Thermochimica Acta, 36 (1980) 387—391
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THERMAL DECOMPOSITION OF SODIUM HEXAFLUOROSILICATE

MILOSLAV VANKA and JOSEF VACHUŠKA

Nuclear Research Institute, 250 68 Řež (Czechoslovakia)

(Received 1 August 1979)

ABSTRACT

Isothermal decomposition of powdered Na_2SiF_6 is found to be a 2/3-order reaction with an activation energy of 182 ± 13 kJ $mole^{-1}$ in the temperature range 644—685 K. The sharp endothermic peak on DTA curves superimposed on the peak of the decomposition reaction itself, reported earlier in the literature, is reversible and accompanied by considerable elongation of Na_2SiF_6 pellet. This effect, probably the result of a solid—solid transition, is observable also in closed-system DTA measurements.

INTRODUCTION

The thermal decomposition of sodium hexafluorosilicate may be used as an alternative method for preparing porous sodium fluoride pellets suitable for use in fluorine chemistry and technology. Data on the decomposition reaction kinetics are rather scarce and some disagreement exists in the literature about interpretation of the experimental results.

In TG/DTA experiments a sharp endothermic peak has been found at about 850 K, superimposed on the main endothermic effect (maximum at 940 K) caused by the decomposition itself. This effect has generally been interpreted as a solid—solid transition in Na_2SiF_6 [1,2]. Istomin and Galkov [3], however, did not find any trace of crystalline phases other than hexagonal Na_2SiF_6 and cubic NaF during X-ray analysis in the temperature range 300—1040 K; they described the peak as an "overheating wave". The same authors found a fine structure in the main effect which seems to suggest a two-stage mechanism for the decomposition reaction. Other authors [1,2], however, have not found a complex reaction mechanism under similar experimental conditions.

Isothermal decomposition of Na_2SiF_6 was found to be a zero-order reaction in the temperature range 830—1000 K. A break on the kinetic curve occurred at 1000 K suggesting a change in the reaction mechanism [3].

In the work described here the thermal decomposition of Na_2SiF_6 powder was studied under both isothermal and non-isothermal conditions. In the isothermal experiments a thin layer of material was used to suppress the influence of diffusion phenomena as much as possible.

EXPERIMENTAL

Isothermal experiments

Samples of 4.8—5 mg of powdered Na_2SiF_6 (technical grade, recrystallized from water, particle size <40 μm) were heated in a platinum boat (approximate area 1 cm^2) in a tube furnace, the temperature of which was controlled to ±1 K. A sample was inserted into the thermostated zone with a thin rod, the sample temperature being stabilized within 3 min. Dry nitrogen evaporated from a Dewar flask was passed over the sample at a velocity of 13 cm s^{-1}. The reaction rate was independent of nitrogen flows which exceeded this value, as well as sample-weight variations within the specified interval. Moisture present in the carrier gas caused irreproducible results owing to hydrolytic processes on the solid-sample surface.

The decomposition was followed by weight changes of individual samples. Maximum weight loss and X-ray diffraction patterns indicated that cubic NaF was the only solid product of the reaction. The silicon contents of completely decomposed samples, determined by colorimetry, were lower than 1%.

Thermoanalytic experiments

TG, DTA and dilatometric analyses were performed at atmospheric pressure in air on a Derivatograph OD-102 (M.O.M., Budapest) equipped with a supplementary dilatometer, at heating rates of 2—8 K min^{-1}.

Several samples of Na_2SiF_6 and its mixtures with NaF (analytical grade) were studied in sealed quartz tubes. Before the DTA runs, the sealed samples were heated to ca. 1070 K and slowly cooled to room temperature. The sample weights were 280 ± 10 mg, the average tube weight being ca. 1.6 g. The degree of Na_2SiF_6 decomposition was confined to well below 1% under these conditions.

Aluminium oxide was used as a reference material in all thermoanalytic experiments.

RESULTS

The isothermal runs were done in the temperature range 644—685 K. The weight losses were correlated with the equation $1 - (1 - \alpha)^{1/3} = kt$, which describes the well-known diminishing sphere kinetics. The corresponding reaction order is 2/3 [4]. A reasonably good fit was observed up to approximately 95% conversion. The apparent activation energy E_A was calculated from the values of the reaction rate $d\alpha/dt$ at $\alpha = 0.5$, and found to be 182 ± 13 kJ $mole^{-1}$.

The TG and DTA curves obtained in a dynamic atmosphere showed two endothermic peaks. The first, a sharp peak starting at 818 K (minimum at 833 K, heating rate 2 K min^{-1}, sample weight 688 mg) was superimposed on the second, which was broader and followed the decomposition observable on the TG curves. The weight loss of samples from the decomposition became apparent from ca. 720 K. We found that the first endothermic

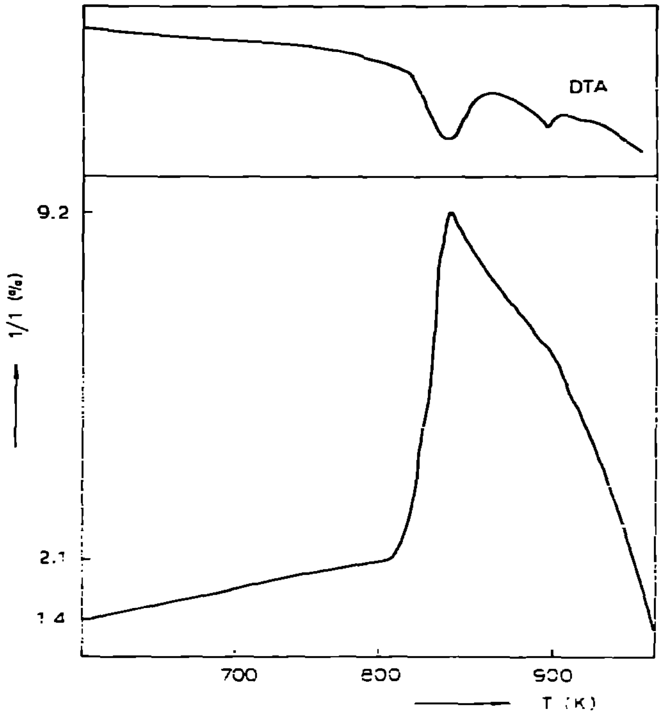

Fig. 1. Dilatometric analysis of Na_2SiF_6 pellets.

effect, described earlier in the literature [1—3], was reversible and the area of the corresponding exothermic peak obtained on cooling was proportional to the quantity of undecomposed hexafluorosilicate present in the sample after the treatment.

On dilatometric analysis an elongation of Na_2SiF_6 pellets was observed at 808 K together with the first endothermic effect. Having reached a maxi-

TABLE 1

DTA of sodium hexafluorosilicate and sodium fluoride mixtures in a closed system

x_{NaF}	Temperature limits within which effect is observed			
	Heating		Cooling	
0	815	950	801	933
0.15	801	936	792	918
0.3	797	935	779	921
0.45	811	937	—[a]	921 (?)
0.6	804	941	—[a]	—[a]
0.75	804	941	—[a]	—[a]
0[b]	809			

[a] Not observed because of destruction of the sealed tube.

[b] Open system, heating rate 2 K min^{-1}.

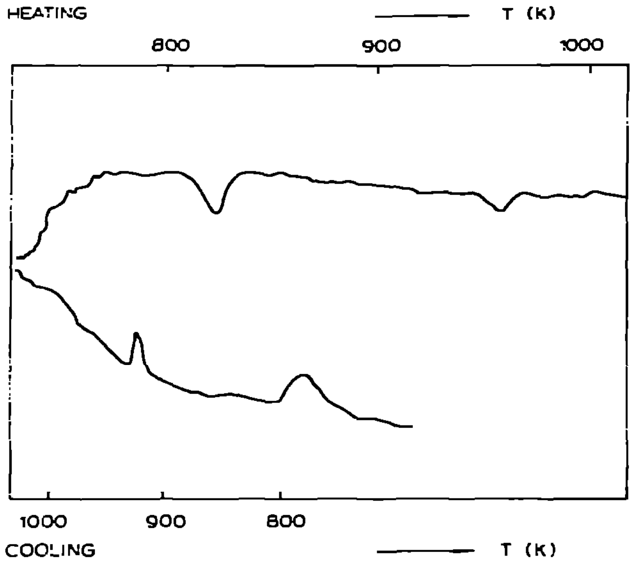

Fig. 2. DTA curve of powdered Na_2SiF_6 in a closed quartz tube.

mum of 9.2%, the pellet size abruptly contracted, obviously owing to the decomposition reaction (see Fig. 1).

No trace of a stepwise decomposition was observed on TG or DTG curves even at a heating rate of 2 K min^{-1}.

A typical DTA curve for Na_2SiF_6 in a closed system is shown in Fig. 2. Two separate endothermic effects were observed on heating, the positions being independent of the sample composition in the range $x_{NaF} = 0$—0.75 (see Table 1). The relative magnitude of the second endothermic effect (above 930 K on heating) increased with the NaF content of the sample. The powdered samples because dispersed over the inner surface of the sealed quartz ampoules after one heating—cooling cycle and no visual marks of melting were apparent.

TABLE 2

Kinetics of sodium hexafluorosilicate isothermal decomposition

Sample type and weight	Temperature at which $d\alpha/dt = 0.01$ (K)	E_A (kJ $mole^{-1}$)	Ref.
Powder, 1 g	943	111.0 ± 8.4	3
Powder, 5 mg	658	186.0 ± 5.7	
Pellets, 0.2 g	791	151.7 ± 8.9	7

DISCUSSION

Both the isothermal kinetic curves and the reaction rates evaluated were different from those reported by Istomin and Galkov [3], who used ca. 1-g samples probably placed in the usual deep crucible. Though the atmosphere used was not reported, it can be concluded that slow removal of gaseous silicon tetrafluoride from the sample surface was the rate-controlling step, resulting in the observed zero-order reaction kinetics. In contrast, the role of diffusion in our isothermal experiments was probably small. The observed 2/3-order kinetics is often applicable in similar experiments, but this can result from a much more complex reaction mechanism than the simple diminishing sphere model (especially in the case of inhomogeneous particle size distribution) [4].

The difference between the reaction rates observed under different conditions also supports the conclusions mentioned above. In order to illustrate this, the temperature at which the reaction rate $d\alpha/dt$ would be equal to 0.01 was calculated from Arrhenius' parameters for different data (see Table 2).

The thermoanalytical experiments seem to confirm that the first endothermic effect at ca. 810 K is probably a phase transition, in agreement with previous work [1,2,5]. We did not succeed, however, in establishing the structure of the assumed high-temperature modification of Na_2SiF_6.

The second endothermic effect observed in the closed-system DTA runs can be explained by melting of a eutectic NaF—Na_2SiF_6 mixture. The existence of such a mixture is assumed by several authors [3,6], but clear experimental evidence is still absent. An alternative explanation of the effect is the possible formation of an intermediate, Na_3SiF_7, the potassium analogy of which is known to be a stable compound. However, conversion of Na_2SiF_6 to Na_3SiF_7 will be negligible in the closed-system experiments, and opinions vary about the existence of Na_3SiF_7 [5,6].

REFERENCES

1 D.L. Deadmore, J.S. Machin and A.W. Allen, J. Am. Ceram. Soc., 45 (1962) 120.
2 R.L. Davidovich, Atlas Derivatogramm Komplexnykh Ftoridov Metallov III—V Grupp, Nauka, Moscow, 1976, pp. 13, 153.
3 S.P. Istomin and A.S. Galkov, Zh. Prikl. Khim., 49 (1976) 2208.
4 B. Delmon, Kinetika Geterogennykh Reaktsii, Mir, Moscow, 1972, pp. 235, 240, 448.
5 L. Kolditz, private communication.
6 R.V. Chernov, Yu.K. Delimarskii and I.G. Kovzun, Ukr. Khim. Zh., 37 (1971) 984.
7 M. Vanka, unpublished results.