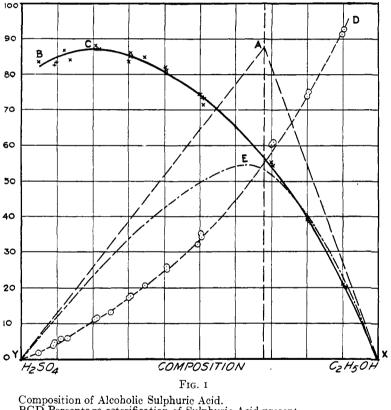# THE SYSTEM: SODIUM SULPHATE, SULPHURIC ACID—ETHYL ALCOHOL

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Butler and Dunnicliff[1] showed that dry ethyl alcohol extracts two thirds of the sulphuric acid from pure dry sodium hydrogen sulphate and leaves behind a residue of the intermediate sulphate $3Na_2SO_4 . H_2SO_4$. The sulphuric acid dissolves in the alcohol and partial esterification takes place. The velocity of this esterification and the equilibrium in alcoholic sulphuric acids have been

FIG. 1

Composition of Alcoholic Sulphuric Acid.
BCD Percentage esterification of Sulphuric Acid present.
YD Percentage of esterification of total Alcohol present.
YEX Percentage of Ethyl Hydrogen Sulphate present.
YAX Maximum possible percentage of Ethyl Hydrogen Sulphate present.

studied by the same authors[2]. At low concentrations of sulphuric acid, the rate of esterification is slow. The percentage conversion of both alcohol and sulphuric acid in alcoholic sulphuric acids has also been determined and the various equilibrium relationships are given in Fig. 1. This diagram is self-

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[1] J. Chem. Soc., 117, 649 (1920).
[2] J. Chem. Soc., 119, 1386 (1921).

explanatory and was plotted from the experimental results on which the second paper referred to above was based.

The object of the work to be described was to investigate the equilibrium between sodium sulphate, sulphuric acid, and ethyl alcohol over a wide range of concentrations.

In the first series of experiments, dry sodium hydrogen sulphate was allowed to react with a known weight of dry ethyl alcohol in a thermostat maintained at 18.3 ± 0.5°C by electrical control. Pure sodium hydrogen sulphate, dry ethyl alcohol and alcoholic sulphuric acids were prepared by standard methods.

Weighed quantities of sodium hydrogen sulphate and alcohol were sealed off in glass bulbs of about 10 c.c. capacity and shaken for about 48 hours in the thermostat. The tube was then allowed to remain stationary in the bath until the solid phase had settled to the bottom. The liquid and the residue ("Rest") were separated and analysed as described below, the same method being used for each analysis.

Since the partial esterification of the sulphuric acid is a complicating factor in the problem, it is necessary to determine

(a)   The acidity due to free sulphuric acid, together with that due to ethyl hydrogen sulphate. The latter was calculated as sulphuric acid and the acidity is called the "Direct Acidity".

(b)   The amount of sulphuric acid converted into ethyl hydrogen sulphate.

(c)   The sodium sulphate and

(d)   the remainder of the constituents (by difference).

Methods of Determination:—

(a)   A weighed amount of the substance was titrated against caustic soda using methyl orange as indicator and the acidity calculated as parts of sulphuric acid per 100 parts of the substance. This is the "Direct Acidity".

(b)   The ester was determined[1] by method 3, and recorded in the Tables as "H_2SO_4 as ester", i.e. percentage of ester × 98/126.

(c)   The sodium sulphate was determined by evaporating a weighed quantity of the substance to dryness in a platinum basin on a water bath. The residue was heated first in an air oven and finally by ignition over a blowpipe before and after treatment with a few drops of nitric acid.

Many estimations were made and a number of analysis are given in Table I. It was desired to find the best method of representing these results graphically and it was thought that, making certain limitations, this might be done by the usual method for a ternary system. Owing to the complication introduced by the esterification of the acid, it was necessary to consider which of three possible ways of condensing the system to one of three components would be best.

1.   (a) sodium sulphate, (b) sulphuric acid assuming that no esterification had taken place, (c) alcohol.

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[1] Butler and Dunnicliff: J. Chem. Soc., **119**, 1385 (1921).

2.   (a) sodium sulphate, (b) "direct acidity" (V.S.), (c) "Solvent" i.e., 100-(a+b).

3.   (a) sodium sulphate, (b) sulphuric acid existing as such and omitting acidity due to the ethyl hydrogen sulphate. This is recorded in the tables as "Free H_2SO_4", (c) "Solvent" = alcohol + ethyl hydrogen sulphate + water.

The first method was shown to be inadmissible by plotting the results. It is not feasible to ignore esterification even though the values at low concentrations of sulphuric acid are small.
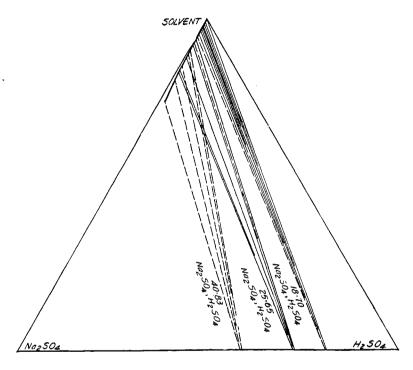

FIG. 2
The System Sodium Sulphate-Sulphuric Acid-Ethyl Alcohol

Method 2 gave a rough convergence of the conjugation lines but a much more satisfactory convergence of the lines to foci on the sodium sulphate—sulphuric acid line was given when the results were plotted according to method 3. These are shown in the continuous lines in Fig. 2 and indicate the existence of solid phases having the formulae $3Na_2SO_4$, H_2SO_4 and $2Na_2SO_4$, H_2SO_4.

It will be seen that the change in the solid phase occurs when the total sulphuric acid is between 5.5 and 6.8 per cent (Free H_2SO_4 = 4.5 − 5.7 per cent, ester 1.0 − 1.13 per cent) and the weight of alcohol used is about 4.5 times the weight of the sodium hydrogen sulphate. These results indicate that at low concentrations of ethyl hydrogen sulphate, the ester has only a small influence on the equilibrium. The effect of the ester on the equilibrium when it is present in large proportions is dealt with later.

TABLE I

Action of Ethyl Alcohol on Sodium Hydrogen Sulphate

Parts of alcohol per unit of sodium hydrogen sulphate	H_2SO_4 as Ester %	Liquid Phase			H_2SO_4 as Ester %	"Rest"			Calculated acidity of solid phase %	
		Free H_2SO_4 %	Na_2SO_4 %	Solvent %		Free Na_2SO_4 %	Na_2SO_4 %	Solvent %		
12.2	0.30	1.58	0.33	98.09	0.15	9.26	36.89	53.85	18.22	3 Na_2SO_4, H_2SO_4
9.9	0.34	2.20	0.42	97.38	0.20	7.68	27.36	64.96	18.65	requires
9.2	0.41	2.43	0.46	97.11	0.18	10.26	39.60	50.14	18.61	18.70% H_2SO_4
8.2	0.41	2.90	0.46	96.64	0.20	10.17	37.43	52.40	18.75	
6.1	0.80	3.55	0.47	95.98	0.40	12.04	44.21	43.75	19.17	
5.0	1.00	4.47	0.41	95.12	0.42	12.70	46.49	40.81	18.89	
4.0	1.13	5.70	0.40	93.90	0.77	10.94	19.80	69.26	26.30	2 Na_2SO_4, H_2SO_4
3.1	1.38	7.35	0.48	92.17	0.70	11.40	25.08	59.62	27.30	requires
2.1	1.42	9.20	0.49	90.31	0.51	16.26	31.84	51.90	26.40	25.65% H_2SO_4
1.5	1.60	10.70	0.50	88.80	0.69	10.30	38.90	41.80	26.90	
1.2	1.44	14.86	0.51	84.63	0.66	21.73	38.80	39.17	27.70	
0.8	3.24	14.51	0.52	81.97	1.04	22.24	42.40	35.36	27.70	

These results obtained graphically were checked by calculation. The "Rest" consists of true solid phase contaminated with true liquid phase, the composition of which has been determined. This contamination was allowed for by subtracting from the values found for free sulphuric acid and sodium sulphate in the "Rest", amounts calculated from the values in columns 4 and 5 respectively in the proportion of

$$\frac{\text{percentage of solvent in the solid phase}}{\text{percentage of solvent in the liquid phase.}}$$

From the net values so obtained for the sulphuric acid and the sodium sulphate in each case, the percentage acidity of each "True solid phase" was calculated and is shown in the 10th column in Table I. This would only be possible if the true solid phase contained no ester in combination. This was shown to be the case by drying a series of samples of "Rest" on porous tiles in desiccators. The maximum amount of ester obtained in the residue was 0.2% of ester and the composition of the "dried" residue corresponded with the values found by calculation and as indicated by the graphic method.

These results show that esterification was never complete (cf. Fig. 1). For this, not less than sixteen days would be necessary at the temperature of the experiment.

By the action of alcohol on sodium hydrogen sulphate, the maximum concentration of acid obtainable in the liquid phase is 17.75 per cent. If quantities of the salt sufficient to obtain higher concentrations are employed it is not possible to separate the liquid phase and the "Rest". Hence it is impossible to investigate this system further by this method.

The equilibrium may be studied at all concentrations of sulphuric acid in two other ways:—

(a)   By the action of alcoholic sulphuric acids on sodium sulphate.

(b)   By the action of alcoholic sulphuric acids on sodium hydrogen sulphate.

It has been shown (loc. cit.) that consistent or complete results are very difficult to obtain by method (a) probably owing to the protective action of the synthetic acid sulphates formed from and adhering to the surface of the particles of sodium sulphate. It was decided therefore to attack pure sodium hydrogen sulphate with alcoholic sulphuric acids prepared and estimated as described (loc. cit.). In order that equilibrium in the alcoholic sulphuric acids should be established, they were allowed to stand for a month before use. The liquid phase and "Rest" were analysed as described above and a number of results are shown in Table II. In these experiments many difficulties arose. In some cases the mixture set to a firm jelly, in others a hard crystalline deposit adhered to the sides of the tube; at the highest concentrations in many of the early experiments, the solid entirely disappeared. This may be due to the formation of a colloidal solution, a supersaturated solution or both. The difficulty due to gelatinisation was a maximum when the alcohol and sulphuric acid were mixed in the proportion of 30:70 to 65:35 by weight but gelatinisation was a more or less constant trouble and it was shown that

TABLE II

Action of Alcoholic Sulphuric Acids on Sodium Hydrogen Sulphate

No.	H₂SO₄ Before action %	H₂SO₄ as Ester After action %	Liquid Phase			H₂SO₄ as Ester in "Rest" %	"Rest"			Calculated acidity of Solid Phase %
			Free H₂SO₄ %	Na₂SO₄ %	Solvent %		Free H₂SO₄ %	Na₂SO₄ %	Solvent %	
1.	8.4	7.66	4.91	0.01	95.08	2.20	14.89	54.34	30.77	19.34
2.	14.3	13.58	6.26	0.81	92.93	2.16	15.94	41.49	39.57	23.79
3.	17.4	16.59	6.97	0.55	92.48	3.92	16.94	43.39	39.67	24.46
4.	21.4	20.92	5.68	0.10	94.22	6.86	20.04	21.69	58.27	43.34
5.	23.0	22.50	6.98	0.82	92.20	6.18	26.90	34.21	38.89	41.54
6.	31.2	30.82	8.37	0.56	91.07	8.56	30.55	40.75	28.70	40.73
7.	34.5	34.34	9.50	0.48	90.02	11.32	29.20	36.33	34.47	41.33
8.	33.4	32.16	14.59	0.42	84.99	25.50	30.84	38.97	30.19	39.94
9.	37.0	37.52	17.01	0.71	82.28	20.53	33.47	43.02	23.51	40.07
10.	39.0	39.32	23.15	1.74	75.11	9.10	36.36	37.97	25.67	43.22
11.	42.2	44.96	19.12	1.98	78.90	28.94	40.41	22.25	37.31	59.56
12.	36.9	55.00	14.69	5.25	80.06	42.08	32.98	17.27	49.75	63.10
13.	30.4	41.92	39.42	2.60	57.98	31.54	46.01	20.02	33.97	55.72
14.	18.0	17.16	63.83	2.72	33.45	12.00	61.94	21.82	16.24	58.88

3Na₂SO₄.H₂SO₄ requires 18.70% H₂SO₄; 2Na₂SO₄.H₂SO₄ requires 25.65% H₂SO₄; Na₂SO₄.H₂SO₄ requires 40.83%; H₂SO₄ and Na₂SO₄.2H₂SO₄ requires 57.98% H₂SO₄.

the liquid phase contained the solid phase in colloidal solution. In order to ensure completion of the reaction the tubes were rotated in the thermostat for 14 days. In the case of the high concentrations (marked with an asterisk) it was not possible to keep the temperature at 18.3° owing to the beginning of the hot season having set in but the temperature in these instances did not exceed 20.4°C and the equilibrium is not very sensitive to a small range of temperature. The contents of many of the tubes became coloured, some pink, some red and, in two cases, brown.

An examination of the results in Table II shows that there are changes of solid phase at the concentration of the alcoholic sulphuric acid as follows:—

(1) The change of phase from $3Na_2SO_4, H_2SO_4$ to $2Na_2SO_4, H_2SO_4$ occurs when the concentrations are between the following limits:—

Total acid	12.56 to 19.84%
H_2SO_4 as ester	7.65 to 13.58%
'Free' H_2SO_4	4.91 to 6.26%

Compare the range of concentration for the same change of phase in the first series.

Total acid	5.47 to 6.83%
H_2SO_4 as ester	1.00 to 1.13%
Free H_2SO_4	4.47 to 5.70%

(2) The change of phase from $2Na_2SO_4, H_2SO_4$ to Na_2SO_4, H_2SO_4 (= $NaHSO_4$) occurs when the concentrations are between the limits:

Total acid	23.56 to 26.60%
H_2SO_4 as ester	16.59 to 20.92%
Free H_2SO_4	6.97 to 5.68%

(3) The change of phase from Na_2SO_4, H_2SO_4 to $Na_2SO_4, 2H_2SO_4$ occurs when the concentrations are between the limits:

Total acid	62.47 to 64.28
H_2SO_4 as ester	39.92 to 44.96
Free H_2SO_4	23.15 to 19.12

(a) Results 1-10 are plotted in Fig. 2 and are indicated by broken lines. No. 11-14 are very irregular and are not shown in the diagram.

(b) Though in the first method of investigation the ethyl hydrogen sulphate appeared to be of minor importance, the results obtained by the second method indicate that this was on account of its low concentration. A study of the two tables will show that the higher the concentration of ester, the greater the concentration of free sulphuric acid with which a given solid phase can be in equilibrium. This influence is shown in Fig. 2 by the crossing of the two sets of lines.

(c) In some cases it will be observed that the percentage of ester in the liquid phase is less after the reaction than before the hydrogen sulphate was mixed with the alcoholic sulphuric acid. This is not due to the decomposition of the ester but to its diminution in percentage owing to the increase in the

amount of the free sulphuric acid present. This increase in the sulphuric acid is due to the extraction of sulphuric acid from the hydrogen sulphate by the alcoholic sulphuric acid. The free sulphuric acid is in excess of the amount possible in an equilibrium mixture of alcoholic sulphuric acids of those concentrations (Table II, Nos. 1-3, vide also Fig. 1) but the time taken by the experiment is insufficient to establish equilibrium in the liquid phase at the temperature of working.

(d)   The analyses given in Table II, Nos. 4-10 show that the solid phase is practically unchanged. This is confirmed by the nearly equal values in columns 2 and 3 which give the percentage of combined acid in the alcoholic sulphuric acid before use and in the liquid phase respectively. The total acidity after the reaction is given by the sum of the figures in columns 3 and 4 and these totals are in ascending order of magnitude with the exception of Nos. 11 and 12, where the results are probably not so accurate as they are up to No. 10 inclusive. In Nos. 4-10 this total is found to be in close agreement with the strength of the alcoholic sulphuric acid before use (values not given in the table). It will also be observed that as the amount of esterification of the alcoholic sulphuric acid increases, it has a greater influence on the nature of the solid phase: compare Nos. 2 and 3, 2 and 4, 10 and 11, 12 and 14.

(e)   Above 65% alcoholic sulphuric acid, the sodium hydrogen sulphate extracts acid from the liquid phase and forms a new solid phase. There is an indication of a compound $2H_2SO_4 . Na_2SO_4$ but the evidence is not conclusive in view of the complications which occur at high concentrations. When the percentage of sulphuric acid is 70 or over, the liquid phase becomes cloudy and a gelatinous substance is present. At concentrations of 80 per cent H_2SO_4 and over, the sodium hydrogen sulphate goes into solution. It was hoped that crystals of the true solid phase might be obtained by freezing and vigorous shaking but though the solution must have been highly supersaturated, all attempts were unsuccessful. In some tubes the solid phase adhered firmly to the walls of the tube as a hard crystalline mass and it is probable that the solid phases formed by the addition of alcoholic sulphuric acid of over 60% strength to sodium hydrogen sulphate were not uniform in composition. In one instance the centrifugalised liquid phase contained 11.5 per cent of sodium sulphate. This was present either as a colloidal sodium hydrogen sulphate probably having the composition $3H_2SO_4 . Na_2SO_4$ or as a supersaturated solution. Many repetitions failed to get absolutely uniform results and those quoted are typical of the values obtained.

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