

Jan KUBISZ *

STUDIES ON SYNTHETIC ALKALI-HYDRONIUM JAROSITES II: THERMAL INVESTIGATIONS

UKD 549.762:13.07:543.226

Abstract. Thermal transformations and weight loss in the range 20—1000°C of synthetic alkali-hydronium jarosites were investigated. Chemical constitution expressed by the following general formula $A_{1-x}(H_3O)_xFe_{3-y}[(OH)_{6-3y}(H_2O)_{3y}(SO_4)_2]$ was confirmed. The DTA curves show six (or five) endothermic and three exothermic peaks at temperatures depending on monovalent cation present. The first four endothermic reactions are connected respectively with: dehydration (removal of H_2O molecules, 190—340°C), deprotonation (removal of H_3O^+ ions, 240—440°C), dehydroxylation (removal of OH^- groups, 300—510°C), and removal of OH^- or H_2O trapped in the collapsed framework of decomposition products (about 540°C). The fifth reaction between 560—930°C is due to the loss of SO_3 , and the sixth at 880°C (recorded only for Na, H_3O -jarosites) to melting of Na_2SO_4 . It was assumed that out of the three exothermic reactions the first at about 510° corresponds to the formation of $\alpha-Fe_2O_3$, the second at 580° probably to liberation of „post-anionic-cages” energy, and the third at 700—780°C, splitting the sulphate dissociation peak, to alkali sulphate formation.

INTRODUCTION

Synthesis of alkali jarosites has yielded alkali and iron deficient minerals with excess water, part of which causes a change of the unit cell dimensions (Kubisz 1961, 1970). Some natural minerals are probably of similar type (Kubisz 1964). It was suggested that hydroxyls of iron coordination polyhedra are partly converted to H_2O molecules (referred to as „additional water”) to balance the lacking Fe^{3+} charge, and alkalis are substituted by H_3O^+ ions. The aim of the present paper was to confirm the proposed (Kubisz 1970) chemical constitution by means of thermal analysis.

Considering the general formula of jarosites two types of endothermic

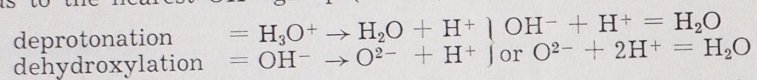
* Institute of Mineralogy and Mineral Deposits, Academy of Mining and Metallurgy, Cracow, Poland.

reactions are to be expected: decomposition of hydrogen-oxygen complexes (H_3O^+ , H_2O , OH^-) and decomposition of sulphate reaction products.

The mechanism of reactions connected with water expulsion is relatively complicated as compared with that of SO_3 removal. According to different activation energies three processes of this type should be distinguished: dehydration (removal of H_2O), deprotonation (removal of H_3O^+), and dehydroxylation (removal of OH^-).

The temperature of dehydration process is determined by the binding energy and lattice positions of H_2O molecules, and structure type of the crystal lattice (disregarding the experimental factors).

Deprotonation and dehydroxylation (compare Freund 1965) are two-steps reactions. In the first step the proton is transferred via hydrogen bonds to the nearest OH^- group (or O^{2-}) forming a H_2O molecule:



The activation energy of this process depends on the transfer distance $\text{O}_d - \text{O}_p$, the height of the potential barrier between donor (O_d) and acceptor oxygen (O_p), and on O—H bond energy. In the second step of the reaction the resulting H_2O molecule migrates to the crystal surface. The velocity and direction of migration of H_2O molecule depend similarly as in the case of the dehydration process on its lattice position and crystal structure type.

The products remaining after removal of hydrogen-oxygen complexes are in an activated state. According to Freund (1965) the energy stored in resulting lattice vacancies (post-ionic „cages”) is liberated spontaneously, the corresponding exothermic effect following close the endothermic ones.

According to the general considerations presented above at least three distinct „water loss” reactions should occur in the investigated jarosites. The temperature of dehydration being the lowest, that of deprotonation intermediate, and that of dehydroxylation the highest.

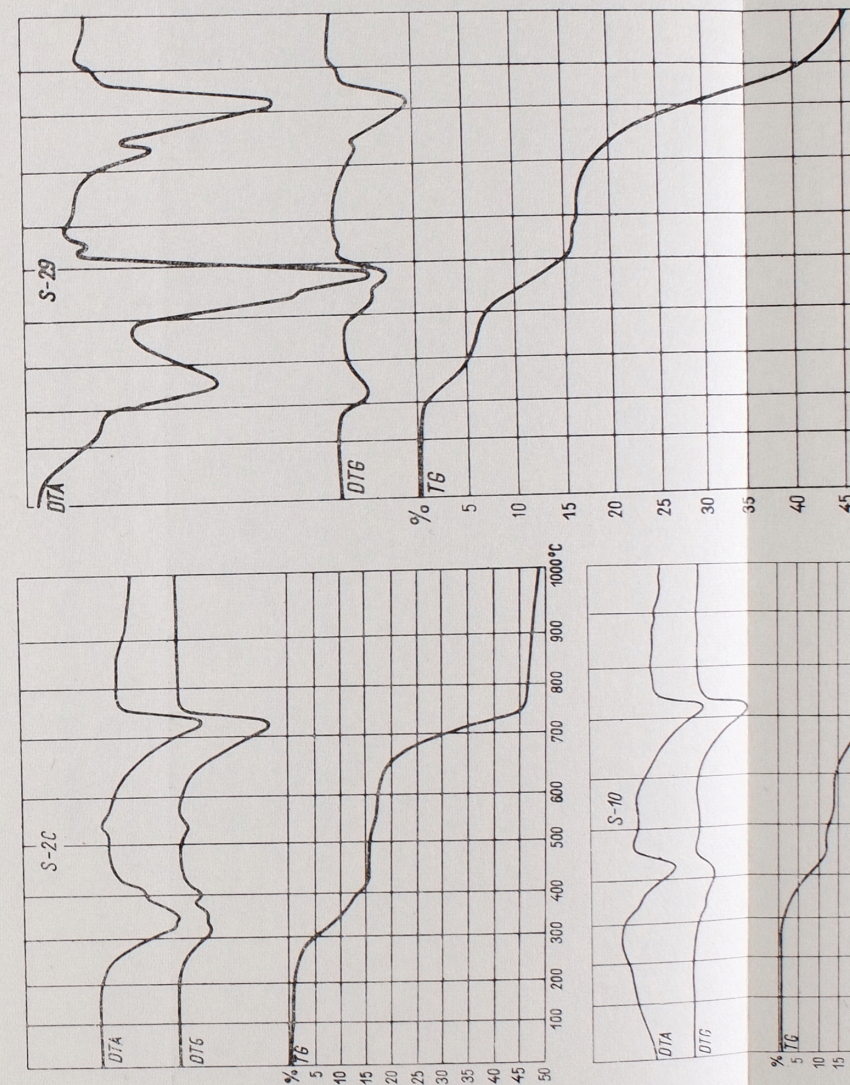
EXPERIMENTAL WORK

The thermal studies were performed with the Derivatograph (after F. and J. Paulik and L. Erdey) registering simultaneously the T, DTA, TG and DTG (derivative of the TG function) curves (Fig. 1). The sample was placed in a platinum crucible, and the temperature measured indirectly in its hollow bottom. Heating rate of $10^\circ\text{C}/\text{min}$ was applied.

The different peak temperatures and shape of curves (Fig. 1) obtained are partly due to differences in the amount of sample (Tabs. 1, 2).

DISCUSSION OF RESULTS

In the case of pure hydronium jarosite which does not contain „additional water” the liberation of hydrogen-oxygen complexes proceeds in



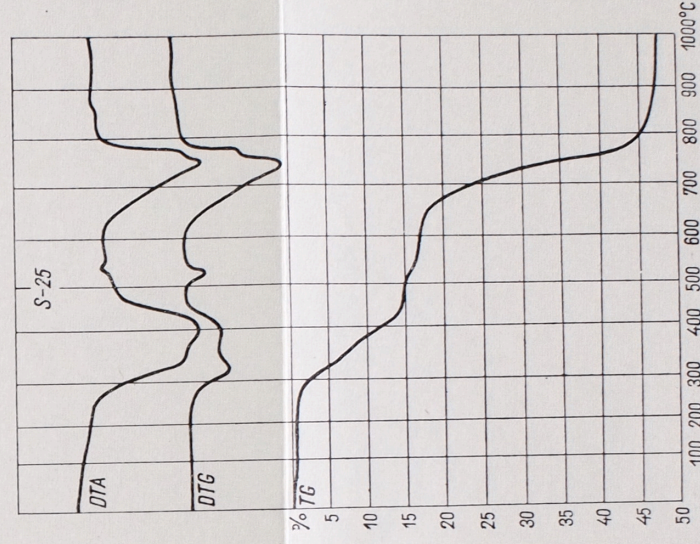
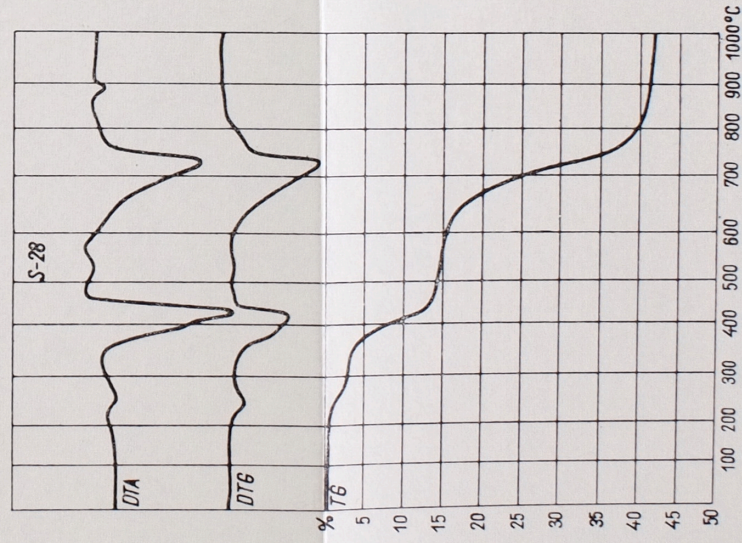
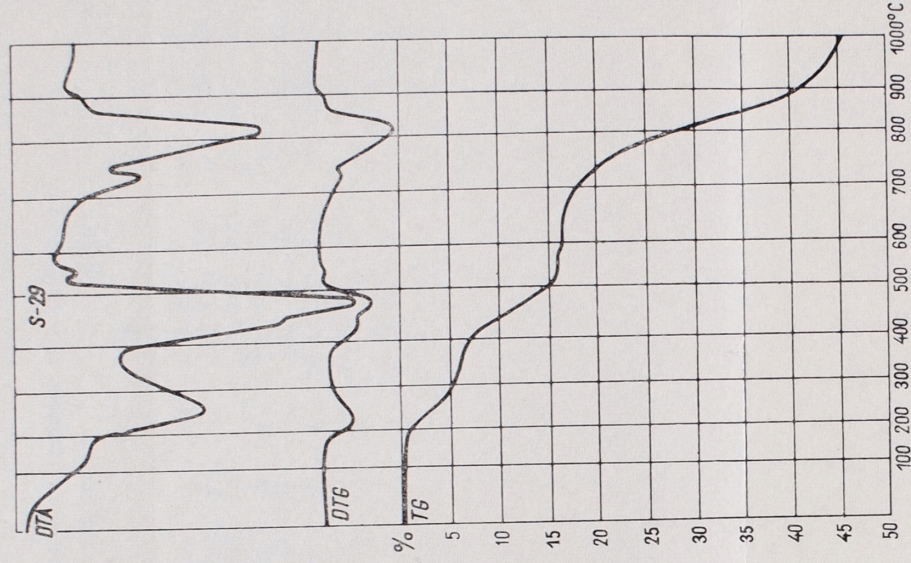
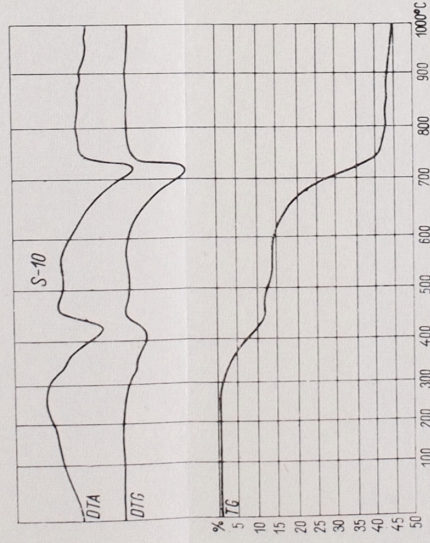
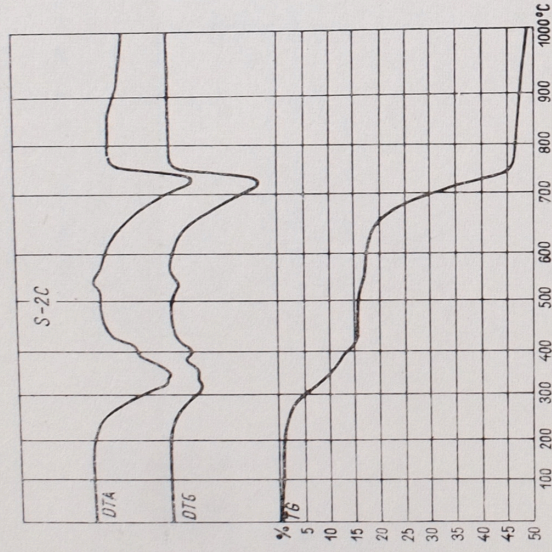


Fig. 1. Examples of derivatographic curves of synthetic alkali-hydronium jarosites
DTA — differential thermal analysis curve, DTG — differential thermogravimetric curve,
TG — thermogravimetric curve. S-2C — hydronium jarosite, S-25, S-29 — $\text{K}_2\text{H}_3\text{O}_2$ -jarosites,
S-10, S-28 — $\text{Na}_2\text{H}_3\text{O}_2$ -jarosites

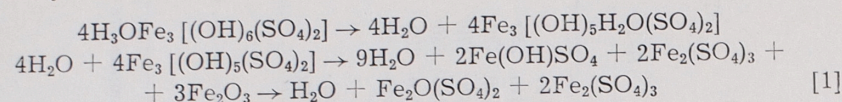
Table 1

Gravimetric data on the endothermic reactions of $K_2H_3O_7$ -jarosites

S-25			S-24			S-4			S-27			S-29		
a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
0-260		0.8	0-220		0.7	0-220		0.6	0-160		0.1	0-180		0.4
260-360	340	5.7	220-320	260	2.8	220-340	280	2.1	160-340	230	4.3	180-340	250	5.3
						340-440	410		340-440	420	3.5	340-440	420	4.1
360-480	410	8.3	320-480	440	11.1	440-520	480	10.4	440-520	460	6.0	440-520	470	5.9
480-560	540	1.3	480-560	540	1.4	520-560	540	0.6	520-550	540	0.5	520-580	550	0.9
560-760	740	18.6	560-720	700	11.8	560-760	750	6.4	550-740	730	4.8	580-740	730	4.5
760-860	780	12.0	720-900	760	16.4	760-880	820	19.3	740-920	810	17.6	740-920	810	21.1
0-560		16.1	0-560		16.0	0-560		13.7	0-550		14.4	0-580		16.6
560-1000		31.2	560-1000		29.2	560-1000		26.0	550-1000		25.4	580-1000		29.1
d		e	d		e	d		e	d		e	d		e
354		1.58	289		4.76	1809		5.64	1456		6.01	560		6.36

a — temperature interval of reaction ($^{\circ}\text{C}$), b — peak temperature of reaction ($^{\circ}\text{C}$), c — weight loss in the given temperature interval (weight, %), d — initial weight of the sample (mg), e — amount of SO_3 bound with K_2O (weight, %).

a different manner as in alkali-hydronium jarosites. Four steps may be distinguished: deprotonation-dehydration-main dehydroxylation-final dehydroxylation.

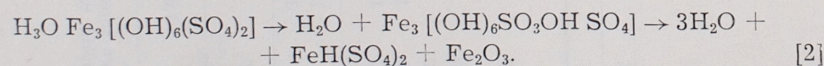


The ratio of water molecules expelled in the above reactions should be equal to 4:4:9:1. However, due to similar activation energies the first three reactions are not distinctly resolved. Therefore it was impossible to establish the exact amount of water (Tab. 2) lost in particular reactions.

In the investigated alkali-hydronium jarosites thermal dissociation is more complicated. „Additional water” is expelled first, prior to deprotonation and dehydroxylation and in higher temperatures alkali sulphates A_2SO_4 ($A = K, Na$) form, besides iron sulphates.

Additional water, filling iron vacancies, is removed between 190–340°C. This process being accompanied by a change of unit cell volume (Kubisz 1970). Maximum of the reaction lies at 260–270°C, depending on the cation present (Tab. 3) and relative amount of this water. The corresponding peak on DTA curves is assymetric and sometimes clearly split (S-4). This may be evidence of two kinds of additional water. One, „compensating”, localized in $\text{FeO}_2(\text{OH}, \text{H}_2\text{O})_4$ polyhedra, and one in iron lattice vacancies. Considering that iron oxy-hydroxide and hydrated iron sulphates, which may be present as slight admixtures, lose water in the same temperature interval, the true nature of the endothermic process described was ascertained by carrying out DTA curves of artificial mixtures of S-29 and varying amounts of $\text{FeO} \cdot \text{OH}$ and $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. These mixtures give three more endothermic reactions (140°, 190°, 320°C) distinctly resolved from the peak representing the loss of additional water.

Deprotonation $\text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O} + \text{H}^+$ and the removal of resulting H_2O molecules takes place at about 320°C in the case of pure hydronium jarosite. The proton of hydronium ion jumps either to sulphate oxygens O_s or to hydroxyl oxygens O_h which most probably lie at a distance less than 3.0 \AA from the monovalent ion. Assuming per analogy with $\text{H}_3\text{OGa}_3[(\text{OH})_6(\text{SO}_4)_2]$ (Johansson 1963) that hydronium in jarosites is closer to O_h oxygens than it is to O_s oxygens, it is more likely for the proton to join hydroxyl groups. Statistically, however, a fraction of hydronium protons will react according to the scheme:



In alkali-hydronium jarosites deprotonation occurs at much higher temperatures (at about 410°C).

Dehydroxylation is connected with destruction of jarosite framework and formation of various sulphates and Fe_2O_3 . Maximum of this reaction

Gravimetric data on the endothermic reactions of Na, H₃O-jarositcs

S-17 (= S-2C)						S-10			S-23			S-26			S-28		
a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
0-220		0.6	0-280		0.5	0-220		0.2	0-220		0.2	0-220		0.2	0-220		0.3
220-340	320	6.1	280-360	340	3.8	220-320	280	2.0	220-320	260	2.1	220-320	260	2.1	220-320	260	2.2
340-400	370	5.0	360-420	400	4.0	320-390	380	3.3	320-400	390	5.1	320-400	390?	5.1	320-400	390?	2.4
400-480	410	3.4	420-480	430	4.7	390-460	420	7.9	400-460	430	5.9	400-460	430	5.9	400-430	420	2.4
															430-500	460	7.0
480-560	530	1.4	480-560	520	1.6	460-560	530	1.4	460-560	530	1.4	460-560	530	1.4	500-560	530	0.5
			560-680	670	6.1	560-690	680	7.9	560-680	670	5.4	560-680	670	5.4	560-700	670	5.7
															700-740	730	6.4
560-800	750	30.2	680-780	730	21.2	690-800	720	18.6	710-800	730	20.8	710-800	730	20.8	740-830	760	12.3
0-560		16.5	0-560		14.6	0-560		14.8	0-560		14.7	0-560		14.7	0-560		14.8
560-1000		33.0	560-1000		31.2	560-1000		27.7	560-1000		28.3	560-1000		28.3	560-1000		27.0
d	e		d	e		d	e		d	e		d	e		d	e	
320	0.00		371	2.19		226	4.92		247	5.65		490	5.62				

a — temperature interval of reaction (°C), *b* — peak temperature of reaction (°C), *c* — weight loss in the given temperature interval weight, %*d* — initial weight of the sample (mg), *e* — amount of SO₃ bound with Na₂O (weight, %).

lies at about 390—480°C. The removal of H_3O^+ ions coordinated to OH^- groups causes the dehydroxylation temperature to be the lowest ($390 \pm 10^\circ\text{C}$) in pure hydronium jarosite. It is intermediate in Na, H_3O - ($440 \pm 10^\circ\text{C}$), and highest in K, H_3O -jarosites ($460 \pm 10^\circ\text{C}$, Tab. 3).

Exothermic peak at about 510°C following close that due to dehydroxylation may be attributed partly to the crystallization of $\alpha\text{-Fe}_2\text{O}_3$ (Kulp and Adler 1950) and partly to the liberation of energy stored in „post-anionic cages” (Freund *loco cit.*).

Table 3

Endothermic reactions* in alkali-hydronium jarosites

Loss of	Jarosite	Mean temperature interval of the reaction, $^\circ\text{C}$	Mean peak temperature (T_{max}), $^\circ\text{C}$
H_2O	K	190—340	260
	Na	220—320	270
	H_3O	?	
H_3O^+	K	340—440	420
	Na	320—400	390
	H_3O	240—350	340
OH^-	K	340?—510	480
	Na	320?—470	440
	H_3O	300?—480	390/410/
SO_3	K	560—930	800/730/
	Na	560—810	730/670/
	H_3O	560—800	750

* In the evaluation of mean temperatures S-25 and S-10 have been treated as hydronium jarosites, together with S-17 (S-2C).

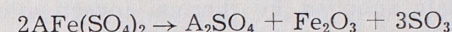
Decomposition of hydroxyl containing reaction products $\text{Fe}(\text{OH})\text{SO}_4$ or $\text{Fe}[\text{SO}_3\text{OH}\text{SO}_4]$ and liberation of H_2O trapped in the collapsed jarosite structure occurs at about $520\text{--}550^\circ\text{C}$. The high activation energy of this reaction is due to low migration ability of H_2O in the collapsed framework rather than to exceptionally high bond energy of these hydroxyls, as suggested by some authors (Cvietkov and Valiashihina 1955).

The second (very weak) exothermic reaction about 580°C may be due to liberation of „post-anionic cages” energy, like the former one, or according to Cvietkov and Valiashihina (1955) to $\alpha \rightarrow \gamma$ transition of Fe_2O_3 .

In the temperature interval of $560\text{--}780^\circ$ (810°) in Na, H_3O - and $560\text{--}850^\circ$ (930°C) in K, H_3O -jarosites respectively decomposition of $\text{Fe}_2(\text{SO}_4)_3$, $\text{Fe}_2\text{O}(\text{SO}_4)_2$ and $\text{AFe}(\text{SO}_4)_2$, and crystallization of A_2SO_4 takes

place ($\text{A} = \text{K, Na}$). The removal of SO_3 is, however, not complete. Part of it (2—4%, Tab. 1, 2), trapped in the collapsed sulphate framework is liberated after the main reaction (small shoulders on the main peaks between $780\text{--}930^\circ\text{C}$, Fig. 1), and a small amount still remains up to 1000°C in the decomposition products.

The sulphate dissociation peak (Fig. 1) is clearly split. Similar phenomenon noticed in other substances is attributed (e.g. Mackenzie 1957) to the presence of several grain classes, or to the formation of transitional phases (Stoch, Żabiński 1964). In the authors opinion this could hardly be the case in the investigated jarosites. More probably the splitting is due to exothermic crystallization of alkali sulphates A_2SO_4 , with molar ratio $\text{A}_2\text{O}:\text{SO}_3 = 1:1$ ($\text{A} = \text{K, Na}$). Their formation from jarosite dissociation product $\text{AFe}(\text{SO}_4)_2$ ($\text{A}_2\text{O}:\text{SO}_3 = 1:4$) requires complete destruction and reorganization of its structure:



The heat of formation of K_2SO_4 is higher than that of Na_2SO_4 , therefore the corresponding exothermic peak is more intense in K, H_3O -jarosites (Fig. 1). There is another phenomenon supporting the proposed explanation of the discussed splitting: The amount of SO_3 liberated before the exothermic deflection (splitting) is inversely proportional to the amount of A_2O present in the particular sample (Tab. 1, 2). This is not so easy to note in the case of Na, H_3O -jarosites where the exothermic reaction maximum is difficult to determine (Tab. 2).

The melting of A_2SO_4 may be observed only on Na, H_3O -jarosite curves (endothermic peak at about 880°C , Fig. 1). K_2SO_4 melts above 1000° , at 1069°C .

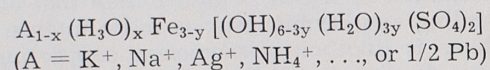
The slight deflection on sulphates dissociation peak (at 645°C) of pure hydronium jarosite (Fig. 1) is most probably due to successive decomposition of $\text{Fe}_2\text{O}(\text{SO}_4)_2$ and $\text{Fe}(\text{SO}_4)_3$. This deflection is sometimes seen around $700\text{--}760^\circ\text{C}$ on A, H_3O -jarosite curves (e.g. S-24, S-29).

Synthetic K, Na, H_3O -jarosites have been investigated thermogravimetrically by Brophy and Sheridan (1965) using a static point method of heating. The samples were held for 24 hours at each temperature point. The resulting TG curve given in their paper shows three water expulsion reactions at $80\text{--}150^\circ$, $240\text{--}280^\circ$, and $365\text{--}470^\circ\text{C}$, which they attribute to the loss of adsorbed water, hydronium and hydroxyls respectively. The reaction temperatures recorded agree well with initial temperatures found by the present author for corresponding reactions in high hydronium minerals (around $150\text{--}190^\circ$, $210\text{--}250^\circ$, and $320\text{--}370^\circ\text{C}$, respectively). This is not the case with temperatures of reaction maxima. It must be remembered, however, that only the initial temperature (if measured in the same manner) is the characteristic one for any given reaction. While the temperature of reaction maximum is a complex function of e.g. graining, weight, and shape of the sample as well as of heating rate and type of sample holder (Stoch 1967). Thus the present author do not agree with Brophy and Sheridan's assignment of the first two reactions. It is more likely that the first reaction recorded by these authors is due to the loss of „additional water” and the

second one to deprotonation ($\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$). It is highly improbable that adsorbed water should be held up to 150° in well crystallized materials like jarosites.

CONCLUSIONS

The results of thermal investigations have shown that three kinds of isoelectronic hydrogen-oxygen complexes are present in the structure of synthetic jarosites with deficient iron content. The H_3O^+ ions, occupying the monovalent cation positions, the H_2O molecules, and OH^- anions, the latter forming coordination polyhedra around Fe^{3+} ions (or filling iron vacancies). Chemical analyses of some natural jarosites (Kubisz 1964) show that similar iron deficient minerals do exist in nature. The analysis of data supplied by thermal investigations supports the chemical constitution of jarosites put forward by the author (Kubisz 1970):



Expulsion of structural water molecules (dehydration) takes place between about 190—340°C. The peak temperature of this reaction being the higher the greater the water content, and beside of this higher in $\text{Na}_2\text{H}_3\text{O}_-$, than in $\text{K}_2\text{H}_3\text{O}_-$ jarosites (Tab. 3). Deprotonation, consisting of proton transfer from H_3O^+ to hydroxyl or sulphate oxygens and subsequent removal of resultant H_2O molecules, occurs between 240—440°C. The peak temperature of this process is lowest in high hydronium jarosites (320—340°C) intermediate in $\text{Na}_2\text{H}_3\text{O}_-$ ($\sim 390^\circ\text{C}$) and highest in $\text{K}_2\text{H}_3\text{O}_-$ jarosites ($\sim 420^\circ\text{C}$) with low hydronium content.

Dehydroxylation takes place in two steps. The destruction of iron-hydroxyl octahedra in the interval of 300—510°C, and the removal of „trapped” water between 510—560°C. Maximum of the main reaction shifts by some ten degrees to lower temperatures from $\text{K}_2\text{H}_3\text{O}_-$ and $\text{Na}_2\text{H}_3\text{O}_-$, to H_3O_- jarosites with increasing hydronium content (Tab. 3).

The process of SO_3 expulsion from the dehydrated jarosite between 560—930°C (highest in $\text{K}_2\text{H}_3\text{O}_-$ members, Tab. 3) is interrupted by exothermic reaction of alkali sulphate (A_2SO_4) crystallization. Maximum of SO_3 loss reaction lies at about the same temperature in H_3O_- and $\text{Na}_2\text{H}_3\text{O}_-$ jarosites. It is however, by some ten degrees higher in $\text{K}_2\text{H}_3\text{O}_-$ members.

Evidently K-O bonds are stronger than Na-O bonds in $\text{AFe}(\text{SO}_4)_2$ which must be destroyed first, prior to SO_3 removal.

It was established that deprotonation, dehydroxylation as well as SO_3 removal require much higher temperatures when K^+ ions are present in jarosite structure. On the other hand hydronium ions which are expelled first in the course of thermal transformations, thus emptying monovalent cation positions of the framework, lower all reaction temperatures.

REFERENCES

- BROPHY G. P., SHERIDAN M. F., 1965: Sulfate studies IV: The jarosite-natrojarosite-hydronium jarosite solid solution series. *Am. Miner.* 50, 1595—1607.
- [CIVIETKOV A. J., VALIASHIHINA E. P.] ЦВЕТКОВ А. И., ВАЛЯШИХИНА Е. П., 1955: Материалы по термическому исследованию минералов. Издательство Акад. Наук СССР. Москва.
- FREUND F., 1965: Zum Entwässerungsmechanismus von Hydroxiden. *Ber. Dtsch. Ceram. Ges.* 42, 23—25.
- JOHANSSON G., 1963: On the crystal structure of a basic gallium sulfate related to alunite. *Arkiv Kemi* 20, 343—352.
- KUBISZ J., 1961: Synteza jarosytów alkalicznych i hydroniowych. *Spraw. z Posiedz. Kom. Oddz. PAN w Krakowie*, 448—449.
- KUBISZ J., 1964: Studium minerałów grupy alunitu-jarosytu. *Pr. geol. Kom. Nauk Geol. PAN Oddz. w Krakowie* 22.
- KUBISZ J., 1970: Studies on synthetic alkali-hydronium jarosites: Synthesis of (potassium) jarosite and natrojarosite. *Mineralogia Polonica* No 1.
- KULP J. L., ADLER H. H., 1950: Thermal study of jarosite. *Amer. J. Sci.* 248, 475.
- MACKENZIE R. C., 1957: The differential thermal investigation of clays. London.
- STOCH L., ŻABIŃSKI W., 1964: Some aspects of the thermal dissociation of minerals as studied by the DTA method. *Bull. Acad. Pol. Sc., Ser. Sc. chim. géol. géogr.* 12, 87—91.
- STOCH L., 1967: Fizyczno-chemiczne podstawy interpretacji wyników termicznej analizy różnicowej. *Pr. miner. Kom. Nauk Miner. PAN Oddz. w Krakowie* 7.

Jan KUBISZ

STUDIUM SYNTETYCZNYCH JAROSYTÓW ALKALICZNO-HYDRONIOWYCH II: BADANIA TERMICZNE

Streszczenie

Badania termiczne serii syntetycznych potasowo-hydroniowych i sodowo-hydroniowych jarosytów, wykonane na derywatografie, potwierdziły zaproponowaną (Kubisz 1970) konstytucję chemiczną minerałów tej grupy. Na krzywych DTA (fig. 1) zaznacza się sześć (lub pięć) endo- i trzy efekty egzotermiczne. Ich temperatury zależą od rodzaju jedno-wartościowych kationów (tab. 3) występujących w danym jarosycie. Pierwsze trzy efekty endotermiczne przyporządkowano odpowiednio: dehydratacji — usunięciu drobin „dodatkowej wody” (190—340°C), deprotonacji — usunięciu jonów H_3O^+ (240—440°C) oraz dehydroksylacji — usunięciu grup OH^- (300—510°C). Czwarty (około 540°C) odpowiada zapewne wydzieleniu grup OH^- lub drobin H_2O uwieczonych pułapkowo w zapadniętej wieżbie krystalicznej produktów rozpadu, piąty (560—930°C) związany jest z wydzieleniem SO_3 , a szósty (880°C) — zaznaczający się tylko na krzywych jarosytów zawierających sód — z topieniem Na_2SO_4 , który tworzy się w czasie przemian termicznych. Ubytki ciężaru próbek podano w tabelach 1 i 2. Efekty egzotermiczne przypisano odpowiednio: pierwszy, około 510°, krystalizacji $\alpha\text{-Fe}_2\text{O}_3$, drugi, około 580°, wydzieleniu energii z „klatek poanionowych” (Freund 1965), a trzeci, około 700—780°C, rozszczepiający przegięcie związane z dysocjacją siarczanów żelaza, krystalizacji siarczanów alkaliów.

Fig. 1. Przykłady krzywych derywatograficznych syntetycznych jarosytów alkaliczno-hydroniowych
 DTA — krzywa termicznej analizy różnicowej, DTG — krzywa różnicowa termogravimetryczna, TG — krzywa termogravimetryczna, S-2C — jarosyt hydroniowy, S-25, S-29 — K_2H_3O -jarosyt, S-10, S-28 — Na_2H_3O -jarosyt

Ян КУБИШ

ИЗУЧЕНИЕ СИНТЕТИЧЕСКИХ ЩЕЛОЧНО-ГИДРОНИЕВЫХ ЯРОЗИТОВ: II. ТЕРМИЧЕСКИЕ ИССЛЕДОВАНИЯ

Резюме

Термические исследования серии синтетических калий-гидрониевых и натрий-гидрониевых ярозитов, произведенные на дериватографе, подтвердили ранее высказанное предположение (Кубиш 1970) о химическом составе минералов этой группы. На кривых ДТА (фиг. 1) намечается шесть (или пять) эндотермических и три экзотермических эффекта. Их температуры зависят от типа одновалентных катионов (табл. 3), находящихся в данном ярозите. Три первых эндотермических эффекта связываются соответственно: с дегидратацией — удалением молекул „дополнительной воды” ($190-340^{\circ}C$), депротонацией — удалением ионов H_3O^+ ($240-440^{\circ}C$) и дегидроксилацией — удалением групп OH^- ($300-510^{\circ}C$). Четвертый эндотермический эффект (около $540^{\circ}C$) соответствует, вероятности, выделению групп OH^- или молекул H_2O , заключенных в ловушках кристаллической решетки продуктов распада, пятый ($560-930^{\circ}C$) связан с выделением SO_3 , а шестой, отмечающийся лишь на кривых ярозитов, содержащих натрий, с плавлением Na_2SO_4 , который возникает в процессе термических изменений. Потери веса образцов приведены в таблицах 1 и 2. Экзотермические эффекты связываются соответственно: первый (около $510^{\circ}C$) с кристаллизацией $\alpha-Fe_2O_3$, второй (около $580^{\circ}C$) с выделением энергии из „последаионных ячеек” (Фройнд 1965) и, наконец, третий (около $700-780^{\circ}C$), расщепляющий перегиб, связанный с диссоциацией сульфатов железа, с кристаллизацией щелочных сульфатов.

ОБЪЯСНЕНИЯ К ФИГУРЕ

Фиг. 1. Примеры дериватографических кривых синтетических щелочно-гидрониевых ярозитов

DTA — кривая термического дифференциального анализа, DTG — дифференциальная термогравиметрическая кривая, TG — термогравиметрическая кривая, S-2C — гидрониевый ярозит, S-25, S-29 — K_2H_3O -ярозит, S-10, S-28 — Na_2H_3O -ярозит