

and (2) that the exceptional behavior of some ions, especially those of higher valence, is to be attributed to a change in their state of hydration with the temperature.

Finally, making use of the data of Dutoit and Dupertuis, it is shown that analogous relations hold for solutions of sodium iodide in six organic solvents of diverse character

In conclusion, I desire to express my thanks to Prof. A. A. Noyes for valuable suggestions in connection with the preparation of this paper.

ON THE NATURE OF PRECIPITATED COLLOIDS.

[SECOND PAPER.]

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In a previous article¹ by one of us, evidence has been given to show that precipitated iron or aluminium hydroxides may be regarded as solid solutions of water in the oxide or in some lower hydrate. In that article, a method was described for determining the composition of the so-called saturated solution of water in the oxide. Briefly the method consisted in slowly drying the moist precipitated hydroxides in the air, at intervals placing them over pure water in a closed vessel immersed in a thermostat for twenty-four hours or more.

In the drying process, a point was reached where the material began to gain in weight when placed over water and the composition at the point where gain in weight first occurred, was that of the saturated solution. The water removed up to this point was considered mechanical water and the water remaining in the oxide was regarded as dissolved. The reasons for this conclusion will be found in the first paper. The results obtained showed that the composition of the "saturated solutions" was practically independent of the method of preparation but varied with the temperature as is the case in general with saturated solutions. It was found that the point where the residues began to take up water, or in other words, the point where mechanical water was removed, could be determined approximately by the mechanical condition of the residues which were moist and somewhat waxy or pasty up to this point and were dry and powdery when more water was removed. This fact was of the greatest assistance in carrying out determinations, for the precipitates could be dried till nearly all the mechanical water was removed before testing them over water in the thermostat for loss or gain in weight.

The errors in the results obtained were considerable. This was partly because the tests for gain or loss in weight showed only the limits be-

¹ THIS JOURNAL, 30, 1388.

tween which the composition of the saturated solution must lie. Occasionally, when the composition was very near that of the saturated solution, the change in weight was so slight that we were uncertain whether gain or loss had occurred. In the work discussed below, we have assumed that gain in weight first occurred when the gain was 0.5 mg. or more. The averages given of the results represent the facts probably with an error of about 1 per cent., possibly somewhat more. We know of no other method for obtaining these results which would be as satisfactory.

The method outlined above has been used to determine the composition of the "saturated solutions" of water in the mixed oxides of (1) iron and aluminium, (2) aluminium and silicon, (3) iron and silicon, (4) aluminium and phosphorus. We wished, if possible, to gain some insight into the nature of the precipitates which form when solutions of a soluble silicate or phosphate and an aluminium or ferric salt are made alkaline. These gelatinous precipitates are commonly called silicates or phosphates of aluminium or iron and a considerable number have been described. The composition of precipitates of this nature can be varied by using different proportions of the constituents in making the precipitation and this is supposed to be due to various different silicates or phosphates, forming mixtures. By choosing the constituents in certain proportions, precipitates of almost any desired composition can be obtained. Some of these have corresponded to definite compounds in their composition and have been so described. There seems to be, however, no special reason why these precipitates should be regarded as compounds except the fact that when two substances in solution form a precipitate, it is usually a definite compound.

In preparing the precipitates containing iron oxide and alumina, solutions of the chlorides containing known amounts of iron and aluminium were mixed in hydrochloric acid solution and precipitated by adding rapidly a slight excess of ammonia. In all cases, the volume, amount of hydrochloric acid and amount of ammonia added were kept nearly constant. The precipitates were washed by decantation till the wash water showed little or no test for chlorine and then transferred to filters and washed again. The precipitates after washing were tested for chlorides by dissolving in an acid—hydrofluoric acid appeared to be the best solvent—and testing with silver nitrate. Never more than an exceedingly faint trace was found. Several precipitates after thorough washing were tested for ammonia by boiling with sodium hydroxide and were found to contain very small amounts. This could not be removed by washing. Traces of ammonia were also found in the mixtures containing silica. It was unnecessary to analyze the iron and alumina mixtures as the proportions could be calculated from the original amounts taken.

The precipitates containing silica were prepared in a similar manner. Sodium silicate was used as a source of silica. These precipitates were analyzed to determine the proportions of each oxide present.

The phosphate precipitates were exceedingly difficult to prepare in pure condition free from chlorides. Most of them were prepared by mixing solutions of sodium phosphate and aluminium chloride in hydrochloric acid solution and precipitating with ammonia. The precipitates containing most phosphate were made by adding aluminium chloride to varying amounts of sodium phosphate without adding ammonia. Precipitates could be obtained in this manner which settled somewhat more readily than when ammonia was used. The more basic precipitates could not be obtained without using ammonia. These last settled very slowly indeed and washing by decantation required one or two weeks. Even then the last of the chlorides was not removed. The proportions of alumina and phosphoric acid in each precipitate were determined by analysis.

Our object in determining the composition of the "saturated solutions" of water in mixtures of iron and aluminium hydroxides was not only to determine the facts in regard to these mixtures but also to furnish material for comparison with the results obtained on the other mixtures where there was the possibility of chemical combination between the constituents. It is reasonable to assume that in mixtures of aluminium and ferric hydroxides, there is no chemical combination of the iron oxide with the alumina.

The precipitates containing the mixed hydroxides should be either (1) a mechanical mixture of the two hydroxides or (2) a solid solution. If a mechanical mixture of the two hydroxides forms, the points on a curve plotted to represent the composition of the saturated solutions with change in the proportions of iron oxide and alumina, should lie on a straight line. If solid solutions of iron oxide and alumina form, dissolving water, these points in general would not lie on a straight line but on one side or the other of it. The case would be not unlike the solution of some substance such as a salt in a mixed liquid solvent, of which many examples are known, the water dissolving in the iron oxide and alumina corresponding to the salt dissolving in a mixed solvent.

The results obtained giving the per cent. of water in mixtures of iron and aluminium hydroxides when gain in weight first takes place over water, are given in Table I. Only four mixtures were used as the general form of the curve was all that was required. The values for pure iron and aluminium hydroxides are interpolated from results given in the previous article.¹

¹ *Loc. cit.*

TABLE I.—ALUMINA-IRON OXIDE SERIES.

	Per cent. of Al_2O_3 .	Per cent. of water in residues when gain in weight first takes place. "Saturated solution."		
		1.	2.	Average.
1.....	0	50.3
2.....	5.3	55.7	54.9	55.3
3.....	38.7	57.2	55.8	56.5
4.....	63.6	58.2	57.0	57.6
5.....	88.0	55.0	..	55.0
6.....	100.0	48.9

These results are shown graphically in Fig. 1, where the composition of the mixed oxides is plotted as abscissa and the amount of water as ordinate.

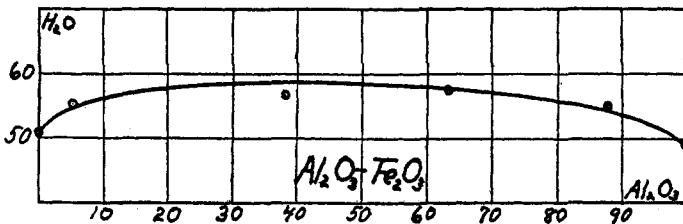


Fig. 1.

The results obtained for the alumina—silica series are in Table II. In covering the series, four determinations were made with each mixture till the main course of the curve was determined and then a smaller number of determinations was made to fill the gaps.

TABLE II.—ALUMINA-SILICA SERIES.

Per cent. of Al_2O_3 in anhydrous oxides.	Per cent. of water in residue when gain in weight first takes place. "Saturated solutions."				Average.	
	1.	2.	3.	4.		
1....	0	56.9	55.5	56.9	..	56.4
2....	2.03	58.9	58.3	58.8	59.0	58.8
3....	12.86	69.3	68.9	69.2
4....	26.03	68.9	68.7	69.4	68.9	69.0
5....	30.88	69.2	69.9	69.4	..	69.5
6....	41.89	69.8	70.0	69.9
7....	44.96	67.3	69.0	67.9	68.3	68.1
8....	61.76	68.4	68.3	68.4
9....	76.13	71.7	71.5	71.1	70.3	71.1
10....	89.48	61.1	64.9	63.6	64.6	63.6
11....	96.35	53.8	58.0	57.6	56.3	56.4
12....	100.00	48.9

The material used in No. 6 in the above table was made by precipitating a water solution of sodium silicate directly with a solution of aluminium chloride without adding ammonia. The precipitate was treated in the same way as the others. The fact that the results are in line with the others is good evidence that the precipitate is of the same nature.

The results are plotted in Fig. 2.

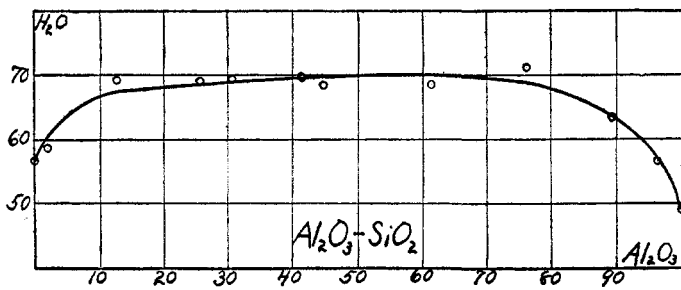


Fig. 2.

The results obtained for the ferric oxide-silica series are in Table III.

TABLE III.—FERRIC OXIDE-SILICA SERIES.

	Per cent. of Fe ₂ O ₃ in anhydrous oxides.	Per cent. of water in residue when gain in weight first takes place. "Saturated solutions."				Average.
		1.	2.	3.	4.	
1....	0	56.9	55.5	56.9	..	56.4
2....	11.30	64.6	61.8	62.9	..	63.1
3....	20.38	63.0	63.7	63.4
4....	24.30	63.8	64.1	64.2	..	64.0
5....	33.30	63.4	61.5	64.0	..	63.0
6....	42.00	58.0	57.8	58.2	..	58.0
7....	55.50	59.5	58.1	56.9	..	58.2
8....	62.48	56.5	57.3	55.0	..	56.3
9....	67.05	55.9	56.5	56.0	56.2	56.2
10....	73.90	57.1	53.6	56.4	..	55.7
11....	81.25	55.7	54.8	55.3
12....	91.27	53.0	54.0	52.9	52.6	53.1
13....	100.00	50.3

The results are plotted in Fig. 3.

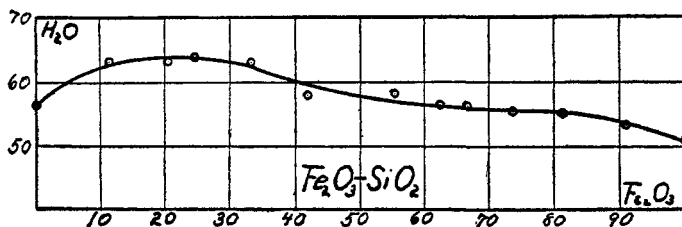


Fig. 3.

In Table IV, the results are given for the last series investigated, containing alumina and phosphoric acid. In preparing these mixtures, two were obtained containing more phosphoric acid in the anhydrous material than corresponded to the compound AlPO_4 and it was only after several attempts, by varying the proportions of aluminium chloride and sodium phosphate, that material was obtained which corresponded

closely to AlPO_4 in composition when ignited. This mixture is No. 3 in the table, containing 41.3 per cent. of P_2O_5 in the ignited residue. (Theory = 41.85.)

TABLE IV.—ALUMINA-PHOSPHORIC ACID SERIES.

	Per cent. of Al_2O_3 in anhydrous oxides.	Per cent. of water in residue when gain in weight first takes place. "Saturated solution."			
		1.	2.	3.	Average.
1.....	35.62	60.5	61.3	61.0	60.9
2.....	37.98	60.5	61.0	61.5	61.0
3.....	41.30	59.3	58.7	59.2	59.1
4.....	45.32	62.9	63.0	61.2	62.4
5.....	57.96	63.0	62.6	..	62.8
6.....	68.68	66.1	63.9	..	65.0
7.....	75.94	66.5	65.7	66.8	66.3
8.....	80.50	67.9	66.9	..	67.4
9.....	85.99	62.9	63.8	..	63.4
10.....	100.00	48.9

One mixture was prepared containing over 90 per cent. of Al_2O_3 in the anhydrous material. It, however, could not be washed thoroughly as it settled very slowly indeed. The results on this mixture agreed with none of the others and were considered unreliable. They are not given in the table. The other results are plotted in Fig. 4.

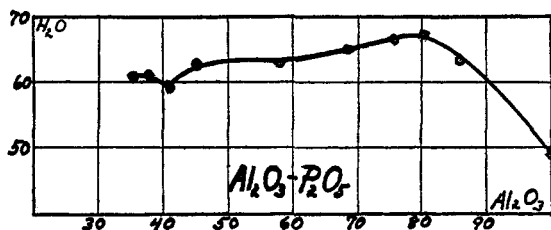


Fig. 4.

The errors due to the method and the nature of the material are considerable, as has already been stated, and this is shown in the figures, where the observed values do not lie closely on the curves as drawn.

The curve for iron oxide and alumina shown in Fig. 1 clearly suggests a solid solution of iron oxide and alumina dissolving water, the mixtures of the two oxides taking up more water than does either oxide alone. Similar cases are known among liquids where a mixture of two dissolves more of a solid than does either one alone. For the sake of comparison, the solubility of potassium permanganate in mixtures of water and acetone, as determined by Herz and Knoch,¹ are given below. The first column gives the number of cubic centimeters of acetone in 100 cc. of water and acetone used as solvent, and the second column the number of milligram equivalents of permanganate in 100 cc. of the solution:

¹ *Z. anorg. Chem.*, 41, 317.

TABLE V.—SOLUBILITY OF POTASSIUM PERMANGANATE IN WATER-ACETONE MIXTURES.

Cc. of acetone in 100 cc. solutions.	Milligram equivalents $KMnO_4$ in 100 cc.
0	148.5
10	162.2
20	177.3
30	208.2
40	257.4
50	289.7
60	316.8
70	328.0
80	312.5
90	227.0
100	67.6

The results are well shown in Fig. 5.

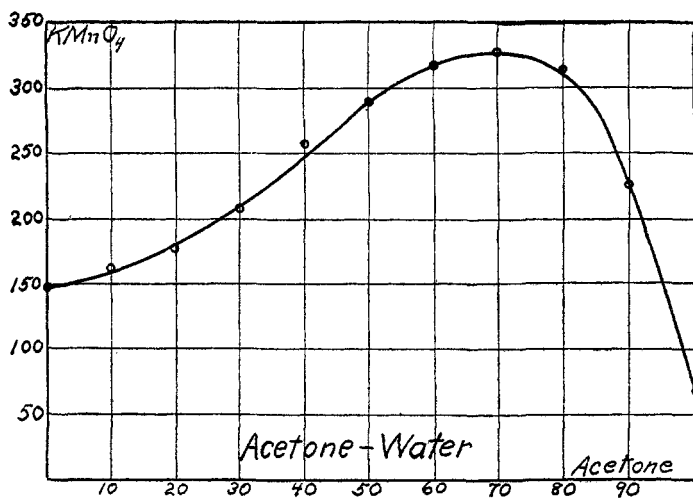


Fig. 5.

The curves where silica or P_2O_5 were present are of the same type.

It is difficult to predict just what form of curve would be obtained in case one or more silicates or phosphates had formed but certainly a decided break in the curve would be expected at the point where any silicate in pure condition formed. On either side of this point, two silicates or a silicate with an excess of either oxide would in that case be present. From the fact that the pure oxides dissolve less water than do the mixtures, it is reasonable to assume that any pure silicate would show a similar behavior. The fact that no break in the curves has been found, together with the general resemblance of the curves to the curve for mixtures of iron oxide and alumina is the best evidence we have secured that all the precipitates are to be considered as solid solutions

of the oxides which dissolve water and that no definite basic phosphates or silicates form. The curve for alumina and phosphoric acid shows a decided drop at the point corresponding to AlPO_4 , the curve rising on either side. This compound probably forms but we do not consider the result conclusive.

We wish to express our thanks to the Committee for the C. M. Warren Fund of the American Academy of Arts and Science for a liberal grant enabling us to carry out this work.

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THE ELECTRICAL CONDUCTIVITY OF FERRIC SULPHATE SOLUTIONS.¹

BY ROGER C. WELLS.

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The interesting behavior of ferric sulphate solutions when diluted or heated has been studied by several investigators chiefly with the desire to find out the composition of the basic precipitates thus formed.² The present paper contains data upon the electrical conductivity of these solutions. The conductivity method has been shown to be an excellent help in following changes in solution and the results here given may prove useful in working out a theory of the state of ferric sulphate in solution.

Preparation of Neutral Ferric Sulphate.—When ordinary ferric sulphate is dissolved in water the solution usually contains an excess of acid. Maus³ long ago, however, pointed out the interesting fact that such a solution, if moderately concentrated, will dissolve ferric hydroxide. It is therefore an easy matter to secure a solution which will analyze "neutral" by first saturating the ordinary solution with ferric hydroxide and then adding sulphuric acid to neutrality. A little ferric hydroxide was precipitated and very thoroughly washed for this purpose. After agitation with the ferric hydroxide and filtration the ferric sulphate solution gave on analysis 0.4239 gram equivalent Fe_2O_3 per liter and 0.4115 gram equivalent SO_3 per liter. After adding the calculated amount of sulphuric acid an analysis gave 0.4173 gram equivalent Fe_2O_3 , 0.4126 gram equivalent SO_3 . A final addition of acid brought up the concentration to 0.4173 gram equivalent Fe_2O_3 , and 0.4170 gram equivalent SO_3 per liter, which was the solution used in all the experiments here described.

Apparatus.—The measurements were made with the usual conduc-

¹ Published by permission of the Director of the U. S. Geological Survey.

² Scheerer, *Pogg. Ann.*, **44**, 453 (1838). Pickering, *J. Chem. Soc.*, **37**, 807 (1880). Moissan, *Traité de chimie minérale*, **4**, 375.

³ *Pogg. Ann.*, **11**, 75 (1827).