

VI.—ON THE PRESENCE OF ACID SULPHATE OF COPPER IN MIXTURES OF AQUEOUS SOLUTIONS OF SULPHURIC ACID AND COPPER SULPHATE—BY CHARLES F. LINDSAY, *Dalhousie College, Halifax, N. S.*

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Anton Schrader* in a paper on the "Electrolysis of Mixtures," measured the conductivity and other properties of solutions containing mixtures of sulphuric acid and copper sulphate, analysing his mixtures for the amount of acid present by titration. In his paper, no methods of any kind are given for the analyses. Prof. MacGregor† has held that Schrader's results point towards the presence of acid sulphate of copper in the solution. At the suggestion of Prof. Mackay this work was undertaken to find if any light could be obtained on this question by chemical analytical methods.

The work was carried out in the Chemical and Physical laboratories of Dalhousie College, and consisted primarily in making up solutions of sulphuric acid and copper sulphate, analysing them, and determining their densities. In the beginning the densities were taken only as a means of calculating the concentration of the mixtures from the concentration of the simple solutions. The work also included the purification of the materials used, and the calibration of burettes and pipettes.

Calibration of Burettes and Pipettes.

All burettes and pipettes were carefully calibrated, by weighing the amount of water of known temperature which they delivered. The burettes used could be read to .01 c.c. They were calibrated for every 2 c.c. throughout their length.

The pipettes, in emptying, were held against the side of the vessel into which they were being emptied, the last drops of water being removed by blowing sharply once.

* Inaugural Dissertation, Berlin, 1897.

† Trans. Roy. Soc. Canada, (2), 4, Sec. 3, 117, 1898-9.

Purification and Analysis of Copper Sulphate.

The copper sulphate was obtained as chemically pure, and after careful re-crystallization, was found to be free from iron and the members of the ammonium sulphide group.

The copper sulphate solutions were analysed by precipitating the sulphate, in known volume, with barium chloride, and weighing as barium sulphate.

The following are the results of three analyses of the same solution :—

Cu SO ₄ in 5 c.c. of solution	=	.5782	grammes.
" " "	=	.5788	"
" " "	=	.5790	"
Mean.....	=	.5787	"

These figures would seem to show that my results might be in error about 0.1 per cent.

Purity and Analysis of Sulphuric Acid.

The sulphuric acid was the best obtainable from Merck, and was taken as chemically pure. The sulphuric acid solutions were analysed volumetrically with standard caustic potash, using as an indicator phenol phthalein.

The following results show with what accuracy such analyses could be carried out :—

2 c.c. H ₂ SO ₄ solution contained	.1627	grammes	H ₂ SO ₄
" " " "	.1625	"	"
" " " "	.1624	"	"
Mean.....	=	.16253	" "

Thus, the possible error of a single measurement would seem to be about 0.11 per cent.

Preparation and Analysis of Mixtures.

Equal volumes of the simple solutions, whose concentrations and densities were known, were mixed at 18°C. The density of the mixture being obtained, the concentration of the mixture with respect to each of the constituents, was obtainable.

The ordinary methods of acid titration are, of course, unavailable in this case, for not only does the copper sulphate itself affect alkalimetric indicators, but the sulphate is precipitated as hydroxide, by the base used for titration. The latter fact is the one used in the method of titration which was employed.

Standard caustic potash solution is added from a burette to the mixture, with constant stirring, until the solution just begins to become cloudy, owing to the beginning of the precipitation of the hydroxide of copper. I found that, using this precipitating point as an indicator, very good determinations of the acid present could be obtained, and would suggest that copper sulphate might be used as an indicator in the determination of free sulphuric acid, in cases where the ordinary indicators are of no use.

The following results of an analysis will show with what accuracy the determination of this precipitating point could be ascertained :

5 c.c. of a mixture $\text{CuSO}_4 + \text{H}_2\text{SO}_4$, began to be cloudy on addition of 43.88 c.c. decinormal caustic potash.

43.97	“	“	“
43.99	“	“	“
44.86	“	“	“

43.92 = mean.

Thus, in these determinations, the difference between the greatest and least values would be about .3%.

A second set of determinations is added :

5 c.c. of a mixture $\text{CuSO}_4 + \text{H}_2\text{SO}_4$, began to become cloudy on addition of 28.94 c.c. of decinormal caustic potash.

28.91	“	“	“	“
28.99	“	“	“	“

28.95 = mean

In this case, the difference between the greatest and least values is about .27%.

It is thus seen not only that the precipitating point is a perfectly definite one, but that it can be determined with considerable accuracy.

The next question is, whether it expresses accurately the amount of acid present.

Concentration.		H ₂ SO ₄		Error.
H ₂ SO ₄	CuSO ₄	Calculated.	Found.	
.416	.361	.2036	.2039	+ .15%
.277	.727	.1356	.1357	+ .08%

Column I. contains the concentration of H₂SO₄ in mixture in gramme-molecules per litre.

“ II. contains the concentration of CuSO₄ in mixture in gramme-molecules per litre.

“ III. contains the amt. of H₂SO₄ in grammes, calculated to be in every 5 c.c. of mixture.

“ IV. contains the same, as found in every 5 c.c. of mixture.

“ V. contains the percentage error.

We thus see that by this means, the sulphuric acid present can be determined with considerable accuracy.

In the above analyses, the mixture under analysis was diluted very much, the reason being, that so far the work has been only to find a good method of analysis, and not to prove or disprove the presence of acid sulphate.

But now a number of analyses were performed on the above mixtures, keeping the mixtures concentrated, and in no case was there any appreciable difference in the amount of caustic potash needed before precipitation would commence.

The results obtained from analyses of the concentrated mixtures, gave, as a rule, slightly less quantities of sulphuric acid. But this I would attribute to the fact that the precipitate would be more easily noticed in the smaller volume than in the larger.

I also made a number of determinations, using standard ammonia in place of the standard potash, but although the precipitating point could be fairly well determined, the results did not agree as well with the amount of sulphuric acid known to be present.

We thus see that this method of chemical analysis for sulphuric acid, while it gives us a good method of analysis for such mixtures, sheds no light on the presence of acid sulphate in solution.

While any recognizable decrease in the amount of sulphuric acid given up to analysis from that known to be present, would yield an almost conclusive proof of the presence of acid sulphate, the result obtained here, does not of necessity lead to the reverse conclusion.

Specific Gravity Measurements.

All specific gravity measurements were made at 18°, and are referred to water at 18°. In these measurements, a pycnometer of the form recommended by Ostwald, and holding about 25 c.c. was used.

The pycnometer was brought to 18° by being placed in a water bath, provided with a mechanical stirrer, whose temperature could easily be kept constant to 1/20 of a degree. When the liquid had come to the temperature of the bath, the meniscus was brought to the mark, the pycnometer taken out, dipped in distilled water, dried carefully with a linen towel, and weighed.

From several successive measurements of the same solution, it would appear that my measurements of density might be in error by about 5 in the fifth place of decimals.

Favre and Valson* have found that, in the case of concentrated solutions of K_2SO_4 and $CuSO_4$, and K_2SO_4 and H_2SO_4 , the density of a mixture of equal volumes of the constituents, is less than the mean value of their densities. From these results they

*Compt. Rend., 77, 907.

drew the conclusion that acid or double sulphate was present in solution. Also McKay† has noticed the same for mixtures of potassium and magnesium sulphates.

In the case of more concentrated solutions of CuSO_4 and H_2SO_4 , I have found the same result to hold. But from lack of time I was unable to push this far.

I give two of my measurements, showing the concentration and density of the constituents, the density of the mixture, and its departure from the mean value.

Parts of H_2SO_4 in 100 parts Solution.	Parts of CuSO_4 in 100 parts Solution.	Density H_2SO_4	Density CuSO_4 .	Mean Value.	Density of Mixture.	Differ- ence.
17.41	16.083	1.12586	1.19108	1.15842	1.15603	.00239
16.23	13.877	1.11525	1.14802	1.13163	1.12952	.00211

†Trans. N. S. Inst. Sci., 9, 348, 1897-98.