919. *Observations on Ammonium Ferric Disulphate Dodecahydrate (Ammonium Ferric Alum) and Some of its Derivatives.*

By Henry Bassett.

Ammonium ferric alum effloresces to yield $NH_4Fe(SO_4)_2,2H_2O$ or $NH_4Fe(SO_4)_2$ under dry tropical conditions. The preparation of a new basic double salt is described; its relation to the ammonium and potassium basic ferric sulphates first prepared in 1827 is discussed.

Some evidence is given for the replacement of ammonium by hydroxonium and of $(SO_4)^{2-}$ by $[(OH)_2(H_2O)_2]^{2-}$ in such salts, and even in the alum. The various colours of ferric alum are explained in a new way.

Ammonium ferric alum is metastable under the dry tropical conditions of central Tanganyika and gradually loses water to yield a white powder consisting of $NH_4Fe(SO_4)_2$ in the form of plates belonging to the hexagonal system. These are relatively large (diameter 0·1—0·2 mm.) because fluctuations in atmospheric humidity permit the occasional formation of films of adsorbed moisture on the primary efflorescence in which crystal growth occurs. The average shade day temperature at Dodoma is near 22° with a maximum of 27·8—33·2° and a night minimum of 10·2—18° according to the time of year. The relative humidity is high in the early morning but becomes very low in the afternoon. At 8·30 a.m. it ranges between 88% in February and 64% in November while at 2·30 p.m. the range is between 57% in February and 27% in November.[1]

Unchanged alum was removed from the product of efflorescence either by leaching with cold water, or by continued exposure to constant weight. The final product then contained 2—2½% of water. A few of the larger purplish fragments were picked out from the effloresced material and analysed to show that the second solid phase was unaltered alum. Anhydrous $NH_4Fe(SO_4)_2$, crystallising in hexagonal plates, was prepared by Lachaud and Lepièrre [2] by prolonged heating of ferrous sulphate in fused ammonium sulphate. Weinland and Ensgraber [3] obtained it by heating ammonium ferric alum with sulphuric acid for some hours. Vegard and Maurstad [4] showed that the *X*-ray diagram corresponded with a hexagonal space lattice having $a = 4{\cdot}825$ Å and $c = 8{\cdot}310$ Å.

Wiedemann [5] says that ammonium ferric alum melts at about 34° to a brown liquid which does not solidify completely on cooling. Erdmann and Köthner [6] give the m. p. as 43—44°, Locke [7] as 40°, Houda and Ishiwara [8] as 37°, and Ephraim and Wagner [9] state that the salt becomes brown at about 33° and is completely melted at 41°.

It seems clear from the careful observations of Welo [10] that ammonium ferric alum has no congruent m. p. but that there is an incongruent m. p. at approximately 37° at which transition occurs from the solid alum to a new solid phase and saturated solution. This indicates that the alum is relatively unstable towards either a lower hydrate or the anhydrous salt. Welo did not determine the nature of the new solid phase which is formed at about 37°.

Crystals of $NH_4Fe(SO_4)_2$ when kept wet at about 25° regenerate the alum after many days. If attempts are made to hasten the process by heating with water, insoluble yellow basic salts are formed. Their formation could explain Lupton's [11] statement that the

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[1] "Summary of Meteorological Observations for 1949," East African Meteorological Department.
[2] Lachaud and Lepièrre, *Bull. Soc. chim.*, 1892, **7**, 356.
[3] Weinland and Ensgraber, *Z. anorg. Chem.*, 1913, **84**, 340.
[4] Vegard and Maurstad, *Z. Kryst.*, 1929, **69**, 519.
[5] Wiedemann, *Wied. Ann.*, 1882, **17**, 569.
[6] Erdmann and Köthner, *Annalen*, 1897, **294**, 2.
[7] Locke, *Amer. Chem. J.*, 1901, **26**, 166.
[8] Houda and Ishiwara, *Sci. Reports Tôhoku Univ.* 1915, **4**, 231.
[9] Ephraim and Wagner, *Ber.*, 1919, **50**, 1105.
[10] Welo, *Nature*, 1929, **124**, 575.
[11] Lupton, *J.*, 1875, **28**, 201.

alum lost 23 out of 24 molecules water at 150° and all at 230°. Somewhat similar statements are made by Adolphs[12] and Masson.[13] The alum would melt partially at about 37° and basic salts would separate from the solution so formed on further heating; a fairly high temperature is required to drive off all water from these basic salts.

The dark solution and the yellow basic salt obtained on warming the anhydrous salt with water were separated by decantation. The yellow solid was dissolved by addition of sulphuric acid. The combined filtered solutions after standing at room temperature for some months yielded pale violet tetragonal bipyramids of $NH_4Fe(SO_4)_2,2H_2O$ *via* the white anhydrous $NH_4Fe(SO_4)$. The preparation and analysis of this compound have been described briefly by Taylor and Bassett.[14] The yellowish-brown solution produced by water and excess of $NH_4Fe(SO_4)_2$ was inoculated with the dihydrate. After a fortnight the original hexagonal plates of $NH_4Fe(SO_4)_2$ had all been converted into aggregates of minute needles of the dihydrate.

The conversion of the original alum into the dihydrate could also be accomplished by treating the solid with a little of the dihydrate. Observations made during these experiments confirmed the opinion that the process of dehydration was complex and involved crystal growth in surface films of solution which were sometimes clearly present. It seems clear from these results that both in absence of any excess of sulphuric acid and also with much of it present the stable sequence of changes is

$$NH_4Fe(SO_4)_2,12HO_2 \rightleftharpoons NH_4Fe(SO_4)_2,2H_2O \rightleftharpoons NH_4Fe(SO_4)_2$$

in the temperature range 25° to 30° though the metastable change

$$NH_4Fe(SO_4)_2,12H_2O \rightleftharpoons NH_4Fe(SO_4)_2$$

can also occur quite readily. No indications of any hydrates intermediate between the dodecahydrate and the dihydrate have been noticed.

When some of the mainly dehydrated alum was kept with a small proportion of water and shaken occasionally at room temperature (25°) for a few hours all the fragments of unaltered alum dissolved but some of the $NH_4Fe(SO_4)_2$ remained undissolved for a long time. The mixture was left to stand in the covered beaker and as evaporation proceeded beautiful yellowish brown hexagonal plates and prisms separated from the brownish solution which crept up the sides of the beaker. Their composition agrees very closely with that required for a basic salt $1\cdot5[(NH_4)_2O],Fe_2O_3,4SO_3,5\cdot5H_2O$. This dissolves readily in water at 25° to give a solution which is nearly colourless when dilute but yellowish brown when concentrated. It has not been recorded previously.

Maus,[15] by spontaneous evaporation of a solution of ammonium ferric alum to which ammonia had been added until the precipitate formed no longer dissolved, obtained crystals with composition very close to that required for $2(NH_4)_2O,Fe_2O_3,4SO_3,4H_2O$. A solution of potassium ferric alum treated in the same way with potassium hydroxide yielded crystals approximating to $2K_2O,Fe_2O_3,4SO_3,6H_2O$. Both of these preparations by Maus and the new one described above form precisely similar hexagonal plates and prisms which indicates some probable close relationship. Maus was of this opinion regarding his two salts but noticed that there was more discrepancy between the analytical and calculated figures for the potassium salt than for the ammonium one, the potassium content found by analysis being much too low.

By rewriting Maus's ammonium salt and the new salt as $(NH_4)_4,Fe_2O,(SO_4)_4,(H_2O)_4$ and $(NH_4)_3,(H_3O),Fe_2O,(SO_4)_4,(H_2O)_4$ the new salt is seen to be derived from Maus's salt by replacement of one quarter of the ammonium by hydroxonium.

The composition found by Maus for his potassium salt agrees closely with that calculated

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[12] Adolphs, Dissertation, Heidelberg, 1904.
[13] Masson, *J.*, 1910, **97**, 862.
[14] Taylor and Bassett, *J.*, 1952, 4438.
[15] Maus, *Pogg. Ann.*, 1827, **11**, 78.

for a mixture of: 70% of $K_4Fe_2O,(SO_4)_4,(H_2O)_4$, 20% of $K_3(H_3O),Fe_2O,(SO_4)_4,(H_2O)_4$, and 10% of $K_3(H_3O),Fe_2O,(SO_4)_3,[(OH)_2(H_2O)_2],(H_2O)_4$.

Justification for postulating small replacement of $[SO_4]^{2-}$ by $[(OH)_2(H_2O)_2]^{2-}$ is derived from the replacement of $(SiO_4)^{4-}$ by $[(OH)_4]^{4-}$ which can occur in silicates. The most striking example of this is found in the garnet group.[16]

Such replacement of $(SO_4)^{2-}$ may well occur to a limited extent in many cases and could explain the small deficiency of sulphate in the fresh supply of ferric alum and in the $NH_4Fe(SO_4)_2$ derived from the old supply.

Partial replacement of ammonium by oxonium probably occurs much more frequently than is realised. It has been shown [17] that $H_2SO_4,Al_2(SO_4)_3,2H_2O$ and $NH_4Fe(SO_4)_2$ are isomorphous and that the former is the hydroxonium salt $(H_3O)Al(SO_4)_2$. Shishkin [18] has shown that replacement of oxonium by ammonium ions can link together structurally similar basic, neutral, and acid salts.

The existence of colourless and yellow varieties of ammonium ferric alum is explicable in terms of small amounts of yellow $[FeOH(H_2O)_5]^{2+}$ ions replacing $[Fe(H_2O)_6]^{3+}$ octahedra [19] of the alum lattice and balanced by replacement of $(SO_4)^{2-}$ by $[OH(H_2O)_3]^-$. If the proportion of $[FeOH(H_2O)_5]^{2+}$ were just right optical bleaching of the violet colour of the pure alum would occur. With more of the yellow ion a yellow alum would result. Ostwald [20] and Perman [21] attributed a similar rôle to colloidal ferric hydroxide but this seems less probable.

EXPERIMENTAL

Analysis.—No manganese was detected by the periodate test in any of the samples used. Iron was precipitated twice with aqueous ammonia solution; a third precipitation was found unnecessary. After ignition, ferric oxide was dissolved in concentrated hydrochloric acid, and its weight corrected for the silica present: dissolved silica in aqueous ammonia is a serious analytical nuisance in tropical conditions. Sulphate was precipitated from acidified solution as barium sulphate, and weighed. Water was estimated by difference.

Product of Efflorescence.—(*a*) A sample (4·4 g.) was treated for 1 hr. with water at 25° with occasional shaking. The residue was filtered off, washed with alcohol, and dried in air (yield 2·8 g.) [Found: $(NH_4)_2O$, 8·8; Fe_2O_3, 30·2; SO_3, 59·0; H_2O, 2·0. Calc. for $NH_4Fe(SO_4)_2$: $(NH_4)_2O$, 9·77; Fe_2O_3, 30·04; SO_3, 60·19%]. (*b*) A sample (14 g.) was exposed in a shallow dish for four months (November to March) (loss 0·1 g.) [Found: $(NH_4)_2O$, 9·7; Fe_2O_3, 29·5; SO_3, 58·2; H_2O, 2·6%]. (*c*) A sample (1·6 g.) was exposed for 5 weeks (June and July) (loss 0·02 g.) [Found: $(NH_4)_2O$, 9·8; Fe_2O_3, 29·8; SO_3, 58·4; H_2O, 2·0%].

Hydration of Ammonium Ferric Disulphate.—(*a*) A sample of the mainly dehydrated alum was treated with water, a large amount of $NH_4Fe(SO_4)_2$ remaining undissolved. On heating it was converted into a yellow basic salt, which, after decantation of the dark solution, was dissolved in the minimum of sulphuric acid. The two solutions were mixed, filtered into a silica dish, and allowed to evaporate at 25—30°. After a few weeks crystals of alum appeared, and in a few more weeks this was converted into white anhydrous $NH_4Fe(SO_4)_2$ which in another four weeks formed pale violet prisms of the dihydrate,[14] soluble with long shaking in 1·7M-hydrochloric acid at 25—30°.

(*b*) Water and excess of the anhydrous disulphate in a stoppered bottle at 25° slowly formed a yellow-brown solution. After a few days this was inoculated with a little dihydrate, and after two weeks the whole had been converted into dihydrate, except for a few large (diameter 1 cm.) crystals of alum.

Conversion of Dodecahydrate into Dihydrate.—A lump of fresh alum, splinters of which were shown to contain no doubly-refracting material [Found: $(NH_4)_2O$, 5·5; Fe_2O_3, 16·6; SO_3, 32·7; H_2O, 45·2. Calc. for $NH_4Fe(SO_4)_2,12H_2O$: $(NH_4)_2O$, 5·4; Fe_2O_3, 16·6; SO_3, 33·2; H_2O, 44·8%], was sprinkled with a little dihydrate and left under a small inverted beaker from July

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[16] Winchell, "Elements of Optical Mineralogy," John Wiley, New York, 5th edn., 1951, Part II, p. 483.

[17] Taylor and Bassett, *J.*, 1952, 4439.

[18] Shishkin, *Zapiski Vsesoyuz Mineral Obshchestva* (*Mém. Soc. russe minéral.*), 1950, **79**, 94—102; *Chem. Abs.*, 1950, **44**, 7612; *Zhur. obshchei Khim.*, 1951, **21**, 456—467; *Chem. Abs.*, 1951, **45**, 6115.

[19] Lipson and Beevers, *Proc. Roy. Soc.*, 1935, *A*, **148**, 664.

[20] Ostwald, "Grundlinien der anorg. Chem.," Leipzig, 1900, p. 585.

[21] Perman, *J.*, 1921, **119**, 1996.

to January. It had become a thin violet shell of the original lump, composed of intergrown nodules of the dihydrate: inside was a mass of similar material stained yellow by a film of basic salt.

Preparation of a Basic Salt.—A sample of the mainly dehydrated alum was shaken with water for several hours at 25°. Unchanged alum dissolved quickly, the anhydrous salt only slowly. On standing and being allowed to evaporate, the mixture yielded yellow-brown hexagonal plates and prisms which were obtained practically free from mother-liquor by means of hardened filter-paper. They became stable in air after losing 2% of moisture {Found: NH_3, 7·5; Fe_2O_3, 24·4; SO_3, 49·0; H_2O, 19·1. $1{\cdot}5[(NH_4)_2O],Fe_2O_3,4SO_3,5\frac{1}{2}H_2O$ requires NH_3, 7·8; Fe_2O_3, 24·3; SO_3, 48·7; H_2O, 19·2%}. The basic *salt* dissolves readily in water at 25°.

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