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THE ELECTROLYTIC FORMATION OF AMMONIUM PERSULFATE AND ITS DECOMPOSITION TO HYDROGEN PEROXIDE

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INTRODUCTION

Two processes are mainly used for the manufacture of hydrogen peroxide by the indirect electrolytic method involving persulfate. In the first a sulfuric acid (sp.g. 1.5) solution is electrolyzed in an undivided cell with platinum electrodes and very high current density (C. D.) and current concentration. This solution is distilled under reduced pressure to yield hydrogen peroxide through the hydrolysis of the persulfuric acid. It is evident that all impurities leading to the catalytic decomposition of the peroxide or per-acid should be avoided. But in commercial practice colloidal platinum from the anode and lead sulfate from the cathode catalyze the decomposition of the peroxide. Thus the solution after distillation cannot be recirculated, and the loss of platinum is very high.

The second process utilizes an acid solution of ammonium sulfate as electrolyte from which ammonium persulfate is obtained. This is allowed to interact with a potassium sulfate solution, and the precipitated potassium persulfate is distilled with sulfuric acid under reduced pressure. The first step may be eliminated and a solution of potassium sulfate electrolyzed directly to precipitate the insoluble per-salt. This process is not used widely due to its obvious complications.

Since the electrolysis of ammonium sulfate proceeds with high efficiency, and since no data was found on the distillation of ammonium persulfate, it was thought advisable to investigate this salt with the view of eliminating the difficulties of the processes now in use and of increasing the overall efficiency for hydrogen peroxide production.

PRIOR INVESTIGATIONS

Ammonium sulfate is particularly suitable for persulfate formation since it is very soluble, and in acid solution the persulfate readily separates out. Thus the concentration of persulfate is kept low and there is consequently little formation of per-monosulfuric acid even in strongly acid electrolytes. Elbs and Schönherr,[1] using a platinum electrode, a temperature of 6° to 7°, and electrolyzing for 30 to 40 minutes, found that the yield of persulfate increases with increase in C. D., concentration of ammonium sulfate, and decrease of acid concentration. Increase of temperature up to 30° has little effect upon the yield of persulfate,[2] but above this it diminishes. An electrolyte containing sufficient acid to correspond to NH_4HSO_4 in composition and a C. D. of 50 amps./dm.^{2} are recommended.[3] The presence of chlorides in small amounts improves the efficiency of the process, and so also does ferro-cyanide, but the product is then contaminated with Prussian Blue.[4]

In order to prevent the reduction of the persulfate at the cathode a porous diaphragm may be used, but as this is undesirable, other means have been employed. The addition of 0.2 percent chromate,[5] which forms an insoluble diaphragm on the cathode, has been found successful. In addition the use of a very high cathodic C. D.,[6] of tin and aluminum cathodes,[7] or of a carbon cathode wound with asbestos string[8] has been proposed. Matsuda, and Matsuda and Nishimori[9] found that electrolysis in an undivided cell without the addition of any salt compared very favorably with experiments using a diaphragm. They also disagreed with the statement that the efficiency of persulfate formation decreased if the solution were allowed to become alkaline during electrolysis. In their work heating of the anode before electrolysis was found to be very beneficial in increasing the yield of persulfate.

Essin and his co-workers[10] have investigated the influence of C. D., concentration, and temperature on the formation of ammonium persulfate mainly to verify a theoretical equation:

$$E = 100 \left\{ \left(\frac{C_0 - 2C}{C_0 - C} \right) - K \right\}$$

where E is the current efficiency, C_0 is the initial concentration of ammonium sulfate, and C that of persulfate in gram equivalents per liter, and K is a constant for a given C. D. and concentration. The constant K is said to be the fraction of sulfate ions reaching the anode which are not directly oxidized. According to this equation, the efficiency will be high if the persulfate concentration is kept low, as was verified by experimental data. Accordingly a flowing electrolyte which is kept streaming past the anode has been proposed.[11]

No data was available on the distillation of ammonium persulfate to yield hydrogen peroxide. Although the distillation of persulfuric acid and potassium persulfate from sulfuric acid[12] is given in the literature, very little data could be found. In the following investigation the exact conditions for the formation of hydrogen peroxide from ammonium persulfate were determined.

EXPERIMENTAL

I. FORMATION OF PERSULFATE

As is evident, the procedure was divided into two parts -- first the electrolytic preparation of ammonium persulfate, and second the decomposition of the persulfate into hydrogen peroxide. In the preparation of ammonium persulfate only improvements in known methods were sought by using different anodes and cathodes, and only solutions not heretofore electrolyzed were submitted to electrolysis.

A. Materials and Apparatus. In all the experiments only C. P. chemicals were used. The electrolyses were carried out in an 800 ml. beaker, using 500 to 600 ml. of solution with the cathode covering the entire inside wall of the container. The anode, in the form of a cylindrical foil, was suspended in the middle of the beaker. The solution was cooled by immersion in continuously circulating cold water, and by this means the temperature was kept at 20° C. ± 3° C. All solutions were filtered before they were submitted to electrolysis. The voltmeter was calibrated in units of 1 volt and the ammeter in units of 1 ampere. The current was regulated by means of a lamp bank inserted in series with the bath.

B. Analysis. The analysis for persulfate was that given by Scott[13] using ferrous sulfate. An aliquot of the persulfate was introduced into an erlenmeyer flask with 25 ml. of standard ferrous ammonium sulfate and stoppered with a bunsen valve. The solution was boiled for a minute, cooled under the tap, and the excess ferrous ammonium sulfate titrated with N/10 potassium permanganate.

The hydrogen peroxide was titrated, in an acid solution, directly with N/10 permanganate.

C. Effect of Anode. Due to the great loss of platinum in the electrolysis of sulfuric acid solutions, it was deemed advisable to find a substitute for that metal. Using a solution of saturated ammonium sulfate and a lead cathode the following metals were tried as anodes at a C. D. of 40 amps./dm.^{2}: tantalum, silver, Duriron, Durichlor, Durimet, lead, and graphite. In all cases no persulfate could be found. The tantalum displayed electrolytic valve action; the silver, Duriron, Durichlor, and Durimet went into solution; the lead became coated with the peroxide; and the graphite disintegrated. As these were the only inexpensive metals insoluble in acid and possessing high oxygen overvoltages, it was necessary to use platinum in all further experiments. For some reason the ammonium sulfate prevented the disintegration of the platinum. Even at the highest concentration of acid (saturated NH_4HSO_4 made 18 N with sulfuric acid) no loss of platinum could be detected on an analytical balance after a three hour run. The surface also remained perfectly smooth. Hence one of the great difficulties encountered in commercial practice has been eliminated.

D. Results of Electrolysis. Table I summarizes the data on electrolysis. Runs 1 to 6 were made at the time when it

Table I

Efficiency of Persulfate Formation in Various $(NH_4)_2SO_4 - H_2SO_4$ Solutions

No.	Solution	Cath.	Loss in wt. of cath.	C. D. amps./dm.²	Efficiency						
					15 min.	30 min	45 min	60 min.	90 min.	120 min	180 min.
1	Sat. $(NH_4)_2SO_4$ with diaphragm	Pb.		25				9.3			
2	Same as 1	Pb.		25				11.2			
3	Sat. $(NH_4)_2SO_4$ no diaphragm	Pb.		25				11.4			
4	Sat. $(NH_4)_2SO_4$ heating anode	Pb.		25				31.8			
5	Sat. $(NH_4)_2SO_4$, 5% H_2SO_4	Pb.		40	79.2		57.6	53.4			
6	Same as 5	Pb.		50	84.7		72.2	61.1	51.7	40.4	
7	Sat. NH_4HSO_4	Al.	.0250g.	50	100	98.9	90.9	82.3*	69.8	62.0	
8	Sat. NH_4HSO_4, 12N. w. H_2SO_4	Al.	.0534g.	50	73.4		64.5	56.3	48.5	42.6	35.0
9	Sat. NH_4HSO_4, 15N. w. H_2SO_4	Al.	.0863g.	50	61.3	54.5	49.7	44.5	37.4	30.7	23.5
10	Sat. NH_4HSO_4, 18N. w. H_2SO_4	Al.	.1705g.	50	23.8	23.4	21.7	20.1	18.3	17.2	16.2

* Persulfate ppts.

was thought that ammonium sulfate would be the circulating material for the continuous production of persulfate and subsequently of hydrogen peroxide. Run 1 was made with a porous diaphragm, and no stirring of the anolyte, while in run 2 the anolyte was stirred. The slight increase in efficiency shows that stirring is beneficial for by that means the concentration of persulfate is reduced at the anode, and also the concentration of depolarizer, i.e. HSO_4 ions, is increased. A comparison of 2 and 3, electrolyses with and without a diaphragm, respectively, indicates that the efficiency is not impaired by the removal of the separating wall even though the distance between anode and cathode is no more than 4 cm. As was expected, an increase in C. D. increased the efficiency. Increase in acid concentration also increased the efficiency up to NH_4HSO_4 formation and then decreased. It was found that a large cathode area was necessary for high efficiency, i.e. low cathodic C. D., for preliminary experiments with high cathodic C. D. gave low yields. In all runs using a lead cathode lead sulfate was found in the electrolyte after electrolysis, the amount increasing with acid concentration. In some cases it was impossible to remove the precipitate by filtration as it was practically in colloidal form. A preliminary run with ammonium acid sulfate solution using a lead cathode gave such a copious precipitate of lead sulfate that it was necessary to abandon that metal as a cathode.

Aluminum was chosen as the best cathode for acid solutions since it does not dissolve rapidly, it does not affect appreciably the current efficiency, its sulfate is not very soluble in acid solution, and aluminum sulfate is one of the few salts which does not catalyze the decomposition of hydrogen peroxide.

Since it was found that appreciable quantities of acid were necessary for good yields of hydrogen peroxide, runs 7 to 10 were inaugurated. Glasstone recommended a C. D. of 50 amps./dm.^{2}, and this was chosen for those runs, although the recent work of Matsuda and Nishimori in acid solutions of approximately the same strength seems to indicate that 40 amps./dm.^{2} is the optimum value.

As the acid concentration was increased the viscosity of the solutions increased appreciably, thus decreasing the current efficiency. The 18 N acid solution was of a thick syrupy consistency, and as was expected its efficiency was very low. It was also noticeable that there was a slight increase in the loss of aluminum as the acid concentration increased.

The effect of heating the anode before electrolysis may be ascertained by a comparison of runs 1, 2, and 3 with run 4. In the former the platinum anode was not heated, but in the latter it was heated to redness before being used. The great benefit derived from this procedure is in full agreement with the recent work of Matsuda and Nishimori.

The results also show that the efficiency decreases with time, due to the increase in concentration of the persulfate, thus corroborating the work of Essin and Matsuda.

II. FORMATION OF HYDROGEN PEROXIDE

A. Apparatus. Due to the fact that hydrogen peroxide is so unstable, it was thought that by flash distillation the hydrogen peroxide would distill off rapidly enough so that it would not remain in contact with substances which might decompose it. Hence the distillation apparatus in Fig. 1 was devised. All parts except the condensor connections were of glass. The column 1, 24 inches long and 2 inches in diameter, was sealed onto a liter round bottom flask 2. Three apertures leading into the column were made for either thermometer or feed inlets. The outside was then wrapped with asbestos paper in which 15 feet of nichrome wire was implanted to provide electrical external heating. The inside was filled up to the topmost aperture with broken raschig rings. The flask was provided with a thermometer well and a drain through the bottom. It was heated by an electric furnace 3, molded to fit the bottom. Funnels 4 were used in obtaining fractions without disturbing the vacuum through the three-way stopcock 5. This is but a slight modification of the apparatus described by Gerhart.[14] All connections between the different paths were made with tin foil lined corks, cemented to the glass with De Khotinsky cement so as to provide a vacuum proof seal. The vacuum was provided by a good water aspirator, capable of giving a vacuum of 20 mm. of mercury. For pressures lower than this a "Hyvac" oil pump was used.

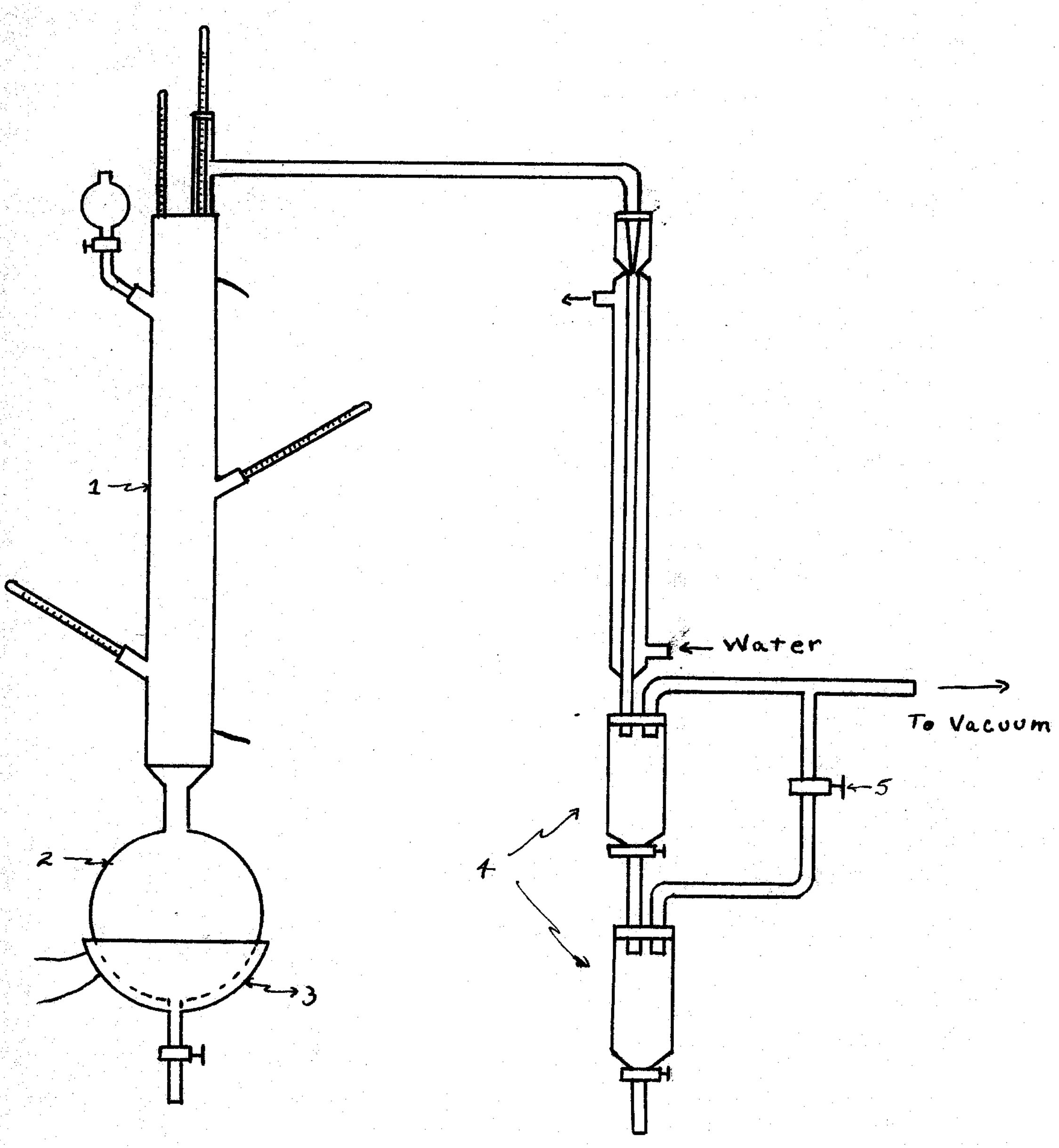


Fig. 1

B. Procedure. In making a run 200 ml. of expected residue was put into flask 2. For instance, if saturated ammonium acid sulfate solution containing ammonium persulfate were to be fed into the column, the flask contained saturated ammonium acid sulfate solution. This was boiled under the desired pressure until first signs of liquid formation were noticed in the condensor. The column was then heated to the desired temperature, and the solution fed in at such a rate as to maintain a constant temperature in the column. After a fixed quentity (75 ml.) had run in, taking on the average about 15 minutes, the pressure was released quickly and the distillate analyzed for hydrogen peroxide.

It was first necessary to determine which temperature and which feed inlet controlled the yield of hydrogen peroxide. Using an acidified solution of ammonium persulfate for the test run, a temperature of 80° C. at the top, and a pressure of 40 mm. of mercury, it was found that the best yields were obtained when using the top inlet. This was most logical as most of the substance would flash before going very far down in the column, and thus the hydrogen peroxide was removed before it had come in contact with the large surface for decomposition offered by the raschig rings.

At this stage a curious phenomenon took place. While the middle thermometer stayed constant at 80° C., the top thermometers would continue to rise, sometimes reaching 140° C. This rise continued until the feed was stopped. Even pure water exhibited the same characteristic. It was thus necessary to use the temperature of the middle thermometer as the temperature of the column. The lower thermometer recorded a temperature but a few degrees higher than the boiling temperature of the solution in the flask.

C. Results. Saturated solutions of ammonium sulfate and saturated solutions of ammonium sulfate containing up to 5% sulfuric acid, these in turn being saturated with ammonium persulfate, yielded but traces of hydrogen peroxide. Only when the acid concentration reached the proportion to form ammonium acid sulfate were appreciable amounts of hydrogen peroxide formed. Even so the yield was much too low for commercial use.

As a check on the column a solution of potassium persulfate in 12 N sulfuric acid was tried, resulting in commercial yields. Hence the low efficiency was not caused by any defect in the column.

Table II lists the results obtained. The percent unchanged persulfate listed in the last column was the amount found in the residue after the completion of a run. This gives a measure of the amount of available oxygen lost through decomposition. All yields were based upon the amount of persulfate originally introduced.

D. Effect of Acid Concentration. It was quite definite that an increase in acid concentration increased the yield. No doubt this was due to both the lowering of the vapor pressure of water and the removal of water through the

TABLE II

Effect of Temperature and Pressure on Yield of Hydrogen Peroxide in Flash Column

No.	Solution	Temp. °C.	Press. mm. Hg.	% Yield	% unchanged Persulfate
1	NH_4HSO_4 sat. w. $(NH_4)_2S_2O_8$	80	25	10.6	
2	Same as 1	80	40	8.4	
3.	"	80	52	9.2	49.6
4	"	80	60	9.7	
5	"	80	80	11.1	
6	"	80	100	13.3	
7	"	80	100	13.3 #	
8	"	80	120	12.4	13.9
9	"	90	100	8.4	19.5
10	"	70	60	11.2	40.9
11	NH_4HSO_4 12N w. H_2SO_4 then nearly sat. w. $(NH_4)_2S_2O_8$	90	22	59.6	
12	Same as 11	90	25	56.9	
13	"	90	60	36.1	
14	"	95	20	53.4	
15	"	95	23	51.2	
16	"	95	40	37.0	
17	"	100	20	38.8	
18	"	100	22	37.8	
19	"	110	30	26.8	

No heat on flask.

hydration of the sulfuric acid. As the vapor pressure of hydrogen peroxide is much less than that of water, it was necessary to remove the water or lower its vapor pressure so that the hydrogen peroxide could distill over.

E. <u>Effect of Pressure</u>. With the saturated ammonium acid sulfate solution, increase of pressure up to 100 mm. of mercury increased the yield. At pressures above 100 mm. the yield decreased. However, with the saturated ammonium acid sulfate solutions made 12 N with sulfuric acid the yield increased with decrease of pressure. It was to be expected that the yield would increase with decrease of pressure, for by that means the quantity of hydrogen peroxide decomposing would be decreased. The unexpected behavior of runs 1 to 10 was inexplicable. There was only a very slight increase with a great increase in pressure, indicating that in this case the yield was quite insensitive to pressure. But for runs 11 to 19 a very slight decrease in pressure increased the yield appreciably. This would indicate that the latter were the more accurate determinations, and due to their high yields, by far the more pertinent ones in this study.

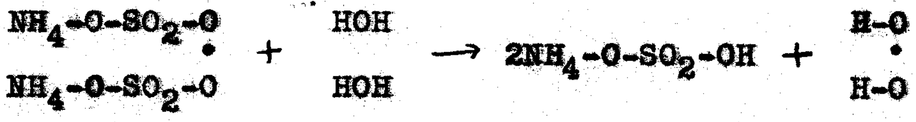
F. <u>Effect of Temperature</u>. At any pressure an increase of temperature up to 90° C. increased the yields, but above that the yield decreased. This temperature, most likely, is the threshold temperature above which rapid decomposition of hydrogen peroxide occurs to decrease the yield.

Run 7 was made with the residue in the flask cold -- only the column was heated. This was made in order to determine whether any hydrogen peroxide came from the distillation of the undecomposed persulfate in the flask. A comparison with run 6 shows that no hydrogen peroxide was realized from that source.

It was feared that some of the loss of persulfate was caused by the oxidation of ammonia to nitrates or nitrites. However, a portion of the distillate when tested with "nitron" failed to indicate even a trace of nitrate.

III. BATCH DISTILLATION

It was observed that solutions of persulfate, on standing over 24 hours, evolved oxygen. Upon titration of the solution, it was found that 95% of the available oxygen was in the form of hydrogen peroxide. If such was the case, the persulfate, on standing, was hydrolyzed to hydrogen peroxide as follows:



$$\begin{array}{c} NH_4\text{-}O\text{-}SO_2\text{-}O \\ \cdot \\ NH_4\text{-}O\text{-}SO_2\text{-}O \end{array} + \begin{array}{c} HOH \\ \\ HOH \end{array} \longrightarrow 2NH_4\text{-}O\text{-}SO_2\text{-}OH + \begin{array}{c} H\text{-}O \\ \cdot \\ H\text{-}O \end{array}$$

This might account for the instability of persulfate solutions on standing through the decomposition of hydrogen peroxide. Upon running a time conversion study, it was found that at the end of 12 hours the hydrolysis reached its peak, and that no appreciable loss in available oxygen took place. From 12 to 24 hours the percent conversion stayed the same, but there was a slight loss in available oxygen. Hence, if a freshly prepared solution of ammonium persulfate were allowed to age for 12 hours and then distilled under reduced pressure, the yield possibly would equal or be greater than that obtained in the flash column. At the same time a complicated, unwieldy piece of equipment would be eliminated.

Table III lists the results of this investigation. An ordinary Claisen flask, heated by an electric furnace as in Part II, A, was connected to an all glass, upright, spiral condensor. At the end of the condensor was attached

TABLE III

Yield of Hydrogen Peroxide on Batch Distillation

No.	Solution	% Yield
1	Sat. NH_4HSO_4 12N w. H_2SO_4 immediately after electrolysis	57.5
2	Same as 1; 12 hr. age	69.5
3	Same as 1; 24 hr. age	65.7
4	Sat. NH_4HSO_4 15N w. H_2SO_4; no age	58.0
5	Same as 4; 12 hr. age	61.3
6	Sat. NH_4HSO_4 18N w. H_2SO_4	24.1
7	Sat. NH_4HSO_4 21N w. H_2SO_4	39.2
8	Sat. NH_4HSO_4 24N w. H_2SO_4	29.0
9	Sat. NH_4HSO_4 12N w. H_2SO_4 feeding slowly into hot residue	16.5
10	Same as 9; feeding rapidly	6.6
11	Same as 9; slow distillation over 4 hrs.	38.2

<u>Note</u>: In all these runs, pressure was 6-10 mm. Hg.

the modified Gerhart equipment for taking fractions. In this case the vacuum was provided by a "Hyvac" oil pump. Reasoning from the results obtained with the flash column, the lowest pressure obtainable was used. A 75 ml. portion of the persulfate solution was added to the flask and boiled rapidly until the first trace of white SO_3 fumes were visible. At this point steady ebullition ceased and violent bumping set in. The whole time consumed for a distillation averaged 30 minutes.

As is indicated in Table III, the yields were slightly better than those obtained in the flash column, and they increased with acid concentration up to 15 N sulfuric acid before beginning to decrease. Allowing the solutions to age from 12 to 24 hours also improved the yield slightly. In no case was any available oxygen found in the residue.

It was thought that feeding the persulfate solution into the hot residue of a previous run might simulate the conditions of a flash distillation. But the results of runs 12 and 13 indicate that the hot solution decomposed the peroxide before it was evolved. Run 14 indicated that rapid distillation was necessary in order to prevent extreme losses through decomposition.

CONCENTRATION OF HYDROGEN PEROXIDE IN DISTILLATE

The volume of distillate decreased with increase in acid concentration in all cases, being 40 ml. for the saturated ammonium acid sulfate solution, 30 ml. for saturated ammonium acid sulfate made 12 N with sulfuric acid, and 20 ml. for all those exceeding 12 N acid. The concentration of peroxide increased in each case, being 0.2 to 0.3% by weight for the first, 0.5 to 0.8% for the second, and 0.6 to 0.8% for the last. The small distillate and the small concentration of peroxide eliminated all possibilities of taking fractions. Even upon doing so, no change in concentration could be detected over the whole range of distillation.

The necessity for obtaining such low concentrations was quite obvious when it was found that the persulfate solutions, when nearly saturated, contained but 2 grams of persulfate per 75 ml. This is equivalent to approximately o.3 grams of hydrogen peroxide. Hence, even with a 100% yield on distillation and the same volumes of distillate, the concentration of the resulting solution would contain but 1.o% to 1.5% of hydrogen peroxide, by weight. At present there seems no way of increasing the concentration of peroxide. If the volume of distillate is decreased by adding more sulfuric acid the yield is reduced; if the solution is electrolyzed longer the current efficiency drops rapidly and the persulfate precipitates; and if the current concentration is reduced the volume of the electrolyzing tank becomes too great for convenience.

CONCLUSIONS

A comparison of Tables I, II, and III shows that for best overall efficiency a solution of saturated ammonium acid sulfate made 12 N with sulfuric acid should be used either in a flash column or for rapid vacuum distillation. The optimum conditions for flash distillation were found to be at a pressure of 20 mm. of mercury or lower, and a column temperature of 90° C.

The disadvantage of low concentration of peroxide is not as great as it may appear, for in all commercial installations a redistillation is necessary. Opposed to this are the advantages of greater overall efficiency, no loss in platinum or raw materials, greater flexibility, and continuity if the flash column is used or semi-continuity for batch distillation. By using batch distillation the complicated expensive equipment now used may be completely eliminated and replaced by simple, inexpensive apparatus. Thus the overall cost for the production of hydrogen peroxide can be greatly reduced.

SUMMARY

Saturated ammonium sulfate with varying proportions of sulfuric acid were submitted to electrolysis to form the persulfate, and subsequently decomposed through vacuum distillation to form hydrogen peroxide in order to determine whether the overall efficiency of hydrogen peroxide formation could be improved. A saturated solution of ammonium acid sulfate made 12 N with sulfuric acid was found to give the best overall efficiency in the flash column and a slightly greater yield through rapid vacuum distillation. The advantages of this process over the ones now in use are:

(1) no loss in platinum;
(2) no loss in raw materials;
(3) it can be made continuous or semi-continuous;
(4) added flexibility of operation.

The only disadvantage encountered was the low concentration of the produced hydrogen peroxide solution.

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