Tr. J. of Chemistry
20 (1996) , 1 – 8.

The Investigation of Aluminum Sulfate-Potassium Chloride Solid Phase Reaction

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Received 19.11.1993

It was found that aluminum sulfate reacts with potassium chloride to produce K_2SO_4, Al_2O_3, and Cl_2 in the solid phase at 700 °C. This reaction was investigated with thermal analysis under air and nitrogen atmosphere. By changing temperature and time parameters, the actual yield of conversion in question was examined analytically and the optimum temperature and time were found for the reaction. The rate expression of the solid phase reaction was also investigated and the rate equation was obtained.

Key Words: aluminum sulfate, Potassium chloride solide phase reaction.

Introduction

Alunite ore, which has the formula of $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$, is found with SiO_2 in nature and by calcination with KCl or $NaCl$ yields K_2SO_4, Al_2O_3 and HCl[1−5]. The calcination of Şaphane Alunite in Turkey with KCl has been studied with the thermal method[6].

It is obvious that the reaction of alunite with KCl has occurred basically between aluminum sulfate and potassium chloride and that is why the solid phase reaction of $Al_2(SO_4)_3 - KCl$ was investigated in this study. The conditions and the kinetic equation of the reaction were found. This reaction may be used to produce $K_2SO_4, \gamma - Al_2O_3$ and Cl_2. It may also give us a new method of producing potassium sulfate and chlorine.

The oldest production method of potassium sulfate was based on the reaction of potassium nitrate with sulphuric acid[7]. In another production method, potassium chloride is reacted with sulphuric acid to produce potassium sulfate and HCI [8]. Another more suitable way of producing potassium sulfate is the reaction of potassium chloride with magnesim sulfate in aqueous solution[9−11]. Potassium sulfate is also obtained from epsomite $(MgSO_4 \cdot 7H_2O)$ and potassium chloride[12]. Another source of potassium sulfate is alunite ore and the amount of K_2O in it is 4-10% [1,2]. In addition to K_2SO_4 and Al_2O_3, alum is also obtained from alunite[13,14].

The $Al_2(SO_4)_3 - KCl$ solid phase reaction which has been investigated in this study is more advantageous than the ones mentioned earlier because it gives us Cl_2 and Al_2O_3 in addition to K_2SO_4.

Material and Methods

Thermal analysis curves of the solid phase reactions of $Al_2(SO_4)_3 + KCl$ were determined with the thermal analysis instrument (NETZSH-STA-429). The reaction was carried out in an air and N_2 atmosphere in the instrument and TG, DTG and DTA curves of the stoichiometric mixtures were obtained. 100 mg of sample was used for analysis and the rate of heat in the instrument was controlled linearly. Rate of heat was 10° C/ min. Kaolinite, sintered at 1600° C as measured with a Pt-Rh/Pt thermocouple, was used. The programme of heat was carried out at 100-900° C. For an investigation of the yield of the solid phase reaction, the mixtures of $Al_2(SO_4)_3 - KCl$ were prepared and the solid phase reactions were carried out in a muffle furnace by changing the time and temperature. The mass obtained from the solid phase reaction was dissolved in boiling water and the undissolved part was separated by filtration. The mass on the filter was completely dissolved in boiling concentrated HCl. Al_2O_3 and SO_3 were analyzed gravimetrically in all of the solutions. The amounts of $K_2SO_4, Al_2(SO_4)_3$ and KCl in the mass dissolved in water and the amounts of Al_2O_3 and SO_3 in the parts which did not dissolve in water were found. Al_2O_3 and SO_3 were analyzed by precipitation of $Al(OH)_3$ with NH_3 and $BaSO_4$ with $BaCl_2$ respectively. The amounts of Cl_2 and SO_3 gases released during the solid phase reaction were calculated stoichiometrically. In this way, the conversion yield of the solid phase reaction was established.

Results and Discussion

The Thermal Curves of Solid Phase Reaction

The TG, DTA and DTG curves of the solid phase reaction that occurred between $Al_2(SO_4)_3$ and KCl are given in Figures 1 and 2. They show the curves obtained in air and N_2 atmosphere, respectively.

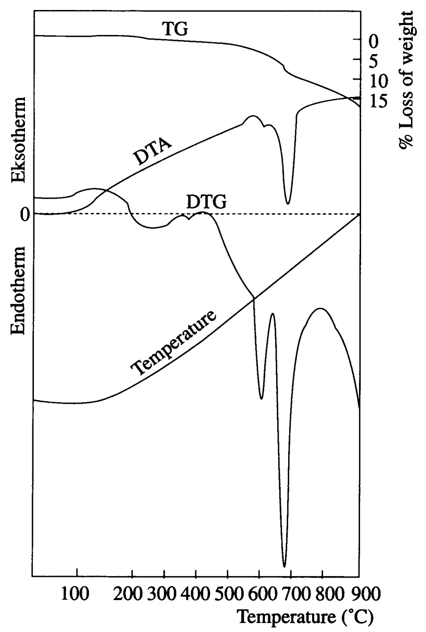

Figure 1. The thermal curves of $Al_2(SO_4)_3 + KCl$ solid phase reactions in air

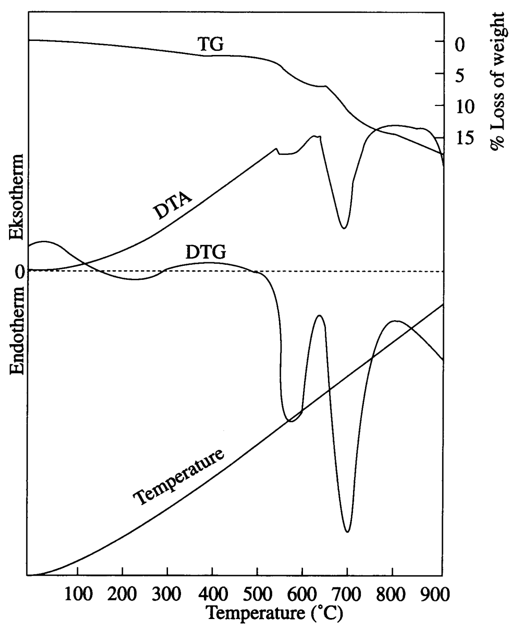

Figure 2. The thermal curves of $Al_2(SO_4)_3 + KCl$ solid phase reaction in nitrogen atmosphere

Endothermic peaks are observed at 600° C and 680° C on DTA in Figure 1 and at 560° C and 680 ° C on DTA in Figure 2. The first endothermic peak at 600° C in Figure 1 belongs to the decomposition of aluminum sulfate:

$$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3. \quad (1)$$

The reaction between $KCl, Al_2(SO_4)_3$ and O_2 forms the endothermic effect at 680° C on the DTA curve in Figure 1:

$$Al_2(SO_4)_3 + 6KCl + 3/2O_2 \rightarrow Al_2O_3 + 3K_2SO_4 + 3Cl_2. \quad (2)$$

The occurance of the endothermic reaction at 560° C on the DTA curve in Figure 2 is caused by reaction (1) and the other endothermic peak ot 680° C on the DTA curve is due to the following reaction:

$$Al_2(SO_4)_3 + 3KCl \rightarrow Al_2O_3 + 3/2K_2SO_4 + 3/2Cl_2 + 3/2SO_2. \quad (3)$$

Figure 1 shows that reaction (1) ending at 635° C causes a weight loss of 4.8% and reaction (2) ending at 800° C causes a weight loss of 5.2% from 635° C to 700° C. When the weight losses occuring from 400° C to 700° C are taken into account we see that the 48% of the total weight loss was caused by SO_3 released at the end of reaction (1) and 52% of the total weight loss was caused by Cl_2 released at the end of the reaction (2). The weight loss in the interval of 800 – 900° C belongs to the decomposition of aluminum sulfate unreacted. Figure 2 shows that reaction (1) ending at 625° C, resulted in a weight loss of 5.6% and the reaction (3), which happened from 625° C to 789° C, resulted in a weight loss of 6.9% in the interval of 625-700° C. The cause of the 44.8% of the weight loss occuring from 625° C to 700° C was SO_3 released at the end of the reaction (1) and the cause of the 55.2% of the weight loss was Cl_2 and SO_2 released during reaction (3). The weight loss occuring in reaction (3) in the inert gas atmosphere is more than the weight loss during reaction (2) because O_2 is added. The reason for this is that reaction (3) releases SO_2 in addition to Cl_2.

The amount of potassium sulfate obtained in equation (2) is more than the amount obtained in equation (3) due to the oxygen in the open air. The solid phase reaction realizes with a lower rate of yield in the inert gas atmosphere and the amount of potassium sulfate obtained is less than the amount obtained in the oper air. Besides the amount of chlorine in the inert gas atmosphere is less than the amount of sulfur dioxide.

The Effect of Temperature on the Solid Phase Reaction

To investigate the effect of temperature on the solid phase reaction, the masses obtained from the solid phase reaction realized at various temperatures were analyzed and the soluble compounds in water were found.

The compositions of the masses obtained from the solid phase reactions made at 600 – 800° C for 60 minutes are given in Table 1.

Table 1. Effect of temperature on the solid phase reaction at 60 minutes

Temperature	Compound (%)			
(°C)	$Al_2(SO_4)_3$	K_2SO_4	Al_2O_3	KCI
600	20.42	22.67	9.09	47.59
650	12.49	44.04	12.05	31.41
700	10.30	45.98	12.89	30.81
800	6.28	45.94	14.61	33.16

The amounts in Table 1 belong to the sum of the reactions (1) and (2). That is to say, the quantities in Table 1 are not related only to reaction (2). The 24.7% of aluminum sulfate taken in stoichiometric ratio reacts according to reaction (1), occuring from 400° C, to 635° C and the 56.1% of it reacts according to reaction (2), occuring from 635° C to 700° C.

The plots of temperature vs. compound % are shown in Figure 3. As can be seen in Figure 3, the increase in the yield of the solid phase reaction depends on temperature. The amounts of potassium chloride and aluminum oxide increase while the amounts of aluminum sulfate and potassium chloride decrease. As can be seen Table 1 and Figure 3 the yield of the total reaction at 700° C is more than the it is at 800° C because, as can be seen from Figure 1, the reaction (2) essentially realizes at 680° C and it ends at 800° C

The plots of the gases formed vs. temperature for the solid phase reaction are given in Figure 4.

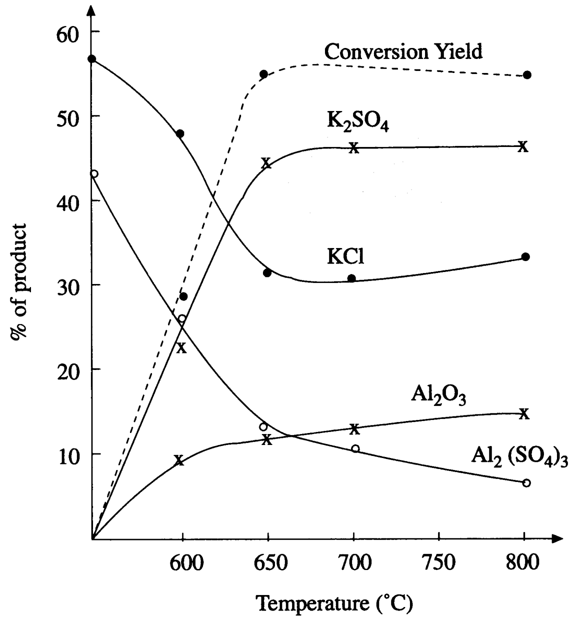

Figure 3. Effect of temperature on the solid phase reaction

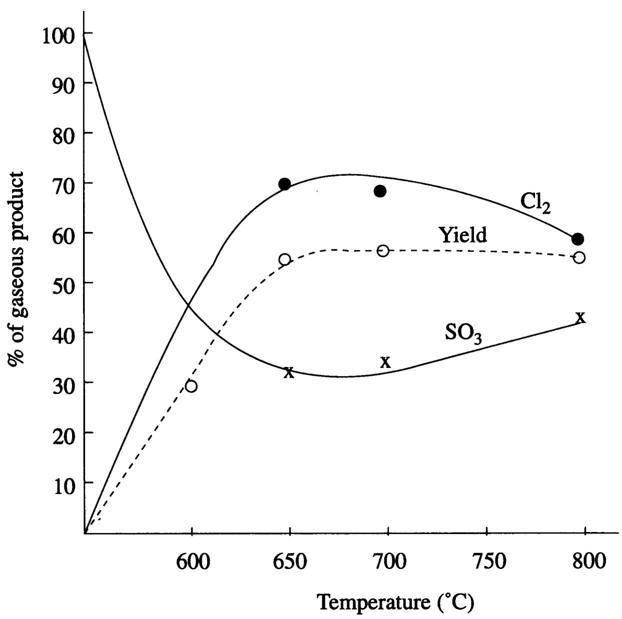

Figure 4. Effect of temperature on the amounts of the gases formed in the reaction

As can be seen from Figure 3 and 4, the optimum temperature for the solid phase reaction is 700° C. The optimum temperature in the above thermal studies was found to be 680° C. This difference in the experimental data was caused by the rate of heating. As shown in the figures, the actual yield of conversion of the reaction can be 57%. The actual yield of conversion depends on the oxygen amount in the furnace.

Effect of the Reaction Time on the Solid Phase Reaction

The compositions of the masses obtained from the solid phase reaction made at different times at 700° C were found. The results are given in Table 2 and Figure 5.

As can be seen from Figure 5, the amount of potassium sulfate and the conversion increases in 30 minutes of reaction times.

The plots of the amounts of the gases formed in the reaction vs. the reaction time are shown in Figure 6.

As can be seen from Figure 6, chlorine formation increases with the reaction time and sulfur trioxide formation decreases with the increase of the reaction time until the 15 th. minute. The amount of aluminum sulfate decomposed to give sulfur trioxide is equal to the amount of aluminum sulfate reacted with KCl to give chlorine in the fifteenth minute. Figure 6 shows a lower increase in the rate of the solid phase reaction after the 15th minute.

Table 2. Effect of reaction time on the solid phase reaction at 700° C

Time	Compound (%)			
(min)	$Al_2(SO_4)_3$	K_2SO_4	Al_2O_3	KCI
0	43.34	0	0	56.65
1	37.46	0.05	1.77	55.55
3	33.29	4.62	4.18	54.00
5	29.51	10.06	5.66	54.75
7	25.16	14.22	7.41	53.19
10	25.47	18.07	7.17	49.27
15	20.46	24.92	9.14	45.47
30	12.45	36.61	12.26	38.67
50	12.55	38.85	11.94	36.64
60	10.30	45.98	12.89	30.81

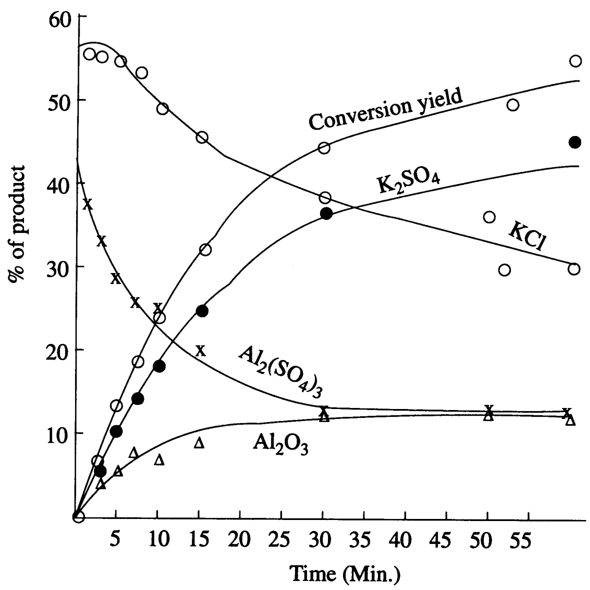

Figure 5. The Compositions of the masses obtained from the solid phase reaction carried out different times at 700° C

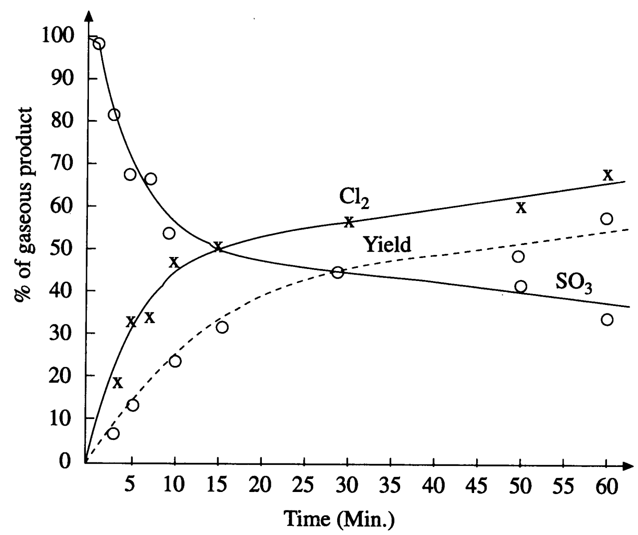

Figure 6. Effect of the reaction time on the amounts of the gases formed in the reaction

The examination of the above studies indicates that the optimum reaction time of the solid phase reaction is 50 minutes. On the other hand, the weight losses occuring in the 60th minute are 47.98% for sulfur trioxide and 52.01% for chlorine. As shown on the thermal curves in Figure 1, these values are 48% for sulfur trioxide and 52% for chlorine.

The values found from thermal curves with analytic values are the same. These results prove that the reactions (1) and (2) recommended in this study are definitely right.

The Kinetics of the Solid Phase Reaction of Aluminum Sulfate- Potassium Chloride Mixture

The rate experession of the solid phase reaction for 700° C was found by van't Hoff differential method. The reaction rate for the reaction can be related to the concentration (x) of reactant by the following equation:

$$v = k \cdot x^n \tag{4}$$

where

n = the order of reaction

k = the rate constant

Taking logarithms of both sides of Eq.(4),

$$\log v = \log k + n \log x \tag{5}$$

If the reaction rate, v, is known at various values of reactant concentration a plot of log v against $log x$ will result in a straight line, and the slope of the line gives the value of the order of reaction with respect to the substance whose concentration is being varied[15].

According to this method, tangents were drawn at the points corresponding to 5,10,20,30 and 50 minutes on the curves of aluminum sulfate and potassium chloride in Figure 6. The slopes of these five tangents were measured to obtain the rates of decomposition, ($v = dx/dt$).

The reaction (2) can be regarded as third-order by van't Hoff's differential method. The rate equation of the reaction (2) can be given the following equation:

$$dx/dt = k \cdot c_a^{1.5} \cdot c_k^{1.5} \tag{6}$$

where dx/dt=the formation rate of K_2SO_4 (%/min)

k = $3.695 \cdot 10^{-5}$ $(\%)^{1.25}/\text{min}$

c_a = the concentration of aluminum sulfate at any time (%)

c_k = the concentration of KCI at any time (%).

The rate of the solid phase reaction (dx/dt) was found separately from the experimental data as above and from equation (6), theoretically. The amounts of $Al_2(SO_4)_3$ and KCI in Table 3 was taken from Figure 5. These results can be compared in Table 3.

Table 3. The experimental and theoretical rates of the solid phase reaction at 700° C

Time	Concentration (%)		The formation rate of K_2SO_4 (%/min)	
(min)	$Al_2(SO_4)_3$	KCI	Experimental	Theoretical
5	29.51	55.55	2.433	2.400
10	23.33	49.27	1.333	1.430
20	16.66	42.00	0.833	0.684
30	14.00	38.67	0.307	0.465
50	13.20	32.66	0.172	0.330

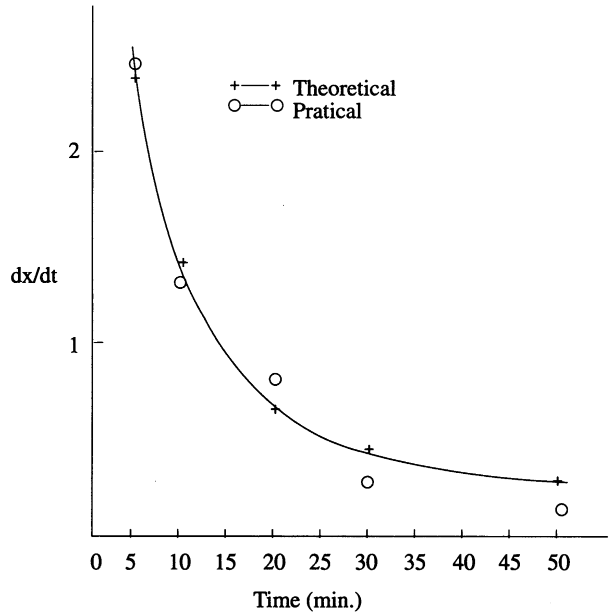

Figure 7. Plots of the experimental and the theoretical reaction rates versus the reaction time

As can be seen from Table 3 and Figure 7 both the rates are in good agreement. As a result the reaction rate can be found correctly from equation(6).

Conclusions

It was found that the solid phase rection between $Al_2(SO_4)_3$ and KCI occured at 700° C given by the following equation:

$$Al_2(SO_4)_3 + 6KCI + 3/2O_2 \rightarrow Al_2O_3 + 3K_2SO_4 + 3Cl_2.$$

This solid phase reaction was studied by thermal and analytic methods.

The optimum temperature and time of these reaction is 700° C and 50 minutes, respectively. The maximum yield in the furnace atmosphere was about 50%. The kinetics of the solid phase reaction was investigated and it was found that the reaction was in the 3rd. order. The rate constant of the reaction was $3.695 \cdot 10^{-5}$ $(\%)^{1.25}$/min. The reaction can be used for production of potassium sulfate, $\gamma - Al_2O_3$ and chlorine. Especially, it will provide a new production possibility for potassium sulfate and chlorine. This reaction can also be employed to take advantage of alunite ore.

References

1. H. Gülensoy and İ. A. Şengil, "Alunit cevheri, Oluşumu ve Bulunuşu hakkında" **Kimya ve Sanayi, 31,** 157-158, 116- 131 (1989).
2. H. Gülensoy and İ. A. Şengil, "Alunit cevherinin değerlendirilmesi hakkında" **Kimya ve Sanayi, 31,** 159-160 67-83 (1989).
3. A. Singevald and O. Braun, "Potassium Sulfate from Alunite and Chloride-Containing Potassium Fertilizer Salts Using the Heat from the Cleavage of Hydrogen Chloride Gas" Ger. Offen., 2507277 (CIC01 D5/06), (1976).

4. S. Jason, "Treatment of Alunite" Financial Mining-Industrial and Shipping Corp. Ger. Offen., 2555875 (CIC01D5/06), (1977).
5. V. I. Kirichenko and A. D. Biba, "Conversion Methods for Complex Treatment of Alunites" Komplksn. **Ispol'z Miner. Syr'ya, 9,** 47-9, (1987).
6. İ. A. Şengil, "Şaphane Aluniti-Potasyum, Sodyum, Baryum veya Kalsiyum klorür karışımlarının Termal Bozunması" **Doğa-Türk Mühendislik ve Çevre Bilimleri Dergisi, 15,** 4, 436-446, (1991).
7. J. W. Mellor, "Inorganic and Theoretical Chemistry" Longmans, London, (1946).
8. F. D. Snell and L. S. Ettre, "Encyclopedia of Industrial Chemical Analysis" John Wiley, 17, USA, (1973).
9. Ü. Sanıgök "Anorganik Endüstriyel Kimya" İstanbul Üniversity, İstanbul, (1987).
10. H. N. terem, "Anorganik Sınai Kimya" Fatih Yayınevi, İstanbul, (1977).
11. M. Nuryagdyu and G. I. Andryasova," Decomposition of Schoenite by a Potassium Chloride Solution" Izv. Akad. Nauk., 70-7(4), (1979).
12. I. D. Sokolov and V. A. Grabovenko, "Effect of Temperature Conditions on the Production of Potassium Sulfate from Epsomite and Potassium Chloride" Khim. Prom-St, 617-18, (1979).
13. İ. A. Şengil and H. Gülensoy, "Şaphane alunit Cevherinden Aluminyum Sülfat üretim Yapan Bir Tesis Üzerinde İncelemeler", **Doğa B, 8,** 2, 158-163, (1984).
14. H. Gülensoy, "Türkiye Alunit cevherlerini Değerlendirme Çalışmaları" TÜBİTAK, MAG-122/A, (1971).
15. G. S. Upadhyaya and R. K. Dube, "Problems in Metallurgical Thermodynamics and Kinetics" Pergamon Press, London, (1977).