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K. Zhumashev[1], A. Narembekova[2], B.B. Katrenov[3]

[1]«Innovatsiya» LLP, Karaganda, Kazakhstan;
[2]Karaganda State Technical University, Kazakhstan;
[3]Zh. Abishev Chemical and metallurgical institute, Karaganda, Kazakhstan
(E-mail: innovaciya_zh@mail.ru)

Determination of the reaction mechanism of the calcium fluoride interaction with ammonium sulphate

Production of ammonium hydrogen fluoride according to the traditional technology using concentrated sulfuric acid is associated with a number of technological difficulties. Considering this, an alternative option for producing ammonium hydrogen fluoride using ammonium sulphate, a by-product of the coke-chemical production has been proposed. Thermodynamic and differential-thermal analyzes of the reaction of the interaction of calcium fluoride with ammonium sulphate were carried out to establish the possibility of using ammonium sulphate as a reagent for the preparation of ammonium fluoride. According to the results of the analysis, the mechanism of the reaction of calcium fluoride with ammonium sulphate was established as the mixture was heated. It is established that there is ammonium sulphate decomposition in the beginning with formation of ammonium hydrosulphate, ammonia, sulfur trioxide and water. Then ammonium hydrosulphate, sulfur trioxide and water interact with calcium fluoride to form ammonium fluoride, fluoric hydrogen and calcium sulphate. Ammonia and fluoric hydrogen then can be also processed on ammonium fluoride. Thus, the possibility of using ammonium sulphate as a reagent for the production of ammonium fluoride from natural calcium fluoride has been established on the basis of the research conducted. The ammonium fluoride then can be processed to ammonium hydrogen fluoride. Thus, the reaction studied can serve as a chemical basis for an alternative technology for the production of ammonium hydrogen fluoride.

Keywords: calcium fluoride, ammonium sulphate, ammonium fluoride, thermal analysis, thermodynamic analysis.

Introduction

Ammonium hydrogen fluoride $NH_4F \cdot HF$ is widely used in heat-and-power engineering, in ferrous and nonferrous metallurgy, in the petroleum industry, as well as in the chemical industry. Ammonium hydrogen fluoride is an expensive imported reagent for enterprises of the Republic of Kazakhstan. Ammonium hydrogen fluoride can be obtained from natural calcium fluoride CaF_2, however, its traditional production technology is based on the reaction of interaction with concentrated sulfuric acid at temperatures above 100 ºC. The implementation of these reactions encounters a number of technological difficulties [1]. Ammonium hydrogen fluoride can also be obtained by dissociating ammonium fluoride NH_4F [2]. Considering this, an alternative method of obtaining $NH_4F \cdot HF$ can be a technology that involves obtaining ammonium fluoride in the first stage, which can then process ammonium hydrogen fluoride.

The main reagents for the production of ammonium fluoride are calcium fluoride and ammonia NH_3. Ammonia is not available in all regions of the Republic of Kazakhstan. In Central Kazakhstan, ammonium sulphate can be a substitute for ammonia, an illiquid by-product of a coke-chemical production containing an ammonium group. With this in mind, it is of interest to determine the possibility of using ammonium sulphate $(NH_4)_2SO_4$ to produce ammonium fluoride [3]. To this end, studies aimed at determining the mechanism of interaction of calcium fluoride CaF_2 with ammonium sulphate $(NH_4)_2SO_4$ have been carried out. The studies included thermodynamic and differential thermal analyzes.

Experimental

Thermodynamic analysis was performed using the HCS-5.1 Chemistry (Outokumpu) software complex [4] and was reduced to calculating the Gibbs energy of chemical reactions, the occurrence of which was the most probable during the interaction of these reagents:

$$CaF_2 + (NH_4)_2SO_4 = CaSO_4 + 2HF\uparrow + 2NH_3\uparrow \quad (1)$$

$$(NH_4)_2SO_4 = NH_4HSO_4 + NH_3\uparrow \quad (2)$$

$$CaF_2 + NH_4HSO_4 = CaSO_4 + NH_4F + HF\uparrow \quad (3)$$

$$(NH_4)_2SO_4 = 2NH_3\uparrow + SO_3\uparrow + H_2O\uparrow \quad (4)$$

$$NH_4HSO_4 = NH_3\uparrow + SO_3\uparrow + H_2O\uparrow \quad (5)$$

$$CaF_2 + H_2O + SO_3 = CaSO_4 + 2HF\uparrow \quad (6)$$

$$NH_3 + HF = NH_4F \quad (7)$$

The results of the thermodynamic analysis of reactions (1)–(7) are presented in Table.

Table

Gibbs energy values for the reaction (1)–(7), kJ (negative values are highlighted in bold)

Temperature, °C	Reaction (1)	Reaction (2)	Reaction (3)	Reaction (4)	Reaction (5)	Reaction (6)	Reaction (7)
0	182.202	100.871	13.475	284.500	183.629	**–102.299**	**–63.893**
100	127.294	97.373	**–8.510**	223.663	126.290	**–96.369**	**–34.468**
200	73.318	93.936	**–29.907**	163.943	70.007	**–90.624**	**–5.327**
300	20.377	90.355	**–52.217**	105.423	15.068	**–85.045**	21.722
400	**–31.436**	86.498	**–74.731**	48.171	**–38.327**	**–79.608**	47.165
500	**–82.035**	82.275	**–96.207**	**–7.749**	**–90.024**	**–74.286**	72.065

From Table 1 it follows that the interaction of calcium fluoride CaF_2 with ammonium hydrogen sulphate NH_4HSO_4 is more probable than with ammonium sulphate $(NH_4)_2SO_4$. The decomposition of ammonium sulphate by reaction (2) with the formation of ammonium hydrosulphate is more probable than the decomposition by reaction (4). Therefore, the interaction of calcium fluoride with ammonium sulphate is probably includes the process of decomposition of the latter with the formation of ammonium hydrosulphate. At temperatures above 300 ºC, ammonium hydrosulphate will begin to decompose according to reaction (5) with the formation of sulfur trioxide SO_3. In return, sulfur trioxide will intensively interact with calcium fluoride, since reaction (6) is exothermic.

Differential-thermal analysis of reactions (1) and (2) was carried out with the Q-1000/D derivatograph of the F. Paulik, J. Paulik and L. Erdey systems of the MOM company in an air atmosphere at a heating rate of 10 ºC/min. The sample weight was 450 mg; calcined alumina served as a reference. Derivatograms (DTA and TG curves) of reaction (1) and decomposition of separately taken ammonium sulphate $(NH_4)_2SO_4$, the results of processing the TG curve with breakdown into three sections are shown in Figures 1 and 2.

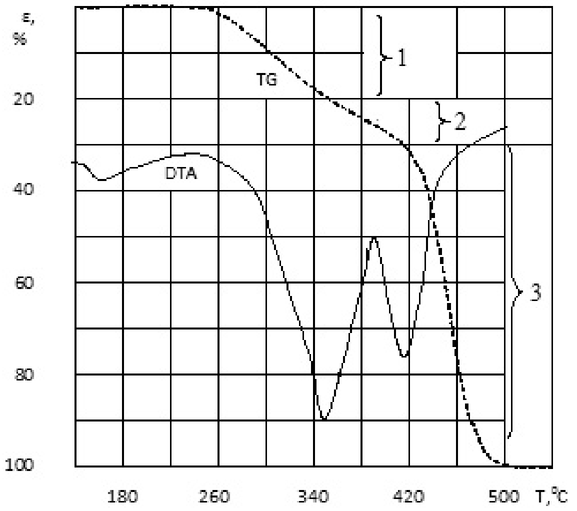

Figure 1. DTA and TG curves of calcium fluoride interaction with ammonium sulphate

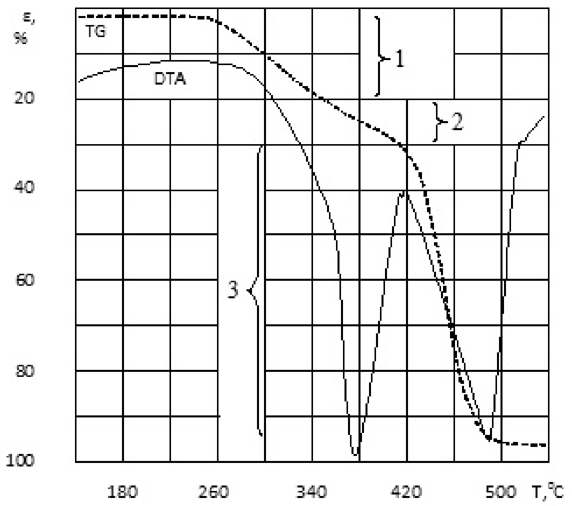

Figure 2. DTA and TG curves of a single ammonium sulphate decomposition

The investigation of the reaction of the interaction of calcium fluoride and ammonium hydrosulphate, DTA reactions (3) and (5) were carried out under the same conditions as for reactions (1) and (2). Derivatograms (DTA and TG curves) of reaction (3) and the decomposition reaction of a single ammonium hydrosulphate NH_4HSO_4, the results of processing the TG curve with breakdown into three (Fig. 3) and two (Fig. 4) sections are shown.

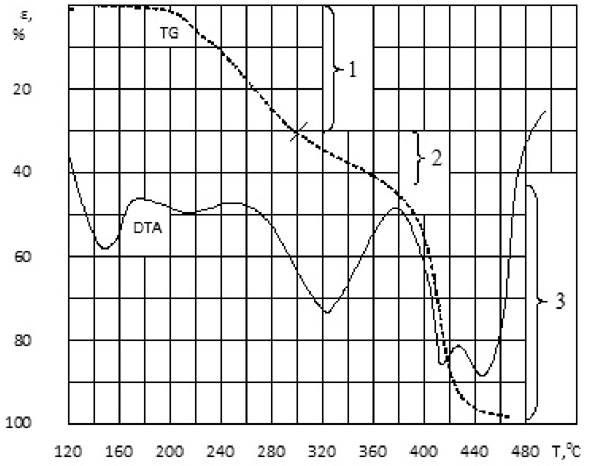

Figure 3. DTA and TG curves of calcium fluoride interaction with ammonium hydrosulphate

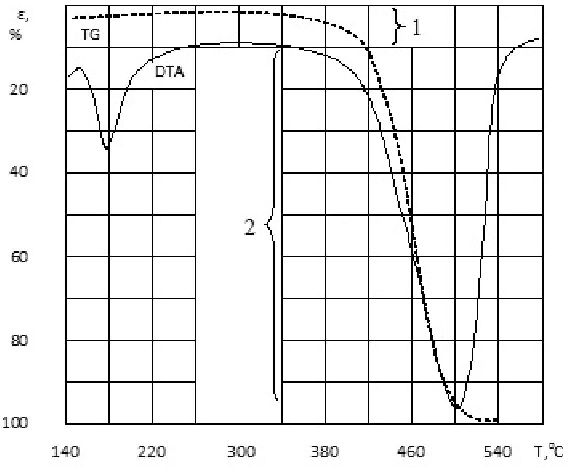

Figure 4. DTA and TG curves of a single ammonium hydrosulphate decomposition

Results and Discussion

Derivatograms presented in Figures 1 and 2 confirm the data of thermodynamic analysis. The decomposition of ammonium sulphate (Fig. 2) proceeds according to reaction (2) with the formation of ammonium hydrosulphate and it begins at 260 °C (section 1 of the TG curve). The total decomposition of $(NH_4)_2SO_4$ is completed at 380 °C, which is evidenced by the endothermic effect. At the same time, the process velocity, according to the decrease in the angle of incidence of the TG curve (section 2), slows down in the temperature range 340–420 °C. This may be due to diffusion difficulty caused by the formation of ammonium hydrosulphate. In this case, reaction (2) is not final, since ammonium hydrosulphate is also decomposed by reaction (5). According to the DTA curve of ammonium sulphate (Fig. 2), the decomposition of ammonium hydrosulphate occurs in the temperature range 420–490 °C (section 3 of the TG curve).

In the interaction of calcium fluoride with ammonium sulphate, first the decomposition of the latter takes place with the formation of ammonium hydrosulphate, which then reacts with calcium fluoride by reaction (3). This explanation is based on the fact that the character of the DTA and TG curves of decomposition of a single ammonium sulphate (Fig. 2) repeats in form the derivatogram (Fig. 1). The main difference between derivatograms (Fig. 1) and (Fig. 2) is the shift of temperature peaks towards low temperatures on derivatogram (Fig. 1). The shift of the peaks can be explained by the flow of the exothermic process of formation of calcium sulphate by the reaction (6). The heat generated during this process partially compensates for the heat consumption for heating and decomposition of ammonium sulphate. In return, the course of reaction (6) indicates that some part of $(NH_4)_2SO_4$ decomposes according to reaction (4) with the formation of sulfur trioxide SO_3 and water. $(NH_4)_2SO_4$ decomposes by reactions (2) and (4) (section 1 of the TG curve) in the temperature range of 260–350 °C. Judging by change of slope of the TG curve, there is an interaction of a calcium fluoride with ammonium sulphate decomposition products (NH_4HSO_4, SO_3 and H_2O) in the temperature range of 350–420 °C (section 2). Judging by the DTA curve, the exothermic process of calcium sulphate formation by the reaction (6) proceeds to a greater degree in the temperature range of 350–390 °C. The reaction (6) indicates that ammonium hydrosulphate begins to decompose by reaction (5). The reaction of calcium fluoride with ammonium hydrogen sulphate (3) takes place at temperatures of 390–420 °C. The remaining part of NH_4HSO_4 is decomposed by reaction (5) in the temperature range of 420–500 °C (section 3). The increase of the DTA curve after 420 °C is explained by heating the calcium sulphate obtained.

Derivatogram presented in Figures 3 and 4 reflects the processes taking place in reactions (3) and (5). The decomposition of ammonium hydrosulphate (Fig. 4) proceeds according to reaction (5) and begins at 340 °C (section 1 of the TG curve). The initial endothermic effect at 180 °C is explained by the melting of NH_4HSO_4 without mass loss. Above 420 °C, the process is more intense and ends at 500 °C (section 2), as evidenced by the endothermic effect.

Judging by the DTA and TG curves, the process of calcium fluoride interaction with ammonium hydrosulphate (Fig. 3) is complex and is accompanied by successive processes in the range of 200–450 °C. Before the interaction, the melting of NH_4HSO_4 takes place first, as evidenced by the presence of an endothermic effect at 150 ºC. The TG curve is straightforward (section 1 of the TG curve) in the temperature range 200–300 ºC, i.e. reaction (3) goes with a constant acceleration factor. The presence of an endothermic effect at 320 ºC indicates the end of this reaction. The angle of incidence of the TG curve decreases in the temperature range of 300–380 ºC, i.e. the velocity of the process slows down, which is probably due to the onset of diffusion hindrance as a result of the formation of a large solid product, calcium sulphate (section 2). The growth of the DTA curve after 320 ºC is explained by heating the calcium sulphate obtained. Unreacted NH_4HSO_4 starts to decompose with the release of sulfur trioxide and water vapor above 380 ºC. The formation of these products contributes to the removal of diffusion difficulties (section 3 on the TG curve), which leads to an increase in the velocity of the process. The dissociation of NH_4HSO_4 proceeds with the absorption of heat, which explains the endothermic effect at 410 ºC. The sulfur trioxide and water react with unreacted calcium fluoride by reaction (6) with the release of heat, which explains the exothermic effect at 430 ºC. The remaining part of NH_4HSO_4 is decomposed by the reaction (5) in the temperature range 430–445 ºC. The growth of the DTA curve after 445 ºC is explained by heating the calcium sulphate obtained.

Conclusion

The results of thermodynamic and differential-thermal analyzes show that as the mixture heats up, the interaction of calcium fluoride with ammonium sulphate proceeds according to the following mechanism:

1) ammonium sulphate decomposes by reaction (2) to form liquid ammonium hydrosulphate, and partially by reaction (4) to form sulfur trioxide and water in the temperature range of 260–350 ºC;

2) calcium fluoride reacts with ammonium hydrosulphate by reaction (3) and with sulfur trioxide and water by reaction (6) with the formation of ammonium fluoride, fluoric hydrogen and calcium sulphate in the temperature range of 350–420 ºC;

3) the remaining part of NH_4HSO_4 is decomposed by reaction (5) with the release of sulfur trioxide and water, which then react with the remaining part of calcium fluoride by reaction (6) above 420 ºC;

4) ammonia and fluoric hydrogen obtained can be also processed into ammonium fluoride by reaction (7).

When the mixture of calcium fluoride and ammonium hydrosulphate is heated, reaction (3) proceeds already in the temperature range of 200–320 ºC. The ammonium fluoride obtained can be used to produce ammonium hydrogen fluoride by decomposing it at a temperature of 138 ºC.

Thus, the possibility of using ammonium sulphate as a reagent for the production of ammonium fluoride from natural calcium fluoride has been established on the basis of the research carried out and the reaction studied (1) can serve as the chemical basis of an alternative technology for the preparation of ammonium hydrogen fluoride.

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К. Жумашев, А. Нарембекова, Б.Б. Катренов

Аммоний сульфаты бар кальций бифторидінің өзара әрекеттесу реакциялар механизмін анықтау

Аммоний бифторидін күкірт қышқылын қолдана отырып, дәстүрлі технологиясымен алу бірқатар технологиялық қиындықтарға алып келеді. Осыны ескере отырып, аммоний сульфатын — кокс-химия өндірісінің жанама өнімі қолдану арқылы аммоний бифторидін алудың балама әдісі ұсынылған. Аммоний фторидін өндіру үшін аммоний сульфатын реагент ретінде қолдану мүмкіндігін анықтау үшін кальций бифторидінің аммоний сульфатымен әрекеттесу реакциясының термодинамикалық және дифференциалды-термиялық талдауы жасалды. Талдаулардың нәтижелері бойынша қоспаны біртіндеп қыздыру кезіндегі кальций бифтордінің аммоний сульфатымен әрекеттесу механизмі анықталды. Аммоний сульфатының әуелі аммоний гидросульфатына, аммиакқа, күкірт триоксидіне және суға ыдырауы анықталған. Сонан соң аммоний гидросульфаты, күкірт триоксиді және су кальций бифторидімен әрекеттесіп, осыдан кейін аммоний фториді, фторлы сутегі, кальций сульфаты деген қосылыстар пайда болады. Аммиак және фторлы сутегі кейін аммоний фторидіне өндіруге болады. Осылайша, өткізген зерттеулерінің негізінде табиғи кальций фторидінен аммоний фторидің өндіру үшін аммоний сульфатын реагент ретінде қолдану мүмкіндігін анықталған. Аммоний фториді кейін аммоний бифторидіне өндіруге болады. Осылайша, зерттелген реакция аммоний бифторидін өндірудің балама технологиясы үшін химиялық негізі бола алады.

Кілт сөздер: кальций бифториды, аммоний сульфаты, аммоний фториді, аммиак, термиялық талдау, термодинамикалық талдау.

К. Жумашев, А. Нарембекова, Б.Б. Катренов

Определение механизма реакции взаимодействия бифторида кальция с сульфатом аммония

Получение бифторида аммония по традиционной технологии с использованием концентрированной серной кислоты сопряжено с рядом технологических затруднений. Учитывая это, предложен альтернативный вариант получения бифторида аммония с использованием сульфата аммония — побочного продукта коксохимического производства. Для установления возможности использования сульфата аммония в качестве реагента для получения фторида аммония были проведены термодинамический и дифференциально-термический анализы реакции взаимодействия бифторида кальция с сульфатом аммония. По результатам проведенных анализов установлен механизм протекания реакции бифторида кальция с сульфатом аммония по мере нагревания смеси. Показано, что вначале происходит разложение сульфата аммония с образованием гидросульфата аммония, аммиака, триоксида серы и воды. Затем гидросульфат аммония, триоксид серы и вода взаимодействуют с бифторидом кальция с образованием фторида аммония, фтороводорода и сульфата кальция. Аммиак и фтороводород затем могут быть также переработаны во фторид аммония. Таким образом, на основании проведенных исследований установлена возможность использования сульфата аммония в качестве реагента для получения фторида аммония из природного фторида кальция. Фторид аммония затем может быть переработан в бифторид аммония. Таким образом, изученная реакция может служить в качестве химической основы альтернативной технологии получения бифторида аммония.

Ключевые слова: бифторид кальция, сульфат аммония, фторид аммония, термический анализ, термодинамический анализ.

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