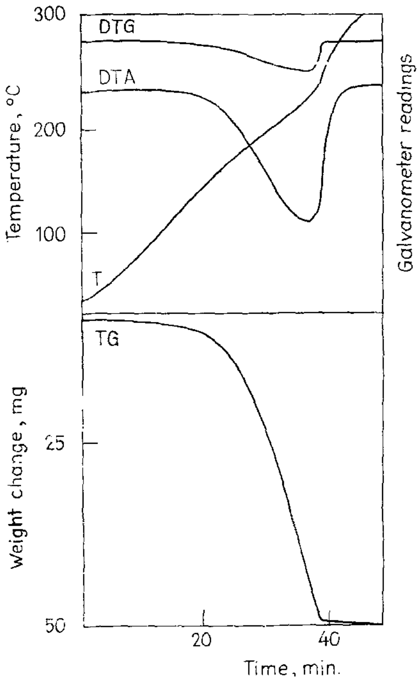

Fig. 7. $CaF_2 \cdot 2\,HF$

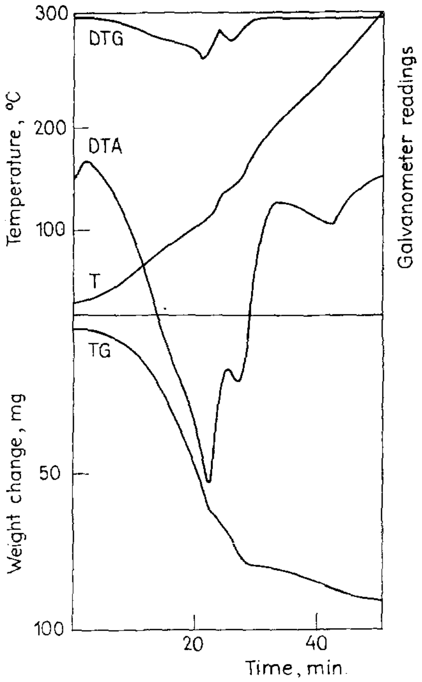

Fig. 8. $SrF_2 \cdot HF$

All processes considered in this paper belong to reactions of the type: A (solid) → B (solid) + C (gas). This process includes several stages: chemical interaction accompanied by the breaking of the bonds and the disappearance of the chemical lattice of substance A, the formation of the lattice of B, etc. Its rate depends on the rate of one or more of these steps. At present there is no strict theory of the unisothermal kinetics of heterogeneous processes, and the concepts "activation energy" (E) and "reaction order" (n), which are the complex functions of the activation energies and reaction orders of the separate stages of the process, are conventional. However, their effective values obtained by investigating the decomposition of substances belonging to the same class may satisfactorily reflect the character of the process and their correlations allow the quantitative estimation of the thermal stability of the compounds.

Some methods were recommended for the calculation of the kinetic parameters of the decomposition process [14–17]. They allow the determination of the effective values of E and n, supposing that the reaction rate obeys the Arrhenius equation:

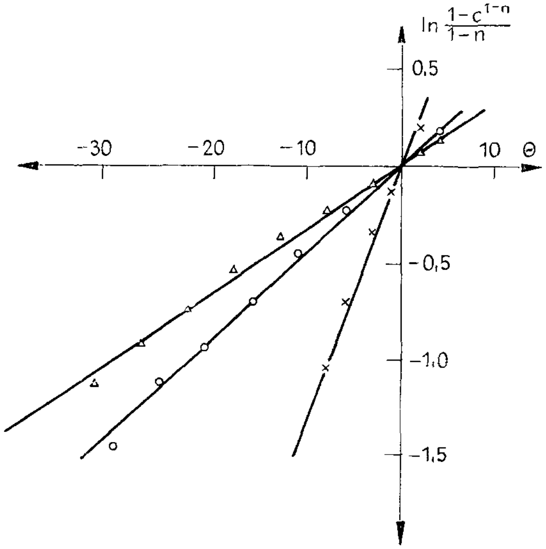

Fig. 9. Calculation of the kinetic parameters for the reactions:

$$\times = BaF_2 \cdot 4.5\,HF \xrightarrow{-\,2{\cdot}5\,HF} BaF_2 \cdot 2\,HF;$$

$$\circ = BaF_2 \cdot 2\,HF \xrightarrow{-\,HF} BaF_2 \cdot HF;$$

$$\triangle = BaF_2 \cdot HF \xrightarrow{-\,HF} BaF_2$$

$$\frac{dC}{dt} = -KC^r.$$

In this study it was possible to use the method of Horowitz and Metzger [15] for the calculation, because the decomposition of the alkaline earth metal hydrofluorides proceeds in a very narrow temperature interval, at a relatively high temperature. In the case when the reaction order $n \neq 1$, the integral expression for the equation of the reaction rate is:

$$1 - C^{1-n} = (1-n)\,l\frac{E\Theta}{RT_s^2}$$

where C = concentration of substance A; R = gas constant, $\Theta = T - T_s$.

The value of T_s may easily be found: it is the temperature of the maximum on the DTG curve [18]. The reaction order is determined by the value of the concentration of the substance capable of decomposition at the temperature where the rate of reaction is maximal (Cs). The $\ln \frac{1 - C^{1-n}}{1 - n}$ vs. Θ plot leads to the activation energy on the basis of the slope of the line (Figs 9, 10). The frequency factor of the kinetic equation was calculated from the equation:

$$\frac{E}{RT_s^2} = \frac{Z}{q} n C_s^{n-1} l \frac{-E}{RT_s}$$

where q is the heating rate.

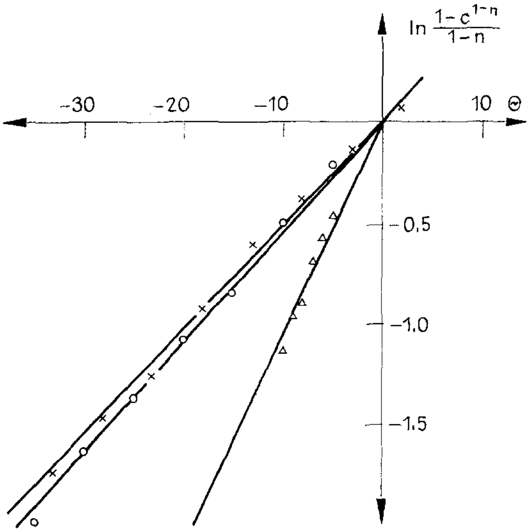

Fig. 10. Calculation of the kinetic parameters for the reactions:

$\times = SrF_2 \cdot 2.5\,HF \xrightarrow{-0{\cdot}5\,HF} SrF_2 \cdot 2\,HF$;

$\circ = SrF_2 \cdot 2\,HF \xrightarrow{-2\,HF} SrF_2$;

$\triangle = CaF_2 \cdot 2\,HF \xrightarrow{-2\,HF} CaF_2$

Kinetic parameters were calculated both for the separate steps of the decomposition of hydrofluorides and for the process of the decomposition of the individual compounds, and similar results were obtained. The average values of the parameters obtained from the series of the experiments are given in Table 2.

It follows from these data that the mechanism of the decomposition of the studied hydrofluorides is often very similar. The values of the activation energy belonging to the release of one HF molecule are rather alike for different hydrofluorides and are 12–17 kcal (with the exception of the first stage of reaction 5). The process of the decomposition of all hydrofluorides is characterized by fractional reaction order, in most cases 1/3, as is often observed for heterogeneous reactions (the decomposition of hydrates, oxalates, carbonates) [16, 18–20]. The reaction order 1/3 has a theoretical basis too, if we consider that the rate of

Table 2

Kinetic parameters for the decomposition reaction of alkaline earth metal hydrofluorides

Decomposition scheme	T_s, °K	n	E kcal mol^{-1}	Z mol^{1-n} min^{-1}
$BaF_2 \cdot 4.5\,HF \xrightarrow{-2.5\,HF} BaF_2 \cdot 2\,HF$	368	0.50	32.1 ± 0.6	9×10^{13}
$BaF_2 \cdot 2\,HF \xrightarrow{-HF} BaF_2 \cdot HF$	373	0.30	12.0 ± 0.5	3×10^{6}
$BaF_2 \cdot HF \xrightarrow{-HF} BaF_2$	497	0.35	16.7 ± 0.6	7×10^{6}
$SrF_2 \cdot 2.5\,HF \xrightarrow{-0.5\,HF} SrF_2 \cdot 2HF$	355	0.18	12.1 ± 0.4	8×10^{6}
$SrF_2 \cdot 2\,HF \xrightarrow{-2\,HF} SrF_2$	418	0.35	24.7 ± 0.5	4×10^{12}
$CaF_2 \cdot 2\,HF \xrightarrow{-2\,HF} CaF_2$	403	0.34	27.3 ± 0.5	3×10^{14}

decomposition of solid substances accompanied by the formation of a gaseous product is proportional to the surface of the decomposing grains [15, 19].

The comparison of the kinetic parameters of the decomposition reaction of hydrofluorides leads to a certain regularity in the change of the stability of these compounds: the temperature of decomposition of hydrofluorides with the same number of HF molecules decreases from barium to calcium. The rate constants calculated from the values of the kinetic parameters show that for reactions of the same type the decomposition of calcium hydrofluorides proceeds at a greater rate as compared with strontium hydrofluorides. Comparison of the rate constants for the successive steps of reactions 3 and 4 shows that the removal of the first HF molecule proceeds at a greater rate. Hence, the thermal stability of hydrofluorides decreases from barium to calcium and with increasing number of the bound HF molecules. This regularity is obviously due to the character of the change of the hydrogen bond strength in the series of the hydrofluorides, and may be evidence of the essential influence of the stage of breaking of the hydrogen bonds in the structure of the hydrofluorides on the rate of the process.

The investigations described are the first attempt to apply the Derivatograph to study the thermal stability of hydrofluorides. The data obtained prove the great possibilities of the Derivatograph for the investigation of such topics, because the application of other methods in the case of these substances is either not possible or the results obtained are not accurate enough. The important advantage of the method is the possibility of studying the kinetics of rapidly proceeding processes and obtaining a complete picture of the process in the entire temperature interval as well as valuable information concerning the conditions of the synthesis of the substances formed during the decomposition process, as shown by the example of alkaline earth metal hydrofluorides. The authors wish to continue the investigation of the thermal behaviour of hydrofluorides by the Derivatograph.

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Résumé. — On a étudié la stabilité thermique des hydrogénofluorures des métaux alcalino-terreux et déterminé les valeurs des énergies d'activation, des ordres de réaction et des constantes de vitesse de réaction à l'aide d'un "Dérivatographe". Après comparaison des paramètres cinétiques on a pu établir une certaine régularité dans le changement de la stabilité thermique en corrélation avec la force de liaison de l'hydrogène dans la structure.

Zusammenfassung. — Die thermische Stabilität von Erdalkalihydrofluoriden wurde mit Hilfe eines Derivatographen untersucht, die Werte der Aktivierungsenergien, der Reaktionsordnung und der Geschwindigkeitskonstanten bestimmt. Der Vergleich der kinetischen Parameter des Zersetzungsvorganges wies auf eine gewisse Regelmäßigkeit in ihrer verschiedenen thermischen Stabilität, die in Zusammenhang mit der Stärke ihrer strukturalen Wasserstoffbindung steht.

Резюме. — Исследование на дериватографе термостабильность гидрофторидов щелочноземельных металлов. Определены значения энергии актизации, порядок реакции и постоянная скорости. Сравнение кинетических параметров процесса распада для целого ряда исследованных гидрофторидов дает возможность обнаружить некоторую регулярность в изменении их термостабильности и ее соотношения с прочностью водородной связи в их структуре.