CXV.—*The System Potassium Sulphate–Aluminium Sulphate–Water at 25°.*

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No one appears to have worked out an isotherm of the system potassium sulphate–aluminium sulphate–water, although several investigators have made determinations· of the solubility of alum (Poggiale, *Ann. Chim. Phys.*, 1843, [iii], **8**, 467; Mulder, *Scheik. Verhandel*, Rotterdam, 1864, 90; Locke, *Amer. Chem. J.*, 1901, **26**, 175; Berkeley, *Phil. Trans.*, 1904, *A*, **203**, 189; Marino, *Gazzetta*, 1905, **35**, ii, 351). Marino also determined the composition of the liquid phases which exist in equilibrium at various temperatures with two solid phases, namely, with crystals of either alum and potassium sulphate or alum and aluminium sulphate.

EXPERIMENTAL.

Methods of Analysis.—As the liquid phases contained aluminium sulphate and potassium sulphate only, the simplest method of analysis was to estimate the total sulphate and the alumina; from

the results, the amounts of the two salts could be calculated. The estimation of sulphate as barium sulphate in presence of aluminium salts was found to be quite trustworthy provided that plenty of hydrochloric acid (about 5 c.c. of the concentrated acid) was added in the cold to the dilute solution (about 500 c.c.). The method of estimating the alumina required a little consideration. The amounts to be estimated varied considerably, and in some cases they were so minute that weighable quantities would have been obtained only by the treatment of inconveniently large volumes of the liquid phases. Schmatolla (*Ber.*, 1905, **38**, 987) found that solutions of aluminium sulphate could be titrated with sodium hydroxide and phenolphthalein at 100°. With aqueous solutions of aluminium sulphate, his titrations were always low, sometimes as much as 0·7 per cent., but when the solution contained excess of barium chloride, he obtained accurate results. Scott (*J. Ind. Eng. Chem.*, 1915, **7**, 1059), however, found that titrations without barium chloride were satisfactory. The inaccuracy of Schmatolla's first method was due to some aluminium sulphate having been carried down by the aluminium hydroxide in the course of titration. Hence it was thought that if very dilute solutions of aluminium sulphate were employed, adsorption might be eliminated and the method rendered quantitative. The method was therefore investigated as follows. Several solutions (100 c.c.) of aluminium sulphate containing quantities of alumina ranging from 0·008 to 0·13 gram were titrated, while boiling, with $N/10$-sodium hydroxide and phenolphthalein, and accurate results were obtained. In the case of solutions which contained an amount of alumina greater than 0·1 gram, difficulty was experienced in determining the end-point exactly, owing to masking caused by the aluminium hydroxide precipitate. The presence of potassium sulphate in solution does not affect the accuracy of the method, which is, under the above conditions, an excellent one for the estimation of alum. Since the time when this method was tested and adopted by the author, two papers have appeared, one by Kolthoff (*Z. anorg. Chem.*, 1921, **112**, 172), who prefers the use of excess of barium chloride, and the other by Tingle (*J. Ind. Eng. Chem.*, 1921, **13**, 420), who found the method satisfactory either with or without the use of barium chloride. This method was employed throughout these determinations, usually in the absence of barium chloride. In the titration of very dilute solutions, the advantages accruing from the use of barium chloride were not apparent.

Equilibrium Determinations.—Saturated solutions (about 150 c.c.) of potassium sulphate and aluminium sulphate in varying propor-

tions were made at a temperature a few degrees above 25°.   Great care was taken to keep the temperature of saturation as low as possible, otherwise considerable hydrolysis ensued and the solution became very turbid.   These solutions were poured into bottles fitted with mechanical stirrers, placed in a thermostat regulated at 25·0 ± 0·1°, and were stirred until equilibrium between the liquid phases and solid phases which had crystallised out had been attained.   Stirring of each liquid phase was generally continued for two or three days, the solid phase was then allowed to settle, and about 20 c.c. of the clear liquid phase were removed, weighed, made up to 250 c.c., and analysed.   In order to ascertain whether equilibrium had been attained, the remaining liquid phase was again stirred for another period of at least a day with the solid phase and a further portion tested.   The solid phase was filtered through a Büchner funnel and weighed portions were analysed. In the cases where the solid phase was alum, the crystals were well-defined and were consequently easily freed from the adhering mother-liquor.   Hence there was no necessity of making a complete analysis ; suitable quantities, however, were dissolved in water, and the solutions boiled and titrated in order to settle definitely the nature of the solid phase.

Although the method of allowing a slightly supersaturated solution to attain equilibrium at 25° gave satisfactory results for those liquid phases which were in equilibrium with alum, much difficulty was experienced in applying this procedure to those solutions which, it was believed, would on crystallisation attain equilibrium with either potassium sulphate or aluminium sulphate. For example, raising the temperature of a solution, the solute of which contained, say, 5 per cent. of aluminium sulphate and 95 per cent. of potassium sulphate, being therefore very dilute with respect to aluminium sulphate, produced considerable hydrolysis of the aluminium salt.   Data obtained in such a way would correspond with the solubility of potassium sulphate in the sulphuric acid liberated.   After that section of the curve indicating the composition of liquid phases in equilibrium with alum had been obtained, it was possible to make up at room temperature solutions which, when stirred with the appropriate solid phases, would attain equilibrium with them.   This procedure was also adopted to obtain data for the two liquid phases, each of which was in equilibrium with two solid phases.   The time required for the various phases, solid and liquid, to attain equilibrium in this way was much longer than in the case of the supersaturated solution ; in some determinations several weeks were necessary.

Results.—The following data were obtained.

	Liquid Phases.			Liquid phases.	
Percentage of K_2SO_4 in the solute.	Grams of water in which 100 grams of solute dissolve to give a saturated solution.	Solid phases.	Percentage of K_2SO_4 in the solute.	Grams of water in which 100 grams of solute dissolve to give a saturated solution.	Solid phases.
100	830	K_2SO_4.	23·3	1150	Alum.
93·4	773	,,	20·1	1028	,,
89·6	679	K_2SO_4 and alum.	16·9	886	,,
87·9	731	Alum.	12·8	754	,,
79·6	999	,,	11·4	685	,,
73·8	1190	,,	8·9	508	,,
53·7	1415	,,	6·5	235	,,
45·5	1424	,,	6·0	211	Alum and $Al_2(SO_4)_3,$ $18H_2O.$
33·7	1384	,,	3·4	245	$Al_2(SO_4)_3,$ $18H_2O.$
30·2	1362	,,	0	261	,,

The above results are represented graphically in Fig. 1, using a slightly modified form of the method first proposed by Jänecke (*Z. anorg. Chem.*, 1906, **51**, 132).

FIG. 1.
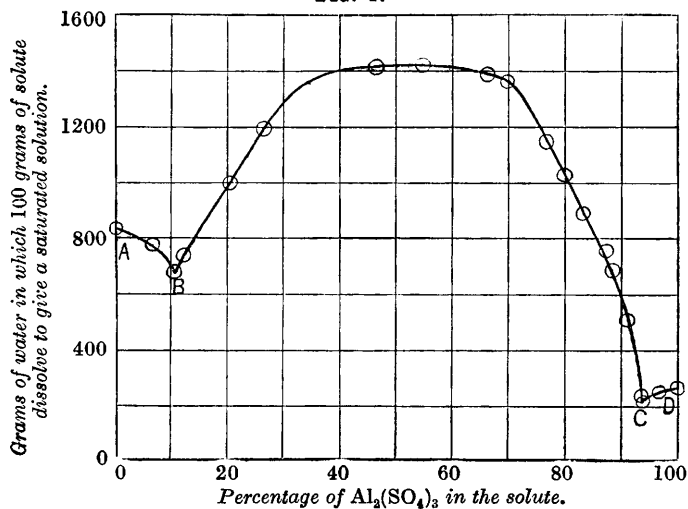
Each of the three branches of the diagram represents saturated solutions in equilibrium with one solid phase only, except those

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solutions which are represented by the two points at which the
curves intersect.   The liquid phases corresponding with AB, BC,
and CD are solutions saturated respectively with potassium sulphate,
alum, and aluminium sulphate (with $18H_2O$).   As the temperature
is fixed, any point, except B and C, on the curves represents a
system having one degree of freedom, namely, one of change in
concentration.   The points B and C represent liquid phases the
compositions of which at 25° are fixed, each solution being in equi-
librium with two solid phases—the former with potassium sulphate
and alum, and the latter with alum and aluminium sulphate crystals.

If curves are drawn from data recorded in Marino's paper, showing
the variation in composition of the solutes of these univariant liquid
phases with temperature, it will be seen that the range of com-
position of solutes of saturated solutions in equilibrium with alum
is considerably diminished on raising the temperature.   Thus the
range at 25° in 100 grams of solute is from 10·4 to 94·0 grams of
aluminium sulphate (Fig. 1), which, incidentally, agrees with the
figures obtained by extrapolation from Marino's results, whereas
the range (as shown by the curves) at 60° is from 35 to 88 grams
of aluminium sulphate.   From the isotherm which has been worked
out, Marino's data, and the variation of solubility of alum with
temperature, a good general knowledge of the system under
consideration may be obtained.

Although the percentage of hydrolysis of aluminium sulphate
at 25° is comparatively low in the liquid phases involved in this
work, appreciably turbid solutions were sometimes obtained,
especially in those solutions the aluminium sulphate concentrations
of which were great.   As the effect of raising temperature is to
enhance hydrolysis, it was decided not to investigate the system at
a higher temperature.

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