Contributions to the formation of oxidic iron(III) compounds in the presence of foreign cations

Part 5 *Hydrolysis of mixed solutions of iron (III) and gallium (III) sulphates*

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The homogeneous precipitation of solids from mixed solutions of iron(III)–gallium(III) sulphates, which gives a complete series of mixed crystals of basic sulphates, was investigated. These alunite–jarosite type compounds show a non-stoichiometric composition. The lattice constant, *a*, of the hexagonal unit cell decreases with increasing substitution of iron by gallium, whereas *c* increases. The volume of the unit cell decreases with increasing proportion of gallium in the solid. The formation of this structure and of mixed crystals are discussed on the basis of appropriate experiments.

1. Introduction

Substitution of cations or anions in solids is a widely used method for modifying their properties in a previously determined way. These substitutions can be controlled most efficiently if the solids are prepared by crystallization from solutions. The situation is relatively uncomplicated if such ions already existing in the solution are inserted into the lattice during crystallization, which may be accompanied by a loss of the hydration shell. In these cases, the extent of substitution, or formation of mixed crystals, is essentially determined by the ionic radii, the concentrations and solubilities. However, little is known about the substitution or formation of mixed crystals in the crystallization of oxidic solids (compounds containing hydroxide or oxide ions within the lattice). In addition to the above criteria, hydrolysis equilibria before and during nucleation, and growth of nuclei also play important roles.

Previous investigations showed that a large amount of gallium(III) can be inserted into the β-FeOOH lattice [1]. This is due to similar ionic radii, similar acidities, and rate constants of water exchange in the hexaquo ions, and similar complexing behaviour. Thus, iron(III) and gallium(III) should be well suited for being used in studying the formation of mixed crystals in various oxidic compounds. The present work reports results of the hydrolysis of mixed $(Fe, Ga)_2(SO_4)_3$ solutions. The reaction conditions were chosen in such a way as to produce basic sulphates of the alunite–jarosite type: $NH_4M_3(OH)_6(SO_4)_2$.

The corresponding pure iron(III) and gallium(III) compounds are well known [2, 3]. Polycations are not formed in solutions of iron(III) sulphate [4]. Hence, the crystallization of basic sulphates should be preceded only by simple hydrolysis equilibria.

Apart from the investigations of the formation of mixed crystals, some experiments have been performed to study the mechanism of the precipitation of ammonio jarosite.

2. Preparation and characterization

Gallium sulphate was prepared from 99.99% gallium metal (VEB Spurenmetalle Freiberg/Sa.) after dissolution in perchloric acid and crystallization of GaOOH [5]. An excess of concentrated H_2SO_4 was then added to the gallium oxide hydroxide with heating, but not complete dissolution was achieved. Therefore, the liquid was separated from the precipitate and evaporated. This gave a viscous solution, from which $Ga_2(SO_4)_3 \cdot 18H_2O$ crystallized. The compound was then filtered, and the adhering sulphuric acid was removed by washing with ethanol and ethanol/ether [6]. All other chemicals were of analytical reagent grade.

The mixtures were prepared from stock solutions, each of which was monomolar with respect to the cations. Hydrolysis was carried out in 0.3 M solutions at 90° C. Homogeneous precipitation was achieved by adding urea (molar ratio urea/M^{3+} = 5). The progress of the reaction was monitored potentiometrically. A break in the pH value curve indicated that the precipitation of basic sulphate had been terminated. The precipitate obtained was filtered, washed with water five times and dried in air.

The samples having the idealized composition $NH_4M_3(OH)_6(SO_4)_2$ where checked for their contents of NH_4, Fe^{3+}, Ga^{3+} and SO_4^{2-}, using standard methods. The hydroxide content results from the condition of electric neutrality. In contrast to the ideal formula, all compounds additionally contain water, whose amount is given by the difference to 100%. The solids were characterized by means of X-ray diffraction (XRD; diffractometer from VEB Freiberger

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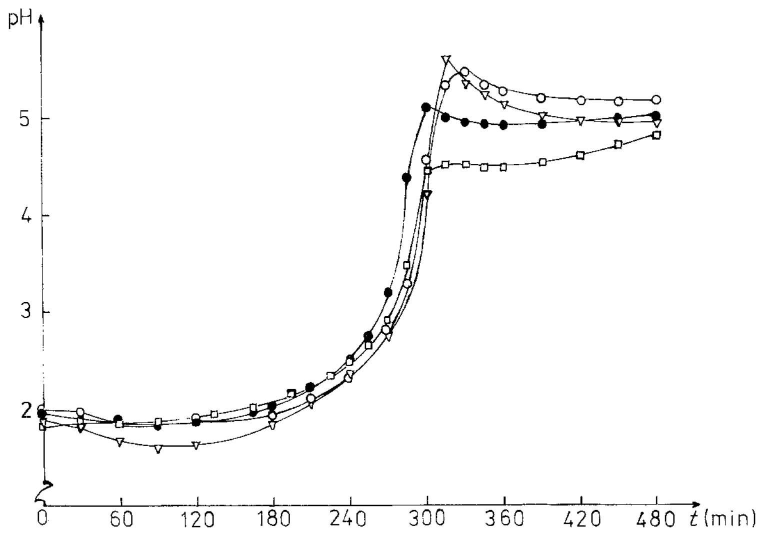


Figure 1 Change of pH with time for selected solutions. (□) 0, (●) 30, (○) 70, (▽) 100 mol % Ga^{3+}.

Präzisionsmechanik), and by TEM measurements (BS 500 Tesla, CSSR). In some experiments, the sulphate content and the degree of neutralization, r (molar ratio OH^-/Fe^{3+}) of pure iron(III) salt solutions were varied by mixing sulphate and nitrate solutions and/or partially precipitating the sulphate by a barium hydroxide solution.

3. Results and discussion

The hydrolysis of mixed $(Fe_{1-x}Ga_x)_2(SO_4)_3$ solutions was studied step by step in the range $0 \leqslant x \leqslant 1$ with $\Delta x = 0.1$. At 25° C, the pH value of the initial solutions increases linearly with increasing gallium content. This is due to the fact that gallium(III) has a stronger tendency to form sulphate complexes [7]. As a consequence of their smaller charge, the sulphato complexes exhibit a lower tendency to hydrolyse than do the hexaquo ions. Fig. 1 shows the changes of the pH during the reaction. The end of the precipitation is indicated by a steep increase in the pH. The time to this break is 290 ± 5 min. For all products isolated a short time after the pH change, the XRD patterns correspond to alunite/jarosite type structures. When the reaction is continued, the pH first shows a small decrease, indicating decomposition of the precipitate. After 15 h, the precipitate also contains α-M_2O_3, or α-MOOH, in addition to the basic sulphate

$$NH_4M_3(OH)_6(SO_4)_2 \rightarrow 3/2M_2O_3 + NH_4^+ + 2SO_4^{2-} + 3/2H_2O + 3H^+,$$

$$NH_4M_3(OH)_6(SO_4)_2 \rightarrow 3\ MOOH + NH_4^+ + 2SO_4^{2-} + 3H^+.$$

The TEM photographs of the basic sulphates show irregularly shaped crystals.

The ideal stoichiometry of the basic salts is $NH_4M_3(OH)_6(SO_4)_2$. It is known from the literature, however, that in general the actual composition does not correspond to this ideal pattern. Typical phenomena include the substitution of monovalent cations by hydronium ions, a lower content of trivalent cations, and the insertion of additional water [8–10]. For this reason, the solids were investigated with respect to their content of NH_4^+, Fe^{3+}, Ga^{3+} and SO_4^{2-}. The proportions of OH^- and H_2O were calculated from the condition of electric neutrality and the difference to 100%. The results obtained are listed in Table I corresponding to the formula $(NH_4)_mFe_nGa_0(OH)_p(SO_4)_q \cdot rH_2O$. The calculations were normalized to $q = 2$ because a great excess of sulphate ions was present in the original solutions. There was no deficit

TABLE I Results of analyses for $(NH_4)_mFe_nGa_o(OH)_p(SO_4)_q \cdot rH_2O$. (The numbers of the samples correspond to the molar proportion of gallium(III) in the initial solution, e.g. 1 = 10 mol %, 3 = 30 mol %, etc.)

No.	m (NH$_4$)	n (Fe)	o (Ga)	$n + o$	$\frac{o}{n+o}$	p (OH)	q (SO$_4$)	r(H$_2$O)
0	1.02	2.72	–	2.72	–	5.18	2	2.72
1	1.00	2.49	0.24	2.73	0.088	5.19	2	2.30
2	1.00	2.19	0.53	2.72	0.195	5.16	2	2.15
3	0.99	1.93	0.78	2.71	0.288	5.13	2	2.19
4	1.00	1.67	1.04	2.71	0.384	5.13	2	2.05
5	1.00	1.38	1.35	2.73	0.495	5.19	2	1.97
6	1.01	1.09	1.60	2.69	0.595	5.08	2	1.65
7	1.01	0.81	1.87	2.68	0.698	5.05	2	1.38
8	1.03	0.55	2.19	2.74	0.799	5.25	2	1.67
9	1.03	0.27	2.49	2.76	0.902	5.31	2	1.21
10	1.05	–	2.93	2.93	–	5.84	2	1.45
10	1	–	2.78	2.78	–	5.54	1.90	1.44

TABLE II Lattice parameters and volumes of the hexagonal unit cell ($a_0 \pm 0.3$ pm, $c_0 \pm 0.6$ pm)

No.	a_0 (pm)	c_0 (pm)	V (10^{-8} pm^3)
0	732.7	1746.5	8.1199
2	729.2	1753.7	8.0757
4	725.8	1757.8	8.0193
5	724.1	1757.9	7.9822
6	722.9	1762.9	7.9784
7	721.6	1763.5	7.9524
8	720.4	1764.0	7.9282
10	717.8	1764.9	7.8751

of ammonium ions, although these were not present in the solution until urea hydrolysis occurred, and at the highest gallium contents they even appeared to be present in excess. In the most solids, only about 90% of the potential sites of trivalent cations were occupied. At the highest contents of gallium the number of vacant sites decreased. Of course, a lower content of trivalent cations also resulted in a lower content of hydroxide ions. Sites in the lattice which, as a consequence, were not occupied might be occupied by water molecules. Although the content of additional water decreased with increasing gallium content, the amount of water present was always greater than would be necessary for filling these gaps.

Structurally, the alunite/jarosite type compounds are composed of corrugated layers with $M(O, OH)_6$ octahedrons and SO_4 tetrahedrons. The monovalent cations are located between these layers. This gives rise to the fundamental question of whether monovalent cations may be present in excess within the lattice. If this is assumed to be the case, then a part of the excessive water might also be present between the layers in the form of H_3O^+ and within the layers in the form of OH^-. The ideal formula of this type of structure would then be completely uncertain.

However, there is still another possible explanation (Table I, bottom row). In this case, all sites of the monovalent cations were assumed to be occupied. Calculations then give a lower content of sulphate, and the number of occupied cationic sites then closely approaches the average of 90%, which supports this explanation. In the literature, we also find analyses which, when normalized to the sulphate, yield an excess of monovalent cations (e.g. rubidium salt in [3]). This might be explained in an analogous way. Compounds of the alunite/jarosite type crystallize rhombohedrally [2, 3]. Insertion of the smaller gallium ion (62 pm as compared with 64.5 pm for iron(III) in an octahedral environment [11]) should have an effect on the lattice parameters. This would also prove the formation of mixed crystals. For some samples, the results for a hexagonal arrangement of the unit cell are summarized in Table II. As was expected, a_0 decreases with increasing proportion of gallium, whereas c_0 first rises more strongly, which is then followed by a smaller increase. The volume of the unit cells decreases linearly with increasing gallium content (Fig. 2). This confirms the formation of a complete series of mixed crystals.

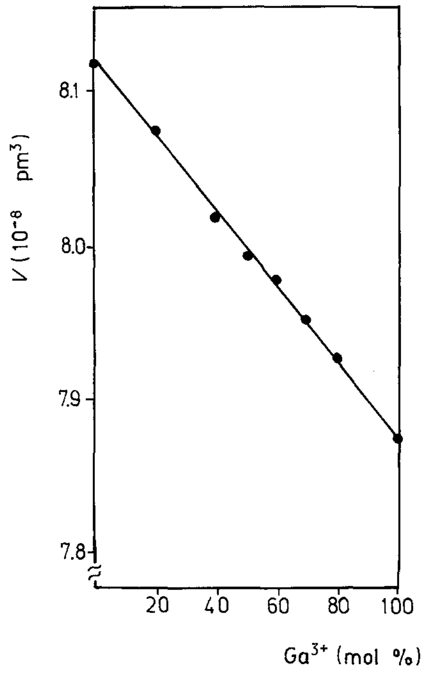
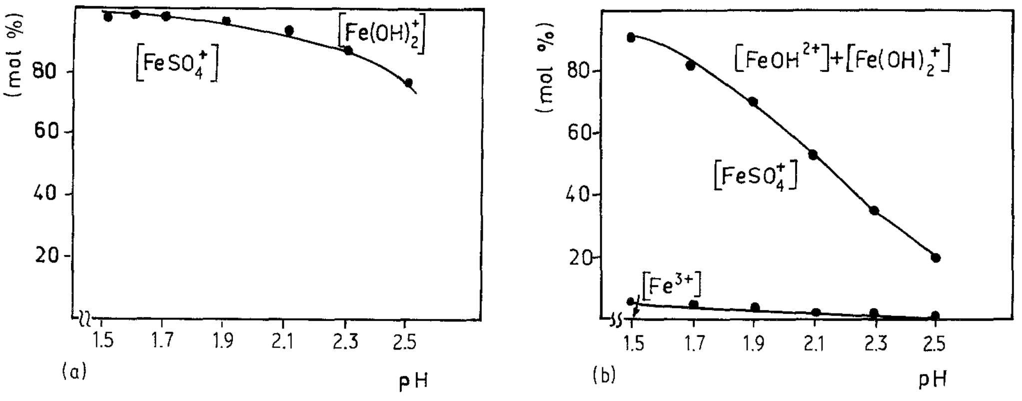


Figure 2 Volumes of unit cells plotted against gallium content in the solid.

It is known from the literature that MO_6 octahedrons, e.g. in oxides with the structure of corund, are more or less distorted [12, 13]. This should apply to a still greater extent to $M(O, OH)_6$ groups. Different distortions of the iron(III) and gallium(III) octahedra will probably also lead to different kinds of corrugation of the tetrahedron–octahedron–tetrahedron layers. This results in a decrease of a_0 and an increase of c_0. Hence the behaviour of the two lattice constants is based on two effects. The decrease in a_0 is due to both the insertion of the gallium ions and increased corrugation of the layers. By contrast, c_0 increases with increasing corrugation. Substitution of the trivalent cations has little effect on c_0 [14]. Thus, the volume of the unit cell during the formation of mixed crystals is only affected by the insertion of the gallium ions. The influence of the inserted water on the lattice parameters cannot be calculated unequivocally because the water proportion strongly intercorrelates with the gallium proportion in the samples available. The additional water probably occupies positions in the MO_6 octahedra (for the purpose of charge compensation) and between the layers.

Dehydration experiments were carried out on sample 2. According to the above concept, this sample contains 0.84 H_2O in octahedra and 1.31 H_2O between the layers (Table I). Removal of up to 0.86 H_2O does not lead to an appreciable change of a_0, whereas c_0 is slightly reduced. This is in good agreement with the expected behaviour of water between the layers. Additional removal of water results in a very small decrease of a_0, whereas c_0 rises again, reaching values which are clearly above those of the initial sample. The volume of the unit cell also increases. This behaviour is somewhat difficult to understand without additional investigation. It does demonstrate, however, the effect of the water content, particularly on c_0, in samples with an alunite/jarosite structure.

Various concepts exist concerning the formation of



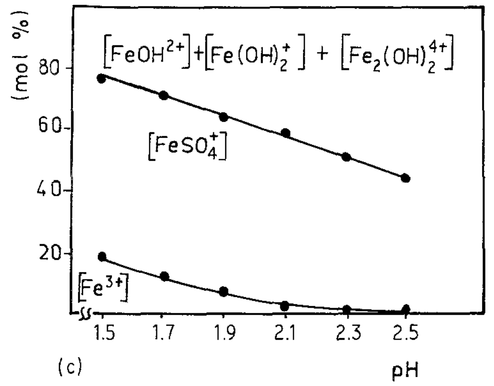


Figure 3 Dependence of molar proportions of various particles in iron(III) sulphate solutions on pH at 80° C. Only particles whose concentration is more than 1 mol % have been taken into consideration. Conversion of constants from [4] to the conditions in Equation 3b was carried out using the Davies equation

$[Fe^{3+}] = 0.3\,mol\,l^{-1}, [SO_4^{2-}] = 0.45\,mol\,l^{-1}, I = 2.67\,mol\,l^{-1}$ (a)

$[Fe^{3+}] = 0.01\,mol\,l^{-1}, [SO_4^{2-}] = 0.015\,mol\,l^{-1}, I = 0.1\,mol\,l^{-1}$ (b)

$[Fe^{3+}] = 0.3\,mol\,l^{-1}, [SO_4^{2-}] = 0.18\,mol\,l^{-1}, I = 2.67\,mol\,l^{-1}$ (c)

compounds with an alunite/jarosite structure. From investigations of the formation of alunite/jarosite mixed crystals, it can be concluded that the hydroxo complexes play a dominant role [15, 16].

Sapieszko *et al.* [4] conclude from equilibrium measurements carried out on iron(III) sulphate solutions that monosulphato and monohydroxo complexes jointly cause oxonium jarosite to be formed. This is in contrast with an extremely large excess of monosulphato complexes in the pH range 1.5 to 2, in which the crystallization of the basic sulphates predominantly proceeds under the reaction conditions chosen (cf. Fig. 1). Fig. 3a presents an estimate of the spectrum of particles for a 0.15 M solution of iron(III) sulphate at 80° C and $I = 2.67\,mol\,l^{-1}$ with the constants given in [4]. The proportion of monosulphato complexes exceeds 95 mol %. Under the given reaction conditions, this estimate can be considered to be too low, because the higher reaction temperature and smaller ionic strength should favour the formation of complexes. Moreover, the relative content of sulphate increases during the reaction, as the basic salt naturally contains less sulphate than does the initial salt. This should compensate for the "dilution" resulting from the precipitation of metal ions. Estimate calculations reveal that the proportion of hydroxo complexes distinctly increases when the overall concentration is reduced (Fig. 3b) or the sulphate content is lowered (Fig. 3c). If the hydroxo complexes have a decisive influence on the reaction, this should facilitate the formation of the basic sulphate. Experiments showed, however, that exactly the opposite is true.

When the initial concentration of the iron(III) sulphate solution is decreased to $0.005\,mol\,l^{-1}$, α-FeOOH but no basic sulphate is formed. Table III presents the results obtained from solutions with decreased sulphate concentrations. Ammonium jarosite is still present as a crystalline product. With decreasing sulphate content, however, the reaction time increases by almost 50% (Fig. 4). This means that much more base is consumed than would correspond to the formation of the basic salt only. Increased degree of neutralization r to 1 or 2, along with the decrease in the sulphate concentration, leads to the formation of α-FeOOH at the smallest sulphate concentration.

In the experiment with a sulphate concentration of $0.18\,mol\,l^{-1}$, and $r = 2$, the ratio of iron(III): hydroxide : sulphate in the initial solution is 3 : 6 : 1.8. This is close to the stoichiometric ratio of 3 : 6 : 2 and also closely approaches the ratio of 3 : 5.7 : 2.2 actually obtained for sample 0. However, this is the experiment in which the highest amount of goethite is found in the solid.

All these experiments suggest that the monosulphato complexes play a dominant role in the crystallization of basic sulphates of the alunite/jarosite type under the reaction conditions given. This is not meant to exclude the possibility of hydroxo complexes being attached to the growing nucleus. However, a part of the hydroxide groups certainly results from coordinated water molecules by cleavage of protons.

TABLE III Hydrolysis products of 0.3 M solutions of iron(III) salts for varying sulphate concentrations and increasing degree of neutralization r (J and G denote ammonium jarosite and goethite, respectively). Reaction times t are also given for $r = 0$

	$[SO_4^{2-}]_o$			
	0.45	0.36	0.27	0.18
$r = 0$	J	J	J	J
t (min)	280	295	330	410
$r = 1$	–	J	J	J ≫ G
$r = 2$	–	J	J	J > G

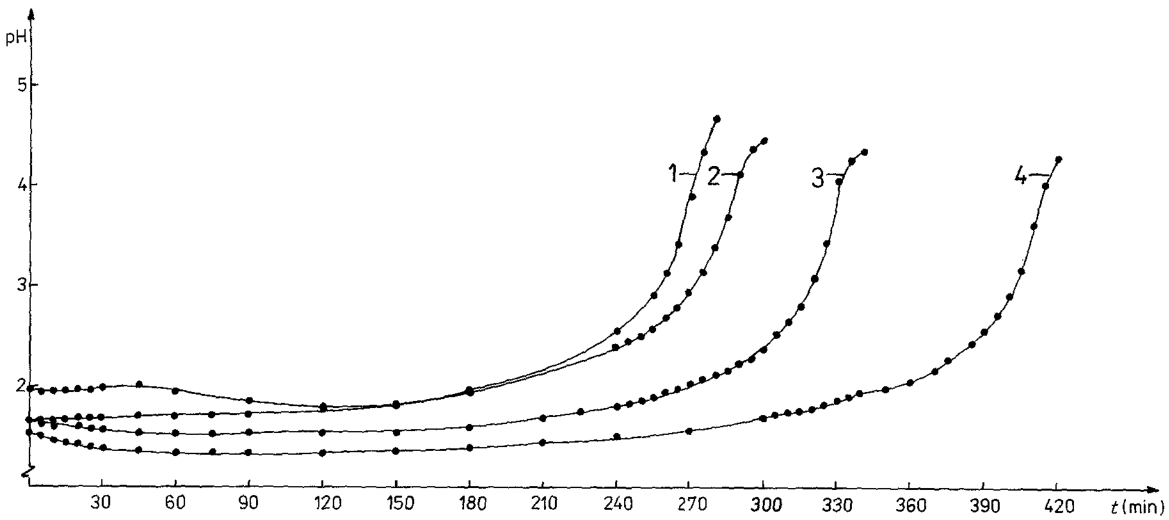


Figure 4 Influence of the sulphate content on the hydrolysis process of 0.3 M solutions of iron(III): (1) 0.45, (2) 0.36, (3) 0.27, (4) 0.18 mol l^{-1} sulphate.

Alunite, $K_3Al(OH)_6(SO_4)_2$ and jarosite $K_3Fe(OH)_6(SO_4)_2$ also form a complete series of mixed crystals. When the salts of the trivalent metals in the corresponding mixed solutions are hydrolysed, iron(III) is enriched in the solid. This fact is attributed to the lower acidity of aluminium(III), and is assumed to demonstrate the role of the hydroxo complexes during crystallization [16]. It cannot, however, disprove the results concerning the role of the sulphate ions. On the one hand, the different acidity would undoubtedly also affect the cleavage of protons involved in the crystallization itself. On the other hand, it should also be taken into account that formation and dissociation of complexes in the case of aluminium(III) proceeds much more slowly than in the case of iron(III). Thus, aluminium(III) is kinetically disadvantaged in the formation of mixed crystals.

Iron(III) and gallium(III) also form a complete series of mixed crystals of the elpasolite-type $K_2Na[(Fe, Ga)F_6]$ [18]. Here the structural units of the lattice are already present in the solution. The formation of a complete series of mixed crystals is due to similar ionic radii, similar complexing behaviour of the two trivalent cations towards fluoride, and similar solubilities of the solids. Without doubt, the complete series of mixed crystals of basic sulphates is also due to a crystallization reaction inserting simple particles into the lattice. Difficulties in the formation of mixed crystals will arise, when the actual crystallization is preceded by hydrolysis and condensation steps [19]. Because gallium(III) and iron(III) are very similar to each other with respect to the ionic radius, the rate of water exchange, the acidity, and the ability to form complexes, complete series of mixed crystals may be expected, whenever simply structured ions present in the solution can be inserted into the lattice without major changes. Cleavage of water from the hydration shell and deprotonation will not obstruct the formation of mixed crystals.

As mixed crystals of any composition can be obtained by means of hydrolysis from mixed solutions of iron(III) sulphate and gallium(III) sulphate, they may serve as precursors for the preparation of binary iron(III)-gallium(III) oxides.

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