to chloride by several evaporations with an excess of hydrochloric acid in a quartz dish. Then the chloride was twice crystallized from a cold solution by saturating with hydrochloric acid gas, with centrifugal drainage of the crystals in each case. As the purified product weighed less than a gram, only one analysis was made. The salt was fused in an atmosphere of dry hydrochloric acid gas in a platinum boat contained in a quartz tube. It was bottled in the Richards "bottling apparatus" and its weight, in vacuum, was found to be 0.72285 g. After solution in water it was precipitated with an equivalent amount of silver, 0.46336 g. (in vacuum) of the latter substance being found to be necessary. When an excess of silver nitrate was added and the precipitate collected and weighed, 0.61583 g. (fused, in vacuum) of silver chloride was obtained. From the amount of silver necessary, the atomic weight of the specimen is computed to be 132.84 (Ag = 107.880; Cl = 35.457), while the silver chloride corresponds to an atomic weight of 132.79. The average result is 132.82, a value essentially identical with the value chosen by the International Committee upon Atomic Weights, 132.81, which depends chiefly upon the work of Richards and Archibald.

It is certainly obvious that the foregoing experiments give no indication of the existence of an unknown alkali element.

The generous assistance of the Carnegie Institution of Washington has facilitated the progress of this work in many ways.

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[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY, YALE UNIVERSITY.]

A METHOD OF DETERMINING THE HYDRATES FORMED BY A SALT.

BY H. W. FOOTE.

Received November 30, 1914.

It is a well-known fact that the addition of sulfuric acid in sufficient quantity to the saturated solution of a hydrated salt with which the acid does not react, will cause the salt to crystallize, either as a lower hydrate or in the anhydrous condition. As an illustration, Taboury[1] has shown recently that beryllium sulfate yields the dihydrate when crystallized from a solution containing two volumes of concentrated sulfuric acid, although the tetrahydrate is the form crystallizing from water. This property of producing a lower hydrate is not peculiar to sulfuric acid alone, for the same effect may be produced by dissolving any other substance, provided it is sufficiently soluble and does not react chemically. Van't Hoff[2] has shown, for instance, that magnesium sulfate crystallizes with only four molecules of water instead of with seven, in the presence of a

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[1] *Compt. rend.*, 159, 180 (1914).

[2] *Sitzungsber. K. Akad. Wiss.* (Berlin), 1899, 340.

saturated solution of magnesium chloride, and the similar dehydrating action of alcohol is well known. Sulfuric acid, however, has one advantage over many substances in producing this result, for it is miscible with water in all proportions, making it possible to reduce the concentration of the water to any desired extent. On the other hand, this acid, at least when concentrated, will react with the majority of salts so that the method is limited chiefly to sulfates.

It is possible, in certain cases, to use this means of preparing lower hydrates to determine all the stable hydrates which a normal sulfate can form at a given temperature. It is evident from the phase rule that the three-component system composed of water, sulfuric acid and sulfate is divariant when the three phases vapor, solution and (solid) hydrate are present, since the phases equal the components in number. At a given temperature, therefore, the hydrate can exist in contact with solutions which vary in composition within certain limits. When two hydrates are present, the system becomes univariant. As a result, at a fixed temperature, there will be but one solution, of definite composition, in equilibrium with the two solid phases and vapor. The proportions of the two solids may, however, be changed so that the composition of the solid residue, as a whole, may be varied while the composition of the solution has a fixed value. It follows that in a series of solubility determinations of a salt, with continually increasing amounts of sulfuric acid, the presence of a pure salt is shown by varying solubility and constant composition of residue, while constant solubility and variable residue show that two salts are present as a mechanical mixture. In this way, it is possible to detect all the stable hydrates of a normal sulfate which form at a given temperature. An exception occurs when an acid sulfate forms before the anhydrous sulfate.

The solubility results are comparable with the vapor pressures of the hydrates alone, without sulfuric acid or solution. At a given temperature, a pure hydrate can exist in contact with pressures of water vapor which vary within certain limits, just as it can exist in contact with solutions of varying concentration. A mixture of two hydrates, on the other hand, has a definite vapor pressure just as it has a definite solubility. The measurement of vapor pressures in the two-component system is one of the standard methods for detecting hydrates and has been used repeatedly. The solubility method, where it can be used, has some advantages over the other, for solubility determinations in general are much simpler to carry out than determinations of vapor pressure, and they are also more accurate. It has an equal advantage with the vapor-pressure method, in showing the range of conditions under which a given hydrate can form.

A number of investigations have been published on the solubility of sulfates in varying concentrations of sulfuric acid, in which the composition of the solid phases has been determined, but these have usually been for the purpose of determining the acid sulfates. In the case of sodium sulfate[1] and of lithium sulfate,[2] each salt forms but one stable hydrate, and these appear on the solubility curves. Kenrick[3] has determined the equilibrium in the system ferrous sulfate, sulfuric acid and water, but an acid sulfate appears before the anhydrous salt is obtained, so that equilibrium between the latter and the monohydrate does not exist in this system. Similarly, an acid sulfate of zirconium is formed immediately following the tetrahydrate, and lower hydrates and the anhydrous salt cannot be obtained by means of sulfuric acid.[4] So far as I am aware, no case has been investigated in which a number of hydrates and the anhydrous salt can all be obtained by means of sulfuric acid. Copper sulfate forms

TABLE I.

Equilibrium in the System $CuSO_4$–H_2SO_4–H_2O *at* 25°.

	Solution.		Residue.		
No.	$CuSO_4$, %.	H_2SO_4, %.	H_2O, %.	Hydrate present.	H_2O, % (calc.)
1	18.47	None	(36.04)[5]	5 H_2O	36.04
2	12.62	11.14	(36.04)[1]	5 H_2O	36.04
3	5.92	25.53	(36.04)[1]	5 H_2O	36.04
4	3.25	36.77	36.12	5 H_2O	36.04
5	2.63	42.15	36.13	5 H_2O	36.04
6	2.59	47.66	36.05	5 H_2O	36.04
7	2.83	49.00	35.57	5 H_2O and 3 H_2O	...
8	2.83	49.20	34.14	5 H_2O and 3 H_2O	...
9	2.84	49.29	28.64	5 H_2O and 3 H_2O	...
10	2.70	50.23	26.23	3 H_2O	25.29
11	2.19	54.78	25.35	3 H_2O	25.29
12	2.11	55.84	19.38	3 H_2O and 1 H_2O	...
13	2.15	55.60	16.12	3 H_2O and 1 H_2O	...
14	0.95	61.79	10.47	1 H_2O	10.14
15	0.17	77.93	10.14	1 H_2O	10.14
16	0.15	83.29	10.87	1 H_2O	10.14
17	0.19	85.46	10.79	1 H_2O	10.14
18	0.44	85.72	9.16	1 H_2O and 0 H_2O	...
19	0.42	85.81	7.64	1 H_2O and 0 H_2O	...
20	0.40	86.04	1.03	Anhydrous	None
21	0.19	92.70	0.83	Anhydrous	None

[1] D'Ans, *Z. anorg. Chem.*, **49**, 356 (1906); **61**, 91 (1909).

[2] Van Dorp, *Z. physik. Chem.*, **73**, 289 (1910).

[3] *J. Phys. Chem.*, **12**, 693 (1908).

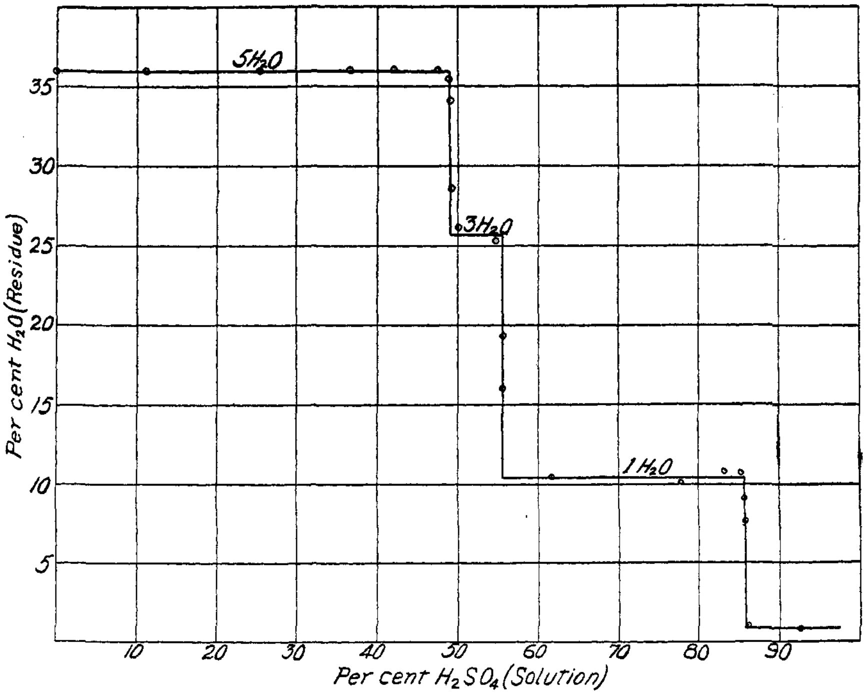
[4] Hauser, *Z. anorg. Chem.*, **54**, 196 (1907).

[5] These values were not determined directly and the calculated value for the pentahydrate is used.

three well-known hydrates and no acid salts interfere. It is, therefore, well suited to illustrate the relations mentioned.

A series of mixtures was prepared containing copper sulfate and water, with continually increasing proportions of sulfuric acid. The mixtures were heated, placed in glass-stoppered bottles sealed with paraffin, and rotated at 25° in a thermostat. No difficulty has been experienced, thus far, in reaching equilibrium after twenty-four hours. Samples for analysis were drawn off through a filter of glass wool. Copper was determined electrolytically and total sulfate by precipitating as barium sulfate. The proportions of copper sulfate and sulfuric acid could then be calculated. The residues were filtered on a filter plate covered with asbestos and washed with strong alcohol. Previous experience had shown that strong alcohol reacts very slowly with dehydrated salts which are insoluble in it. A small amount of acid, averaging less than 1%, always remained in the residue and causes an error in the water determination, giving somewhat high results. Chiefly for this reason, the analysis of the solutions is somewhat more accurate than that of the residues. The results obtained are given in Table I.

The results have been divided into groups in each of which either the solution or the residue remains constant in composition while the other varies. The percentage of copper sulfate falls off rapidly to rather low



values with increasing content of sulfuric acid so that the change in composition of solution is better illustrated by the results for sulfuric acid. In the figure, the results have been plotted. Ordinates represent percentage of water in the residue, and abscissas, the percentage of sulfuric acid in solution. This brings out clearly the range of conditions under which each hydrate forms, this being represented by the length of the horizontals. The conditions for the trihydrate are very narrow while the pentahydrate forms under the widest range, being stable in contact with solutions containing as much as 49% of sulfuric acid.

Solutions which are in equilibrium with two solid hydrates should have the same vapor pressure as that of the hydrates themselves.[1] The vapor pressure of the solutions in Nos. 7–9 of the table, for instance, should be equal to that of a mixture of the solid pentahydrate and trihydrate. Whether this way of determining the vapor pressures of hydrates will offer any advantage in accuracy or convenience has not yet been tested. Where the solubility of the salt is slight, as it is in the solution in equilibrium with anhydrous salt and monohydrate (Nos. 18–19), the vapor pressure of the solution is nearly that of the sulfuric acid solution alone.

I plan to extend this method to a number of sulfates which form more than one stable hydrate.

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ELECTRIC SYNTHESIS OF COLLOIDS.

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The present work was undertaken with a view to elucidate the process of formation of sols by the electric method first utilized by Bredig[2] for the preparation of sols in water, and subsequently modified by Svedberg[3] for obtaining sols in non-aqueous media and of various substances besides metals. Bredig's own method is now a general one and has been extended by others to media other than water.

Much difference of opinion exists as to the process of formation of the sol by these methods. Wo. Ostwald, and others,[4] hold that the process is of an electro-chemical nature and the substance goes into the liquid in the atomic form, under electric forces and afterwards becomes aggregated. Benedicks[5] and others lay stress on the thermal side of the process and are of the opinion that the metal partly volatilizes and partly

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[1] Foote and Scholes, THIS JOURNAL, 33, 1309 (1911).

[2] *Z. angew. Chem.*, 1898, 951.

[3] *Ber.*, 39, 1703 (1906).

[4] Cf. Ostwald's *Grundriss der Kolloid Chemie.*

[5] *Z. Chem. Ind. Kolloide*, 11, 263 (1912).