LXIX.—*The Action of Alcohol on the Sulphates of Sodium.*

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THE literature dealing with the solubility relationships of the sulphates of sodium is given by Foote (*J. Ind. Eng. Chem.*, 1918, **10**, 896), and Saxton (*ibid.*, 897) draws certain important conclusions relating to the composition of the solid sulphates of sodium prepared according to a method by which these were washed first with a mixture of sulphuric acid, water, and alcohol, then with alcohol, and finally with ether.

The present paper shows (1) that sodium sulphate and sodium hydrogen sulphate are acted on by a mixture of alcohol and sulphuric acid, and (2) that the washing with alcohol would decompose sodium hydrogen sulphate alone or in the presence of sodium sulphate, but would not decompose the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$. Saxton does not state how many times his compounds were washed with alcohol or ether, or if the washing was continued until the washings were neutral. It is shown below that, with or without preliminary washings with alcohol, many days' extraction with ether are required completely to remove the acidity from sodium sulphate or hydrogen sulphate which has been treated with alcoholic sulphuric acid. This point appears to be of great importance in connexion with the results given in Saxton's paper.

Lunge ("Sulphuric Acid and Alkali," 1909, Vol. II, Part I, 29) states that the compound $\text{Na}_3\text{H}(\text{SO}_4)_2$, observed by Thomson and Mitscherlich, is stable in air (see also D'Ans, *Ber.*, 1906, **39**, 1534), that (*loc. cit.*, p. 24) water decomposes sodium hydrogen sulphate into neutral sulphate and free sulphuric acid (compare Pascal and Ero, *Bull. Soc. chim.*, 1919, [iv], **25**, 25), and that alcohol deprives powdered sodium hydrogen sulphate of all free acid (see also Roscoe and Schorlemmer's "Treatise on Chemistry," 1913, Vol. II, pp. 261 and 341, where a similar statement is made regarding potassium hydrogen sulphate).

Pascal and Ero (*loc. cit.*) have studied the ternary system $\text{Na}_2\text{SO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$. They state that a fused mixture of sodium sulphate and hydrogen sulphate is converted on cooling through 179° into the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$. Further, that nitre-cakes having an acidity inferior to 36 per cent. of sulphuric acid, on cooling after the retort is tapped, must pass through that temperature, and must therefore consist of a mixture of sodium hydrogen sulphate and the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$.

EXPERIMENTAL.

This work was undertaken as part of a research on the recovery of sulphuric acid from nitre-cake by means of spirits of wine (commercial ethyl alcohol). Experiments on commercial nitre-cakes were somewhat anomalous, but showed that nitre-cake, whether dry or moistened with 10 per cent. of water, when washed with either commercial (undried) alcohol or with absolute alcohol gave a residue having an acidity corresponding with about 18·7 per cent. of sulphuric acid, and that even in cases where the water added to the nitre-cake was as much as 60 per cent. of the weight of the cake, the residue had an acidity of about that value.

In view of the statements mentioned above regarding the action of alcohol on sodium hydrogen sulphate, it was expected that the residues resulting from these experiments would be free from acid. The fact that they invariably showed an acidity approximating to 18·5 per cent. suggested the formation of an acid salt having an acidity inferior to that of sodium hydrogen sulphate. The subsequent work was undertaken with the object of elucidating this point.

It is now known, as the result of this work, that exhaustive extraction of nitre-cake by commercial alcohol containing even small percentages of water leads to the progressive diminution in the acidity of the residue after each extraction, and finally results in complete extraction of the acid. The constancy of the value (about 18·5 per cent.) obtained in the above experiments is due to the fact that the residues were not washed exhaustively with alcohol. Washing with the alcohol was only repeated four or five times. The progressive extraction of nitre-cake by commercial spirit has been studied by the authors, and the acidity in the residue after each extraction has been determined. Full details of this part of the work will be published in a subsequent paper on the commercial aspect of the subject, but the values given in table I will illustrate the points sufficiently for the present purpose, and will explain one of the several reasons why an investigation of the subject with pure materials was undertaken.

TABLE I.

Successive Extraction of Nitre-cake by Moist Alcohol. (About 5 per cent. of Water.)

						Sulphuric acid. Per cent.
Acidity of original cake						33·0
Acidity of residue after	6th extraction with alcohol...					16·4
”	”	12th	”	”	...	8·8
”	”	18th	”	”	...	1·6

It will be shown that pure, dry alcohol extracts acid from pure sodium hydrogen sulphate until the residue contains only 18.69 per cent. (calc.: 18.7 per cent.) of acidity as sulphuric acid, and that neither in the cold nor when heated has dry alcohol any further action on it.

The results quoted for commercial nitre-cake were obtained because the solid, that is, the nitre-cake or partly extracted nitre-cake, was not washed until the washings were neutral. In fact, the above results (table I) show that, with commercial spirits of wine, a neutral washing could not have been obtained until all the acidity had been extracted from the cake.

Preparation of Materials.—Sodium sulphate was prepared by neutralising a solution of pure sodium carbonate with pure sulphuric acid. The solution was evaporated to dryness and fused until neutral.

Sodium hydrogen sulphate, prepared from the calculated quantities of pure sodium carbonate and pure sulphuric acid, was fused at 200° until no further loss was observed. The salt is hygroscopic. It gave the following analysis:

	Found. Per cent.	Calc. Per cent.
Free acid as H_2SO_4	40.76	40.83
Sodium sulphate formed on ignition	59.10	59.18
" SO_4 " as Na_2SO_4	39.80	40.00
" SO_4 " estimated as BaSO_4	67.60	67.53

In all experiments in which pure, dry sodium sulphate of hydrogen sulphate was used, the sulphate was fused and poured into a hot agate mortar, quickly ground up as soon as solidification had set in, and transferred to a weighing bottle.

Sulphuric acid (100 per cent.) was prepared by mixing calculated quantities of pure sulphuric acid with fuming sulphuric acid. The strength was 100.38 per cent., and the concentration was reduced to 100.10 per cent. by exposure to a moist atmosphere.

Ethyl Alcohol.—Pure absolute alcohol was left in contact with lime for several days and then distilled. This operation was repeated until the strength of the distillate, as determined from its density, was 99.80 per cent. by weight.

Alcoholic sulphuric acids were made up by mixing refined alcohol with 100 per cent. sulphuric acid. The approximate strength was obtained by weighing, and the actual strength was determined by titration. Esterification takes place slowly (at 18—19°), and at that temperature about three weeks are required for equilibrium to be established. The percentage "total" acidity, a , is found by evaporating a weighed portion of the alcoholic sulphuric acid to pastiness with excess of standard sodium or potassium hydroxide, and then heating in an air-oven for half

an hour at 120°. This ensures complete decomposition of the ethyl hydrogen sulphate. The percentage acidity by direct titration, b , is found by titrating a known weight of the alcoholic sulphuric acid with standard alkali hydroxide. The percentage esterification of the sulphuric acid present is given by

$$\frac{2(a-b)}{a} \times 100.$$

These values (see figure and tables V and VI) have been carefully verified. They differ considerably from those previously available. This work on ethyl hydrogen sulphate will be the subject of a subsequent paper.

Ethyl Ether.—Commercial "pure" ether was dried over calcium chloride, then by exposure to metallic sodium with intermittent shaking, and was finally distilled from sodium.

The Action of Pure, Dry Alcohol on Pure, Dry Sodium Sulphate and its Crystalline Hydrates.

Alcohol has no action on neutral, anhydrous sodium sulphate. Sodium sulphate is sparingly soluble in dilute alcohol.

When the sulphates $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ are treated with dry, cold alcohol, the whole of the water of crystallisation is extracted and the anhydrous sulphate remains. When a super-saturated solution of sodium sulphate in water is treated with warm alcohol (D 0.850), the heptahydrate crystallises out (Löwel, *Ann. Chim. Phys.*, 1851, [iii], **33**, 334; 1857, **49**, 32).

The Action of Pure, Dry Alcohol on Pure, Dry Sodium Hydrogen Sulphate.

The first experiments were carried out with ordinary "absolute" alcohol not specially dried. The dried, powdered hydrogen sulphate was shaken for a short time with excess of this alcohol, filtered, and then washed repeatedly with the same substance. The acidity of the residue fell rapidly to about 18.7 per cent. of sulphuric acid, the washings being strongly acid, and then continued to fall, but very slowly, and the washings were only faintly acid. Two samples, after very exhaustive washing, contained acidities of 17.53 and 17.46 per cent. respectively, and the washings still showed faint acidity. The experiments were repeated with specially dried alcohol prepared as described above, and similar results were obtained. The acidity, as before, rapidly fell to about 18.7 per cent., and then decreased very slowly, but in this

case exhaustive washing reduced the acidity only to 18.07 per cent. and 18.31 per cent. in duplicate samples.

Now, an acidity of 18.7 per cent. corresponds with that of the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and it was concluded that the rapid reduction of the acidity to approximately this value was due to the formation of this salt. It was further concluded that the reduction of the acidity below 18.7 per cent. was due to water in both cases. The method of extraction on an open filter favoured the absorption of atmospheric moisture by the alcohol.

Attempts to eliminate the effect of atmospheric moisture by carrying out the extraction in a Soxhlet apparatus produced similar results; prolonged extraction invariably gave a residue having an acidity slightly below 18.7 per cent. In this case, it was decided that water from another source was responsible, partly, at any rate, for the anomalous results. It has been shown repeatedly in the course of this work that ethyl hydrogen sulphate is invariably formed when alcohol acts on sodium hydrogen sulphate, and it follows that an equivalent quantity of water must be present as a result of this reaction.

In an extraction in a Soxhlet apparatus, this water would dilute the alcohol and would distil over with it, and the effect would be the same as that produced by the undried alcohol in the method of extraction by washing on a filter. Attempts were made to eliminate this water by placing in the flasks of the extraction apparatus (1) anhydrous copper sulphate, and (2) magnesium powder, the latter in the hope that magnesium sulphate and hydrogen would be formed and the production of ethyl hydrogen sulphate prevented. Both failed, owing to the difficulties in carrying out the extraction, caused mainly by violent bumping in the flask. It was finally decided that the best method of attacking the problem was to allow an excess of dried alcohol to remain in contact with the salt for a time sufficient to permit of equilibrium being reached, and then to remove the liquor from the sphere of action as quickly as possible by washing with a neutral solvent. The solvent adopted was ether, dried as described above. A blank experiment, carried out by extracting some dried sodium hydrogen sulphate (acidity, 40.76 per cent.) with the ether in a Soxhlet apparatus, gave, after prolonged extraction, residues containing 40.57 and 40.68 per cent. of sulphuric acid, showing that ether is without action on the hydrogen sulphate. Dried sodium hydrogen sulphate was shaken continuously in a shaking machine with dried alcohol for twenty-four hours, and then filtered off rapidly. The

residue was wrapped in clean paper and extracted in a Soxhlet apparatus with the dried ether until the runnings were neutral. The residue obtained by this method invariably had an acidity lying between 18.66 and 18.74 per cent. of sulphuric acid. Similar results were obtained when the hydrogen sulphate, instead of being shaken with alcohol, was digested with it for several hours under a reflux condenser.

The conclusion is that the action of dry alcohol, either hot or cold, on dry sodium hydrogen sulphate results in the formation of the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, containing 18.7 per cent. of acidity as sulphuric acid.

Thus, dry alcohol extracts two-thirds of the acidity from sodium hydrogen sulphate, and the statement found in certain standard works (*loc. cit.*) that sodium hydrogen sulphate is decomposed by alcohol with the formation of neutral sulphate, requires revision. Complete extraction of the acid only takes place when the alcohol is contaminated with water.

The action of alcohol on potassium hydrogen sulphate was next examined. The "pure" material was fused until no further loss of weight could be detected. The acidity was 36.15 per cent. (calc.: 36.03 per cent.). Several samples were treated with alcohol and extracted with ether, as in the case of the sodium salt, and the acidity in the residue was estimated. In all the samples the acidity lay between 35.59 and 35.84 per cent. It is thus evident that the decomposition of potassium hydrogen sulphate by dry alcohol is negligible. This result is recorded independently by Borntraeger (*Annali Chim. Appl.*, 1919, **12**, 1).

The action of several other aliphatic alcohols on sodium hydrogen sulphate was examined to see if their behaviour is similar to that of ethyl alcohol. The results are given in table II.

TABLE II.

Action of certain Aliphatic Alcohols on Dry Sodium Hydrogen Sulphate.

Alcohol.	Boiling point under 610 mm. pressure.*	Acidity of residue. Per cent.
Methyl alcohol	59.5°	18.68
Ethyl alcohol	72.5°	18.68
n-Butyl alcohol	110-111°	18.65
Amyl alcohol	125.0°	18.66

* Normal pressure at the laboratory at which the work was done.

*The Nature of the Reaction between Alcohol and Sodium
Hydrogen Sulphate.*

During the investigation of the reaction by repeated washings with alcohol on a filter, the washings were collected and the acidity was determined by titration. It was noticed that the acid found in the washings was always less than that which had disappeared from the salt. It was suspected that this discrepancy was due to the formation of ethyl hydrogen sulphate. The liquors were examined for this substance, and its presence was confirmed.

The method of analysis employed for determining in these alcoholic extracts both the total acidity and the extent of conversion into ethyl hydrogen sulphate is that described above under "alcoholic sulphuric acids."

The question then arose: Is the ethyl hydrogen sulphate formed as a result of direct action between the alcohol and the hydrogen sulphate, or is its formation a secondary reaction between the alcohol present and the sulphuric acid extracted directly from the hydrogen sulphate?

The solution of the problem involved an examination of the reaction occurring when dry alcohol and dry sulphuric acid are mixed in varying proportions. The detailed results of this examination will be given in a separate paper, and it is sufficient to state here that:

(1) At the ordinary temperature (18° to 19°) equilibrium between the product, ethyl hydrogen sulphate, and the reacting substances is reached very slowly, and requires about two or three weeks for completion.

(2) The extent of the conversion depends on the proportions in which the reacting substances are present.

The curve indicates the percentage esterification of the total sulphuric acid present for varying proportions of alcohol and sulphuric acid after equilibrium has been attained.

The answer to the question proposed was found by a comparison of results obtained with acid alcoholic liquids prepared from sodium hydrogen sulphate with the values on the above curve.

Since the action represented by the equation

takes some time to reach equilibrium, it follows that, if the presence of ethyl hydrogen sulphate in the liquor prepared from sodium hydrogen sulphate is due to this reaction, the examination of such liquors immediately after the substances have been shaken together should show percentage conversion lower than those on the above curve. If, on the other hand, the ethyl hydrogen sulphate is pro-

duced as a result of direct action between the alcohol and the hydrogen sulphate, the value should lie either on its curve or above it, according as the reaction $\text{EtHSO}_4 + \text{H}_2\text{O} \rightarrow \text{EtOH} + \text{H}_2\text{SO}_4$ reaches equilibrium quickly or slowly. (The velocity of this reaction was not studied quantitatively during this work, but it has been observed that the hydrolysis takes place slowly.) Quantities

of sodium hydrogen sulphate and alcohol in varying proportions were shaken for twenty-four hours and filtered. Table III (p. 657) shows the degree of conversion of the sulphuric acid in the filtrate into ethyl hydrogen sulphate.

The values in the fifth column lie far below those on the curve, and it appears, therefore, that the formation of ethyl hydrogen sulphate is a secondary reaction between alcohol and sulphuric acid, the latter being produced as the result of a primary reaction between alcohol and hydrogen sulphate. It has not been found possible to ascertain the precise nature of this primary reaction.

Experiments were performed in order to ascertain whether the

TABLE III.

Sodium hydrogen sulphate. Grams.	Ethyl alcohol. Grams.	Acidity of filtrate as percentage of sulphuric acid.		Esterifica- tion. Per cent.	Acid ex- tracted. Theory = 2.72 grams. Grams.
		By direct titration.	Total.		
10	12	18.12	18.31	2.07	2.69
10	12	18.44	18.73	3.10	2.77
10	18	12.90	13.10	3.05	2.71
10	21	10.99	11.30	5.48	2.68
10	24	9.70	9.98	5.61	2.66
10	24	9.74	10.04	5.97	2.68

process of extraction of the acid is practically instantaneous or whether it takes some time. The results are shown in table IV, from which it will be seen that the extraction is rapid, but not instantaneous. Powdered sodium hydrogen sulphate was vigorously shaken with alcohol for the time shown in the third column. As the time of shaking increased, the mixture became more viscous. The actual time allowed for filtration is shown in the fourth column. The total quantity of acid extracted from the 5 grams of hydrogen sulphate was calculated from the acidity of the filtrate. The tests, although not of a high degree of accuracy, are sufficiently conclusive to give the desired information.

TABLE IV.

Estimation of the Rate of Extraction of Sulphuric Acid from Sodium Hydrogen Sulphate by means of Alcohol.

Sodium hydro- gen sul- phate. Grams.	Alcohol. Grams.	Time dur- ing which the mix- ture was shaken. Minutes.	Time allowed for filtra- tion. Minutes.	Weight of filtrate. Grams.	Percent- age of acid in filtrate. Theory 8.8.	Weight of acid actu- ally re- covered. Grams. Theory 1.36.
5	14.1	1.0	0.75	6.097	5.07	0.75
5	14.0	2.0	1.0	2.925	6.97	1.05
5	14.0	4.0	2.0	2.188	8.02	1.22
5	14.0	8.0	3.0	1.981	{ 8.27 8.39	{ 1.24 1.28

The maximum amount of extraction shown in this table amounts to 94.1 per cent. of that theoretically possible. From the last column of table III, it will be seen that when the extraction is continued for twenty-four hours, the acid extracted from the sodium hydrogen sulphate agrees with that demanded by theory, assuming the quantitative conversion of the sodium hydrogen sulphate into the compound $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$. Subsequent investigation showed that extraction for two hours is more than sufficient to ensure the completion of this reaction.

The Action of Alcoholic Sulphuric Acid on Pure, Dry Sodium Sulphate.

Powdered sodium sulphate was mixed with more than twice its weight of alcoholic sulphuric acid, shaken for seventy-two hours, and then filtered off. The acid in the filtrate was determined as in the alcoholic sulphuric acids. The salt was quickly removed from the filter, wrapped in clean paper, and extracted by means of ether in a Soxhlet apparatus until the runnings were neutral. During the shaking, all mixtures become more or less gelatinous. The time during which the extraction lasted is given in the second column of table V. The figure in brackets indicates the number of hours of that time during which the continuous extraction in the Soxhlet apparatus was proceeding. For the rest of the time the substance was lying immersed in the ether. The times only give an approximate idea of the time taken for extraction, as, owing to the difficulty of judging the end-point, it is probable that some samples were left exposed to the action of the ether longer than was absolutely necessary. The two results shown under Nos. 6 and 7 in table V illustrate the considerable length of time required in these cases to complete the reaction.

TABLE V.

Action of Alcoholic Sulphuric Acid on Dry Sodium Sulphate.

No.	Time extracted.		Percent- age of acid in the alco- holic sulphuric acid.	Percentage con- version into ethyl hydrogen sulphate of constituents.		Acidity in residue as per- centage of sul- phuric acid.	Notes.
				Acid.	Alcohol.		
1	6½	days (20)	9.19	82.5	3.9	0.57	
2	—		20.41	87.7	10.6	1.53	
3	8½	days (36)	29.9	83.7	17.5	5.83	
4	9	days (41)	40.6	81.0	26.2	10.83	
5	9	days (41)	50.6	72.5	34.0	12.49	
6	11	days (53)	70.2	54.5	60.4	19.98	incomplete.
	18	days (102)	70.2	54.5	60.4	18.80	neutral washings.
7	15	days (65)	78.8	41.0	71.5	27.69	incomplete
	23	days (117)	78.8	41.0	71.5	18.59	neutral washings.

From these results it will be observed that sodium sulphate combines with sulphuric acid presented to it as alcoholic sulphuric acid. The amount of combination increases with the strength of the alcoholic sulphuric acid used, but is not directly proportional to it. The table gives the results after the sodium sulphate had

been left in contact with the alcoholic sulphuric acid for seventy-two hours with constant shaking. Owing to pressure of work, it was not possible to examine the influence of time on the action of alcoholic sulphuric acids on sodium sulphate.*

The Action of Alcoholic Sulphuric Acid on Dry Sodium Hydrogen Sulphate.

Sodium hydrogen sulphate was mixed with about six times its weight of alcoholic sulphuric acid and shaken for twenty-four hours. The solid was then filtered off, wrapped in clean paper, and placed in a Soxhlet apparatus for extraction with dry ether. The acidity of the residue in the paper was estimated as soon as the runnings from the apparatus were neutral. The observed results are given in table VI.

TABLE VI.

Action of Alcoholic Sulphuric Acid on Dry Sodium Hydrogen Sulphate.

No.	No. of hours extracted.	Strength of alcoholic sulphuric acid as percentage of sulphuric acid.	Percentage conversion of constituents into ethyl hydrogen sulphate.		As percentage of sulphuric acid.	
			Acid.	Alcohol.	Acidity in filtrate after shaking.	Acidity of residue
1	13	9.1	82.5	3.9	13.5	18.83
2	34	21.6	87.1	11.3	28.8	18.64
3	38	29.9	83.7	17.5	32.9	26.31
4	82	40.6	81.0	26.2	39.1	27.69
5	38	50.6	72.5	34.0	50.1	23.62
	?	50.6	72.5	34.0	50.1	18.93
6	34	60.6	64.5	44.5	57.5	33.60
	74	60.6	64.5	44.5	57.5	18.63
7	50	70.2	54.5	60.4	67.8	27.86
8	86	78.8	41.0	71.5	78.1	23.63

* It is necessary to exercise great care in testing the runnings with litmus paper as, when the acid is small in quantity, its presence is not indicated until all the ether has evaporated from the paper.

In the cases of specimens treated with alcoholic sulphuric acids of the higher acid-contents, it was observed that the liquor in the flask of the Soxhlet apparatus separated into two layers. This was due to the presence of ethyl hydrogen sulphate. This substance was also found in washings in which no separation into layers had occurred. The solubility of ethyl hydrogen sulphate in ether is less than one per cent., and consequently, if there is much ethyl hydrogen sulphate present, it shows itself by causing the appearance of two layers in the flask.

These remarks apply also to the next section.

From these figures it is evident that alcoholic sulphuric acid reacts with sodium hydrogen sulphate. It appears that alcoholic sulphuric acids of which the strength is about 20 per cent. and less extract acid from the hydrogen sulphate and leave a residue of the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, whilst acids of 30 per cent. and more also react with the hydrogen sulphate and give another sulphate of sodium, which has previously been prepared by a different method, having the formula $\text{Na}_2\text{SO}_4, 2\text{NaHSO}_4$ and an acidity of 25.65 per cent. The formation of this compound has not been definitely proved, but, if it is formed, it is decomposed by exhaustive extraction with ether, giving the compound

The mixtures of alcoholic sulphuric acid and sodium hydrogen sulphate become gelatinous during the shaking, and, if the substance in the Soxhlet apparatus is examined during the extraction, crystals of considerable size are found. These crystals seem to be formed in the bottle or during the extraction, for the hydrogen sulphate was always carefully powdered before exposing it to the action of the alcoholic sulphuric acid. The crystals probably consist of the compound $\text{Na}_2\text{SO}_4, 2\text{NaHSO}_4$, as they are not observed when the product of the extraction is the compound

The extraction was fairly rapid at first, and the litmus with which the runnings were tested showed a bright pink coloration. After some time the extraction became very slow, and the acidity towards litmus paper was obvious, but extremely weak (see footnote, p. 659). This will explain the various times shown in the table for extraction; for example, one sample, after actual extraction for eighty-two hours and remaining in ether for the remainder of a fortnight when the extraction was not proceeding, showed an acidity of 27.7 per cent. The remainder of the sample was then replaced and was extracted for twenty-four hours more, and when not under continuous extraction was left in the dry ether, the whole experiment lasting about three days. After this treatment the acidity was 24.7 per cent. As a comparison, it may be stated that the ethereal extraction of sodium hydrogen sulphate, after treatment with alcohol, takes only a few hours to complete.

It will be observed that the acidity of the filtrates in cases 1, 2, and 3 is greater than the original acidity of the alcoholic sulphuric acid; in all other cases it is about the same or a little less.

Discussion of certain Properties of the Intermediate Sulphate,
 $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$.

The compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, which is so readily formed by the action of dry alcohol on dry sodium hydrogen sulphate, is dealt with by Pascal and Ero (*loc. cit.*), although the substance was prepared by a different method from that described in this paper. In the course of the present work it has been necessary to study this compound in some detail, and the results do not confirm the observations of Pascal and Ero, who state that the intermediate sulphate decomposes at 174° with partial liquefaction. Specimens of the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, were prepared by extraction of sodium sulphate by alcohol, and the statement that the substance is unchanged in air was confirmed. The acidity of the different samples ranged from 18.66 to 18.78 per cent. A weighed quantity of the substance was then heated in a platinum basin in an oil-oven, and cooled and weighed at intervals. The temperature of the bath was raised about 4° or 5° at a time until the temperature reached 215° . The salt was kept in the bath for about half an hour at each temperature, and weighed after each heating. It showed no signs of melting, and its weight was constant. Over the whole period of a particular experiment, 7.3038 grams of the substance lost 0.0254 gram. The acidity at the commencement of the experiment was 18.67 per cent., and the acidity after the prolonged heating was 18.74 per cent. This result has been frequently confirmed. The only difference in the substance after heating was that the colour had changed to a pale grey. The salt as prepared is snow-white. Every attempt on the part of the authors to determine the melting point resulted in failure. Even when heated to 260° the substance did not melt. It seemed possible that Pascal and Ero, having prepared their specimens from solutions, might have determined the melting point of a substance containing water, and that the presence of water would cause it to melt. A sample of the intermediate sulphate was prepared by the recrystallisation of nitre-cake (33 per cent. of sulphuric acid), and gave the following analysis:

	I.	II. Calculated from I, assum- ing the salt dehydrated.	III. Theory for the dry salt.
	Found. Per cent.		
Acidity as H_2SO_4	18.45 } 18.50 }	19.28	18.70
SO_4 determined as BaSO_4	70.58	73.41	73.29
Na_2SO_4 produced on fusion ...	77.42 } 77.43 }	80.69	81.30
Water	3.95 } 4.02 }	—	—

The salt obtained by recrystallisation contained a slight excess of acid above that required for the intermediate compound. On heating, water was given off, but fusion did not take place. The authors are unable to account for the observations quoted in the paper mentioned (*loc. cit.*). The substance, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, decomposes before it melts, the residue after heating being fused sodium sulphate.

The Action of Pure, Dry Alcohol on Mixtures of Pure, Dry Sodium Sulphate and Pure, Dry Sodium Hydrogen Sulphate before and after Heating the Mixtures.

The next series of experiments was carried out with the object of elucidating the composition of commercial nitre-cake. It is usually assumed that nitre-cake is a mixture of sodium hydrogen sulphate and sodium sulphate, but recently Pascal and Ero (*loc. cit.*) have stated that, at the ordinary temperature, it is a mixture of the intermediate sulphate, $\text{Na}_2\text{SO}_4 \cdot \text{NaHSO}_4$, and the hydrogen sulphate. Pascal and Ero's statement is based on a study of the melting points of mixtures of neutral sulphate and sulphuric acid, and their conclusions are not therefore necessarily applicable to nitre-cake. It occurred to the authors that a study of the action of alcohol on (1) mixtures of sodium sulphate and hydrogen sulphate, and (2) commercial nitre-cake, would probably throw light on the subject, and experiments were accordingly carried out on these lines. As a preliminary experiment, it was necessary to ascertain if there is any evolution of sulphuric acid from such mixtures when heated to 215° , as the conclusions drawn depend on the assumption that, before extraction with alcohol, the total amount of acid in the mixture is the same as the amount of acidity in the mixture when weighed out for the experiment. Results show that mixtures of sodium sulphate and sodium hydrogen sulphate do not lose sulphuric acid when heated to 215° .

(a) *Table VII. Nos. 1 to 7.*—Dry sodium sulphate and dry sodium hydrogen sulphate were shaken with excess of alcohol for twenty-four hours. The solid was then filtered off and extracted with dry ether until the runnings were neutral.

(b) *Table VII. Nos. 8 to 13.*—In all these cases the salts were treated as above, except that, before the alcohol extraction, the mixed salts were heated in an oil-oven for four hours at 200 — 215° . In No. 13 the mixture was heated for six and a-half hours to see if the reaction became quantitative if given sufficient time. The analyses indicate that the reaction was complete in the shorter time, namely, **four hours**.

The values shown in column vii are found by calculation, assuming that all the sodium hydrogen sulphate is converted into the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, and that as much sodium sulphate as possible combines with the sulphuric acid so liberated, also forming the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$.

It will be seen that, in every case, the acidity of the residue is greater than it would be if the hydrogen sulphate only took part in the reaction (column iv), but less than the value shown in column vii. Participation of the sodium sulphate in the reaction is indicated in every case, although (see column viii) its conversion into the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, is never complete.

Two explanations are possible of the part taken by the sodium sulphate in the reaction:

(1) That, in the presence of alcohol, some of the sulphate combines directly with the sodium hydrogen sulphate. No evidence in favour of this possibility has been found.

(2) That the alcoholic sulphuric acid produced by the action of the alcohol on the sodium hydrogen sulphate reacts with a portion of the sulphate, forming the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$.

Sulphuric acid acts on sodium sulphate in the presence of water, and it seemed not unlikely that it might act on sodium sulphate in the presence of alcohol. This point was thoroughly investigated, and the results obtained (p. 658) show conclusively that (*a*) anhydrous sodium sulphate is acted on by alcoholic sulphuric acid at the ordinary temperature, and (*b*) that the amount of interaction increases with the strength of alcoholic sulphuric acid employed.

In the second series of analyses, obtained in experiments in which the substances under consideration were heated, it will be seen that the heating of the two salts in contact results in a very considerable formation of the compound, $\text{Na}_2\text{SO}_4\cdot\text{NaHSO}_4$, as indicated by the increased acidity of the residue after extraction (see table VII, columns v to viii, and compare Nos. 8 to 13 with Nos. 1 to 7). The mixtures (except No. 13) were heated for four hours at $200\text{--}215^\circ$. Prolonged heating does not increase the yield of intermediate sulphate. Considering the difficulties of complete admixture and the fact that the mixtures never completely fused, the results lead one to expect a still higher conversion to the compound under ideal conditions. It appears that if the ratio $\text{Na}_2\text{SO}_4:\text{NaHSO}_4$ is greater than unity, the degree of conversion to the double compound is greater than when the ratio $\text{NaHSO}_4:\text{Na}_2\text{SO}_4$ is greater than unity.

TABLE VII.

Action of Pure, Dry Alcohol on Mixtures of Sodium Sulphate and Sodium Hydrogen Sulphate both before and after Heating.

Mixtures of sodium sulphate and sodium hydrogen sulphate not heated after mixing.

Expt. No.	Composition of mixture.		Corresponding with approximate molecular proportions.	Initial acidity of mixture. Per cent. H_2SO_4 .	Acidity of residue. Per cent. H_2SO_4 .	Calculated acidity of residue assuming complete conversion of NaHSO_4 into $\text{Na}_2\text{H}(\text{SO}_4)_2$, the Na_2SO_4 remaining unaffected. Per cent. H_2SO_4 .	Calculated acidity of residue assuming maximum possible conversion of both NaHSO_4 and Na_2SO_4 into the compound $\text{Na}_3\text{H}(\text{SO}_4)_2$. Per cent. H_2SO_4 .	Conversion of Na_2SO_4 into $\text{Na}_3\text{H}(\text{SO}_4)_2$ expressed as the percentage of the total Na_2SO_4 originally present which could have been so converted.
	Na_2SO_4 . Per cent.	NaHSO_4 . Per cent.						
1	70.3	29.7	$2\text{Na}_2\text{SO}_4 : \text{NaHSO}_4 \dots$	12.1	7.74	4.40	12.1	43.4
2	54.2	45.8	$\text{Na}_2\text{SO}_4 : \text{NaHSO}_4 \dots$	18.7	9.88	7.08	18.7	23.9
3	37.2	62.8	$\text{Na}_2\text{SO}_4 : 2\text{NaHSO}_4 \dots$	25.6	13.20	10.31	18.7	34.5
4	20.0	80.0	$\text{Na}_2\text{SO}_4 : 4.7\text{NaHSO}_4$	32.6	17.31	13.92	18.7	71.0
5	17.0	83.0	Composition of nitre-cake if it were a mixture of Na_2SO_4 and NaHSO_4 .	33.8	15.98	14.59	18.7	33.6
6	8.6	91.4	Approximately $\text{Na}_2\text{SO}_4 : 13\text{NaHSO}_4$.	37.3	17.16	16.57	18.7	26.6
7	0.0	100.0	$\text{NaHSO}_4 \dots\dots\dots$	40.8	18.69	18.70	18.7	—

Mixtures of sodium sulphate and sodium hydrogen sulphate heated at 200—215° after pulverisation and intimate mixing.

8	70.3	29.7	2Na ₂ SO ₄ : NaHSO ₄ ...	12.1	11.50	4.40	12.1	92.2
9	64.8	35.2	3Na ₂ SO ₄ : 2NaHSO ₄ ...	14.4	14.85	5.30	15.2	96.3
10	54.2	45.8	Na ₂ SO ₄ : NaHSO ₄ ...	18.7	15.71	7.08	18.7	74.2
11	37.2	62.8	Na ₂ SO ₄ : 2NaHSO ₄ ...	25.6	17.01	10.31	18.7	80.6
12	29.7	70.3	Na ₂ SO ₄ : 3NaHSO ₄ ...	28.7	17.29	11.84	18.7	79.5
13	37.2	62.8	Na ₂ SO ₄ : 2NaHSO ₄ ...	25.6	16.94	10.31	18.7	79.0
Mixture heated 6½ hours.								

Substances prepared from sodium nitrate and sulphuric acid, that is, nitre-cakes.

14	17.0	83.0	Nitre-cake from factory retort.	33.8	18.78	14.59	18.7	100.0
15	54.2	45.8	Nitre-cake prepared in laboratory to give molecular proportions.	19.0	18.58	7.08	18.7	99.0
16	70.6	29.4	Na ₂ SO ₄ : NaHSO ₄ .	12.0	11.96	4.35	12.00	—
Col.	i.	ii.	Nitre-cake prepared in laboratory.	iv.	v.	vi.	vii.	viii.
			iii.					

Constitution of Nitre-cake.

The results given in table VII provide conclusive evidence regarding the constitution of nitre-cake. It will be noticed from experiments Nos. 14, 15, and 16 that:

(a) When the original acidity of the cake is more than 18·7 per cent., extraction with dry alcohol reduces it to 18·7 per cent., indicating a complete conversion of the sodium hydrogen sulphate present in the cake into the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$.

(b) When the original acidity of the cake is about 18·7 per cent., treatment with dry alcohol leaves it unaltered.

(c) When the original acidity of the cake is less than 18·7 per cent., treatment with dry alcohol again leaves it unaltered.

Experiments 1 to 6 having shown that when mixtures of sodium sulphate and sodium hydrogen sulphate are extracted with alcohol the sodium sulphate is never completely converted into the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, it follows from the above results that nitre-cakes of 18·7 per cent. acidity and more contain no sodium sulphate at all. Cakes of more than 18·7 per cent. acidity consist of a mixture of sodium hydrogen sulphate and the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and cakes of less than 18·7 per cent. acidity comprise a mixture of sodium sulphate and the compound,

containing no hydrogen sulphate at all, for, if hydrogen sulphate were present, extraction with alcohol would reduce the acidity. Finally, a cake of 18·7 per cent. acidity consists of the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and contains neither sulphate nor hydrogen sulphate.

The molecular proportions of a nitre-cake of known acidity may be calculated from one of the two formulæ given below:

(a) If the acidity of the nitre-cake is 18·7 per cent. sulphuric acid or less, $x = 1 - \frac{142y}{4900 - 120y}$, where x = the molecular proportion of sodium sulphate, $(1 - x)$ = the molecular proportion of the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, in the cake, and y = its acidity as percentage of sulphuric acid.

(b) If the acidity is 18·7 per cent. of sulphuric acid, or more, but not exceeding 40·83 per cent., $x = \frac{4900 - 120y}{142y}$, where x = the molecular proportion of the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, $(1 - x)$ = the molecular proportion of sodium hydrogen sulphate in the nitre-cake, and y = its acidity as percentage of sulphuric acid.

Summary and Conclusions.

(1) Dry alcohol acts on dry sodium hydrogen sulphate, with the formation of the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and the liberation of sulphuric acid, which dissolves in the alcohol, and is subsequently converted partly into ethyl hydrogen sulphate. Prolonged action of alcohol does not extract any further quantity of the acid.

(2) Methyl, *n*-butyl, and amyl alcohols also react with sodium hydrogen sulphate, with the formation of the same intermediate sulphate.

(3) Dry ethyl alcohol does not decompose dry potassium hydrogen sulphate.

(4) Moist alcohol will completely decompose sodium hydrogen sulphate, giving first the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, and finally normal sodium sulphate. Sodium sulphate is sparingly soluble in moist alcohol.

(5) Alcoholic sulphuric acid reacts with sodium sulphate in the cold (18°), with the formation of an acid sulphate. The amount of the interaction increases with the strength of the alcoholic sulphuric acid employed.

(6) When alcoholic sulphuric acid acts on sodium hydrogen sulphate, the intermediate sulphate, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, is formed if the strength of the alcoholic sulphuric acid corresponds with 20 per cent. or less. When the alcoholic sulphuric acid has a strength corresponding with 30 per cent. of sulphuric acid or more, the compound, $\text{Na}_2\text{SO}_4, 2\text{NaHSO}_4$, is probably produced; if so, this compound is slowly decomposed by constant extraction with pure, dry ether, and finally yields the compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$.

(7) The compound, $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, is formed when dry sodium sulphate is heated with dry sodium hydrogen sulphate.

(8) Nitre-cake consists of the compound $\text{Na}_2\text{SO}_4, \text{NaHSO}_4$, alone or mixed with either sodium hydrogen sulphate or sodium sulphate, according as the acidity is equal to, greater than or less than 18.7 per cent. of sulphuric acid.

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