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.

SHEFFIELD LABORATORY, NEW HAVEN, CONN.

THE ELECTRICAL CONDUCTIVITY OF FERRIC SULPHATE SOLUTIONS.[1]

BY ROGER C. WELLS.

Received July 15, 1909.

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. Maus[3] 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-

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[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 minerale*, **4**, 375.

[3] *Pogg. Ann.*, **11**, 75 (1827).

tivity apparatus.[1] The electrically heated and regulated thermostat was constant to 0.02°. For large volumes of solution dip electrodes were constructed. It was found very important to determine the cell

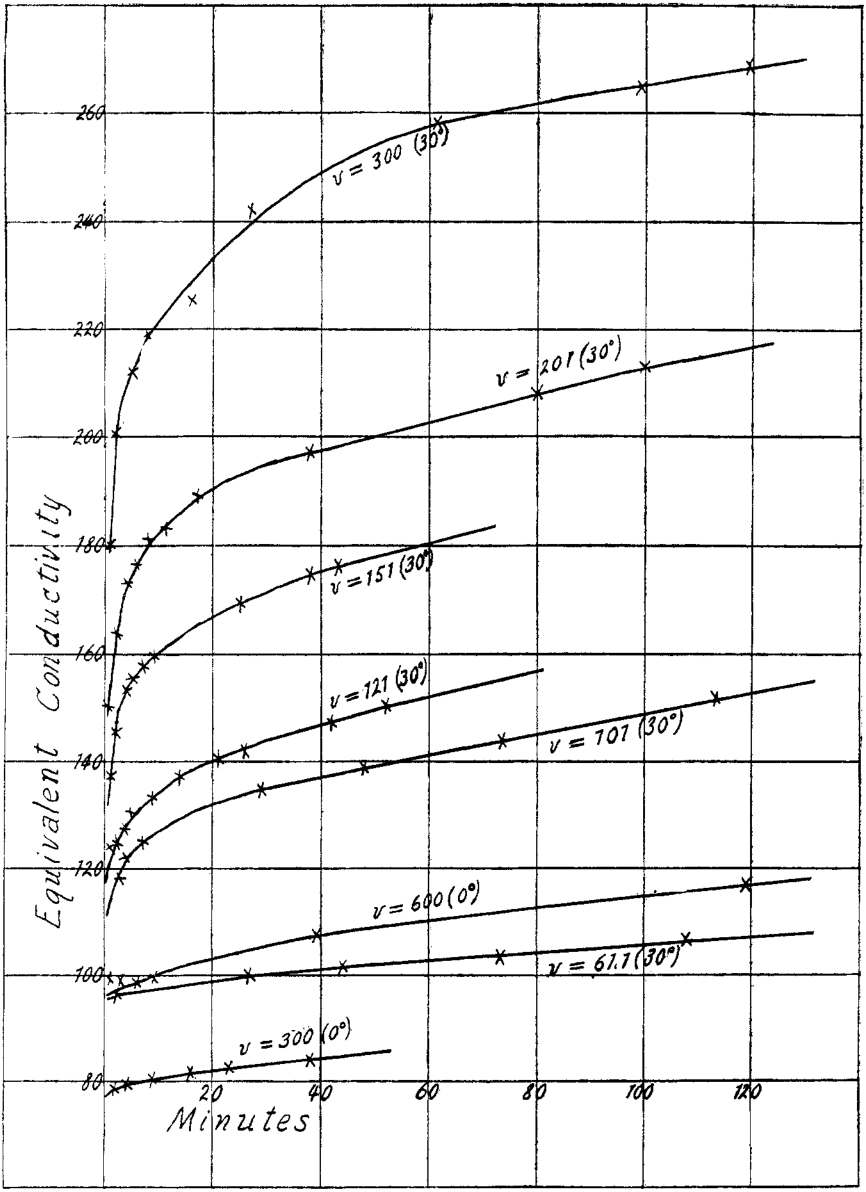

Fig. 1.

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[1] Ostwald-Luther, Physik-chem., Messungen, p. 395.

factors with exactly as much solution and with the electrodes in the same position as obtained in actual measurements. Pure potassium chloride was made up to 0.02 N for determining the cell factors. Sufficiently pure water was employed to make the correction a very small fraction in most cases. In the tables v represents the number of liters containing a gram equivalent of salt ($1/6\ Fe_2(SO_4)_3$ in grams) and $\Lambda = 1000\ \kappa\ v$ the equivalent conductivity where κ is the specific conductivity.

The Behavior of Ferric Sulphate on Dilution.—When a concentrated solution of ferric sulphate is diluted a precipitate appears on standing or warming which has usually been designated "basic salt." It contains ferric oxide and sulphate. The composition of such "basic salts" has been shown by Cameron and Robinson to be indefinite.[1] The formation of this precipitate, however, is sufficient evidence of the tendency of dilute ferric sulphate to hydrolyze. Furthermore, one would certainly expect the hydrolysis of ferric sulphate to occur from analogy with ferric chloride. The latter salt has been studied by Goodwin,[2] who found that the conductivities of the dilute solutions increase with time, a phenomenon becoming very marked at high dilutions and accompanied by the formation of a yellow precipitate.

Similar changes occur with ferric sulphate. By the method of successive dilutions values were obtained for the conductivity up to $v = 16$ at 25° without observing any irregularity. At higher dilutions a slow increase became evident, much more marked at higher than at lower temperatures.

Time curves for such observations were obtained for a number of dilutions and temperatures. The results are given in Table I and some are plotted in Fig. 1.

TABLE I.

	Time.	Equivalent conductivity.		Time.	Equivalent conductivity.
$v = 19.12$	1 min. after			5 days	82.3
$t = 25°$	diluting.	57.2		8 "	82.3
	15 min.	57.7	$v = 38.24$	1 min.	73.2
	30 "	57.8	$t = 25°$	4 "	73.6
$v = 25.15$	0.66 min.	69.7		10 "	73.9
$t = 30°$	2 "	70.3	$v = 61.12$	1 "	96.9
	4 "	70.5	$t = 30°$	3 "	97.6
	15 "	70.7		27 "	100
	38 "	71.2		44 "	101
	1 hr. 16 min.	71.3		1 hr. 13 min.	103
	4 hrs. 26 min.	72.2		1 hr. 48 "	106
	6 hrs. 6 min.	73.2		4 hr. 53 "	117
	18 hrs.	77.2		6 hr. 38 "	121
	3 days	80.0		18 hr.	131

[1] *J. Physic. Chem.*, **11,** 641 (1907).

[2] *Z. physik. Chem.*, **21,** 1 (1896).

TABLE I (*Continued*).

	Time.	Equivalent conductivity.
	22 hr.	132
	3 days	137
	8 "	151
$v = 61.12$	1 min.	95·7
$t = 30^\circ$	2 "	95·7
	6[1] "	96
	12[2] "	96·5
	32 "	98
	53 "	99·7
	104 "	102
	111 "	103
	248 "	113
	22 hrs.	131
$v = 101$	1.5 min.	107
$t = 30^\circ$	2.7 "	118
	4 "	122
	7 "	125
	29 "	135
	48 "	139
	73 "	144
	131 "	152
	140 "	156
	158 "	163
	3 days	193
	6 "	194
$v = 121$	0.5 min.	124
$t = 30^\circ$	1·5 "	123
	2·5[1] "	125
	3·5 "	127
	4·5[3] "	132
	9 "	133
	14 "	137
	21 "	141
	26 "	142
	36 "	146
	42 "	147
	52 "	151
$v = 151$	1 min.	137
$t = 30^\circ$	2[4] "	146
	3 "	151
	4 "	153
	5 "	155
	7 "	158
	8 min.	158
	9 "	160
	25 "	169
	38 "	175
	43 "	176
$v = 201$	0.66 min.	150
$t = 30^\circ$	2 "	164
	4 "	173
	8 "	181
	17 "	189
	38 "	197
	80 "	208
	110 "	215
	20 hrs.	245
	7 days	272
$v = 300$	2 min.	78.4
$t = 0^\circ$	4 "	79·5
	6 "	80.4
	9 "	80.4
	16 "	81.6
	38[5] "	84
$v = 300$	0.5 min.	118
$t = 29^\circ$	1[2] "	127
	2 "	149
	4 "	156
	8 "	194
	10 "	201
	17 "	214
	36 "	236
$v = 300$	1 min.	189
$t = 30^\circ$	2 "	198
	3 "	206
$v = 300$	1 "	180
$t = 30^\circ$	3 "	202
	5 "	212
	8 "	219
	16 "	228
	27 "	242
	61 "	258
	99 "	265
	119 "	269
	18 hrs.	294
	3 days	303

[1] Solution clear.

[2] Ppt. appears.

[3] Ppt. visible.

[4] Ppt.

[5] Solution remains a clear very pale yellow.

TABLE I (*Continued*).

	Time.	Equivalent conductivity.		Time.	Equivalent conductivity.
	4 days.	306		6 min.	248
	7 "	302		8 "	236
v = 600	1 min.	99.6		10 "	240
t = 0°	3 "	98.7		14 "	246
	6 "	98.3	v = 600	1 "	247
	9 "	99.5	t = 30°	2 "	260
	39 "	107.7		3 "	266
	119[1] "	117		19 "	295
v = 600	0.5 min.	202		110 "	327
t = 28.9°	1.5 "	226		1 day	353
	3 "	229		2 "	337
	4 "	237		5 "	342

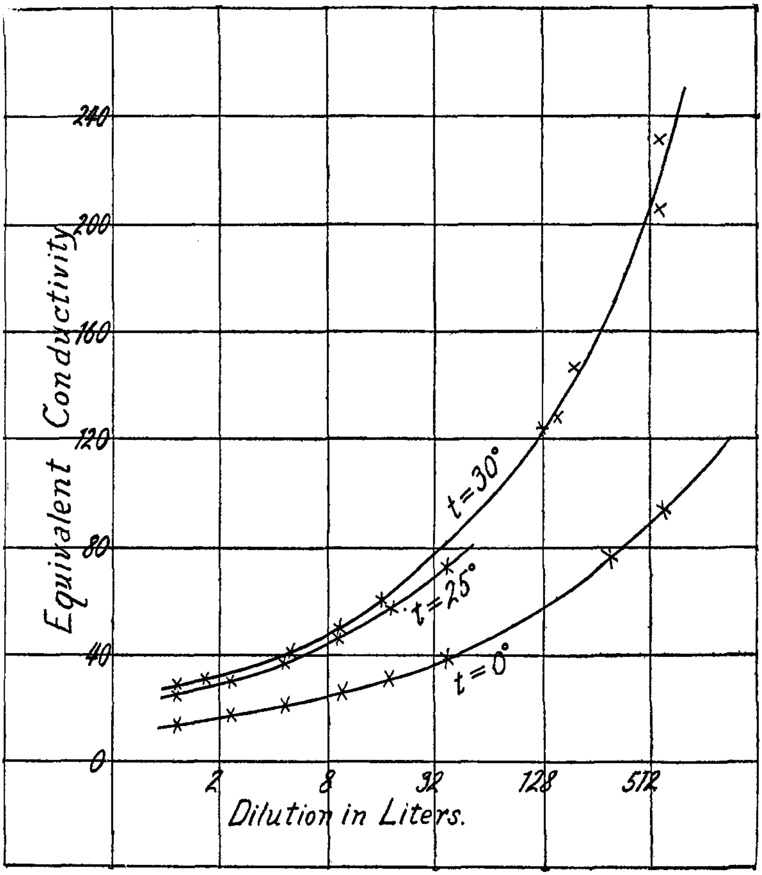

Fig. 2.

The True Conductivities of Ferric Sulphate Solutions.—If the curves

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[1] Solution shows a very pale yellow opalescence.

derived from the above measurements are considered it will be seen that it is possible to extrapolate values for the conductivities at zero time which may reasonably be taken as "the conductivities of ferric sulphate solutions." These extrapolated values form a continuous curve with those obtained by the method of successive dilutions of the concentrated solution. By repetition, fairly concordant values were thus obtained and are plotted in Fig. 2 for the temperatures 0°, 25° and 30°. The curves enable one to read off the values for the conductivity at the customary dilutions and also show the temperature coefficient of the conductivity at the various dilutions. The data from which the first part of the curves are plotted are given in Table II.

TABLE II.

	Dilution.	Equivalent conductivity.
0°	1.195	13.30
	2.390	16.48
	4.780	20.14
	9.560	24.69
	19.12	30.72
	38.24	38.4
	300.1	76.0
	600.0	95.0
25°	1.195	24.89
	2.390	29.34
25°	4.780	36.19
	9.560	45.32
	19.12	57.2
	38.24	73.2
30°	1.195	26.24
	1.794	29.55
	5.382	41.09
	16.15	59.50
	48.45	89.50
	145.3	145.7

Discussion of the Results.—After considering the results above it seems reasonable to conclude that there are at least two reactions to be considered. The first is either a hydration or hydrolysis which attains equilibrium immediately after a change either of concentration or temperature, the second is a rearrangement or further hydrolysis which results in the formation of a basic precipitate and which occurs with a measurable speed.

The first reaction of hydration or hydrolysis is practically the reaction occurring on solution of the salt in water. Equilibrium is here attained easily and quickly. After warming or cooling the more concentrated solutions of ferric sulphate their conductivities return to their original values at the original temperatures. Changes of temperature, however, cause an interesting change of color. The original solution used above was reddish yellow at room temperature. On warming it became cherry-red, on cooling it turned a pale straw color. This change in color is presumably a matter of hydration. Sulphuric acid produces a straw color, which suggests that the red color is due to ferric hydroxide. In the case of ferric chloride, however, Goodwin concluded that a 0.9 normal solution which had stood for over a year did not contain any *colloidal* ferric hydroxide[1] and the chances that a ferric sulphate solution would

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[1] *Z. physik. Chem.*, 21, 12 (1896).

contain it are less, since sulphuric acid causes the coagulation of colloidal ferric hydroxide solutions. Hence if ferric hydroxide exists in the red solution it must be in some other state than the free or colloidal state. This peculiar state is further indicated by the abnormally low conductivity of ferric sulphate at low dilutions. It compares with values for some other salts at 25° as follows:

	$v = 1$.	$v = 32$.	$v = 1024$.
$\frac{1}{2}(NH_4)_2SO_4$	77.9	121.2	147.5
$\frac{1}{2}MgSO_4$	33.4	72.0	116.1
$\frac{1}{2}FeSO_4$	32.7	69.0	123.8
$\frac{1}{2}CuSO_4$	29.7	65.0	117.3
$\frac{1}{2}BeSO_4$	..	31.2	58.2
$\frac{1}{3}LaCl_3$	..	35.3	43.8
$\frac{1}{3}FeCl_3$	..	109.0	...
$\frac{1}{3}Al(C_2H_3O_2)_3$	..	7.1	...
$\frac{1}{6}Fe_2(SO_4)_3$	22.0	70.0	(220.0)

No change in conductivity of the original solution after a very long time has as yet been detected. It seems unlikely that such a change would occur since a temporary rise of temperature does not cause one. Scharizer has reached the conclusion that even concentrated solutions of ferric sulphate are somewhat hydrolyzed.[1] Whether this is so or not, the abnormally high values at high dilutions indicate a hydrolysis, but this first hydrolysis seems to be distinct from that occurring later with the measurable speed, since it reaches equilibrium practically instantaneously and is not accompanied by a precipitation.

I have computed the extent of the increase of this first hydrolysis with dilution in an extremely approximate way as follows:

Taking $\Lambda = (1 - x)\Lambda_1 + x\Lambda_2$ where x is the per cent. of hydrolysis, Λ the observed conductivity, Λ_1 the hypothetical conductivity of the non-hydrolyzed salt and Λ_2 that of sulphuric acid,[2] then

$$x = \frac{\Lambda - \Lambda_1}{\Lambda_2 - \Lambda_1}. \qquad (1)$$

It is now possible to assume minimum and maximum values for Λ_1 between which the truth probably lies.

As far as hydrolysis is concerned, maximum values could not be assumed greater than the values actually obtained and if these were taken there would be no hydrolysis indicated. For minimum values I have assumed, that starting with $\Lambda_1 = 22$ at $v = 1$ the value for Λ_1 increases with dilution *as much as it does for* $FeSO_4$, giving the values shown in the second column. In the third column are the actual values of Λ, in the fourth those for sulphuric acid and in the fifth the value computed by (1) for x on this assumption. The values of x are of course

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[1] *Z. Kryst.*, **46**, 427.

[2] Ley, *Z. physik. Chem.*, **30**, 232 (1899).

only a first approximation and indicate only the increase of hydrolysis from $v = 1$.

v.	Λ_1 (assumed).	Λ (actual).	$\Lambda_2(H_2SO_4)$.	x.
1	22	22	208.0	0
4	33	35	227.0	1.0
16	45	55	261.0	4.6
64	57	87	311.0	12.0
256	73	135	360.0	22.0
1024	90	(205)	376.0	(40.0)

Of course the hydrolysis here indicated precludes the possibility of getting a value for Λ_∞ or a value for λ_{Fe}.

The second stage of the hydrolysis, which occurs with measurable speed when v is greater than 3 or 4 results in the precipitation of "basic salt." The formation of this precipitate, by removing iron oxide, causes the reaction to proceed further than it otherwise would so that notwithstanding the removal of both ferric oxide and sulphate from the solutions the conductivity continues to increase. This indicates a very complete hydrolysis and as a matter of fact the iron is the more completely removed from solution the further it is diluted, being completely removed at the highest dilution. The conductivity is then solely due to the sulphuric acid remaining in solution. Although final values of the conductivity were found as given below no attempt was made to determine the specific reaction velocity or the order of the reaction from the data on account of the removal of the products by precipitation.

FINAL VALUES OF THE CONDUCTIVITY, 30°.

v.	Λ.
25.1	82.3
61.0	151.0
101.0	194.0
201.0	272.0
300.0	303.0
600.0	344.0

An interesting confirmation of the fact that the composition of the "basic salt" is indefinite is given by its color. At $v = 60$ it is brownish yellow, at $v = 100$ orange, at $v = 200$ yellow and at $v = 400$ straw color. The precipitate barely forms at all at 0° even at high dilutions and is then almost white.

Summary.—At low dilutions the conductivity of ferric sulphate solutions is abnormally low, at high dilutions abnormally high. Upon dilution a "basic salt" forms by hydrolysis and precipitates. The speed of formation of the "basic salt" increases enormously with rise of temperature and increasing dilution. By direct measurement at low dilutions and by extrapolation at high dilutions the conductivities of ferric sulphate solutions before the formation of the basic precipitate can be determined. Values of the same are given for 0°, 25°, and 30°. These values seem to indicate that ferric sulphate begins to be hydrolyzed even at a dilution of a few liters. It is proposed that the hydrolysis occurs in two stages, the first occurring with great rapidity, but not accompanied by any precipitation; the second with measurable speed and being identical with the formation of the "basic salt."

U. S. GEOLOGICAL SURVEY, WASHINGTON, D. C.,
July 8, 1909.

[CONTRIBUTION FROM THE LABORATORIES OF THE MALLINCKRODT CHEMICAL WORKS, ST. LOUIS.]

THE PRESENCE OF IODATE IN COMMERCIAL POTASSIUM IODIDE.—A FALLACY.

BY LAUNCELOT W. ANDREWS.

Received July 13, 1909.

The belief appears to be generally held that commercial potassium iodide frequently contains iodate. Thus, the *Pharmacopoeia* prescribes a test for iodate in the iodides and many procedures have heen published for making the test, differing from one another mainly in the choice of the kind of acid used in acidifying and in the amount of it employed. Now, it is not at all apparent how there can be any iodate present in the salt, since the latter is subjected in the course of manufacture to fusion with charcoal and likewise to reducing agents in solution. The production of a blue coloration when the solution of an iodide is mixed with starch paste and acidified with hydrochloric acid, is by no means to be looked upon as evidence of the presence of iodate, although the non-appearance of such coloration is good evidence of its absence. Most commercial samples of potassium iodide contain traces of iron. This iron is commonly present in one of two conditions, or in both. One form is that found in ordinary dust containing coal smoke or soot, in which condition the metal passes readily into solution as ferric chloride, when acted on by dilute hydrochloric acid. The other form is that of anhydrous ferric oxide in a state of extremely fine subdivision. This form dissolves slowly in the dilute acid, even in the presence of the iodide. It is produced by long boiling of saturated solutions of the iodide with ferric hydroxide. Its state of division is often such that this oxide will pass in part through an ordinary filter paper, but is almost entirely retained by the "toughened" paper of the "Dreverhoff" or "S. and S." brands.

A sample of iodide containing iron, in either form, will of course liberate iodine on acidification with hydrochloric acid, the formation of the iodine following more quickly and with more dilute acid when the iron is in the first, more soluble form. If, however, the solution of the iodide (of potassium) is acidified by the addition of potassium bitartrate and